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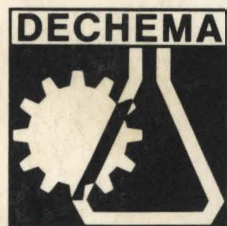
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Metal Extraction

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Metal Extraction

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The Cobalt Catalysed Oxidation of Solvent Extraction Diluents

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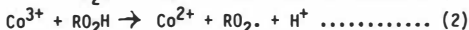
Solvent extraction for the separation and recovery of cobalt from nickel is now well established commercially.⁽¹⁾ While chloride liquors containing nickel and cobalt have been processed by solvent extraction for many years, it is only relatively recently that sulphate liquors have been so processed and even yet in only two plants ie. Nippon Mining Co Ltd ⁽²⁾ and Rustenburg Refiners Pty Ltd ⁽³⁾ are such liquors processed using totally sulphate based flowsheets. The extractant originally chosen for both plants was di 2-ethyl hexyl phosphoric acid (DEHPA) but, because cobalt leakage from the cobalt circuit was found to cause hydroxyoxime degradation problems in the subsequent nickel extraction circuit, Nippon Mining soon switched to the more selective alkyl phosphonic acid extractant, PC88A. ^(4,5) Rustenburg Refiners on the other hand faced no such downstream problems and still operate their plant using DEHPA as the extractant.

The first plant scale unit in Rustenburg Refiners' operations was commissioned in 1979 and this operated satisfactorily for the first few years up to 1982. In that year a larger plant was commissioned which was operated much more as a closed unit operation than the previous plant. After the first year of this latter operation, performance slowly deteriorated with eventually a serious fall off in both separation factor and phase break. Replacement of 40% of the solvent inventory in June 1983 only provided a temporary respite and further performance deterioration was soon experienced. Preliminary examination of the solvent phase suggested that oxidative degradation of the aromatic diluent had occurred. This paper presents the results of a study of this unusual problem.

General Considerations

Although no previous cases of diluent oxidation in solvent extraction plants treating cobalt containing solutions had been reported; it was strongly suspected that the degradation problem in the MRR plant was probably associated with the cobalt as it is a known oxygen carrier which can catalyse oxidation reactions, particularly when present in the hexa-coordinate as opposed to the tetrahedral form. Thus it is reported that cobalt compounds catalyse the oxidation of aromatic hydrocarbons ^{6,7,8} including p xylene ⁹ which can be converted at high temperature and pressure to terephthalic acid.

Oxidative degradation of the aromatic hydrocarbons in the plant diluent is thought therefore to have proceeded through an initial slow build up of peroxy or hydroperoxide compound followed by reaction with cobalt ions liberating free radicals¹⁰ as in equations 1 and 2 where R is alkyl.



Because phenols can terminate autoxidation chain reactions by free radical capture eg. $\text{AH} + \text{RO}_2\cdot \rightarrow \text{A}\cdot + \text{RO}_2\text{H}$; $\text{A}\cdot + \text{RO}_2\cdot \rightarrow \text{AO}_2\text{R}$ and $2\text{A}\cdot \rightarrow \text{A-A}$ (where AH is a substituted phenol), the addition of a phenol antioxidant would be expected to inhibit the oxidative degradation.

Experimental Approach

To study this diluent oxidation problem, it was considered that oxidation tests carried out in an autoclave using air under pressure would give oxidation rates sufficiently high relative to oxidation by air at atmospheric pressure that it would be possible to confirm that cobalt was indeed promoting diluent oxidation and that this technique would then provide the basis for a general and in-depth study of this unusual problem. Preliminary tests proved satisfactory and therefore this technique was adopted for the study.

Loaded organic phases containing either the metal salt or the sodium salt of the extractant were charged to a 11 stirred electrically heated autoclave wherein they were contacted with appropriate aqueous solutions usually at an organic to aqueous ratio of 3:1. Air was introduced to the autoclave at a pressure of 150 psi and the operating temperature was 50°C for most tests. The rate of oxidation was determined by measuring the change in oxygen content in samples taken of the overgas while maintaining overpressure by introducing successive measured charges of air as demanded by pressure drop. The oxidised organic phases were stripped of metal and examined for the presence of oxidative degradation products of the diluent by IR spectroscopy and combined gas chromatography/mass spectrometry (GCMS).

Although the major part of the study has been concerned with cobalt, the following metal ions were also studied ie. Ni^{2+} , Cu^{2+} , Fe^{3+} and Mn^{2+} . Both an alkyl phosphonic acid (PC88A Daihachi Chemical Co Japan) and an alkyl phosphinic acid (Cyanex 272, American Cyanamid Corp.) were studied as well as DEHPA. A range of aromatic and aliphatic diluents were also examined. A summary of all systems studied is given in table 1.

Results

Preliminary oxidation tests showed that organic phases containing an aromatic diluent, Solvesso 150, oxidised quite rapidly in the autoclave and that the final solutions contained degradation products of the diluent which matched closely those found in the sample from the Rustenburg Refiners plant. An ion chromatogram of the plant sample contained a number of small peaks between the last of the solvent peaks and the TBP peak (absent in the chromatogram of the fresh solvent) which correlated with phenyl ethanones of molecular weight 148 and 162 and with methylesters of

benzoic acid. Further preliminary tests also showed that significant degradation only occurred in the presence of cobalt when the plant cobalt/nickel system was considered. Thus for work associated with the Rustenburg Refiners plant problem oxidative testwork was restricted to cobalt.

a) Effect of Diluent Aromaticity

The comparative oxidation results for the aromatic diluent Solvesso 150, Escaid 100 (aromaticity 25%) and aliphatic Escaid 110 are shown in Fig 1. The figure shows that the higher the aromatic content of the diluent, the faster was the rate of oxidation.

Examination of the rate plot for Solvesso 150 in Fig 1 shows that there was an initial small induction period in the oxidation of about 2 hours after which the oxidation rate was constant. This induction period is consistent with a gradual build up in the solvent of peroxy or hydroperoxide compounds followed by reaction with cobalt ions liberating free radicals ⁽¹⁰⁾ as shown above in equations (1) and (2).

No such induction period was apparent for Escaid 100 or Escaid 110.

(b) Effect of Cobalt Loading

For this study only the organic phase was taken for autoclaving to eliminate any possible contribution to the rate from the cobalt present in the aqueous phase. The results obtained are shown graphically in Fig 2. Fig 4 shows that the oxidation rate increased with the metal loading up to a maximum in the range $10\text{--}15\text{ g l}^{-1}$, but decreased on further increase in the loading to 20 g l^{-1} . The lower oxidation rate at high cobalt loading may be associated in some way with an increase in the proportion of tetrahedral cobalt present ⁽¹¹⁾, because it would be expected that in this co-ordination state cobalt would be less able to promote the transfer of oxygen. However, other factors such as solvent viscosity and oxygen solubility may also be playing a part. Moreover, at the higher cobalt concentration of 20 g l^{-1} there was also less diluent available for reaction because to achieve this loading it was necessary to increase the concentration of DEPHA from 0.5M up to 0.8M.

Fig 2 also shows that at all cobalt loadings there was an appreciable induction period (much longer in fact than when aqueous phase was present, Fig 1). The length of this induction increased progressively as the cobalt loading decreased - indeed no constant rate was reached even after 34h at the loading of $2\text{ g l}^{-1}\text{ Co}$.

(c) Effect of Temperature

The effect of increase in temperature on the diluent oxidation rate is shown in Fig 3 for Solvesso 150 and Escaid 110. The results show that at room temperature Solvesso 150 oxidised slowly but that the oxidation rate increased rapidly with temperature

eg. at 50°C the rate is approximately 13 times that at room temperature while at 70°C the rate increase is nearly 40 times. With Escaid 110 however little oxidation occurred at all at room temperature and significant oxidation only appeared at temperatures > 50°C.

(d) Effect of Oxygen Partial Pressure

The effect of oxygen partial pressure on diluent oxidation rate was also examined by reacting the aromatic solvent in the autoclave under several different oxygen-nitrogen atmospheres. The results which are presented graphically in Fig 4 show that the oxidation rate exactly doubled on increasing the oxygen concentration from 5 to 10 per cent but on further increasing the oxygen level to 30 per cent there was little, if any, increase in rate.

From these data, assuming that the apparent linear relationship between the rate of oxidation and O_2 partial pressure is maintained as the oxygen content is reduced to 0.2 atmospheres (ie. normal air pressure) then the oxidation rate under plant conditions is predicted to be of the order of $20m.M\ l^{-1}\ hr^{-1}$.

(e) Change of Extractant

The testwork using DEPHA as extractant was extended to include both a phosphonic acid (PCB8A) and a phosphinic acid (Cyanex 272). Solvesso 150 was used as diluent in each case and the results in figure 5 show that using the phosphonic acid as extractant, diluent oxidation was faster than in the comparable test with DEHPA but that for the phosphinic acid, oxidation was slower. This result for PCB8A is particularly surprising as it was believed that, as these reagents progressively load cobalt increasingly in the tetrahedral form, an order of oxidative stability of the solvent of phosphoric < phosphonic < phosphinic would have been found. Other factors are obviously involved but it has not been possible in this study to determine what these are.

(f) Effect of Metal Ion

The ability of metal ions other than cobalt to promote diluent oxidation was also examined. Using DEHPA as extractant and oxidation conditions as before manganese, a known oxidation catalyst was found to catalyse oxidation of Solvesso 150 at a rate comparable with that of cobalt, as shown in Fig 6. Copper also catalysed diluent oxidation to an appreciable extent but the activity of both nickel and ferric iron was very low. From the figure, the catalytic activity is seen to decrease in the order $Co > Mn > Cu > Fe\ III > Ni$.

(g) Effect of Antioxidant

Initial testwork showed that phenols were very effective in preventing diluent oxidation. For plant use, a proprietary antioxidant, Ionol CP (Shell Chemicals Ltd)

was selected. Little or no oxygen uptake by the organic phase was recorded in either of two extended autoclave tests in which loaded solvent prepared with Ionol CP (0.1^{w/o}) stabilised Solvesso 150 and Escaid 110 were autoclaved for 15 and 38 days respectively. A gradual loss of antioxidant in both tests was recorded by GC analyses and is shown in Fig 7. Extrapolations of these rate plots show that for Solvesso 150 consumption of antioxidant would be complete in 17 days compared with 50 days for Escaid 110. For any plant application therefore monitoring of the antioxidant concentration is essential. While GC was used for most of the Ionol CP analyses HPLC was also found to be satisfactory.

(h) Implications for Plant Operation

The results of this study showed that over time aromatic diluents will oxidize severely in the Rustenburg Refinery cobalt solvent extraction system. Aliphatic diluents are significantly more stable and are preferred. Addition of antioxidant to the organic phase will reduce the oxidation rate of both aliphatic and aromatic diluents, but as the antioxidant is consumed in the process it is essential that the concentration be monitored and controlled. Based on these results and continuous countercurrent testwork at Warren Spring Laboratory a solvent formulation containing Escaid 110 modified with TBP and Ionol CP as antioxidant was introduced into the Rustenburg Refinery plant in 1983. Since that time there has been no problem with diluent oxidation.

CONCLUSIONS

In alkyl phosphorus acid extraction systems, metal ions, particularly cobalt and manganese, are capable of catalysing the oxidative degradation of commercial solvent extraction diluents with attendant problems of poor phase separation and loss in solvent selectivity.

In the cobalt, DEHPA system the rate of oxidation increases with increasing diluent aromaticity, temperature and cobalt solvent loading. The oxidation rate is also dependant on the oxygen partial pressure at low oxygen concentrations.

Phenolic antioxidants are effective in conferring diluent stability. However it is essential to monitor and maintain the antioxidants concentration for long term satisfactory plant performance.

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TABLE 1 - Loaded Organic Phases Studied in Testwork

All organic phases contained 5 v/o TBP as phase modifier
Volume of organic phase taken - 240 ml except where indicated by * or +

Variable Examined	Organic Phase Composition			Aqueous Phase Taken
	Extractant (Concn 0.5M)	Diluent	Metal Loaded	
Diluent Aromaticity	DEHPA	Solvesso 150	Co, 13.0 g l ⁻¹	CoSO ₄ (~ 16 g l ⁻¹ Co)
" "	"	Escaid 100	Co, 13.6 g l ⁻¹	" (~ 16 g l ⁻¹ Co)
" "	"	Escaid 110	Co, 13.0 g l ⁻¹	" (~ 16 g l ⁻¹ Co)
Solvent Loading	DEHPA	Solvesso 150	Co, 2.0 g l ⁻¹	No Aqueous Phase
" "	"	"	Co, 5.0 g l ⁻¹	"
" "	"	"	Co, 10.0 g l ⁻¹	"
" "	"	"	Co, 14.2 g l ⁻¹	"
" "	"	"	Co, 20.5 g l ⁻¹	"
Temperature 17-70°C	DEHPA	Solvesso 150	Co, 13 g l ⁻¹	CoSO ₄ (~ 16 g l ⁻¹ Co)
" "	"	Escaid 110	Co, 13 g l ⁻¹	" (~ 16 g l ⁻¹ Co)
Oxygen Partial Pressure 0.5 to 3 Bar	DEHPA	Solvesso-150	Co, 13 g l ⁻¹	CoSO ₄ (~ 16 g l ⁻¹ Co)
"	"	Escaid 110*	Co, 13 g l ⁻¹	" (~ 16 g l ⁻¹ Co)
Extractant Type	DEHPA	Solvesso 150	Co, 13.0 g l ⁻¹	CoSO ₄ (~ 16 g l ⁻¹ Co)
" "	PC88A	"	Co, 14.0 g l ⁻¹	" (~ 15 g l ⁻¹ Co)
" "	Cyanex 272	"	Co, 15.6 g l ⁻¹	" (~ 14 g l ⁻¹ Co)
Metal Ion	DEHPA	Solvesso 150	Ni, 12.0 g l ⁻¹	NiSO ₄ (~ 17 g l ⁻¹ Ni)
" "	"	"	Fe III, 9.3 g l ⁻¹	Ferric Alum (17.4 g l ⁻¹ Fe)
" "	"	"	Cu, 16.2 g l ⁻¹	CuSO ₄ (~ 16 g l ⁻¹ Cu)
" "	"	"	Mn, 11.5 g l ⁻¹	MnSO ₄ (~ 16 g l ⁻¹ Mn)
Antioxidant Addition	DEHPA	Solvesso 150	plus Ionol CP	CoSO ₄ (~ 16 g l ⁻¹ Co)
" "	"	Escaid 110		CoSO ₄ (~ 16 g l ⁻¹ Co)

* 640 ml Organic Phase

+ 480 ml Organic Phase

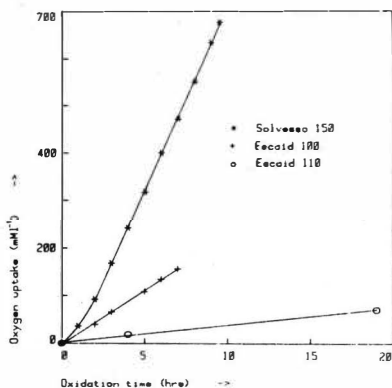


FIG.1 RATE OF OXYGEN UPTAKE BY COBALT LOADED D2EHPA IN DIFFERENT DILUENTS.

D2EHPA Concn: 0.5M
Modifier: TBP, 5%
Temp: 50°C

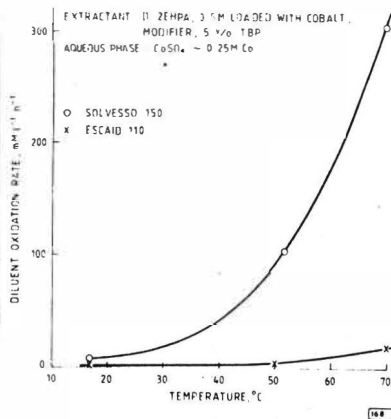


FIG.3 EFFECT OF INCREASE IN TEMPERATURE ON DILUENT OXIDATION RATE

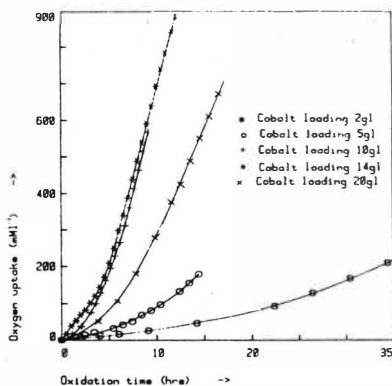


FIG.2 RATE OF OXYGEN UPTAKE BY COBALT LOADED D2EHPA IN SOLVESSO 150.

Effect of increase in cobalt concn.
D2EHPA: 0.5M
Modifier: TBP, 5%
Temp: 50°C

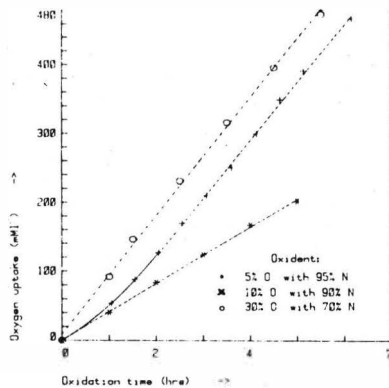


FIG.4 RATE OF OXIDATION OF COBALT LOADED D2EHPA IN SOLVESSO 150.

Effect of oxygen partial pressure.
D2EHPA Concn: 0.5M
Co loading: 13g/l
Modifier: TBP, 5%

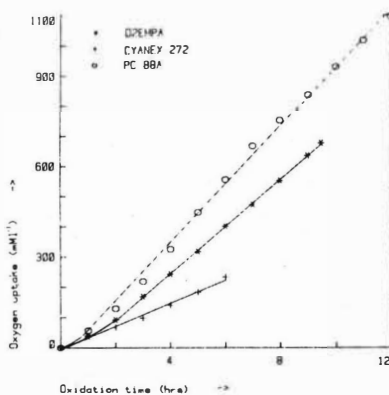


FIG 5 COMPARISON OF OXIDATION RATES FOR COBALT ORGANIC PHASES IN SOLVESSO 150.

Modifier: TBP, 5%

Temp: 52 C

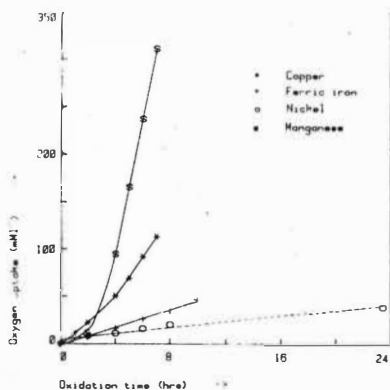


FIG 6 RATE OF OXYGEN UPTAKE BY METAL LOADED

D2EHPA IN SOLVESSO 150.

Effect of metal form change.

D2EHPA Conc: 0.5M

Modifier: TBP, 5%

Temp: 52 C

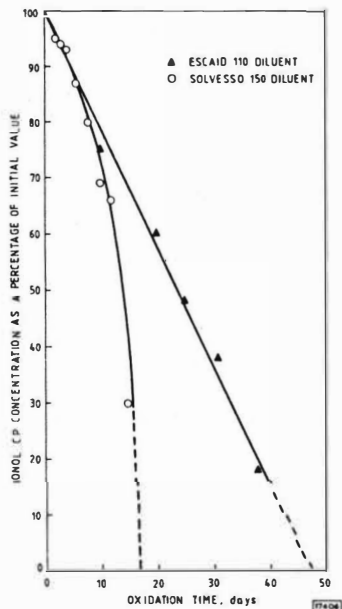


FIG 7 DECREASE IN CONCENTRATION OF IONOL CP DURING EXTENDED AUTOCLAVE TESTS.

The Role of Aryl Aldoxime Reagents in the Technical and Economic Advancement of Copper Production by Solvent Extraction

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The use of o-hydroxyaryloximes as extractants in large scale processes for the production of copper by solvent extraction is well established. Other classes of chemical compounds have been investigated and proposed for this application but have failed on mainly technical grounds. Certain hydroxy oxime formulations are pre eminent in being able to meet the considerable number of exacting requirements of a successful solvent extraction reagent.

The earliest reagents used for the commercial solvent extraction of copper were based on formulations of a ketoxime, 2-hydroxy-5-nonylbenzophenone oxime (1,2). While this was seen as a considerable innovation at the time the product (LIX 64N) was a weak extractant suited mainly to the recovery of copper from relatively dilute leach solutions. Since this time new oxime extractants and formulations have been developed giving greatly improved performance and plant economics, and it is these developments and ongoing research into improved products that is the subject for this paper.

In the early 1970's ICI and Acorga identified the need for stronger extractants with improved properties to allow the application of solvent extraction to more concentrated, acidic leach solutions, and which would also offer considerable economies in plant design and operating costs. In the course of the synthesis and evaluation of more than one hundred and fifty compounds, we identified an aryl aldoxime, namely 2-hydroxy-5-nonylbenzaldoxime as offering many of the properties we were looking for. This compound, now known as P50 oxime was a strong extractant with very fast extraction kinetics and was far more selective for copper over iron and other metals than the earlier ketoxime reagents. The distinct advantages of nonyl salicylaldoxime (P50) over other contenders were recognised by the granting of patents to ICI in most industrialised and copper producing countries (3).

Although P50 oxime had most of the improved properties we were looking for its high strength as an extractant made it more difficult to strip with normal spent tankhouse electrolyte than the weaker ketoxime reagents. It could have been used in solvent extraction circuits specifically designed for it but a considerable amount of the reagent would have been carried round the circuit in the copper loaded form requiring the use of a large excess of reagent. Various attempts were made to modify the chemistry of the P50 molecule itself but these always resulted in major changes in properties, making the reagent too weak and destroying other advantages such as the very fast kinetics (4). It was further discovered in the course of our work however

that if controlled amounts of certain compounds such as alkyl phenols, alcohols and esters were added as modifiers to P50, a considerable improvement could be made in the stripping, without unduly affecting the extraction performance (5,6).

These discoveries were put into effect in 1976 with the launching of the reagents Acorga P5100 and Acorga P5300 which were formulations of P50 oxime incorporating nonyl phenol as the modifier. The reagent Acorga P5100, based on a 1:1 ratio of P50 to nonyl phenol, is a strong extractant but with a much better transfer efficiency than the unmodified aldoxime, and capable of giving excellent copper recovery in plants employing fewer and smaller mixer settlers than the earlier solvent extraction plants. Acorga P5300 contained a higher proportion of modifier and was a slightly weaker extractant.

The effect on the economics of the solvent extraction process following the introduction of these Acorga reagents was quite dramatic. By the late 1970's solvent extraction plants were being commissioned which were approximately one third the size of earlier operations of equivalent copper production capacity, and are currently reported to be making copper for less than \$660 per tonne (30c/lb) (7). These new reagents also achieved our objective of opening up the potential for solvent extraction to treat much stronger, acidic solutions from vat leaching operations. Over the years 1979-82 there was a 70% increase in the amount of installed solvent extraction capacity for copper, virtually all of which is accounted for by the installation of plants using the second generation aldoxime based reagents.

Nonyl phenol was initially chosen as the modifier in Acorga reagents because, being a starting material for the manufacture of P50 oxime, it was convenient to use, readily available, and gave products of highly satisfactory performance in many applications. The success of these reagents in the late 70s and the recognition of their overwhelmingly superior properties and economic benefits does not mean, however, that there has since been a lack of progress in reagent development - quite to the contrary.

1981 saw the introduction of the reagent Acorga PT5050, which is based on a 2:1 weight ratio of P50 oxime and tridecyl alcohol. This reagent was initially developed to meet specific requirements for a particular customer, but has since found wide spread acceptance at a number of operations. In 1985 it was, we believe, the single solvent extraction reagent purchased in greatest tonnages world wide. In the early development of Acorga PT5050 it was recognised that its properties differed from Acorga P5100 in a number of areas. For example, it was found that Acorga PT5050 had even better selectivity than the nonyl phenol modified Acorga P5100. Other differences also became apparent with respect to hydrolytic stability, Kinetics

and phase separation. It has since been clearly recognised that the choice of modifier can have subtle effects on various properties of extractants.

Use of mixtures of aldoximes with weak ketoximes has also been proposed as an alternative means of obtaining extraction and strip characteristics similar to those of modified aldoxime reagents (8). This approach, however, can introduce some of the adverse properties of ketoxime reagents such as their inferior copper-iron selectivity and kinetics. The effect of different modifiers on the properties of extractants, and how this can be directed to the tailoring of improved reagents to meet specific requirements, is considered below with respect to some of the more important reagent parameters.

Selectivity

We investigated copper-iron selectivity by contacting Escaid solutions of various extractant formulations containing 25g per litre P50, or the molar equivalent of other oximes, with two fresh portions of aqueous feed, then analysing the organic phase. Data was acquired using two different feed solutions; feed (A) which contained 3g/litre of Cu^{2+} , 3g/litre of Fe^{3+} at pH 2.0, and feed (B) which contained 3g/litre of Cu^{2+} , 30g/litre of Fe^{3+} at pH 2.0. The results, expressed as the ratio of copper to iron extracted for contact with each of the two feed solutions, are displayed in Table 1.

Table 1 Copper-Iron Selectivity of Various o-Hydroxyaryloxime formulations.

<u>Extractant Composition</u>	<u>Commercial Formulation</u>	<u>Copper-Iron ratio</u>	
		<u>in extract</u>	
		<u>Feed A</u>	<u>Feed B</u>
P50(C_9 salicylaldoxime)+ nonylphenol	Acorga P5100	1859	386
P50 + alcohol (1)		5972	736
P50 + alcohol (2)		5384	515
P50 + alcohol (3)	Acorga M5615	6024	976
P50 + ester (1)		5898	971
P50 + ester (2)		7435	1210
C_{12} salicyl aldoxime plus tridecanol	LIX 622	1444	208
C_{12} salicyl aldoxime + C_9 benzophenone oxime	LIX 864	170	33
C_{12} salicylaldoxime + C_9 acetophenone oxime	LIX 984	790	120

These results show that a combination of either alcohol (3) or the ester (2) with the nonyl salicylaldoxime P50 can provide products offering exceptional selectivity for copper over iron under even the most arduous of conditions (high Fe/Cu ratio in the feed and high pH). Some of the deficiencies of the concept of mixtures of aldoximes and ketoximes are self evident from these data.

Kinetics

The rates of extraction and stripping of copper with certain o-hydroxyaryl- aldoximes such as Acorga P50 are known to be very fast, and much faster than with ketoxime reagents (4). We have recently had cause to evaluate reagents for a project where the operating temperature in the extraction circuit is likely to be between 0 and 5°C, and as the benefits of solvent extraction become more universally appreciated we see further potential for its application in colder climates, and also for dealing with some low temperature mine waters. It might be expected that operating at lower temperatures will slow down extraction rates considerably and this can become a matter of major concern if low stage efficiencies result in a loss of copper. The kinetic properties of various hydroxyoxime formulations at 0°C and 25°C are illustrated in Table 2.

Table 2 Rates of extraction and stripping for various reagents at 0° and 25°C.

<u>Extractant formulation</u>	<u>Approach to equilibrium, %</u>			
	<u>0°C</u>		<u>25°C</u>	
	<u>Extract</u>	<u>Strip</u>	<u>Extract</u>	<u>Strip</u>
	(30sec)	(15sec)	(30sec)	(15sec)
P50 oxime (C9 salicylaldoxime)	97.3	89.7	100	98
P50 oxime plus nonylphenol (Acorga P5100)	64.4	72.6	96.2	99.4
P50 oxime plus tridecanol (Acorga PT5050)	85.6	90.6	96.5	100
Ketoxime reagent (LIX 64N)	62.8	42.1	86.3	81.7
P50 plus LIX 64N	75.4	45.2	94.1	87.9
C12 salicylaldoxime plus LIX 64N	64.0	43.4	81.6	64.5

The experimental methods for carrying out this comparison are described elsewhere (9). The reagent concentrations used were 0.3 molar oxime and the aqueous feed 6g/l Cu^{2+} and 3g/l Fe^{3+} at pH 2.0.

The main point of interest in these data lies in the different effects observed between the alcohol and nonyl phenol modifiers on the kinetics of the extractant under low temperature conditions. A combination of P50 oxime with an alcohol modifier clearly offers the best approach to obtaining high stage efficiencies under these conditions (other than using the unmodified aldoxime and accepting a lower transfer efficiency). The economic significance of obtaining high stage efficiencies in solvent extraction processes is readily appreciated when it is considered that an improvement of only 1% in copper recovery in a plant with a capacity of 20,000 tonnes per annum recovers extra copper with a market value of approximately \$300,000.

Phase Separation

A similar order of preference of reagents to that shown above has also been observed with regard to phase separation rates. Again, the tridecanol modified reagent

Acorga PT5050 stood up very well under the low temperature conditions that caused a considerable slowing down of phase separation rates with other extractant formulations (10).

Hydrolytic Stability

A concern with oxime based reagents in solvent extraction processes is that their rate of hydrolysis when contacted with strip acid be at an acceptable rate, such that the losses by this cause are as small as possible. In practice this is the case, and the majority of oxime extractants have half lives under real operating conditions of several years. In the course of our recent work however, we have noted interesting differences in the relative effects of different modifiers and formulations on the hydrolytic stability of oximes, enabling us to formulate strong oxime extractants even more resistant to hydrolysis than those hitherto available.

It is evident from previous work carried out by ourselves and others that accelerated degradation tests carried out at elevated temperatures can give quite misleading results and the data can not be accurately extrapolated to indicate the rate of hydrolysis at realistic operating temperatures and acidities (11). Long term stability tests have been carried out independently in which solutions of extractants were stirred continuously with strip acid for several months at temperatures of 30°C. The results are displayed in Table 3.

Table 3 - Half lives of various hydroxy oxime formulations stirred continuously with strip acid at 30°C

<u>Extractant formulation</u>	<u>Half life (years)</u>
P50 oxime + nonylphenol (Acorga P5100)	2.2
P50 oxime + tridecanol (Acorga PT5050)	3.82
P50 oxime + alcohol (3) (Acorga M5615)	4.57
Dodecylsalicylaldoxime + tridecanol	3.25
Dodecylsalicylaldoxime + 2 hydroxy-5-nonyl acetophenone oxime (aldoxime-Ketoxime mixture)	3.05

These results show up clear differences in the rate of hydrolysis of an oxime when formulated with different modifiers and shown how careful selection of modifier can be used to effect a considerable improvement in reagent stability.

Entrainment and Crud

Crud can be a nuisance with certain siliceous leach solutions and manifests itself as a mass of solid stabilised emulsion in the settlers. Modifiers are not the primary cause of such cruds, since cruds can be readily generated simply by contacting siliceous feed solutions with reagent free Kerosene: they can however have some influence on the amounts of crud generated. Entrainment of organic in

aqueous adversely affects tankhouse operations and represents a source of reagent loss, so that steps are usually taken to minimise it. Entrainment of aqueous in the loaded organic phase represents another means of transfer of iron to the tankhouse electrolyte. Under conditions, of high iron concentration in the feed, iron transference to the electrolyte by this means can outweigh the high selectivity advantages of the reagent.

We have examined a number of extractant formulations using different modifiers, including alkyl phenols, fatty alcohols, and esters. In particular we have looked at the effect of structural differences in compounds to see if their interfacial properties can be related to the generation of crud and entrainment. In experiments using small pilot scale mixer settlers, various extractant solutions were contacted with real mine solutions and periodic measurements made of entrainment levels (parts per million) and rate of crud generation (mm per hour). Results for some of these formulations are displayed in Table 4 and show clear differences between various modifiers examined. The particular alcohol (3) gave marked improvements in entrainment levels over other alcohols tested as modifiers under most operating conditions, and this trend was confirmed in later experiments carried out using a different feed solution.

Table 4 Entrainment levels (ppm) and crud generation (m.m.hr⁻¹) for formulations of P50 oxime with various modifiers

Modifier	<u>Organic continuous dispersion</u>			<u>Aqueous continuous dispersion</u>		
	<u>Entrainment (ppm)</u>		<u>Crud</u> mm hr ⁻¹	<u>Entrainment(ppm)</u>		<u>Crud</u> mm hr ⁻¹
	O in A	A in O		O in A	A in O	
alcohol(1)	147	675	1.6	90	117	0.75
alcohol(2)	313	792	3.4	50	350	5
alcohol(3)	73	467	2.2	120	0	0.75
Ester (1)	300	1125	14	360	3000	11.5
Ester (2)	53	25	0.57	94	50	1.0

The results with the two esters also reveal marked differences with respect to both entrainment and crud generation. In earlier work the ester (1) had shown considerable promise as a modifier for o-hydroxybenzaloximes because of the resulting very high Cu-Fe selectivity and good hydrolytic stability. It was rejected however on account of its adverse properties with respect to the amounts of entrainment and crud generated. The data in Table 4 show how these problems can be overcome by use of an alternative ester, No (2) in the table. Extension of this study to other reagent formulations showed that by careful selection of the modifier, extractant formulations can be produced having better performance with regard to crud and entrainment levels than formulations containing no modifier at all.

The ACORGA M Range of Extractants for Copper

We believe the approach pioneered by ICI and Acorga based on an understanding of the principles of modifier effects offers the preferred way forward to the formulation of extractants of improved performance, and also offers the technically exciting facility of tailoring reagents to optimise specific plant requirements. A result of this is the new Acorga M Range of extractants based on formulations of P50 oxime with modifiers selected on the basis of our current work. Typical members of this Range are Acorga M5397 and Acorga M5615, both of which are strong extractants, similar in strength to Acorga P5100; but with sharply improved properties in specific areas.

Trials have been carried out recently for a major commercial solvent extraction plant currently using a mixture of reagents, but which wished to increase throughput and reduce transfer of iron to the tankhouse. The feed solution at this operation contains approximately 3.5gpl Cu^{2+} , 3.5gpl Fe^{3+} and pH 1.5. The entrainment levels with Acorga M5615 - particularly of aqueous in organic - were less than half those obtained with Acorga P5100 and a very marked improvement on the level of entrainment currently being experienced in the plant with mixed ketoxime/aldoxime reagents. The copper/iron transfer ratios obtained using the different reagent solutions were as follows:

<u>Reagent</u>	<u>Cu/Fe ratio</u>
Current plant organic	171
25 v/o Acorga P5100	310
25 v/o Acorga M5615	1088

In another operation, a means of reducing aqueous in organic (A in O) entrainment was needed, whilst still maintaining organic phase continuity: large scale pilot trials were carried out and careful studies were made of entrainment levels at a number of points in the operation. Numerous measurements were made over several days and the averages of the figures recorded are shown in Table 5.

Table 5 Entrainment levels during trials of Acorga M5615

<u>Measurement point</u>	<u>Entrainment</u>
Aqueous in organic stream from 1st extract stage	98ppm
Aqueous in organic stream from 2nd strip stage	26ppm
Organic in aqueous stream from 2nd extraction stage	40ppm
Organic in aqueous from 1st strip stage	14ppm

Entrainment levels of aqueous in the organic stream exiting the first extraction stage of greater than 1000ppm had often been recorded during trials with a competitive reagent. In addition, there was a substantial reduction in crud generation with Acorga M5615.

Important benefits of Acorga M5615 are thus seen to be with regard to selectivity and entrainment. In addition, this reagent offers substantial improvements in hydrolytic stability over other aldoxime formulations. Its utility will no doubt lie in the economic as well as technical benefits it can bring to a particular solvent extraction operations.

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Where experiments reported in this paper involve commercial reagents the reagents have been used in the form received from the manufacturers and are assumed to be representative of the commercial product.

Interest in chloride hydrometallurgical processes has been increasing in recent years. Many different processes have been proposed in attempts to treat a wide variety of materials, including complex sulphide ores, Red Sea muds and scrap metals (1). Most of these processes involve dissolution of the valuable base metals, followed by stages to separate and purify the metal constituents. Removal of lead by cooling and precipitation of the chloride is often suggested; however the solubility of lead chloride is a complex function of chloride activity (2) and alternative means of lead removal need to be investigated. Solvent extraction and ion exchange are two well-known hydrometallurgical separation techniques, but whereas the behaviour of metals such as copper, zinc, cobalt and nickel when undergoing extraction from chloride media is reasonably well known, the detailed behaviour of the often associated lead is not. Furthermore the common base metal solvent extraction reagents were developed for use in sulphate media, in which the solubility of lead is extremely low; clearly with chloride solutions this is no longer the case.

Studies have been made of the solvent extraction of lead from chloride and nitrate solutions using carboxylic acids (3,4), and also from acetate solutions using Lix 34 (5). The solvent extraction of lead from chloride solutions with amines has received greater attention (6,7), and has been proposed as an alternative to crystallisation for lead removal from chloride solutions. However, this technique is most effective at low to moderate chloride concentrations (less than 4 M); at higher concentrations extraction is reduced, suggesting that the complex anion $PbCl_4^{2-}$, which predominates in solutions of high chloride activity, is not extractable (6,7). The solvent extraction of lead from solutions of moderate chloride activity (2 M) using an alkyl phosphoric acid has been investigated, and shown to be non-stoichiometric (8).

This paper reports the solvent extraction of lead from chloride solutions of concentration ranging from 0 to 5 M, using the following commonly available solvent extraction reagents: di-(2-ethylhexyl)phosphoric acid (D2EHPA) - (supplied by Union Carbide Inc), Versatic 10 (Shell Chemical Co), Lix 34, Lix 54, Lix 70, Alamine 336 and Aliquat 336 (General Mills Inc) and Kellex 100 (Ashland Chemical Company). Values are presented for distribution coefficients, stability constants, inferred complex structures and the effects of pH and temperature upon extraction.

EXPERIMENTAL

Organic solutions were prepared by mixing the required volume of "as received" extractant with kerosene ("heavy distillate", BDH Ltd), also nonyl phenol (30%) was added to Kellex 100 and dodecanol to Alamine 336 (13% v/v) and Aliquat 336 (15%)

as phase modifiers. The functional groups, structures and physical properties of these extractants are adequately described elsewhere (9); in summary they represent extractants based upon alkyl phosphoric and carboxylic acids, alkarylsulphonamide, β -diketone and hydroxyoxime structures, 8 hydroxyquinoline and tertiary and quaternary amines.

All the pH-dependent extractions at constant temperature were conducted in an AKUFVE instrument, using aqueous solutions of constant ionic strength (5 M, based upon molarity at 20°C) with A.R. grade sodium perchlorate as backing electrolyte. Lead analysis was carried out by sampling and subsequent sample dilution before atomic absorption spectrophotometry. At the start of a particular extraction, or stripping, experiment involving the incremental addition of alkali (8 M sodium hydroxide) or acid (8 M hydrochloric or 4 M perchloric acid) an organic phase sample was also taken, stripped with 2 M NaCl solution at pH 1 and the strip solution analysed for lead. Subsequently organic lead concentrations were calculated by mass balance using the aqueous lead concentration, and the distribution coefficient (D) readily followed. The gradient of the linear relation between log D and pH was calculated over the region $-1 < \log D < 1$. Extractions conducted over a range of temperatures, to provide data for enthalpy calculations, were performed in a glass mixer/settler unit (10); solution temperature was maintained to within $\pm 0.5^\circ\text{C}$ by the use of a thermostatic water bath.

Extractions using the amines were performed by a "shake flask" technique, using 25 cm³ phase volumes. The flasks were shaken at room temperature ($\sim 20^\circ\text{C}$) for 7 h before the phases were allowed to disengage, followed by sampling and analysis.

RESULTS AND DISCUSSION

Most of the experimental results are presented in Table 1 on the basis of a linear relation between log D and pH. Many simplifications and assumptions must be made in proposing this linear relation (9), however, it does provide a simple means of representing the extraction data in tabular form, and has the advantage that the other parameter frequently used to represent extraction data, extraction efficiency, can be inferred from it.

The extraction equation for lead undergoing solvent extraction with an acidic or chelating organic extractant (HA) can be represented by the equation:



where p is the degree of polymerisation of the extractant in the organic phase, m the number of molecules of extractant required per atom of lead extracted and superscript bars represent the organic phase. Equation (1) does not take into account any polymerisation of the organic lead complex; this has been neglected because the log D vs pH relations provided in Table 1 all show correlation coefficients

TABLE 1 Extraction of lead from chloride solutions at 25°C using various extractants. Initial lead concentration 500 mg.l⁻¹, ionic strength (NaCl and NaClO₄) 5 M.

Chloride concn. (M)	Extractant concn. (% v/v)	pH of half extraction	Gradient by regression	Correlation coefficient	Number of points
Extractant D2EHPA					
0.02	5	1.27	2.0	0.998	4
0.02	10	0.90	2.0	0.990	4
0.02	15	0.69	2.0	0.990	4
0.02	20	0.56	2.0	0.990	5
0.5	20	1.56	2.0	0.990	7
1.0	20	2.00	2.0*		8
1.8	20	2.55	2.0*		6
3.0	20	3.80	curved		8
4.0	20	-	curved		7
5.0	20	-	curved		7
Extractant Versatic 10					
0.02	5	3.91	2.0	1	4
0.02	10	3.62	2.0	1	4
0.02	15	3.40	2.0	0.998	5
0.02	20	3.29	2.0	0.999	6
0.5	20	4.14	1.9	0.993	6
1.0	20	4.61	2.1	1	7
2.0	20	5.10	1.9	0.994	7
3.0	20	5.43	2.2	1	5
4.0	20	5.74	2.3	1	4
5.0	20	5.79	1.9	0.997	6
Extractant Lix 34					
0.02	5	4.70	1.7	1	5
0.02	10	4.46	1.6	0.998	5
0.02	15	4.27	1.8	0.986	5
0.02	20	4.02	1.3	1	4
0.5	20	5.07	2.0	0.998	4
1.0	20	5.42	1.4	0.996	6
2.0	20	5.97	1.9	0.997	4
3.0	20	6.25	2.2	0.995	6
Extractant Lix 54					
0.02	30	5.58	1.8	0.990	5
0.02	50	5.08	2.0	0.995	5
1.0	50	6.41	1.8	0.995	4
2.0	50	6.90	1.8	0.994	5
Extractant Lix 70					
0.02	10	4.82	1.8	0.998	5
0.02	15	4.62	1.7	0.999	3
0.02	20	4.49	1.9	0.997	4
0.5	20	5.42	1.8	0.994	4
1.0	20	5.86	1.7	0.999	6
2.0	20	6.39	1.9	0.999	6
3.0	20	6.75	1.8	0.999	6
4.0	20	7.00	1.7	1	5
5.0	20	7.16	1.8	1	5
Extractant Kelex 100					
0.02	7.4	3.15	1.9	0.998	5
0.5	7.4	3.97	1.9	0.997	4
1.0	7.4	4.37	2.1	1	5
2.0	7.4	4.86	1.8	0.999	7
3.0	4.5	5.36	1.9	0.999	5
3.0	6.0	5.30	1.9	1	6
3.0	7.4	5.14	2.0	1	6
4.0	7.4	5.40	1.7	0.998	4
5.0	7.4	5.49	1.9	1	4

*Based over a limited range - see Figure 1

approaching unity and polymerisation of the extracted species is usually associated with curvature of this relation. The stoichiometry of equation (1) provides the following mathematical relation (allowing for the formation of aqueous lead chloro-complexes):

$$\log D = 2\text{pH} + \log k + \frac{m}{p} \log[(\text{HAA})_p] - \log \left(1 + \sum_{i=1}^{i=4} \beta_i [\text{Cl}^-]^i \right) \quad (2)$$

where k is the extraction equilibrium coefficient and β_i the stability constant for the aqueous lead chloride complex, thus

$$\text{Pb}^{2+} + i\text{Cl}^- = \text{PbCl}_i^{(2-i)+} \quad \text{and} \quad \beta_i = \frac{[\text{PbCl}_i^{(2-i)+}]}{[\text{Pb}^{2+}][\text{Cl}^-]^i} \quad \text{where } i=1 \text{ to } 4$$

It is well recognised that equations such as (1) and (2) should be written in terms of activities and not concentrations (2). However, the use of aqueous media of constant ionic strength facilitates the assumption of constant activity coefficients, so that the data presented in Table 1 should be consistent and quantitatively comparable.

Values of m (equation (2)) can be calculated by considering the variation of pH of half extraction ($\text{pH}_{0.5}$ - defined as the pH at which equal concentrations of lead exist in each phase) with extractant concentration, for a constant value of $\log D$ (usually taken at $\log D = 0$):

$$\frac{d \text{pH}_{0.5}}{d \log [(\text{HAA})_p]} = \frac{-m}{2 \cdot p} \quad (3)$$

The values of p were assumed to be 2, 2, 2, 1, 2 and 1 for D2EHPA, Versatic 10, Lix 34, Lix 54, Lix 70 and Kelex 100 respectively. Substituting these values into equation (3) provides the species PbA_2 for the extracted structure formed with Kelex 100, and $\text{PbA}_2 \cdot 2\text{HA}$ for the other extractants. These structures neglect the possibility of solvating molecules associated with the organic lead complex, either as transferred water or organic solvent.

Further useful information can be obtained from the variation of $\text{pH}_{0.5}$ with chloride concentration, for a fixed concentration of a particular extractant. Equation (2) was used to predict the variation of $\text{pH}_{0.5}$ ($\Delta \text{pH}_{0.5}$) with chloride concentration, for given values of β_1 to β_4 (2), but failed to provide values for $\Delta \text{pH}_{0.5}$ as large as those observed experimentally. If single ion chloride activity coefficients (γ_{Cl^-}) are introduced into the final term of equation (2) then it becomes:

$$\dots -\log \left(1 + \sum_{i=1}^{i=4} \beta_i [\text{Cl}^-]^i \gamma_{\text{Cl}^-}^i \right) \quad (4)$$

It can be seen that to provide values of $\Delta \text{pH}_{0.5}$ equal to those observed γ_{Cl^-} would need to take values considerably greater than unity. Such values would be expected in certain electrolytes at moderate to high chloride concentrations, but in 5 M sodium chloride γ_{Cl^-} has been estimated to be 0.941 (2).

An alternative explanation for the observed large values of $\Delta \text{pH}_{0.5}$ may be due to the formation of inextractable complexes of lead with ligands other than chloride. Table 1 shows that the differences between $\text{pH}_{0.5}$ at $[\text{Cl}] = 3$ and at $[\text{Cl}] = 0.02$ for the extractants Kelex 100, Versatic 10, Lix 34 and Lix 70 are 1.99, 2.14, 2.23 and 2.26 respectively, and the values of $\text{pH}_{0.5}$ at $[\text{Cl}] = 0.02$ are 3.15, 3.29, 4.02 and 4.49, i.e. the value of $\Delta \text{pH}_{0.5}$ is itself pH dependent. Therefore, it is likely that an inextractable lead complex, possibly involving hydroxide ions is formed. Published stability constants (for lead hydroxide) indicate that concentrations of this species are insignificant below pH 6, and only extremely low up to pH 8 (11). However, the hydroxy-chloro lead compounds $\text{Pb}_2(\text{OH})_3\text{Cl}$ and $\text{Pb}(\text{OH})_2\text{PbCl}_2$ are known to exist and it is possible that these are formed and not extracted in aqueous solution. If the effect of all these hydroxide-related species are combined in the general term $\alpha(\text{OH}^-)$, equation (2) can be extended:

$$\log D = 2\text{pH} + \log k + \frac{m}{p} \log \left[\frac{(\text{HA})}{\text{p}} \right] - \log \left(1 + \sum_{i=1}^{i=4} \beta_i [\text{Cl}^-]^i \right) - \log (1 + \alpha(\text{OH}^-)) \quad (5)$$

Thus on increasing the pH, and consequently the concentration of OH^- , progressively lower values of $\log D$ would be obtained using equation (5) than are calculated using equation (2). This effect may also explain why the gradient of the $\log D - \text{pH}$ line is generally slightly below the expected value of 2.

Equation (5) demonstrates that on considering the extrapolated value of $\log D$ at pH of zero, then the term $\log (1 + \alpha(\text{OH}^-))$ tends to zero. Therefore, despite the obvious occurrence of a hydroxide related complex values of $\log k$, and consequently k , can be reliably obtained by rearranging equation (5) thus:

$$\log k = \log D + \log \left(1 + \sum_{i=1}^{i=4} \beta_i [\text{Cl}^-]^i \right) - \frac{m}{p} \log \left[\frac{(\text{HA})}{\text{p}} \right] \quad (6)$$

Extraction coefficients derived using equation (6) are: 1.5 , 1.3×10^{-7} , 6.6×10^{-7} , 4.2×10^{-11} , 7.7×10^{-7} and 2.9×10^{-5} for the extractants D2EHPA, Versatic 10, Lix 34, Lix 54, Lix 70 and Kelex 100 respectively. The common base metal hydroxyoxime extractants Lix 64N and Acorga P5300 (20% v/v in kerosene) were also used, but no measurable lead extraction took place below pH 7, and at this pH precipitation of basic lead salts occurred. However, an indication of the complexing power of Lix 64N for lead can be obtained by considering the closely related extractant Lix 70, which is more acidic by virtue of substitution of a chlorine atom, and is a stronger cation exchange extractant. Thus under comparable conditions, the value of $\text{pH}_{0.5}$ for extraction of zinc by Lix 70 was found to be one pH unit less than that for Lix 64N. Assuming similar behaviour with lead in 2 M chloride solution, the $\text{pH}_{0.5}$ value for Lix 64N would be 7.4, and the corresponding k value 1.6×10^{-10} .

The calculated extraction coefficients clearly indicate that of those examined, D2EHPA is the strongest extractant for lead in aqueous chloride solution. However, Figure 1 shows that lead extraction proceeds in a manner consistent with equation (5) only for chloride concentrations $< 0.5 \text{ M}$; at higher concentrations the observed

extraction coefficient is much less than predicted by equation (6). Many possible explanations of this behaviour were tested, for example, formation of extractable lead chloride species and/or an aqueous lead-D2EHPA complex and/or extraction of sodium from the aqueous phase with consequent depletion of the extractant, but none could account for such a large deviation from theoretical behaviour. D2EHPA was the only extractant to show behaviour inconsistent with equation (5), consequently log D - pH relations for the rest of the extractants can be inferred from Table 1.

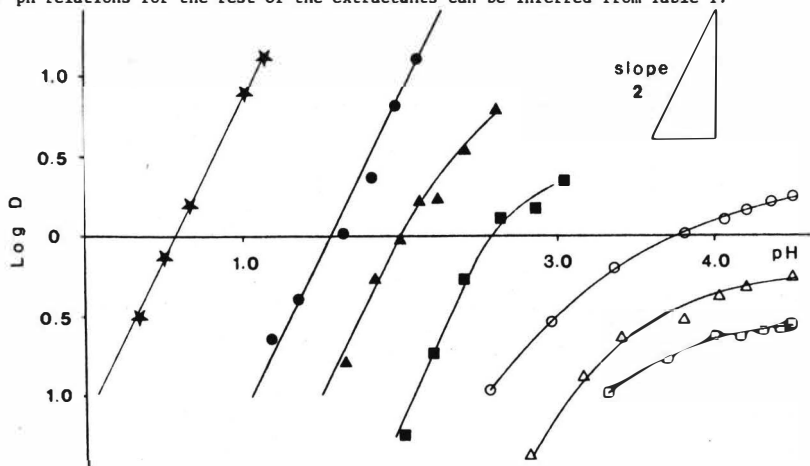


Figure 1 Extraction of lead from chloride solutions with 20% v/v D2EHPA in kerosene. Initial lead concentration 500 mg.l^{-1} ; ionic strength (NaCl & NaClO_4) 5 M, temperature 25°C . Chloride concn. (M): \star - 0.02, \bullet - 0.5, \blacktriangle - 1.0, \blacksquare - 1.8, \circ - 3.0, \triangle - 4.0 and \square - 5.0.

Rapid lead extraction rates were noted for the acidic extractants, less than five minutes was required to reach equilibrium. The chelating agents Lix 34, Lix 70 and Kelex 100 took slightly longer and Lix 54 required at least eight minutes to equilibrate. Accurate pH control was also very difficult with Lix 54, and the phase disengagement of Lix 70, in a glass mixer/settler unit, was poor at 25 at 43°C .

Accurate kinetic studies were beyond the scope of this study, but investigation of the effect of temperature on extraction was examined for the extractants D2EHPA, Versatic 10, Lix 70 and Kelex 100. Table 2 shows the variation of $\text{pH}_{0.5}$ with temperature for the four extractants. Enthalpy was calculated via the Gibbs-Helmholtz equation, arranged for enthalpy variation:

$$\frac{d(\ln k)}{d(1/T)} = \frac{d(\ln D)}{d(1/T)} = \frac{-\Delta H}{R} \quad (7)$$

which shows that ΔH may be derived from the gradient of a graph of $\log D$ vs $1/T$. It appears that lead extraction is exothermic for D2EHPA, Lix 70 and Kelex 100, consequently an increase in temperature is accompanied by a decrease in extraction. The enthalpy values are approximately twice those reported for extraction of copper

Table 2 Effect of temperature and calculated enthalpies of extraction of lead from 2 M chloride solution. Initial lead conc. 500 mg.l^{-1} ; ionic strength 2 M.

Extractant (conc in kerosene)	Temperature (C)	pH 0.5	Gradient of equation (7)	Correlation coefficient	Enthalpy (KJ/mole)
D2EHPA (20% v/v)	26	2.40	2116	0.963	-40.5
	45	2.57			
	60	2.89			
Versatic 10 (20% v/v)	25	5.00	No temperature variation		
	42	5.04			
	56	4.99			
Lix 70 (20% v/v)	25	6.02	2794	0.997	-53.5
	43	6.34			
	62	6.54			
Kelex 100 (4.5% v/v)	26	5.09	2882	0.989	-55.2
	45	5.31			
	65	5.64			

with hydroxyoximes (12). However, no account has been taken of any variation of the concentration of lead chloro-complexes with temperature, which if endothermic could reduce the free lead concentration and the distribution coefficient. Lead extraction using the tertiary amine Alamine 336 and the quaternary compound Aliquat 336 (Figure 2) gave the same pattern of extraction in relation to chloride concentration that has been noted before (6,7). Both produced greater than 75% extraction of lead at chloride concentrations less than 1 M, but extraction was less

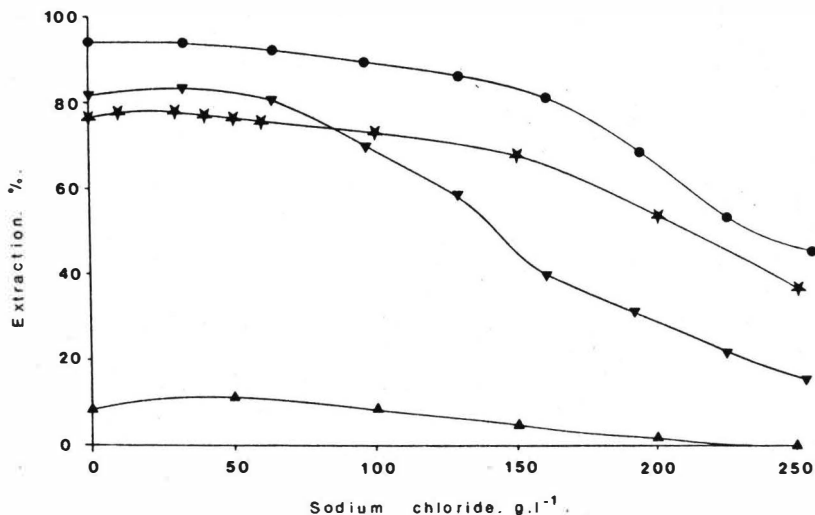


Figure 2 Extraction of lead from chloride solutions with amine extractants. Initial lead conc. 500 mg.l^{-1} , ionic strength (NaCl & NaClO_4) 5M, temperature 25C. Alamine 336: * - 160 g.l^{-1} in kerosene, • - 160 g.l^{-1} in Shell-solve, ref 6 Aliquat 336: ▲ - 50 g.l^{-1} in kerosene, ▼ - 50 g.l^{-1} in Shell-solve, ref 6.

than 50% from 5 M sodium chloride solution, for all the extractant concentrations used (up to 160 g.l^{-1} extractant). For both amines, extraction was improved by the use of an aromatic diluent (Shellsolve) in preference to an aliphatic one (kerosene).

CONCLUSIONS

All the acidic and chelating reagents investigated will extract lead from aqueous chloride solutions, under certain conditions of pH and chloride concentration. All these reagents provided extraction behaviour consistent with accepted cation exchange theory (equation (1)), except for D2EHPA at chloride concentrations greater than 0.5 M. The commercial application of this reagent at high chloride concentrations is unlikely, due to the observed considerable decline in extraction below the predicted value. The chelating agents, originally designed for solvent extraction of copper, gave low equilibrium extraction coefficients, indicating that they form only weak lead complexes. Lead extraction by D2EHPA, Lix 70 and Kelex 100 was depressed on increasing the temperature, but Versatic was unaffected.

The amines Alamine 336 and Aliquat 336 both showed reduced lead extraction on increasing the chloride concentration. Extraction in both cases was improved by the use of an aromatic diluent.

Selection of an appropriate solvent extraction reagent depends on the metals present and the separations desired. This work has shown how some of the common reagents behave toward lead chloride solutions, and should be of use to the hydrometallurgist whether the metal is extracted for subsequent recovery, as a means of impurity removal or even as a study of the conditions to be avoided during the solvent extraction of more valuable metals, in the presence of aqueous lead chloride.

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MATHEMATICAL MODELS FOR THE RATE OF METAL EXTRACTION:
WHICH ONE DESCRIBES YOUR SYSTEM?

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The study of the rate of extraction in a given system has as a final objective the development of a design equation that includes mass transfer and chemical reaction parameters. In order to establish the dependence of the extraction rate on these parameters the relative importance of mass transfer and chemical reaction rates has to be investigated at different concentrations and hydrodynamic conditions. In addition knowledge of the location of the rate controlling chemical reaction is required before a mathematical model for the rate of extraction can be developed. All this information has to be provided by a set of experimental data obtained usually in a single laboratory contactor. One of the main limitations of the experimental techniques more widely used, is the narrow range of conditions under which they can be operated. Besides, the description of their hydrodynamic behaviour is in most cases insufficient to allow modelling from results obtained under simultaneous mass transfer and chemical reaction control [1]. The assumption of chemical control in cases of mixed control leads to models that do not represent the mechanism of transfer and hence may not fit results outside the range of conditions used to establish them [2]. Danesi and Chiarizia [3] published a critical review of mathematical models used to describe the kinetics of extraction of metal ions and indicated the need to identify the rate controlling mechanisms in order to select the right one. Criteria used to establish the nature of the rate controlling steps were analysed by Danesi [4] who pointed out that in many cases the evidence they provide is inconclusive.

The difficulties encountered in modelling metal extraction are apparent in the literature, where examples are formed of different chemical kinetic models, proposed for the same system [2,5] as well as of different models that fit the same experimental results [6].

In this work simulated experimental results are analysed with the purpose of selecting a mathematical model for the rate of transfer. Three models that describe different rate controlling mechanisms and location of the reaction are found to fit the data. Conclusions derived from numerical analysis of these three models are used to propose an experimental procedure to select the right one.

'Experimental'

It was assumed that the simulated experimental results were obtained using an experimental technique that provided a well defined interfacial area. The rate controlling mechanisms of extraction are unknown but combined mass transfer and chemical control is not ruled out. All experiments were conducted at the same hydrodynamic conditions. The stoichiometry of the overall reaction is:



where bars indicate species in the organic phase.

The location of the rate controlling reaction is not known but it was assumed was either the interface or the aqueous diffusional film. Experimental results for the variations of interfacial flux with the concentrations of metal ion and extractant are indicated by crosses in Figures 1 and 2.

Mathematical Models and Analysis of Results

Three mathematical models that include mass transfer coefficients fit well the experimental results. The model for very fast interfacial reaction proposed by Chapman et al [7] gives the following expression:

$$K_E = \frac{\left(C_{MRb} + \frac{R}{K_{MR}}\right) \left(C_{Hb} + \frac{2R}{K_H}\right)^2}{\left(C_{Mb} - \frac{R}{K_M}\right) \left(C_{HRb} - \frac{2R}{K_{HR}}\right)^2} \quad (1)$$

This model assumes that the interfacial reaction is at equilibrium.

Hughes and Rod proposed the following model for mass transfer with chemical reaction in the aqueous film:

$$\left(\frac{R}{(\theta C_{Mb})^{\frac{1}{2}} C_{HRb}} \right)^2 = \left(1 - \frac{R}{K_M C_{Mb}} \right) \left(1 - \frac{2R}{K_{HR} C_{HRb}} \right)^2 \quad (2)$$

where

$$\theta = \frac{k_2 D_{HR}}{P_{HR}}$$

This model was developed for a pseudo first order reaction of the form:

$$R = k_2 C_M C_{HR} \quad (2a)$$

where C_M is in excess.

For reactions taking place at the interface at intermediate or slow rate, Ortiz et al [2] developed the equation:

$$\left(\frac{2}{K_I K_H} - \frac{2}{K_M K_{HR}} \right) R^2 + \left(\frac{C_{Hb}}{K_I} + \frac{2C_{Mb}}{K_{HR}} + \frac{C_{HRb}}{K_M} \right) R - C_{Mb} C_{HRb} = 0 \quad (3)$$

Equation 3 corresponds to a reaction rate given by:

$$R = k_I C_M C_{HR} C_H^{-1} \quad (3a)$$

In order to facilitate calculations the following simplification was introduced.

$$K_M = K_{HR} = K_H = \frac{1}{2} K_{MR}$$

It was assumed that the equilibrium constant K_E was known from equilibrium studies and that approximate values of the mass transfer coefficients could be estimated. A value $K_E = 1 \times 10^{-4}$ was used in the calculations. On the other hand the rate constants of chemical reaction in equations (2) and (3) are unknown. Equations (1) to (3) were solved for different values of k_2 and k_I . For $K_M = 1 \times 10^{-4} \text{ ms}^{-1}$, $k_2 = 1 \times 10^3 \text{ kmol}^{-1} \text{ m}^3 \text{ s}^{-1}$ and $k_I = 3.16 \times 10^{-7} \text{ ms}^{-1}$, the three equations fitted the 'experimental' results as shown in Figures 1 and 2. Therefore, a model could not be selected from this 'experimental' set of results. It should be pointed out that although the experimental data are simulated, they represent well the type of results obtained in contactors with no facilities for changing the mass transfer coefficients[1].

Numerical Analysis of the Models

Figure 3 shows the response of the models to changes in the mass transfer coefficients. It can be seen that at $K_M = 1 \times 10^{-4}$ m/s the three models give close values of R but they diverge as soon as K_M is changed. Model 1 has the highest order of dependence on K_M as expected from a model for very fast reaction. Model 2 has just reached a plateau, i.e. a region where R becomes independent of the mass transfer coefficients, while Model 3 is still in the mixed regime. Hence at the conditions of the experiments it is very easy to select the right model by changing the mass transfer coefficients. However, in a different extraction system and concentration ranges the divergence between Models 2 and 3 may not be as large. This is shown in Figure 4 curve (a) for $C_M = 0.01$ and $C_{HR} = 0.001$. Here the two models remain close over the entire range of K_M . However, as reported by Hughes and Rod [6], due to the heterogeneous nature of the reaction a change in the ratio C_M/C_{HR} for constant rate of reaction (i.e. $C_M C_{HR} = \text{const}$) is followed by a change in the rate of extraction if the reaction takes place in the aqueous film. This is shown by curve (b) obtained with Model 2 for $C_M = 0.001$ and $C_{HR} = 0.01$. This is not the case for interfacial reactions so the curve for $C_M = 0.001$ and $C_{HR} = 0.01$ calculated with Model 3 overlaps with curve (a). This difference in the behaviour of the two models indicates a way to establish the location of the rate controlling reaction.

Plots of the extraction flux versus C_M and C_{HR} at the conditions of curve (a) for the two models are given in Figures 5 and 6. It can be seen that although the dependence of R on C_{HR} is similar for Models 2 and 3, the values obtained by varying C_M are quite different.

Conclusions and Recommendations on Experimental Procedure

An example is given in which simulated experimental results, obtained in a wide interval of metal and extractant concentrations but at the same hydrodynamic conditions, could be fitted by three quite different mathematical models. Numerical analysis of the sensitivity of these models to variations in the mass transfer coefficients showed that their overlapping was confined to a narrow region that contained the 'experimental' conditions. Simulation

at a different range of concentrations showed that the models for interfacial reaction [2] and reaction in the aqueous diffusional film can overlap over a very wide interval of mass transfer coefficients. However, by changing metal and reactant concentrations at $C_M C_{HR} = \text{const}$ the two models give different results. Besides, the response of these two models to variations in metal concentration at the conditions of the plateau is quite different.

The above conclusions suggest that in order to select or derive a mathematical model the experimental data should cover a range of mass transfer coefficients and the conditions for a plateau established. If the dependence of the extraction flux on the concentrations of reactants is determined at the plateau conditions, then the effect of the mass transfer coefficients is eliminated.

The location of the rate controlling reaction can be investigated by changing the ratio C_M/C_{HR} at $C_M C_{HR} = \text{constant}$ in the plateau region.

An alternative approach that overcomes some of the experimental limitations is discussed elsewhere [8].

List of Symbols

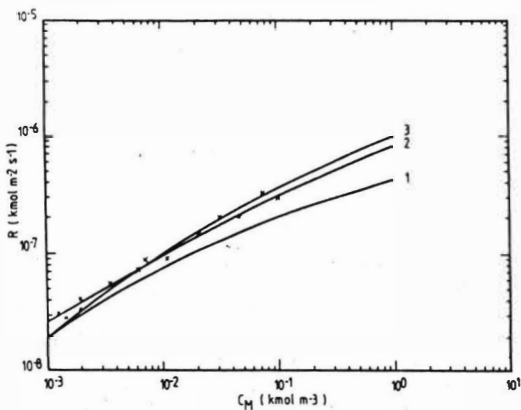
C_j	= concentration of component j, kmol m^{-3}
D	= diffusivity, $\text{m}^2 \text{s}^{-1}$
k_2	= rate constant of a second order reaction, $\text{kmol}^{-1} \text{m}^3 \text{s}^{-1}$
k_I	= surface area based rate constant for the forward reaction, ms^{-1}
K_E	= equilibrium constant
K_j	= mass transfer coefficient of component j, ms^{-1}
P	= partition coefficient
R	= interfacial flux, ms^{-1}

Subscripts

H	= hydrogen ion
HR	= extractant
M	= metal ion
MR	= metal complex
b	= bulk phase

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Note - In Figs. 1, 2 and 3:
 $K_E = 10^{-4}$, $k_I = 3.16 \times 10^{-7}$,
 $k_2 = 10^3$, $D_{HR} = 10^{-9}$, $P_{HR} =$
 100 , $C_H = 10^{-3}$ and $C_{HR} = 10^{-7}$.

Fig. 1 Models 1, 2 and 3:
 $K_M = 10^{-4}$; $C_{HR} = 10^{-1}$.

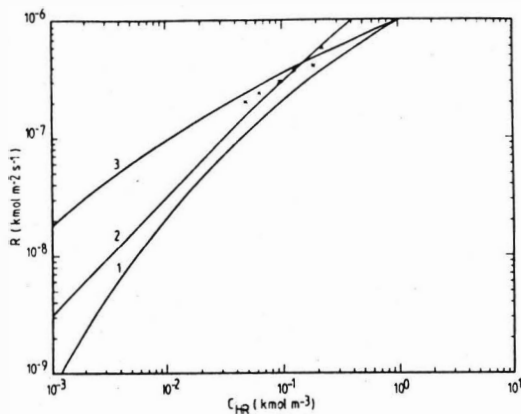


Fig. 2 Models 1, 2 and 3:
 $K_M = 10^{-4}$; $C_M = 10^{-1}$.

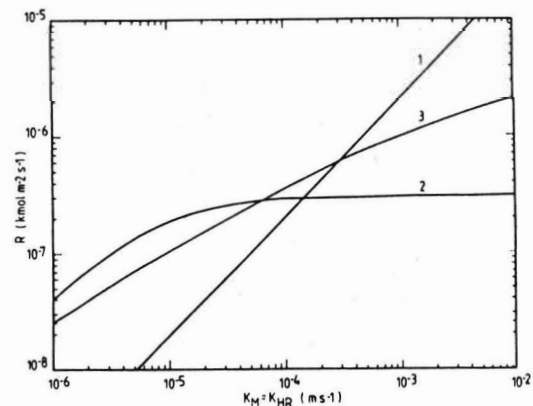
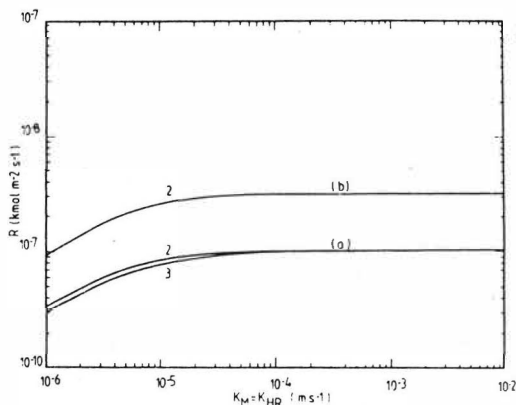


Fig. 3 Models 1, 2 and 3:
 $C_M = 10^{-1}$; $C_{HR} = 10^{-1}$.



Note - in Figs. 4, 5 and 6:
 $k_1 = 10^{-7}$, $k_2 = 10^3$, $C_H = 10^{-3}$,
 $\dot{M}_{HR} = 10^{-9}$, $P_{HR} = 100$.

Fig. 4 Model 2 -

(a) $C_M = 10^{-2}$; $C_{HR} = 10^{-3}$

(b) $C_M = 10^{-3}$; $C_{HR} = 10^{-2}$.

Model 3 -

(a) $C_M = 10^{-2}$; $C_{HR} = 10^{-3}$ and

$C_N = 10^{-3}$; $C_{HR} = 10^{-2}$.

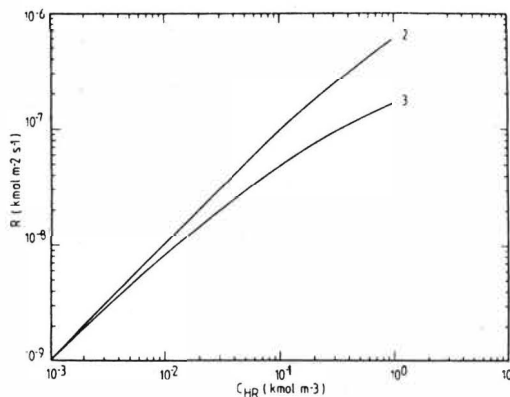


Fig. 5 Models 2 and 3:

$K_M = 10^{-4}$, $C_M = 10^{-2}$.

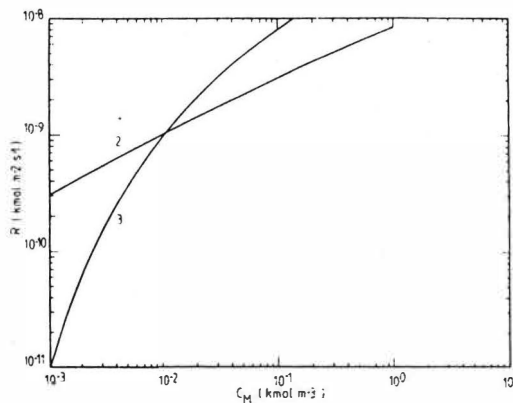


Fig. 6 Models 2 and 3:

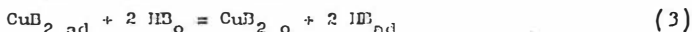
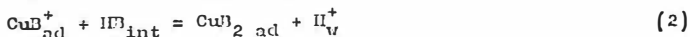
$K_M = 10^{-4}$, $C_{HR} = 10^{-3}$.

THE HYDROPHILE-LIPOPHILE BALANCE OF HYDROXYOXIMES, THEIR ADSORPTION AND THE RATE OF COPPER EXTRACTION

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Hydroxyoximes of the following formula show an explicit amphiphile structure, where: R denotes a long alkyl, usually a branched nonyl or dodecyl group, Y stands for a phenyl, hydrogen or methyl group, and X denotes hydrogen, chlorine or a short alkyl chain. On one side of the molecule they contain two hydrophilic groups, i.e. hydroxyl and oxime groups, and on the other side a long alkyl. Consequently, although the affinities of the hydrophilic groups for the aqueous phase are small, the hydroxyoxime can adsorb at the organic/aqueous interfaces and decrease the interfacial tension in those systems. Depending upon their long alkyl chain and 1 or 2 aromatic rings they are very hydrophobic and are soluble in organic nonpolar diluents. When adsorbed at the interface they are mainly immersed in the organic phase. However, as the length of the alkyl decreases they can penetrate with their hydrophilic heads more deeply into the aqueous phase. Their solubility in the aqueous phase also increases. Thus, their behaviour at the interface depends upon the so-called hydrophile-lipophile balance (HLB) which is generally employed in surfactant physical chemistry (1).

Taking into account the surface activity of hydroxyoximes, their solubility in the aqueous and organic phases, and the dissociation constants of the phenolic group the interfacial mechanism was deduced. Among the different proposals which are similar in their basic points and are only slightly different in their specific items, the following scheme will be discussed (2):



where: subscripts w and o denote a water phase and an organic phase, respectively; subscripts ad and int denote the molecules in the interfacial monolayer and at the border of the sublayer from which the hydroxyoxime molecule is transferred into the monolayer without diffusion.

When adsorption is neglected, which is never the case in real systems

(3), it is thought that the rate of extraction is limited by eq.2.

$$\bar{r} = \frac{k_2 K_1 a [\text{Cu}^{2+}]_w [\text{IO}]_{\text{ad}} [\text{IO}]_{\text{int}}}{[\text{H}^+]_w} \quad \text{and} \quad \bar{r} = \frac{k_2 a [\text{CuB}_2]_o [\text{IO}]_{\text{ad}} [\text{H}^+]_w}{K_3 [\text{IO}]_o^2} \quad (4)$$

Assuming that the equilibrium of oxime adsorption at the interface is quickly established the oxime concentration at the interface is appr. equal to the surface excess. In regions of low and high oxime concentrations the surface excess is proportional to the bulk concentration or is constant, respectively. Thus, $[\text{IO}]_{\text{ad}} = \Gamma = \alpha [\text{IO}]_o$ or $[\text{IO}]_{\text{ad}} = \Gamma = \text{const}$ (4-6). Neglecting diffusion and assuming that the oxime concentration in the aqueous phase is proportional to the oxime concentration in the organic phase the following boundary equations are obtained:

$$\bar{r} = k \frac{[\text{Cu}^{2+}]_w [\text{IO}]_o^2}{[\text{H}^+]_w} \quad \text{and} \quad \bar{r} = k [\text{CuB}_2]_o [\text{H}^+]_w \quad (5)$$

$$\text{or} \quad \bar{r} = k \frac{[\text{Cu}^{2+}]_w [\text{IO}]_o}{[\text{H}^+]_w} \quad \text{and} \quad \bar{r} = k \frac{[\text{CuB}_2]_o [\text{H}^+]_w}{[\text{IO}]_o^2} \quad (6)$$

which may be used to explain the change of the order of the extraction rate against oxime concentration.

However, the use of the equilibrium surface excess does not explain the influence of the oxime structure, especially the length of the alkyl upon the extraction rate, although such attempts are described in the literature (7,8). This means that some other explanation must exist. The discussion of these problems is the subject of our present work.

Experimental

Individual and well defined hydroxyoximes and intermediates were used. The extraction rate was determined by the short contact method (9). The conditions for the kinetic measurements were as follows: temperature, 293 K; oxime concentration in octane, 0.003-0.05 M; copper concentration, 0.015 M; pH of the aqueous phase, 3.0. Interfacial tension was measured at 293 K by the drop volume method using mutually presaturated organic and aqueous phases. The aqueous phase was adjusted by sulphuric acid to pH = 2. The hydrophile-lipophile balance was determined by reversed-phase gas chromatography using ethanol as a polar agent and n-alkanes as nonpolar standards according to the method described previously (10).

Results and Discussion

Regardless of the method used, the applied series of hydroxyoxime homologues and the extraction conditions, the rate of copper extraction increases as the length of the alkyl decreases. For 2-hydroxy-5-alkylbenzaldehyde oximes having a straight alkyl (only in such a case is the oxime structure similar and the influence of alkyl branching upon the extraction rate eliminated) the highest and the lowest extraction rates were observed for oximes having the methyl and dodecyl group in the 5 position, respectively (Fig.1). (More data about the extraction rate as determined by the short contact method, is presented in another paper (11)). This means that the extraction rate decreases as oxime hydrophobicity increases. However, more hydrophobic compounds usually show higher surface activity, i.e. more effectively decrease the interfacial tension, as in the case of the investigated oximes (Fig.2). In the case of alkylphenols the surface activity also increases for the first few homologues having a straight alkyl. However, for alkylphenols having a long and branched alkyl the surface activity is much smaller (Fig.3). This phenomenon is not observed in aromatic diluent/water systems, in which the interfacial tension decreases as the length of the alkyl chain decreases (Fig.4). This different behaviour in octane/water and toluene/water systems can be explained in terms of the cohesion energy between the solvent molecules, the alkyl and the aromatic ring of alkylphenol, as well as by the interactions between hydrocarbon molecules and water, which are quite different for the considered systems. The interactions between octane and alkyl and between toluene and the aromatic ring seem to be more important in the octane/water and toluene/water systems, respectively.

The adsorption of hydroxyoximes can be described by different, partly equivalent, adsorption isotherms, e.g. Gibbs, Henry, Langmuir, Freundlich or Temkin. The application of the Henry isotherm is restricted to only very low oxime concentrations, and is only used for some quick preliminary model calculations of adsorption kinetics. For all other isotherms satisfactory approximations are obtained, although the error of approximation depends upon the considered range of oxime or alkylphenol concentration. The application of the fundamental Gibbs isotherm is limited by the inconvenience and errors of differentiation. The use of the Langmuir isotherm is convenient for adsorption kinetics calculations. The application of the semiempirical Temkin isotherm is very convenient for surface excess calculations.

For the same bulk concentrations the surface excess and the molecular area are of a similar order of magnitude for oximes having various alkyl length. Moreover, in the case of salicyl oximes having a straight alkyl the surface excess slightly increases as the length of the alkyl increases (Fig. 4). Thus, the order of changes is quite different as for that observed for the extraction rate. Compounds having a branched alkyl exhibit lower surface excess, but they extract more quickly.

This behaviour of hydroxyoximes and the relationships observed between the extraction rate and the surface activity of hydroxyoximes can be discussed from the point of view of cohesion energy (12). It is well-known that the cohesive energies (C) of organic solvent for organic solvent (C_{OO}) and water for water (C_{WW}) oppose miscibility and promote phase separation, while the cohesive energy between an organic solvent and water molecules (C_{OW}) promotes miscibility and opposes separation. However in hydrocarbon/water systems: $C_{WW} > C_{OO} \sim C_{OW}$. When in such systems extractant molecules are present which have a lipophilic segment (L) and a hydrophilic segment (H) then 10 possible cohesive energies can be considered: C_{LO} , C_{LL} , C_{OO} , C_{OH} , C_{OL} and C_{HH} , C_{HH} , C_{HW} , C_{HL} , C_{HO} (Fig. 6). The relative magnitude of these ten cohesive energies determines the miscibility and phase relations in this three-component system. If the cohesive energy of any component is greater than the other cohesive energies, that component will separate out as a separate phase. If the cohesive energies of the lipophilic segment of the extractant molecule for the organic solvent (C_{LO}) and of the hydrophilic segment or segments for water molecules (C_{HL}) are greater than the other eight cohesive energies then the extractant molecule is well adsorbed and orientated between the separated organic solvent and water phase. Thus, the magnitude and the ratio of these two cohesive energies determine the behaviour of the extractant molecules: $R = C_{LO}/C_{HL}$. If the cohesive energy on the organic side is greater than the cohesive energy on the water side ($R > 1$) then the extractant molecules are dragged more strongly into organic phase layers. Furthermore, if R is much greater than 1 then the extractant is dissolved in the organic phase and separates from the water phase. If R is much less than 1 then the extractant is dissolved in the water phase and separates from the oil phase.

At the interface which is saturated by the extractant molecules we can assume that C_{OH} and C_{HL} are effectively zero due to lack of access. The same is true of C_{LO} in terms of cohesive energies. The limited degree of contact permits neglecting C_{OW} . Thus, the R coefficient becomes the ratio of the cohesive energy of a mole of lipophilic

together with its associated organic solvent to that of a mole of hydrophile, together with associated water (Fig.7).

In the homologue series of hydroxyoximes having a straight alkyl the hydrophilic segments are the same while the length of the alkyl chain varies. If the alkyl chain increases its molar volume and dispersion (London) interactions increase, then the cohesive energy between the lipophilic segments of the hydroxyoxime molecules, as well as the cohesive energy between the lipophilic segments of hydroxyoxime molecules and the molecules of the hydrocarbon solvent also increase. As a result, oxime molecules are dragged more deeply into the organic phase, and a more vertical position of the oxime molecule and its lipophilic segment is achieved. The adsorbed molecules are more densely packed at the monomolecular layer and their mobility is limited. When the alkyl is branched its molar volume increases but the dispersion energies decrease due to the sterical hindrance. As a result the cohesive energy decreases and the hydroxyoxime molecules become less hydrophobic. Simultaneously, they occupy a greater statistically area in the monolayer at the interface.

All this means that the surface excess cannot be directly related to the extraction rate, and its values do not explain the increase of the extraction rate for more hydrophilic oximes, although in the case of the individual oxime the extraction rate increases as the surface excess increases (Fig.8). It is necessary to point out here that in the region in which the interface is almost saturated and the surface excess is appr. constant, the extraction rate further increases and more sharply for less hydrophobic compounds, i.e. having a short alkyl chain. It seems for us that the rate of copper extraction in the homologue series of hydroxyoximes depends mainly upon the depth of penetration of the oxime hydrophilic groups into the aqueous layers near the interface and upon oxime solubility in the aqueous phase. The approach of the copper hydrated ion to the oxime molecule, and then the oxime molecule to the strongly orientated, charged and partly hydrated intermediate complex, must be enhanced as the oxime molecule and then the intermediate complex are more deeply immersed in the aqueous phase. As a result, the extraction rate increases for more hydrophilic compounds (Fig.9) whose hydrophilicity can be quantitatively measured by the so-called hydrophile-lipophile balance. Similar relations are observed for other extraction systems in which different techniques of extraction rate determination, as well as other oximes and diluents, were used (6,13).

For nonionic surfactants the HLB values on the Griffin scale are in the range of 0-20. The HLB value of 10 is considered as the arbitrary limit between hydrophilic and hydrophobic compounds. Derivatives having higher HLB values show higher affinity for the aqueous phase, are better soluble in the aqueous phase and when adsorbed at the interface they are mainly immersed in the aqueous layers; while compounds having HLB values below 10 show higher affinity for the organic phase and when adsorbed at the interface they are mainly immersed in the organic phase. The HLB values for hydroxyoximes are in the range of 1.6-3.4 on the Griffin scale, which corresponds to their high hydrophobicity and affinity for the organic nonpolar phase. As HLB increases oxime solubility in the aqueous phase also increases according to the following approximate relation: the logarithm of oxime concentration = $a + b \text{ HLB}$ (12).

The relation between the initial extraction rate and oxime HLB is similar to that observed previously by us (6,13), in which kinetic data were obtained by means of other techniques. The extraction rate tends to well-defined asymptotes at the region of the lowest and the highest HLB values, which can be considered as regions of pure interfacial and volume processes, respectively. Assuming this, the contribution of the volume reaction to the overall reaction rate can be calculated as $B = (r - r_s)/(r_v - r_s) \cdot 100\%$, where: r denotes the measured reaction rate, and r_s and r_v stand for the extraction rates of the interfacial and bulk processes, respectively, as determined from the asymptotes of the relation $r = \phi(\text{HLB})$. The shaded area in Fig.10 shows the influence of the alkyl length in 2-hydroxy-5-alkylbenzaldehyde oxime upon the contribution of the volume reaction. For salicyl oximes the contribution of the volume reaction sharply decreases as the length of the alkyl increases, but for almost the whole investigated region the volume reaction cannot be neglected. In the case of 2-hydroxy-5-alkylbenzophenone oximes the contribution of the volume reaction is small and does not exceed 20%. Thus, in the whole investigated region the reaction proceeds mainly at the interface.

When oximes have similar molecular mass their surface concentration and orientation at the interface become the important parameters, as in the case of 2-hydroxy-5-(1,1,4,4-tetramethylbutyl)-benzaldehyde oxime (II) and 2-hydroxy-3,5-di-(*t*-butyl)-benzaldehyde oxime (III). Compound II extracts copper quicker than its analog having a straight alkyl, but it exhibits lower surface activity. This means that II is more hydrophilic than its analog having the straight alkyl, and

therefore III penetrates more deeply into the aqueous layers near the interface. III adsorbs very weakly and extracts copper very slowly. The bulky t-butyl group disturbs the vertical orientation of the oxime molecule at the interface, inhibiting in this way the penetration of the phenolic group into the aqueous layers and contact with copper ions. The bulky Y group in oximes of formula I has a less negative effect on the extraction rate because it is further away from the reaction site.

In the case of 2-hydroxy-5-alkylbenzophenone oximes the Z isomer retards extraction. The same effect on the extraction rate is exhibited by alkylphenols, although this effect is not great, especially when the Z isomer and alkylphenol concentrations are not great and a freshly formed interface is considered. It is not surprising that although the Z isomer forms dimers more easily than the E isomer (14), which is connected with their different structures and different energies of hydrogen bond formation (Fig.11), the Z isomer exhibits higher surface activity, decreasing the interfacial tension more efficiently and at lower concentrations than the E isomer. This means that the extent of oxime dimerization does not determine the adsorption equilibrium of hydroxyoximes, and the negative effect of strong Z oxime dimerization is with the surplus compensated by hydration forces, i.e. cohesion energy between the hydrophilic groups of the oxime and water molecules, occurring at the interface. These forces are stronger for the E isomer which, as a result, becomes more hydrophilic and less surface active in comparison to the Z isomer.

If adsorption equilibrium is achieved the interface should be densely occupied by the molecules of the more surface active Z isomer. In the presence of alkylphenols the interface should be occupied to an important extent by the alkylphenol molecules, which should strongly influence the extraction rate. However, this is not observed because the decrease of the extraction rate is not great. This suggests that either adsorption equilibrium is not achieved or the adsorbed molecules are very mobile. This problem will be discussed in our next paper.

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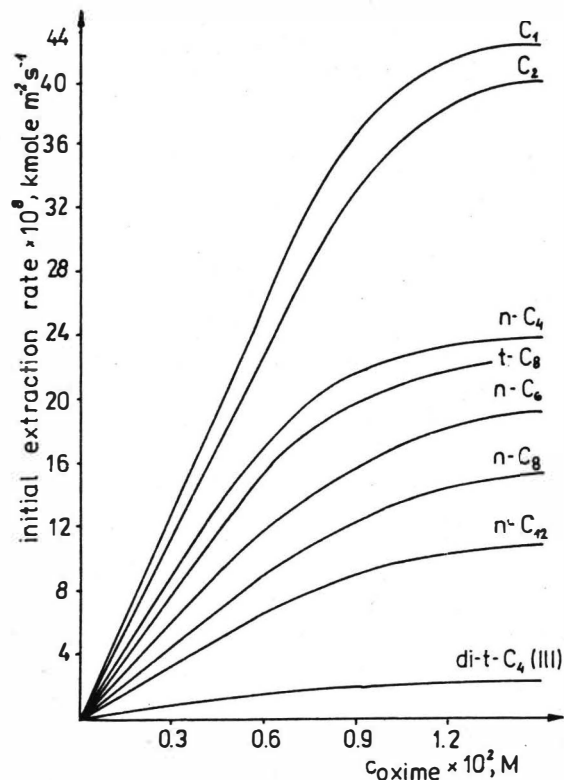


Fig. 1. The influence of alkyl length upon the rate of copper extraction by 2-hydroxy-5-alkylbenzaldehyde oximes

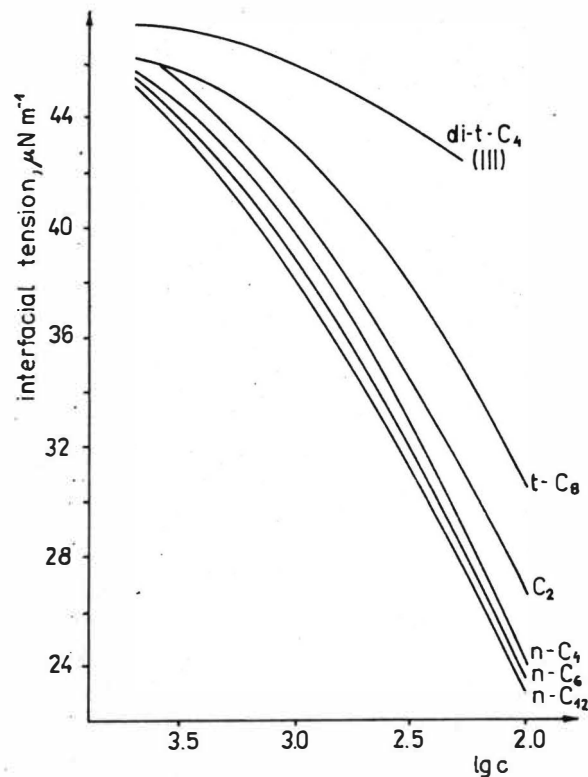


Fig. 2. The interfacial tension for 2-hydroxy-5-alkylbenzophenone oximes

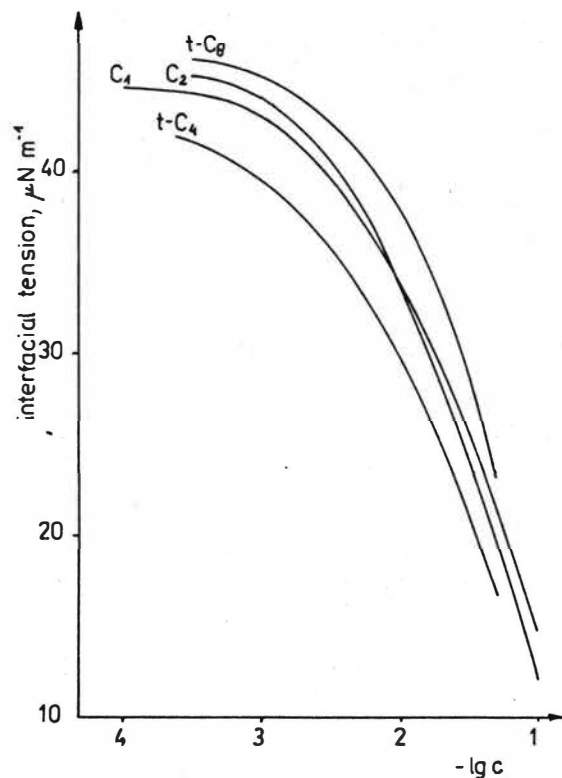


Fig. 3. The interfacial tension for alkylphenols in octane/water interface

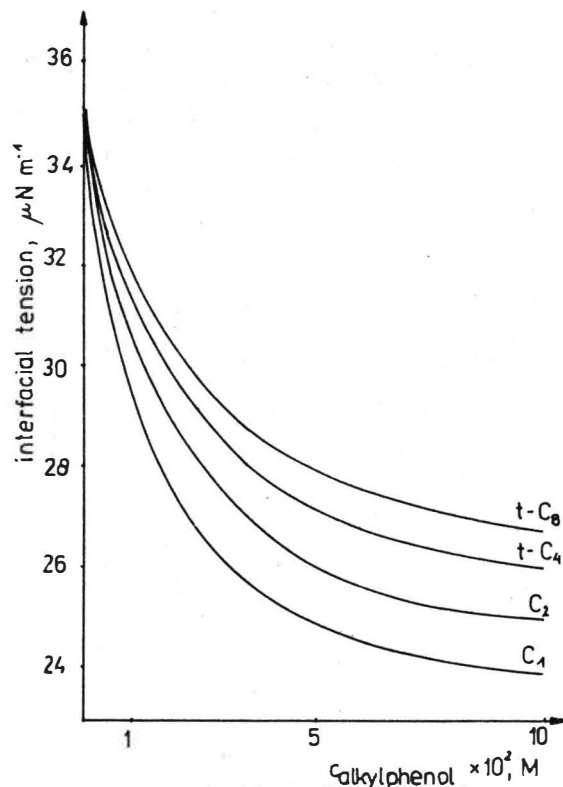


Fig. 4. The interfacial tension for alkylphenols in toluene/water interface

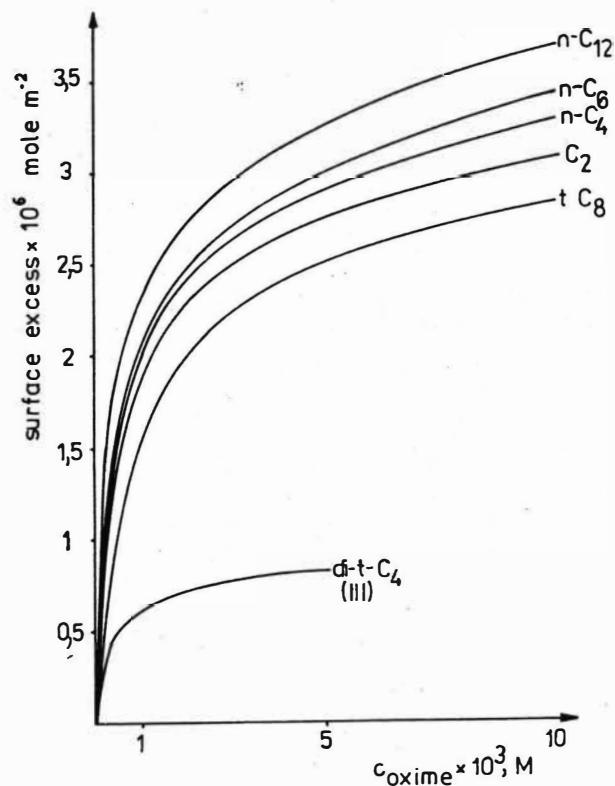


Fig. 5. The surface excess for 2-hydroxy-5-alkylbenzaldehyde oximes

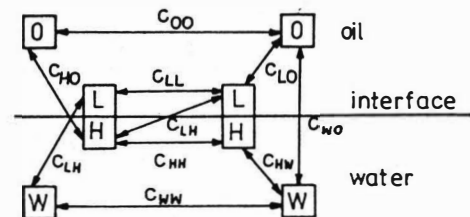


Fig. 6. Cohesion energy types

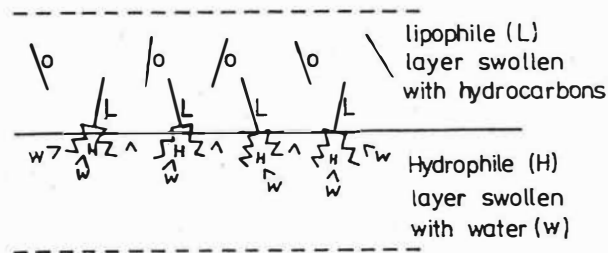


Fig. 7. The interfacial zone

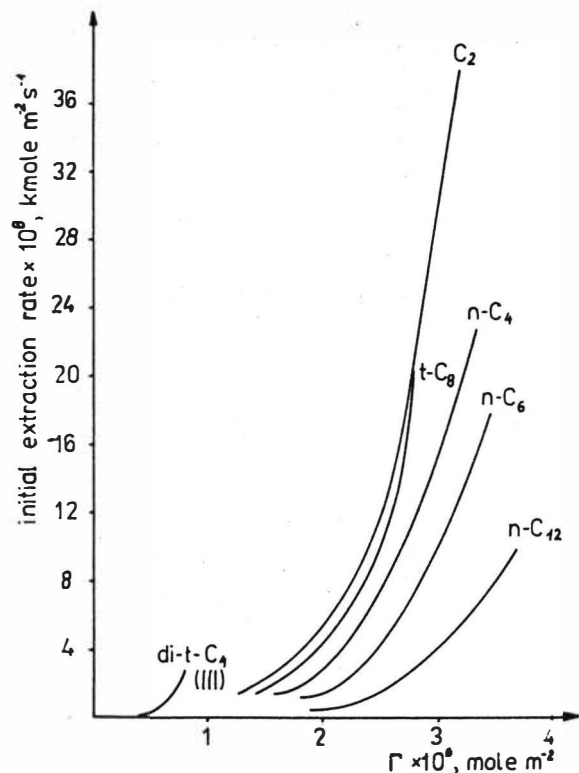


Fig. 8. The initial extraction rate and the surface excess for 2-hydroxy-5-alkylbenzaldehyde oximes

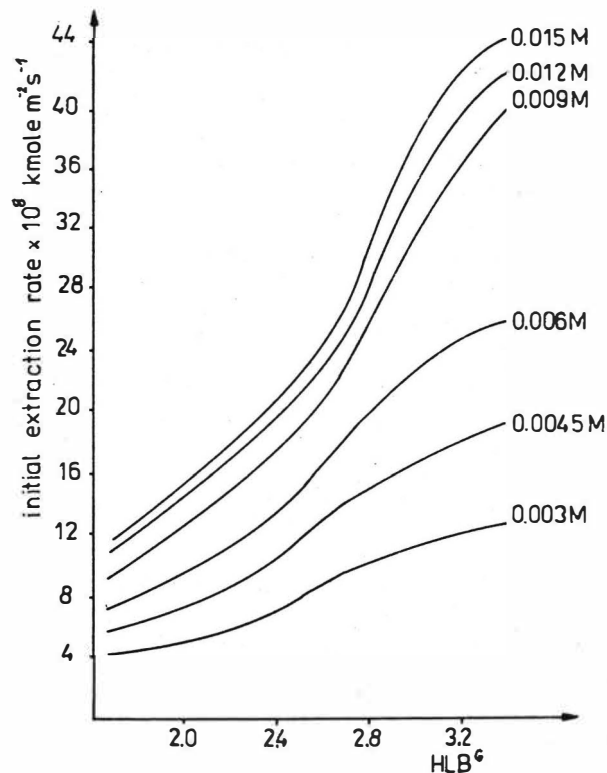


Fig. 9. The influence of HLB upon the extraction rate for 2-hydroxy-5-alkylbenzaldehyde oximes

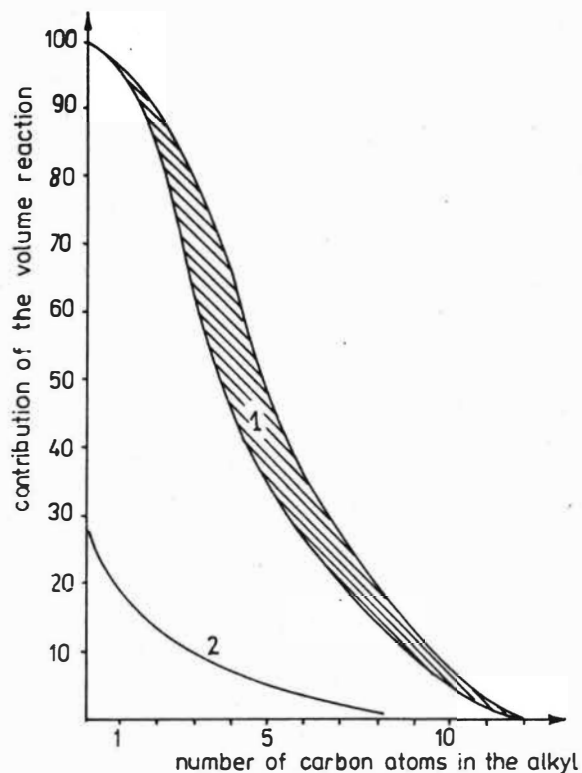
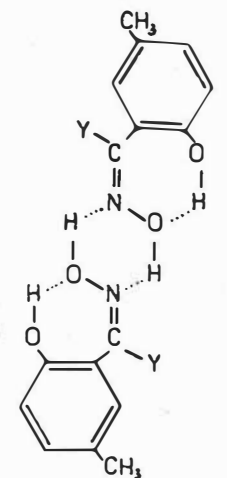
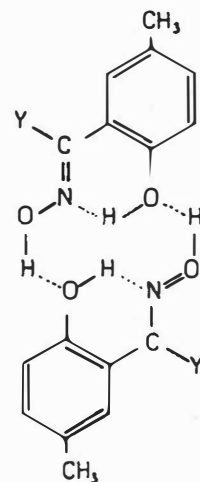


Fig. 10. The contribution of the volume reaction
(1- 2-hydroxy-5-alkylbenzaldehyde oxime
2- 2-hydroxy-5-alkylbenzophenone oxime)



dimer of [Z]- oxime



dimer of [E]- oxime

Fig. 11. The structure of dimers for E and Z izomers
(14)

Uranium Recovery from Phosphoric Acid by Solvent Extraction: A Review of the Freeport Experience

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Freeport-McMoRan is a world-class natural resources company based in New Orleans, Louisiana. The company is active in the exploration, development, and production of oil and gas, sulfur, gold, copper, nickel and cobalt, phosphoric acid, and uranium oxide. These operations stretch from the marshes of the Mississippi River delta to the dry tropical coast of northeastern Australia, and from the mountain tops of New Guinea to the floor of the Gulf of Mexico. But while many of Freeport-McMoRan's activities are taking place far from its New Orleans headquarters, one of its biggest success stories has unfolded right along the nearby banks of the Mississippi River.

In 1966, Freeport Chemical Company was formed, and plans were laid for sulfuric and phosphoric acid plants at Uncle Sam, Louisiana, between New Orleans and Baton Rouge. At the time of its construction, the Uncle Sam complex was the largest sulfuric and phosphoric acid facility in the world; design production capacities were for 5800 tonnes of sulfuric acid and 2050 tonnes of P_2O_5 per day. One of the basic raw materials, the phosphate rock, was known to contain low concentrations of several valuable elements, and the potential for commercial extraction of uranium from the wet process phosphoric acid was recognized immediately at Freeport's Research and Development center.

The concept of the solvent extraction process is, of course, simple: first, the uranium-bearing phosphoric acid is intimately mixed with an immiscible solvent capable of extracting the uranium; next, the two liquids are allowed to disengage, and the barren acid and pregnant solvent are separated; finally, the uranium is stripped from the loaded extractant and is recovered.

But while the concept is simple, the challenge was formidable. Wet process phosphoric acid presents almost every undesirable circumstance to be encountered in a solvent extraction process:

- The feed is lean (about 150 ppm U_3O_8), and the uranium occurs as a mixture of species [$U(VI)$ and $U(IV)$].
- Phosphoric acid is a complexing medium, and its tenacious affinity for uranium poses a special challenge to efficient extraction.
- The presence of numerous metallic impurities requires a high degree of solvent selectivity.
- The presence of humates and fine solids promotes the formation of abundant interfacial crud.
- The relatively high viscosities of the acid and organic streams are an impediment to phase disengagement, and the disparity in the densities of the two phases complicates the engineering of the hydraulics of the system.
- The high temperature of the freshly produced feed acid (about 65°C) could be a problem when dealing with organic solvents.

Facing these challenges, Freeport initiated process development work in January, 1967 -- more than a year in advance of the first phosphoric acid production at Uncle Sam. The first phase of the project focused mainly on four points: 1) the pretreatment of the acid prior to extraction; 2) the definition and demonstration of the extraction chemistry; 3) the invention of complimentary stripping techniques; 4) the study of the physical chemistry and hydrodynamics of the acid/solvent system.

It was during this early period that two key developments took place. The first was the discovery of the now classic extractant combination of DEHPA and TOPO (di-2-ethylhexylphosphoric acid and trioctylphosphine oxide), which was reported in 1969 by workers at the Oak Ridge National Laboratory.⁽¹⁾ The other was the invention of reductive stripping in Freeport's laboratories later that same year. ⁽²⁾ (Figure 1.) This latter discovery was significant because it is the key to Freeport's two-circuit process which offers several advantages over single-circuit designs.

Following a four-year hiatus, work was resumed with a pilot plant consisting of the operations comprising the primary circuit. Key achievements included simplification of the acid pretreatment, development of crud handling techniques, adoption of economical oxidation methods, and development of the ability to operate the solvent extraction system at high temperatures.

Simultaneously, development of the secondary circuit was proceeding at Research and Development, where attention was focused on secondary extraction and stripping chemistry, the rejection of impurities from the loaded secondary extract, and the regeneration of the stripped solvent. In addition, final product recovery schemes and methods for controlling organic entrainment were evaluated. (It may be of interest to note that the secondary circuit was designed without ever having been piloted.)

The process which ultimately evolved is depicted in Figure 2. It is a two-circuit design in which the primary circuit serves to selectively extract and concentrate the uranium. The small, but uranium-rich loaded strip acid stream is then fed to the secondary circuit where the uranium is actually recovered.

The advantage of this design derives mainly from the fact that the actual product recovery occurs in the diminutive secondary circuit. In addition to the actual extraction of the uranium from the feed acid, there are three important process steps common to both single-circuit and two-circuit systems. These are the removal of impurities from the pregnant extract, the alkaline stripping of the uranium from the loaded solvent, and the acid regeneration of the stripped solvent. In single circuit systems, these operations must all be sized to accommodate the entire solvent flow. (Figure 3.) In contrast, Freeport's two-circuit design permits these process steps to be performed on the much smaller solvent stream of the secondary circuit. (Figure 2.) And because the secondary circuit equipment is so small, its impact on total capital costs is also small.

The process illustrated in Figure 2 was the basis for Freeport's first commercial uranium recovery operation. Freeport Uranium Recovery Company (FURC) was formed in 1976, and our plant at Uncle Sam began production in November, 1978. This facility can process 5000 liters per minute of ordinary black acid.

Feed Preparation. Freeport's technology distinguishes itself from others at the very outset of the process: there is no elaborate pretreatment of the acid. The FURC plant is fed with fresh black filter acid (27-29% P_2O_5) from the neighboring Freeport Chemical phosphoric acid plant. This acid is processed through a simple gravity clarifier to remove excessive solids. The slurry underflow from the clarifier is returned to the attack/filtration system of the acid plant, and the clarified overflow proceeds to the oxidation section. There is no use of activated carbon or clays, no filtration of the acid, and no intentional cooling of the acid. Oxidation of the acid prior to extraction is necessary to convert any U (IV) to U (VI), because the DEHPA/TOPO extractant is specific for the

more highly oxidized species. The primary oxidation system is another distinguishing feature of the plant. It is both simple and economic. There is no use of expensive peroxide or of contaminating oxidants such as chlorates or nitrates. The design and operation of this oxidation system is proprietary.

Primary Extraction. The primary extraction circuit was designed to use the well-known solvent formulation consisting of DEHPA(0.5M) and TOPO(0.125M) in kerosene. There are five elevated extraction stages which are situated above the primary stripping stages. The system was designed to accept 4400 liters of acid per minute, and to operate at 60°C, with an O/A ratio of about 1:1. Raffinate acid exiting the extraction section contains less than 15 ppm U_3O_8 .

Crud Handling. The consequence of eliminating any costly extensive pretreatment of the feed acid is that the residual carbonaceous matter (humates) and fine solids promote the formation of crud -- a three-phase gelatinous emulsion which accumulates at the acid-solvent interface in the mixer-settlers. Equipment was designed and patented which enables the crud to be removed periodically without interrupting the solvent extraction process. (3) A patent has also been obtained for a process to treat the crud and to recover the associated solvent values. (4)

Solvent Deentrainment. In order to avoid solvent loss and potential damage to rubber lined equipment in the phosphoric acid plant, it is essential that solvent entrainment in the raffinate acid be minimized (less than 50 ppm). Provision has been made to deentrain solvent from the raffinate in flotation cells; but because of operating techniques developed through experience, the solvent level in the raffinate is typically below the allowed limit before the raffinate reaches the deentrainment equipment.

Primary Stripping. Stripping is accomplished in five stages with a small stream split from the raffinate exiting primary extraction. Because the stripping process depends upon the reduction of U (VI) to U (IV) by dissolved Fe (II) in the strip acid, the supply of ferrous ions is replenished as the strip acid passes through the stripping circuit. While the chemical process of reductive stripping has been disclosed in our patent, the detailed design and operation of the strip acid reduction system is a proprietary feature of our commercial technology. As the loaded strip acid leaves the system, the net effect of the primary circuit has been to concentrate the uranium by approximately fifty-fold (from about 150 ppm to about 7500 ppm U_3O_8).

Secondary Extraction. The loaded strip acid is re-oxidized before being fed to secondary extraction. Secondary extraction employs the same DEHPA/TOPO solvent formulation used in primary extraction. The circuit comprises five extraction stages and achieves greater than 99% extraction efficiency. Secondary raffinate is returned to primary extraction.

Solvent Washing. The pregnant secondary solvent is successively washed with clean (low-iron) phosphoric acid and with water to remove coextracted iron and entrained P_2O_5 . The iron removal step is patented. (5)

Secondary Stripping. The clean pregnant solvent is stripped of uranium with a dilute solution of ammonium carbonate. Because the uranium is stripped as the hexavalent species, no reduction is required (in contrast to primary reductive stripping).

Solvent Regeneration. Because the stripping step effectively neutralizes the di-2-ethylhexyl phosphoric acid, it must be converted back to the acid form in order to reestablish its extraction potency. The effect of returning ammonia to the secondary extractors can be disastrous, and therefore the stripped secondary solvent stream is regenerated with mineral acid prior to being recycled to the secondary extraction circuit. This process step is covered in the same patent which disclosed the iron removal technique.

Product Recovery. The uranium-laden strip solution is processed through a multi-step product recovery scheme which is designed to reduce ammonia and CO_2 consumption and to yield a product of exceptional purity. In the final step, the yellow cake is calcined and drummed. The product is 98% U_3O_8 .

By 1980, annual production at Uncle Sam had surpassed the plant's design capacity of 314,000 kilograms of U_3O_8 . But even before construction of this facility was complete, work on process improvements was underway at R&D -- especially in the areas of solvent formulation and stripping chemistry. By the end of 1979, certain process modifications had been demonstrated in a pilot plant, and these improvements were incorporated into the design of our second uranium recovery unit, the Sunshine Bridge plant. This second FURC plant processes black acid from Agrico's Faustina plant near Donaldsonville, Louisiana. Construction was completed in only 18 months from the start of engineering; plant operations began in May, 1981, and design operating rates were achieved within three weeks of plant completion. The Sunshine Bridge unit consists only of a primary circuit comprising four extraction stages and four stripping stages; unlike the Uncle Sam plant, all extractors and strippers are situated adjacent to one another on the same level. The loaded strip acid produced at Sunshine Bridge is transported by truck for further processing in the secondary circuit of the Uncle Sam plant, which was enlarged to accommodate this extra duty. The Sunshine Bridge plant was designed to process 386,000 tonnes of P_2O_5 (as 29% acid) per year, and to produce 190,000 kilograms of U_3O_8 per year.

In 1981, Freeport agreed to provide technical aid to another major U. S. company (IMC) with large uranium recovery commitments. Portions of our technology were licensed for use in their operations with an aggregate capacity of 900,000 kilograms of U_3O_8 per annum. With this further extension of the application of our technology, Freeport was emerging as the clear leader in uranium recovery from phosphoric acid. Today our technology is still dominant in the industry.

The success of Freeport's operating experience can be gauged in several ways:

Production Statistics. Table 1 summarizes processing and production data for the Uncle Sam and Sunshine Bridge plants for every whole year of operation since start-up. Excepting 1982 (during which phosphoric acid production was depressed, and feed rates to the FURC plants were below plan), the plants have together processed 108% of their combined design acid feed capacities, and have produced 102% of their combined design capacities for U_3O_8 . During the peak year of 1984, the Uncle Sam FURC plant operated at 115% of design feed rate, and it produced 115% of design U_3O_8 capacity.

Extraction Efficiency. Extraction efficiency in the primary circuits is typically greater than 90%, and is greater than 99% in the secondary circuit; as mentioned, primary raffinates average less than 15 ppm U_3O_8 .

Operating Factor. The plants operate on a three-week wash cycle and a twelve-month major maintenance cycle. The average operating factor is 90-95%.

Product Quality. As already stated, the 98% U_3O_8 product is exceptionally pure. It meets all converter specifications, and no shipment has ever been rejected.

Commercial Performance. One indication of the commercial success of Freeport's uranium recovery ventures is the fact that FURC has shown a profit for every quarter since the start-up of our first unit at Uncle Sam. Another indication is given by the production rankings given in Table 2. These data show that those operations which have incorporated Freeport technology have proven to be the hardest survivors in the declining uranium market of the last several years.

An important component in Freeport's success is its continuing commitment to research and development. Freeport's scientists, engineers, and technicians have accumulated almost two decades of process development experience related to uranium recovery from phosphoric acid. Beyond the original process development effort, there are three accomplishments which can be cited as prime examples of the many achievements of our R&D program. The first of these is the development of a computerized mathematical model of the extraction system. Essentially it is a means for rapidly solving the coupled McCabe-Thiele problems of the extraction and stripping circuits. But what makes the model especially valuable is that it incorporates multivariant non-linear correlations which relate the extraction and stripping coefficients to a number of key operating conditions; these correlations have been developed from both laboratory and plant data. The model has become a powerful tool which allows us to make rapid recommendations for optimizing plant operations at Uncle Sam and Sunshine Bridge, and which can be used in the preliminary design of new systems. The second accomplishment is the development of an acid testing program which allows us to verify the compatibility of our process with other phosphoric acid supplies or with acid which might be produced from yet undeveloped phosphate rock resources. The evaluation of the acid focuses on six characteristics: 1) chemical composition of the acid; 2) amenability to gravity clarification; 3) oxidation requirement; 4) capacity for crud formation; 5) hydrodynamic behavior in combination with solvent; and 6) extractability of the uranium. We have had the opportunity to apply this testing program to the evaluation of acids from six domestic (U.S.) and three foreign sources. The third accomplishment is the very recent development of a new process for recovering solvent from crud. The new treatment method is capable of recovering over 90% of the solvent associated with the crud formed in the extraction system, and work is currently in progress to implement this new technology at both the Uncle Sam and Sunshine Bridge plants.

In review, Freeport has invested two decades in process development covering every aspect of uranium recovery from phosphoric acid. Our knowledge ranges from the liberation of the uranium during phosphoric acid production, to the certified analysis of the calcined yellow cake. We have experience at all levels, from the laboratory to full scale production plants.

- A strong research and development program.
- A proven process.
- An unexcelled product.
- And an unmatched technical and commercial success.

These are the things that we believe have made Freeport-McMoran the industry leader in the recovery of uranium from phosphoric acid.

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3. Cognevich, U. S. Patent No. 4,126,551 (1978).
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TABLE 1. PROCESSING AND PRODUCTION DATA FOR FREEPORT'S
UNCLE SAM AND SUNSHINE BRIDGE URANIUM PLANTS

<u>Year</u>	<u>Acid Processed (Tonnes P_2O_5)</u>		<u>Uranium Oxide Produced (Kg U_3O_8)</u>	
	<u>Uncle Sam</u>	<u>Sunshine Bridge</u>	<u>Uncle Sam</u>	<u>Sunshine Bridge</u>
1979	658,769	-	281,488	-
1980	707,825	-	315,576	-
1981	693,121	-	322,868	-
1982	522,917	410,358	238,173	153,671
1983	703,286	471,073	345,165	187,491
1984	784,237	525,927	362,438	196,491
1985	667,786	454,351	304,427	193,459

Note: The Uncle Sam plant was designed to process 682,000 tonnes P_2O_5 (as 29% acid) and to produce 314,000 kilograms U_3O_8 per annum. The Sunshine Bridge plant was designed for 386,000 tonnes P_2O_5 and 190,000 kilograms U_3O_8 . Data are presented for whole years of operation since start-up.

TABLE 2. RANKINGS OF URANIUM OXIDE PRODUCERS EMPLOYING
FREEPORT TECHNOLOGY VERSUS OTHER U. S. PRODUCERS

<u>Year</u>	<u>Company</u>	<u>U_3O_8 Production</u>	<u>Rank</u>
1980	Freeport	315.5 tonnes	17th
1984	IMC*	771.8 tonnes	2nd
1984	Freeport	558.9 tonnes	3rd

*Portions of Freeport's technology were licensed to IMC in 1981.

Source:

U. S. Department of Energy, Statistical Data of the Uranium Industry (1983).

U. S. Department of Energy, 1984 Uranium Industry Annual (1985).

Corporate annual reports and Forms 10-K.

FIGURE 1.
REDUCTIVE STRIPPING

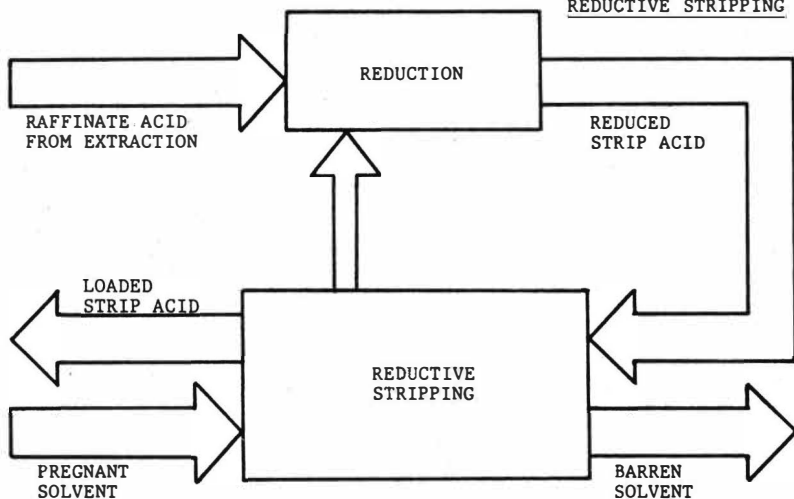


FIGURE 3. SINGLE-CIRCUIT
SOLVENT EXTRACTION SYSTEM

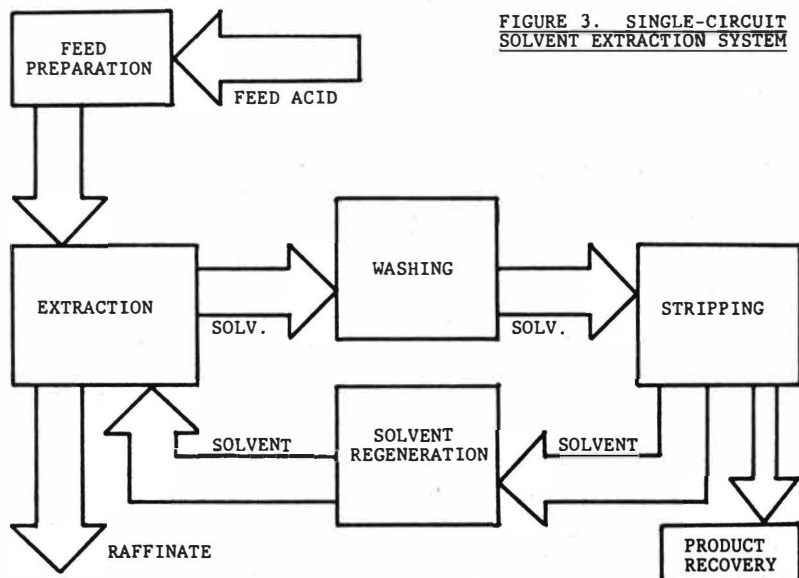
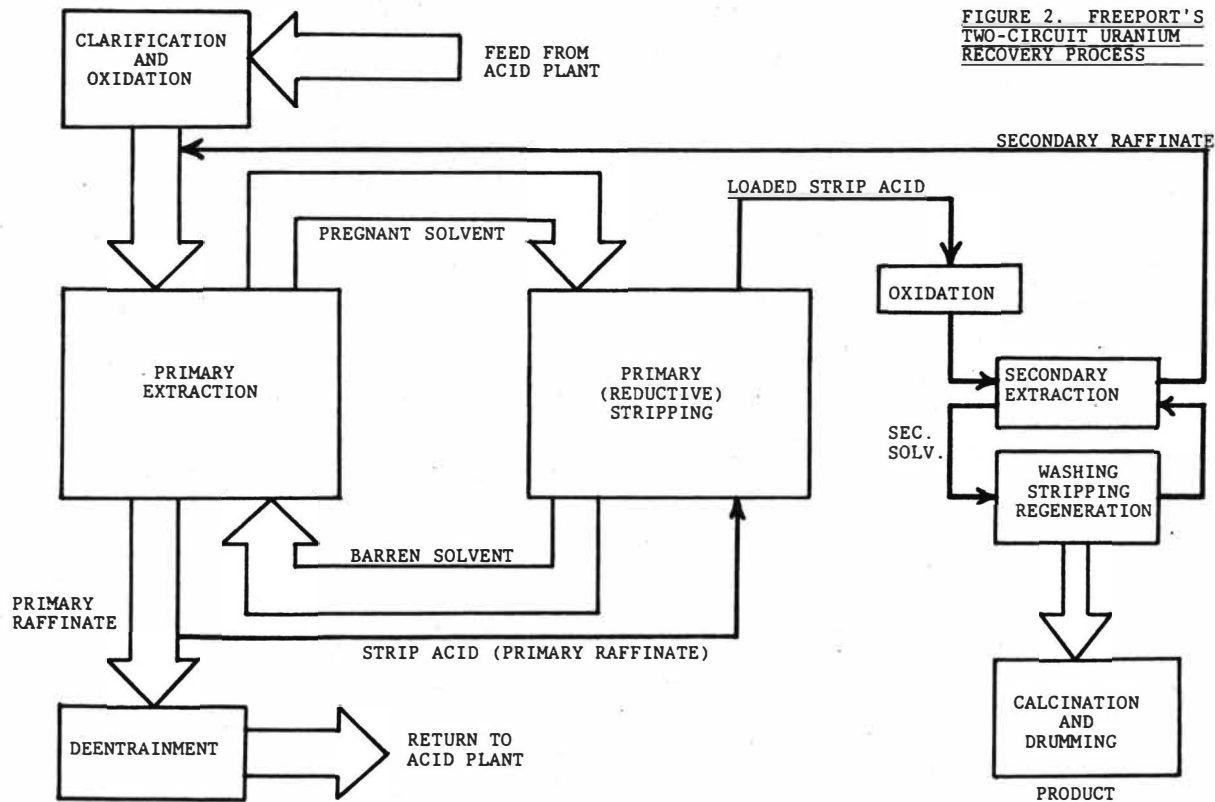


FIGURE 2. FREEPORT'S
TWO-CIRCUIT URANIUM
RECOVERY PROCESS



Prediction of Extractor Performance from Tracer Experiments with Stationary Continuous Phase

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Experimental tests on the model equipment are needed for the chemical engineering design of extraction columns. The pilot plant experiments are material and time consuming if they are carried out under steady state conditions, since the approach of the extraction system to equilibrium is usually slow. In case of process development, sufficient amounts of the process liquids may be difficult to obtain. These difficulties can be avoided if the experiments are carried out under unsteady state conditions. The aim of this contribution is to show how the information obtained from tracer experiments can be used for predicting the extractor performance.

The method is based on tracer experiments in two phase system. Non-reacting tracers are used to characterize the longitudinal mixing of the phases, the reacting tracer, i.e. the component extracted in the studied process, to characterize the extraction rate. Interpretation of the multiple tracer experiments in two phase systems with a stagnant phase was theoretically studied by Shinnar et al. (1). In our case, when longitudinal mixing occurs both in the mobile dispersed and the stationary continuous phase, the tracer data from both phases are needed for the evaluation of the mass transfer rate.

The back-flow model with constant flows of phases has been applied to the modelling of a vibrating plate extractor. The transient behaviour of the extractor, operating with the continuous phase stationary, is described by the following set of differential equations with $Q = 0$:

$$v \frac{dC_i}{dt} = qC_{i+1} - (Q + q)C_i + QC_{in} - J_i A \quad i = 1 \quad (1a)$$

$$\bar{v} \frac{d\bar{C}_i}{dt} = (\bar{Q} + \bar{q})\bar{C}_{i+1} - (\bar{Q} + \bar{q})\bar{C}_i + J_i A \quad (2a)$$

$$v \frac{dC_i}{dt} = qC_{i+1} - (Q + 2q)C_i + (Q + q)C_{i-1} - J_i A \quad i = 2, n-1 \quad (1b)$$

$$\bar{v} \frac{d\bar{C}_i}{dt} = (\bar{Q} + \bar{q})\bar{C}_{i+1} - (\bar{Q} + \bar{q})\bar{C}_i + (\bar{Q} + \bar{q})\bar{C}_{i-1} + J_i A \quad (2b)$$

$$v \frac{dC_i}{dt} = -(Q + q)C_i + (Q + q)C_{i-1} - J_i A \quad i = n \quad (1c)$$

$$\bar{v} \frac{d\bar{C}_i}{dt} = \bar{Q} \bar{C}_{in} - (\bar{Q} + \bar{q})\bar{C}_i + \bar{q}\bar{C}_{i-1} + J_i A \quad (2c)$$

valid for each extracted component. If the dependence of the mass transfer rate on the concentrations is known

$$J_i = J(k, K, C_i, \bar{C}_i) \quad (3)$$

the set of Eqs (1)-(3) can be solved for given values $n, Q, v, \bar{v}, q, \bar{q}, K, k$, and A at specified initial conditions. The dispersed phase flow Q , number of stages n and the volume of the stage $V = v + \bar{v}$ are known or can be easily related to the experimental equipment. Equilibrium constant K is determined from equilibrium data. The backflows of phases q, \bar{q} , hold-up of the dispersed phase $X = v/V$ and the product of the rate constant and interfacial area kA remain as the parameters of the model to be estimated from the tracer data. The method of fitting the response curves and the method of moments will be applied to this estimation problem.

In the linear case, when the equilibrium is described by a constant distribution coefficient $m = \bar{C}/C$, and the rate equation assumes the form

$$J = k(C - \bar{C}/m) \quad (4)$$

the moments of the response curve in the mobile phase can be expressed from the analytical solution of Eqs (1)-(2) by means of the dimensionless parameters:

$$\begin{aligned}\tau &= v/Qt = VX/Qt, & \alpha &= q/Q \\ E &= m\bar{v}/v = m(1-X)/X, & \bar{\alpha} &= \bar{q}/Q \\ N &= kA/Q\end{aligned}$$

When the reacting tracer is injected into the first stage as a δ -input, then the mean of the response curve in the n -th stage

$$\mu = n(1 + E)\tau \quad (5)$$

represents the mean dimensionless residence time of the tracer in both phases of the system. The corresponding dimensionless variance is given by Eq. (6), valid exactly for $\bar{\alpha} = 0$, (or $N \rightarrow \infty$):

$$\sigma^2/\mu^2 = \frac{1}{n} \left\{ (1 + 2b) - \frac{2b(1+b)}{n} \left[1 - (b/(1+b))^n \right] + 2 \left(\frac{E}{1+E} \right)^2 \frac{1}{N} \right\} \quad (6)$$

where $b = \alpha + m\bar{\alpha}$

It can be approximated by the relation

$$\sigma^2/\mu^2 = \frac{1}{n} \left(1 + 2\alpha + 2m\bar{\alpha} + 2 \left(\frac{E}{1+E} \right)^2 \frac{1}{N} \right) \quad (7)$$

when backmixing is low and the number of stages very large. It follows from Eq. (5) for $E = 0$ that the hold-up in the column can be determined from the mean of the residence time of the non-reacting tracer ν_0 ,

$$X = \mu_0 Q t / (nV) \quad (8)$$

and that the ratio of the means for the reacting and nonreacting tracer is related to the hold-up and the equilibrium distribution coefficient m :

$$\mu/\mu_0 = 1 + E = 1 + m(1 - X)/X \quad (9)$$

The dimensionless variance of the residence time of the reacting tracer, which according to Eq. (6) linearly increases with the reciprocal mass transfer number N , contains information about the rate parameter kA .

As the equilibrium relation is generally nonlinear, the differential equations must be solved numerically to obtain the response to the reacting tracer injection and its moments. The above given relationships proved useful for obtaining the initial guesses for the numerical solution of the parameter estimation problem in the general non-linear case.

The method was applied to the determination of the separation efficiency of a vibrating plate extractor for the extraction of Ce(III) from nitrate solutions by di-2-ethylhexylphosphoric acid (DEHPA). The extraction is governed by the reaction



The concentration of the nitric acid in the aqueous phase was 0.5 mole/l, the con-

centration of DEHPA (\pm HL) in kerosene 0.92 mole/l.

The extraction column (Fig. 1) with diameter 50 mm and overall height 5000 mm had 48 plates. The plates perforated with 2.5 mm I.D. holes with 5 per cent free area were equipped with downcomers having 15 per cent free area for the passage of the continuous phase. The distance of the plates was 100 mm. The dispersed aqueous phase was introduced through a distributor into the top of the column. Its outlet at the bottom was automatically controlled to keep constant liquid level in the column. The position of the interface in the bottom was held constant by means of an expansion vessel attached to the column. The changes in the hold-up in the column were automatically compensated by the exchange of the continuous phase between the column and the vessel.

The following experimental procedure was adopted for the tracer experiments. After the flowrate of the circulating dispersed phase and the frequency of the vibration were set, the column was operated at least one hour to reach hydrodynamic equilibrium. The approach of the hold-up to the steady state was indicated by the changes of the liquid level in the expansion vessel. When the steady hold-up was reached, the δ -type injections were introduced:

- 1) Organic soluble dye was injected into the continuous phase on the 17th plate and the phase sampled on the 23rd plate.
- 2) Water soluble dye was introduced into the inlet of the dispersed phase, i.e. on the first plate and the phase sampled below the lowest plate.
- 3) Reacting tracer (0.1 M Ce^{3+} in 0.5M HNO_3) was injected into the inlet of the dispersed phase and the samples taken below the lowest plate as in 2).

The agitation intensity in particular experiments was varied by changing the vibration frequency at constant amplitude, $2A = 8$ mm. A special series of experiments with one phase system was designed to determine the dependence of the backflow on the frequency.

A computer program has been developed for solving the set of differential equations (1)-(2) by Runge-Kutta-Merson method. The column was modelled as a 24-stage extractor with the stage height 0.20 m (= twice the distance of the plates). The rate equation of the type

$$J = k(C \cdot (\overline{\text{HL}})_2 / (H^+)^2 - [\overline{C} \cdot (H^+) / (\overline{\text{HL}})_2] / K)$$

was used for the description of Ce(III) transfer rate. The value of the equilibrium constant was determined by laboratory experiments:

$$K = (\overline{C}/C) [(H^+) / (\overline{\text{HL}})_2]^3 = 0.309$$

Typical measured and calculated responses in the continuous phase are illustrated by Fig. 2. Fig. 3 indicates that the backflow evaluated by the curve fitting is linearly dependent on the vibration frequency and that this dependence is common for the one phase and the two phase data.

Typical responses in the dispersed phase are shown in Fig. 4. The hold-up and the backflow in this phase were determined by fitting the mean and the variance of the non-reacting tracer response. The mass transfer parameter was estimated by fitting the variance of the reacting tracer response, while the mean served as a check of the equilibrium constant used. The knowledge of the hold-up at the given dispersed phase flow enabled us to determine the relative velocity of phases w , important for the calculation of the throughput in the countercurrent arrangement, which is given by Eq (10):

$$w = U/X + \bar{U}/(1 - X) \quad (10)$$

The experimental conditions and the calculated parameter values are given in Tab. I.

Tab. I. Parameters estimated from the experimental data

Q	f	μ_0	μ_0^2/σ_0^2	μ	μ^2/σ^2	X	q	\bar{q}	kA	w
$10^{-6} \frac{m^3}{s}$	$\frac{1}{s}$	s	-	s	-	-	$10^{-6} \frac{m^3}{s}$	$10^{-6} \frac{m^3}{s}$	$10^{-6} \frac{kmole}{s}$	$10^{-3} \frac{m}{s}$
1.18	3.00	772	0.184			0.103	2.25	4.58		6.26
1.18	3.33	1162	0.176	2674	0.326	0.157	2.15	5.00	20.4	4.11
1.82	3.00	794	0.162	1757	0.570	0.162	2.93	4.58	6.95	6.14
1.82	3.33	1228	0.142	2068	0.302	0.267	2.49	5.00	12.2	3.73

The obtained parameter values and the same computer program were then used for predicting the separation efficiency of the column at countercurrent extraction with the flow ratio $U/\bar{U} = 3.33$ and with the inlet concentrations $C = 0.010$, $(H^*) = 0.37$, $C = 0.000$, $(H^*)_2 = 0.46$ mole/l. The throughputs of the phases which would produce the same hold-up as in the experiments, were predicted from Eq. (10). With regard to the high intensity of agitation employed, the backflows of the phases were assumed to be independent on the phase flows. By solving the model with these parameters the output concentrations were obtained and the number of theoretical stages corresponding to the computed separation was calculated. The calculated fraction extracted η and the column efficiency characterised by HETS values are given in Tab. II.

Tab. II. Extractor performance estimated from the tracer data

U	\bar{U}	f	X	u	\bar{u}	kA	η	HETS
$10^{-3} \frac{m}{s}$	$10^{-3} \frac{m}{s}$	$\frac{1}{s}$	-	$10^{-3} \frac{m}{s}$	$10^{-3} \frac{m}{s}$	$10^{-6} \frac{kmole}{s}$	-	m
0.398	1.33	3.33	0.157	1.18	2.73	20.4	0.894	1.68
0.605	2.02	3.00	0.162	1.60	2.50	6.95	0.764	2.87
0.450	1.50	3.33	0.267	1.34	2.73	12.2	0.863	1.87

The HETS values in Tab. II, which are high in comparison with those achieved in systems where physical extraction occurs, show that the efficiency of the column for the studied Ce(III)-DEHPA extraction is relatively low due to the reaction kinetics.

The method proved useful for predicting the extractor performance from relatively simple experiments. The reliability of the prediction depends on the adequacy of the mathematical model of the extraction process occurring in the equipment. The method is not restricted to the use of a particular model. In extraction processes with slowly coalescing systems, especially in the region near the flooding, the hold-up profile and the forward mixing (channelling) can have considerable effect on the overall column efficiency. Under these conditions more realistic models [2]-[4], which take these phenomena into account, are recommended for the interpretation of the tracer experiments. In order to estimate the sensitivity of the predicted HETS to the model used, the same tracer data from the dispersed phase were interpreted by the model with the backflow in the continuous phase and partial stage bypassing in

the dispersed phase. The by-pass coefficient as well as kA values were evaluated from the tracer data. Although the kA values differed significantly from those obtained from the backflow model, the fraction extracted and the HETS values predicted for the countercurrent extraction remained practically unchanged.

Symbols

A	interfacial area, m^2
C	concentration, $kmole.m^{-3}$
E	extraction ratio
f	frequency, s^{-1}
J	interfacial flux, $kmole.m^{-2}.s^{-1}$
k	rate constant, ms^{-1} , $kmole.m^{-2}.s^{-1}$
K	equilibrium constant
m	distribution coefficient, $(\bar{C}/C)_{equil}$
n	number of stages
N	mass transfer number
q	backflow, $m^3.s^{-1}$
Q	flow of the phase, $m^3.s^{-1}$
t	time, s
U	superficial phase velocity, ms^{-1}
u	superficial backflow velocity, ms^{-1}
v	phase volume in the stage, m^3
V	volume of the stage, m^3
w	relative velocity of phases, ms^{-1}
X	hold-up of the dispersed phase
α	backflow coefficient
τ	dimensionless time
in	refers to the inlet

barred symbols refer to the continuous phase

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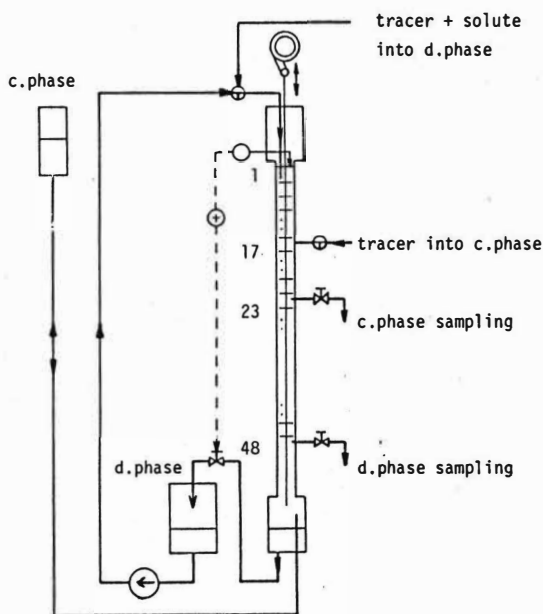


Fig. 1 Experimental equipment

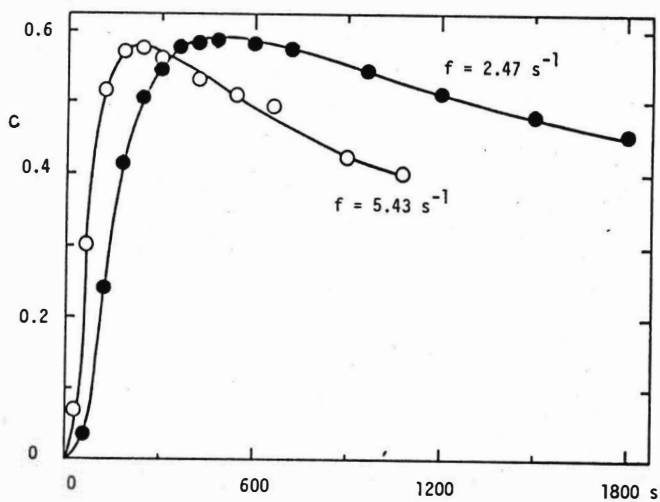


Fig. 2 Response curves in the continuous phase

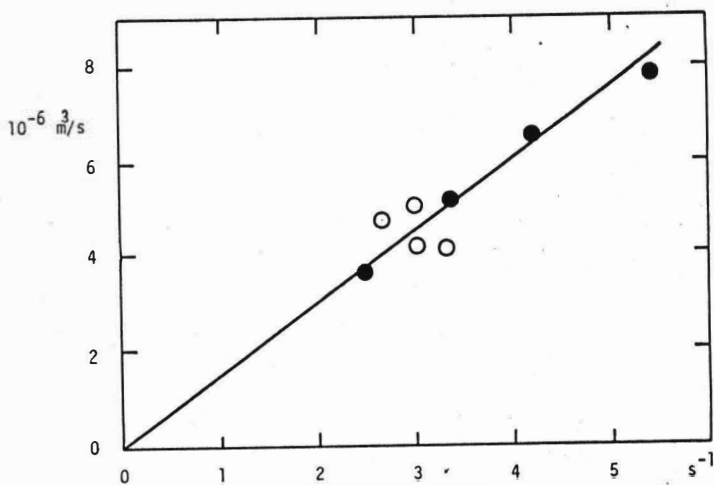


Fig. 3 Dependence of the backflow in the continuous phase on the vibration frequency (● one phase, ○ two phase system)

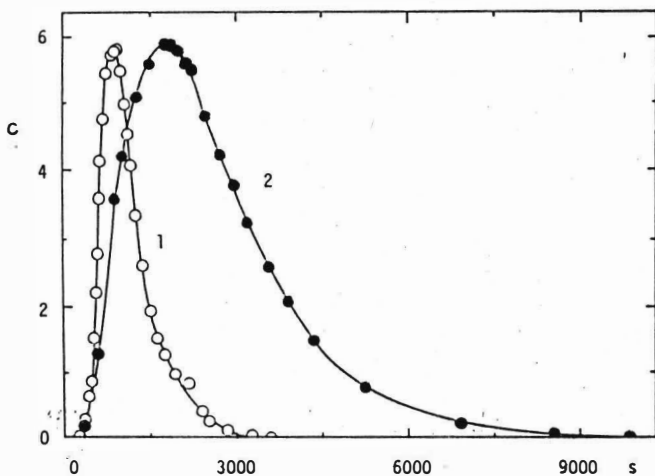


Fig. 4 Response curves in the organic phase, $f = 3.33 \text{ s}^{-1}$, 1 - nonreacting tracer, 2 - reacting tracer

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1. Introduction

Solvent extraction techniques have been utilized as an important technique for the separation and concentration of metals in commercial scale processes. So far, solvent extraction of metals have been extensively studied with extractants containing oxygen or/and nitrogen as donor atoms. However, relatively few works have been conducted on the extractants containing sulfur as a donor atom.

It is well known that metals classified into so called "soft acids" such as gold, silver, mercury, copper(I) and palladium are selectively and effectively extracted by extractants containing sulfur or phosphorus as donor atoms, which are classified into so called "soft bases". Among the sulfur containing extractants, extraction properties of dialkyl sulfides, petroleum sulfides and O,O'-dialkyldithiophosphoric acids have been extensively investigated, especially in Soviet.

Actually, dialkyl sulfides are now commercially utilized for the separation of palladium from platinum at the Inco's Acton precious metal refinery in United Kingdom¹⁾ and for the recovery of precious metals from various wastes such as spent catalysts in Japan.

Recently, American Cyanamid Co. Developed a new commercial extractants for the recovery of silver and palladium, CYANEX 471, the active species of which is triisobutylphosphine sulfide (TIBPS).²⁾ Besides these, various sulfur containing extractants have been developed mainly for analytical purposes.³⁾ Many sulfur containing compounds are marketed as commercial chemicals such as collectors in flotation and additives to lubricating oil. These may be utilized also as extractants⁴⁾. However, extraction behaviors of these reagents have not been well examined.

In the present work, as a part of a series of quantitative and systematic investigations on the sulfur containing extractants, the authors synthesized a new-type sulfur containing carboxylic acid, α -butylthiolauric acid (α -BTLA), to investigate its extraction properties for various metals. In addition, we also investigated those of two trialkylphosphine sulfides, triisobutylphosphine sulfide (TIBPS) and trioctylphosphine sulfide (TOPS), for various metals, especially for mercury(II). TIBPS and TOPS are produced and marketed as a commercial metal extractant under the trade name "CYANEX 471" by American Cyanamid Co. as mentioned earlier and as a commercial chemical by Nippon

Chemical Industry Co. Ltd., respectively.

2. Experimental

2.1 Reagents

The structural formulas of the extractants used in the present study are shown below.



α -BTLA was synthesized in good yield from α -bromolauric acid, produced and marketed by Shell Chemical Co. as a commercial metal extractant, and 1-butanethiol in methanol in an atmosphere of nitrogen. The product was purified by vacuum distillation. The identification of the product was carried out by IR spectra and NMR spectra.

TIBPS was purified from CYANEX 471 donated by American Cyanamid Co. by recrystallization from ethanol-water mixture. TOPS was used as received from Nippon Chemical Industry Co. Ltd., without further purification. Toluene was used as a diluent in all experiments. The concentration of α -BTLA was determined by titration with potassium hydroxide dissolved in ethanol using phenolphthalein as an indicator. Those of TIBPS and TOPS were determined on a gravimetric basis.

2.2 Procedure

Equal volumes of the aqueous and organic phases of known concentrations were shaken in a stoppered glass flask at a constant temperature of 30 °C in a thermostated water bath. The phases were shaken for a few h. Equilibrations were ascertained to be attained within these shaking times in a preliminary experiment. After equilibration, the two phases were separated and analysed for metal concentrations in both phases. Metal concentration in the aqueous phase was determined by titration with EDTA in its high concentration region and by atomic absorption spectrochemical analysis in its low concentration region. That in the organic phase was calculated from the mass balance of its concentration in the aqueous phase before and after the equilibration or determined in the same manner after stripping with 1 mol/dm³ aqueous ammonium thiocyanate solution in the cases of silver and mercury.

3. Results and Discussion

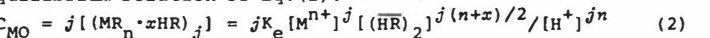
3.1 Extraction properties of α -BTLA

Prior to the quantitative investigations of extraction equilibria with α -BTLA, preliminary experiments were carried out to examine the qualitative relation between the distribution ratio and pH in the extraction of various metals, i.e. Ag(I), Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Pb(II), Mn(II), Al(III) and Fe(III), from 1 mol/dm³ aqueous ammonium nitrate solution as shown in Fig. 1.⁵⁾

The relation between the logarithm of the distribution ratio and pH gives straight lines the slope of which are equal to the valencies of the metals, which suggests that α -BTLA behaves as a chelating or a non-chelating acidic extractants in the extraction of these metals from nitrate media.

3. 1. 1. Extractions of Silver(I) and Calcium(II) from Nitrate Media^{5,6)}

First, the extraction equilibria of silver(I) and calcium(II), which are one of the typical "soft acids" and "hard acids", respectively, from nitrate media were investigated. Silver and calcium were extracted from 1 mol/dm³ aqueous ammonium nitrate and sodium nitrate solutions, respectively. Assuming that α -BTLA behaves as a non-chelating acidic extractant similar to other carboxylic acids such as Versatic acid from the result shown in Fig.1, the stoichiometric relation of the extraction reaction of metals with α -BTLA can be generally described by Eq.(1).⁷⁾



where $(\overline{HR})_2$ denotes the dimeric species of α -BTLA in the organic phase which is predominant in non-polar diluents and $(MR_n \cdot xHR)_j$ denotes the extracted metal complex existing as a j -meric species solvated by x molecules of neutral carboxylic acid, HR. If only a single species was assumed to exist in the organic phase for simplicity, the total metal concentration in the organic phase is expressed by Eq.(2) from the equilibrium relation of Eq.(1).

$$C_{MO} = j[(MR_n \cdot xHR)_j] = jK_e [M^{n+}]^j [(\overline{HR})_2]^j [(n+x)/2] / [H^+]^j n \quad (2)$$

Here, the concentration of the unreacted dimeric species of α -BTLA, $[(\overline{HR})_2]$, is nearly equal to its initial concentration and constant in the region of low loading ratio of metal to carboxylic acid. In the extraction of silver, it should be taken into account that metal ion in the aqueous solution is existing not only as an extractable free aquo-ion but also as unextractable ion-pair, $AgNO_3$, or ammine complexes, $Ag(NH_3)_i^+$. The concentration of the free aquo-ion, $[Ag^+]$, is calculated from total metal concentration in the aqueous phase, C_{MW} , pH and nitrate ion concentration according to Eq.(5) taking account of the formation of an ion-pair expressed by Eq.(3) and those of ammine

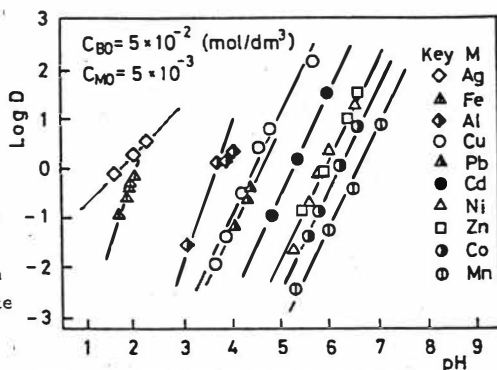
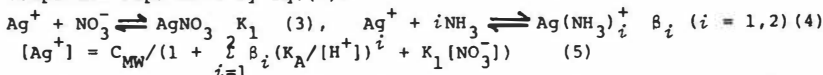


Fig.1 Equilibrium distribution of various metals from 1 mol/dm³ NH₄NO₃ solution

complexes expressed by Eq.(4).



In Eq.(5), K_A denotes the dissociation constant of ammonium ion.

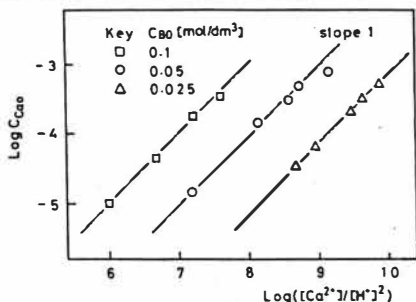
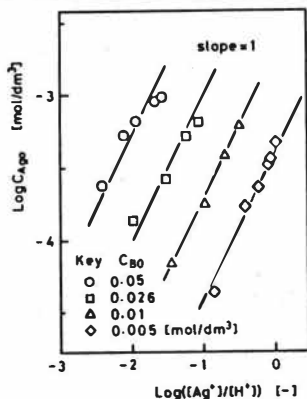
Following values were used in the subsequent calculations: $K_1 = 1.82 \text{ dm}^3/\text{mol}^8$, $\beta_1 = 2.51 \times 10^3 \text{ dm}^3/\text{mol}^8$, $\beta_2 = 2.51 \times 10^7 (\text{dm}^3/\text{mol})^2$ and $K_A = 2.8 \times 10^{-10} \text{ mol/dm}^3$.

However, it is not necessary to take account of the existence of ammine complex and, consequently, Eq.(5) is approximated by Eq.(6) under the present experimental conditions since the extraction takes place at low pH as shown in Fig.1. $[\text{Ag}^+] = \frac{C_{\text{MW}}}{1 + K_1 [\text{NO}_3^-]} \quad (6)$

Logarithm of Eq.(2) gives

$$\log C_{\text{MO}} = j \log ([\text{M}^{n+}]/[\text{H}^+])^n + \frac{j(n+x)}{2} \log C_{\text{B}_0}/2 + \log j K_e \quad (7) \text{ where } C_{\text{B}_0}$$

denotes the initial total concentration of the extractant.



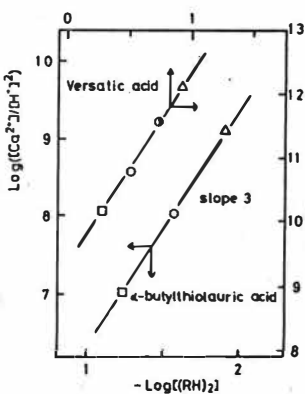
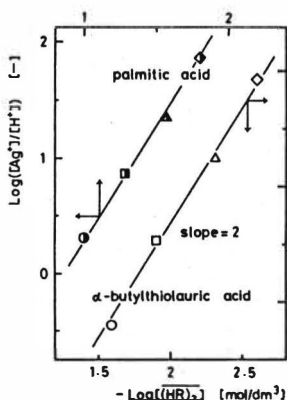
Figs. 2 and 3 Relation between $\log C_{\text{MO}}$ and $\log [\text{M}^{n+}]/[\text{H}^+]^n$ for the extractions of silver(I) and calcium(II) with α -BTLE (C_{MO} = metal concentration in organic phase)

The experimental results are illustrated in Figs. 2 and 3 as log-log plots of C_{MO} against $[\text{M}^{n+}]/[\text{H}^+]^n$ according to Eq.(7) for the extraction of silver(I) and calcium(II), respectively. The plotted points in Figs 2 and 3 evidently lie on straight lines of slope 1 corresponding to each C_{B_0} , which indicates that $j = 1$ in both extraction systems; that is, metal carboxylates are existing as monomeric species in the organic phase. In this case, Eq.(7) is rewritten as follows.

$$\log [\text{M}^{n+}]/[\text{H}^+]^n = -\frac{n+x}{2} \log C_{\text{B}_0}/2 + \log C_{\text{MO}} - \log K_e \quad (8)$$

The values of the intercepts of the straight lines in Figs.2 and 3 with the constant values of C_{MO} , e.g. $\log C_{\text{MO}} = -3.5$ in Fig.2 and $= -4.0$ in Fig.3, were plotted against $\log C_{\text{B}_0}/2$ according to Eq.(8) as shown in Figs. 4 and 5. In these figures, experimental results of the extractions of silver(I) with palmitic acid and of calcium(II) with Versatic acid are also illustrated for comparison. In both cases, $\log C_{\text{MO}} = -3.5$. In Fig.4, good linear relationships of slope 2 are observed for both

carboxylic acids as expected from Eq.(8), suggesting that $\alpha = 3$ in Eq.(1). Therefore, it can be concluded that silver(I) is extracted as the complex, $\text{AgR} \cdot 3\text{HR}$, according to the stoichiometric relation described by Eq.(9) with both carboxylic acids.



Figs.4 and 5 Relation between $\log [M^{n+}]/[H^+]^n$ and $-\log[(\overline{\text{HR}})_2] (= -\log C_{B0}/2)$ in the extractions of silver(I) and calcium(II)

$\text{Ag}^+ + 2(\overline{\text{HR}})_2 \rightleftharpoons \overline{\text{AgR} \cdot 3\text{HR}} + \text{H}^+$ (9) Also in Fig.5, good linear relationships of slope 3 are observed for both carboxylic acids, suggesting that $\alpha = 4$ in Eq.(1). It can be concluded that calcium(II) is extracted as $\text{CaR}_2 \cdot 4\text{HR}$ according to the stoichiometric relation described by Eq.(10) for both carboxylic acids.

$\text{Ca}^{2+} + 3(\overline{\text{HR}})_2 \rightleftharpoons \overline{\text{CaR}_2 \cdot 4\text{HR}} + 2\text{H}^+$ (10) The extraction equilibrium constants of silver(I) and calcium(II) with these carboxylic acids were evaluated from the intercepts of the straight lines with the ordinates in Figs.4 and 5 as listed in Table 1.

From Table 1, it is obvious that there are very large differences between the extraction equilibrium constants with α -BTLA and palmitic or Versatic acids not only in the extraction

	Table 1. Extraction equilibrium constants of silver(I) and calcium(II)	
	$\text{Ag}(\text{dm}^3/\text{mol})$	$\text{Ca}(\text{dm}^3/\text{mol})$
α -BTLA	2.88×10^1	3.98×10^{-8}
palmitic acid	6.03×10^{-3}	-
Versatic acid	-	1.58×10^{-13}

of silver(I) but also in that of calcium(II). The difference in the extraction of silver(I), which is classified into "soft acids", may be attributable to the strong affinity of a sulfur atom of α -BTLA to silver. However, it cannot explain that in the extraction of calcium(II), which is classified into "hard acids", since it has no affinity to calcium. Beneitez et al.¹⁰⁾ found that the presence of a sulfur atom decreases the pK_a of the carboxylic acid and increases the extractions of various metals in their studies with S-tert-dodecylthioglycolic acid. It may be considered that alkylthio group at α -position also increases the acidity of carboxylic acid, which contributes the remarkable enhance-

ment of the extraction equilibrium constants. Hence, pK_a of α -BTLA in the aqueous phase was measured by pH titration method¹¹⁾ using a water-dioxane mixture containing α -BTLA, the ratio of which was variously changed. As the result, pK_a was evaluated as $pK_a = 3.9$. On the other hand, pK_a of Versatic acid in 1 mol/dm³ aqueous ammonium nitrate solution had been previously evaluated by the authors as $pK_a = 5.9$.¹²⁾ Therefore, it is considered that this large difference of pK_a between these two carboxylic acids is responsible for the large differences of the extraction equilibrium constants of silver(I) and calcium(II).

3.1.2. Extraction of Mercury(II) from Chloride Media¹³⁾

Next, we investigated the extraction equilibrium of mercury(II), a representative "soft acid", from aqueous sodium chloride solutions.

Figure 6 shows the effect of pH on the distribution ratio in the extraction of mercury(II) with α -BTLA. It is evident that the distribution ratio is independent of pH over the whole pH contrary to the extractions of silver(I) and

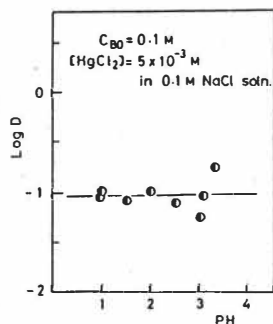


Fig.6 Effect of pH on the distribution ratio of mercury(II) in the extraction with α -BTLA

calcium(II) from nitrate media. This fact is considered to suggest that α -BTLA does not behave as a cation-exchange extractant as in the extraction of silver and calcium but as a solvating extractant in that of

mercury(II) from chloride media. This behavior of α -BTLA as a solvating extractant is considered to be caused by a strong affinity of a sulfur atom of this reagent to mercury(II).

pH was kept constant at pH=2 in the subsequent experiments. Figure 7 shows the effect of chloride ion concentration on the distribution ratio of mercury(II). Apparently, the distribution ratio decreases with increasing chloride ion concentration. This decrease is due to the increase of unextractable anionic mercury-chloride complexes, $HgCl_3^-$ and $HgCl_4^{2-}$, with increasing chloride ion concentration. Based on the solvating extraction reaction, the stoichiometric relation is described by Eq. (11) taking account of the coordination number of mercury(II) (=4).

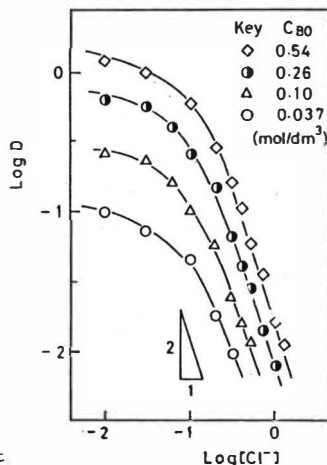
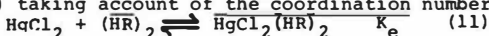


Fig.7 Effect of chloride ion concentration on the distribution ratio of mercury(II) in the extraction with α -BTLA

The equilibrium relation for the above reaction is described by

$$K_e = [\text{HgCl}_2(\text{HR})_2] / [\text{HgCl}_2][(\text{HR})_2] \quad (12)$$

In Eq. (12), the concentration of the unreacted dimeric species of the extractant, $[(\text{HR})_2]$, is nearly constant and equal to $C_{B0}/2$ under the present experimental conditions as in the preceding section. The concentration of the neutral chloro complex, $[\text{HgCl}_2]$, can be calculated from the total metal concentration in the aqueous phase, C_{MW} , and chloride ion concentration according to Eq. (13).

$$[\text{HgCl}_2] = \beta_2 [\text{Cl}^-]^2 C_{MW} / (1 + \sum_{i=1}^4 \beta_i [\text{Cl}^-]^i) \quad (13)$$

where β_i denotes the stability constant of the i th chloro complex of mercury(II). $\text{Hg}^{2+} + i\text{Cl}^- \rightleftharpoons \text{HgCl}_i^{(2-i)-}$ β_i (14)

Following values of β_i was used in the subsequent calculations.

$$\beta_1 = 5.8 \times 10^6, \beta_2 = 1.45 \times 10^{13}, \beta_3 = 9.72 \times 10^{13}, \beta_4 = 1.26 \times 10^{15} \quad (14)$$

Since tetrachloro complex, HgCl_4^{2-} , is predominant in the high concentration region of chloride ion ($[\text{Cl}^-] > 1 \text{ mol/dm}^3$), Eq. (13) is approximated by Eq. (15) under these conditions. $[\text{HgCl}_2] = \beta_2 C_{MW} / \beta_4 [\text{Cl}^-]^2$ (15)

Distribution ratio of mercury(II) is described by Eq. (16) from Eqs. (12) and (13) and is further approximated by Eq. (17) in the high concentration region of chloride ion.

$$D = [\text{HgCl}_2(\text{HR})_2] / C_{MW} = K_e (\beta_2 [\text{Cl}^-]^2 / 1 + \sum_{i=1}^4 \beta_i [\text{Cl}^-]^i) [(\text{HR})_2] \quad (16)$$

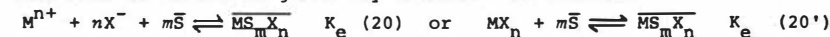
$$D = K_e \beta_2 [(\text{HR})_2] / \beta_4 [\text{Cl}^-]^2 \quad (17) \quad \text{Logarithm of Eq. (17) gives Eq. (18).}$$

$$\log D = -2 \log [\text{Cl}^-] + a \quad (18) \quad \text{where } a = \log(\beta_2/\beta_4) + \log K_e + \log [(\text{HR})_2] \quad (19)$$

The plotted points in Fig. 7 are apparently lying on straight lines of slope -2 in the high concentration region of chloride ion as expected from Eq. (18). The intercepts of these straight lines with the ordinate, a , are plotted against $\log [(\text{HR})_2]$ as shown in Fig. 8. As is evident from Fig. 8, the plotted points are lying on a straight line of slope 1 as expected from Eq. (19). The extraction equilibrium constant, K_e , was evaluated from the intercept of this straight line with the ordinate as $K_e = 5.5 \text{ dm}^3/\text{mol}$. The solid lines in Fig. 7 are the calculated curves based on Eq. (16) using this value of K_e and β_i mentioned above. The curves are in good agreement with the experimental results over the whole concentration region of chloride ion.

3.2 Extraction Properties of Trialkylphosphine Sulfides

Since trialkylphosphine sulfides ($= S$) undoubtedly behave as neutral solvating extractants, the stoichiometric relation of the extraction reactions of metals is generally described as follows.



The equilibrium relation for the above extraction reaction is described

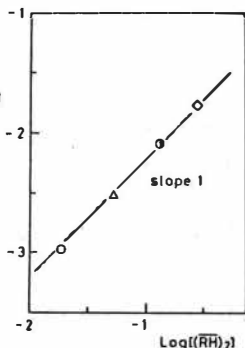


Fig. 8 Relation between a and $\log [(\text{HR})_2]$

by Eq.(21) or Eq.(21') analogous to Eq.(12) in the preceding section.

$$K_e = \frac{[MS_mX_n]}{[M^{n+}][X^-]^n[\bar{S}]^m} \quad (21) \quad K'_e = \frac{[MS_mX_n]}{[MX_n][\bar{S}]^m} \quad (21')$$

Distribution ratio is expressed by Eq.(22) or Eq.(22').

$$D = \frac{[MS_mX_n]/C_{MW}}{[M^{n+}][X^-]^n[\bar{S}]^m/C_{MW}} = K_e \quad (22) \quad D = \frac{K'_e [MX_n][\bar{S}]^m}{C_{MW}} \quad (22')$$

Distribution equilibria of metals with trialkylphosphine sulfides were analysed on the basis of Eq.(22) or (22') in the following sections.

3.2.1. Extraction of Silver(I) with TIBPS from Nitrate Media¹⁵⁾

As mentioned in 3.1.1, the formations of an ion-pair and ammine complexes in the aqueous phase should be taken into account in the extraction of silver from nitrate media.

Combination of Eqs.(5) and (22) gives the distribution ratio of silver(I) as follows.

$$D = \frac{K_e [NO_3^-] [\bar{S}]^m}{1 + \sum_{i=1}^2 \beta_i (K_A/[H^+])^i + K_1 [NO_3^-]} \quad (23)$$

In the regions of low concentration of nitrate ion and low pH, the formations of the ion-pair and ammine complexes can be ignored and, in addition, the concentration of the unreacted extractant, $[\bar{S}]$, is approximated to its initial concentration, C_{B0} . From Eq.(23), logarithm of the distribution ratio is expressed by Eqs.(24) and (25) in these regions.

$$\log D = \log [NO_3^-] + a \quad (24) \quad \text{where } a = m \log C_{B0} + \log K_e$$

Figure 9 shows the effect of nitrate ion concentration on the distribution ratio in the extractions from nitric acid and aqueous ammonium nitrate solution based on Eq.(24). Straight lines of slope 1 were obtained for both media in the low concentration region of nitrate ion. The values of a defined by Eq.(25) were evaluated from the intercepts of these straight lines with the ordinate for each C_{B0} and were plotted against $\log C_{B0}$ as shown in Fig.10. Obviously, the plotted points lie on a straight line of slope 2, which suggests that $m=2$. Therefore, the stoichiometric relation of this extraction reaction is expressed by Eq.(26).

$Ag^+ + NO_3^- + 2\bar{S} \rightleftharpoons AgS_2NO_3 \quad K_e \quad (26)$ The extraction equilibrium constant was evaluated from the intercept of the straight line with the ordinate as $K_e = 7.08 \times 10^6 \text{ (dm}^3/\text{mol)}^3$ for both media.

However, in the high concentration region of nitrate ion, the distribution ratios for both media deviate downward from the straight lines

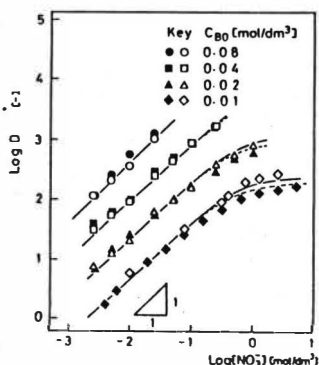


Fig.9 Effect of nitrate ion concentration on the distribution ratio in the extraction of silver with TIBPS (open keys = HNO_3 , closed keys = NH_4NO_3)

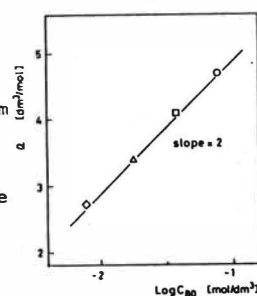


Fig.10 Relation between a and $\log C_{B0}$

with increasing concentration of nitrate ion. Furthermore, those from aqueous ammonium nitrate solution are slightly lower than those from nitric acid. This is due to the formations of the ion-pair and ammine complexes in the aqueous phase as mentioned earlier and also to the decrease in the concentration of the free extractant. Figure 11 shows the effect of pH on the distribution ratio in the extraction from 1 mol/dm³ aqueous ammonium

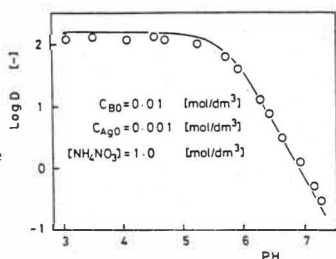


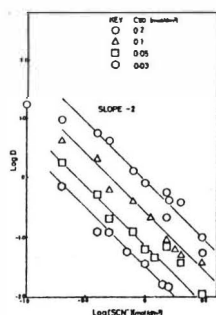
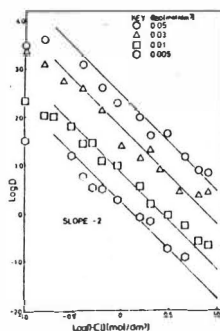
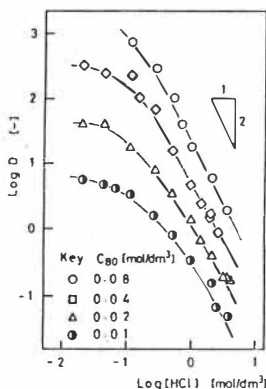
Fig.11 Effect of pH on the distribution ratio of silver in the extraction with TIBPS

The decrease of the distribution ratio at high pH can be attributable also to the increase of the ammine complexes. The curves in Figs.9 and 11 are the calculated results based on Eq.(23) using the extraction equilibrium constant evaluated earlier and the stability constants of the ammine complexes listed in 3.1.1. and taking account of the mass balance of the extractant and silver expressed by Eqs.(27) and (28), respectively.

$$C_{B0} = [\bar{S}] + 2[\bar{AgS}_2NO_3] \quad (27) \quad C_M \text{ initial} = C_M^{MW} + [\bar{AgS}_2NO_3] \quad (28)$$

3.2.2. Extractions of Mercury(II) with TIBPS¹⁶¹ and TOPS

In the preliminary experiments, it was found that trialkylphosphine sulfides are the much more effective extractants to mercury(II) than other sulfur containing extractants. Hence, detailed investigations on the extraction equilibria of mercury(II) from hydrochloric acid with TIBPS and TOPS were conducted. In addition, the extraction from aqueous ammonium thiocyanate solution with TIBPS was also studied to examine the ability of this aqueous solution as a stripping solution. Figures 12 and 13 shows the effect of hydrochloric acid concentration on the distribution ratio in the extractions with TIBPS and TOPS, respectively. Figure 14 shows the effect of thiocyanate ion concentration in the extraction from aqueous ammonium thiocyanate solution with TIBPS. As observed in the extraction with α -BTLA, the plotted points lie on straight lines of slope -2 in the high concentration region of anions, which can be attributable to the formations of unextractable tetrachloro or tetrathiocyanate complexes, HgX_4^{2-} ($X = Cl^-$ or SCN^-), in the aqueous phase as discussed in 3.1.2. Logarithm of the distribution ratio is approximately described by Eqs.(29) and (30) analogous to Eqs. (18) and (19). $\log D = -2\log[X^-] + a$ ($X^- = Cl^-$ or SCN^-) (29) where $a = m\log[\bar{S}] + \log(\beta_2/\beta_4) + \log K_e$ ($[\bar{S}] \approx C_{B0}$) (30) The intercepts of the straight lines of slope -2 with the ordinate in Figs.12-14 were plotted against C_{B0} according to Eq.(30) as shown in Fig.15. In Fig.15, it is evident that the plotted points lie on straight lines of slope 2, which suggests that $m=2$; that is, mercury(II) is extracted according to the stoichiometric relation expressed by Eq.(31).



Figs. 12, 13 and 14 Effect of the concentration of anionic species in the extractions from hydrochloric acid with TIBPS and TOPS and from aqueous ammonium thiocyanate solution by TIBPS

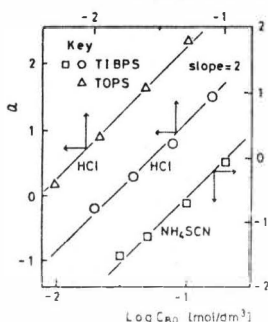
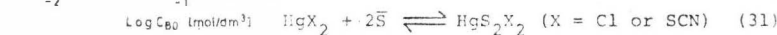
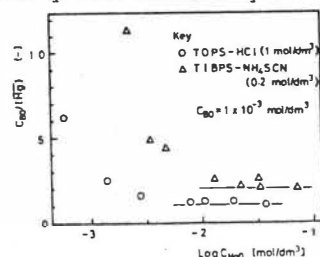


Fig. 15 Plot of α against $\log C_{80}$

Fig. 16 Experimental result of loading test



The extraction equilibrium constants were evaluated as follows: $K_e = 3.98 \times 10^5$ (TIBPS - HCl), 7.2×10^6 (TOPS - HCl), 1.8×10^6 (TIBPS - NH_4SCN) $[(\text{mol}/\text{dm}^3)^{-2}]$. However, from the results of the loading tests shown in Fig. 16, it is considered that mercury (II) is extracted as metal:extraction 1:1 dimeric complexes, $(\text{HgCl}_2)_2\text{S}_2$, from hydrochloric acid in the regions of high loading ratio as found with dialkyl sulfides.¹⁷

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Extraction Properties of Some Neutral Polydentate Organic Compounds Containing Sulfur and Nitrogen

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The neutral monodentate extragents are widely adopted in chemistry. The reagents containing several heteroatoms have become available owing to the fine organic synthesis techniques. Apriori, the mutual effect of atoms in the structure of an organic molecule is estimated by the inductive and resonance effects as well as by the CNDO/2 method, i.e. by variations in σ - and π -electron density of the heteroatoms. Moreover, the heteroatoms of one type (e.g. of sulfur) may be assumed as active centres whereas those of the other type (e.g. of nitrogen or oxygen) - as electron - active -substituents. The effect of the latter on the former should be conditioned by their electronegativities, types, configurations, and the carbon chain length. The donor centre and the electron-active substituent may exchange their roles with respect to the type of a metal. Proceeding from the general considerations stated above, the physico-chemical and spectral methods have been employed to analyze the investigation results of the extraction behaviour of aminosulfides and aminoketosulfides as related to the platinum metals and gold, to observe the complex formation reactions for such systems, and to consider the complexes' structures and compositions.

The chemical properties of the platinum metal and gold extractions are greatly influenced by the duration of the contact phase period. With the small period of phase contact the platinum metals are extracted according to the anion-exchange mechanism, an increase in the phase contact period favours the involvement of the donor centres into the inner sphere of the ion being a complex forming agent. Aminosulfides and aminoketosulfides can be employed as group extragents for the noble metals.

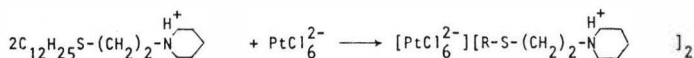
Introduction

A novel class of extragents consisting in aminosulfides and aminoketosulfides has been suggested for extracting Si, Au, Hg, and Pt metals thus taking into account the evergrowing interest of scientists to researches of nitrogen- and sulfur-containing compounds as noble metal ligands and proceeding from the coordination chemistry of the metals mentioned above [1]. The aminosulfide and aminoketosulfide geometries have been assumed to promote a free access for the donor atoms in forming the ion associate with the Pt metal acid complexes with their further involvement into the in-

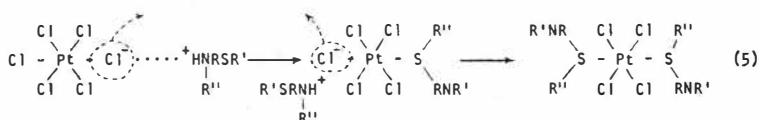
Extraction Chemistry

Palladium and Gold Extractions. Preliminary experiments afforded the estimation of the extraction equilibria settings to be 5-10 min. for Au(III) and Pd(II) extractions. As it follows from the distribution coefficient values for gold ($D > 10^3$) and palladium ($D > 10^2$), those metals are effectively extracted from HCl by aminosulfides and aminoketosulfides. According to the elemental analysis data of extracts saturated by a metal, Pd(II) is extracted as a monosolvate and Au(III) - as a semisolvate to give the following ratios, Pd:Cl:N:S=1:2:1:1; Au:Cl:N:S=2:6:1:1. The ^1H NMR spectral assignments made for the extract phases and for the extracted complexes isolated allow us to conclude that Au and Pd extractions involve both the nitrogen atom and sulfur atom of the reagent in complex formation. It should be noted that an increase in the metal concentration in the organic phase promotes the metal extraction process to be accompanied by the isolation of the extracted complexes to the third phase. The compounds formed possess low solubilities evidently due to the association thus impeding the quantitative description of the extraction equilibria. The extraction coefficient becomes considerably higher with an increase in temperature and with a decrease in the aqueous phase acidity.

Platinum Extractions. The most attractive results have been obtained with Pt(IV) extractions by aminosulfides and aminoketosulfides. The period of 20 min has been sufficient for establishing the equilibrium state in such systems. The Pt(IV) extractions by thioesters at room temperature take several days to reach the equilibrium state and those by aliphatic amines are considered noneffective, hence amino(keto)sulfides appear undoubtedly advantageous. Thus, the introduction of the amine nitrogen into a sulfide molecule produces essential effect on the rate of Pt(IV) extraction from the hydrochloric medium. An increase in the HCl concentration results in a considerable decrease in the Pt(IV) extraction by aminosulfides and aminoketosulfides. The HCl solution of 0.1-0.5 mol/l gives the most effective Pt(IV) extractions, the procedure of which is not accompanied by the third phase formation with the contact phase period below 5 minutes. The electron spectrum assigned for the extraction phase reveals an intensive absorption band in the region of 37000 cm^{-1} , which has been referred to a charge transfer from the chlorine ion to that of metal in hexachloroplatinate (IV)-ion. The ^1H NMR spectra show the largest additional shift for the proton signals of methylene groups at nitrogen atoms to compare it to the extragent spectrum. Taking into consideration the extract electronegativities and the electrophoregrams of the extracted complex phases isolated within the given period of phase contact, the platinum extraction proceeds by the phase exchange mechanism with the production of ion associates which can be easily isolated and identified. Therefore, the extragent donor centre, nitrogen, can be protonated, i.e. the platinum extraction with a short phase contact period is described by the following equation,



However, with an increase in the content phase period the H^1 NMR spectra show an additional shift of the proton signals of methylene groups at the sulfur atoms (1.5p. p.m.) and those signals at the nitrogen atoms appear analogous in complex formation with HCl. The Raman spectrum interpretation of the Pt(IV) complexes with amino(keto)sulfides isolated within the long contact phase period prove their trans-configurations. The sulfur atoms possess a sufficient trans-effect to lead to a relaxation of the Pt-Cl bond trans-positioned to the sulfur atom involved to result further in the chlorine atom substitution by the sulfur one and in the formation of the end complex with trans-configuration.





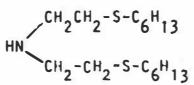
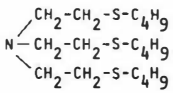

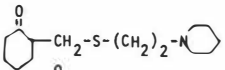
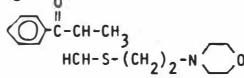
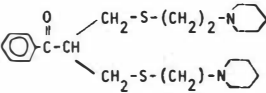
Thus, the Pt(IV) extractions by aminosulfides and aminoketosulfides occur in two stages. The production of ion association with the extraction proceeding by the anion exchange interphase mechanism in the first one and the substitution of chlorine ions in the Pt(IV) acid complex by the ligand sulfur atoms with further realization of the introduction mechanism in the second stage.

Complex Formation in the Neutral Media. With the complex formation in neutral media the nitrogen atoms are not protonated, which should determine both the compositions and the rates of production of the compounds. The ratio of Pt:Cl comprises 1:4 for all compounds. The Pt:Ln ratio is conditioned by the total content of sulfur and nitrogen atoms in Pt(IV) complexes with aminosulfides containing primary (DTEA) and secondary (BHEA) atoms of the amine nitrogen. Accounting for the coordination number of six inherent to the Pt(IV) complexes, the ligand sulfur and nitrogen atoms have been supposed to participate in complex formation, the H^1 NMR spectral assignments being the evidence. A comparison of the spectra of the Pt(IV) chlorode complexes with the DTEA and BHEA aminosulfides to those of the ligands reveals a shift of the proton signals at sulfur and nitrogen atoms. The Pt(IV) complex formation with the aminosulfides containing primary and secondary atoms of the amine nitrogen takes 3-5hs. The slowest is the complex formation in a neutral medium (2-3 days) with the ligands containing tertiary atoms of the amine nitrogen, i.e. with the aminosulfides of PEDS, MEDS, as well as with aminoketosulfides. The elemental analysis results prove the ratio of Pt:Cl:S to be 1:4:2 for all compounds thus allowing to suggest the following complex compositions: $PtCl_4 \cdot 2PEDS$, $(PtCl_4)_2 \cdot 2TBEA$, etc.

Rhodium Extractions. The studies into the contact phase period effecting Rh(III) extractions from the newly prepared HCl solution of 2 mol/l have demonstrated the extraction equilibrium to set up for 5 hs. The preliminary boiling of the Rh(III) so-

in an alcohol-benzene medium [5]. The aminosulfide and aminoketosulfide individualities and purities have been assigned by the elemental and functional analysis data, as well as by the IR, H^1 and C^{13} NMR spectral characteristics and by TL and GLC chromatographic descriptions. Table I presents some physico-chemical characteristics and conventional names of the components. A series of N-containing extragents represent strong bases to extract HCl. Thus, 1-(3-thiapentadecyl)-pyperidine extracts HCl to give monohydrochloride. The extraction constant for HCl has been determined by the potentiometric method, $\lg K_{ex} = 5.41 \pm 0.2$.

Table I. Structural Formulae and Some Physico-Chemical Properties

N : Conv. : Names :	Full Name	Structural Formula	b.p. _o C : m.p.	γ_{20}^{20} : γ_{20}^{20}	n_D^{20} : n_D^{20}
1 PEDS	Pyperidinoethyl-dodecyl-sulfide	$C_{12}H_{25}-S-(CH_2)_2-N$ 	158 (2mm)	0.9154	1.4875
2 MEDS	Morpholinoethyl-dodecyl-sulfide	$C_{12}H_{25}-S-(CH_2)_2-N$ 	170 (5mm)	0.9497	1.4875
3 DTEA	2-Dodecylthioethyl-amine	$C_{12}H_{25}-S-(CH_2)_2-NH_2$	170 (4mm)	0.8886	1.4739
4 BHEA	Bis(2-hexylthioethyl)-amine		200 (2mm)	0.9267	1.4930
5 TBEA	Tris(2-butylthioethyl)-amine		230 (2mm)	0.9676	1.5100
6 BAES	Dibutylaminoethyl-sulfide	$C_8H_{17}-S-(CH_2)_2-N$ 	163 (1mm)	1.8638	1.4710
7 PEC	2-(pyperidinoethyl-thiomethyl)cyclohexanone		100 (2mm)	1.0614	1.5290
8 PMP	1-Phenyl-2-(morpholinoethylthiomethyl)-1-propanone		210 (3mm)	1.1141	1.5537
9 BPP	Bis(pyperidinoethylthiomethyl)-1-phenyl-1-ethanone		100 (1mm)	1.0960	1.5570

ner coordination sphere of the complex forming ion, i.e. here the extraction of Pt metals is conducted by the reagent with a directing effect [2]. Besides, the labilization of the ligand exchange to the extragene donor atoms has been supposed to occur in the Pt metal acid complexes owing to the appearance of the ion-associative complex on the extraction initial stage; hence, the EDA bond formed between the complex forming ion and the polydentate reagent donor atoms should stabilize the oxidation degree of the metal ion with which it is transferred from the aqueous phase to the organic one [3]. The polyfunctional reagents may take the part of both the monodentate and polydentate chelate forming reagents. The cycle formation leads to a gain in the extraction free energy,

$$-RT \ln K_{ex} = \Delta G_{ex} = \Delta G_{complex} - \Delta G_{aq} + \Delta G_{solv} \quad (1)$$

$$\Delta G_{ex} = \Delta H_{ex} - T \Delta S_{ex}$$

The enthalpy factor contributes much to the extraction process, still with extracting metals by the polydentate extragents of equal importance is the other factor of free energy, i.e. the entropy one, which depends on several items:

- ΔS - solvation of the coordination compound under extraction;
- + ΔS - translational component of min molecules;
- + ΔS - relational component.

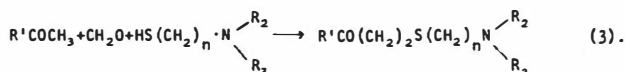
The total component of entropies and enthalpies is exactly the one to result in the total gain of free energy in extracting by the polydentate reagent

The investigation results of metal extractions by the polyfunctional organic compounds discussed have revealed the approach based on the coordination chemistry thesis to be the most perspective, that approach implying the close interconnection between the organic reagent reactivity and the structure and composition of the coordination compound formed in the course of extraction taking into consideration both the contribution of solvation to the organic phase and that of hydration to the aqueous one.

Extragen Syntheses

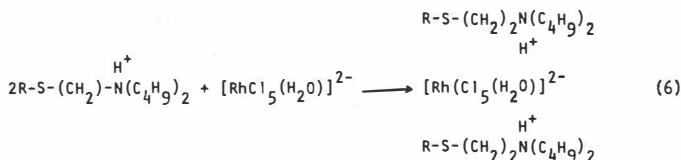
Aminosulfides and aminoketosulfides have been for the first time produced and identified in the Institute of Chemistry of the USSR Acad.Sci.Bashkirian Branch.

Aminoketosulfides have been synthesized in accordance with the amination reaction[4],



A number of the original structure aminosulfides has been obtained in reactions of the related amine Cl-derivatives with mercaptanes in the presence of caustic soda

lution in HCl of 2 mol/l during one hour decreases both the period of establishing the equilibrium down to 3 hs and the Rh(III) distribution coefficient. The lower Rh(III) distribution coefficients have been also observed with solutions kept for a week or longer. Many an author investigating the Rh(III) complex behaviour in aqueous solutions come across the so-called 'aging' phenomenon for the Rh(III) chloride solutions consisting in the process of aquation and hydrolysis. The problem of slow kinetics of the ligand exchange has also appeared with the Rh(III) extractions by teraalkylammonium chloride. In the case under consideration, a decrease in the Rh(III) extraction is evidently connected with the higher aquation which interfere with the extraction. Indeed, the absorption electron spectrum recorded for the solution boiled has revealed the higher content of the $\text{RhCl}_3(\text{H}_2\text{O})_2^-$ complex than that of $\text{RhCl}_5\text{H}_2\text{O}^{2-}$. That has been the reason for further employment of either the newly prepared Rh(III) solutions in 2 mol/l of HCl or the diluted initial Rh(III) solution in 6 mol/l of HCl with the working concentrations of hydrochloric acid. Quite natural should be an assumption that Rh(III) is extracted from the acidic medium by aminosulfides as ion associates by the ion exchange mechanism,



To prove the assumption said above, the electron absorption spectra have been recorded for the extract phases in chloroform with respect to the contact phase period in extractions from 0.1 mol/l and 2 mol/l of HCl. The spectra have been compared to those of the Rh(III) solution in 2 mol/l of HCl to find out changes in the electron absorption spectra with an increase in the phase contact period. Thus, the contact phase period of below 15 min results in the extract electron spectra shaped as for the $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ acid complex (with extractions from 2 mol/l of HCl). With the Rh(III) extractions from 1 mol/l of HCl the electron spectrum shapes of the extract phases are indicative of the extraction proceeding by the anion exchange mechanism during 5 minutes only. A decrease in the extraction period by the said mechanism with the negligible distribution coefficient ($D=0.05$) may be explained by the share of the $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ acidic complex considerably lowered in the aqueous phase. Furtheron, the decelerated involvement of donor atoms into the inner coordination sphere of the Rh(III) complex should evidently take place. The phase contact period growing up to 5 hs results essentially in no changes of the distribution coefficient.

Iridium Extractions. Our studies have been carried out for the Ir(III) and Ir(IV) extractions from hydrochloric acid solutions by amino(keto)sulfides. The period of interphase equilibrium settings comprises 30 min for Ir(III) and 50 min for Ir(IV) extractions. The initial stage for extracting both Ir(III) and Ir(IV) proceeds

according to the interphase ion exchange mechanism to be conformed by the ^1H NMR and electron absorption spectral data. With extractions of small Ir(IV) concentrations ($10^{-6} - 10^{-4}$ mol/l) from 0.1 mol/l of HCl iridium is completely reduced to the three-valence state. However, iridium is stabilized in the oxidation degree of +4 with an increase in its concentration in the organic phase and with the involvement of the extragent reactive centres (N and S donor atoms) to the inner sphere of iridium (confirmed by the ^1H NMR spectra showing a shift of the methylene proton signals at N and S atoms for 1 p.p.m.). The stabilization said above is influenced by the extragent type and the number of donor atoms involved in the very EDA bonding of ligand-complex forming ion. The difference in the extraction mechanism implies some novel routes of separating the platinum metals alongside with their group isolations by the employment of aminosulfides and aminoketosulfides as extragents.

Iron and Copper Extractions. The effect of iron and copper, those being the most concomitant elements, has been investigated for the platinum metal extractions. Considerable contents of base metals of $10^3 - 10^4$ as related to noble metals do not impede the quantitative extractions of the latters. Iron and copper are practically unextractable by PEDS in chloroform (Table 2).

Table 2. Distribution Coefficients ($\lg D$) of Fe(II) and Cu(II) Extracted by PEDS. $C_{\text{Me}} = 2 \cdot 10^{-3} \text{ M}$; $C_{\text{R}} = 0.05 \text{ M}$; Contact Phase Period = 60 min.

Metal	$C_{\text{HCl}}, \text{ M}$					
	0.1	0.4	0.9	1.7	3	6
Fe	-3.0	-2.7	-2.5	-2.2	-2.3	-0.2
Cu	-2.1	-2.1	-1.8	-2.0	-1.8	-1.6

Therefore, the sulfur containing amines allow to draw a quantitative differentiation between the noble metals and base ones.

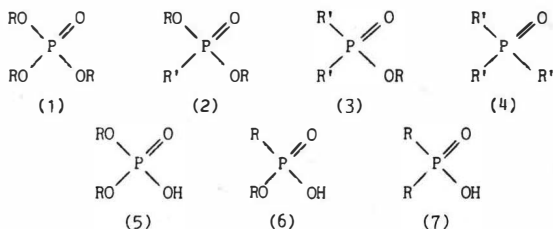
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Some Aspects of the Design of Selective Organophosphorus Extractants for Zinc, Cobalt, and the Rare-earth Metals.

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Organophosphorus compounds are widely used in commercial processes for the selective solvent extraction of metals. Neutral (solvating) extractants, such as types (1) to (4), are used for the extraction of uranium, thorium, iron, the rare-earth metals, zirconium, hafnium, niobium, tantalum, platinum, and iridium. Acidic (cation exchange) extractants, such as types (5) to (7), are used for the extraction of uranium, cobalt, zinc, vanadium, and the rare-earth metals.



These reagents present an interesting opportunity to examine the effects on extraction behaviour of the progressive replacement of C-O-P linkages by direct C-P bonds, and of changes in the identity of the substituent alkyl (or aryl) groups R and R'. In this paper we describe the extraction and selectivity characteristics of the neutral organophosphorus compounds (1) to (4) for which R = R' = n-butyl, cyclohexyl, phenyl, etc. towards

- (a) zinc(II), iron(III), and indium(III) in chloride media, and
- (b) scandium(III), yttrium(III) and the lanthanides(III) in nitrate media.

We also describe the extraction and selectivity characteristics of the series of organophosphorus acids (5) to (7) for which R = n-octyl, 2-ethylhexyl, cyclooctyl, etc. towards cobalt(II), nickel(II), zinc(II), copper(II), calcium(II), and magnesium(II) in non-complexing (nitrate) media.

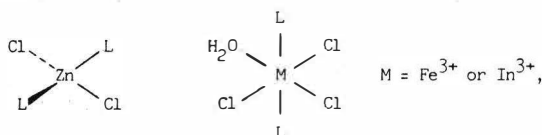
Extraction of zinc(II), iron(III), and indium(III) from sodium chloride solutions.

The extraction of metals from chloride solutions of low acidity by neutral organophosphorus compounds (L) can be represented as,



It was shown by slope analysis treatment of metal distribution data, and by analysis of chloride contents of loaded organic phases that the extracted complexes have the stoichiometries ZnCl_2L_2 , FeCl_3L_2 and InCl_3L_2 , although anomalous values of the coefficients n and m were obtained for the extraction of zinc(II) and iron(III) by tri-n-butyl phosphate (Table 1), indicating the presence of

complexes of the probable stoichiometries ZnCl_2L_3 and $[\text{M}^*(\text{H}_2\text{O})_x\text{L}_5][\text{FeCl}_4^-]$, where $\text{M}^* = \text{H}^+$ or Na^+ . In general, however, it is likely that the extracted complexes are tetrahedral for zinc(II), and trans-octahedral for iron(III) and indium(III),



the incorporation of water into the octahedral complexes being more likely than the existence of five-coordinate species. The inability to incorporate a third neutral organophosphorus ligand into the octahedral complexes can be understood in terms of the fact that the first two such ligands can occupy trans-positions, whereas a third would be required to occupy a sterically unfavourable position cis to both existing organophosphorus ligands. As a result of the trans-position of these ligands in the octahedral complexes, and the similarly sterically favourable position of the ligands in the tetrahedral zinc(II) complexes, however, it was found that the structure of the organophosphorus ligands themselves do not exert a profound effect upon the extraction strength or selectivities within a given class of compounds. Thus, for the series of isomeric di-n-butyl butylphosphonates $(\text{n-C}_4\text{H}_9\text{O})_2\text{R}'\text{PO}$, where $\text{R}' = \text{n-butyl, iso-butyl, sec-butyl or tert-butyl}$, metal extraction differs only to a small extent between members of the series (Fig. 1.). In contrast the metal distribution equilibria for most of the compounds in this study can be well correlated with the electron-donating or withdrawing nature of the substituent groups, using expressions of the type: $\log D = \log D_0 + \rho^* \Sigma \sigma^*$, where σ^* represents the polar substituent constants for alkyl and alkoxy groups bound to phosphorus available in the literature (1), and ρ^* is the reaction constant measuring the susceptibility of the reaction site (here, the phosphoryl group) to polar effects (Fig. 2.).

It is clear, therefore, that in the separation of zinc(II) and indium(III) from iron(III) by neutral organophosphorus compounds, the nature of the optimum extractant would depend largely upon the suitability of the extraction and stripping characteristics under the prevailing conditions, with little influence of structural effects on selectivities being evident.

Extraction of scandium(III), yttrium(III), and the lanthanides(III) from sodium nitrate solutions.

It was shown by slope analysis of distribution data, and by analysis of nitrate contents of loaded organic phases, that in the extraction of the trivalent rare-earth metals from sodium nitrate solutions of low acidity by neutral organophosphorus compounds (L),



the extracted complexes were usually of the stoichiometry $M(NO_3)_3 \cdot L_3$, although in the extraction of scandium(III) with sterically hindered compounds such as tri-cyclohexylphosphine oxide and di-n-butyl tert-butylphosphonate, complexes of the type $Sc(NO_3)_3 \cdot L_2$ are formed (Table 2). The incorporation of three organophosphorus ligands into the extracted complexes causes distinct steric effects to become apparent. Thus, the extraction of the rare-earth metals by the series of compounds (1) to (4) for which $R = R' = n$ -butyl exceeds that of the series for which $R = R' =$ cyclohexyl (Fig. 3.), whereas the reverse is true for the extraction of zinc(II) and iron(III) described above, where steric effects are less important. Moreover, with the n-butyl compounds the maximum extraction occurs near the middle of the lanthanide series (europium), whereas for their more hindered cyclohexyl analogues, the maximum extraction is shifted towards the metals of larger cationic radius (to praseodymium and cerium for the compounds shown in Fig. 3.).

Enigmatically, the extraction of the small scandium(III) ion (radius 0,068nm is less affected by the steric complexity of the extractant than are the larger lanthanide ions (radii 0,085 to 0,106nm). However, this may be the result of a less sterically hindered situation arising in the $Sc(NO_3)_3 \cdot L_3$ or $Sc(NO_3)_3 \cdot L_2$ complexes with monodentate nitrate ligands (six-coordinate cation) than in the $M(NO_3)_3 \cdot L_3$ lanthanide complexes with bidentate nitrate ligands (nine-coordinate cations). Better separation factors can be obtained for scandium(III) over yttrium(III), for example, using the cyclohexyl series (2) to (4) than with the corresponding n-butyl series (values for the latter in parentheses): $\beta_Y^{Sc}(2)$ to (4): 27 (3), 62 (4,5), and 35 (9). Separation factors also increase through the series of isomeric di-n-butyl butylphosphonates $(n-C_4H_9O)_2R'PO$, β_Y^{Sc} : 3, 5, 8 and 14 for the compounds with $R' = n$ -butyl, iso-butyl, sec-butyl, and tert-butyl, respectively. For the last-named series of extractants the dependence of extraction upon steric factors can be quantified by use of expressions of the type

$$\log D = \log D_0 + \delta E_s,$$

where E_s represents the steric substituent constants of the alkyl groups (here R') available in the literature (2), and δ is a constant indicating the susceptibility of the reaction site to steric effects. Representative correlations are shown in Fig. 4.

Extraction of base metals by organophosphorus acids.

The selectivity series for the extraction of divalent base metals by organophosphorus acids, such as di(2-ethylhexyl)phosphoric acid ($Zn > Cr > Ca \approx Mn > Cu > Fe > Co \approx Mg > Ni \approx V$) shows no correlation with the Irving-Williams series, but instead appears to reflect the ease with which the respective metal cations adopt the tetrahedral coordination (or, for Cu^{2+} and Cr^{2+} , a tetragonally distorted octahedral coordination) favoured by the bulky dimeric ligands (3). In view of

the different steric requirements of the tetrahedral (Zn, Mn, and Co), tetragonal or square-planar (Cu and Cr), and octahedral complexes (Ni, Ca, and Mg), differences in the type of organophosphorus acid (5) to (7) and in the steric complexity of the substituent alkyl groups might be expected to exert a considerable effect on the degree of selectivity observed for certain pairs of metals. The organophosphorus acids used in this study were prepared in order to investigate the effect of reagent structure on the extraction of cobalt, nickel, zinc, copper, calcium, and magnesium. The results obtained are summarized in Table 3 in terms of the differences between the $pH_{0,5}$ values for certain pairs of metals (e.g., $\Delta pH_{0,5}^{Ni-Co}$) under standard conditions. Clear trends are apparent in the separations between the pairs Co/Ni, Co/Ca, Zn/Cu, and Mg/Ca, which increase across the series (5) to (7) with a given substituent group, and with increase in the steric complexity of the alkyl group for a given reagent type. Both these effects are, in fact, related to steric factors, since the substituent alkyl groups are brought progressively closer to the metal-coordinating site in traversing the series (5) to (7).

The marked effects on Co/Ni selectivity and Co/Ca selectivity are clearly a result of the less sterically crowded situation that pertains in the tetrahedral cobalt complex $Co(HA_2)_2$ compared with the octahedral nickel and calcium complexes $M(HA_2)_2(H_2A_2)_n(H_2O)_{2-n}$. The rather smaller effect on Zn/Cu selectivity results from the relatively small differences expected between the steric requirements of the tetrahedral zinc and square planar copper complexes. Changes with respect to Mg/Ca selectivity are also distinct. Calcium is strongly extracted by the less sterically hindered reagents such as di-n-octylphosphoric acid ($\Delta pH_{0,5}^{Mg-Ca} = 1.12$ pH unit) due to the more favourable additional solvation of the larger Ca^{2+} ion (0.099nm, cf. Mg^{2+} 0.064nm) by undissociated molecules of the extractant. The selectivity for calcium over magnesium becomes smaller as the steric complexity of the extractant is increased, and for very hindered extractants such as di(2-ethylhexylphosphinic acid, where additional solvation of the cations is very difficult, the selectivity reverts to that expected on the basis of the higher stability constants for the formation of ionic complexes by the cation with the higher charge-to-radius ratio ($\Delta pH_{0,5}^{Mg-Ca} = -0.56$ pH unit).

Under the conditions used in this study, the nickel complexes of the more sterically hindered extractants, at least, appear to exist mainly as the species $Ni(HA_2)_2(H_2O)_2$, since plots of $\log D - 2 \log [H_2A_2]$ against pH give straight lines of slope 2. We have obtained an interesting confirmation that the two water molecules are present in the first coordination sphere of the cation (with, of course, possible additional water molecules held by hydrogen bonding). Thus, when water was removed from toluene solutions containing the pale green octahedral complex of, for example, dicyclooctylphosphinic acid by azeotropic evaporation of a small amount of the solvent, dark blue solutions were obtained with the spectral characteristics of tetrahedral nickel complexes $Ni(HA_2)_2$. (Fig. 5). Re-addition

of water to these solutions rapidly regenerated the original pale green nickel complex.

References

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Table 1. Stoichiometric coefficients of metal complexes $MCl_n L_m$ extracted by neutral organophosphorus compounds.

Extractant	Zn^{2+}		Fe^{3+}		In^{3+}	
	n	m	n	m	n	m
$(n-C_4H_9O)_3PO$	1,9	2,9	3,9	4,7		
$(n-C_4H_9O)_2n-C_4H_9PO$	2,0 ^a	2,2	2,9 ^a	2,0		2,3
$(c-C_6H_{11}O)(c-C_6H_{11})_2PO$	2,0		3,0			
$(C_2H_5O)(n-C_8H_{17})_2PO$		1,9		1,7	2,9	2,0
$(n-C_4H_9)_3PO$	2,0	2,2	2,9	2,0	3,0	

^a $(n-C_4H_9O)_2 iso-C_4H_9PO$

Table 2. Stoichiometric coefficients of metal complexes $M(NO_3)_3 L_m$ extracted by neutral organophosphorus compounds.

Extractant	Value of coefficient m					
	Sc	Y	La	Nd	Gd	Yb
$(n-C_4H_9O)_2n-C_4H_9PO$	2,97		3,35		3,02	3,28
$(n-C_4H_9O)_2t-C_4H_9PO$	2,05				2,91 ^a	2,94 ^b
$(C_2H_5O)(n-C_8H_{17})_2PO$		2,75	3,29	2,77	2,76	
$(n-C_4H_9)_3PO$	2,78				2,76	
$(c-C_6H_{11})_3PO$	2,10		2,59		2,59	2,62

^a Europium

^b Dysprosium

Table 3. Separations of divalent metal ions by solutions of organophosphorus acids (0,20M) in toluene at 20°C.

Extractant and alkyl group (R)	Separation of pH _{0,5} values (pH units)			
	Ni-Co	Ca-Co	Cu-Zn	Mg-Ca
(RO) ₂ POOH				
n-octyl	0,21	-1,30	1,25	1,12
2-ethylhexyl	0,53	-0,82	1,51	0,88
2-octyl	0,60	-0,39	1,64	0,59
cyclooctyl	0,64		1,61	
R(RO)FOOH				
n-octyl	0,83	-0,47	1,45	0,94
2-ethylhexyl	1,42	0,31	1,74	0,35
cyclooctyl	1,42	0,74	1,74	-0,09
R ₂ POOH				
n-octyl	1,28	0,38	1,60	0,48
2-ethylhexyl	1,93	1,50	1,62	-0,56
cyclooctyl	1,89		1,74	
2,4,4-trimethylpentyl	1,84	1,40		-0,51

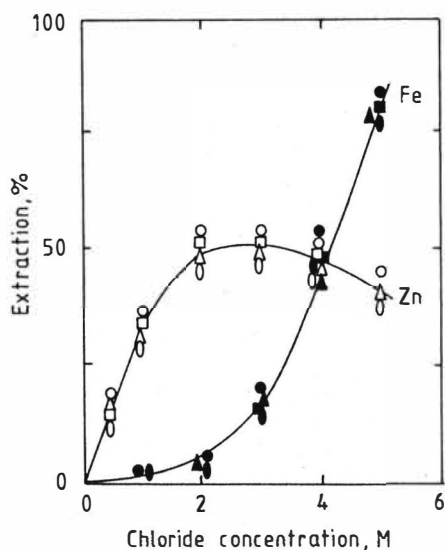


Fig. 1. Extraction of zinc(II) and iron(III) by solutions of di-n-butyl alkylphosphonates (1,0M) in xylene. Alkyl groups: (○) n-butyl, (Δ) iso-butyl, (□) sec-butyl, (●) tert-butyl.

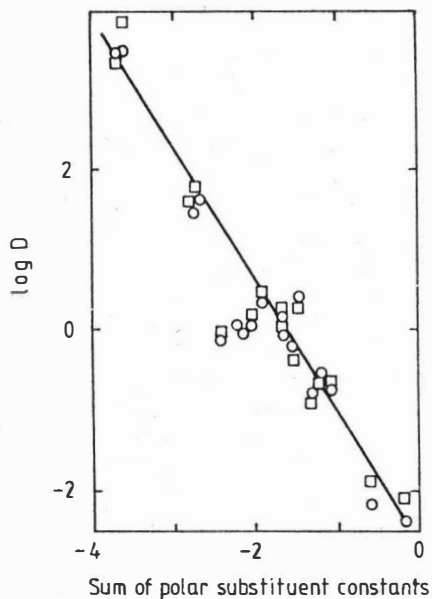


Fig. 2. Extraction of zinc(II) from 2M NaCl (O) and iron(III) from 4M NaCl (□) by neutral organophosphorus compounds (1,0M) in xylene as a function of the sum of the polar substituent constants of the groups attached to the phosphoryl donor-group.

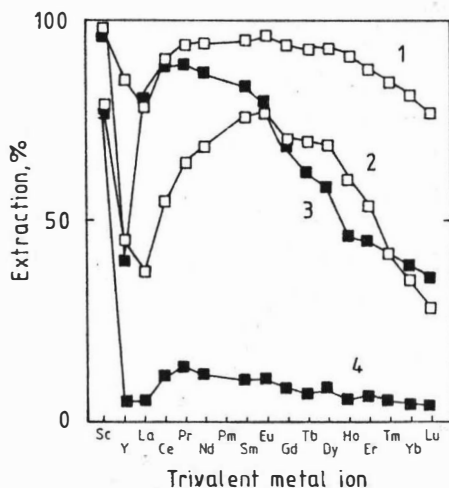


Fig. 3. Extraction of rare-earth metals from solutions of NaNO_3 (1,0M) by toluene solutions of :
 1. $(n\text{-C}_4\text{H}_9)_3\text{PO}$ (0,1M)
 2. $(n\text{-C}_4\text{H}_9\text{O})(n\text{-C}_4\text{H}_9)_2\text{PO}$ (0,25M)
 3. $(c\text{-C}_6\text{H}_{11})_3\text{PO}$ (0,1M)
 4. $(c\text{-C}_6\text{H}_{11}\text{O})(c\text{-C}_6\text{H}_{11})_2\text{PO}$ (0,25M)

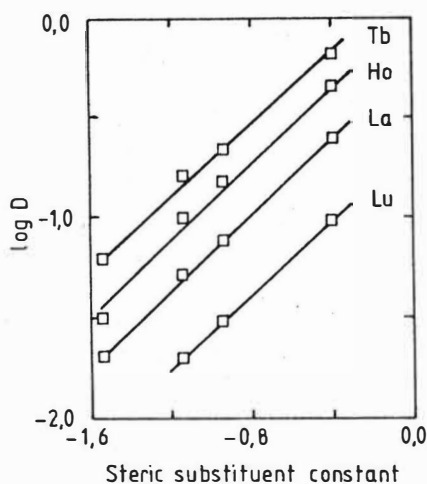


Fig. 4. Extraction of lanthanides from solutions of NaNO_3 (1.0M) by solutions of the isomeric di-n-butyl butylphosphonates (1.0M) in toluene as a function of the steric substituent constants of the isomeric butyl groups.

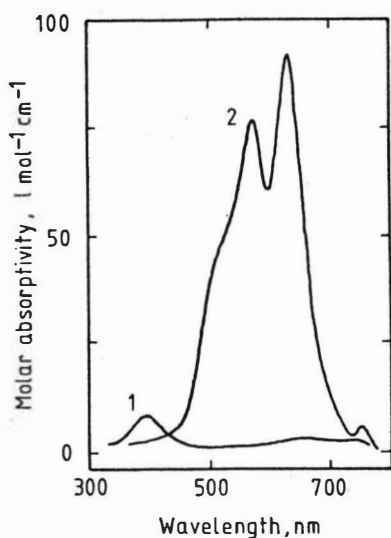


Fig. 5. Electronic spectra of toluene solutions of nickel complexes of dicyclooctylphosphinic acid (H_2A_2):
 1. $\text{Ni}(\text{HA}_2)_2(\text{H}_2\text{O})_2$;
 2. $\text{Ni}(\text{HA}_2)_2$

Solvent Extraction of Nickel(II) and Cobalt(II) from Acidic Leach Liquors by Synergistic Mixtures of Bis(alkyl)phosphoromonothioic Acids and Oximes or Substituted 8-Quinolins

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Although the solvent extraction of nickel(II) and cobalt(II) from acidic leach liquors has been extensively investigated during the last two decades, no commercial plant has been developed up to the present. However, recent works carried out by J.S. Preston [1,2] on the mixtures of organophosphorus acids and non-chelating oximes showed promising perspectives. Indeed, it was observed that the addition of non-chelating oximes such as 2-ethylhexanal oxime (EHO) to a solution of an organophosphorus acid (e.g. bis[2-ethylhexyl]phosphoric acid, denoted HL) produced marked synergistic effects, which enabled these two metals to be extracted under acidic conditions (pH 0 - 3) and then easily stripped. Nevertheless, it was found that the extraction of nickel(II) and cobalt(II) by such mixtures is poorly selective towards most other base metal cations, especially aluminium(III) which is usually present in the leach liquors. In previous communications [3, 4], we recommended the use of "soft" (according to the R.G. Pearson's hard and soft acids and bases principle [5]) extractants to achieve the selective recovery of nickel(II) and cobalt(II). Effectively, base metal cations such as Mg(II), Al(III), Mn(II), Cr(III), Fe(III), Co(III) are typical hard acids, whereas Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) are rather soft acids (in fact borderline). The hard and soft acids and bases principle is that hard acids (metals) prefer to bind to hard bases (complexing agents) and soft acids prefer to bind to soft bases. Among the "soft" extractants, the *o,o*-bis(alkyl)phosphorodithioic acids or more precisely their conjugated bases were found to be very efficient for the selective extraction of nickel(II) from high acidic media (pH ~ 0). However, these compounds present the drawback to be poorly stable against hydrolysis as soon as the temperature exceeds about 30°C [6]. The *o,o*-bis(alkyl)phosphoromonothioic acids possess a lesser degree of softness than their dithio analogues. When used alone in solution, they do not extract Ni^{2+} and Co^{2+} from high acidic media (e.g. pH ~ 0) and, at lower acidity (e.g. pH ~ 4), they are not selective of these two metal cations over other base metal cations. On the other hand, we showed that the replacement of the organophosphorus acids by *o,o*-bis(alkyl)phosphoromonothioic ones in the synergistic extractant mixtures proposed by J.S. Preston allows the selective recovery of Ni^{2+} , and at a lesser degree the one of Co^{2+} , towards base metal cations such as Al(III).

In the first part of the present paper we show that in spite of their "intermediate softness" the long chain *o,o*-bis(alkyl)phosphoromonothioic acids are fairly stable against hydrolysis for periods of months, even up to about 50°C. Then, we further in-

investigate the extraction of nickel(II) and cobalt(II) by the mixtures of *O,O*-bis(2-ethylhexyl)phosphoromonothioic acid (HL') and non-chelating oximes. Finally, we examine the possibilities of synergism arising from the mixtures of *O,O*-bis(2-ethylhexyl) phosphoromonothioic acid and substituted 8-quinolinols.

Experimental

The extraction experiments were carried out by shaking the mixture of aqueous and organic solutions inside a thermostated pear-shaped vessel the movement of which was reproducible (Agitelec equipment, Sté Toulemonde et Cie, Paris). The solution of metal cations were titrated by atomic absorption with a Video 11 Instrument Laboratory spectrophotometer.

O,O-Bis(2-ethylhexyl)phosphorodithioic acid (> 90%), *O,O*-bis(2-ethylhexyl)phosphoromonothioic acid (70%), 2-ethylhexanal oxime (99%), 7-(α -carbomethoxyanilinobenzyl)-8-quinolinol (99%) and 5-lauroyl-8-quinolinol (99%) were prepared in the laboratory. The percentages given in brackets represent the degree of purity. *O,O*-Bis(2-ethylhexyl) phosphoromonothioic acid contained about 30% of 2-ethylhexanol. Since long chain alcohols are often used as additives in liquid-liquid extraction, we did not try to eliminate the excess of 2-ethylhexanol. 2-Ethylhexanal oxime was a mixture of its two syn (30%) and anti (70%) isomers. 7-(4-Ethyl-1-methyloctyl)-8-quinolinol (99%) was isolated from "Kelex 100" (Shering) as previously reported [7]. The other reagents were analytical grade.

The stability of *O,O*-bis(2-ethylhexyl)phosphoromonothioic acid against hydrolysis was studied by shaking this reagent with acidic or neutral aqueous phases at different temperatures. The means of investigation used were acidimetric and gravimetric titrations, microanalyses and ^1H and ^{31}P NMR spectrometry.

Results and discussion

(1) Stability of *O,O*-bis(2-ethylhexyl)phosphoromonothioic acid against hydrolysis

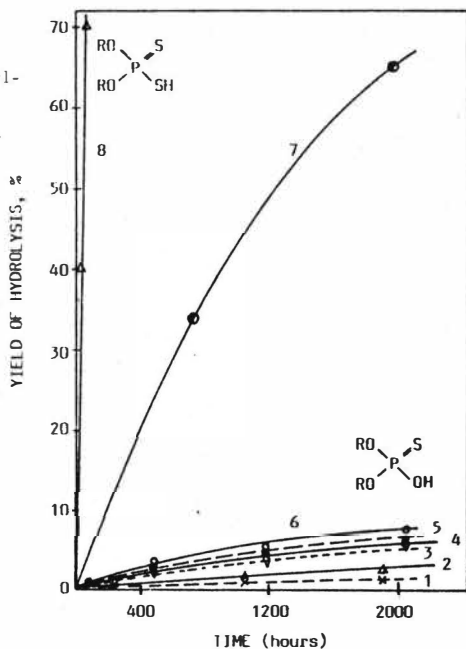
In figure 1, the yield of hydrolysis of *O,O*-bis(2-ethylhexyl)phosphoromonothioic acid (HL') has been plotted as a function of time for various temperatures. Examination of this figure shows that HL' is fairly stable against hydrolysis up to about 50°C. At 45°C, for instance, its yield of degradation is less than 2.5% after 3 months in contact with 1 mol.l⁻¹ HCl. Comparison of curves 4 and 8 in figure 1 also shows that the *O,O*-bis(alkyl)phosphoromonothioic acids are much more resistant against hydrolysis than their dithio analogues. However, beyond 65°C the degradation of HL' cannot be ignored (curve 7 in figure 1). The hydrolysis compounds we found in the aqueous phases were orthophosphoric acid as well as several other non-identified acidic phosphorus-containing compounds giving rise to ^{31}P NMR signals in the range -5.5 to 0 ppm (with

FIGURE 1

Yield of hydrolysis of *O,O*-bis(2-ethylhexyl)phosphoromonothioic acid (HL') and *O,O*-bis(2-ethylhexyl)phosphorodithioic acid (HL'') under various conditions.

- [1] HL', 25°C, 1 mol.L⁻¹ HCl
- [2] HL', 45°C, 1 mol.L⁻¹ HCl
- [3] HL' (0.92 mol.kg⁻¹) in kerosene, 65°C, 1 mol.L⁻¹ HCl
- [4] HL', 65°C, 1 mol.L⁻¹ HCl
- [5] HL' (0.92 mol.kg⁻¹) in kerosene, 65°C, H₂O
- [6] HL', 65°C, H₂O
- [7] HL', 85°C, 1 mol.L⁻¹ HCl
- [8] HL'', 65°C, 1 mol.L⁻¹ HCl

Unless otherwise stated, HL' and HL'' were used undiluted. The aqueous phases in contact with HL' or HL'' were either water or 1 mol.L⁻¹ HCl.



5×10^{-2} mol.L⁻¹ H₃PO₄ as internal standard). Up to 65°C, no phosphorus-containing compound other than *O,O*-bis(2-ethylhexyl)phosphoromonothioic acid was observable at significant level in the organic phases under study. On the other hand, five phosphorus-containing compounds were found in the organic phase left in contact with 1 mol.L⁻¹ HCl at 85°C during three months: *O,O*-bis(2-ethylhexyl)phosphoromonothioic acid ($\delta_p = -64.8$ ppm, 48%); bis(2-ethylhexyl)phosphoric acid ($\delta_p = 0.5$ ppm; 17%) and three other compounds A ($\delta_p = -69.0$ ppm, 2%), B ($\delta_p = -29.9$ ppm; 17%) and C ($\delta_p = -0.5$ ppm; 16%). The chemical shifts given in brackets are referenced to 85% H₃PO₄ as external standard. The percentage of each compound has been determined by integration of the ³¹P NMR signals. From bibliographical data we deduce that A and B could be a *O,O,O*-trialkylphosphorothioate and a *O,O,S*-trialkylphosphorothioate, respectively (the literature gives δ_p -67 to -68.5 ppm for (RO)₃P=S [8, 9] and δ_p -28 ppm for (RO)₂P(=O)SR [8, 10] with R = C₂H₅ and C₃H₇). It must be pointed out that (RO)₃P=S can be formed by a mere reaction of esterification between (RO)₂P(=S)OH and 2-ethylhexanol. Such a reaction could be, at least partially, avoided by using *O,O*-bis(alkyl)phosphoromonothioic acids free of alcohol. However, 2-ethylhexanol is thought to be among the hydrolysis products of *O,O*-bis(2-ethylhexyl)phosphoromonothioic acid. Finally, compound C could be 2-ethyl-

hexyl phosphoric acid $[(RO)P(=O)(OH)_2]$, in agreement with the existence of a second acidity in the acidimetric titration curves.

(2) Solvent extraction by mixtures of *o,o*-bis(2-ethylhexyl)phosphoromonothioic acid and non-chelating oximes

Thermodynamic aspect

The results discussed in our previous communications [3, 4] are summarized in table I. The synergistic effects observed for Ni^{2+} and Co^{2+} when non-chelating oximes are added to bis(2-ethylhexyl)phosphoric acid (HL) or *o,o*-bis(2-ethylhexyl)phosphoromonothioic acid (HL') are due to the formation of mixed complexes. In the absence of oxime, the extracted cobalt complexes (with HL or HL') show electronic spectra characteristic of tetrahedral symmetry. The addition of non-chelating oximes causes transformation of the blue tetrahedral species to pink octahedral ones. The nickel complexes are always octahedral.

The complexes of nickel(II) and cobalt(II) extracted by the mixture of HL' and 2-ethylhexanal oxime (EHO) are now investigated in more details by the slope analysis

Table I : Metal extraction by various organic phases at 20°C : pH values at 50% metal extraction (phase ratio = 1).

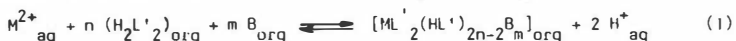
Extractants ^(a) (each 0.5 M)	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Al^{3+}	Mn^{2+}	Mg^{2+}
HL ^(b)	4.1	3.7	2.9	1.4	1.5	2.8	3.8
HL' ^(c)	3.3	2.9	< 0	0.3	1.4	3.1	3.4
HL'' ^(c)	0	0	< 0	0	> 3	3.0	> 4
HL + EHO ^(b)	1.6	2.0	1.0	1.6	1.5	2.0	3.7
HL' + EHO ^(c)	0.4	1.3	< 0	1.0	1.7	> 3	3.8

HL: bis(2-ethylhexyl)phosphoric acid; HL': *o,o*-bis(2-ethylhexyl)phosphoromonothioic acid; HL'': *o,o*-bis(2-ethylhexyl)phosphorodithioic acid; EHO: 2-ethylhexanal oxime.

(a) The concentration of the extractants is expressed as the number of moles of monomer per litre of solution; (b) from reference [2]; (c) initial aqueous phases contained 0.05 mol.L^{-1} metal cations in 1.0 mol.L^{-1} $(H, Na)_2SO_4$; HL', HL'' and EHO were in solution in kerosene.

Type of reagents : --- soft or borderline; ☐ hard.

technique. *O,O*-Bis(alkyl)phosphoromonothioic acids exist mainly as the dimeric species $H_2L'_2$ in non-polar solvents [11]. The extraction of a divalent metal cation, M^{2+} , by a dimerized acidic extractant, $H_2L'_2$, in the presence of a non-chelating oxime, B, can be represented by the general reaction :



where aq means aqueous and org organic. Hence the following expression can be derived:

$$\log D = \log K_{ex} + n \log [H_2L'_2] + m \log [B] + 2 pH \quad (2)$$

where K_{ex} is the equilibrium constant for eqn. (1) and D represents the distribution coefficient of the metal between the organic and the aqueous phases. Inspection of eqn. (2) shows that plots of $\log D$ against pH at constant $[H_2L'_2]$ and constant $[B]$ should consist of straight lines with slope 2.0. Similarly, plots of $\log D - 2 pH - m \log [B]$ against $\log [H_2L'_2]$ and plots of $\log D - 2 pH - n \log [H_2L'_2]$ against $\log [B]$ should consist of straight lines with slopes n and m, respectively. Such plots for the extraction of nickel(II) from 0.2 mol.L^{-1} (Na, H)ClO₄ by mixtures of HL' and EHO in dodecane at 25°C gave straight lines in all cases (figure 2). As expected, the metal distribution shows second order dependence on pH (slope $[1.93 \pm 0.24]_{95\%}$). It was also found that $n = [1.72 \pm 0.21]_{95\%}$ and $m = [3.28 \pm 0.32]_{95\%}$. Such results lead us to propose the formula $NiL'_2(HL'_2)(EHO)_3$. It must be pointed out that J.S. Preston found the same stoichiometry for the mixed complex of nickel(II) formed by bis(2-ethylhexyl)phospho-

FIGURE 2

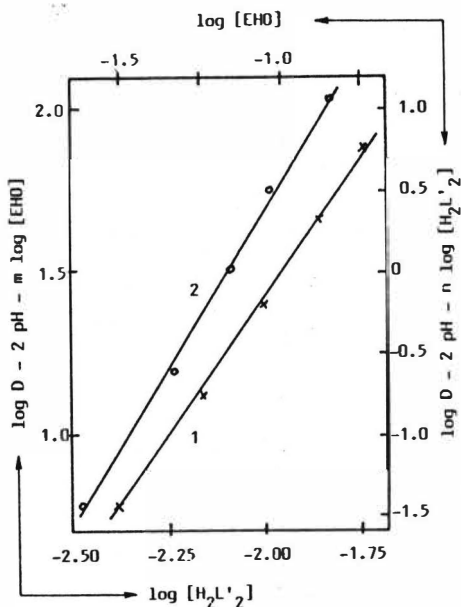
Extraction of Ni(II) by mixtures of *O,O*-bis(2-ethylhexyl)phosphoromonothioic acid (HL') and 2-ethylhexanal oxime (EHO) in dodecane, at 25°C.

(1) $\log D - 2 pH - m \log [EHO] = f(\log [H_2L'_2])$

initial concentrations: $[EHO] = 0.15 \text{ mol.L}^{-1}$; $[HL']$ between 4.5×10^{-3} and $1.5 \times 10^{-2} \text{ mol.L}^{-1}$ and $[Ni^{2+}] = 2.0 \times 10^{-3} \text{ mol.L}^{-1}$

(2) $\log D - 2 pH - n \log [H_2L'_2] = f(\log [EHO])$

initial concentrations: $[HL'] = 1.5 \times 10^{-1} \text{ mol.L}^{-1}$; $[EHO]$ between 2.5×10^{-2} and $1.5 \times 10^{-1} \text{ mol.L}^{-1}$ and $[Ni^{2+}] = 2.0 \times 10^{-3} \text{ mol.L}^{-1}$.



ric acid and 2-ethylhexanal oxime [2]. However, from the asymptotic limits of the distribution isotherms of nickel(II) between aqueous solutions (pH 1.7) and kerosene containing HL' (7.3×10^{-2} or 1.3×10^{-1} mol.L⁻¹) and an excess of EHO (4.2×10^{-1} mol.L⁻¹), a metal/thiophosphorus ligand (as L' or HL') stoichiometry of 1:2 was derived, which suggests that several mixed complexes can exist depending upon the conditions of extraction.

Similar experiments have been performed with cobalt(II). Plots of log D against pH at constant $[H_2L'_2]$ and constant [B], as well as plots of log D - 2 pH against $\log[H_2L'_2]$ at constant [B] consist of straight lines. The slopes obtained indicate that the distribution ratio shows second order dependence on pH [1.98 ± 0.15]_{95%} and first order dependence on the concentration of HL' [0.85 ± 0.25]_{95%}. On the other hand, plots of log D - 2 pH against $\log[B]$ at constant $[H_2L'_2]$ did not give a straight line. Here again, the existence of several complexes cannot be precluded.

Kinetic aspect

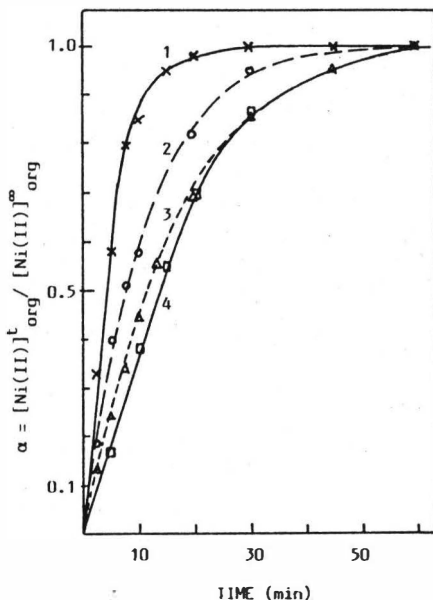
The rate of extraction is one of the most important factors in industrial applications. In figure 3, the dimensionless organic concentration α has been plotted as a function of the contact time for various pH ($\alpha = [Ni(II)]^t_{org} / [Ni(II)]^\infty_{org}$, where

FIGURE 3

Fraction α of Ni(II) extracted into the organic phase as a function of time at various pH, at 25°C (phase ratio = 1).

- (1) pH = 1.2 (2) pH = 1.0
(3) pH = 0.9 (4) pH = 0.7

Initial concentrations: $[HL'] = [EHO] = 0.2$ mol.L⁻¹ in dodecane and $[Ni^{2+}] = 2.0 \times 10^{-3}$ mol.L⁻¹ in 0.2 mol.L⁻¹ (H, Na)ClO₄.



$[\text{Ni(II)}]_{\text{org}}^t$ represents the concentration of nickel(II) extracted into the organic phase after time t and where $[\text{Ni(II)}]_{\text{org}}^{\infty}$ denotes its concentration at equilibrium). The experiments have been performed at non-controlled interfacial area (agitation cell). Examination of figure 3 shows that the extraction of nickel(II) by the mixture of *o,o*-bis(2-ethylhexyl)phosphoromonothioic acid and 2-ethylhexanal oxime is much more rapid than the extraction of nickel by previously described synergistic extractant mixtures such as LIX 65 N + Versatic 911 acid [12] or LIX 63 + carboxylic acids [13]. Indeed, in this latter case, contact time of several hours were required in order to attain equilibrium at room temperature.

(3) solvent extraction by mixtures of *o,o*-bis(2-ethylhexyl)phosphoromonothioic acid and substituted 8-quinolinols

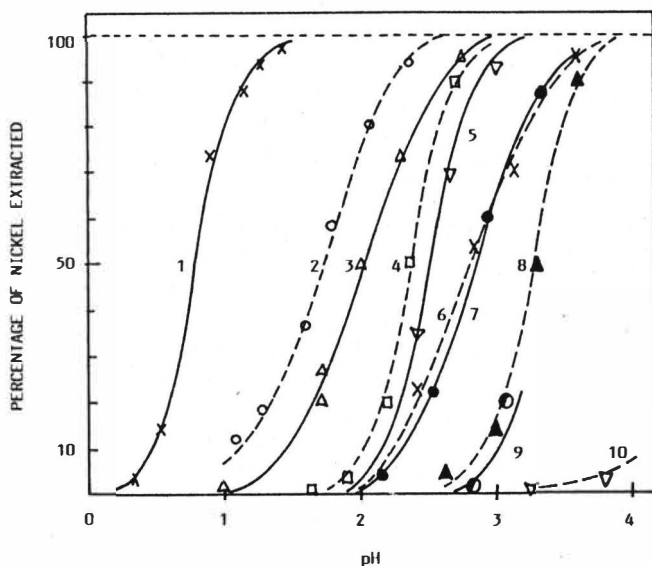


FIGURE 4: Extraction of nickel(II) by various organic phases at 25°C (phase ratio = 1).

Initial conditions: (1) $5 \times 10^{-2} \text{ M Ni(II)}$; 0.5 M HL' + 0.5 M 5-CloXH in CHCl_3 , (2) $5 \times 10^{-3} \text{ M Ni(II)}$; $5 \times 10^{-2} \text{ M HL'}$ + $5 \times 10^{-2} \text{ M 5-CloXH}$ in CHCl_3 , (3) $5 \times 10^{-2} \text{ M Ni(II)}$; 0.5 M HL' + 0.5 M 7-C₁₁oxH in kerosene, (4) $5 \times 10^{-3} \text{ M Ni(II)}$; $5 \times 10^{-2} \text{ M HL'}$ + $5 \times 10^{-2} \text{ M 5,7-Cl}_2\text{oxH}$ in furfural, (5) $5 \times 10^{-2} \text{ M Ni(II)}$; 0.5 M HL' + 0.5 M 5-LoXH in CHCl_3 , (6) $5 \times 10^{-2} \text{ M Ni(II)}$; 0.5 M HL' + 0.5 M 5-CMABoxH in CHCl_3 , (7) $5 \times 10^{-3} \text{ M Ni(II)}$; $5 \times 10^{-2} \text{ M 5-CloXH}$ in CHCl_3 , (8) $5 \times 10^{-2} \text{ M Ni(II)}$; 0.5 M HL' in kerosene, (9) $5 \times 10^{-2} \text{ M Ni(II)}$; 0.5 M 7-C₁₁oxH in kerosene, (10) $5 \times 10^{-3} \text{ M Ni(II)}$; $5 \times 10^{-2} \text{ M HL'}$ in CHCl_3 .

In the purpose to find an alternative way, the extraction of nickel(II) by mixtures of *O,O*-bis(2-ethylhexyl)phosphoromonothioic acid and substituted 8-quinolinols has been investigated. Five 8-quinolinols were tested : 7-(4-ethyl-1-methyloctyl)-8-quinolinol (7-C₁₁oxH), 7-(α -carbomethoxyanilinobenzyl)-8-quinolinol (7-CMABoxH), 5-lauroyl-8-quinolinol (5-LoxH), 5,7-dichloro-8-quinolinol (5,7-Cl₂oxH) and 5-chloro-8-quinolinol (5-CloxH). The experimental results are reported in figure 4. Examination of this figure, in particular curves 3, 8 and 9, and curves 2, 7 and 10, shows that synergistic effects occur in the extraction of nickel(II). 5-Chloro-8-quinolinol appears as the most efficient additive for extraction of Ni²⁺ from high acidic media. Moreover, the separation of Ni²⁺ could be selective towards aluminium(III) and at a lesser degree towards zinc(II). Indeed, with the mixture of HL' ($5 \times 10^{-1} \text{ mol.L}^{-1}$) and 5-CloxH ($5 \times 10^{-1} \text{ mol.L}^{-1}$) in CHCl₃, the pH values at 50% extraction (pH_{0.5}) were 0.8, 1.5 and 2.1 for nickel(II), zinc(II) and aluminium(III) [each initially $5 \times 10^{-2} \text{ mol.L}^{-1}$ in 1.0 mol.L^{-1} (H, Na)₂SO₄], respectively. On the other hand, the extraction of aluminium(III) (pH_{0.5} = 2.1) and the one of zinc(II) (pH_{0.5} = 1.5) interfere with the extraction of cobalt(II) (pH_{0.5} = 1.4).

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MIXED-METAL COMPLEXES FORMED DURING SOLVENT EXTRACTION WITH CARBOXYLIC ACIDS

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Introduction

Despite much fundamental research work done since the late 1950's, carboxylic acids have found few applications as commercial solvent extraction reagents. The reasons for this include the fact that these reagents extract iron ahead of most other base metals, they are not very specific for many transition metals and they have a rather high aqueous solubility, particularly at the relatively high pH at which many base metals are extracted. However there has been a recent renewal of interest in these extractants because they possess the correct acidity and thermal stability to allow certain metals to be stripped from loaded carboxylate solutions by direct hydrolysis with water at 130 - 200°C. Iron carboxylates precipitate hematite by this process, whereas mixed solutions of iron with nickel, cobalt, magnesium and manganese precipitate magnetic spinel ferrites. This process might make solvent extraction an economic process for removing waste iron from metallurgical process streams, and is currently being investigated as a means of producing oxides for ceramics applications. The success of this hydrolytic stripping process will be crucially dependent on the purity of the carboxylate solutions that can be prepared by solvent extraction. Although extraction data indicate that iron is extracted well ahead of other base metals, Mühl and coworkers have found evidence of coextraction in carboxylate systems, which lowers the separation factors for iron and base metals [1]. Coextraction was attributed to the formation of mixed carboxylate complexes. This paper presents work done to characterize the extent of coextraction of a variety of metals with iron, to determine whether coextraction might be controlled by manipulation of the aqueous solution chemistry, and to identify any mixed-metal carboxylate complexes which might form in the organic solution.

Experimental Procedure

Solvent extraction tests were done using a 33 vol % solution of Neo-Decanoic acid, produced by Exxon Chemical Co., in kerosene. The organic solutions were equilibrated overnight at the desired temperature with an equal volume of aqueous solution, 0.05M in the metal of interest, with a total ionic strength of 2.0M after pH adjustment with sodium carbonate, then the equilibrium pH was measured. Distribution

coefficients were determined by stripping the organic solutions with 6.0 M HCl and measuring all metal concentrations by atomic absorption spectrophotometry.

UV/visible spectrophotometry was done on a Cary 17D spectrophotometer with a carboxylic acid/kerosene reference. Infrared spectrophotometry was done with a Perkin-Elmer 180 spectrophotometer, and high resolution mass spectra were obtained with a Kratos MS 50 Fast Atom Bombardment (FAB) spectrometer.

Results and Discussion

Figure 1 shows the percentage extraction of Fe^{3+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} and Mg^{2+} from sulphate solutions as a function of pH. These extraction curves agree well with those reported previously [2-5], with the order of extraction closely following the order of hydrolysis of these ions. Figure 2 shows the effect of different anions on the distribution coefficients of Fe^{3+} , Cu^{2+} , Zn^{2+} and Ni^{2+} . It is evident that for each of these ions extraction occurs at progressively higher pH's going from nitrate to chloride and sulphate solutions, but to different extents for the different metals. This effect is due to increasingly strong complexation by chloride and sulphate ions, and can be predicted accurately for chloride, and less well for sulphate, by a mathematical model describing extraction [6].

Figures 1 and 2 suggest that solvent extraction with carboxylic acids would give very effective separation of iron from copper, zinc, nickel and other divalent metal ions. In practice, however, it may be difficult to obtain such good separations. Figure 3 shows extraction curves for iron and nickel alone, along with curves for iron in the presence of nickel, and nickel in the presence of iron, in nitrate, chloride and sulphate solutions at 25°C. It is evident that at low pH nickel is strongly coextracted with iron, this effect increasing on going from nitrate to chloride and sulphate solutions. Similar behaviour was observed for nickel with iron at 60°C, and for manganese, cobalt and magnesium with iron at 25°C, all in sulphate solutions. Zinc was found to coextract with iron in a similar manner, although to a lesser extent, whereas coextraction of copper was not detected in nitrate solutions, but was evident at very low pH in chloride and sulphate solutions. It is evident from Figure 3 that if iron was to be removed from process streams by carboxylic acids, the most satisfactory separations would be achieved by maximizing the loading of iron in the organic, or by using nitrate solutions.

Since the divalent metals are not extracted from single metal aqueous solutions at the low pH's at which coextraction occurs, it is evident that the carboxylate species which form during coextraction must be different from those which form during the extraction of divalent metals alone, and have higher formation constants. Since the metals which coextract most strongly with iron are those with the most

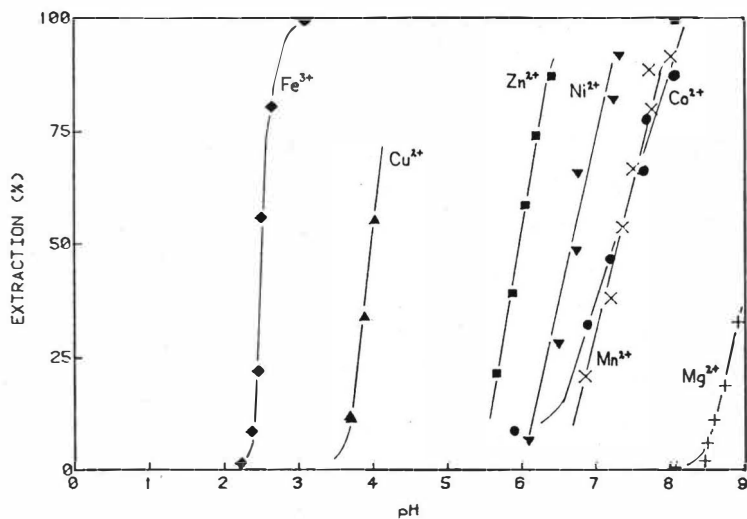


Figure 1: Extraction of Metal Ions from Sulphate Solutions with Neo-Decanoic Acid in Kerosene at 25°C, $[M]_{\text{tot}} = 0.05\text{M}$, $[\text{SO}_4^{2-}]_{\text{tot}} = 0.6\text{M}$

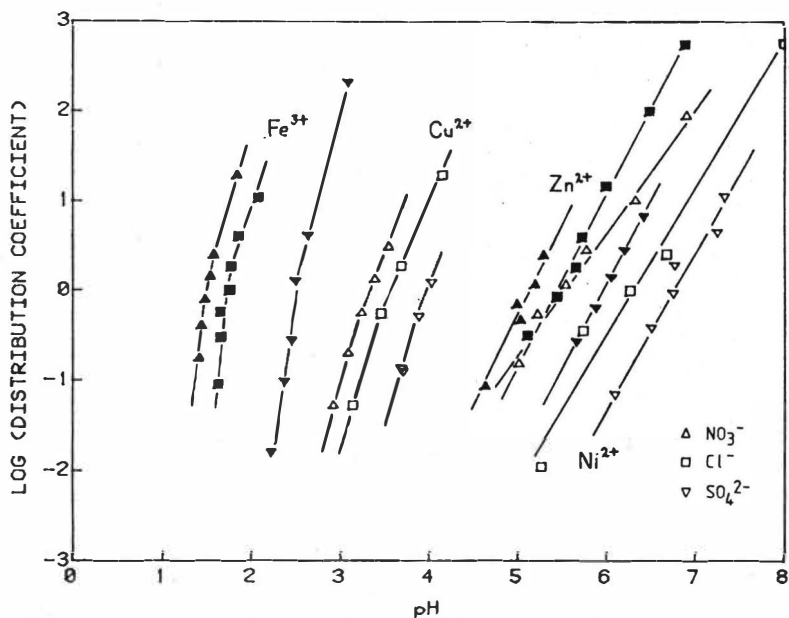


Figure 2: Extraction of Metal Ions from Nitrate, Chloride and Sulphate Solutions with Neo-Decanoic Acid in Kerosene at 25°C, $[M]_{\text{tot}} = 0.05\text{M}$

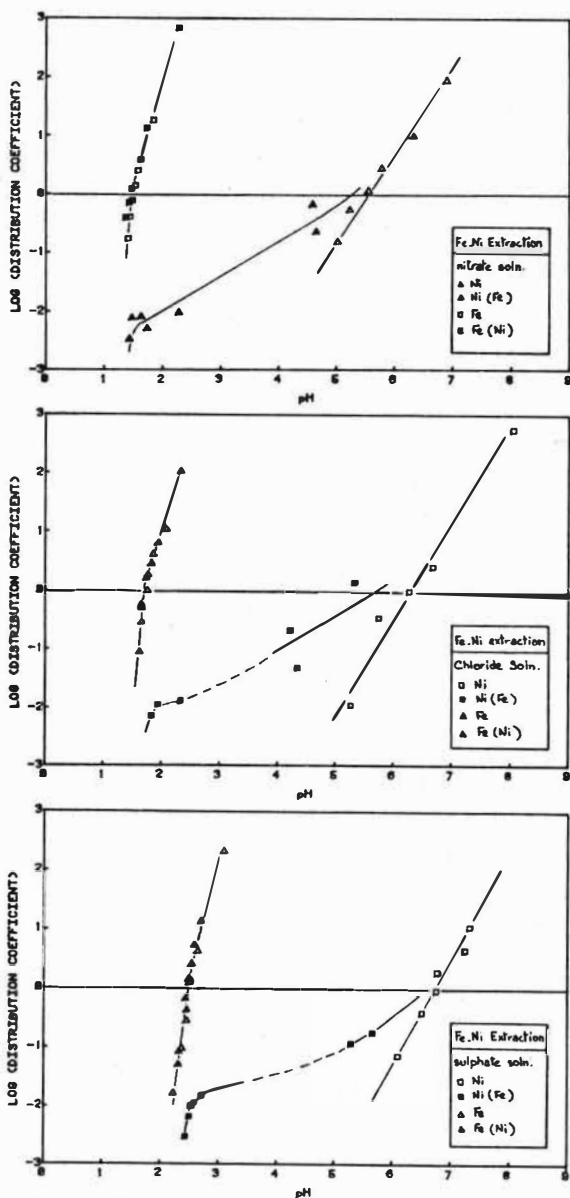


Figure 3: Extraction of Iron and Nickel with Neo-Decanoic Acid From Single and Mixed Nitrate, Chloride and Sulphate Solutions

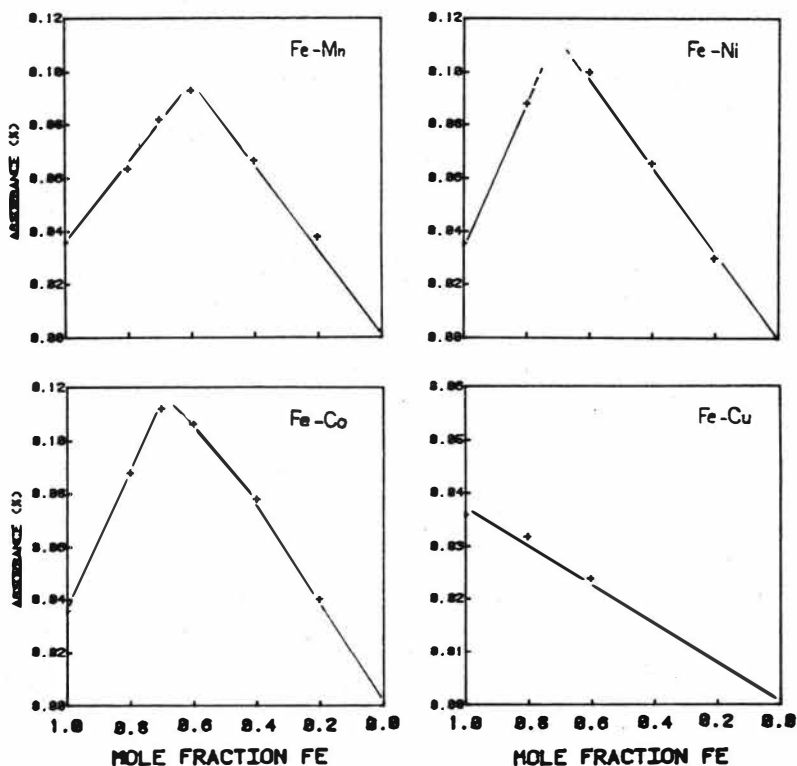


Figure 4: Variation in the Absorbance at 450nm for Carboxylate Solutions Containing Iron and One Divalent Cation

dissimilar extraction behaviour, it is likely that the new species are mixed metal carboxylate complexes. To investigate the nature of any such mixed complexes, various techniques were used to examine mixed metal carboxylate solutions.

As shown in Figure 4, UV/visible spectrophotometry showed deviations from Beer's Law of additivity of absorbances for carboxylate solutions containing iron with manganese, cobalt or nickel in various ratios. This indicates the presence of mixed species. The maximum deviation from linearity at 450nm corresponded to complexes containing Fe(III) and M(II) in the ratio 3:2, 2:1 and 2:1 for Mn, Co and Ni respectively. Solutions containing iron with copper, zinc and magnesium showed

additive absorbances; however this does not indicate the absence of any mixed complexes, but rather that there were no mixed complexes which absorb at 450nm in these solutions. The importance of wavelength is demonstrated by Figure 5, which shows the corrected absorbance of iron-nickel carboxylate solutions at various wavelengths. This plot shows the existence of two distinct complexes, with Fe:Ni ratios of 2:1 and 3:1 which are active at different wavelengths.

Infrared spectroscopy gave further evidence of the existence of mixed metal carboxylate species. Figure 6 shows the carbonyl region of the spectra of (a) iron, cobalt and mixed iron-cobalt carboxylate solutions and (b) iron, manganese and mixed iron-manganese solutions. It is evident that the spectra of both mixed solutions are not the sums of the spectra of the single metal solutions; for example the iron peak

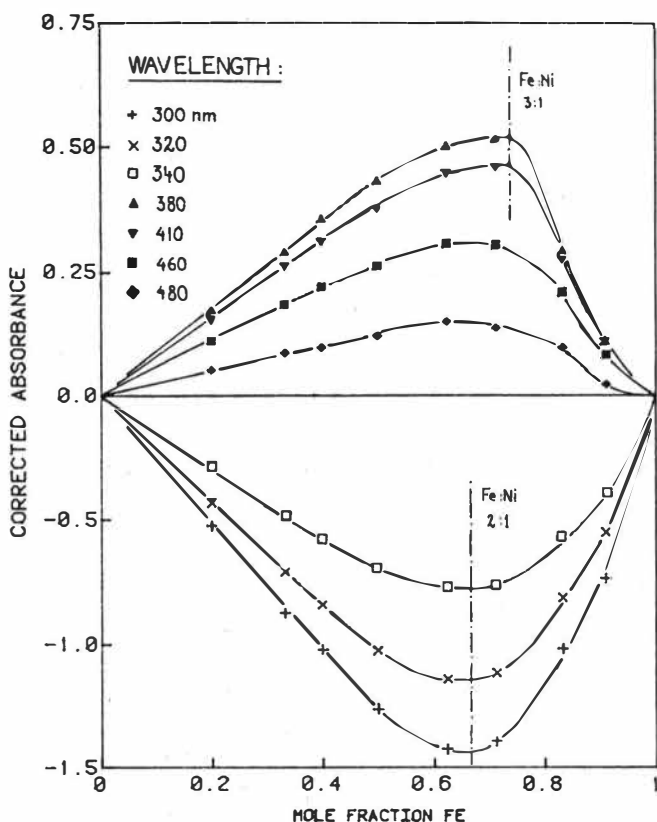


Figure 5: Continuous Variation Method Plots for Iron-Nickel Carboxylate Solutions

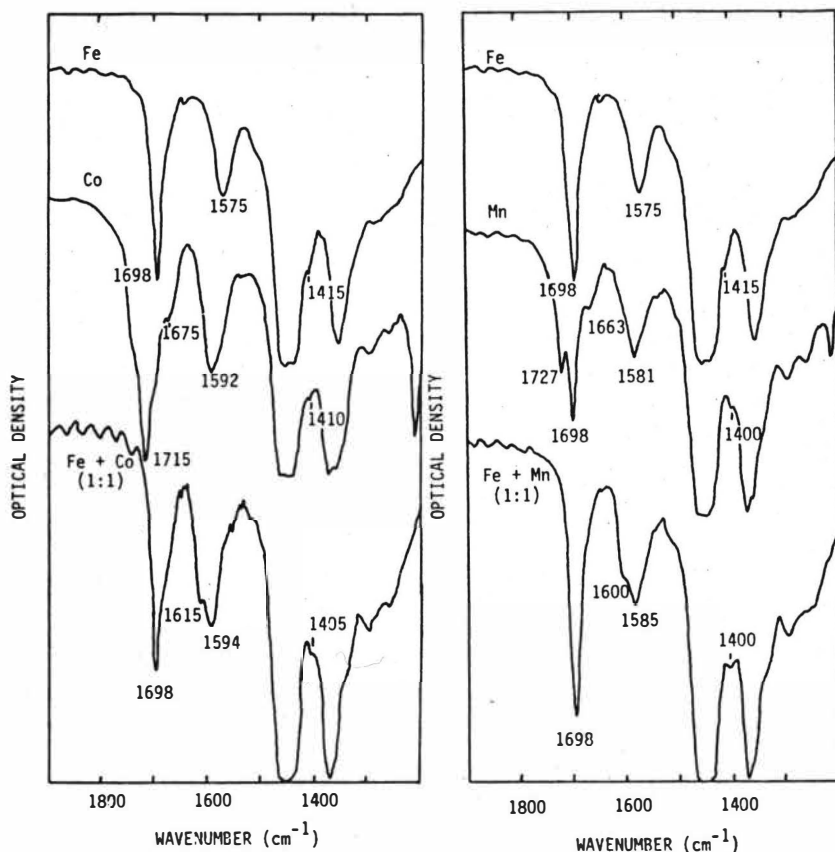


Figure 6: Infrared spectra of (a) Fe and Co, (b) Fe and Mn Carboxylate Solutions

at 1575 cm^{-1} and the cobalt peak at 1592 cm^{-1} which are probably due to bidentate chelation and monodentate coordination respectively do not appear in the mixed iron-cobalt solution. Instead these peaks appear to have shifted to the higher frequencies of 1615 and 1594 cm^{-1} , which suggests that there are mixed iron-cobalt complexes with the same type of coordination as in the single complexes, but with somewhat weaker metal-ligand bonds. A similar effect is seen for the iron-manganese system, and the iron-nickel system which has been discussed at length [7]

Fast atom bombardment mass spectrometry was done on nickel, iron and mixed iron-nickel carboxylate solutions; this also indicated that the mixed solution contained

species that were distinctly different from the species present in the single metal solutions. Ions corresponding to the main peaks in the spectra are shown in Table I. These do not correspond to neutral species, which suggests that the complexes are broken up within the spectrometer. Moreover, the species present after evaporation during mass spectrometry may be different from those present in solution. However, on the basis of these data the most likely complexes appear to be NiR_2 and $(\text{NiR}_2)_2$ in nickel carboxylate solutions, $(\text{Fe}(\text{OH})\text{R}_2)_3$ in iron carboxylate solutions and $\text{Fe}_2\text{Ni}(\text{OH})_3\text{R}_6$ in mixed iron-nickel solutions.

Acknowledgements

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Table I: Main Peaks in FAB Spectra of Nickel and Iron Carboxylate Solutions and Corresponding Species

Nickel		Iron		Iron and Nickel	
m/z *	Corresponding Species	m/z	Corresponding Species	m/z	Corresponding Species
458	NiR_2	697	$\text{Fe}_3(\text{OH})\text{R}_3$	699	$\text{Fe}_2\text{Ni}(\text{OH})\text{R}_3$
629	Ni_2R_3	868	$\text{Fe}_3(\text{OH})\text{R}_4$	870	$\text{Fe}_2\text{Ni}(\text{OH})\text{R}_4$
802	Ni_2R_4	1039	$\text{Fe}_3(\text{OH})\text{R}_5$	1041	$\text{Fe}_2\text{Ni}(\text{OH})\text{R}_5$
		1210	$\text{Fe}_3(\text{OH})\text{R}_6$	1213	$\text{Fe}_2\text{Ni}(\text{OH})\text{R}_6$

* m/z is mass to charge ratio

LIQUID-LIQUID EXTRACTION OF PALLADIUM (II) FROM THE
 $\text{PtCl}_4\text{-PdCl}_2\text{-HCl-H}_2\text{O-XYLENE-CYANEX 471 SYSTEM}$

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INTRODUCTION

The refining of the platinum group metals on a continuous basis to produce the high purity individual metals require the availability of a separation and concentration technology such as liquid-liquid extraction. The liquid-liquid extraction process, to be successful, must have a complexing extractant that is selective for the desired metal. The complexity of the extraction process increases when very dilute concentration of the desired metal is to be recovered, as in the case of the leached platinum and palladium from spent automotive catalytic converters. (1,2)

Cleare et al. (3,4) discussed the various ways in which the desired separations can be achieved by the proper manipulation of the chemistry of the platinum group metals. The new platinum refinery of Matthey Rustenberg Refiners utilizes liquid-liquid extraction processing for the separation of the platinum group metals.(5) This paper reports on the liquid-liquid extraction equilibria of the $\text{PtCl}_4\text{-PdCl}_2\text{-HCl-H}_2\text{O-xylene-Cyanex 471 System}$.

Cyanex 471 has potential in the separation of palladium (II) from platinum(IV) and palladium(II) chloride solutions. Palladium extraction occurs through a solvating mechanism. The loading capacity of Cyanex 471 extractant increases with increasing concentration of extractant in the solvent. A phase modifier, p-nonylphenol, may be used to enhance loading. In the absence of the modifier, the extracted palladium complex precipitates as a dark brown solid at a loading of 10.5 g/l palladium and a Cyanex 471 concentration of 120 g/l. Modification with 10% p-nonylphenol doubles the solubility of the Cyanex 471 in the solvent, xylene. The exact chemical formula and structure of Cyanex 471 has not been made public by American Cyanamid.

EXPERIMENTAL

Reagents

The palladium and platinum used in this study were obtained from Alpha Products. The platinum(IV) chloride had a stated purity of 99.98% in aqueous hydrochloric acid solution, while the reported purity of the palladium(II) was 99.998%. The other chemicals used were of reagent grade purity.

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Cyanex 471 is an experimental phosphine-based sulfide extractant, developed and provided by the Industrial Products Division of American Cyanamid Company.

Analytical Work

Two analytical methods were used to determine palladium and platinum concentrations. A Bausch and Lomb Spectronic 700 Spectrophotometer was used for analysis at higher palladium(II) concentrations of 100-500 ppm, in the absence of platinum(IV). The concentration was determined by a method based on the palladium(II)-tin(II) chloride colorimetric system developed by Ayres et al. (6,7). At low palladium concentrations of 0-100 ppm or whenever there was platinum(IV) present, a Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer was used, following the method described by Potter (8). Calibration tests on both instruments showed very good accuracy.

When the Bausch and Lomb Spectrophotometer was used, the following procedure was followed. To an aliquot of palladium(II) chloride solution in a 25-ml flask were added 10 ml of mixed acid (2.4 M in hydrochloric acid and 2.3 M in perchloric acid). A green color was developed by the addition of 2 ml of 0.5 M tin(II) chloride solution 1 M in hydrochloric acid. The mixture was diluted to volume. After 30 minutes its absorbance was measured at 635 nm. This procedure follows Beer's law between 4.0 and 40.0 ppm palladium. A calibration curve was initially completed using a standard palladium(II) chloride solution.

The atomic absorption procedure was used with a standard for both the platinum and palladium hollow cathode lamps. After correct adjustments of the lamp positions, burner heat position, gas flows and energy levels, the samples were measured against the standards at wavelengths of 247.6 and 265.9 nm for palladium and platinum, respectively. The results were then tabulated using the Perkin-Elmer PRS-10 Printer Sequencer.

Distribution Ratio Studies

A known volume of aqueous solution was equilibrated with an equal volume of the organic solution containing Cyanex 471. This was accomplished in 60 ml separatory funnels by shaking the two phases in an automatic shaker for at least one hour, and allowing the phases to separate for a minimum of 30 minutes.

After phase separation in the 60 ml separatory funnels, the aqueous phase was removed and analysis performed by either the spectrophotometric or atomic absorption method. The final HCl concentration in the aqueous phase was determined by titration using phenolphthalein as an indicator. All experiments were carried out at 296K. The distribution ratio, D_c of the system was defined to be $D_c = \bar{C}_M / C_M$ where \bar{C}_M is the metal concentration in the organic phase and C_M is the metal concentration in the aqueous phase. The percent extraction was defined to be C_M / C_{M0} , where C_{M0} is the initial metal concentration in the aqueous phase.

RESULTS AND DISCUSSION

Calibration Curve

Using a standard solution of 101.8 ppm PdCl_2 ($9.565 \times 10^{-4} \text{ mol/dm}^3$) in 0.12 M HCl, the procedure of Ayres and Alsop (6) was followed. Aliquots of the standard were tested in ten equal increments ranging from 4.07 to 40.7 ppm. A reference blank gave an absorbance reading of 8.7 on the digital readout, with the decimal point on the digital readout set to read tenths. This reference absorbance was then subtracted from all future absorbance readings. A linear regression analysis was then done on the ten calibration runs. The following equation was obtained:

$$C_M = 4.45 \times 10^{-6} (\text{actual absorbance})(\text{dilution factor}) \quad (1)$$

where C_M is the concentration of Pd in mol/dm^3 , actual absorbance is the absorbance reading minus the 8.7 reference absorbance, and the dilution factor is the volume of the original sample divided by the total volume of the diluted sample actually used in the spectrophotometric analysis. This equation had a correlation coefficient, r^2 , of 0.9998, which shows excellent accuracy. After all analytical work with the spectrophotometer was completed, the standard solution was rechecked. All readings were within 1% of the original calibration readings.

PdCl_2 -HCl- H_2O -xylene-Cyanex 471 System

The distribution ratio, D_c , was measured for the PdCl_2 -HCl- H_2O -xylene-Cyanex 471 system as a function of Cyanex 471 and HCl concentrations at initial Pd concentrations in the aqueous phase of 509 and 30.61 ppm Pd. Figure 1 shows D_c obtained

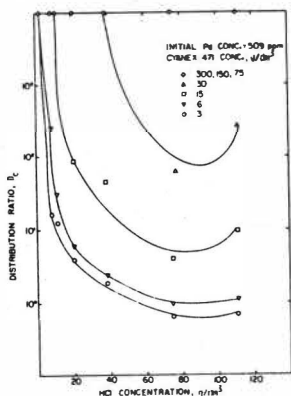


FIGURE 1.
Effect of HCl concentration on the extraction equilibria of palladium with Cyanex 471 in xylene, at $C_{\text{MO}} = 509$ ppm.

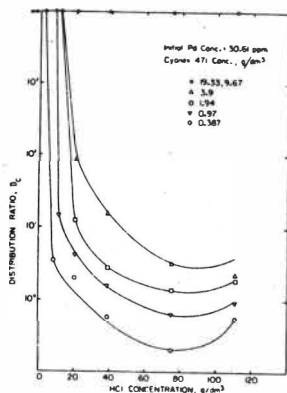


FIGURE 2.
Effect of HCl concentration on the extraction equilibria of palladium with Cyanex 471 in xylene, at $C_{\text{MO}} = 30.6$ ppm.

for various Cyanex 471 concentration versus HCl concentration at an initial Pd concentration of 509 ppm. Figure 2 shows D_c obtained for different Cyanex 471 concentrations versus HCl concentration at an initial Pd concentration of 30.61 ppm. The amount of Cyanex 471 required to achieve 100% extraction increases with an increase in Pd concentration. For all Cyanex 471 values below the 100% extraction level, the distribution ratio first decreases with increasing HCl concentration, then passes through a minimum between 70 and 75 g/dm³ HCl (about 2 M HCl) and finally increases slowly.

Initial liquid-liquid batch equilibria studies found that the HCl concentration in the aqueous phase increased slightly as palladium complexed with Cyanex 471 and was extracted into the organic phase. This increase in HCl concentration led to the incorrect assumption that cation exchange was the mechanism by which extraction occurred and to the erroneous conclusion that only a stronger acid could effectively strip the Pd from the organic phase. After finding in batch stripping studies that concentrated HCl did not strip effectively, volumetric analysis of the aqueous phase showed a decrease in aqueous phase volume. This finding led to the correct conclusion that a solvating mechanism is the extraction mechanism with H₂O being co-extracted. This in turn resulted in the increased HCl concentration in the aqueous phase.

Palladium loading

The maximum extent to which palladium can be loaded into the organic phase is 87% of stoichiometric loading, where 2 moles of Cyanex 471 extractant react with 1 mole of palladium in the presence of 10% p-nonylphenol phase modifier. This maximum loading represents 20.5 g/dm³ Pd in a xylene solution of 120 g/dm³ Cyanex 471 modified with 10% p-nonylphenol. At the maximum loading the extracted palladium complex precipitates as a dark brown solid.

PtCl₄-PdCl₂-HCl-H₂O-xylene-Cyanex 471 System

When PtCl₄ was added to the palladium(II) chloride system, the extraction chemistry became very complicated. Figure 3 shows the distribution ratio $D_{c,Pd}$ of palladium and Figure 4 shows the distribution ratio of platinum $D_{c,Pt}$ obtained for different Cyanex 471 concentrations versus HCl concentration. Initial palladium and platinum concentrations in the aqueous phase were 15.3 and 31.3 ppm, respectively. The distribution ratio of palladium goes through at least two minimums,

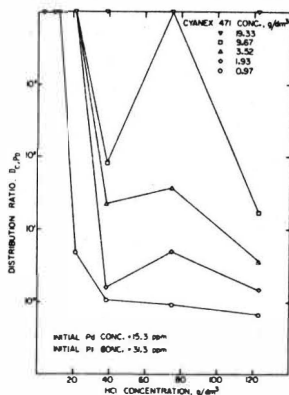


FIGURE 3.
Effect of HCl concentration on the extraction equilibria of palladium in the presence of platinum with Cyanex 471 in xylene.

indicating at least two competing complexing reactions at the aqueous-organic interface. The distribution ratio of platinum varies greatly with both HCl and Cyanex 471 concentrations, indicating multiple complexing reactions at the aqueous-organic interface. The limiting reaction at each point could depend on parameters such as free ion concentration, HCl concentration, Cyanex 471 concentration, palladium complex concentration or possibly others.

The fact that Cyanex 471 can still extract 100% of the palladium while simultaneously extracting as much as 4% of the platinum under certain conditions suggests very strongly that Cyanex 471 could be used to separate palladium from platinum in chloride solutions. Figure 5 shows the separation factor Pd/Pt defined as $Pd/Pt = D_{cPd}/D_{cPt}$ obtained for various Cyanex 471 concentrations versus HCl concentration. Infinite separation factors in the dilute HCl range demonstrate the feasibility of this type of separation in an extraction column. The unknown composition of Cyanex 471 makes the present study of the complexing reactions difficult.

Palladium stripping

Concentrated HCl was the first to be tried based on the incorrect cation exchange mechanism assumption. Maximum stripping of palladium was 11% at 8 M HCl when tested between 6-12 M HCl. After the correct solvating mechanism was understood, various compounds which form strong ligands with palladium were tried. Sodium carbonate and sodium hydroxide were both tried, but neither stripped any palladium from the organic phase. Next a sodium thiosulfate fixer solution was tried. This solution consisted of 240 g/dm³ Na₂S₂O₃·5H₂O, 15 g/dm³ Na₂SO₃, and 7.5 g/dm³ H₃BO₃. This solution effectively stripped 100% of the palladium in all cases if the solution was fresh. If the solution was more than a few hours old, the S₂O₃²⁻ ions began to decompose in the H₂O. Ammonium thiosulfate can be

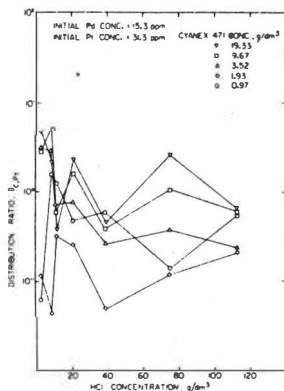


FIGURE 4.
Effect of HCl concentration on the extraction equilibria of platinum in the system PdCl₂-PtCl₄-HCl-H₂O-Cyanex 471-xylene

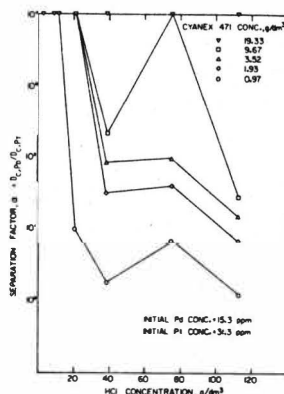


FIGURE 5.
Effect of HCl concentration on the separation factor of palladium and platinum in the PdCl₂-PtCl₄-HCl-H₂O-Cyanex 471-xylene system.

used in place of sodium thiosulfate to accomplish the same result. Aluminum potassium sulfate can also be added to help stabilize the stripping solutions but was not used because aluminum interferes with palladium detection in both the atomic absorption and spectrophotometric analytical procedures.

CONCLUSION

Cyanex 471 is an extractant which has remarkable potential in separating palladium(II) from chloride solutions containing platinum(IV) and palladium(II). Liquid-liquid extraction equilibria studies have given infinite separation factors in the dilute HCl region demonstrating that Cyanex 471 could be applied to conventional commercial solvent extraction process to recover palladium(II) from spent automotive catalysts. The distribution equilibria and solution chemistry of the $\text{PdCl}_2\text{-HCl-H}_2\text{O-xylene}$ -Cyanex 471 system is complicated by the presence of PtCl_4 . The system becomes extremely complex with various complexing reactions competing at the interface.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. Harvey J. Jensen for his assistance with the equipment set-up and the Industrial Products Division of American Cyanamid Company for providing the Cyanex 471 reagent. The authors also wish to acknowledge the financial support in the form of a graduate assistantship and research support from the U.S. Bureau of Mines under the Mining and Minerals Resources Research Institute Generic Center Program (Grant Number G1125132, Sub-account No. 1901- Mineral Industry Waste Treatment and Recovery Generic Center).

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SOLVENT EXTRACTION AND PHOTOMETRIC DETERMINATION OF NICKEL(II)
BY MIXTURES OF DIARYLTHIOCARBAZONES AND 2,2'-BIPYRIDYL

A. Majeed Kiwan, F.M. Hassan and F. Haydar

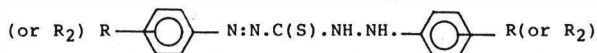
Department of Chemistry, Faculty of Science
University of Kuwait, Kuwait.

The relatively slow extraction rate of nickel(II) by diphenylthiocarbazone (H_2Dz ; $Ph\ N:N.CS.NH.NH.Ph$) and the multiband absorption spectrum (340, 475, 565 and 675 nm) of its complex ($Ni(HDz)_2$) renders this reagent rather unpopular for the extraction and photometric determination of nickel(II). However, in the presence of nitrogen bases, Math and Freiser¹ have reported that the rate of nickel extraction was enhanced and the absorption spectra of its complex had improved due to the collapse of its multiband absorption spectrum into a single band near 525 nm. These changes were attributed to the formation of the ternary nickel complex ($Ni(HDz)_2L$, $L:2,2'$ -bipyridyl or 1,10-phenanthroline), which was considered to form the basis of a highly sensitive method for nickel determination².

As part of our interest in metal extractions by diarylthiocarbazones and due to the lack of information on the extraction equilibria of ternary complexes, we report here some results on several nickel(II) diarylthiocarbazone bipyridyl complexes. The interactions of nickel bisdiarylthiocarbazones, $Ni(HRDz)_2$ with 2,2'-bipyridyl in chloroform (single phase) were also investigated.

Experimental:

Diarylthiocarbazonates (H_2RDz)



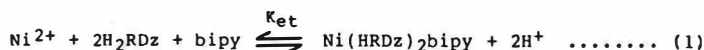
These reagents were prepared from the aryl anilines by the nitroformazyl method³ and purified as described elsewhere⁴.

Extraction Constants (K_{eb}) of Nickel Bisdiarylthiocarbazonates. $(\text{Ni}(\text{HRDz})_2)$.

These were determined in the usual manner by equilibrating nickel(II) (5 ml. $\sim 2 \times 10^{-4}M$) in 0.5M sodium perchlorate adjusted to different pH values with equal volumes of diarylthiocarbazonates ($\sim 4 \times 10^{-5}M$) in chloroform. Equilibration was carried out by mechanically shaking the two phases for one hour. The concentrations of free H_2RDz , $\text{Ni}(\text{HRDz})_2$ were determined spectrophotometrically, $[\text{Ni}^{2+}]$, by difference and $[\text{H}^+]$, pH-metrically.

Extraction Constants (K_{et}) of Ternary Nickel Complexes, $(\text{Ni}(\text{HRDz})_2 \text{ bipy})$.

These were determined by equilibrating known amounts of nickel(II), diarylthiocarbazonate and 2,2'-bipyridyl in a two phase system consisting of equal volumes (5ml) of 0.5M sodium perchlorate (with different pH's) and chloroform. The extraction constant of the ternary complex is defined as the equilibrium constant of equation 1.



The concentrations of free diarylthiocarbazonate and of the ternary nickel complex were determined spectrophotometrically. Since 2,2'-bipyridyl forms water-soluble complexes with nickel(II), the concentrations of free Ni^{2+} and of 2,2'-bipyridyl were computed from the known values of their stability constants ($\log K_1 = 6.80$, $\log K_2 = 6.46$ and $\log K_3 = 5.2$)⁵. The partition coefficient, of bipy ($P_{\text{bipy}} = [\text{bipy}]\text{CHCl}_3/[\text{bipy}]_{\text{aq}}$) was determined and found to be 350.

Formation Constant (K_{ft}) of the Ternary Nickel Complexes ($\text{Ni}(\text{HRDz})_2\text{bipy}$) in Chloroform.

Known amounts of nickel bis-diarylthiocarbazonates and 2,2'-bipyridyl were mixed together in chloroform to form the ternary complex. Its formation constant in this single phase is the equilibrium constant of equation (2).



The concentrations of nickel complexes were determined spectrophotometrically from their characteristic spectral data whereas the concentration of free 2,2'-bipyridyl was determined by difference.

RESULTS AND DISCUSSIONS

Visible Spectra of Nickel bisdiarylthiocarbazonate Complexes, $\text{Ni}(\text{HRDz})_2$.

The nickel(II) complexes with diarylthiocarbazonates investigated here, show multiband absorption spectra the data (λ_{max} and ϵ_{max}) of

which are summarized in Table 1. They are basically different from those of other $M(\text{HRDz})_n$ complexes which with the exception of Pd(II) and Pt(II) complexes show single well defined absorption bands⁶. Their spectral data show that introduction of Cl-atoms at C-4 and C-4' of the phenyl rings of diphenylthiocarbazone has raised the ϵ_{max} at 675 nm from 19.3×10^3 to 22.6×10^3 . On the other hand, when Cl atoms were introduced at C-2 and C-2', or C-3 and C-3' the corresponding ϵ_{max} values decreased slightly to 17.8×10^3 and 16.3×10^3 respectively. Further introduction of methyl groups at C-2 and C-2' of 4,4'-dichlorodiphenylthiocarbazone, raised the ϵ_{max} of value at 675 nm to 31.1×10^3 . The λ_{max} values of the longest wavelength bands of Ni(HRDz)_2 are always shifted (2-15 nm) bathochromically on substitution.

Visible spectra of ternary complexes, Ni(HRDz)_2 bipy.

The spectral data of ternary nickel complexes (Table 1) indicate that they are intensely coloured with single well-defined absorption bands in the region 507-523 nm, depending on the nature and position of substituents.

When diphenyl-, 2,2'-dimethylphenyl-, 2,2'-dichlorodiphenyl-, 3,3'-dichlorodiphenyl-, and 3,3'-dichloro-2,2'-dimethyldiphenyl-thiocarbazones were used, the spectral data (ϵ_{max} and λ_{max}) of ternary species formed in the two phase systems were different from the corresponding values of ternary complexes formed in the single phase (Table 1).

Tabel 1

Spectral characteristics of binary and ternary nickel(II) complexes with diarylthiocarbazonates and 2,2'-bipyridyl in chloroform

Diarylthio- carbazone, H ₂ RDz	λ_{\max} ($\epsilon_{\max} \times 10^{-3}$) Ni(HRDz) ₂	λ_{\max} ($\epsilon_{\max} \times 10^{-3}$) Ni(HrDz) ₂ bipy
1) Diphenyl	478(25.2); 556(22); 660(193)	512 ^t (61.5) 507 ^s (46.5)
2) 2,2'-dimethylphenyl	422(16.8); 510 ^b (20.7); 550(24.6); 662(22.4)	506 ^t (56.7) 508 ^s (40.3)
3) 2,2'-dichlorophenyl	430(22.4); 470 ^b (23.0) 560 ^b (23.0); 670(17.8)	512 ^t (52.0) 511 ^s (42.5)
4) 3,3'-dichlorophenyl	475 ^b (23.0); 560(19.2) 675(16.7)	519 ^t (54.3) 522 ^s (41.1)
5) 4,4'-dichlorophenyl	475 ^b (41.9); 550 ^b (33.8) 675(22.6)	523 ^t (72.6) 525 ^s (73.2)
6) 3,3'-dichloro- 2,2'-dimethylphenyl	424(25.2); 508(22.5) 550(24.9); 670(22.1)	511 ^t (47.7) 508 ^s (42.3)
7) 4,4'-dichloro- 2,2'-dimethylphenyl	426(30.1); 508 ^b (28.6) 556(32.6); 670(30.1)	518 ^t (58.9) 514 ^s (58.7)
8) 5,5'-dichloro- 2,2'-dimethylphenyl	427(26.1); 508 ^b (24.6) 554(27.8); 670(24.6)	514 ^t (49.8) 511 ^s (50.3)

b: broad ; s: single (chloroform) phase

t: two-phase system consisting of chloroform and 0.5M sodium perchlorate solution.

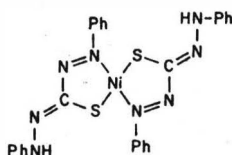
The ϵ_{\max} values of the former complexes are generally 10 to 48% greater than those of the latter complexes depending on the type

and position of substituents, though the λ_{\max} values differed only by 2-6 nm. On the other hand, 4,4'-dichlorophenyl-, 4,4'-dichloro-2,2'-dimethyl-, and 5,5'-dichloro-2,2'-dimethylphenylthiocarbazones gave the same ternary nickel species in both single and two phase systems (Table 1).

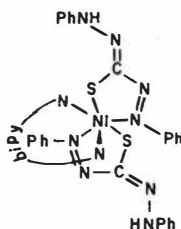
All ternary nickel bis-diarylthiocarbazonate 2,2'-bipyridyl complexes are intensely coloured with ϵ_{\max} ranging from 46.5×10^3 to 73.2×10^3 (Table 1). The latter value which corresponds to $\text{Ni}(4,4'\text{-Cl}_2\text{HDz})_2\text{bipy}$ is about 48% greater than that of $\text{Ni}(\text{HDz})_2\text{phen}$, viz. 49.5×10^3 at 525nm) which was considered² to form the basis of a highly sensitive method for the determination of $\text{Ni}(\text{II})$.

Structure of binary and ternary nickel complexes:

Nickel(II) bis-diphenylthiocarbazonate, $\text{Ni}(\text{HDz})_2$ was reported⁷ to have a square planar configuration I and when this complex was mixed with 2,2'-bipyridyl in benzene, it gave the octahedral ternary complex, II.

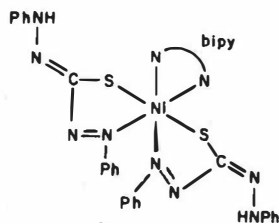


I



II

The latter structure suggests that addition of 2,2'-bipyridyl to $\text{Ni}(\text{HDz})_2$ results in a cleavage of an Ni-S (rather than Ni-N) bond prior to the final molecular arrangement of the complex. The other ternary species which is formed in the two phases may be represented by the isomeric structure III, in which the two sulphur atoms occupy trans-positions.



III

Extraction constants (K_{eb} and K_{et}) of binary and ternary complexes

The extraction data given in Table 2 indicate that introduction of Cl-atoms at C- 3' and 3' and C- 4 and 4' of the phenyl rings of diphenylthiocarbazonate raised K_{eb} from $10^{-4.17}$ to $10^{-2.9}$ and $10^{-3.2}$ respectively. Introduction of methyl groups at C-2 and 2' decreased K_{eb} to $10^{-6.62}$. Further introduction of Cl atoms in the latter complex at C- 3 and 3', C- 4 and 4' and C- 5 and 5' had negligible effects on K_{eb} . The extraction constants (K_{et}) of ternary nickel complexes $Ni(HRDz)_2bipy$ are 10^{15-16} greater than the corresponding values (K_{eb}) of the binary complexes $Ni(HRDz)_2$. Their high values ($10^{9.01}$ - $10^{12.65}$) confirm the remarkable synergic effect of 2,2'-bipyridyl on the extraction of nickel diarylthiocarbazonates.

Formation constants (K_{ft}) of ternary nickel complexes.

In Table 2, are listed, the formation constants of $Ni(HRDz)_2bipy$ in chloroform. Their values range from $\log K_{ft}$ 3.27 to 5.25 depending on the diarylthiocarbazonate. Our K_{ft} value for $Ni(HDz)_2bipy$ is close to Frieser et al's value¹. The variations in K_{ft} values of $Ni(HRDz)_2bipy$ may be rationalized in terms of the different pK_a of H_2RDz and the steric effects of their substituents (R).

Table 2

Extraction and formation constants of $\text{Ni}(\text{HRDz})_2$ and $\text{Ni}(\text{HRDz})_2\text{bipy}$ in single and two-phase^a systems.

Diarylthio-carbazone, H_2RDz	$\log K_{\text{eb}}$ $\text{Ni}(\text{HRDz})_2$	$\log K_{\text{ft}}$ $\text{Ni}(\text{HRDz})_2\text{bipy}$	$\log K_{\text{et}}$ $\text{Ni}(\text{HRDz})_2\text{bipy}$
1) Diphenyl	-4.17	4.20 (lit.4.63)	11.40
2) 2,2'-dimethylphenyl	-6.62	3.27	9.01
3) 2,2'-dichlorophenyl	-4.30	4.62	11.03
4) 3,3'-dichlorophenyl	-2.9	5.25	12.65
5) 4,4'-dichlorophenyl	-3.2	4.87	11.84
6) 3,3'-dichloro-,2,2'-dimethylphenyl	-6.50	4.23	10.02
7) 4,4'-dichloro-,2,2'-dimethylphenyl	-6.23	4.06	9.41
8) 5,5'-dichloro-,2,2'-dimethylphenyl	-5.97	4.21	10.02

a) Chloroform and 0.5M sodium perchlorate solution.

ACKNOWLEDGEMENT:

We are grateful to the Research Council, Kuwait University for the financial support (SC008 and SC026) of this work.

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With modern theories of solution the extraction equilibrium distribution model on two-metal system is established by thermodynamic method. In this system, cobalt and copper are co-extracted from sulphuric acid solution by (2-ethylhexyl) phosphonic acid-mono (2-ethylhexyl) ester (EHEHPA).

Because the aqueous phase contains sulphuric acid, cobalt sulphate and cupric sulphate, there is a mixed electrolyte solution with dissociation equilibrium. Based on the Pitzer's electrolyte theory, some assumptions and approximations have been made. The simple expression of the activity coefficient for single ion in a mixed electrolyte solution is obtained as follows:

$$\ln \gamma_{\pm} = \frac{1}{2} z_{\pm}^2 f'(z) + 2 \sum_a m_a (B_{Ma} + (\sum m_z) C_{Ma}) + \sum_a \sum_c m_c m_a (z_a^+ z_c^- B_{ca} + 2 z_{\pm} C_{ca})$$

$$f'(z) = -2 A \phi \left[\frac{2 \psi}{1 + 1.2 z \psi} + \frac{2}{1.2} \ln (1 + 1.2 z \psi) \right]$$

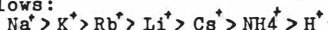
Combining the electricity equilibrium, material balance and dissociation equilibrium in H₂SO₄-CoSO₄-CuSO₄ aqueous solution and extraction equilibrium with the simplified Pitzer's expression, the activity coefficient and the equilibrium concentrations for all ions and the osmotic coefficient can be calculated by computer. The mean relative deviation between the experimental and calculated pH values is less than 0.02. Our calculated results show that the above equations work very well for the metal-extraction system with dissociation equilibrium in the aqueous phase.

Based on the experimental data of the equilibrium concentrations of constituents in both phases and the activity coefficient of diluent determined by the gas-chromatography, the activity coefficients for EHEHPA, Co(HR₂)₂, Cu(HR₂)₂ and the dissolved water in organic phase and the thermodynamic extraction equilibrium constants K_{Co} and K_{Cu} are obtained by means of the "working reference state method" proposed by authors. The organic phase is treated as quinary component system by the improved Scatchard-Hildebrand solution theory. 10 terminal parameters A_{ij} in our improved Scatchard-Hildebrand equation for organic phase are optimized on computer. In the region of 0.5-1.542M (the initial concentrations of extractant), the values of K_{Co} and K_{Cu} are kept constant respectively. The calculated values of activity coefficient are consistent with the experimental values. Thus, it seems to be possible to establish the theoretical model for two metal extraction equilibria in place of empirical ones.

The salting effect of D2EHPA in the solutions of alkali chlorides

Jui-Fang Lu, Hong-Bing Ding, Yi-Gui Li, Teng Teng,
Dept. of Chemical and Chemical Engineering, Tsinghua University, Beijing/China

The solubility of di(2-ethylhexyl) phosphoric acid (D2EHPA) in aqueous solutions of HCl, LiCl, NaCl, KCl, RbCl, CsCl and NH₄Cl is determined with the P(32) tagged D2EHPA. The results show that all of these salts give the salting-out effect to D2EHPA. The solubility of D2EHPA, $S_0=0.087$ g/l, and its dissociation constant, $K_a=10^{-11}$, in water at 25°C are measured by pH titration method. From these data the salting constants of D2EHPA in these solutions are evaluated. They are 0.267 for LiCl, 0.322 for NaCl, 0.283 for KCl, 0.277 for RbCl, 0.260 for CsCl, 0.177 for NH₄Cl and 0.0699 for HCl (>1M). The salting-out sequence of the cations on D2EHPA is as follows:



Some salting effect theories, such as electrostatic theory (Debye-Hückel formula), McDevit-Long Theory and scaled particle theory with various ion radii are applied to these systems. Among them it is found that when the improved McDevit-Long theory and the Gouy-Chapman ion radii, Weddington ion radii or Latimer ion radii are used, the salting constants calculated are coincident with the experimental data. After various types of interactions between particles in solution such as electrostatics, dispersion, dipole, induced-dipole attractions and hard-sphere repulsion are considered, the scaled particle theory is improved by the authors. The improved salting effect formula gives better results if the parameters needed are chosen properly.

The applicability of Pitzer's formula in the salting effect is also tested. It seems that the Pitzer's formula can be used to these systems except hydrochloric acid.

The results show also that if sufficient acid or unextracted salts are present in aqueous phase, the solubility loss of acid extractants in aqueous phase will be reduced.

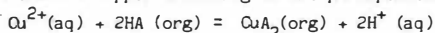
As the manuscript was not available at the 28th May 1986, the deadline for printing this book, we only print the short abstract of the paper.

Solvent Extraction of Copper(II) from Chloride solutions by Non-chelating Nitrogen-donor ligands.

K.H. Solderhoff, Council for Mineral Technology, Randburg, South Africa.

Introduction

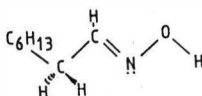
Hydrometallurgical processes, particularly those using chloride leachants, are receiving some attention as an alternative to conventional pyrometallurgical methods for the treatment of complex sulphide ores. Consequently, solvent extraction reagents that will selectively extract individual metals from concentrated chloride solutions are required. Solvent extraction is used extensively for the commercial-scale recovery of copper from solutions obtained by leaching of low-grade ores with dilute acids. The most commonly used extractants are of the ortho-hydroxyoxime type and belong to a class of weakly acidic chelating ligands, which extract copper according to the pH-dependent equilibrium:



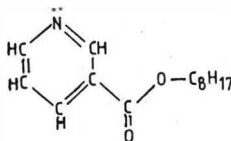
In contrast, reagents of the non-chelating nitrogen donor type (e.g. those containing $\text{C}=\text{NOH}$ as the only functional group) are able to extract copper from chloride solutions by a solvating mechanism that is largely independent of pH. In this work, the factors influencing the extraction of copper with aldioximes were investigated and comparisons were drawn between the behaviour of these extractants and other nitrogen donor ligands such as n-octyl-3-pyridine carboxylate and ACORGA CLX-20.

The structures of the extractants used are shown below:

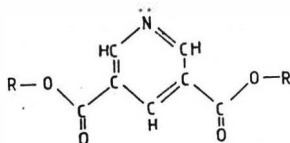
Octanal oxime



n-octyl-3-pyridine
carboxylate



ACORGA CLX-20



Experimental

The extractants were dissolved in toluene and an approximate ten fold excess extractant to metal concentration was used. Equal volumes of organic and aqueous phases were shaken until equilibrium was reached. (15 minutes for Cu, Co and Fe and 1 hour for Ni and Zn). When the two phases were clearly separated, metal concentrations in the aqueous phase were determined by titration against EDTA or by atomic absorption. Iron determinations were done by titration against sodium thiosulphate. The difference between initial and final aqueous metal concentrations was assumed to be equal to the metal concentration in the organic phase.

Results and Discussion

Extraction of copper with octanal oxime

Octanal oxime (OCOX) is a non-chelating ligand and is expected to extract copper from chloride solutions by a general reaction:



The distribution coefficient of the metallic species between the two phases is

$$D = [\text{MCl}_n(\text{OCOX})_m] / [M^{n+}]$$

including the expression for the equilibrium constant of reaction (1), and assuming the activity coefficients of $(\text{MCl}_n(\text{OCOX})_m)$ and (M^{n+}) species are equal to one:

$$D = K_{\text{ext}} \times \{\text{Cl}^{-}\}^n \times \{\text{OCOX}\}^m \dots\dots\dots (2)$$

The stoichiometry of the extraction reaction can thus be studied by the slope analysis technique, where logarithmic plots of the distribution coefficient (D), versus the chloride and oxime activities will have slopes equal to n and m respectively.

Two complicating factors must however be taken into account:

- (1) The formation of aqueous $(\text{MCl}_a)^{2-a}$ charged complexes, which are not extractable.
- (2) The association of oxime in the organic phase.

According to equation (1), two chloride molecules are expected to be extracted with every divalent metal for the preservation of electrical neutrality. Thus the slope of $\log D$ versus $\log \{\text{Cl}\}$ is expected to have a value of two. Such plots are shown in figure 1, and values slightly lower than two were obtained. The discrepancy is due to the formation of aqueous $(\text{CuCl}_a)^{2-a}$ charged complexes that are not extractable, but are present in the aqueous phase. Thus the distribution coefficient is equal to:

$$\begin{aligned}
& \frac{[MCl_n(OCOx)_m]}{([M^{2+}] + [MCl^+] + [MCl_2] + [MCl_3^-] + \dots)} \dots\dots\dots (3) \\
D = & \\
& \frac{[MCl_n(OCOx)_m]}{[M^{2+}] (1 + \beta_a [Cl]^a)} \\
& \\
& \frac{[MCl_a]^{2-a}}{[M^{2+}] [Cl]^a} \\
\beta_a = &
\end{aligned}$$

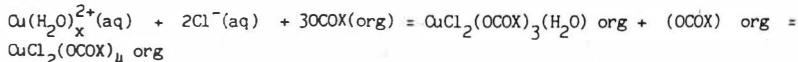
taking logs and incorporating the equilibrium constant expression

$$\begin{aligned}
\log D = \log K_{\text{ext}} + n \log \{Cl\} + m \log \{OCOx\} \\
- \log (1 + \beta_a [Cl]^a) \dots\dots\dots (4)
\end{aligned}$$

the slope of $\log D$ versus $\log \{Cl\}$ plot at constant oxime concentration is decreased due to the last term of equation (4).

Vapour pressure osmometry was used to measure the association of octanal oxime in toluene. The species present in solution were identified and formation constants for dimers and trimers calculated by graphical and numerical methods¹. (Table 1). The species diagram is shown in figure 2. The monomer concentrations at given analytical oxime concentrations were then used in the log-log plots of D versus oxime activities as shown in figure 3. The slope of 3.5 probably represents an average value for the formation of both $CuCl_2(OCOx)_3$ and $CuCl_2(OCOx)_4$.

The extraction of Cu^{2+} by octanal oxime from chloride solutions thus proceeds as follows:

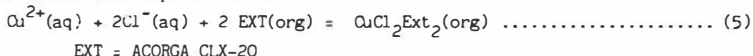


The stoichiometry of the reaction was confirmed by direct analysis of copper, chloride and water content in the organic phase as well as by metal loading curves.

The effect of pH: Extraction from chloride solutions should ideally be independent of pH but as can be seen in figure 4, below pH of approximately two, the extraction decreases considerably. Two factors contribute to this decrease. First, octanal oxime is a Lewis base by virtue of its nitrogen lone pair and therefore a certain amount of protonation of extractant in the organic phase can occur. The protonated octanal oxime, however, is partially soluble in the aqueous phase and this enhances the decrease of extraction at low pH.

Extraction of copper with n-octyl-3-pyridine carboxylate and ACORGA CLX-20.

N-octyl-3-pyridine carboxylate (NOPC) and ACORGA CLX-20, a pyridine dicarboxylic ester, function as nitrogen donors via a mechanism which is similar to that of extraction of CuCl_2 with octanal oxime. ACORGA CLX-20 has been patented by ICI for the selective extraction of copper from chloride solutions, and the extraction mechanism has been reported to be²



The above mechanism was confirmed in this work to apply both to NOPC and ACORGA CLX-20.

Selectivity of extractants for copper

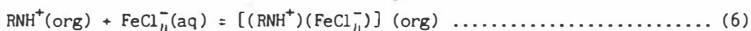
The extraction curves for Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} from chloride solutions with both octanal oxime and n-octyl-3-pyridine carboxylate are shown in figure 5. The stoichiometries of the respective complexes formed in the organic phase are also depicted. The metals are extracted in the order predicted by the Irving-Williams stability series for octahedral compounds



Octanal oxime extracts from lower chloride concentrations than NOPC. This is not expected on the basis of their relative pKa measured in 80% ethanol. (Table 2). NOPC has an higher affinity for protons and should therefore also form stronger complexes with metal cations. The stability of the octanal oxime complexes can be explained in terms of the stoichiometry of the extraction reaction. As described previously, three to four oxime ligands are coordinated to the metal ions of copper, nickel and cobalt, while only two NOPC ligands are present in the corresponding metal/NOPC complexes. This decrease in the number of extractant molecules incorporated into the metal complex is due to the bulkiness of the NOPC ligand.

A valid comparison of extractant strength can be drawn between NOPC and ACORGA CLX-20, since their extraction reactions have the same stoichiometry. ACORGA CLX-20 is the weaker extractant of the two and therefore extracts from higher chloride concentrations. This is due to the two carboxylic ester groups, which withdraw electron density from the coordinating nitrogen to a greater extent than in NOPC, which possesses only one such group.

Extraction of iron(III) from chloride solutions of low pH occurs by a mechanism in which the protonated extractant associates with the negatively charged FeCl_4^{-} species (6). The extraction of iron(III) from lithium chloride solutions with ACORGA CLX-20 at different acid concentrations is shown in figure 6. It can be seen that extraction increases with increasing chloride and acid concentration.



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Table 1. Formation constants for dimers (β_2) and trimers (β_3) of octanal oxime in toluene at 25°C.

Method	β_2	β_3
Graphical	5.24	13.77
Numerical	6.25	12.01

Table 2. Relative pKa of extractants in 80% ethanol.

n-octyl-3-pyridine carboxylate	2.17
octanal oxime	1.92
ACORGA CLX-20	1.87

Figure 1. Extraction of Cu(II) from chloride solutions with octanal oxime. Aqueous phases: $[Cu^{2+}] = 0.008M$, $[NaCl] = 0.01-0.5M$. Organic phases : a (0.05M), b(0.1M), c (0.2M), d (0.4M), e (0.8M).

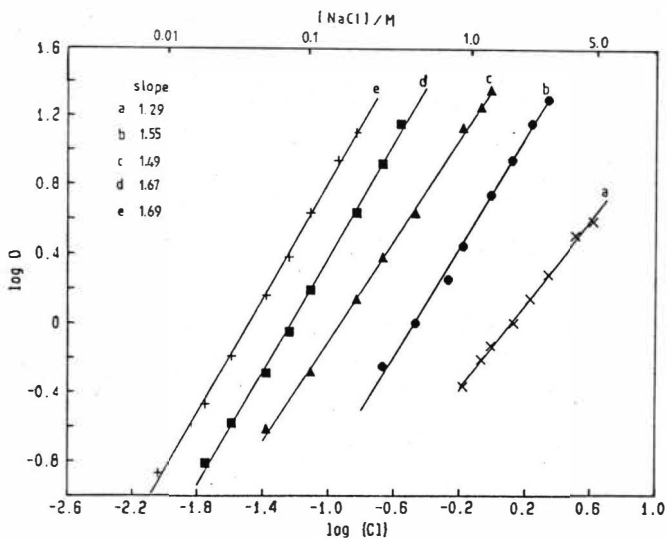


Figure 2. Species distribution diagram for octanal oxime in toluene.

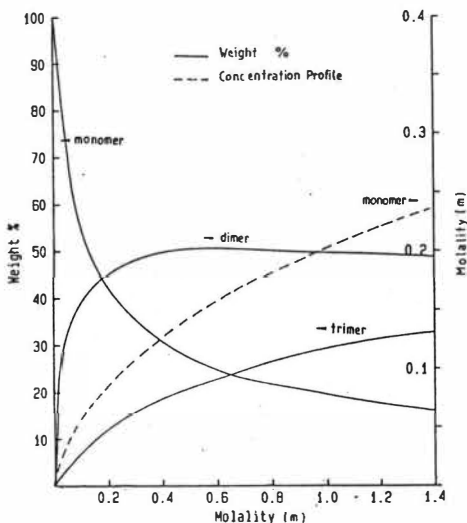


Figure 3. $\log D$ dependence on octanal oxime concentration (----) analytical oxime concentrations (____) monomer oxime concentrations.

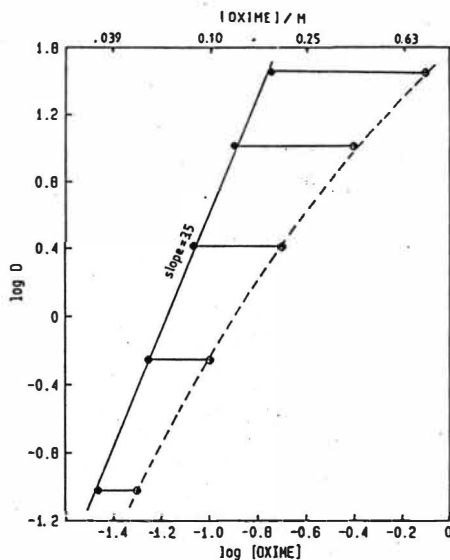


Figure 4. Effect of pH on the extraction of Cu(II) from chloride solutions with octanal oxime ($[Cl] = 1.0M$)

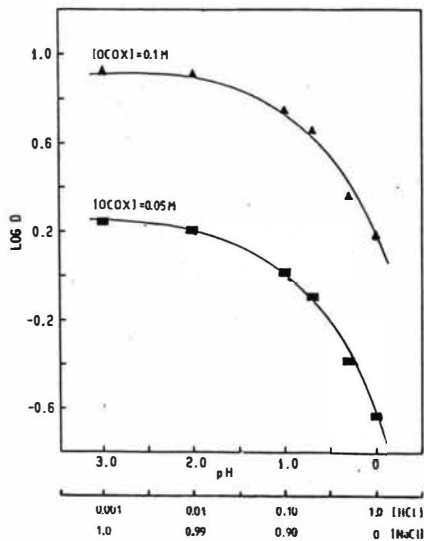


Figure 5. Extraction at Cu(II), Co(II), Ni(II) and Zn(II) with actaral oxime and n-octyl-3-pyridine carboxylate.

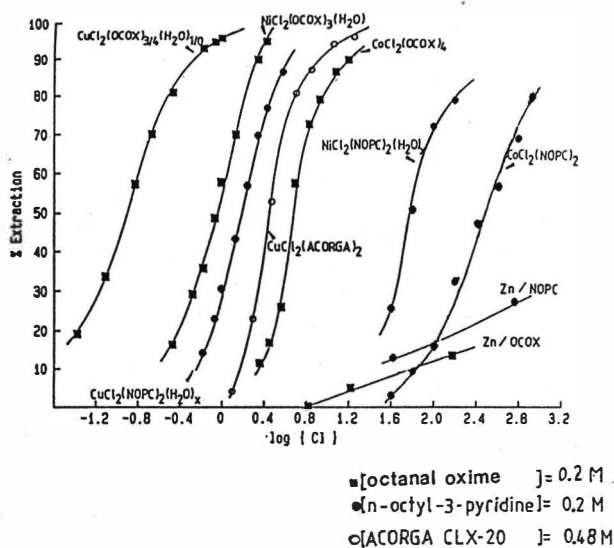
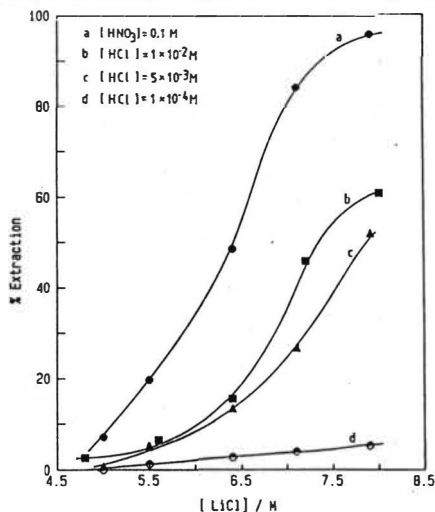


Figure 6. Extraction of Fe(III) from lithium chloride solutions with ACORGA CLX-20.



Characterization of Chelating Ion Exchange Resins by FT-IR Spectroscopy and High-Resolution Solid-State ^{13}C NMR : Application to the Solvent-Impregnated Resins

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Although there is already a long history of the study of chelating ion exchange resins, only few papers have been devoted to their physico-chemical characterization. In the present paper, we propose to investigate ion exchange resins, and more especially the solvent-impregnated ones, by FT-IR spectroscopy and high-resolution solid-state ^{13}C NMR. The solvent-impregnated resins are attractive because the combination of appropriate extractants, adsorbents and eventually additives allows the formulation of efficient reactive stationary phases for both analytical and industrial purposes. Such resins can be prepared conveniently by adsorption of extractants and additives on a macroporous solid. The fixation of metal cations on impregnated resins has been extensively investigated, but, to date, little is known on the physico-chemical interactions between the solvent (extractants and additives) and the solid support. These interactions, however, play a determining role on most of the macroscopic behaviours of the impregnated resins, especially the leakage of the reagents and their extractive properties.

The example of a long hydrocarbon chain oxine derivative, 7-(4-ethyl-1-methyloctyl)-8-quinolinol ("Kelex 100") adsorbed on a macromolecular resin, the Amberlite XAD-7 support, has been chosen in this work because of its potential interest in the hydrometallurgy of gallium [1] and germanium [2]. FT-IR and high-resolution solid-state ^{13}C NMR spectra of 7-(4-ethyl-1-methyloctyl)-8-quinolinol-impregnated resins are reported and discussed. A special attention is focused on the inner sites by which the molecules of extractant could be anchored on Amberlite XAD-7. The influence of this anchorage on the chelation ability of 7-(4-ethyl-1-methyloctyl)-8-quinolinol is also examined in the case of the fixation of gallium(III).

Experimental

Reagents : 7-(4-Ethyl-1-methyloctyl)-8-quinolinol (HL) was isolated from "Kelex 100" (Shering) as previously reported [3]. The Amberlite XAD-7 resin (Rohm and Haas Company) of practical grade quality was carefully washed with ethanol and water, and impregnated with HL in a classical way. Aqueous gallium(III) solutions were prepared from gallium oxide (Rhône-Poulenc Co).

Apparatus : The spectroscopic instruments used were a Nicolet 7199 Fourier transform infrared spectrometer ($4000 - 400 \text{ cm}^{-1}$) [32 co-added interferograms were scanned at 2 cm^{-1} resolution] and an IFS 113V Bruker Fourier transform infrared spectrometer ($400 - 60 \text{ cm}^{-1}$) [100 co-added interferograms were scanned at 4 cm^{-1} resolution] for FT-IR and far FT-IR spectroscopy, respectively; a Varian FT 80A model and a Bruker WM 500 model for ^1H and ^{13}C NMR measurements in solution. High-resolution solid-state ^{13}C NMR experiments were performed at 75.47 MHz on a Bruker CXP 300 spectrometer, using high power proton decoupling ($H_1 = 51 \text{ kHz}$) and rapid magic-angle rotation (3.5 kHz - 4.0 kHz spinning speeds) in boron nitride rotors.

Two basic pulse programs were employed to investigate the solid samples :

(i) The normal cross-polarization sequence (FLIP) under the Hartmann-Hahn condition. Cross-polarization durations were 1 ms. In this experiment spin-temperature inversion techniques were used to minimise base line noise and roll [4]. Flip-back was also systematically employed to shorten the delay time between two successive pulse sequences [5]. (ii) The second sequence is the single pulse excitation sequence [6 - 8]. The carbon magnetization is excited by a 90° pulse and is observed in the presence of a strong dipolar proton decoupling. This experiment detects only the ^{13}C spins for which $T_1(^{13}\text{C})$ is much shorter than the period of time t_{rep} between two successive excitation pulses. Therefore a low value for t_{rep} discriminates against regions with long $T_1(^{13}\text{C})$ which usually correspond to the rigid domains in the samples under study. Here, t_{rep} was taken as 2 s. No digital broadening was applied prior to Fourier transformation of the free induction decay.

Results and discussion

The Amberlite XAD-7 support, a polyacrylate adsorbent possessing a macroporous structure (porosity : 0.53 ml/ml [9]) and a high surface area ($450 \text{ m}^2/\text{g}$ [9]), has often been recommended for the preparation of solvent-impregnated resins; that is why it has been used in the present study. Two typical impregnated supports containing respectively 0.31 and 0.73 g/g of HL (gram of HL per gram of dry Amberlite XAD-7) have been prepared and investigated. It must be pointed out that, in the two cases, the content of HL is significantly lower than the loading capacity of the support (1.7 g/g [10]), so that all HL is presumably adsorbed on the inner surface of the support, and not merely retained by capillarity in its pores. More precisely, the lowest concentration (0.31 g/g) is lower than the amount m_0 of HL ($m_0 \sim 0.4 \text{ g/g}$) needed to form one monolayer on the surface of the resin, whereas the highest concentration (0.73 g/g) is higher than m_0 .

Typical ^{13}C magic-angle spinning NMR spectra are represented in figure 1. Magic-angle spinning experiments using cross-polarization technique allow a preferential observation of the rigid parts of the samples. On the other hand, the single pulse excitation

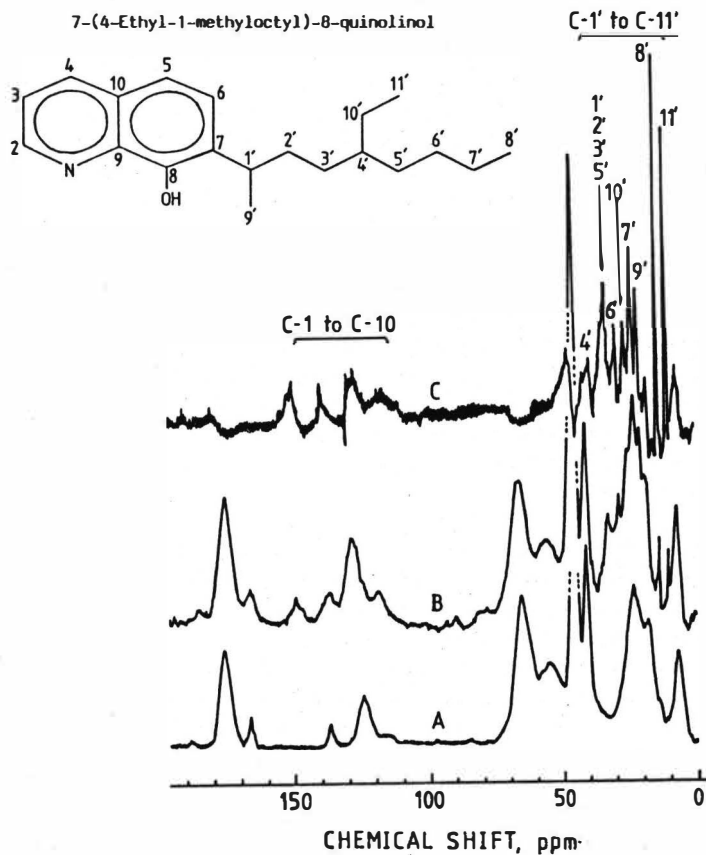


Figure 1 : ^{13}C solid-state NMR spectra of Amberlite XAD-7 and 7-(4-ethyl-1-methyloctyl)-8-quinolinol-impregnated (0.73 g/g) Amberlite XAD-7. (A) FLIP / Amberlite XAD-7 [n.s. 1200]; (B) FLIP / HL (0.73 g/g) on Amberlite XAD-7 [n.s. 6467]; (C) Single pulse sequence / HL (0.73 g/g) on Amberlite XAD-7 [n.s. 2397]; n.s. = number of scans. The chemical shifts are referenced to tetramethylsilane.

with short repetition time (2 s) spectra are rather representative of the fast relaxing mobile sites, i.e. the ^{13}C atoms with short $T_1(^{13}\text{C})$.

At 0.73 g/g, the single pulse excitation spectrum of impregnated Amberlite XAD-7

(spectrum C in figure 1) mainly presents a series of sharp and well resolved signals associated with the aliphatic carbons of the 7-(4-ethyl-1-methyloctyl)-8-quinolinol molecules. In the FLIP spectrum (spectrum B in figure 1) we find the strong and typically broad signals given by the Amberlite XAD-7 support, but also the sharp signals corresponding to the aliphatic carbon atoms of adsorbed HL. The signals given by the aliphatic carbons C-8' and C-11' are much more intense in the single pulse excitation spectrum than in the FLIP one, which means that the two carbons C-8' and C-11' are very mobile. For the other aliphatic carbons of HL, the comparison between single pulse excitation and FLIP spectra is more difficult because of the presence of the broad signals of the support. Nevertheless, we can roughly estimate that the carbons (C-1' + C-2' + C-3' + C-5'), C-6', C-7', C-9' and C-10' also give rise to stronger signals in the pulse excitation spectrum than in the FLIP one, but this time to a much lesser extent than in the case of C-8' and C-11'. That means that C-1', C-2', C-3', C-5', C-6', C-7', C-9' and C-10' have a reduced mobility. In the 110 - 160 ppm chemical shift range where the signals associated with the aromatic carbons of HL are expected, several broad signals are observable. Among them, only the one close to 150 ppm can be unambiguously attributed to the response of an aromatic carbon of HL, possibly C-2 or/and C-8.

At 0.31 g/g, the FLIP spectrum of impregnated Amberlite XAD-7 (spectrum A in figure 2) is similar to the one recorded at 0.73 g/g (spectrum B in figure 1), but, of course, with a weaker relative intensity for the signals corresponding to the carbon atoms of 7-(4-ethyl-1-methyloctyl)-8-quinolinol. On the other hand, the single pulse excitation spectrum of low loaded (0.31 g/g) Amberlite XAD-7 is very different from the one recorded at 0.73 g/g. Indeed, to observe some signals associated with the carbon atoms of adsorbed HL it has been necessary to record the spectrum with a large number of scans (about 13000). Under such a condition, the broad signals given by Amberlite XAD-7 which usually do not appear in the single pulse spectra are very amplified (spectrum B in figure 2). Moreover, their chemical shifts and their intensities do not coincide with those measured on the various FLIP spectra, which suggests that Amberlite XAD-7 is an heterogeneous polymer. Anyway, the absence of most of the sharp signals associated with HL cannot be explained by a mere effect of dilution, but is indicative of an increased rigidity of the adsorbed molecules.

The preceding observations shows that 7-(4-ethyl-1-methyloctyl)-8-quinolinol behaves differently depending on whether its concentration is smaller or higher than the one needed to form one monolayer on the surface of the resin. In the first case, the molecules of adsorbed HL, or more precisely their alkyl chains, appear as rigid, which means that these latter greatly participate to the adsorption phenomenon. In the second case, the molecules of 7-(4-ethyl-1-methyloctyl)-8-quinolinol in excess of the first monolayer do not present any inner site by which they would be firmly held. Their retention would be rather the result of weak interactions. Are such conclusions in agreement with the FI-IR data?

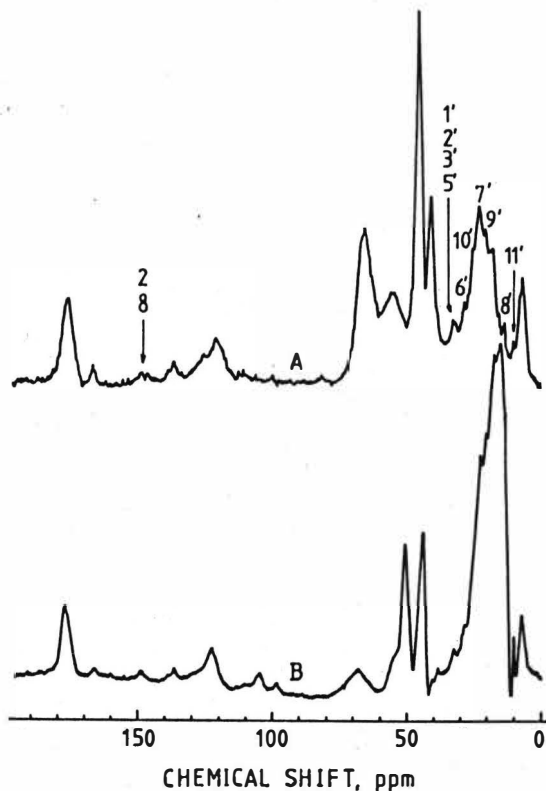


Figure 2 : FLIP and single pulse excitation spectra of 7-(4-ethyl-1-methyloctyl)-8-quinolinol-impregnated (0.31 g/g) Amberlite XAD-7.
 (A) FLIP [n.s. 3655]; (B) single pulse sequence [n.s. 12683] ; n.s. = number of scans.

Examination of table I where the main fundamental frequencies of 7-(4-ethyl-1-methyloctyl)-8-quinolinol are listed shows a slight shift in the frequency of the stretching modes of the methyl and methylene groups of HL during adsorption on Amberlite XAD-7. However, this shift cannot be attributed to the interactions between HL and the macroreticular support since such interactions are expected to lower the vibrational frequencies. The shift we observe in table I might be due to the overlap with the two broad absorption bands associated with the support and located at 2973 and

Table I : Assignments of the main fundamental frequencies (in cm^{-1}) of 7-(4-ethyl-1-methyloctyl)-8-quinolinol (HL)

HL as a film on a CsBr disc	HL on Amberlite XAD-7 : 0.73 g/g [polyethylene pellet]	HL on Amberlite XAD-7: 0.31 g/g [polyethylene pellet]	Assignments
3386.3	(a)	(a)	Stretching frequency of intra-molecularly hydrogen-bonded OH
3055.0	(a)	(a)	Aromatic C-H stretching
2957.4	2958.7	2959.9	Stretching modes
2926.5	2928.4	2929.9	of the methyl
2870.6	2871.1	2871.9	and methylene
2858.0	2858.1	2861.1	groups
1576.2	1576.3	1576.3	Ring vibration
1505.1	1505.9	1505.9	Ring vibration
1462.8	(a)	(a)	Ring vibration + bending mode of the methyl or methylene groups
1434.7	(a)	(a)	Ring vibration
1408.2	(a)	(a)	Ring vibration
1376.3	(a)	(a)	Ring vibration + bending mode of the methyl or methylene groups
1330.9	(a)	(a)	Ring vibration
1278.9	(a)	(a)	O-H in-plane bending mode
1244.2	(a)	(a)	-
1091.8	(a)	(a)	C-O stretching
1041.0	(a)	(a)	Ring vibration
826.0	826.0	826.6	Out-of-plane ring C-H bending
802.6	802.7	803.1	Out-of-plane ring C-H bending
724.5	724.1	724.0	Ring breathing
687.4	687.3	687.4	Out-of-plane ring C-H bending
459.4	(a)	(a)	C-O in-plane bending mode

(a) not clearly observable because of the bands of Amberlite XAD-7

2893 cm^{-1} , respectively. In a similar way, such an effect might conceal the decrease in frequency expected from the adsorption phenomenon. Table I also shows that the frequency of the out-of-plane ring C-H bending and ring breathing vibrations does not suffer any significant shift during adsorption. Considering that for benzene, toluene, p-xylene and mesitylene the most marked differences in the positions of the absorption bands between the liquid and adsorbed (on silica) states occur for the extrapla-

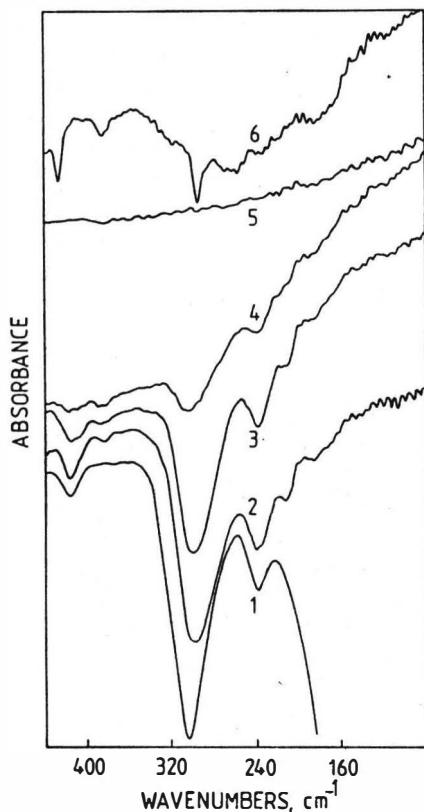


Figure 3 : Far FT-IR spectra of: (1) GaL_3 in solution (0.3 mol.L^{-1}) in cyclohexane; (2) GaL_3 as a film on a polyethylene disc; (3) HL (0.73 g/g) on Amberlite XAD-7 after complete reaction with aqueous gallium(III) [polyethylene pellet]; (4) = (3) but with HL at 0.31 g/g ; (5) = (3) but before reaction with aqueous gallium(III); (6) pure HL between two discs of polyethylene.

nar deformational vibrations of the ring C-H bonds (shift between 3 and 10 cm^{-1}) [11], we can conclude that the cycles of HL are not much involved in the adsorption process, neither at high nor at low loading. This conclusion is not in contradiction with the NMR experiments which are, indeed, little informative on the behaviours of the aromatic carbons of HL because of the difficulty to observe their solid-state NMR signals.

At this point of the discussion, we can underline that the anchorage of 7-(4-ethyl-1-methyloctyl)-8-quinolinol on Amberlite XAD-7 mainly by its alkyl chain is favourable to the extraction of metal cations : the quinolinol groups keep by this way the mobility required to easily form metal complexes. For instance, in liquid-liquid systems (e.g. water/dodecane) 7-(4-ethyl-1-methyloctyl)-8-quinolinol forms a three-liganded octahedral complex of gallium(III) : GaL_3 . After adsorption on Amberlite XAD-7, HL still efficiently reacts with gallium(III) to form the three-liganded complex GaL_3 . Moreover, the similarity in the FT-IR spectral pattern between GaL_3 in solution and the complex formed directly on the support lead us to conclude that the two complexes exhibit the same stereochemistry (figure 3). Such observations shows that the presence of the solid Amberlite XAD-7 support does not create any significant steric hindrance.

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INTRODUCTION

Upon mixing together water or an aqueous electrolytic solution, a hydrophobic hydrocarbon often called "oil", and an adequate amphiphilic compound or combination of amphiphilic compounds, it is possible to obtain a macroscopically homogeneous fluid of low apparent viscosity which is in general optically transparent and isotropic (1, 2). A medium of this kind is frequently called a "microemulsion" (3).

The classification proposed by Winsor (4) may be instrumental in defining certain typical systems that contain phases of the microemulsion kind. A Winsor IV (W IV) system is, considered on the macroscopic scale, a single-phased medium that is the result of the complete "mutual solubilization" of all the constituents of the original mixture. If its water and oil contents are high enough, a W IV system may be considered as a microemulsion. Winsor I (W I) and Winsor II (W II) systems are macroscopically diphasic media in which one of the phases is a microemulsion. In a W I system (Figure 1a), the microemulsion forms the lower phase and is in equilibrium with an excess organic phase. Symmetrically, in a W II system (Figure 1c), the microemulsion forms the upper phase, and is in equilibrium with an excess aqueous phase. Finally, a Winsor III (W III) system (Figure 1b) is a triphasic medium in which the microemulsion forms the middle phase and is in equilibrium simultaneously with an excess organic phase and an excess aqueous phase.

PRESENTATION OF PROCESS

It has been already suggested (5, 6) that multicomponent systems used in metallic species extraction processes could in fact be W II systems. Hirasaki (7) has shown that the association of metallic cations with anionic surfactant micelles can be described by taking into consideration only electrostatic interactions and consequently depends essentially on the concentration and valence of the cations.

On this basis, we have designed a process aimed at concentrating dilute solutions of metallic cations. This process is an extraction-reextraction sequence (see Figure 2).

The extraction stage consists in mixing the aqueous solution of cations with appropriate amounts of oil, anionic surfactant and cosurfactant so as to obtain a W II system. As mentioned earlier, the existence of this type of system is favored by the presence of metallic cations in the aqueous component. According to Belloq et al. (8) a microemulsion belonging to a W II system may be described as a dispersion of water droplets in a continuous oil phase. The water droplets are delimited by a monomolecular membrane of interspersed surfactant and cosurfactant molecules. The cations to be concentrated and the surfactant counterions, generally Na^+ , are electrostatically associated with the membrane. If the metallic cations to be concentrated are divalent and their concentrations are comparable with that of the surfactant counterions they are then more absorbed than the surfactant counterions and their concentration in the microemulsion phase is higher than their concentration in the excess aqueous phase. By a good selection of process conditions a microemulsion may be formed that contains most of the cations to be extracted and only part of the water from the original solution.

After having been separated from the excess aqueous phase, the microemulsion undergoes the reextraction part of the process. This consists in adding concentrate acid to the microemulsion, which lowers the surfactant hydrophilicity and consequently induces the formation of a new excess aqueous phase and the shifting of the metallic cations towards this aqueous phase which may become concentrated than the original aqueous phase ($C_2 > C_0$).

Globally one extraction-reextraction cycle may be considered as one equilibrium stage of separation. One can thus think of a multistage process consisting of several successive extraction-reextraction cycles.

The search of optimal process conditions (temperature, oil/water and cosurfactant/surfactant weight ratios, active mixture concentration, and oil, surfactant and cosurfactant nature) can be performed by direct experimental planning or by mathematical simulation of the process. Actually, we have chosen to work on the

simulation of the phase equilibrium and the component distribution. This simulation is based on the pseudophase model (9-12). The objective of the simulation is to orientate us in the experimental search of the optimal conditions for a extraction-reextraction cycle as well as to illuminate us on the way to perform a "multistage" process.

PSEUDOPHASE MODEL

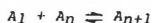
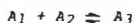
It is well known that the geometrical features of real microemulsion are complicated (direct and inverted spherical micelles, lamellar systems, bicontinuous domains...). Anyway, we can imagine that the microemulsion consists of three domains : (I) a polar domain composed of water (or brine) and some amount of cosurfactant (alcohol) ; (II) a non-polar domain composed of the oil, with some cosurfactant and a small quantity of water ; (III) amphiphilic interfacial domain composed of the surfactant and of the remaining cosurfactant.

These three domains may formally be treated as separated macroscopic phases and are called "aqueous pseudophase", "oil pseudophase", and "membrane pseudophase", respectively.

The pseudophase model is based on three main ideas : (I) the three "pseudophases" behave as true macroscopic phases ; (II) the pseudophases obey thermodynamic laws ; (III) alcohol is associated in non-polar media, according to consecutive association equilibria $2A_1 \rightleftharpoons A_2$, $A_1 + A_2 \rightleftharpoons A_3 \dots$, and all equilibrium constants (K_1 , $K_2 \dots$) are equal (K).

The composition equilibria is considered as an equilibrium between pseudophases which is governed by four constants :

(I) K : self-association constant of alcohol in the oil pseudophase, (see Nomenclature section)



$$K = \frac{x_{A_2,0}}{x_{A_1,0}^2} = \frac{x_{A_3,0}}{x_{A_1,0} x_{A_2,0}} = \dots$$

(II) k_M : the partition constant of the alcohol between oil and membrane pseudophases,

$$k_M = x_{A,M}/x_{A_1,0}$$

(III) k_W : the partition constant of the alcohol between oil and aqueous pseudophases,

$$k_W = x_{A,W}/x_{A_1,0}$$

(IV) : the weight ratio water/alcohol in the oil pseudophase

$$E = x_{W,0}/x_{A,0}$$

Let's consider a Winsor's type III system (Figure 3a). In the pseudophase model, this type of system is constituted by a gas phase and five liquid phases (Figure 3b) : the real aqueous phase (W), the actual oil phase (O) and the three pseudophases (O', M', W') within the actual microemulsion phase. Using the phase rule we obtain (12) that the maximum number of phases or pseudophases showing discrete compositions is equal to four. This leads to the conclusion $O=O'$ and $W=W'$.

This model does not predict the type of the systems (one-, two-, three-phases). However this model allows to calculate the composition of each actual demixing phase (excess oil phase and excess aqueous phase).

PHASE DIAGRAMS

Studying the behaviour of the systems that will be used is a prerequisite to the design of a reliable extraction-reextraction process.

As an illustration of the experimental results, the relative phase volume of each phase is presented (Figure 4) as a function of the temperature and water

salinity in a three-dimensional diagram. The formulation of the system, which contains sodium dodecyl sulfate (SDS), i.e. an anionic surfactant, is indicated in the caption of Figure 4. It is readily seen from this diagram that in conformity with the model behaviour recalled in Figure 1, an isothermal increase of the water salinity results in a $W I \rightarrow W III \rightarrow W II$ transition and an increase in temperature at constant salinity results in a $W II \rightarrow W III \rightarrow W I$ transition. The region where a microemulsion phase is in equilibrium with an aqueous phase ($W II$ system) corresponds to higher salinities and lower temperatures.

It was observed that, if the aqueous solution of the cations to be extracted is colored (green for nickel for instance) the microemulsion phase is colored, while the excess aqueous phase is slightly colored only and the excess oil phase is colorless. This proves that the metallic cations to be extracted migrate preferentially into and accumulates consequently in the microemulsion phase.

QUANTITATIVE ASSESSMENT OF THE PROCESS

Extraction Stage

In order to quantify the previous observations we have measured the concentrations of all components in the different phases for a system whose characteristics are indicated in the caption of Table 1. The concentrations of the different components reported in Table 1 vary as the active mixture overall concentration increases, the temperature being held at 30°C.

The system remains of the $W I$ type up to 5% in active mixture. It is of the $W III$ type between 5 and 9%, and of the $W II$ type above 9%. Only the concentrations in the microemulsion phase show large variations. For small concentrations of active mixture there is no excess aqueous phase. When an aqueous phase appears, nickel remains in the microemulsion phase. Finally the microemulsion becomes diluted as more and more oil is incorporated into it.

In this extraction stage the maximum nickel concentration in the microemulsion phase does not coincide with the maximum extracted amount. The mass balance shows that the fraction of extracted nickel (i.e. nickel located in the microemulsion phase) is equal to 92% of the original amount of nickel when the active mixture overall concentration is 13%, while it is only equal to 77% when the active mixture overall concentration is 7%. This value corresponds to the maximum concentration of nickel in the microemulsion phase.

Reextraction Stage

A complete extraction-reextraction cycle was carried out using the system defined by the data reported in table 2.

At 30°C, a $W II$ system was obtained whose aqueous phase contained only 18% of the original nickel (1300 ppm), 3.6% of the pentanol and 0.3% of the SDS. After the separation of the microemulsion from this aqueous phase, concentrated (36% weight) hydrochloric acid was added to the microemulsion so as to induce the separation of a new excess aqueous phase and promote the shifting of nickel cations into this aqueous phase.

In Figure 5 are plotted, for both the microemulsion phase and the new excess aqueous phase, the concentrations of the different components versus the overall concentration is maximum when the acid concentration is equal to 0.5 mole per liter. At lower acid concentrations, the process is less efficient because the shifting of nickel cations towards the excess aqueous phase is rather weak. On the other hand, adding too large amounts of acid results only in diluting the excess aqueous phase and consequently the lowering of the nickel concentration in it.

At 0.5 mol/l of acid the concentration of nickel in the aqueous phase culminates to 14500 ppm. This concentration is three times larger than the concentration of nickel in the original aqueous solution. The rate of nickel recovery is 72%. The aqueous phase also contains 1% of the pentanol and 0.1% of the SDS originally incorporated in the system.

AGREEMENT BETWEEN THE PSEUDOPHASE MODEL AND EXPERIMENTS

The pseudophase model was tested on the system used in the extraction experiment, shown in Table 1. Water + $Ni Cl_2$ have been considered as one unique pseudocomponent. The pseudophase model contains four unknown parameters to be determined. These parameters have been estimated by means of an identification based on a GAUSS-NEWTON method and by comparing theoretical and experimental concentrations.

Let us recall that in this model the composition of the actual oil (aqueous) phase are assumed to be respectively equal to the composition of the oil (aqueous) pseudophase. Composition of actual microemulsion phase is calculated by mass balance using the experimental phase weight fractions. Calculated data corresponding to the optimal set of parameters ($K = 95$, $k_w = 1.1$, $k_M = 70$, $\epsilon = 0.20$) are provided in Table 4.

Correlation between calculated and experimental concentrations in the three phases is shown in Figure 6.

CONCLUSIONS

Pseudophase model is a good instrument to simulate the non-ionic component partition in microemulsion systems. Up to this point, an expansion of the model that will allow us to simulate the ion partition is going on.

This simulation is based on the hypothesis that the association of metallic cations with anionic surfactant micelles can be described in terms of electrostatic interactions only (7).

In the present paper we have presented some results on the concentration process in one single extraction-reextraction cycle. The next step will be to study the "multistage" process in the aim of concentrating the aqueous solution by successive extraction-reextraction cycles. At the same time the study on the separation of several cations in aqueous solution will start.

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NOMENCLATURE

A	alcohol
S	surfactant
O	oil, oil phase
W	water, aqueous phase
M	microemulsion phase
O'	oil pseudophase
M'	membrane pseudophase
W'	aqueous pseudophase
A ₁ , A ₂ ...A _i	imeric alcohol
X _{i,j}	weigh fraction of the i component in the j phase or pseudophase

TABLE I.
Experimental Composition of the Oil, Microemulsion and Aqueous Phases in
Extraction Experiment as a function of Overall Active Mixture Concentration.
Overall composition (weight): n-decane/water=1; 1-pentanol/SDS=3; Ni in
water 0.5. The concentrations are expressed in % weight.

Oil phase

A.M.	Water	Pentanol	Decane	SDS	Ni·10 ³
3.5	0.96	3.60	95.4	0.010	61.0
5.0	0.48	4.86	94.6	0.012	8.9
7.0	1.00	8.77	90.1	0.083	15.7
9.0	2.38	8.61	88.5	0.439	44.0
11.0	--	--	--	--	--
13.0	--	--	--	--	--

Microemulsion phase

A.M.	Water	Pentanol	Decane	SDS	Ni
3.5	89.8	2.04	5.7	1.97	0.46
5.0	61.7	5.78	24.8	6.72	0.82
7.0	41.7	8.46	41.9	6.92	0.88
9.0	32.9	9.65	50.8	5.75	0.70
11.0	22.5	10.89	62.1	4.12	0.39
13.0	24.8	12.53	57.3	4.74	0.47

Aqueous phase

A.M.	Water	Pentanol	Decane	SDS·10 ³	Ni
3.5	--	--	--	--	--
5.0	98.8	0.99	0.00	6.6	0.17
7.0	98.7	1.04	0.00	8.4	0.18
9.0	98.8	1.08	0.00	3.4	0.12
11.0	98.8	1.04	0.00	9.2	0.11
13.0	98.9	1.02	0.00	9.9	0.09

TABLE 2.
Overall Composition in Reextraction Experiment. The concentrations are
expressed in % weight.

Component	%
Water (5000ppm Ni)	45.69
N-Decane	40.74
SDS	3.33
1-Pentanol	10.23

TABLE 3.
Composition of the Microemulsion and Aqueous Phases in Reextraction
Experiment as a function of Overall Acid Concentration (in mol/l). The
concentrations are expressed in % weight.

Microemulsion phase

m H ⁺	Water	Pentanol	Decane	SDS	Ni
0.00	19.07	15.2	62.7	2.80	0.287
0.06	9.83	16.7	71.1	2.05	0.319
0.19	7.15	17.2	72.8	2.56	0.228
0.51	4.61	17.6	75.0	2.77	0.045
0.94	4.38	17.3	75.6	2.75	0.018
1.39	4.01	17.4	75.7	2.85	0.021
2.20	5.34	17.3	74.6	2.79	0.013

Aqueous phase

m H ⁺	Water	Pentanol	Decane	SDS-10 ³	Ni
0.00	--	--	--	--	--
0.06	97.6	1.03	0.71	49.0	0.53
0.19	97.1	0.89	0.70	20.0	1.11
0.51	97.4	0.83	0.00	15.0	1.45
0.94	97.6	0.90	0.00	5.9	1.27
1.39	97.6	1.18	0.00	5.4	1.03
2.20	97.4	1.61	0.00	8.7	0.84

TABLE 4.
Calculated Composition of the Oil, Microemulsion and Aqueous Phases in
Extraction Experiment as a function of Overall Active Mixture Concentration.
The concentrations are expressed in % weight.

Oil phase

A.M.	Phase wt fract.	Water+ NiCl ₂	Pentanol	Decane	SDS
3.5	0.475	0.753	3.631	95.62	--
5.0	0.449	1.097	5.288	93.61	--
7.0	0.376	1.548	7.459	90.99	--
9.0	0.260	1.989	9.587	88.42	--
11.0	--	--	--	--	--
13.0	--	--	--	--	--

Microemulsion phase

A.M.	Phase wt fract.	Water+ NiCl ₂	Pentanol	Decane	SDS
3.5	0.525	91.22	1.715	5.40	1.667
5.0	0.206	62.35	5.041	26.54	6.068
7.0	0.274	41.16	7.614	44.84	6.387
9.0	0.415	30.91	9.432	54.24	5.422
11.0	0.713	22.59	11.138	62.41	3.857
13.0	0.723	22.27	13.069	60.16	4.495

Aqueous phase

A.M.	Phase wt fract.	Water+ NiCl ₂	Pentanol	Decane	SDS
3.5	--	--	--	--	--
5.0	0.345	99.02	0.977	0.00	--
7.0	0.350	98.97	1.027	0.00	--
9.0	0.325	98.94	1.055	0.00	--
11.0	0.287	98.92	1.074	0.00	--
13.0	0.277	98.91	1.088	0.00	--

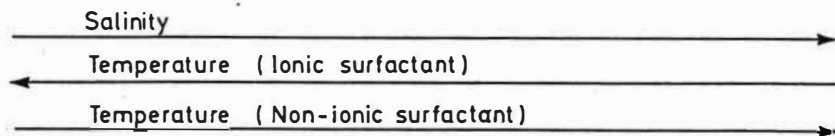
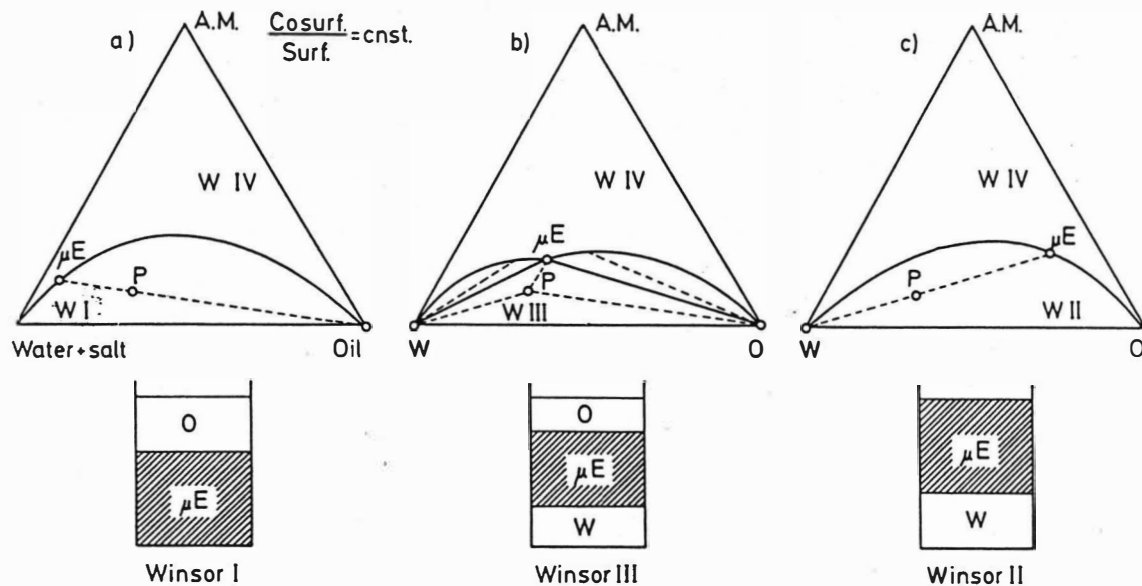


Figure 1. Idealized evolution of pseudoternary phase diagrams (A.M. = active mixture; W = water or aqueous solution; O = oil).

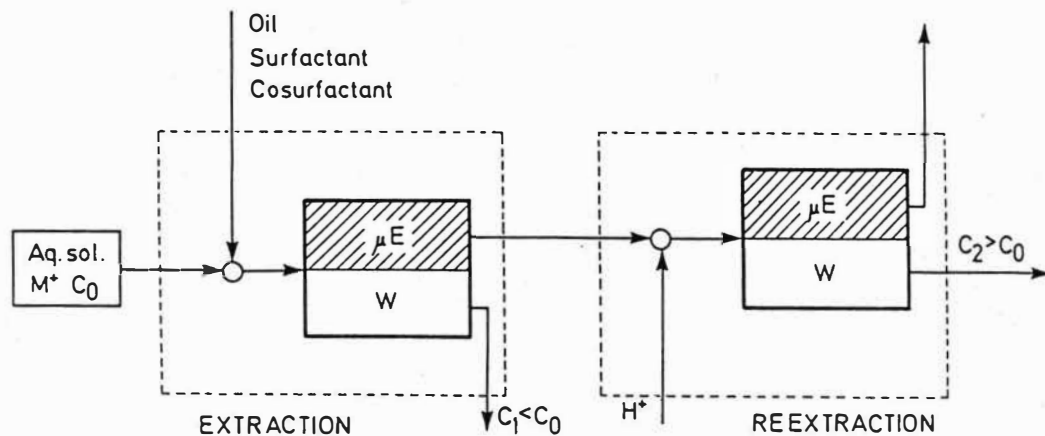


Figure 2. Sketch of the extraction-reextraction process.

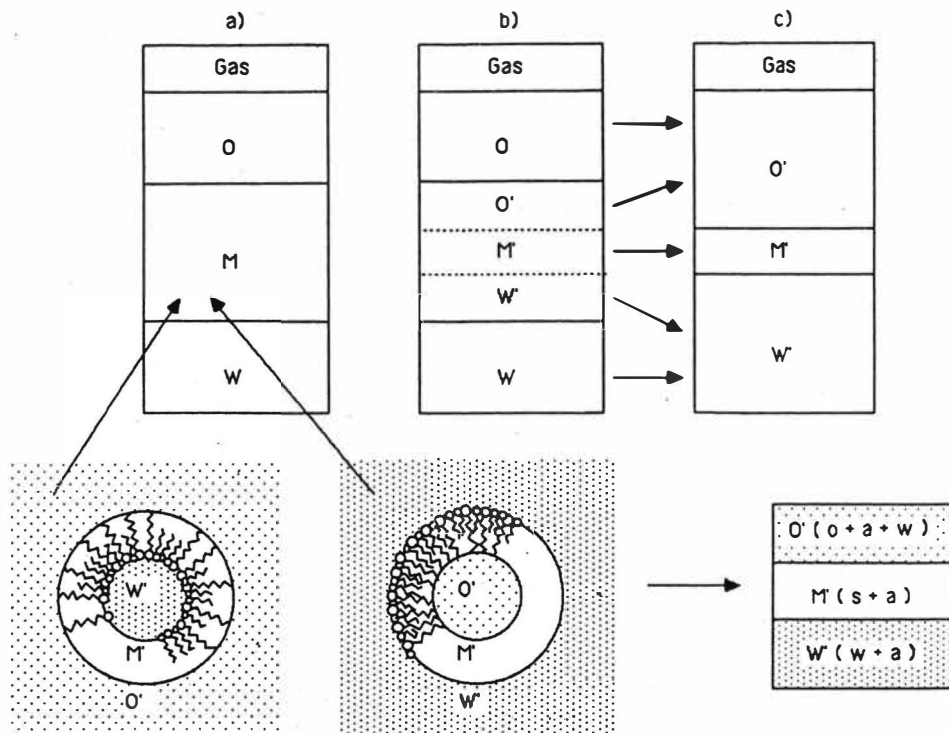


Figure 3. Pseudophase model.

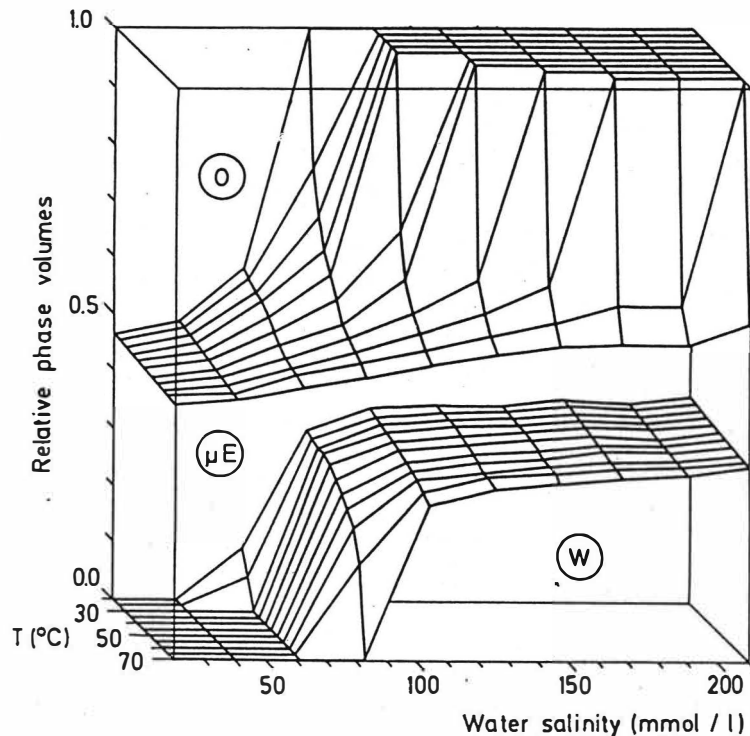


Figure 4. Three-dimensional phase diagram: Relative phase volumes versus temperature and water salinity (NiCl_2); O = oil phase; μ E = microemulsion phase; W = aqueous phase. Overall composition (weight): n-decane/water=1; 1-pentanol/SDS=3; SDS+pentanol=9%.

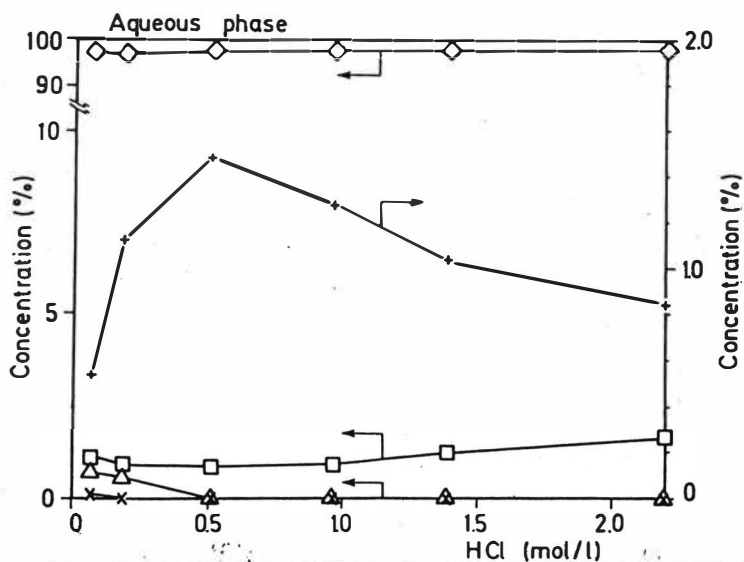
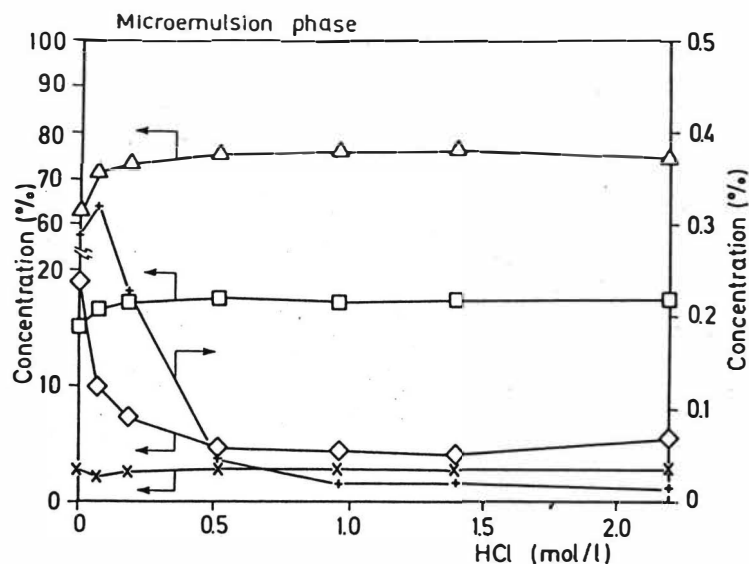
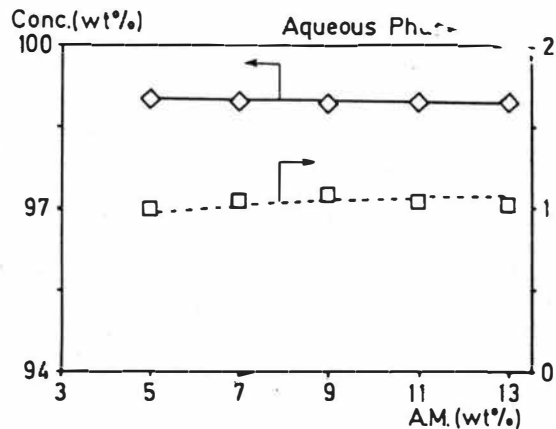
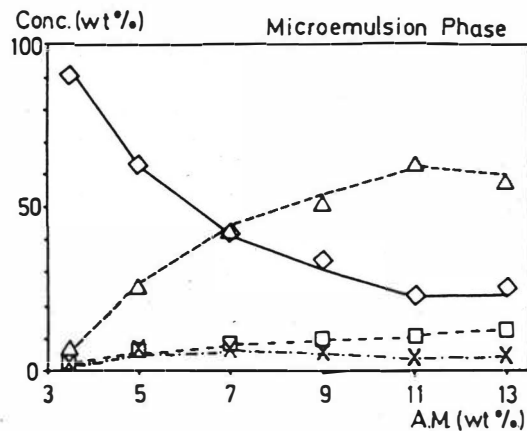
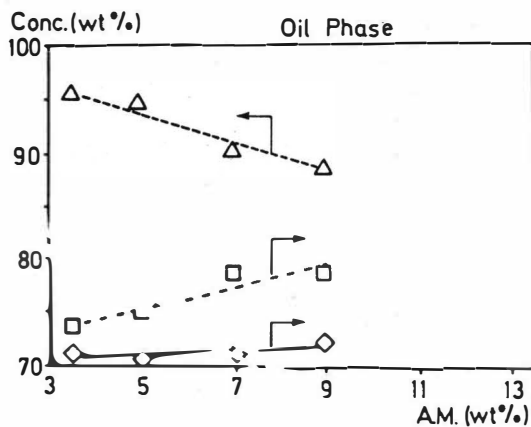


Figure 5. Reextraction stage. Composition of the microemulsion and aqueous phases versus the acid concentration at 30°C. Overall composition is in Table 2. Concentration are expressed in % weight. (+ Ni; \diamond water; \square 1-pentanol; \triangle n-decane; X SDS).



	exp.	calc.
Water	◇	—
1-Pentanol	□	---
n-Decane	△	---
SDS	X	---

Figure 6. Extraction stage. Calculated and Experimental Composition of the oil, microemulsion and aqueous phases versus the percentage of active mixture at 30°C.

The Extraction of Hexavalent Metals (Chromium, Molybdenum and Tungsten) from Alkaline Solutions by Long-Chain Alkyl Quaternary Ammonium Compounds

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Abstract

The extractions of hexavalent metals (chromium, molybdenum and tungsten) from sodium hydroxide solutions by trioctylmethylammonium compound ($R_3R'NCl$ or $R_3R'NOH$) in benzene have been examined under different conditions. As a results, it is found that these metals are taken up from alkaline solutions through anion exchange reactions by the following equations: $MO_4^{2-}(aq) + 2R_3R'NOH(org) \rightleftharpoons (R_3R'N)_2MO_4 + 2OH^-(aq)$ where $M = Cr, Mo$ and W . The formation of the species, $(R_3R'N)_2M$, is also supported by the facts that the characteristic vibrations of moiety appear in the infrared spectra of organic extracts, and that a band in the absorption spectra of organic solutions follows the Beer's law over the range of sodium hydroxide concentration studied.

Introduction

The extraction of metals in strong alkaline solutions is of significance for hydrometallurgy. The extractable metals exist as either form of hydroxo- or oxo- species. For the uptake of metals from their hydroxy anions, it is known that alkylated hydroxy quinolines are effective extractants. We have confirmed that zinc(II), lead(II) and gallium(III) are extracted from aqueous solutions containing their anions by 7(5,5,7,7-tetramethyl-1-octen-3-yl)-8-hydroxyquinoline (KELEX 100)(1-3). In contrast, as it is expected that quaternary ammonium compounds are suitable for the uptake of anion through ion-exchange reaction, the extraction of chromium(VI) from sodium hydroxide solutions by trioctylmethylammonium compound ($R_3R'NCl$ or $R_3R'OH$)(4,5). Thus the present work is extended to investigate the extraction of hexavalent metals (chromium, molybdenum and tungsten) from sodium hydroxide solutions by long-chain alkyl ammonium compound.

Experimental

Reagent

Trioctylmethylammonium chloride ($> 99\%$ $R_3R'NCl$, TOMAC, Koei Chemical Co., Ltd.) without further purification was diluted with benzene. A stock solution of trioctylmethylammonium hydroxide ($R_3R'NOH$) was prepared as follows: 0.05 mol dm^{-3} TOMAC in benzene was shaken with 2 mol dm^{-3} sodium hydroxide solution for 5 min; the organic solution was centrifuged and equilibrated with a fresh solution of sodium hydroxide; the procedure was repeated five times. Aqueous solutions of hexavalent metals were prepared by dissolving their sodium metalates ($NaCrO_4 \cdot 4H_2O$, $Na_2MoO_4 \cdot 2H_2O$ and $Na_2WO_4 \cdot 2H_2O$) in sodium hydroxide solutions of selected concentration, and in general the metal concentration was 0.005 mol dm^{-3} . All chemicals used were of analytical reagent grade.

Extraction and analytical procedure

Equal volumes (15 cm^3 each) of organic and aqueous phase placed in stoppered centrifugal glass tube were shaken by mechanical shaker at 20°C , except the experiments on temperature effect. Preliminary experiments showed that the equilibration is complete in 5 min. The mixture was centrifuged and separated, and then aliquots of both phases were pipetted to determine the distribution coefficient of hexavalent metal (the ratio of the equilibrium concentration of metals in organic phase to that in aqueous phase, E_a°). Chromium and tungsten in the organic phase were stripped with 2 mol dm^{-3} NaOH in the presence of 2-ethylhexyl alcohol. Molybdenum in the organic phase was stripped with 2 mol dm^{-3} NaOH + 2 mol dm^{-3} HCl in the presence of 2-ethylhexyl alcohol. The concentrations of chromium, molybdenum and tungsten in aqueous solution were assayed spectrophotometrically utilizing the maximal absorption of chromate, molybdate and tungstate ions at 366 nm ($\epsilon = 4800$), 460 nm ($\epsilon = 11726$) and 400 nm ($\epsilon = 11455$), respectively. The concentrations of sodium accompanied by chromium and molybdenum extracted into organic phase were determined by atomic absorption spectrophotometry using Hitachi Ltd. Model 170-50-A for the aqueous solutions adjusted to pH 0.5 by hydrochloric acid after stripping them with 2 mol dm^{-3} KCl and 2 mol dm^{-3} KOH + 2 mol dm^{-3} HCl, respectively.

The concentration of chloride and the water content in the organic phase were examined by Volhard's and Karl-Fisher's methods as indicated previously(6).

Absorption and infrared spectroscopies

The infrared spectra of the samples prepared by evaporation of the organic diluent were measured on a Japan Spectroscopic Co., Ltd.

grating models IRA-I ($4000-650\text{ cm}^{-1}$) and IR-F ($700-200\text{ cm}^{-1}$) using a capillary film between thallium halide plates or polyethylene films. The absorption spectra were determined on a Hitachi model 340 grating spectrophotometer equipped with automatic baseline compensater, using matched $1.0 \times 1.0\text{ cm}$ fused silica cells.

Results and discussion

Extraction by trioctylmethylammonium chloride and hydroxide

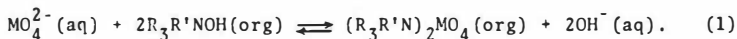
In the extractions of hexavalent chromium, molybdenum and tungsten from sodium hydroxide solutions containing 0.005 mol dm^{-3} sodium metalates by TOMAC at 20°C , the distribution isotherms of hexavalent metals between sodium hydroxide solutions and TOMAC in benzene gave the results that the extraction efficiency is in the order $\text{Cr} > \text{Mo} > \text{W}$, but the distribution coefficient decreases with increasing the hydroxide ion concentration in aqueous phase and then their decreases become gentry at the hydrochloric acid concentrations above ~ 4 , 3 and 4 mol dm^{-3} . In the extraction by TOMAC, however, the formation of the species $\text{R}_3\text{R}'\text{NOH}$ can not be neglected during the extraction process, although the chloride form is more stable than the hydroxide one as expected from the energies of hydration of chloride and hydroxide ions(7).

On the one hand, the distribution isotherms of hexavalent metals by $\text{R}_3\text{R}'\text{NOH}$ in benzene reveal that an enhancement of the extraction of hexavalent metals by $\text{R}_3\text{R}'\text{NOH}$ in comparison with $\text{R}_3\text{R}'\text{NCl}$ is consistent with the order of substitution of anions(8). In the extraction of hexavalent chromium, molybdenum and tungsten at the concentration of sodium hydroxide below 5 mol dm^{-3} , the dependence of distribution coefficients on sodium hydroxide concentrations indicates a typical extraction behaviour through anion-exchange reaction which shows the monotonous decrease in the distribution coefficient with increasing the concentration of hydroxide ion concentration in aqueous phase. In contrast, a slight increase of the distribution coefficient is observed at higher sodium hydroxide concentrations, since the Na^+ cation in aqueous phase affects the chemical potential of MO_4^{2-} ions where $\text{M} = \text{Cr}, \text{Mo}$ and W in aqueous phase. However, since anomalous rise does not occur in the extraction from potassium hydroxide solutions, it is inferred that the existance of hexavalent metals in potassium hydroxide solutions are more stable than that in sodium hydroxide ones at a constant concentration of sodium hydroxide in 0.3 mol dm^{-3} .

When the concentrations of the metals in the organic phase are plotted

as a function of the molar at a fixed total concentration in 0.01 mol dm^{-3} of initial aqueous metal and $R_3R'NOH$, the maxima appear at the molar fraction of 0.33. In addition the repeated extractions of metals from fresh aqueous solutions containing metals in $0.005 \text{ mol dm}^{-3}$ by $R_3R'NOH$ at a constant sodium hydroxide concentration in 0.2 mol dm^{-3} give the molar ratio $[R_3R'NOH]/[M]$ of two in the organic phase. These results indicate that the stoichiometric composition of the metal organic species possesses $(R_3R'N)_2MO_4$.

Accordingly it is postulated that hexavalent metal is extracted into the organic phase through the reaction



Infrared and absorption spectra

The metal-saturated organic extracts from 0.2 mol dm^{-3} sodium hydroxide solution with 0.02 mol dm^{-3} $R_3R'NOH$ in benzene were examined by infrared spectrophotometry. The spectrum of $R_3R'NOH$ exhibits bands at 3400 and 1650 cm^{-1} due to the OH stretching and bending modes, respectively. By comparison with the data for metal-saturated organic extracts, it is seen that the absorption due to OH stretching and bending bands are decreased in their intensities by the extraction of metals, in accordance with the expectations from equation(1). Even in the spectra of the metal-saturated organic extracts, however, an appearance of OH bands arises from entrainment of water associated with metals. The spectra of the organic extracts by $R_3R'NOH$ reveal the M-O stretching bands at 845 , 830 and 780 cm^{-1} for chromium, 830 and 765 cm^{-1} for molybdenum and 820 cm^{-1} for tungsten, respectively, suggesting the shift of the M-O stretching frequencies of $Na_2CrO_4 \cdot 4H_2O$ at 930 , 882 and 830 cm^{-1} , $Na_2MoO_4 \cdot 2H_2O$ at 890 , 850 and 820 cm^{-1} and $Na_2WO_4 \cdot 2H_2O$ at 950 , 850 and 830 cm^{-1} to lower frequencies. From these it is inferred that the species $(R_3R'N)_2CrO_4$, $(R_3R'N)_2MoO_4$ and $(R_3R'NCl)_2WO_4$ are formed in the extraction of hexavalent chromium, molybdenum and tungsten from sodium hydroxide solutions by $R_3R'NOH$.

The absorption spectra of the organic solutions extracted from sodium hydroxide solutions with 0.02 mol dm^{-3} $R_3R'NOH$ in benzene show an absorption maximum at 27000 cm^{-1} , assigned to the transition $^1A_1 \rightarrow ^1T_2$, consistent with those of aqueous sodium chromate solutions being in a tetrahedral environment. Accordingly it is presumed that the extracted species from aqueous solution containing hexavalent molybdenum and tungsten in sodium hydroxide solutions by $R_3R'NOH$ are also in tetra-

hedral arrangement.

Temperature effect

The extractions of hexavalent chromium, molybdenum and tungsten from aqueous solutions containing $0.005 \text{ mol dm}^{-3}$ sodium metalates in 0.5 mol dm^{-3} sodium hydroxide with $0.05 \text{ mol dm}^{-3} \text{ R}_3\text{R}'\text{NOH}$ in benzene at temperatures between 10 and 40 °C give the results that the distribution coefficients decrease with rising temperature in these extraction systems. Thus the value of heat of reaction (change in enthalpy, $-\Delta H$) is estimated as 8.4, 20.2 and 10.2 kJ mol^{-1} for chromium, molybdenum and tungsten, respectively.

Effect of anion on quaternary ammonium salts

When the extraction of hexavalent chromium, molybdenum and tungsten from aqueous solutions containing $0.005 \text{ mol dm}^{-3}$ sodium metalates in 0.2 mol dm^{-3} sodium hydroxide are carried out with 0.02 mol dm^{-3} trioctylmethylammonium salts, replaced by various anions such as NO_3^- , SCN^- , HSO_4^- and ClO_4^- , in benzene at 20 °C, it is seen that the extraction efficiency of quaternary ammonium compounds is in the $\text{OH} > \text{Cl} > \text{HSO}_4 > \text{ClO}_4$, corresponding to the dimension of equilibrium constant (7).

Acknowledgement

We with to thank the Koei Chemical Industry Co., Ltd. for a sample of TOMAC.

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The Extraction of Mercury(II) from Hydrochloric Acid Solutions by Alkyl-Sulphide and Sulphoxide

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Abstract

The extraction of mercury(II) from hydrochloric acid solutions by dihexylsulphide (DHS, R_2S) and dihexylsulphoxide (DHSO, R_2SO) in benzene have been investigated under different conditions. The infrared and Raman spectral studies have been carried out for the organic extracts. As a result, the equilibrium equations are proposed on the basis of distribution data.

Introduction

It is known that the presence of sulfur atom facilitates combination with the class b metal ions. Accordingly sulfur containing compounds such as diethyldithiocarbamate, xanthate, dithio- β -isoindigo, dithizone, mercaptanes, sulphide and sulphoxides have been used as the solvent extractants of platinum, silver and mercury. Especially, it has been found that alkyl-sulphide and sulphoxide were effective in the extraction of mercury(1-4).

Therefore we undertake this work in order to obtain further information on the extraction of mercury(II) from hydrochloric acid solutions by dihexylsulphide (DHS, R_2S) and dihexylsulphoxide (DHSO, R_2SO).

Experimental

Reagents

DHS (Daiichi Chemical Industry Co., Ltd., 99.5 %) was used without further purification, and DHSO was synthesized by means of oxidation from DHS as follows(5): 1) 35 cm³ each of acetic acid and acetic anhydride and 20 cm³ of aqueous solution of hydrogen peroxide in 30 % were added to 50 cm³ of DHS dropwisely for during 1 hr; the mixture was cooled with ice, and then the resulting mixture was stripped for 3 hr at 0 °C. 2) After end of the reaction was confirmed by TLC, DHSO extracted into chloroform was washed at first with water and then with 10 % sodium carbonate, and finally with water again. 3) White crystal been

got from the removal of chloroform by evaporater was refined by recrystallization method.

Aqueous solutions of mercury(II) were prepared by dissolving its chloride in hydrochloric acid of the selected concentration. The used chemicals were of analytical reagent grade.

Extraction and analytical procedure

Equal volumes (15 cm^{-3} each) of DHS or DHSO in benzene and aqueous solutions containing chlorides were placed in 50 cm^3 stoppered conical flasks and shaken for 10 min in a water bath thermostatted at 20°C , except the experiments on temperature effect. Preliminary experiments showed that equilibrium was complete 10 min.

The mixture was quickly separated by centrifuge, and metal in organic phase was stripped with hydrochloric acid of 1 mol dm^{-3} . The concentration of metal in aqueous solutions was determined by EDTA titration at pH 10 for mercury(II), in the presence of excess Mg-EDTA using Eriochrome black T (BT) as indicator(6). The distribution coefficient, E_a° , was obtained as the ratio of the equilibrium concentration of mercury (II) in the organic phase to that in aqueous phase. The concentration of chloride and the water content in the organic phase were examined by Volhard's and Karl-Fisher's methods indicated previously(7).

The infrared spectra of the organic extracts were measured on a JASCO infrared recording spectrophotometer Model IRA-1 ($4000-650 \text{ cm}^{-1}$) and IR-F ($700-200 \text{ cm}^{-1}$) using a capillary film between tellurium halide plates or polyethylene films. The Raman spectra of the organic extracts were measured on a JASCO Laser Raman Spectrophotometer Model R-300.

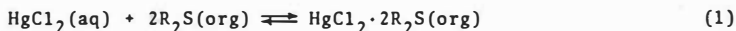
Results and discussion

Extraction of mercury(II) by DHS

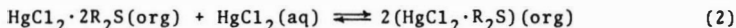
The extraction of mercury(II) from hydrochloric acid solutions containing 1 g dm^{-3} ($0.0368 \text{ mol dm}^{-3}$) HgCl_2 by DHS in benzene at 20°C gave the results that the distribution coefficient decreases with increasing the concentration of hydrochloric acid in aqueous phase. The log-log plots of E_a° vs. [DHS] at constant hydrochloric acid concentration showed the straight lines with the following slopes: 1.90, 1.90, 1.92 and 1.75 at 0.01, 0.1, 0.5 and 1 mol dm^{-3} HCl, respectively.

In the extraction of mercury(II) by DHS, when the continuous variation of $[\text{Hg}]_{\text{org}}$ is plotted as a function of $[\text{Hg}]_{\text{initial aq}}$ at a fixed total concentration, $[\text{Hg}]_{\text{initial aq}} + [\text{DHS}]_{\text{initial}}$, maxima appear at the molar fractions of 0.5 and 0.33 at initial aqueous hydrochloric acid concentrations in 0.1 and 1 mol dm⁻³, respectively. In contrast, when the repeated extractions of mercury(II) from fresh aqueous solutions containing 0.1 mol dm⁻³ HgCl₂ with 0.2 mol dm⁻³ DHS in benzene are carried out at a constant hydrochloric acid concentration in 0.02 mol dm⁻³, the molar ratio of $[\text{Hg}]/[\text{R}_2\text{S}]_{\text{initial}}$ in the organic phase approaches a limiting value of unity, suggesting that the stoichiometrical species $\text{R}_2\text{S} \cdot \text{HgCl}_2$ is formed in the increase of mercury(II) loading.

Accordingly it is considered that the extraction of mercury(II) by DHS is expressed as follows:



and with increasing the loading of mercury(II) in the organic phase



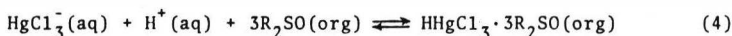
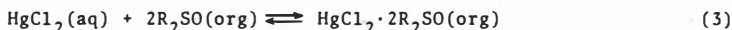
Extraction of mercury(II) by DHSO

In the extraction of mercury(II) from hydrochloric acid solutions containing 1 g dm⁻³ (0.0368 mol dm⁻³) HgCl₂ by DHSO, the distribution coefficient decreases with increasing aqueous acidity below about 2 mol dm⁻³, but above this acidity the extraction curve rises. The log-log plots of E_a° vs. the equilibrium concentration of DHSO give straight lines with slopes of the values as follows: 1.60, 1.62, 1.60 and 1.60 at 0.01, 0.1, 0.5 and 1 HCl mol dm⁻³, respectively. This suggests that the distribution coefficient has the second power dependence on $[\text{DHSO}]$, indicating that the formation of di-solvate in the extraction at low aqueous acidity by DHSO.

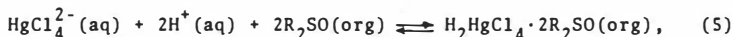
In the extraction of mercury(II) at aqueous low acidity ($[\text{HCl}]_{\text{initial aq}} \leq 2 \text{ mol dm}^{-3}$), the continuous variation of $[\text{Hg}]_{\text{org}}$ as a function of molar fraction of $[\text{Hg}]_{\text{initial aq}} / ([\text{Hg}]_{\text{initial aq}} + [\text{DHSO}]_{\text{initial}})$ at a fixed total $[\text{Hg}]_{\text{initial aq}} + [\text{DHSO}]_{\text{initial}}$ maxima appear at the molar fraction of 0.5 and 0.33 at initial aqueous hydrochloric acid concentrations in 0.1 and 1 mol dm⁻³, respectively. The repeated extractions of mercury(II) from fresh aqueous solutions containing 0.1 mol dm⁻³ HgCl₂ with 0.2 mol dm⁻³ DHSO in benzene at a constant hydrochloric acid concentration of 0.2 mol dm⁻³ give the result that the molar ratio $[\text{Hg}]/[\text{R}_2\text{SO}]_{\text{initial}}$ in

the organic phase approaches a limiting value of unity, suggesting that the stoichiometrical species $R_2SO \cdot HgCl_2$ is formed in the increase of mercury(II) loading.

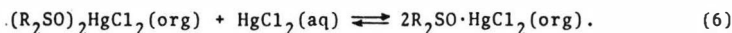
Further the extraction of mercury(II) from aqueous solutions at higher acidity ($[HCl]_{initial} \geq 2 \text{ mol dm}^{-3}$) by DHSO has been surveyed by the similar manners to its extraction at low acidity ($[HCl]_{initial} \geq 1 \text{ mol dm}^{-3}$), and consequently the following equilibrium equations are inferred : as the aqueous species of mercury(II) depends on the aqueous acidity,



and



and when mercury(II) loading increases



Infrared spectra

Several times repeated extractions of mercury(II) from fresh aqueous solutions containing $0.1 \text{ mol dm}^{-3} HgCl_2$ with 0.2 mol dm^{-3} DHS or DHSO in benzene at a constant concentration of hydrochloric acid in $20^\circ C$ gave the molar ratios $[DHS]$ and $[DHSO]/[Hg]/[Cl]$ of $1 : 1 : 2$ and $1 : 1 : 2$, respectively. The saturated organic extracts so obtained were examined by infrared spectrophotometry.

In the extraction by DHS, the spectra of the organic extract exhibits the absorption due to the C-S stretching vibration at 720 cm^{-1} and the Hg-Cl stretching frequency at 290 cm^{-1} in accordance with the distribution data.

In the extraction by DHSO, the spectra of the organic extracts exhibit the absorptions due to the S=O stretching vibration at 990 cm^{-1} , shifted from the band which appears at 1050 cm^{-1} in a free DHSO, and the Hg-O and Hg-Cl stretching frequency at 365 and 300 cm^{-1} , respectively, in agreement with the distribution data.

Further Raman spectra of the organic extracts by DHS and DHSO reveal

the HgCl_2 band at 280 and 310 cm^{-1} , respectively, suggesting the formation of the species $\text{R}_2\text{S}\cdot\text{HgCl}_2$ and $\text{R}_2\text{SO}\cdot\text{HgCl}_2$. In contrast, the organic extracts of mercury(II) from 1, 3 and 7 mol dm^{-3} hydrochloric acid solutions containing 100 g dm^{-3} HgCl_2 by DHSO in benzene at 20°C give the absorption bands at 310, 285 and 270 cm^{-1} assigned to HgCl_2 , HgCl_3^- and HgCl_4^{2-} , respectively, corresponding to the equilibrium equations (3)-(6).

Temperature effect

The extraction of mercury(II) from hydrochloric acid solutions containing 1 g dm^{-3} ($0.0368\text{ mol dm}^{-3}$) with DHS and DHSO of 0.1-0.2 mol dm^{-3} in benzene in the range of temperature between 10 and 50°C gave the results that the distribution coefficients decrease with rising temperature in both cases. From this the heats of reaction (change in enthalpy, $-\Delta H$) are estimated as follows; by DHS, 32.9 and 14.9 kJ mol^{-1} at 0.01 and 0.5 mol dm^{-3} HCl, respectively; by DHSO, 20.3, 26.2 and 35.2 kJ mol^{-1} at 0.01, 0.5 and 6 mol dm^{-3} HCl, respectively.

Acknowledgement

We wish to thank the Daihachi Chemical Industry Co., Ltd. for a sample of DHS.

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Extraction of Zn(II) by organophosphorous compounds.

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The use of acidic esters of ortophosphoric acid has been investigated and the mechanism of extraction have been clarified and reported for several systems and reviewed by Kolarik (1).

In the last years the introduction of commercial extractants CYANEX 272 (American Cyanamid Company), SME 418 (Shell Chemical Co.), PC 88A (Daihachi Chemical Industry Company) has increased the interest in the use of phosphonic and phosphinic acids as extractants in hydrometallurgy processing of metals. Nevertheless only few studies have been reported on the extraction of metals (2,3) being most of them concerning to the separation of Cobalt and Nickel (4-6) but practically none of them have been devoted to the determination of the extracted species in the organic phase.

In the present work we have studied the degree of aggregation and its formation constants of di(-2-ethylhexyl)phosphoric acid (DEHPA), 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (HEH(EHP)) and di-n-octyl phosphinic acid (HDOP) in toluene at 25°C in order to clarify the extraction mechanism. Finally a detailed study of the extraction of Zn(II) by these organophosphorous reagents have been undertaken. Its objective is to determine the composition of the extracted species as well as their equilibrium constants.

Reagents and experimental procedure.

The extractants DEHPA (BDH) and HEH(EHP) (Shell Chemical Co. SME 418) were purified before utilization. The extractant HDOP was synthesized from the alkene and hypophosphorous acid (7).

The aggregation of DEHPA, HEH(EHP) and HDOP dissolved in toluene at 25°C was followed by vapor pressure osmometry. Osmometric measurements were carried out with a Knauer vapor pressure osmometer. Benzil was utilized as standard. The osmometric data were collected in the form ($\Delta R, B$) where B is the concentration (mol.kg^{-1}) of the different organophosphorous compounds.

The distribution equilibria studies were carried out at 25°C, shaking equal volumes (15 ml) of the organic phase and the aqueous phase until the equilibrium is reached. The composition of the organic phase was $C \text{ mol.dm}^{-3}$ of HA in toluene. The composition of the aqueous phase consisted of 0.1 mol.dm^{-3} (Na^+ , H^+ , Zn^{2+}) ClO_4^- and 0.1 mol.dm^{-3} (Na^+ , H^+ , Zn^{2+}) NO_3^- . The zinc concentration was determined by a 2380 Perkin Elmer atomic absorption spectrophotometer.

Results

Aggregation studies.

The aggregation process can be represented by the equation



where the formation constant is

$$\beta_n = \frac{|B_n|}{|B_1|^n} = |B_n| b^{-n} \quad (2)$$

The mass balance is given by

$$B = b + \sum n \beta_n b^n \quad (3)$$

The measured property ΔR can be expressed as

$$\Delta R = k_0 S \quad (4)$$

where S is the sum of the concentration for all solute species given by the expression

$$S = b + \sum \beta_n b^n \quad (5)$$

For benzil in toluene solutions, $B = S$ and the calibration constant k_0 can be obtained.

From experimental data ($\Delta R, B$) by using equation (4) the average aggregation \bar{n} can be calculated by

$$\bar{n} = B / S \quad (6)$$

By rearranging, equation (3) can be written as:

$$\log (B/b - 1) = \log n \beta_n + (n - 1) \log b \quad (7)$$

where b is the free monomer concentration calculated from the equation

$$\log b = \log b_0 + \int_{S_0}^S (1/\bar{n}) d \ln S \quad (8)$$

by graphical integration.

Thus, a plot of $\log (B/b - 1)$ as a function of $\log b$ would give a

straight line with an intercept equal to $\log n\beta_n$ and slope equal to $(n - 1)$. In fig. 1 it is seen that the data could be fitted by a straight line having a slope 1, which indicates that the degree of aggregation is 2. The constants are given in table I.

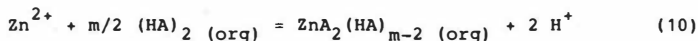
Metal distribution studies.

The distribution coefficient of Zinc(II) between the organic and aqueous phase was obtained directly as the ratio of the total zinc concentration in both phases.

$$D = \frac{[Zn^{2+}]_{(org)}}{[Zn^{2+}]_{(aq)}} \quad (9)$$

Values of D were measured as a function of pH for different total concentration of extractants at constant metal concentration of $10^{-4} \text{ mol. dm}^{-3}$ (Fig. 2,3,4).

The extraction of Zinc(II) with the cationic extractants can be written



where HA refers to DEHPA, HEH(EHP) and HDOP. K_m is the extraction constant defined by

$$K_m = \frac{[ZnA_2 (HA)_{m-2}]_{(org)} [H^+]^2}{[Zn^{2+}] [(HA)_2]_{(org)}^{(m/2)}} \quad (11)$$

A preliminary graphical treatment obtained by plotting $\log D$ against $\log (HA)_2 (org)$ at constant pH showed that two species of type $ZnA_2 (HA)_2$ and $ZnA_2 (HA)_{m-2}$ were formed in organic phase.

Assuming that this two species are formed and taking into account the distribution coefficient the following function can be obtained:

$$\frac{D [H^+]^2}{K_4 [(HA)_2]_{(org)}^2} = 1 + \frac{K_m [(HA)_2]_{(org)}^{(m-4)/2}}{K_4} \quad (12)$$

In order to determine the value of m and the extraction constants, the data plotted as $\log D - 2 \text{ pH} - 2 \log [(HA)_2]_{(org)}$ against $\log [(HA)_2]_{(org)}$ were compared with the theoretical function $\log Y = \log (1 + X^1)$, where Y and X are the normalized variables defined as:

$$Y = \frac{D |H^+|^2}{K_4 |(HA)_2|_{(org)}^2} \quad (13)$$

$$X = \frac{K_m^{2/(m-4)} |(HA)_2|_{(org)}}{K_2^{2/(m-4)}} \quad (14)$$

$$\text{and } i = (m-4)/2 \quad (15)$$

Values of m were found to be 3, 2, 2, for DEHPA, HEH(EHP) y HDOP respectively.

A refinement of the model obtained was performed using a version of the general minimizing program LETAGROP (8), especially adapted to the treatment of distribution data, LETAGROP-DISTR (9). In this program the computer searches for the best set of formation constants that would minimize the error squares sum defined by:

$$U = \sum (\log D_{\text{exp}} - \log D_{\text{calc}})^2 \quad (16)$$

where D_{exp} is the distribution ratio of zinc determined experimentally and D_{calc} is the calculated D value obtained by solving the mass balance equations for HA , Zn^{2+} , ClO_4^- or NO_3^- , using a given set of complexes and their equilibrium constants. The program also calculates the standard deviation $(\log D)$, defined by

$$\sigma(\log D) = \left| \sum (\log D_{\text{exp}} - \log D_{\text{calc}})^2 / N_p \right|^{1/2} \quad (17)$$

The results are given in Table II.

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Reagent	$\log \beta_2$
DEHPA	4.62
HEH (EHP)	3.38
HDOP	2.15

Table I. Equilibrium constants for the association of different organo-phosphorous compounds in toluene at 25°C.

Reagent	Method	$\log K_4$	$\log K_3$	$\log K_2$
DEHPA	Graphical	-1.32	-2.58	---
	Numerical	-1.33±0.10	-2.51±0.18	---
HEH (EHP)	Graphical	-2.06	---	-4.30
	Numerical	-2.06±0.09	---	-4.35±0.05
HDOP	Graphical	-1.87	---	-3.95
	Numerical	-1.87±0.06	---	-3.92±0.04

Table II. Equilibrium constants for the extraction of Zn(II) by organo-phosphorous compounds dissolved in toluene at 25°C.

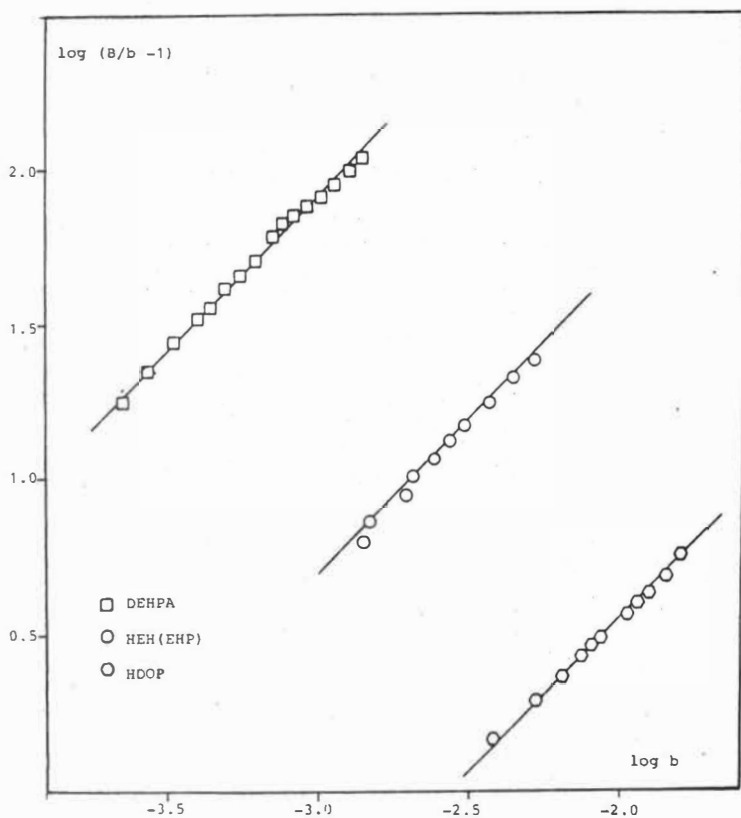


Fig. 1. The experimental points $\log (B/b-1)$ vs $\log b$ for different organophosphorous acids.

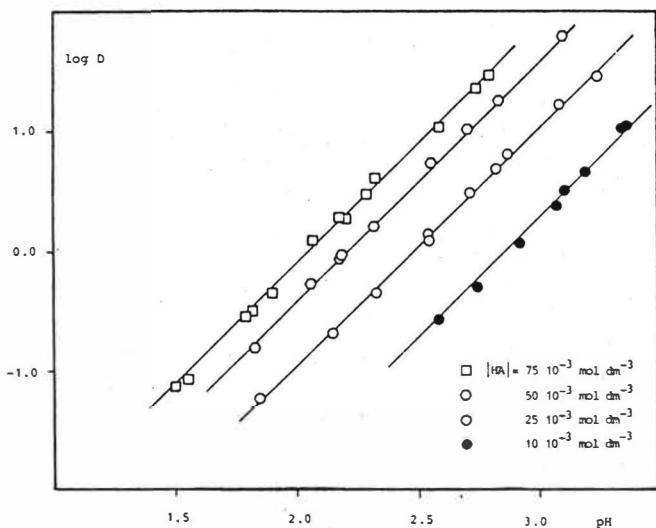


Fig. 2 log D plotted as a function of pH for the extraction of Zn(II) in perchlorate medium by different concentrations of DEHPA (HA) dissolved in toluene.

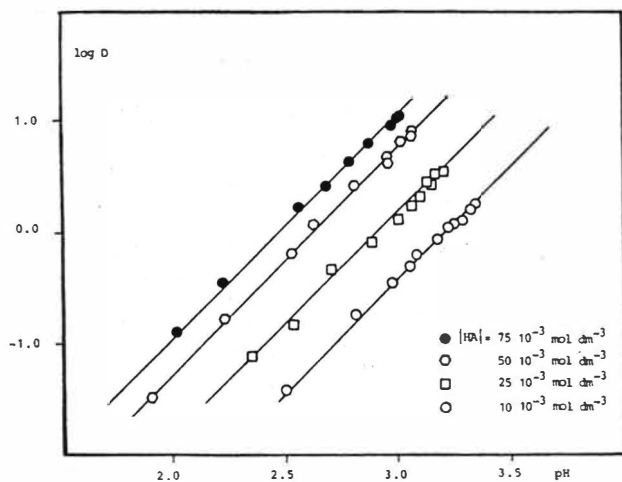


Fig. 3. log D plotted as a function of pH for the extraction of Zn(II) in perchlorate medium by different concentrations of HEH(ENP) (HA) dissolved in toluene.

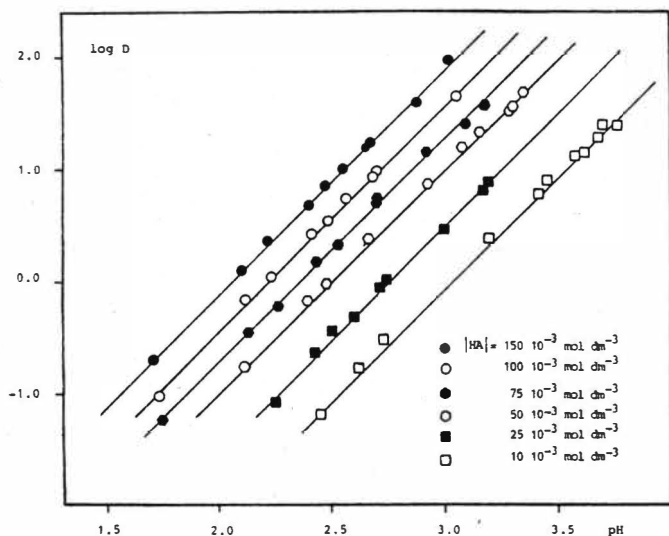


Fig. 4. $\log D$ plotted as a function of pH for the extraction of Zn(II) in nitrate medium by different concentrations of HDOP (HA) dissolved in toluene.

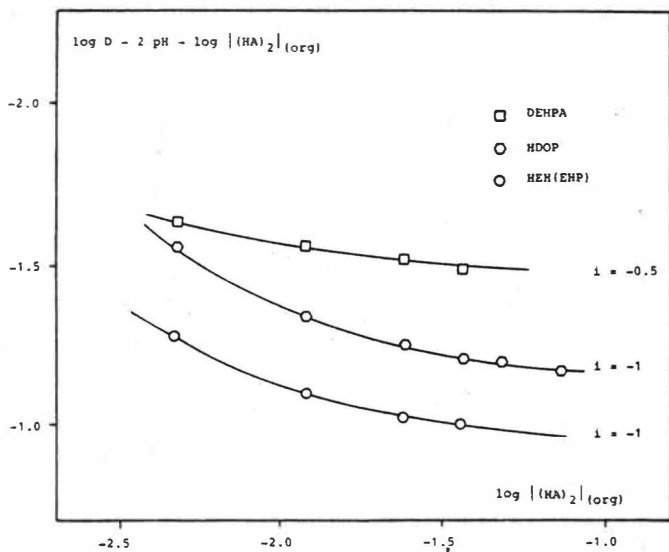


Fig. 5. $\log D - 2 \text{ pH} - 2 \log |(HA)_2|_{(org)}$ plotted as a function of $\log |(HA)_2|_{(org)}$ for the extraction of Zn(II) by different extractants. The full-drawn lines correspond to the theoretical function $\log Y = \log (1 + X^i)$.

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For the modelling of solvent extraction columns, it is necessary to have some models capable to predict the compositions of the equilibrated liquid phases. Liquid-liquid equilibrium data are necessary whether the description of column behaviour is carried out in terms of equilibrium stages, or in terms of the mass transfer concept.

In the last years, calculation models for the prediction of the behaviour of multicomponent mixtures have been proposed, starting from binary equilibrium data.

Different methods have been developed (Wilson, NRTL, UNIQUAC) for the solution of non-electrolyte systems, and other methods based on the "Group-Solution Concept" (ASOG, UNIFAC) for systems containing electrolytes. In this second case, the supporting idea consists in the possibility of taking a solution as a mixture of mutually interacting molecular groups.

According to the principles which form the basis of the proposed methods, the aim of the present work is the research of a mathematical model suitable for the prediction of liquid-liquid equilibrium data in systems in which five components are present, some of which are electrolytes.

In particular, the considered system is composed by water-hydrochloric acid-ferric chloride-tributylphosphate-isocumene. In this system, also complexing reactions occur, and normally this system gives rise to two liquid phases.

In order to study this complex system, equilibrium data obtained from simplified two-liquid-phase systems have been discussed; specifically, data obtained from three-components systems, one of which was water, have been utilized. Part of these data have been taken from the literature, others have been obtained by experimental tests.

The model obtained was used in the modelling of a liquid-liquid solvent extraction pilot plant; in this case, the influence of the temperature is negligible, because such plants usually work at ambient temperature.

The validity of the model proposed was checked by experimental tests.

As the manuscript was not available at the 28th May 1986, the deadline for printing this book, we only print the short abstract of the paper.

Synergism, Antagonism and Selectivity in the LIX63-HDNNS Metal Extraction System

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There have been a number of reports in which the addition of the acidic liquid cation exchanger dinonylnaphthalene sulfonic acid (HDNNS or HD) to chelating reagents has been found to produce synergistic extraction and/or improved kinetics (1-6). Of particular interest is the mixed system consisting of this sulfonic acid and the anti-isomer of 5,8-diethyl-7-hydroxy-6-dodecanone oxime (H_2L , the active extractant in the commercial reagent LIX63, a product of Henkel). The selective extraction of Cu(II), Ni(II), and Co(II) from Fe(III) has been reported (2,3). The synergistic extraction of nickel and cobalt by this sulfonic acid-hydroxyoxime mixture has been attributed to the ability of HDNNS micelles to solubilize both the hydroxyoxime molecules and the metal ions (2,4) and the ability of the oxime to chelate these metals without deprotonating (5). In this paper, new data on the behavior of Fe(III) are compared with the results previously reported for Ni(II) and Co(II).

Experimental

The anti-isomer of 5,8-diethyl-7-hydroxy-6-dodecanone oxime (H_2L) was extracted from commercial LIX63 (Henkel) using the copper oximate method previously described (8). Commercial HDNNS was supplied by King Industries Inc. (Norwalk, CT, U.S.A.) and was purified using methods already available in the literature (4,9). Details of the extraction procedures are given elsewhere (5,7). Hexane was used as the organic phase diluent. The aqueous phase contained Ni(II), Co(II), or Fe(III) nitrate at 5.0×10^{-3} kmol m^{-3} . The ionic strength was controlled with 1.0 kmol m^{-3} KNO_3 .

Results and Discussion

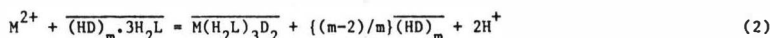
Plots of $\log D$ vs $\log[HD]$ are presented in Figure 1 for Ni(II) and Co(II), and in Figure 2 for Fe(III). It can be seen that for all three metals, in the absence of the oxime, straight lines with slopes close to unity are obtained. On the other hand, as shown in Figure 1, in experiments conducted with aqueous solutions at pH 1, as HDNNS concentration is increased at a constant concentration of H_2L , D_{Ni} and D_{Co} both go through maxima. In the case of D_{Fe} , a maximum is observed for pH 2.5 but not for pH 1. The effect of pH on Fe(III) extraction is further illustrated in Figure 3 which shows that when the pH is less than 1.4, the D_{Fe} of the mixed system is lower than that of the pure system, while when the pH exceeds 1.4 the opposite effect is observed. It is interesting to note that the slope of the $\log D_{Fe}$ vs pH plot is about 2 for the mixed extractant system, whereas it is only about 0.5 for the pure HDNNS system.

The fact that in the pure HDNNS systems all three metals gave $\log D$ vs $\log[HD]$ plots with slopes of about 1 indicates that the active extractant is the micellar HDNNS species (5):



In the mixed extractant system, the organic phase contains a variety of species, i.e., HDNNS and H_2L monomers, pure HDNNS micelles, and mixed HDNNS- H_2L micelles. The molecular interaction of HDNNS and H_2L has been demonstrated by infrared spectroscopy (4). Continuous variation experiments (5) have shown that in the case of Ni(II) and Co(II), the extracted species in the mixed system has the stoichiometry $M/H_2L/HDNNS = 1/3/2$. Thus it has been suggested (5) that the organic phase species responsible for the observed enhanced extraction is an "active" mixed micelle of stoichiometry $(HD)_m \cdot 3H_2L$, and that the peaks in the distribution curves (Figure 1) are attributable to variations in concentration of this active species. Thus the extraction reaction can be written as:

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In Equation 2, the hydroxyoxime is shown as a neutral ligand in view of the previous finding (8) that in acidic solutions H_2L can form complexes without deprotonating.

The results presented in Figures 2 and 3 suggest that Fe(III) extraction follows Equation 2 only when the pH exceeds 1.4. In fact, for pH values less than 1.4, the presence of H_2L leads to antagonistic extraction of Fe. The effect of pH on the synergistic/antagonistic extraction of Fe is attributable to the nature of the aqueous species transferred into the organic phase (7). Between pH 2.0 and 3.5, the predominant Fe(III) species is $Fe(OH)_2^+$ which carries a charge of plus two and is therefore extractable according to Equation 2. This analysis is consistent with the $\log D_{Fe}$ -pH plot for the mixed extractant system (Figure 3) which shows a slope of 2 (instead of the slope of 3 expected for the extraction of Fe^{3+}). On the other hand, the fact that no synergistic extraction of iron occurs below pH 1.4 suggests that the predominant Fe(III) species under these conditions, i.e., Fe^{3+} , forms mixed complexes with difficulty. It is likely that when Fe^{3+} is surrounded by three H_2L molecules, further interaction between the ferric ion and three bulky HDNNS molecules becomes sterically unfavorable. On the other hand, no such steric difficulties are envisaged for the formation of the species $\{Fe(OH)(H_2L)_3D_2\}$ because only two HDNNS molecules are involved.

The mixed complex formed with Ni^{2+} appears to be stronger than the corresponding $Fe(OH)_2^+$ complex. For example, as can be seen in Figure 2, for 10^{-3} molal HDNNS and a fixed H_2L concentration of 0.1 molal, the presence of nickel at pH 2.5 decreases $\log D_{Fe}$ from 2.75 for the nickel-free system to a low value of 0.6. It can be seen from the proposed structures (I and II) that the nickel complex would exhibit a higher stability since it is more completely chelated by the H_2L molecules. In the case of $Ni(H_2L)_3D_2$ (I) all three oxime molecules function as bidentate ligands whereas the presence of the hydroxyl ligand in $Fe(OH)(H_2L)_3D_2$ (II) forces one of the oxime molecules to act as a monodentate ligand.

This mixed LIX63-HDNNS system has been suggested as a selective extractant for Cu^{2+} , Ni^{2+} , and Co^{2+} in the presence of Fe^{3+} (2,3). The strong effect of pH on Fe distribution, as discussed above, is therefore noteworthy. At pH 1.0 the selectivity is very high and follows the nickel or cobalt distribution behavior. However, there is little or no selectivity when the pH is raised to 2.5. This behavior can be attributed to the synergistic extraction of Fe as $Fe(OH)_2^+$ at the higher pH. Thus it is concluded that in order to ensure significant Ni/Fe or Co/Fe selectivity, extraction should be conducted under pH conditions that keep iron as trivalent (Fe^{3+}) rather than as a divalent ($Fe(OH)_2^+$) species.

Acknowledgement

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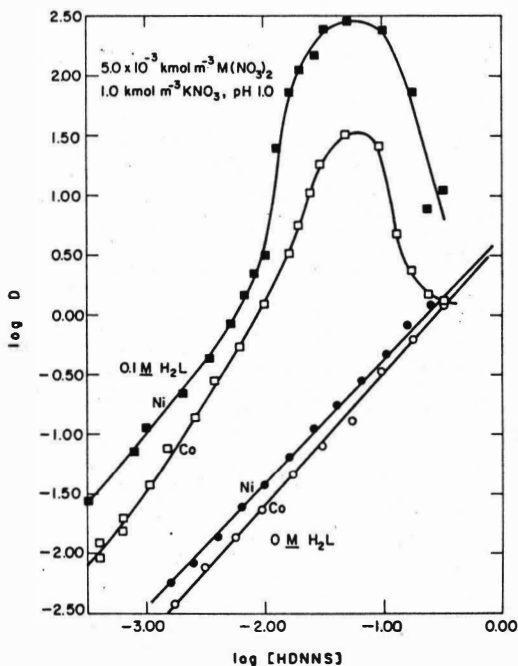
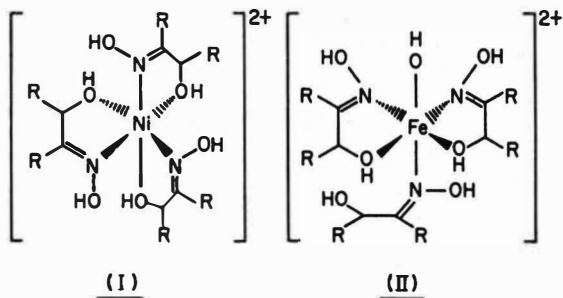


Figure 1. Effect of HDNNS on Ni or Co distribution.



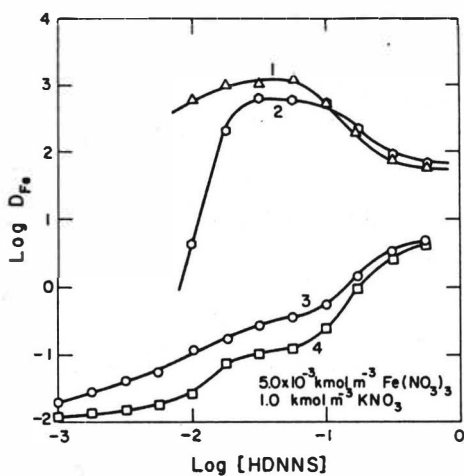


Figure 2. Effect of HDNNS on Fe distribution ($0.1 \text{ kmol m}^{-3} \text{ H}_2\text{L}$):
 (1) pH = 2.5, no Ni; (2) pH = 2.5, $5 \times 10^{-3} \text{ kmol m}^{-3} \text{ Ni}$;
 (3) pH = 1.0, no Ni; (4) pH = 1.0, $5 \times 10^{-3} \text{ kmol m}^{-3} \text{ Ni}$.

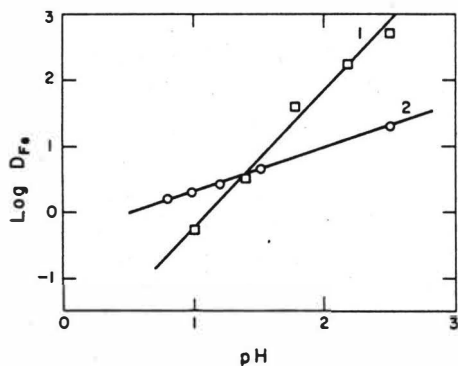


Figure 3. Effect of pH on Fe distribution ($1.0 \text{ kmol m}^{-3} \text{ KNO}_3$):
 (1) $0.1 \text{ kmol m}^{-3} \text{ HD} + 0.1 \text{ kmol m}^{-3} \text{ H}_2\text{L}$, (2) $0.1 \text{ kmol m}^{-3} \text{ HD}$.

Oxidation and Reduction in Metal Chelate Extraction Systems.

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In many liquid-liquid systems, the extraction of metal ions with a chelating extractant proceeds rapidly and the equilibrium is established within a short time except when the rate of complex formation is low. However, it has been found in our laboratory, that the extraction proceeded slowly when oxidation of the metal ions occurred in the organic phase. The present paper describes the extraction of manganese(II) and cobalt(II) as β -diketonate complexes which is controlled by oxidation of the metal ion in the chelate in the organic phase. It also describes that the rate and equilibrium of this oxidation is sometimes quite different when the ligand, solvent, and partial pressure of the oxygen in the gas phase was different.

Experimental.

All the procedures were made at 298K. Solvent extraction experiments were carried out as follows. An aqueous 1 mol/dm³ sodium perchlorate solution containing trace amounts of Mn²⁺ or Co²⁺ was buffered by sodium hydrogen carbonate at pH 8 and it was vigorously agitated with the same volume of a solvent containing a β -diketone (which will be denoted by HA) for a certain time. Experiments were also made in one liquid phase systems. The organic solutions of the complexes was prepared by dissolving the crystals of the complex in the solvent or by extracting the metal ions from an aqueous solution by ordinary solvent extraction procedures. The total amount of the metal ions in the two phases was determined by atomic absorption spectrometry and the amount of the trivalent metal ions in a complex in the organic phase was

determined by spectrometry or by estimation on the basis of the difference in the two-phase distribution behavior of the divalent and trivalent complexes.(1)

1. Oxidation of Manganese(II) β -diketonate complexes.

The results obtained in the early stage of the present study has been published.(2) It was observed that the extraction of manganese(II) in the aqueous phase with acetylacetone(Hacac) into carbon tetrachloride at pH 8 reached one transient equilibrium within a short time by a vigorous two-phase agitation and this was assumed to be the extraction equilibrium of this metal ion as the $Mn^{II}(acac)_2$ complex. However, the distribution ratio gradually increased thereafter and reached another equilibrium after several hours. Figure 1 shows an example in which the pH was 8 and the acetylacetone concentration in the initial organic phase was 0.1 mol/dm^3 . As seen from the figure, the distribution ratio, $D=[Mn]_{ORG}/[Mn]$, increases even after 8 hours. It was also found that the $Mn^{II}(acac)_2$ complex in the organic phase was easily stripped by washing with the same aqueous solution as above and an equilibrium for this backward extraction was established by a vigorous two-phase agitation within a short time, for example, within 3 minutes. However, when the $Mn^{III}(acac)_3$ complex dissolved in the same organic solvent was washed by the same aqueous solution, the distribution ratio decreased very slowly and after several hours, an equilibrium was established which was the same one as that approached by the forward extraction of manganese(II) with acetylacetone after an agitation of the two phases for a long time. By an extrapolation, it was concluded that about one month was necessary to reach the second equilibrium, which should be the final one.

It was also found that such an increase in the extraction by a prolonged two-phase agitation did not occur when the solvent

was polar like as 4-methyl-2-pentanone(MIBK) or when it was a non-polar organic solvent contained an adduct forming ligand such like as trioctylphosphine oxide.

This was explained in terms that the extracted $Mn^{II}(acac)_2$ in the organic phase was oxidized into $Mn^{III}(acac)_3$ by the atmospheric oxygen dissolved in the solvent and this did not occur in the aqueous phase and in the polar or adduct-forming solvents.

Such an oxidation of $Mn^{II}(acac)_2$ in a nonpolar solvent was also observed in the single liquid systems and the results supported the above assumption that the complex is oxidized only in non-polar solvents. The rate of oxidation is much higher in chloroform and benzene than in carbon tetrachloride and the rate was found to be dependent on the ligand concentration and the partial pressure of oxygen in the gas phase.

The oxidation of manganese(II) β -diketonates was also observed when the ligand was benzoylacetone(Hbza) and dibenzoylmethane(Hdbm). Figure 2 gives the extraction curves of manganese initially in the divalent state in the aqueous phase. The data are given by the distribution ratio of the total manganese, $D = ([Mn(II)]_{org} + [Mn(III)]_{org}) / ([Mn(II)] + [Mn(III)])$, as a function of the ligand(β -diketonate anion) concentration in the aqueous phase. As seen from the change in the extraction curves obtained by a two-phase agitation for different times, the distribution ratio at a certain given $[A^-]$ increased very much by a prolonged agitation. This should also be due to an oxidation of the $Mn^{II}(acac)_2$ to the $Mn^{III}(acac)_3$ complex by the oxygen dissolved in the organic phase. However, the rate of oxidation of the complex which were formed by the phenyl substituent of acetylacetone was different; the rate of oxidation of $Mn^{II}(bza)_2$ was similar to that of $Mn^{II}(acac)_2$ but that of $Mn^{II}(dbm)_2$ was much higher. Oxidation of manganese(II) β -diketonate complexes by atmospheric oxygen was also found in the single organic solution

systems. It was found that all of the three manganese(II) β -diketonate complexes were quantitatively oxidized to the corresponding manganese(III) complex when the solution was left standing for a long time. Figure 3 gives the change in the absorbance of the carbon tetrachloride solution of the β -diketonate complexes each in the presence of 0.1 mol/dm^3 of the reagent as a function of the standing time. From Fig. 3, it is seen that the rate of oxidation of the $\text{Mn}^{\text{II}}(\text{dbm})_2$ complex is much higher than that of the $\text{Mn}^{\text{II}}(\text{acac})_2$ and $\text{Mn}^{\text{II}}(\text{bza})_2$ complex. The quantitative oxidation of the $\text{Mn}^{\text{II}}(\text{dbm})_2$ complex was achieved within a few minutes but that for the other two took more than one hour. From these, it can be concluded that the results of the experiments in the one organic solution systems agree with the findings in the solvent extraction experiments though the time necessary to attain the final equilibrium was much longer in the two phase systems.

2. Oxidation of Cobalt(II) β -diketonate complexes.

It is known that cobalt(II) in metal chelate extraction systems containing such reagents as acetylacetone and nitrosonaphthol is oxidized to cobalt(III) under the presence of oxidizing reagent and since cobalt(III) complexes are kinetically inert, they can be separated from those which are co-extracted with them if the organic phase is washed by acid solutions.(3) The separation of cobalt(II) and cobalt(III) in an aqueous solution or in an organic solvent by a liquid-liquid distribution method which utilizes the difference in the kinetic behavior of this metal in these two oxidation states is useful in the study of these metal ions.(1) The present study was carried out mainly by using this method.

It was found that a similar kind of oxidation of cobalt(II) β -diketonate chelates occurred by atmospheric oxygen in non-polar

solvents but the results were different from those obtained with the corresponding manganese(II) chelates. Since the rate of oxidation of the cobalt(II) complexes were much lower than that of the manganese(II) complexes, it was not possible to observe an increase in the distribution ratio in solvent extraction systems with β -diketones in a short time and only experiments in one solvent system were made.

Bis(acetylacetonato)cobalt(II) complex in air-saturated carbon tetrachloride was oxidized to the trivalent state. The rate was dependent on the acetylacetone concentration but not very much on the partial pressure of oxygen in the gas phase. When the concentration was 0.1 mol/dm^3 , the half time was estimated to be about 10 hours. However, when the ligand was benzoylacetone, the oxidation under the identical conditions was negligible; even after 24 hours, the change in the amount of the $\text{Co}^{\text{II}}(\text{bza})_2$ complex was nearly the same to that at initial. Figure 4 shows these results.

These results indicate that the oxidation of manganese(II) and cobalt(II) complexes with acetylacetone and its phenyl substituents occurs only in the nonpolar solvents and it could also occur in the organic phase consists of a non-polar solvent in extraction systems containing these reagents. However, since the rate of oxidation in the solvent extraction systems is not very high, it is possible that only the extraction equilibrium of the divalent metal or an apparent equilibrium of metal extraction in which the metal is in the both oxidation states could be observed and the latter may cause a poor producibility of the results.

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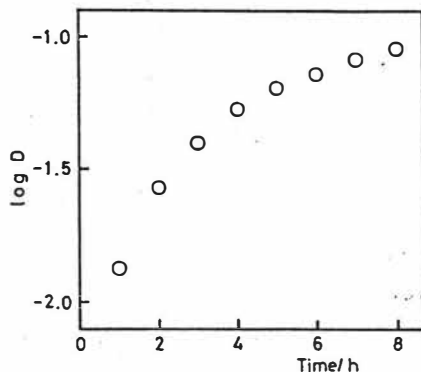


Figure 1. Increase in the distribution ratio of manganese initially in the divalent state in the aqueous phase in solvent extraction system with acetylacetone, as a function of two-phase agitation time. Org.phase: carbon tetrachloride saturated with air and initially containing 0.1 mol/dm^3 acetylacetone. aqueous phase: 1 mol/dm^3 sodium perchlorate solution at pH 8.

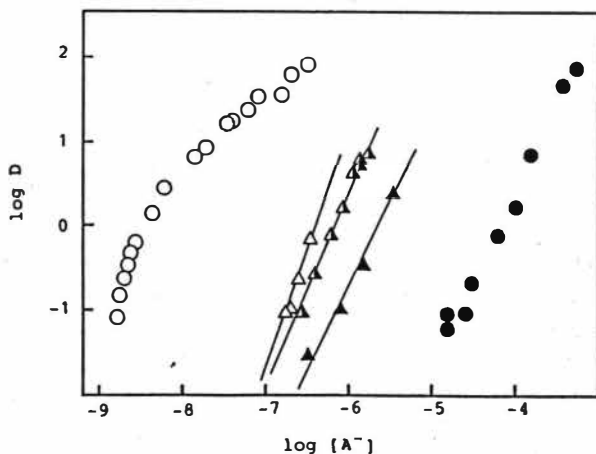


Figure 2. Extraction curves of manganese obtained after agitation for different time. They are given by the distribution ratio as a function of the β -diketonate ion concentration in the aqueous phase. The aqueous phase was 1 mol/dm^3 sodium perchlorate. The solvent was carbon tetrachloride initially containing 0.1 mol/dm^3 of benzoylacetone (circles) or dibenzoylmethane (triangles) and the two phase agitation was made \bullet : for short time and \circ : for 48 hours with benzoylacetone or \blacktriangle : 30 sec., \triangle : 30 min., and Δ : 48 hours with dibenzoylmethane.

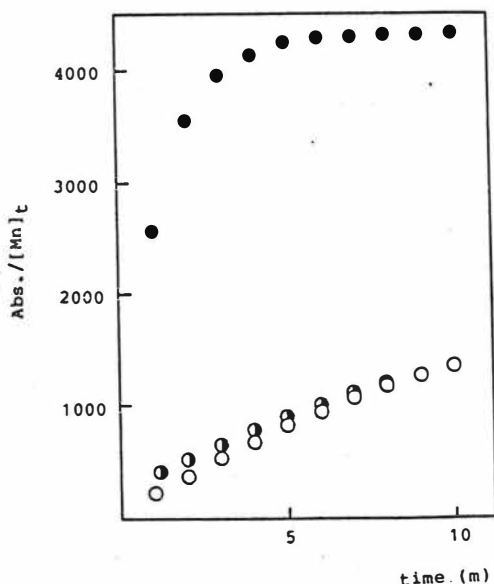


Figure 3. Increase in the absorbance of carbon tetrachloride solution containing manganese β -diketonate in which the metal ions are in the divalent state at initial. Each solution initially contain 0.1 mol/dm^3 of the β -diketonate. The complex is ○:acetylacetonate, ●:benzoylacetonate, and ●:dibenzoylmethanate.

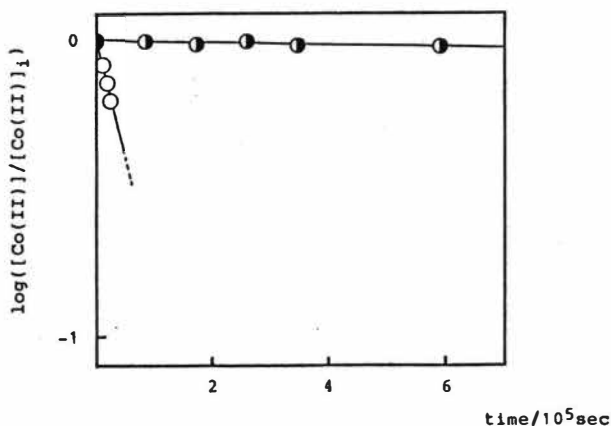


Figure 4. Decrease in the amount of divalent cobalt β -diketonate complex in carbon tetrachloride given as a function of time. Each solution contains 0.1 mol/dm^3 of the β -diketonate.

○: acetylacetonate and ●:benzoylacetonate.

Soluble Losses in the Solvent Extraction of Gold from Alkaline Cyanide Solutions by Modified Amines

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Introduction

The application of solvent extraction for the treatment of alkaline gold cyanide leach solutions could offer several advantages over the Merrill-Crowe and carbon adsorption processes, including faster rates of reaction and greater selectivity (1). Such an application of solvent extraction has received little attention until recently when it was reported that amines modified by certain organophosphorus compounds could selectively extract gold from alkaline cyanide solution (2-4). To be commercially viable, the loss of the organic reagents to the aqueous raffinate must be kept low. In this regard, research was initiated to determine the soluble loss of these reagents and the conditions under which this loss is minimized.

Experimental

Based on previous work, the secondary amine, Adogen 283 (ditridecyl amine), at 0.5 molar in the organic phase, was used as the extractant for all experiments in this investigation. The gold extraction and modifier soluble loss were measured by contacting equal volumes of the organic and the aqueous feed solution (10 ppm gold) under given conditions until equilibrium was achieved. The aqueous phase was then analyzed for gold and phosphorus content using a DCP plasma spectrometer.

Organophosphorus Modifiers

Figure 1 shows that the effective extraction of gold from alkaline cyanide solutions with 0.5 M amine is possible with the addition of organophosphorus modifiers. As the polarity of the modifier is increased, the basicity of the extractant increases; that is, the percent extraction-vs.-pH curve is shifted to higher pH values (4). It has been established that the polarity of the modifiers increases in the order: trialkyl phosphate < dialkyl alkyl phosphonate < alkyl dialkyl phosphinate < trialkyl phosphine oxide. Thus, only 10% trioctyl phosphine oxide (TOPO) is as effective as 25% dibutyl butyl phosphonate (DBBP) or 50% tributyl phosphate (TBP). The polarity of the modifier also affects its solubility in the aqueous phase, as shown in Figure 2. For modifiers with constant n-alkyl chain length, such as TBP and DBBP, the increase in polarity results in an increase in solubility. TOPO has a lower solubility than either TBP or DBBP because of the greater hydrophobicity of the longer n-octyl chains attached to the molecule. Thus, two major factors affecting modifier solubility can be seen to be the polarity of the molecule and the length of the n-alkyl chains of the molecule, that is, its hydrophobicity. These effects have also been reported in the literature for other organophosphorus compounds (5). In any case, note that even TOPO, the least soluble of the commercially available modifiers, has a soluble loss of over 100 ppm at pH 9 to 10, the desired range of extraction. Such a condition would

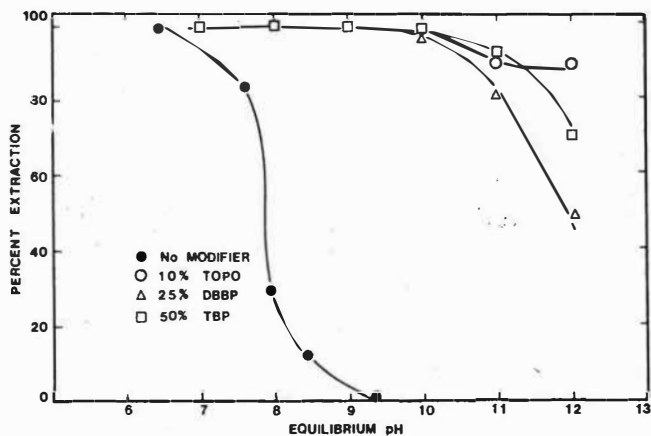


Figure 1. The effect of modifier type on the extraction of gold from cyanide solution. Organic: 0.5 M secondary amine (Adogen 283) plus modifier in Chevron IX solvent.

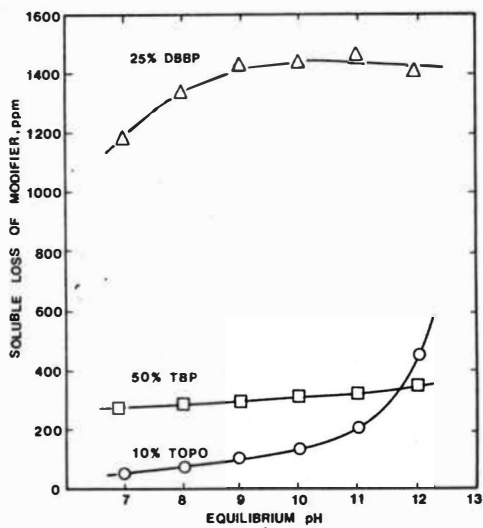


Figure 2. The effect of modifier type on the soluble loss to the aqueous phase. Organic: 0.5 M secondary amine (Adogen 283) plus modifier in Chevron IX solvent.

be unacceptable from the standpoint of process economics for cyanide solutions containing low concentrations of gold. Obviously, if the process is to be commercialized, a modifier with a much lower soluble loss must be found.

Trialkyl Phosphates

The members of the trialkyl phosphate family should have lower solubilities than the more polar phosphonates or phosphine oxides, so the solubilities of several such molecules were measured as a function of pH and alkyl chain length and structure. Figure 3 shows the results. The lowest solubility is shown by tri-n-octyl phosphate (TOP), at less than 20 ppm for pH 9 to 10. Interestingly, the experimental results show a greater solubility for tri-n-hexyl phosphate (THP) than for TBP, even though the longer hexyl groups are expected to reduce the soluble loss by promoting its hydrophobicity. The soluble loss of tri-sec-butyl phosphate (TSBP), as much as 130 gpl, is truly staggering. Although branching has been known to increase solubility in many circumstances, a soluble loss of this magnitude seems unreasonable. These results are probably due to hydrolysis of the phosphate in alkaline solution; the resultant dialkyl phosphoric acid is much more water soluble and would account for the high losses shown in Figure 3. The extraction characteristics for these trialkyl phosphates are shown in Figure 4. For equimolar additions, the extraction is roughly equivalent. There is a slight trend toward decreased extraction with an increase in alkyl chain length and branching, probably due to steric effects.

Tri-n-octyl Phosphate

In view of the low solubility of TOP in the aqueous phase, less than 20 ppm, the use of TOP might be preferred to the use of other organophosphorus compounds as modifiers provided its extraction characteristics are acceptable. Such seems to be the case as shown in Figure 5. First, the basicity of the secondary amine (0.5 M) can be systematically controlled by appropriate additions of TOP, the pH_{50} shifting from 7.9 in the absence of TOP to almost 11.0 at 75% TOP, in which case there is no kerosene diluent present. Second, it is evident from Figure 5 that good stripping can be achieved for the TOP system with the extent of extraction close to zero at pH 12 and above. It should be noted that the maximum TOP addition is about 75%, since 0.5 M Adogen 283 corresponds to about 25% of the solution volume. Therefore, at 75% TOP, the modifier might more aptly be termed a diluent rather than a modifier. The ΔpH_{50} for 0.5 M amine in pure TOP is thus the maximum ΔpH_{50} that can be attained in the TOP modified amine system. This maximum ΔpH_{50} of 3.1 units is smaller than the maximum ΔpH_{50} found for the TBP modifier, but it must be remembered that the molecular weight of TOP is much greater than TBP. A solution of 0.5 M amine in pure TOP is only 1.62 M TOP, whereas 1.62 M TBP corresponds to about 45% TBP. The ΔpH_{50} for 45% TBP is roughly 3.1 pH units for 0.05 M amine in hexane (6), so on an equimolar basis it is evident that TOP is as effective a modifier as TBP.

As mentioned previously, TOP is the least water-soluble organophosphorus modifier studied, as demonstrated in Figure 6. Below pH 9, the loss of TOP to the raffinate would

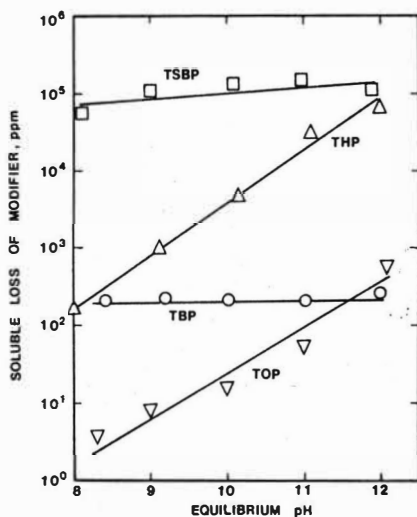


Figure 3. The effect of alkyl phosphate chain length and structure on soluble loss. Organic: 0.5 M secondary amine (Adogen 283) plus 1.5 M modifier in kerosene.

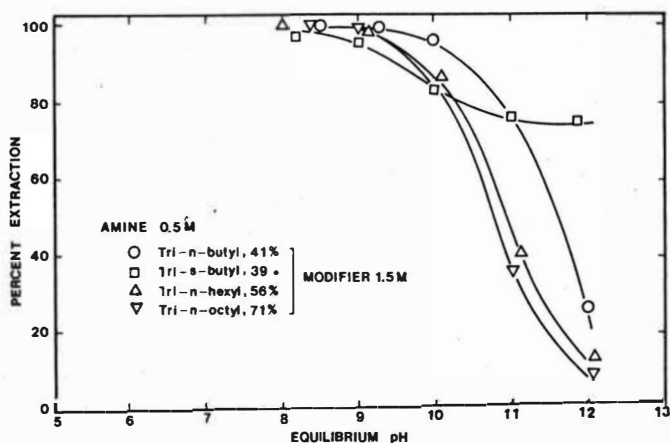


Figure 4. The effect of alkyl phosphate chain length and structure on the extraction of gold from cyanide solution. Organic: 0.5 M secondary amine (Adogen 283) plus 1.5 M modifier in kerosene.

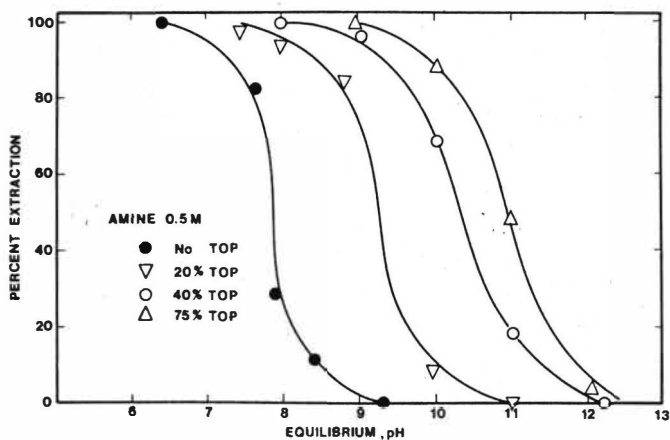


Figure 5. The effect of TOP concentration on the extraction of gold from cyanide solution. Organic: 0.5 M secondary amine (Adogen 283) plus TOP in kerosene.

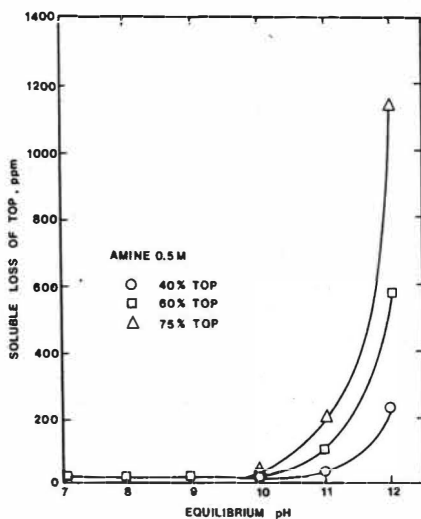


Figure 6. The effect of TOP concentration on the soluble loss to the aqueous phase. Organic: 0.5 M secondary amine (Adogen 283) plus TOP in kerosene.

be less than 15 ppm. At higher pH values, the soluble loss of TOP is seen to be very pH dependent, increasing dramatically above pH 10; this may be due to alkaline hydrolysis of the molecule. However, note that even with 0.5 M amine in pure TOP the soluble loss of TOP is less than 50 ppm at pH 10. Since the gold extraction step would be carried out at pH 10 or below, a target level of 50 ppm soluble loss could be met with the TOP modifier. Although the soluble loss at pH 12 is much higher, stripping solution flowrates would be orders of magnitude smaller than extraction flowrates, so the higher aqueous TOP distribution under these conditions would not be so critical.

Other factors influencing the soluble loss of the tri-n-octyl phosphate modifier are the concentration of modifier in the organic phase and the ionic strength of the aqueous phase. The first effect is shown in Figure 6 and is significant above pH 10. The effect of ionic strength is given in Table 1. As the ionic strength is increased, soluble loss decreases, due to the salting-out effect. This effect has also been observed for TBP with a variety of monovalent salts (7). From a practical standpoint, the salting effect is of little value in the treatment of dilute leach solutions, since these solutions generally are at low ionic strength, and it would be very costly to add salt to such dilute solutions. However, in the treatment of higher-grade solutions, such as spent cyanide electroplating wastes or carbon eluates, the salting phenomenon would be present and has been found to be significant in solvation extraction (8).

Table 1. The Effect of Ionic Strength (Na_2SO_4) on the Soluble Loss of TOP at pH 13

Organic: 0.5 M Amine in TOP (25% Amine/75% TOP)

Ionic Strength (M)	Soluble Loss of TOP (ppm)
0	1200
3.0	142
6.0	58
12.0	28

The effect of amine concentration in the organic phase was studied, and, as can be seen in Figure 7, a five-fold increase in amine concentration, from 0.1 to 0.5 M, at 40% TOP resulted in a shift in pH_{50} from 8.75 to 10.30, for a ΔpH_{50} of 1.55 units. Further, an increase in amine concentration was found to decrease soluble losses of TOP to the aqueous phase, as shown in Figure 8. These results suggest some type of interaction between amine and modifier, which decreases the activity of the free modifier, thus resulting in a lower loss to the aqueous phase. Such a phenomenon may also be related to amine basicity, and research in this area continues.

Engineering Significance

For commercial treatment of alkaline gold cyanide solutions, it seems that an organic phase with 0.5 molar amine and 50% TOP in a kerosene diluent would be suitable. This combination shows good extraction of gold from pH 9 to 10 with a soluble loss of less

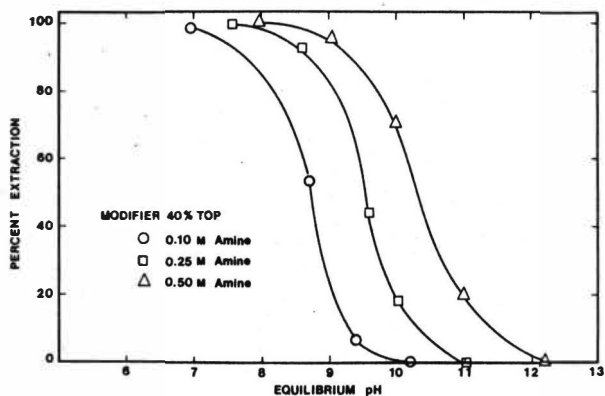


Figure 7. The effect of amine concentration on the extraction of gold from cyanide solution. Organic: secondary amine (Adogen 283) plus 40% TOP in kerosene.

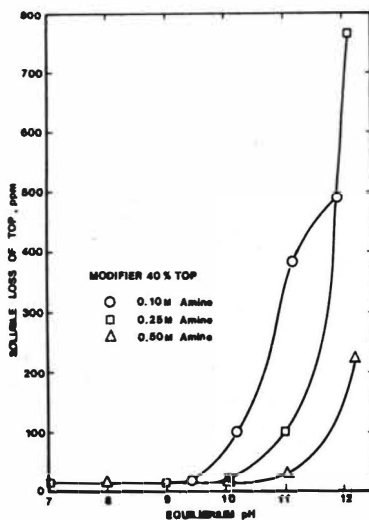


Figure 8. The effect of amine concentration on the soluble loss of TOP to the aqueous phase. Organic: secondary amine (Adogen 283) plus 40% TOP in kerosene.

than 20 ppm. The soluble loss of the amine was also measured under these conditions and found to be less than 10 ppm. A conservative, make-up solvent cost analysis based on experimentally measured losses -- soluble (30 ppm) and entrained (30 ppm) -- for the amine/TOP system suggests an operating cost of less than \$0.70 per 1000 gallons of solution treated for a conventional mixer/settler circuit (9).

The reaction kinetics appear to be rather rapid, and it is anticipated that only modest mixing will be required to achieve a satisfactory extraction rate, a situation which should lower solvent loss by entrainment. An even further reduction in solvent loss might be expected for solvent-impregnated resins including polymerized solvent networks, the use of which, for the recovery of gold from heap and agitation leach solutions, will be discussed in another publication (10).

Acknowledgements

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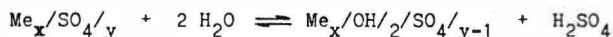
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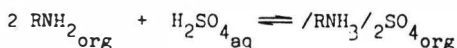
Extraction studies of some metal sulphates $/Al^{3+}, Fe^{3+}, UO_2^{2+}, Zr^{4+}/$ by benzene solutions of primary amine PRIMENE JMT have been carried out from "neutral" solutions.

On the ground of the results of chemical analysis and IR spectra of the organic phase is supposed that the extraction of metal sulphates from "neutral" aqueous solutions by Primene JMT is realized in the simplest case according to the following schemes

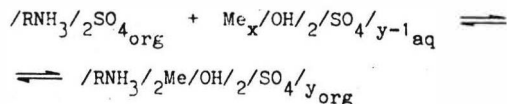
a/ At low aqueous acidity the hydrolysis of $Me_x/SO_4/y$ occurs



b/ Free amine reacts with sulphuric acid



c/ By the reaction between primary amine sulphate and the species $Me_x/OH/2/SO_4/y-1$ from the aqueous phase the adduct in the organic phase forms



Some problems of solvent extraction thermodynamics

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The most complicated problem of extraction thermodynamics is the correct description of equilibrium in systems with non-ideal organic phase. Now the activity coefficients of extractants and extracted compounds in the organic phase of the most of systems cannot be directly determined and should be calculated from the activities of other components. The cross-differentiation relations are used for this task in multicomponent solutions. Usually the deduced equations are simple enough, include one or two parameters and are fit for computer calculations.

In systems where water concentration is a linear function of extractant concentration and water activity the equations with one constant called a hydration parameter can be used to calculate activities of extractant and other components.

The equations with two solvation parameters have been deduced to describe the effect of alcohols on extraction of metals with amines. The mutual influence of hydration and solvation with alcohols on extraction equilibrium is analysed.

In order to calculate solute activities from solvent ones in multicomponent solutions the special method has been developed.

As the manuscript was not available at the 28th May 1986, the deadline for printing this book, we only print the short abstract of the paper.

Electron Density Distribution in Organic Compounds and their Efficiency as Extraction Agents

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The searching for any correlation between organic compounds structure and their extraction capacity (EC) is one of the most important problems in the metal extraction theory and, as such, it is stated in some form or solved at some level throughout the history of this branch of knowledge. This problem can be considered as the part of the general organic chemistry theory which already comprises such a notion as the molecular engineering (1). The perspective studies are now under way in the pharmaceutical chemistry; it is this field of science where the term "ligand planning" had first appeared.

There exist two essentially different methodological approaches to this problem. The first one is based on developing the physically substantiated model. The second approach uses the formalism which allows to process the experimental data accumulated. The present work falls in the first direction. And we proceed here from the following statement of principal importance. The choice of the optimal structure of an agent should be started from finding the complex of extracted metal which has optimal composition. In this case the problem of choice of an extraction agent (EA) is reduced to the choice of the optimal ligand of a complex. The complex with optimal electronic structure is supposed to have completely occupied bounding molecular and atomic orbitals (MO and AO) of a valent shell of the central atom (c.a.). Besides, the electronic structure of an extracted compound should be such that the vacant AO and MO have high energy, i.e. that some energy slit between the high occupied and the low unoccupied molecular orbitals (HOMO and LUMO) should exist. It was supposed that such complexes should be characterized by the correspondence between the electronegativity of a valent state of c.a. (χ_{VC}) and the total electronegativity of donor atoms of the extraction agent ($\sum \chi_{DA}$) (2).

Various types of extraction agents are used for extraction of metals, that leads to formation and extraction of various types of compounds. As examples in the given paper are mainly considered the

complexes of metals which are formed in extraction systems containing helating bidentant agents (HA) and electrodonor mono- and poly-dentant bases (B) with P, S or O-donor atoms. In extraction systems with arbitrary set of HA and B agents one could expect the formation of the following complexes: coordinatively saturated neutral complexes MA_n and coordinatively unsaturated hydrated complexes $MA_n(H_2O)_m$, complexes with the mixed coordination sphere MA_nB_m and MX_nB_m (X-acidoligand); anion complexes of $MA_n^{(q-n)-}$ and $MA_nB_m^{(q-n)-}$ composition, cation complexes $MA_p^{(n-p)+}$ and MB_m^{n+} . The charged complexes are extracted in the presence of hydrophobic anions or cations, respectively, in the form of triple complexes of ion associates type.

The separation coefficient of M_i and M_j metals in the extraction systems with HA, $S_{i,j}$ is described by the equation:

$$S_{i,j} = \frac{K_{ex, M_iA}}{K_{ex, M_jA}} = \frac{\beta_{M_iA} \cdot P_{M_iA}}{\beta_{M_jA} \cdot P_{M_jA}} \quad (1)$$

The extraction of the other types of complexes is expressed by similar equations. Hence, the selectivity of an extraction system is defined by the ratio of stability and partition constants provided, however, that the extracted complexes have a composition of the same type.

The stability constant of a complex is an integral quantity which reflects the sum of free energies of processes associated both with rupture and formation of chemical bonds and with the solvation effects of different nature for all components of a complex formation reaction.

Since it's difficult to take into account theoretically all energy contributions when the complex formation energy is calculated, a great number of various approximate schemes have been developed so far, which allow to estimate more or less reliably the constants or the succession of constants for one-type reactions (3,4). The approaches developed within the framework of perturbation theory (5) seem to be the most successive ones. To calculate the complex formation energy we have used the approximation which supposes that the energy of c.a.-agent interaction (ΔE) can be represented as a sum

$$\Delta E = E_{es} + E_{pol} + E_{exc} + E_{ct} + E_d \quad (2)$$

Here E_{es} is the electrostatic energy of interaction between non-dis-

turbed multielectronic systems, E_{pol} is their mutual polarization energy, E_{exc} is the component caused by electron exchange between complex components, E_{ct} is the charge transfer energy which corresponds to the interaction between the electrons of one component and the vacant orbitals of the other one and vice versa, E_d is the energy of dispersion interaction between the systems. One should emphasize that the above scheme is valid when the geometry of agents varies only slightly. In opposite cases the decomposition of interaction energy should include also the energy of corresponding geometric variations.

When c.a. represents the cation of an alkali metal, the main contribution into ΔE is made by its electrostatic and polarization components (6). The electrostatic component may be obtained from the distribution of molecular electrostatic potential (MEP) of a ligand (7) and the polarization one - by using the experimental values of bond polarizabilities (8). MEP are calculated from the data of quantum-chemical calculations (for molecules) (9) or from the diffraction data (for crystals) (10); the latter method allows to take into account the peculiarities of electronic structure of a ligand in the solid phase.

Within the framework of the above approach the distribution of the sum of electrostatic and polarization components can be considered to be an analogue of the true surface of potential energy which reflects the features of the cation ligand interaction. In the case where c.a. are the cations of transition and post-transition metals, the Klopman approximation of expression (2) is widely used (11), where E_{es} is calculated in the point charge approximation, E_{ct} - by using the characteristics of HOMO of the donor and LUMO of the acceptor of electrons; the other terms in eq. (2) are neglected. The Klopman equation suggests that the character of interaction is mainly determined by the difference between energies of HOMO of the donor (E_D) and LUMO of the acceptor (E_A); if this difference is great, the interaction is primarily electrostatic one, if it is small, the situation is opposite. Thus, the $E_D - E_A$ difference determines the character of donor-acceptor interaction of a pair of donor-acceptor agents.

Using some simplifying approximations, Klopman has calculated the parameters characterizing metals. It was found that the stability constants and the coordinative saturation of MA_n complexes of some metals containing soft helating agents with sulphur donor atoms

correlate with Klopman's parameters; the similar dependence is also valid for extraction constants (12).

Therefore, the complex formation energy for model systems can be now estimated to a sufficiently good precision. In practice, however, it remains still much to be done in order that a priori calculations of any metal-ligand combination would actually allow not only to place ligands in the order corresponding to complex formation energy, but would provide some numerical characteristics as well. One of the difficulties lies here in the fact that in the general case the ratio of electrostatic and covalent contributions into the complex formation energy varies monotonously. An account should also be taken of the fact that the increase of electron density on donor atoms of functional groups of agents leads to the change in composition of extracted complexes of metals. As a result, the compositions of complexes of metals M_1 and M_j under comparison are different and eq. (1) becomes unacceptable.

For the case of coordinatively saturated complexes, not coordinatively interacting with water, the distribution between the phases is primarily determined by the energy of formation of a cavity in the water structure (E_{cav}) which can be expressed by eq. (3):

$$E_{cav} = \gamma \cdot S \quad (3)$$

where γ denotes the surface tension of a solvent and S is the surface of a cavity. Hence, E_{cav} is dependent on the volume of an extracted complex. The energy of non-specific interaction is defined by intermolecular contacts, i.e. again by the volume of a molecule in the first approximation. A number of approaches (13-16) has been developed for estimating the distribution of such a type of compounds in twophase systems and, what is essential, the extraction of such different complexes as, for example, $GeCl_4$ and chromium tri-(acetylacetonate) (III) are equally well described within the framework of the Hildebrand's theory of regular solutions (13).

It follows from the above considerations that the stability and the partition constant of an extracted complex is determined by the initial electronegativities of c.a. and donor atoms of EA as well as by the re-distribution of electron density in an extracted complex. Moreover, the stoichiometry and the charge of a complex are dependent on the electron density distribution in a metal complex.

At present there are many examples of extraction systems in which the variation of compound structure due to the electron density

change on the atoms in functional groups can be observed, so that one may consider this phenomenon as a common fact. Moreover, the analysis shows that the correspondence between χ_{VS} and $\sum \chi_{DA}$ may be contemplated. One should emphasize here that the limits of variation of effective charges within the framework of one VS are specific for any VS and are determined by the electronic structure of an element.

The complex formation leads to changing both electronic and geometric structure of an agent. The energy required for changing the structure in the EA-ligand transition is generally determined by the correspondence between the agent structure and the electronic and stoichiometric structures of the given VS of DA. The energy of conformation transitions for molecules of complicated extragents may be significant and comparable with the total complex formation energy (17).

Approaches to construction of group and selective extraction agents should be different. The first ones must possess, apparently, rather mobile electronic or geometric structure. For relatively simple structures the ability of complex formation with a variety of metals is stipulated by electron mobility. Moreover, the ligands in complexes of various metals must exist actually in the form of various tautomers. The analysis of the data on extraction of complexes formed by nitrosohydroxylamines (18) confirms this point of view.

The selective extraction agents, on the opposite, must possess a rather rigid electronic and stereochemical structure, on one hand, and the structure maximally satisfying the requirements of a single VS of one c.a. only - on the other. To solve this far more complicated problem it is necessary to take into account simultaneously both electronic and stereochemical requirements. In this case the organic compound which, while interacting with the given VS of c.a., forms a coordinatively saturated complex characterized by the presence of a rather wide energy slit between LUMO and HOMO, can be considered to be optimal with respect to EA structure. The value of a slit can be calculated by using the methods discussed above or on the basis of the Phillips dielectric theory (19). Thus, the most correct beginning of the agent construction process is the construction of a complex possessing specified properties (structure, stability and coordinative saturation). The sought EA should become the ligand of a complex.

The problem stated may be represented as the succession of smaller problems of choosing VS of c.a. and the set of donor atoms satisfying the VS requirement as well as the problems of construction of a ligand, choice of the EA structure, searching for the rational system of synthesis. The choice of VS of c.a. and donor atoms is mainly based on the hypothesis of some correspondence between χ_{VS} of o.a. and $\sum \chi_{DA}$ is supposed to be stable within some limits of effective charge on the c.a. frame and is determined, in its turn, by the type of AO of a valent shell, by their hybridization, i.e. by the coefficients at AO in MO of VS of c.a. The VS chosen in such a way determined by itself the optimum polyedron of a coordination sphere with donor atoms distributed over the sphere surface, their nature and VS. The distribution of donor atoms over the coordination sphere surface determines, in its turn, the optimum cavity of EA and becomes the initial one in choosing the structure or structures of ligands. Having determined the structure of ligands, one may proceed to construction of the structure of EA with the view that the electronic and geometric structure of EA may considerably differ from the ligand structure. Some parts of the EA construction program compiled in the above manner represent by themselves rather large and complicated problems.

Therefore, a priori construction of EA supposes the choice of the "best" structures from the variety of alternative ones, which requires, in its turn, the choice of quantitative parameters, characterizing the notions "better - worse", and the optimization of the objective function with respect to a set of parameters of various physical nature. The problems of such a type are typical problems of systems analysis (20).

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Modelling of Equilibrium Data for the Solvent Extraction of Copper from Multicomponent Aqueous Solution of Weak Electrolytes by Hydroxyoximes

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Abstract

The chemical model for the copper/LIX 64N system has been developed on the basis of knowledge of the extraction chemistry. The model is thermodynamically rigorous as the activity data are employed. The presence of a few undissociated species in the aqueous solution is taken into account. The solution of a set of mass balances, dissociation equilibria and activity coefficients equations gives values of the copper cations and hydrogen cations activities in the aqueous phase. In the organic phase the extractant aggregation and formation of the inert oxime-diluent complex have been examined for obtaining the most suitable form of the extractant mass balance. The aggregation and the thermodynamic extraction constants are the parameters of the model, which should be determined on the basis of experimental data for the solvent extraction equilibria. The thermodynamical description of the phase equilibria in the solvent extraction systems covers a wide range of concentrations and makes it possible to predict equilibrium composition in the system containing a few extracted metals.

Introduction

The determination and description of equilibrium data for the solvent extraction of metal ions or salts by organic extractants is a beginning of the design of hydrometallurgical processes. Equilibrium data are frequently reported graphically or as a mathematical model. The distribution ratio of a metal between organic and aqueous phases is often represented graphically as a function of the hydrogen cation concentration ($\log D$ vs. pH , [1]). Although such informations are readable, data presented in this way are incomplete in more detailed calculations.

Some workers [2] have presented equilibrium data by means of reaction equilibrium constants, but the experimental range was usually limited to the dilute solutions, where deviations from ideality could be neglected. Another way of analytical description of phase equilibria is use of regression method for correlating experimental data over a broad range of conditions [3]. Such completely empirical

polynomials can be convenient and useful for calculations in a specified system studied, but the obtained parameters have no obvious physical significance and do not allow direct extrapolation to extreme conditions or to solutions modified by additional components.

In this paper, the experimental equilibrium data are described on the ground of thermodynamical analysis of metal extraction process. The model is illustrated by data for the solvent extraction of copper by LIX 64N [4].

Activity Coefficients in Weak Electrolyte Solutions

The precise description of nonideal aqueous solution of electrolytes is the ground for the modelling of equilibrium between a concentrated aqueous solution and an organic immiscible solution of an extractant. Strong electrolyte interactions cannot be described by means of chemical equations. Their contribution to chemical potential should be taken into account by means of activity coefficients.

In many aqueous electrolyte systems of hydrometallurgical interest, not only strong electrolytes but also weak ones are present. In the rigorous thermodynamic description of weak electrolyte solutions a presence of a few undissociated species has to be taken into account. For instance, in the solvent extraction of copper, the sulfuric acid and copper sulfate are weak electrolytes. Two partially dissociated solutes, HSO_4^- and CuSO_4 , dissociate according to the following equations:



To calculate the composition of real weak electrolyte solution one has to solve the set of dissociation equilibrium equations:

$$m_{\text{HSO}_4^-} = m_{\text{H}^+} m_{\text{SO}_4^{2-}} \gamma_{\text{H}^+, \text{SO}_4^{2-}}^3 / (\gamma_{\text{H}^+, \text{HSO}_4^-}^2 K_1), \quad (3)$$

$$m_{\text{CuSO}_4} = m_{\text{Cu}^{2+}} m_{\text{SO}_4^{2-}} \gamma_{\text{Cu}^{2+}, \text{SO}_4^{2-}}^2 / (\gamma_{\text{CuSO}_4} K_2), \quad (4)$$

mass balances:

$$2 m_{(\text{H}_2\text{SO}_4)} = m_{\text{H}^+} + m_{\text{HSO}_4^-}, \quad (5)$$

$$m_{(\text{CuSO}_4)} = m_{\text{Cu}^{2+}} + m_{\text{CuSO}_4}, \quad (6)$$

$$m_{(\text{H}_2\text{SO}_4)} + m_{(\text{CuSO}_4)} = m_{\text{SO}_4^{2-}} + m_{\text{HSO}_4^-} + m_{\text{CuSO}_4} \quad (7)$$

and activity coefficient correlations:

$$\ln \gamma_{MX} = (\ln \gamma_{MX})_{i=1} + \nu_M / \nu \sum_m D_{MXm} m_m, \quad (8)$$

$$\ln \gamma_m = \sum_c D_{cXm} m_o + \sum_a \Omega_{aXm} m_a + 2 \sum_n \lambda_{mn} m_n. \quad (9)$$

K_1 and K_2 are dissociation constants of HSO_4^- and CuSO_4 , respectively. The parentheses in subscripts refer to apparent molality. γ_{MX} and γ_m are the activity coefficients of $M_{\nu_M} X_{\nu_X}$ electrolyte and molecular solute m (e.g. undissociated CuSO_4). The first term in Eq.(8) corresponds to the ion-ion interactions [5, 6], the second - to the ion-molecule ones.

In order to describe the presence of undissociated molecules, the Pitzer basic equation for strong electrolytes [5] has been modified by introducing a set of new interaction parameters [6]. The thermodynamic model for both ionic and molecular solutes in aqueous electrolyte systems includes therefore binary and ternary ion-ion interaction and difference parameters (β^0 , β^1 , C , θ and γ [5]), second and third virial coefficients for neutral-neutral interactions (λ , μ), and the observable binary salt-molecule interaction (D) and difference (Ω) parameters for ion-neutral interactions [6]. D_{MXm} represents the interactions between salt MX and molecular solute m . Ω_{aXm} represents the differences between the interactions of molecular solute m with two unlike salts sharing one common cation. The model is designed to predict the composition and the activity coefficients in aqueous weak or strong electrolyte solutions, including mixtures with any number of solutes. With this model, activity data for the aqueous solutions of sulfuric acid and copper sulfate have been correlated. The results show better agreement between experimental data and the correlations than in the instance of the treatment of bivalent metal sulfates as strong electrolytes [6].

Thermodynamic Analysis of Metal Extraction

For extraction of ions of a bivalent metal (e.g. copper) by a chelating extractant HR , the basic equilibrium equation is



where HR represents the active β -hydroxyoxime in LIX 64N and CuR_2 is the copper chelate in the organic phase. Taking into account the nonideality in the aqueous phase and putting it aside in the organic phase, the equilibrium constant K can be expressed as follows

$$K = C_{\text{CuR}_2} / (C_{\text{HR}}^2 a), \quad (11)$$

$$\text{where } a = \frac{a_{\text{Cu}^{2+}}}{a_{\text{H}^+}^2} = \frac{m_{\text{Cu}^{2+}} \gamma_{\text{Cu}^{2+}}^2}{m_{\text{H}^+}^2 \gamma_{\text{H}^+}^2} \frac{\gamma_{\text{SO}_4^{2-}}^2}{\gamma_{\text{H}^+}^3 \gamma_{\text{SO}_4^{2-}}}. \quad (12)$$

Mean activity coefficients of electrolytes in the aqueous solution are calculated according to the modified Pitzer's model, described above. Assuming that the extractant is monomer in the organic phase, its mass balance takes the form

$$C_{RG} = C_{HR} + 2 C_{CuR_2} \quad (13)$$

where the C_{RG} is the total concentration of active oxime in the organic phase. It is conserved throughout the extraction process. Combining the equilibrium equation (11) with the mass balance (13) one obtains the relation

$$C_{CuR_2} = 0.5 C_{RG} - \frac{1}{2\sqrt{K}} \sqrt{C_{CuR_2} / a} \quad (14)$$

This is the equation of straight line with the slope $1/(2\sqrt{K})$ and the ordinate intercept $0.5 C_{RG}$. It is shown in Fig. 1. Using the method of least squares, the unknown values of C_{RG} (the total concentration of active oxime in the solution of technical LIX 64N in an organic diluent) and K (the equilibrium constant of the reaction (10)) can be obtained. At higher LIX concentrations, one can notice (Fig. 1) significant deviations from the expected straight line according to Eq. (14). So one can draw the conclusion that the concentration of active oxime is smaller than the concentration of unbound LIX. This can be caused by formation of oxime complexes, which do not extract copper ions. When the activity coefficients in the aqueous phase are neglected, the deviations from the expected straight line are visible at the lower LIX concentrations (dashed line in Fig. 1). The total concentration of active oxime obtained from the ordinate intercept ($C_{RG} = 0.179 \text{ mol/dm}^3$ in 20% vol. LIX 64N) is found to be identical with value obtained according to "ultimate loading" method [4]. If the extractant dimerization and formation of oxime-diluent complexes are taking into account, two additional equilibrium equations should be considered:

$$2 HR = (HR)_2 \quad \text{with } K_d = C_{(HR)_2} / C_{HR}^2 \quad (15)$$

for dimerization, and

$$HR + n DIL = HR(DIL)_n \quad (16)$$

$$\text{with } \Phi = K_s C_{DIL}^n = C_{HR(DIL)_n} / C_{HR} \quad (17)$$

for oxime (HR) - diluent (DIL) complex [7]. Thus, the extractant mass balance takes the form:

$$C_{RG} = C_{HR} + 2 C_{CuR_2} + 2 K_d C_{HR}^2 + \Phi C_{HR} \quad (18)$$

Assuming, that metal can be extracted only by free monomer HR, from Eq. (11) and Eq. (18) it follows:

$$\left(\frac{1}{C_{CuR_2}} - \frac{2}{C_{RG}} \right) a = \frac{2 K_d}{K C_{RG}} + \frac{1 + \Phi}{C_{RG} \sqrt{K}} \sqrt{\frac{a}{C_{CuR_2}}} \quad (19)$$

Fig. 2 illustrates Eq. (19) applied to experimental data of various LIX concentrations. From Fig.2 it follows that the reaction (15) can be neglected ($K_d \approx 0$) and Eq.(19) can be transformed to the form:

$$\frac{1}{C_{CuR_2}} = \frac{2}{C_{RG}} + \frac{1 + \Phi}{C_{RG} \sqrt{K}} \frac{1}{\sqrt{(C_{CuR_2} a)}} \quad (20)$$

Eq.(20) represents the set of straight lines with different slopes and ordinate intercepts, depended on LIX concentration (Fig.3).

From Fig.3 it follows, that the term $(1 + \Phi)/\sqrt{K}$ is depended on LIX concentration. It is a linear function of C_{RG} (Fig.4). Therefore, interactions between oxime and diluent may be described by coefficient φ , defined by equation

$$\Phi = \varphi C_{RG} \quad (21)$$

where φ is concentration independent and is constant for specified extractant-diluent system. Then the dependence presented in Fig.4 can be expressed by the linear relation

$$\frac{1 + \varphi C_{RG}}{\sqrt{K}} = \alpha C_{RG} + \beta \quad (22)$$

The straight line slope (α) and ordinate intercept (β) are determined using the method of least squares and then the model parameters can be calculated ($\varphi = \alpha \sqrt{K}$; $K = \beta^{-2}$).

For $CuSO_4 - H_2SO_4$ / LIX 64N - Escaid 100 solvent extraction system [4] the equilibrium constant K was found to be $16.0 \text{ dm}^3/\text{kg } H_2O$ and the diluent parameter φ was found to be $4.23 \text{ dm}^3/\text{mol}$. The total concentration of active oxime in various LIX solutions are reported in Table 1.

Table 1. The total concentration of active oxime in various LIX 64N solutions in Escaid 100.

% vol. LIX 64N	5	10	20	50
$C_{RG}, \text{ mol/dm}^3$	0.0439	0.091	0.184	0.485

If in the extraction system the diluent was replaced by another one, only one parameter (φ) should be determined for the new system. Thus the effect of diluent on extraction equilibrium can be wholly described by the diluent parameter φ . This effect is shown in Fig.5 for the copper extraction by 20% LIX 64N in various diluents [7]. The diluent parameters calculated for a few diluents are reported in Table 2.

Table 2. The diluent parameters for various diluents of LIX 64N.

Diluent	φ	Diluent	φ
dekalin	0.83	trichloroethylene	6.54
trimethylpentane	2.07	bromobenzene	7.72
n-heptane	3.09	chlorobenzene	10.44
Escaid 100	4.23	toluene	14.85

Conclusions

The precise description of nonideal aqueous solution of weak electrolytes is the base of presented mathematical model of solvent extraction equilibria. Dissociation constants of weak electrolytes and parameters of activity coefficient correlations should be obtained on the basis of thermodynamic properties of aqueous solutions. The equilibrium constant K , diluent parameter φ and total concentration of active extractant C_{RG} are the parameters of the model, which should be determined by treatment of experimental data for the solvent extraction equilibria. The model covers a wide range of concentrations and allows direct extrapolation to multicomponent systems or to other diluents.

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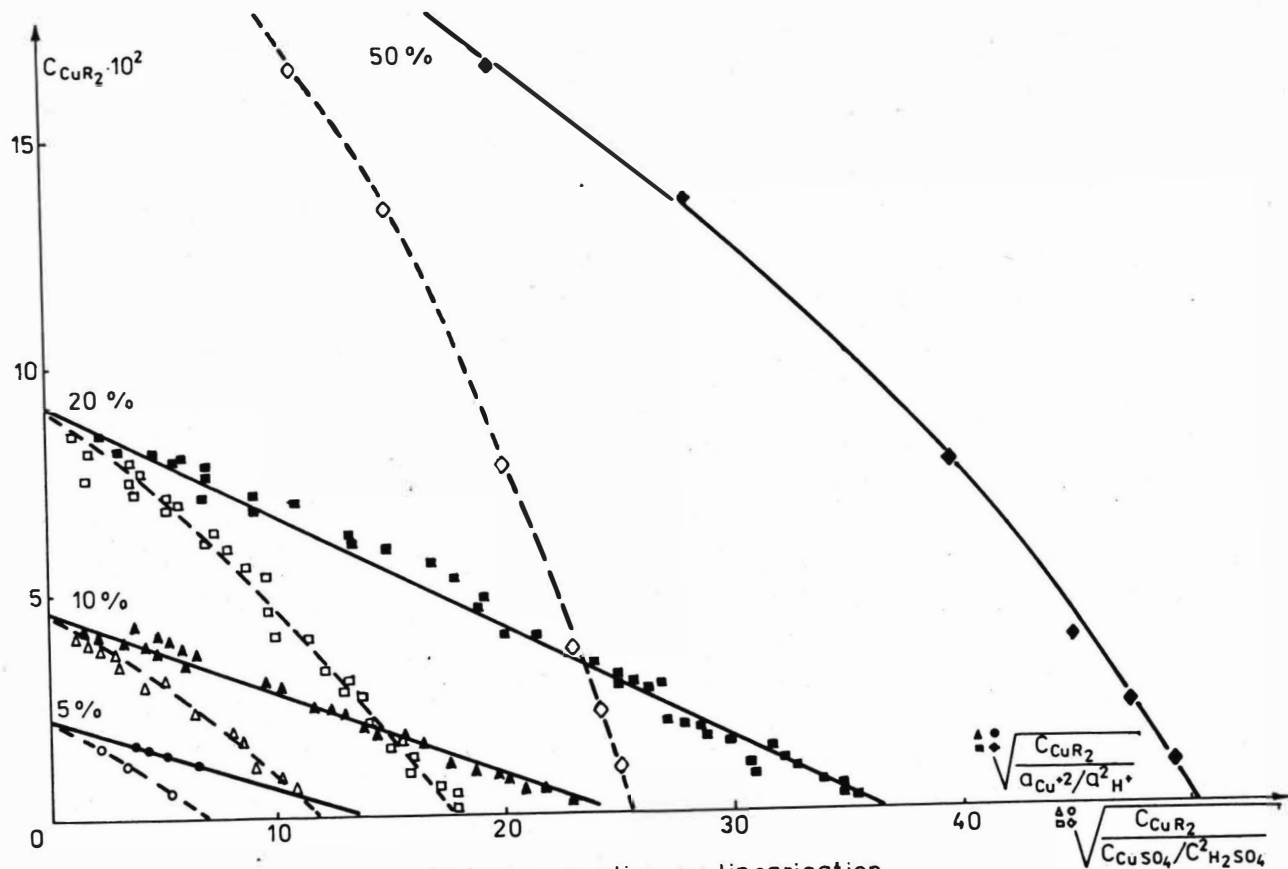


Fig.1. Effect of activity coefficient correction on linearisation of equilibrium data acc. to Eq.14

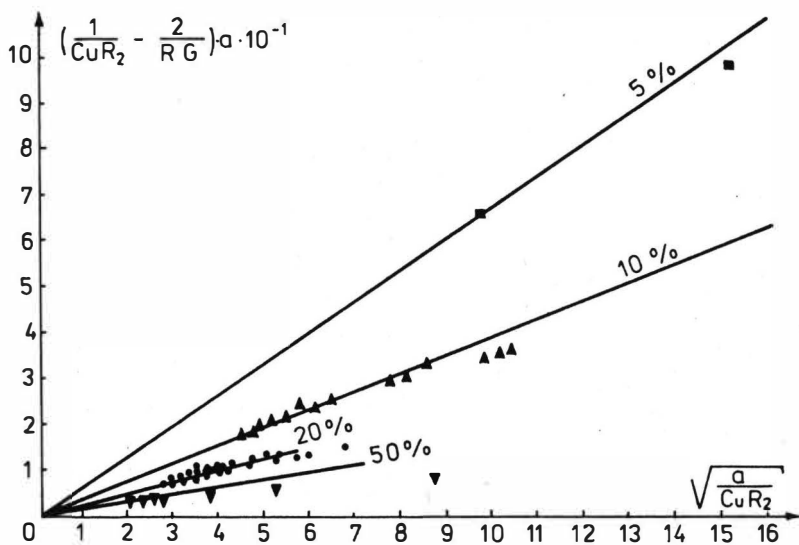


Fig.2. Linearisation of equilibrium data
acc. to Eq. 20

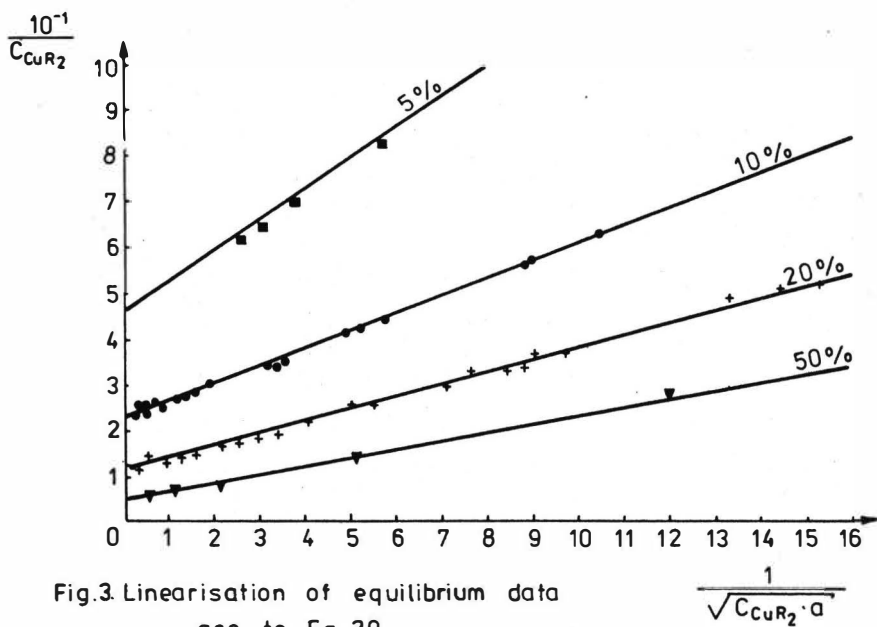


Fig.3. Linearisation of equilibrium data
acc. to Eq. 20

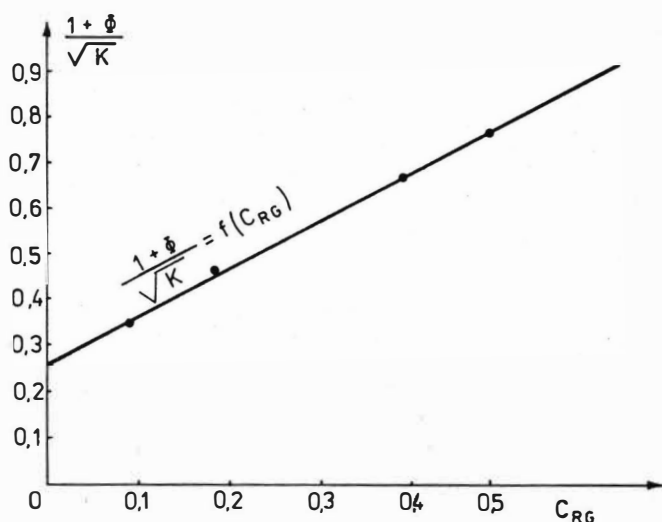


Fig. 4. The dependence of Φ value on the LIX concentration C_{RG}

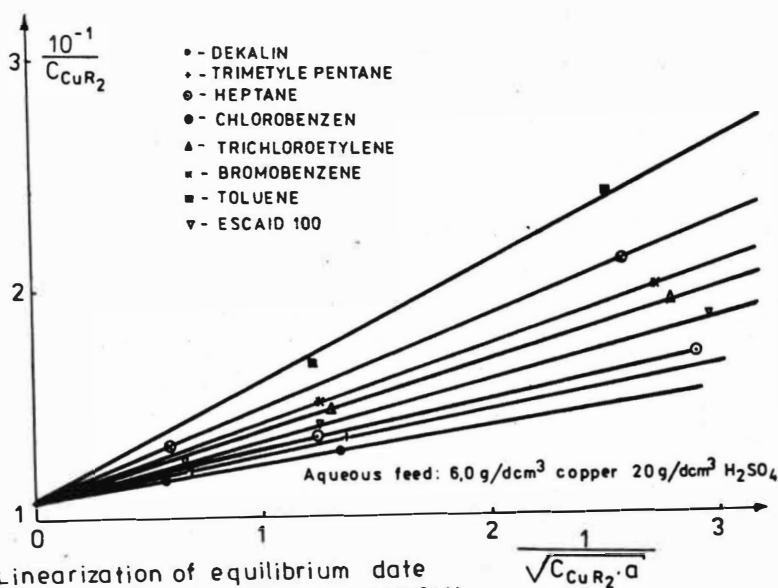


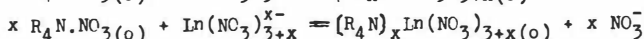
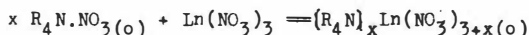
Fig 5 Linearization of equilibrium data acc. to Eq 20 for 20% vol LIX 64N in various diluents.

Studies on Extraction Mechanism of the Rare Earth with Quaternary Ammonium Salts

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1. Introduction

The quaternary ammonium salts are important extractants used for the rare earth separation. However, the reaction mechanism of extraction is not well known yet. For instance, there are two proposed way to form the same extracted complexes through either nucleophilic mechanism or ion exchange mechanism. In the case of nitrate system, for example:



Which one is correct?

Moreover, the extraction behaviour of the quaternary ammonium salts strongly depends on the anion existed in extraction system. For example, in the nitrate system the distribution ratio of rare earth decreases with the increase of atomic number of the rare earths, while in the thiocyanate system it behaves contrarily. Why so?

In order to explain these phenomena more clearly, a study on the coordination chemistry of lanthanide nitrates and thiocyanates in aqueous solution, the structural determination of the extracted complexes and the comparison of the IR spectra of the loaded organic phase and those of the solid extracted complexes were carried out.

2. The coordination chemistry of lanthanide nitrates and thiocyanates in aqueous solution

According to the definitions:

$$Y = \frac{(Ln) + (LnL) + (LnL_2) + (LnL_3) + (LnL_4) + \dots}{(Ln)} = 1 + \sum_{i=1}^6 \beta_i (L)^i$$

and

$$Y_{(1)} = 1 + \beta_1 + \beta_2 + \beta_3 + \dots = 1 + \sum_{i=1}^6 \beta_i$$

where the charges of the complexes are omitted for simplicity and Y is the coordination degree, namely the ratio of total concentration of metal ion to the concentration of the free metal ion and $Y_{(1)}$ is the coordination degree when $(L) = 1$ M. $\beta_1, \beta_2, \beta_3, \dots$ are the cumulation equilibrium constants of the species LnL, LnL_2, LnL_3, \dots respectively. Plotting $Y_{(1)}$ versus atomic number Z of rare earths, we can find that

$Y_{(1)}$ decreases with the increase of Z in nitrate system, while in the thiocyanate system it behaves contrarily. It is shown in Figure 1. Also, it is noted that the dominant species of the rare earth complexes in polar solvent, say water, present as LnI , LnI_2 , LnI_3 . The tendency toward forming anion complexes, such as LnI_4 , LnI_5 , LnI_6 is very weak (1).

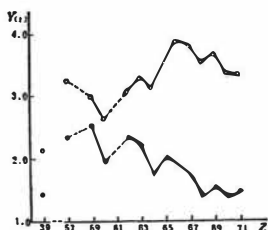
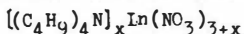


Fig. 1. The Variation of $Y_{(1)}$ with Z

- nitrate system
- thiocyanate system

3. The structural determination of the extracted complexes by single crystal X-ray diffraction

The previous results obtained in our laboratory with either slope analysis or saturation method indicated that the mole ratio of the extractant, say methyl trialkyl ammonium nitrate, to the light rare earth in extracted complexes is three in the saturated organic phase. The extracted complexes may have a general formula $(R_3CH_3N)_3Ln(NO_3)_6$ (2). However, it is very difficult to get the same results for the heavy rare earths. Currently, a series of tetrabutyl ammonium polynitrate lanthanides was synthesized and characterized. They can be represented by the general formula as follows



where $x=3$, when Ln is La, Pr or Nd, and $x=2$, when Ln is Eu-Lu or Y. The complex of Sm can be of both constitutions according to the condition of synthesis.

The structures of $[(C_4H_9)_4N]_3Nd(NO_3)_6$ (3) and $[(C_4H_9)_4N]_2Er(NO_3)_5$ (4) have been studied by single crystal X-ray diffraction. They are monoclinic with space group $P 2_1/C$ and $P 2_1/A$ respectively. The unit cell parameters were found as follows

	$[(C_4H_9)_4N]_3Nd(NO_3)_6$	$[(C_4H_9)_4N]_2Er(NO_3)_5$
a(Å)	16.896(2)	14.410(3)
b(Å)	23.059(3)	16.775(7)
c(Å)	17.443(3)	20.755(7)
b(degree)	90.584(11)	107.390(20)
Z	4	4
d(g/cm ³)	1.216	1.335
V(Å ³)	6795.32	4787.68

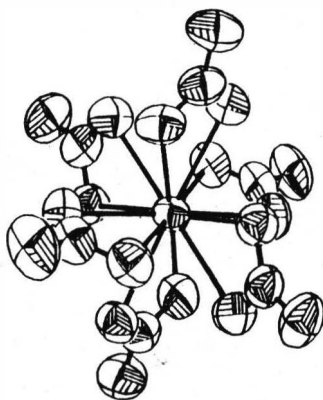


Fig.2 The configuration of $\text{Nd}(\text{NO}_3)_6^{3-}$ anion.

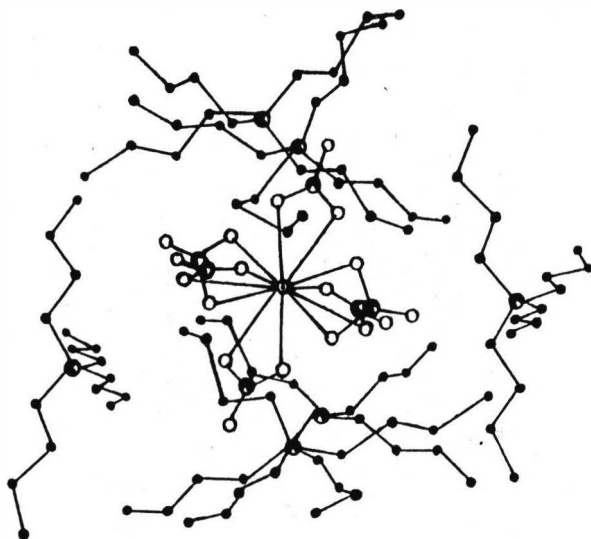


Fig.3 The crystal structure of $((\text{C}_4\text{H}_9)_4\text{N})_3\text{Nd}(\text{NO}_3)_6$.

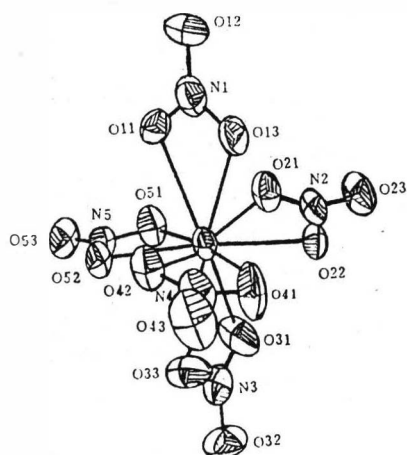


Fig.4 The configuration of $\text{Er}(\text{NO}_3)_5^{2-}$ anion.

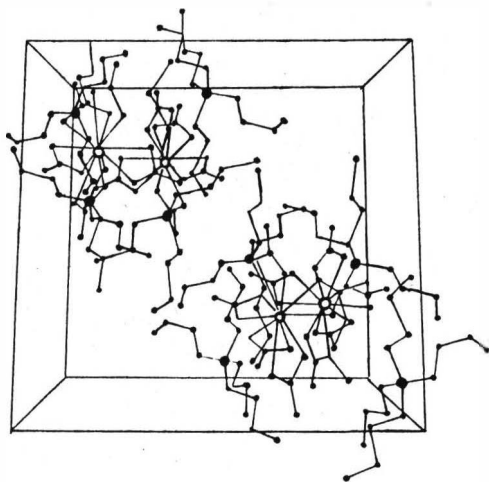


Fig.5 The crystal structure of $[(\text{C}_4\text{H}_9)_4\text{N}]_2\text{Er}(\text{NO}_3)_5$.

The nitrate groups coordinate with the central Nd or Er ion bidentately. Therefore, the coordination number of Nd is 12, and that for Er is 10. The structural configuration of the anion in crystals is shown in Figure 2 and 4. In the case of $[(C_4H_9)_4N]_3Nd(NO_3)_6$, the anion $Nd(NO_3)_6^{3-}$ may be described as a distorted octahedron if each of the six nitrate groups is considered to occupy a single coordination position and the anion $Er(NO_3)_5^{2-}$ may be described as a distorted trigonal bipyramid in the same way. The cell packings are shown in Figures 3 and 5. The anions and cations interact electrostatically, but there is no chemical bonding between them.

Martin and his co-workers synthesized a series of $[(C_4H_9)_4N]_3Ln(NCS)_6$ and the structure of $[(C_4H_9)_4N]_3Er(NCS)_6$ has been determined (5). The erbium ion coordinates with six thiocyanate ions through nitrogen atoms. The average bond length of Er-N is 2.34 Å. Basically, Er-N-C-S has an approximately linear arrangement.

4. The comparison of IR spectra between the pregnant organic phase and those of solid extracted complexes

The saturated organic phase have been prepared with methyl-trialkyl ammonium nitrate and thiocyanate when octanol and kerosene were used as diluents by liquid-liquid extraction. The far IR spectra have been studied for 0.1 M solution of the above systems. In the nitrate system, the dependence of the vibrational frequency of Ln-O bond on the atomic number Z in anions $Ln(NO_3)_{3+x}^{x-}$ shows that it roughly keeps constant around $191-192\text{ cm}^{-1}$ from La-Nd and then jumps to 221 cm^{-1} at Sm. After that, it keeps constant around 221 cm^{-1} until Lu. In the thiocyanate system, that of Ln-N bond in anions $Ln(NCS)_6^{3-}$ varies slowly from 189 cm^{-1} at La to 201 cm^{-1} at Er and then it jumps to 220 cm^{-1} at Tm. After that, it turns to be flat again. Either the vibrational frequency of Y-O bond or that of Y-N bond is higher than that of all lanthanides (6).

On the other hand, a series of far IR spectra of solid complexes $[(C_4H_9)_4N]_xLn(NO_3)_{x+3}$ have been studied. It is very interesting to find that the dependence of the vibrational frequency of Ln-O bond is the same as that found in the liquid $[R_3CH_3N]_xLn(NO_3)_{3+x}$ series. The comparison is shown in Figure 6. The jump of vibrational frequency may reflect the change of the coordination number.

5. Conclusions

(1) The studies of the coordination chemistry of lanthanide nitrates and thiocyanates in aqueous solution indicate that the formation of

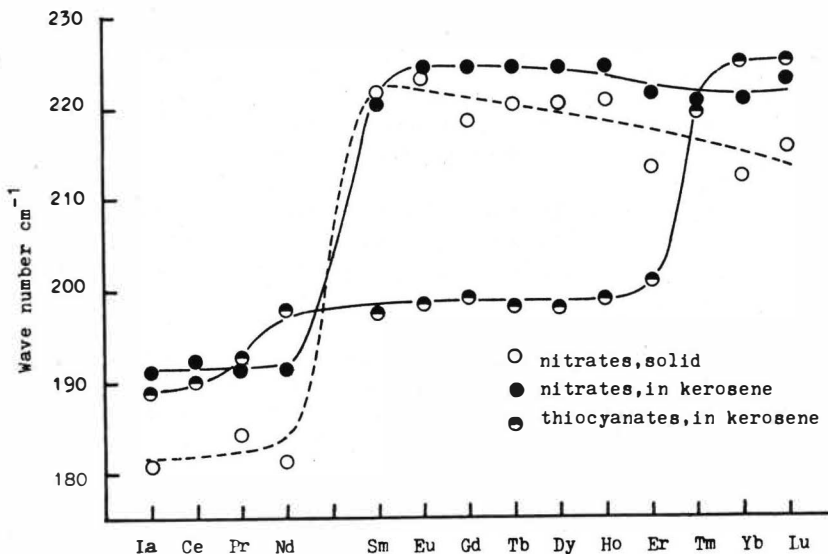


Fig.6 Dependence of vibrational frequency of Ln-O or Ln-N bond on the atomic number Z

the complex anions could not be observed in polar solvents, but the species $\text{Ln}(\text{NO}_3)_6^{3-}$, $\text{Ln}(\text{NO}_3)_5^{2-}$ and $\text{Ln}(\text{NCS})_6^{3-}$ can be found in solid extracted complexes. It has been concluded that the extraction mechanism should be nucleophilic rather than ion exchange.

(2) Comparing the results of the coordination chemistry of lanthanides in aqueous solution and the far IR spectra of saturated organic phase, we can find that the dependence of the distribution ratio on the atomic number is mainly dependent on the complex formation in the aqueous phase rather than the stability of the extracted complexes in the organic phase.

The results of the structural studies give an additional information, that the difference of the coordination number between the light and the heavy rare earths is the main reason why the slope of the straight line of $\log D$ of the extraction of the heavy rare earths plotted versus \log of the concentration of the quaternary ammonium nitrate as extractant is two instead of three.

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Studies on the extraction properties of rare-earth with α -isopropyl-
beta-isobutyl acrylic acid

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The extraction properties of rare earths with α -iso-propyl- β -isobutyl acrylic acid-n-hexane solution were studied. The distribution ratio and extraction $pH_{1/2}$ values for the fifteen rare earth ions, and the separation coefficients for the sixteen pairs of neighbouring rare earth elements were determined under $(HA)=1.0M$, and $(RE_1^{3+})=(RE_2^{3+})=0.02M$. All the $pH_{1/2}$ values are lower and the separation coefficients for Y^{3+}/La^{3+} (3.45) and Lu^{3+}/Y^{3+} (2.72) are higher than that with the other carboxylic acids. The extraction equilibrium of La^{3+} , Nd^{3+} , Eu^{3+} , Er^{3+} , and Y^{3+} by the α,β -acrylic acid-n-hexane solution from lanthanide chloride aqueous solution were studied under $(HA)=2.0-0.2M$, and $(RE^{3+})=0.02-0.001M$. The compositions of the extracted species in the organic phase and the apparent equilibrium constants (K) of extraction reaction were determined by Fletcher method. The extracted species of La and Y exist in the form of $REA_3 \cdot 3HA$, with the apparent equilibrium constants K , 6.46×10^{-13} and 1.23×10^{-12} respectively, while Nd, Eu and Er in the form of $(REA_3 \cdot 3HA)_2$, with the apparent equilibrium constants K , 4.79×10^{-11} , 5.75×10^{-11} , and 3.31×10^{-11} respectively.

As the manuscript was not available at the 28th May 1986, the deadline for printing this book, we only print the short abstract of the paper.

Mathematical Model For Extraction Of Rare Earths With D2EHPA

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ABSTRACT

The mathematical models of extraction of rare earths with D2EHPA in the systems of both single metal extraction and two metal separation have been investigated. For equilibrium systems of extraction of one component with D2EHPA, the model is

$$Y = A1 \cdot X^{A2} \cdot H^{A3} \cdot (L_0 - A4 \cdot Y)^{A5}$$

It has been developed directly from the main extraction reaction of rare earths with D2EHPA



The optimized parameters $A3$, $A4$ and $A5$ are close to values which are developed directly from the reaction. The model has been used to predict the results of different extraction systems of rare earths with D2EHPA. All of the results calculated by using the model compare quite well with the experimental results. The mathematical model not only can be used to calculate extraction results but also can be used to explain and study extraction reaction mechanism, association of extractant, and the composition of extractive complex.

In equilibrium systems of extraction separation of two components, the mathematical models

$$Y1 = A11 \cdot X1^{A12} \cdot H^{A13} \cdot (L_0 - A14 \cdot Y1)^{A15} \cdot X2^{A16} \cdot Y2^{A17}$$

$$Y2 = A21 \cdot X2^{A22} \cdot H^{A23} \cdot (L_0 - A24 \cdot Y2)^{A25} \cdot X1^{A26} \cdot Y1^{A27}$$

have also been developed. In these models the optimized parameters are also close to the values expected from the reaction. The calculated values conform to the experimental results quite well.

INTRODUCTION

A research method, computer aided experiment (CAE) and computer aided design (CAD), for extraction separation technique which differs from previous methods, has been developed because of the rapid development of the electronic computer. The establishment of the mathematical models for extractions systems is one of keynote of the method. The mathematical models can be divided into three categories, a) empirical model, b) semitheoretical model and c) thermodynamic model. For extraction of rare earths there are polynomial, distribution coefficient and other semitheoretical models (1-5).

The purpose of this research was to build up the mathematical model for extraction of rare earths by D2EHPA[di(2-ethylhexyl)phosphoric acid] based on reaction equations and partial equilibrium data on the system and to try to predict extraction results and study extraction reaction mechanism.

ESTABLISHMENT OF EXTRACTION MODEL

The extraction of lanthanide ions by D2EHPA in non-polar solvents from aqueous solutions having rather low acidities is considered to be an ion exchange reaction. For the system, the main extraction reaction can be presented



in which Re^{n+} means lanthanide ion and $(\text{HL})_2$ expresses a dimer of D2EHPA. The concentration equilibrium constant for the extraction reaction is

$$K = \frac{[\text{Re}(\text{HL}_2)] [\text{H}^+]^n}{[\text{Re}^{n+}] [(\text{HL})_2]^n} \quad (2)$$

from which we have

$$[\text{Re}(\text{HL}_2)] = K [\text{Re}^{n+}] [\text{H}^+]^{-n} [(\text{HL})_2]^n \quad (3)$$

$(\text{HL})_2$ is replaced by $\text{Lo}-n[\text{Re}(\text{HL}_2)]$ (Lo means initial concentration of extractant in organic phase, then

$$[\text{Re}(\text{HL}_2)] = K [\text{Re}^{n+}] [\text{H}^+]^{-n} [\text{Lo}-n[\text{Re}(\text{HL}_2)]]^n \quad (4)$$

for convenience gives

$$Y = A1 * X^{A2} * H^{A3} * (\text{Lo}-A4Y)^{A5} \quad (5)$$

in which Y expresses the concentration of the rare earth in the organic phase, X means the concentration of the rare earth in aqueous solution, H acidity of the system and the parameters A1 means K, A2, A3, and A4 (or A5) mean coefficients of Re^{n+} , H^+ , and $(\text{HL})_2$ respectively in reaction (1).

Equation (5) is a mathematical model for extraction of a single metal ion by D2EHPA. It can be seen that for deduction of equation (5) only one hypothesis, that the concentration equilibrium constant K is considered a real constant has been introduced. In fact K is a hypocritical constant which slightly varies with variation of concentration of each component in the equilibrium condition in the system. It is considered a constant when the range of concentrations of the components of the system is not very wide. Thus it can be thought that equation (5) reflects an inherently essential relation among various species in equilibrium condition for the extraction process.

We could say that in equation (5) the optimized parameters from A1 to A5 which are obtained by using equilibrium experimental data of Y, X and H which are measured exactly under a certain pressure and temperature can be used to predict and study reaction mechanism, composition of extracted species and association of extractant.

Using Y1 and Y2 to express concentrations of the lanthanide ions in the organic phase respectively, X1 and X2 stand for concentrations of the ions in the aqueous phase respectively and presuming that the influence of concentrations of one metal ion in the aqueous and organic phases on the extraction of another ion is also an exponential function, we have the mathematical models

$$Y1 = A11 * X1^{A12} * H^{A13} * (\text{Lo}-A14 * Y1)^{A15} * X2^{A16} * Y2^{A17} \quad (6)$$

$$Y2 = A21 * X2^{A22} * H^{A23} * (\text{Lo}-A24 * Y2)^{A25} * X1^{A26} * Y1^{A27} \quad (7)$$

for equilibrium systems of extraction separation of two components. The parameters in equations (5), (6) and (7) will be optimized using the SUMT (Sequential Unconstrained Minimization Technique) method based on Hooke-Jeeves Pattern Search with equilibrium data of various extraction conditions. A generalized FORTRAN program (HJSUMT) has been designed based on the SUMT method(6).

RESULTS AND DISCUSSION

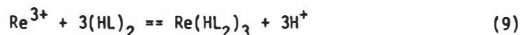
1. System DyCl_3 -- HCl -- H_2O -- 1.0M D2EHPA--Kerosene(7)

This is a system involving extraction of a single metal. The mathematical model was developed:

$$Y = 4.3961 * X^{0.3126} * H^{-3.8403} * (1.0-4.8612Y)^{2.4556} \quad (8)$$

for the system by using the HJSUMT method to optimize the parameters of equation (5)

based on ten groups of experimental data. The extraction of trivalent lanthanide ions by D2EHPA was reported previously to be



for which equation (4) becomes

$$[\text{Re}(\text{HL}_2)_3] = K[\text{Re}^{3+}][\text{H}^+]^{-3}[\text{Lo-3Re}(\text{HL}_2)_3]^3 \quad (10)$$

It can be found from the equation (8) that optimized parameters A2 0.3126, A3 -2.8403 and A5 2.4556 are near the values expected from equation (10) 1.0, -3.0 and 3.0. The extractant (D2EHPA) exists as a dimer in the organic phase when it extracts the metals. For the optimization of the parameters we have not used the hypothesis that D2EHPA exists on a dimer in organic solutions. If we considered that the extractant is dimeric, the optimized parameter A4 becomes $4.8612/2 = 2.4306$ which is close to the value of 3.0 developed directly from equation (10).

If we presume that D2EHPA is dimeric in the solution, the mathematical model was optimized

$$Y = 4.3961 \times 10^{-0.3126} \times H^{-2.4009} \times (0.5 - 2.9700 \times Y)^{1.2075} \quad (11)$$

based on the same ten groups of data. In equation (11) A1 and A2 were fixed and only A3, A4 and A5 were optimized by the HJSUMT method. It can be seen that A4 in equation (11) is closer to 3.0 than the one in equation (8). The extractant indeed exists as a dimer in organic solution.

From different considerations in the mathematical models, the optimized parameters from A1 to A5 which express the coefficients of the extraction reaction have been obtained. It probably implies that the mathematical model for extraction of rare earths could be used to predict the reaction mechanism, association of extractant, and composition of extracted species and no doubt could be considered to supply a convenient method for the study of extraction mechanism of metals by D2EHPA.

Table 1 gives a comparison of experimental results and calculated values using equation (8). As may be seen from table 1 the extraction model has a high prediction accuracy not only when it is used to calculate extraction results under the experimental conditions of the ten data groups marked with an asterisk but also when it is used to predict results in the experimental range outside these conditions.

Table 1. Comparison of equilibrium experimental values and predicted values for extraction of dysprosium

No.	Aqueous Phase Conc. (M)		Organic Phase Conc. Dy(3+) (M)		Relative Errors-%
	Dy(3+)	Acidities	Exp.	Cal.	
1	0.1307	1.1476	0.1284	0.13098	2.01
2	0.2454	1.1613	0.1331	0.13493	1.37
3	0.7698	1.1646	0.1364	0.14287	4.74
4	0.9553	1.3233	0.1293	0.13620	5.34
5	0.8471	1.3325	0.1287	0.13485	4.78
6	0.5115	1.3609	0.1298	0.12954	0.20
7*	0.4200	1.3690	0.1285	0.12756	0.73
8*	0.7725	1.5042	0.1234	0.12558	1.77
9*	0.1550	1.6894	0.1002	0.10229	2.08
10*	0.6558	1.7171	0.1159	0.11403	1.61
11*	0.8711	1.8404	0.1091	0.11096	1.71
12*	0.5454	1.8747	0.1087	0.10518	3.23
13*	1.0089	2.0704	0.0997	0.10252	2.82
14*	0.6166	2.0749	0.1029	0.09771	5.04
15*	0.2851	2.1578	0.0887	0.08687	2.03
16*	0.1829	2.2065	0.0791	0.08057	1.81

Table 1 (contd)

17	0.8280	2.5552	0.0813	0.08230	1.19
18	0.3162	2.5582	0.0742	0.07281	1.80
19	0.4832	2.5825	0.0775	0.07610	1.82
20	0.9069	2.5862	0.0808	0.08211	1.68
21	0.6397	2.6013	0.0813	0.07819	3.76
22	0.3244	2.7429	0.0661	0.06696	1.37
23	0.5754	2.8115	0.0718	0.07030	2.04
24	0.9294	2.9033	0.0689	0.07212	4.62
25	0.3314	2.9281	0.0603	0.06151	2.07

note: The values with * are used to build up the model.

In order to test the suitability of the model, equation (8) has been adopted to estimate concentrations of dysprosium in organic solution for the system $\text{DyCl}_3\text{--HCl--H}_2\text{O--1.0M D2EHPA--Amsco(8)}$. The results are shown in Table 2. It should be noted that the range of experimental conditions for both the equilibrium concentrations of lanthanide ion (0.06 - 2.5M) and extraction acidities (1.3 - 5.1M) are much wider than the ones (0.1 - 1.0M and 1.37 - 2.2M) of the system which we have discussed above. It is apparent that the values calculated are close to the experimental results for 49 groups of data in Table 2. This indicates that the mathematical model for extraction of rare earths with D2EHPA has a certain extensive property.

Table 2. Comparison of experimental results and calculated results using C. Owen's data.

No.	Aqueous Phase Conc. (M)		Organic Phase Conc. Dy(3+) (M)		Relative Errors %
	Dy(3+)	Acidities	Exp.	Cal.	
1	0.065	1.38	0.108	0.11114	2.91
2	0.065	1.37	0.108	0.11173	3.45
3	0.265	1.38	0.128	0.12323	3.72
4	0.270	1.37	0.128	0.12393	3.18
5	0.510	1.37	0.132	0.12904	2.24
6	0.509	1.37	0.132	0.12903	2.25
7	0.768	1.37	0.130	0.13221	1.70
8	0.766	1.34	0.132	0.13371	1.30
9	1.010	1.35	0.130	0.13527	4.06
10	1.250	1.37	0.127	0.13586	6.98
11	1.480	1.37	0.126	0.13709	8.80
12	1.490	1.36	0.125	0.13762	10.10
13	1.730	1.41	0.123	0.13633	10.83
14	1.730	1.42	0.121	0.13585	12.28
15	1.980	1.47	0.118	0.13453	14.00
16	1.980	1.43	0.116	0.13638	17.57
17	2.230	1.44	0.116	0.13678	17.92
18	2.470	1.43	0.113	0.13798	22.10
19	2.470	1.47	0.116	0.13616	17.38
20	2.450	1.55	0.116	0.13250	14.23
21	2.440	1.47	0.116	0.13607	17.30
22	0.116	2.81	0.040	0.05527	38.17
23	0.316	2.78	0.059	0.06553	11.07
24	0.317	2.78	0.059	0.06556	11.12
25	0.564	2.75	0.066	0.07205	9.17
26	0.565	2.74	0.066	0.07239	9.68
27	0.817	2.72	0.069	0.07662	11.05
28	0.817	2.74	0.069	0.07597	10.11
29	1.080	2.76	0.068	0.07805	14.78
30	1.080	2.76	0.069	0.07805	13.12
31	1.340	2.73	0.069	0.08112	17.57
32	1.600	2.61	0.070	0.08683	24.04
33	1.590	2.62	0.070	0.08643	23.47
34	1.850	2.65	0.070	0.08690	24.14

Table 2 (contd)

35	1.850	2.60	0.069	0.08858	28.37
36	2.090	2.74	0.070	0.08513	21.62
37	2.100	2.68	0.071	0.08714	22.73
38	0.276	4.98	0.017	0.02299	35.25
39	0.518	5.00	0.023	0.02642	14.86
40	0.518	4.99	0.024	0.02653	10.54
41	0.761	4.94	0.028	0.02953	5.48
42	0.762	4.94	0.228	0.02954	5.51
43	1.010	4.92	0.032	0.03168	1.02
44	1.000	4.92	0.032	0.03161	1.23
45	1.250	5.04	0.036	0.03164	12.12
46	1.260	5.01	0.036	0.03206	10.94
47	1.420	5.10	0.042	0.03177	24.35
48	1.430	5.03	0.042	0.03269	22.17

2. System $YCl_3-HCl-H_2O$ -D2EHPA-Amsco(9)

This is also a system of extraction of a single component. The difference between this system and example 1 is that the concentration of extractant in the organic phase is not only 1.0M. In the system 0.31, 0.42, 0.56 0.72 and 2.0M were used respectively to extract trivalent yttrium. We only utilized partial equilibrium data of extraction of yttrium by 1.0M D2EHPA to optimize parameters of equation (5), then estimated extraction under all extractive conditions using the model obtained. The model was presented as follows:

$$Y = 20.4768 \times 10^{-6} \times H^{-2.6254} \times (L - 6.0526 \times Y)^{2.1223} \quad (12)$$

It can be found that not only A3 -2.63, A4/2 3.03 and A5 2.12 approach the values desired, -3.0 and 3.0, but also A2 0.61 approximates 1.0. The experimental data and quantities calculated by the model are shown in Table 3. The data with an asterisk in Table 3 were used to optimize the model. Although the experimental conditions for values calculated by the model are much wider both with respect to concentration of extractant and acidities than that of the data with the asterisk, the calculated results are satisfactory.

Table 3. Experimental results and calculated values of the system $YCl_3-HCl-H_2O$ -D2EHPA

No.	Aqueous Phase Conc. (M)		Initial Extractant Conc. (M)	Organic Phase Conc. Y(3+) (M)		Relative Errors-%
	Y(3+)	Ac.		Exp.	Cal.	
1	0.0802	3.05	0.31	0.01350	0.01146	15.13
2	0.2670	2.94	0.31	0.01600	0.01797	12.29
3	0.0865	3.99	0.31	0.00733	0.00731	0.22
4	0.2750	3.94	0.31	0.01340	0.01202	10.27
5	0.0887	4.43	0.31	0.00527	0.00601	13.96
6	0.2770	4.41	0.31	0.01080	0.01000	7.42
7	0.2730	4.51	0.42	0.01760	0.01611	8.47
8	0.0635	3.07	0.56	0.02960	0.02763	6.66
9	0.2420	3.04	0.56	0.04630	0.04034	12.87
10	0.0764	4.02	0.56	0.01830	0.01955	6.81
11	0.2540	4.04	0.56	0.03260	0.02945	9.68
12	0.0798	4.53	0.56	0.01430	0.01615	12.97
13	0.2630	4.42	0.56	0.02740	0.02632	3.94
14	0.0551	3.01	0.72	0.03950	0.04022	1.83
15	0.2260	3.05	0.72	0.06290	0.05639	10.35
16	0.0626	3.55	0.72	0.03100	0.03352	8.14
17	0.2350	3.57	0.72	0.05390	0.04876	9.54
18	0.0688	4.05	0.72	0.02540	0.02842	11.89
19	0.2430	4.08	0.72	0.04540	0.04228	6.88

Table 3 (contd)

20	0.0738	4.50	0.72	0.02060	0.02457	19.28
21	0.2490	4.45	0.72	0.03920	0.03817	2.64
22	0.0434	1.99	1.00	0.10400	0.09098	12.52
23*	0.0962	1.98	1.00	0.12000	0.10298	14.18
24	0.4790	2.02	1.00	0.13700	0.12169	11.17
25*	0.9300	2.01	1.00	0.13600	0.12853	5.49
26	1.4000	2.01	1.00	0.13400	0.13217	1.37
27*	2.5800	2.00	1.00	0.13400	0.13717	2.37
28	0.0367	2.34	1.00	0.06170	0.07714	25.03
29*	0.1900	2.81	1.00	0.10500	0.09083	13.50
30	0.3780	2.78	1.00	0.11500	0.10168	11.59
31*	0.7450	2.75	1.00	0.12000	0.11136	7.20
32	1.2500	2.75	1.00	0.12100	0.11759	2.81
33*	2.3600	2.64	1.00	0.12400	0.12621	1.79
34*	0.0555	3.65	1.00	0.04580	0.05233	14.25
35*	0.2410	3.61	1.00	0.08350	0.07738	7.33
36*	0.4650	3.69	1.00	0.09460	0.08647	8.59
37	0.9190	3.48	1.00	0.10300	0.10056	2.37
38*	1.4800	3.40	1.00	0.10300	0.10844	5.28
39	2.1800	3.33	1.00	0.11100	0.11444	3.10
40*	0.1190	5.22	1.00	0.03610	0.04034	11.74
41	0.2210	4.92	1.00	0.05300	0.05387	1.64
42	0.4620	4.92	1.00	0.06620	0.06604	0.24
43	0.6020	4.89	1.00	0.07150	0.07089	0.85
44*	0.9160	4.83	1.00	0.07680	0.07871	2.49
45	1.1700	4.83	1.00	0.08220	0.08269	0.59
46	1.3600	4.89	1.00	0.08680	0.08425	2.94
47	1.4100	4.59	1.00	0.08760	0.08913	1.75
48*	1.7100	4.76	1.00	0.09640	0.08970	6.96
49*	0.1070	6.48	1.00	0.02060	0.02670	29.62
50	0.5270	6.44	1.00	0.05330	0.04922	7.66
51*	1.0800	6.18	1.00	0.07890	0.06382	19.11
52	0.0955	7.91	1.00	0.01340	0.01703	27.11
53	0.6090	7.69	1.00	0.05990	0.03981	33.54
54	0.0135	9.89	1.00	0.00408	0.00346	15.11
55	.00013	.421	1.00	0.09090	0.10385	14.25
56	.00069	.432	1.00	0.14600	0.12274	15.93
57	.00077	.506	1.00	0.10300	0.11636	12.97
58	.00302	.531	1.00	0.14300	0.12857	10.09
59	0.0084	0.99	1.00	0.13600	0.11965	12.02
60	0.0401	1.37	1.00	0.12800	0.11236	12.22
61	0.1860	1.37	1.00	0.14500	0.12892	11.09
62	2.1600	1.26	1.00	0.14400	0.14795	2.74
63	0.2050	3.51	2.00	0.18400	0.19355	5.19
64	0.4310	3.54	2.00	0.22200	0.21342	3.87
65	0.9220	3.55	2.00	0.24600	0.23222	5.60
66	1.5400	3.42	2.00	0.25900	0.24709	4.60
67	1.9500	3.57	2.00	0.28300	0.24814	12.32
68	2.1400	3.44	2.00	0.28900	0.25318	12.40
69	0.2080	5.06	2.00	0.12100	0.14400	19.01
70	0.4030	5.21	2.00	0.16000	0.16163	1.02
71	0.8800	4.81	2.00	0.19200	0.19647	2.33
72	1.3500	4.68	2.00	0.21400	0.21179	1.03
73	1.6100	4.13	2.00	0.25400	0.22998	9.46
74	0.0575	8.04	2.00	0.04710	0.04733	0.48
75	0.5070	7.62	2.00	0.14500	0.11499	20.69
76	0.5230	7.86	2.00	0.14600	0.11164	23.54
77	0.0237	9.95	2.00	0.02270	0.01926	15.16
78	0.0476	9.67	2.00	0.03240	0.02956	8.76

note: The values with * are used to build up the model.

3. System $\text{LuCl}_3\text{--YbCl}_3\text{--HCl--H}_2\text{O--1.0M D2EHPA (10)}$

For the system of extraction separation of two metal ions the model equations (6) and (7) are used. the concrete mathematical models are obtained

$$Y(Lu) == 1.8931 * X(Lu)^{1.0682} * H^{-2.8965} * [1.0 - 7.4467 * Y(Lu)]^{2.4871} \\ * X(Yb) - 1.0531 * Y(Yb) - 1.3274 \quad (13)$$

$$Y(Yb) == 1.4574 * X(Yb)^{1.2000} * H^{-3.0183} * [1.0 - 7.4534 * Y(Yb)]^{2.8793} \\ * X(Lu) - 1.1355 * Y(Lu) - 1.1237 \quad (14)$$

for the system by the HJSUMT program based on equilibrium data. In equations (13) and (14) not only A13 and A23, A14/2 and A24/2, A15 and A25 are consistent with expected values -3 and 3 but also A12 and A22 are approximately equal to 1. The effect of one component in aqueous and organic phases on the extraction of another one is expressed as the negative exponent. This may illustrate that the characterization of the parameters is a reflection of the essential relationships of various components of the equilibrium system on the model. Table 4 shows a comparison with relative errors of two results.

Table 4. Comparisons of two kinds of results of extraction separation of Lu(3+) and Yb(3+) of D2EHPA

Aqueous Phase Conc. (M)			Organic Phase Conc. (M)				Relative Errors-%	
Lu	Yb	HCl	Exp		Cal.		Lu	Yb
			Lu	Yb	Lu	Yb		
0.024	0.228	4.92	0.0219	0.106	0.0211	0.1066	3.58	0.03
0.051	0.203	4.96	0.0407	0.0877	0.0414	0.0875	1.65	0.20
0.074	0.178	5.00	0.0560	0.0732	0.0565	0.0730	0.86	0.29
0.098	0.150	4.96	0.0716	0.0590	0.0719	0.0595	0.40	0.89
0.123	0.126	5.04	0.0841	0.0469	0.0839	0.0468	0.27	0.31
0.144	0.102	4.98	0.0953	0.0365	0.0952	0.0370	0.13	1.45
0.172	0.076	4.96	0.1078	0.0246	0.1072	0.0257	0.53	4.75
0.196	0.049	4.96	0.1156	0.0176	0.1159	0.0156	0.30	11.1
0.218	0.025	4.91	0.1251	0.0087	0.1251	0.0071	0.03	18.1

4. System YbCl₃--TmCl₃--HCl--H₂O--1.0M D2EHPA(..)

The same procedure of optimization has been used for this system as compared with the system 3, equations (15) and (16) were developed.

$$Y(Yb) == 1.8582 * X(Yb)^{1.0937} * H^{-2.4360} * [1.0 - 7.841 * Y(Yb)]^{2.5621} \\ * X(Tm) - 0.5144 * Y(Tm) - 1.3377 \quad (15)$$

$$Y(Tm) == 1.8395 * X(Tm)^{1.0400} * H^{-2.4930} * [1.0 - 5.2316 * Y(Tm)]^{2.5350} \\ * X(Yb) - 0.2550 * Y(Yb) - 0.7060 \quad (16)$$

It should be noted that the first parameters which identify the concentration equilibrium constants in equations (13) and (15) are larger than the ones in equations (14) and (16) respectively. That is because Lu(3+) and Yb(3+) are easier to extract than Yb(3+) and Tm(3+) respectively by D2EHPA. The consistency between calculated datum and experimental result is not very satisfactory for extraction of thulium for the secondary group of data in table 5. It is considered that the experimental

results may be not reasonable, because the distribution coefficient of thulium should decrease gradually with the decrease of concentration of thulium in equilibrium aqueous solution (other conditions keep invariable). The distribution coefficients calculated based on the experimental data are 0.224, 0.172 and 0.192 respectively for No. 1, 2 and 3 for extraction of thulium. The second distribution coefficient which is less than the third one is not reasonable. However the distribution coefficients calculated 0.217, 0.197 and 0.183 based on the predicted data are satisfactory.

Table 5. Comparison of two kinds of extraction separation results of Yb(3+) and Tm(3+) by D2EHPA

No.	Aqueous Phase Conc. (M)			Organic Phase Conc. (M)				Relative Errors %	
	Yb	Tm	HCl	Exp.		Cal.		Yb	Tm
				Yb	Tm	Yb	Tm		
1	0.120	0.125	4.89	0.084	0.028	0.0842	0.0271	0.17	3.21
2	0.179	0.064	4.92	0.106	0.011	0.1059	0.0126	0.07	14.83
3	0.218	0.026	4.99	0.116	0.005	0.1160	0.0048	0.00	4.86
4	0.134	1.292	5.24	0.032	0.103	0.0319	0.1030	0.15	0.00
5	0.013	0.164	4.83	0.019	0.076	0.0185	0.0761	2.69	0.04

CONCLUSION

The mathematical models reduced from the reaction of rare earths with D2EHPA for one metal ion system

$$Y = A1 \cdot X^{A2} \cdot H^{A3} \cdot (Lo - A4 \cdot Y)^{A5}$$

and for two metal components

$$Y1 = A11 \cdot X1^{A12} \cdot H^{A13} \cdot (Lo - A14 \cdot Y1)^{A15} \cdot X2^{A16} \cdot Y2^{A17}$$

$$Y2 = A21 \cdot X2^{A22} \cdot H^{A23} \cdot (Lo - A24 \cdot Y2)^{A25} \cdot X1^{A26} \cdot Y1^{A27}$$

can be used not only to predict extraction results but also to explain and study reaction mechanism of extraction of rare earths by D2EHPA, association of extractant, and compositions of extractive complexes.

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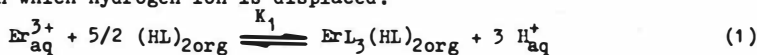
Extraction Mechanism of Erbium(III) and Aluminium(III) by
2-ethylhexylphosphonic acid mono-2-ethylhexyl ester

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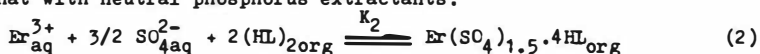
Although 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (referred to as HEH/EHP and denoted as HL) is an excellent extractant for the separating and purifying lanthanides and other elements(1), the chemistry of the extraction process is not well understood. Only the extraction mechanism of lanthanides(III) in the chloride and nitrate system(2,3), cerium(IV) in the sulphate system(4) and aluminium(III) in the chloride and sulphate system(5-7) by HEH/EHP has been investigated. It was the purpose of this study to determine the extraction mechanism of Er(III) in the sulphate and Al(III) in the nitrate by HEH/EHP.

Extraction mechanism of erbium(III)

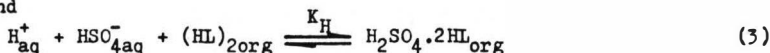
The partition equilibria of Er(III) between sulphuric acid and HEH/EHP in octane were investigated. The extraction mechanism of Er(III) at different acidities has been discussed with the methods of slope, IR and NMR. Figure 1 shows the effect of acidity of equilibrium aqueous phase on Er(III) extraction by HEH/EHP. The data of Fig. 1 determine two different extraction reactions. The equilibrium curve of $\text{LogD}-\text{Log}[H^+]_{\text{aq}}$ determines a straight line having a slope of -3.0 at low aqueous acidity. It is indicated that Er(III) can be extracted from sulphate system by the ion-exchange reaction. The shape of the equilibrium curve for $\text{LogD}-\text{Log}[H_2SO_4]_{\text{aq}}$ suggests the possibility of Er(III) extraction by other reactions at high aqueous acidity. Figure 2 shows the LogD as a function of the equilibrium concentration of free HEH/EHP. The slopes of the plot of Fig.2(a) are 2.5 at low aqueous acidity. For high aqueous acidity the data of Fig.2(b) determine a straight line having a slope of 2.0. Thus, the extraction mechanism of Er(III) in the sulphate system by HEH/EHP could be written as follows: at low aqueous acidity, Er(III) is extracted by a cation-exchange reaction in which hydrogen ion is displaced:



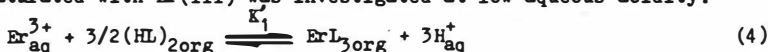
and at high aqueous acidity by a solvation reaction similar to that with neutral phosphorus extractants:



and



The extraction mechanism for the case that the organic phase is saturated with Er(III) was investigated at low aqueous acidity:



The solid complex of ErL_3 species has been obtained. The equilibrium constant for the reaction of Equation (1) is

$$\text{Log} K_1 = \text{Log} D + \text{Log} (1 + \sum_i \beta_i [\text{SO}_4]_{\text{aq}}^i) + 3 \text{Log} [\text{H}^{+}]_{\text{aq}} - 5/2 \text{Log} [\text{HL}]_{2\text{org}} \quad (5)$$

and that of Equation (2) is

$$\begin{aligned} \text{Log} K_2 = \text{Log} D + \text{Log} (1 + \sum_i \beta_i [\text{SO}_4]_{\text{aq}}^i) + 2 \text{Log} (1 + K_H [\text{H}^{+}]_{\text{aq}} [\text{HSO}_4]_{\text{aq}}) \\ - 1.5 \text{Log} [\text{SO}_4]_{\text{aq}} - 2 \text{Log} [\text{HL}]_{2\text{org}} \end{aligned} \quad (6)$$

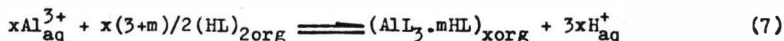
The equilibrium constants K_1 and K_2 are as follows:

$$\text{Log} K_1 = 2.11 \text{ and } \text{Log} K_2 (17.9\text{N } \text{H}_2\text{SO}_4) = 4.08.$$

The effect of different solvents and temperatures on the Er(III) extraction was observed. The thermodynamic functions (ΔH , ΔZ and ΔS) of the extraction reaction were calculated. The IR and NMR studies were carried out for the extracted complex. The data of the IR and NMR are in good agreement with the obtained extraction mechanism.

Extraction mechanism of aluminium(III)

The partition equilibrium of Al(III) between nitric acid and HEH/EHP in hexane were investigated. The extraction mechanism of Al(III) has been discussed with the methods of slope, saturation, IR and NMR. Writing the equilibrium equation for the extraction of Al(III) from nitrate system by HEH/EHP as:

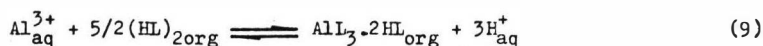


permits an equilibrium constant K to be written:

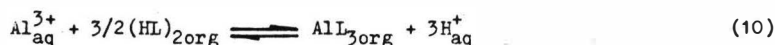
$$K = \frac{[(\text{AlL}_3 \cdot m\text{HL})_{\text{x}}]_{\text{org}} [\text{H}^{+}]_{\text{aq}}^{3x}}{[\text{Al}^{3+}]_{\text{aq}}^x [\text{H}_2\text{L}_2]_{\text{org}}^{x(3+m)/2}} \quad (8)$$

where x represents the polymerization degree of Al(III) and m the solvation number of HEH/EHP. The relationship between $\text{Log} D$ and pH was investigated at various HEH/EHP concentrations. The results are shown on Fig. 3. The data of Fig. 3 determine a straight line for each HEH/EHP concentration with the slope of 2 to 3. For higher equilibrium aqueous pH the slope is less than 3. This may be due to complexing between Al^{3+} and OH^{-} in the aqueous phase. A plot of $\text{Log} D - 3\text{pH}$ versus

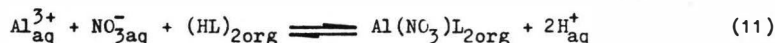
Log[HL]_{2org}, shown on Fig. 4, was made. The slope of the plot of Fig. 4 is 2.5. Thus, m=2. The determination of polymerization degree of aluminium containing species is shown on Fig. 5. The plot of Fig. 5 was found to be a straight line with the slope near to 1. It may be considered that aluminium containing species extracted from nitric acid solutions by HEH/EHP is a monomer. Thus, the extraction reaction of aluminium(III) in the nitrate system by HEH/EHP could be written as follows:



Extraction mechanism for the case that the organic phase is saturated with Al(III) could be written as follows:



and



The composition of extracted complex by saturated method may be considered as $[\text{Al}(\text{NO}_3)_{0.5}\text{L}_{2.5}\cdot n\text{H}_2\text{O}]_n$. The IR and NMR studies were carried out for the extracted complex. The results on the IR and NMR are in satisfactory agreement with the above extraction mechanism.

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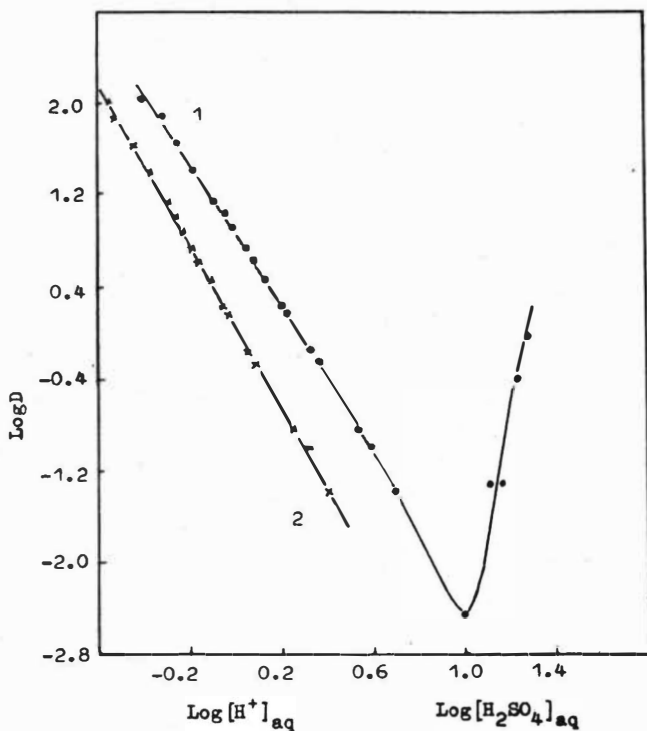


Fig. 1 Effect of acidity of equilibrium aqueous phase on Er(III) extraction by HEH/EHP
 (1) $\text{Log} D - \text{Log} [\text{H}_2\text{SO}_4]_{\text{aq}}$ (2) $\text{Log} D - \text{Log} [\text{H}^+]_{\text{aq}}$

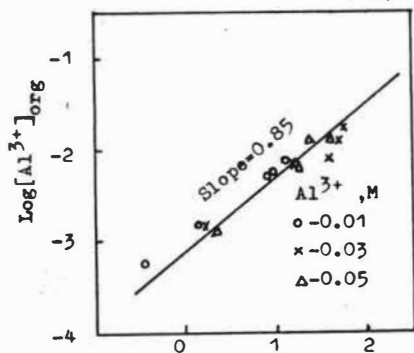


Fig. 5 Determination of polymerization degree of aluminium containing species extracted from nitric acid solutions by HEH/EHP

$$\text{Log} [\text{Al}]_{\text{aq}} + 3\text{pH} + 2.5 \text{Log} [(\text{H L})_2]_{\text{org}} - 2.5 (\text{Al})_{\text{org}}$$

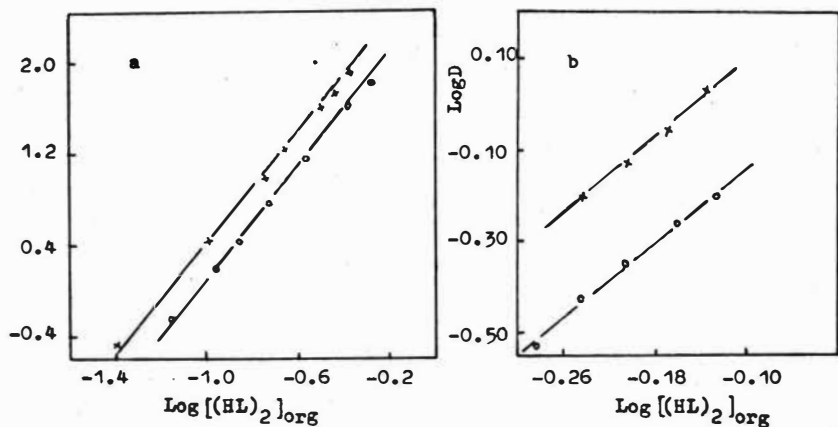


Fig. 2 Effect of HEH/EHP concentration on Er(III) extraction
 (a) $\text{LogD}-\text{Log}[(\text{HL})_2]_{\text{org}}$: x - 0.22N H₂SO₄ o - 0.31N H₂SO₄
 (b) $\text{LogD}-\text{Log}[(\text{HL})_2]_{\text{org}}$: x - 19.0N H₂SO₄ o - 17.9N H₂SO₄

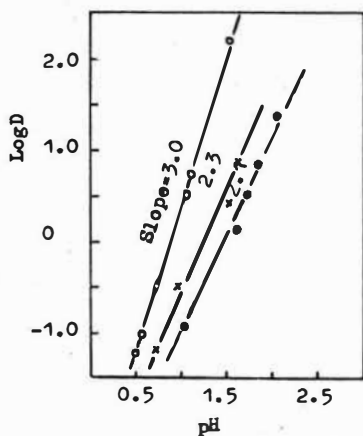


Fig. 3 Extraction of Al(III) from nitric acid solutions by HEH/EHP at various concentrations (HL)_{org}, M
 o-0.90 x-0.54 .-0.36

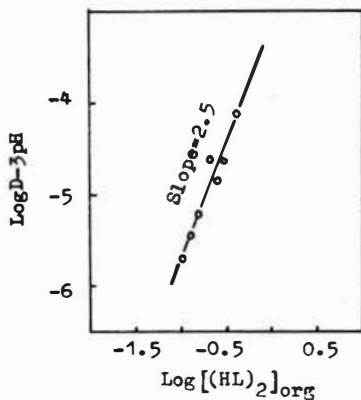


Fig. 4 Effect of HEH/EHP concentration on Al(III) extraction

Extraction systems for the separation of rare-earth elements of yttrium subgroup

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Moscow/USSR

The manuscript was not available at the 28th May 1986, the deadline for printing this book.

THE EFFECT OF SURFACTANTS ON THE EXTRACTION OF COPPER
FROM CHLORIDE SOLUTIONS

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Surfactants are being increasingly used in metal extraction using liquid surfactant membrane processes. Their main function is to -physically- stabilize the water-in-oil emulsion. However, the surfactants used may chemically influence the extraction of the metals.

The present paper presents the results of a study of the chemical effect of the surfactants on the extraction of copper by tri-n-lauryl ammoniumchloride. Emulsifiers representing the three different types of surfactants, i.e. anionic, cationic and non-ionic, were considered. The distribution of copper between aqueous chlorides solutions and toluene solutions of TLAHCl in the presence of varying concentrations of the different surfactants were determined.

The results of the study were considered in terms of complex formation between the different components involved. The decrease of the extraction of copper as a result of the addition of the surfactant was explained by its complexation with the amine salt. The enhancement of the copper extraction as a result of the addition of the surfactant was explained by the formation of mixed species, i.e. ammonium salt-surfactant-copper chloride. The formation constants of the different suggested species were determined. Estimates of the aggregation of the surfactants in the organic phase were obtained as well as their corresponding aggregation constants.

Interactions between surfactants and the ammonium salts were examined independantly using spectrophotometric methods in order to confirm results from metal distribution studies.

As the manuscript was not available at the 28th May 1986, the deadline for printing this book, we only print the short abstract of the paper.

Extraction of Divalent Metals from Chloride Solutions

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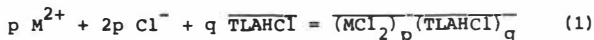
The extraction of divalent metal chlorides by long-chain tertiary amines has been studied by different authors (1-6) who described different aspects of the behaviour of these type of systems and gave details of their practical applications.

The interest for these systems has increased recently mainly because their close connections to some hydrometallurgical processes. In this sense, metal chloride hydrometallurgy, seems to demand deeper knowledge of the behaviour of the individual extraction systems.

Specific Interaction Theory (S.I.T.) (15) was employed in order to make a comparative study of the extraction of Cd(II), Pb(II), Zn(II) and Cu(II) chlorides by Tri-n-laurylammonium Chloride (TLAHCl), in aromatic diluents, and correlate the results at different ionic strength. The extractant TLAHCl represents in this case a model reagent for the behaviour of long-chain amines. The results obtained were expressed in terms of speciation in both phases.

Results of the Individual Systems

The extraction of a divalent metal ion by long-chain tertiary amine dissolved in organic diluent may be represented by the following general reaction:



(bars represents the organic phase)

Assuming ideal behaviour in the organic phase and taking into account that distribution data were taken at constant ionic strength, the stoichiometry extraction constant may be written

$$K_{pq} = \frac{|(MCl_2)_p|(TLAHC1)_q|}{|M^{2+}|^p|Cl^-|^{2p}|TLAHC1|^q} \quad (2)$$

Table I summarizes the results of the extraction of Zn(II), Cu(II), Pb(II) and Cd(II) at different ionic strength.

These results have been collected from different previous work (8,10,12,14) and have been expressed in terms of speciation and stability constants at both aqueous and organic phases.

As seen two different models have been determined which correspond to the different organic diluent employed in the study. Hence for Zn(II), Cu(II) and Pb(II) the species at the organic phase have the form $MeCl_2(TLAHC1)_2$ and $MeCl_2(TLAHC1)_5$ when toluene is used as organic solvent. In addition to this a trimer of the form $Me_3Cl_6(TLAHC1)_6$ has been found for the Zn(II) system in spite of its little relevance in the experimental conditions used. On the other hand, the Cd(II), studied in benzene, has been found to exist as $CdCl_2(TLAHC1)_2$ and $CdCl_2(TLAHC1)_3$ in the organic phase. These diverse results take into account the different behaviour of the TLAHC1 organic solutions with respect to the diluent. Thus, while TLAHC1 aggregates with a dimers formation in benzene(16), trimers are formed in toluene solutions(17).

The corresponding chlorocomplexes formed at the aqueous phase for the different metals are also contained in Table I, the values given for the stability constant of these complexes have been corrected to the given media from those reported in the literature(7,9,11,13) using the Specific Interaction Theory (S.I.T.).

Dependence of the Extraction Constants on the Ionic Strength

In order to correlate the values of the extraction constants at different ionic strength the following general equation was used:

$$\log K^I = \log K^0 - \frac{\Delta Z^2 A \sqrt{I}}{1 + 1.5 \sqrt{I}} + b(i,k) I_k \quad (3)$$

$$\text{with } \Delta Z^2 = \sum n_j Z_j^2 - \sum r_j Z_j^2$$

where n_j denotes the stoichiometric coefficients of the reacting ionic species of charge Z_j and r_j are the corresponding coefficients for the ionic species formed in eq. (1), K^I and K^0 represent respectively extraction constant at I and 0 ionic strength. $b(i,k)$ are the specific interaction coefficients between the species i and k , $A = 0.5107$ and I represents the ionic strength in mol.kg^{-1} .

Results of the different systems are given in Table II.

Conclusions

Results in Table I indicate that the extraction of the different metals may be explained assuming the formation of two species in the organic phase which composition seems to be independent of both the metal extracted and the chloride content in the aqueous phase. Nevertheless, the stoichiometry of these species strongly depends on the nature of the aromatic diluent. Hence, higher number of amine molecules bounded to the metal in toluene than in benzene was found which correspond to the higher aggregation of the amine salt in that diluent.

Quantitative results show that extraction efficiency follows the order $\text{Cd} > \text{Zn} > \text{Pb} > \text{Cu}$ (Fig. 1). Furthermore, when Cl^- concentration increases enhancement of the extraction is observed for all the metals except lead(II). On the other hand, only in this system coextraction of metal by the organic diluent was detected.

In order to clarify these results let us consider first the behaviour of the metal ion in the aqueous phase as chloride concentration increases (Fig. 1).

From this figure it seems that anionic metal chlorocomplex formation plays important role on the extraction reaction. Nevertheless two different situations has to be considered. In the case of Cd(II), Zn(II) and Cu(II) it is evident that anion formation in the aqueous phase produces enhancement of the extraction. This fact may give some support to the idea that the metallic anions participate in the extraction reaction. In the case of lead(II), however, the decrease of the extraction as lead anionic complexes increases (Fig. 1) may suggest a extraction reaction of different nature. Coextraction of lead by the organic solvent may suggest that neutral lead chloride directly participate on the extraction reaction facilitating the exchange reactions taking place in organic phase.

Data for different systems has allowed correlations of extraction constants at different ionic strength.

Table II contains the extrapolated values for constant at zero ionic strength and the values of the specific interaction coefficients for different ions in solution. Although the b_{i-k} values seems to be larger than those of the already reported (18), their magnitudes follow the order expected. In any case the use of solvent extraction as indirect technique to generate thermodynamic data in the aqueous phase must be considered as a useful tool.

Finally the applicability of these studies in the field of metal separation should be considered. Thus, from the results obtained the experimental conditions for some separations, i.e. Cd(II) from lead(II) or Zn(II) from Cu(II) can be easily designed.

These consequences will strength our future work on the practical determinations of the extraction mechanisms from kinetic data.

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TABLE I. RESULTS OF THE DIFFERENT SYSTEMS IN TERMS OF SPECIATION AND STABILITY CONSTANTS

Metal ion: Zn(II)

Organic diluent: Toluene

Aqueous solution	1.0M NaCl	2.0M NaCl	3.0M NaCl	species	phase	ref.
stability constants						
log β_{11}	-0.58	-0.93	-1.24	$ZnCl^+$	aq.	7
log β_{12}	-0.77	-1.14	-1.45	$ZnCl_2$	*	*
log β_{13}	-0.88	-1.22	-1.49	$ZnCl_3^-$	*	*
log β_{14}	-0.90	-1.30	-1.68	$ZnCl_4^{2-}$	*	*
log β_{122}	4.50	4.59	4.43	$ZnCl_2(TLHCl)_2$	org.	8
log β_{125}	9.71	9.94	8.76	$ZnCl_2(TLHCl)_5$	*	*
log β_{166}	15.54	10.30	--	$Zn_3Cl_6(TLHCl)_6$	*	*

Metal ion: Cu(II)

Organic diluent: Toluene

Aqueous solution	1.0M LiCl	2.0M LiCl	3.0M LiCl	species	phase	ref.
stability constants						
log β_{11}	0.19	0.13	0.13	$CuCl^+$	aq.	9
log β_{12}	-2.00	-1.85	-1.60	$CuCl_2$	*	*
log β_{13}	-1.70	-1.72	-1.68	$CuCl_3^-$	*	*
log β_{14}	-3.18	-3.20	-3.17	$CuCl_4^{2-}$	*	*
log β_{122}	1.61	1.84	2.27	$CuCl_2(TLHCl)_2$	org.	10
log β_{125}	5.73	6.21	6.79	$CuCl_2(TLHCl)_5$	*	*

Metal ion: Pb(II)

Organic diluent: Toluene

Aqueous solution	1.0M NaCl	2.0M NaCl	3.0M NaCl	species	phase	ref.
stability constants						
log β_{11}	0.73	0.65	0.61	$PbCl^+$	aq.	11
log β_{12}	0.99	0.90	0.89	$PbCl_2$	*	*
log β_{13}	0.84	0.76	0.78	$PbCl_3^-$	*	*
log β_{14}	0.10	0.05	0.06	$PbCl_4^{2-}$	*	*
log β_{122}	4.62	4.54	4.48	$PbCl_2(TLHCl)_2$	org.	12
log β_{125}	8.51	8.38	8.32	$PbCl_2(TLHCl)_5$	*	*

Metal ion: Cd(II)

Organic diluent: Benzene

Aqueous solution	1.0M NaCl	3.0M NaCl	species	phase	ref.
stability constants					
log β_{11}	2.27	2.20	$CdCl^+$	aq.	13
log β_{12}	3.41	3.20	$CdCl_2$	*	*
log β_{13}	3.57	3.40	$CdCl_3^-$	*	*
log β_{122}	9.35	10.09	$CdCl_2(TLHCl)_2$	org.	14
log β_{123}	11.28	11.59	$CdCl_2(TLHCl)_3$	*	*

Table II. Extrapolated values of the constants for the different systems calculated by using eq. (3). Interaction coefficients are also given.

Metal	Species	K^0	$b(i,k)$
Zn^{2+}	$ZnCl_2(TLAHCl)_2$	5.68	0.09
	$ZnCl_2(TLAHCl)_5$	11.37	
Cu^{2+}	$CuCl_2(TLAHCl)_2$	1.89	0.08
	$CuCl_2(TLAHCl)_5$	6.07	
Pb^{2+}	$PbCl_2(TLAHCl)_2$	5.80	-0.02
	$PbCl_2(TLAHCl)_2$	9.72	
Cd^{2+}	$CdCl_2(TLAHCl)_2$	9.80	0.49
	$CdCl_2(TLAHCl)_3$	11.78	

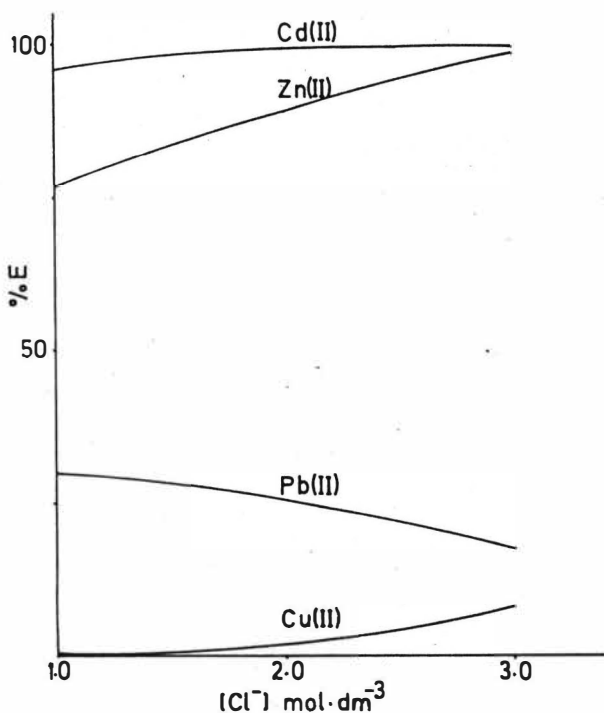


Fig. 1.- Percent of metal extracted plotted v.s. chloride concentration in the aqueous phase.

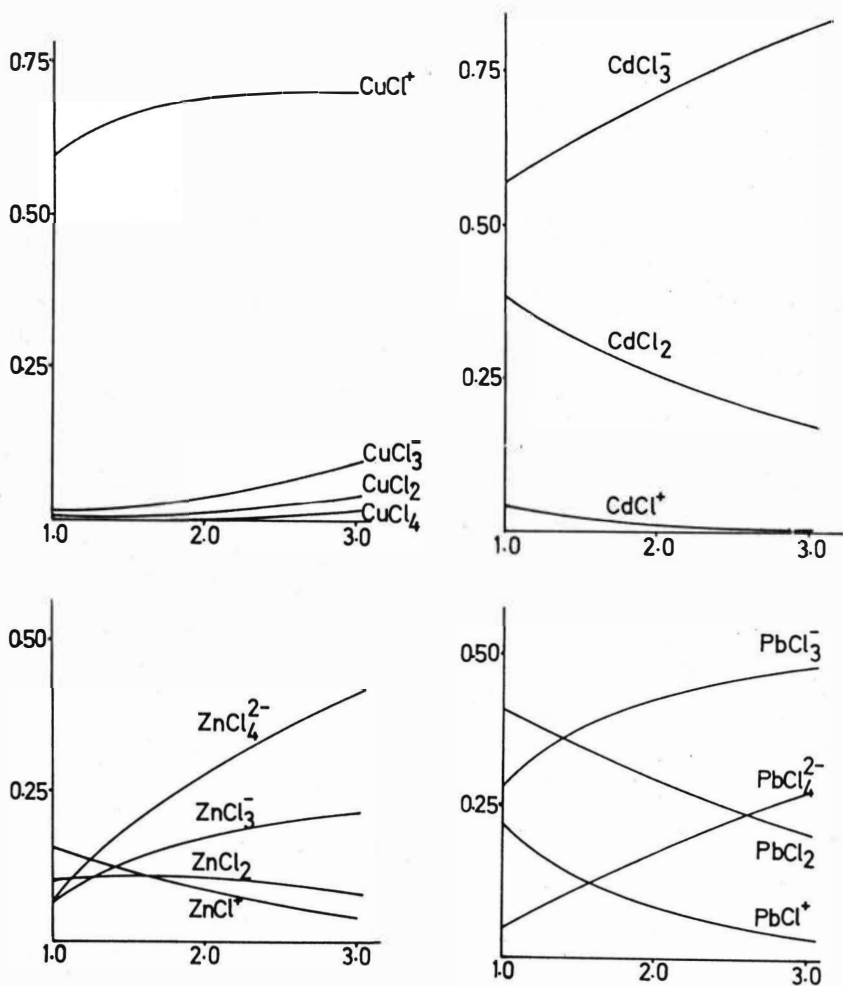


Fig. 2.- Fraction of metal chloride complexes plotted v.s. chloride concentration (mol.dm⁻³) in the aqueous solution.

The Catalytic Effect of LIX63 in the Extraction of Cu^{2+} and CuCl^+ with LIX34

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INTRODUCTION

The active component of the extractant LIX34 (registered trade mark of Henkel Corporation) is by the manufacturer reported (1) to have a relative molar mass of 438, thus being the largest chelating extractant molecule commercially available. It is an 8-(alkaryl)sulfonamidoquinoline (1), but the exact structure of the alkaryl group has not to our knowledge been disclosed by the manufacturer. Nakashio et al. (2) have stated that the active component of LIX34 is 8-(dodecylphenyl)sulfonamidoquinoline ($M_r=452$) and the same structure is reported by Flett et al. (3). Przeszlakowski and Iwaniuk (4) have assumed it to be 8-(nonylphenyl)sulfonamidoquinoline ($M_r=410$).

In isolating the active component of LIX34 (lot no. 6M16105) for kinetic studies we have found it to consist of at least eight isomers of a compound with the relative molar mass 438, as determined by gas chromatography - mass spectrometry. We thus conclude that the alkyl substituents on the benzene ring contain a total of eleven carbon atoms and support the M_r -value reported by the manufacturer (1). The detailed structure of the alkaryl group will be discussed elsewhere (5).

In addition to its large size the active component of LIX34, hereafter denoted HR, has several other properties which make it an interesting compound to compare with other chelating extractants. Because of its different structure HR does not exhibit the syn-anti isomerism of the hydroxy oximes and it is chemically stable. In comparison with 8-hydroxy-7-dodecenyloquinoline (Kelex 100, registered trade mark of Sherex Chemical Co.) HR has the advantage of not extracting acids.

A previous paper (6) from our laboratory reported a preliminary study of the kinetics of copper(II) extraction with HR from aqueous perchlorate solutions containing chloride. Chloroform was used as diluent in the extract phase in order to avoid complications arising from extractant aggregation, and the rate experiments were performed in a Lewis cell. Later investigations in our laboratory include a thorough study (7) of the catalytic effect of anti-5,8-diethyl-7-hydroxy-6-dodecanone oxime (hereafter denoted HB = the active component of LIX63, registered trade mark of Henkel Corporation) on the extraction of Cu^{2+} in a Lewis cell from aqueous perchlorate solutions of constant ionic strength (1000 mol/m^3 ; NaClO_4) using HR in chloroform as extractant. This study has recently been extended to systems containing chloride, and it is now possible to present a kinetic model which explains the catalytic effect of HB on the initial extraction rate of Cu^{2+} and CuCl^+ with HR in a Lewis cell. The calculated distribution of

copper species in the aqueous phase is based on a study of chloride complex formation which will be reported separately (8).

EXPERIMENTAL

Solvents and chemicals. All aqueous solutions were prepared from distilled water which had been further deionized with a Milli-Q Water Purification System. All other solvents and chemicals were of p.a. quality except for the extractants of which HB was isolated from commercial LIX63 according to the method of Tammi (9) and HR as the sodium salt from LIX34 using the method of Sandström (15). Because HR consists of several isomers differing in the alkaryl group care was taken to perform the rate experiments with a reagent of constant isomer distribution, as determined by gas chromatography.

Apparatus and experimental technique. The Lewis cell has been described in (16). It contained 150 cm³ of each phase, both phases being stirred independently in opposite directions at 3.75 s⁻¹, as measured with a digital photo tachometer. The Lewis cell was thermostated at 25.0°C and pH was maintained at the desired value to within 0.01 unit by manual addition of sodium hydroxide. To avoid disturbances due to precipitation of KClO₄ KCl was replaced by NaCl in the pH electrode (Radiometer GK2401-C). The extract (chloroform) phase was continuously pumped to a VARIAN DMS 90 UV-Visible spectrophotometer which recorded the absorbance of the complex CuR₂ at 473 nm.

THEORY AND EXPERIMENTAL RESULTS

1. Extraction of Cu²⁺ from chloride-free solutions with HR only

Nakashio et al. (2) have applied Langmuir's adsorption isotherm in modelling the Cu²⁺ extraction rate of 8-(dodecylphenyl)sulfonamidoquinoline, a compound which is structurally similar to HR. According to their results the rate-limiting step is a reaction between the charged intermediate and a second extractant molecule, both adsorbed at the interface. Using this approach an expression can be developed for the initial extraction rate with HR only.

If the first reaction step is fast equilibrium is maintained both at the interface and in the aqueous phase adjacent to it. Omitting the charges for simplicity we may write



$$[\text{CuR}]_i = K_1 [\text{Cu}]_i [\text{HR}]_i [\text{H}]_i^{-1} = K_1 K_{\text{DHR}}^{-1} [\text{Cu}]_i [\overline{\text{HR}}]_i [\text{H}]_i^{-1} \quad (2)$$

$$\text{where } K_{\text{DHR}} = [\overline{\text{HR}}]_i / [\text{HR}]_i \quad (3)$$

$[\overline{\text{HR}}]_i$ indicates the concentration of HR in the organic phase in the immediate vicinity of the interface while $[\text{HR}]_i$, $[\text{H}]_i$, $[\text{Cu}]_i$ and $[\text{CuR}]_i$ are the corresponding concentrations on the aqueous side of the

interface. At the interface itself concentrations are expressed per unit area and distinguished by the subscript "ads". If the free fraction of the interface is denoted θ the adsorption equilibria for the species HR and CuR may be written

$$\overline{\text{HR}}_i + \theta \xrightleftharpoons{K_{\text{HR}}} \text{HR}_{\text{ads}} \quad (4)$$

$$\text{CuR}_i + \theta \xrightleftharpoons{K_{\text{CuR}}} \text{CuR}_{\text{ads}} \quad (5)$$

For the interfacial concentrations $[\text{HR}]_{\text{ads}}$ and $[\text{CuR}]_{\text{ads}}$ one thus obtains the expressions

$$[\text{HR}]_{\text{ads}} = K_{\text{HR}} \theta [\overline{\text{HR}}]_i \quad (6)$$

$$[\text{CuR}]_{\text{ads}} = K_{\text{CuR}} \theta [\text{CuR}]_i \quad (7)$$

where θ in this case is given by equation (8):

$$\theta^{-1} = 1 + K_{\text{CuR}} S_{\text{CuR}} [\text{CuR}]_i + K_{\text{HR}} S_{\text{HR}} [\overline{\text{HR}}]_i \quad (8)$$

Here S_{CuR} and S_{HR} are the interfacial areas occupied by one mole of CuR and HR, respectively. The adsorption of the extraction product CuR_2 is assumed to be negligible. Assuming the rate controlling elementary reaction (9) and expressing $[\text{CuR}]_i$ with equation (2) we obtain the following equation for the initial extraction rate N_{Cu} :

$$\text{CuR}_{\text{ads}} + \text{HR}_{\text{ads}} \xrightarrow{k_9} \overline{\text{CuR}}_{2i} + \text{H}_i \quad (9)$$

$$\begin{aligned} N_{\text{Cu}} &= \frac{k_9 K_1 K_{\text{CuR}} K_{\text{HR}} [\text{Cu}]_i [\overline{\text{HR}}]_i^2}{K_{\text{DHR}} [\text{H}]_i (1 + K_{\text{CuR}} S_{\text{CuR}} K_{\text{DHR}}^{-1} [\text{Cu}]_i [\overline{\text{HR}}]_i [\text{H}]_i^{-1} K_{\text{HR}} S_{\text{HR}} [\overline{\text{HR}}]_i)^2} \\ &= \frac{k'_{10} [\text{Cu}]_i [\overline{\text{HR}}]_i^2}{[\text{H}]_i (1 + K'_{\text{CuR}} [\text{Cu}]_i [\overline{\text{HR}}]_i / [\text{H}]_i + K'_{\text{HR}} [\overline{\text{HR}}]_i)^2} \end{aligned} \quad (10)$$

The differences between the bulk concentrations and the corresponding concentrations close to the interface were calculated from the experimental extraction rate using appropriate mass transfer coefficients for the aqueous and organic interfacial films:

$$[\text{Cu}]_i = [\text{Cu}] - N_{\text{Cu}}/k_{\text{Cu}} = [\text{Cu}] - N_{\text{Cu}}/7.0 \times 10^{-6} \text{ m/s} \quad (11)$$

$$[\text{H}]_i = [\text{H}] + 2N_{\text{Cu}}/k_{\text{H}} = [\text{H}] + 2N_{\text{Cu}}/4.0 \times 10^{-5} \text{ m/s} \quad (12)$$

$$[\overline{\text{HR}}]_i = [\overline{\text{HR}}] - 2N_{\text{Cu}}/k_{\text{HR}} = [\overline{\text{HR}}] - 2N_{\text{Cu}}/1.3 \times 10^{-5} \text{ m/s} \quad (13)$$

The film coefficients in the equations (11) - (13) are based on estimates for our Lewis cell made by Paatero (10), who studied copper extraction with 2-hydroxy-5-nonylbenzophenone oxime isolated from LIX65N (registered trade mark of Henkel Corporation). His k_{HR} value ($1.5 \times 10^{-5} \text{ m/s}$) was modified for our extractant by estimating the

corresponding diffusivities according to Wilke and Chang (11).

The experimental rate data covered the following concentration ranges: (13.3 - 100) mol m⁻³ copper(II), (10-90) mol m⁻³ HR, (3.16 - 31.6) mol m⁻³ H⁺. Fitting of the data to equation (10) by nonlinear regression analysis yielded the following constants:

$$k_{10} = k_9 K_1 K_{CuR} K_{HR} / K_{DHR} = (3.19 \pm 0.48) \times 10^{-9} \text{ m}^4 \text{mol}^{-1} \text{s}^{-1} \quad (14)$$

$$K_{CuR} = K_1 K_{CuR} S_{CuR} / K_{DHR} = (2.69 \pm 0.48) \times 10^{-3} \text{ m}^3 \text{mol}^{-1} \quad (15)$$

$$K_{HR} = K_{HR} S_{HR} = (7.73 \pm 1.38) \times 10^{-3} \text{ m}^3 \text{mol}^{-1} \quad (16)$$

2. The effect of HB on the extraction of Cu²⁺ with HR

As shown by Figure 1 the rate curves obtained when adding small increments of HB to the Lewis cell clearly indicate that HB catalyzes the extraction by at least two mechanisms, one predominating at low and the other one at higher HB concentrations.

HB may be expected (12,13) to form a complex CuB⁺ (analogous to CuR⁺) whose equilibrium concentration in the aqueous film is given by equation (17), which is analogous to equation (2) (K₁₇ is the equilibrium constant analogous to K₁ in reaction (1)):

$$[CuB]_i = K_{17} K_{DHB}^{-1} [Cu]_i [\overline{HB}]_i [H]_i^{-1} \quad (17)$$

Since CuB₂ is not formed at low pH an uncharged complex can only be formed with HR at the interface where CuB⁺ is strongly adsorbed:



The same mixed complex is formed according to reaction (19). The



further reaction of CuRB to the more stable end product CuR₂ (12,13), is a fast homogeneous reaction which regenerates the catalyst HB without affecting the kinetic expression. HB is more interfacially active than HR and it is thus strongly adsorbed at the interface. Terms describing the adsorption of CuB⁺ and HB must therefore now be included in the expression for θ where the new primed constants K'_{CuB} and K'_{HB} are analogous to K'_{CuR} and K'_{HR} (defined in equations (15) and (16), respectively):

$$\theta^{-1} = 1 + K'_{CuR} [Cu]_i [\overline{HR}]_i [H]_i^{-1} + K'_{CuB} [Cu]_i [\overline{HB}]_i [H]_i^{-1} + K'_{HR} [\overline{HR}]_i + K'_{HB} [\overline{HB}]_i \quad (20)$$

The individual rate contributions of reactions (18) and (19) cannot be distinguished since they are described by equations of the same form. Obviously they represent the interfacial catalytic mechanism responsible for the rapid rate increase at low $[\overline{HB}]$. The effect at high $[\overline{HB}]$ could only be modelled by assuming a pseudo-first order reaction in

which HB diffuses into the aqueous film where it simultaneously reacts with CuR^+ , which is maintained at constant equilibrium concentration:



In order to obtain good agreement with the experimental data at low pH (down to 1.50) it was necessary to assume that HB becomes partly inactivated by protonation while diffusing into the aqueous phase:



A similar approach has recently been taken by Nicol et al. (14) in studying homogeneous reaction kinetics with a much less basic aromatic hydroxy oxime in 80% ethanol.

Development of rate expressions according to the model outlined above, including the noncatalytic rate equation (10) modified by using the θ -expression given by (20), yielded the following expression for the total extraction rate N_{tot} ($=A+B+C$) in the presence of HB:

$$\begin{aligned} N_{\text{tot}} &= k_{10} [\text{Cu}]_i [\overline{\text{HR}}]_i^2 \theta^2 / [\text{H}]_i + \\ & (k_{18} K_{17} K_{\text{CuB}} K_{\text{HR}} / K_{\text{DHB}} + k_{19} K_{17} K_{\text{CuR}} K_{\text{HB}} / K_{\text{DHR}}) [\text{Cu}]_i [\overline{\text{HR}}]_i [\overline{\text{HB}}]_i \theta^2 / [\text{H}]_i + \\ & \frac{[\overline{\text{HB}}]_i}{(1 + K_{22} [\text{H}]_i) K_{\text{DHB}}} (D_{\text{HBaq}} k_{21} K_{17} K_{\text{DHR}}^{-1} [\text{Cu}]_i [\overline{\text{HR}}]_i [\text{H}]_i^{-1})^{0.5} \\ & = \frac{k_{10} [\text{Cu}]_i [\overline{\text{HR}}]_i^2 \theta^2}{[\text{H}]_i} + \frac{k_{23} [\text{Cu}]_i [\overline{\text{HR}}]_i [\overline{\text{HB}}]_i \theta^2}{[\text{H}]_i} + \\ & \frac{k_{23} [\overline{\text{HB}}]_i}{(1 + K_{22} [\text{H}]_i)} ([\text{Cu}]_i [\overline{\text{HR}}]_i / [\text{H}]_i)^{0.5} = A + B + C \quad (23) \end{aligned}$$

In equation (23) D_{HBaq} stands for the diffusivity of HB in the aqueous film and k_{10} is given by equation (14). The constants K_{22} , k_{23} and K_{23} as well as the new constants K_{CuB} and K_{HR} in θ (equation (20)) were determined as follows by nonlinear regression analysis of the experimental data:

$$K_{22} = (0.0188 \pm 0.0039) \text{ m}^3 \text{mol}^{-1} \quad (24)$$

$$\begin{aligned} k_{23} &= k_{18} K_{17} K_{\text{CuB}} K_{\text{HR}} / K_{\text{DHB}} + k_{19} K_{17} K_{\text{CuR}} K_{\text{HB}} / K_{\text{DHR}} \\ &= (2.05 \pm 0.25) \times 10^{-6} \text{ m}^4 \text{mol}^{-1} \text{s}^{-1} \quad (25) \end{aligned}$$

$$\begin{aligned} K_{23} &= (k_{21} K_{17} D_{\text{HBaq}} / K_{\text{DHR}})^{0.5} / K_{\text{DHB}} \\ &= (0.615 \pm 0.026) \times 10^{-6} \text{ m}^{2.5} \text{mol}^{-0.5} \text{s}^{-1} \quad (26) \end{aligned}$$

$$K_{\text{CuB}} = K_{17} K_{\text{CuB}} K_{\text{CuB}} / K_{\text{DHB}} = (0.128 \pm 0.038) \text{ m}^3 \text{mol}^{-1} \quad (27)$$

$$K_{\text{HB}} = K_{\text{HBSHB}} = (2.84 \pm 0.31) \text{ m}^3 \text{mol}^{-1} \quad (28)$$

Equation (23) agrees quite well with the experimental data, as illustrated in Figure 1.

3. The effect of HB on the extraction of Cu^{2+} and CuCl^+

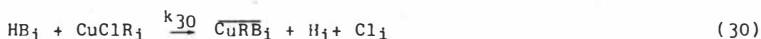
A separate study yielded the values $1.4 \text{ dm}^3\text{mol}^{-1}$ and $0.60 \text{ dm}^6\text{mol}^{-2}$ for the stability constants of CuCl^+ and CuCl_2 , respectively (8). Using these constants it was possible to compare the copper(II) extraction rates from solutions with and without chloride having equal concentrations of free cupric ion. An estimate of the extraction rate for CuCl^+ could then be obtained by subtraction. Somewhat surprisingly, the resulting difference was found to pass a distinct minimum as a function of the HB concentration except at the lowest HR concentrations, where a slight monotonous increase was noted.

In the absence of HB the extraction rate of CuCl^+ could best be described by assuming an interfacial reaction between $\text{CuClR}_{\text{ads}}$ and HR_{ads} to be rate controlling:



The rate expression thus contained θ^2 but attempts to include a term describing the adsorption of CuClR in the expression for θ (eq. (20)) failed to give a significant constant $K_{\text{CuClR}} (=K_{31}K_{\text{CuClR}}K_{\text{DHR}}^{-1})$. This probably means that CuClR is very weakly adsorbed but reacts rapidly with HR_{ads} (high k_{29}). A model assuming a homogeneous reaction between CuClR_i and HR_i in the organic film also fitted the rate data reasonably well, and the ability of CuClR to penetrate into the bulk of the extract phase was manifested as a sudden turbidity caused by the liberation of HCl drops. This turbidity was observed spectrophotometrically in experiments with high CuCl^+ and low HR concentrations, but the interfacial mechanism (29) appeared to be rate-controlling with normal concentration ratios.

Addition of HB rapidly displaces the weakly adsorbed CuClR from the interface, thus decreasing the rate according to (29) and causing the experimentally observed minimum. The increasing rate at high $[\text{HB}]$ is best explained by a pseudo-first order reaction (30) in the aqueous film between CuClR_i (at equilibrium concentration) and HB diffusing from the interface. The equilibrium concentration of CuClR in the aqueous film is expressed by equation (31).



$$[\text{CuClR}]_i = K_{31}K_{\text{DHR}}^{-1} [\text{CuCl}]_i [\text{HR}]_i [\text{H}]_i^{-1} \quad (31)$$

The models outlined above gave two new terms, D_1 and D_2 , to be added to the terms A, B and C in equation (23):

$$\begin{aligned} N_{\text{CuCl}} &= k_{32} \frac{[\text{CuCl}]_i [\text{HR}]_i^2 \theta^2}{[\text{H}]_i} + k_{32} \frac{[\text{HB}]_i [\text{CuCl}]_i^{0.5} [\text{HR}]_i^{0.5}}{(1+K_{22}[\text{H}]_i)[\text{H}]_i^{0.5}} \\ &= \quad \quad \quad D_1 \quad \quad \quad + \quad \quad \quad D_2 \quad \quad \quad (32) \end{aligned}$$

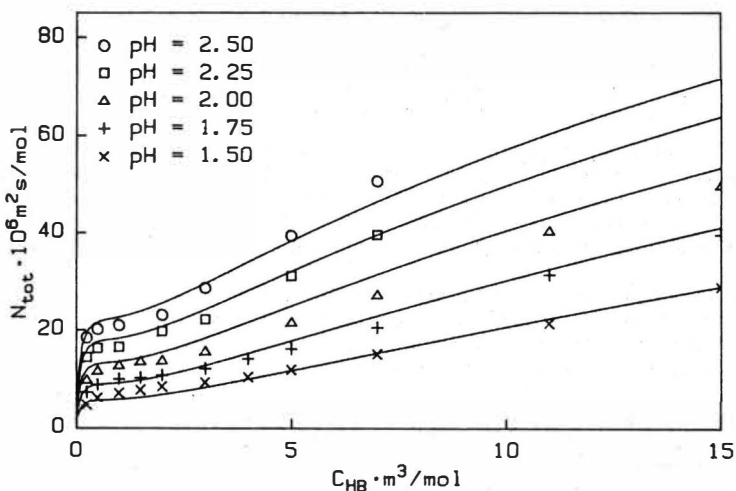


Figure 1. The effect of $[HB]$ at different pH values and constant $[Cu]$ ($=33.3 \text{ mol m}^{-3}$) and $[HR]$ ($=33 \text{ mol m}^{-3}$). Curves according to equation (23).

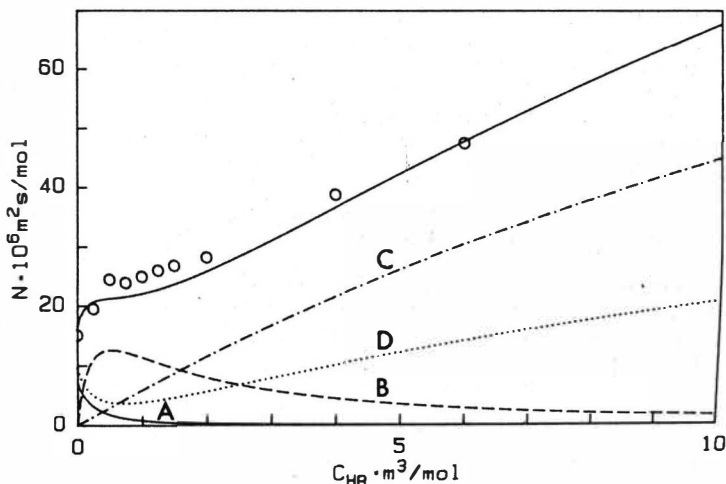


Figure 2. Effect of $[HB]$ on the total extraction rate at constant total $[Cl]$ ($=400 \text{ mol m}^{-3}$), $[Cu]$ ($=33.3 \text{ mol m}^{-3}$), $[CuCl]$ ($=19.0 \text{ mol m}^{-3}$), $[HR]$ ($=50 \text{ mol m}^{-3}$) and pH ($=2.00$). Curves showing contributions from the terms A, B, C and D ($=D_1+D_2$) computed with equations (23) and (32).

For k_{32} and k_{32}^* regression analysis gave

$$k_{32}^* = k_{29}K_{31}K_{CuClR}/K_{DHR} = (8.19 \pm 0.72) \times 10^{-9} \text{ m}^4\text{mol}^{-1}\text{s}^{-1} \quad (33)$$

$$k_{32} = (D_{HBaq}k_{30}K_{31}/K_{DHR})^{0.5}/K_{DHB} \\ = (0.397 \pm 0.025) \times 10^{-6} \text{ m}^2.5\text{mol}^{-0.5}\text{s}^{-1} \quad (34)$$

The distribution of aqueous copper species was computed from the stability constants of CuCl^+ and CuCl_2 and the mass transfer through the aqueous film was assumed to be approximately described by equation (13) using the total extraction rate for Cu(II) . Since HB is not consumed $[\text{HB}]_1$ was always assumed equal to $[\text{HB}]$.

Figure 2 illustrates the contributions of the different terms A, B, C and D ($=D_1+D_2$) in the total rate model, which is the sum of equations (23) and (32). It is of particular interest to note that curve D has a minimum, in agreement with experiments.

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Interphase Transfer Kinetics from Transport Measurements Through Supported Liquid Membranes*

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Supported Liquid Membranes (SLM) consist of thin layers of organic solutions of solvent extraction reagents (carriers) absorbed on microporous polymeric films (1). When SLM's are interposed between two different aqueous solutions of suitable composition (Feed and strip) they can perform selective separations of chemical species. The permeation through SLM's can be described as the combination in a single stage of an extraction and a stripping step, occurring in non-equilibrium conditions. The permeability coefficient of metal species through SLM's has been derived (1) by combining two diffusional resistances (through the aqueous boundary layer and the SLM itself) and one chemical resistance, arising from possible slow chemical reactions. When the permeating metal species are present at low concentrations, the equation correlating the pseudo first order rate constant of the slow chemical reaction between the metal-containing species and the carrier, to the SLM permeability coefficient, P (cm/s), is

$$P = \frac{K_1}{K_1 \Delta_a + K_{-1} \Delta_o + 1} \quad (1)$$

In Equation (1) K_1 and K_{-1} are the forward and reverse pseudo first order rate constants of the above mentioned reaction. This is assumed to take place at the interface or in an aqueous zone very close to the interface. Δ_a and Δ_o are the aqueous and liquid membrane diffusional parameters (1). They are defined as $\Delta_a = d_a/D_a$ and $\Delta_o = d_o/D_o$, where D_a = aqueous diffusion coefficient of metal species, d_a = thickness of aqueous boundary layer, D_o = liquid membrane diffusion coefficient of the metal-carrier complex, d_o = thickness of the SLM. By

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considering that the distribution ratio of the metal species between the organic liquid membrane and the adjacent aqueous feed solution, K_d , is equal to:

$$K_d = \frac{K_1}{K_{-1}} \quad (2)$$

Equation (1) can be rearranged in the form

$$P^{-1} = \Delta_a + \Delta_a/K_d + K_1^{-1} \quad (3a)$$

or

$$R_T = R_a + R_o + R_c \quad (3b)$$

where P^{-1} = total membrane resistance (R_T), Δ_a = aqueous film diffusion resistance (R_a), Δ_o/K_d = membrane diffusional resistance (R_o) and K_1^{-1} = chemical resistance (R_c). By independently measuring P , K_d , Δ_a , and Δ_o , the pseudo first order rate constant of the forward chemical reaction can be evaluated from:

$$K_1 = (P^{-1} - \Delta_a - \Delta_o/K_d)^{-1} \quad (4)$$

The rate law describing the slow chemical process can be in turn derived by experimentally studying the dependence of K_1 on the concentration of the various components of the system. From the rate law we can then derive useful information on the mechanism controlling the extraction of the metal species into the organic phase which is used as liquid membrane.

In this work the above described approach has been used for studying the extraction kinetics of Eu^{3+} and few other selected lanthanide and actinide cations, by bis(2-ethylhexyl) phosphoric acid (HDEHP) in n-dodecane from aqueous solutions containing a polyaminocarboxylic acid (HEDTA) and lactic acid (HL). HDEHP represents in this case the SLM carrier. The system has practical interest for the separation of lanthanide from actinide cations present in nuclear waste streams (TALSPEAK process (2)) and is characterized by slow extraction kinetics (2,3). Since actinide cations are more strongly complexed by HEDTA than the lanthanide cations, the latter are better extracted by HDEHP. In this way a separation between the two groups is possible. Lactic acid, a complexant itself, is added to the system to speed up the slow extraction reactions by HDEHP. Figure 1A shows the formulas and abbreviations of the reagents used in this investigation. A schematic description of the SLM system studied is given in Figure 1B. The permeability coefficient of Eu^{3+} (and the other selected cations) through the SLM was measured for various concentrations of the aqueous complexing reagents at different acidities. The following concentration ranges were studied: from 0 to

0.09 M for HEDTA, from 0 to 1.0 M for HL and from $1.3 \times 10^{-4} M$ to $8.5 \times 10^{-3} M$ for H^+ . The permeability coefficient, P , was calculated from the slope of the straight lines obtained by plotting on a semilogarithmic scale the metal species concentration in the feed solution vs time. Figure 2A shows two of such plots as well as the equation used to calculate P . C and C_0 are the metal species concentrations in the feed solution at time = t (sec) and time = 0, respectively. Figure 2B shows an example of primary data in the form of $\log K_d$ vs $[HL]$ and $\log P$ vs $[HL]$ plots. Similar sets of data were obtained by varying the HEDTA and the H^+ concentrations, while keeping the HL and H^+ concentrations constant ($[HEDTA]$ variation) and the HL and HEDTA concentrations constant ($[H^+]$ variation), respectively. The values of Δ_a and Δ_o , necessary to calculate K_1 , were evaluated from permeation experiments performed in absence of HEDTA. In this situation the chemical reactions can be considered instantaneous and the following values were obtained: $\Delta_a = 6.3 \times 10^2$ (s/cm) and $\Delta_o = 1.2 \times 10^4$ (s/cm). The independence of Δ_a from $[HL]$ and $[HEDTA]$ was verified by directly measuring the diffusion coefficient of Eu^{3+} in aqueous solutions by the capillary method. The pseudo first order rate constants, calculated by Eq. (4), were then plotted vs $[HL]$, $[HEDTA]$ and $[H^+]$ on log-log scales. The $\log K_1$ vs $\log [HL]$ plot is shown in Figure 3A. A straight line with slope + 1 is in this case obtained. Similar plots, obtained by plotting $\log K_1$ vs $\log [HEDTA]$ and $\log K_1$ vs $\log [H^+]$, gave straight lines with slopes equal to -1($HEDTA$) and + 1 (H^+). Each set of experimental data was also plotted in terms of R_T , R_C , R_A , and R_O vs $[HL]$, $[HEDTA]$ and $[H^+]$ in order to evaluate the variation of the various resistances with the chemical composition of the system. An example of such a plot is shown in Figure 3B.

From the logarithmic dependencies of K_1 on the concentrations it follows that the extraction of the metal species can be described by the rate law

$$\text{Rate} = K \frac{[Eu]_T [HL]_T [H^+]_e}{[H_3Y]_T} \quad (5)$$

In Eq. (5) K is a combination of rate and equilibrium constants and the subscripts T and e indicate total and equilibrium aqueous concentrations. Rate law (5) can be used to obtain information on the mechanism of the extraction reaction and the accelerating role of lactic acid. From the metal ion complex formation constants (4), the following approximate relations hold in the concentration range investigated by us:

$$[Eu]_T \sim [EuY] = [Eu^{3+}] [Y^{3-}] \quad (6)$$

$$[HL]_T \sim [HL] = [H^+] [L^-] \quad (7)$$

$$[H_3Y]_T \sim [H_2Y^-] = [Y^{3-}] [H^+]^2 \quad (8)$$

By substituting Eqns. (6), (7), (8) into Eqns. (5) we then obtain

$$\text{Rate} \propto [\text{Eu}^{3+}] [\text{L}^-] \propto [\text{EuL}^{2+}] \quad (9)$$

Rate Eqn. (9) indicates that to a first approximation the predominating step of the extraction reaction is



and explains the increase in extraction rate with the increase in lactic acid concentration. A more refined treatment of the rate law (5), taking into account also the concentrations of the less abundant species, leads to the extraction mechanism schematically described in Figure 4.

Assuming that the same mechanism also holds for the other actinide and lanthanide trivalent cations, the pseudo first order rate constants of Pm^{3+} , Am^{3+} and Cf^{3+} were evaluated. Similar numerical values were obtained in spite of appreciable differences in the permeation rates. The lanthanide cations were in all cases showing higher values of the permeability coefficients. This result indicates that no kinetic selectivity is present in the system and that the faster permeabilities of the lanthanide cations is entirely attributable to the higher K_d values of these ions.

As far as the possibility of studying interphase mass transfer kinetics from transport measurements through SLM's is concerned, the new method possesses the following advantages over previously used techniques (constant interfacial area stirred cell, highly stirred flasks, falling or rising drop):

1. the diffusional contributions through the boundary layers or inside the droplets of the dispersed phase are never neglected,
2. very small volumes of organic phase are needed (about 0.100 ml),
3. very simple equipment is required.

The major disadvantage, common also to the previously used techniques, is that chemical resistances lower than 10^2 sec/cm are difficult to measure.

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Aqueous Complexing Agents

$$\begin{array}{c} \text{HO}-\text{CH}_2-\text{CH}_2 \qquad \qquad \text{CH}_2\text{COOH} \\ \qquad \qquad \qquad \diagdown \qquad \diagup \\ \qquad \qquad \qquad \text{N}-\text{CH}_2-\text{CH}_2-\text{N} \\ \qquad \qquad \qquad \diagup \qquad \diagdown \\ \text{HOOCCH}_2 \qquad \qquad \text{CH}_2\text{COOH} \end{array} = \text{HEDTA or H}_3\text{Y}$$

$$\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{COOH} = \text{HL (lactic acid)}$$

SLM Carrier (0.1 F in n-dodecane)

$$\begin{array}{c} \text{I}[\text{CH}_3-(\text{CH}_2)_3-\text{CH}-\text{CH}_2-\text{O}]_2\text{P} \\ \qquad \qquad \qquad \text{CH}_2 \\ \qquad \qquad \qquad \text{CH}_3 \end{array} \begin{array}{c} \text{O} \\ \parallel \\ \text{OH} \end{array} = \text{HDEHP or HX}$$

SLM Support

Celgard® 2500, 25μm thick microporous polypropylene

FEED	SLM	STRIP
$[\text{NaCl}] = 1 \text{ M}$ $[\text{HEDTA}] = 0 \text{ to } 0.09 \text{ M}$ $[\text{HL}] = 0 \text{ to } 1.0 \text{ M}$ $[\text{H}^+] = 1.3 \times 10^{-4} \text{ to } 8.5 \times 10^{-3} \text{ M}$ $[\text{Eu(III)}] = \text{tracer}$	0.1 F HDEHP in $n\text{-dodecane}$ $\text{Celgard}^{\text{®}} 2500$	1 M HCl


Eu(III) 

Fig. 2A

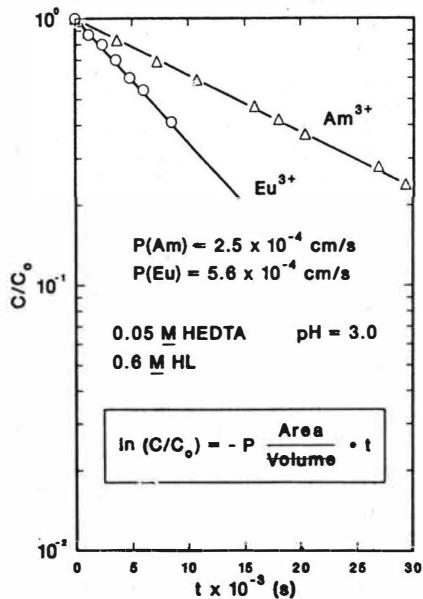


Fig. 2B

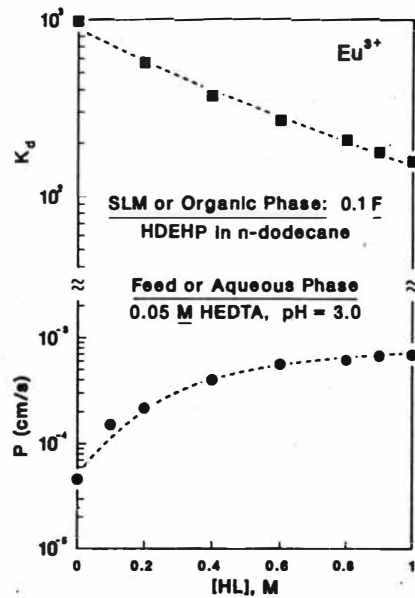


Fig. 3A

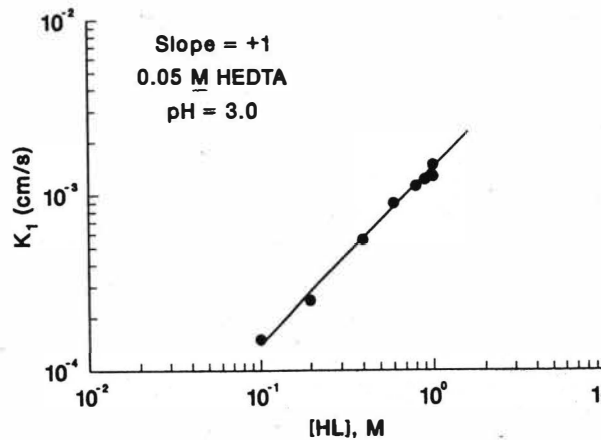


Fig. 3B

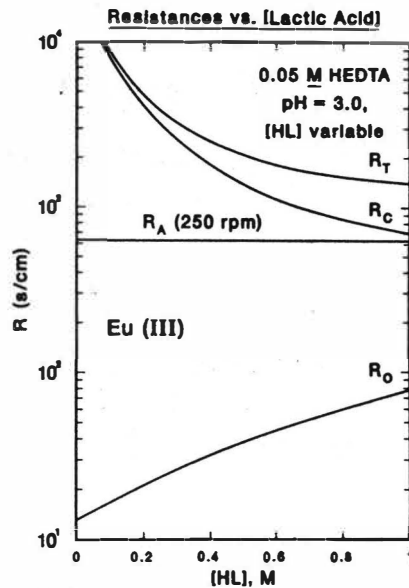
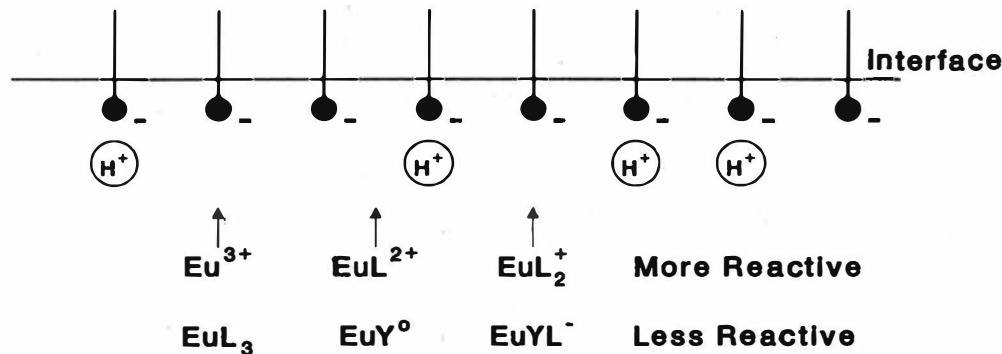


Fig. 4

Organic Phase (SLM)

Adsorbed layer of HDEHP molecules
HDEHP is partly dissociated



Aqueous Phase (Feed)

Eu aqueous species in equilibrium

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1. Introduction

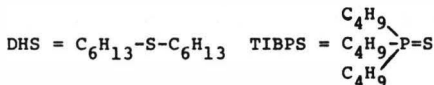
It is well known that sulfur containing extractants are highly selective to palladium(II). National Institute for Metallurgy of South Africa developed a separation process for the refining of precious metals using solvent extraction techniques which have potential economic advantages over conventional selective precipitation process on a commercial scale.¹⁾ In this process, dihexyl sulfide was used as a selective extractant to palladium(II) over platinum(IV); that is, palladium can be separated from platinum utilizing a very large difference in the extraction rates between these metals. A similar process was developed by INCO and has been successfully operated at their Acton precious metal refinery at West London,²⁾ where dioctyl sulfide has been used instead of dihexyl sulfide. However, dialkyl sulfides have a big drawback of slow extraction rate of palladium. Recently, American Cyanamid Co. developed a novel commercial extractant, CYANEX 471, the active species of which is triisobutylphosphine sulfide.³⁾ This reagent is said to have a superior extraction rate of palladium to dialkyl sulfides.

Extensive works have been done on the extractions of various metals by various sulfur containing extractants, especially dialkyl sulfides, their oxides and dialkyldithiophosphoric acids. However, the majority of these works are limited to those on extraction equilibria or their hydrometallurgical applications and no works have been done on the extraction kinetics with these extractants. In the present study, extraction kinetics of palladium with a dialkyl sulfide and a trialkylphosphine sulfide from chloride media were investigated to elucidate their extraction mechanism.

2. Experimental

2.1 Reagents

As a dialkyl sulfide, SFI-6, which was supplied by Daihachi Chemical Industry Co., Ltd., Japan, was used without further purification. This commercial extractant contains dihexyl sulfide, abbreviated as DHS hereafter, with the purity above 98%. As a trialkylphosphine sulfide, triisobutylphosphine sulfide, abbreviated as TIBPS hereafter, was used. This reagent was purified from CYANEX 471, donated by American Cyanamid Co., by recrystallization from ethanol-water mixture. Toluene was used as a diluent. Palladium(II) was extracted from aqueous NH_4Cl solutions



with DHS and from HCl with TIBPS. Organic solutions were prepared on a gravimetric basis by diluting the extractants with toluene to a required concentration.

2.2 Measurement of Extraction Rates

The Lewis cell was used for the measurement of extraction rate with DHS. The extraction rate was measured at 303 K as follows. After the introductions of equal volumes of the aqueous and organic phases, the stirring of both phases was initiated in opposite directions at a constant speed of 150 rpm. In the preliminary experiment, the extraction rate was confirmed to be independent of the stirring speed in the range greater than 150 rpm. The time variation of palladium concentration in the organic phase was measured by atomic absorption spectrochemical analysis after stripping of palladium with $2 \text{ mol/dm}^3 \text{ NH}_3$.

A batch-type stirred glass cell was used for the measurement of the extraction rate with TIBPS. The cell was fitted with four baffles. Stirring was carried out using an impeller with six flat blades connected with a speed controller. After the introductions of equal volumes of hydrochloric acid and the organic solution, stirring was initiated and aqueous samples were taken at time intervals to measure the time variation of palladium concentration in the aqueous phase. In the preliminary experiment, it was found that the extraction rate is independent of the stirring speed over the range 1300-1500 rpm. Then, the subsequent experiments were carried out at a constant stirring speed of 1400 rpm.

3. Distribution Equilibria of Palladium and Interfacial Adsorption Equilibria of the Extractants

Prior to the kinetic study, the distribution equilibria of palladium and interfacial adsorption equilibria of the extractants were investigated. But, only loading tests were carried out in the study of the distribution equilibria to examine the mole ratios of palladium extracted in the organic phase to the extractants since palladium was completely extracted under the conditions of excess concentrations of the extractants over palladium, which made it difficult to carry out the quantitative analysis. Figure 1 shows the results of the loading tests, which indicate that the mole ratio asymptotically approaches to 2 in the extraction with DHS and to 1 in that with TIBPS. The stoichiometric relations of these extraction reactions are considered to be described as follows. $\text{PdCl}_2 + 2\text{S} \rightleftharpoons \text{PdS}_2\text{Cl}_2$ (1) for the extraction with DHS. And $2\text{PdCl}_2 + 2\text{S} \rightleftharpoons \text{Pd}_2\text{S}_2\text{Cl}_4$ (2) for that with TIBPS.

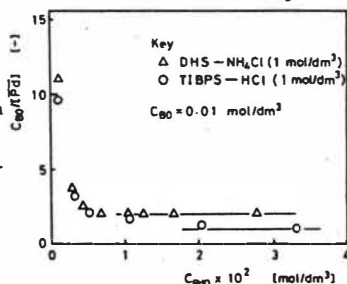


Fig.1 Results of the loading test

Figure 2 shows the relation between the interfacial tension (γ) and the concentrations of the extractants (C_{B0}). These results indicate that both DHS and TIBPS are interfacially active and adsorbed at the interface. Based on the Langmuir's monolayer adsorption model, adsorptions of these extractants are expressed by $\bar{S} \rightleftharpoons S_{ad}$ K_{ad} (3) Interfacial tension is correlated with the extractant concentration in the organic phase based on the Gibbs' adsorption isotherm as expressed by Eq. (4).⁵⁾

$\gamma = \gamma_0 - (RT/S_s) \ln(1 + K_{ad}(\bar{S}))$ (4) where γ_0 is the interfacial tension between toluene and the aqueous phase. S_s denotes the interfacial area occupied by unit mole of the extractant.

K_{ad} and S_s were evaluated from the experimental results shown in Fig.2 according to Eq. (4) as listed in Table 1. The solid lines in Fig.2 are the calculated curves based on Eq. (4) using these values. These are in good agreement with the experimental result

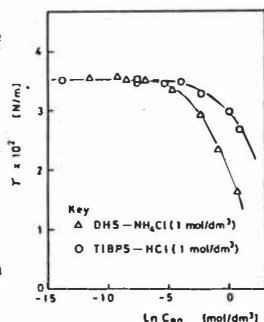


Fig.2 Relation between interfacial tension and the extractant concentration

4. Experimental Results

4.1 Extraction Rate with DHS

Initial extraction rate was calculated from the linear relation between the palladium concentration in the organic phase and contact time.

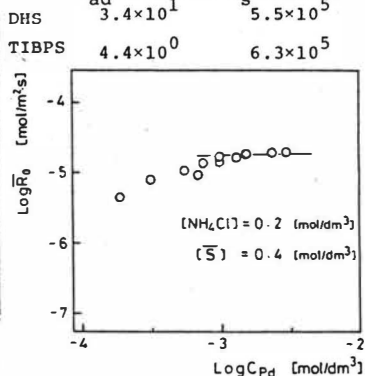
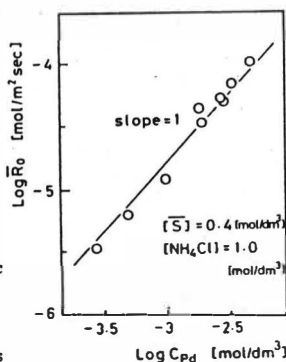
Figure 3 shows

the effect of

the effect of palladium concentration in the aqueous phase on the initial extraction rate from 1 mol/dm³ NH₄Cl solution. The plots are lying on a straight line of slope 1 in this concentration region. Figure 4 shows that in the extraction from 0.2 mol/dm³ NH₄Cl solution. Although the initial extraction rate increases with increasing palladium concentration in its low concentration region as in Fig.3, it tends toward a constant value in its high concentration region.

Table 1. Interfacial adsorption equilibrium constants

	K_{ad} [dm ³ /mol]	S_s [m ² /mol]
DHS	3.4×10^1	5.5×10^5
TIBPS	4.4×10^0	6.3×10^5



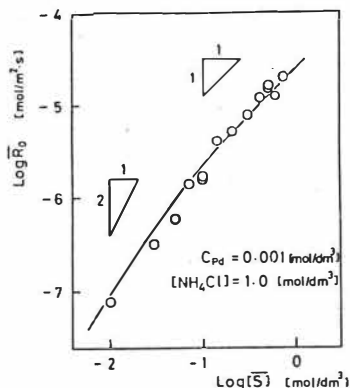


Fig.5 Effect of DHS concentration on the initial extraction rate

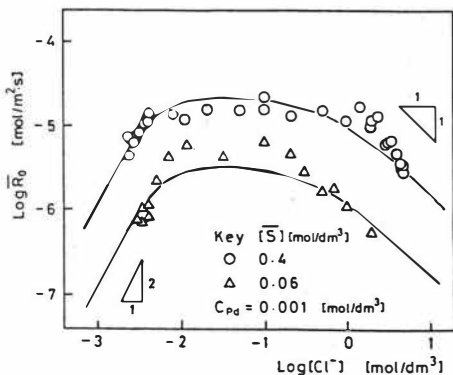


Fig.6 Effect of chloride ion concentration on the initial extraction rate

Figure 5 shows the effect of DHS concentration on the initial extraction rate from 1 mol/dm³ NH₄Cl solution. The plots are lying on a straight line of slope 2 in the low concentration region of DHS and on that of slope 1 in the high concentration region. The effect of chloride ion concentration on the initial extraction rate is shown in Fig. 6 for both concentration regions of DHS. The plots lie on straight lines of slope 2 and on those of slope -1 in the low and high concentration regions of chloride ion, respectively, while the initial extraction rate appears to be independent of the chloride ion concentration in the intermediate concentration region.

4.2 Extraction Rate with TIBPS

In the extraction with TIBPS, the apparent pseudo-first order forward reaction rate constants (k_f) were obtained from the time variation of the palladium concentration in the aqueous phase (a) on the basis of Eq.(5) assuming that the rates of the forward and reverse extractions are pseudo-first order with respect to palladium in the aqueous and organic phase, respectively.

Figure 7 shows the effect of chloride ion concentration on k_f . The plotted points lie on a straight line of slope -1 in its

low concentration region and appear to approach to a constant value as it increases. Figure 8 shows the effect of the concentration of TIBPS in the organic phase on k_f . The plotted points appear to lie on a straight line with the slope of about 0.75.

$$\frac{a_i - a_e}{a_i} \ln \frac{a_i - a_e}{a_t - a_e} = k_f t \quad (5)$$

(The subscript, i and e, denote initial and equilibrium state, respectively)

5. Extraction Mechanisms of Palladium(II)

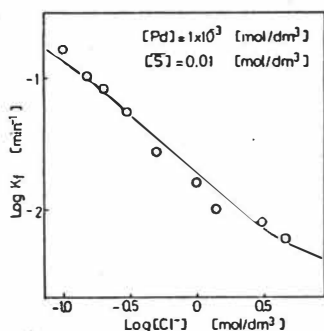


Fig. 7 Effect of chloride ion concentration on k_f .

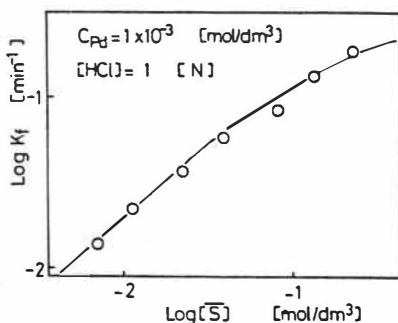


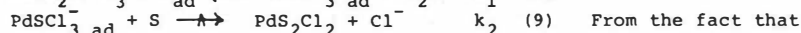
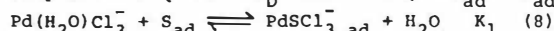
Fig. 8 Effect of TIBPS concentration on k_f .

The classical heterophase homogeneous reaction mechanism of the extraction kinetics of metals⁴⁾ where complex formation with the extractant dissolved in the aqueous phase is rate-determining would not be able to give reasonable interpretations to the experimental results mentioned in the preceding sections. Therefore, taking account of the fact that both extractants are interfacially active, the experimental results were analysed on the basis of the heterogeneous interfacial reaction model.

5.1 Rate Mechanism in the Extraction with DHS

The extraction rate with DHS was analysed on the basis of the interfacial reaction scheme proposed for the extraction kinetics of nickel with a hydroxyoxime in the previous paper⁶⁾ as follows.

First, the extractant in the organic phase is physically partitioned to the aqueous phase and is adsorbed at the interface. The extractant adsorbed at the interface undergoes the complex formation with aquatrichloro complex of palladium, $\text{Pd}(\text{H}_2\text{O})\text{Cl}_3$, which is much more labile compared with other chloro complexes,⁷⁾ to form the intermediate complex, PdSCl_3 , at the interface. Subsequently, the extractant molecule in the aqueous phase attacks the intermediate complex to form the final



the reaction order with respect to DHS is greater than 1 in its low concentration region, the interfacial reaction step described by Eq. (9)

is considered to be rate-determining and, consequently, the initial extraction rate is expressed as follows: $\bar{R}_0 = k_2 \theta_{\text{PdS}} [\text{S}] = k_2 K_D [\text{S}] \theta_{\text{PdS}}$ In Eq. (10), θ_{PdS} is the fractional coverage of the intermediate (10)

complex and is expressed on the basis of the Langmuir's monolayer adsorption model as follows:
$$\theta_{\text{PdS}} = \frac{K_{\text{ad}} K_1 [\text{Pd}(\text{H}_2\text{O})\text{Cl}_3] [\text{S}]}{1 + K_{\text{ad}} [\text{S}] + K_{\text{ad}} K_1 [\text{Pd}(\text{H}_2\text{O})\text{Cl}_3] [\text{S}]} \quad (11)$$

Combination of Eqs.(10) and (11) gives the following rate expression.

$$\bar{R}_0 = \frac{k_2 K_D K_{ad} K_1 f_3 ([Cl^-]) C_{Pd} [\bar{S}]^2}{1 + K_{ad} [\bar{S}] + K_{ad} K_1 f_3 ([Cl^-]) C_{Pd} [\bar{S}]} \quad (12)$$

$$\text{where } f_3 ([Cl^-]) \equiv \beta_3 [Cl^-]^3 / (1 + \sum_{i=1}^4 \beta_i [Cl^-]^i) \quad (13)$$

In Eq.(13), β_i denotes the stability constant of the i th chloro complex of palladium. $Pd^{2+} + iCl^- \rightleftharpoons PdCl_i^{(i-2)-}$ β_i (14)

Under the present experimental conditions, Eq.(13) is approximated as $f_3 ([Cl^-]) \approx \beta_3 [Cl^-]^2 / \sum_{i=1}^4 \beta_i [Cl^-]^{i-1}$ (15)

The proposed rate expression, Eq.(12), can be approximated by Eq.(16) in case the extractant concentration, $[\bar{S}]$, is low enough and by Eq.(17) in case it is high enough.

$$\bar{R}_0 \approx k_2 K_D K_{ad} K_1 f_3 ([Cl^-]) C_{Pd} [\bar{S}]^2 \text{ for low } [\bar{S}] \quad (16)$$

$$\bar{R}_0 \approx k_2 K_D K_1 f_3 ([Cl^-]) C_{Pd} [\bar{S}] / (1 + K_1 f_3 ([Cl^-]) C_{Pd}) \text{ for high } [\bar{S}] \quad (17)$$

Equation (16) suggests that the initial extraction rate is first order with respect to palladium in the aqueous phase and second order with respect to the extractant in its low concentration region while Eq.(17) suggests that it is first order with respect to the extractant in its high concentration region. Equation (17) is further approximated by Eq.(18) in case $f_3 ([Cl^-]) C_{Pd}$ is low enough and by Eq.(19) in case it is high enough. $\bar{R}_0 \approx k_2 K_D K_1 f_3 ([Cl^-]) C_{Pd} [\bar{S}]$ (18) $\bar{R}_0 \approx k_2 K_D [\bar{S}]$ (19)

Equations (15) and (18) suggest that initial extraction rate is second order and inversely first order with respect to chloride ion in its low and high concentration region, respectively. Equation (19) suggests that it is dependent neither on chloride ion concentration nor on palladium concentration in the aqueous phase in case $f_3 ([Cl^-])$ is high enough. These tendencies expected from Eqs.(16)-(19) can qualitatively interpret the experimental results.

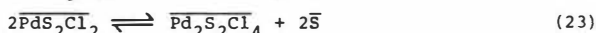
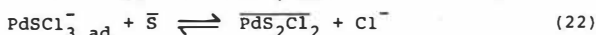
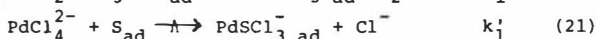
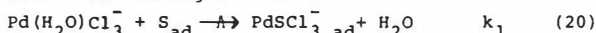
The parameters, β_i/β_3 ($i=1-3$), K_1 and $k_2 K_D$ in Eq.(12), were evaluated by the nonlinear least square method from the results shown in Fig.6 using K_{ad} evaluated earlier as follows: $\beta_1/\beta_3 = 2.2 \times 10^{-4}$, $\beta_2/\beta_3 = 2.2 \times 10^{-3}$, $\beta_4/\beta_3 = 1.6 \times 10^1$, $K_1 = 1.1 \times 10^4$, $k_2 K_D = 6.8 \times 10^{-8}$ [m/s].

The solid lines in Figs.5 and 6 are the calculated results from Eq.(12) using these values. The curves are in fairly good agreement with the experimental results.

5.2 Rate Mechanism in the Extraction with TIBPS

The concentration dependencies of the reactant species, chloride ion and the extractant, on the extraction rate are quite different between DHS and TIBPS from the comparison of Figs.5 and 6 with Figs.7 and 8. The interfacial reaction scheme expressed by Eqs.(20)-(23) were proposed instead of that in the extraction with DHS expressed by Eqs.(8) and (9) to interpret the concentration dependencies on the extraction

rate shown in Figs.7 and 8.



Here, the intermediate complex, PdSCl_3^- , is simultaneously formed at the interface either from aquatrachloro complex as in the extraction with DHS or from tetrachloro complex. These steps are considered to be rate-determining in the extraction with TIBPS from the experimental result that the reaction order with respect to the extractant is less than 1 as shown in Fig.8. Consequently, the rate expression of the extraction with TIBPS is described as follows:

$$\bar{R}_0 = (k_1[\text{Pd}(\text{H}_2\text{O})\text{Cl}_3^-] + k'_1[\text{PdCl}_4^{2-}])\theta_s \quad (24) \quad \theta_s \text{ denotes the fractional coverage of TIBPS and is described by Eq.(25) based on the Langmuir's monolayer adsorption model and based on the assumption that the subsequent step expressed by Eq.(22) is rapid.}$$

$\theta_s = K_{\text{ad}}[\bar{\text{S}}]/(1 + K_{\text{ad}}[\bar{\text{S}}]) \quad (25)$

\bar{R}_0 is ultimately rewritten as Eq.(26) from Eqs.(24) and (25) and taking account of the fractions of the chloro complexes of palladium in the aqueous phase.

$$\text{Under the present experimental conditions,} \quad \bar{R}_0 = \frac{k_1\beta_3[\text{Cl}^-]^3 + k'_1\beta_4[\text{Cl}^-]^4}{1 + \sum_{i=1}^4 \beta_i[\text{Cl}^-]^i} \cdot \frac{K_{\text{ad}}[\bar{\text{S}}]}{1 + K_{\text{ad}}[\bar{\text{S}}]} \cdot C_{\text{Pd}} \quad (26)$$

the great majority of palladium is existing as aquatrachloro or tetrachloro complexes in the aqueous phase. Consequently, \bar{R}_0 is approximated as follows:

$$\bar{R}_0 = \frac{k_1\beta_3 + k'_1\beta_4[\text{Cl}^-]}{\beta_3 + \beta_4[\text{Cl}^-]} \cdot \frac{K_{\text{ad}}[\bar{\text{S}}]}{1 + K_{\text{ad}}[\bar{\text{S}}]} \cdot C_{\text{Pd}} \quad (27)$$

The interfacial reaction rate constants, k_1 and k'_1 , were evaluated by the nonlinear least square method from the results shown in Figs.7 and 8 using the values of K_{ad} evaluated earlier and β_3 and β_4 shown below as follows: $\beta_3 = 2.0 \times 10^{10}$, $\beta_4 = 7.9 \times 10^{11}$, $k_1 = 6.1 \times 10^{-1}$, $k'_1 = 1.7 \times 10^{-3}$. The solid lines in Figs. 7 and 8 are the calculated results based on Eq.(27) using these values. The calculated curves are in good agreement with the experimental results.

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THE KINETICS OF EXTRACTION OF TUNGSTEN BY PETROLEUM SULFOXIDE

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INTRODUCTION

The extraction of tungsten has been studied by using petroleum sulfoxide (PSO) and butyl alcohol mixture⁽¹⁾. By this extraction technology, the recovery of tungsten values in scheelite or wolframite will be achieved. In comparison with dibutyl sulfoxide (DBSO)⁽¹⁾, the extractant PSO has the advantage of low solubility in water, but requires somewhat higher aqueous acidity at which the solubility of tungstic acid is too low for practical application. This difficulty can be overcome if organic phase is pre-equilibrated with hydrochloric acid of proper concentration and then is made in contact with the aqueous solution of high tungsten content at much low acidity. In this way hydrochloric acid transfers from the organic phase to the aqueous phase to furnish sufficient H^+ so that the tungsten species in the aqueous phase reacts with H^+ and PSO to form extraction complex which then transfers to the organic phase. Thus the concentration of tungsten in the aqueous phase is lowered rapidly and precipitation does not occur. Therefore, the extraction involves counter-diffusional processes of hydrochloric acid and tungsten complexes and it is interesting to study the kinetics of both processes.

The results obtained by using a simple Lewis cell and a stirred cell as well as an AKUFVE system to determine mass transfer coefficient k_L and rates R_{HCl} and $R_{W_2O_5}$ in the extraction of tungsten by petroleum sulfoxide are reported and an empirical rate equation is presented.

APPARATUS

A simple Lewis cell was used. The cell itself is a glass cylinder with a jacket and the temperature of circulating water can be kept within $\pm 0.5^\circ C$. The upper stirrer axle is a hollow pipe through which the lower stirrer axle extends into the heavy phase. The stirrers in two phases were driven by motor and pulleys and rotate in opposite directions at controllable speeds which can be measured by a photodetector and a tachometer. The cell has a total volume of $234.7 \times 10^{-6} m^3$ and a plane interface of $2.35 \times 10^{-3} m^2$.

The experiments in a stirred cell and AKUFVE 110 system were run with the organic phase as dispersed droplet phase. The stirring speeds in both were much higher than that in the Lewis cell and also measured by the same method. In these systems the drop size distribution and specific surface area were measured and recorded continuously.

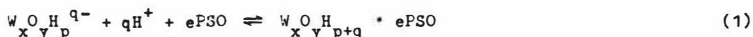
RESULTS AND DISCUSSION

The extraction of tungsten by petroleum sulfoxide-butanol mixture, which contains HCl by pre-equilibration with hydrochloric acid of appropriate concentration, may be composed of the following consecutive steps:

1. HCl solvate ($HCl \cdot S$, where S is the extractant) in the organic phase transfers to the interface and at the interface or in the vicinity of it $HCl \cdot S$ decomposes into H_2O and hydrochloric acid;
2. hydrochloric acid dissociates into H^+ and Cl^- in the aqueous phase;
3. H^+ and PSO combine with tungsten species to form extractable complexes at the reaction zone in the vicinity of the interface;

4. transfer of extractable complexes from reaction zone to the bulk of organic solvent.

The transport of $\text{HCl}\cdot\text{S}$ from the bulk of organic solvent to the interface offers the main resistance of step 1, because HCl distributes in favor of aqueous phase. Due to the same reason and insolubility of PSO in water, $\text{HCl}\cdot\text{S}$ decomposes in contact with water. The dissociation of hydrochloric acid is an instantaneous one and step 2 can be neglected in the rate of extraction. In weak hydrochloric acid the species of isopolytungstic acids are very complex and change markedly with variation of H^+ and tungsten concentration. The general formula of anions is $\text{W}_x\text{O}_y\text{Hp}^{q-}$ (1). These anions will react with H^+ and PSO in the following manner:



Under mild and inadequate agitation it has been observed that a heavy organic phase formed sinks to the bottom beneath the aqueous phase. While the stirring speed increases, the third phase dissolves quickly in the light organic phase. In regard to the appearance of the "third phase", it is very likely that the tungsten species react with H^+ and PSO at the locality where H^+ and PSO are generated and sufficient to provide a favorable condition in forming the extractable complexes which are heavier than and insoluble in the aqueous phase and may temporarily separate from both original phases. Therefore, the step 4 is considered to offer only a little resistance to mass transfer of the complexes.

The above discussion indicates that among the four steps the transport of HCl and the interfacial reaction of formation of extractable complexes, i.e. steps 1 and 3, are the key steps controlling the overall extraction process and should be deliberated.

The equation of transfer of $\text{HCl}\cdot\text{S}$ from the bulk of solvent to the interface may be written as

$$R_{L,\text{HCl}\cdot\text{S}} = K_{L,\text{HCl}\cdot\text{S}} a \{ [\text{HCl}\cdot\text{S}]_o - [\text{HCl}\cdot\text{S}]_i \} \quad (2)$$

where $R_{L,\text{HCl}\cdot\text{S}}$ - rate of transfer of $\text{HCl}\cdot\text{S}$, $\text{kmol/s}\cdot\text{m}^3$
 $K_{L,\text{HCl}\cdot\text{S}}$ - mass transfer coefficient, m/s
 a - interfacial area per unit volume, m^2/m^3
 $[\text{HCl}\cdot\text{S}]_o, [\text{HCl}\cdot\text{S}]_i$ - concentrations of the solvate in the bulk of organic phase and the reaction zone near the interface respectively

The decomposition of $\text{HCl}\cdot\text{S}$ in aqueous phase near the interface is



And the decomposition rate,

$$R_{r,\text{HCl}\cdot\text{S}} = k_{r,\text{HCl}\cdot\text{S}} [\text{HCl}\cdot\text{S}]_i - k'_{r,\text{HCl}\cdot\text{S}} [\text{H}^+][\text{Cl}^-][\text{S}]_i \quad (4)$$

where $R_{r,\text{HCl}\cdot\text{S}}$ - the decomposition rate, $\text{kmol/s}\cdot\text{m}^3$
 $k_{r,\text{HCl}\cdot\text{S}}, k'_{r,\text{HCl}\cdot\text{S}}$ - forward and reverse reaction constants respectively
 $[\text{S}]_i$ - concentration of extractant at the interface

$$\text{The rate of transfer of } HCl = R_{HCl} = R_{L,HCl \cdot S} = R_{r,HCl \cdot S} \quad (5)$$

From Eqs. (2)-(5), the rate equation can be derived:

$$R_{HCl} = \frac{k_r HCl \cdot S \quad k_L HCl \cdot S \text{ am} \{ [HCl \cdot S]_O - K_{HCl} [H^+][Cl^-][S]_i \}}{k_{L,HCl \cdot S} a + k_{r,HCl \cdot S} m} \quad (6)$$

where K_{HCl} - a value concerning equilibrium constant of dissociation

For mass transfer controlling,

$$k_{L,HCl \cdot S} a \ll k_{r,HCl \cdot S}$$

then

$$R_{HCl} = k_{L,HCl \cdot S} a \{ [HCl \cdot S]_O - K_{HCl} [H^+][Cl^-][S]_i \} \quad (7)$$

For reaction controlling,

$$k_{r,HCl \cdot S} \ll k_{L,HCl \cdot S} a$$

it follows

$$R_{HCl} = k_{r,HCl \cdot S} m \{ [HCl \cdot S]_O - K_{HCl} [H^+][Cl^-][S]_i \} \quad (8)$$

The Rate Equation of Formation of Extractable complexes from Tungsten Species, H^+ and PSO

As discussed above, PSO is almost insoluble in water (about 0.05 vol-%) but is very concentrated in the organic phase (most of runs were carried out with 50 vol-% PSO, i.e. 2.91 kmol/m³). The additional hydrogen ion required for favorable extraction is supplied by HCl·S which generated H^+ and PSO (also BuOH) at (or near) the interface. The simplest form of rate expression governed by kinetic factors appears to be

$$R_{WO_3} = \varphi k_{r,WO_3} [WO_3]^a [H^+]^\beta [PSO]_O \quad (9)$$

where R_{WO_3} - transfer rate of tungsten species
 φ - stoichiometric ratio
 k_{r,WO_3} - rate coefficient of complexing reaction
 $[WO_3], [H^+], [PSO]_O$ - concentrations of respective substances

Due to that the tungsten species in weak hydrochloric acid ($pH \approx 2$) is complicated and its reaction mechanism seems unclear, the values of $\varphi k_{r,WO_3}$, a and β can only be found experimentally.

Interfacial Area in Lewis Cell and Stirred Cells

In Lewis cell the stirring speed was kept sufficient low to prevent any tendency of disturbance at the interface. When the stirring speed in one phase was set at 0.5 S⁻¹, no disturbance was observed unless the speed in another phase exceeds 1 S⁻¹. When the stirring speeds of both phases were set at 0.8 S⁻¹, ripples appear at the interface. If the stirring speeds increase beyond 1 S⁻¹, the interface will entirely be destroyed. Therefore, most of

experiments of this investigation were carried out with stirring speeds of 0.5 S^{-1} for both phases. Under these conditions, the uniformity of the bulk concentrations of both phases could be maintained. The interfacial area of the Lewis cell is $2.35 \times 10^{-3} \text{ m}^2$ and the cell volume is $235 \times 10^{-6} \text{ m}^3$ so that the specific area "a" will be $10 \text{ m}^2/\text{m}^3$.

In contrary to the case in Lewis cell, the stirring speed in the stirred cell and AKUFVE system is much high and mixing intensity will bring one phase into droplets dispersed in the other and flow pattern may be turbulent. The evaluation of "a" is important for the interfacial reaction as well as the diffusion process in any type of stirred cell. As it was briefly stated before, there were devices to measure drop size distribution and hold up and these data were processed to yield interfacial area per unit volume "a" by microcomputer.

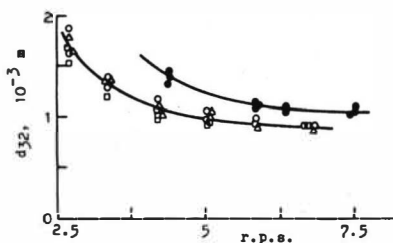


Fig. 1 d_{32} vs. r.p.s. (40°)

Stirred cell: \bigcirc PSO/BuOH=1(v);
 \triangle PSO/OctOH=4/1(v);
 \square PSO/OctOH=3/2(v).
 AKUFVE: \bullet PSO/BuOH=1(v).

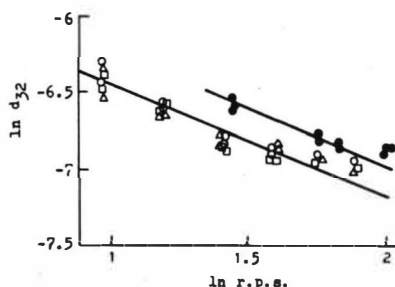


Fig. 2 $\ln d_{32}$ vs. \ln r.p.s. (40°C)

Stirred cell: \bigcirc PSO/BuOH=1(v);
 \triangle PSO/OctOH=4/1(v);
 \square PSO/OctOH=3/2(v).
 AKUFVE: \bullet PSO/BuOH=1(v).

From drop size distribution curves, it indicates that the higher the stirring speed is, the less asymmetrical DSD and the more uniform the drop size will be. The data obtained were used to plot the curves in Figs. 1 and 2. They show that d_{32} decreases with increasing stirring speed N but approaches a certain value as a limit, i.e. $N > 5 \text{ S}^{-1}$, $d_{32} \approx 0.9 \times 10^{-3} \text{ m}$ in the stirred cell used in this investigation and $N > 6 \text{ S}^{-1}$, $d_{32} = 1.06$ in the mixing chamber of AKUFVE 110. The variation of value "a" with stirring speed in the stirred cell is illustrated in Fig. 3. In Fig. 2 the plots of $\ln d_{32}$ vs. $\ln N$ for both the stirred cell and AKUFVE give straight lines with a slope of -0.8 , i.e. $d_{32} \propto N^{-0.8}$, which is about the value -0.75 put forward by Shinnar⁽²⁾.

It reveals in Figs. 1 and 3 that beyond a certain stirring speed, further increase of it offers no advantages. Not only the value "a" increases no more, but also the droplet diameter becomes about $1 \times 10^{-3} \text{ m}$. Droplets of this size are liable to behave as rigid spheres moving in the continuous phase so that the transfer coefficients of inside and surrounding drops are impaired.

Transfer of $\text{HCl} \cdot \text{S}$ and Generation of H^+ , Cl^- and S

Fig. 4 shows the change of mass transfer coefficient with changing hydrodynamics of the upper and lower phase, i.e. by fixing a stirring speed in one phase and varying that in the other. When the speeds of both phases are $< 0.5 \text{ S}^{-1}$, K increases rapidly with increasing stirring speed. This tendency slows down thereafter. It seems interesting that beyond the rapid increase region two lines separate from each other and the effect of increasing Re_0 at a fixed value of Re_a appears somewhat more pronounced than vice versa.

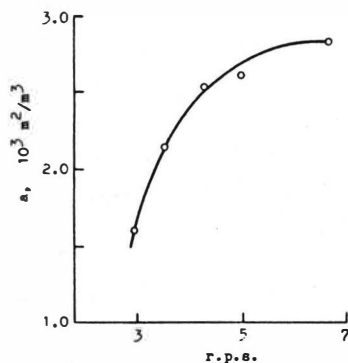


Fig. 3 a vs. r.p.s. (40°)

Stirred cell: PSO/BuOH=1(v)

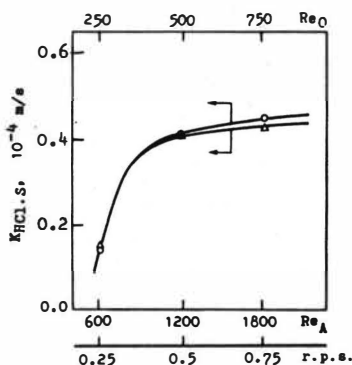


Fig. 4 Effect of Re_O & Re_A on $K_{HCl.S}$ (40°)

Solvent: PSO/BuOH=1(v),
 $[HCl]_O = 0.771 \text{ kmol/m}^3$, $[WO_3] = 0.168 \text{ kmol/m}^3$.
 Lewis cell: Δ $Re_O = 500$, \circ $Re_A = 1200$.

Perhaps this is an indication that the organic phase offers a little more resistance than the aqueous. From the shape of the curves the process is governed by mass transfer.

The two curves in Fig. 5 show the effect of stirring speed on the mass transfer coefficient $K_{HCl.S}$ and extraction rate on volume basis in the stirred cell. The curve, $R_{HCl.S}$ vs. N , rises first rapidly then flattens down gradually. This trend is in agreement with the curve in Fig. 3.

For temperature effect and Arrhenius plot, there are two sets of data, one of low stirring speed in Lewis cell and another of high speed in the stirred cell, all experimental points at changing temperatures fall on respective straight lines, as shown in Fig. 6. The two lines all give a slope of $-(1 \pm 0.1) \times 10^3$ and a value E of 8.4 kJ/mol (2.0 kcal/mol). The low value of E indicates that it is much below the range of activation energy of a chemical reaction.

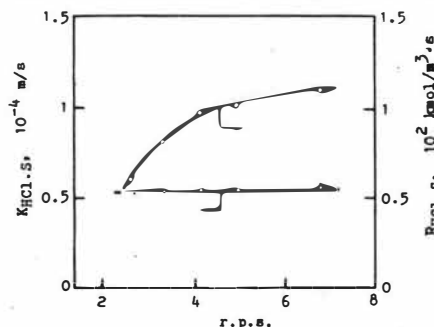


Fig. 5 K & R vs. r.p.s. (40°) stirred cell

PSO/BuOH=1(v), $[HCl]_O = 0.712$, $[WO_3] = 0.190 \text{ kmol/m}^3$.

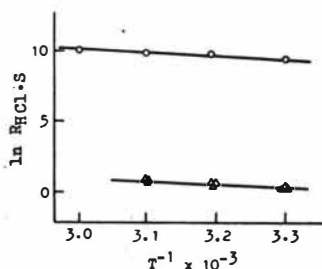


Fig. 6 $\ln R_{HCl.S}$ vs. T^{-1}

\circ Stirred cell: 6.8 s^{-1} , $a = 2.85 \times 10^3 \text{ m}^2/\text{m}^3$
 $[HCl]_O = 0.712 \text{ kmol/m}^3$
 Δ Lewis cell: 0.5 s^{-1} , $a = 10 \text{ m}^2/\text{m}^3$
 $[HCl]_O = 0.65 \text{ kmol/m}^3$

Extraction of Tungsten

When the extraction data of tungsten in Lewis cell were plotted in the same manner as those of HCl, Fig. 7 was obtained. The line with Re_A fixed rises more rapidly with increasing Re_0 than the case with Re_0 fixed and Re_A varied. The curve of the latter case is less susceptible to the change of Re_A and becomes rather flat. Perhaps it can be explained that the flow of organic phase will carry more HCl and PSO to the reaction zone near the interface and the transport of these two is more important than that of the tungsten species in aqueous phase. The temperature dependence on R_{WO_3} (kmol/s.m²) is shown in Fig. 8 from which the apparent activation energy has been found, i.e. $E = 20,600$ kJ/kmol (4,940 kcal/kmol). Therefore, in Lewis cell the extraction of tungsten is still governed by mass transfer.

Fig. 9 shows that R_{WO_3} increases with increasing stirring speed, more rapidly at low than at high speeds. But R'_{WO_3} which is on unit interfacial area basis, varies very little with stirring speed.

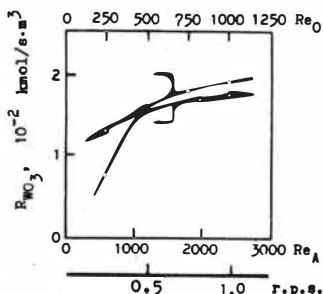


Fig. 7 R_{WO_3} vs. Re (40°)

Solvent: PSO/BuOH=1(v),
 $[HCl]_0=0.77$, $[WO_3]=0.173$ kmol/m³
 Lewis cell: Δ $Re_0=500$, \circ $Re_A=1200$.

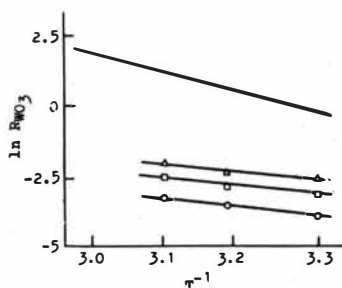


Fig. 8 $\ln R_{WO_3}$ vs. T^{-1}

Stirred cell: 6.8 s⁻¹; $a=2850$ m²/m³;
 $[HCl]_0=0.712$ kmol/m³;
 $[WO_3]=0.0854$ kmol/m³.

Lewis cell: 0.5 s⁻¹; $a=10$ m²/m³;
 $[HCl]_0=0.65$ kmol/m³.
 $[WO_3]$: Δ 0.259, \square 0.173,
 \circ 0.083 kmol/m³.

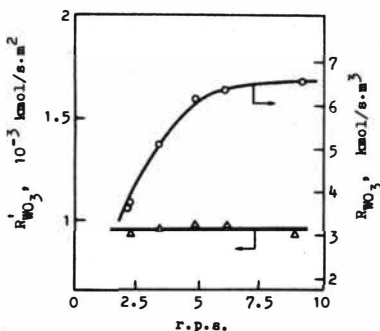


Fig. 9 R'_{WO_3} and R_{WO_3} vs. r.p.s. (40°)

Solvent: PSO/BuOH=1(v). Stirred cell
 Concns: $[HCl]_0=0.712$, $[WO_3]=0.190$ kmol/m³.

Fig. 9 shows that when the stirring speed is below 4 s^{-1} , R_{WO_3} increases rapidly with increasing agitation intensity, and then becomes unchanged. The latter stage falls to the region of chemical reaction control.

The experimental data at different temperatures were used to plot the values of $\ln R_{\text{WO}_3}$ vs. T^{-1} (see the upper line of Fig. 8) and the apparent activation energy has been found to be about $52.3 \times 10^3 \text{ kJ/kmol}$ ($12.5 \times 10^3 \text{ kcal/kmol}$). In comparison with the value of $20.4 \times 10^3 \text{ kJ/kmol}$ obtained in Lewis cell at low stirring speed, this value of $52.3 \times 10^3 \text{ kJ/kmol}$ indicates that the extraction falls in the chemical reaction control region. The transition from the region of diffusion control to chemical reaction control depends upon the intensity of mixing.

The overall rate of the extraction of WO_3 can be expressed as an empirical equation as already mentioned before (Eq. 9). To obtain the values of α and β , $\log R_{\text{WO}_3}$ vs. $\log [\text{WO}_3]$ with a fixed concentration of H^+ and also $\log R_{\text{WO}_3}$ vs. $\log [\text{H}^+]$ with a fixed concentration of WO_3 were plotted. Two straight lines were drawn as shown in Figs. 10 and 11. From the slopes the values of α and β have been found to be 1.91 and 0.949 respectively. Since the solvent used in most experiments contains a constant concentration (50 vol-% PSO) and the term $[\text{PSO}]_0$ is included a constant C:

$$R_{\text{WO}_3} = C [\text{WO}_3]^{1.91} [\text{H}^+]^{0.949} \exp(-E/RT) \quad (10)$$

$$\text{where } C = \phi k'_{r, \text{WO}_3} [\text{PSO}]_i$$

Similar experiments were carried out in AKUFVE 110 system, the result is in agreement with that obtained in the stirred cell.

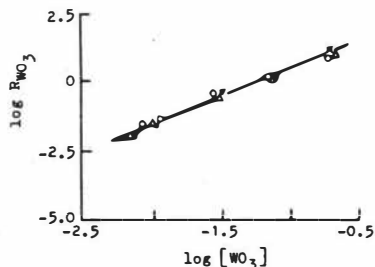


Fig. 10 $\log R_{\text{WO}_3}$ vs. $\log [\text{WO}_3]$

40°C ; $\text{PSO/BuOH}=1(\text{v})$; $[\text{HCl}]=0.717 \text{ kmol/m}^3$.
 $a, \text{ m}^2/\text{m}^3$: \circ 2500; \times 2610; \triangle 2850.

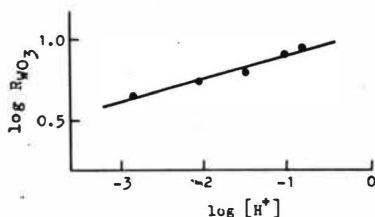


Fig. 11 $\log R_{\text{WO}_3}$ vs. $\log [\text{H}^+]$ (40°C)

$a=2850 \text{ m}^2/\text{m}^3$; $[\text{WO}_3]=0.187 \text{ kmol/m}^3$.

CONCLUSIONS

From the results reported above the following conclusions may be drawn:

- (1) The transport process of hydrochloric acid is controlled by diffusion under all conditions.

- (2) Under practical conditions the extraction rate of tungstic species is governed by the complexing reaction and the overall rate equation may be expressed as follows:

$$R_{\text{WO}_3} = C [\text{WO}_3]^{1.91} [\text{H}^+]_0^{0.949} \exp (-52.3 \times 10^3/RT)$$

where C depends upon mainly the concentration of extractant.

The ranges of experimental conditions are

$$T = 20^\circ\text{C} - 80^\circ\text{C}, \quad N > 4 \text{ s}^{-1}, \quad [\text{H}^+]_0 = 0.1 - 1.2 \text{ kmol/m}^3$$

$$[\text{WO}_3] = 0 - 0.5 \text{ kmol/m}^3, \quad [\text{PSO}]_0 = 50 \text{ vol-\% in equal volume of butanol.}$$

- (3) It seems that transfer of hydrochloric acid from the organic phase into aqueous phase almost keeps pace with the consumption of H^+ to form extractable tungsten complexes so that there is no precipitation of "tungsten acid" occurred.

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The Extraction Kinetics and Mechanism of Palladium(II) with Trialkylmethyl Ammonium Chloride in Octane

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INTRODUCTION

Recently there are many reports on the extraction kinetics of metals by some acidic and oxime extractants [1-5], whereas the investigations on the extraction kinetics of metals by the amine type extractants are rarely reported. As one part of the systematic investigations on the extraction of palladium(II) with amine type extractants, the present paper reports the main results of the extraction kinetics of palladium(II) with trialkylmethyl ammonium chloride (hereafter TAMACl) from hydrochloric acid. A PVC membrane Pd(II) ion-selective-electrode was used as a continuously monitor techniques. The enthalpy and the corresponding equilibrium constants obtained from the kinetic data are in good accordance with that obtained from the equilibrium data. The extraction mechanism is also discussed.

EXPERIMENTAL PROCEDURES

The liquid-liquid extraction kinetic data have been obtained using an apparatus shown in Figure 1. This apparatus allows one to continuously monitor the concentration variations of metal ion in the aqueous phase with the extraction time. All the kinetic experiments described here were carried out at stirring speeds of 220±20 rpm where the plateau region of the mass transfer rate vs stirring speed was located so it is possible to assume that the extraction process is controlled by chemical reaction.

DATA TREATMENT

The kinetic data of the concentration vs time have been analyzed by assuming a first order reversible reaction for the palladium(II) transfer, i. e.



which led to the integrated kinetic equation

$$(a_i - a_e) a_i^{-1} \ln (a_i - a_e) (a_t - a_e)^{-1} = AV^{-1} k_f t \quad (2)$$

$$a_e a_i^{-1} \ln (a_i - a_e) (a_t - a_e)^{-1} = AV^{-1} k_b t \quad (3)$$

where a_i , a_e and a_t represent the concentration of Pd(II) in the aqueous phase at initial, equilibrium and t moment, respectively; A and V , the interfacial area between two phases and the volume of the organic phase, respectively ($A = 25\text{cm}^2$ in the present study); k_f and k_b , the mass transfer coefficients from aqueous to organic and from organic to aqueous, respectively; and t , the extraction time in minute. By plotting the left member of Equation (2) or (3) as a function of time, straight line should be obtained, which allowed the evaluation of k_f or k_b as functions of TAMACl concentration in the organic phase, of hydrogen ion and chloride ion concentration in the aqueous phase, and of other factors affecting k_f and k_b .

RESULTS

Verification of the first order reversible reaction of Pd(II) transfer

Figure 2 shows the plot based on Equation (2) from one set of the experimental data obtained in the present study. Obviously, it is a first order plot, the good linearity of which proves that the above assumption is correct.

Extractant concentration dependency

The plots of Figure 3 show the effect of the concentration of monomeric TAMACl in the organic phase on the mass transfer coefficients k_f and k_b , respectively. These results indicate that with increasing of TAMACl concentration in the organic phase, the absolute value of slope of line decreases for k_f and increases for k_b .

Hydrogen ion and chloride ion concentration dependency

Figures 4 and 5 show the effect of concentration of hydrogen ion and chloride ion in the aqueous phase on k_f and k_b , respectively. The trends of the plots shown in Figures 4 and 5 are similar to that of plots for the extraction of TcO_4^{2-} by tri-alkylmethyl ammonium nitrate (TAMAN) from nitric acid[6].

Specific interfacial area dependency

Figure 6 shows the effect of specific interfacial area, i. e. the ratio between the interfacial area of the interface and the volume of the organic phase, on the initial extraction rate. It can be seen that the initial extraction rate is proportional to the specific interfacial area. This result implies that the extraction process studied in this study may be controlled by interfacial reaction.

Temperature dependency

Figure 7 shows the effect of temperature on k_f and k_b . The apparent activation energy could be calculated from the Arrhenius equation

$$\lg k = - \frac{E}{2.303RT} + C$$

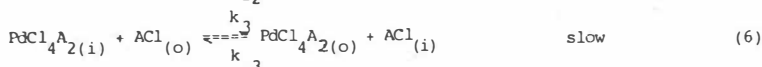
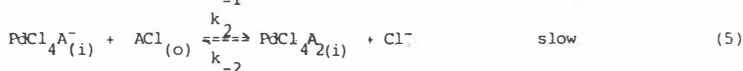
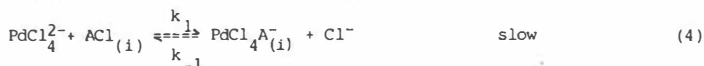
where E is the activation energy in KJ/mol. The values calculated for forward and

backward extraction are +10.4 KJ/mol and +14.6 KJ/mol, respectively. From these results the enthalpy ΔH for this extraction process were calculated to be -4.2 KJ/mol which is in good accordance with the result obtained from extraction equilibrium (-4.3 KJ/mol)[7].

DISCUSSION

Extraction mechanism

Considering that TAMACl being a strong surfactant and the experimental results stated above, we suggest that under the experimental conditions in the present study, the extraction mechanism for the extraction of Pd(II) by TAMACl from hydrochloric acid may be expressed by the following interfacial reactions:



where ACl represents TAMACl ($\text{A}=\text{R}_3\text{CH}_3\text{N}$); subscripts (i) and (o) denote the interface and organic, respectively. By applying the steady-state approximation, we may obtain

$$k_f = \frac{k_1 k_2 k_3 [\text{ACl}]_{(o)}^2 [\text{ACl}]_{(i)}}{k_{-1} k_{-2} [\text{Cl}^-]^2 + k_{-1} k_3 [\text{Cl}^-] [\text{ACl}]_{(o)} + k_2 k_3 [\text{ACl}]_{(o)}^2} \quad (7)$$

$$k_b = \frac{k_{-1} k_{-2} k_{-3} [\text{Cl}^-]^2 [\text{ACl}]_{(i)}}{k_{-1} k_{-2} [\text{Cl}^-]^2 + k_{-1} k_3 [\text{Cl}^-] [\text{ACl}]_{(o)} + k_2 k_3 [\text{ACl}]_{(o)}^2} \quad (8)$$

Considering that the interface was saturated with TAMACl under the experimental conditions in this study, the concentration of TAMACl at interface, $[\text{ACl}]_{(i)}$, can be regarded as a constant, thus the kinetic experimental results shown in Figure 4 and 5 can be interpreted well in terms of Equations (7) and (8). From Equations (7), (8), (9) and (10) we can further obtain

$$D = \frac{[\text{Pd(II)}]_{(o)} k_f}{[\text{Pd(II)}] k_b} \quad (9)$$

where D is the distribution ratio of Pd(II) between two phases, and then obtain

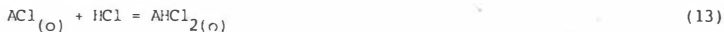
$$D = K_{\text{ex}} \frac{[\text{ACl}]_{(o)}^2}{[\text{Cl}^-]^2} \quad (10)$$

where $K_{\text{ex}} = k_1 k_2 k_3 / k_{-1} k_{-2} k_{-3}$. Equation (12) is exactly the same as the corresponding equation of distribution ratio for this extraction system[7]. The values of equilibrium constants obtained from the kinetic data and from the equilibrium data are $10^{5.13}$ and $10^{5.30}$, respectively. The good agreement between these two values indicate

that the mechanism stated above is reasonable.

Effect of acidity

The effect of acidity in the aqueous phase on k_f and k_b may be caused by the following reaction [8]



For the associate $AlHCl_2$ thus formed has no extractability for $PdCl_4^{2-}$ so the trends for k_f and k_b with the acidity can be explained as the decreasing of effective concentration of extractant in the organic phase with increasing of acidity.

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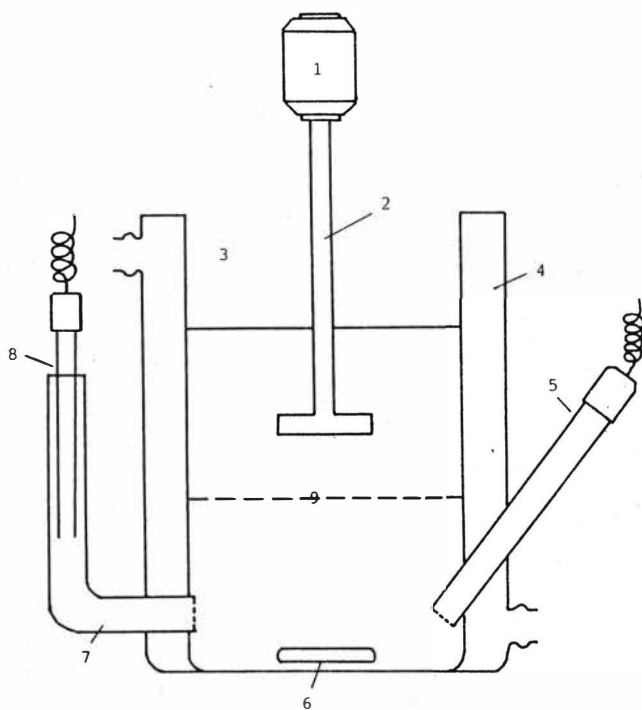


FIG. 1: APPARATUS USED TO STUDY THE EXTRACTION KINETICS IN THE PRESENT INVESTIGATION.

1. MOTOR; 2. STIRRER; 3. REACTING CELL; 4. THERMOSTAT;
5. REFERENCE ELECTRODE; 6. MAGNETON; 7. PVC MEMBRANE Pd(II) ION-SELECTIVE-ELECTRODE; 8. SATURATED CALOMEL ELECTRODE; 9. INTERFACE BETWEEN TWO PHASES.

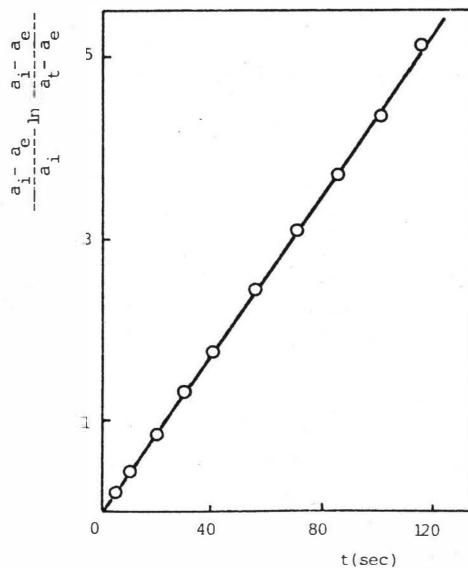


FIG. 2: THE FIRST ORDER RATE PLOT FOR EXTRACTION OF Pd(II)

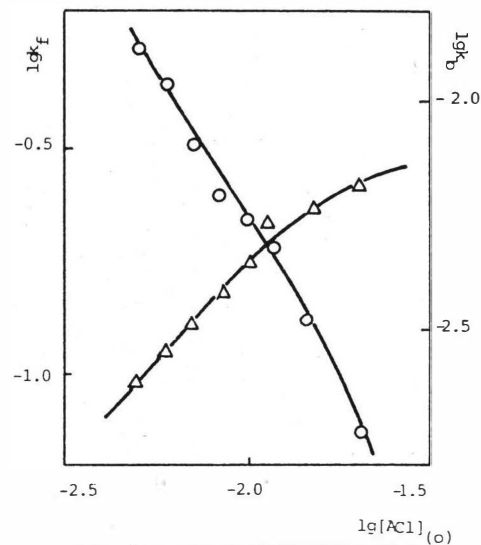


FIG. 3: EFFECT OF EXTRACTANT CONCENTRATION ON MASS TRANSFER COEFFICIENTS, $k_f(\Delta)$; $k_b(o)$.

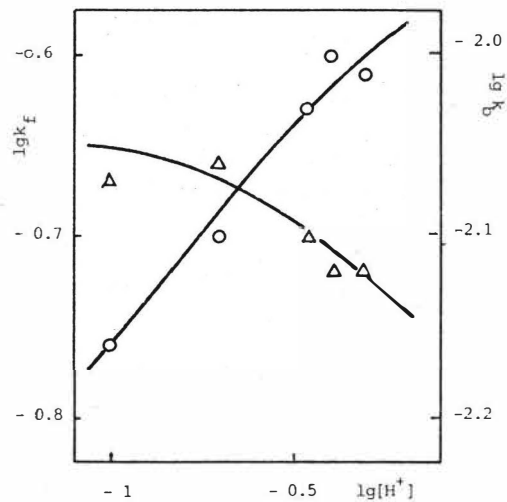


FIG. 4: EFFECT OF HYDROGEN ION CONCENTRATION ON MASS TRANSFER COEFFICIENTS, $k_f(\Delta)$; $k_b(\circ)$.

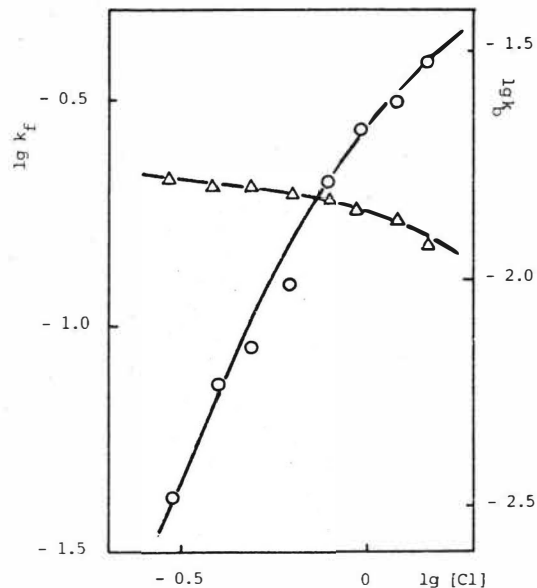


FIG. 5: EFFECT OF CHLORIDE ION CONCENTRATION ON MASS TRANSFER COEFFICIENTS, $k_f(\Delta)$; $k_b(\circ)$.

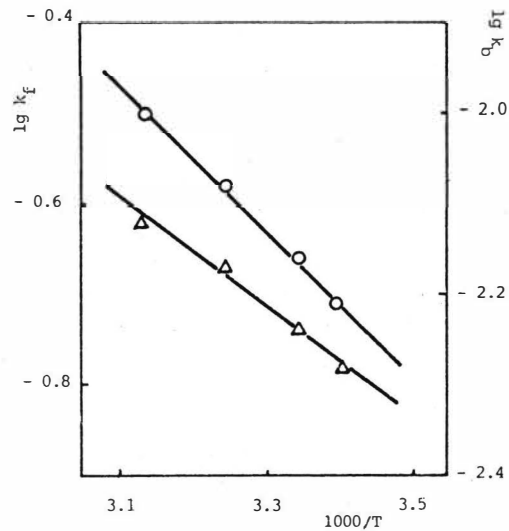


FIG. 6: EFFECT OF TEMPERATURE ON THE MASS TRANSFER COEFFICIENTS, $k_f(\Delta)$; $k_b(\circ)$

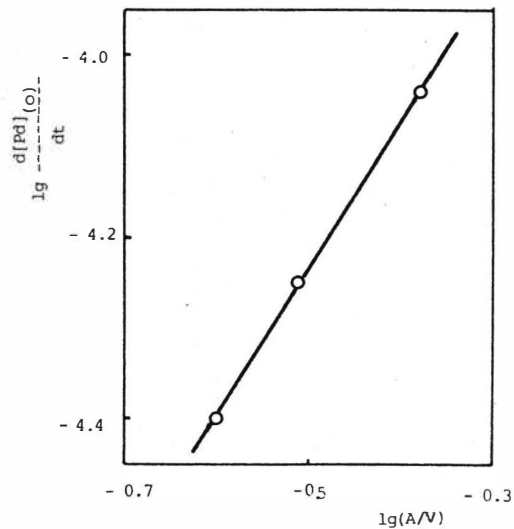


FIG. 7: DEPENDENCY OF INITIAL EXTRACTION RATE ON SPECIFIC INTERFACIAL AREA.

THE INTERFACIAL PROPERTIES AND METAL EXTRACTION KINETICS OF SOME ACIDIC ORGANOPHOSPHOROUS EXTRACTANTS

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This work consists of two parts. Firstly, the interfacial tension of Di-ethylhexyl phosphoric acid(HDEHP) and 2-ethylhexyl-2-ethylhexyl phosphonic acid(HEH(EHP) in liquid-liquid systems have been studied as a function of concentration of extractant temperature and the solubility parameter of diluents by using the Du Nuoy ring method[1]. From the experimental data,a series of interfacial activity parameters were calculated by use of the Gibbs adsorption equation and the Langmuir isotherm equation. Secondly, the kinetics of extraction of Mg(II) from sulfate solution into octane, and of Fe(III) from nitrate solution into heptane with HEH(EHP) have been investigated, the single drop method was used for the former system, the constant interfacial area stirring cell method and the highly stirring method [2] were used for the latter one.From the kinetic data and the interfacial properties of HEH(EHP) it was proposed that the rate-determining steps in these two extraction systems may be the reactions taking place at the organic/aqueous interface. By applying the steady-state approximation, the apparent initial extraction rate equations were derived. The results are reported below.

DETERMINATION OF THE INTERFACIAL ACTIVITY PARAMETERS

The molecular state adsorbed at interface

The interfacial tension data measured by the Du Nuoy ring method at $298 \pm 1K$ could be treated by the Gibbs adsorption equation

$$\Gamma = - \frac{1}{2.303RT} \frac{d\gamma}{d \lg C} \quad (1)$$

and the Langmuir adsorption isotherm equation

$$\Gamma = \Gamma_{\infty} \frac{KC}{1 + KC} \quad (2)$$

where Γ = surface excess of extractant; Γ_{∞} = surface excess at saturated adsorption; C = bulk concentration of the extractant; K = adsorption constant; γ = interfacial tension measured experimentally.

Since HDEHP and HEH(EHP) exist both as monomer and dimer in diluent, then

$$C_F = C_1 + 2 C_2 = C_1 + 2K_2 C_1^2 \quad (3)$$

where C_F = formula weight concentration of extractant; C_1 = concentration of the

monomer; C_2 = concentration of the dimer; K_2 = dimerization constant. If K_2 is known the values of C_1 and C_2 under different C_F can be calculated. The values of γ measured experimentally at corresponding concentrations are plotted against $\lg C_1$ and $\lg C_2$, respectively (Figure 1), then the values of Γ can be obtained by introducing the values of slope at points on these curves into Equation (1). The plots of the calculated values of Γ against C_1 and C_2 , respectively were shown in Figure 2. By comparing these plots with Equation(2), it can be seen that for the HDEHP-kerosene- H_2O system, the Γ vs C_1 curve is in agreement with Equation(2), while the Γ vs C_2 curve is not. From this, it is possible to consider that the monomer will be predominant at kerosene/water interface. It is also true for HEH[EHP].

Estimation of the interfacial activity parameters

Since HDEHP and HEH[EHP] exist as dimers predominantly in most nonpolar solvents, Generally, it can be regarded that $C_1 \ll C_2$, thus the concentration of the dimer is approximately one-half of C_F , and that of the monomer can be calculated by

$$C_1 = (C_2 K_2^{-1})^{\frac{1}{2}} = [C_F (2K_2)^{-1}]^{\frac{1}{2}} \quad (4)$$

By introducing Equation (4) into Equations (1) and (2)

$$\Gamma = - \frac{1}{2.303RT} \frac{d\gamma}{d(1/2 \lg C_F)} \quad (5)$$

$$\Gamma = \Gamma_{\infty} \frac{K' C_F^{\frac{1}{2}}}{1 + K' C_F^{\frac{1}{2}}} \quad (6)$$

can be obtained, where $K' = K(2K_2)^{-\frac{1}{2}}$; values of K' may be used as a measure of the strength of interfacial adsorption activity. The plot of γ vs $1/2 \lg C_F$ based on Equation(5) is shown by curve 3 in Figure 1, from which the values of Γ were calculated, then the Γ vs $C_F^{\frac{1}{2}}$ curve was plotted (curve c in Figure 2). The agreement between the Γ vs $C_F^{\frac{1}{2}}$ curve thus obtained with the relation characterized by Equation (6) shows that under the concentration range used in the present study, the approximately treatment stated above is feasible.

The Langmuir adsorption isotherm (Γ vs $C_F^{\frac{1}{2}}$ plot), was shown in Figure 3, from the horizontal segment of this plot, surface excess at saturated adsorption, Γ_{∞} , and the minimum bulk concentration needed to saturate the organic/aqueous interface, C_{\min} , can be obtained. From Equation(6), when $\Gamma = 1/2 \Gamma_{\infty}$, $K' = C_F^{-\frac{1}{2}}$, so the value of K' can be obtained from that of $C_F^{\frac{1}{2}}$ corresponding to the value of $1/2 \Gamma_{\infty}$ on the vs $C_F^{\frac{1}{2}}$ plot. Since the molecules at saturated adsorption orientate in closest packing, the interfacial area occupied by the adsorbed extractant molecules, A_I , can be calculated by dividing the reciprocal of Γ_{∞} by Avogadro's number [1], this value approximates to the cross-section area of the adsorbed molecules. Γ_{∞} , C_{\min} , A_I and K' are a set of parameters characterizing the interfacial activity of extractants.

Effect of diluent and temperature on the interfacial activity parameters

The results listed in Tables 1 and 2 show the effect of diluent on the interfacial activity parameters of HDEHP and HEH[EHP], respectively and that in Table 3 shows

the effect of temperature on these parameters.

Table 1 Effect of diluents on interfacial activity parameters of HDEHP
(at 298±1 K; aqueous phase: pure water)

Diluent	$\sqrt{\omega} \times 10^{10}$ (mol cm ⁻²)	A_{I} (Å ²)	C_{min} (mol dm ⁻³)	K' (mol dm ⁻³) ^{-1/2}	$D_{\text{Co(II)}}^{**}$	$\Delta\sigma^*$
Kerosene	2.17	76.5	0.250	5.32	5.89	8.55
Cyclohexane	2.38	69.8	0.490	3.28	3.89	8.15
CCl ₄	2.34	70.9	0.640	2.56	1.55	7.75
Benzene	2.31	71.9	0.774	2.22	0.59	7.20
Chloroform	2.32	71.6	0.865	2.10	0.34	7.05

* $\Delta\sigma = \sigma_w - \sigma_d$, where σ_w is the solubility parameter of water (16.35); σ_d , the solubility parameter of diluent, here the σ_d of kerosene is replaced by that of dodecane.

** $D_{\text{Co(II)}}^{**}$ is the distribution ratio of Co(II) [3].

Table 2 Effect of diluents on interfacial activity parameters of HEH[EHP]
(at 298±1 K; aqueous phase: pure water)

Diluent	$\sqrt{\omega} \times 10^{10}$ (mol cm ⁻²)	A_{I} (Å ²)	C_{min} (mol dm ⁻³)	K' (mol dm ⁻³) ^{-1/2}	$D_{\text{Cr(III)}}^{**}$	$\Delta\sigma^*$
Kerosene	2.38	69.8	0.0064	42.6	0.912	8.55
CCl ₄	2.01	82.6	0.010	38.5	/	7.75
Benzene	1.85	89.7	0.25	8.70	0.112	7.20
Chloroform	2.28	72.8	0.36	5.00	0.100	7.05

*same illustrations as in Table 1.

** $D_{\text{Cr(III)}}^{**}$ is the distribution ratio of Cr(III).

Table 3 Effect of temperature on interfacial activity parameters of HEH[EHP]

Temperature (K)	$\sqrt{\omega} \times 10^{10}$ (mol cm ⁻²)	A_{I} (Å ²)	C_{min} (mol dm ⁻³)	K' (mol dm ⁻³) ^{-1/2}
293±1	2.32	71.4	0.40	58.5
298±1	2.38	69.8	0.64	42.6
303±1	2.38	69.8	0.79	27.4
308±1	2.31	72.6	1.21	22.6

From the results listed in Table 1, 2 and 3, it can be seen that:

1. In ordinary case, the interfacial concentration of these two extractants is more than their bulk concentration in the aqueous phase, it is favourable for the reactions taking place at the organic/aqueous interface. Furthermore, under the same

conditions, the larger the adsorption constant, K' , the higher is the distribution ratio of the extracted species.

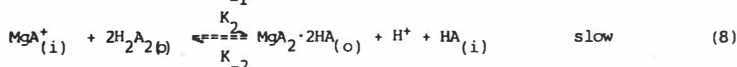
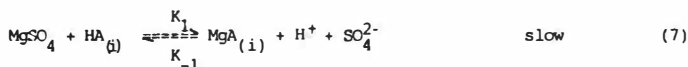
2. The strength of interfacial activity depends on both the temperature and the nature of diluents. The greater the difference of polarity between water and the diluent used in the system, the stronger is the interfacial activity; the higher the temperature, the weaker is the interfacial activity.

EXTRACTION KINETICS OF Mg(II) AND Fe(III) WITH HEH[EHP]

In 1970s, Roddy et al [4] had investigated the extraction kinetics of Fe(III) with HDEHP and proposed that the extraction rate was controlled by series and parallel reactions taking place at the interface. In recent years, we have studied the extraction kinetics of Ni(II) with HDEHP [5], of Cr(III) and Zn(II) with HEH[EHP] [6,7], the results obtained also proved that the rate-determining steps were the interfacial reactions. The present paper reports the results of extraction kinetics of Mg(II) from sulfate solution, and Fe(III) from nitrate solution with HEH[EHP].

Extraction kinetics of Mg(II) from sulfate solution with HEH[EHP]

The extraction kinetics of this system has been studied by means of single drop method[5]. According to the dependency of the initial extraction rate on the specific interfacial area shown in Figure 4 and the experimental kinetic data, it can be considered that the rate-determining steps may take place at the interfacial region, i. e.



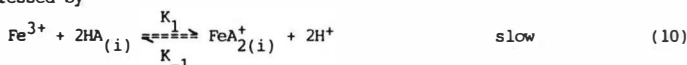
According to Equations (7) and (8), the initial extraction rate equation for the forward extraction may be expressed by

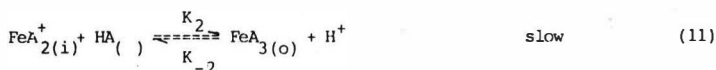
$$R^0 = \frac{K_1 K_2 [\text{Mg}^{2+}] [\text{H}_2\text{A}_2]_{(o)}^2}{K_{-1} [\text{H}^+] [\text{SO}_4^{2-}] + K_2 [\text{H}_2\text{A}_2]_{(o)}^2} \quad (9)$$

By examining the effect of temperature on the extraction rate, in the temperature range of 293-323K, the activation energy for this extraction process was calculated to be 37.1 KJ/mol.

Extraction kinetics of Fe(III) from nitrate solution with HEH[EHP]

Extraction kinetics of this system has been studied using two methods. when the constant interfacial area stirring cell method was applied, the extraction mechanism may be expressed by

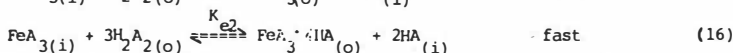
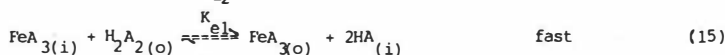
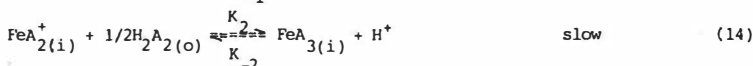
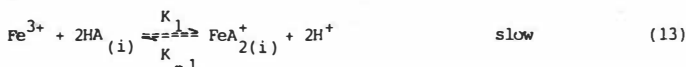




The initial extraction rate equation for the forward extraction is

$$\frac{d[\text{Fe}]}{dt} = a_i \frac{\text{K}_1 [\text{Fe}] [\text{HA}]_{(i)}^3}{\text{K}_{-1} \text{K}_2^{-1} [\text{H}^{+}]^2 + [\text{HA}]_{(i)}} \quad (12)$$

where $[\text{ }]$, $[\text{ }]_{(i)}$ and $[\text{ }]_{(o)}$ represent the concentration of species in the aqueous phase, interface and in the organic phase, respectively; a_i , the specific interfacial area. When the highly stirring method was used, the extraction mechanism may be expressed by



Initial extraction rate is

$$\frac{d[\text{Fe}]}{dt} = \text{K}'_f [\text{Fe}] - \text{K}'_b [\text{Fe}]_{(o)} \quad (17)$$

where

$$\begin{aligned} \text{K}'_f &= a_i \frac{\text{K}_1 \text{K}_2 [\text{H}_2\text{A}_{2(o)}]^{\frac{1}{2}} [\text{HA}]_{(i)}^2}{\text{K}_{-1} [\text{H}^{+}]^2 + \text{K}_2 [\text{H}_2\text{A}_{2(o)}]^{\frac{1}{2}}}; \\ \text{K}'_b &= a_i \frac{\text{K}_{-1} \text{K}_{-2} [\text{H}^{+}]^2 \text{Y}^{-1}}{\text{K}_{-1} [\text{H}^{+}]^2 + \text{K}_2 [\text{H}_2\text{A}_{2(o)}]^{\frac{1}{2}}}; \\ \text{Y} &= \frac{[\text{H}_2\text{A}_{2(o)}] [\text{HA}]_{(i)}^{-2} (\text{K}_{e1} + \text{K}_{e2} [\text{H}_2\text{A}_{2(o)}])}{\text{K}_1 \text{K}_2 \text{K}_{e1}} = 1.79; \quad \lg \frac{\text{K}_1 \text{K}_2 \text{K}_{e1}}{\text{K}_{-1} \text{K}_{-2}} = 4.87 \end{aligned}$$

From the results of extraction kinetics of Mg(II) and Fe(III) with HEH[EHP] stated above, it is logically to propose that due to the interfacial activity of HEH[EHP], the interaction between the extractant molecules adsorbed at the organic/aqueous interface and the metal ions (Mg(II) and Fe(III) in the present study) in the aqueous may be the rate-determining step and is in agreement with the conclusion proposed by Roddy[4].

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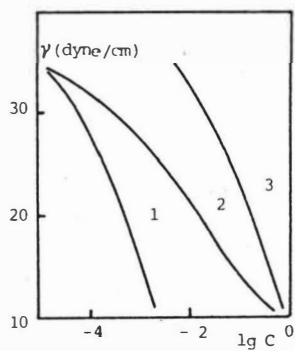


FIG. 1: γ -- $\lg C$ CURVE

1: γ -- $\lg C_1$; 2: γ -- $\lg C_2$;
3: γ -- $1/2 \lg C_F$

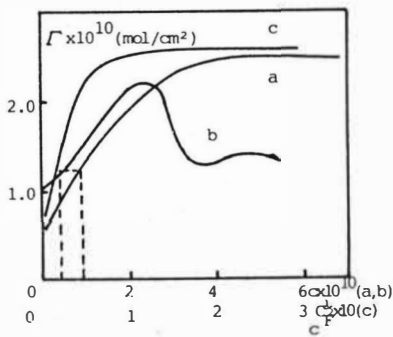


FIG. 2: Γ -- C CURVE

a: Γ -- C_1 ; b: Γ -- C_2 ;
c: Γ -- $C_F^{1/2}$

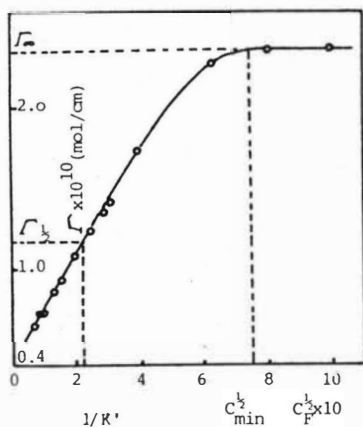


FIG. 3: LANGMUIR CURVE

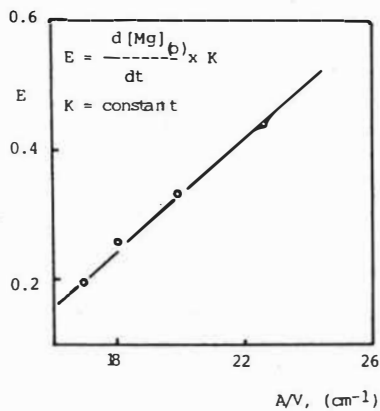


FIG. 4: DEPENDENCY OF INITIAL
EXTRACTION RATE ON SPECIFIC
INTERFACIAL AREA

The importance of dynamic interfacial tension in some commercial metal extraction systems

J.M. Rodrigues de Carvalho, Lisboa/P

Manuscript was not available up to 30 June 1986

II-295-300

Study on the Decomposition of Scheelite Concentrate by LEACHEX Process

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INTRODUCTION

One of the conventional methods of processing scheelite concentrate is to leach the mineral with hydrochloric acid and then to extract the metal values from the leach liquor by a solvent. In this leaching process, one of the reaction products, "tungstic acid", is sparingly soluble in aqueous acid solution and will precipitate onto the surface of unreacted ore particles. This solid film will seriously hinder the reactant acid from diffusing in and one of the products CaCl_2 from diffusing out. In consequence, the overall decomposition rate of scheelite decreases as the reaction proceeds and the leaching process turns to be very slow. Usually the drawback may be lessened by very fine grinding of the ore, raising of the reaction temperature and using a large excess of concentrated acid. For example, ore particles of -325 mesh, a temperature of 368K and two to three times the stoichiometric amount of 8 M acid are used, even so, the percentage decomposition of scheelite can hardly attain 95% in 5 hours.

Other means of accelerating the decomposition rate of scheelite is the use of a ballmill type reactor in which the insoluble "tungstic acid" film covering unreacted particles can be constantly rubbed off so as to reduce the diffusional resistance. But the choice of the material of construction for the mill may offer difficulty.

A complexing leaching process proposed by Xuin et al. (1) is to decompose the mineral by hydrochloric acid in the presence of phosphate so that a soluble tungstatophosphoric acid is formed in stead of the insoluble "tungstic acid" and the percentage decomposition may attain 95% in an hour or so. The only drawback is the unnecessary introduction of phosphorous impurity which is usually detrimental to most tungsten products.

A combined leaching and extraction method named LEACHEX has been developed and reported by one of the authors (2) to process minerals and recover the valuables in them. Unlike the conventional process, LEACHEX process decomposes the mineral by hydrochloric acid in the presence of a suitable organic solvent. In this process leaching and extraction are accomplished simultaneously in a single equipment, LEACHEX reactor. During processing, the reaction product "tungstic acid" is immediately removed from reaction mixture by being extracted into an organic solvent prior to its possible precipitation on the surface of the ore particles. Thus, the concentration of "tungstic acid" in aqueous phase is kept at a low level and the barrier to diffusion of both the reactant and reaction product in the conventional leaching can be avoided. In consequence, the decomposition rate of the mineral is greatly accelerated.

In the present study, the rate controlling step of the LEACHEX process for the decomposition of scheelite concentrate and the effects of various parameters, such as temperature, concentration of HCl in aqueous phase and size of ore particles, have been investigated and the reaction kinetic correlation is proposed.

EXPERIMENTAL

Material: The scheelite concentrate used is from Jiangxi, China, and consists of 66.9% WO_3 and 16.8% CaO . The ore screened through standard sieve into five fractions shown in Table 1 is used to examine the effect of particle size on the rate of the reaction. The WO_3 content and the density of each fraction are also included in the Table.

Table 1 Some properties of ore fractions

size, mesh	size, μm	WO_3 , %	density, kg/m^3
-40 to +60	280 to 450	74.0	6060
-60 to +100	152 to 280	72.0	5580
-100 to +120	125 to 152	70.1	5440
-120 to +160	98 to 125	67.8	5620
-180 to +200	76 to 90	65.2	4960

Hydrochloric acid, extractant and diluent are chemical pure reagent. Other chemicals used in analyses are all of A.R. grade.

Experimental apparatus and procedure: A 250 ml three-mouth round bottom flask immersed in a thermostatically controlled water bath was used as LEACHEX reactor. The flask was provided with reflux condenser, thermometer and stirrer. Temperature was kept constant and controlled within $\pm 1^\circ\text{K}$. The aqueous phase containing hydrochloric acid was fully mixed with the organic phase at the reaction temperature. The concentration of the acid in the equilibrated aqueous phase was taken as initial concentration, $[\text{HCl}]$. Then the liquid phase mixture and a weighed portion of the ore were added into the reactor and the stirrer was started. At regular intervals, samples of about 2 ml of both aqueous phase and organic phase were withdrawn and analysed for WO_3 by means of thiocyanate photometric method.

Unless otherwise stated, the experimental conditions of Table 2 were used.

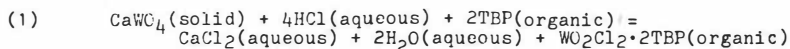
Table 2 Experimental conditions

aqueous phase	about 8 M HCl
organic phase	pure TBP
solid phase	crushed ore containing of all sizes
stirring speed	6 s^{-1}
temperature	as indicated in each case
phase ratio	solid : liquid : organic = $1 \text{ kg} : 0.015 \text{ m}^3 : 0.015 \text{ m}^3$

RESULTS AND DISCUSSIONS

The LEACHEX system

According to De and Rahaman (3), pure TBP can extract tungsten almost quantitatively from 8 - 10 M hydrochloric acid solution and disolvate $\text{WO}_2\text{Cl}_2 \cdot 2\text{TBP}$ is formed. Our preliminary experiments shown that TBP is one of the best solvents with very high distribution coefficient and good phase disengaging property. Therefore, this solvent was used in the subsequent study. In consequence, the overall reaction can be written as follows:



Determination of the rate controlling step

The overall LEACHEX process may consist of the consecutive steps as follows:

- 1 Diffusion of the molecules of hydrochloric acid in bulk aqueous phase through the liquid film surrounding the ore particle.
- 2 Diffusion of the molecules of hydrochloric acid through solid film, if existing, to the reaction zone.
- 3 Decomposition reaction at the surface of unreacted ore.
- 4 Diffusion of the molecules of reaction products through the liquid

and solid films to the bulk of aqueous phase.

5 Diffusion of the molecules of tungsten species to liquid-liquid interface and extraction of tungsten species by solvent.

6 Diffusion of the molecules of the extraction complex into the bulk of organic phase.

To simplify the kinetic study on noncatalytic heterogeneous reaction, researchers always focus their attention on the rate controlling step of the overall process, and then deduce a mathematical model for this controlling step and examine the validity of the model by experimental results.

As revealed by Xuin et al., the specific surface area of scheelite concentrate (grinding to -200 mesh) is only $0.05 \text{ m}^2/\text{g}$, the decomposition reaction of CaWO_4 can only occur at the surface of the ore particles. As the reaction proceeds, reaction products, CaCl_2 and "tungstic acid", are produced. One of them, "tungstic acid", is extracted by TBP immediately instead of precipitating onto the surface of unreacted ore particles. At the same time the impurities mingled with the CaCO_3 particles are disintegrated and separated from the unreacted cores. So the surface of unreacted ore particles is exposed to hydrochloric acid and the decomposition reaction continues. During the process stated above, no solid "tungstic acid" is formed and no inert solid remains on the surface of unreacted core to form solid film to hinder the diffusion of reactant and reaction products, which is proved to be true by following facts.

Firstly, the analyses of the aqueous and organic phases are shown in Table 3. From the values of fractional conversion, x , and concentrations of WO_3 in aqueous and organic phases, $[\text{WO}_3]_{\text{aq}}$ and $[\text{WO}_3]_{\text{org}}$, it is obvious that "tungstic acid" is extracted into solvent as soon as it is formed. Therefore, $[\text{WO}_3]_{\text{aq}}$ is always kept at low values and in no case it tends to precipitate out provided adequate TBP is present.

Table 3 A set of experimental data of LEACHEX process

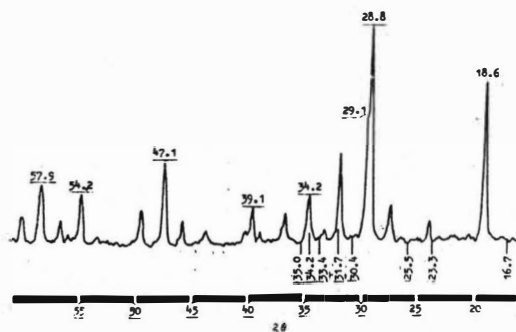
temperature, 353K; $[\text{HCl}]_0$, 8.26 M; ore, -60 to +100 mesh; solvent, pure TBP; other conditions see Table 2.

time, min.	$[\text{WO}_3]_{\text{aq}}, \text{M}$	$[\text{WO}_3]_{\text{org}}, \text{M}$	x	$D(\text{WO}_3)$
1	8.62×10^{-4}	0.0207	0.124	24.0
2	8.62×10^{-4}	0.0339	0.203	39.3
5	1.08×10^{-3}	0.0552	0.335	51.1
10	1.76×10^{-3}	0.0888	0.549	50.4
20	2.59×10^{-3}	0.131	0.780	50.6
30	3.02×10^{-3}	0.152	0.905	50.3

Secondly, the sample of acid insoluble residue taken out at any stage of reaction is grey instead of yellow as it is taken from a conventional leaching. This indicates the absence of yellow tungstic acid on particles in the LEACHEX process.

Thirdly, the x-ray diffraction analysis of the residual solid from LEACHEX process (Fig. 1) confirms the absence of solid tungstic acid.

Due to the absence of solid film covering the unreacted ore particles, the diffusions of hydrochloric acid in one direction and the products in the opposite direction through the solid film can be ruled out. Among the six consecutive steps outlined before, step 2 and step 4 can be neglected. The only resistance to diffusional process is due to a stagnant liquid film surrounding the undecomposed ore particles. The rate of the diffusion of molecules of the reactant and products depends on the properties of the system and hydrodynamic conditions, e. g.



minutes to reach extraction equilibrium, but the time required for complete reaction is about ten times as long as that for extraction. So extraction of metal value is not a rate controlling step and only the decomposition reaction is the rate controlling step of overall LEACHEX process. In addition, the apparent activation energy of 55,200 J/mol (13,200 cal/mol) and first order reaction rate with respect to the surface area of the ore particles (see below) provide further evidences of this conclusion.

Reaction kinetic consideration

As the reaction proceeds, the concentration of HCl in aqueous phase, $[HCl]$, is decreasing. From material balance

$$(2) \quad [HCl] = [HCl]_0 (1-ax)$$

$[HCl]_0$ is initial concentration in aqueous phase, a is a constant and can be found from experimental data, x is fractional conversion of WO_3 . In case the rate of the overall process is limited by chemical reaction, the rate equation may be written as

$$(3) \quad \frac{dx}{dt} = K (1-x)^{2/3} (1-ax)^n$$

where n is the order of reaction, and K depends on conditions and represents the initial rate of the process.

1, Effect of temperature

The reaction rate depends strongly on temperature. The effect of temperature on the rate of the LEACHEX process ranged from 327 to 363K is shown as fractional conversion x vs. time in Fig. 4. These data were analysed by using Eq. (3). It was confirmed that K is a constant for each set of initial conditions. To determine the apparent activation energy of the reaction, the logarithms of K 's were plotted against $1/T$ in Fig. 5. An apparent activation energy of 55,200 J/mol (or 13,200 cal/mol) has been obtained and it indicates that the rate of the overall process is governed by chemical reaction according to F. Habashi (4).

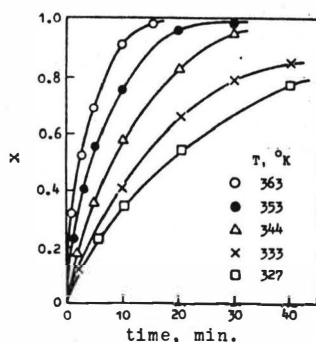


Fig. 4 Temperature dependence

$[HCl]_0$, 8.35 M;
other conditions see
Table 2.

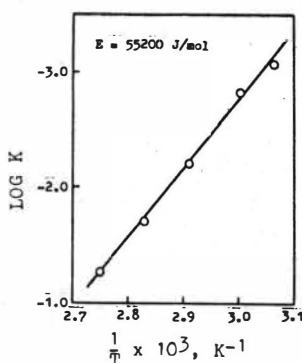


Fig. 5 Arrhenius plot

Data are taken from
Fig. 4.

2, Effect of initial concentration of HCl

In Fig. 6 the fractional conversion of WO_3 , x , was plotted as a function of reaction time with different initial concentrations of HCl in aqueous phase. The fractional conversion has been found to increase rapidly with increasing concentration of HCl. When $[\text{HCl}]_0$ is $\geq 9 \text{ M}$ (355K) decomposition reaction goes to completion within 15 minutes. Plotting $\log K$ vs. $\log [\text{HCl}]_0$ led to a straight line (Fig. 7) which gives a slope equal to about 4.

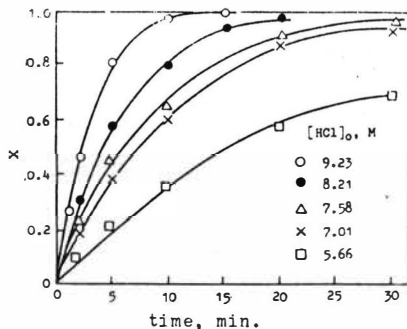


Fig. 6 Plot of x vs. t for different $[\text{HCl}]_0$
temperature, 355K;
other conditions see Table 2.

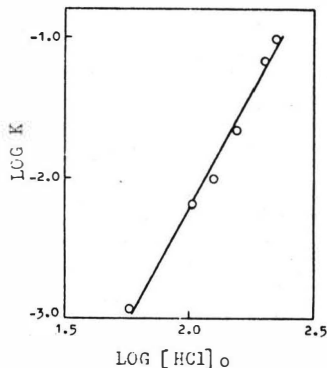


Fig. 7 Effect of $[\text{HCl}]_0$ on K
Data are from Fig. 6.

3, Effect of particle size

Because the density of the ore varies with size of the ore particles, specific surface area, S , in stead of radius was used in evaluation and was calculated from the mean values of particle size and density. Fig. 8 gives the curves of the fractional conversion vs. time for

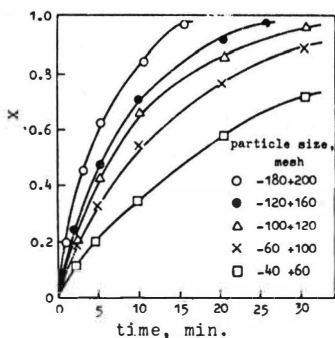


Fig. 8 Plot of x vs. t for different particle sizes
 T , 353K; $[\text{HCl}]_0$, 8.35 M;
other conditions see Table 2.

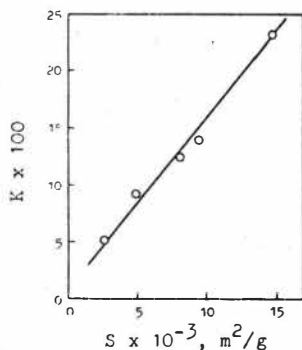


Fig. 9 Effect of S on K
Data are taken from Fig. 8.

different particle sizes. The fact that K is directly proportional to S (Fig. 9) is consistent with result predicted by the unreacted-core-shrinking model.

4, Effect of concentration of TBP in organic phase

From the theoretical model the reaction rate is independent of the TBP concentration provided that there is sufficient TBP to form disolvate. Experimental results listed in Table 4, confirm the prediction and support again the conclusion that the rate of the LEACHEX process is not limited by extraction of tungsten by TBP.

Table 4 Effect of TBP concentration on the rate of the LEACHEX process

temperature, 353K; $[HCl]_0$, 8.96 M; organic phase, TBP in M in kerosene; other conditions see Table 2.

TBP concentration, M	1.46	1.83	2.19	2.92	3.65
initial rate K	0.236	0.230	0.234	0.244	0.232

Reaction kinetic correlation

The kinetic equation may be expressed by an empirical one with relevant parameters in exponent form. The constants were estimated by microcomputer model PDP-11 with optimization method and rounded. A kinetic equation is thus obtained as follows:

$$(4) \quad \frac{dx}{dt} = K (1-x)^{2/3} (1-ax)^{4.0}$$

$$(5) \quad K = 4.35 \times 10^5 \exp(-55,200/RT) \cdot [HCl]_0^{4.0} \cdot S^{1.0}$$

Comparison of different methods

By LEACHEX process, the decomposition of scheelite concentrate is greatly accelerated by many folds. The curves in Fig. 10 illustrate the different rates between different methods. Because of high reaction rate of LEACHEX process, the decomposition of mineral may be carried out at much lower temperature and be able to use larger particles of the ore than the conventional leaching process. therefore, the energy consumption is low. In addition, a partial separation of impurities may be realized and the flow sheet of processing scheelite concentrate can be simplified.

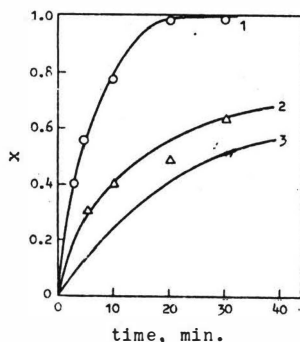


Fig. 10 Rates of different methods

temperature, 353K;
1, LEACHEX process; $[HCl]_0$,
8.36 M; ore, -40 mesh;
2, leaching with HCl and
 PO_4 ; $[HCl]_0$, 8.0 M; ore,
-40 to +200 mesh(1);
3, conventional leaching
with HCl; $[HCl]_0$, 7.70 M;
ore, -320 mesh(5).

CONCLUSIONS

The results obtained from the present investigation are summarized as follows:

1 LeACHEX process for the decomposition of scheelite concentrate is a competitive method with many advantages over other methods, such as simple flow sheet, high reaction rate and low energy consumption. It may also be used to process other minerals.

2 The overall rate of LEACHEX process for the decomposition of scheelite concentrate is controlled by the decomposition reaction.

3 Using the unreacted-core-shrinking model, an empirical kinetic equation can be written as Eqs. (4) and (5).

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Many Researches have been performed on the rate of metal extraction by chelating agents. Nevertheless, considerable disagreement still exists about the mechanism of metal transfer. There exist three main reasons for this disagreement. The first is the interpretation of the kinetic data. The kinetic data have been interpreted with the help of reaction orders with respect to metal ion, chelating agent and hydrogen ion. In metal extraction by chelating agents, the rate processes accompanied with extraction are complicated and the diffusion effect cannot be eliminated from the overall extraction rate. Thus, the mechanism of metal transfer is not well understood only by this approach. The second is concerned with the locus of metal complex formation. Two loci were proposed, i.e., aqueous phase (1) and interfacial zone (2). The commercial chelating agents are strongly surface-active and less soluble in the aqueous phase. The interfacial reaction would play major role in complex formation. The third is the heterogeneous nature of the complex formation. The copper extraction rate by commercial chelating agents was reported to be controlled by the formation of 1:2 metal-chelating agent complex. This is not well interpreted by usual reaction kinetics for metal complex formation. The aim of the present work is to formulate the rate of metal extraction by taking into account the reaction processes in the aqueous phase and in the interfacial zone, and to interpret the complicated features of metal extraction. Also, we discuss, from kinetic view point, the key factors which are important for selecting molecular form of chelating agent and the diluent of the chelating agents.

Reaction Processes: Consider the reaction processes accompanied with divalent metal M^{2+} extraction by hydroxyoxime HR. The equilibrium relationship is obtained by considering the reaction processes shown in Table 1. The reaction processes in the aqueous phase are described by Fig.1 from kinetic view point. We postulate that the concentration of MR_2 , $[MR_2]$, is much greater than $[MR^+]$ and that pK_a for HR is much greater than pH. At this condition, a stationary state method for MR^+ and R^- is available and this provides the rate of formation of 1:2 complex MR_2 :

Table 1 Reaction processes for metal extraction equilibrium

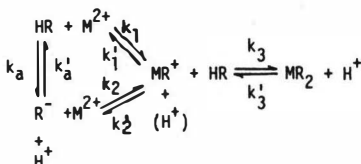
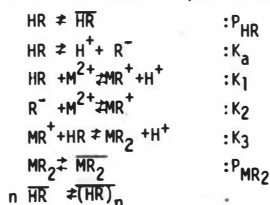


Fig.1 Reaction processes of metal complex formation

$$r = k_b([HR] - [MR_2][H^+]^2 / K_1 K_3 [HR][M^{2+}]) \quad (1a)$$

$$k_b = k [M^{2+}] / [1 + k([H^+] / K_a + k_2[M^{2+}] / K_a)] \quad (1b)$$

Chelating agent of commercial use is composed of polar and apolar parts. The monomer hydroxyoxime in the interfacial zone interacts with water molecules and takes perpendicular orientation of non-polar rest part of the chelating agent molecule to the interface. Thus, the interfacial zone where polar part of the chelating agent exists functions as a phase similar to the aqueous bulk phase. The reaction processes concerned with the interface are shown in Fig.2. The stationary states for R^- and MR^+ in the interfacial zone are expressed as

$$k_3^* \theta_{HR} - k_1^* [H^+]_i \theta_{R^-} - k_2^* [M^{2+}]_i \theta_{R^-} + k_2^* \theta_{MR^+} = 0 \quad (2)$$

$$k_1^* [M^{2+}]_i \theta_{HR} - k_1^* [H^+]_i \theta_{MR^+} + k_2^* [M^{2+}]_i \theta_{R^-} - k_2^* \theta_{MR^+} - k_3^* [X_{HR}]_i \theta_{MR^+} + k_3^* [H^+]_i \theta_{MR_2} = 0 \quad (3)$$

The rate of MR_2 formation in the interfacial zone per unit area is described as

$$r^* = k_3^* [X_{HR}]_i \theta_{MR^+} - k_3^* [H^+]_i \theta_{MR_2} \quad (4)$$

Here, the asterisk is the term concerned with the interface and the subscript i represents the value adjacent to the interface. Since the species of adsorption is mainly HR , the surface fraction covered by species I, θ_I , is expressed by Langmuir isotherm:

$$\theta_I = K_I^S [I]_i / (1 + K_I^S [HR]_i), K_I^S = \text{adsorption equilibrium constant of species } I \quad (5)$$

Substitution of Eqs.(2) and (3) into Eq.(4) with Eq.(5) yields

$$r^* = k_s ([HR]_i - [H^+]_i [MR_2]_i / K_1 K_3 [HR]_i [M^{2+}]_i) \quad (6)$$

$$k_s = k_b [1 + K_{HR}^S / (1 + K_{HR}^S [HR]_i)] \quad (7)$$

In the above derivation, we used the approximations:

$$k^* / \Gamma^\infty = k, \Gamma^\infty = \text{saturated surface concentration} \quad (8)$$

$$K_{HR}^S = K_{R^-}^S = K_{MR^+}^S \quad (9)$$

$$[X_{HR}] \equiv [HR] \quad (10)$$

The reaction rate constants concerned with the interface can be related to those in the aqueous phase with the help of Eq.(8). Adsorption equilibrium constants of species with group R approximately agree with each other, if the electrical potential near the interface is weak. Eq.(10) is a key assumption to interpret the complicated features of the metal extraction by chelating agents. The rotational motion of the adsorbed species MR^+ is strongly restricted due to amphiphilic nature of the chelating agent. Thus, it is natural to consider that the MR^+ complex in the interfacial zone reacts with the HR which has been dissolved into the aqueous phase. The interfacial reaction rate, Eq.(6) with Eq.(7), is expressed in term of the reaction rate constants in the aqueous phase.

Eqs.(6) and (7) are applicable to surface-active chelating agents. In case of surface-inactive agents, the surface excess quantity of HR is zero. Even in this case, interfacial reaction can take place. Taking this into account, Eqs.(6) and (7) are

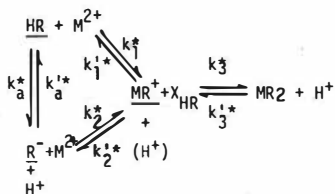


Fig.2 Reaction processes of metal complex formation in interfacial zone. The species with underline represent adsorbed state.

rewritten as

$$r^* = k_s^* ([HR] - (1/K_1 K_3) [H^+]^2 [MR_2]_i / [M^{2+}]_i [HR]_i) \quad (11a)$$

$$k_s^* = k_b [\delta P_{HR} + P_{HR}^{\infty} K_{HR} / (1 + K_{HR} [HR]_i)], K_{HR}^S [HR] \approx \bar{K}_{HR}^S [\bar{HR}], k_{HR}^S = \bar{K}_{HR}^S P_{HR} \quad (11b)$$

δ is the thickness of the interfacial zone and P_{HR} is the partition coefficient of HR, which is defined by $P_{HR} = [\bar{HR}] / [HR]$, the term with overline representing the value in the organic phase.

Metal extraction rate: The rate of metal extraction is obtained by solving the diffusion equations with complex formation in the aqueous stagnant phase

$$Dd^2[HR]/dx^2 = -2Dd^2[MR_2]/dx^2 = 2k_b([HR] - 2[MR_2]/K), K = 2K_1 K_3 [M^{2+}][HR]/[H^+]^2$$

with the use of the boundary conditions:

$$\text{At } x=L, [HR]=[HR]_b, Dd[HR]/dx + 2Dd[MR_2]/dx = 0, -Dd[HR]/dx = (V/A)(2k_b)([HR]_b - 2[MR_2]_b/K)$$

$$\text{At } x=0, Dd[MR_2]/dx + k_s^*([HR]_i - 2[MR_2]_i/K) = k_0([MR_2]_i - [MR_2]_b), [MR_2]_i P_{MR_2} = [MR_2]_b$$

The resultant expression of the metal extraction rate is given by

$$j = (1/2R_0 P_{HR}) (R_a^{-1} + R_s^{-1}) / (R_a^{-1} + R_s^{-1} + R_0^{-1}) ([HR]_i - [MR_2]_i [H^+]_i^2 / K_{ex} [HR]_i [M^{2+}]_i) \quad (12)$$

$$R_0^{-1} = 2k_0 K_{ex} P_{HR} [M^{2+}]_i [HR]_i / [H^+]_i^2, R_s^{-1} = 2k_s^*, R_f = (1 + K^{-1}) \coth \zeta_b / (k_w \zeta_b)$$

$$\bar{R}_f + \bar{R}_f = (1 + K^{-1}) \sinh(2\zeta_b) / (2k_w \zeta_b), R_b = (A/V) \coth \zeta_b \sinh(2\zeta_b) / (2k_b), R_a^{-1} = R_f^{-1} + R_b^{-1} \quad (13)$$

Here, k_w and k_0 are the mass transfer coefficients in the aqueous and the organic phases, respectively. A and V are the interfacial area and the volume of the aqueous phase. D is the diffusion coefficient in the aqueous phase. K_{ex} is the overall equilibrium constant of metal extraction. The metal flux is expressed by the resistances. The equivalent circuit of metal flow is shown in Fig.3.

When $R_b \gg R_s, R_f \gg R_0$, the initial rate is simply expressed by

$$j = j_f + j_s \quad (14)$$

$$j_f = P_{HR}^{-1} [k_b D (1 + K^{-1})^{-1/2}]^{1/2} [HR]_i = \text{contribution of aqueous phase reaction} \quad (15a)$$

$$j_s = k_b [\delta + P_{HR}^{\infty} / ([HR]_i + 1/K_{HR}^S)] [HR]_i = \text{contribution of interfacial reaction} \quad (15b)$$

Experimental results and discussion:

1) Effect of P_{HR} : The extraction rate given in the preceding section can interpret the complicated features of Cu(II) extraction by several hydroxyoximes. Miyake et al. (3) reported the rate of Cu(II) extraction by o-hydroxy acetophenone oxime (HAPO) in benzene solution. This oxime is soluble in the aqueous phase, P_{HR} being 40, and is surface-inactive. The reaction rate constants are necessary for evaluating the metal flux. The k_1 value was observed for Cu(II)-HAPO in 80% methanol solution, the value being $2.5 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. From this, we assume that k_1 is $1 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

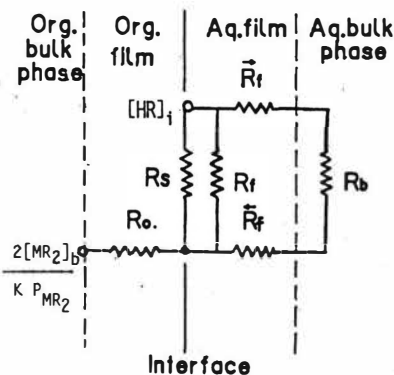


Fig.3 Equivalent circuit for conversion from HR to MR_2

k'_a can be estimated from the value for diffusion controlled reaction rate constant. k_2 is given by the value estimated from Eigen's mechanism. Also, we assume that MR_2 formation is controlled by the formation of MR^+ , i.e., $k_3K_1 = \infty$ (Strictly, k_3K_1 value should be $1 \times 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, so as to fit the data). The experimental Cu(II) fluxes are compared with the calculated ones from Eq.(12) in Fig.4. In this case the contribution of the interfacial reaction to overall flux is negligibly small. The experimental results can be reproduced by the calculation with the rate constants mentioned above, and the metal complexes are formed in the aqueous stagnant film. The rate determining step for MR_2 formation is the reaction to yield MR^+ .

The observed rates of Cu(II) extraction by 2-hydroxy-5-nonyl acetophenone oxime (HNAPO) in n-heptane solution are shown in Fig.5. In this case, $P_{HR} = 1700$, and HNAPO is much less soluble in the aqueous phase than HAPO. The results calculated from Eq.(12) agree well with the experimental fluxes, when using the parameter values shown in the figure. The terms concerned with the interface are obtained from the interfacial tension lowering. The rate constants are the same as in HAPO system except for k_3K_1 which is decided for the calculated value to fit the experimental one. In this case, the interfacial reaction to yield 1:2 complex MR_2 from MR^+ dominates the metal extraction rate.

The change of the rate determining step with P_{HR} can be interpreted in term of the second term of the denominator in Eq.(1b), $(k P_{HR} [H^+] / k_3 K_1 [HR])$. This term is much smaller than unity when P_{HR} is small, yielding that the rate determining step being

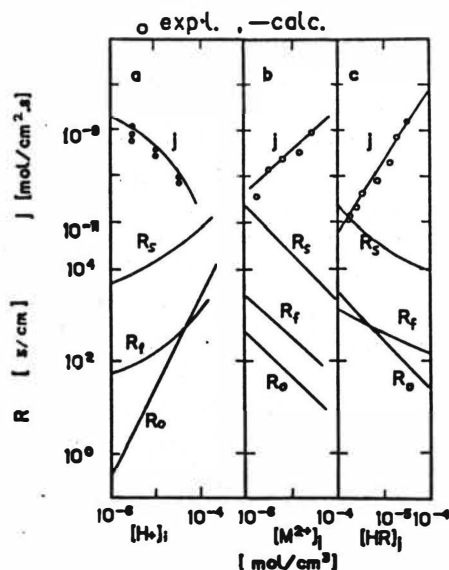


Fig.4 Comparison of calculated flux with experimental one in Cu(II)-HAPO in benzene and the contribution of resistances to overall flux. R_e is much larger than the other resistances.

Condition of calculation:

$$k_1 = 10^6 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

$$k_a = 70 \text{ s}^{-1}$$

$$k'_a = 3.5 \times 10^{13} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

$$k_2 = 5 \times 10^{11} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

$$k_3 = \text{infinite}$$

$$K_{HR}^S = 0, \delta = 10^{-7} \text{ cm}$$

$$(a) [Cu^{2+}]_i = 1.5 \times 10^{-5}, [HR]_i = 7.9 \times 10^{-6}$$

$$(b) [H^+]_i = 1.0 \times 10^{-5}, [HR]_i = 8.0 \times 10^{-6}$$

$$(c) [H^+]_i = 3.2 \times 10^{-5}, [Cu^{2+}]_i = 1.5 \times 10^{-5}$$

in mol/cm^3

MR⁺ formation process. When P_{HR} is large, the term becomes greater than unity, rate determining step being MR₂ formation process.

Effect of diluent: The rates of Cu(II) extraction by HNAPO in several diluents are shown in Fig.6 with the experimental condition. At this condition, the rate of extraction reduces to

$$j = j_s = (k_3 K_1 [\overline{\text{HR}}]_i [\text{M}^{2+}]_i / P_{\text{HR}}) (\delta [\text{HR}]_i + \Gamma^\infty [\text{HR}]_i / (1/\overline{K}_{\text{HR}}^S + [\text{HR}]_i)) / [\text{H}^+]_i \quad (16)$$

because $R_B \gg R_f, R_S \gg R_O$. The $\overline{K}_{\text{HR}}^S$ is much greater than $[\text{HR}]_i$, and $\delta \ll \Gamma^\infty [\text{HR}]_i$. Thus, Eq.(16) is simply expressed by

$$j = (k_3 K_1 \Gamma^\infty / P_{\text{HR}}) [\text{HR}]_i [\text{M}^{2+}]_i / [\text{H}^+]_i \quad (17)$$

The concentration dependencies of j are the same as having been reported by several investigators for commercial chelating agents. The experimental data for heptane, toluene, benzene and their mixtures are in proportional to P_{HR}^{-1} , and can be explained by Eq.(17).

Key factors for metal extraction rate: The effects of substitutional group of the oxime and of the diluent are also shown in Fig.6. The broken curve is the result of calculation from Eq.(15a), i.e., the contribution of complex formation in aqueous phase to the overall flux. When P_{HR} is small, the aqueous phase reaction dominates the extraction rate. The dotted curves are the result calculated from Eq.(15b) by taking $\overline{K}_{\text{HR}}^S$ as the parameter. The experimental results for HNAPO change along the curve with the parameter value $\overline{K}_{\text{HR}}^S = \infty$, and the interfacial reaction dominates the extraction rate because HNAPO takes large P_{HR} and $\overline{K}_{\text{HR}}^S$ values. From this figure, the important factor for metal extraction rate is the solubility of chelating agent into the aqueous phase. The adsorption constant is also important for the extraction rate, because interfacial reaction increases the rate. The resistance ratio R_f / R_S can be evaluated from Eq.(13) as

$$R_f / R_S = (P_{\text{HR}} / L) (\delta + \Gamma^\infty \overline{K}_{\text{HR}}^S / (1 + \overline{K}_{\text{HR}}^S [\text{HR}]_i)) \epsilon_b \coth \epsilon_b \quad (18)$$

Here, L is the thickness of aqueous stagnant film. When this ratio is large compared with unity, the interfacial reaction dominates the extraction rate.

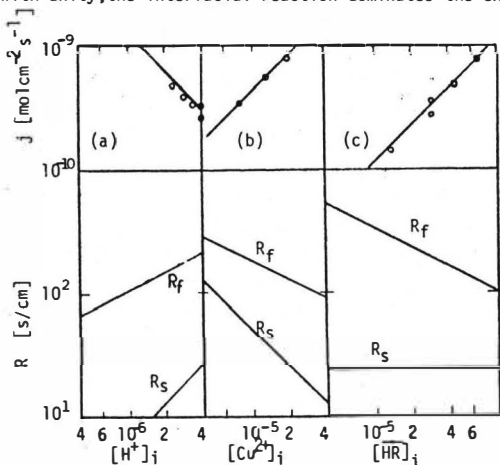


Fig.5 Comparison of calculated flux with experimental one in Cu(II)-HNAPO in heptane solution R_O and R_B are negligible.

Condition of calculation:

$$k_1 = 10^6 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

$$k_a = 1.4 \times 10^{10} \text{ s}^{-1}$$

$$k_d = 3.5 \times 10^{13} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

$$k_2 = 5 \times 10^{11} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

$$k_3 K_1 = 2.2 \times 10^7 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

$$\overline{K}_{\text{HR}}^S \gg 5 \times 10^6 \text{ cm}^3 / \text{mol}$$

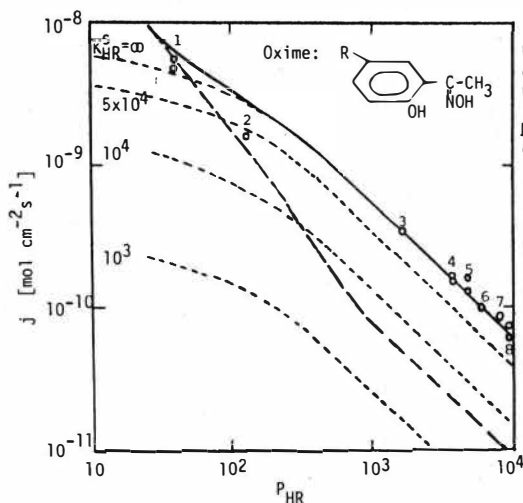
$$\Gamma^\infty = 1.8 \times 10^{-3} \text{ mol} / \text{cm}^2 \quad \delta = 10^{-7} \text{ cm}$$

$$(a) [\text{Cu}^{2+}]_i = 2 \times 10^{-5}, [\text{HR}]_i = 2.9 \times 10^{-5}$$

$$(b) [\text{H}^+]_i = 4.0 \times 10^{-6}, [\text{HR}]_i = 7 \times 10^{-5}$$

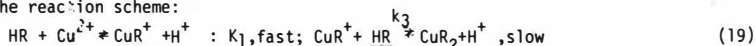
$$(c) [\text{H}^+]_i = 4.0 \times 10^{-6}, [\text{Cu}^{2+}]_i = 2 \times 10^{-5}$$

$$\circ \text{ obs.} \quad \text{—} \text{ calc.}$$

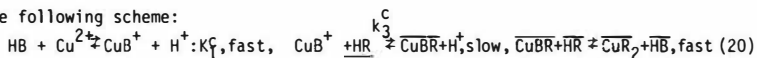


Catalysis of oxime : Many studies have been performed on the catalysis of oxime for Cu(II) extraction, e.g., for LIX65N-LIX63 system. However, the mechanism of the catalysis has not been elucidated. Many investigators analyzed their kinetic data in term of reaction orders, without extracting the catalytic effect from overall extraction rate. Here, we discuss the catalytic role of 5,8-diethyl-6-hydroxy-7-oximinododecane (DEHO) in Cu(II) extraction by HNAPO in benzene.

In Cu(II) extraction by HNAPO, Eq.(17) is applicable. This equation is simply derived by the reaction scheme:



Here, HR is the HR species adsorbed. The reaction to yield 1:1 metal complex is fast and is in equilibrium state. The reaction to yield 1:2 metal complex controls the extraction rate. It can be shown that this scheme is equivalent to that previously shown in Fig.2. LIX63 has the characteristics: 1) pK_a is greater than that of LIX65N or HNAPO(4), 2) Solubility of LIX63 into aqueous phase and the adsorption equilibrium constant are in the same order of magnitude as those of LIX65N and HNAPO(5). From these characteristics, we can estimate that the reaction processes concerned with the interface does not take part in the catalytic effect, because LIX63 shows the catalytic effect even when $[LIX63]$ is much smaller than $[LIX65N]$ or $[HNAPO]$. LIX63 composes five membered chelate ring, and the hydroxyl hydrogen of LIX63 is labile, these leading to the increase in the formation constant of 1:1 metal complex. Taking these into account, the catalytic role of LIX63 (denoted as HB) is interpreted by considering the following scheme:



This scheme is analogous to the model proposed by Ashbrook(6). The catalytic effect

is described as

$$j^C = (k_3^C k_1^C / P_{HB}) I^{\infty} [HB]_i [Cu]_i [H^+]_i^{-1}, \text{ when } \bar{K}_{HR}^S [HR] \gg 1 \quad (21)$$

Combining Eq.(21) with Eq.(17), the overall extraction rate, r , is related to the rate without HB, $j_{[HB] \rightarrow 0}$:

$$j/j_{[HB] \rightarrow 0} = 1 + (k_3^C k_1^C / k_3 k_1) (P_{HR} / P_{HB}) ([HB] / [HR]) \approx 1 + G [HB] / [HR] \quad (22)$$

Figure 7 shows the catalytic effect of DEHO in Cu(II) extraction by HNAPO in benzene solution. The experimental data can be fitted by Eq.(22), yielding that $G=30$.

Experimental: Reagents used in this work are the same as in the report(3) except for DEHO, which was purified from LIX63 by the procedure reported in the literature(7). Mass transfer experiments were performed with the use of quartz cell of Lewis type. The absorbance of the complex was measured by using position-scanning spectrophotometer(8) at 25.0°C. The interfacial tension was measured by the pendant drop method at 25°C.

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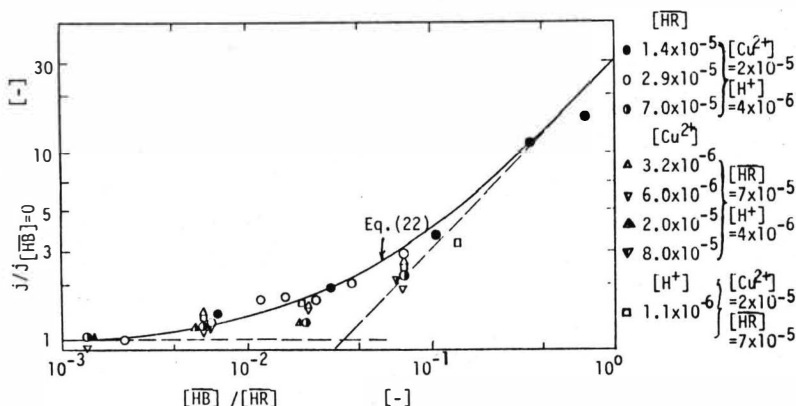


Fig.7 Catalytic effect of DEHO in Cu(II) extraction by HNAPO in benzene solution

Diffusion Measurement of the Hydroxyoximes in LIX64N by FT-NMR Technique

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ABSTRACT

Experimental self-diffusion coefficients of the anti- and syn-isomers of 2-hydroxy-5-nonylbenzophenone oxime and anti-5,8-diethyl-7-hydroxy-6-dodecanone oxime obtained by the NMR Fourier-transform pulsed field gradient spin-echo method are presented. The diffusion coefficients were measured at varying solute concentrations using CCl_4 and CDCl_3 as solvents. Values estimated with the Wilke and Chang correlation agree reasonably well with the present experimental values extrapolated to infinite dilution.

INTRODUCTION

Knowledge of the diffusivity of the various extractants is necessary for studies of mass transport in conventional and in liquid membrane extraction systems, but hardly any experimental data even for the most common reagents have been available. In the commercial extractant LIX64N by Henkel Co., USA, the main extracting compound is 2-hydroxy-5-nonylbenzophenone oxime (HNBPO), and the catalyst is 5,8-diethyl-7-hydroxy-6-dodecanone oxime (DEHO). These oximes exist as anti- and syn-isomers and in nonpolar solvents they have a tendency to self-associate. The aggregates may contain up to four monomers in hydrocarbon solutions (1,2). Most correlations available for the estimation of diffusion coefficients, as for example the Wilke-Chang correlation (3) often used in solvent extraction studies, are empirical modifications of the Stokes-Einstein equation valid for spherical solutes in diluted systems. The association of solvent molecules is taken into account with a correction factor, but the correlations neither take the association of the solute molecules into account nor are they able to distinguish different isomers.

The present paper reports measurements of the self-diffusion coefficients of anti-HNBPO, syn-HNBPO and anti-DEHO obtained by the Fourier-transform NMR pulsed field gradient spin-echo (FT-PGSE) method. In this method the mean square displacement of the nucleus (tagged via nuclear spin) is measured and one obtains the values of self-diffusion coefficients for the molecular motion of each component at the existing composition of the uniform mixture. The self-diffusion coefficient is determined by the frictional properties of the system and does not contain a thermodynamic contribution. The FT-PGSE technique offers a convenient method for measuring individual self-diffusion coefficients in multicomponent systems. Previously it has been used to study for example the association in micellar (4-6) and microemulsion (7-9) solutions.

EXPERIMENTAL

Chemicals: The pure anti- and syn-isomers of 2-hydroxy-5-nonylbenzophenone oxime were isolated from LIX65N (Lot.no. 5M19324) by methods described previously (10). The free anti-isomer was thus prepared by dissolving the copper complex in the solvent in question and this was then stripped with sulfuric acid (150 g/dm^3) and washed with water. The pure anti-5,8-diethyl-7-hydroxy-6-dodecanone oxime was isolated from LIX63 (Lot.no. 4M10123) following the method by Tammi (11). CDCl_3 (Fluka, >99.8% D) and CCl_4 (Merck, >99.5%) were used without further purification. The water was distilled water which was deionized with a MilliQ water purification system.

Diffusion measurements: The self-diffusion coefficients were measured using pulsed field gradient spin-echo FT-NMR method (8,12,13). The measurements were performed on a Bruker CXP-100 spectrometer, operating at 90 MHz for ^1H , at the ambient probe temperature $26.5 \pm 0.5 \text{ }^\circ\text{C}$. The diffusion coefficients were evaluated by a non-linear least squares curve fitting to the relation

$$A = A_0 \exp[-\gamma^2 g^2 D \delta^2 (\Delta - \delta/3)] \quad (1)$$

where A and A_0 represent the amplitudes of a NMR line with and without a pulsed field gradient, D the self-diffusion coefficient, g the magnitude of the applied field gradient and γ the magnetogyric ratio. Δ and δ are time parameters in the experiment, as described previously (12). Δ was kept constant at 140 ms and δ was varied between 20 and 80 ms. The gradient was calibrated using pure water, where $D = 2.30 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at $25 \text{ }^\circ\text{C}$ (14). A typical standard deviation for a self-diffusion coefficient fitted to equation (1) is 3%.

RESULTS AND DISCUSSION

The concentration dependency of the self-diffusion coefficients for anti-HNBPO and anti-DEHO is shown in Figure 1 and Figure 2, respectively. CCl_4 and CDCl_3 were used as solvents. The former represents a medium in which self-association of the oximes is known to take place, while in the latter solvent the oximes are essentially monomeric (10).

DEHO is the smaller molecule of the two oximes. The molar volume of DEHO is estimated according to Le Bas (15) to be $389.6 \text{ cm}^3/\text{mol}$ which can be compared to $430.3 \text{ cm}^3/\text{mol}$ for HNBPO. Consequently, DEHO diffuses about 10-20% faster than HNBPO in both solvents. The two isomers of HNBPO are of the same size, but the syn-isomer diffuses slightly slower than anti-HNBPO (Table 1), which can be attributed to the higher self-association tendency of the syn-isomer (10). The measurement of the diffusion coefficients for the copper complexes of the oximes was not possible due to rapid spin-spin relaxation.

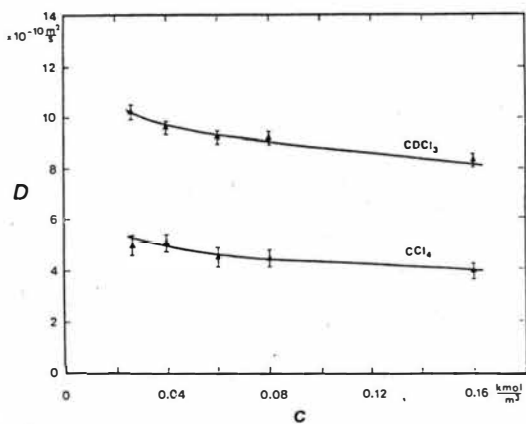


Figure 1: The concentration dependence of the self-diffusion coefficient of anti-HNBPO dissolved in CDCl₃ and in CCl₄.

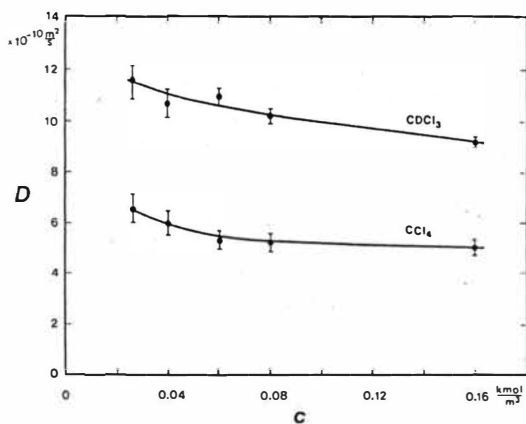


Figure 2: The concentration dependence of the self-diffusion coefficient of anti-DEHO dissolved in CDCl₃ and in CCl₄.

The diffusivity of both anti-HNBPO and anti-DEHO decreased with increasing concentration in both solvents (Figures 1 and 2). According to osmometric measurements in CHCl_3 (10) the mean aggregation number, \bar{n} , of anti-HNBPO increases only to 1.15 within the examined concentration range (0.026 - 0.160) kmol/m^3 . Self-association cannot therefore alone explain the decrease in diffusivity observed in CDCl_3 and the effect must mainly be attributed to other types of molecular interactions, such as hydrocarbon chain entanglement etc., that slow down the mobility of the oximes. Viscosity, being a macroscopic sum of all molecular interactions involved, reflects the same effect. Previous measurements of the viscosity of 2,2,4-trimethylpentane and CHCl_3 solutions proved that the addition of anti-HNBPO causes an almost linear increase in the viscosity of the solutions. For example at $c = 0.16 \text{ kmol/m}^3$ the viscosity of a CHCl_3 solution is $0.620 \text{ g m}^{-1}\text{s}^{-1}$ instead of $0.541 \text{ g m}^{-1}\text{s}^{-1}$ for pure CHCl_3 . If one assumes in an analogous manner to the Wilke-Chang correlation (Equation 2, below) that $D = \eta^{-1} \bar{n}^{-0.6}$, where η is the viscosity of the mixture and the mean size of diffusing solute species is assumed to be directly proportional to \bar{n} , the observed increases in η and \bar{n} are correlated to the observed concentration dependency of the self-diffusion coefficient.

The values for the mutual diffusion coefficient D_{AB}° at infinite dilution calculated according to the Wilke and Chang correlation

$$D_{AB}^\circ = 7.4 \cdot 10^{-8} (\psi M)_B^{0.5} T \eta_B^{-1} V_A^{-0.6} \quad (2)$$

and the Tyn and Calus correlation (16)

$$D_{AB}^\circ = 8.93 \cdot 10^{-8} T \eta_B^{-1} V_A^{1/6} V_B^{-1/3} (P_B/P_A)^{0.6} \quad (3)$$

are shown in Table 1. The latter correlation was chosen to be tested in this work as it has been shown by Hayduk and Minhas (17) to give a smaller average error of 14.2% in comparison to 16.1% for the Wilke-Chang correlation for polar and non-polar substances using 756 data-points. In the above equations ψ is the association parameter for the solvent, M_B is the molar mass of the solvent, T is the temperature, η_B is the viscosity of the pure solvent, V_A and V_B are molar volumes, and P_A and P_B are the parachors. The following values were used in Equations 2 and 3 for the calculation of D_{AB}° shown in Table 1: $V_{\text{HNBPO}} = 430.3 \text{ cm}^3/\text{mol}$, $V_{\text{DEHO}} = 389.6 \text{ cm}^3/\text{mol}$, $V_{\text{CCl}_4} = 103.0 \text{ cm}^3/\text{mol}$ (18), $V_{\text{CDCl}_3} = 88.6 \text{ cm}^3/\text{mol}$ (18), $P_{\text{HNBPO}} = 859.8$, $P_{\text{DEHO}} = 680.6$, $P_{\text{CCl}_4} = 229.8$ and $P_{\text{CDCl}_3} = 190.1$ (calculated according to Ref. 19), $\eta_{\text{CCl}_4} = 0.904 \text{ g m}^{-1}\text{s}^{-1}$ and $\eta_{\text{CDCl}_3} = \eta_{\text{CHCl}_3} = 0.541 \text{ g m}^{-1}\text{s}^{-1}$ corresponding to the temperature of 25°C .

The values for D_{AB}° calculated according to Equations 2 and 3 (Table 1) approximately agree with the experimental values for D extrapolated to zero concentration (see Figures 1 and 2). At infinite dilution the self-diffusion coefficient should theoretically equal the mutual diffusion coefficient, which has also experimentally been verified in

Table 1: Calculated mutual diffusion coefficients, D_{AB}^0 , at infinite dilution, calculated diffusion coefficients, D , at the oxime concentration of 0.160 kmol/m^3 , and experimental self-diffusion coefficients, D , measured at the concentration of 0.160 kmol/m^3 .

Solvent	Solute	Wilke-Chang		Tyn-Calus		Experim. at
		D_{AB}^0	D	D_{AB}^0	D	$c=0.16 \text{ kmol/m}^3$ D
		$10^{-10} \text{ m}^2/\text{s}$		$10^{-10} \text{ m}^2/\text{s}$		$10^{-10} \text{ m}^2/\text{s}$
CCl_4	anti-HNBPO	7.9	5.5	7.8	5.9	3.9 ± 0.3
	syn-HNBPO	7.9	4.4	7.8	4.9	3.2 ± 0.3
	anti-DEHO	8.4	---	8.8	---	5.0 ± 0.3
CDCl_3	anti-HNBPO	11.5	9.2	12.2	10.0	8.2 ± 0.3
	anti-DEHO	12.2	9.8	13.7	11.3	9.2 ± 0.2

several binary systems (20). It looks like the relative diffusivity of the oximes is well predicted by both correlations. The calculated values are, however, too high within the concentration range that is most often of interest in practical applications. In order to take into account the concentration effect, the values of D_{AB}^0 were recalculated according to the Wilke-Chang and the Tyn-Calus correlations by multiplying the molar volume and parachor values of the oximes by \bar{n} valid at the concentration in question and using η for the mixture. The corrected values for the diffusion coefficients are also shown in Table 1. The difference between the calculated and measured values is relatively seen smaller in CDCl_3 , where the compounds are essentially monomeric, than in CCl_4 , where the self-association is more prominent. This reveals the difficulty of handling association phenomena in empirical correlations for diffusion coefficients.

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Extraction Rates of Divalent Metal Ions with Acidic Organo-phosphorus Extractants

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We have proposed a general extraction model to evaluate the extraction rate of metal ions by the chelating extractants [1,2]. The following informations are required to predict the extraction rate by this model.

(1) Physicochemical properties of extractants, for example, the distribution constant between the organic and aqueous phases, the proton dissociation constant, the aggregation in the organic phase and the interfacial adsorption properties.

(2) Extraction ability such as extraction constant and the rate constants of the complex formation.

(3) Mass transfer coefficients of both organic and aqueous stagnant layers.

The purpose of this paper is to show that this general extraction model is applicable to the prediction of extraction rate of divalent metal ions by acidic organophosphorus extractants.

EXPERIMENTAL

(1) Preparation of organic and aqueous phases

Di(2-ethylhexyl)phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (EHPNA), active species of PC88A (Daihachi Chemical Ind. Co., Ltd., Osaka, Japan) were used as extractants. D2EHPA was purified according to the procedure of Partridge and Jensen [3], but EHPNA was used without purification. The diluents used were benzene and n-heptane of analytical grade.

Copper(II), cobalt(II) and zinc(II) solutions were prepared by dissolving their perchlorate salts into deionized water.

The pH was adjusted at 4.0 with sodium hydroxide or perchloric acid, and the ionic strength was adjusted to 0.2 mol/dm^3 with sodium perchlorate. All inorganic chemicals were of analytical grade.

(2) Measurement of physicochemical properties of extractants.

The distribution of extractant between organic and water phases was measured by the usual method [2,4]. The concentration of extractant in water was measured by the procedure of Komasa et

al.[4]. The dimerization constants of extractant in organic phases were measured by the vapor pressure osmometric method (Corona 114). The interfacial tension was measured by the pendant drop method[5].

(3) Extraction of metal ion.

The distribution of metal ions was obtained by the usual method[2]. The concentration of metal ion in the organic phase was completely stripped with 6mol/dm^3 HCl and the concentration of metal in the aqueous phase was analyzed with an atomic absorption spectrophotometer (Nippon Jarrell Ash AA-782).

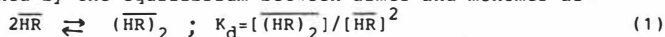
The transfer cell and the experimental procedures were the same as mentioned in the previous papers[2,6].

All experiments were carried out at 298K.

RESULT AND DISCUSSION

(1) Physicochemical properties of extractants

The aggregation of extractant in the organic phase can be explained by the equilibrium between dimer and monomer as

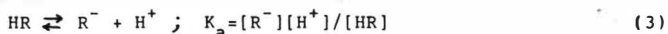


,where - denotes the species in organic phase. The obtained dimerization constants are summarized in Table 1. This result means that the activity of extractant in organic phase can be interpreted in terms of the ideal mixture of monomer and dimer species of acidic organophosphorus extractant.

The distribution ratio of extractant between the organic and aqueous phases was shown by

$$D_{\text{HR}} = (2[(\overline{\text{HR}})_2] + [\overline{\text{HR}}]) / ([\text{HR}] + [\text{R}^-]) \quad (2)$$

The proton dissociation of extractant in aqueous phase was defined as



Therefore, Eq.(2) can be rewritten by the use of Eqs.(1) and (3) as follows.

Table 1. Physicochemical properties of acidic organophosphorus extractants.

Reagent Diluent	D2EHPA		EHPNA	
	Benzene	n-Heptane	Benzene	n-Heptane
K_d [dm^3/mol]	1×10^4	3×10^4	3×10^2	8×10^3
p_{HR} [-]	110	130	510	600
pK_a	1.9	1.9	2.2	2.2
Γ_{HR} [mol/cm^2]	8.0×10^{-11}	1.7×10^{-10}	1.0×10^{-10}	1.2×10^{-10}
K_{HR} [cm^3/mol]	4×10^7	2×10^8	5×10^7	8×10^7

$$D_{HR} = (1 + 2K_d[\overline{HR}])P_{HR}/(1 + K_a/[H^+]) \quad (4)$$

where P_{HR} was defined by

$$HR \rightleftharpoons \overline{HR} \quad ; \quad P_{HR} = [\overline{HR}]/[HR] \quad (5)$$

The pH dependence of the distribution ratio of extractant (EHPNA) is shown in Fig. 1. From the data of the lower pH region, the value of P_{HR} was calculated and the value of K_a was calculated from the higher pH region. These values are summarized in Table 1. The value of P_{HR} in benzene is lower than that in n-heptane, and that of D2EHPA is lower than that of EHPNA. The pK_a is very low, i.e., the organophosphorus acid is the strong acid. This is the characteristics of these acidic organophosphorus extractants compared to the chelating agents such as o-hydroxyoxime[2] and β -diketone[11].

This extractant mainly exists as dimer in the organic phase. However, it is deduced that this extractant mainly exists as monomer at the organic-aqueous interface, for the intermolecular hydrogen bond of extractant is destroyed by the water molecules. Therefore, the adsorptive species of extractant can be considered as both HR and R^- . The effect of the concentration of extractant on the interfacial tension can be expressed by the Gibbs equation as follows.

$$-d\gamma = \Gamma_{HR} d\mu_{HR} + \Gamma_R d\mu_R \quad (6)$$

From the equilibrium relation, the following equations apply.

$$d\mu_{HR} = d\mu_{HR} = d\mu_R + d\mu_H \quad (7)$$

Therefore, Eq.(6) can be rewritten by

$$-d\gamma = (\Gamma_{HR} + \Gamma_R) d\mu_{HR} - \Gamma_R d\mu_H \quad (8a)$$

Under the condition of constant pH, Eq.(8a) becomes as

$$-d\gamma = (\Gamma_{HR} + \Gamma_R) d\mu_{HR} \quad (8b)$$

If the interfacial excess quantities of HR and R^- can be expressed by the Langmuir adsorption isotherm of two components system, Eq.(8b) becomes as follows.

$$-d\gamma = b[\overline{HR}]/(1 + a[\overline{HR}]) d\mu_{HR} \quad (9a)$$

$$\text{where } a = K_{HR} \{1 + K_R K_a / (K_{HR} P_{HR} [H^+])\} \quad (9b)$$

$$b = \Gamma_{HR}^\infty K_{HR} \{1 + \Gamma_R^\infty K_R K_a / (\Gamma_{HR}^\infty K_{HR} P_{HR} [H^+])\} \quad (9c)$$

By the integration of Eq.(9a) using the relation,

$$d\mu_{HR} = RT d \ln [\overline{HR}] \quad (10)$$

the following equation is obtained.

$$\gamma_0 - \gamma = RT b \ln(1 + a[\overline{HR}])/a \quad (11)$$

Here, γ_0 is the interfacial tension at $[\overline{HR}] = 0$. Assuming that the Langmuir constants and the saturated interfacial excess quantities of HR and R^- are approximately equal, Eq.(11) can be simplified as

$$\gamma_0 - \gamma = RT \ln \{1 + K_{HR} (1 + K_a / (P_{HR} [H^+])) [\overline{HR}]\} \quad (12)$$

The change of interfacial tension by the concentration of

extractant is shown in Fig.2. Here, the abscissa was monomer concentration calculated by considering the dimer and monomer equilibrium. The solid line in Fig.2 was calculated from Eq.(12) by use of the values of Γ_{HR}^{∞} and K_{HR} shown in Table 1.

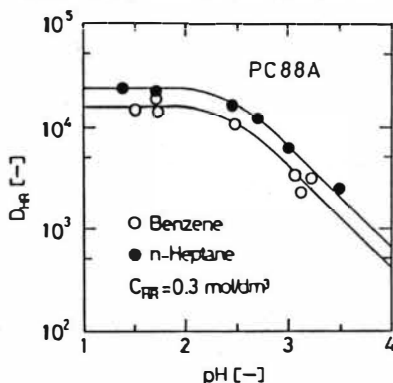


Figure 1. Effects of pH and diluent on the distribution ratio of extractant at pH=4.0.

(2) Extraction equilibrium

The overall reaction of divalent metal ion with the acidic organophosphorus extractant is expressed by



$$K_{ex} = \frac{[\overline{MR_2(HR)_m}][H^+]^2}{[M^{2+}][HR]^{2+m}} \quad (13a)$$

$$K_{ex(d)} = \frac{[\overline{MR_2(HR)_m}][H^+]^2}{[M^{2+}][HR]_2^{1+m/2}} \quad (13b)$$

K_{ex} defined by Eq.(13a) is related to $K_{ex(d)}$ defined by Eq.(13b) as follows.

$$K_{ex(d)} = K_{ex}(k_d)^{1+m/2} \quad (13c)$$

The value of m was obtained from the slope of $\log D_M [H^+]^2$ vs. $\log [HR]_2$ as 2 for Cu(II) and Co(II) and 1 for Zn(II), where D_M is the distribution ratio of metal ion, $D_M = [\overline{MR_2(HR)_m}]/[M^{2+}]$. This results were the same as reported by Komasaawa et al.[7] and Nakashio et al.[8]. The obtained extraction constants are summarized in Table 2. The extraction constant in n-heptane is greater than that in benzene. This result is similar to that of Komasaawa et al.[9].

(3) Extraction rate of divalent metal ion

The extraction mechanism of metal ion is expressed by the following five steps[2].

Step(I): The diffusion process of extractant in the organic stagnant layer is expressed by

$$J_{HR} = k_{o(m)} g([HR]_b - [HR]_i) \quad (14a)$$

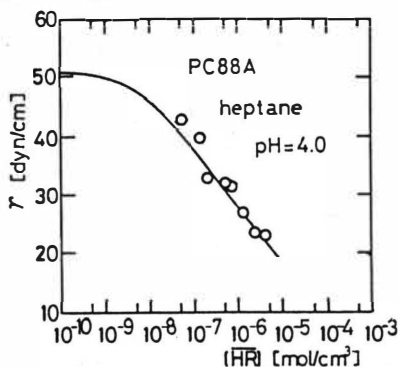


Figure 2. Change of interfacial tension with concentration of extractant.

Table 2. Parameterns for calculation of extraction rate

Metal ion	Zinc(II)	Copper(II)	Cobalt(II)
m	1	2	2
$K_{ex(d)}$ (Benzene)	$5.0 \times 10^{-3} *$	2.0×10^{-5}	2.0×10^{-6}
$K_{ex(d)}$ (n-Heptane)	$3.0 \times 10^{-2} *$	1.0×10^{-4}	1.0×10^{-5}
$k_a(M)$ [cm/s]	1.1×10^{-3}	1.1×10^{-3}	1.1×10^{-3}
$k_o(C)$ [cm/s]	8.3×10^{-4}	6.8×10^{-4}	4.4×10^{-4}
$k_o(m)$ [cm/s]	1.1×10^{-3}	9.0×10^{-4}	5.7×10^{-4}
$k_1 [dm^3/(mol s)]$	1.0×10^7	2.5×10^9	7.9×10^5
$k_2 [dm^3/(mol s)]$	6.3×10^7	1.6×10^{10}	5.0×10^6
δ [cm]	1×10^{-7}	1×10^{-7}	1×10^{-7}

* unit $(mol/dm^3)/0.5$

$$\text{where, } g = 1 + 2K_d(k_o(d)/k_o(m))([\overline{HR}]_b + [\overline{HR}]_i) \quad (14b)$$

The coefficient g was introduced to take into account the diffusion of both monomer and dimer of the extractants, where $k_o(m)$ and $k_o(d)$ are the mass transfer coefficients in the organic stagnant layer for monomer and dimer of extractant, respectively. These values were estimated by use of the observed mass transfer coefficient of complex, $MR_2(HR)_m$ [2].

Step(II): Adsorption process of extractant. Only monomer species adsorb at the interface as described above. It is assumed that the adsorption rate is very fast and the equilibrium relation applies.

Step(III): The diffusion process of metal ion in the aqueous stagnant layer is expressed as

$$J_M = k_a(M)([M]_b - [M]_i) \quad (15)$$

where $k_a(M)$ is the mass transfer coefficient in the aqueous stagnant layer for metal ion. The value was estimated from the zinc extraction rate as 1.1×10^{-3} cm/s, the detail will be described below.

Step (III): The complex formation process proceeds mainly at the organic-aqueous interface, for the extractant has very low overall solubility in the aqueous phase. The reaction paths of complex formations are shown in Fig.3. The proton dissociation rate is very fast because the pK_a of extractant is very low [2]. If the rate of 1:1 complex formation is rate determining step, the final complex formation rate is expressed as follows.

$$\frac{d[MR_2(HR)_m]}{dt} = k_f([\overline{HR}]_i[M]_i - [MR_2(HR)_m]_i[H]_i/K_{ex}[\overline{HR}]_i^{m+1}) \quad (16a)$$

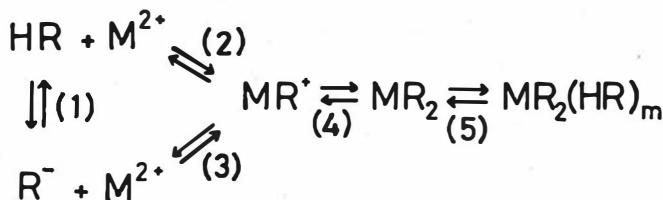


Figure 3. Scheme of reaction between divalent metal ion and acidic organophosphorus extractant.

$$k_f = (k_1 + k_2 K_a / P_{\text{HR}} [\text{H}^+]_i) E_{\text{HR}} / \{1 + (E_{\text{HR}} + 1)(1 + 2E_{\text{HR}} / K_3 (E_{\text{HR}} + 1) [\overline{\text{HR}}]_i / 2K_5 P_{\text{com}} [\overline{\text{HR}}]_i^m)\} \quad (16b)$$

$$E_{\text{HR}} = \delta + \Gamma_{\text{HR}}^{\infty} K_{\text{HR}} / \{1 + K_{\text{HR}} [\overline{\text{HR}}]_i (1 + K_a / P_{\text{HR}} [\text{H}]_i)\} \quad (16c)$$

Here, E_{HR} means the effective concentration of extractant at the interface and that is derived by considering the adsorption of extractant. δ is the length of the interfacial region and the value is about 10^{-7} cm. Assuming that the concentration of MR^+ and MR_2 is negligible small compared to that of $\text{MR}_2(\text{HR})_m$ at the interface, Eq.(16b) is simplified as

$$k_f = (k_1 + k_2 K_a / P_{\text{HR}} [\text{H}^+]_i) E_{\text{HR}} \quad (17)$$

The values of the rate constants can be estimated by assuming the Eigen's mechanism, that are summarized in table 2.

Step(IV): The final complex formed at the interface diffuses to the organic bulk phase through the organic stagnant layer. The rate is expressed as

$$J_C = k_{o(C)} ([\text{MR}_2(\text{HR})_m]_i - [\text{MR}_2(\text{HR})_m]_b) \quad (18)$$

where, $k_{o(C)}$ is the mass transfer coefficient in the organic stagnant layer for the complex. The value was calculated by use of the data of stripping rate of metal complex, because the stripping rates were proportional to the concentration of complex in organic phase and independent of pH in aqueous phase.

Step(V): The diffusion process of the proton in the aqueous stagnant layer is expressed by

$$J_H = k_{a(H)} ([\text{H}^+]_i - [\text{H}^+]_b) \quad (19)$$

where, $k_{a(H)}$ is the mass transfer coefficient of the proton in the aqueous stagnant layer. It is assumed that the value is 5 times as large as $k_{a(M)}$, for the proton diffusivity is very large, and is about 10 times that of metal ion[11].

As the complex concentration in the bulk organic phase is negligible small at the initial period of the extraction, the forward extraction rate was derived by Eqs.(15), (16) and (17) as follows.

$$J_f = [\text{M}]_b / \left\{ \frac{1}{k_{a(M)}} + \frac{1}{(\delta k_f [\overline{\text{HR}}]_i) + [\text{H}^+]_i^2 / (k_{o(C)} K_{\text{ex}} [\overline{\text{HR}}]_i^{m+1})} \right\} \quad (20)$$

Each term in denominator of Eq.(20) means the resistance of mass transfer of metal ion, the resistance of complex formation at the interface and the mass transfer resistance of complex, respectively. The interfacial concentrations of HR and H^+ can be estimated by Eq.(14) and (19), respectively.

Figure 4 shows the effect of extractant concentration on the forward extraction rate for zinc. The dotted line is the extraction rate limited by the diffusion of zinc ion in the aqueous stagnant layer. The broken line is the extraction rate limited by the diffusion of extractant in the organic stagnant layer. The solid lines are the values calculated from Eq.(20) by use of the values shown in Table 2. The zinc extraction rate was limited by the diffusion of zinc ion at high extractant concentration. On the other hand, at the lower extractant concentration the diffusional resistances of the extractant and the complex contributed to the extraction rate. Therefore, the extraction rate is almost independent of the diluent.

Figure 5 shows that the effect of extractant concentration on the extraction rate for copper. The solid lines show that the calculated values by use of values shown in Table 2. At the high $[(HR)_2]$, the observed data was explained by this model. However, at the lower $[(HR)_2]$, the observed values are very lower than the calculated values. If the values of K_{ex} are reduced to (1/5)(for benzene) and (1/2)(for n-heptane) of the value obtained from the equilibrium study, the whole observed extraction rate is interpreted satisfactorily by this model as

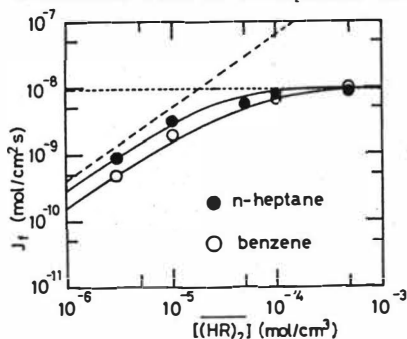


Figure 4. Effects of concentration of extractant and diluent on extraction rate of Zn(II). $[Zn^{2+}] = 8.5 \times 10^{-6} \text{ mol/cm}^3$ pH = 4.0

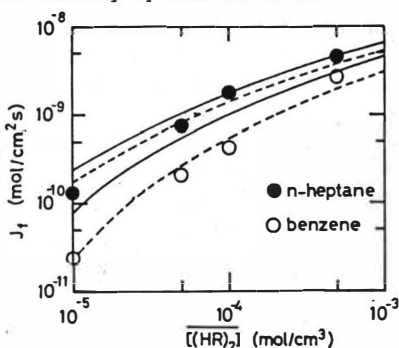


Figure 5. Effects of concentration of extractant and diluent on extraction rate of Cu(II). $[Cu^{2+}] = 8.5 \times 10^{-6} \text{ mol/cm}^3$ pH = 4.0

shown by the broken lines. The extraction rates of cobalt also shows the similar behavior, i.e., to explain the observed extraction rate the value of K_{ex} should be lower than that obtained by the equilibrium study. The same conclusion has been mentioned by Komasaawa et al.[10]. The reasonable interpretation cannot be given at the present stage. The further study are required from the view of the interfacial physical chemistry such as the interfacial potential and the specific adsorption of proton and metal ion at the organic-aqueous interface. In all these experiments of the forward extraction, the reaction resistance of 1:1 complex formation at the interface was negligible small.

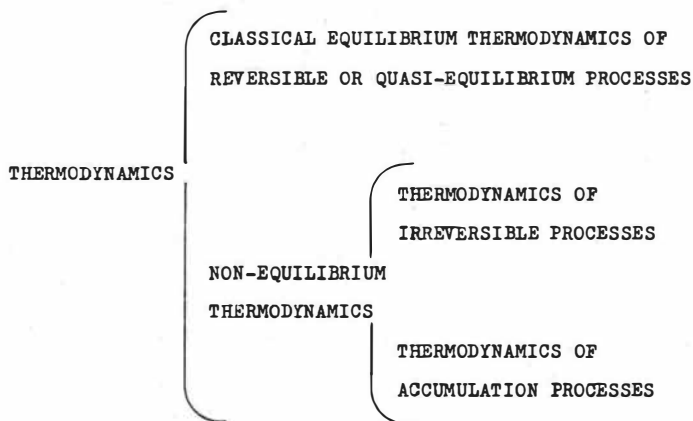
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Regularities of Thermodynamics of Accumulation Processes Applied to Metal Extraction Kinetics

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Presently, the Thermodynamics of Accumulation Processes /TAP/ is one of the two branches of the Non-Equilibrium Thermodynamics. The Thermodynamics of Irreversible Processes is another branch of the entire Non-Equilibrium Thermodynamics. A contemporary idea about the various branches of the thermodynamic knowledge is presented here:



TAP became study-object in Bulgaria since 1967; it deals with the phenomena associated with the introduction, transformation and accumulation of mass and/or energy in the affected systems i.e. in non-isolated, open or closed, systems. The phenomena - processes and effects - due to the work done upon the systems by positive exogenous impacts /influences/ during the measurable impact time t , are called accumulation processes and effects. TAP always deals with processes which proceed with real rates. It is suggested that the impact is positive when a mass dm /or Δm / and/or energy dE /or ΔE / is introduced in the system; in that case the free potential Φ of the system increases, causing a sybatic increase of the system internal energy U . Another part of U is the bound energy B of the system i.e. $U = \Phi + B$. The Gibbs energy and the Helmholtz energy represent the free potential Φ of the system in separate cases. The TAP-regularities are deduced for positive influences, but they could be

applied at negative impacts also, as the signs before the terms of the expressions are changed respectively. The negative influences are however, studied in TAP as far only as they always provoke an accumulation of a part of U under some energy form included in Φ . It can be defined, in general, that fundamental TAP-objects are all phenomena, which are associated with an increase of the free potential Φ of the system during the time t : $d\Phi/dt > 0$.

TAP is not opposed to the Thermodynamics of Irreversible Processes, on the contrary, TAP should be considered as a connecting link between the classical equilibrium thermodynamics and the Thermodynamics of Irreversible Processes, since the beginning of every irreversible process is always preceded by the introduction and accumulation of a mass and/or energy /i.e. by accumulation phenomena/ in an equilibrium - before the impact - system. The interdependence and the difference between the regions of application of the regularities of the classical equilibrium thermodynamics, of the Thermodynamics of Irreversible Processes and of the TAP can be explained by means of Fig.1. The approximately-wavelike curve ABCDEF reflects the alteration of Φ in an affected system in the time period $/t_6 - t_1/$. The following processes are presented by the graphics, in various parts of the whole time period: /1/ Equilibrium or quasi-equilibrium processes - from t_1 to t_2 ; from t_3 to t_4 and from t_5 to t_6 - in which Φ does not change with the time, in accordance with the Clausius' ideas; the independence of Φ from t is shown by the corresponding parts of the curve, which are parallel to the t -axis; the possibility of some of those periods to last - without external impacts - infinitely long times is shown by dotted parts of the curve and of the t -axis; /2/ Irreversible processes - in the period from t_4 to t_5 , which are object of the Thermodynamics of Irreversible Processes and, /3/ Accumulation processes - in the period from t_2 to t_3 , in which the Φ -value increases from Φ_1 to Φ_2 as a result of some work, executed upon the system. It is obvious from the figure that an irreversible process could not proceed in an equilibrium system without a preliminary realization of an accumulation process at least, in the same system.

All processes and effects are examined in TAP at the macroscopic level, which, as known, is characteristic for the thermodynamics in general, but by a full use of the idea about the elementary energy kinds /forms, types/. The elementary energy kinds are defined by pairs of conjugated intensity $/P/$ and capacity $/X/$ factors /variables of state/. The product of a given pair: P_x and X_x , represents an extensive function E_x , which is considered as a quantity of energy

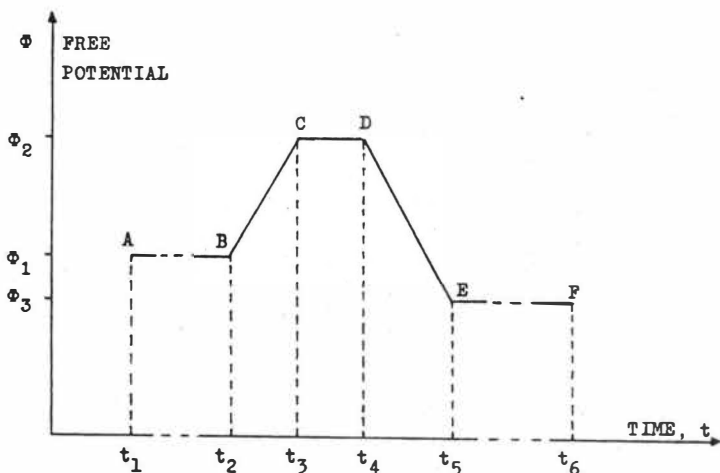


Fig.1. Alterations of the free potential Φ of an affected system with the time t in different process types.

ABCDEF - approximated curve connecting the consecutive Φ - values; Φ_1 , Φ_2 and Φ_3 - initial, maximum and final values of the free potential; t_1, t_2, t_3, t_4, t_5 and t_6 - consecutive time-points.

/labour/ of the elementary kind "r" and has the dimension of energy. It is suggested that P_r and X_r of each determined E_r are measurable macroscopic factors. The definition "monoenergetic conjugation" is accepted for the conjugation existing between the intensity and capacity factors of one and the same elementary energy kind. Between E_r , P_r and X_r there exist the following relations:

$$E_r = P_r \cdot X_r \quad [ML^2T^{-2}] \quad /1/ ; \quad dE_r = X_r dP_r + P_r dX_r \quad /2/$$

$$dE_r/dt = X_r dP_r/dt + P_r dX_r/dt \quad /3/$$

$$/ P_r = 0 / \Leftrightarrow / X_r = 0 / \Leftrightarrow / E_r = 0 / \quad /4/$$

$$E_r = P_r \cdot X_r = \Psi_r^0 = \text{constant} ; \quad / P_j \neq r = \text{constant} / \quad /5/$$

$$P_r = \Psi_r^0 / X_r ; \quad X_r = \Psi_r^0 / P_r ; \quad / P_j \neq r = \text{constant} / . \quad /6/$$

Eq./3/ shows that E_r depends on t through P_r and X_r ; the identity /4/ - that the monoenergetically conjugated factors can participate in the phenomena interpretation or can be eliminated only together ;

Eqs./5/ and /6/ - that the product of P_r and X_r is a constant in systems where all other intensity factors $/ P_j \neq r /$ have constant values.

According to TAP, the "energivity" of a system is defined by the number and by the kinds of the elementary energies, which form the internal energy U . In a similar manner, the energivity of an impact or of a result of the impact in the system is determined by the number and kinds of the elementary energies participating in the energy action or in the processes in the system respectively. According to the number n of the elementary energies involved, an impact or its result could be "monoenergetic", "bi-energetic" or "polyenergetic". An increase of the initial number n characterizing the system's energivity is considered as a polyenergetization phenomenon. It is essential to be emphasized that the energivity has a quantitative as well as a qualitative aspects: the contents of that concept comprises both the number and the kinds of the elementary energies involved in the impacts or in some generalized thermodynamic function as U , Φ or B . In a concrete investigation n equals the number of the elementary energy kinds, which are indispensable and sufficient for the characterization of an affected system or of an impact in a degree, corresponding to the purposes of the thermodynamic study. A rule for the polyenergetization of the impacts' effects in the affected system has been derived in TAP as a consequence of the Second Thermodynamic Principle. That rule claims that a monenergetic effect in the affected system could not be realized even by monoenergetic impact. Therefore, the result of each impact in the affected macrosystem consists in the changes of the values of two factors of different elementary energy kinds at least.

All processes and effects in an affected are expressed in TAP by the alteration rates and by the final changes respectively of the intensity and/or capacity factor values of various elementary energy kinds, existing or appearing in the system: dP/dt ; dX/dt or $\Delta P/\Delta t$; $\Delta X/\Delta t$ for processes and: dP ; dX or ΔP ; ΔX for effects. Those alterations are positive for accumulation processes and effects. The internal energy U , as well as the free potential Φ and the bound energy B of an affected system are considered as summations of the quantities of the elementary energy kinds:

$$dU = d\Phi + dB = \sum_{r=1}^n dE_r = \sum_{r=1}^n d/P_r \cdot X_r / \quad /7/$$

$$U = \Phi + B = \sum_{r=1}^n E_r = \sum_{r=1}^n P_r \cdot X_r \quad /8/$$

The application of Eq./8/ in its integral form has been postulated in TAP and the consequences demonstrated. In TAP relationships have been deduced, which were applied in the development of industrial technologies [1]; in the determination of qualitative transformations in crystallization processes [2]; in the interpretation of the changes in the stellar plasma, in the arc plasma and in the plasma for thermonuclear fusion [3], and in the investigation of biologic phenomena [4]. The present work illustrates the application of TAP-regularities in the kinetics of noble metals' extraction.

Some authors [5] accept that the extraction of Pt from HCl-solutions by bipropylsulphide is a process of transition region i.e. it is limited by both chemical and diffusion kinetics, but when the same extracting agent and solutions are used, the extraction of Pd is controlled by diffusion kinetics and that there are chemical kinetics' limitations for the processes of extraction of Rh or Ru. The use of TAP-regularities, however, permits conclusions to be made, which do not correspond to that acceptance. An Extended Arrhenius Equation for the rate constant k has been used in this study.

A well known equation, proposed by S. Arrhenius in 1889 is still the basic relation of the chemical kinetics:

$$\ln k = \ln A' - E'_0/RT \quad /9/$$

where k is the reaction rate constant; A' is the so-called factor of the molecules' impacts frequency and, according to the Arrhenius' ideas, is a constant independent of the temperature T , K; E'_0 is the activation energy and is supposed to be an independent constant also; R is the gas constant. However, A' and E'_0 proved to be functions of T ; E'_0 is also called "apparent activation energy". Moreover, Eq./9/ corresponds to reaction system activations caused by temperature increases, which have been the only means available in the Arrhenius' time. An extension of Eq./9/ was necessary nowadays, since now there exist more possibilities of surpassing the kinetic limitations. Processes with magnetic, ultrasoundic and with other activating impacts are developed. From the point of view of TAP, the activation of a reaction system is an accumulation process which, in general, can be accomplished by impacts of various kinds. Using the Arrhenius' equation written in a form similar to that accepted in the Activated Complex Theo-

ry [6], we have:

$$\ln k = \ln A.T / - \Delta\Phi''/RT = \ln A + \ln T - \Delta\Phi''/RT \quad /10/$$

where A is a constant strictly independent of T and $\Delta\Phi''$ is, according to TAP, equal to the following difference:

$$\Delta\Phi'' = \Phi'' - \Phi \quad /11/$$

Φ'' and Φ are the free potentials of the activated, reactable molecules' system and of the inactivated molecules' system before the impact, respectively. Φ'' is considered constant. According to Eq./8/,

Φ of the initial system can be expressed as a summation of elementary energy terms. Assuming, for a simplification of the derivations, a hypothetic monoenergetic expression of Φ :

$$\Phi_r = E_r = P_r.X_r \quad /12/$$

we can write Eq./11/ in the following form:

$$\Delta\Phi_r'' = \Phi_r'' - P_r.X_r \quad /13/$$

Differentiating Eq./13/ with respect to P_r ; taking into account that Φ_r'' is a constant and using Eq./6/, we obtain:

$$d\Delta\Phi_r''/dP_r = -X_r = -\Psi_r^0/P_r \quad /14/$$

From Eq./14/ we derive:

$$d\Delta\Phi_r'' = -\Psi_r^0.dP_r/P_r = -\Psi_r^0.d/\ln P_r/ \quad /15/$$

Integrating Eq./15/ and assuming that when $P_r \rightarrow 0$, $\Delta\Phi_r''$ is equal to an integration constant $E_{0,r}$, we obtain:

$$\Delta\Phi_r'' = E_{0,r} - \Psi_r^0.\ln P_r \quad /16/$$

Substituting $\Delta\Phi_r''$ from Eq./16/ in Eq./10/ we have:

$$\ln k = \ln A + \ln T - E_{0,r}/RT + \Psi_r^0/RT.(\ln P_r) \quad /17/$$

Therefore, for a polyenergetic impact we can write:

$$\ln k = \ln A + \ln T - E_0/RT + \sum_{r=1}^{n-1} \Psi_r^0/RT.(\ln P_r) \quad /18/$$

As far as E_0 is a constant independent of all P_r and X_r /including T/, it can be accepted as activation energy according to the Arrhenius' ideas. Eq./18/ contains the unknown coefficients Ψ_r^0/RT . Designating $\Psi_r^0/RT \Leftrightarrow \Psi_r$, and taking into account that T is the intensity factor of the heat work, we can accept that the same coefficient for the term $\ln T$ in Eq./18/ is equal to unity:

$$\Psi_T^0/RT = 1 ; \Psi_T.\ln T = \ln T. \quad /19/$$

Thus we obtain the possibility of experimental determination of relative values of Ψ_r for the various impact kinds by comparing their

kinetic influences with that of the heat impact. Furthermore, we can include the term $\ln T$ in the summation:

$$\ln k = \ln A - E_0/RT + \Psi_T \cdot \ln T + \sum_{r=1}^{n-1} \Psi_r \cdot (\ln P_r) ; \quad /20/$$

$$\ln k = \ln A - E_0/RT + \sum_{r=1}^n \Psi_r \cdot (\ln P_r) \quad /21/$$

Eqs./20/ and /21/ are the two forms of the Extended Arrhenius' Equation, expressing the relation between the rate constant k , activation energy E_0 and values of the intensity factors of various impact kinds. The experimentally determined mean values of the relative coefficients Ψ_r have been published [7]: for chemical /concentration/ impact $\Psi_r = 0.15$; for ultrasonic impact $\Psi_r = 0.04$; for impact by increased surface $\Psi_r = 0.04$ etc. It is easy to show that Eqs./20/; /21/ are more general than Eq./9/, since in separate cases they can be transformed in the later. If we assume, e.g., that in Eq./20/ all impacts excepting the heat impact are negligible ones i.e. that all $\Psi_{r \neq T} = 0$, or all $P_r \rightarrow 0$, $\Psi_T = 1$, we obtain Eq./9/:

$$\ln k = \ln A - E_0'/RT + \ln T = \ln A \cdot T - E_0'/RT = \ln A' - E_0'/RT \quad /22/$$

An assessment of the kind of the limitations in the extraction processes can be based on experimental data and on an Extended Arrhenius Equation for the extraction rate constant k_e :

$$\ln k_e = \ln A - E_0/RT + \Psi_T \cdot \ln T + \sum_{r=1}^{n-1} \Psi_r \cdot (\ln P_r) \quad /23/$$

Here P_r / $r = 1, 2, 3, \dots$ / can represent the concentrations of: metal ions or complexes to be extracted - C_{Me} ; extracting agent - C_e and of the acid in the mixture - C_a . Since the extraction rate w_e for a certain metal is proportional to k_e and to the time t : $w_e = k_e \cdot t$, if $t = \text{constant}$ for two extraction cases: 1 and 2 with equal metal recoveries, we can write:

$$w_{e,1} = w_{e,2} ; k_{e,1} \cdot t = k_{e,2} \cdot t ; \ln k_{e,1} = \ln k_{e,2} \quad /24/$$

Substituting an expression as Eq./23/ for each $k_{e,i}$ in the last equation of /24/; accepting that $n=3$, as well as that the intensity factors are: T , C_{Me} and C_e and, using a transition in Brigg's logarithms we obtain the approximate equation:

$$\log T_1 + \Psi_r \cdot \log C_{Me,1} + \Psi_r \cdot \log C_{e,1} = \log T_2 + \Psi_r \cdot \log C_{Me,2} + \Psi_r \cdot \log C_{e,2}$$

from which we can derive an expression for Ψ_r :

$$i_r = \log(T_1/T_2) / \log\left(\frac{C_{Me,2} \cdot C_{e,2}}{C_{Me,1} \cdot C_{e,1}}\right) \quad /25/$$

Using equations like Eq./25/, our experimental data and those of other authors [5] for extraction of Pt, Pd, Rh and Ru, we obtained the mean values of Ψ_r , which are shown in Table 1.

Table 1. Values of Ψ_r for Extraction of Noble Metals by Bipropylsulphide /T= 293-413 K/ and Evaluated Degrees of Process Limitations.

Metal	C_{HCl} , M	Ψ_r -value	Degree of process limitations, per cent	
			Chemical kinetics	Diffusion kinetics
Pt	0.1 - 0.5	0.027	18	82
	0.5 - 2.0	0.07	46.7	53.3
Pd	1.1	0.046	31	69
Rh	1.1	0.042	28	72
Ru	1.1	0.042	28	72

The last two columns' values in Table 1 are calculated as follows:

Type of kinetics	Part of unity	Ψ_r -value	Product
Chemical	x	0.15	0.15 x
Diffusion	y	0	0
Mixed kinetics	1.00	/e.g./ 0.042	0.042

Therefore: $0.15 x = 0.042$; $x = 0.28$, i.e. $x = 28$ per cent.

The Ψ_r -values in Table 1 correspond to those obtained for other surface-dependent processes in transition region by experiments based on TAP-ideas, e.g. leaching with ultrasonic impact. The values ensure the choice of optimum industrial extraction process performances.

Conclusions.

1. All processes of extraction of Pt, Pd, Rh and Ru from HCl-solutions by bipropylsulphide are limited by diffusion kinetics /about 70 per cent of the control/ and by chemical kinetics /about 30 per cent/. The chemical limitations increase with the HCl-concentration.
2. The Extended Arrhenius Equation of TAP could be applied for an evaluation of the degree of various type process limitations.

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Kinetics and Mechanism of Cobalt Extraction with 2-ethylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester

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Researches on the solvent extraction kinetics of metals with organo-phosphorous acid extractants, especially with di-2-ethylhexyl phosphoric acid (HDEHP) have been reported^[1,2,3]. As the kinetic regime is determined by diffusion process and the rate of chemical reactions occurring in the biphasic system and the complexity of the interface, some conclusions are disputing. In this work, the kinetics and mechanism of cobalt(II) extraction with 2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester (EHEHPA, HA) in n-hexane from acetic acid-sodium acetate buffer solutions have been investigated in an improved Lewis type cell.

Experiments Reagents: EHEHPA was purified by using copper salt methods. It has been confirmed that the content is more than 99% by electrometric titration. Water was prepared by twice distillation. The initial composition of aqueous phase and organic phase were $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ - NaClO_4 - NaAc - HAc and n-hexane-EHEHPA, respectively. The pH in aqueous phase was controlled by NaAc - HAc buffer solutions and NaClO_4 was used to adjust ion strength of the solution. All other chemicals were A.R. grade, such as NaAc , HAc , NaClO_4 , HClO_4 , CoCl_2 and so on.

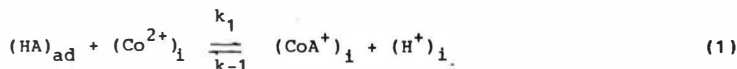
Measurement of Extraction Rates A new technique has been developed in which cobalt(II) concentrations in organic phase can be measured continuously by a flow cell connecting with a double beam spectrophotometer and the output signal transferred into a microcomputer through an Analog-Digital Card to collect the experimental data simultaneously. The extraction processes were carried in an improved constant interfacial area cell. The schematic diagram of the apparatus is shown in Figure 1. The parts which contacted with liquids such as impeller and horizontal baffle, cylindrical grids, are made up of corrosion-resistant materials i.e. Teflon and Titanium. Being stirred, the liquid in the bulk phases transfer from the centre part to all around and form circle cycle, going up and down. The diversified directional liquid motions make the both bulk phases well-disturbed immediately and the interfacial area is always constant. The volumes of organic and aqueous phases are both 440 ml. The detail were described in the paper (4). In this system, the kinetics plateau in different conditions begins at

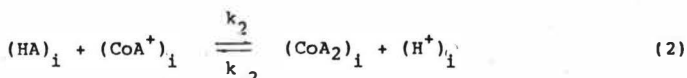
approximately the same stirring speed of 160 rpm. All experiments were carried out at $25 \pm 0.5^\circ\text{C}$ and at the plateau region of the curve of extraction rates vs. stirring speed. One of the typical results is shown in Figure 2. The initial extraction rates were calculated from the slope of the straight part of the time vs. concentration curves.

Results and Discussion

(1) As shown in Figure 3 and Figure 4, the extraction rates were proportional to the special interfacial area as varying species concentrations and were increased by the addition of an anionic surfactant, but decreased by the addition of a cationic surfactant. The interface tension test showed the strong adsorption of extractant HA on the interface (5). The surfactants effect the mass transfer rate by the electrostatic effect and the space effect. It was also observed that the solubility of EHEHPA in aqueous is less than that of HDEHP. Referring to the research results of extraction kinetics with HDEHP^[1,2,3], the control step of the extraction reaction of Co(II) with EHEHPA are mostly occurred in the liquid-liquid interface. (2) The initial extraction rates R_o was obtained under various experimental conditions: The effect of Co(II) concentrations on R_o is shown in Fig. 5. R_o was proportional to the initial concentration in the range of low [Co(II)], but in the high [Co(II)] the slope of $\log R_o$ vs. $\log [\text{Co(II)}]$ was only slightly greater than zero. This phenomena may be explained as following; When the [Co(II)] is low, the R_o was controlled by reaction kinetics. As the concentration of Co(II) is getting higher, the reaction rate increases faster than the diffusion, and eventually the process falls into the diffusion regime. The effect of EHEHPA concentrations on R_o is shown in Fig. 6. The result was similar to that in Fig.5. As [HA] increases, the interface adoption of HA trends towards saturation and limits the mass transfer rate.

The effect of pH on R_o and [H], [CoA₂] on stripping rate R_o' in kinetics regime also have been measured. From all of above results, it could be concluded that changing the species concentrations, the extraction process may shift from reaction regime to diffusion regime. (3) Mechanism and Kinetics: As mentioned above, the liquid-liquid interface is saturated with the adsorption of EHEHPA and the chemical reaction occurred at the interface, so diffusion of the species to and from the interface through the stagnant organic and aqueous layers determined the mass transfer rate. Referring to the equilibrium equation of EHEHPA (6), the reaction mechanism can be described as:





where the subscript "i" denotes the species in aqueous and organic stagnant layer and subscript "ad" denotes those adsorbed on the interface. The $[HA]_{ad}$ is considered to be constant, and $[HA]_i$ varies with the reaction and diffusion. The equation of reaction rate has been derived as follow:

$$R = \frac{k_1 k_2 [HA]_{ad} [HA]_i [Co]_i - k_{-1} k_{-2} [CoA_2]_i [H]_i^2}{k_{-1} [H]_i + k_{-2} [HA]_i} \quad (3)$$

and together with the mass transfer equation (flux)_i

$$\begin{aligned} N &= \frac{D_{Co}}{\delta_{aq}} ([Co] - [Co]_i) \\ &= \frac{D_{HA}}{\delta_{org}} ([HA] - [HA]_i) \\ &= \frac{V}{A} R \end{aligned} \quad (4)$$

it form a model describing the over all mass transfer. Where D are the diffusion coefficient and δ_{aq} , δ_{org} are the thickness of stagnant layer of aqueous and organic phase, respectively.

The initial extraction rate R_0 can be calculated from Eq. (3) and (4) by giving the initial conditions and the estimate values of parameters. The solid line in Fig. 5 and Fig. 6 are the calculation results of the above model assuming the reverse reaction terms of Eq. (3) are negligible.

Conclusions

The kinetics and mechanism of extraction of cobalt(II) with EHEHPA can be fairly well explained by the reaction model that the extraction rate is determined by the formation of interfacial extracting coordination compound in case of slow extraction rate at low reacting species concentration and by diffusion process in both aqueous and organic stagnant layer when the reaction rate is high.

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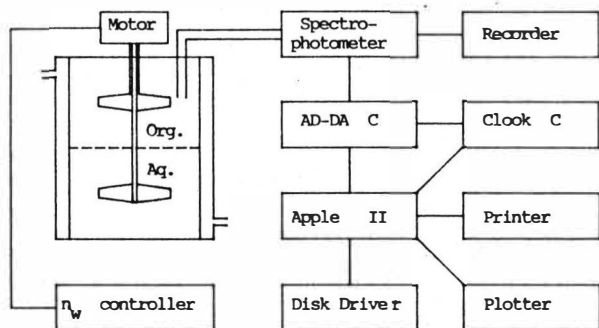


Figure 1. Diagram of the computer-assisted extraction measurement system.

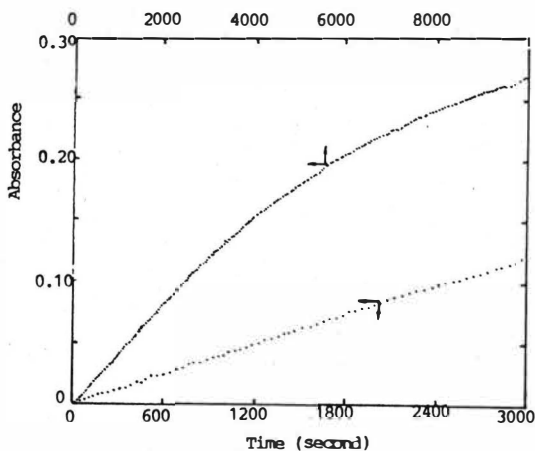


Figure 2. Typical result of kinetics determination.

The extraction of $C_0(II)$ with EHEHPA in n-hexane from dilute acetic acid-acetate buffer solutions.
 $[EHEHPA] = 0.035M$, $[C_0(II)] = 0.006M$ pH = 4.594 $t = 25^\circ C$

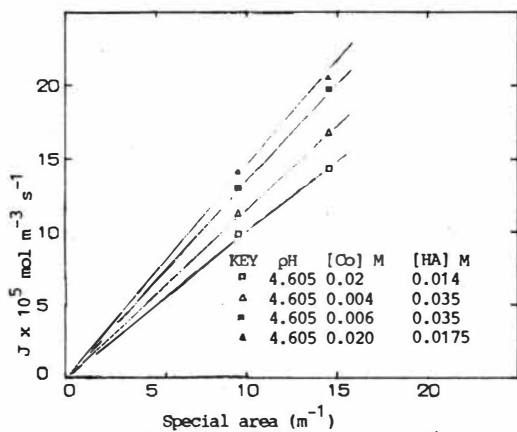


Figure 3. Effect of special area on mass transfer rate

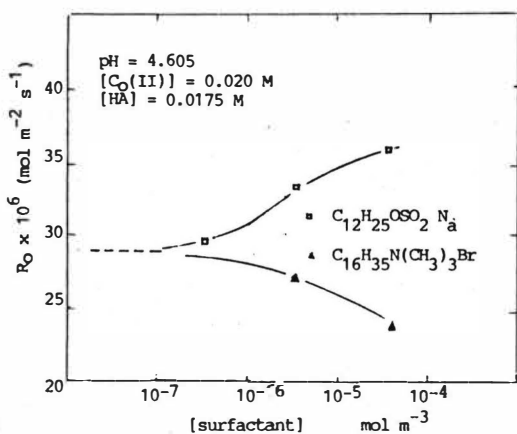


Figure 4. Effect of surfactants on initial forward extraction rate

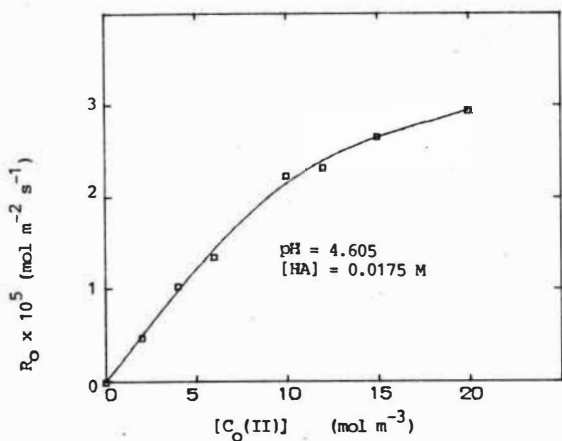


Figure 5. Effect of Cobalt concentration on initial forward extraction rate

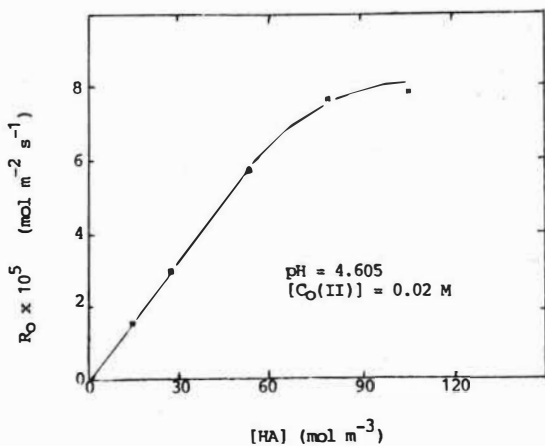


Figure 6. Effect of initial extractant concentration on initial forward extraction rate

PHASE TRANSFER AND MICELLAR CATALYSIS IN METAL SOLVENT EXTRACTION:
A KINETIC MODEL FOR THE LIX63-HDNNS SYSTEM

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There is considerable interest in the discovery and application of combinations of reagents which improve the performance of hydrometallurgical extraction systems. The improvement sought may relate to the loading capacity (synergism), the rate of extraction and/or stripping (catalysis), higher selectivity, phase separation or a combination of these characteristics. It has been found that mixtures of the hydroxyoxime LIX63 and dinonylnaphthalene sulfonic acid (HDNNS) can selectively extract nickel and cobalt from acidic solutions which also contain iron. Variations in the extractant concentrations affect both the extent and the rate of metal extraction. It has been reported that in the presence of LIX63, the Ni distribution coefficient increases dramatically in the neighborhood of the critical micelle concentration of the sulfonic acid (1,2). Furthermore, when the concentration of HDNNS is increased for a given constant concentration of LIX63, the distribution coefficient of Ni(II) (Figure 1) and the interfacial extraction flux (Figure 2) increase, peak, show a region where there is no significant variation and eventually approach the values corresponding to the pure HDNNS (i.e., oxime-free) system (3,4).

On the basis of these and other results available in the literature, it has been suggested that both phase transfer and micellar catalytic processes are operative in the LIX63-HDNNS system (1). The phase transfer catalysis is a result of the fact that HDNNS is (a) highly interfacially active, as demonstrated by interfacial tension data (2), (b) a very strong acid which deprotonates to give a highly negatively charged organic/aqueous interface, as demonstrated by electrophoresis data (5), (c) a liquid cation exchanger capable of extracting metals in highly acidic solutions, as demonstrated by equilibrium distribution studies (3). On the other hand, the micellar catalysis is a result of the fact that HDNNS micelles solubilize LIX63 molecules (as demonstrated by interfacial tension and IR data (2)) as well as metal ions. Thus the oxime and metal concentrations at the microscopic micellar organic/aqueous core interface are much higher than those at the macroscopic organic/aqueous interface. This concentrative effect permits the oxime in the mixed micelle to react with metal ions in the aqueous core to give a mixed complex which apparently does not form in the absence of mixed micelles of the right sulfonate and oxime combinations.

In this paper, a preliminary kinetic model is presented which attempts to simulate the effects of the concentrations of the various species on the interfacial flux for the system $\text{KNO}_3\text{-HNO}_3\text{-Ni(NO}_3)_2\text{/LIX63-HDNNS-hexane}$. A mechanism is proposed for the extraction reaction which draws from the speciation of the organic reagents, incorporates the K⁺-H⁺ interchange undergone by HDNNS, and assigns the role of phase transfer catalyst to HDNNS. The pseudo-steady state approach consisting of systematically taking one step as rate-controlling while the other steps are maintained at equilibrium is followed (6). Four possible rate equations are thus derived. Kinetic data obtained in a quiescent interface cell using the initial rate technique with HDNNS as the only extractant is used to evaluate the constants in the derived models, and to decide which of the models fits the "pure" system data best. The model thus found is then used to generate fluxes corresponding to the "mixed" system, which are compared with experimental data obtained with the rising drop technique.

The Proposed Mechanism

It has been found that HDNNS (or HD) dissolved in heptane extracts potassium from an aqueous solution, as follows (7):

$$K^+ + \overline{HD} = \overline{KD} + H^+ \quad (1)$$

A fraction \overline{X} is defined as

$$\overline{X} = \frac{\text{HDNNS monomer concentration in K form}}{\text{Total HDNNS monomer concentration}} = \frac{C_{KD}}{C_D} = \frac{C_{KD}}{C_{KD} + C_{HD}} \quad (2)$$

At pH > 2.3, $\overline{X} = 1$, while $\overline{X} = 0$ at pH = 0 and higher acidity. A linear variation of \overline{X} between pH = 0 ($\overline{X} = 0$) and pH = 2.5 ($\overline{X} = 1$) has been assumed.

HDNNS is a very strong surfactant which aggregates in organic solution forming reversed micelles (2,8)

$$k m \overline{KD} + (1-k)m \overline{HD} = \overline{[(K_k, H_{1-k})D]_m}; K_p = \frac{C_P}{C_D} \quad (3)$$

The acidic and potassium forms of the micelles coexist in the same concentration ratio as the monomers as given by eqn (2). The aggregation number, m, was found to be 7 (8). Infrared spectroscopy studies have shown that LIX63 molecules are solubilized by HDNNS micelles to produce mixed micelles (2), as follows

$$\overline{[(K_k, H_{1-k})D]_m} + q HL = \overline{[(K_k, H_{1-k})D]_m \cdot q HL}; K_A = \frac{C_A}{C_P \cdot C_L^q} \quad (4)$$

where q was found to be equal to 3 for catalytic or "active" mixed micelles (3). A number of other aggregates of reagent molecules may form (e.g., those containing one or two LIX63 molecules per mixed micelle), but are of no direct relevance to the reaction scheme because only the HDNNS monomer, and the pure and active mixed micelles are assumed to partake in it. All the species, however, are included in the mass balances whose solutions are used as inputs by the models. The HDNNS balance for the single extractant system is stated as follows

$$C_{DT} = C_D + m C_P \quad (5)$$

For the mixed reagent system, the balances are two coupled nonlinear algebraic equations. Because the balances relate to organic phases which have undergone negligible extents of conversion (i.e., before extraction starts or under conditions of initial rate experiments), they include no term representing a metal-bearing species. The HDNNS balance in the mixed system is given by:

$$C_{DT} = C_D + C_B + m C_P + m C_{M1} + m C_{M2} + m C_A \quad (6)$$

The corresponding mass balance for LIX63 is:

$$C_{LT} = C_L + C_B + C_{M1} + 2 C_{M2} + 3 C_A \quad (7)$$

To solve eqns. 6 and 7 for C_D and C_L , the aggregation equilibrium constants and the monomer concentrations related to eqns 3,4 and similar ones for the rest of the aggregate species are substituted in place of the aggregate concentrations in the balances. The values of all aggregation constants have been estimated previously by treatment of extraction equilibrium data (4).

The following formulation is made simpler by considering the potassium form of the micelles only, as applies to the higher pH range (> 2.3), but it nevertheless has general validity. The HDNNS monomer adsorbs at the macroscopic interface

$$\overline{KD} = KD, i; C_{KD, i} = \frac{K'_a C_{KD}}{1 + K''_a C_{KD}} \quad (8)$$

Provided the adsorption process is described by an isotherm of the Langmuir type, then $C_{KD, i}$ is a constant at HDNNS concentrations above the CMC (i.e., $1 \ll K''_a C_{KD}$, eqn. 8). Because of its strong acidity, HDNNS ionizes readily conferring a negative charge to the interface, as was confirmed experimentally by Lin (5). The resulting electrostatic potential favors the interaction between the sulfonate and metal ions:

$$KD, i = K^+ + D^-, i \quad (9)$$

$$D^-, i + M^{2+} = MD^+, i \quad (10)$$

Reversed micelles such as those formed by aggregation of HDNNS in organic solvents (eqn. 3) have the ability to solubilize polar substances within the hydrophilic cavity created at the micellar core. Such microenvironments present special conditions which can promote synergo-catalytic effects, generally known as micellar catalysis (7). Results obtained from ongoing research indicate that the time scale of electrolyte solubilization by pure HDNNS micelles is much shorter than the time scale of the overall metal extraction (10). About 10 water molecules per surfactant molecule were found to saturate pure HDNNS micelles, comparing well with the literature value of 11, for n-heptane as solvent (11). The charged complex produced by step 10 thus has a high probability of being solubilized by a micelle in its neighborhood, together with a microvolume of adjacent aqueous phase. In view of this argument, it is proposed that charged complexes solubilized within micellar polar cores react with HDNNS molecules from the micellar palisade to form neutral complexes at the microscopic interface between palisade and solubilized electrolyte. The neutral complex, now truly an organic phase species, lodges in the palisade.

$$MD^+, i + \overline{KD} = \overline{MD}_2 + K^+ \quad (11)$$

When the micelle involved in the solubilization-reaction process is an active mixed micelle, very favorable conditions are set for LIX63 to chelate the metal. The application of the methods of slope analysis and continuous variation to metal distribution data have shown that the stoichiometry of the final product in this case is M/HDNNS/LIX63 = 1/2/3 as results from the following reaction (3):

$$\overline{MD}_2 + (\overline{KD})_m \cdot qHL = \overline{MD}_2 \cdot qHL + (\overline{KD})_m \quad (12)$$

When a pure micelle is involved, there is no chelation and the reaction is

$$\overline{MD}_2 + (\overline{KD})_m = \overline{MD}_2(\overline{KD})_{m-2} + 2 \overline{KD} \quad (13)$$

The total interfacial flux is given by the sum of the fluxes due to pure and active micelles as

$$J_T = J_p + J_a = k_p C_{MD_2} C_p + k_a C_{MD_2} C_a = k C_{MD_2} C_p \quad (14)$$

$$\text{where } k = k_p + k_a \frac{C_a}{C_p} \quad (15)$$

Pure and mixed micelles compete for metal ions in the solubilization-reaction process. As the formal concentration of HDNNS is increased while the formal concentration of LIX63 is kept constant, the ratio between active and pure micelles shifts in favor of the less efficient pure micelle. Inspection of eqns. 12 and 13 shows that reactions at micellar pseudointerfaces regenerate HDNNS monomers and micelles. The regenerated monomer may subsequently adsorb at the macroscopic interface completing a cycle as phase-transfer catalyst (eqn. 8).

Derivation and Evaluation of the Models

Steps 8, 10, 11, and 12, 13 of the mechanism are taken in turn as the controlling (slowest) step, with all the others considered at equilibrium. From the pseudo-steady-state assumption applied to the slowest step, different expressions for C_{MD} were obtained. Substitution of these expressions into eqn. 14 resulted in the model equations 16 to 19 (Table 1). The constants in the models were evaluated by regression analysis. The software package "Minitab" was used to regress data obtained in a quiescent interface, nondispersive stirred cell. Eighteen sets of data from experiments involving the single reagent (HDNNS) system were used to correlate J_p to pH, C_M , and C_{DT} . The kinetic constant determined by the package is k_p (eqn. 15).

The values of C_p and C_D used were taken from the solution to the organic phase speciation; C_D was found as the root of eqn. 5 by bisection or Newton-Raphson algorithms and C_p was computed from eqn. 3. A value of $K_A = 4.5 \times 10^{18}$ was adopted (4). The concentration of free potassium in the aqueous phase (C_K) was computed from the balance on total potassium as follows:

$$C_{KT} = C_K + C_{KD} + mC_p \quad (20)$$

The concentration of adsorbed monomer was assumed to be constant and negligibly small throughout. This is a simplifying assumption which allows omitting $C_{KD,i}$ in eqn. 20.

Eqn. 16 shows the highest correlation coefficient and lowest summation of residuals, closely followed by eqn. 18. The summation of residuals was computed as $\sum [\log (J_{p,exp}/J_{p,pred})]^2$. The experimental fluxes can be compared with the fluxes predicted by eqns. 16 and 18 in Figure 3. Comparable data obtained with rising drop experiments are also shown in Figure 3, where good agreement is seen at low values of C_{DT} . At higher values of C_{DT} , both models predict fluxes smaller than those experimentally found. Once the values of the rate constants k were determined, total fluxes J_T were simulated with eqns. 16, 18. The ratio C_A/C_p was obtained for each pair C_{DT}, C_{LT} as described next. An optimization routine was used to find the roots (C_D, C_A) of the system of eqns. 6, 7 and C_p and C_A were then computed from eqns. 3, 4; $K_A = 5.0 \times 10^{16}$ was adopted (4).

Figure 4 shows predictions of J_T as various values of the constant k are inserted into eqns 15, 18. Predicted values of J_T are seen to increase and peak as C_{DT} is increased. However, the peaks are located at higher C_{DT} values than those peaks found experimentally with rising drop experiments. For $C_{LT} = 5.0 \times 10^{-6}$ kmol/m³, $k_A = 1.7 \times 10^6$ gives the best fit of the data.

The authors hope to refine the models by explicitly incorporating interfacial and mass transport parameters into the rate constants. Current research on monolayers (12) will provide basic information useful in this context. Ongoing experimental research with a quiescent interface cell (10) is expected to provide kinetic extraction data for the mixed system under conditions where the transfer rate is independent of the hydrodynamic environment. Such data may yield insight into diffusive contributions to the overall rates obtained with the rising drop technique. It is also expected that such work will provide further insight into the micellar catalytic effects previously observed.

Acknowledgement

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Notation

- C = Concentration, kmol/m^3
- HDNNS = Dinonylnaphthalene sulfonic acid
- $\overline{\text{HD}}$ = HDNNS monomer
- $(\overline{\text{HD}})_m$ = HDNNS micelle,
- HL = The active hydroxyoxime extractant in purified LIX63
- J = Interfacial flux, $\text{kmol/m}^2\text{s}$
- k = Rate constant
- K = Equilibrium constant
- $\overline{\text{KD}}$ = HDNNS monomer, potassium form
- $(\overline{\text{KD}})_m$ = HDNNS micelle, potassium form
- m = Aggregation number of HDNNS, 7
- M = Metal (Ni(II)) ion
- q = Aggregation number of LIX63 in active micelles, 3
- \overline{X} = Fraction of HDNNS monomer concentration in potassium form

Superscripts

-: A bar over a species means it belongs in the organic phase

Subscripts

- | | |
|----------------------------------|--|
| A, a = Active mixed micelle | LT = Formal (total) LIX63 |
| B = Binary HDNNS-LIX63 aggregate | MD_2 = Neutral sulfonate complex |
| D = HDNNS monomer, both forms | $\text{MD}^+_{,1}$ = Charged sulfonate complex |
| DT = Formal (total) HDNNS | M1 = Aggregate, $(\overline{\text{KD}})_m \cdot \overline{\text{HL}}$ |
| K = Free potassium ion | M2 = Aggregate, $(\overline{\text{KD}})_m \cdot 2\overline{\text{HL}}$ |
| KT = Formal (total) potassium | P, p = Pure micelle |
| L = LIX63 monomer | |

Table 1. Analysis of Rate Models

<u>Controlling Step</u>	<u>Eqn. No.</u>	<u>Derived Rate eqn.</u>	<u>Eqn. No.</u>	<u>Correlation Coefficient R</u>	<u>Sum of Residuals Squares</u>	<u>Returned constants (Pure System)</u>
Adsorption of monomer	8	$J_T = k C_P C_M \frac{C_{KD}^2}{C_K^2}$	16	0.990	0.717	$k_p = 153.0$
Reaction with adsorbed monomer	10	$J_T = \frac{k C_P C_M}{\alpha C_K + \beta \frac{C_K^2}{C_{KD}}}$	17	0.808	4.981	
Formation of neutral complex	11	$J_T = \frac{k C_M C_{KD}}{\epsilon C_K + \eta \frac{C_K}{C_P}}$	18	0.988	0.911	$\frac{\epsilon}{k_p} = 19212.0$ $\frac{\eta}{k_p} = 1.0825 \times 10^{-5}$
Reaction in micellar pseudophase	12 13	$J_T = k \frac{C_M C_P C_{KD}}{C_K^2}$	19	0.842	1.933	

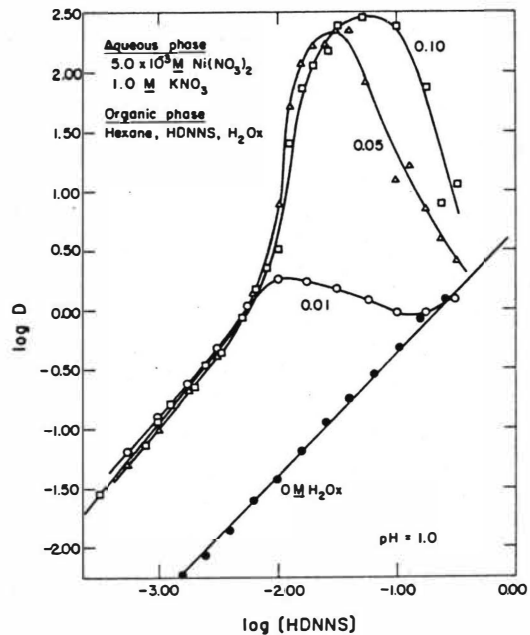


Figure 1. Effect of HDNNS on nickel distribution (3).

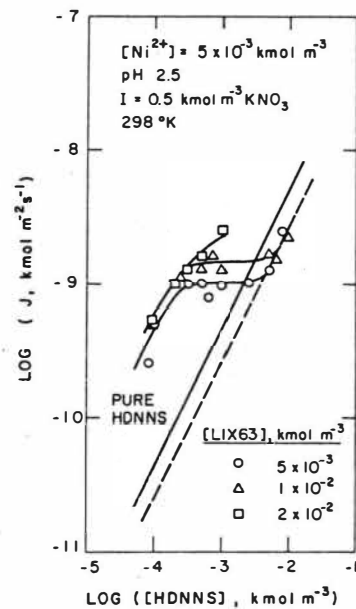
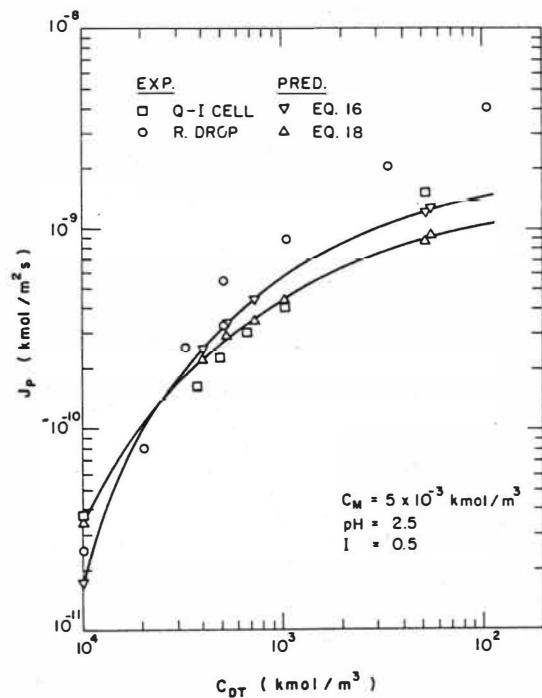
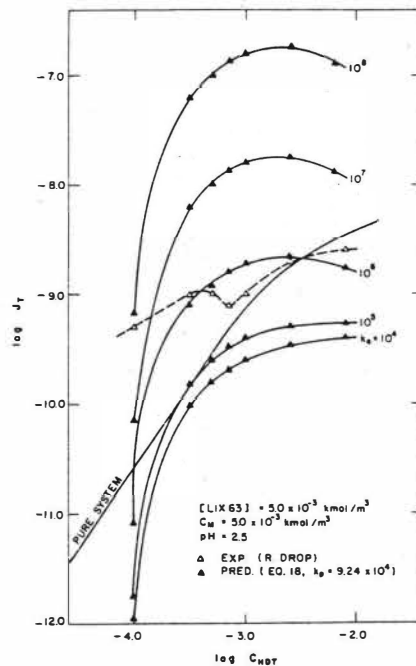


Figure 2. Effect of HDNNS and LIX63 on nickel flux into rising drops (4).

Figure 3. Effect of C_{DT} on J_P .Figure 4. J_T predicted by Equation 18.

Comparisons between Single Drop and Stirred Cell Techniques in the Modelling of the Stripping of Zinc from Di(2-ethylhexyl) Phosphoric Acid

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The mechanism and rate of extraction of zinc by di(2-ethylhexyl) phosphoric (HDEHP) acid in n-heptane was investigated by Ajawin et al [1,2,3]. They studied the effect of hydrodynamic conditions on the extraction rate and proposed a mathematical model for the interfacial flux that included mass transfer and chemical reaction parameters at conditions in which the reverse reaction could be neglected. In the present work the stripping reaction is studied and a mathematical model for the stripping flux is developed. The selection of laboratory contactor to be employed is discussed, first using the mathematical model for the rate of extraction to account for the effect of mass transfer coefficients.

Comparisons Between Single Drop and Stirred Cell Techniques

Figure 1 shows the variation of the interfacial flux with mass transfer coefficients for three sets of reactant concentrations calculated with the model for the extraction flux [3]. The concentrations were selected so that the rate of extraction in the chemical regime, given by $k_1 C_Z C_O^{-1}$ is the same for the three curves. The pH value has been kept constant at 2.5. It can then be seen that the values of the mass transfer coefficients for which a plateau region is reached vary with the ratio C_O/C_Z . Then it is a combination of relative concentrations and hydrodynamic conditions what determines the rate controlling mechanism. This situation makes the interpretation of experimental results difficult unless the effects of mass transfer coefficients and concentrations can be assessed separately. A method to overcome this limitation is proposed elsewhere [4]. Two experimental techniques that provide interfacial fluxes were considered: the single drop and the stirred non-dispersive cell. The first does not permit the study of the effect of changing the mass transfer coefficients on the extraction rate and could only be used if its hydrodynamic conditions are well defined, while the second requires careful mechanical design and vibration free mounting to avoid interfacial ripples.

According to their hydrodynamic behaviour drops can be classified as: (i) noncirculating, (ii) nonoscillating with internal circulation and (iii) oscillating. Each of these types have different values of both the disperse and continuous phase mass transfer coefficients. Table 1 contains values of mass transfer coefficients for circulating and oscillating drops calculated from correlations [5] for the physical properties of the system under study. Figure 2 shows the variation of interfacial flux with zinc concentration simulated with the extraction model for single circulating drops. It can be seen that results for the rising and falling drops are different. This is due to the change of disperse phase required by the buoyancy forces. At the conditions of curves (1) and (2) the system is not in the chemical regime and the dependence of R on C_z includes the resistance to mass transfer. Therefore the slopes of the curves do not give the order of the reaction. At lower extractant concentrations, curves (3) and (4), the flux is low enough for the resistance to mass transfer to become negligible. In this case the system is in chemical regime and the slope gives the order of the reaction but the interfacial flux is so low that a long drop residence time would be required to achieve detectable concentration changes in the drop. If the drops are non-circulating another set of curves would be obtained for the same concentrations. It can be concluded that experimental results obtained with the single drop may not be in the chemical regime and since the mass transfer coefficients cannot be changed the interpretation of results would be difficult. A stirred cell was therefore selected [6].

Experimental

Experiments were conducted in a modified Nitsch cell. The cell and experimental procedure are the same as detailed elsewhere [1]. The n-heptane used was of knock-testing quality, HDEHP obtained from BDH was purified following the technique of Partridge and Jensen [7]. The rest of the chemicals were of Analar grade and were used without further purification. The pH of the aqueous phase was adjusted by H_2SO_4 and the ionic strength by H_2SO_4 and Na_2SO_4 . The concentration of zinc was determined by atomic absorption spectrophotometry. All experiments were conducted at $25 \pm 0.1^\circ C$ at an ionic strength of 1.0 kmol m^{-3} .

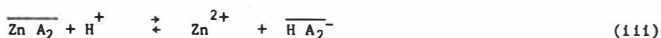
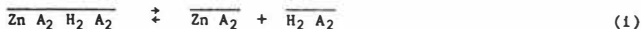
Location of the Rate Controlling Chemical Reaction and Conditions for Chemical Control

A series of experiments were conducted to establish the region of chemical control. This involved measurement of the rate of stripping at different stirring speeds and concentrations to determine the conditions at which a "plateau" of the type shown in Figure 1 curve (3) is reached. It was found that for $C_{Z0} = 5.2 \times 10^{-4} M$, $C_0 = 0.1 M$ and $pH = 1.96$ there was no further increase in the stripping rate for $N > 300$ rpm. Hence all experiments were conducted at $N = 320$ rpm and concentrations that did not lead to higher fluxes.

Under conditions of chemical control the rate of transfer was found to be proportional to the interfacial area thus indicating that the rate controlling reaction takes place either at the interface or in one of the diffusional films. Discrimination between these two possibilities is discussed together with the experimental results.

Kinetics and Mechanism of Chemical Reaction

As the reaction between zinc and HDEHP is reversible the same mechanism as for extraction was proposed for stripping:



where bars indicate species in the organic phase. It was assumed that step (iii) was the slowest and therefore rate controlling as in the extraction process [2,8]. The rate of stripping would then be given by:

$$r = K_3 C_{ZnA_2} \cdot C_H \quad (1)$$

By writing C_{ZnA_2} in terms of total zinc concentration in the organic phase C_{Z0} , introducing the equilibrium constants of reactions (i), (ii) and (v)

and using the activity of HDEHP, Equation (1) becomes:

$$r = \frac{k' C_{Z0} C_H}{(K_{E1}/K_{E2}) a_0 + \sqrt{a_0}} \quad (2)$$

where K_{E1} and K_{E2} are the overall equilibrium constants for the formation of $ZnA_2H_2A_2$ and ZnA_2HA respectively obtained by regression, from equilibrium studies [8], have values $K_{E1} = 0.0633$ and $K_{E2} = 0.0064$.

Experimental Results

Figure 3 shows a plot of $\log r$ versus pH at $C_{Z0} = 5.2 \times 10^{-4}M$ and $C_0 = 0.1M$. Results are well fitted by a straight line of slope -1. The stripping rates at pH = 2.05 and $C_0 = 0.1M$ and different initial organic zinc concentrations are plotted in Figure 4. The slope in this case is 1. Finally Figure 5 shows the variations of stripping rate with HDEHP activity in the organic phase plotted as $\log r$ versus $\log (9.89 a_0 + \sqrt{a_0})$. A straight line of slope -1 fits well the experimental results. This slope analysis confirms equation (2). The three values of k' obtained from these results are in very good agreement giving an average value of $1.0 \times 10^{-3} m^{3/2} kmol^{-1/2} s^{-1}$. The surface area based constant, $k'_I = 8.2 \times 10^{-5} m^{5/2} kmol^{-1/2} s^{-1}$ was obtained by dividing the volume-based value by the interfacial area per unit volume of aqueous phase.

Hughes and Rod [9] have proposed a mathematical model for extraction with a pseudo first order reaction taking place in the aqueous diffusional film. They have shown by numerical analysis that at the conditions of the plateau and keeping the product $C_M C_X$ constant changes in the ratio C_M/C_X are followed by changes in R . Since this is not the case for interfacial reactions [3,10] results at $C_{Z0} \cdot C_H = \text{constant}$ and different C_{Z0}/C_H values were compared to establish the location of the rate controlling reaction. Points 1 and 2 in Figures 3, and, 4 satisfy the imposed conditions and show that the rate of stripping is independent of C_{Z0}/C_H in the chemical regime. This indicates that the location of the rate controlling reaction is likely to be the interfacial region.

Mathematical Model

For an interfacial reaction in the mixed regime of chemical and mass

transfer control the concentrations in Equation (2) are interfacial and their values are obtained from the equations for the fluxes of the species involved. These equations are linked by the stoichiometry of reaction [8]

$$R = k_{ZO} (C_{ZO} - C_{ZO1}) = \frac{1}{2} K_H (C_H - C_{H1}) = \frac{1}{1.8} K_O (a_{O1} - a_O) \quad (3)$$

when subscript 1 indicates interfacial values.

Substituting k' for k_I in Equation (2), so that the flux rather than the volumetric rate of reaction is obtained, and combining the resulting equation with Equation (3) gives an expression for the interfacial flux of the form:

$$AR^4 + BR^3 + CR^2 + DR + E = 0$$

where

$$\begin{aligned} A &= \frac{4}{K_{ZO}^2 K_H^2} + \frac{4.7 \times 10^{10}}{K_O^2} - \frac{8.6 \times 10^5}{K_{ZO} K_H K_O} \\ B &= \frac{-4C_H}{K_{ZO} K_H} - \frac{8C_{ZO}}{K_{ZO} K_H} + \frac{5.2 \times 10^{10} a_O}{K_O} + \frac{4.3 \times 10^5 C_H}{K_{ZO} K_O} + \frac{8.6 \times 10^5 C_{ZO}}{K_H K_O} \\ &\quad - \frac{4.8 \times 10^5 a_O}{K_{ZO} K_H} - \frac{2.6 \times 10^8}{K_O} \\ C &= \frac{4 C_{ZO}^2}{K_H^2} + \frac{C_H^2}{K_{ZO}^2} + \frac{8 C_{ZO} C_H}{K_{ZO} K_H} + 1.4 \times 10^{10} a_O^2 - \frac{4.3 \times 10^5 C_{ZO} C_H}{K_O} \\ &\quad + \frac{2.4 \times 10^5 C_H a_O}{K_{ZO}} + \frac{4.8 \times 10^5 C_{ZO} a_O}{K_H} - 1.5 \times 10^8 a_O \\ D &= 2C_{ZO} C_H \left[-\frac{2C_{ZO}}{K_H} - \frac{C_H}{K_{ZO}} - 1.2 \times 10^5 a_O \right] \\ E &= C_{ZO}^2 C_H^2 \end{aligned}$$

Equation (4) shows how the overall transfer rate is governed by the mass transfer coefficients of the species in addition to the rate constant of

chemical reaction. An analysis of the order of magnitude of the different terms leads to substantial simplifications of Equation (4) but it is outside the scope of this paper.

Nomenclature:

a_0	activity of dimeric HDEHP
C_H	concentration of hydrogen ion
C_M	concentration of metal
C_O	concentration of dimeric HDEHP
C_X	concentration of extractant
C_Z	concentration of zinc in aqueous phase
C_{ZO}	concentration of zinc in organic phase
k_I	surface area based extraction reaction rate constant
k'	volume based stripping reaction rate constant
k_I'	surface area based stripping reaction rate constant
K_H, K_O, K_{ZO}	mass transfer coefficients of hydrogen ion, organic HEDHP and organic zinc respectively
r	initial reaction rate of zinc
R	initial flux of zinc across interface
σ	interfacial tension

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Table 1: Mass transfer coefficients for single drops.

Phase	$K \times 10^5 [\text{m.s}^{-1}]$	$\sigma \times 10^3 [\text{Nm}^{-1}]$
Nonoscillating circulating drops	0.6	20
Oscillating drops	2.0	20

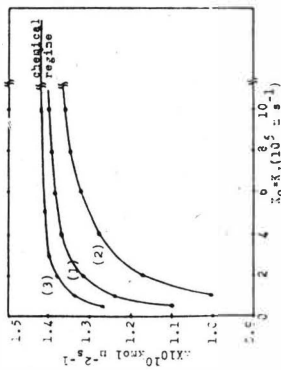


Fig. 1. Variation of the interfacial flux, J , with mass transfer coefficients, K , for three different cases. $\tau_0=0.001$.
(1) $C_0=0.01$, $C_2=0.0001$; (2) $C_0=0.001$, $C_2=0.0001$.
(3) $C_0=0.01$, $C_2=0.001$.

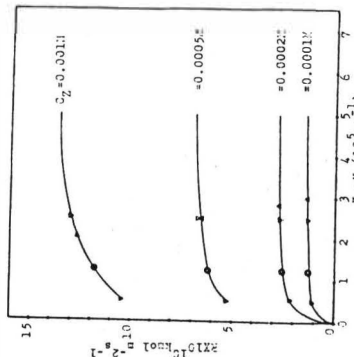


Fig. 2. Variation of simulated fluxes for a single drop, $C_0=0.01$.
 $C_2=0.001$, $\tau_0=0.001$, $\tau_1=1$ falling oscillating drop.
 $C_2=0.001$, $\tau_0=0.001$, $\tau_1=1$ falling oscillating drop.
 $C_2=0.001$, $\tau_0=0.001$, $\tau_1=1$ falling oscillating drop.
 $C_2=0.001$, $\tau_0=0.001$, $\tau_1=1$ falling oscillating drop.

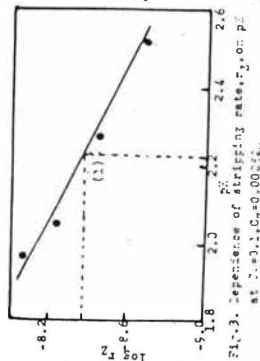


Fig. 3. Dependence of stripping rate, T_0 , on p at $\tau_0=0.001$, $C_0=0.001$.

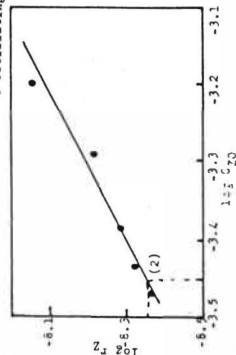


Fig. 4. Dependence of stripping rate, T_0 , on organic zinc concentration at $p=2.05$, $C_0=0.01$.

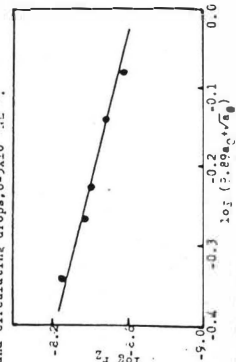


Fig. 5. Dependence of stripping rate, T_0 , on organic zinc activity at $p=2.27$, $C_0=0.01$.

The Role of Aggregate Formation in Solvent Extraction of Calcium

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In solvent extraction processes involving hydrometallurgical separations, spent nuclear fuel reprocessing, and nuclear waste processing operations, metal ions transfer across the boundary between two immiscible liquids. Hence, the properties of the liquid/liquid interface can often influence the extraction process. This suggests that one, therefore, should be able to control the extraction rate by proper manipulation of the nature of the liquid/liquid interface.

In an earlier communication (1) from this laboratory, aggregates, possibly reversed micelles, were proposed to form in the system di(2-ethylhexyl)phosphoric acid (HDEHP)/n-hexane/ CaCl_2 solution under certain conditions. The objective of the present study was to determine whether the amount of calcium extracted and the rate of extraction become significant when reversed micelles form. The interfacial tension (γ), equilibrium distribution coefficient (K_D), and mass transfer coefficient (k_{AO}) were obtained for the system HDEHP/n-hexane/0.01 mol dm^{-3} CaCl_2 solution.

The sources and methods of purification of water and CaCl_2 for preparing aqueous solutions, n-hexane and HDEHP for making organic solutions, and HCl for adjusting pH have been described elsewhere (1). NaOH used for adjusting pH was E. Merck Suprapur Grade. ^{45}Ca was obtained from Amersham as calcium chloride in aqueous solution. This solution was diluted 200 times and used for the mass transfer experiments. Rionfluor and Econofluor-2 (New England Nuclear) were used as scintillation cocktails for distribution equilibria and kinetics experiments, respectively. A solution of Nachromix (Godax) in concentrated sulfuric acid was used for cleaning glassware as well as the mass transfer cell.

The experimental set-up and methods for measuring γ of liquid/liquid extraction systems by the Wilhelmy plate technique have been described elsewhere (1,2).

A Lewis-type stirred, constant area (11.9 cm^2) mass transfer cell was employed to determine the aqueous-to-organic mass transfer coefficient (k_{AO}). The cell was jacketed so as to keep the temperature constant during each run. The organic and aqueous phases were independently stirred by two identical flat-blade stirrers, symmetrically positioned 15 mm above and below the liquid/liquid interface. Bodine synchronous (KYC-768) electric motors were used for this purpose, while Bodine (Model 2414) gear reducers were employed for varying the stirring speed.

Initially, we constructed a mass transfer cell very similar to that described by Vandegrift and Horwitz (3). Problems, however, due to rocking of the interface were experienced at stirrer speeds greater than 80 rpm. This problem was minimized by

employing eight vertical baffles (four above and four below the interface) and by placing a thin (3 mil) ring of FEP film (Dupont 300C) at the liquid/liquid interface. One side of the Teflon film is hydrophilic, and this side faced the aqueous phase.

An additional advantage of this Teflon ring is that it offers a simple means of varying the interfacial area. Also curvature effects become minimized, and hence the contact area can be calculated geometrically. When the organic phase is stirred at high speeds, a disturbance sets in at the air/organic interface and is transmitted to the organic/aqueous interface. This was eliminated by placing a TFE disc (1/8" thick having a hole for the upper stirrer to pass through) on top of the upper vertical baffles in the organic phase to dampen the waves. After incorporating these modifications, a plot of the mass transfer coefficient versus stirring speed exhibited more or less a plateau for speeds > 150 rpm (maximum speed employed was 300 rpm). Thus for stirring speeds > 150 rpm the present system is considered to be in a kinetic regime. However, at 300 rpm a slight disturbance was observed at the liquid/liquid interface. Hence, 150 rpm was used in all experiments.

For studying the distribution equilibria of calcium the following procedure was employed. In a series of bottles (25 ml capacity), 10.04 ml of aqueous solution ($0.01 \text{ mol dm}^{-3} \text{ CaCl}_2$) was introduced into each bottle along with 10 μ l of diluted $^{45}\text{CaCl}_2$ solution. Fifty μ l of these solutions were then transferred into glass scintillation vials containing 10 ml of Biofluor and were weighed on a semi-microbalance. The samples were then counted in a Beckman 215 liquid scintillation counter. Afterwards, 10 ml of HDEHP solution was added to each bottle, and the two phases were allowed to equilibrate overnight after shaking and adjusting the pH to the desired value. After equilibration, the pH was checked again and adjusted if required, and 50 μ l of the organic and aqueous phases were withdrawn and weighed separately in scintillation vials containing 10 ml of Biofluor. From the counts and the weight of each sample, the counts for a fixed volume (0.1 ml) of the three different types of samples mentioned above were calculated. The counts are proportional to the concentration of the calcium in each sample. The ratio of counts for the same volume of organic sample to that for the aqueous sample at equilibrium gives the distribution coefficient (K_d) if the efficiency of counting is the same in both phases. The efficiencies were found to be approximately 90% for both phases using $^{45}\text{CaCl}_2$ standard solution purchased from Amersham. The percent calcium extracted is expressed as $100 \times C_0/C_a$ where C_a is the counts for the aqueous phase before extraction and C_0 is that for the organic phase after extraction.

The experimental technique for obtaining mass transfer coefficients was as follows: Equal aliquots (39 ml) of aqueous and organic phases were introduced into the clean mass transfer cell and equilibrated at $20 \pm 0.05^\circ\text{C}$ for about 15 hours. Due consideration was given to the surface chemical cleanliness of the system. After equilibration, 50 μ l of diluted $^{45}\text{CaCl}_2$ solution was injected into the aqueous phase

with a hypodermic syringe inserted through a Teflon-lined septum. A small volume (50 μ l) of the organic phase was withdrawn with a Finn pipet at various times and weighed in a glass scintillation vial containing 10 ml of Econofluor-2. It was confirmed from interfacial tension measurements that negligible contamination occurred upon using Finn pipet tips in the mass transfer experiments. Sampling of the organic phase at different time intervals was continued for three hours. Seven hours after starting the experiment, samples from the organic and aqueous phases were also withdrawn to obtain readings for infinite time (equilibrium). Seven hours were sufficient for obtaining equilibrium. In addition to determining the radioactivity at infinite time in the organic phase, K_d also was evaluated at the end of the experiment using Biofluor, as before, because it is suitable for use in both aqueous and organic phases.

The γ -log [HDEHP] $_2$ curves for the system HDEHP/n-hexane/0.01 mol dm $^{-3}$ CaCl $_2$ solution at equilibrium pH 3.0 and 3.5 are shown in Figs. 1 and 2, respectively. The break in the slope of the two curves around 1.6×10^{-3} and 1.0×10^{-3} mol dm $^{-3}$ at pH 3.0 and 3.5, respectively, suggests that aggregates are formed beyond these concentrations which correspond to the critical dimeric HDEHP concentrations, i.e., [HDEHP] $_2^{\text{crit}}$ for the formation of reversed micelles. Preliminary quasi-elastic light scattering measurements suggested that these aggregates are not microemulsions or liquid crystals in view of their smaller size. The ability of sodium di(2-ethylhexyl)

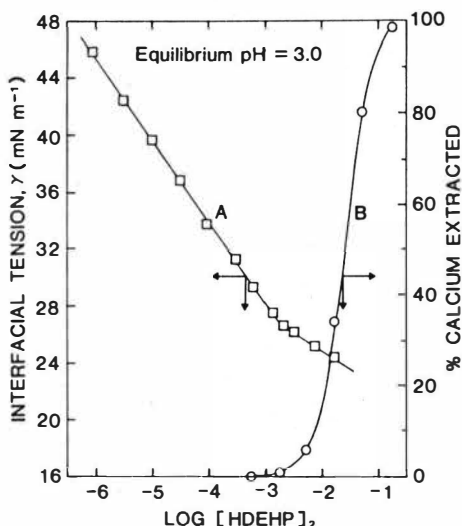


Fig. 1. (A) Interfacial tension and (B) percent calcium extracted as a function of log [HDEHP] $_2$ for the system HDEHP/n-hexane/0.01 mol dm $^{-3}$ CaCl $_2$ solution at pH 3.0 and 20°C.

phosphate to form reversed micelles has been documented in the literature (4,5). Hence, we believe the aggregates in our systems are reversed micelles. Reversed micelles have polar cores and are thus capable of solubilizing the aqueous phase and making Ca^{2+} more accessible for complexation with HDEHP.

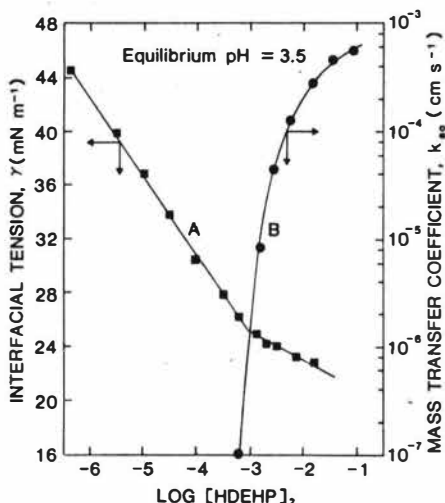
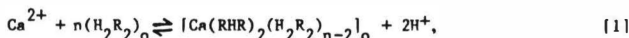


Fig. 2. (A) Interfacial tension and (B) mass transfer coefficient as a function of $\log [\text{HDEHP}]_2$ for the system HDEHP/n-hexane/ $0.01 \text{ mol dm}^{-3} \text{ CaCl}_2$ solution at pH 3.5 and 20°C .

HDEHP is known to exist in dimeric form in most organic solvents (6-9). The overall reaction for the extraction of calcium by dimerized HDEHP can be represented by the following reaction (10):



where H_2R_2 is the dimeric HDEHP and the subscript o refers to the environment of the species in the organic phase. The extraction equilibrium constant, K_{ex} , for this process is given by

$$K_{\text{ex}} = \frac{[\text{Ca}(\text{RHR})_2(\text{H}_2\text{R}_2)_{n-2}]_o [\text{H}^+]^2}{[\text{Ca}^{2+}] [\text{H}_2\text{R}_2]_o^n}. \quad [2]$$

Equation [2] can also be written in terms of K_d as

$$K_{\text{ex}} = \frac{K_d [\text{H}^+]^2}{[\text{H}_2\text{R}_2]_o^n}. \quad [3]$$

Henceforth, the subscript o will be dropped and $[\text{H}_2\text{R}_2]_o$ will be written as $[\text{HDEHP}]_2$.

Eq. [3] can be rearranged to Eq. [4], i.e.,

$$(\log K_d - 2\text{pH}) = \log K_{ex} + n \log [\text{HDEHP}]_2. \quad [4]$$

According to Eq. [4] a straight line of slope n and intercept $\log K_{ex}$ will be obtained on plotting $(\log K_d - 2\text{pH})$ versus $\log [\text{HDEHP}]_2$.

A plot of $(\log K_d - 2\text{pH})$ versus $\log [\text{HDEHP}]_2$ at pH 3.0 is depicted in Fig. 3 and has a slope of 2.01 (correlation coefficient, $r = 0.9971$) for $[\text{HDEHP}]_2, \leq 5 \times 10^{-3}$ mol dm^{-3} . Hence, n in Eq. [1] clearly can be taken as 2. Thus, the overall reaction for the extraction of calcium by dimeric HDEHP can be written as

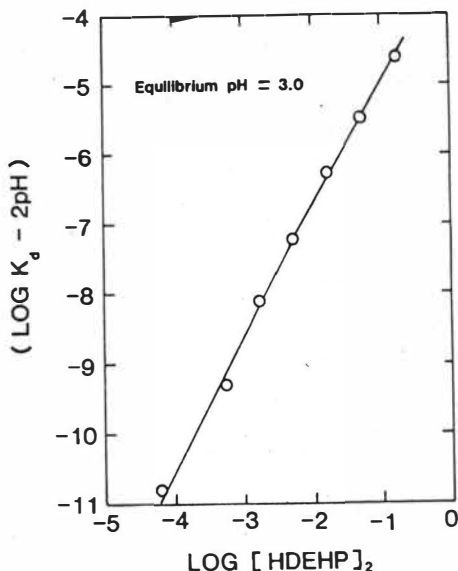
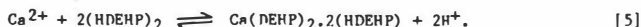


Fig. 3. $(\log K_d - 2\text{pH})$ vs. $\log [\text{HDEHP}]_2$ curve at pH = 3.0 for the system HDEHP/n-hexane/0.01 mol dm^{-3} CaCl_2 solution at 20°C .

Cox et al. (10) also reported the value of 2 for n for the extraction of metal ions by organophosphorus acids. As mentioned earlier, the intercept of the $(\log K_d - 2\text{pH})$ versus $\log [\text{HDEHP}]_2$ curve gives the value of $\log K_{ex}$. The extraction equilibrium constant thus evaluated for the system under consideration is 3×10^{-3} . It is to be emphasized that the stoichiometry shown in Eq. [5] is that for the pre-micellar concentration range. In the micellar range the slope of $(\log K_d - 2\text{pH})$ versus $\log [\text{HDEHP}]_2$ curve becomes less than 2.

In addition to the γ - $\log [\text{HDEHP}]_2$ curve Fig. 1 also shows the percent calcium

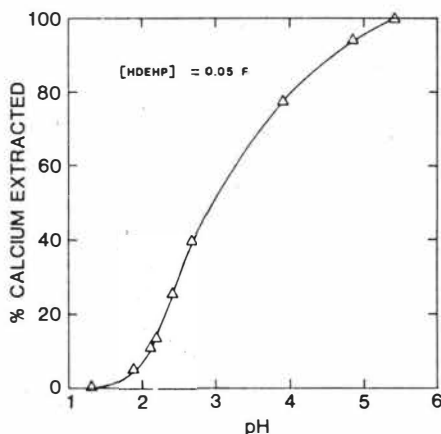


Fig. 4. Percent calcium extracted as a function of equilibrium pH for the system HDEHP/n-hexane/0.01 mol dm⁻³ CaCl₂ solution at [HDEHP] = 0.05 F and 20°C.

extracted as a function of log [HDEHP]₂ at pH 3.0 (curve B). Only when the reversed micelles begin to form above [HDEHP]₂^{crit} does the amount of calcium extracted become appreciable. Thus, reversed micelles appear to play an important role in enhancing calcium extraction.

Figure 4 shows the percent calcium extracted as a function of pH at constant [HDEHP] = 0.05 F, where F is the formula weight concentration of HDEHP. The calcium extracted increases gradually with pH, and around pH 5.4 almost 100% extraction is achieved.

The extraction of calcium from an aqueous solution to a nonpolar organic diluent can be represented in a simplified way as



where the subscript a refers to the aqueous phase, and k_{ao} and k_{oa} are the mass transfer coefficients from the aqueous to organic and from the organic to aqueous phases, respectively. The rate equation (11) for the interphase transfer of calcium is:

$$-\ln \left(1 - \frac{[\text{Ca}]_o^t}{[\text{Ca}]_o^\infty} \right) = \left[\frac{A}{V_o} \left(1 + \frac{V_o}{V_a} K_d \right) k_{oa} \right] t, \quad (7)$$

where $[\text{Ca}]_o^t$ and $[\text{Ca}]_o^\infty$ are the concentrations of calcium in the organic phase at time t and at infinite time (equilibrium), respectively, A is the interfacial area, and V_o

and V_a are the volumes of organic and aqueous phases, respectively. K_d can be written in terms of the mass transfer coefficients (3) as

$$K_d = \frac{k_{AO}}{k_{OA}} \quad [8]$$

A plot of $-\ln(1 - [Ca]_O^t/[Ca]_O^\infty)$ versus t should give a straight line passing through the origin and having a slope $A/V_O[1 + (V_O/V_A)K_d]k_{OA}$ from which k_{OA} can be calculated. Knowing k_{OA} and K_d , one can calculate k_{AO} from Eq. [8].

Since $\gamma\text{-log } [HDEHP]_2$ curves were already obtained at pH 3.0 and 3.5, mass transfer experiments were performed under essentially identical conditions arbitrarily selecting an equilibrium pH 3.5. Figure 2 shows k_{AO} as a function of $\log [HDEHP]_2$ (curve B) along with the $\gamma\text{-log } [HDEHP]_2$ curve (curve A) for comparison. It is seen from Fig. 2 that there is a marked increase in k_{AO} in the vicinity of $[HDEHP]_2^{\text{crit}}$. This is likely due to the formation of reversed micelles beyond the critical concentration and thus more calcium can be solubilized and transferred into the organic phase. Since the reversed micelles have an aqueous microenvironment, the bulk HDEHP molecules can come into contact with this microenvironment, ionize and interact with the solubilized Ca^{2+} to form calcium-HDEHP complexes. Thus, in addition to the heterogeneous interfacial chemical reaction between Ca^{2+} and HDEHP at the n-hexane/aqueous interface, reaction can take place at the reversed micelle/n-hexane interface. This probably leads to the significant increase in k_{AO} when reversed micelles are present. However, below the critical concentration, k_{AO} becomes very small due to the absence of reversed micelles. Below $[HDEHP]_2 = 5 \times 10^{-4} \text{ mol dm}^{-3}$, there is virtually no transfer of calcium, and it is difficult to obtain mass transfer data because the concentration of extracted calcium in the organic phase is very low.

The nature of the molecular aggregates presently is being investigated in greater detail using a variety of techniques including intensity light scattering and vapor pressure osmometry. Quasi-elastic light scattering techniques also are being extended to solvent extraction systems in an attempt to determine the size and size distribution of the aggregates.

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Transfer of Multicomplexed Ions Across the Interface Between two Immiscible Electrolyte Solutions; Fe(II,III), Ni(II) and Zn(II) Ions Complexed by Bidentate Nitrogen Bases

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INTRODUCTION

Although charge transfer across the interface between two immiscible electrolyte solutions is subject to steadily increasing interest, investigations have been restricted mainly to ions and systems which are supposed to be suitable as models for ionic transfer of alkali and alkaline earth ions, whereas the transfer of complexed transition metal ions from water into the organic solvent phase was - up to now - neglected with one exception: Freiser mentioned recently that he was going to investigate this type of system.

Phase transfer of complexed transition metal ions seems to be of some importance for solvent extraction processes which are now becoming common in hydrometallurgic metal-extraction and metal-winning. Data for single-ion phase transfer may hopefully be applied to develop a general theory of the kinetics of the extraction process.

EXPERIMENTAL

The aqueous 10^{-2} M base electrolyte solutions were prepared from doubly distilled water, LiCl (p.a. Fluka) and NiSO_4 , FeSO_4 or ZnSO_4 (p.a. Merck). The complexing agents (o-phenanthroline, p.a. Fluka or 2,2-bipyridine, p.a. Merck) were then added as methanolic solution. Concentration ratios of metal cation to complexing agent were 1:1, 1:2, 1:3 or 10:1. The Fe(II) - o-phenanthroline complex was oxidized to the Fe(III) complex by titration with $\text{Ce}(\text{SO}_4)_2$ (p.a. Merck). The aqueous reference solution of 10^{-2} M tetraphenylarsonium chloride (TPACl) was prepared from p.a. product (Fluka). The chloride contents of all aqueous solutions was checked by an argentometric titration.

Nitrobenzene base electrolyte solutions were freshly prepared from nitrobenzene (puriss., p.a. Fluka) and tetraphenylarsonium 3,3'-bis(undecahydro-1,2-dicarba-3-cobalta-closododecabor)-ate (TPADCC).

This salt was prepared by precipitation from aqueous solutions of tetraphenylarsonium chloride (TPACl, p.a. Fluka) and cesium salt of DCC-anion (CsDCC). The precipitated salt (TPACDD) was purified by recrystallization from water/acetone mixture.

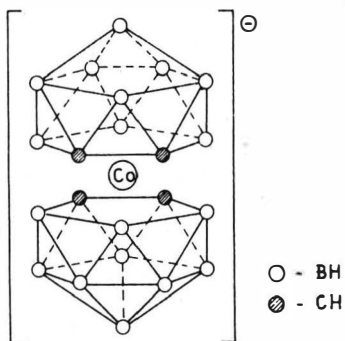
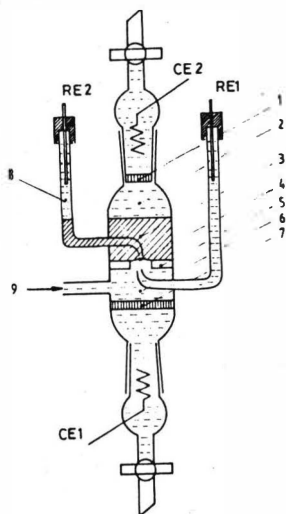


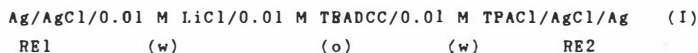
Fig. 1: Structure of the 3,3'-bico-(undecahydro-1,2-dicarbaborato)cobaltate anion. (Dicarbollylcobaltate, DCC)

Fig. 2: Four-electrode cell for voltammetric measurements at liquid/liquid interfaces. 1 and 7 glass-frits; 2 aqueous solution; 3 nitrobenzene phase; 4 nitrobenzene/water interface across 0.25 cm² orifice; 5 glass wall; 6 aqueous phase; 8 reference aqueous solution; RE1, RE2 reference electrodes, CE1 and CE2 counter electrodes; 9 microsyringe



An all-glass four-electrode cell, which is shown in Fig. 2 is used for experimentation. With the help of the microsyringe (9) the water/nitrobenzene interface is adjusted in the round orifice (area 25.0 mm²) made in the glass wall (5) located between the tips of two Luggin capillaries. The lower-density aqueous phase occupies the bottom of the cell, whereby a flat and reproducible interface is formed. Prior to the experiment the cell is washed with acetone, then with distilled water and finally dried in a dry-box. The cell is immersed in a water bath and thermostated at 25.0 ± 0.1°C. The reference electrodes RE1 and RE2 are Ag/AgCl electrodes, which repeatedly are renewed by anodic polarization in 0.1 M KCl solution with a current density of 5 mA/cm² for 2 hours; platinum wires serve as the counter electrodes CE1 and CE2.

The potential difference E of the galvanic cell(I)



is controlled potentiostatically. Since the potentials of the Ag/AgCl reference electrode RE1 and RE2 practically cancel each other, the potential difference E can be written as:

$$\Delta E = \Delta \phi_{\text{TPA}^+}^{\circ} - RT/F \ln \{ \gamma_{\text{TPA}^+}^{\circ} / \gamma_{\text{TPA}^+}^w \} \quad (1)$$

subscripts: w = aqueous phase, o = organic phase,

where $\gamma_{\text{TPA}^+}^{\circ}$ and $\gamma_{\text{TPA}^+}^w$ are the activity coefficients of TPA⁺ ion in the nitrobenzene and aqueous phase, respectively. ΔE is the Galvani potential difference across the interface, which is given by $\phi_w = \phi_o$ and which is related to the formal potential difference for the TPA⁺ ion $\Delta \phi_{\text{TPA}^+}^{\circ}$

$$\Delta \phi_{\text{TPA}^+}^{\circ} = \Delta \phi_{\text{TPA}^+}^{\circ} + RT/F \ln \{ \gamma_{\text{TPA}^+}^{\circ} / \gamma_{\text{TPA}^+}^w \} \quad (2)$$

The standard potential difference $\Delta \phi_{\text{TPA}^+}^{\circ}$ for the TPA⁺ ion had been calculated from the standard Gibbs transfer energy of the TPA⁺ ion from water into the nitrobenzene phase.

$$\Delta \rho_{TPA^+}^0 = \Delta \Delta G_{TPA^+}^{o,w \rightarrow o} / F \quad (3)$$

The value $\Delta \rho_{TPA^+}^0 = -0.372$ V for the TPA^+ ion transfer from water to nitrobenzene was calculated from extraction data.

Voltammetric measurements are performed either by using a four-electrode potentiostat with Ohmic potential drop compensation by positive feedback or with a conventional three-electrode Wenking potentiostat. In this case the controlled potential difference between both reference electrodes RE1 and RE2 is referred virtually to ground potential by an appropriate difference amplifier impedance converter. Again IR-compensation is performed by positive feedback. The potential-sweep voltammograms (max. rate: 0.2 V s^{-1}) are plotted on an XY-recorder or recorded on a Tectronix-Oscilloscope.

RESULTS

According to Fig. 3 which shows the cyclic voltammogram for the interface water/nitrobenzene together with an corrected cyclic voltammogram for transfer of the three nickel complexes of o,o'-bipyridyl (oBP) (ML_2^{2+} , ML_2^{2+} , ML_3^{3+}) the "window" of the interfacial potential (compare Eq. (1)) which allows voltammetric observation of ion-transfer extends from 0.08 V to 0.68 V.

Fig.3 depicts single sweep voltammograms corrected for base electrolyte currents of different ions from aqueous solutions containing Ni^{2+} -cations and o-bipyridine in different concentration ratios: $c(Ni^{2+})^{tot}/c(oBP)^{tot} = 1/2$ (full line); $1/1$ (dashed-dotted line), $1/3$ (dashed line, left hand side) and $10/1$ (dashed line, right hand side).

Fig. 3: Voltammograms indicating phase-transfer of Nickel II ions complexed by o-bipyridine reveal the transfer of three different species: Nickel II-ions being complexed with one (NiL_2^{2+}), two (NiL_2^{2+}) and three (NiL_3^{3+}) o-bipyridyl molecules. Interesting enough the peaks for transfer of ML_2^{2+} , ML_2^{2+} and ML_3^{2+} are equally separated from one another by the voltage difference $E = 0.17$ V. Thus the exchange of any two water molecules by one molecule of bidentate ligand oBP changes the standard Gibbs transfer energy for nickel ions by the same amount

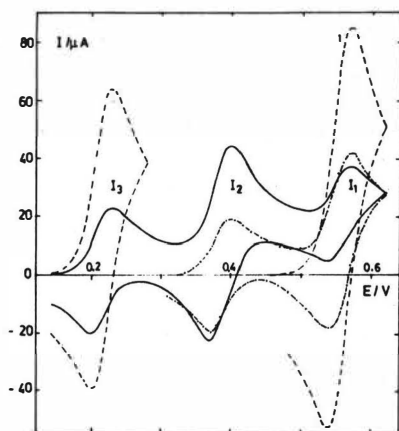


Fig. 3

irrespective of how many water molecules in the inner hydration-sphere of nickel are already exchanged by the ligand
($\Delta\Delta G^\circ(\text{transfer}) = 33 \text{ kJ/mol}$).

Applying convolution-analysis of peak voltammograms, i.e. performing convolution potential sweep voltammetry yields in convolution half-wave potentials and - by logarithmic reduced representation - in logarithmic slopes of current/voltage curves which for all three peaks discussed so far amount to $0.030 + 0.002 \text{ V}$ per decade. This slope is indicative for a reversible transfer process. Half-wave potentials and convoluted limiting currents are collected in Table 1.

the height of any individual reversible peak for transfer of a chemically stable and well defined species is proportional to its concentration in the aqueous bulk phase and proportional to the square root of its diffusion coefficient in water. Comparing the peak heights of voltammograms for solutions containing $10^{-3} \text{ M Ni}^{2+}$ nearly completely complexed either as ML_2^{3+} or as ML^{2+} reveals that obviously the diffusion coefficient of ML^{2+} is considerably higher than that of ML_2^{3+} .

SUMMARY

Transfer from water to nitrobenzene of Iron (II) and (III), Ni(II) and Zn(II) complexed in the aqueous phase by one, two and three molecules of o-phenanthroline and o,o'-bipyridine is investigated using cyclic voltammetry. The kinetically inert complexes of Fe(II), Fe(III) and Ni(II) are keeping their ligand-metal bonds intact and are transferred reversibly from water into nitrobenzene. The uncomplexed metal ions are not transferred within the voltage range limited by transfer of the ions of the aqueous and nonaqueous supporting electrolyte. Ease of phase-transfer is greatly enhanced by complexation with the organic ligand and successive addition of the first, second and third bidentate nitrogen base changes the Gibb's transfer enthalpy of the Ni(II) by approximately equal amounts ($\Delta\Delta G^\circ = -37 \text{ kJ/mol}$). The molecular structure of the complex ligand bears only a minor but clearly discernible influence on the Gibb's transfer enthalpies as demonstrated for Ni(II)-phenanthroline and bipyridine complexes. Comparative investigation of phase transfer of Fe(II)- and Fe(III)-trisphenanthroline complexes reveals that due to higher charge of the Fe(III)-complexes they are more strongly solvated in aqueous and hence less easily extracted into nitrobenzene than Fe(II)-complexes.

Table 1

Half-wave potentials ($E_{1/2}$), limiting convoluted current (m_d) and diffusion coefficients (D_w) in water of multi-complexed transition metal ions

Sol.No	$E_{1/2}/V$			$m_d/As^{1/2}m^{-1}$			D_w/m^2s^{-1}		
	ML	ML ₂	ML ₃	ML	ML ₂	ML ₃	ML	ML ₂	ML ₃
Ni ²⁺ -o,o'-bipyridin									
3	0.557	0.385	0.214	1.37	2.5	1.65	$1.3 \cdot 10^{-9}$	$8.7 \cdot 10^{-10}$	$7.5 \cdot 10^{-10}$
Ni ²⁺ -phenanthroline									
7	0.543	0.352	0.158	0.688	1.94	0.98	$5 \cdot 10^{-10}$	$3.4 \cdot 10^{-10}$	$2.8 \cdot 10^{-10}$
Fe ²⁺ -phenanthroline									
11	-	-	0.150	-	-	3.1	-	-	$2.9 \cdot 10^{-10}$
Fe ³⁺ -phenanthroline									
13	-	-	0.331	-	-	-	-	-	(?) *)

*) Not determined because of uncertainty concentration of species ML_3^{3+} .

Extraction Kinetics Investigation Under Conditions of Non-Stationary Surface of Phase Contact

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Much attention has been drawn to extraction kinetics investigations lately. Among a lot of research methods reactor ones are of considerable interest because they provide experimental conditions which are the closest to those existing in the real extraction apparatus (1). When the extraction kinetics investigation is carried out under the conditions of non-stationary surface of phase contact (PCS) it is generally difficult to control PCS because its value suddenly changes when two phases are dispersed into each other. Using unique apparatus and experimental techniques a number of workers are engaged in studies of mass transfer processes under stationary PCS conditions (2,3). Presented here the extraction kinetics investigations method for the conditions of non-stationary PCS simplifies the construction of the reactor and the implementation of the experiment.

If the reaction accompanying the mass transfer process is of the first order, the mass transfer rate is given by

$$dy_t/dt = a_t k_o (y_t^e - y_t) / V_o \quad (1)$$

where y_t - current concentration of metal in the organic phase;

$y_t^e = \alpha x_t$ - equilibrium concentration of metal by the local equilibrium with the water phase;

α - distribution coefficient;

x_t - current concentration of metal in the water phase;

a_t - current value of PCS;

t - time;

k_o - mass-transfer coefficient;

V_o - volume of the organic phase.

It may be written as (4);

$$dy_t/dt = k_o (I + \alpha) a_t (y - y_t) / V_o \quad (2)$$

where y - equilibrium concentration of metal in the organic phase.

Integration of Equation 2 in the range of 0 to t and 0 to y_t at the constant distribution coefficient results in

$$\ln(I - I_t) = - k_o (I + \alpha) / V_o \int_0^t a_t dt \quad (3)$$

where I_t - extent of extraction. Approximation of PCS against time

$$a_t = lmt / \beta (I + lt) \quad (4)$$

where l and m are parameters characterizing the rate of changing PCS and equilibrium value of the PCS, respectively; β - proportionality factor and substitution a_t in Equation 3 gives:

$$\ln(I - I_t) = -k_o(I + d)MA/V_o \quad (5)$$

where $A = t - (I/l)\ln(I + It)$. Analysing the dependencies $\ln(I - I_t)$ on A one may conclude of the process under non-stationary conditions of PCS and of localization and orders of the limiting step of the reaction.

This method has been tried when investigating the extraction of gallium from potash solutions by p-tert-butyl phenolformaldehyde oligomer (5) and re-extraction of nickel and copper from phase containing disulphide p-tert-butyl phenol (6). To investigate the kinetics of extraction the photometric unit connected to the titrator T-107 was used. The construction of this unit allows to carry out the agitation in the reactor by a magnetic stirrer and to control, simultaneously, the PCS by light scattering (7). The stroboscopic tachometer 2TCT-32-456 was used to measure the rotation speed of the stirrer. The unit was fed through the power stabilizer G-0,5. The reactor was a glass vessel with a ground tight conical cap supplied with a capillary for removing air (Fig.1). The inner diameter of the vessel was 33 mm. The magnetic agitator was a cylinder the 7mm in dia. and 22mm long. The upper part of the reactor was filled by means of a syringe. In any case water and organic phase ratio was a unit. The extraction system was balanced with respect to macroelements before the introduction of the elements under investigation. Change in PCS was determined from Equation 6 using the photocurrent values obtained (7)

$$\beta a_t = (P_o/P - I) \quad (6)$$

where P_o - photocurrent value in the extraction system before agitation; P - photocurrent value of the agitated extraction system. The coefficient β depends upon refraction indices of dispersed phase and dispersion medium as well as the reactor construction.

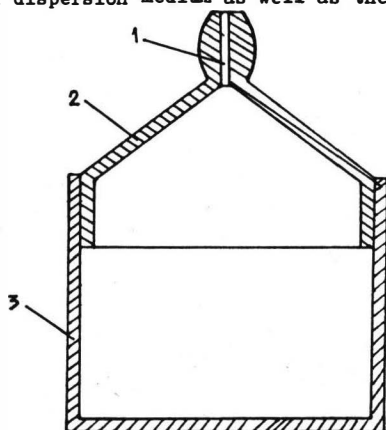


FIGURE 1. The reactor for extraction kinetics investigation.

- 1 - capillary
- 2 - cap
- 3 - glass

The distribution of the radioactive isotopes Ga-67 between IM solution of extractant in toluene and IM potassium carbonate solution was studied. Under these conditions gallium was extracted rather slowly: the equilibrium was achieved only after two hours of intensive agitation ($n=1265$ r/min, $\Delta=7.33$). In order to determine the extraction rate of gallium was found for different stirring speeds. The values a_t were determined using the photocurrent values obtained by Equation 6 and by least square method l and m parameters in Equation 4 were calculated. Curves $\ln(I - I_t)$ vs. A were plotted using the time and agitation intensity data as they affect the gallium extraction taking into account the PCS changes. The control by means of F -test showed that all experimental data were described by linear regression equation adequately with probability of 0.95. The parameters of these equations $y=bx$ are listed in Table I.

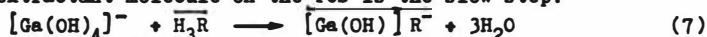
Table I.

Parameters of regression equation for dependences $\ln(I - I_t)=f[t - (I/l)\ln(I + It)]$. Gallium extraction by solution of 0.1M p-tert-butyl phenolformaldehyde oligomer in toluene.

Stirring speed n , r/min	Parameter $b \cdot 10^3$	Correlation coefficient
620	4.71	0.990
670	4.57	0.991
785	9.20	0.998
860	11.21	0.996
1265	24.02	0.989

It is clear from Equation 5, that $b=k_o(I + \Delta)m/V_o\beta$. Hence, it was found that $k=k_o/\beta$. Taking into account that in these experiments $\beta = \text{const}$, it is possible to make a conclusion on the process regime from the dependence k vs. n . Figure 2 shows that when stirring speed is increased beginning from $n=800$ r/min mass-transfer coefficient is not changed and, consequently, the process occurs in kinetic regime. Independences of mass-transfer coefficients upon stirring speed change and upon phase contact surface testify about localization of limit step of the process on the PCS (8). Indirectly this fact was proved by low gallium extraction rate in constant interfacial area stirred cell. When the extraction process was carried out in the cell with PCS of 45cm^2 and with stirring speed of 180 r/min during 30 minutes, the value of gallium distribution coefficient was only 0.05 per cents from equilibrium one, while when this extraction was carried out in the reactor, the value of distribution coefficient was

equal to 50 per cents. In order to determine the order of limit step of reaction with respect to extractant the dependences of gallium extraction rate upon time with different extractant concentrations were studied. This order is equal to one (Figure 3). The order with respect to gallium is equal to one too, because above mentioned dependences of extraction rate upon time were linear (Table I). By means of dilution method it was established that ratio of gallium to extractant in the extraction complex is equal to one. Taking this fact into account it is possible to propose the following mechanism of gallium extraction. Interaction of tetrahydroxogallate ion with the extractant molecule on the PCS is the slow step:



Then the formed anion associates with potassium and this complex transfers into bulk organic phase:

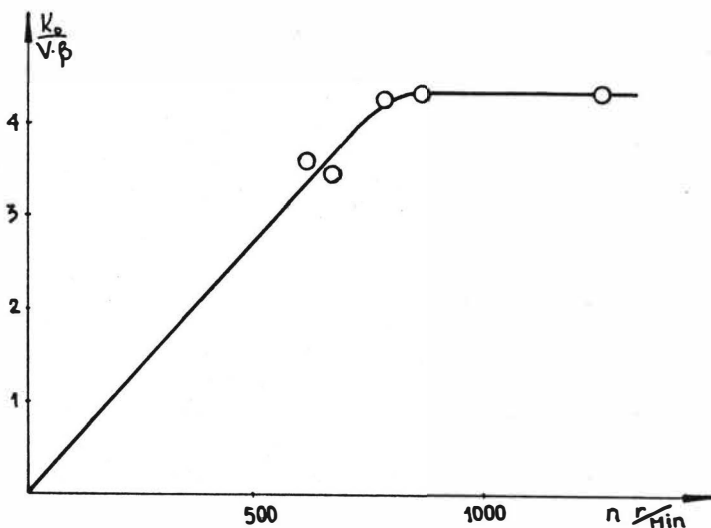
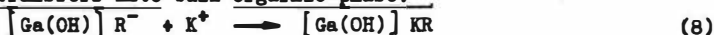


FIGURE 2. Influence of the stirring speed on gallium mass-transfer coefficient.

Time of equilibrium in re-extraction process in the system: disulphide p-tert-butyl phenol - sulphuric acid is equal to 1 hour for nickel and to 30 minutes for copper. The organic phase, which contained $4.09 \cdot 10^{-3} \text{M}$ nickel and $1.10 \cdot 10^{-3} \text{M}$ copper and which was used for re-extraction kinetics investigation had been obtained by extraction of 0.1 M extractant solution in toluene from the solutions contained instead of these metals 200 gramm/liter $(\text{NH}_4)_2\text{SO}_4$ and $\text{pH}=10$. Re-ex-

traction was carried out by sulphuric acid solutions. The control by means of F-test showed that experimental dependences $\ln(I - I_t)$ on A in the cases of nickel and copper re-extraction were described by linear regression equation $y = b_0 + b_1 x$ adequately with probability of 0.95. Parameters of this equation are listed in Table 2.

Table 2.

Parameters of regression equation for dependences $\ln(I - I_t) = f[t - (I/l)\ln(I + lt)]$ for nickel and copper re-extraction from organic phase containing disulphide p-tert-butyl phenol and toluene.

Stirring speed n, r/min	N i c k e l			C o p p e r		
	Parameters b_0	$b_1 10^2$	Correlation coefficient	Parameters b_0	b_1	Correlation coefficient
670	0.371	2.80	0.959	0.456	0.284	0.937
785	0.386	2.60	0.961	0.482	0.182	0.963
860	0.432	4.20	0.959	0.532	0.217	0.948
1050	0.476	3.65	0.912	0.599	0.189	0.953
1265	0.559	3.24	0.926	0.511	0.394	0.978

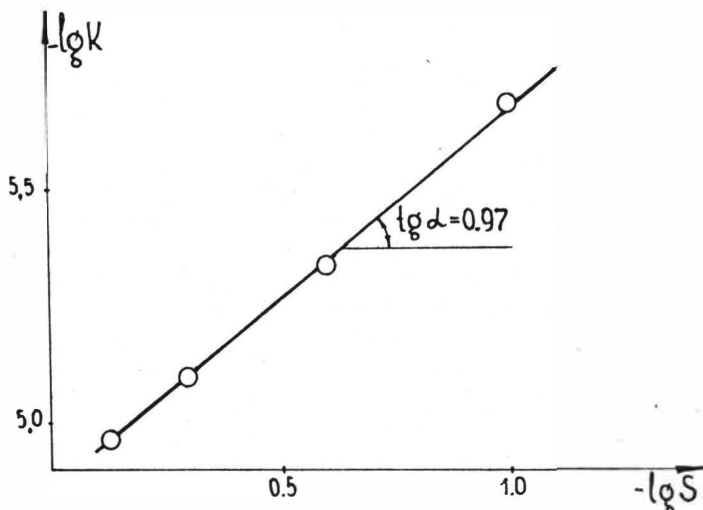


FIGURE 3. Determination of the order with respect to extractant in the process of gallium extraction.

Figure 4 shows that when the stirring speed increasing, the mass-transfer coefficient in this range of stirring speed is constant both in the process of nickel re-extraction and in the process of copper re-extraction. Independences of mass-transfer coefficient upon stirring speed, and so upon the PCS, testify that beginning from $n=670$ r/min re-extraction processes both nickel and copper occurs in kinetics regime, and the limit step of the process localize on the PCS (8).

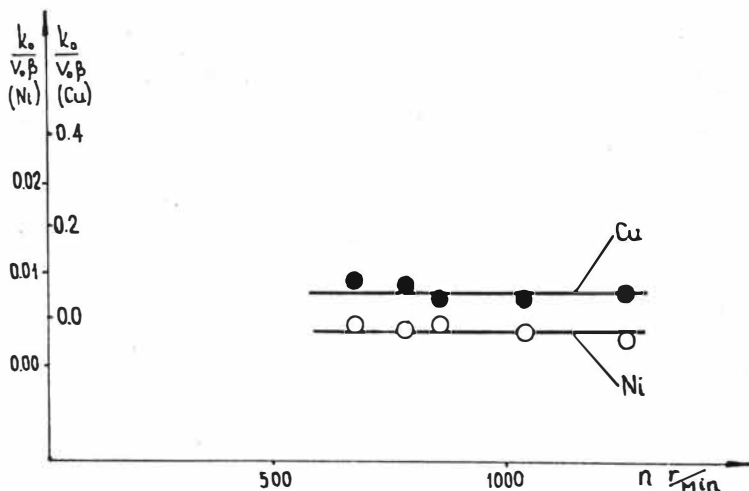


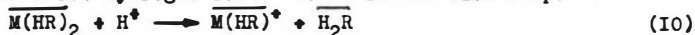
FIGURE 4. Influence of the stirring speed on nickel and copper mass-transfer coefficients.

The orders with respect to nickel and copper are equal to one because above-mentioned dependences of re-extraction rate upon time were linear (Table 2). In order to determine the order of limit step of reaction with respect to hydrogen ion the dependences of re-extraction rate of nickel and copper upon time with different sulphuric acid concentrations were studied. During nickel re-extraction this order is equal to one (Figure 5), but during copper re-extraction this order is changing from one to zero with increasing sulphuric acid concentration more than 0.25M (Figure 6). It was established by means of dilution method and studying $\lg \alpha_m$ vs. pH curves that nickel and copper extraction carries out according to Equation 9 (without taking hydration into account).



Taking this fact into account it is possible to propose the following mechanism of nickel and copper re-extraction (when $I_{H_2SO_4} < 0.25M$).

Apparently, the destruction of $M(HR)_2$ complex and the addition of the first hydrogen ion H^+ to it is the slow step:



The addition of the second hydrogen ion H^+ to this complex occurs very quickly because of unstability of the intermediate complex:



The formed ions of nickel (II) and copper (II) diffuse in bulk organic phase.

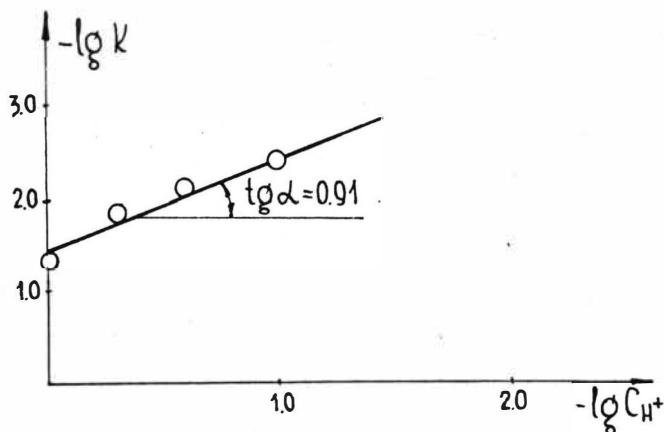


FIGURE 5. Determination of the order with respect to hydrogen ion in the process of nickel re-extraction.

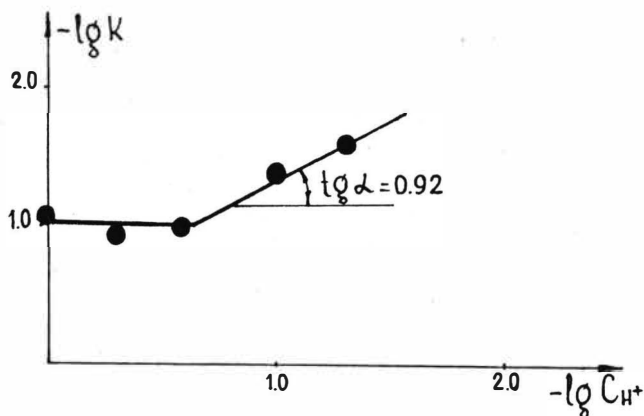


FIGURE 6. Determination of the order with respect to hydrogen ion in the process of copper re-extraction.

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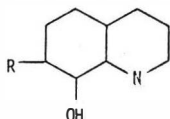
ROLE OF THE INTERFACE IN THE KINETICS AND MECHANISM OF EXTRACTION OF NICKEL BY 8-QUINOLINOLS

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Solvent extraction processes such as those involving metals and chelating extractants, in addition to being of high interest to such diverse groups as analytical chemists and hydrometallurgists, provide unique opportunities to evaluate the role of liquid-liquid interface in complex mass transfer processes. In fact, over the last twenty years, lively controversy has developed over this role. Two extreme positions based on extraction kinetics studies have received most of the attention: (1) The rate of extraction of a metal ion in the aqueous phase by a "hydrophobic" chelating extractant in the organic phase reflects the formation of a metal chelate species entirely in the interface [1]; (2) The bulk, aqueous phase is the site of the rate-determining chelate formation reaction [2]. A significant barrier to resolution of this issue lies in the difficulties of the experimental techniques used by both factions. The concern of those championing the interfacial mechanism for conducting experiments under conditions of fixed, well-defined interfacial area led them to use Lewis cell and falling (or rising) drop methods in which relative movement of two phases is slow enough to make them subject to diffusion control. On the other hand, use of high speed stirring by those who believe in the bulk aqueous phase mechanism, while effectively eliminating diffusion, did not until recently permit the interfacial area to be measured, and hence the role of the interface could not be fully assessed. With the recent development in this laboratory of a high speed stirring apparatus incorporating a micro-porous Teflon filter element [3], it became possible to observe interfacial adsorption of extractants [4] under steady-state conditions and to apply properly such findings to extraction kinetics [5]. More recently, by combining extraction experiments with interfacial tension measurements, and applying Gibbs' adsorption isotherm, we can reliably measure and control the interfacial area [6] and thus study its effect on the overall extraction kinetics in a wide variety of extraction systems.

We have been particularly interested in the kinetics and mechanism of metal chelate extraction systems. Previous studies [7, 8] have demonstrated that nickel extraction by 8-quinolinol (oxine) (A) occurs via two reaction pathways: (1) reaction between nickel and neutral oxine and (2) reaction of metal with ligand anion. In each case, it has been postulated that these rate determining reactions occur in the bulk aqueous phase. Recent work in this laboratory [4,5] has revealed that, in cases where the ligand anion is a surface active species, the extraction may, at least partially, proceed through a reaction path involving the

interfacial region. Haraguchi and Freiser [9] have found that for KELEX 100 (8), the pH value is affected by high speed stirring, indicating that the distribution of the ligand anion is sensitive to changes in interfacial area. To help answer the question of whether the rate determining steps for the extraction of nickel by oxine and its higher molecular weight analog, KELEX 100, are taking place in the bulk aqueous phase or in the interfacial region, this system has been studied with the new apparatus. The nickel/oxine system affords one the opportunity to test the applicability of the apparatus as a diagnostic tool in determining reaction mechanisms in typical solvent extraction systems.



- (A) R = H
(B) R = dodeceny

EXPERIMENTAL

8-Quinolinol (oxine) (Eastman Kodak) was purified by recrystallization from ethanol. 7-Dodeceny-8-quinolinol (KELEX 100) was obtained from Sherex Chemicals and was purified by washing 100 mL of undiluted KELEX 100 with about 20 L of 1 M sulfuric acid. The yellow aqueous phase containing the major impurity (oxine) was discarded and the washing continued until the aqueous phase was colorless. The solution was washed with water and the light brown organic phase evaporated on a rotary evaporator until only the purified KELEX 100 remained. All other chemicals were of analytical grade. Phosphate and THAM buffers, sodium perchlorate and sodium hydroxide solutions were washed with solutions of KELEX 100 in chloroform to remove metal impurities. Chloroform was washed with water twice before use. Nickel solutions were prepared from nickel perchlorate and standardized by complexometric titration with EDTA at pH 10 with murexide as the indicator.

Apparatus: The extraction kinetics apparatus described previously [3] was used with some minor changes, such as the introduction of a computer controlled data acquisition unit. The absorbance readings from the Cary 219 were sent at chosen intervals (usually 1 Hz) to an Apple II Plus computer. A Pascal software program was written to collect and store the data on floppy disks. Stirrer rotation rates were measured with an analog tachometer (precision of $\pm 2\%$).

Procedure: The spectrophotometer was first zeroed at the desired wavelength by pumping clean chloroform through the flow cell. The Morton flask was immersed in a water bath being held at 22°C , and the phase separator and stirrer were incorporated into the system. To the reaction vessel was added 100 mL of chloroform which was 10^{-3} M in ligand concentration. Next, 90 mL of aqueous buffer (10^{-3} M buffer and 0.1 M NaClO_4) was added and, following thermal equilibration, the peristaltic pump was started to circulate the organic phase through the flow cell.

The stirrer was set to the desired stir rate and the mixture was allowed to equilibrate for 5 minutes.

The kinetics of extraction was started by the rapid (<1 sec) injection of 10 mL of 10^{-3} nickel solution. The reaction process was monitored at the respective wavelength maxima: 390 nm for $\text{Ni}(\text{Ox})_2$ and 487 nm for $\text{Ni}(\text{KELEX})_2$. These two wavelengths correspond to different electronic transitions.

The experiments were carried out under pseudo-first order conditions with ligand in the organic phase in large excess over nickel ion in the aqueous phase. The pseudo first order rate constants, k_{obs} , were determined from

$$\ln \frac{A_e - A_0}{A_e - A_t} = k_{\text{obs}} t$$

where A_e is the absorbance at equilibrium, A_0 is the absorbance at time zero, and A_t is the absorbance at time t .

Interfacial tension was determined by the drop-volume method using a Gilmont micro buret and polyethylene tip.

RESULTS AND DISCUSSION

In a previous study [6], it was demonstrated that the amount of interfacial area, or average droplet size, a liquid-liquid dispersion can be measured as a function of stirring rate. This allows the measurement of extraction rate under varying interfacial area, and thus, the evaluation of the role of the interfacial area in solvent extraction kinetics. It has been assumed that since the chloroform and aqueous phases in the pH range used in this study were found to have identical interfacial tension (32.5 dyn/cm) to the system used previously (butyldithizone), the relation between specific interfacial area (interfacial area divided by volume) and stirring rate, are essentially the same [6] (see Table 1). It should be pointed out that, while subject to small absolute errors in interfacial area, our method [6] for determining this clearly demonstrates a good linear relationship between stirring speed and interfacial area in the range of 2000-4000 r.p.m. for the chloroform-aqueous phase pairs used. This results in a high degree of internal consistency on which are based the major conclusions concerning the respective roles of bulk aqueous and interfacial pathways.

The rates of extraction of nickel with oxine and KELEX 100 were found to be dependent on hydrogen ion concentration raised to a fractional power [7, 9], indicating two concurrent pathways whose rate determining steps involve either neutral and anionic forms of the ligand. These two paths have been previously presumed to occur strictly in the bulk aqueous phase. Finding that an increase in interfacial area can cause a drop in absorbance of the neutral reagent in the bulk

organic phase under alkaline conditions suggests that the ligand anion is surface active [5]. This leads to the possibility that the reaction of nickel with ligand anion may, in part, utilize an interfacial reaction mechanism.

It was determined from the drop in absorbance of the species in the organic phase upon stirring, that at pH 11.3, the oxine anion exhibited an interfacial excess of 3×10^{-12} mol/cm², while for KELEX 100 the excess by 6×10^{-12} mol/cm², twice that of oxine. Even in the case of KELEX 100, the value of Γ is equivalent to each

molecule occupying about 2800 \AA^2 of interface, a value much larger than that expected for an interface saturated with a monolayer of the molecules. The quite small Γ values indicate that these species are only weakly surface active, yet still sufficiently so to produce the kinetic effects observed.

In order to evaluate the role of the interface in the extraction kinetics of nickel with 8-quinolinols, the rates of reaction were measured as a function of specific interfacial area. The results are illustrated in Figure 1 for oxine and Figure 2 for KELEX 100. The experiments were run over a range of pH values to see how the ratio of neutral to ligand anion would affect the balance between the two possible pathways (bulk and interfacial). The results, which indicate that the extraction pH is very important in determining what combination of mechanisms is operative, can be rationalized by the reaction scheme illustrated in Figure 3. This scheme allows for three distinct concurrent reaction pathways:

- Path 1: Reaction between metal and neutral ligand in the bulk aqueous phase.
- Path 2: Reaction of metal with ligand anion in the bulk aqueous phase.
- Path 3: Reaction of metal and ligand anion in the interface.

Evidence in support of this reaction scheme is seen in Figures 1 and 2. In the low pH range, the reactions are practically independent of specific interfacial area. In this range the neutral form of the ligand predominates, and its reaction with nickel ion occurs in the bulk (path 1). The fact that neutral ligand shows unobservably low surface active tendencies lends support to the likelihood of a strictly bulk phase reaction.

With increasing pH, increases in both slopes and intercepts in both figures is observed, indicating the dual anion mechanisms. The significance of the increasing intercept is that, in the limit of zero interfacial area, the rate increases with pH, as required by a bulk phase reaction of the ligand anion.

The increase of the observed rate with interfacial area is heightened with increasing pH, demonstrating that the ligand anion participates in a rate determining step at the interface (path 3).

These findings are represented quantitatively by the following derived relations:

$$-\frac{d(\text{Ni})}{dt} = k_{\text{obs}} (\text{Ni}) \quad (1)$$

$$-\frac{d(\text{Ni})}{dt} = (k_{\text{HL}} + k_{\text{L}} \frac{K_{\text{a}}}{[\text{H}^+]}) \frac{[\text{HL}]_{\text{o}} [\text{Ni}]}{K_{\text{D}}} + k_{\text{i}} K_{\text{M}} K_{\text{L}} a_{\text{d}} \frac{K_{\text{a}}}{[\text{H}^+]} \frac{[\text{Ni}] [\text{HL}]_{\text{o}}}{K_{\text{D}}} \quad (2)$$

$$k_{\text{obs}} = (k_{\text{HL}} + k_{\text{L}} \frac{K_{\text{a}}}{[\text{H}^+]}) \frac{[\text{HL}]_{\text{o}}}{K_{\text{D}}} + k_{\text{i}} K_{\text{M}} K_{\text{L}} a_{\text{d}} \frac{K_{\text{a}}}{[\text{H}^+]} \frac{[\text{HL}]_{\text{o}}}{K_{\text{D}}} \quad (3)$$

where k_{obs} is the observed pseudo first order rate constant, k_{HL} is the second order rate constant of metal plus neutral ligand in the bulk aqueous phase, k_{L} is the second order rate constant for metal plus ligand anion in the bulk aqueous phase, k_{i} is the interfacial rate constant, K_{a} is the acid dissociation constant ($\text{p}K_{\text{a}}$ 9.90 and 10.40 for oxine and KELEX 100, respectively [10]), K_{D} is the distribution constant of the neutral ligand ($10^{2.6}$ and $10^{5.52}$ for oxine and KELEX, respectively [10]), K_{M} is the distribution constant of the metal between the interface and bulk aqueous phase, K_{L} is the distribution constant of the ligand anion between the interface and the bulk aqueous phase, d is the thickness of the interface, and a is the specific interfacial area. A plot of k_{obs} vs. a (Figures 1 and 2) permits the evaluation of all the rate constants, provided the other values are known. The excellent linearity seen in the plots confirms the applicability of Equation 3.

The only unknown values in Equation 3 are K_{M} , K_{L} , and d . Since it is assumed that the metal is not surface active, K_{M} is taken as unity. The values of the product of (K_{L} , d) can be obtained by measurement of $\Delta \text{pH}_{1/2}$, the change in $\text{pH}_{1/2}$ to a lower value upon generation of a large interfacial area, $\text{pH}_{1/2}$ being the pH at which 50% of the ligand has left the organic phase and transfers to the interfacial and bulk aqueous phases. This relation has been previously derived by Watarai and Freiser [5]

$$10^{\Delta \text{pH}_{1/2}} - 1 = K_{\text{L}} a_{\text{d}} \quad (4)$$

The observed shift in $\text{pH}_{1/2}$ for oxine was 0.03 ± 0.01 and that for KELEX 100 was 0.8 ± 0.6 , yielding the values from Equation 4 of (K_{L} , d) as $10^{-3.6 \pm 0.2}$ for oxine and $10^{-1.7 \pm 1.0}$ for KELEX 100.

The values of the slopes and intercepts of the lines in Figures 1 and 2 can be used to evaluate all three rate constants, as well as the degrees of contribution of the three pathways. Results are in Table 2 along with values from other studies. A similar ligand, 8-mercaptoquinoline, is included for comparative purposes.

There is fairly good agreement with Yamada et al. [2] in the case of oxine kinetics. It must be pointed out that this study was done at a slightly lower temperature (22°C) than that of Yamada (25°C). Nevertheless, one must realize

that their study was done under the assumption of a completely bulk phase reaction mechanism as opposed to this study's finding of a combination of bulk and interfacial reactions of the ligand anion. The 10 times higher interfacial rate constant can be understood in terms of the differences in many physical properties between the bulk and interfacial phases. It is possible that the dielectric constant at the interface is somewhere between that of the bulk solvents, yielding a much lower dielectric constant than that of bulk water. This would be expected to be a more conducive environment for the reaction between two oppositely charged ions as is the case here. In addition, the geometric orientation of the weakly surface active chelating agent may be affected by the different environment that the interface provides. The number of degrees of freedom for the ligand anion should be lower at the interface, than in bulk water, due to the presence of dispersive forces which tend to orient the species in such a way as to reduce its free energy. The polar chelating group is expected to be pointing towards the aqueous phase which will also enhance the chances of reaction. These factors would all lead to the observed larger interfacial rate constant found for oxine.

The observation of a consistent difference between bulk rate constants for the neutral and anionic species of both oxine and KELEX 100, $10^{2.4}$ times greater for the respective anions, lends support to the validity of these rate constants. This difference reflects the greater facility for substitution that the anion possesses over the neutral ligand.

Although the more hydrophobic KELEX 100 anion is more highly adsorbed into the interfacial region than is the 8-quinolinolate (i.e., K' is higher) and thus a greater proportion of the reaction of the anion with Ni^{2+} takes place in that region, it is interesting to note that the rate constants, k_L and k_i , are not different. Thus, the interfacial region would seem to have an essentially aqueous character. Further investigation is necessary to obtain a general answer to the question of how the interfacial and bulk rate constants compare to one another.

The finding in this study of a three path reaction mechanism for the extraction of a well known, simple, chelating system indicates the complexity that may be involved. The usefulness of the new extraction kinetics apparatus as a diagnostic tool for evaluating the role of the liquid-liquid interface in solvent extraction systems has been demonstrated. The ability to differentiate between bulk phase and interfacial reactions can be very important in the design of improved extractants, as well as in the understanding of the fundamental chemical properties of the liquid-liquid interface.

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Table 1. Interfacial Area Dependence of Stir Rates

Stir Rate (RPM)	Interfacial Area (cm ²)	Specific Int. Area (cm ⁻¹)
2000	11,600	116
2500	14,600	146
3000	17,600	176
3500	20,600	206
4000	24,500	245
6000	27,500	275

Table 2. Summary of Rate Constants for Nickel Extraction With Oxine and Its Analogs

Extractant	Log k_{HL} (M ⁻¹ s ⁻¹)	Log k_L (M ⁻¹ s ⁻¹)	Log k (M ⁻¹ s ⁻¹)
Oxine ^a	2.97	5.46	6.7±0.2
Oxine ^b	3.55	5.73	
Thiooxine ^c	3.45	5.45	
KELEX 100 ^a	4.4	6.8	6.7±1.0
KELEX 100 ^d	3.74		6.92

^aPresent work

^bReference 7

^cReference 11

^dReference 9

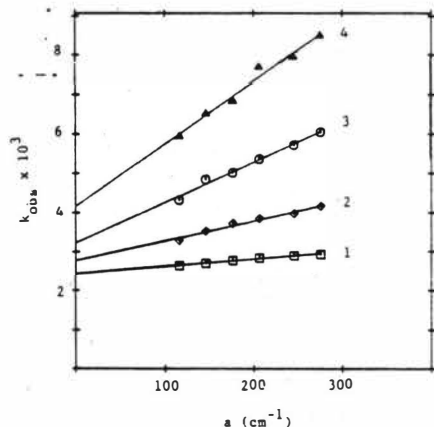


Figure 1. Specific Interfacial Area Dependency of Nickel Extraction by Oxine. (1) pH 6.54; (2) pH 6.77; (3) pH 7.03; (4) pH 7.15. Conditions: (Oxine = 1×10^{-3} M; $(\text{NaClO}_4) = 0.1$ M; $\text{Ni} = 1 \times 10^{-4}$ M.

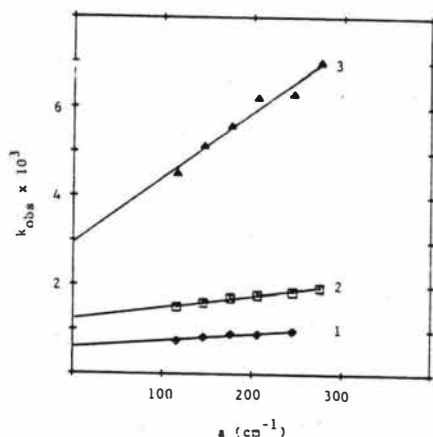


Figure 2. Specific Interfacial Area Dependency of Nickel Extraction by KELEX 100. (1) pH 7.27; (2) pH 7.7; (3) pH 8.45. Conditions: (KELEX) = 1×10^{-2} M; $(\text{NaClO}_4) = 0.1$ M; $(\text{Ni}) = 1 \times 10^{-4}$ M.

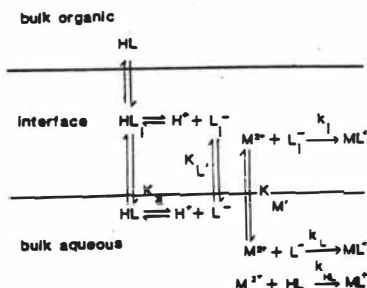


Figure 3. Reaction Scheme for 8-Quinolinols

TRANS-EFFECT IN EXTRACTION KINETICS: PALLADIUM EXTRACTION BY 7-(1-VINYL-3,3,5,5-TETRAMETHYLHEXYL)-8-QUINOLINOL

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Experimental

A series of vials containing 10.0 mL each of aqueous and organic phase were shaken for predetermined time intervals at a speed of 280 oscillations/min. After the vial was removed and allowed to settle for 30 seconds, the aqueous phase was removed, centrifuged and analyzed for palladium by adding excess thiocyanate to give 0.4 M solution and measuring the absorbance of the $\text{Pd}(\text{SCN})_4^{2-}$ complex at 310 nm [12, 13].

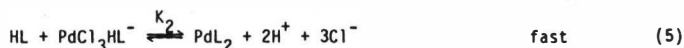
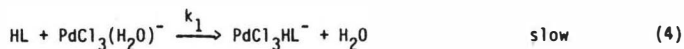
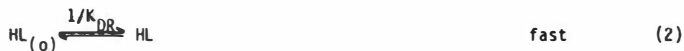
The observed rate constants, k_{obs} , were determined from:

$$\ln \frac{[\text{Pd}]_{t=0}}{[\text{Pd}]_{t=t}} = k_{\text{obs}} t \quad (1)$$

where t is the sampling time, $[\text{Pd}]_{t=0}$ and $[\text{Pd}]_{t=t}$ are the aqueous phase concentrations of the metal at initial time, t_0 , and time t , respectively.

RESULTS AND DISCUSSION

In the absence of thiocyanate, the dependence of the observed rate constant, $\log k_{\text{obs}}$, on $\log [\text{H}^+]$, $\log [\text{HL}]_0$, and $\log [\text{Cl}^-]$ was linear with slopes close to zero, 1, and -1, respectively (Table 1). These results are reminiscent of those reported for palladium extraction by LIX 65N [14] and dioctyl sulfide [15], and indicate that the extraction mechanism can be represented by the following steps:





for which the rate expression is:

$$-\frac{d[\text{Pd}]}{dt} = k_1 [\text{PdCl}_3(\text{H}_2\text{O})^-] [\text{HL}] \quad (7)$$

which, by suitable substitution, becomes

$$-\frac{d[\text{Pd}]}{dt} = \frac{k_1 \alpha_{\text{PdCl}_4^{2-}} [\text{Pd}]_T [\text{HL}]_0}{K_{DR} K_{f4} [\text{Cl}^-]} \quad (8)$$

where

$$\alpha_{\text{PdCl}_4^{2-}} = \frac{[\text{PdCl}_4^{2-}]}{[\text{Pd}]_T} = \frac{\beta_4 [\text{Cl}^-]}{\beta_3 + \beta_4 [\text{Cl}^-]} \quad (9)$$

and β_3 , β_4 represent the overall formation constants for $\text{PdCl}_3(\text{H}_2\text{O})^-$ and PdCl_4^{2-} , respectively ($\log \beta_3 = 10.2$, $\log \beta_4 = 11.5$ [16]).

Using the value of $K_{DR} = 10^{5.52}$ [17], $K_{f4} = 19.95$ [16] and $\alpha_{\text{PdCl}_4^{2-}}$ values, the rate data yields a value of k_1 as $8.91 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$, which is lower than $3.74 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ reported for palladium extraction by LIX 65N [14], which may result from the alkenyl group being possibly close enough to the chelating center to exert steric hindrance.

The effect of thiocyanate on the extraction rate is seen to be quite complex (Figure 1a). At low thiocyanate concentrations ($\leq 2 \times 10^{-4} \text{ M}$), the extraction rate is enhanced at an increasing order which reaches a limit of 1.01 ± 0.06 . At higher concentrations, it remains constant for a short range before decreasing with a thiocyanate order of -0.92 ± 0.03 . The UV-VIS spectra of the aqueous solutions (prior to extraction) in the thiocyanate range of $1 \times 10^{-5} - 5 \times 10^{-4} \text{ M}$ (Figure 2) display a series of shifts which indicate the presence of mixed complexes. First there is a bathochromic shift with increasing thiocyanate in the thiocyanate band at 280 nm (which corresponds to PdCl_4^{2-} [18]) up to 292 nm when the thiocyanate concentration reaches the value of $5 \times 10^{-5} \text{ M}$. Then follows a hypsochromic shift to 280 nm. At still higher concentrations ($5 \times 10^{-4} \text{ M}$), a

shoulder appears as well as a new band at 310 nm (corresponding to $\text{Pd}(\text{SCN})_4^{2-}$ [12, 13]). Therefore, the effect of thiocyanate (Figure 1a) can be interpreted in terms of the presence of a mixture of complexes of the type $\text{PdCl}_{4-x}(\text{SCN})_x^{2-}$ ($x = 0-4$) in the aqueous phase.

A plot of the fractions of these complexes:

$$\alpha_{\text{PdCl}_{4-x}(\text{SCN})_x^{2-}} = \frac{\beta_x [\text{SCN}^-]^x [\text{Cl}^-]^{-x}}{1 + \beta_1 [\text{SCN}^-] [\text{Cl}^-]^{-1} + \beta_2 [\text{SCN}^-]^2 [\text{Cl}^-]^{-2} + \beta_3 [\text{SCN}^-]^3 [\text{Cl}^-]^{-3} + \beta_4 [\text{SCN}^-]^4 [\text{Cl}^-]^{-4}}$$

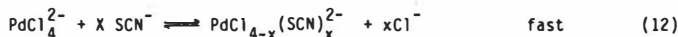
where $x = 1-4$ and $\log \beta_1 = 6.03$, $\log \beta_2 = 10.93$, $\log \beta_3 = 14.52$, and $\log \beta_4 = 17.55$ [19], as a function of thiocyanate concentration (Figure 1b), reveals that in the thiocyanate range where the species $\text{PdCl}_3(\text{SCN})^{2-}$, $\text{PdCl}_2(\text{SCN})_2^{2-}$ and $\text{PdCl}(\text{SCN})_3^{2-}$ are predominant, the extraction rate increases with thiocyanate concentration, while it decreases with increasing $\text{Pd}(\text{SCN})_4^{2-}$ concentration (Figure 1a).

A more detailed interpretation of the system is obtained by plotting the observed rate constant against the various $\alpha_{\text{PdCl}_{4-x}(\text{SCN})_x^{2-}}$ fractions ($x = 1-4$). Only one

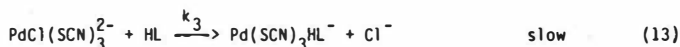
such plot, that involving $\alpha_{\text{PdCl}(\text{SCN})_3^{2-}}$ (for $\text{PdCl}(\text{SCN})_3^{2-}$) shows a consistent high positive correlation. Over the entire $[\text{SCN}^-]$ range employed, a linear least squares fit results in the relation:

$$k_{\text{obs}} = (2.66 \pm 0.55) \times 10^{-3} x \alpha_{\text{PdCl}(\text{SCN})_3^{2-}} + (0.056 \pm 0.18) \times 10^{-3} \quad (11)$$

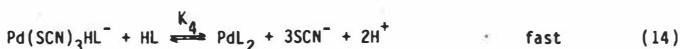
The course of the extraction can be explained as follows: There is a rapid exchange equilibrium between thiocyanate and chloride



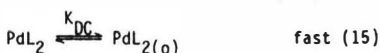
where $x = 1-4$. Of these complexes, the $\text{PdCl}(\text{SCN})_3^{2-}$ reacts most rapidly with the ligand. The monodentate addition of the first ligand is rate determining:



and is followed by chelation and the rapid addition of the second:



and extraction of the neutral complex:



The observed rate expression can be derived by considering equation 13, i.e.,

$$-\frac{d[\text{Pd}]}{dt} = k_3 [\text{PdCl}(\text{SCN})_3^{2-}] [\text{HL}] \quad (16)$$

$$= k_3 \alpha_{\text{PdCl}(\text{SCN})_3^{2-}} [\text{Pd}] [\text{HL}]_0 / K_{\text{DR}} \quad (17)$$

where $\alpha_{\text{PdCl}(\text{SCN})_3^{2-}}$, the fraction of $\text{PdCl}(\text{SCN})_3^{2-}$ present in the aqueous solution, is equal to:

$$\alpha_{\text{PdCl}(\text{SCN})_3^{2-}} = \frac{\beta_3 [\text{SCN}^-]^3 [\text{Cl}^-]^{-3}}{1 + \beta_1 [\text{SCN}^-] [\text{Cl}^-]^{-1} + \beta_2 [\text{SCN}^-]^2 [\text{Cl}^-]^{-2} + \beta_3 [\text{SCN}^-]^3 [\text{Cl}^-]^{-3} + \beta_4 [\text{SCN}^-]^4 [\text{Cl}^-]^{-4}} \quad (18)$$

The variation in $\log k_{\text{obs}}$ with $[\text{SCN}^-]$ may be considered to have three segments (Figure 1a), which have slopes of +1, 0, and -1, respectively, as the major different aqueous palladium species are $\text{PdCl}_2(\text{SCN})_2^{2-}$, $\text{PdCl}(\text{SCN})_3^{2-}$, and $\text{Pd}(\text{SCN})_4^{2-}$ predominate in turns.

For example, in the thiocyanate range of 5×10^{-5} - 1.6×10^{-4} M, the use of the term $\beta_2 [\text{SCN}^-]^2 [\text{Cl}^-]^{-2}$ corresponding to the dominance of $\text{PdCl}_2(\text{SCN})_2^{2-}$ permits the simplification of equation 18 to:

$$\alpha_{\text{PdCl}(\text{SCN})_3^{2-}} = K_3 [\text{SCN}^-] / [\text{Cl}^-] \quad (19)$$

where $K_3 = \beta_3 / \beta_2$ is the formation constant of $\text{PdCl}(\text{SCN})_3^{2-}$. Substituting equation 19 in 17 gives the rate expression:

$$-\frac{d[\text{Pd}]}{dt} = \frac{k_3 K_3 [\text{Pd}] [\text{SCN}^-] [\text{HL}]_0}{K_{\text{DR}} [\text{Cl}^-]} \quad (20)$$

which agrees well with the observed first order dependence of the extraction rate on thiocyanate (Figure 1a) and KELEX 100 (Table IIA) concentrations, and the independence of the solution pH (Table IIC) in this region. Using the value of $K_3 = 10^{3.59}$ and the $K_{\text{DR}} = 10^{5.52}$ yields a formation rate constant of $(4.42 \pm 0.26) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

In the third segment of Figure 1a, $\text{PdCl}(\text{SCN})_3^{2-}$ and $\text{Pd}(\text{SCN})_4^{2-}$ are the predominant species present in the aqueous solution (Figure 1b). Therefore, equation 18 can be simplified to give:

$$\alpha_{\text{PdCl}(\text{SCN})_3^{2-}} = \frac{B_3}{B_3 + B_4 [\text{SCN}^-] [\text{Cl}^-]} \quad (21)$$

Kinetic studies carried on in this region (Table IIB) yielded results which, in combination with the inverse first order dependence on thiocyanate ion (Figure 1a), are expected when $B_4 [\text{SCN}^-] [\text{Cl}^-] \gg B_3$, and therefore

$$\alpha_{\text{PdCl}(\text{SCN})_3^{2-}} = [\text{Cl}^-] / K_4 [\text{SCN}^-] \quad (22)$$

where $K_4 = B_4 / B_3$ is the formation constant of $\text{Pd}(\text{SCN})_4^{2-}$. Substituting equation 22 in 17 gives the rate expression:

$$-\frac{d[\text{Pd}]}{dt} = \frac{k_3 [\text{Pd}] [\text{HL}]_0 [\text{Cl}^-]}{K_4 K_{\text{DR}} [\text{SCN}^-]} \quad (23)$$

Using $K_4 = 10^{3.03}$ and the observed rate constant values measured when more than 90% of the metal is in the $\text{Pd}(\text{SCN})_4^{2-}$ form, yields a formation rate constant of $(2.32 \pm 0.09) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, which is somewhat smaller than the $(4.42 \pm 0.26) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, calculated earlier.

In the second segment of Figure 1a, the term $B_3 [\text{SCN}]^3 [\text{Cl}^-]^{-3}$, corresponding to $\text{PdCl}(\text{SCN})_3^{2-}$, predominates in equation 18 and, therefore, the dependence of the

extraction rate on thiocyanate concentration tends to approach zero order (Figure 1a). Using a maximum value of $\alpha_{\text{PdCl}(\text{SCN})_3^{2-}} = 0.483$, and the corresponding $\log k_{\text{obs}} = -2.88$, yields a formation rate constant, k_3 , of $4.52 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$. Averaging the k_3 values calculated for the three regions in Figure 1a gives a value of $(3.75 \pm 1.01) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, which is 42-fold higher than that measured in the absence of thiocyanate.

The $\text{PdCl}(\text{SCN})_3^{2-}$ complex which is involved in rate determining step is square-planar in which the Pd-Cl bond is greatly weakened by the "trans-effect" of the thiocyanate ion and, therefore, causes the enhancement in the extraction rate. This view was strengthened by the changes in the extraction rates studied as a function of thiocyanate, iodide, and bromide concentrations (Figure 3). The rates decreased in the same order as the labilizing "trans-effect" of these ions [20-22].

The insignificant contribution of $\text{PdCl}_2(\text{SCN})_2^{2-}$ in the rate determining step can be explained by its existence mainly in the trans-form [23], and therefore there is no effect of thiocyanate ion in weakening the Pd-Cl bond. The importance of $\text{PdCl}(\text{SCN})_3^{2-}$ rather than $\text{PdCl}_3(\text{SCN})^{2-}$ is puzzling and may be due to differences in the electronic configuration of the two species.

In conclusion, the presence of as little as $2 \times 10^{-4} \text{ M}$ thiocyanate has given rise to more than a six hundred-fold enhancement in the observed rate (from $2.29 \times 10^{-6} \text{ s}^{-1}$ to $1.51 \times 10^{-3} \text{ s}^{-1}$) in palladium extraction from 1 M chloride solution at pH 5.5 with $2 \times 10^{-2} \text{ M}$ KELEX 100. The implications of these findings to other platinum metals is currently under study in our Laboratory.

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TABLE I. KINETICS DATA FOR PALLADIUM EXTRACTION BY KELEX 100

A. Dependence on $[HL]_0$ *
 $[Pd]_T = 1.0 \times 10^{-4}$ M, $[Cl^-] = 0.5$ M, pH=5.31, $[NaOAc] = 1 \times 10^{-2}$ M, Ionic Strength fixed to 1.0 with Na_2SO_4

$[HL]_0 \times 10^{-2}$ M	Log k_{obs}
1	-5.56
1.5	-5.46
2.5	-5.24
4	-5.04
5	-4.88
6	-4.92

B. Dependence on $[Cl^-]$ **
 $[Pd]_T = 1 \times 10^{-4}$ M, $[HL]_0 = 5 \times 10^{-2}$ M, pH=5.25
 $[NaOAc] = 1 \times 10^{-2}$ M, ionic strength fixed to 1.0 with Na_2SO_4

$[Cl^-]$, M	$\alpha_{PdCl_4}^{2-}$	Log k_{obs}
0.2	0.800	-4.50
0.3	0.857	-4.70
0.5	0.909	-4.88
0.6	0.923	-4.94
0.8	0.941	-5.13
1.0	0.952	-5.24

* Slope of Log k_{obs} vs. Log $[HL]_0 = 0.92 \pm 0.07$

** Slope of Log k_{obs} vs. Log $[Cl^-] = -1.03 \pm 0.06$

TABLE II. KINETIC DATA FOR PALLADIUM EXTRACTION BY KELEX 100 IN THE PRESENCE OF SODIUM THIOCYANATE

A. Dependence on $[HL]_0$ at $[SCN^-] = 1 \times 10^{-4}$ M *
 $[Pd]_T = 3 \times 10^{-5}$ M, $[Cl^-] = 1.0$ M, pH=5.70,
 $[NaOAc] = 1 \times 10^{-2}$ M

$[HL]_0 \times 10^{-3}$ M	Log k_{obs}
4	-4.01
8	-3.64
12	-3.43
16	-3.28
20	-3.20

B. Dependence on $[HL]_0$ at $[SCN^-] = 1.6 \times 10^{-3}$ M **
 $[Pd]_T = 3 \times 10^{-5}$ M, $[Cl^-] = 1.0$ M, pH=5.70,
 $[NaOAc] = 1 \times 10^{-2}$ M

$[HL]_0 \times 10^{-3}$ M	Log k_{obs}
4	-3.97
8	-3.64
12	-3.42
16	-3.32
20	-3.17

* Slope for Log k_{obs} vs. Log $[HL]_0 = 1.18 \pm 0.03$

** Slope for Log k_{obs} vs. Log $[HL]_0 = 1.13 \pm 0.04$

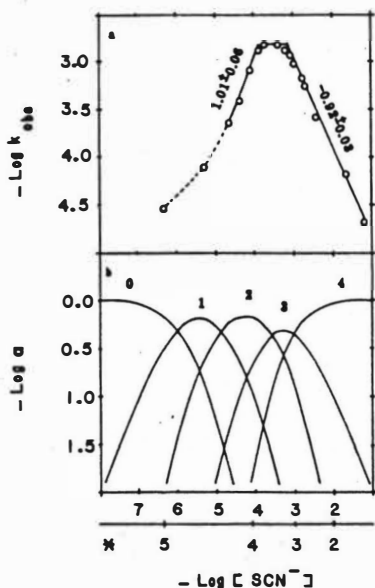


Figure 1a. Effect of Equilibrium Thiocyanate Concentration on Rate of Pd Extraction by KELEX 100. $[Pd] 3 \times 10^{-5} M$; $[NaOAc] 1 \times 10^{-2} M$; $[NaCl] 1.0 M$; $[KELEX] 2 \times 10^{-2} M$; pH 5.70 (* indicates initial $[SCN^-]$, i.e., uncorrected for complex formation).

1b. Fraction of $PdCl_4^{2-}$ species as a function of thiocyanate concentration.
 (0) $PdCl_4^{2-}$, (1) $PdCl_3(SCN)^{-}$, (2) $PdCl_2(SCN)_2$, (3) $PdCl(SCN)_3$, (4) $Pd(SCN)_4^{2-}$.

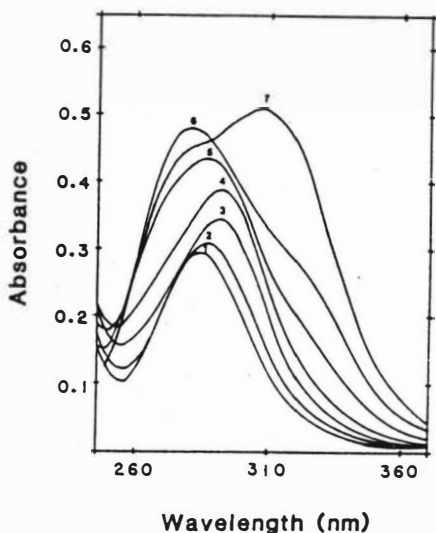


Figure 2. Absorption Spectra of the $Pd(II)$ Complexes at Different Thiocyanate Concentrations:

$[Pd]_T 3 \times 10^{-5}$; $[NaCl] 1.0 M$; $[NaOAc] 1 \times 10^{-2} M$; pH 5.70; $[NaSCN]$, (1) $1 \times 10^{-5} M$, (2) $1.6 \times 10^{-5} M$, (3) $3 \times 10^{-5} M$, (4) $5 \times 10^{-5} M$, (5) $1 \times 10^{-4} M$, (6) $2 \times 10^{-4} M$, (7) $5 \times 10^{-4} M$.

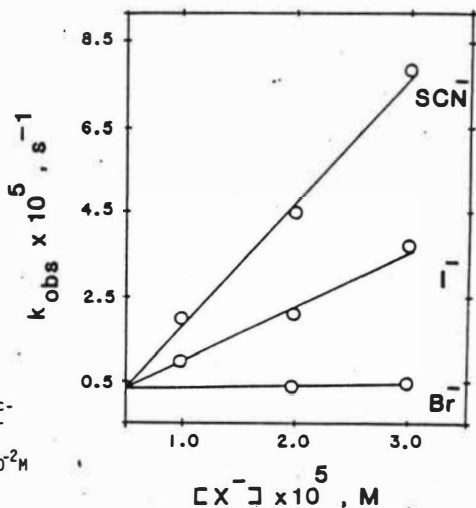


Figure 3. Observed Rate Constant as a Function of Initial Bromide, Iodide and Thiocyanate Concentrations:

$[Pd] 3 \times 10^{-5} M$, $[NaCl] 1.0 M$, $[NaOAc] 1 \times 10^{-2} M$, $[KELEX] 2 \times 10^{-2}$, pH 5.70.

New Extractant for Arsenic Separation from Industrial Solutions

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Arsenic bearing ores are often used as feed materials in metallurgical processes. Consequently, As is contained in many solutions and residues from which it must be separated in order to improve the purity of the final products. Copper refining electrolytes are the most important exemplum of such industrial solutions, but As separation is performed in many other cases, for instance on Ni bearing leach solutions from Ni ores or on leach solutions from copper drosses. In all cases, As must be extracted from sulfuric acid solutions.

Among the different techniques used or studied for As separation, solvent extraction seems the most promising. TBP is used as the main extractant in most of the processes patented (1, 2, 3, 4, 5). In the last years, SAMIM - Centro Ricerche Veneto has developed a new process based on 2-ethyl-1-hexyl alcohol (6,7), for which an industrial prototype is presently under construction at the SAMETON copper refinery of Porto Marghera.

The extractant presently available are characterized by low extraction yields using quite high O/A ratios. Moreover, TBP has a negligible extraction yield with respect to the 3+ form, which limits its use to the cases in which the 5+ form is present. In order to improve these characteristics, in our laboratories a new series of extractants (called ENIM 100) has been designed and synthesized. These new extractants have been tested for the afore-mentioned applications until pre-pilot scale and the results of one of them is reported in the present work. The use of ENIM 100 for As separation from hydrometallurgical solutions is covered by an Italian patent which has been extended to several foreign countries.

ENIM 100

ENIM 100 is a series of extractants which must be used with a solvent, either aromatic or aliphatic, and preferably with a phase modifier. Optimum concentrations vary in the range of 5 to 10 %.

The main characteristics of the extractants are the following:

- low volatilities, which allow to use ENIM 100 also at temperatures higher than ambient;
- low solubilities in the aqueous phase and good stabilities, which reduce the loss of extractant during the extraction and stripping operations, with a consequent saving in operating costs;
- negligible loading of H_2SO_4 and H_2O
- Absence of toxicity and of polluting effects;
- costs comparable to other commercial extractants of similar characteristics.

EXPERIMENTAL

Up to now, most of the interest was concentrated in the extraction of arsenic from copper refining electrolytes, in which arsenic is mainly present in the 5+ form. The experiments described in the following paragraphs were thus performed on artificial solutions simulating a copper refining electrolyte, except when the use of an industrial solution is specified. No difference in the extraction

yields was noticed between industrial and artificial solutions containing As^{5+} . Typical concentrations (in g/l) of a copper refining electrolyte are: Cu 60, As 10, H_2SO_4 150-200, Pb 0.02, Zn 2, Fe 1, Ni 10, Sn 0.05, Bi 0.012, Cl 0.03, Sb 0.5, Glue 2 mg/l, Thiourea 1 mg/l.

Shake-out tests

For preliminary tests the following informations were derived. There is no influence in initial As^{5+} concentration (at constant H_2SO_4 conc. of 150 g/l and O/A 2/1) in the range from 4 to 14 g/l on extraction yields. Also the effect of temperature at different acidities (initial As^{5+} 10 g/l), shown in Fig. 1, is not evident even if a slight inverse relationship can be noticed. On the contrary, the increase of extraction yields with acidity is quite important and a careful choice of the optimum acid concentration at which to operate is advisable. Several tests were performed also to evaluate the selectivity of ENIM 100 with respect to other metals present in solution and the effect of glue and thiourea additions. Selectivity was very good and no effect of the organic additives on the extraction results was noticed.

As far as stripping is concerned, no significant influence of the stripping solution pH on the stripping yields was noticed within the range 1 to 9. For this reason, water can be used without any pH adjustment.

Also increasing arsenic concentrations in the organic phase (from 1 to 7 g/l, saturation loading) do not affect stripping yields.

The effect of temperature on stripping yields is also very limited; it is quite drastic, though, on phase separation times: at 20°C the separation is very difficult while at 30, 40, 50°C separation times become 3', 1' and 45" respectively. For this reason it is preferable to maintain all the solutions at the temperature of the feed, that is around 50°C. The effect of contact times on the stripping yields (at T 50°C and O/A 2/1) is shown in Fig. 2. It is evident the strict correlation between the two parameters, which will greatly influence the choice of the reactor for the stripping operation.

Extraction and stripping isotherms (Figg. 3 and 4) were derived both for the As^{3+} and As^{5+} forms. It is clearly seen that quite high extraction yields can be obtained with low O/A ratios (typical extraction yields of As^{5+} for TBP in the same operating conditions are equal to or lower than 30 % with O/A = 5/1). Still, stripping yields are very interesting.

From the above, it can be concluded that, with regard to extraction, both extraction and phase separation characteristics are such as to allow a very simple operation and the use of simple equipment. As far as stripping is concerned, slow kinetics, both during stripping and phase separation, suggest a more careful choice of the apparatus and of the operating conditions.

Pre-pilot tests

Pre-pilot tests were performed, using industrial solutions, both for the extraction and stripping operations.

Extraction experiments were carried out on a mixer settler and on two pulsed columns with the following characteristics:

Mixer: Ø 190 mm
height 90 mm
Vol. 2.5 l

Settler: mm 500 x mm 250 x mm 80
Vol. 10 l

Column A: height 1500 mm

Ø 52 mm

n. plates 38

30 % hole surface

pulse generator:

cam operated bellows

vol. 3.2 l

Column B: height 2000 mm

Ø 52 mm

n. plates 52

30 % hole surface

pulse generator:

cam operated bellows

vol. 4.2 l

Table I shows the operating conditions and the extraction yields. In all cases O/A was equal to 2/1 (organic flowrate 40 l/h, aqueous flowrate 20 l/h) and the acidity 180 g/l H_2SO_4 .

As expected from the overall extraction characteristics, a mixer settler of limited dimension is already sufficient for optimum extraction.

As far as stripping is concerned, column B was used by itself or put in series with an other column with the same characteristics (See Tab. II) (O/A 2/1, organic flowrate 40 l/h and aqueous flowrates 20 l/h). Low extraction yields were reached in both cases even if the doubling of the contact time (obtained with the two columns) has a good effect on the final results due to the low kinetics pointed out in the previous paragraph. An even longer contact time, obtained with the use of a Graesser contactor (Ø 150 mm, length 1000 mm, number of compartments 35, vol. 18 l, organic flowrate 20 l/h, aqueous flowrate 10 l/h) gives the extraction yields corresponding to the theoretical stage. The use of this kind of reactor is also advisable since a drastic mixing of the two phases causes the formation of emulsions.

CONCLUSIONS

Pre-pilot tests confirmed the information obtained from the preliminary tests, that is the optimum conditions of the extraction process and a slightly more difficult control of the stripping parameters, in any case overcome by the use of the proper reactor. Further tests will be needed to minimize the loss of extractant due to solubilities and entrapments problems, both through the choice of the most proper compounds of the series ENIM 100 and of the most suitable operating conditions and reactors. Additional information will be collected about selectivity.

The whole process will be scaled up to a level similar to that used for 2-ethyl-1-hexyl alcohol in order to compare the results. In the meantime application of ENIM 100 to the extraction of other cations will be developed. Interesting results are presently available on Mo and V extraction from HCl solutions.

Table I: EXTRACTION - Operating conditions and yields

Reactor	T °C	aqueous solution initial As conc., g/l	Organic solution initial As conc., g/l	Yield %
Mixer settler	55	11.2	1.1	58.9
Column A	56	10.5	2.1	53.3
Column B	59	10.5	2.5	61.0

Table II: STRIPPING - Operating conditions and stripping yields

Reactor	T °C	Aqueous solution initial As conc., g/l	Organic solution initial As conc., g/l	Yield %
Column B	62	0	7.4	13.0
Column B+B	65	0	4.9	44.0
Graesser	50	0	6.1	65.5

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FIGURE 1
EFFECT OF TEMPERATURE AND H2SO4 CONC. ON EXTRACTION YIELDS

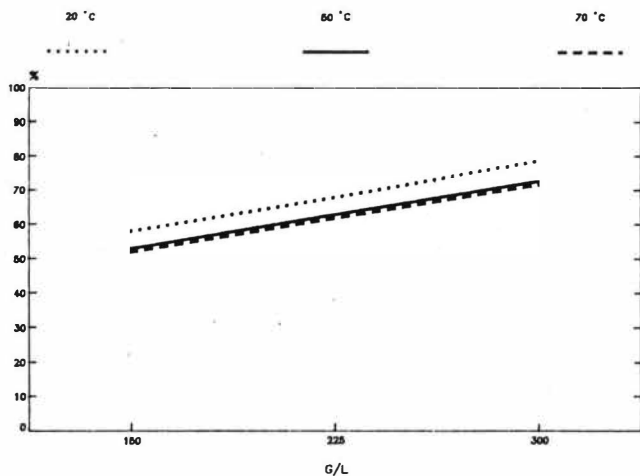


FIGURE 2
EFFECT OF CONTACT TIME ON STRIPPING YIELDS

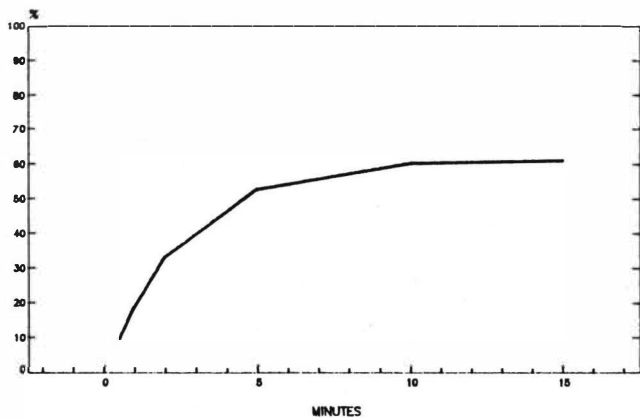


FIGURE 3

EXTRACTION ISOTHERMS

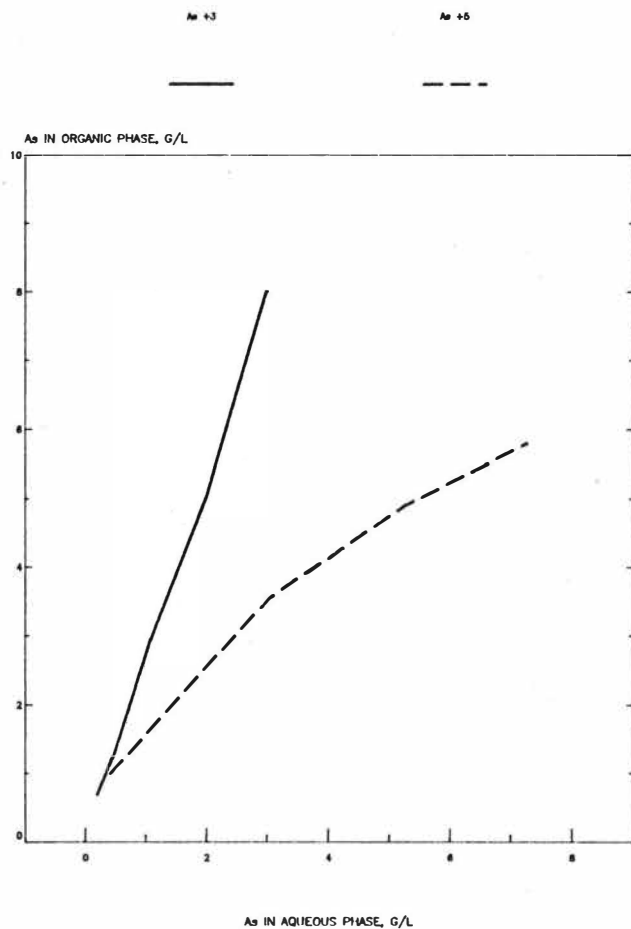
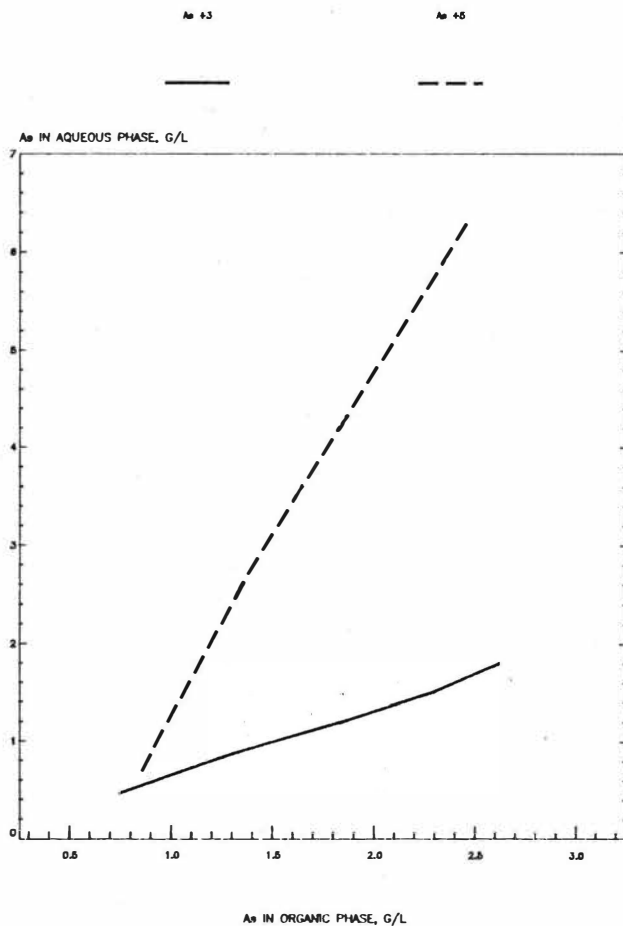


FIGURE 4

STRIPPING ISOTHERMS



THE LANGMUIR FILM BALANCE - A NOVEL REACTOR SYSTEM FOR SOLVENT EXTRACTION INTERFACIAL STUDIES

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INTRODUCTION

The fact that metal solvent extraction takes place in a biphasic system, with the various reactants confined predominantly to either the aqueous phase or the organic phase, coupled with the fact that metal extractants are, to varying degrees, interfacially active, suggests a possible role of interfacial activity in the extraction process (1-5). In this connection, physico-chemical studies of model reagents as well as purified commercial extractants spread as monomolecular films at the air/water interface should provide valuable insight into extractant/aqueous-phase interactions (6). For example, measurements of monolayer dissolution kinetics can lead to estimates of aqueous solubilities, diffusion coefficients, and surface ionization constants (7-9). Film balance techniques can also be used to measure reaction kinetics in monolayer films with the advantage of being able to control surface concentration and molecular orientation by direct manipulation of the spread film (10). Identification of reaction products and determination of reaction equilibrium constants may be achieved by collecting monolayer films and subjecting this material to chemical analysis. A number of commercial extractants and their homologues have already been shown to spread as monomolecular films at the air/water interface (11-13). Monolayer techniques coupled with analytical tools such as electron spin resonance spectroscopy and dynamic light scattering can be used to obtain structural details of interfaces on a molecular level (14). In principle, these methods could be applied to the study of solvent extraction systems.

Preliminary pressure-area isotherms obtained in this laboratory for HDNNS and the purified active reagent in LIX65N at the air/water interface were reported previously (13). The scope of these film balance studies has now been expanded to include both the equilibrium and dynamic properties of the monolayers. This paper reports and discusses the results of monolayer dissolution experiments conducted in an effort to obtain a more complete description of the extractant/aqueous-phase interactions.

EXPERIMENTAL

Materials. Dinonylnaphthalene sulfonic acid (HDNNS) was obtained from King Industries, Inc. (Norwalk, CT). The sodium salt of HDNNS was used throughout this study; detailed procedures for the preparation and purification of NaDNNS are given elsewhere (15). Elemental analysis (performed by Galbraith Lab, Knoxville, TN) of the purified material gave: C, 69.79; H, 9.15; O, 10.04; S, 6.38; Na, 4.39%; $C_{28}H_{43}O_3Na$ requires: C, 69.71; H, 8.92; O, 9.96; S, 6.64; Na, 4.77%.

The anti-isomer of 2-hydroxy-5-nonylbenzophenone oxime (HBPO) was purified from the as-received, commercial reagent (LIX65N, Lot No. 80K265006, Henkel Corp.) as described in the literature (16). Nonaqueous titration of the oxime with tetrabutylammonium hydroxide indicated a purity of 99.7 wt% (molecular weight 339.5). The purified, anti-isomer was stored as the copper oximate. Elemental analysis (performed by Galbraith Lab., Knoxville, TN) of the copper oximate gave: C, 71.36; H, 7.71; N, 3.56; O, 8.49; Cu, 8.55%; $C_{46}H_{56}N_2O_4Cu$ requires: C, 71.40; H, 7.57; N, 3.79; O, 8.65; Cu, 8.59%. When needed, the free oxime was obtained by contacting a hexane solution of the copper oximate with 4 mol dm^{-3} H_2SO_4 for three cycles.

Spreading solutions were made with purified hexane (Photrex, J. T. Baker) at NaDNNS or oxime concentrations of approximately 10^{-3} mol dm^{-3} . The hexane was purified

by column chromatography using silica gel (60/200 mesh, Applied Science, State College, PA) and activated alumina (80/200 mesh, Fisher Scientific). Water used in all experiments was purified by reverse osmosis (Millipore-R04) and deionization (Millipore Milli-Q). The pH of subphase solutions was adjusted by additions of KOH (Fluka, puriss) or Ultrex grade HNO_3 (J. T. Baker). A constant ionic strength was maintained with $0.1 \text{ mol dm}^{-3} \text{ KNO}_3$ (Fluka, purum).

Measurement of Film Loss. All monolayer experiments were conducted with a Lauda film balance which was interfaced to a micro computer for data collection (15). The rate of dissolution at constant film pressure (Π) was measured by monitoring the decrease of film area (A_t) with time (t). Monolayers were spread at initial areas of about $150 \text{ Å}^2 \text{ molecule}^{-1}$ and immediately compressed at a rate of 7.5 cm min^{-1} to the desired Π . The rate of film contraction was then followed while maintaining a constant surface pressure. The initial time ($t=0$) of an experiment was taken as the time when the first drop of spreading solution touched the subphase. All subphases were made fresh for each run in order to eliminate any possible effects of contamination from previous experiments. All data reported represent the average of three or more experiments conducted at 18°C .

RESULTS AND DISCUSSION

Dissolution Kinetics. With few exceptions, most studies of monolayer dissolution have indicated that this process is controlled by diffusion in the aqueous phase (7-9). If the dissolution process is diffusion controlled, equilibrium will be established almost immediately after spreading, between the monolayer and a thin aqueous film of thickness α extending only a few molecular distances away from the surface (see Figure 1). The surfactant concentration within this aqueous film will depend upon the surface pressure (Π) and the monolayer density (Γ) as described by the Gibbs equation. Once in the aqueous phase, the solute molecules will diffuse away from the surface, through a stagnant layer of thickness (δ), and will eventually be removed to the bulk of the subphase solution by convective currents.

The dissolution behavior of both NaDNNS and HBPO is consistent with the diffusion-controlled mechanism of Ter Minassian-Saraga (7). According to this model, the rate of interfacial desorption is controlled by diffusion into the bulk aqueous phase from the saturated aqueous layer (region α , Figure 1) located immediately beneath the spread monolayer. During the initial, nonsteady-state period of desorption, the rate of film contraction can be expressed by the following equation (7):

$$\frac{d \ln A_t}{d\sqrt{t}} = k_i = 2K_D \sqrt{\frac{D}{\pi}} \quad (1)$$

where π is the numerical constant, D is the diffusion coefficient of the solute in the subphase, and K_D is given by C_α/Γ ; C_α is the solute concentration in the aqueous phase immediately below the spread film and Γ is the surface density of the spread monolayer. Typical $\ln A_t$ vs. \sqrt{t} plots for the first 25 minutes are shown in Figure 2. The area A_0 obtained by extrapolating to zero time represents the film area that would be observed in the absence of film dissolution. The area per molecule (A) within the monolayer can be obtained by dividing A_0 by the number of molecules spread. The adsorption density is then given by $\Gamma = A_0/A$. After 20-60 minutes, the concentration gradient within the diffusion layer (of thickness δ) becomes constant and dissolution reaches a steady-state. The rate of film contraction is then given by Equation 2 (7):

$$\frac{d \ln A_t/A_0}{dt} = k_s = K_D \frac{D}{\delta} \quad (2)$$

In Figure 3, $\ln A_t/A_0$ vs. t plots for $\Pi = 25 \text{ mN m}^{-1}$ are shown. It can be seen from this figure that in the region $t > 20 \text{ min.}$, both the NaDNNS and HBPO curves exhibit trends that are consistent with Equation 2. For both reagents, dissolution increases with increase in surface pressure (15), indicating a lack of significant van der Waals interactions that might present a surface energy barrier to dissolution.

Figure 4 shows the effect of pH on the initial dissolution rate constant k_i . It can be seen that in the case of NaDNNS, there is little pH dependence on k_i . This

result is consistent with the low pKa value (0.57) of naphthalene sulfonic acid (17). In contrast, Figure 4 indicates that the k_i values obtained for HBPO at different pH values lie on a sigmoidal curve that resembles a titration curve. The rapid increase in dissolution rate at high pH is attributable to the deprotonation of the hydroxyoxime. The surface pKa was estimated as 11.5 by fitting the kinetic data to the following equation (8):

$$k_i = \frac{k_{i,\max}}{1 + [H^+]/K_a} \quad (3)$$

where $k_{i,\max}$ represents the maximum dissolution rate that would be observed when the monolayer is completely ionized, and K_a is the acid dissociation constant. The bulk phase pKa has been reported to be about 8.5 (18-20). The difference of 3 units between the surface and bulk phase pKa value of HBPO is in agreement with reports in the literature for other acid dissociation systems (21). This behavior has been attributed to the differences in pH between the bulk aqueous phase and the charged interfacial region, and a simultaneous increase in the dissociation constant due to head-group interactions within the monolayer film (21).

Extractant Dissolution and Metal Extraction. If metal complexation with extractant molecules takes place in the bulk aqueous phase or within an aqueous diffusion zone adjacent to the interface, an intermediate step in both mechanisms would involve the interfacial desorption of the extractant (HR) into the aqueous phase:

$$HR_{int} = HR_{aq}$$

It is therefore of interest to compare the rate of extractant dissolution into the aqueous phase with the rate of metal extraction. Since the dissolution of both NaDNNS and HBPO at the a/w interface is limited by diffusion rather than a surface energy barrier, the contribution to the free energy of desorption (ΔG^0) from R-chain cohesion must be small compared to other free energy contributions. Therefore, ΔG^0 at both the air/water and organic/water interfaces should be very similar. Accordingly, it is expected that the dissolution rates at both interfaces are comparable.

Kinetic experiments with a quiescent interface cell have indicated that metal complexation by HDNNS occurs at the oil/water interface (22). Extraction rates of metal ions from the lanthanide series with interfacially saturated HDNNS solutions were on the order of 10^{-11} mol cm⁻² s⁻¹. Initial desorption rates of NaDNNS, when expressed as a flux ($-\Gamma \, d \ln A_s/dt$), were approximately 10^{-14} mol cm⁻² s⁻¹ at a constant surface pressure of 25 mN m⁻¹. The relative magnitude of metal extraction rates and aqueous phase dissolution rates is thus consistent with an interfacial extraction mechanism. In Table 1, the initial extractant flux ($-\Gamma \, d \ln(A_s/A_s^0)/dt$) is listed along with copper extraction rates obtained from the literature^o for HBPO (20,23,24). The fact that the rate of copper extraction is 4 to 6 orders of magnitude greater than the rate of extractant dissolution strongly suggests that the metal chelation reaction occurs at the interface rather than in an aqueous diffusion zone or in the bulk aqueous phase.

Table 1. Comparison of the dissolution rate of HBPO and the rate of Cu extraction.

$\Gamma(\text{HBPO})$ (mol cm ⁻² x 10 ¹⁰)	[HBPO] ₃ (mol dm ⁻³)	Species	J_2 (mol cm ⁻² s ⁻¹)	pH	Reference
3.0		HBPO	9.5×10^{-15}	4	This Work
---	2×10^{-6}	Cu	8×10^{-10}	4	[23]
1.8-1.9 ^a	1.3×10^{-2}	Cu	1.1×10^{-9}	4	[24]
1.8-1.9 ^a	1.7×10^{-2}	Cu	1.5×10^{-8}	1.6	[20]

In all the extraction systems, a constant ionic strength was maintained with Na₂SO₄.

^a Γ was estimated from the interfacial tension data of Al-Diwan et al. (25) and Komazawa et al. (20).

ACKNOWLEDGEMENTS

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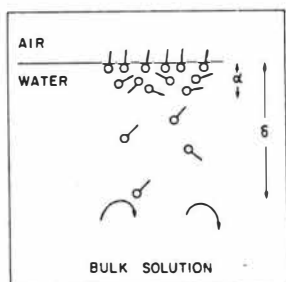


Figure 1. Schematic illustration of a monolayer/aqueous system.

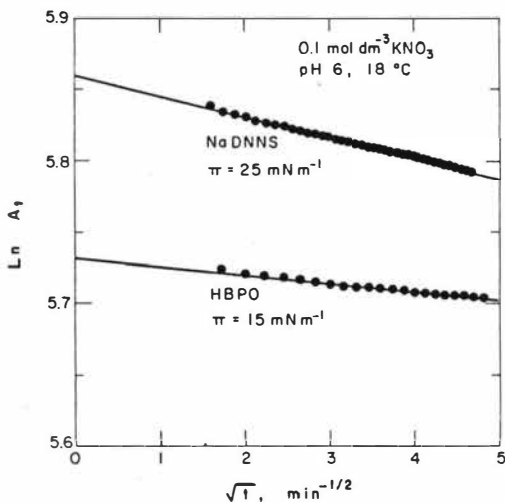


Figure 2. Typical initial desorption plot for NaDNNS and HBPO at constant π .

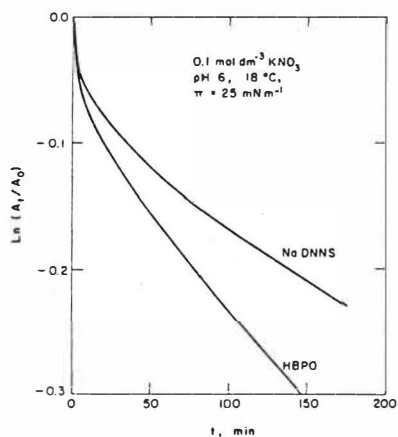


Figure 3. Dissolution from NaDNNS and HBPO monolayers maintained at a constant surface pressure. The values of A_0 were obtained from $\ln A_t$ vs. \sqrt{t} plots.

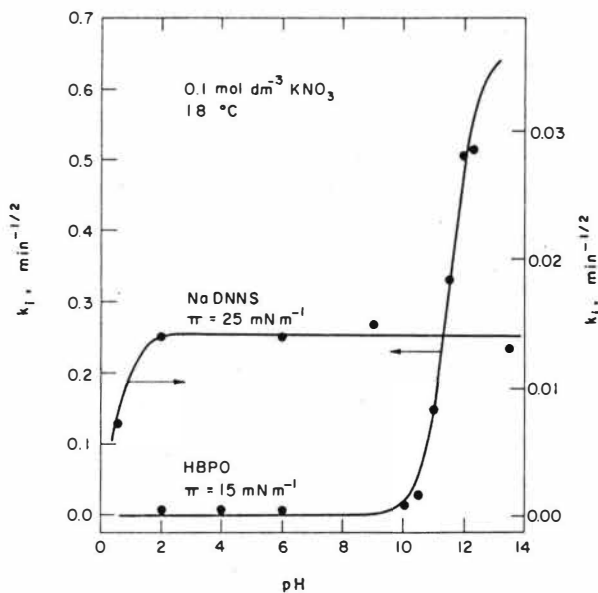


Figure 4. Influence of pH on the initial desorption rates of NaDNNS and HBPO monolayers

The Adsorption of Model 4-Alkylphenylamines at the Aqueous/Organic Interfaces

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The separation of platinum, palladium, iridium, rhodium and ruthenium as a group from copper, nickel, iron and cobalt by extraction with 4-octylphenylamine dissolved in toluene from 3 N hydrochloric acid has been described by Vasilyova et al. (1). These results were fully confirmed by Pohlandt (2-4), who showed that 4-octylphenylamine is an effective group extractant for the noble metals. All these metals can be extracted efficiently from 3 N HCl, i.e. from a concentration that represents a compromise between the maximum extractions for palladium and rhodium individually. Platinum, iridium and gold can be extracted quantitatively at hydrochloric acid concentrations of 2-11 N, and ruthenium at concentrations of 2-9 N. The extraction of rhodium increases with increasing acid concentration up to 8 N, but the extraction of palladium decreases rapidly with increasing HCl concentration. The noble metals can also be extracted from nitric acid, sulphuric acid and from mixed systems containing different mineral acids. The equilibrium is established rather slowly, and 10-30 min of shaking is necessary to obtain high, i.e. above 90%, extraction.

Back extraction of the platinum-group metals can be carried out with 7 N perchloric acid. Platinum, rhodium and ruthenium are not extracted at a perchloric acid concentration of more than 3 N, iridium at a concentration of more than 4 N, and palladium at a concentration of more than 7 N. Only the extractability of gold remains high up to a perchloric acid concentration of 7 N. Thus, only gold cannot be extracted.

Platinum-bearing materials can contain different base metals: zinc, tin, antimony, selenium, tellurium, lead, arsenic, nickel, copper, cobalt, chromium and bismuth. When extraction is carried out from 3 N HCl solution tellurium, arsenic, nickel, cobalt and iron are not extracted, zinc, selenium, chromium and tin are slightly extracted, and only antimony, lead and bismuth are extracted to a considerable extent. Furthermore, their back-extraction is possible. However, these last metals are usually minor constituents and their extraction is not very important.

Some problems can be encountered both in the extraction and stripping stages. Stable emulsions can be formed if the quality of 4-octyl-

phenylamine is not good. In back extraction precipitation can be observed both in the aqueous and organic phases when chloroform, benzene or petroleum ether are used as diluents. This precipitation can be avoided using diisobutylketone as a diluent.

The results described in the literature prove the high effectiveness of 4-octylphenylamine as a noble metal extractant. Thus, it can be used for analysis of these metals in different materials. It is also stressed that this extractant may find application in the industrial concentration and separation of noble metals by liquid-liquid extraction or by use of resins impregnated with 4-octylphenylamine.

The aim of this work was to determine the surface activity at the organic/aqueous interfaces of model 4-alkylphenylamines having a different length of the alkyl. This seems for us an important parameter in extraction kinetics and may influence the formation of stable undesired emulsions.

Experimental

Model 4-alkylphenylamines containing from 6 to 16 carbon atoms in their straight alkyl were used. Their analytical data is given in Table 1. Their spectrophotometric data and the method of their synthesis were described and discussed previously (5).

Table 1: The analytical data of 4-alkylphenylamines

Alkyl	b.p. °C/mm Hg	m.p. °C	D ₂₀ ⁴	Density g/cm ³	Purity ^x %	Elemental analysis, % calculated/found		
						C	H	N
n-C ₆ H ₁₃	150/6	-	1.5315	0.9258	97.1	81.4	10.7	7.9
						81.4	10.6	7.9
n-C ₈ H ₁₇	138-140/2	-	1.5216	0.9131	98.4	82.0	11.2	6.8
						81.9	11.2	6.7
n-C ₁₀ H ₂₁	164/2	-	1.5126	0.9025	98.6	82.4	11.6	6.0
						82.4	11.6	6.0
n-C ₁₂ H ₂₅	185-187/2	29-30	-	-	98.1	82.7	11.9	5.4
						82.5	11.8	5.5
n-C ₁₄ H ₂₉	209/2	39-41	-	-	96.6	83.0	12.1	4.9
						83.1	12.0	4.8
n-C ₁₆ H ₃₃	246-247/2	50-51	-	-	98.1	83.3	12.3	4.4
						83.3	12.3	4.3

^x - as determined by gas chromatography

The interfacial tension was measured by the ring method at 13-20°C using presaturated phases. The diameter of the platinum ring was 6.06 mm, while the diameter of the wire used for the ring construction was

0.27 mm. The ratio of the glass dish diameter to the diameter of the platinum ring was about 10. The height of each phase was about 7 mm. Solutions of 4-alkylphenylamines dissolved in n-heptane, toluene and benzene were used as the organic phases, and redistilled water and 3.16 N HCl as the aqueous phases. These phases of 35 cm³ volume each were presaturated for 2.5 hrs using a mechanical shaker. Then the dispersion was poured into a separation funnel and stored there for 12 hrs. 30 cm³ of the aqueous phase was then taken, disregarding 5 cm³ near the interface, and added into a glass dish of 66 mm diameter and 35 mm height. The platinum ring was inserted into the aqueous phase, just below the surface and 30 cm³ of the organic phase was delicately added. The ring was then inserted at the interface and after an appropriate time of stabilization the interfacial tension was measured by pulling the ring from the interface into the organic phase. Usually only several minutes were necessary to obtain constant interfacial tension. After each measurement the ring was dried with filter paper, rinsed with benzene, potassium dichromate and sulphuric acid solution, and with redistilled water and dried. The accuracy of the method was checked using systems for which the interfacial tension is given in the literature. Similar values of the interfacial tension were registered with an error not exceeding 1.5%.

Results and Discussion

In systems containing redistilled water as the aqueous phase the surface activity of amines is moderate (Figs 1 and 2), as in the case of the hydroxyoxime extractants. An essential decrease of the interfacial tension is observed at concentrations of 1 mole m⁻³ and 10 mole m⁻³ for the aliphatic and aromatic hydrocarbons used as diluents respectively. A region of constant low interfacial tension is not achieved.

Much higher interfacial activity is observed in systems containing HCl (Fig. 3). Depending upon the length of the alkyl the decrease of the interfacial tension is observed at 10⁻⁴ mole m⁻³ for n-hexadecylphenylamine and at 0.1 mole m⁻³ for 4-hexylphenylamine. In this case for amines containing 6, 8 and 10 carbon atoms in the alkyl, the curves typical for surfactants were obtained. This can be explained by the relatively high protonation of the initial amine. Thus, a region of low constant interfacial tension was obtained, and the existence of explicit points of inflexion suggests substantial solubility of all the extractants in the aqueous phase and their association in this phase. The values of the hypothetical critical

micelle concentration (c_m) of 2.95, 0.79 and 0.32 mole m^{-3} obtained for alines containing 6, 8 and 10 carbon atoms in the alkyl decrease as the length of the alkyl increases. These values fit fairly well the general straight line relation: $\log c_m = a + b n$, where n denotes the number of carbon atoms in the alkyl, and the constants a and b are in our case equal to 2.19 and -0.26, respectively. For alines having a longer alkyl this region was not achieved, probably due to their insolubility in the aqueous phase. This problem must be reconsidered after obtaining more information about aline's solubility and surface activity in the aqueous phase and their distribution between the considered phases.

From the practical point of view the system containing HCl is the most important. For this system the values of the surface excess, molecular area and the free energy of the aline's adsorption were calculated. Using the Gibbs isotherm the gradients for the straight line parts of the relation $\Gamma = \Psi(\log c)$ were calculated by a.s.e., and then used to estimate the surface excess in this region, $\Gamma = 1/(2.303 RT)(-d\sigma/d \log c)$. The constants of the Temkin isotherm: Π_T and Γ_T were calculated by matching the adsorption isotherm to the experimental data (3,6):

$$\log c + \frac{\Pi_T}{RT} = \frac{\Pi_T}{RT} \Pi^{0.5} \quad (1)$$

where: $\Pi = \sigma - \sigma^0$, σ - the interfacial tension for the considered aline concentration c and σ^0 - the interfacial tension in the system which does not contain aline ($c = 0$). The free energy of micellization and the surface excess were calculated from the following relations:

$$-\Delta G_T^0 = RT \Pi_T \quad \text{and} \quad \Gamma_T = \frac{2 \Pi_T^{0.5}}{2.303 \Pi_T} \quad (2) \text{ and } (3)$$

Langmuir constants were obtained by matching the isotherm (eq.4) to the experimental data. The surface excess and the free energy of micellization were calculated according to relations 5 (7) and 6 (8):

$$\frac{c}{\Pi} = \frac{1}{\Pi_T} + \frac{c}{\Pi_T} \quad \text{and} \quad \Gamma = \frac{\Pi_T c}{RT \frac{1}{\Pi_T} + \frac{c}{\Pi_T}} \quad (4) \text{ and } (5)$$

$$-\Delta G_L^0 = RT \ln \left(\frac{\Pi}{c} \right)_0, \text{ where } \left(\frac{\Pi}{c} \right)_0 = \lim_{c \rightarrow 0} \frac{\Pi}{c} = \frac{1}{\Pi_T} \quad (6)$$

Satisfactory results were obtained by matching the Temkin and Langmuir isotherms to the experimental data (Figs 4 and 5). The values of all the considered parameters are given in Table 2, and a comparison of the surface excess values is presented in Table 3 and Fig. 6.

The obtained results show that the surface excess calculated according to the Temkin isotherm is similar to that estimated from the Gibbs

Table 2. The adsorption parameters for 4-alkylphenylamines for benzene/3.16 N HCl interface

Alkyl		Gibbs		Langmuir		Temkin
C ₆	c	0.1 - 3.5	c	0.02 - 3.5	c	0.13 - 3.5
	D	13.83	A	31.8	K	-4.71
	R	0.993	B	6.72	B	75600
			R	0.998	R	0.975
			ΔG	4.6	ΔG	-11.5
C ₈	c	0.02 - 0.9	c	0.01 - 0.6	c	0.02 - 2.5
	D	11.30	A	35.2	K	-4.99
	R	0.996	B	1.61	B	70200
			R	0.999	R	0.953
			ΔG	1.1	ΔG	-12.2
C ₁₀	c	0.02 - 0.3	c	0.02 - 0.3	c	0.02 - 0.3
	D	9.04	A	38.4	K	-5.46
	R	0.998	B	0.40	B	73400
			R	0.998	R	0.992
			ΔG	-2.2	ΔG	-13.3
C ₁₂	c	0.005 - 0.3	c	0.005 - 0.3	c	0.005 - 0.3
	D	6.91	A	41.0	K	-6.53
	R	0.999	B	0.91	B	102000
			R	0.998	R	0.983
			ΔG	-0.23	G	-15.9
C ₁₄	c	0.004 - 0.4	c	0.004 - 0.3	c	0.004 - 0.3
	D	5.60	A	50.8	K	-6.42
	R	0.994	B	0.61	B	104000
			R	0.998	R	0.975
			ΔG	-1.21	ΔG	-15.1
C ₁₆	c	0.006 - 0.1	c	0.002 - 0.1	c	0.002 - 0.1
	D	5.35	A	93.4	K	-4.61
	R	0.995	B	0.84	B	87300
			R	0.993	R	0.995
			ΔG	-0.43	ΔG	-11.2

where: c in mole m⁻³, D = -d γ /d log c · 10³, B_L in mole m⁻²N⁻¹, A_L in m N⁻¹, ΔG_L and ΔG_T in kJ mole⁻¹, K_T in dimensionless form, B_T in m^{1.5}N^{0.5}mole⁻¹ and R stands for regression coefficient (subscripts T and L were omitted).

isotherm, although the exact shapes of the curves are somewhat different. The application of eq.5 is restricted only to low amine concentrations. Therefore only the values of surface excess calculated from eq.5 for low amine concentrations are given in Table 3. Generally agreement between all three isotherms is observed in the region of low extractant concentrations. At higher concentrations the surface excess is constant according to the procedure applied for the Gibbs isotherm, while it slowly increases to an asymptote value according to the Temkin isotherm. The differences of 0.3 · 10⁻⁶ mole m⁻² are normal and must be acceptable as systematic errors connected with the application of different models. Moreover, in this region the basic assumptions used during the isotherm's derivations are not fulfilled. Thus, it seems for us that the application of the Temkin

isotherm is the most convenient for surface excess calculations, and that this isotherm gives a reasonable picture, i.e. approximate, but very probable of the surface excess change with increasing extractant concentration (Fig.7).

Table 3. The values of the surface excess

Alkyl	Concentration mole m ⁻³	Surface excess, mole m ⁻² · 10 ⁵		
		Gibbs	Langmuir	Temkin
C ₈	0.025	2.02	1.71	1.38
	0.98	2.02	-	2.31
C ₁₀	0.011	1.62	1.41	1.08
	0.29	1.62	-	1.93
C ₁₂	0.005	1.24	1.49	0.85
	0.32	1.24	-	1.21
C ₁₄	0.004	1.00	1.81	0.88
	0.4	1.00	-	1.24
C ₁₆	0.006	0.95	1.09	0.72
	0.096	0.95	-	0.99

For the considered amines the surface excess decreases as the length of the alkyl increases. As a result of this, the molecular area increases by about $10 \cdot 10^{-20} \text{ m}^2$ and $5 \cdot 10^{-20} \text{ m}^2$ per methylene group in aromatic hydrocarbon/aqueous solution and heptane/water systems, respectively (Fig.8). This effect can be explained by the repulsive electrostatic forces which influence more strongly the position of the alkylphenylamine molecules when they are more strongly adsorbed, with the cationic group tending toward the interface, and are due to the stronger cohesion energy on the organic phase side which occur for derivatives having a longer alkyl. This is supported by the values of the adsorption free energy, which as a result of the amine protonation are much higher in a system containing HCl, and which increase for the first homologues as the length of the alkyl increases. Homologues having a longer alkyl cannot be considered because they exhibit bad solubility in the system and promote the formation of stable emulsions which disturb the measurements.

Our results show that rather a semiquantitative description of the surface excess was obtained. These values significantly depend upon the model used and vary for different models. All adsorption isotherms can be considered for very low amine concentrations, which are not-significant for extraction. In an important region of higher concentrations the basic assumptions used to derive the adsorption models are not fulfilled. Due to this the models do not match the experimental points over the whole experimental region. By changing this region, or broadening it more or less, different values of the adsorption parameters are then obtained.

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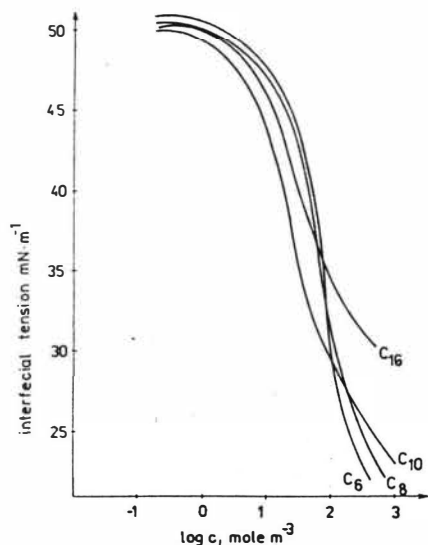


Fig. 1. Surface activity of 4-alkylphenylamines (heptane / water).

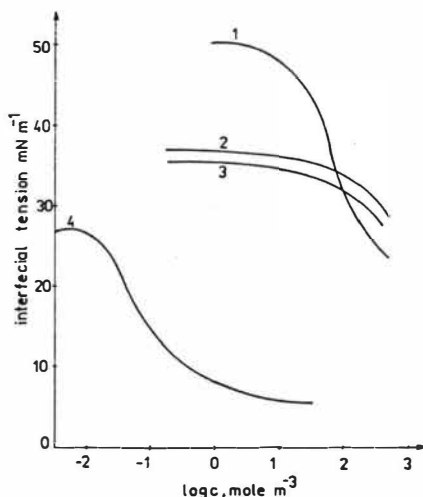


Fig. 2. Surface activity of 4-octylphenylamine (1- heptane / water, 2-toluene / water, 3-benzene / water, 4-benzene / 3.16 N HCl).

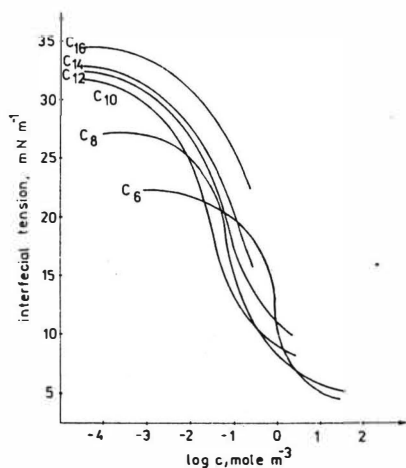


Fig. 3. Surface activity of 4-alkylphenylamines (benzene/3-16 N HCl).

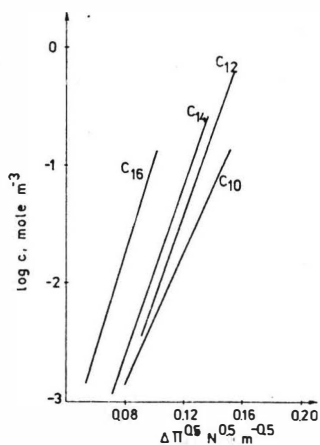


Fig. 4. Temkin isotherms.

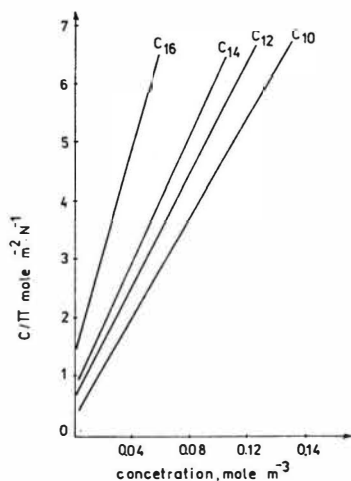


Fig. 5. Langmuir isotherms.

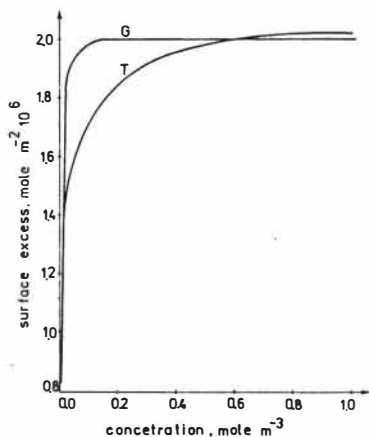


Fig. 6. Surface excess for 4-octylphenylamine.

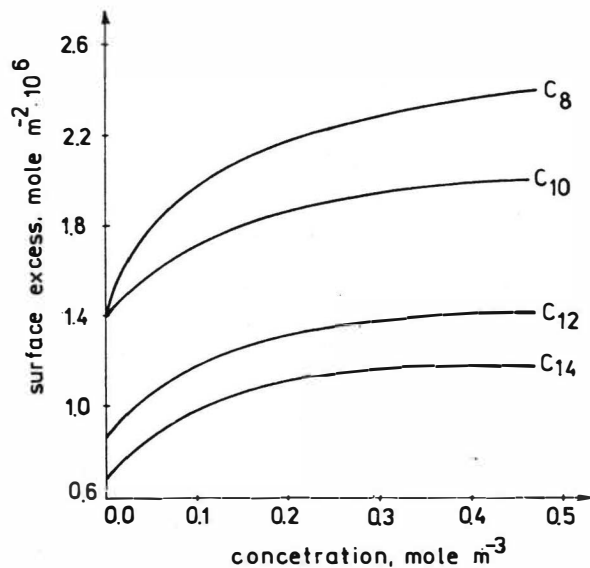


Fig. 7. Surface excess according to the Temkin isotherm

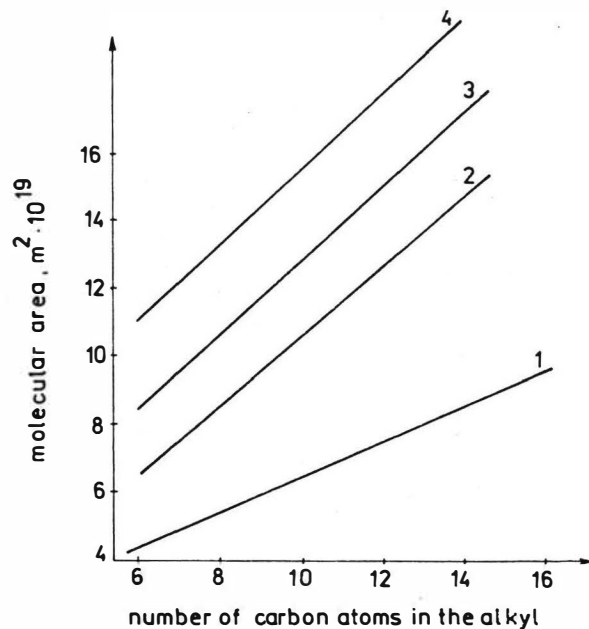


Fig. 8. Molecular area (1-heptane / water, 2- benzene / 3.16 N HCl, 3- benzene / water, 4 - toluene / water).

Solvent Extraction Application to Separation of Rare-Earth Metals in Non-Ferrous Metallurgy

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Solvent extraction is the main method for separation, purification and concentration of the rare-earth metals (RE) on industrial scale in the non-ferrous metallurgy. The first industrial-capacity plant for lanthanum isolation from RE mixture was put on stream in 1962 (1). Nowadays this advanced technology is being developed in the direction of sharp increase of quantities processed as well as the number of metal items recovered. Besides lanthanum separation the extraction technology is largely being used for production of cerium, praseodymium, neodymium, samarium, europium, gadolinium and, to a lesser extent, of heavier RE. Large-scale yttrium separation and thorough purification processes are completely based on solvent extraction.

Because of RE close resemblance in chemical properties, multistage separation plants, namely countercurrent extraction cascades with apparatus of mixer-settler type having diverse capacity are run in industry (1). There are from some tens to some hundreds apparatus in individual sets. The cascade stage number and the plant throughput are dependent considerably on the selectivity of the extraction system used which is quantitatively characterized by a separation factor (α) value. A higher selective system involves less apparatus number and a higher total plant output, ensuring improved economic efficiency as a result. That is why the careful investigation of different class extractants and extraction system parameters became an urgent problem.

We have investigated RE extraction with neutral oxygen-containing compounds, as well as with organic acids and amines of various classes from nitrate, chloride, thiocyanate and other type solutions including complex ones.

Neutral phosphororganic compounds, namely trialkyl phosphates, trialkyl phosphonates and trialkylphosphine oxides, among them tributyl phosphate (TBP) being of especial attention, have been extensively tried (2-4). The works carried out made it possible to ascertain RE extraction sequence depending on atomic number, as well as effects of different parameters (extractant type, salt anion type, acidity, salt

concentration, salting-out agent content, relative amounts of elements under separation, temperature etc.) on system selectivity. Similar, but smaller-scale experiments were concerned with study of other type neutral extractants, i.e. alcohols, ketones and other ones. Thus, it has been shown that extraction with neutral phosphororganic reagents from concentrated nitrate solutions can be successfully applied to RE sum isolation as well as to isolation of individual lighter elements, namely lanthanum, cerium, praseodymium and neodymium, the cerium preoxidation to tetravalent state being expedient.

Separation of the heavy elements by means of their nitrate extraction with neutral phosphororganic extractants is ineffective. To achieve the selectivity required it is necessary to add into an aqueous phase polyaminoacetic acids as complex-forming agents.

Monobasic phosphoric $(RO_2)POOH$, phosphonic $(RO)RPOOH$ and phosphinic R_2POOH acids (R is a normal or branched alkyl containing from 4 to 8 carbon atoms or an aromatic radical) are of a higher selectivity for entire lanthanoid series than the neutral phosphororganic compounds, essential alteration in the substitutional radical structure being of no practical importance for separation factor (α) values (5-7). In particular, α values for adjacent lanthanoids or yttrium series keep within the limits of 2.6-2.8 for such structurally different acids as dibutyl phosphoric, di(2-ethylhexyl)phosphoric (HDELHP), methyl(2-ethylhexyl)phosphonic, diheptylphosphinic, dioctylphosphinic and phenyl(2-ethylhexyl)phosphinic ones. At the same time the extractive power of the phosphororganic acids strongly depends on substituting radical structure. For example, the thulium distribution coefficients for six above-mentioned acids differ more than three orders of magnitude under comparable conditions.

Unlike neutral oxygen-containing compounds and phosphororganic acids the alkyl structure in monocarboxylic acids influences selectivity greatly, α -branching effect being the most significant (8, 9). Depending on branching position the selectivity increases following the order acids of normal structure $< \beta$ -branched $< \alpha$ -branched $< \alpha, \alpha$ -branched $< \text{polybranched}$.

The separation factors on RE extraction with tertiary and quaternary amines from concentrated nitrate solutions are not rather large, however the extraction sequence is unusual - the extractabi-

lity monotonously decreases from lanthanum to lutetium. When using thiocyanate solutions the extractability increases following normal sequence and α values for heavier RE from erbium to lutetium reach great magnitudes.

Two commercially available extractants - TBP and HDEHP - are mainly practised for RE extraction now (1). The separation technology using TBP is considered to be the most efficient for industrial-scale production. The separation factor for TBP increases both with increase of the RE nitrate concentration and that of the salting-out agent, the salting-out efficiency increasing in the order $\text{NH}_4\text{NO}_3 < \text{Ca}(\text{NO}_3)_2 < \text{Al}(\text{NO}_3)_3 < \text{LiNO}_3$. The separation factor (α) values of 1.8-2.0 for cerium subgroup elements satisfy requirements of commercial production.

The flowsheet for RE preparation using an extraction system of the type 100% TBP-RE nitrates-salting-out agent is in current application to separation of natural RE into heavier, middle and lighter metals and isolation of lanthanum, cerium, praseodymium, neodymium and yttrium as oxides. The main source of the cerium series elements is usually loparite and of the yttrium ones is yttrosynchisite (1).

TBP can be sufficiently effective for RE sum recovery from solutions after digestion of other type minerals. For instance, RE extraction from nitrate solutions after apatite decomposition is rather effective in spite of large quantities of calcium phosphate being present (10). Satisfactory results have been obtained for RE refining from thorium and other radioactive impurities containing in solutions after yttrosynchisite processing (11).

As to phosphororganic acids, HDEHP is used on industrial scale, especially for extraction of europium, samarium and gadolinium from their chloride solutions (12).

Aliphatic carboxylic acids of normal structure are applied for purification of RE solutions from other metal impurities containing in accompanying minerals (13). Possibilities for tertiary amine application to RE separation as compare with phosphororganic extractants are constrained owing to their low selectivity (14), but the quaternary amines are fairly suitable for separation of the middle elements of the lanthanoid series.

An important trend in extraction technology improvement is the search for effective systems basing on new types of extractants, namely organic oxides, viz. phosphine oxides, sulphoxides and amine oxides, monobasic carboxylic and phosphororganic acids etc.

Petroleum sulphoxides proved to be rather effective for high-purity yttrium oxide separation. According to its physical and chemical properties (complex stability constants, distribution coefficients) yttrium is located inside of the lanthanoids series and usually occupies a site in the holmium-erbium range, sometimes displacing into the gadolinium-dysprosium one and even into cerium subgroup range. That is why all the methods of yttrium purification are based on two separation systems at least. The first system (when yttrium is within the holmium-erbium range) serves for yttrium purification from all the elements from lanthanum to dysprosium inclusive, the second one is selected with the purpose to shift yttrium to cerium series range according to value of its distribution coefficient and refine it from lanthanoids not separated earlier (elements from holmium to lutetium).

The conditions for yttrium thorough purification from the entire lanthanoid series in a single extraction system by extraction from simple chloride or joint thiocyanate-chloride solutions using petroleum sulphoxides as extractants have been found (15). Under predetermined concentrations of metal, salting-out agent and extractant yttrium removes outside lanthanoid range, being concentrated predominantly in the aqueous phase and the lanthanoids in the organic one. This yttrium shift outside the lanthanoid series is of a such large value, that the commercial process for yttrium deep purification from lanthanoid impurities, based on extraction with petroleum sulphoxides, has been developed (15). The yttrium-lanthanoids separation factor ($\alpha_{RE, Y}$) varies under optimal process conditions from 3 to 10 depending on element order number.

The technology is protected by patents both in the USSR and abroad (16). The method of yttrium thorough purification by means of extraction with petroleum sulphoxides allows to reduce a number of technological operations and equipment items, as well as production area owing to single-cascade operation.

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A Study of Oxidizing Process of Cobalt(II) in the Bis(2-ethylhexyl) dithiophosphoric Acid--Additives Solvent Extraction System

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The extraction of cobaltous ion and nickelous ion by bis(2-ethylhexyl)dithiophosphoric acid (HL) has been reported by Sabot et al. (1-3). The central metallic cobaltous ion of extracted chelate compounds is oxidized quite easy to cobaltic ion in the process of extraction by oxygen in the air. The problems can occur when the stability of cobaltic chelate compound is so great that even concentrated acids will not allow the metal to be stripped. If we put the some additives (B) (for examples: pyridine(py), 2.3.4 trimethylpyridine, 2.3 dimethylpyridine, 2.6dimethylpyridine, 3.5 dimethylpyridine, trioctylphosphine oxide(Topo), tributylphosphite(TBP), octanol) into the system indicated above and the oxidation of cobaltous ion in the extracted chelate compound can be restrained in varying degree in the solvent extraction process. In this paper the formation constants of mixed type chelate compounds have been measured and the mechanism that the oxidation of cobaltous ion can be restrained by additives has been studied by means of interfacial tension, visible spectra and infrared spectra.

Experiments and Results

Bis(2-ethylhexyl)dithiophosphoric acid was used as received from Kuanming Metallurgical Institute and was purified by basewashing prior to use. n-heptane (c.p grade) was selected as an appropriate diluent and pyridine, 3-methylpyridine, 2.3-dimethylpyridine, 2.6-dimethylpyridine, 3.5-dimethylpyridine of chemical pure grade were used throughout as

additives. The aqueous phase were normally prepared by cobaltous sulfate of analytical reagent and sodium sulfate (A.R.) was used without further purification in order to keep ionic strength constant. The concentration of cobalt chelate compounds in organic phase was obtained by measuring the concentration of cobalt in the scrub raffinate (aqueous).

1. Measurements of Interfacial Tension

Interfacial tension measurements were carried out with a k 8600 type ring tensiometer made in West Germany. The aqueous and organic phases were equilibrated in advance and the interfacial tension recorded. The hexane was used as a diluent in the organic phase and the sodium ion concentration was kept constant at 1 M by the appropriate addition of Na_2SO_4 . The data were treated according to published procedures(4). The results are displayed graphically in fig.1.

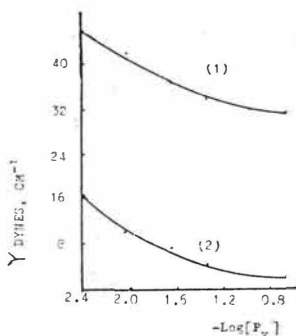


Fig. 1 Variation of interfacial tension with the concentration of pyridine ($t = 30 \pm 0.1^\circ\text{C}$)
Organic phase (1) Py + Hexane
(2) Py + Hexane + 5.170×10^{-3} MHL

2. Measurements of Electronic Spectra of Complex Compounds

The visible spectra of extractives in the different organic phase were measured respectively by UV-240 type made in Japan. The visible spectra of oxidizing process of extractives in organic phase without additive and containing additive pyridine are shown in fig.2 and fig.3 respectively. The visible spectrum of extractives containing different pyridine concentration is given in fig.4. We also measured the visible spectra of extracted organic phase at the present of different kinds of additives. All spectral measurement were used

1 cm colorimetric cell and the heptane as reference substance.

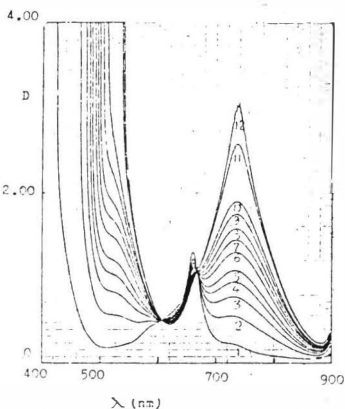


Fig. 2 The visible spectrum of oxidizing process about the central metallic cobaltous ion in the organic phase without additive condition.
organic phase [HL] $2.5 \times 10^{-2} M$
aqueous phase [Co(II)] $7.94 \times 10^{-3} M$
Time of curves measurement (minute)
(1) 1 (2) 10 (3) 20 (4) 30 (5) 40 (6) 60
(7) 90 (8) 100 (9) 130 (10) 160 (11) 270 (12) 330

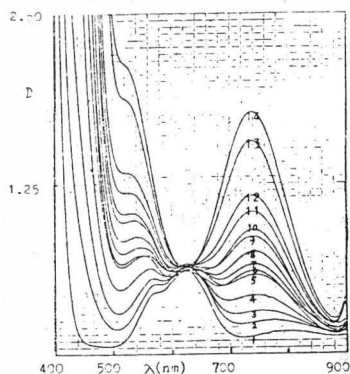


Fig. 3 The restrainable visible spectrum of oxidizing process about the central metallic ion in the organic phase containing additive pyridine
Organic phase [HL] $2.5 \times 10^{-2} M$
aqueous phase [Co(II)] $7.94 \times 10^{-3} M$
[Py] $1.0 \times 10^{-2} M$
Time of curves measurement (hours)
(1) 1 minute (2) 1.4 (3) 3.6 (4) 5.4 (5) 9 (6) 10
(7) 12 (8) 17 (9) 22.7 (10) 30 (11) 42.6 (12) 53.8
(13) 65.7 (14) 78.8

3. Measurements of Infrared Spectra

The infrared spectra of extractant HL, free pyridine, the extractives in organic phase without additive and containing pyridine and after the achievement of oxidation equilibrium extracted organic phase containing pyridine have been studied respectively by Perkin-Elmer 580 B infrared spectrophotometers in the range of $400-1350 \text{ cm}^{-1}$. The extracted organic phase containing pyridine were all washed by water prior to measure in order to remove a part of free pyridine. It was

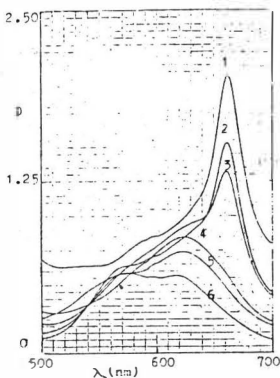


Fig. 4 The visible spectrum of extracted organic phase containing different pyridine concentration
Organic phase HL $2.5 \times 10^{-2} M$
aqueous phase [Co(II)] $7.94 \times 10^{-3} M$
No.: 1 2 3 4 5 6
[HL]:[Py] 1:0 1:1 1:2 1:4 1:10 1:50

the optical density of chelate compounds containing any additive concentration. Then, we have obtained by

$$\log \frac{[\text{CoL}_2 \cdot \text{Bn}]}{[\text{CoL}_2]} = \log \frac{D_0 - D}{D - D_\infty}$$

$$\log \frac{D_0 - D}{D - D_\infty} = n \log[B] + \log K$$

The number of additive molecule in the mixed type chelate compounds and formation constant can be obtained by plotting $\log \frac{D_0 - D}{D - D_\infty}$ to $\log[B]$. The values of $\log K$ and n were measured respectively at the present of all kinds of additives and room temperature ($\sim 298\text{K}$), The results can be seen in fig.5 and table 2.

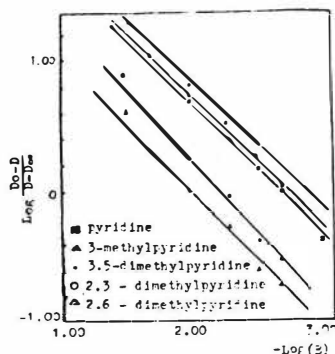


Fig. 5 The observed $\log \frac{D_0 - D}{D - D_\infty}$ as a function of the $-\log[B]$
 $[\text{CoL}_2] = 9.99 \times 10^{-4} \text{M}$

Table 2 The composition and Formation constant of Mixed Type Chelate Compounds at the present of Different Additives

Additives	n	log K
3,5 dimethylpyridine	0.96	2.85
3. methylpyridine	0.97	2.73
pyridine	0.95	2.67
2,3 dimethylpyridine	1.07	2.23
2,6 dimethylpyridine	1.02	1.99

5. Determinations of Oxidation Degree of Cobaltous Chelate Compounds at the presence of all Kinds of additives

As have been discussed above, the CoL_2 solution first was prepared, then additive B was added into it immediately. After 10 hours we measured respectively their optical density at 735nm (the characteristic absorption wavelength of oxidation products) when adding different additives. The values of the corresponding optical density of using different additives fully displayed the oxidation degree of cobaltous chelate compounds. The results are given in table 3.

reported (5) that pyridine molecule has nine strong bands in the range of $400-1350\text{cm}^{-1}$. These strong bands have been observed similarly by us. When pyridine molecule is bonded into extracted chelate compounds, all these strong bands are shifted relevantly in the mixed type chelate compounds except for two bands at 992cm^{-1} and 1032cm^{-1} are covered by the p-o-c broad absorption band ($950-1100\text{cm}^{-1}$) of extractant HL. When the organic phase reached oxidation equilibrium, these bands of pyridine would return once again to the originated site as shown in table 1

Table 1 Infrared Spectra of pyridine in the range of $400-1350\text{cm}^{-1}$

Free Pyridine	405	604	705	748	1070	1147	1218
Pyridine in the Extractives	429	615	680	754	1120	1222	1258
Pyridine after the Achievement of oxidation Equilibrium	405	599	698	745	1070	1152	1222

4. Determinations of Composition and Formation Constant for mixed Type Chelate Compounds

After adding additive B into the extraction system, supposing original extractive CoL_2 takes place addition reaction with B in monomer form, we obtain a simple equilibrium equation



The value of formation constant may be expressed by as follows

$$K = \frac{[\text{CoL}_2 \cdot \text{Bn}]}{[\text{CoL}_2] [\text{B}]^n}$$

The equation can be reduced to line equation

$$\log \frac{[\text{CoL}_2 \text{Bn}]}{[\text{CoL}_2]} = n \log [\text{B}] + \log K$$

Suppose that characteristic absorption peaks of CoL_2 in monomer form and CoL_2 in mixed type chelate compounds at 660nm all obey beer's law. Under the same extractant concentration condition, D_0 and D_∞ stand for the optical density of CoL_2 without additive and adding enough additive to convert completely CoL_2 into CoL_2Bn respectively, while D represents

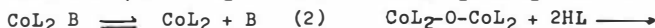
Table 3. The D^{735} of Oxidation products of Using Different Additives (Stationary Time: 10 hours in Air)

Additives Concentration (M)	3,5-dimethyl- pyridine	3-methyl- pyridine	pyridine	2,3-dimethyl- pyridine	2,6-dimethyl- pyridine
5.0×10^{-3}	0.400	0.472	0.476	0.960	1.010
1.0×10^{-3}	0.210	0.240	0.427	0.770	0.778

Discussion

In fig. 2 and fig. 3 it is shown that no matter whether the additive is added or not, the visible spectra of extractives all vary with the time and the strength at 735nm vary directly proportional to time in bis(2-ethylhexyl)dithiophosphoric acid extraction system. The appearance new peak at 735nm is characterized as cobaltic oxidation products, so it is indicated further that oxidation of cobaltous can be restrained greatly by using different kinds of additives. D. S. Flett et al. have reported that the variation in interfacial tension of kelex100/versatic 911 mixed solution with versatic 911 concentration indicates that there is a weak interaction between the two extractants. This interaction confirmed by NMR studies, effectively removes the kelex100 from the interface thus preventing the oxidation reaction. From this point of view, we determined the variation in interfacial tension of HL/B mixed solution with additive (B) concentration by means of interfacial tension ring method test and obtained results (Fig. 1) which is different obviously from that of D.S. Flett (6). This is because additive pyridine is a weaker surfactant active agent than extractant HL, so it is unable to compete with extractant HL for efficient occupation interface. In fig. 1 it is shown that it is not an interfacial controlling process that oxidation of cobaltous extractive can be prevented by using different pyridine kinds of additives in our studying system. From fig. 4 we can see that there is a characteristic sharp absorption peak of CoL_2 at 660nm, this peak value decreases gradually with the increase in concentration of additives, in the meanwhile, two new absorption peaks of mixed type chelate compounds formed from CoL_2 with additives B

are appeared at 570nm and 620nm, their peak values increase gradually with the increase in concentration of additives. The mixed type chelate compounds have been proved further by infrared spectra. The characteristic absorption frequency of pyridine molecule in mixed type chelate compounds has shifted evidently (see table 1). As has been pointed out in literature (5), The infrared spectrum of the pyridine molecule is considerably modified when the non-bonding pair of electrons on the nitrogen atom is donated into the vacant orbital of an electron - acceptor. The effects on frequency and intensity might be expected to depend both on the symmetry of the vibration and on the chemical nature of the bond involved. Thus it can be seen that nitrogen atom in pyridine molecule is coordinated into the cobaltous chelate compound CoL_2 to form more stable mixed type chelate compound CoL_2B . When the organic phase reached oxidation equilibrium, the characteristic absorption frequency of the pyridine molecule would return once again to the original site. We consider that this is the result of pyridine molecule come off mixed type chelate compounds and that oxidation of the cobaltous chelate compound CoL_2 can be prevented by the formation of mixed type chelate compound CoL_2Bn . For this reason, an additive is considered restraint ability of oxidation the more strong, the more stable its mixed type chelate compound and it depends on the formation constant of mixed type complexes of different kinds of additives formed. From fig 4 it can be seen that the extent of formation of mixed type chelate compound CoL_2Bn also depends upon to ratio of CoL_2 to B, even though $[\text{CoL}_2]:[\text{py}] = 1 : 1$, CoL_2 hasn't yet all change to CoL_2B . It is not until $[\text{CoL}_2]:[\text{py}] = 1 : 50$ that mixed type chelate compound is formed nearly completely. The experiments also have demonstrated that there is a dissociation equilibrium for mixed type chelate compound CoL_2B in the presence of additive B and product CoL_2 is oxidated quite easy to CoL_2 by oxygen in the air, so it is conceivable that the oxidation process of cobaltous chelate compound may be as follows



The result of experiment (table 2) indicates that the composition of different kinds of mixed type chelate compound are all

CoL B and we can infer the sequence of restraint ability of different kinds of additives from the formation constant (table 2) as follows:

3,5dimethylpyridine > 3 methylpyridine > pyridine >
2.3 dimethylpyridine > 2.6 dimethylpyridine.

This sequence is just in accordance with the measurement results (table 3) experimentally of extent of oxidation of extracted chelate compounds, thus, the mechanism proposed above gets proof once again. Different pyridine kinds of additives are all Lewis base, their coordinate nitrogen atom has an electron - donor ability. The stability of mixed type chelate compounds is directly proportional to the electron - donor ability of the incoming additives. 3.5 dimethylpyridine and 3 methylpyridine are the much stronger base than pyridine, therefore former mixed type chelate compounds have a higher stability than that later one. In addition to the electronic effect, also the experimental data (table 3) shown that the dependence of stability on the size of the incoming additive is more important for the 2.6 dimethylpyridine and 2.3 dimethylpyridine. Although they are the much stronger base than the pyridine, the much small size of the pyridine became the dominant factor for preventing the oxidation of CoL₂. It is well-known that steric hindrance effects play a important role in substituting group of α position of pyridine. It is understood that 2.6 dimethylpyridine formation constant and preventing the oxidation reaction ability are the least of all pyridine kinds of additives in our research.

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Extractive chromatographic separation of selenium (IV), and tellurium (IV) and associated elements with trioctylphosphine oxide

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The extraction chromatographic separation with TBP was used for the separation of selenium(IV) and tellurium(IV) from other elements (1-3). TOA (4,5) was also utilized for the separation of tellurium(IV) from tin, lead and antimony(V). Amberlite LA-2 (6) was used for separation from indium. Bis(-2-ethylhexyl) phosphoric acid (HDEHP) (7) was used for the separation of tellurium and antimony.

EXPERIMENTAL

Apparatus and reagents :

The apparatus and column used was similar to one described earlier (8).

The stock solution of selenium(IV) and tellurium(IV) were prepared by fusing 0.59 g of powdered element in sodium hydroxide or aquaregia respectively. The solution after removing excess of acid or alkali was made up to 100 ml with distilled water containing 1% hydrochloric acid. The solutions were standardised gravimetrically (9). They contained 3 mg/ml of concerned element. The diluted solution containing 50 µg/ml of selenium or tellurium were prepared by appropriate dilution.

General procedure :

An aliquot of solution was taken. The solution was made upto 6 M in hydrochloric acid containing 7 M lithium chloride for extraction of selenium while it was made to 4 M hydrochloric acid for extraction of tellurium. The solution was passed on column. The extracted selenium or tellurium were stripped with mineral acids and salts. Twenty fractions, each of 2 ml ; were collected. Selenium(IV) from the each fraction was determined spectrophotometrically with 3,3' diamino-benzidine at 345 nm (10). Tellurium(IV) from the stripped solution was determined as its iodide complex at 340 nm (11).

RESULTS AND DISCUSSION

Extraction studies :

The studies of selenium(IV) from 1-6 M hydrochloric acid in the presence of 1-7 M lithium chloride showed that it was extracted at 6 M hydrochloric acid containing 7 M lithium chloride. While similar studies for tellurium(IV) from 1-6 M hydrochloric acid, showed that it was extracted at 4-6 M hydrochloric acid. Thus the optimum conditions for the extraction of selenium(IV) was 6 M hydrochloric acid containing 7 M lithium chloride while that for tellurium(IV) was 4 M hydrochloric acid.

Effect of stripping agent :

The study of stripping of selenium(IV) or tellurium(IV) showed that selenium was stripped with 1-6 M of all mineral acids or their salts. While tellurium(IV) was stripped with 1-3 M of all mineral acids or salts.

Separation of selenium(IV) or tellurium(IV) from binary mixtures :

Selenium(IV) was extracted with 6 M hydrochloric acid containing 7 M lithium chloride while tellurium(IV) was extracted with 4 M hydrochloric acid in the presence of any of the diverse ions. It was seen that on passing the mixture containing selenium(IV) or tellurium(IV) and any of the ions like alkali and alkaline earths, chromium(III), manganese, cobalt, nickel, copper, cadmium, aluminium and lead were not extracted and passed through the column. However selenium(IV) or tellurium(IV) were extracted. They were stripped with 6 M or 1 M hydrochloric acid respectively. It was possible to separate selenium(IV) or tellurium(IV) from any of these elements in binary mixtures in the concentration ratio of 1:200.

Separation of selenium(IV) from multicomponent mixtures :

The mixture of copper, selenium(IV) and tellurium(IV) was passed on the column from 6 M hydrochloric acid containing 7 M lithium chloride, when copper was not extracted while selenium(IV) was first stripped with 6 M and finally tellurium with 1 M hydrochloric acid.

When the mixture of cadmium|manganese, selenium(IV), and scandium was passed through the column from 6 M hydrochloric acid containing 7 M lithium chloride, cadmium or manganese were unextracted. The extracted selenium(IV) was stripped with 6 M hydrochloric acid and scandium with 2 M hydrochloric acid.

Table - 1

Separation of Selenium(IV) from Multicomponent Mixtures

Mixture	Taken μg	Found μg	% Recovery	Eluant	Eluant volume ml
1 Cu	51	50.5	99	6 M HCl + 7 M LiCl	10
Se(IV)	60	60.2	100.3	6 M HCl	10
Te(IV)	180	178	98.9	1 M HCl	12
2 Cd/Mn	70	69	98.6	6 M HCl + 7 M LiCl	8
Se(IV)	60	59.5	99.2	6 M HCl	10
Sc	50	50.5	101	2 M HCl	10
3 Co/Tl(I)	80	80.5	100.6	6 M HCl + 7 M LiCl	8
Se(IV)	60	59	98.3	6 M HCl	10
Th	50	50	100	2 M HCl	10
Ga	15	14.7	98	0.1 M HCl	8
4 Ni	50	48.5	99	6 M HCl + 7 M LiCl	8
Se(IV)	60	60.2	100.3	6 M HCl	10
Ge	22	22.1	100.5	2 M HCl	12
Fe(III)	62.5	63	100.8	0.25 M HCl	16
Mo(VI)	50	49.6	99.2	0.1 M HCl	16
5 Pb/Mg	75	75.5	100.7	6 M HCl + 7 M LiCl	8
Se(IV)	60	59.8	99.7	6 M HCl	10
Zr	75	75	100	2 M HCl	10
Ga	75	74.8	98.8	0.1 M HCl	8
Cr(VI)	51	50	98	H ₂ O	22
6 Al	70	71	101.4	6 M HCl + 7 M LiCl	8
Se(IV)	60	60.5	100.8	6 M HCl	10
Te(IV)	180	180	100	1 M HCl	12
Sn(IV)	59	59.2	100.3	2 M HNO ₃	10
Au	100	99	99	7 M HNO ₃	14

Cobalt/thallium(I), selenium(IV), thorium and gallium were separated by passing their mixture from 6 M hydrochloric acid containing 7 M lithium chloride when cobalt or thallium were not extracted while extracted selenium(IV) was stripped with 6 M hydrochloric acid, thorium with 2 M hydrochloric acid and gallium with 0.1 M hydrochloric acid.

When the mixture of nickel, selenium(IV), germanium, iron(III) and molybdenum(VI) passed on column from 6 M hydrochloric acid containing 7 M lithium chloride, nickel was not extracted. The extracted selenium(IV) was stripped with 6 M hydrochloric acid, germanium with 2 M hydrochloric acid, iron(III) with 0.25 M hydrochloric acid, and molybdenum(VI) with 0.1 of hydrochloric acid.

When a mixture of lead or magnesium, selenium, zirconium, gallium, chromium was passed from 6 M hydrochloric acid containing 7 M lithium chloride, lead or magnesium was not extracted while the extracted selenium(IV) was stripped with 6 M hydrochloric acid, zirconium with 2 M hydrochloric acid, gallium with 0.1 M hydrochloric acid and chromium(VI) with water.

The separation of aluminium, selenium(IV), tellurium(IV), tin(IV) and gold was carried out by passing the mixture through column with 6 M hydrochloric acid containing 7 M lithium chloride, when aluminium was not extracted. Selenium(IV) was backstripped with 6 M hydrochloric acid, tellurium(IV) with 1 M hydrochloric acid, tin(IV) with 2 M nitric acid and finally, gold with 7 M nitric acid (Table 1).

Separation of tellurium(IV) from multicomponent mixtures :

When the mixture of lead, selenium(IV) and tellurium(IV) was passed on column from 6 M hydrochloric acid containing 7 M lithium chloride lead was not extracted while extracted selenium(IV) was stripped with 6 M hydrochloric acid and tellurium(IV) with 1 M hydrochloric acid.

When the mixture containing nickel/arsenic(III), tellurium(IV), iron(III) and molybdenum(VI) in 4 M hydrochloric acid was passed through the column, nickel or arsenic(III) was not extracted at this acidity while the extracted tellurium(IV), iron(III) and molybdenum(VI) were stripped respectively with 2 M, 0.25 M and 0.1 M hydrochloric acid.

The mixture of cobalt, germanium, tellurium(IV), gallium and tin(IV) in 5 M hydrochloric acid was passed through the column. Cobalt was not extracted. The extracted germanium was stripped with 4 M hydrochloric acid, tellurium(IV) with 2 M hydrochloric acid, gallium with 0.1 M hydrochloric acid and tin(IV) with 2 M nitric acid.

Table - 2

Separation of Tellurium(IV) from Multicomponent Mixtures

Mixture	Taken μg	Found μg	% Recovery	Eluant	Eluant volume ml
1 Pb	75	76	101.3	6 M HCl + 7 M LiCl	8
Se(IV)	60	59.5	99.2	6 M HCl	10
Te(IV)	50	49.8	99.6	1 M HCl	12
2 Ni/As(III)	50	49.5	99	4 M HCl	8
Te(IV)	50	50.1	100.2	2 M HCl	16
Fe(III)	62.5	63	100.8	0.25 M HCl	14
Mo(VI)	50	51	102	0.1 M HCl	16
3 Co	80	80.3	100.6	5 M HCl	8
Ge	22	21.8	99.1	4 M HCl	30
Te(IV)	50	49.8	99.0	2 M HCl	16
Ga	15	15.3	102	0.1 M HCl	8
Sn(IV)	59	59.2	100.3	2 M HNO ₃	10
4 Cu	51	50.5	99	6 M HCl + 7 M LiCl	10
Se(IV)	60	60.2	100.3	6 M HCl	10
Te(IV)	50	50.2	100.4	1 M HCl	12
Cr(VI)	51	50	98	H ₂ O	22
5 Mg	75	75.5	100.7	4 M HCl	8
Te(IV)	50	50	100	2 M HCl	16
In	75	74.1	98.8	0.25 M HCl	20
Mo(VI)	50	50.5	101	0.1 M HCl	16
Cr(VI)	51	50	98	H ₂ O	22
Tl(III)	100	99	99	5% Hydrazine sulphate in 0.5 M H ₂ SO ₄	
6 Cu	51	50.2	98.4	6 M HCl + 7 M LiCl	10
Se(IV)	60	59.5	99.2	6 M HCl	10
Ge	22	22.2	101.9	4 M HCl	30
Te(IV)	50	49.5	99	1 M HCl	12
Sn(IV)	59	59.2	100.3	2 M HNO ₃	10
Au(III)	100	101	101	7 M HNO ₃	14

When the mixture of copper, selenium(IV), tellurium(IV) and chromium(VI) was passed from 6 M hydrochloric acid containing 7 M lithium chloride, copper was not extracted. Selenium(IV) was stripped with 6 M hydrochloric acid, tellurium(IV) with 1 M hydrochloric acid and finally chromium with water.

The mixture of magnesium, tellurium(IV), indium, molybdenum(VI), chromium(III) and thallium(III) when passed from 4 M hydrochloric acid, magnesium was not extracted. The extracted tellurium(IV) was stripped with 2 M hydrochloric acid, indium with 0.25 M hydrochloric acid, molybdenum(III) with 0.1 M hydrochloric acid, chromium(III) with water and finally thallium(III) with 0.5 M sulphuric acid containing 5% hydrazine sulphate.

When the mixture containing copper, selenium(IV), germanium, tellurium(IV), tin(IV), and gold was passed from 6 M hydrochloric acid containing 7 M lithium chloride, copper was not extracted, while extracted selenium(IV) was stripped with 6 M hydrochloric acid, germanium with 4 M hydrochloric acid, tellurium(IV) with 1 M hydrochloric acid, tin(IV) with 2 M nitric acid and gold with 7 M nitric acid (Table 2).

All the elements during separations the selenium and tellurium were determined spectrophotometrically with suitable chromogenic reagents (12).

The separation of selenium from iron, lead, arsenic, bismuth, copper, nickel and cobalt is important, as they are associated with selenium in minerals. The separation of tellurium from lead, bismuth, iron, copper and antimony is of significance as they are present in tellurium minerals. The time required for separation and determination is about 2 hrs.

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Synergistic Solvation Extraction of Tungsten(VI) in Weakly Acidic Solutions by the Mixture of Tertiary Amine and Alcohol as Solvent

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ABSTRACT

The addition of alcohol to tertiary amine to enhance its solvation extraction of W(VI) in weakly acidic solutions was studied. Mechanism of synergism was proposed. The compositions of the extraction species under different conditions were determined with their schematic structures proposed.

INTRODUCTION

Tertiary amine, just like primary and secondary amines, can extract tungsten(VI) from weakly acidic dilute tungstate solutions by the mechanism of solvation extraction⁽¹⁾. As there is no active hydrogen atom in the molecule of tertiary amine, much lower extraction can only be obtained in comparison with those by primary and secondary amines through solvation mechanism. Large excess amount of tertiary amine has to be used to arrive a high percent of extraction. In the present work, the synergistic effect of alcohol on the solvation extraction of tungsten(VI) by tertiary amine was investigated.

EXPERIMENTAL

An electric shaker was used to carry out the extraction experiments. For temperature studies, the experiments were performed in a thermostat. Tungsten(VI) was analyzed by the thiocyanate photometric method. Perchloric acid volumetry was used for the analysis of amine. Solution pH was measured by a pH meter. Tungsten(VI) solution was prepared from sodium tungstate and the calculated amount of sulfuric acid, based on gram atoms of W(VI) in stock solution, was added during extraction. The extractants and other reagents used were analytical grade or chemical pure grade.

RESULTS AND DISCUSSIONS

Effect of the addition of alcohol on the extraction of W(VI) The effect of the addition of alcohol on the extraction of W(VI) by different classes of amines is shown in Fig. 1. The results indicate that

the effect of alcohol on extraction of W(VI) by different classes of amines with different mechanisms of extraction is different. It can be seen that alcohol gives a synergistic effect on the extraction of W(VI) by tertiary amine with solvation mechanism. However, it gives antagonistic effect on the extraction of W(VI) by tertiary amine with anion exchange mechanism or by primary amine with solvation mechanism. It may be considered that tertiary amines are not very effective in solvation extraction toward W(VI) as there is no active hydrogen atom in the molecules of tertiary amines. By addition of alcohol into the organic phase, active hydrogen atoms are brought into the system and thus to enhance the effectiveness of tertiary amine in solvation extraction. When the tungsten(VI) is extracted by tertiary amine with anion exchange mechanism, it is dependent on the salt-forming tendency of nitrogen atoms in the molecules of tertiary amine, and has no relation with the presence or absence of active hydrogen atoms. Addition of alcohols into the organic phase will decrease the salt-forming tendency of tertiary amines due to the formation of hydrogen bonds between tertiary amines and alcohols and thus decrease the results of extraction by anion exchange. When W(VI) is extracted by primary amines with solvation mechanism, very good results will be obtained as there are two active hydrogen atoms in each molecule of primary amine. Addition of alcohols into the organic phase will also decrease the fraction of extraction due to the formation of hydrogen bonds between primary amines and alcohols.

The amount of W(VI) extracted by a mixture of tertiary amine and alcohol increases linearly with increasing of amount of acid added as shown in Fig. 2. It can be considered that with increasing of the amount of acid added, the amount of neutral species of W(VI) to be extracted also increases resulting higher fraction of W(VI) extracted. The effect of initial concentration of W(VI) on fraction of extraction into the organic phase is shown in Fig. 3. It may be considered that species of W(VI) existed in the aqueous and organic phase are mainly monotungstate with low initial concentration of W(VI) while with high concentration of W(VI), it forms isopolyanions in the aqueous phase. The point of intersection of the straight lines in Fig. 3 corresponds to the initial W(VI) concentration in the aqueous phase of about 0.3 g/l which can be taken as the boundary point of forming polyanions under the conditions studied.

The effect of temperature on W(VI) extraction by a mixture of tertiary amine and alcohol was studied as shown in Fig. 4. It can be seen that in the range of the temperature studied, the distribution

coefficient of W(VI) decreases with increasing of temperature. Temperature has been found to have very low influence on the extraction of W(VI) by tertiary amine with anion exchange mechanism⁽¹⁾. Therefore, it may be taken as another evidence that mechanism of extraction under the conditions studied in the present work is by solvation and not by anion exchange.

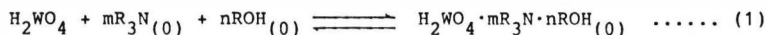
The effect of different alcohols on solvation extraction of W(VI) by tertiary amine was investigated with the results given in Table 1. It can be seen that the synergistic effect of alcohols with different structures is different. The different classes of alcohols and also the steric effect of alkyl groups in alcohol have some influence on the results while cyclohexyl alcohol gives much higher synergistic effect in comparison with alcohols derived from alkanes.

Table 1 Effect of addition of alcohols of different structures to the organic phase on the extraction of W(VI) by tertiary amine
 aq.: W(VI) 0.1803 g/l, acid added: $N_H + f_{W(VI)} = 1.5$;
 org.: TDA 0.02 M, ROH 0.16 M in n-octane;
 O/A = 1, Temperature, $\sim 20^\circ\text{C}$, Contact time, 5 min.

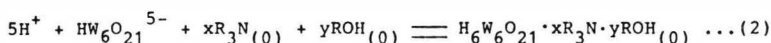
Alcohol	cyclohexanol	n-octanol	n-heptanol	2-ethylhexanol	octanol-2
E %	67.3	40.0	39.6	36.6	33.3

Studies on the composition of the synergistic extraction species

The aqueous solution chemistry of tungsten(VI) is very complex and the different species existed in the solutions depend not only on the acidity of the solution and concentration of tungsten(VI) but also on ionic strength of the solution and temperature. A number of studies have been reported in the literatures⁽²⁻⁶⁾. Based on the results reported and the experimental conditions as well as the results of the present work, tungsten(VI) may be considered to exist mainly as monotungstate with addition of small amount of acid into the solution and as paratungstate with addition of large amount of acid. Therefore, for the determination of the composition of the synergistic extraction species, it may be assumed that the extraction reactions can be expressed as:



with the addition of small amount of acid and as



with the addition of large amount of acid respectively.

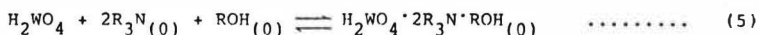
Under the present experimental conditions, the extraction of W(VI) by tertiary amine or alcohol alone is very low and thus only the synergistic extracted complexes will be considered. Hence, the following expressions were derived from Equations 1 and 2 respectively;

$$\frac{DY}{[H^+]^2} = K_{ex} \beta_2 [R_3N]_{(0)}^m [ROH]_{(0)}^n \dots (3)$$

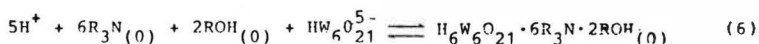
$$\text{and } \frac{D}{[H^+]^5} = K_{ex}' [R_3N]_{(0)}^x [ROH]_{(0)}^y \dots (4)$$

where $Y = 1 + \beta_1(H^+) + \beta_2(H^+)^2$ and subscript 0 stands for the organic phase; D is the distribution coefficient of W(VI); K_{ex} & K_{ex}' are the equilibrium constants of Equations 1 and 2 and β_1 & β_2 are the formation constants of $HW_6O_{21}^{5-}$ & H_2WO_4 respectively ($\beta_1 = 4.5 \times 10^3$, $\beta_2 = 7.1 \times 10^5$ (5,6) at 25°C.)

Based on Equations 3 & 4, straight lines should be obtained by plotting the left sides of the equations versus concentrations of tertiary amine or alcohol at the constant concentrations of alcohol or tertiary amine respectively on logarithm-logarithm scale. Results are shown in Figs. 5 and 6 respectively. From the slopes of these straight lines, the number of moles of tertiary amine and alcohol associated respectively with the synergistic extraction species under different conditions can be found. The mole ratio of tertiary amine to W(VI) in extraction species was further studied by the method of continuous variation as shown in Fig. 7. The results obtained were consistent with the results of the slope method as given in Figs. 5 and 6. Therefore, the extraction reactions can be represented as:



with $N_H/f_{W(VI)} \leq 1.5$ and



with $N_H/f_{W(VI)} = 2.0$ respectively.

The apparent equilibrium constants of extraction reactions as given by Equations 5 and 6 were calculated from the experimental

results to be $\log K_{2X} = 8.12 \pm 0.16$ for Eqn. 5 at $26 \sim 27^\circ\text{C}$ and $\log K_{ex}' = 35.43 \pm 0.32$ for Eqn. 6 at about 25°C respectively.

Discussion of the mechanism of synergistic extraction The infrared spectra of the organic phase before and after extraction of W(VI) were studied and compared. The IR absorption bands of the stretching vibration of the -OH group in the alcohol were found at 3630 cm^{-1} (monomer) and 3320 cm^{-1} (polymer) before extraction of W(VI) and a stronger and broader absorption band was found at about 3380 cm^{-1} after loaded with W(VI). The band at $\sim 3380\text{ cm}^{-1}$ was found to be enhanced by increasing of the amount of W(VI) extracted and also by decreasing of the amount of alcohol in the organic phase. Therefore, it may be considered that the hydrogen bonds are formed between the active H atom of alcohol and tungstate-tertiary amine complex during extraction and the alcohol is taken part in the formation of synergistic extraction species.

It was observed that when the organic phase containing tertiary amine alone was slowly added to the W(VI) solution without addition of salting-out agents, milky white turbidity appeared rapidly at the interface. The turbidity increased with time and then diffused into both phases gradually and finally all aqueous phase became opaque as pale-milky liquid. When the organic phase containing both alcohol and tertiary amine was added to the W(VI) solution, only a little turbidity appeared for quite a long time.

The mechanism of synergistic extraction of W(VI) with alcohol and tertiary amine can be suggested. During solvation extraction of W(VI) by tertiary amine, the hydrated tungstate-tertiary amine complexes were formed first at the interface. These complexes have a strong hydrophilic property and will exist in the aqueous side in emulsion form. With the addition of alcohol into the organic phase, hydroxyl groups of alcohol will react with these complexes and replace the water molecules in the complexes either partially or completely. The hydrophilic property of the complexes will be decreased and they will be transferred into the organic phase rapidly. The alcohol in the extraction system studied can be considered as being able to accelerate the dehydration of the hydrophilic complexes formed on the one hand and to enter the extracted species directly through the formation of hydrogen bonds. The structure of the extracted species may be represented as shown in Fig. 8.

CONCLUSIONS

The synergism of alcohol toward tertiary amine in the solvation extraction of W(VI) is probably through the formation of hydrogen bonds between the hydroxy-hydrogen atom of alcohol and tungstate-tertiary amine complex and thus the alcohol is taken part in the formation of synergistic extraction species. In the meantime the replacement of water molecules in the hydrated tungstate-tertiary amine complexes by molecules of alcohol takes place also. The composition of the extraction species has been determined by using of the slope method and the method of continuous variation. The structure of synergistic extraction species was suggested. The synergistic system studied in the present work has indicated that active hydrogen atoms play an important role in the solvation extraction by amines.

NOMENCLATURE

A or a:	the aqueous phase
D:	the distribution coefficient
E:	percent extraction
$f_{W(VI)}$:	number of gram formula weight of W(VI)
K_{ex} :	the equilibrium constant of extraction reaction
M:	molar concentration
N_{H^+} :	number of gram equivalents of H^+
O or o:	the organic phase
T:	temperature ($^{\circ}C$)
β_1, β_2 :	the formation constants of HWO_4^- and H_2WO_4 respectively
R_3N :	tertiary amine
TOA:	tri-n-octyl amine
TDA:	tri-n-decyl amine
ROH:	alcohol or n-octanol

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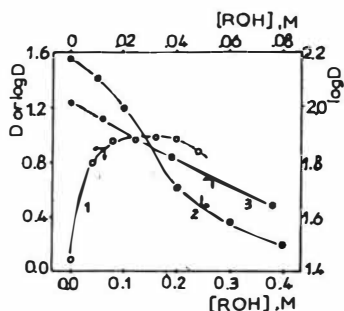


Fig. 1 Effect of the addition of n-octanol on the extraction of W by different classes of amines with different mechanisms.

O/A=1, diluent: n-octane

1. solvation extraction, 0.02 M TDA, aq.: 0.1803 g/l W, $N_H/f_W=1.5$, $\sim 12^\circ\text{C}$., 5 min., (ordinate: D.)

2. anion exchange extraction, 0.01 M TDA, aq.: 0.1803 g/l W, pH 1.24, $\sim 12^\circ\text{C}$., 5 min., (ordinate: log D.)

3. solvation extraction, 0.02 M primary amine N-1923, aq.: 0.190 g/l W, pH 3.91, $\sim 25^\circ\text{C}$., 10 min., (ordinate: log D.)

Fig. 2 Amount of W(VI) extracted by the mixture of tri-n-decyl amine and n-octanol as a function of the amount of acid added. aq.: 0.1803 g/l W, O/A=1, 10-17 $^\circ\text{C}$., 5 min., diluent: n-octane. org.: 1. 0.01 M TDA & 2% ROH; 2. 0.02 M TDA & 2% ROH 3. 0.0425 M TDA & 0.12 M ROH

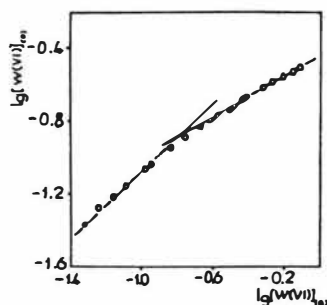
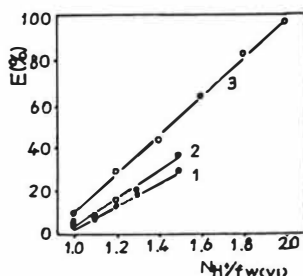


Fig. 3 Amount of W(VI) in the organic phase as a function of the amount of W(VI) in the aqueous phase at equilibrium. aq.: $N_H/f_W=1.5$, org.: 0.05 M TDA & 0.10 M n-octanol in $n\text{-C}_8\text{H}_{18}$ O/A=1, $\sim 18^\circ\text{C}$., 5 min.

Fig. 4 Effect of temperature on the distribution coefficient of W. aq.: 0.001 M W, $N_H/f_W=1.4$ O/A=1, 5 min. org.: 0.0987 M TOA & 0.10 M n-octanol in n-octane.



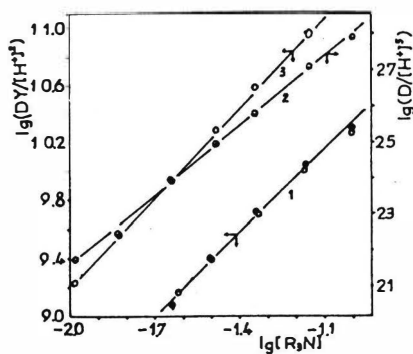


Fig. 5 Plot of $\log (DY/(H^+)^2)$ or $\log (D/(H^+)^5)$ vs. $\log (R_3N)$.
 aq.: 0.001 M W, O/A=1, 5 min.
 1. $N_{H^+}/f_W=1.0$, 0.15 M n-octanol, O-TOA, O-TDA, $\sim 25^\circ\text{C}$., (slope 1.9)
 2. $N_{H^+}/f_W=2.0$, 0.15 M n-octanol, O-TOA, $\sim 25^\circ\text{C}$., (slope 6.2)
 3. $N_{H^+}/f_W=1.5$, 0.20 M n-octanol, O-TOA, $26-27^\circ\text{C}$., (slope 2.1)

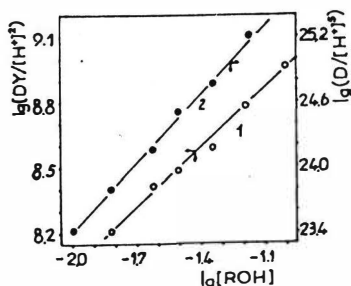


Fig. 6 Plot of $\log (DY/(H^+)^2)$ or $\log (D/(H^+)^5)$ vs. $\log (ROH)$.
 aq.: 0.001 M W, O/A=1, 5 min.
 1. $N_{H^+}/f_W=1.5$, 0.0104 M TOA, $26-27^\circ\text{C}$., (slope 0.9).
 2. $N_{H^+}/f_W=2.0$, 0.0297 M TOA, $\sim 28^\circ\text{C}$., (slope 2.1).

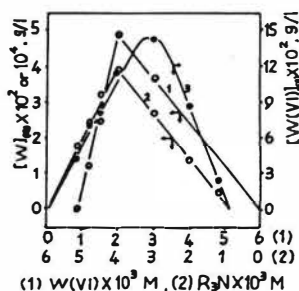
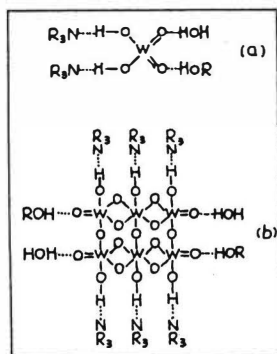


Fig. 7 Studies on the composition of the extraction species by the method of continuous variation (n-octanol=0.10 M)
 O/A=1, 5 min.
 1. $N_{H^+}/f_W=1.0$, $\sim 24^\circ\text{C}$., (ordinate $(W) \times 10^4$)
 2. $N_{H^+}/f_W=1.5$, $\sim 19^\circ\text{C}$., (ordinate $(W)_O \times 10^2$)
 3. $N_{H^+}/f_W=2.0$, $\sim 23^\circ\text{C}$.

Fig. 8 Schematic representation of the proposed synergistic extraction species of W(VI) with tertiary amine and alcohol.
 a. with small amount of acid added, $N_{H^+}/f_W \leq 1.5$,
 b. with large amount of acid added, $N_{H^+}/f_W=2.0$,
 (dotted line: H bond).



Method for Prediction of Equilibrium Values in Practical Solvent Extraction Systems
(Application to Ammoniacal-Copper Systems)

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Introduction. The development of more selective extractants has expanded greatly the consideration of and the use of solvent extraction in metal recovery processes. However, in many cases, the full capability of the extractant is not known and a great deal of experimental work is required to produce the necessary data so that process evaluation and optimization studies can be made. Some progress has been made at establishing extraction mechanisms and at predicting metal extraction from ammoniacal solutions (1-4). However, most models are limited in some respect, and a further need was recognized for a solvent extraction model that was applicable to practical systems, accurate, and easy to use. Toward these goals, fundamental research into the equilibrium modeling of the solvent extraction of metals has been pursued by the Bureau of Mines, U.S. Department of the Interior. As the first part of this research, the extraction of copper from ammoniacal solutions with LIX 64N was investigated. The primary goal of this research was to develop a mathematical model that could predict the equilibrium distribution of metal ions to within 5 pct of the actual concentrations. Additional goals of this effort were to develop a model that required only limited initial condition parameters and could accurately predict equilibrium values in practical situations, i.e., relatively high metal loading from high-ionic-strength solutions such as might be obtained in industrial leaching processes.

Experimental. Aqueous solutions were prepared from analytical grade reagents. The extractant (LIX 64N) and commercial kerosene (Kermac 470B) were used as-received without purification and were mixed as required to nominal concentrations of 1, 10, and 25 vol-pct extractant. As recommended by Ritcey (5), the solvents were conditioned before use. The effective concentration of extractant (RH_{TI}) within each solvent was determined through an "ultimate" loading capacity determination with copper. This type of determination is often used in commercial copper solvent extraction plants (6). The concentrations of the constituents in the feed liquors were chosen based upon available industrial data and the physical constraints of the systems (table 1).

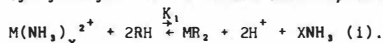
TABLE 1. - Range of concentrations used in feed liquors

Systems	Constituents' concentration range, mol/L, and pH range				
	Cu	NH ₄ T	SO ₄	CO ₂ T	pH
Cu-NH ₄ -SO ₄	0.002-0.25	0.2-7.8	0.1-2.4	NAP	7.23-9.78
Cu-NH ₄ -CO ₂04 - .24	1.2-8.1	NAP	0.7-2.2	7.89-10.22

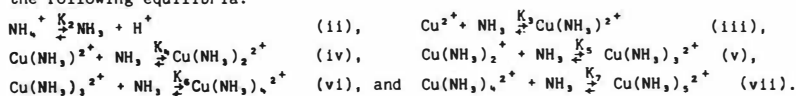
NAP Not applicable.

Shake-out tests were performed in separatory funnels that were shaken mechanically in a thermostatically controlled apparatus. In order to reduce the number of variables to be considered, the O/A ratio and temperature were held constant at 1 and $40^\circ \pm 1^\circ$ C, respectively. Equilibration in shake-out tests was allowed to proceed for 30 min, which was found to be more than sufficient to reach chemical and thermal equilibrium. In all cases, analytically determined equilibrium copper concentrations were checked by determining material balances; where necessary, slight adjustments were made. Duplicate and in some cases triplicate shake-out tests and analyses were made for some selected conditions. The estimated standard deviation for replicate tests was about 1 pct of the mean value of the extracted copper concentration. Partly because of the volatile nature of some of the aqueous components, comparison of pH measurements in replicate tests was found to be about 0.1 pH unit. However, the accuracy of the pH measurements was estimated to average ± 0.02 pH unit.

Chemistry of Systems. The extraction of divalent cations from ammoniacal solutions by hydroxyoximes has often been represented simply by



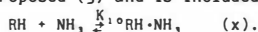
This equation shows the possible influence that H^+ and free NH_3 have on the extraction equilibrium. However, since this study was carried out under basic conditions and when considering only metal extraction, the H^+ ion effect can be essentially ignored in favor of the more important NH_3 concentration. The loading behavior of the $Cu-NH_3-SO_4-LIX$ 64N system was investigated in the initial studies. A series of tests was made by contacting solvent with aqueous solutions that had increasing copper concentrations. An "ideal loading curve" was generated for low through medium copper-loading levels on the solvent; i.e., essentially all of the copper in the aqueous phase was extracted by the solvent. However, as the solvent reached about 80 pct of its maximum loading, the extraction data deviated from the ideal curve. At that approximate level, the solvent loading did not increase at a constant proportion as the total copper in the system was increased; instead, it tapered off to a maximum loading level somewhat less than that measured in the "ultimate" loading capacity tests. Generally, the data indicated that the point of deflection from the "ideal loading curve" and the final solvent loading capacity were affected strongly by the free NH_3 concentration in the equilibrium raffinate. Higher free NH_3 concentrations usually indicated more NH_3 was coordinated with copper in the aqueous phase, resulting in suppression of copper extraction. These and other data indicated that complex interactions in the aqueous phase affected the extraction of copper. The aqueous chemistry of the ammoniacal-sulfate system can be represented by the following equilibria:



When considering the ammoniacal-carbonate system, additional equilibria must be considered:



Ignored in this model were complications such as dissolved CO_2 in the aqueous phase, and formations of $Cu-NH_3-Y$ complexes where Y may be HCO_3^- , NH_2COO^- , or similar compounds. Spectroscopic data indicated that complexes of this type were formed, but they could not be specially identified, and equilibrium constants were not available. An additional complicating reaction between the monomeric extractant and NH_3 has been proposed (3) and is included:



Equilibrium Constants and Expressions. In several cases literature values were adequate, but in other cases it was necessary to develop empirical expressions to describe equilibria in the high-ionic-strength solutions of this investigation. In the sulfate system the following expression was developed for reaction ii:

$$pK_2 = 9.476 + 0.2985 (\mu_1)^{0.5} \quad (\text{xi}),$$

where $pK_2 = -\log (K_2)$ @ $20^\circ C$. Literature values (8) were extrapolated to above ionic strength 2, and equations for $Cu-NH_3$ complex formations were developed from the extrapolated data. The equations that apply at $25^\circ C$ follow:

$$\begin{aligned} \log K_1 &= 4.04 + 0.10 \mu_1 & (\text{xii}), & \log K_4 = 3.42 + 0.10 \mu_1 & (\text{xiii}), \\ \log K_3 &= 2.79 + 0.10 \mu_1 & (\text{xiv}), & \log K_6 = 2.01 + 0.10 \mu_1 & (\text{xv}), \text{ and} \\ \log K_7 &= -0.75 + 0.10 \mu_1 & (\text{xvi}). \end{aligned}$$

These relationships fitted the measured average coordination number of $Cu-NH_3$ complexes in the high-ionic-strength sulfate solutions of this investigation. Where necessary, the values for the equilibrium constants were corrected to $40^\circ C$ with the van't Hoff equation using literature values (8) for ΔH 's. The $CO_3^{2-}-HCO_3^-$ equilibrium was measured, and a weighted average value from these data was selected for the equilibrium constant ($K_9 = 7.2 \times 10^9$ at $40^\circ C$). A literature value (1) was used for the equilibrium constant for NH_2COO^- formation ($K_5 = 2.2$ at $40^\circ C$). Linear regression analysis techniques applied to sulfate-system data produced an equilibrium constant ($K_{10} = 0.48$) that was appropriate for the $RH-NH_3$ equilibrium. Equilibrium constants based on the stoichiometry of reaction i and on variations of it were developed with data from the sulfate system. However, none of the tested forms was adequate to fit the data over a reasonable range of conditions. Therefore, statistical regression analyses of the data were made, and the following equation resulted:

$$CuR_2 = S (CuA)^{0.021} (NH_3)^{-0.097} (\mu_1)^{-0.009} \quad (\text{xvii}).$$

This equation had an estimated relative standard deviation of about 5 pct with the data it was developed from.

Supplemental Equations. A model based upon the above-mentioned relationships must deal primarily with equilibrium values, which usually are not available. A

reasonable approach for such a model involves the simultaneous solution of pertinent equations. A subroutine (ZSPOW) from the IMSL, Inc. library (9) was selected to solve the nonlinear system of this model. Additional equations were needed to balance the number of unknowns of the sulfate and carbonate systems. In the sulfate system, charge and material balances for NH_4^+ , Cu^{2+} , RH^+ , and an equation for the average coordination number were necessary. In the carbonate system, some modifications to the balances of the sulfate system were necessary to reflect the different chemistry involved. In addition, the average coordination number equation was replaced with a CO_2 material balance, and equilibrium equations viii and ix were included.

Model Flow Charts. A composite flow chart for the sulfate and carbonate computational models is shown in figure 1. The method of solution used by the ZSPOW subroutine is a local method; therefore, a successful solution depends on a good starting point. The initial estimates program provides estimated values for the required equilibrium variables from limited-initial-parameter inputs. Empirical correlations, conventional equilibrium expressions, and material balances were used to estimate the starting point. Scaling factors for the variables are generated in the programs so that the convergence criteria of the ZSPOW subroutine will function properly. In both models the μ_1 of the equilibrium raffinate was estimated and then used to adjust the pertinent equilibrium constants before final solution of the equations was accomplished.

Results and Discussion. The sulfate system model was developed using a 25-vol-pct LIX 64N extraction system; however, the model was found to apply equally well with 10-vol-pct and even reasonably well with 1-vol-pct extractants. The sulfate system model was appropriately modified and also applied successfully to the carbonate system. These models were tested with shake-out data produced over industrial-level ranges of aqueous components and with solvent-copper loadings ranging from about 25 pct up to near 100 pct of the maximum loading capacity of the solvent. With few exceptions, the models predicted the copper loadings on the solvent to within 5 pct of the measured values (figure 2) and predicted equilibrium pH values to within 0.1 to 0.3 pH unit of the measured values. Generally, the carbonate system model was not quite as accurate as the sulfate system model. In the sulfate system (with 10- and 25-vol-pct extractants), the average error in the predicted copper loading was 3.6 pct, and the average error in the predicted pH was 0.12 pH unit. Results from a typical comparison test are shown in table 2. In the carbonate system (with 10- and 25-vol-pct extractants), the average error in the predicted copper loading was 4.2 pct, and the average error in the predicted pH was 0.22 pH unit. The slightly reduced accuracy in the carbonate system model was likely caused by the previously mentioned aqueous phase complexities (e.g., Cu-NH_3 -Y complexes) that were not accounted for in the model. Of the separate 96 shake-out test comparisons made with these models, convergence on reasonable results was experienced in 85 cases (89 pct).

In certain cases, the models can converge, with very small negative values being reported for some aqueous copper species. In those cases, the final output from the models was adjusted so that values ≥ 0.0 were reported. In their present form, these models can be used in process optimization studies in applicable systems.

TABLE 2. - Typical comparison of predicted results and measured data (Cu-NH₃-SO₄-LIX 64N model)

Source of data	Principal equilibrium constituents, ¹ mol/L, where applicable								
	NH ₄ ⁺	NH ₃ free	RH·NH ₃	X	H ⁺	CuR ₂	RH free	CuA	pH
Predicted...	4.46	0.55	0.016	4.19	1.801x 10 ⁻⁹	0.163	0.06	9.37x 10 ⁻⁴	8.75
Observed....	² 4.4	.5	.02	4.05	1.34x 10 ⁻⁹	.16	² 0.06	4.2 x 10 ⁻³	8.87

¹Initial parameters (mol/L); solvent, $RH_{TI} = 0.40$, $CuR_{2I} = 2.0 \times 10^{-4}$; liquor, $CuA_I = 0.16$, $SO_4^{2-} = 2.2$, $NH_{4T} = 5.0$, $NH_{3I} = 0.3$.

²Determined by difference calculations.

Copies of these mathematical models can be obtained by writing to the authors. More complete and detailed reports concerning these models will be forthcoming. Continuing studies are underway to expand the range and utility of these models, and to investigate other metal extraction systems.

Notation List.

- O/A Organic to aqueous volume ratio
- NH_{4T} Equivalent total ammonia, includes NH_4^+ , NH_3 , + $Cu(NH_3)_2^+$ + NH_2COO^- , mol/L
- CO_{2T} Equivalent total carbon dioxide, includes CO_3^{2-} + HCO_3^- + NH_2COO^- , mol/L
- M Divalent metal such as Cu or Ni
- X Average coordination number of Cu-NH₃ complexes
- RH Free extractant in the solvent phase, mol/L
- K Equilibrium constant for reactions
- $RH \cdot NH_3$ Ammonia loaded on solvent phase, mol/L
- ν_I Ionic strength, $\nu_I = 1/2 \sum_i c_i z_i^2$
- c_i Concentration of i^{th} species in aqueous phase, mol/L
- z_i Charge of i^{th} species in aqueous phase
- CuR_2 Cu-extractant complex in solvent phase, mol/L
- S Constant, $S = 0.45(RH_{TI})$
- RH_T Total extractant concentration in solvent, includes CuR_2 + $RH \cdot NH_3$ + RH , mol/L
- CuA Total aqueous Cu species, may be either initial liquor or raffinate, mol/L
- Cu_T Total Cu in system, includes both phases, mol/L
- mol/L Mole per liter
- ΔH Enthalpy, kilojoule per mole
- I Subscripts refer to initial condition parameters, except does not apply to ionic strength term

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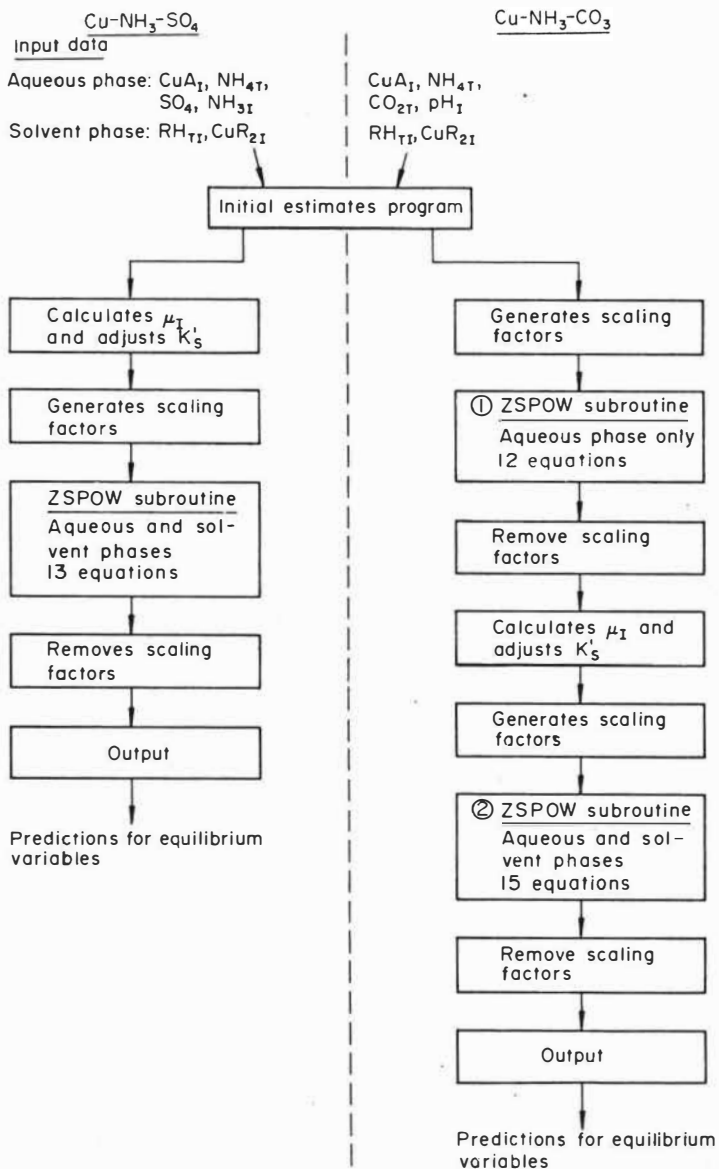


FIGURE 1. - Simplified Cu-NH₃-(SO₄ or CO₃)-LIX 64N model flow charts.

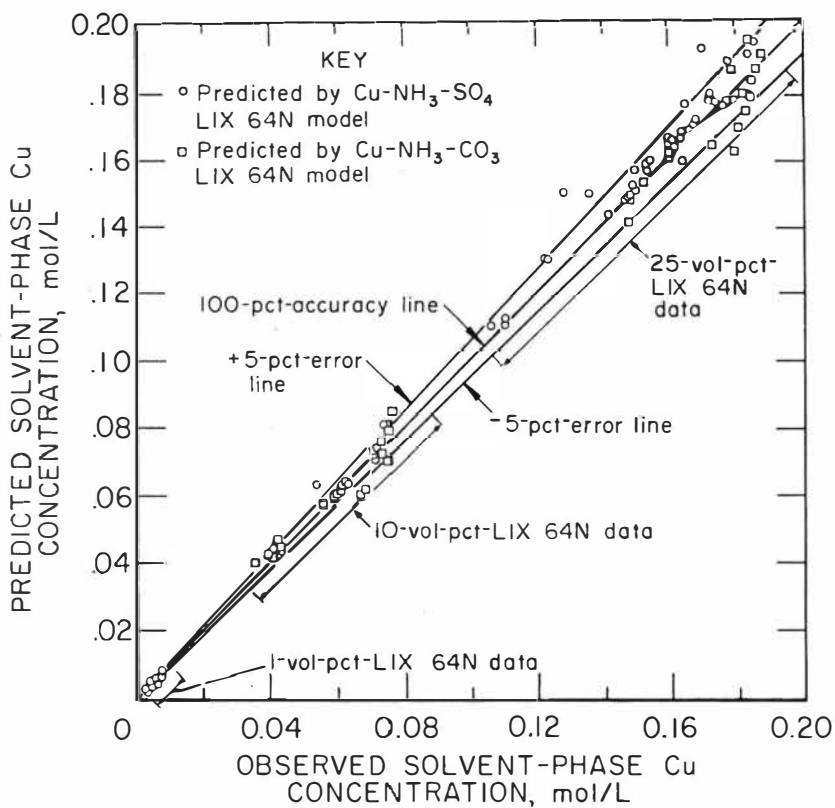


FIGURE 2. - Comparison of predicted results of copper loading versus observed results.

Separation of Gallium(III) from Strongly Alkaline Liquors by Extraction with 7-(4-Ethyl-1-methyloctyl)-8-quinolinol ("Kelex 100")-Impregnated Resins

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In recent years there has been an increased interest in the metal extraction from alkaline solutions. Among the various metals studied, the recovery of gallium either from the liquors formed in the Bayer process or from alkaline leach solutions of residual products formed during the refining of zinc has been extensively investigated. Several extractants have been proposed, but 8-quinolinol derivatives such as 7-(4-ethyl-1-methyloctyl)-8-quinolinol ("Kelex 100") were found to be particularly efficient for the liquid-liquid extraction of gallium(III) from high alkaline media [1-3]. Because the use of solid stationary phases for recovery of metal species is attractive, especially for the treatment of diluted solutions, we have decided to investigate in the present paper the possibility of gallium(III) recovery by 7-(4-ethyl-1-methyloctyl)-8-quinolinol-impregnated resins. Indeed, solvent-impregnated resins have attracted considerable attention since liquid ion-exchangers such as LIX 63 (an aliphatic alpha-hydroxyoxime), "Kelex 100", etc., and high specific area macroreticular adsorbents have become commercially available. The combination of appropriate extractants, adsorbents and eventually additives allows the formulation of efficient resins for both analytical and industrial purposes.

The first part of the paper deals with the treatment of typical aluminate solutions formed in the Bayer process. The influence of various parameters such as the amount of extractant loaded on the support, the presence of additives, the concentration of gallium(III) in the aluminate solution ($1.5 \text{ mol.L}^{-1} \text{ AlO}_2\text{Na}$, $3.5 \text{ mol.L}^{-1} \text{ NaOH}$) is reported. The influence of the nature of the macroporous support is also examined in a preliminary discussion. In the second part of the paper, the extraction of gallium(III) from alkaline solutions containing Zn(II) and Pb(II) is investigated.

Experimental

Reagents : 7-(4-Ethyl-1-methyloctyl)-8-quinolinol (HL) was isolated from "Kelex 100" (Shering) as previously reported [4]. The Amberlite XAD-2 and XAD-7 supports (Rohm and Haas Company) of practical grade quality were carefully washed with ethanol and water, and impregnated with HL in a classical way. Aqueous gallium(III) solutions were prepared from gallium oxide (Rhône-Poulenc Co). Versatic 10 and Versatic 911 acids (Shell) were used as delivered. The other reagents from Prolabo and Merck were all analytical grade.

Extraction and analytical procedures : The liquid-liquid experiments were carried out by shaking the mixture of aqueous and organic solutions inside a thermostated pear-shaped vessel the movement of which was reproducible (Agitelec equipment, Sté Ioulemonde et Cie, Paris). The solid-liquid extraction experiments were performed in the same way, but samples of impregnated resins were used instead of the organic solutions. After a given period of time, the two phases were separated and the metal cations remaining in the aqueous phase were titrated by atomic absorption with a Video II Instrument Laboratory spectrophotometer. In the case of the extraction experiments from the Bayer solutions ($1.5 \text{ mol.L}^{-1} \text{ AlO}_2\text{Na} + 3.5 \text{ mol.L}^{-1} \text{ NaOH}$), the non-aqueous phases (organic solutions or resins) were also analyzed. In this purpose, they were rinsed with water, then shaken with a $5 \text{ mol.L}^{-1} \text{ H}_2\text{SO}_4$ solution in which aluminium(III) and gallium(III) were totally stripped. The two metals recovered in this latter solution were titrated by atomic absorption.

Results and Discussion

The solvent-impregnated resins can be prepared by adsorption of liquid ion-exchangers (e.g. "Kexel 100") on a macroporous solid. The nature and the physical characteristics of this solid have been shown to have a great importance on the extractive behaviours of the resulting solvent-impregnated resins [5]. In figure 1, the yield of gallium(III) extracted at equilibrium has been plotted as a function of aqueous sodium hydroxide concentration for two typical commercially available adsorbents, Amberlite XAD-2 (polystyrene) and Amberlite XAD-7 (acrylic ester) and two concentrations of 7-(4-ethyl-1-methyloctyl)-8-quinolinol (HL), namely 0.3 and 0.7 g/g (gram of HL per gram of dry support). The aliphatic adsorbent (Amberlite XAD-7) gives much better results than the aromatic one (Amberlite XAD-2). The chemical nature of the two supports, more than the other parameters [porosity (ml/ml): (a) 0.42, (b) 0.55; surface area (m^2/g): (a) 330, (b) 450; average pore diameter (\AA): (a) 90, (b) 80 with (a) = Amberlite XAD-2 and (b) = Amberlite XAD-7], could be responsible of such a difference. Indeed, we have shown that 7-(4-ethyl-1-methyloctyl)-8-quinolinol is adsorbed on aliphatic Amberlite XAD-7 mainly by its alkyl chain [6], which is favourable to the extraction of metal cations since the quinolinol groups keep by this way a great mobility. On the other hand, in the case of Amberlite XAD-2 the existence of a strong interaction between the cycles of the support and those of HL cannot be precluded. Such an interaction might partially inhibit the extraction of metal cations both by its electronic effects and its tendency to reduce the mobility of the chelating groups.

Figure 1 also shows that there is a sharp decrease in the yield of extraction of gallium as soon as the concentration of sodium hydroxide exceeds about 3.5 mol.L^{-1} .

The work presented below shows further aspects of the extraction of gallium(III) by

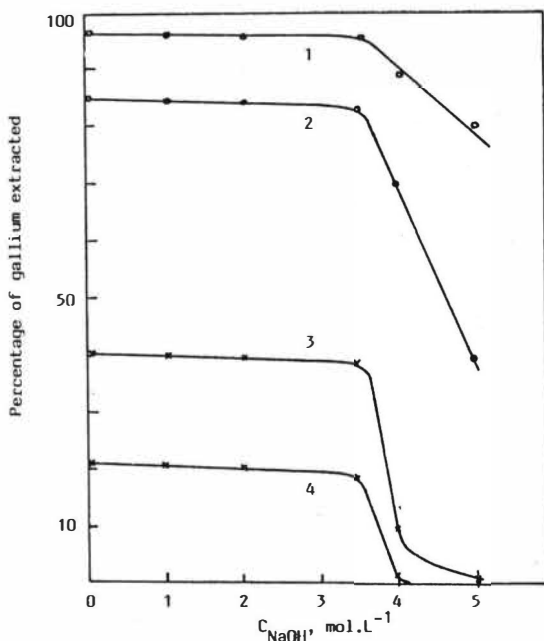


Figure 1 : Percentage of extraction of gallium(III) by 7-(4-ethyl-1-methyloctyl)-8-quinolinol-impregnated resins as a function of aqueous NaOH concentration, at equilibrium at 25°C.

(1) Amberlite XAD-7 with HL at 0.7 g/g; (2) Amberlite XAD-7 with HL at 0.3 g/g; (3) Amberlite XAD-2 with HL at 0.7 g/g; (4) Amberlite XAD-2 with HL at 0.3 g/g.

In all cases the ratio γ = number of moles of impregnated HL/number of moles of Ga(III) to be extracted was equal to 10.

7-(4-ethyl-1-methyloctyl)-8-quinolinol adsorbed on Amberlite XAD-7.

(1) Extraction of gallium(III) from aluminate solutions formed in the Bayer process

The liquid-liquid extraction of gallium(III) from alkaline media by "Kelex 100" in solution in a mixture of kerosene and long chain alcohols is efficient, but very slow since several hours are necessary to attain equilibrium. To improve the rate of extraction, the addition of long chain carboxylic acids (e.g. Versatic acids) has been recommended. In alkaline media, the presence of such compounds gives to the organic phase a structure of microemulsion, which considerably increases the rate of

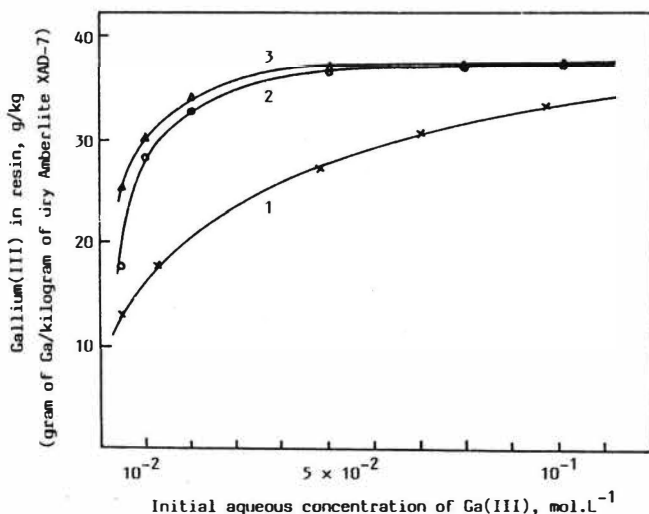


Figure 2 : Extraction of gallium(III) from aqueous solutions containing 1.5 mol.L^{-1} AlO_2Na + 3.5 mol.L^{-1} NaOH by various impregnated resins, at 25°C .
 (1) Amberlite XAD-7 with HL (0.55 g/g); (2) Amberlite XAD-7 with HL (0.55 g/g) + n-octanol (0.1 g/g); (3) Amberlite XAD-7 with HL (0.55 g/g) + n-decanol (0.1 g/g) + Versatic 911 acid (0.05 g/g).

phase transfer: in most cases the equilibrium can be obtained within less than two minutes [7]. Because of the existence of such a drastic influence, a special attention has been paid below to the potential effects of carboxylic acids on the extractive behaviours of "Kelex 100"-impregnated resins. The experimental results are reported in figures 2 to 5.

Figure 2 shows the extraction of gallium(III) from aqueous solutions containing 1.5 mol.L^{-1} sodium aluminate + 3.5 mol.L^{-1} sodium hydroxide and increasing concentrations of gallium(III). The presence of n-octanol or both n-octanol and Versatic 911 acid seems to improve the accessibility of the molecules of 7-(4-ethyl-1-methyloctyl)-8-quinolinol, but does not significantly modify their asymptotic capacity towards gallium(III). In figure 3, the relative extraction of gallium(III) and aluminium(III) from aluminate solutions is considered. Examination of the various curves, including the one concerning a liquid-liquid system, does not show any dramatic difference in the selectivity of the extraction of gallium(III) towards aluminium(III). However, it can be noticed that for the aluminate solutions containing gallium(III) at low concen-

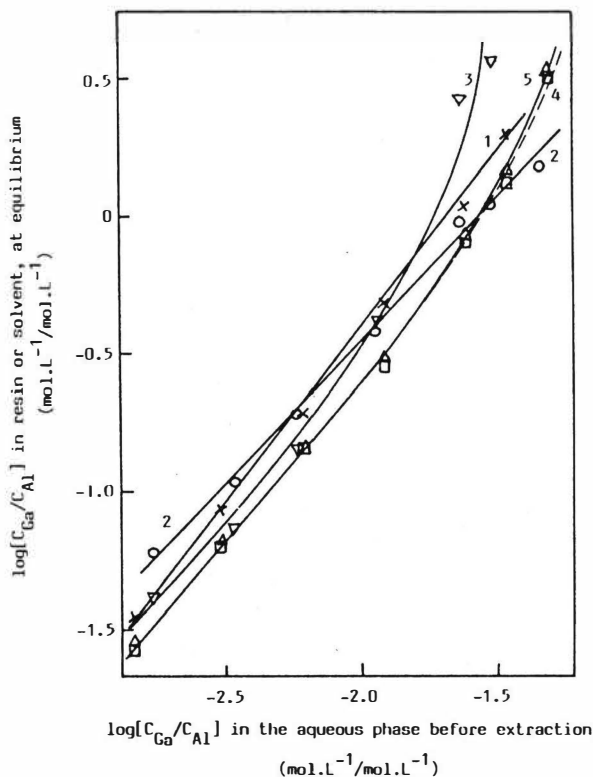


Figure 3 : Relative extraction of Ga(III) and Al(III) from aqueous solutions containing $1.5 \text{ mol.L}^{-1} \text{ AlO}_2\text{Na} + 3.5 \text{ mol.L}^{-1} \text{ NaOH}$ and increasing concentrations of Ga(III), at equilibrium at 25°C .

(1) Liquid-liquid system ($V_{\text{aq}}/V_{\text{org}} = 1$); organic phase: HL (80 g/L) + n-decanol (100 g/L) + Versatic 10 (50 g/L) in kerosene; (2) Amberlite XAD-7 with HL (0.3 g/g); (3) Amberlite XAD-7 with HL (0.6 g/g); (4) Amberlite XAD-7 with HL (0.3 g/g) + n-decanol (0.15 g/g) + Versatic 10 (0.075 g/g); (5) Amberlite XAD-7 with HL (0.6 g/g) + n-decanol (0.19 g/g) + Versatic 10 (0.09 g/g).

In all cases 1.2 g of HL (in solution or adsorbed) was used for the treatment of 15 ml of aqueous phase.

Figure 4

Fraction α of metal extracted by various impregnated resins as a function of time, at 25°C.

- (1) Al(III); Amberlite XAD-7 with HL ($[X]$ 0.3 g/g and $[O]$ 0.55 g/g
- (2) Ga(III); Amberlite XAD-7 with HL (0.55 g/g) + n-decanol (0.1 g/g) + Versatic 911 (0.05 g/g)
- (3) Ga(III); Amberlite XAD-7 with HL (0.55 g/g) + n-octanol (0.1 g/g)
- (4) Ga(III); Amberlite XAD-7 with HL (0.55 g/g).

Initial aqueous phase: Ga(III) $[1.4 \times 10^{-2} \text{ mol.L}^{-1}]$ + Al(III) $[1.5 \text{ mol.L}^{-1}]$ + NaOH $[3.5 \text{ mol.L}^{-1}]$.

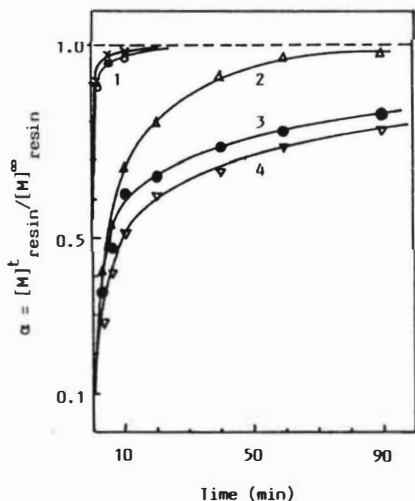


Figure 5

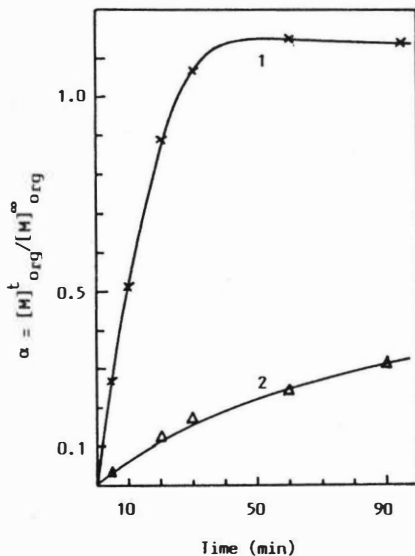
Fraction α of metal extracted by an organic solution of "Kelex 100" as a function of time, at 25°C ($V_{aq}/V_{org} = 1$).

- (1) Al(III); (2) Ga(III)

Initial conditions:

Organic phase: HL (40 g/L) + n-octanol (80 g/L) in kerosene.

Aqueous phase: Ga(III) $[1.4 \times 10^{-2} \text{ mol.L}^{-1}]$ + Al(III) $[1.5 \text{ mol.L}^{-1}]$ + NaOH $[3.5 \text{ mol.L}^{-1}]$.



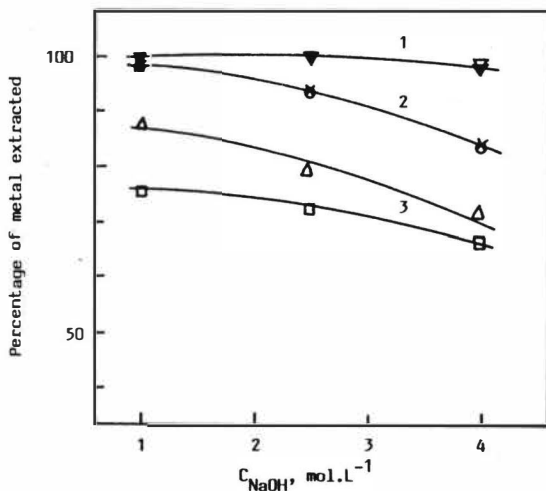


Figure 6 : Percentage of extraction of Pb(II), Zn(II) and Ga(III) by 7-(4-ethyl-1-methyloctyl)-8-quinolinol-impregnated resins as a function of aqueous NaOH concentration, at 25°C.

(1) Pb(II) 2.0 g/L; [∇] R₁, [∇] R₂; (2) Ga(III) 0.5 g/L; [\times] R₁, [\circ] R₂; (3) Zn(II) 1.0 g/L [Δ] R₁, [\square] R₂.

R₁ = Amberlite XAD-7 with HL (0.35 g/g), R₂ = Amberlite XAD-7 with HL (0.63 g/g). In all cases, 0.14 g of HL was used for the treatment of 10 ml of aqueous phase.

tration ($C_{Ga} < 10^{-2}$ mol.L⁻¹) the Amberlite XAD-7 resin moderately loaded with HL (0.3 g/g) gives the highest selectivity coefficients (curve 2). In figures 4 and 5, the dimensionless organic concentration α has been plotted as a function of the contact time for impregnated and liquid-liquid systems, respectively ($\alpha = [Ga(III)]^t_{org/resin} / [Ga(III)]^\infty_{org/resin}$, where $[Ga(III)]^t_{org/resin}$ represents the concentration of the gallium extracted after time t and where $[Ga(III)]^\infty_{org/resin}$ denotes its concentration at the equilibrium). Examination of these two figures shows that in the two cases, Al(III) is much more rapidly extracted than Ga(III). It can also be observed that the chelation of the two metal species is more rapid in impregnated system (figure 4) than in liquid-liquid system (figure 5), unless the organic phase has the structure of a microemulsion since in this latter case the equilibrium is generally reached within two minutes for both Al(III) and Ga(III). Comparison of curves 2,3 and 4 in figure 4 exhibits that the coimpregnation of additives such as alcohols and Versatic

911 with "Kelex 100" increases the fixation rate of gallium(III). Nevertheless the kinetics remains rather slow. Indeed, after reaction with the most external molecules of HL, gallium(III) must diffuse inside the pores of the macroreticular support before its chelation and such a diffusion is probably the limiting step of the process. However, we have observed that this kinetics is acceptable when the "Kelex 100"-impregnated resins are used in columns at 40 - 50°C.

(2) Extraction of gallium(III) from alkaline solutions containing Zn(II) and Pb(II)

The extraction of zinc(II), lead(II) and gallium(III) from sodium hydroxide solutions by two 7-(4-ethyl-1-methyloctyl)-8-quinolinol-impregnated resins is shown in figure 6. As a result, it is seen that these three metals are efficiently extracted by impregnated "Kelex 100". I. Sato et al. [2] found similar results with 7-(5,5,7,7-tetramethyl-1-octen-3-yl)-8-quinolinol (HQ) in kerosene and showed that Zn(II), Pb(II) and Ga(III) are extracted as ZnQ_2 , PbQ_2 and GaQ_3 , respectively. From a practical point of view, we can conclude that "Kelex 100" allows the global recovery of zinc, lead and gallium, but not their selective separation.

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Introduction

Extraction systems where a mixture of diisopropyl ether (IPE) and n-alcohol appears as solvent and hydrochloric acid as aqueous medium are interesting because of the formation of three liquid phases and synergistic enhancement of extraction.

The formation of the three-phase system has been recently observed in the system $\text{HCl-H}_2\text{O-IPE-n-pentyl alcohol}$ (metal not present) at certain initial concentration of hydrochloric acid and alcohol (as component of solvent mixture) (1). A strong dependence of equilibrate phase volumes and even of a number of co-existing phases upon temperature was also found in this system.

Excellent efficiency of extraction of tetrachlorometallic acids with IPE at a high initial concentration of hydrochloric acid under conditions of the third liquid phase (heavy organic phase) formation is well known (2-9). However at lower initial concentrations of hydrochloric acid the efficiency of pure IPE as extractant significantly decreases. Under such conditions it is possible to obtain good efficiency of extraction if mixed solvent IPE-n-alcohol is used. A preliminary examination of the distribution of the metals forming tetrachlorometallic acids under different experimental conditions by paper chromatography (10) and of the extraction (11) carried out in the system $\text{FeCl}_3\text{-HCl-H}_2\text{O-IPE-n-alcohol}$ with $\text{C}_1\text{-C}_5$ alcohols shows that the most interesting system is the one including n-pentyl alcohol. n-Pentyl alcohol is the lowest among n-alcohols whose mixture with IPE along the whole range of volume ratios of the binary mixture is heterogeneous (1). This allows to define the distribution ratio of extraction with pure alcohol and so to calculate the synergistic effect according to expression $\Delta D = D_M - (D_{\text{IPE}} + D_{\text{alc}})$ where ΔD is synergistic enhancement of extraction, and D_M , D_{IPE} , D_{alc} are distribution ratios of extraction with the solvent mixture, IPE and alcohol respectively. It has been confirmed by more detailed investigations that the addition of n-pentyl alcohol to IPE under given conditions causes a synergistic enhancement of extraction (1, 12, 13). Therefore it seems promising to extend the investigation of extraction to systems containing the next higher n-alcohol i.e. n-hexyl alcohol.

In this paper are presented the results of an investigation of systems $\text{HCl-H}_2\text{O-IPE-n-hexyl alcohol}$ (I) and $\text{FeCl}_3\text{-HCl-H}_2\text{O-IPE-n-hexyl alcohol}$ (II). In system I the influence of temperature (15-40 °C at the initial acid concentration of 6.6-9.1 mol.dm⁻³ and initial alcohol concentration of 5-30 % vol.) on phase transformation

was investigated, as well as the influence of initial acid concentration ($6.6\text{--}9.1 \text{ mol}\cdot\text{dm}^{-3}$) and initial alcohol concentration ($5\text{--}30 \text{ \% vol.}$) at 20°C on the phase volume and acid distribution. In system II the influence of alcohol concentration ($10\text{--}90 \text{ \% vol.}$) at three levels of acid concentration ($1.0, 3.0$ and $5.1 \text{ mol}\cdot\text{dm}^{-3}$) at 20°C on the volume of equilibrate phases and iron(III) distribution was studied.

Experimental

Materials.

IPE, Fluka or Merck, C.P. was purified, distilled and dried. Purification was achieved with successive treatments by ferrous sulphate, potassium permanganate and sodium hydroxide. After washing with water it was distilled and the middle fraction (bp. $66.8\text{--}67.8^\circ\text{C}$) was collected. The IPE prepared in this way contained $1.9 \text{ mg H}_2\text{O}\cdot\text{cm}^{-3}$. n-Hexyl alcohol used was The British Drug Houses, p.a. ($n_D^{20} 1.417\text{--}1.419$). Other chemicals used were of analytical reagent grade.

Procedure.

The separations were made in 15 mL graduated cuvettes which were selected from a large group in order to assure accurate volume calibrations. The systems were prepared by vigorous shaking of components and placed in a water bath with a thermostat kept by automatic control at $t \pm 0.05^\circ\text{C}$. The shaking was repeated in the same manner at 15-min intervals for 1 h . The initial volume ratio of the organic phase to the aqueous phase (r^1) was always 1.0 . The volumes of the equilibrated phases were determined before sampling.

Methods of Analysis.

The concentration of hydrochloric acid in the samples of aqueous and organic phases was determined by acid-base titration (phenolphthalein end point). Samples of organic phases were diluted in a suitable quantity of water (approximately $1:20$) without previous treatment. The concentration of iron(III) in the samples of aqueous phase and in the pretreated samples of organic phases was determined by complexometric titration using Titriplex III and 2-oxy-5-sulphobenzoic acid as indicator.

Results and Discussion

The strong influence of temperature on extraction systems containing IPE observed in previous investigation (14, 15) was also found during examination of $\text{HCl-H}_2\text{O-IPE-n-hexyl alcohol}$ system where initial acid concentration (C_{HCl}^1) was varied from 6.6 to $9.1 \text{ mol}\cdot\text{dm}^{-3}$ and alcohol concentration in mixed solvent (c_{alc}^1) from 5 to 30 \% vol. in the temperature range from 15 to 40°C . Results are given in Table 1. At initial acid concentration $C_{\text{HCl}}^1 = 6.6$ and $7.1 \text{ mol}\cdot\text{dm}^{-3}$ in a full range of initial alcohol concentration as well as at initial alcohol

Table 1

Number of coexisting liquid phases in the system: $\text{HCl} - \text{H}_2\text{O} -$
 n -hexyl alcohol in the temperature range from 15 to 40 °C*

c_{HCl}^i (mol.dm ⁻³)	Initial alcohol concentration c_{alc}^i (% vol.)					
	5	10	15	20	25	30
6.6	2	2	2	2	2	2
7.1	2	2	2	2	2	2
7.6	2	3 → 2 (15-19 °C)	2	2	2	2
8.1	2	2 → 3 → 2 (15-19-30 °C)	3 → 2 (20-25 °C)	3 → 2 (15-19 °C)	2	2
8.6	2	2 → 3 → 2 (20-25-40 °C)	2 → 3 → 2 (15-19-35 °C)	3 → 2 (25-30 °C)	2	2
9.1	2	2 → 3 (35-40 °C)	2 → 3 (25-30 °C)	1 → 2 → 3 (15-19-25 °C)	1 → 2 (15-19 °C)	2

* 3 → 2 - three-phase system transfers in the two-phase system
 or due to an increase of temperature (at temperatures
 2 → 3 given in parentheses) or vice versa

1 → 2 - homogeneous system transfers in the two-phase system
 due to an increase of temperature (at temperatures
 given in parentheses)

Initial phase volume ratio $r^i = 1.0$.

concentration $c_{\text{alc}}^i = 5, 25$ and 30 % vol. in a full range of acid concentrations the systems were two-phase ones. The influence of temperature on the formation of three-phase systems and on the transformation of two-phase systems to three-phase ones and vice versa was established at higher acid concentrations (7.6-9.1 mol.dm⁻³). Especially interesting are systems with initial acid concentration $c_{\text{HCl}}^i = 8.1$ and 8.6 mol.dm⁻³ and initial alcohol concentration $c_{\text{alc}}^i = 10$ % vol. as well as systems with $c_{\text{HCl}}^i = 8.6$ mol.dm⁻³ and $c_{\text{alc}}^i = 15$ % vol. These systems, by increase of temperature, transform from two-phase to three-phase ones and then again back to two-phase systems. A homogeneous system with initial concentrations

$c_{\text{HCl}}^i = 9.1$ and $c_{\text{alc}}^i = 20$ % vol. by a temperature rise of only 10°C (i.e. from 15 to 25°C) transforms to a two-phase one and finally to a three-phase system.

Figure 1 shows the influence of acid concentration on phase volume fractions at 20°C at three levels of alcohol concentration. Volume changes of equilibrate phase at higher acid concentrations (over $8.1 \text{ mol}\cdot\text{dm}^{-3}$) or under conditions of three phase formation are very strong.

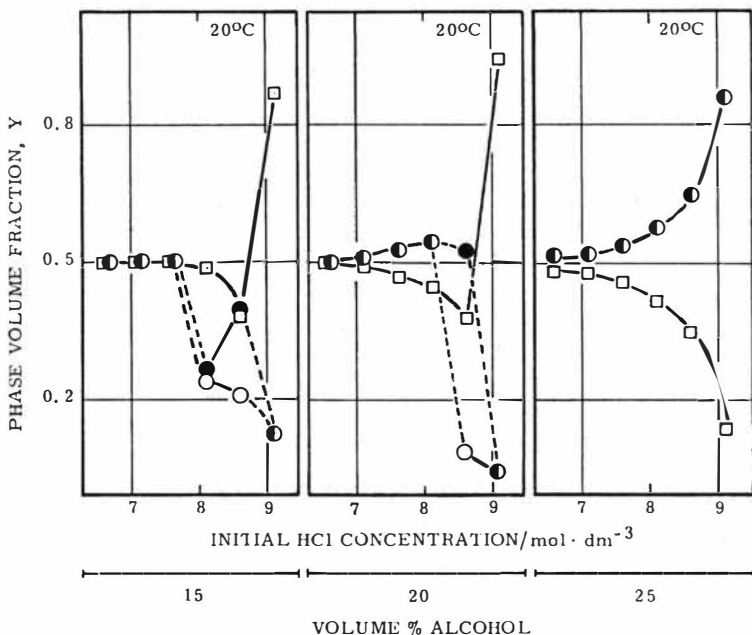


Figure 1. Volume fraction of equilibrated phases vs. the initial acid concentration at different initial concentration of alcohol. System: $\text{HCl-H}_2\text{O-IPE-n-hexyl alcohol}$. Initial phase volume ratio $r^i = 1.0$. Aqueous phase - □, organic phase - ●, light organic phase - ○, heavy organic phase - ●.

The change of hydrochloric acid concentration in organic phases as a result of the influence of initial acid concentration at 20°C is given in Figure 2. At initial alcohol concentration $c_{\text{alc}}^i = 10$ % vol. and initial acid concentration $c_{\text{HCl}}^i = 8.1 \text{ mol}\cdot\text{dm}^{-3}$ (Fig. 2a) the third (heavy organic) phase appears which

contains more than a 16 times higher concentration of acid than the light organic phase. This concentration is at the same time about 80 times higher than the acid concentration in the system with pure IPE under equal other experimental conditions (16). At a higher initial concentration of alcohol, $c_{\text{alc}}^i = 25\% \text{ vol.}$, (Fig. 2b) the third phase does not appear and acid concentration in the organic phase does not reach a maximum value but increases with increase in initial acid concentration.

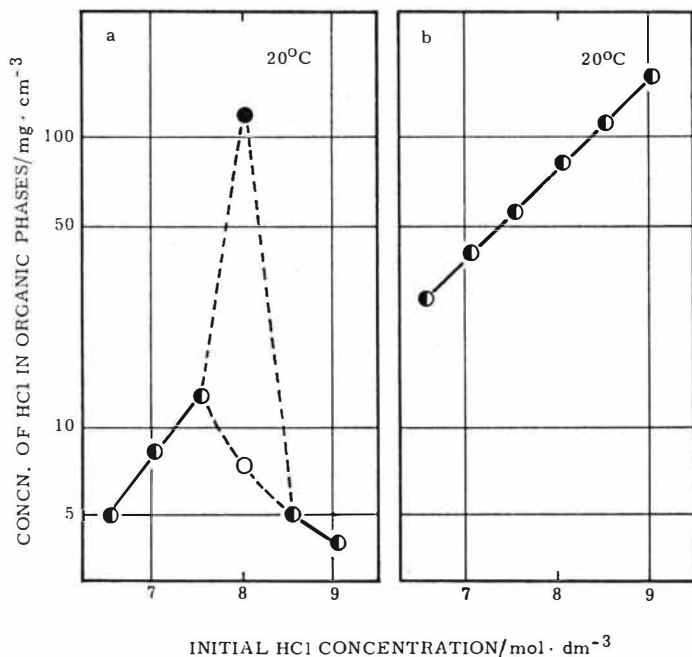


Figure 2. Concentration of hydrochloric acid in the equilibrated organic phases vs. the initial concentration of acid. System: $\text{HCl-H}_2\text{O-IPE-n-hexyl alcohol}$. Initial concentration of alcohol $c_{\text{alc}}^i = 10\% \text{ vol.}$ (a) and $25\% \text{ vol.}$ (b). Initial phase volume ratio $r^i = 1.0$. Organic phase - \bullet , light organic phase - \circ , heavy organic phase - \bullet .

The change of hydrochloric acid concentration in organic phases as a result of the influence of initial alcohol concentration at 20°C is given in Figure 3. At initial acid concentration $c_{\text{HCl}}^i = 7.1 \text{ mol}\cdot\text{dm}^{-3}$ acid concentration in the organic phase increases with the increase of initial alcohol concentration (Fig. 3a). At initial acid concentration $c_{\text{HCl}}^i = 8.1 \text{ mol}\cdot\text{dm}^{-3}$ enhanced extraction

appears to be the result of third phase formation. Excluding the effect caused by the appearance of the third phase higher initial concentrations of acid and alcohol contribute to acid extraction.

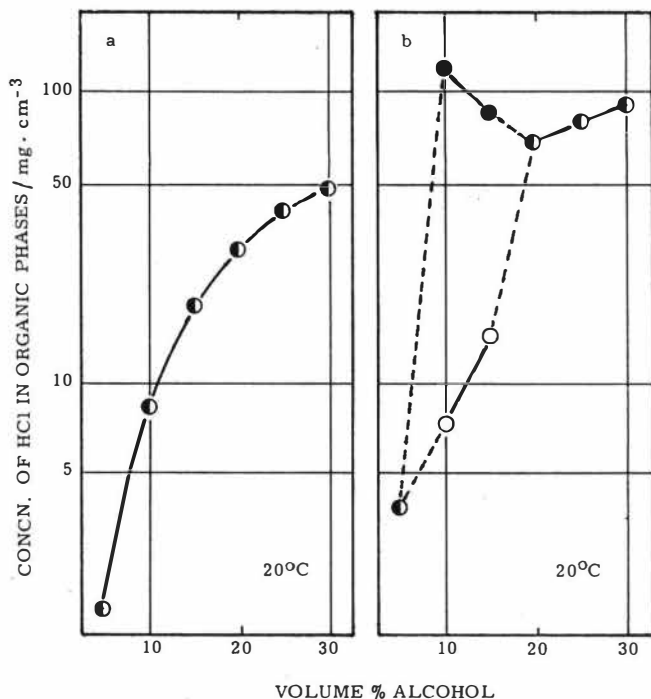


Figure 3. Concentration of hydrochloric acid in the equilibrated organic phases vs. the initial concentration of alcohol. System: $\text{HCl}-\text{H}_2\text{O}-\text{IPE}-n\text{-hexyl alcohol}$. Initial concentration of acid $c_{\text{HCl}}^1 = 7.1 \text{ mol} \cdot \text{dm}^{-3}$ (a) and $8.1 \text{ mol} \cdot \text{dm}^{-3}$ (b). Initial phase volume ratio $r^1 = 1.0$. Organic phase - ● , light organic phase - ○ , heavy organic phase - ● .

In spite of this the acid distribution ratios are not very high as is seen from Figure 4. This is the result of high acid concentration in the aqueous phase. However, the partial distribution ratio between the heavy organic phase and the aqueous phase in the system mentioned above ($c_{\text{HCl}}^1 = 8.1 \text{ mol} \cdot \text{dm}^{-3}$, $c_{\text{alc}}^1 = 10 \text{ \% vol.}$) is also 80 times higher than in the system with pure IPE. The distribution ratio of any two-phase system presented in Figure 4 is even higher than the distribution ratio

in the system with pure IPE (e.g. D_c in the system defined by $c_{HCl}^i = 8.1 \text{ mol.dm}^{-3}$, $c_{alc}^i = 20 \text{ \% vol.}$ is over 44 times higher).

The existence of the synergistic effect of mixed solvent IPE-n-hexyl alcohol was examined in systems containing $0.147 \text{ mol.dm}^{-3}$ of iron(III) in the initial aqueous phase. The initial acid concentration was $c_{HCl}^i = 1.0, 3.0$ and 5.1 mol.dm^{-3} and the initial alcohol concentration varied from 10 to 90 % vol. at 20°C .

At a low initial concentration of acid, $c_{HCl}^i = 1.0 \text{ mol.dm}^{-3}$, extraction of iron(III) was very poor and distribution ratios did not exceed a value of 0.01. With increase in initial acid concentration extraction improved as shown in Figure 5. In both cases ($c_{HCl}^i = 3.0$ and 5.1 mol.dm^{-3}) the synergistic effect was evident and enhancement of extraction had a maximum at initial alcohol concentration $c_{alc}^i = 40 \text{ \% vol.}$ The values of the synergistic effect calculated according to the expression in the introduction were 0.77 and 9.2.

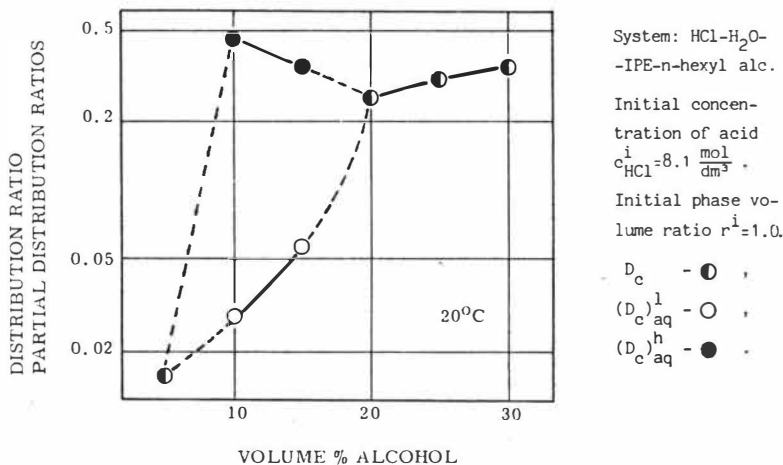


Figure 4. Distribution ratio (D_c) and partial distribution ratios ($(D_c)_{aq}^1$ and $(D_c)_{aq}^h$) vs. the initial concentration of alcohol

Acknowledgment

This work was performed with support of the Self-Management Council for Scientific Research of S.R. Croatia.

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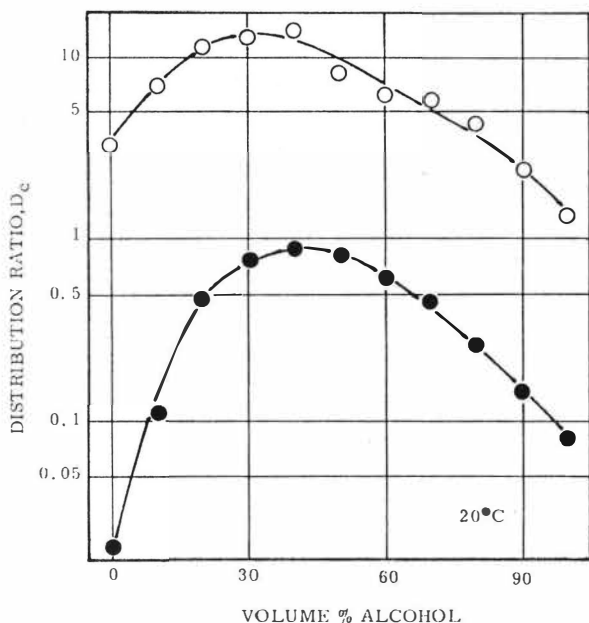


Figure 5. Distribution ratio of iron(III) vs. the initial concentration of alcohol.

System: $\text{FeCl}_3\text{-HCl-H}_2\text{O-IPE-n-hexyl alcohol}$. Initial phase volume ratio $r^1 = 1.0$. Initial acid concentration c_{HCl}^1 : 3.0 mol.dm^{-3} - ● , 5.1 mol.dm^{-3} - ○ .

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Solvent extraction of d transition metals using cationic exchanges and polyimines

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Abstract will be available in Munich

Properties of Bis(4-acylpyrazol-5-ones) in Liquid-Liquid Extraction Systems.

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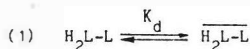
Since Jensen (1) emphasized the great interest of 4-acylpyrazol-5-ones as extractive agents, their properties in two-phase systems have been extensively studied(2). Like β -diketones, they are acidic chelating compounds but they have lower pK_a . Their synthesis is easy and consists in the one-step reaction of an acid chloride with a pyrazol-5-one in dioxan solution in the presence of $Ca(OH)_2$ (1). By using a bis (acid chloride), $ClCO-(CH_2)_n-COCl$, a bis (4-acylpyrazol-5-one) with two acidic chelating groups, separated by n methylen groups, may be obtained (3).

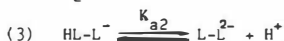
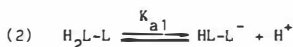
The behaviour of these complexing and extracting agents towards metal cations is expected to depend on the length of the hydrocarbon chain between the two active parts of the molecule :

- if $n \leq 7$, the coordination of the four oxygen donor atoms of the bis(acylpyrazolone) on the same metal atom is unlikely and polynuclear metal species are expected to be extracted,
- if $n \geq 8$, the length is then sufficient to allow a folding of the extractant and its tetracoordination to a single metal atom : on this assumption, the ligand would closely surround the extracted metal, which might decrease its hydration. Of course, the extraction of polynuclear species remains possible.

The present work supports these hypotheses. It deals with the extractions of $Cu(II)$, $Zn(II)$, $Co(II)$ and $In(III)$ from 1M $(Na,H)ClO_4$ solutions at 25°C with the bis(acylpyrazolones) H_2L-L and $H_2L'-L'$ (fig.1) in chloroform or toluene.

Dissociation and distribution equilibria of H_2L-L . The distribution coefficient of H_2L-L , d , between a $(Na,H)ClO_4$ 1M aqueous solution and $CHCl_3$ is defined from equilibria 1,2 and 3 :



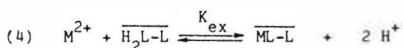


$$d = \frac{[\text{H}_2\text{L-L}]}{([\text{H}_2\text{L-L}] + [\text{HL-L}^-] + [\text{L-L}^{2-}])}^{-1}$$

K_d has been determined at low pH (where $d = K_d$) by spectrophotometric measurements, and the value of $K_{a1}K_{a2}K_d^{-1}$ estimated from a two-phase acido-basic titration.

From these data, the following values are obtained : $\log K_d \sim 4.3$ and $-\log (K_{a1}K_{a2})^{1/2} \sim 6.5$, to be compared to the pK_a of the parent compound HPMBP : $\text{pK}_a \sim 4$ (2).

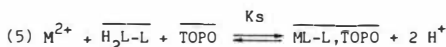
Extraction of copper (II) with $\text{H}_2\text{L-L}$. The slopes of the distribution curves $\log D$ vs pH and $\log D$ vs $\log [\text{H}_2\text{L-L}]$ (fig. 2, 3), 2 and 1 respectively, show that copper is extracted as CuL-L . No effect of the copper concentration (from 0.15 to $1.5 \cdot 10^{-3}\text{M}$) was observed, which indicates the extraction of mononuclear species, according to (4).



with $\text{M} = \text{Cu}$, $\log K_{\text{ex}} = 0.05$ (toluene) and -0.35 (CHCl_3).

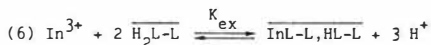
For the same normality of the extractants, the extraction of copper is better with $\text{H}_2\text{L-L}$ than with HPMBP in spite of the higher acidity of the latter (fig. 2, 3) : it may be explained by the low hydration of CuL-L compared to that of Cu(PMBP)_2 , due to the tetracoordination of L-L^{2-} on the same copper atom. No synergic effect was observed in the presence of TOPO whereas $\text{CuL}_2\text{,TOPO}$ species are usually extracted with single acylpyrazolones HL (4), which strongly supports this assumption.

Synergic extractions of cobalt (II) and zinc (II) with $\text{H}_2\text{L-L}$ and TOPO in CHCl_3 . The extractions of Co and Zn with $\text{H}_2\text{L-L}$ alone in CHCl_3 are limited by a third-phase formation. $\log K_{\text{ex}} \sim -6.8$ (equilibrium 4) has been estimated for $\text{M} = \text{Zn}$. If TOPO is added to the $\text{H}_2\text{L-L}$ chloroform solution, the third phase disappears and a synergic extraction is observed, following the equilibrium (5)



determined from experimental distribution curves $\log D$ vs pH or $\log [\overline{H_2L-L}]$ or $\log [\overline{TOPO}]$. $\log K_s = -3.23$ and -5.10 for $M = Zn$ and Co respectively. The stoichiometry of $\overline{ZnL-L, TOPO}$ is in agreement with the usual pentacoordination of $Zn(II)$. Generally, in the presence of \overline{TOPO} , $Co(II)$ is extracted with simple acylpyrazolones HL as $\overline{CoL_2(TOPO)_2}$: in the present case, a steric hindrance due to the folding of $L-L^{2-}$ around Co prevents it from the coordination of a second $TOPO$. The difference $\log K_s(Zn) - \log K_s(Co)$ (~ 2) may be explained by the different lipophilicities of the extracted species. It indicates the presence of H_2O in the cobalt species.

Extraction of indium (III) with H_2L-L or $H_2L'-L'$ in toluene or $CHCl_3$. Owing to its valency, the extraction of one In^{3+} cation requires at least 1.5 bis(acylpyrazolone). That means that at least one acidic chelating group remains free or may be coordinated to a second indium atom. Thus, the analysis of the extraction curves is undoubtedly difficult. Nevertheless, equilibrium (6) describes the In extraction from perchlorate medium at low pH and high extractant/metal ratio:



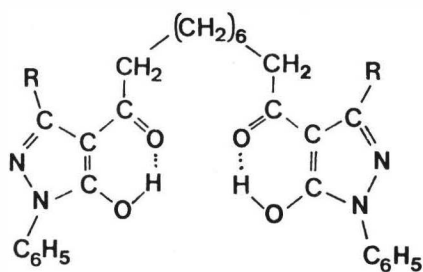
with $\log K_{ex} = 1.4, 1.0$ and 1.1 for the H_2L-L /toluene, $H_2L-L/CHCl_3$ and $H_2L'-L'$ /toluene systems respectively.

By increasing pH and (or) decreasing the extractant/metal ratio, K_{ex} increases showing the inadequacy of equilibrium (6): the stoichiometry of the extracted species tends towards 1.5 and polynuclear species are extracted. This is supported by the distribution curves and the elementary analysis of solid complexes crystallized from the organic phases.

In most cases, bis(acylpyrazolones) are better extractants than the single ones (i.e. HPMBP). This is mainly due to the possibility of its tetracoordination on a single metal atom but also to the formation of polynuclear species. Their low solubility in usual diluents will certainly limit their industrial use in solvent extraction but they remain promising ligands if they are bound on polymeric matrices.

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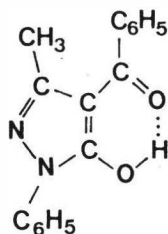
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$H_2 L-L$: $R = CH_3$

$H_2 L'-L'$: $R = C_6H_5$

1,10 - bis[1-phenyl-3-(methyl or phenyl)-5-hydroxyl-4-pyrazolyl]-1,10-decanedione.



= **HPMBP**

1-phenyl-3-methyl-4-benzoylpyrazol-5-one (enol).

TOPO = tri-n-octylphosphine oxide.

Figure 1 : The extractants

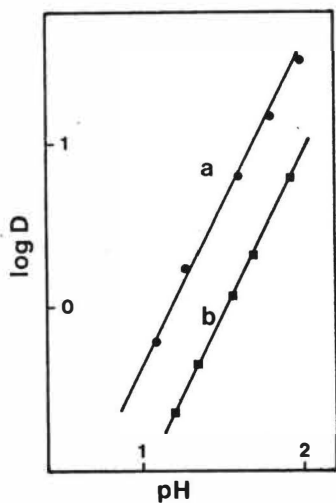


Figure 2 : Extraction of Cu with a) - $\text{H}_2\text{L-L}$ 0.01M and
b) - HPMBP 0.02M in CHCl_3 : log D vs pH (slopes 2)

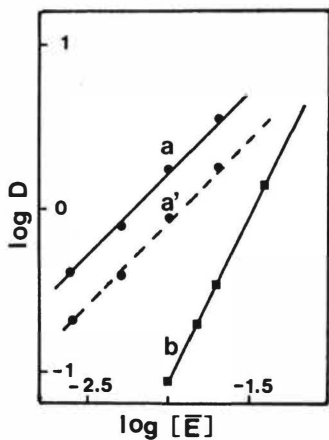


Figure 3 : Extraction of Cu with $\text{H}_2\text{L-L}$ or HPMBP in CHCl_3 (pH = 1.28) :
a) $[\bar{\text{E}}] = [\text{H}_2\text{L-L}]$, slope 1
a') $[\bar{\text{E}}] = 1/2[\text{H}_2\text{L-L}]$, slope 1
b) $[\bar{\text{E}}] = [\text{HPMBP}]$, slope 2.

Structural Effects of Organic Ligand in Metal Extraction

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The role of solvent extraction has increased steadily to the present situation when it is developed as one of the most important methods in isolation and separation of metal ions. Metal extraction, which is based on the formation of complexes by organic ligands with metal ions or corresponding ionic species, may be regarded as a multi-componental coordination process between heterogenous phases. The radical property of extractive separation is, however, dependent chiefly on the stability of metal complexes which are closely related both to the structure of ligands and to the nature of metal ions. The present paper describes the recent progress in our Laboratory for the structure-reactivity studies of organic ligands in metal extraction.

As illustrated by our early investigations the reactivity of the coordinating atoms or group, the steric effect and the solubility of the ligands are the principal structural factors in extraction of metals. Quantitative examination of the contribution of these structural effects to the extraction performances of ligand will provide an experimental basis for the molecular design of extractants with expected properties.

Reactivity of coordinating atom or group - The electronic effect in extraction

It is well demonstrated by numerous experimental data that extraction behaviours of phosphorus-based ligands are closely related to their chemical structures. As shown by us the distribution ratio (D) of cerium, promethium and yttrium in extraction by neutral organophosphorus esters increased in order of magnitude as the increasing of C-P bonds in the molecule. It is clearly evidenced by the increase of Δ_{POD} , a parameter introduced by our Laboratory for the direct evaluation of Lewis basicity of phosphoryl oxygen, or by the increase in polarity of groups directly linked to the phosphorus atom (σ^*). All of these are attributed to the electronic effect of substituents bonded to coordinating atom or group. As expected, a linear free energy relationship exists in plotting D versus Δ_{POD} or σ^* .

The nature of phosphoryl oxygen in neutral organophosphorus ligand may be represented directly by charge density (q_o), bond order ($P_{P=O}$), bond energy ($E_{P=O}^*$) as well as energy of molecular orbital ($\Sigma\lambda_i$) calculated by HMO method⁽¹⁾. The contribution of these structural parameters to the extraction behaviours of neutral organophosphorus compounds was examined. The Dce of these compounds are enhanced as the increasing of q_o and q_p . Meanwhile, the $\Sigma\lambda_i$ is the function of Σo^*

$$\Sigma o^* = - 3.84 + 0.168 \Sigma\lambda_i \quad (r=0.997)$$

In extraction of metal ions by acidic phosphorus esters, $>P(O)OH$ serves as coordinating group. The extraction performance of these ligands towards rare earths as well as cobalt and nickel was studied⁽²⁾. It is shown that the Kex for lanthanide extraction are enhanced as the increasing Σo^* and the decreasing pK_a . A linear relationship exists between these parameters. However, there is no such relationship in extraction of cobalt and nickel due to the steric requirements in this process.

The structure parameters calculated by HMO method gave promising results in quantitative examinations of extraction by acidic phosphorus based ligands. The Kex of Nd, Sm, Y and Yb extraction are governed chiefly by the charge density of hydroxyl oxygen atom (HOMO) in grouping $>P(O)OH$. The plot of Kex againsts q_o (HOMO) values of these compounds gives straight line as anticipated, owing to the direct influence of q_{OH} on the pK_a of ligands. A quantitative relationship also exists between $\Sigma\lambda_i$ and Σo^* of acidic organophosphorus extractants. i.e.

$$\Sigma o^* = - 4.12 + 0.166 \Sigma\lambda_i \quad (r=1.00)$$

It is demonstrated that the mentioned microscopic structural parameters being closely related to the pK_a of the compounds are the determinant factors for the extraction behaviour of the acidic phosphorus-based ligand. As indicated by our recent investigation using NMR spectroscopy and CNDO/2 calculation, the contribution of PO in $>P(O)OH$ of ligand could be neglected in lanthanide extraction, though the process takes place via the dimer of acidic phosphorus esters with the participation of phosphoryl oxygen⁽³⁾. Based on the fact that pK_a of ligand is a function of Kex in lanthanide extraction, a series of linear relationship between these two parameters was derived while the steric effect is not so important.

Aromatic hydroxyoximes are another interesting class of chelating extractants which received extensively studies in recent ten years. A systematic structure-reactivity investigations of aromatic hydroxyoximes in copper extraction was reported by us.⁽⁴⁾

In contrast with the literature data, which indicate the pKa or the charge density of phenolic hydroxyl oxygen is the dominating structure factor of aromatic hydroxyoximes, we recently found that the contribution of charge density of hydroxyamido nitrogen is extremely important in copper extraction (Table 1).

Table 1 Structure and reactivity of 2-HO-X-C₆H₃-C(Y)=NOH

No.	X	Y	logK _{ex}	pKa	q _O	q _N	log p
1	H	C ₆ H ₅	-0.96	10.78	1.9347	1.3293	1.67
2	5-s-C ₈ H ₁₇	C ₆ H ₅	-0.78	11.12	1.9369	1.3294	6.09
3	5-s-C ₈ H ₁₇ O	C ₆ H ₅	-1.08	11.48	1.9376	1.3294	5.36
4	4-s-C ₈ H ₁₇ O	C ₆ H ₅	0.29	10.99	1.9347	1.3452	5.36
5	3-NO ₂ , 5-t-C ₈ H ₁₇	C ₆ H ₅	2.41	7.7	1.9311	1.3298	5.74
6	3-Cl, 5-s-C ₈ H ₁₇	C ₆ H ₅	1.97	10.45	1.9377	1.3294	6.80
7	H	4'-C ₁₂ H ₂₅ C ₆ H ₄	-0.31	11.29	1.9347	1.3409	8.04
8	5-s-C ₈ H ₁₇	2'-ClC ₆ H ₄	-0.73	11.08	1.9369	1.3337	6.80
9	5-s-C ₈ H ₁₇	4'-CH ₃ OC ₆ H ₄	-0.92	11.08	1.9369	1.3444	6.02
10	5-s-C ₈ H ₁₇ O	CH ₃	-0.61	10.83	1.9371	1.3781	4.58
11	4-s-C ₈ H ₁₇ O	CH ₃	0.51	10.56	1.9342	1.3934	4.58
12	4-s-C ₈ H ₁₇ O	C ₃ H ₇	0.48	10.94	1.9342	1.3934	5.56
13	4-s-C ₈ H ₁₇ O	C ₅ H ₁₁	0.32	10.46	1.9342	1.3934	6.64
14	4-s-C ₈ H ₁₇ O	C ₇ H ₁₅	1.28	10.68	1.9342	1.3934	7.72
15	4-i-C ₈ H ₁₇ O	CH ₃	0.14	10.02	1.9342	1.3934	4.56

The high q_N value of the aromatic hydroxyoximes will provide either higher content of E form, the active ingredient for metal extraction or, higher stability constants of the complexes with transition metals resulting from back donation of the latter. As illustrated by regression analysis, a fair correlation coefficient was obtained in treating q_O and q_N to K_{ex} of copper extraction.

$$\log K_{ex} = 433.3 - 231.3 q_O + 10.36 q_N \quad (r=0.90)$$

If the distribution constant ($\log p$) of ligand calculated by Hansch equation was added as a term in addition to q_o and q_N in multiple linear regression, a better correlation ratio was resulted.

$$\log K_{ex} = 468.3 - 249.4 q_o + 10.09 q_N + 0.088 \log P \quad (r=0.93)$$

The experimental K_{ex} in copper extraction by aromatic hydroxyoxime (K_{ex}^{obs}) in Table 1 well consist with calculated K_{ex} (K_{ex}^{calc}) from these empirical equations (Fig 1).

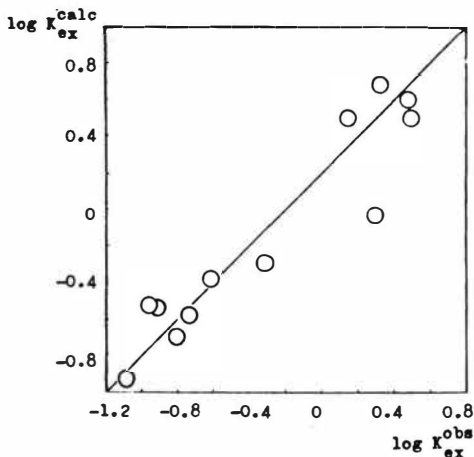


Fig. 1 $\log K_{ex}^{calc}$ versus $\log K_{ex}^{obs}$ in copper extraction by hydroxyoximes

Since the polar constants of long chain alkyl and alkoxy groups are still insufficient in the literature, the QSAR studies of organic compounds bearing such groups was inhibited. Here we report eighteen constants, an extension of Kabachnik's scale, of long chain alkyl and alkoxy groups based on the ionization constant determination of a series of mono-basic alkylphosphates and alkylphosphonates. It was observed that there is an excellent linear relationship between σ^P value and group connectivity, a term introduced recently by Hanson, as a parameter for the polarity of alkyl substituents. A preliminary study was performed on the influence of steric and self-coiling effect to the pK_a value of mono-basic phosphates and phosphonates comprising long chain alkyl and alkoxy groups (Table 2).

Based on our experimental data. The extraction constants of rare earth (K_{ex}^{RE}) by acidic phosphorus-based ligands are therefore

correlated linearly with the σ^P constants of the substituents while the steric effect offers no significant influence on the extraction process.

$$\log K_{ex}^{Nd} = 2.85 - 4.18 \Sigma \sigma^P \quad r = 0.997 \quad (1)$$

$$\log K_{ex}^{Sm} = 4.12 - 4.12 \Sigma \sigma^P \quad r = 0.954 \quad (2)$$

$$\log K_{ex}^{V} = 5.82 - 4.41 \Sigma \sigma^P \quad r = 0.998 \quad (3)$$

$$\log K_{ex}^{Vb} = 6.67 - 4.39 \Sigma \sigma^P \quad r = 0.991 \quad (4)$$

So we can predict extraction ability of ligands based on the polarity of the substituents by these empirical equations.

Table 2 The polar constants of some long-chain alkyl and alkoxy groups

No	Group	σ^P	S*	$\Sigma \frac{n_i}{4i^2 - 1}$	σ_{calc}^P	$\Delta \sigma^P$
1	CH ₃	-0.00±0.045	0.064	0.133	-0.00	0.00
2	i-C ₃ H ₇	-1.14±0.030	0.032	0.467	-1.12	0.02
3	cyc-C ₆ H ₁₁	-1.24±0.025	0.027	0.540	-1.30	-0.06
4	n-C ₈ H ₁₇	-1.14±0.015	0.013	0.471	-1.13	0.01
5	i-C ₈ H ₁₇	-1.21±0.055	0.055	0.506	-1.21	0.00
6	n-C ₈ H ₁₇	-1.28±0.040	0.035	0.533	-1.28	0.00
7	n-C ₄ H ₉ O	-0.42±0.055	0.057	0.445	-0.42	0.00
8	i-C ₄ H ₉ O	-0.46±0.065	0.066	0.457	-0.45	-0.01
9	n-C ₄ H ₉ O	-0.61±0.035	0.050	0.495	-0.56	0.05
10	i-C ₆ H ₁₃ O	-0.55±0.075	0.106	0.489	-0.54	0.01
11	n-C ₈ H ₁₇ O	-0.50±0.015	0.015	0.471	-0.49	0.01
12	i-C ₈ H ₁₇ O	-0.57±0.040	0.044	0.506	-0.59	-0.02
13	n-C ₈ H ₁₇ O	-0.68±0.035	0.031	0.533	-0.67	0.01
14	n-C ₁₂ H ₂₅ O	-0.50±0.020	0.014	0.480	-0.52	-0.02
15	n-C ₁₃ H ₂₇ O	-0.72±0.010	0.007	0.547	-0.71	0.01
16	n-C ₁₃ H ₂₇ O	-0.86±0.010	0.007	0.609	-0.89	-0.03
17	i-C ₁₄ H ₂₉ O	-0.61±0.020	0.014	0.540	-0.69	-0.08
18	n-C ₁₅ H ₃₁ O	-0.85±0.010	0.007	0.614	-0.91	-0.06

* S refers to standard deviation

Spatial Structure of ligand and coordination compound - The steric effect in extraction

Steric factors consisting of shielding, conformation and strain effects can either assist or hinder the extraction process, which is governed by the formation of thermodynamic stable complexes. However, the degree of the influence of the steric effect of ligand is

dependent on the ionic radius and structure of metal ions as well as the composition and the structures of extracted species.

In the structure-reactivity studies of the extraction of Ce, Pm and Y by dialkylphenylphosphonates and dibutylalkylphosphonates it was shown that the steric effect of alkyl group in the former is considerably greater than that in the latter, owing to the significant steric hinderance arising from two ester alkyl groups in the molecule of dialkylphenylphosphonates. Meanwhile the D value for heavy rare earths is comparatively larger than that for light ones when the structure effect of organic ligands are similar due to lanthanide contraction. In contrast with the result reported by Eremen and Shvedov, our data clearly demonstrated that the steric effect of ligand plays a major role in their extractive separation properties. The size of the extractant appears to be of great importance in separating those metal ions which forms coordination compounds with various compositions. As early as 1964, we stated that the steric bulk of the extractant gives excellent property in Th/U separation, for example DSOMP (378) is superior to TBP (36). Analogous result was declared by Horwitz et al. in 1981, who correlated steric effect of the ligand with the thermodynamic function ΔS in extraction reaction. The steric effect of alkyl group of sulfoxides in lanthanide extraction shows similar order $nC_{18}H_{17} > iC_8H_{17} > sC_8H_{17}$.⁽⁵⁾

For the quantitative study of steric effect of ligands the focus of our attention was to examine the behaviours of acidic phosphorus esters which are of great importance in extractive separation of metal ions. Since the correlation analyses of Kex in nickel or cobalt extraction with σ^P and Charton's v , a commonly used parameters for steric effects, gave only unsatisfied results, it is therefore necessary to establish a new parameter, reflecting steric effect of substituents of ligands in cobalt nickel separation by mono-basic alkylphosphonates and alkyl-phosphates.

Based on the general quantitative expression between extraction constants with polar and steric effect of substituents of ligand, $\log K_{ex} = \rho \Sigma \sigma^P + \delta \Sigma E_{PA}^M + C$ two series of parameters E_{PA}^{CO} and E_{PA}^{Ni} were evaluated besides E_{PA}^{RE} for lanthanide extraction (Table 3).

Table 3. Substituent Steric Parameters of Phosphorus-based Ligands

NO.	Substituents	ν	E_{PA}^{Co}	E_{PA}^{Ni}	E_{PA}^{RE}	Ex,ex
1	CH ₃	0.52	-0.48	-0.51		-0.037
2	i-C ₃ H ₇	0.76	-1.01	-1.39		0.216
3	Cyc-C ₆ H ₁₁	0.87	-1.08	-1.92	-1.32	0.218
4	n-C ₆ H ₁₃					0.010
5	n-C ₇ H ₁₅					0.011
6	n-C ₈ H ₁₇	0.68	-0.96	-1.48	-1.26	0.011
7	i-C ₈ H ₁₇	1.16	-1.16	-1.94	-1.71	0.086
8	s-C ₈ H ₁₇	1.07	-1.20	-2.10	-1.88	0.277
9	n-C ₆ H ₁₃ O					0.008
10	n-C ₇ H ₁₅ O					0.010
11	n-C ₈ H ₁₇ O	0.61	-0.12	0.00	-0.25	0.012
12	i-C ₈ H ₁₇ O	0.76	-0.36	-0.46	-0.48	0.023
13	s-C ₈ H ₁₇ O	0.92	-0.57	-0.85	-0.76	0.169
14	n-C ₁₂ H ₂₅ O	0.65	-0.21	-0.38		0.021
15	i-C ₁₄ H ₂₉ O		-0.40	-0.48		

Cyc-C₆H₁₁ is $\overline{CH_2(CH_2)_4CH-}$; i-C₈H₁₇ is C₄H₉CH(C₂H₅)CH₂-;
s-C₈H₁₇ is C₇H₁₃CH(CH₃)-; i-C₁₄H₂₉ is C₇H₁₅CH(C₅H₁₁)CH₂-.

An excellent LFER existed, however, in correlating log K_{ex} to E_{PA}^M in addition to ξ , indicating the applicability of these parameters for the steric effect of ligand substituents in metal extraction including cobalt, nickel and rare earth.

$$\log K_{ex}^{Co} = -1.96\xi + 2.03 \xi E_{PA}^{Co} - 6.33 \quad r=0.973 \quad (5)$$

$$\log K_{ex}^{Ni} = -3.67\xi + 2.43 \xi E_{PA}^{Ni} - 8.66 \quad r=0.982 \quad (6)$$

$$\log K_{ex}^{Nd} = -2.69\xi + 2.89 \xi E_{PA}^{RE} - 2.62 \quad r=0.999 \quad (7)$$

$$\log K_{ex}^{Sm} = -3.31\xi + 3.12 \xi E_{PA}^{RE} - 2.21 \quad r=0.999 \quad (8)$$

$$\xi = \Sigma \sigma P$$

It is expected to use E_{PA}^{Co} or E_{PA}^{Ni} in extraction of those metals which possess identical configuration of coordination compounds in extraction process as cobalt or nickel. As shown by our systematic studies, E_{PA}^{RE} substituent steric parameter of acidic phosphours esters in lanthanide extraction works well in actinide extraction by neutral phosphours esters.

It is also found that the separation factor, one of the most important characteristics in extractive separation, is linearly related to the difference between steric parameters in extraction of a pair of metal ions. It is useful in the design of extractant molecules with a higher cobalt/nickel separation factor. The theoretical predication is well supported by experimental data.

The E_{PA}^M value is an empirical parameter, since it consists of residual factors together with steric effect. It is therefore necessary to evaluate the steric contribution of the substituents with elimination of other structure influence. A theoretical calculation based on molecular mechanics (Allinger's MM2 program) was thus performed for this purpose. The calculated parameters including bond length, bond angle, rotation barrier and dipole moment of various alkylphosphotates and phosphinates, were proved to be consistent with the experimental data. In order to estimate the steric effect of substituents, dialkyl t-butyl phosphate or dialkyl t-butylphosphinate was chosen as model compound for the simulation of steric environment of the complexes in this preliminary study. The optimum geometry of the model structure and its parent acid were determined by the molecular mechanics program, the most stable structure were selected to compare with each other. It was found that the difference of the local steric energy of hydroxyl oxygen in both two compounds is closely correlated with the degree of the size of substituent and can thus be used as a measurement of the steric effect of the substituents(E_s, ex). A series of E_s, ex of alkyl and alkoxy groups were evaluated. (Table 3). the molecular mechanics calculation of coordination compounds with metal ions is still in progress.

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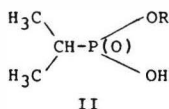
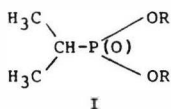
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Isopropylphosphonic Esters - A New Class of Potential Extractants for Lanthanides

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Extraction of lanthanides by phosphorus-based ligands has been studied extensively only with tributylphosphate (TBP) and di(2-ethylhexyl) phosphoric acid (D2EHPA). The wide application of these extractants are markedly inhibited by their insufficiently large separation factor and comparatively higher acidity required in extraction or stripping process. Various efforts have been made for the development of more powerful extractants. The structure-reactivity studies of ligands in metal extraction is, however, considered to be one of the effectual ways to develop such new reagents.⁽¹⁾ Steric effects associated either with the spatial structure of ligands or with the geometric configuration of the complexes formed play an important role in extraction process, especially for the separation of elements with monotonously varying atomic radius like the lanthanides.⁽²⁾ This is well demonstrated by the higher selectivity during the extraction of lanthanides by di(1-methylheptyl) methylphosphonate (DSOMP). The influence of chemical structure of dialkyl alkylphosphonates or monoalkyl alkylphosphonates on their extraction behaviour of 3d elements has been reported elsewhere⁽³⁾, but the data for the rare earth elements are insufficient.

In this paper, the influence of chemical structure of isopropylphosphonic esters on their extraction properties of rare earths was presented. Since in these new ligand molecules, namely compounds I and II, a bulky isopropyl group was directly bonded to the phosphorus atom and therefore a remarkable steric effect could be observed. Meanwhile various degrees of spatial conformation of ligands would be achieved by introducing different structure of ester alkyl groups.



- I $R = nC_4H_9-(DNBPP)$; $isoC_4H_9-(DIBPP)$; $secC_4H_9-(DSBPP)$
 $tC_4H_9-(DTBPP)$; $cycC_6H_{11}-(DCHPP)$; $nC_8H_{17}-(DNOPP)$
 $C_4H_9CH(C_2H_5)CH_2-(DIOPP)$; $C_6H_{13}CH(CH_3)-(DSOPP)$
- II $R = nC_8H_{17}-(MNOPP)$; $C_4H_9CH(C_2H_5)CH_2-(DSOPP)$
 $C_6H_{13}CH(CH_3)-(MSOPP)$; $nC_{12}H_{25}-(MDDPP)$
 $C_7H_{15}CH(C_5H_{11})CH_2-(MANPP)$; $C_{11}H_{23}CH(CH_3)-(MMDPP)$
 $C_7H_{15}CH(C_7H_{15})-(MHOPP)$.

Extraction of Rare Earths by Dialkyl Isopropylphosphonates (I)

DNBPP, DIBPP and three isomeric dioctyl isopropylphosphonates were synthesized by direct alcoholysis of the complex resulting from reaction of isopropyl chloride, phosphorus trichloride and aluminum trichloride. DSBPP and DTBPP were prepared by the solvolysis of isopropylphosphonyl dichloride with corresponding sodium alcoholate. The identity of these products was checked by acetylated paper chromatography. The high purity of dialkyl isopropylphosphonates thus obtained are verified by elemental analyses, IR and proton NMR spectra. (4)

Influence of ester alkyl group on distribution ratio (D) and separation factor (β) in extraction of La, Pr, Nd, Sm and Y from 3.0N HNO_3 are represented in Figure 1 and Table 1. These data were compared with that from TBP and DSOMP.

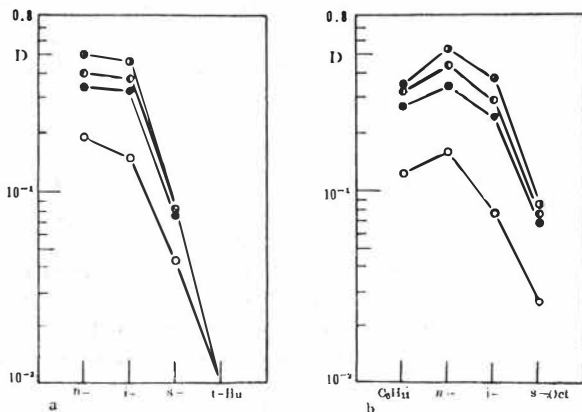


FIG. 1 Extraction of lanthanides by $(CH_3)_2CHP(O)(OR)_2$
 La(O), Pr(●), Nd(○), Sm(●); 3N HNO_3
 (a) $R = n-C_4H_9$, $iso-C_4H_9$, $sec-C_4H_9$, $tert-C_4H_9$
 (b) $R = Cyclo-C_6H_{11}$, $n-C_8H_{17}$, $iso-C_8H_{17}$, $sec-C_8H_{17}$

Table 1. Extraction of Lanthanides by dialkyl Isopropylphosphonates
 $iC_3H_7P(O)(OR)_2$

R	Abbr.	D				β		
		La	Pr	Nd	Sm	Pr/La	Nd/Pr	Sm/Nd
n C_4H_9-	DNBPP	0.138	0.344	0.401	0.496	1.88	1.17	1.24
i C_4H_9-	DIBPP	0.149	0.326	0.371	0.461	2.01	2.19	1.14
s C_4H_9-	DSBPP	0.043	0.075	0.080	0.079	1.83	1.74	1.07
t C_4H_9-	DTBPP	0.01	0.01	0.01	0.01	-	-	-
cyc $C_6H_{11}-$	DCHPP	0.123	0.275	0.331	0.357	2.24	1.20	1.08
n $C_8H_{17}-$	DNOPP	0.157	0.344	0.434	0.537	2.19	1.26	1.24
n $C_4H_9CH(C_2H_5)CH_2-$	DIOPP	0.076	0.233	0.292	0.375	3.06	1.25	1.28
n $C_6H_{13}CH(CH_3)-$	DSOPP	0.026	0.067	0.075	0.084	2.55	1.12	1.12
$CH_3P(O)(OC_8H_{17}S)_2$	DSOMP	0.233	0.529	0.646	0.770	2.27	1.22	1.19
$(C_4H_9O_3)_3PO$	TBP	0.043	0.082	0.082	0.142	1.94	1.01	1.72

It is evidently shown that the D values in lanthanides extraction by dialkyl isopropylphosphonates with the same carbon number of alkoxy group decrease with strengthening the isomerization of the alkyl radical, i.e. the steric hindrance towards phosphorus atom enhanced. The following order was observed: DNOPP>DIOPP>DSOPP; DNBPP>DIBPP>DSBPP>DTBPP (Fig. 1). The lower extraction ability of DCHPP is attributed to the greater steric hindrance arising from geometric conformation of the cyclohexyl group. There is no obvious influence of number of carbon atoms in alkoxy group on their extraction behaviours.

As anticipated, the extractive ability of dialkyl isopropylphosphonates is superior to TBP due to the higher basicity of phosphoryl oxygen. The fact that the D values of extraction by dialkyl isopropylphosphonates are less than those by DSOMP can be explained either by hyperconjugation of methyl group (Baker-Nathan effect) in the latter

The calculated values of the relative entropy change are all positive. Considering the change of the relative thermodynamic functions for praseodymium and lanthanum extraction by dialkyl isopropylphosphonates with various alkoxy group it can be said that the hindered ester of isopropylphosphonic acid reveals both a smaller relative enthalpy change and less reverse contribution to the extractive separation.

Extraction of Rare Earths by Mono-alkyl Isopropylphosphonates (II).

Mono-alkyl isopropylphosphonates were synthesized by partial alcoholysis of isopropylphosphonyl dichloride and followed by hydrolysis⁽⁷⁾. For the structure-reactivity studies higher purity of extractants is necessary due to the fact that even a trace of impurities may cause considerable experimental errors. The viscous syrupy acidic phosphorus-based ligand may be purified through their copper complex, a simple and effective method developed in our laboratory as early as 1964⁽⁸⁾. The purity of compounds II prepared was checked by silicon-loaded paper chromatography, potentiometric titration, elemental analyses as well as IR and proton NMR spectra.

Influence of structure of alkoxy group on extraction constant (K_{ex}) and separation factor (β) in extraction of lanthanum, europium and lutetium as representative of light, medium and heavy rare earth respectively from nitrate system are as shown on Table 2.

Table 2 Influence of the structure of R of $iC_3H_7P(O)OR(OH)$ on the extraction separation for rare earths

Extractant		pK_a	K_{ex}			β		
R	abbr.		La	Eu	Lu	Eu/La	Lu/Eu	Lu-La average
$C_8H_{17}-$	MOPP	3.84	8.94×10^{-2}	9.42	*	105.4	—	—
$C_4H_9CH(C_2H_5)CH_2-$	MEHPP	3.97	7.07×10^{-3}	1.46	6.48×10^3	206.5	4438	2.67
$C_6H_{13}CH(CH_3)-$	MMHPP	4.22	1.67×10^{-3}	5.56×10^{-2}	3.68×10^1	33.29	661.9	2.04
$C_{12}H_{25}-$	MDDPP	3.79	1.37×10^{-2}	6.47	*	472.3	—	—
$C_7H_{15}CH(C_5H_{11})CH_2-$	MANPP	4.01	1.68×10^{-3}	1.14	5.89×10^3	678.6	5167	2.93
$C_{11}H_{23}CH(CH_3)-$	MDPP	4.22	2.25×10^{-4}	2.98×10^{-2}	2.43×10^1	132.4	815.4	2.29
$C_7H_{15}CH(C_7H_{15})-$	MHOPF	4.48	2.14×10^{-6}	2.36×10^{-4}	8.46×10^{-2}	110.3	358.5	2.13

* The viscosity of the organic phase is too high.

linked to the phosphorus atom in the former.

The remarkable separation behaviour of dialkyl isopropylphosphonates in the lanthanide extraction under investigation is very interesting. With proper degree of isomerization in alkoxy alkyl group, both DIOPP and DSOPP possess excellent separation factor for Pr/La, 3.06 and 2.55 respectively. Both values are greater than those for TBP (1.94) and DSOMP (2.27) under same conditions. Meanwhile, the β value of Pr/La for DIBPP is 2.19 which lies between the values for TBP and DSOMP. The higher separation factors of Pr/Nd for these three extractants in comparison with those from TBP were also revealed. Analogous to the extraction of thorium, an intense influence of steric hindrance was also observed on lanthanides extraction. It is, however, reasonable to consider that the ionic radius of lanthanides (La^{3+} 1.016Å) is close to that of thorium (1.02Å). In contrast with the result reported by Eremen⁽⁵⁾ and Shvedov⁽⁶⁾, the present study clearly shows that the steric effect of extractants plays an extremely important role in their separation behaviour. We can, therefore, to a limited extent, design selective ligands for extraction of certain metal ions by utilizing the steric hindrance in solvent extraction. With the aid of the present results, this proposition has received an additional experimental support.

The thermodynamic functions of extraction reaction of lanthanum and praseodymium nitrate with various dialkyl isopropylphosphonates were estimated and the contribution of the structure of ester alkyl group to these parameters were discussed.

The distribution ratios of lanthanum and praseodymium nitrate extraction by DNOPP, DIOPP, DNBPP, DIBPP, and TBP at various temperatures were estimated. All of D values decrease with the increase of temperature. The plot of $\log D$ versus $1/T$ was found to be a straight line for all extraction systems under investigation. ΔH° was estimated. The relative free energy change of $\text{Pr}(\text{NO}_3)_3$ to $\text{La}(\text{NO}_3)_3$ extraction can be expressed as $\Delta G_r^\circ = \Delta(\Delta G_r^\circ) \equiv -RT \ln K_{\text{Pr/La}} = -RT \ln \beta$ Pr/La, where $\beta = K_{\text{Pr}}/K_{\text{La}} = D_{\text{Pr}}/D_{\text{La}}$ under the same condition. Relating ΔG_r° to ΔH_r° ($\Delta H_r^\circ = \Delta H_{\text{Pr}}^\circ - \Delta H_{\text{La}}^\circ$), the relative entropy change can also be calculated. It follows that the separation between Pr and La resulted from the favorable extraction of the former and it is caused neither by the difference of enthalpy, nor by the difference of relative bond energy between the complex formed and the hydrated lanthanide ion.

As demonstrated by the data on Table 2, slight variation in structure of ester alkyl group can have very dramatic effect on the efficiency of these compounds in extractive separation of rare earths. The Kex values in lanthanide extraction by mono-alkyl isopropylphosphonates markedly decreased with strengthening the isomerization of the ester alkyl radical locating near the reaction center of the ligand, i.e. mono-alkyl isopropylphosphonates with straight chain alkyl group, MNOPP, MDDPP gave, as a rule, highest Kex value though the phase separation was difficult, in lutecium extraction due to the high viscosity of the loaded organic phase resulting from the poor lipophilicity of the ligand.

The Kex values are sharply depressed, usually in two orders of magnitude, by putting α -branch chain in ester alkyl group (MSOPP, MNDPP, MHOPP), upon which, the bulky the branch chain is, the lower the Kex will be. Meanwhile, the separation factors in such cases are also decreased evidently. It is attributed to the steric hindrance of phosphorus-based ligand in extraction process. However, the mono-alkyl isopropylphosphonates bearing β -substituted ester alkyl group, MIOPP, MANPP gave considerable high Kex and β values in lanthanide extraction. In such case, the spatial structure of substituents shows remarkable assistance to the extraction. As shown by these data the steric effects of ligand can have either hindrance or assistance to extraction reaction depending on the geometric requirements of the coordination process. Moreover, such effect of ligand was considerably intensified from extraction of light to heavy rare earths due to the lanthanide contraction. Table 2 also indicated that the pKa values of the compounds under investigation showed, to a certain extent, relationship with the structure of alkyl groups. It is necessary to point out that Kex is correlated linearly with the polar and steric constants of phosphorus-based ligand suggested by us recently for the lanthanide extraction⁽⁹⁾.

The extraction chemistry of lanthanides by MANPP was studied. In comparison with commercial available D2EHPA, MANPP is distinguished for its higher extraction selectivity in rare earths separation from chloride medium than from nitrate system. Extraction mechanism was discussed based on the investigation of the extraction equilibrium by slope methods. The thermodynamic function ΔH and ΔG of the extraction reaction, was estimated by examining the temperature effects on extraction equilibrium. The plots of the estimated ΔG as well as Kex versus atomic number of lanthanide reveal an obvious tetrad

effect. All lanthanides may be divided into four subgroups: La-Ce-Pr-Nd, (Pm)-Sm-Eu-Gd, Gd-Tb-Dy-Ho, Er-Tm-Tb-Lu. Gd lies both in the second and the third subgroups, Y locates between Ho and Er due to the appropriate ionic radius.

The composition and the structure of the coordinated compounds of MANPP with Eu and Yb, (LnL_3) was elucidated by elemental analyses, IR, proton NMR and differential thermal analyses.

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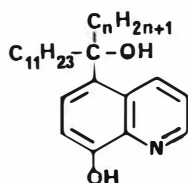
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NEW 5-SUBSTITUTED 8-QUINOLINOLS FOR EXTRACTION OF GALLIUM(III) FROM ALUMINATE BAYER LIQUORS.

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Until now, Ga(III) is extracted from Bayer liquors (1.5M AlO_2Na , 3.5M NaOH) by a 7-alkylsubstituted 8-quinolinol (1). The rate of phase transfer is slow; it may be accelerated by tensioactive species such as carboxylic acids which confer to the organic phase the structure of a microemulsion (2).

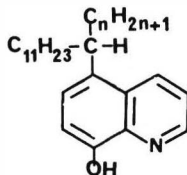
We thought that the 5-substituted 8-quinolinols would have a better access to the water/solvent interface than the 7-substituted ones and would give rise to more rapid kinetics than the latter, even without additives. We synthesized the three following molecules and studied the extraction of Ga(III) and Al(III) from both thermodynamic and kinetic point of view, firstly by investigating the new molecules as extractants, secondly by using them as "Kelex 100" modifiers.



YOL n



YEN n



YAN n

The new extractants are much more acidic than "Kelex 100" (3). Biphaseic pK_a for YOL5, YEN5 and "Kelex 100" are 11.5, 10.9 and higher than 14, respectively. Consequently, the new extractants HL are fully ionized, as ion pairs L^-Na^+ , in the organic phase in equilibrium with 3.5M NaOH. We recall that in the same conditions "Kelex 100" is only partially ionized.

1) PROPERTIES OF THE NEW MOLECULES AS EXTRACTANTS

1) Thermodynamics.

The distribution coefficient D_{Ga} from 3.5M NaOH in absence of aluminate has been studied for the three above compounds (fig.1). The behaviour of YOL compounds is surprising. It appears that at high concentration ($> .05\text{M}$) YOL compounds are partially soluble in aqueous phase with micelles formation. The partition of YOL may be studied by spectrophotometry of both phases. The spectral characteristics are: λ_{max} 335nm ϵ 2810 $\text{cm}^{-1}\text{mol}^{-1}$ for the maximum of absorbance in the organic phase and λ_{max} 248nm ϵ 23850 $\text{cm}^{-1}\text{mol}^{-1}$ in the aqueous one. The micelles in aqueous solution may include gallium ion (λ_{max} 253nm, ϵ 34610 $\text{cm}^{-1}\text{mol}^{-1}$). This phenomenon explains the shape of the figure 1 curves: at low concentration of YOL the extraction of Ga is classical at upper concentration, the formation of micelles in aqueous phase compete with complexes formation in organic phase.

From the above data it is possible to calculate $\log D_{\text{Ga}}$ versus $\log \text{L}^-$, L^- being the equilibrium concentration of the basic form L^- of the extractant. If, and only if, we assume the formation of 1:3 complexes with YAN5 and 1:2 complexes with YEN10, we obtain straight lines, the slopes of which being 3 and 2 respectively. Assuming in the two cases the formation of octaedic species, the formulas of the extracted compounds are $\text{Ga}(\text{YAN5})_3$ and $\text{Ga}(\text{YEN10})_2(\text{OH})_2\text{Na}^+$. The formation of 1:2 complexes instead of 1:3

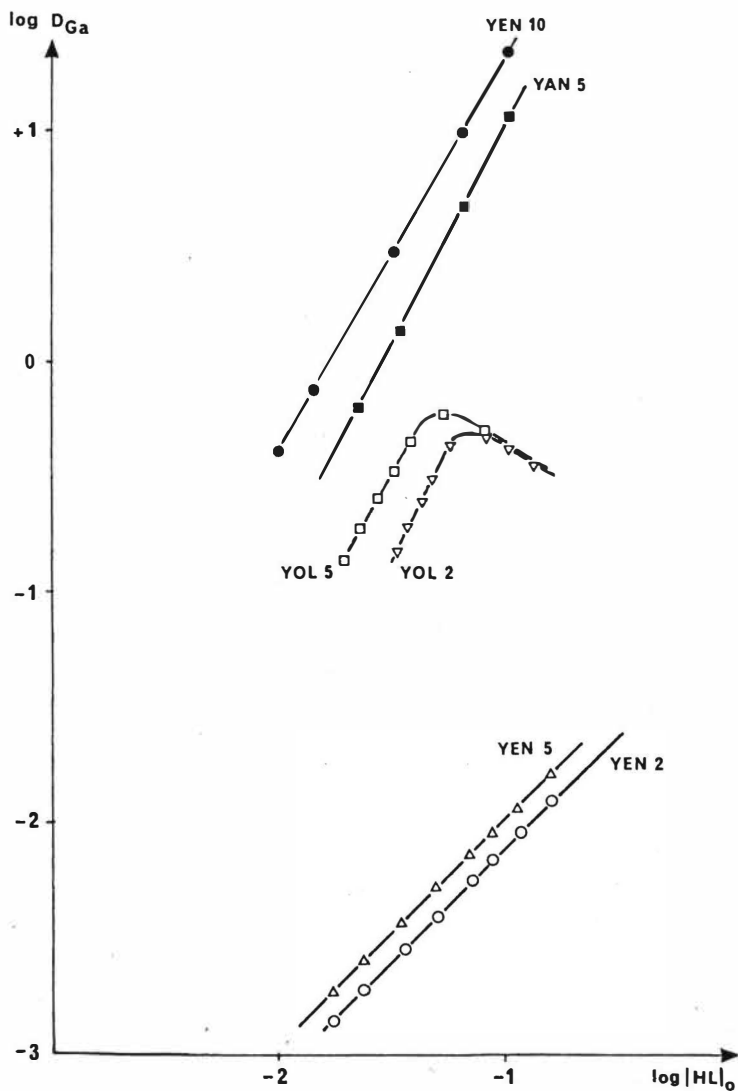


Figure 1.- Variation of gallium(III) distribution versus total extractant concentration;

Organic phase: Kerosene + n-octanol 2.5% V/V + variable concentration of the extractants (logarithmic scales).

Aqueous phase: 3.5M NaOH + 1.5M $NaClO_4$ + $1.43 \cdot 10^{-2}M Ga(OH)_4^-$.

complexes as usual may be due to an high steric hindrance, YEN10 molecule having a tertiary carbon with two long chains (C_{10} and C_{11}).

Conditional extraction constants for the medium 1.5M NaOH have been deduced from the curves $\log D = f(\log L^-)$. We find 7.5 and 4.0 for their logarithms, for $Ga(YAN5)_3$ and $Ga(YEN10)_2(OH)_2$. An accuracy of .5 unit is expected (4).

In presence of 1.5M AlO_2Na , the extraction of $Ga(III)$ is lower (figure 2). Comparison of figures 1 and 2 clearly indicates that simultaneous extraction of Al and Ga occurs. The only extractant which exhibits a reasonable selectivity is YEN10. The stoichiometry of the aluminum extracted complexes have been studied: it is 1:3 for YAN5 and 1:2 for YEN10. The logarithm of the conditional extraction constants are 7.7 for $Al(YAN5)_3$ and 3.5 for $Al(YEN10)_2(OH)_2$. The selectivity of the gallium/aluminium separation is therefore 0.6 for $YAN5$ and 4.0 for YEN10.

2) Kinetics.

As we wrote previously, the reasons for which we synthesized such molecules were based on kinetic considerations. So, we studied the rate of phase transfer in gallium extraction in a constant interfacial area cell. We used an agitation speed = 44rpm, an order of magnitude for which the diffusion of the species is not the limiting step. The rate of phase transfer is independent of the octanol percentage in the organic phase, in the range 2-8% (V/V). The initial rate V^0 of phase transfer is proportional to the gallium concentration in the aqueous phase and to the extractant concentration in the organic one. In this phase, the extractant is under its basic form L^- . So, we can write:

$$V^0 = k Ga(OH)_4^- \text{ aq } L^- \text{ org}$$

From the slope of the straight lines $V^0 = f(\text{Ga concentration})$ and $V^0 = f(L^-)$ it is possible to calculate the rate constant k . We obtain $1.2 \cdot 10^{-11}$ for YAN5 and $1.05 \cdot 10^{-11}$ for YEN10, if we expressed V^0 in $\text{mol.m}^{-2}.\text{s}^{-1}$ and the concentrations in mol.m^{-3} . With "Kexel 100", the interpretation of the results is more complicated because of the existence in organic phase of the two HK and $K^- Na^+$ forms. The rate of phase transfer is first order versus the concentration of gallium in aqueous phase and first order versus the concentration of HK form in organic phase. In the following conditions: extractant concentration: 0.1M, gallium concentration: $7.1 \cdot 10^{-4} M$ the initial extraction rates are 1.35, 0.85, 0.75 for "Kexel 100", YAN5, YEN10 respectively. "Kexel 100" gives the highest extraction rate, on the opposite way of what was expected.

3) Interfacial properties.

We measured the interfacial tension γ_i between organic and aqueous phases using several concentrations of extractants. Although at equilibrium the species are $L^- Na^+$ and $(HK + K^- Na^+)$, we note all of them HL in this paragraph. Figure 3 illustrates the obtained results. At very low HL concentration, γ_i is approximately constant (part I of the curves). Then γ_i decreases linearly with $\log HL$ (part II) and, lastly, is constant again (part III). The intersection of the straight lines I and II occurs for a concentration in tensioactive species HL equal to the critical adsorption concentration (CAC) which is the concentration at which the species begin to be adsorbed at the interface. The intersection of straight lines II and III occurs for a concentration of the tensioactive product equal to the critical micellar concentration (CMC) which is the lower concentration of HL in the bulk of the organic phase allowing the formation of micelles in this phase. The interfacial concentration of the adsorbed species may be derived from the slope of the part II of the curves (5). We can write:

$$L^-_i = - \frac{10^{-3} \delta \gamma_i}{2.3RT \delta \log L^-}$$

in which the units are mol.m^{-2} for interfacial concentration L^-_i , N.m.K⁻¹ for

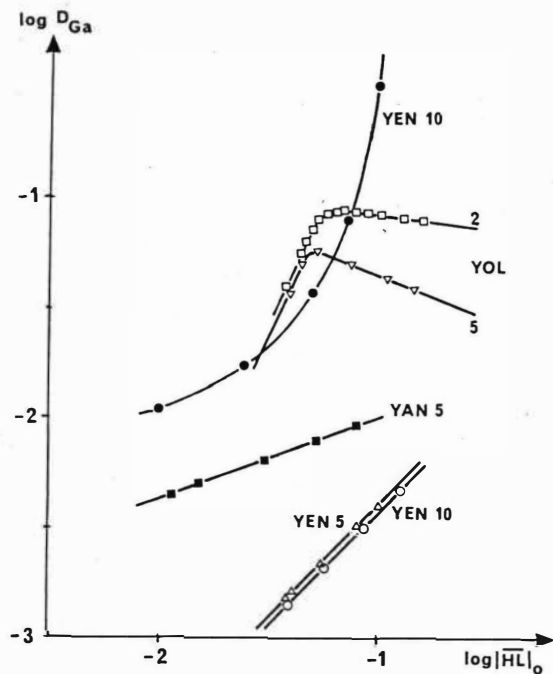


Figure 2. - Variation of Gallium(III) distribution coefficient in presence of large amount of Al(III).

Same conditions as in figure 1, but 1.5M AlO_2Na in aqueous phase instead of 1.5M $NaClO_4$.

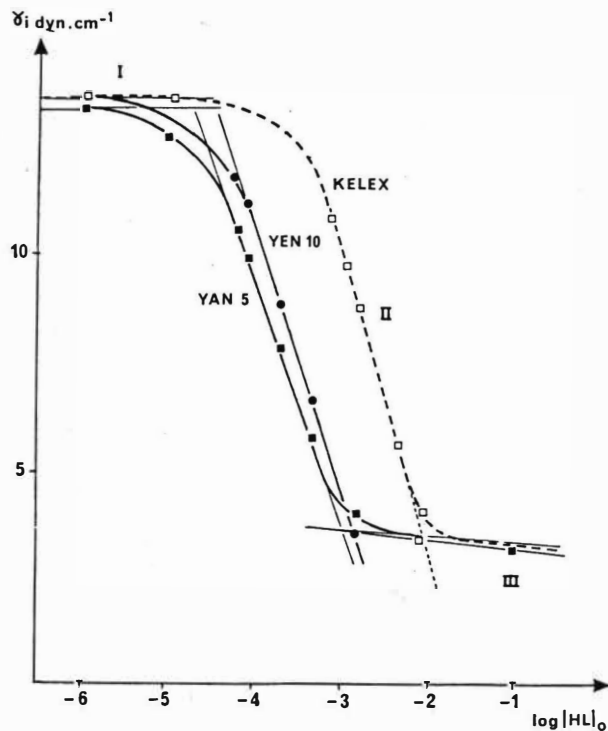


Figure 3. - Variation of the interfacial tension versus the total concentration of the extractants in the organic phase.

$T = 19.8^\circ C$

the gas constant R , dyne.cm^{-1} for the interfacial tension and mol.l^{-1} for the extractant concentration.

Instead of the interfacial concentration, one can consider the disponible area A_i for each molecule at the interface. We have:

$$A_i = \frac{10^{20}}{L_i \cdot N} \text{ } ^{\circ} \text{ } A^2$$

N being Avogadro number. The table I allows comparison between phase transfer rates and interfacial concentrations: interfacial concentrations of YAN5 and YEN10 are lower than the "Kelex 100" one; the rates of phase transfer are lower too. Nevertheless, an inversion occurs for YAN5 and YEN10 derivatives. It seems difficult to draw significant correlation from a such small number of results.

TABLE I

Relation between the interfacial concentration of extractants and the initial rate of phase transfer.

extractant	YAN5	YEN10	KELEX 100
CCA (mol.l^{-1})	$1.8 \cdot 10^{-5}$	$3.2 \cdot 10^{-5}$	$3.2 \cdot 10^{-4}$
CCM (mol.l^{-1})	$1.0 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	$1.5 \cdot 10^{-2}$
L_i (mol.m^{-2})	$1.6 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$
A_i (\AA^2)	158	144	129
V^0 ($\text{mol.m}^{-2} \cdot \text{s}^{-1}$)	$.85 \cdot 10^{-7}$	$.75 \cdot 10^{-7}$	$1.3 \cdot 10^{-7}$

II) NEW MOLECULES AS "KELEX 100" MODIFIERS

The new molecules HL have been tested as "Kelex 100" modifiers. The organic extraction phase was a mixture of kerosene + 2.5% (V/V) octanol + 0.1M "Kelex 100". We added to this phase variable amounts of the extractants HL.

1) Solubilization of water in the organic phase.

Addition of tensioactive species to a mixture of kerosene and alcohol may induces the formation of a microemulsion (6). In extraction systems, the microemulsion is a water in oil one which constitutes the organic phase. This microemulsion is in equilibrium with an excess of water. In such a system, large amounts of water are solubilized in the organic phase. By reciprocity, high concentration of water in the organic phase indicates, with a good probability, the formation of a microemulsion. In our case, the studied L^- species were strongly tensioactive. So, we determined the water concentration in the organic phase, by Karl Fisher titration. We observed that water concentration increases linearly with the concentration of modifiers, so long as the modifier concentration is lower than 10^{-2}M . As an exemple, in absence of modifiers, with only "Kelex 100" and alcohol, we had .2M of water in kerosene, an addition of .01M of YAN5 or YEN10 increases to .4M or .6M respectively, the water concentration.

In presence of YAN or YEN derivatives, it seems that the organic phase becomes a microemulsion. We have shown recently (7) that the use of such an organic phase allows an enhancement of the transfer rate.

2) Extraction of gallium(III) from sodium aluminate solutions.

Distribution coefficients of both gallium and aluminum have been determined for typical concentrations, namely $1.5M AlO_2Na$ and $1.5 \cdot 10^{-2}M Ga(III)$. By addition of modifiers, the distribution coefficients of the two species vary. The selectivity of the separation which is expressed by the ratio of the distribution coefficient D_{Ga}/D_{Al} is given figure 4 when the concentration of the modifiers increase from zero to $0.07M$. Most of them, but YEN10 and YAN5, induce a loss in selectivity.

From a kinetical point of view, all the modifiers increase the initial rate of phase transfer V , determined at constant interfacial area. Linear variations have been obtained. So, the rate of phase transfer may be calculated using the following relation:

$$V = V_K(1 + \alpha L^-)$$

V_K being the rate of phase transfer for "Kelex 100" alone, L^- the modifier concentration, α is a constant depending on the modifier, the values of which are given in the table II. It is clear that YEN2 and YEN5 are very efficient. Unfortunately YEN10 has not been tested.

TABLE II

Values of α constant for the various modifiers.

Modifier	YOL2	YOL5	YEN2	YEN5	YAN5
α	92	96	100	111	22

III) CONCLUSIONS.

5-substituted 8-quinolinols extract gallium(III) and aluminum(III) from strongly basic solutions. Because they are much more acidic than "Kelex 100" they are much less selective. Used as extractants, YAN5 and YEN10 are the only acceptable ones although they induce low rates of phase transfer, even lower than "Kelex 100" one.

Used as modifiers, they involve the formation of a microemulsion in the organic extraction phase, due to their high tensioactive properties. Therefore, the rate of phase transfer is increased, the effect is of the same order of magnitude than those obtained by using long chain carboxylic acids.

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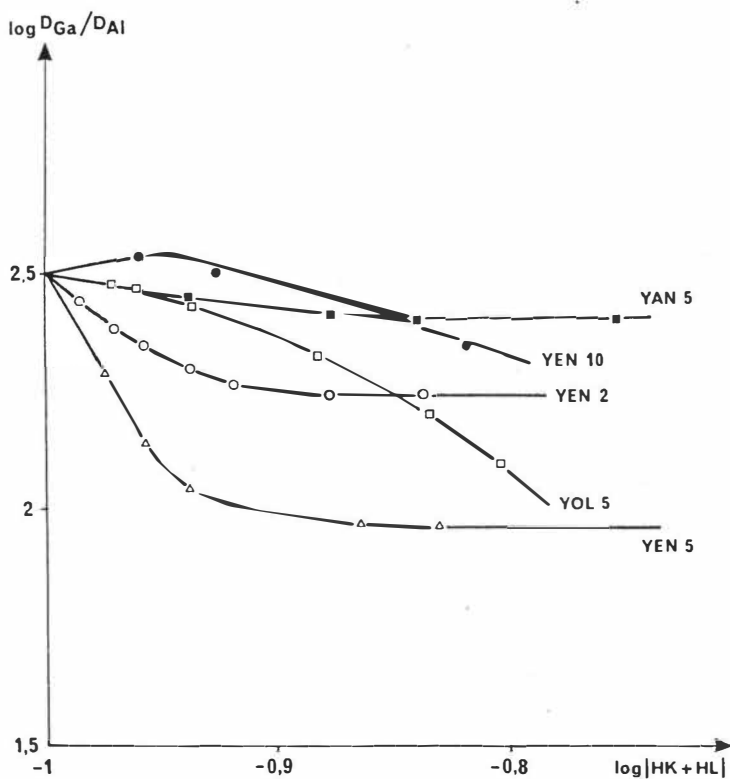


Figure 4. - Variation of the selectivity of gallium / aluminum separation versus the logarithm of the total concentration of "Kelex 100" + modifier.

Organic phase: Kerosene + n-octanol 2.5% V/V + 0.2×10^{-2} M "Kelex 100" + variable HL

Aqueous phase: 3.5M NaOH, 1.5M AlO_2Na , 1.43×10^{-2} M $Ga(OH)_4^-$.

Kinetics of extraction of Cu(II) by a new pyrazolone extractant:

1-phenyl-3-methyl-4-stearoyl-pyrazol-5-one

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Abstract:

The kinetics of copper extraction from sulfate media by a pyrazolone in Solvesso 150 was studied using a known interfacial area cell, called Lewis cell. The influence of hydrodynamical parameters (stirring speed, volumes of solutions, interfacial area) was evaluated, as well as the influence of chemical ones (copper sulfate and extractant concentrations, acidity). The extractant interfacial adsorption and mass-transfer coefficients were measured in the absence of chemical reaction. The results suggest an interfacial mechanism for extraction, where the rate controlling step is the reaction between the extractant in the organic phase and the adsorbed first copper complex CuR^+ .

Introduction:

1-phenyl-3-methyl-4-alkyl-pyrazolones-5 are chelating reagents. Since 1960, they have been studied, mostly by Russian and Indian workers, for their good extraction abilities (1,6). They are widely used in analytical chemistry for separation and concentration before titration. It has been reported that chemical and physical properties of pyrazolones (especially: - high extractive strengths, - quantitative extraction at low pH values, - excellent selectivity, - readiness at stripping), make them suitable reagents for industrial purposes. Lately S.N.P.E. (7) synthesised a series of alkyl-pyrazolones and tested them as substitution reagents for other commercial extractants (Lix 65N, Acorga P5100, Relex 100, etc...). One of the most promising among these derivatives is 1-phenyl-3-methyl-4-stearoyl-pyrazol-5-one. The determination of extraction kinetics and mechanisms with this new reagent is necessary to choose proper reactors, to size extracting units and to test whether substitution of other extractants with pyrazolone can be done without modifying existing plants.

At the present time, very little information is available for metal-pyrazolones systems (8,9). From the literature about other chelating extractants, the following general conclusions may be drawn:

- The reaction is very often said to take place at the aqueous-organic interface. A large number of the proposed mechanisms involve adsorbed species and therefore the extractant interfacial concentration has to be studied.
- The possible contribution of interfacial mass-transfer resistances to the extraction kinetics must be estimated; then apparatus should allow the measurement, or, at least, a precise calculation of interfacial area and mass-transfer coefficients.
- Thermodynamics of extraction and of solutions has to be investigated to explain:
 - . slower extraction rates when approaching equilibrium
 - . the kinetic mechanism and expression of the rate of extraction from concentrated aqueous solutions.

To avoid fitting or estimating hydrodynamical parameters, a known interfacial area cell was chosen for the kinetic studies. Additional non reactive transfer experiments were achieved in the same cell. The results of these studies and surface tension measurements between the two liquids are reported in appendix I and II respectively. The purpose of this work is to represent the initial rates of copper extraction by the chosen pyrazolone for a whole range of reactant concentrations.

Experimental:

Reagents:

1-phenyl-3-methyl-4-stearoyl-pyrazol-5-one is provided by S.N.P.E. and Solvesso 150 supplied by ESSO is used as a diluent. Aqueous solutions are prepared by dissolving copper sulfate in twice-distilled water. pH is fitted with sulfuric acid. All chemicals are analytical grade (Normapur qualities, Prolabo).

Set-up and mode of operation:

The modified Lewis cell (fig. 1) is a thermostated glass reactor ($T = 35 \pm 0.5^\circ\text{C}$) provided with annular and plate Teflon separators which maintain the interfacial area at $10.4 \cdot 10^{-4} \text{ m}^2$. Teflon baffles prevent vortexing, they are perforated to avoid stagnant pockets. The volumes of aqueous and organic phases are $1 \cdot 10^{-4} \text{ m}^3$ each, they are stirred in opposite directions with six-blade titanium impellers. The stirring speed is measured with a stroboscope. The copper load of the organic phase is continuously analysed on a circulating loop by spectrophotometry (Waters 450 U.V., wavelength 440 nm). The spectrophotometer is calibrated for each run by sampling the organic phase ($0.2 \cdot 10^{-6} \text{ m}^3$ samples) and titrating copper by atomic absorption (Varian AA 275). The use of the spectrophotometer in line makes the experiments faster and reduces the number of samples needed; therefore the cell can be smaller and requires smaller quantities of extractant. The pH is measured by Tacussel U6 pH-meter. For initial pH lower than 3, it does not need to be controlled because its variation is small during the short time of the experiment; for pH higher than 3, it is controlled by adding concentrated soda.

Interfacial area A and aqueous phase volume V can be varied using different sets of baffles and Teflon separators. The extraction rate is studied as a function of stirring speeds, interfacial area, aqueous phase volume, extractant and cupric sulfate concentrations and pH.

Results:

Fig. 3, 4, 5, 6 show the variation of the initial extraction rate $\rho_s = -\frac{\bar{V}}{A} \frac{d(\overline{\text{CuR}_2})}{dt}$ with the stirring speeds in both phases (N, \bar{N}), the extractant and copper sulfate total concentrations and pH respectively. The extraction rate ρ_s is independent of A and V, and of both stirring speeds N and \bar{N} when N and \bar{N} are higher than 150 rpm, for the concentrations in figure 3. Figures 4, 5 and 6 show that the rate of extraction increases with $[\overline{\text{RHT}}]$, $[\text{CuSO}_4]$ and pH respectively.

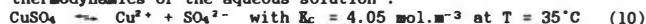
Discussion:

Conclusions from figure 3, the use of $N = \bar{N} = 200 \text{ rpm}$ and the values found for ρ_s which are always lower than $11 \cdot 10^{-5} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, suggest that the cell is operated under conditions of chemical control in the experiments presented in figures 4, 5 and 6. Using the mass-transfer correlation presented in appendix I and calculating interfacial concentrations from ρ_s for each experiment leads to the same conclusions. A linear regression of results in figure 4 shows ρ_s is proportional to the concentration of extractant. Then a multiple regression of $\ln(\rho_s / [\overline{\text{RHT}}])$ upon $\ln([\text{CuSO}_4])$ and pH yields:

$$\rho_s = 1.99 \cdot 10^{-9} \cdot \frac{[\text{CuSO}_4]^{0.49}}{10^{-0.47 \cdot \text{pH}}} [\overline{\text{RHT}}] \quad (\text{SI}), \quad \text{with an average error } e = 0.15$$

$$e = \frac{1}{n} \sum_{i=1}^n \left| \frac{\rho_{s \text{ calc}} - \rho_{s \text{ exp}}}{\rho_{s \text{ exp}}} \right|$$

The following dissociation equilibria are introduced to take into account the thermodynamics of the aqueous solution:



and using extended Debye-Huckel relations:

$$\log \frac{[\text{Cu}^{2+}][\text{SO}_4^{2-}]}{[\text{CuSO}_4]} = \log K_c + \frac{0.128 \sqrt{I}}{1 + 0.0512 \sqrt{I}} - 5.2 \cdot 10^{-5} \cdot I \quad (12)$$

$$\log \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \log K_a + \frac{0.0645 \sqrt{I}}{1 + 0.0538 \sqrt{I}} + 9.9 \cdot 10^{-4} \cdot I \quad (13)$$

with $I = \frac{1}{2} \sum Z^2 [X_i]$ ionic strength of the solution

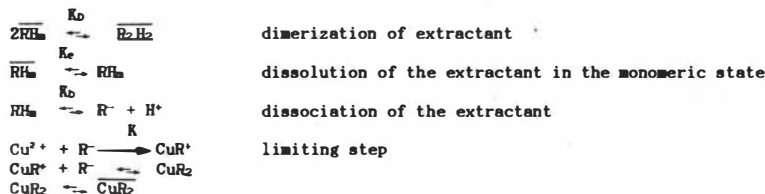
A second multiple regression yields:

$$\rho_a = 7.53 \cdot 10^{-8} \cdot \frac{[\text{Cu}^{2+}]^{0.54} [\overline{\text{RH}}]}{[\text{H}^+]^{0.55}} \quad \text{with an average error } e = 0.14$$

Then, initial fractional orders cannot be attributed to thermodynamics properties of the aqueous phase. According to all preceding remarks, experimental results can be explained according to two hypothesis. Chelating reaction occurs either with adsorbed species at the interface or within the diffusion film, after dissolution of the extractant into the aqueous phase.

Reaction in the aqueous phase:

Supposing following scheme.



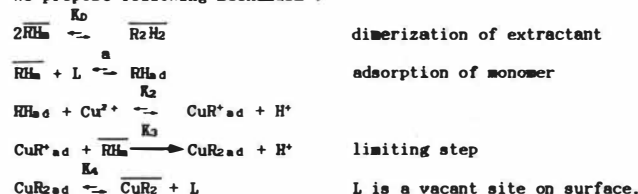
following Hatta's theory for mass-transfer with chemical reaction and assuming a fast reaction regime leads to:

$$\rho_a = \sqrt{2 \cdot K_b \cdot K \cdot D_{\text{RH}} \cdot \frac{[\text{Cu}^{2+}]}{[\text{H}^+]}} \cdot K_e \cdot [\overline{\text{RH}}]$$

where D_{RH} is the diffusion coefficient of RH in aqueous solution. Orders 0.5, -0.5, 1 for $[\text{Cu}^{2+}]$, $[\text{H}^+]$, $[\overline{\text{RH}}]$ respectively are almost identical to experimental orders. Checking this scheme would need, as previously done for LIX 65N in the laboratory [17], to identify K, K_e , K_b and K_D precisely for the pyrazolone and the diluent studied; this work is in progress. But as stripping results, that will be presented elsewhere, can't be analysed with a reaction occurring in the aqueous phase, we think that the nearness of experimental and predicted orders might be accidental. Orders 0.5 for $[\text{Cu}^{2+}]$, -0.5 for $[\text{H}^+]$ conceal real mechanism.

Reaction with adsorbed species :

We propose following mechanism :



Extraction rate expression is : $\rho_s = K_2 \cdot K_3 \cdot [RH]_d \cdot \frac{[Cu^{2+}]}{[H^+]}$

The expression of $[RH]_d$ takes into account the intermediate complex CuH^{+}_d at the interface considering that sites blocked-up by CuR^+ and RH are of same sizes. Finally, the expression of ρ_s is :

$$\rho_s = \frac{C_s \cdot a \cdot K_2 \cdot K_3 [RH]_0^2 [Cu^{2+}]}{[H^+] (1 + a [RH]_0) (1 + K_2 \frac{[Cu^{2+}]}{[H^+]})} \quad (a)$$

With $C_s = 1.01 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2}$ and $a = 0.69 \text{ mol}^{-1} \cdot \text{m}^3$, a linear regression gives raw values of K_2 and K_3 , these values are substituted into equation (a), and K_2 being kept constant K_3 is adjusted to minimize the average error e . Appendix II gives an order of magnitude for K_3 . Neglecting dimerization yields $K_2 = 0.118$ and $K_3 = 0.537$ with an average error $e = 0.17$ on 47 analysed data (fig. 7). Using $K_3 = 2 \cdot 10^{-3} \text{ m}^3 \cdot \text{mol}^{-1}$ yields $K_2 = 0.118$ and $K_3 = 0.57$; experiments with varying concentration of extractant are better fitted but the overall error is slightly higher ($e = 0.20$).

Conclusion:

In a whole range of extractant concentration, cupric sulfate concentration and pH ($20 \leq [RH] \leq 330 \text{ mol} \cdot \text{m}^{-3}$, $20 \leq [CuSO_4] \leq 560 \text{ mol} \cdot \text{m}^{-3}$, $1 \leq \text{pH} \leq 3.5$) initial extraction rates may be calculated from the following empirical kinetic law:

$$\rho_s = 1.99 \cdot 10^{-9} \cdot \frac{[CuSO_4]^{0.49} [RH]_0}{10^{-0.47 \cdot \text{pH}}} \quad (\text{SI})$$

Extraction reactions most likely occur on the interface and involves adsorbed species. The interfacial area would be blocked-up with extractant and the first copper complex CuR^+ . The limiting step would be the reaction between adsorbed CuR^+ and an unadsorbed extractant monomere. This mechanism leads to the expression:

$$\rho_s = \frac{4.7 \cdot 10^{-9} [RH]_0^2 [Cu^{2+}]}{[H^+] (1 + 0.69 [RH]_0) (1 + 0.118 \frac{[Cu^{2+}]}{[H^+]})}$$

It is in agreement with the results and conclusions of a study on the stripping rate performed in our laboratory. This work will be presented elsewhere.

Appendix I: Mass-transfer characteristics of the cell

The mass-transfer characteristics of the cell are measured using the system benzene in the organic phase/water and titrating benzene transferring to water by spectrophotometry (wavelength 203 nm). The benzene transfer is studied as a function of the stirring speeds in both phases in the range 50-300 rpm. In this range, the mass-transfer coefficient of benzene into water is found to vary as $N^{0.67}$; When $N = 200 \text{ rpm}$, \bar{N} has no influence on K_L in the range $100 \leq \bar{N} \leq 300 \text{ rpm}$. This result is in agreement with Olander's experimental correlation (18):

$$K_L = A \cdot \nu^{-0.11} \cdot D^{0.44} \cdot N^{0.67}$$

where ν is the kinematic viscosity of the solution ($\text{m}^2 \cdot \text{s}^{-1}$) and D is the diffusion coefficient of the transferring species ($\text{m}^2 \cdot \text{s}^{-1}$). For water, $\nu = 0.7237 \cdot 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$ [19]; from [20] and with temperature and viscosity corrections according to Wilke and Chang correlation [14], $D = 1.50 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$. Then, A is fitted for our apparatus: $A = 7.66 \cdot 10^{-5} \text{ (SI)}$.

Appendix II: Interfacial tension measurement

Interfacial tension between the extractive solution and the aqueous solution without copper is measured at 35°C with Prolabo tensiometer using the stirrup detachment method. The interfacial tension is studied as a function of extractant or copper complex concentration. Figure 8 shows the variation of interfacial tension with the extractant concentration. The saturation of the interface by the extractant molecules occurs for weak concentration of extractant (10 mol.m^{-3}). When the overall extractant concentration increases so does the degree of aggregation of the extractant characterized by a dimerization equilibrium constant $K_D = \frac{[R_2H_2]}{[RH]^2}$. The predominant species changes from a monomer RH to a dimer and the surface tension no longer increases. From figure 8, and assuming that only monomers adsorb at the interface, one may find the maximal surface excess of the monomer C_s from the Gibb's adsorption equation:

$$C_s = - \left(\frac{1}{RT} \frac{d\Gamma}{d \ln [RH]} \right) \quad \text{where} \quad \begin{array}{l} T = \text{absolute temperature} \\ R = \text{universal gas constant} \end{array}$$

The adsorption constant a is then given by SZYSZKOWSKI equation:

$$\Gamma_0 - \Gamma = RT C_s \ln (1 + a \cdot [RH])$$

If we neglect the part of the curve Γ versus $[RH]$ after the inflection point (that is to say the last data) $[RH] = [RH]$; we obtain a and C_s . Taking into account the last point, yields a fitted order of magnitude for K_D : $10^{-3} < K_D < 3 \cdot 10^{-3} \text{ mol.l}^{-1}$. A new calculation of C_s and a with the average value $K_D = 2 \cdot 10^{-3} \text{ mol.l}^{-1}$, taking into account dimerization on the whole range of extractant, gives very close values of C_s and a : $C_s = 1.01 \cdot 10^{-6} \text{ mol.m}^{-2}$; $a = 0.69 \cdot \text{mol.l}^{-1}$.

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Nomenclature:

A	interfacial area	m^2
a	adsorption constant of RH, $a = [RH_{ad}] / ([RH_m] \cdot [L])$	$mol^{-1} \cdot m^3$
C _s	surface excess of the extractant monomer	$mol \cdot m^{-2}$
D _i	diffusion coefficient of species i	$m^2 \cdot s^{-1}$
Γ	interfacial tension	$N \cdot m^{-1}$
Γ ₀	interfacial tension without extractant	$N \cdot m^{-1}$
K _a	dissociation constant of HSO ₄ ⁻	$mol \cdot m^{-3}$
K _b	dissociation constant of RH	$mol \cdot m^{-3}$
K _c	dissociation constant of CuSO ₄	$mol \cdot m^{-3}$
K _d	dimerization constant	$m^3 \cdot mol^{-1}$
K	kinetic constant for $Cu^{2+} + R^- \xrightarrow{K} CuR^+$	$s^{-1} mol^{-1} \cdot m^3$
K _e	dissolution constant of extractant	
K ₂	equilibrium constant $K_2 = [CuR^+_{ad}] \cdot [H^+] / ([RH_{ad}] \cdot [Cu^{2+}])$	
K ₃	kinetic constant for $CuR^+_{ad} + RH_{m} \xrightarrow{K_3} CuR_{2ad} + H^+$	$mol^{-1} \cdot m^3 \cdot s^{-1}$
K ₄	desorption constant for CuR ₂	$mol \cdot m^{-3}$
N, \bar{N}	stirring speeds	rpm
RH	extractant	
RH _m	extractant in the monomeric form	
ρ _s	initial extraction rate	$mol \cdot m^{-2} \cdot s^{-1}$
V, \bar{V}	volumes	m^3
ν	kinematic viscosity	
\bar{x}	all values concerning the organic phase	
x _{exp}	experimental value	
x _{cal}	calculated value	

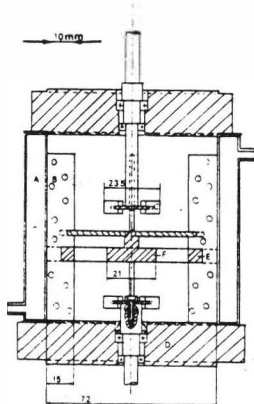


Fig. 1: The stand-on-underecor cell dimensions in mm: -
 A: Thermostated jacket;
 B: Perforated baffles; C: Titanium impellers; D: Teflon cover;
 E: Teflon ring; F: Teflon central separator.

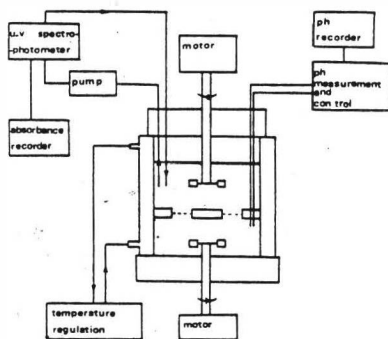


Fig. 2: Experimental set-up.

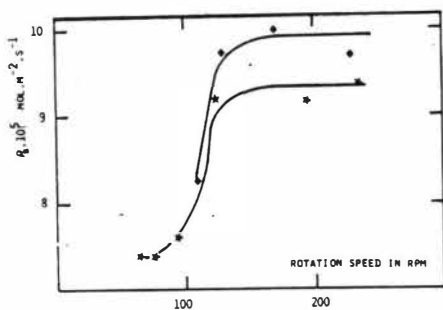


Fig. 3: Effect of stirring speeds N and \bar{N} on initial extraction rate.
 $[\text{CuSO}_4] = 95 \text{ mol.m}^{-3}$, $(R\bar{N}) = 227 \text{ mol.m}^{-3}$, no H_2SO_4 added,
 $\text{pH} = 3.5$ non controlled, $T = 35^\circ\text{C}$
 $\ast N = 200 \text{ rpm } \bar{N} \text{ is varied, } \diamond \bar{N} = 200 \text{ rpm } N \text{ is varied.}$

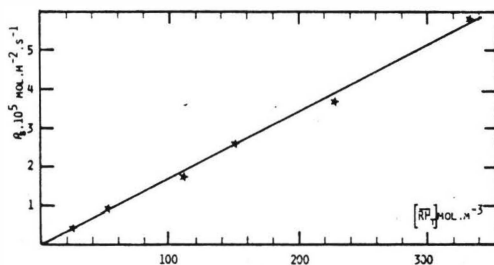


Fig. 4: Influence of total extractant concentration on initial extraction rate
 $[\text{CuSO}_4] = 95 \text{ mol.m}^{-3}$, $[\text{H}_2\text{SO}_4] = 9.3 \text{ mol.m}^{-3}$, $\text{pH} = 2.2$,
 $T = 35^\circ\text{C}$, $N = \bar{N} = 200 \text{ rpm}$.

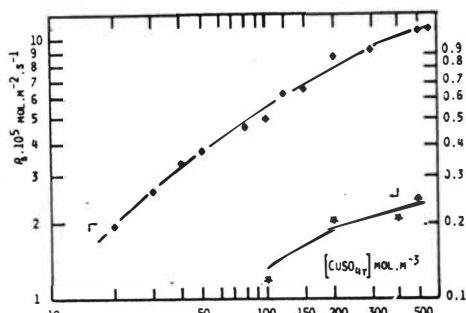


Fig. 5: Effect of total CuSO_4 concentration on the initial extraction rate
 $7.2 \leq [\text{H}_2\text{SO}_4] \leq 16.6 \text{ mol.m}^{-3}$, to fit $\text{pH} = 2$,
 $T = 35^\circ\text{C}$, $N = \bar{N} = 200 \text{ rpm}$, $\diamond [R\bar{N}] = 270 \text{ mol.m}^{-3}$,
 $\ast [R\bar{N}] = 7 \text{ mol.m}^{-3}$

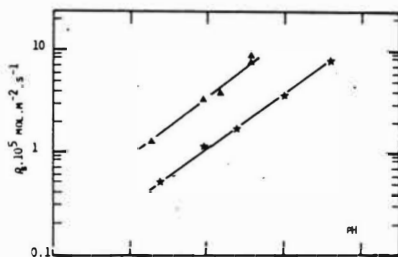


Fig. 6: Effect of pH on the initial extraction rate
 $[\text{CuSO}_4] = 95 \text{ mol} \cdot \text{m}^{-3}$, pH controlled, $T = 35^\circ\text{C}$
 $\star [\text{RH}] = 84 \text{ mol} \cdot \text{m}^{-3}$, $\Delta [\text{RH}] = 230 \text{ mol} \cdot \text{m}^{-3}$,
 $N = \bar{N} = 200 \text{ rpm}$.

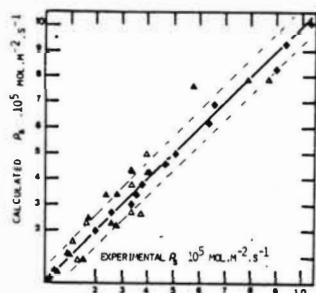


Fig. 7: Comparison between experimental and calculated values of the initial extraction rate.

Δ variable $[\text{RH}]$
 \triangle ——— $[\text{H}^+]$
 \diamond ——— $[\text{Cu}]$

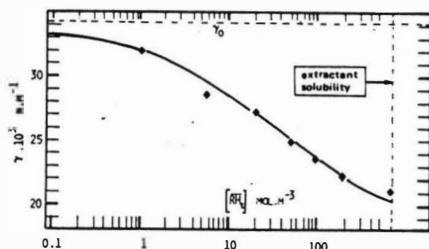


Fig. 8: Effect of extractant concentration on interfacial tension,
 \diamond experimental data, --- calculated values.
 Aqueous phase pH = 2 set with H_2SO_4 .
 Organic phase: pyrazolone in Solvesso 150, $T = 35^\circ\text{C}$.

Some experiences in the separation of Co-Ni with PC 88A and Cyanex 272 in mixed sulphate-chloride media

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Introduction

Sulphate and mixed sulphate-chloride solutions are conventional aqueous media for the separation of cobalt and nickel with solvent extraction processes. Recently developed organophosphorous acid reagents based on alkyl phosphonic and alkyl phosphinic acids /e.g. PC 88A, Cyanex 272/ permit a more efficient separation of Co from Ni in sulphate solution than was possible with the established extractant di-2-ethylhexyl phosphoric acid /D2EHPA/. In the last years a few papers (1, 2, 3) have been appeared on the solvent extraction separability of Co and Ni with 2-ethyl-hexyl phosphonic acid mono-2-ethylhexyl ester /PC 88A/ and di-/2,4,4-trimethylpentyl/phosphinic acid /Cyanex 272/ reagents. The author of reference (1) qualitatively shows that in media containing Cl^- and SO_4^{2-} ions the formation of Co and Ni chloro and sulphato complexes must be taken into account, however no significant change in the separation coefficients can be expected between the two metal ions since the stability constants of the corresponding chloro and sulphato complexes are very similar. As a result of metal-chloro and - sulphato complex formation the Extraction % - pH curves measured at different chloride and sulphate concentrations will be shifted as Figs. 1 - 4 show. The authors of papers (3) and (4) explain these shifts so that the measured pH values in such solutions are lower than their actual values. In this paper we show that the extraction of Co and Ni with PC 88A and Cyanex 272 reagents from media containing Cl^- and SO_4^{2-} ions can be quantitatively described considering only the chloro and sulphato complexes of these elements. On the basis of this model it can be shown that a significant change in the separation coefficient of the Co and Ni can be expected only at very high $> 3 \text{ mol/dm}^3$ Cl^- ion concentrations due to the formation of the CoCl_4^{2-} species.

Reagents, Experiments

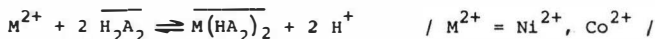
Cyanex 272 sample was a gift of Cyanamid /Canada/ Ltd, for which the authors are very grateful. PC 88A was the product of Daihachi Chemical Industry Co. /Japan/. Shell MSB 210 solvent has been used and 2.5 vol%

tributyl phosphate /TBP/ as phase modifier. The effect of the latter material to the extraction of Co and Ni could be neglected in the frame of the model to be described, due to its relatively low concentration. All other reagents used were of analytical grade. The distribution of Co and Ni was measured with shaking funnel experiments at room temperature. Equal volumes of solvent and aqueous solution were contacted for 5 minutes. After separating the phases the metal content of the aqueous phase was analysed with AAS. In the course of our studies the distribution of Co and Ni has been investigated between the organic solvent and aqueous solution of nearly constant ionic strength /I=5.0/ containing perchlorate - chloride or perchlorate-sulphate ions as a function of pH at different chloride and sulphate concentrations.

Our experimental data are shown on Figs. 1 - 4. It can be seen that with increasing chloride or sulphate concentrations the Extraction % - pH curves shift parallel towards higher pH values. Plotting the log D values as a function of pH straight lines can be obtained in wide pH ranges. The slope of these curves was 1.00 ± 0.05 in case of Ni - PC 88A and Ni - Cyanex 272 systems both in chloride and in sulphate solutions. The slope of different Co systems varied between 1.25 - 1.70 indicating a more complex process. According to reference (1) taking into account monomeric reagent concentrations integer numbers can be obtained in case of Co.

Computations, Results and Discussions

Now we would like to explain the observed shifts of curves with increasing chloride and sulphate concentrations with the help of a simple model. We consider a simple extraction equilibrium



with a constant K_{ex} :

$$K_{ex} = \frac{[\overline{M(HA_2)_2}][H^+]^2}{[M^{2+}][\overline{H_2A_2}]^2} \quad / 1 /$$

The distribution constant D in chloride medium is as follows:

$$D = \frac{[\overline{M(HA_2)_2}]}{[M^{2+}](1 + \sum_i K_i^M [Cl^-]^i)} \quad / 2 /$$

here K_1^M is the stability constant of the i -th metal-chloro species. According to reference (5) in case of Ni^{2+} one has to consider only the formation of $NiCl^+$ species,

$$K_1^{Ni} = \frac{[NiCl^+]}{[Ni^{2+}][Cl^-]} \quad / 3a /$$

while in case of Co^{2+} the formation of $CoCl_4^{2-}$ should be also taken into account:

$$K_1^{Co} = \frac{[CoCl^+]}{[Co^{2+}][Cl^-]} \quad / 3b /$$

$$K_4^{Co} = \frac{[CoCl_4^{2-}]}{[Co^{2+}][Cl^-]^4} \quad / 3c /$$

In our experimental range the total analytical concentration of Cl^- ion and of reagent H_2A_2 is much higher than the concentration of Co^{2+} or Ni^{2+} therefore their equilibrium concentrations are nearly equal to their total /analytical/ concentrations. With these simplifications combining eqs. /1/, /2/, /3/ we can derive the equations as follows: for the extraction of Ni^{2+} from Cl^- medium

$$\frac{1}{D_{Ni}} = \frac{[H^+]^2}{K_{ex} [H_2A_2]^2} + \frac{[H^+]^2}{K_{ex} [H_2A_2]^2} \cdot K_1^{Ni} [Cl^-] \quad / 4 /$$

Plotting $1/D_{Ni}$ values as a function of Cl^- concentrations at constant pH values we get straight lines. Fig. 5. shows these lines in case of PC 88A and Cyanex 272. The value of stability constant of $NiCl^+$ formation can also be determined and was in good agreement with the data of the literature (5). A plot corresponding to eq. /4/ in case of Co^{2+} resulted straight lines only at lower Cl^- concentrations indicating the significance of $CoCl_4^{2-}$ species too. Taking into account this species we can derive an equation as follows:

$$\frac{1}{D_{Co}} = \frac{[H^+]^2}{K_{ex} [H_2A_2]^2} \left(1 + K_1^{Co} [Cl^-] + K_4^{Co} [Cl^-]^4 \right) \quad / 5 /$$

In the knowledge of K_1^{Co} and K_4^{Co} we can plot $1/D_{Co}$ as a function of $1 + K_1^{Co} [Cl^-] + K_4^{Co} [Cl^-]^4$ at constant pH values. According to Ref.(5) using $K_1^{Co} = 1.0$ and $K_4^{Co} = 7.1 \times 10^{-3}$ values we could obtain straight lines in the full chloride concentration range in the case of both

PC 88A and Cyanex 272 as Fig. 6. shows, indicating the validity of our assumptions.

Similar models have been derived for the explanation of extraction behaviour of Co^{2+} and Ni^{2+} in sulphate and mixed sulphate-chloride media too.

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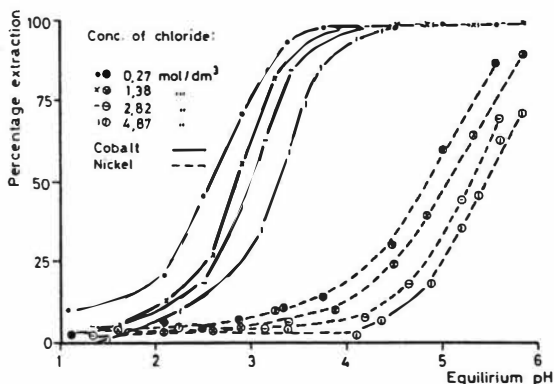


Figure 1. Extraction of cobalt and nickel by Cyanex 272 at different chloride concentrations
 Organic phase: 20 vol% Cyanex 272, 2.5 vol% TBP in MSB 210
 Aqueous phase: 0.051 mol/dm^3 Co, 0.086 mol/dm^3 Ni as chlorides, NaCl , NaClO_4 ; $I = 5.0$

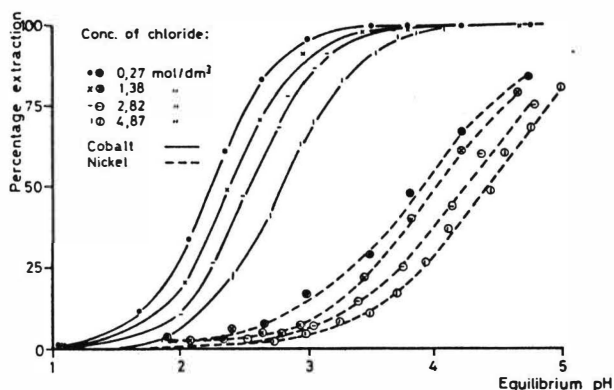


Figure 2. Extraction of cobalt and nickel by PC 88A at different chloride concentrations
 Organic phase: 20 vol% PC 88A, 2.5 vol% TBP in MSB 210
 Aqueous phase: 0.051 mol/dm^3 Co, 0.086 mol/dm^3 Ni as chlorides, NaCl , NaClO_4 ; $I = 5.0$

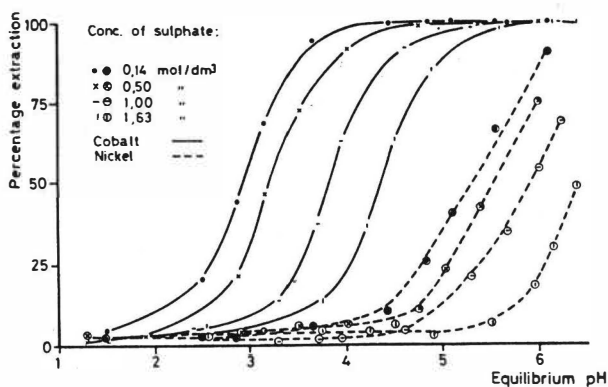


Figure 3. Extraction of cobalt and nickel by Cyanex 272 at different sulphate concentrations

Organic phase: 20 vol% Cyanex 272, 2.5 vol% TBP in MSB 210
 Aqueous phase: 0.051 mol/dm³ Co, 0.086 mol/dm³ Ni as sulphates, Na₂SO₄, NaClO₄; I = 5.0

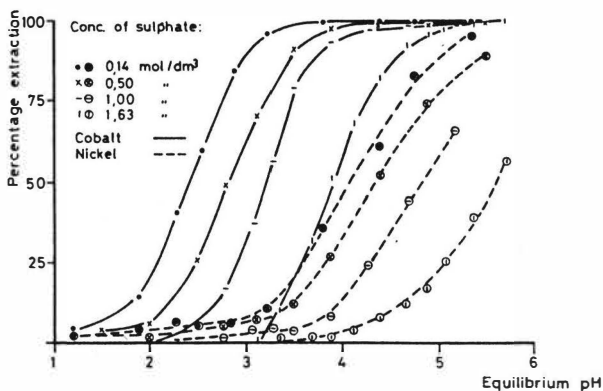


Figure 4. Extraction of cobalt and nickel by PC 88A at different sulphate concentrations

Organic phase: 20 vol% PC 88A, 2.5 vol% TBP in MSB 210
 Aqueous phase: 0.051 mol/dm³ Co, 0.086 mol/dm³ Ni as sulphates, Na₂SO₄, NaClO₄; I = 5.0

Chloride - Nickel

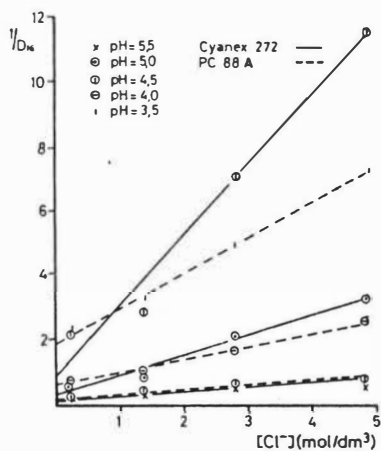


Figure 5.
Plot of $Ni^{2+}-Cl^-$ system according
to eq. /4/

Chloride - Cobalt

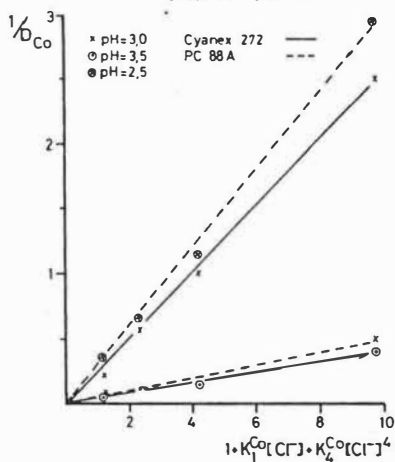


Figure 6.
Plot of $Co^{2+}-Cl^-$ system according
to eq. /5/

Complex Formation of Noble Metals with Polydentate Reagents under Extraction Conditions

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Our organization is continuously expanding and developing the studies into the syntheses and extraction and complex-forming properties of the sulfur containing reagents to produce some new effective extract agents.

As has been shown, Au (III) is extracted from the acidic medium according to the interphase anion exchange mechanism, the period of phase contact being less than two minutes, thus forming the ion associates. The latter have been isolated and described. When the period of phase contact exceeds two minutes, there takes place the further involvement of the ligand coordination sphere of Au (III).

The involvement of the ligand donor atoms into the inner coordination sphere of a metal ion has been observed with Pd(II) extractions by aminosulfides. The extraction of Pd(II) by aminoketosulfides proceeds by stages. The ion associates are first formed and then the involvement of some of the ligand atoms into the inner coordination sphere of the metal ion occurs. The extraction proceeds according to the mixed mechanism.

IR, Raman, and ^1H NMR spectral methods have been employed to investigate the complexes isolated, the compositions and configurations thereof being described.

Introduction

The report presented considers the investigations of complex formation of Au(III) and Pd(II) chlorides with aminosulfides and aminoketosulfides under the extraction conditions. Of special interest are nowadays the studies into the ligand properties of polydentate reagents containing primary, secondary, and tertiary atoms of the amine nitrogen.

To attain the profound realization of the extraction equilibrium mechanisms of interactions of amino- and aminoketo-sulfides and noble metals, it is necessary to confront the results obtained in extractions with the information on compositions and structures of the complexes extracted. Thus, a single viewpoint is provided for considering the complex formation process. Proceeding from the assumption that the coordination of the ligand donor atoms is determined by the conditions of complex formation, the noble metal complexes with aminosulfides and aminoketosulfides have been isolated from acidic and neutral media by the direct and extractational methods.

Table 1. Structural Formulae, Conventional and Full Names, Some Physico-Chemical Characteristics of the Reagent Studied



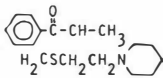
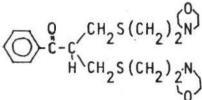


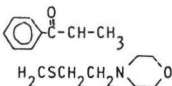
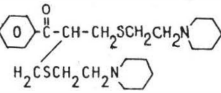
N	Convent. Names	Full Names	Structural Formulae	b.p.s. m.p.s. (°C)	ρ_4^{20}	n_D^{20}
1	PEDS	pyperidinoethyl-dodecylsulfide	$C_{12}H_{25}SCH_2CH_2N$ 	158 /2mm/	0.9154	1.4875
2	MEDS	morpholinoethyl-dodecylsulfide	$C_{12}H_{25}SCH_2CH_2N$ 	170 /5mm/	0.9497	1.4875
3	BHEA	bis(2-hexylthioethyl)amine	$HN(CH_2)_2SC_6H_{13}$ $(CH_2)_2SC_6H_{13}$	200 /2mm/	0.9267	1.4930
4	TBEA	tris(2-butylthioethyl)amine	$N(CH_2)_2SC_4H_9$ $(CH_2)_2SC_4H_9$ $(CH_2)_2SC_4H_9$	230 /2mm/	0.9676	1.5100
5	PPP	1-phenyl-2-pyridinoethylthiomethyl)-1-propanone		135 /4mm/	1.0562	1.5500
6	BMP	bis(morpholinoethylthiomethyl)-1-phenyl-1-ethanone		depr. /1mm/ 100	1.1710	1.5745
7	TPP	1,1,3,3-tetrakis(pyperidinoethylthiomethyl)-2-propanone	$O=C(CH_2SCH_2CH_2N$  $)_2CH_2SCH_2CH_2N$  $)_2$	depr. /1mm/ 100	1.0842	1.5525
8	PMP	1-phenyl-2(morpholinoethylthiomethyl)-1-propanone		210 /1mm/	1.1141	1.5537
9	DTEA	2-dodecylthioethylamine	$C_{12}H_{25}S(CH_2)_2NH_2$	170 /4mm/	0.8886	1.4739
10	BPP	bis(pyperidinoethylthiomethyl)-1-phenyl-1-ethanone		depr. /1mm/ 100	1.0960	1.5670
11	BHEA	bis(2-hexylthioethyl)amine	$HN(CH_2)_2SC_6H_{13}$ $(CH_2)_2SC_6H_{13}$	200 /2mm/	0.9267	1.4930

Table 1 presents the structural formulae, conventional and full names, some physico-chemical characteristics of the reagent studied, synthesized, and identified for the first time in the Institute of Chemistry of the Bashkirian Branch of the USSR Academy of Sciences.

The Complex Formation of Au(III) with Aminosulfides and Aminoketosulfides under Extraction Conditions

The coordination chemistry of Au(III) is distinctive by a great variety of compounds with N- and S-containing ligands of the plane-square structure [1-4]. The majority of Au(III) complexes are relatively unstable and suffer reduction under the light effect as well as under redox conditions. As it follows from the scanty literature data on the complex formation of Au(III) with ligands containing both sulfur and nitrogen atoms, the composition and structure of the compounds formed depend on the ligand structures [5].

The elemental compositions of the Au(III) chloride complexes isolated by the direct method in the neutral medium are given in Table 2 to illustrate and prove all the ligands under study to form the compounds, the content of metal in which is equivalent to the total content of S and N atoms, the ratio of Au:Cl being 1:3.

Table 2. Elemental Compositions of the Complexes of Noble Metals with Some Amino- and Aminoketo-Sulfides, Isolated by the Direct Method from the Neutral Medium

Ligands ↓ Contact Period →	Au(III) 30 min	Pd(II) 30 min
$C_{12}H_{25}SCH_2CH_2NH_2$	$(AuCl_3)_2 \cdot L$	$PdCl_2 \cdot L$
$NH(CH_2CH_2SC_6H_{13})_2$	$(AuCl_3)_3 \cdot L$	$(PdCl_2)_3 \cdot 2L$
Contact period →	3-5 hours	30 minutes
$C_{12}H_{25}SCH_2CH_2NR_2$	$(AuCl_3)_2 \cdot L$	$PdCl_2 \cdot L$
$N(CH_2CH_2SC_4H_9)_3$	$(AuCl_3)_4 \cdot L$	$(PdCl_2)_2 \cdot L$
$C_6H_5COCHCH_3$	$AuCl_3 \cdot L$	$PdCl_2 \cdot L$
$H_2CSCH_2CH_2NR_2$	$(AuCl_3)_2 \cdot L^*$	
$C_6H_5COCH(CH_2SCH_2CH_2NR_2)_2$	$(AuCl_3)_2 \cdot L$	$(PdCl_2)_2 \cdot L$
$O=C\left(\begin{array}{c} H \\ \\ CH_2SCH_2CH_2NR_2 \\ \\ CH_2SCH_2CH_2NR_2 \end{array}\right)_2$	$(AuCl_3)_4 \cdot L$	$(PdCl_2)_4 \cdot L$

* heated to ($\sim 40^\circ C$).

The complexes represent the nonhydroscopic pulverous substances temperately soluble in usual organic solvents and stable for 2-3 weeks in a dark room at 5-10°C. With the complex formation of Au(III) and aminosulfides containing the primary and secondary atoms of the amine nitrogen, there occurs the involvement (within 30 min.) of donor atoms of the S and N ligands into the inner coordination sphere of the metal ion in the neutral medium. It is proved by the ^1H NMR spectral assignments of the complexes (Table 3), where an additional chemical shift of the proton signals has been observed at the sulfur and intropen atoms to compare them with those of ligands.

The successive character of the complex formation of Au(III) with BHEA aminosulfide by the direct method has been confirmed by the ^1H NMR spectra; which allow to make an assumption that the proton signals of methylene groups at the nitrogen atoms are shifted to the lower field for approx. 0.6 p.p.m. and those at the sulfur atoms - for 0.3 p.p.m. at the initial stages of complex formation. The largest additional shift is observed for the single proton signal at the ligand nitrogen atom. That signal is intensively shifted to the lower field region up to 10 p.p.m. Thus, the complex formation includes all the ligand donor atoms with their involvement into the inner coordination sphere of Au(III) where the electron donor-acceptor bonding Au - N is formed first.

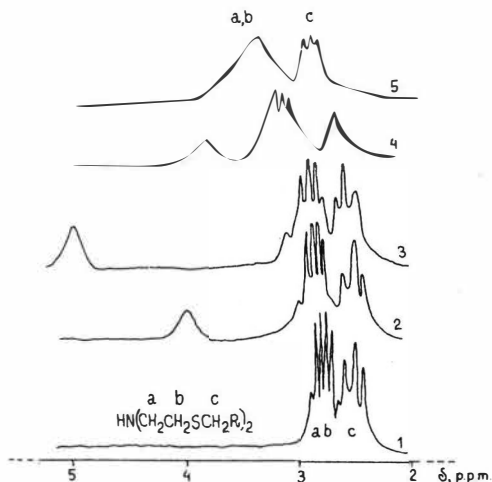


Figure 1. ^1H NMR Spectra of BHEA Aminosulfide (1) and of its Complex with Au(III) Chloride Obtained by the Direct Method (5). Spectra 2-4 Illustrate the Successive Shift of the Ligand Proton Signals in the Process of Complex Formation (100 MHz, Solvent - D-Chloroform).

In contrast to aminosulfides with the content of primary and secondary atoms of the amine nitrogen, the complex formation with aminosulfides containing the tertiary nitrogen atoms proceeds more slowly. The formation of Au(III) complexes with such ligands as MEDS, PEDS, TBEA coordinated by all donor atoms has been established possible with the prolonged period of reagent contact (3-5 hs) and temperate heating (40°C) only (Table 2). The successive formation of Au(III)-PEDS complex ascertained by the ^1H -NMR spectral data has shown the additional chemical shift to occur for the proton signals of both sulfur and nitrogen atoms, still first are shifted to the lower field region those at the sulfur atoms. The complex formation of Au(III) and aminoketosulfides containing the tertiary nitrogen atoms with the reagent contact period of 2-3 min. results in the compounds possessing the Au:Cl:S:N ratio of 1:3:1:1 (Table 2). The ^1H -NMR spectra reveal the largest additional chemical shift for the proton signals of methylene groups at the sulfur atoms (0.6 p.p.m.). At the same time, the prolonged period of reagent contact favour the proton signals at the nitrogen atoms to start shifting towards the lower field region, which is indicative of their coordination by Au(III) (0.6-1 p.p.m.).

The isolation of the Au(III) complexes with amino- and aminoketosulfides by the extraction method (3 mol/l HCl medium, 2-3 min of contact phase period) gives the orange-red ointment-like substances well soluble in organic solvents. The elemental analysis data of the complexes obtained prove the Au:Cl:N ratio to be 1:4:1 irrespective of the number of sulfur atoms in the ligand molecules (Table 3).

Table 3. The Elemental Competitions of Noble Metal Complexes with some Aminosulfides and Aminoketosulfides Isolated by the Extraction Method from 3 mol/l of HCl Medium (Phase Contact Period - 2-5 min.).

Ligands (L)	Au(III)	Pd (II)
$\text{C}_{12}\text{H}_{25}\text{SCH}_2\text{CH}_2\text{NH}_2$		$\text{PdCl}_2 \cdot \text{L}$
$\text{NH}(\text{CH}_2\text{CH}_2\text{SC}_6\text{H}_{13})_2$		$(\text{PdCl}_2)_3 \cdot 2\text{L}$
$(\text{CH}_2\text{CH}_2\text{SC}_4\text{H}_9)_3$	$\text{HAuCl}_4 \cdot \text{L}$	$(\text{PdCl}_2)_2 \cdot \text{L}$
$\text{C}_6\text{H}_5\text{COCHCH}_3$ $\text{H}_2\text{CSCH}_2\text{CH}_2\text{NR}_2$		$\text{H}_2\text{PdCl}_4 \cdot \text{PdCl}_2 \cdot 2\text{L}$
$\text{C}_6\text{H}_5\text{COCH}(\text{CH}_2\text{SCH}_2\text{CH}_2\text{NR}_2)_2$	$(\text{HAuCl}_4)_2 \cdot \text{L}$	$\text{H}_2\text{PdCl}_4 \cdot \text{PdCl}_2 \cdot \text{L}$
$\text{CO} \left(\begin{array}{c} \text{CH}_2\text{SCH}_2\text{CH}_2\text{NR}_2 \\ \text{CH} \\ \text{CH}_2\text{SCH}_2\text{CH}_2\text{NR}_2 \end{array} \right)_2$	$(\text{HAuCl}_4)_4 \cdot \text{L}$	$(\text{H}_2\text{PdCl}_4)_2 \cdot (\text{PdCl}_2)_2 \cdot \text{L}$

Thus, the complex formation of Au(III) with aminosulfides and aminoketosulfides in the acidic medium proceeds with the initial formation of ion associates (according to the interphase anion exchange mechanism) with the subsequent involvement of the ligand donor atoms into the inner coordination sphere of Au(III). The lowering of the aqueous phase acidity favours the acceleration of involving the ligand nitrogen atoms and that is the reason for the failure of our attempt to isolate. The intermediate ion associates from 0.1 mol/l of HCl solutions with 1-2 min of the contact phase period. The electron spectra of absorption of the Au(III) complexes with aminosulfides and aminoketosulfides were recorded with the employment of acetonitrile. The interpretation of the electron spectra of absorption of the Au(III) complexes with the ligands investigated provides a conclusion that they possess the plane-square structure, which is most likely tetrahonally twisted, the given conclusion being in agreement with the literature data [6].

Table 4. The Characteristics of the Electron Absorption Spectra of Au(III) Complexes with Some Aminosulfides and Aminoketosulfides (Solvent - Acetonitrile).

Assignment	HAuCl ₄ ·PMP		(AuCl ₃) ₂ ·PPP		(HAuCl ₄) ₂ ·BMP	
	ν , cm ⁻¹	ϵ , l/mol·cm	ν	ϵ	ν	ϵ
$^1A_{1g} \rightarrow ^1A_{2u}$	22000	25	22320	73	23820	120
$^1A_{1g} \rightarrow ^1E_g$	25630	100	25680	230	25840	450
$^1A_{1g} \rightarrow ^1A_{2u}, ^1E_u(1)$	30960	2500	30800	3700	30800	6400
$\pi \rightarrow \pi^*$ benzene	35920	1200	35760	900	36960	3300
$\pi \rightarrow \pi^*$ conj.	40240	6250	39600	2800	40560	17000
$^1A_{1g} \rightarrow ^1E_u$	43600	25300	43600	30400	43760	53000

Raman spectra of the Au(III) complexes with the ligands under study could not be recorded because of their fast decay in the light of the helium-neon laser.

The Complex Formation of Pd(II) with Aminosulfides and Aminoketosulfides.

The literature reports numerous coordinational Pd(II) compounds with such ligands as organic sulfides, amines, etc. There exists a limited number communications concerning the Pd(II) complexes with the reagents containing both sulfur and nitrogen atoms [7,8].

Irrespective of the production method, all the Pd(II) complexes with aminosulfides and aminoketosulfides remain stable for several years; they possess limited solubi-

lities in usual organic solvents, which impedes their study. Those complexes represent yellow-to-brown pulverous substances. As it follows from the consideration of the elemental compositions of Pd(II) complexes with aminosulfides isolated by the direct method (interactions of Na tetrachloropalladate (II) and ligands in diethyl ether), the complex formation results in the compounds with the Pd:Cl ratio 1:2 and that of Pd:L varies with regard to the total sum of S and N atoms in the ligand molecules. The electrophoregrams of the complexes give no evidence to any shifts of coloured spots from the starting line to indicate the absence of electrolytic dissociation. The assignments of proton signals in the ^1H -NMR spectra of the TBEA aminosulfide and $(\text{PdCl}_2)_2 \cdot \text{TBEA}$ complex proves the additional chemical shift to occur for the proton signals of methylene groups both of sulfur atoms (~ 0.6 p.p.m.) and nitrogen ones (~ 1 p.p.m.), thus providing a conclusion that all the ligand donor atoms take part in the complex formation.

The complexes of Pd(II) with aminosulfides isolated by the extraction method (contacting the aqueous and organic phases with the content of Pd(II) in 3 mol/l of HCl solution and ligand solution in chloroform, respectively) do not differ by their compositions and physicochemical properties from those obtained by the direct method (Table 3). The ^1H -NMR spectra of the complexes, with the TBEA aminosulfide in particular, isolated by the direct and extraction methods coincide entirely. Therefore, the complex formation of Pd(II) with aminosulfides is accompanied by the involvement of the donor atoms of ligand sulfur and nitrogen into the inner coordination sphere of the metal ion to result in the complexes identical by their compositions and structures with either method of their production. The elemental analysis results for the Pd(II) complexes with the aminoketosulfides isolated by the direct method prove the Pd:Cl:S:N ratio to be 1:2:1:1. The complexes' electrophoregrams give no shifts of the coloured spots, which is indicative of the absence of ion associates. There is an additional chemical shift of the proton signals at S and N atoms in the ^1H -NMR spectra of the complexes mentioned as compared to those of ligands. Thus, the $\text{PdCl}_2 \cdot \text{PPP}$ complex spectrum reveals the additional chemical shift of the proton signals at donor atoms for 1 p.p.m.

The absorption electron spectra of the Pd(II) complexes with aminoketosulfides give intensive bands of the charge transfer in the region of 35000 and 40000 cm^{-1} , which are inherent to complexes of the $\text{PdCl}_2 \cdot 2\text{L}$ type. The electrophoregrams of the complexes given present a considerable shift of the coloured spots from the starting line towards the anode and a small one - towards the cathode. The electrolytic motion towards the anode has been assumed to take place owing to the presence of the PdCl_4^{2-} ions in the complex structures and that towards the cathode - to the presence of complexes with protonated atoms of the ligand nitrogen. The absorption electron spectra of the Pd(II) complexes with the aminoketosulfides isolated by the extraction method show an intensive broad in the region of 41000 cm^{-1} characteristic for the

PdCl_4^{2-} ion. The charge transfer bands are probably submerged and cannot be observed due to their much lower intensity in the given region of the $\text{PdCl}_2 \cdot 2\text{L}$ complexes' spectra than that in the PdCl_4^{2-} ion spectrum. Thus the extraction of Pd(II) by aminoketosulfides proceeds by stages. The ion associates are first formed, then there occurs the involvement of the ligand sulfur atoms into the inner coordination sphere of Pd(II) . At the same time, the tetrachloropalladate $(\text{II})^-$ ions are bound up with the ligands through the nitrogen protonated atoms and hence the extraction proceeds according to the mixed mechanism. The $^1\text{H-NMR}$ spectral observations of the successive formation of the complexes given have shown that the additional chemical shift of the proton signals occurs at the nitrogen atoms in the first place and that at the sulfur atoms - in the second. The nitrogen atoms in aminoketosulfides have been experimentally established more basic than those in aminosulfides. The difference found in complex formations of Pd(II) with the ligands discussed and consisting in the fast involvement of the aminosulfide nitrogen atoms into the inner coordination sphere of the metal ion is therefore explained by the lower basicity of the nitrogen atoms as compared to those in aminoketosulfides as well as by the absence of ketogroups stabilizing the electron densities of sulfur atoms.

The plane-square structures of the Pd(II) complexes may be of *cis*- and *trans*- configurations [9]. To determine the configurations of the complexes under study, their Raman spectra have been recorded and the characteristics are given in Table 5.

Table 5. The Band Assignment in the Raman Spectra of Pd(II) Chloride Complexes (cm^{-1})

Assignment	: $\text{PdCl}_2 \cdot 2\text{DHS}$: $(\text{PdCl}_2)_3 \cdot 2\text{BHEA}$: $\text{PdCl}_2 \cdot \text{PPP}$
$\delta_{\text{Cl-Pd-S}}$	135	130	163
$\gamma_{\text{Pd-S}}$	320	314	317
$\gamma_{\text{Pd-Cl}}$	304	305	305

The spectra of all complexes show a band in the region of $300\text{--}315\text{ cm}^{-1}$, which is invariably referred to the symmetric vibrations of the $\gamma_{\text{Pd-Cl}}$ bonding thus being indicative of the *trans*-configuration of Pd(II) complexes [6,9-15]. The second band active in Raman spectra corresponds to the Pd-S bonding vibrations. It is considerably less intensive than that of the $\gamma_{\text{Pd-Cl}}$ bonding, is positioned nearby within the interval of $294\text{--}330\text{ cm}^{-1}$ and therefore its assignment is difficult. As it follows from the interpretations of the spectral assignments, all the Pd(II) complexes investigated have been proved *trans*-isomers (C_{2v} symmetry). With the *cis*-configurations according to the Raman spectra, active should be the vibrations appearing as two bands of $\gamma_{\text{Pd-S}}$ [16,17].

Conclusions

The studies into the complex formation of Au(III) and Pd(II) with aminosulfides and aminoketosulfides have proved the extraction from the active medium to proceed first according to the interphase anion exchange mechanism with the formation of ion associates and further the reagent donor atoms are involved into the inner coordination sphere of the metal ions. The complex formation in the neutral medium provides the relatively slow involvement of the ligand donor atoms into the inner coordination sphere of the metal ions to compare it to the complex formation period in the acidic medium.

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Extraction of Alkali and Alkaline Earth Metals
with Dibenzo[14]-crown-4-oxyacetic and-capronic acid

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The title compounds were synthesized on the base of an improved procedure using sodium amide.

The extraction of Li, Na, K, Rb as well as Mg, Ca, Sr, Ba with ligand solutions in CHCl_3 was studied in the dependence on pH and ligand concentration realizing equilibrium conditions. The resulting data were used to evaluate the composition of species existing in the organic phase. This method gave good results especially with dibenzo[14]-crown-4-oxyacetic acid. Some disturbances were observed in the case of dibenzo[14]-crown-4-oxyacetic acid because of the water solubility of this extractant. The capronic acid derivative, at all, is an essentially better extractant than the acetic compound. For the extraction of alkali metal ions with dibenzo[14]-crown-4-oxyacetic acid the following extraction rates were found: Li 40 %, Na 2,4 %, K 0,9 %, Rb 0,3 %. Li is extracted as the expected 1:1 species, whereas the other alkali metals form 1:2 compounds. These measurements were made in the presence of tetramethyl ammoniumhydroxide. Using other bases to adjust pH, for example triethanoleamine, the sequence of extraction is changed in favour of K, this fact finds an explanation by the similarity of ionic radii of K and Ca. Ca as well as the other alkaline earth metals form 1:2 complexes of the sandwich type with the crownethercarbonic acids studied here. These compounds, at all, are excellent extractants for the higher alkaline earth metals and reach quantitative results. Separations are possible by varying pH. This is unequivocally a result of the favourable combination of donor atoms in these compounds. Such an effect was not observed using a mixtures of hydroxydibenzo[14]-crown-4 and capronic acid to extract alkali and alkaline earth ions. All results given above are demonstrated by a series of graphical plots of $\lg D$ versus pH or $\lg c_L$.

Crown Ethers as Synergic Ligands in The Solvent Extraction of Metal Ions by Thenoyl-trifluoroacetone

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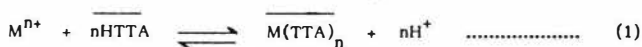
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Recently, crown ethers found many applications in solvent extraction of several metal ions especially alkali and alkaline earth metals (1-3). Different approaches were developed to solubilize the anion associated with the metal cation to be extracted by the CE in the organic phase. One of these is the use of organic-soluble-aqueous-insoluble cation exchanger, thus avoiding the problem of anion transference (4). This concept represents a case of synergism, if the CE is regarded as a neutral donor and the liquid cation exchanger is the acidic extractant. In this contribution, the B-diketone thenoyltrifluoroacetone (HTTA) is introduced as the organic soluble ligand to be associated with the metal cation and CEs as synergic ligands. The systems given in this paper are Co(II)-0.10 M (H^+ , $NaClO_4$)/CEs + HTTA-chloroform; selected lanthanides (III)-0.10 M (H^+ , $NaClO_4$)/CEs + HTTA-chloroform and actinides Am(III) or Pu(IV)/CEs + HTTA-chloroform. The results are discussed in terms of the synergic ability of the CEs to form adducts with the metal TTA-chlate and the principle of correspondence between the CE and the ionic radii of the metal ions extracted.

Chemical Equilibria of Investigated Systems

Description of the equilibria encountered when extracting with CEs is governed by the system used for solubilizing the anion associated with the metal to be extracted in the organic phase. When anion-solvating diluent or large highly polarizable anion is used for this purpose, a chemical model based on ion pair formation can satisfactorily explain the extraction equilibria. For the systems studied, the B-diketone HTTA acts as acidic extractant and CEs act as neutral extractants, this justifies using a chemical model similar to that used for extraction of metal adducts. Therefore, the equilibrium encountered for our systems can be presented by the following equations.

In absence of crown ether, the extraction of M^{n+} by HTTA is given by (5):



where the barred symbols refer to the organic phase species. At constant ionic strength and assuming that the activity coefficient in the organic phase to be unity,

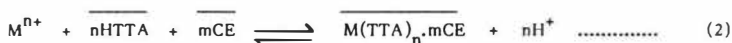
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a conditional extraction constant for this system, K_{no} , is given by:

$$K_{no} = \frac{[M(TTA)_n] [H^+]^n}{[M^{n+}] [HTTA]^n}$$

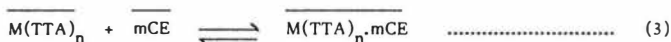
In the presence of crown ether, the extraction equilibrium becomes



The conditional extraction constant, K_{nm} , is given by:

$$K_{nm} = \frac{[M(TTA)_n.mCE] [H^+]^n}{[M^{n+}] [HTTA]^n [CE]^m}$$

The formation of the adduct in the organic phase can be represented by



The formation constant of the adduct, B_{nm} , is given by

$$B_{21} = \frac{[M(TTA)_n.mCE]}{[M(TTA)_n] [CE]^m} = \frac{K_{nm}}{K_{no}}$$

The System Co(II)-0.10 M (H^+ , $NaClO_4$)/CEs-HTTA

The synergic ability of different structurally related CEs on the extraction of cobalt by HTTA in chloroform was investigated. The crown ethers employed are dicyclohexyl 24-crown-8 (Dch 24 C8), 18-crown-6 (18 C6), dicyclohexyl 18-crown-6 (Dch 18 C6), 15-crown-5 (15 C5), dibenzo 18-crown-6 (Db 18 C6), and 12-crown-4 (12 C4). Investigating the various parameters affecting the extraction equilibria based on the synergic extraction model represented by equations 1-3, slope analysis indicated a molar composition of $Co(TTA)_2.CE$ for the adduct extracted whatever is the CE used. The extraction constants obtained, table (1), indicated the following:

i- B_{21} increase slightly with the increase in cavity diameter of the CE; for the unsubstituted ligands 12 C4 < 15 C5 < 18 C6, and Dch 18 C6 < Dch 24 C8 for substituted ligands, ii- no specific cavity size is required for the formation of the extracted adduct, iii- B_{21} largely increase with the number of oxygen donor within the cavity of the crown ether, 12 C4 < 15 C5 < 18 C6 < Dch 24 C8, and iv- B_{21} increase with the basicity of the oxygen in the crown as exemplified by the sequence

18 C6 > Dch 18 C6 > Db 18 C6 as a result of the electron withdrawing ability of the substituents; dicyclohexyl and dibenzo groups.

It can be therefore concluded that the stability of the adduct is mainly a contribution of increasing oxygen donor or basicity rather than correspondence between the cavity size of the CEs and the Co(II) diameter.

TABLE 1

Extraction and formation constants of different $\text{Co(TTA)}_2\text{.CE}$ species extracted by HTTA and different crown ethers in chloroform from aqueous perchlorate medium of constant ionic strength of 0.1 (H^+ , NaClO_4).

Crown Ether*	Cavity Diameter**, Å	$K_{21} \times 10^6$	$B_{21} \times 10^{-3}$
18 C6	2.6 - 3.2	7.5	4.1
Dch 18 C6	2.6 - 3.2	6.5	3.7
Db 18 C6	2.6 - 3.2	1.4	0.79
Dch 24 C8	4.5 - 5.6	11.0	6.2
15 C5	1.7 - 2.2	2.7	1.53
12 C4	1.2 - 1.5	0.48	0.28

*) For abbreviation see text.

**) See reference (7).

The effect of dielectric constant and temperature on Co(II) extraction by HTTA/Db 18 C6 dissolved in nitrobenzene-toluene mixture of different compositions, to give diluent media of different dielectric constants, was investigated. Slope analysis of the experimental results indicated that, in all media, cobalt is extracted by HTTA as Co(TTA)_2 and in presence of Db 18 C6 as $\text{Co(TTA)}_2\text{.CE}$. The extraction constants for the different equilibria encountered; K_{20} , K_{21} and B_{21} are given in table (2). From this table, it is clear that both K_{20} and K_{21} increase by increasing the dielectric constant of the diluent mixture. On the contrary B_{21} increases by decreasing the dielectric constant of the diluent. This was previously observed in different synergistic systems (7) and is generally explained on the basis of the increased hydrophobic character of the adduct formed. Investigating the effect of temperature on the systems studied and applying the conventional thermodynamic relations ΔG , ΔH and ΔS for the extraction system used in different diluents were evaluated. The obtained values given in table (2) indicated the following: i- ΔH for the chelate and mixed equilibria are positive and reflect the endothermic character of these reactions, ii- plotting ΔS against ΔH for the overall equilibrium (K_{21}), gave a linear relation with slope around 200. This result proves the compensation effect (8) and indicate that the complexation enthalpy and entropy are dominated by hydration

TABLE 2

Thermodynamic values for Co(II) extraction by HTTA and HTTA + Db 18 C6 in nitrobenzene (Nb), toluene (Tol) and their mixtures, from perchlorate aqueous media having constant ionic strength; 0.1 (H^+ , $NaClO_4$) at pH 5.2, using acetate buffer.

Nb-Tol %	$-\log K_{20}$	$-\log K_{21}$	$\log B_{21}$	ΔG Kcal/ mole	ΔH Kcal/ mole	ΔS Cal/deg/ mole
100- 00	7.43 ± 0.01			10.13	13.09	9.93
80- 20	7.59 ± 0.01			10.35	12.12	5.94
65- 35	7.76 ± 0.01			10.58	12.26	5.64
50- 50	8.02 ± 0.01			10.94	12.45	5.07
35- 65	8.27 ± 0.01			11.28	12.58	4.36
20- 80	8.65 ± 0.01			11.79	12.67	2.95
00-100	9.25 ± 0.01			12.61	13.13	1.75
100- 00		3.18 ± 0.01		4.34	3.66	- 2.28
80- 20		3.26 ± 0.01		4.45	3.29	- 3.89
65- 35		3.36 ± 0.01		4.58	3.11	- 4.93
50- 50		3.56 ± 0.01		4.85	2.97	- 6.31
35- 65		3.70 ± 0.01		5.05	2.75	- 7.72
20- 80		3.97 ± 0.01		5.41	2.52	- 9.70
00-100		4.35 ± 0.01		5.93	1.14	-16.07
100- 00			4.26 ± 0.01	-5.81	- 9.52	-12.45
80- 20			4.33 ± 0.01	-5.90	- 9.24	-11.21
65- 35			4.40 ± 0.02	-6.00	- 9.56	-11.95
50- 50			4.47 ± 0.02	-6.10	- 9.70	-12.08
35- 65			4.57 ± 0.02	-6.23	- 9.70	-11.64
20- 80			4.69 ± 0.02	-6.39	-10.25	-12.95
00-100			4.89 ± 0.02	-6.67	-11.94	-17.69

and formation of the adduct is through the substitution of water in the $Co(TTA)_2$ chelate, iii- the entropy variation for the adduct is slightly changed with ϵ of the medium and the variation of ΔG with the change in dielectric constant is related to ΔH . Therefore, the free energy variations of the adduct is governed by the enthalpy variation of the system, and iv- the high negative values of ΔS for the adduct indicates its ordered structure. It is found that the relation between $\log K_{20}$ or $\log B_{21}$ against $\log \epsilon$ gave a straight line relationship with positive or negative slopes, respectively. This was related in a linear free energy relationship represented by the following equations;

$$\log K_{20} = -9.95 + 1.6 \log \epsilon$$

for the cobalt chelate complex, Co(TTA)_2 and

$$\log B_{21} = 5.13 - 0.56 \log \epsilon$$

for the cobalt adduct, $\text{Co(TTA)}_2\text{-CE}$, where CE stands for Db 18 C6.

The Systems Ln -0.10 M (H^+ , NaClO_4)/CEs-HTTA

Investigating the synergic effect of the crown ethers Db 18 C6, 15 C5 and 12 C4 with mixture of different molar ratios of HTTA in chloroform and the different crowns, it is found that Yb^{3+} , Tm^{3+} and Eu^{3+} are synergically extracted only with 15 C5. Both Db 18 C6 and 12 C4 showed no or slight synergic extraction. Slope analysis based on the aforementioned equilibria indicated that the main extracted adduct with 15 C5 for the aforementioned lanthanides has the molar formula $\text{Ln(TTA)}_3\cdot 2\text{CE}$. The extraction constant of this adduct as related to the three lanthanide investigated gave the sequence $\text{Eu}^{3+} > \text{Tm}^{3+} > \text{Yb}^{3+}$, table (3), a sequence which is observed in other synergic extraction systems (9).

TABLE 3

Extraction constants K_{30} and K_{32} and formation constants B_{32} of Eu^{3+} , Tm^{3+} and Yb^{3+} with HTTA and HTTA-15 C5 adducts in chloroform

Cation	$\log K_{30}$	$\log K_{32}$	$\log B_{32}$
Eu^{3+}	-10.02 ± 0.01	4.90 ± 0.02	5.12 ± 0.01
Tm^{3+}	-9.75 ± 0.01	4.65 ± 0.01	5.10 ± 0.02
Yb^{3+}	-9.63 ± 0.01	4.61 ± 0.01	5.02 ± 0.01

To interpret the inability of Db 18 C6 and 12 C4 to form adducts with the Ln(TTA)_3 , the concept of correspondence between the CE cavity and the ionic radii of the metal ion should be consulted (1 & 10). The ionic radii of the lanthanides investigated ranges from 1.25 \AA^0 for Nd^{3+} to 1.12 \AA^0 for Yb^{3+} . These radii correspond with the cavity diameter of 15 C5 which is in the order of $1.7\text{--}2.2 \text{ \AA}^0$. With Db 18 C6 or 12 C4, the cavity diameter of these CEs are either large ($2.6\text{--}3.2 \text{ \AA}^0$) or small ($1.2\text{--}1.5 \text{ \AA}^0$) to accommodate the host lanthanide metal chelate. This is also observed for the lanthanides Nd^{3+} , Er^{3+} and the actinides Am^{3+} and Pu^{4+} , table (4), where the synergic factor for the extraction using 15 C5 is higher than that obtained using 18 C6, under similar extraction conditions.

TABLE 4

Distribution ratio and synergic factor for Nd^{3+} , Eu^{3+} , Am^{3+} and Pu^{4+} using 0.1 M HTTA and 15 C5 or 18 C6 mixture in chloroform extracted from different aqueous media.

Cation (a)	Aqueous Media	15 C5		18 C6	
		D_{mix}	S.F.	D_{mix}	S.F.
Nd^{3+}	0.35 M HNO_3	0.02	0.7	0.04	0.5
	Acetate buffer (b)	0.82	5.9	0.56	4.3
	Perchlorate buffer (c)	1.4	6.4	0.99	4.1
Er^{3+}	0.35 M HNO_3	0.04	2.0	0.05	0.5
	Acetate buffer	40	4.8	28	4.4
	Perchlorate buffer	51	5.3	28	3.4
Am^{3+}	0.35 M HNO_3	0.02	0.5	0.03	0.6
	Acetate buffer	2.8	93.0	2.1	13
	Perchlorate buffer	1.3	12.0	1.9	19
Pu^{4+}	0.35 M HNO_3	2.6	1.7	3.7	1.7
	Acetate buffer	23.0	3.5	17	3.0
	Perchlorate buffer	14.0	2.2	11	1.5

(a) Cation concentrations: Nd^{3+} , Er^{3+} and Am^{3+} = 0.01 g/l and Pu^{4+} = 0.1 g/l.

(b) Acetate buffer: 0.15 M sodium acetate and 1.35 M acetic acid; pH 3.5.

(c) Perchlorate buffer: 0.05 M sodium acetate, 0.04 M sodium perchlorate and 1.0 M acetic acid; pH 3.0.

In table (4), it is clear that the composition of the aqueous medium affect the extraction by the mixed system. In general, extraction of all metal ions from 0.35 M HNO_3 is always lower than that at pH 3.0 and containing acetate or perchlorate buffers. Again D_{mix} for Nd^{3+} and Er^{3+} from perchlorate solution is higher than that from acetate. For Am^{3+} and Pu^{4+} , D_{mix} using acetate buffer is higher than that when perchlorate buffer is employed. These variations are mainly related to the complexing abilities of the used actinides or lanthanides to perchlorate or acetate solutions.

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Liquid-liquid Extraction of Metals in the Absence of Usual Organic Solvents

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Liquid-liquid extraction, one of the most efficient technological and analytical methods for the separation of substances, is based on their non-uniform distribution between the aqueous solution and the organic solvent. It is known that the energy of extraction process can be presented as a sum of the energies of the compound formation (G_{form}), its solvation (G_{solv}) and hydration (G_{hydr}): $G = G_{\text{form}} + G_{\text{solv}} - G_{\text{hydr}}$. Therefore, in the extraction of substances having a high G_{hydr} , such as complexes of metals with water-soluble organic reagents, high-charge inorganic complex ions or coordinatively hydrated complexes, the use of traditional extraction systems does not always produce the desired results.

To extract such compounds we proposed (1) using the systems whose both phases contain considerable quantities of water, so as to reduce the hydration effect on the transfer of the substance from one phase to another. Extraction systems of this kind are based on using a water-soluble non-ionic polymer - polyethylene glycol, whose salting out from the aqueous solution results in the formation of a second liquid phase. Of undoubted practical interest is also the possibility of using systems where conventional solvents, not infrequently toxic, volatile and explosive, would be absent.

The scarcity of data in literature, concerning the PEG - salt - water systems that can be obtained at room temperature, as well as the absence of criteria for the choice of an electrolyte to act as the salting-out agent, made it necessary to study phase equilibria in PEG-water-salt solutions. Figure 1 shows phase diagrams for the systems based on PEG 2000 and different inorganic salts.

It is of interest to note that heterogeneous systems were obtained only for the salts whose anions occupy a position at the beginning or, on the contrary, at the end of the known lyotropic series of the salting-out of polymers (2), i.e. exert a clear-cut structurizing or destructurizing effect on water. The salts whose anions affect the water structure insignificantly, viz. chlorides, bromides, nitrates, do not salt out PEG at room temperature. Cations have a much lower salting-out capacity with respect to PEG than anions, and in the presence of effective salting-out anions their action is levelled off. Thus, the width of heterogeneity region differs slightly for the systems based on CuSO_4 , CdSO_4 , NiSO_4 , MgSO_4 , MnSO_4 , Li_2SO_4 . Therefore, when considering the influence of the nature of cation on the possibility of a two-phase system with a given salt being formed one should first of all take into account the solubility of the salt with this cation, and not its salting-out capacity. For instance, for K_2SO_4 and Na_2SO_4 that have a relatively low solubility in water no heterogeneous systems with PEG 2000 have been obtained, despite the fact that the sulphate is an efficient salting-out agent.

As seen from the data presented in Fig.1 (curves 1, 4, 6) the heterogeneity region in the systems based on $(\text{NH}_4)_2\text{SO}_4$ in the presence of the acid is narrowed down, and in the presence of alkali it widens. An opposite effect is observed in the systems based on KSCN and KI (curves 7 and 9). Moreover, a heterogeneous system with KI can never be obtained in the absence of acid.

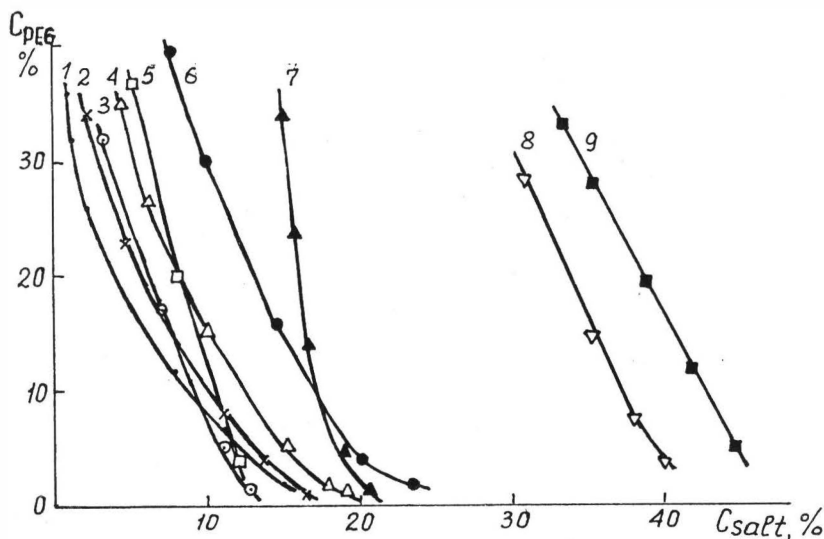


Fig. 1. Phase diagrams of systems:

- 1 - $\text{PEG}-(\text{NH}_4)_2\text{SO}_4\text{-NaOH (1M)-H}_2\text{O}$, 2 - $\text{PEG}-(\text{NH}_4)_2\text{HPO}_4\text{-H}_2\text{O}$,
- 3 - $\text{PEG-K}_2\text{CO}_3\text{-H}_2\text{O}$, 4 - $\text{PEG}-(\text{NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$, 5 - $\text{PEG-NH}_4\text{F-H}_2\text{O}$,
- 6 - $\text{PEG}-(\text{NH}_4)_2\text{SO}_4\text{-H}_2\text{SO}_4\text{ (1M)-H}_2\text{O}$, 7 - $\text{PEG-KSCN-HCl (0.6M)-H}_2\text{O}$,
- 8 - $\text{PEG-NaClO}_4\text{-H}_2\text{O}$, 9 - $\text{PEG-KSCN-H}_2\text{O}$.

Thus, the ability of quite a large number of electrolytes to salt out PEG with the formation of a second liquid phase, as well as the possibility of working with considerable concentrations of acids and alkali, make the proposed system sufficiently flexible and universal.

Using radiometric and photometric methods the distribution of a number of metal cations has been studied in the $\text{PEG 2000 - H}_2\text{O - (NH}_4)_2\text{SO}_4$ system. The metal ions were shown to be non-uniformly distributed between the phases, with the ratio of the metal concentration in the PEG phase to its concentration in the salt phase, i.e. the distribution coefficient D , being less than unity for all the studied metals. With increasing $(\text{NH}_4)_2\text{SO}_4$ concentration in the system, the D values for metals decrease, amounting from 0.1 to 0.01.

Presented in the table are the data on the extraction of a number of elements with reagents constituting the chromotropic acid derivatives (arsenazo III, thoron, arsenazo M, etc.). Extraction of water-soluble metal chelates containing sulphonic groups is known to present considerable problems (3). The metal:reagent ratio in such compounds is, as a rule, equal to 1:1; that is why the metal cation can retain a part of its positive charge, because of which anions of the CCl_3COO^- , ClO_4^- and similar types have to be introduced into the system. In conventional extraction systems it is necessary to introduce bulky organic cations (diphenyl guanidine, etc.) into the system to compensate the sulphonic group charge. As a result a part of the added cations and anions are extracted in the form of

Table

Extraction of metals with reagents (R) of the arsenazo III group in the PEG 2000 (15.4%) - $(\text{NH}_4)_2\text{SO}_4$ (14.1%) - H_2O system

Reagent	Metal	Extraction $C_{R,M}$	conditions Opt. pH	log D
Arsenazo III	Th(IV)	$1 \cdot 10^{-3}$	2.0-5.0	1.5-2.2
	U(VI)	$1 \cdot 10^{-3}$	4.0	1.3
	Bu(III)	$1 \cdot 10^{-3}$	3.5	0.9
	Fu(III)	$3 \cdot 10^{-2}$	3.5	2.8
	Ln(III)	$3 \cdot 10^{-2}$	3.5	1.5
Thoron	Co(II)	$1.1 \cdot 10^{-2}$	7.5	2.2
	Bi(III)	$1.8 \cdot 10^{-2}$	5.0	1.5
	Fe(III)	$1.8 \cdot 10^{-2}$	4.0	1.8
Arsenazo M	Fe(III)	$1.8 \cdot 10^{-2}$	3.0	1.4
Chlorophosphonazo	Fe(III)	$1.8 \cdot 10^{-2}$	4.0	1.3
Chrome dark-blue	Fe(III)	$1.8 \cdot 10^{-2}$	3.0-8.0	2.1-2.3
Eriochrome black T	Co(II)	$1.8 \cdot 10^{-2}$	8.0	0.6
	Cu(II)	$1.1 \cdot 10^{-2}$	5.0	2.4

the corresponding salts. In addition to this, "intramolecular ionization" causes enhanced hydration of some fragments of the reagent molecule, and, therefore, high solvating ability solvents, e.g., alcohols, are used for the extraction. As seen from the presented results, in PEG-based systems numerous metals are extracted by reagents of this kind without any additional compounds being introduced.

We have studied metal extraction by organic reagents of another class also containing hydrophylic sulphonic groups: complexones (aminoacetic acid derivatives) of triphenylmethane family, viz. methylthymol blue and xlenol orange. In conventional extraction systems their metal complexes can only be extracted in the presence of quaternary ammonium bases (4) or carboxylic acids (5). In PEG-based systems, with a concentration of these reagents equal to about 0.01 M, the extraction percentage of Bi, Fe (III), Zr and Eu amounts to 90-95 in the absence of any additional components.

Earlier it was shown that alizarin complexone can be used to extract actinide and lanthanide complexes from carbonate solutions (6) into PEG water solutions. Figure 2 shows the D vs. pH dependences for a number of elements in a system based on ammonium sulphate. High values of D were obtained, e.g. for europium, while the extraction of rare earth metal complexes with alizarin complexone into alcohols fails to achieve their quantitative recovery even in the presence of triphenyl guanidine (7).

Extraction of number of metals with water-soluble substituted 8-hydroxyquinolines has been studied. 7-Chloro-8-hydroxyquinoline-5-sulphonic acid extracts quantitatively Fe (III), Co, In, Zr within a pH range of 5-8.

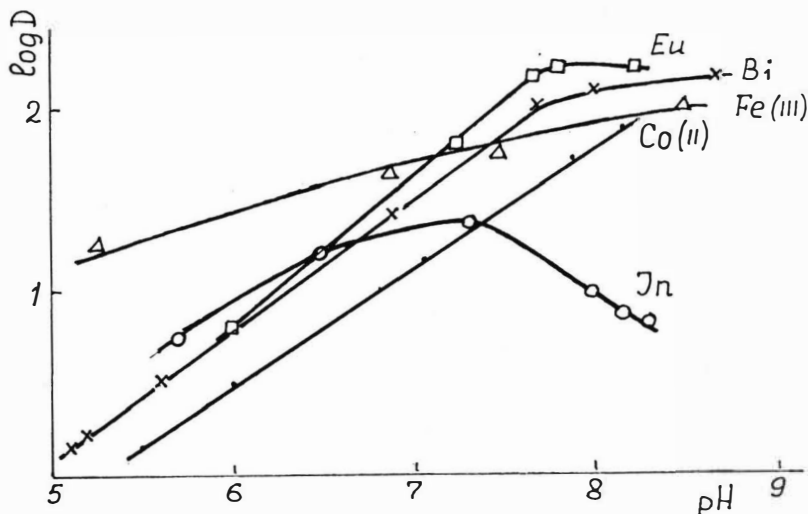


Fig.2. Extraction of metal complexes with alizarin complexone in the PEG 2000 (15.4%) - $(\text{NH}_4)_2\text{SO}_4$ (14.1%) - H_2O system; $C_R = 1.1 \cdot 10^{-2} \text{ M}$, $C_{Me} = 1 \cdot 10^{-5} \text{ M}$.

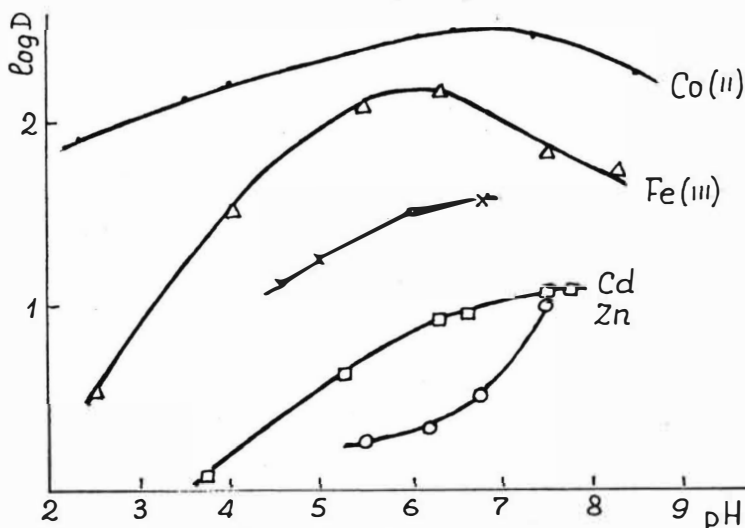


Fig.3. Extraction of metal complexes with PAR in the PEG 2000 (15.4%) - $(\text{NH}_4)_2\text{SO}_4$ (14.1%) - H_2O system; $C_R = 2.2 \text{ M}$, $C_{Me} = 1 \cdot 10^{-5} \text{ M}$.

Figure 3 shows the pH dependences for a number of metals in the form of their complexes with 4-(2-pyridylazo)-resorcinol (PAR). Despite the absence of sulphonie groups in the reagent molecule, the extraction of its complexes with metals into organic solvents also presents difficulties. The hydrophilicity of the complexes is in this case caused by the coordinative unsaturation of the central metal atom, which necessitates introducing solvating additives, e.g., alcohols (8) or carboxylic acids (9), into the system. Anion complexes, formed at high pH values are extracted in the form of ion pairs only in the presence of quaternary ammonium bases (10) or triphenyl guanidine (8). Even in the presence of such additives the D values are, as a rule, not high. Efficient extraction of metal complexes with this reagent in PEG-based systems in a wide range of pH indicates that hydration of the central metal atom and the negative charge of the complex compound do not hinder the passage of the complex into the PEG phase, in distinction to the conventional extraction systems.

However, not all organic reagents and their complexes with metals are extracted into the PEG phase. One of the factors determining their distribution in the system is the presence of aromatic rings in the reagent molecule. Insertion of, e.g., EDTA into a PEG-based system does not lead to an increase in the D of metals.

Earlier it was shown that inorganic complexes of many elements can be efficiently extracted in PEG 2000- $(\text{NH}_4)_2\text{SO}_4$ - H_2O systems containing NH_4SCN and KI (1).

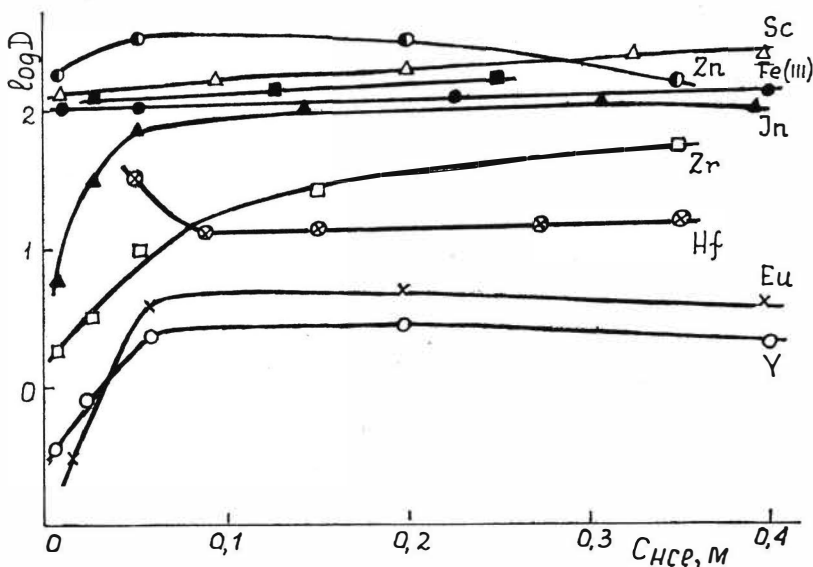


Fig. 4. Extraction of metals in the PEG 2000 (19.5%) - HCl - H_2O system; $C_{\text{Me}} = 1 \cdot 10^{-5} \text{ M}$.

Figure 4 presents the data on the extraction of a group of metals in a system based on KSCN in the presence of HCl . In the absence of sulphate, exerting a masking influence on a number of metals, high D values were obtained for the elements whose thiocyanate complexes are not extracted in a system based on $(\text{NH}_4)_2\text{SO}_4$.

The results obtained show that the use of a new type of extraction systems based on PEG holds promise for the solution of various problems.

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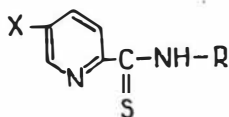
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New Extractants for the Recovery of Noble Metals

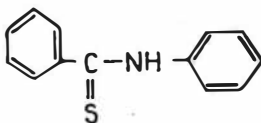
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Limited sensitivity and selectivity of the conventional methods of determining noble metals (NM) make it obviously necessary to perform their joint preconcentration, including extractive concentration. Also important for analytical chemistry and industry is the NM separation from one another in mixtures and from the accompanying elements. These problems are solved by extracting NM with organic reagents containing sulphur- and nitrogen-donating atoms. It is imperative in this connection to search for new, more efficient extractants of this type.

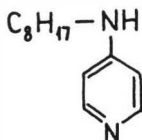
The object of the work was to study NM extraction with thiobenzanilide (TBA), six N-substituted α -thiopicoline amides (TPA), 4-octylaminopyridine (OAP), and 1-(3-thiapentadecyl)-piperidine (TPDP), to develop extractive methods for the separation of NM mixtures and the methods for selective joint recovery of these metals (see Formulae I-IX and Table 1).



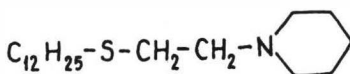
N-Substituted α -thiopicoline amides (I-VI)



Thiobenzanilide (VII)



4-Octylaminopyridine (VIII)



1-(3-Thiapentadecyl)-piperidine (IX)

Table 1

N-Substituted α -thiopicoline amides

R	X	Designation of reagent
n-C ₄ H ₉ -	H	I
C ₆ H ₅ -	H	II
o-CH ₃ -C ₆ H ₅ -	H	III
C ₆ H ₅ -CH ₂ -	H	IV
o-CH ₃ -O-C ₆ H ₄ -	H	V
C ₆ H ₅ -	C ₂ H ₅ -	VI

Techniques and procedures. TBA was obtained by recrystallizing the commercial compound from ethanol. TPA, OAP and TPDP were synthesized using conventional procedures (1-3). Extraction of elements was studied with the help of ^{110m}Ag , ^{198}Au , ^{109}Pd , ^{197}Pt , ^{192}Ir , ^{59}Fe , and ^{64}Cu radionuclides. Solutions of metals (radionuclides and carriers) were prepared in 6 or 11 M HCl. NM concentration in the experiments was 10^{-5} - 10^{-4} M, the volumes of aqueous and organic phases were 4-5 ml. As a rule, the extraction from hydrochloric acid media was studied.

Extraction of Noble Metals

Reagents distribution in two-phase systems. In the chloroform-HCl solution system practically the whole of TBA is in the organic phase when contacting with 0.1-12 M HCl solutions, and N-TPA - with HCl solutions in the range from 0.1 to 3-5 M. When the phases are in contact the reagents have been potentiometrically established to extract hydrochloric acid with the formation of 1:1 adduct. N-TPA reextraction at contact with 6-12 M HCl solutions is caused by the second HCl molecule being added to the reagents. OAP and TPDP at contact with 0.01-3 M solutions also extract hydrochloric acid with the formation of monohydrochlorides.

Ag, Au, Pd, Pt and Ir extraction with the help of TBA. In normal conditions, TBA solutions in chloroform quantitatively extract Ag, Au(III) and Pd, but practically do not extract Pt(IV) and Ir (III, IV). Silver can be fully extracted with 0.025 M TBA solution in chloroform from 0.3-5 M HCl; TBA is thus one of the most powerful silver extractants from hydrochloric acid media. Gold and palladium are quantitatively extracted from 0.1-12 M HCl with the help of 0.001 and 0.025 M TBA solutions, respectively. The minimum contact time of the phases, needed for complete extraction of 20-40 μg Ag, Au and Pd, amounts to 1, 3 and 5 min.

Platinum is quantitatively extracted at room temperature only in the presence of SnCl_2 or KI. Iridium is completely recovered after its solution has been heated on a water bath in a mixture with TBA solution in dioxane in the presence of SnCl_2 or KI. Platinum is extracted in the presence of SnCl_2 better than in the presence of KI: quantitative extraction of platinum from 0.1-12 M HCl is achieved with the help of 0.001 M TBA solution in the presence of 0.02 M SnCl_2 or with the help of 0.01 M TBA solution in the presence of 0.25 M KI solution. The minimum contact time of the phases, needed for the maximum extraction of 40 μg of platinum with 0.001 M TBA solution, amounts to 3 and 10 min in the presence of SnCl_2 and KI, respectively.

For iridium, on the contrary, KI is preferable. The minimum heating time for a quantitative formation of iridium compound with TBA in the aqueous phase amounts to 75 min in the presence of SnCl_2 and to 40 min in the presence of KI, the complete extraction of 4-6 μg of iridium in the presence of 0.04 M TBA being achieved with 1-3 and 0.3-11.5 M HCl, respectively, in the aqueous phase. For the extraction of iridium compound with TBA is convenient a mixture of chloroform and n-butanol in the ratio of 7:1 (in the case of chloroform the degree of iridium recovery does not exceed 88%), 0.5 min contact of phases is sufficient. On the whole, TBA is characterized by a high degree of Ag, Au, Pd, Pt and Ir extraction in a wide range of the values of extractive system parameters.

Au, Pd, Ag and Pt extraction with the help of TPA. TPA solutions in chloroform quantitatively extract palladium and gold (III). With 0.001 M TPA this is achieved in a rather narrow HCl concentration range (2 - 5 M). For the maximum recovery of 20-40 μg of gold with

0.002 M TPA solutions it is sufficient for the phases to be in contact during 15 s, and of 20-40 μg of palladium - from 3 to 10 min, depending on the TPA used. Silver is practically not extracted from hydrochloric acid media with 0.001 M TPA solutions; 0.05 M solution of reagent III extracts from 1 M HCl solution not more than 28% of silver. Platinum (IV) is practically neither extracted with 0.001 M TPA solutions in normal conditions, but is well extracted with them in the presence of SnCl_2 or KI. For the maximum extraction of platinum ($2.5 \cdot 10^{-3}$ M) it is necessary to have a 1000- or 4000-fold excess of SnCl_2 or KI, respectively, and the minimum contact time of the phases in this case is from 5 to 10 min.

Platinum, rhodium, iridium and ruthenium extraction with the help of TPDP. At pH 0-2, iridium, platinum and rhodium are extracted with 0.05 M TPDP solution within 60 min of the contact of phases. The maximum ruthenium (III) extraction is achieved at pH 3-4 and amounts to about 19%. The time for the equilibrium to be established in the extraction with 0.05 M TPDP solution from 1 M HCl for platinum (IV) is 15 min, for the extraction of iridium (IV) and iridium (III) from 0.1 M HCl it is 30 and 45-50 min, respectively. In the extraction of rhodium and ruthenium the equilibrium is not reached even after 2 h of the contact of phases. During its extraction, iridium (IV) is reduced by the extractant to iridium (III). The degree of NM recovery depends on the nature of solvents, increasing in the series of octanol < chloroform < 1,2-dichloroethane.

Iridium, palladium, platinum and rhodium extraction with the help of OAP. OAP quantitatively extracts iridium (IV) from HCl solutions as soon as after 5 min of the contact of phases at room temperature. The maximum of extraction is attained at 0.2 M HCl, complete iridium recovery is reached at 0.1-3 M HCl. OAP is a more efficient reagent in comparison with the previously studied 2-octylaminopyridine (4): when the latter is used iridium solution in a mixture with extractant solution has to be heated in the presence of SnCl_2 during 40 min, whereas OAP recovers iridium rapidly and completely at room temperature. Palladium, platinum (IV), rhodium and iridium (III) are quantitatively extracted in the conditions of iridium (IV) extraction.

The Chemism of Extraction

The composition of extracted compounds was determined by the method of molar ratios and the method of the shift of equilibriums, in a number of cases - by the element analysis of compounds isolated in their solid state. The nature of coordination was estimated from the electron or IR spectra of complexes by comparing them with the spectra of free reagents.

TBA. Ag, Pt and Au are extracted as individual compounds with the M:R ratio equal to 1:2, 1:2 and 1:1, respectively, and Pd as a mixture of several compounds. All the compounds are electron-neutral, which follows from the data on the electrophoresis of the extracts or from a good extractability of compounds with low-polarity hexane or carbon tetrachloride. An adsorption band at 410 nm in TBA electron spectrum, corresponding to the $n \rightarrow \pi^*$ transition in the thiocarbonyl group, is absent in the spectra of complexes, which is indicative of coordination via the sulphur atom. The band of N-H bond valence vibrations at $3170\text{-}3120\text{ cm}^{-1}$ in the IR spectra does not disappear in going from TBA to its complexes with gold and silver; most probably the hydrogen thioamide atom is not split off. The absence of this band in the IR spectrum of TBA compound with platinum makes it possible to assume the presence of platinum coordination bond with the thioamide nitrogen atom, apart from the sulphur atom. Gold (III) in the complexing with TBA is first reduced to gold (I) which forms a

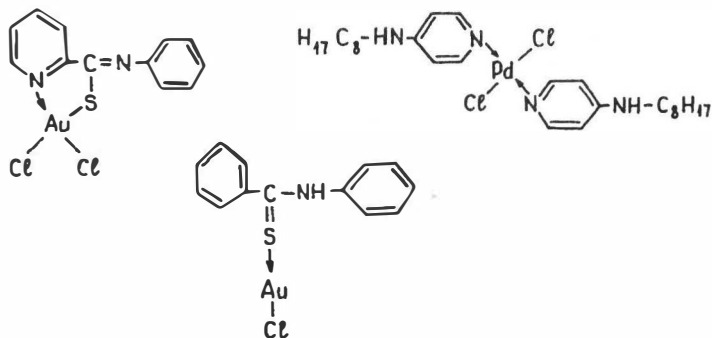
complex with another TBA molecule. The composition of gold and silver compounds thus answers to the formulae $\text{Ag}(\text{HR})_2\text{Cl}$ and $\text{Au}(\text{HR})\text{Cl}$ (HR is the TBA molecule), and the coordination is actualized via the sulphur atom. The composition of platinum compound with TBA, extracted in the presence of SnCl_2 , answers to the formula PtR_2 , the coordination is actualized via the sulphur atom and, presumably, via the thioamide nitrogen atom.

TPA. Au, Pd and Pt are extracted, almost in all cases, as individual compounds with the M:R ratio equal to 1:1, 1:2 and 1:2, respectively. The structure of compounds was studied with reagent III taken as the example. In complexing with III, gold (III) is not reduced; gold (III) is extracted with an almost equimolar quantity of III; the Au:R:Cl ratio in the compound is close to 1:1:2, which is more characteristic for gold (III) complexes. Formation of NM complexes with III is accompanied by the splitting off of thioamide hydrogen, indicative of which is the disappearance in IR spectra of the N-H bond vibration band (in an uncoordinated reagent at 3200 cm^{-1}). A considerable high-frequency shift observed in the IR spectra for the band answering to the S-C-N group vibration (from 1525 to $1595\text{--}1550\text{ cm}^{-1}$) indicates a substantial increase in the degree of C-N bond dual binding in III with the complexing. In its free state III, similarly to TBA, exists mainly in thion form, and the degree of the binding of carbon and nitrogen atoms in the thioamide group is close to that of a single bond. A strong shift of the S-C-N group band indicates the coordination via the sulphur atom. This is confirmed by the electron absorption spectra of the complexes lacking the band of $n \rightarrow \pi^*$ transition in the thiocarbonyl group, present in the spectrum of uncoordinated III at 440 nm . Vibration bands of the pyridyl group in the IR spectrum of III at 400 and 590 cm^{-1} are shifted with the complexing to $360\text{--}361$ and 590 cm^{-1} , respectively, which shows that NM are coordinated with the heterocyclic nitrogen atom. This is confirmed by the hypsochromic shift of the band of $\pi \rightarrow \pi^*$ transition from 283 to $262\text{--}272\text{ nm}$ in the electron spectra, mainly caused by the pyridyl group absorption, in going from III to its complexes with NM. NM compounds with N-TPA are readily extracted from $0.1\text{--}3\text{ M}$ HCl solutions with low-polarity benzene and carbon tetrachloride, which is indicative of the electroneutrality of these compounds. The composition of the compounds of III with Pt (in the presence of SnCl_2), Pd and Au, extracted from $0.1\text{--}4\text{ M}$ HCl, thus answers to the formulae PtR_2 , PdR_2 and AuCl_2R (where R is the deprotonated molecule of III), the coordination bonds are actualized with the sulphur and the heterocyclic nitrogen atoms, i.e., III, and it seems that the other TPA too, act as bidentate chelating ligands in NM extraction from acid media.

TPDP. The presence of nitrogen- and sulphur-donating atoms in the TPDP molecule provides grounds for the assumption that NM are extracted by two mechanisms: fast extraction by the anion-exchange mechanism and the formation of coordinationally solvated compounds. The character of NM extraction confirms this assumption. Although platinum and iridium are extracted rather fast, after the phases have been in contact for more than 2 h the NM distribution coefficients start gradually rising - new compounds are apparently formed in the extracts. Comparison of the electron absorption spectra of the extracts, obtained at different moments of the contact of phases, showed that at the initial moment of platinum and iridium extraction the anion-exchange mechanism is actualized, with the participation of nitrogen atom. With time an M-S coordination bond appears in the formed ionic associate, i.e., a coordinationally solvated compound arises. Rhodium is only extracted with the formation of coordinationally solvated compounds, no ionic associate with the extractant being formed. The M:R ratio in the iridium compound is

equal to 1:3.

OAP. The realization of two extraction mechanisms is possible: anion exchange and the formation of coordinationally solvated compounds. A high rate of iridium extraction testifies in favour of the first mechanism, the irreversibility of the extraction system and the difference between the extract electron spectrum and the initial aqueous phase spectrum are indicative of the second mechanism. According to the electrophoresis data, negatively charged iridium complexes are mainly present in the extracts, but a neutral complex is also present there. A palladium complex has been isolated in the solid state, the Pd:OAP:Cl ratio in the complex is equal to 1:2:2. In the IR spectra the band of the pyridine ring C=C and C=N bond vibrations is observed to shift from 1590 to 1605 cm^{-1} in going from uncoordinated OAP to its complex with palladium. At the same time, the frequency of the side chain C-N bond vibrations decreases. This suggests palladium coordination via the heterocyclic nitrogen atom. The complex appears to constitute a trans-isomer, which is indicated by its high mobility in chromatographic analysis. Small quantities of another palladium compound are present in the extract, the Pd:OAP ratio in it is higher than 2. It is immobile in chromatographic analysis. The structures of gold compounds with III and TBA and of palladium compound with OAP can be represented by the following formulae:



The Use of Extraction for Analytical Purposes

NM extraction in the presence of iron, nickel and copper. Iron and nickel traces do not interfere in most cases with the extraction of NM traces, and are not themselves extracted together with NM. Iron (III) interferes with platinum and iridium extraction if its quantity exceeds that of SnCl_2 or KI because they are oxidized by iron (III). Copper (II) is not being extracted when NM are recovered with the help of TPA, but at a 10^3 -fold ratio with respect to NM it hinders their quantitative isolation. In NM extraction with the help of TBA, copper (II) does not interfere with palladium and gold isolation, it hinders silver extraction at a 10^4 - 10^5 -fold excess, platinum and iridium extraction - at a 10^4 -fold ratio; copper itself is extracted to a considerable degree. Reextraction has been used to separate copper from NM: copper is separated from Ag, Au and Pd after the extract has been washed with a mixture of 0.25% potassium permanganate solution and 4% EDTA solution in the ratio of 1:3, prepared 3-5 s prior to reextraction. To separate copper from platinum the extract is washed with a mixture of the same solutions, but in the ratio of 1:9, to separate copper from

iridium - with 1 M thiourea solution. The degree of copper reextraction is 98-99%.

Iron (III) and copper (II) traces in a 10^3 - 10^4 -fold ratio practically do not hinder NM extraction with the help of TPDP, and themselves do not pass with it into the extract. In NM extraction with the help of OAP, iron (III), copper (II), cobalt (II), manganese (II) and zinc (II) do not interfere with NM extraction in a 10^4 - 10^5 -fold ratio. For NM to be separated from non-noble metals more completely it is necessary to wash the obtained extract with 0.1 M HCl solution.

Methods of extractive separation of NM mixtures. A scheme has been developed for the isolation of individual NM groups from a mixture of Ag, Au, Pd, Pt and Ir microquantities. First the sum of Ag, Au and Pd is extracted from 0.5-1.2 M HCl solution with 0.025 M TBA solution in chloroform. HCl and SnCl_2 solutions are then added to the aqueous phase, and platinum is extracted from 2.5-3 M HCl solution with 0.001 M TBA solution in chloroform. After that, TBA solution in dioxane (up to 0.01-0.04 M TBA) is added to the aqueous phase, the mixture is heated at 100°C (90 min), cooled, 1 ml 1 M thiourea solution and a mixture of chloroform with n-butanol (7:1) are added, and iridium is extracted. This scheme has been used in atomic-adsorption determination of palladium, platinum and iridium in copper-nickel ore.

A scheme has been developed for the separation of a mixture of Ag, Au, Pd, Pt and Ir microquantities. First the sum of Pd and Au is isolated from 0.5-1.0 M HCl solution with 0.001 M solution of a mixture of reagents III and VI in chloroform. The metals are separated by selective reextraction of gold with 4% EDTA solution. From the remaining aqueous phase silver is extracted with 0.025 M TBA solution. Pt and Ir are then isolated in accordance with the above scheme. The separation schemes are characterized by a high (90-99%) degree of recovery for each NM and a high degree of their separation. They are suitable for NM mixtures containing traces of Fe, Ni and Cu. They provide complete Fe and Ni separation from NM, copper can be additionally separated by washing the obtained extracts with appropriate reextractants. The schemes are simple, take little time to accomplish, and are convenient for use in the analysis of platinum-containing stocks.

A method of NM extractive concentration. The sum of palladium, platinum, rhodium and iridium is extracted from 0.1-3 M HCl solution with 0.035 M OAP solution in chloroform at room temperature during 10 min of the contact of phases. The aqueous phase is discarded, the organic phase is washed with 0.1 HCl solution. The method has been used to determine NM with the help of atomic-emission spectroscopy with inductively coupled plasma.

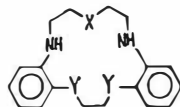
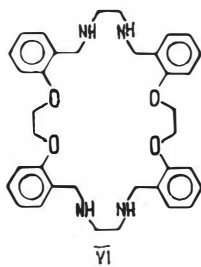
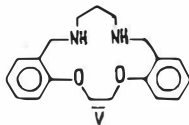
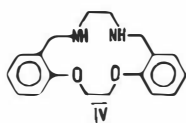
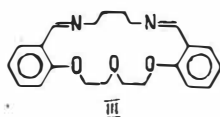
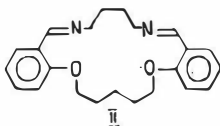
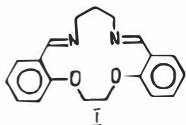
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Solvent Extraction of Transition and Post-transition Metals with Azamacrocyclic Compounds

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Macroheterocyclic compounds are promising for use as highly selective extractants /1/. Relatively well studied are oxygen-containing macrocycles: crown ethers and, partially, cryptands /2/, and also tetraazamacrocycles /1/. At the same time, N,O-, N,S- and N,O,S-containing macrocycles have been studied to a small extent /3,4/, despite the fact that these very compounds extract transition and post-transition metals. In the present work the authors have studied compounds I-XXVII, differing in the number, nature and arrangement of heteroatoms and in the size of the ring.



VII: X = CH₂, Y = O

VIII: X = Y = O

X: X = S, Y = O

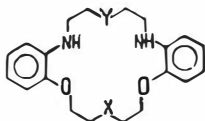
IX: X = NTs, Y = O

XI: X = Y = S

XII: X = NTs, Y = S

XIII: X = O, Y = S

XIV: X = CH₂, Y = S



XV: X = Y = CH₂

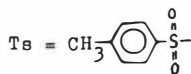
XX: X = NTs, Y = CH₂

XXIII: X = Y = NTs

XVI: X = O, Y = CH₂

XXI: X = O, Y = NTs

XXIV: X = CH₂, Y = NH



Under the above conditions some of these compounds extract, partially or quantitatively, Ag (I), Hg (II), Pd (II), Au (III), Cu (II), Ni (II), Tl (I) and Co (II). These elements are grouped in a single block in the periodic table (Fig.1), the first four ions representing soft acids (according to Pearson) and the last ions lying between the soft and the hard ones. Soft cations (especially, silver and mercury) are extracted with numerous macrocycles, and the less soft ones (Ni, Tl and Co) are extracted in significant amounts only with some of the compounds. The set of extracted elements is thus primarily determined by electronic factors.

Na 2,3	Mg 2																		
K 2	Ca 1,2,3	Sc 3	Ti ^{IV} 3		Cr ^{III} 3	Mn ^{II} 1,2,3	Fe ^{III} 1,2,3	Co ^{II} 1,2,3	Ni 1,2,3	Cu ^{II} 1,2,3	Zn 1,2,3	Ga 1,4						Se ^{IV} 3	
			Zr 3				Ru ^{III} 3		Pd 1,2,3	Ag 1,2,3	Cd 1,2,3						Sn ^{IV} 1,2,3	Sb ^{III} 3	Te ^{IV} 3
	Ba 2,3	Ce ^{III} 3						Ir ^{IV} 5		Au ^{III} 1,2,3	Hg ^{II} 1,2,3	Tl ^I 1,2,3					Pb 1,2	Bi ^{III} 2	

Selectivity of metal extraction

Selectivity of the interaction of a macrocycle with metals must be determined to a considerable extent by the possibility of a conformational change in the macrocycle during the complexing. Conformationally more rigid compounds must be more selective. Among compounds I-XXVII, Schiff bases (I-III) have the highest conformational rigidity. And they are the most selective out of all the compounds that have been investigated: practically, only silver is extracted. Similar compounds IV, V without double bonds are less selective: in addition to silver, quantitatively extracted are mercury and copper, and in the case of compound VI - also Co, Zn and Pd. A lower selectivity of these macrocycles seems to be associated with their

higher conformational flexibility, and in the case of VI - also with a large size of the relatively flexible ring.

Silver is extracted with compounds I-III from neutral or weakly acid media (Fig.2), the degree of extraction increasing in the following series of solvents: o-xylene < chloroform < 1,2-dichloroethane < nitrobenzene. Silver extraction is quantitative and selective under the following conditions: solution of macrocycle II in 1,2-dichloroethane (0.01 M) in the presence of picrate (0.001 M), pH 4.5-5.4; contact of phases 10 min. The extraction of Hg (II), Cu (II), Pd (II) and Co (II) in this case amounts to only a few percent, and the other 12 elements are practically not extracted.

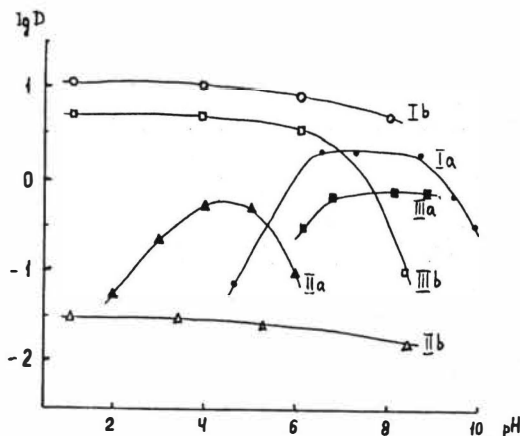


Fig. 2. Extraction of silver (Ia-IIIa, see conditions in Fig.1) and of picric acid (Ib-IIIb, 0.01 M reagents in chloroform, 0.001 M picrate) with reagents I-III.

Compounds VII-XXVII mainly extract mercury or other metals. By their selectivity these macrocycles occupy an intermediate position between I-III and IV-VI.

Selective extraction is achieved for metals that do not require introducing a special counterion. Compounds IX and XXIII, for instance, selectively extract mercury (II). Extraction depends but slightly on the presence of picrate (macrocycle IX) or dipicrylamine (XXIII). The degree of mercury extraction is constant in a wide range of acidity: 2 M H_2SO_4 - pH 4 (XXIII) and pH 2-7 (IX) (Fig.3). The nature of solvent does not exert any substantial effect on the degree of extraction: distribution coefficients for chloroform, benzene and toluene are almost the same.

Other dibenzo-15-crown-5 analogues (X-XV) extract from acetate-nitrate solutions, besides mercury, also copper in the absence of special counterions; and dibenzo-18-crown-6 analogues (XV-XXXVI) extract palladium, the degree of mercury extraction being much lower than for reagents IX and XXIII. Inclusion of picrate (IX-XIV) or dipicrylamine (XV-XXVII) enhances the mercury extraction, but selectivity in this case decreases: reagents X-XIV and XVI-XXVII also extract copper and silver, and XIX-XXVII - nickel as well;

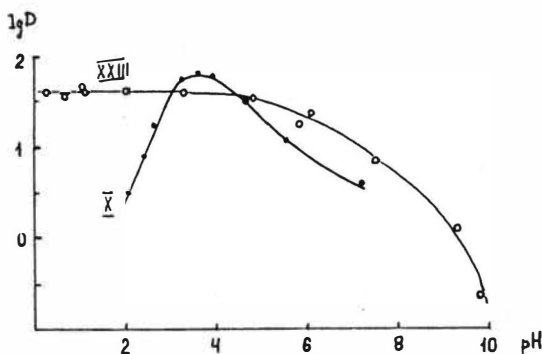


Fig.3. Mercury extraction with 0.001 M reagents in chloroform: X - in the presence of 0.001 M picrate, XXIII - without special counterions.

XVII, XVIII, XXI-XXVII - thallium (I); XX, XXVI, XXVII - cobalt. To compare the selectivity of reagents, extracting mercury in the presence and in the absence of special counterions, given below is the degree of the extraction of other elements in the conditions that are optimal for mercury extraction (0.001 M reagents in chloroform):

Reagent	Extraction conditions	Degree of extraction, %				
		Ag(I)	Au(III)	Cu(II)	Hg(II)	Pd(II)
IX	pH 6 (0.2 M acetate)	7	8	1.5	81	5
X	pH 6; $1 \cdot 10^{-3}$ M picrate	10	3	15	98	3
XXIII	0.1 M H_2SO_4	0.1	22	0.3	97	14

Influence of the number, nature and arrangement of donor atoms. It is of interest to compare a series of structurally similar reagents as the extractants for the same element. The degree of copper extraction (R, %) with dibenzo-18-crown-6 analogues (XV-XXV) in fixed conditions (see Fig.1, pH 8) is shown below:

Reagent	XXIV	XXIII	XXI	XXV	XXII	XX	XIX
X and Y	CH_2, NH	NTs, NTs	O, NTs	NH, CH_2	NTs, O	NTs, CH_2	CH_2, NTs
R, %	92	81	30	29	28	27	17

Reagent	XVIII	XVI	XVII	XV	No reagent
X and Y	O, O	O, CH_2	CH_2, O	CH_2, CH_2	
R, %	9.9	7.9	6.9	4.0	2.2

If a substituent X in the molecule is fixed and Y is varied (or, vice versa, Y is fixed and X is varied), then copper extraction will increase in the following sequence of varied substituents (sometimes sign "<" turns into sign " \approx "): $CH_2 < O < NTs < NH$. On the whole this dependence is also observed for silver and nickel, but does not hold true for palladium. For thallium (I) the extraction increases in a different series of substituents: $CH_2 < NTs < O, NH$. This seems to be associated with a greater hardness of thalli-

um ion. The mutual arrangement of donor centres is not so significant as their nature, since isomeric reagents have similar extractive properties (XVI and XVII; XIX and XX; XXI and XXII; XXIV and XXV).

For reagents XI-XIV with fixed Y=S heteroatoms the extraction of mercury and silver increases in the following sequence of varied substituents X: $\text{CH}_2 < \text{O} < \text{NTs} < \text{S}$ (the conditions are as shown in Fig. 1, pH 6):

Reagent		XI	XII	XIII	XIV
2Y, X		2S,S	2S,NTs	2S,O	2S,CH ₂
R,%:	Hg	53	30	30	20
	Ag	57	43	17	11

It is of interest to note that mercury is extracted more efficiently by reagents with Y=O (IX, X), and not with Y=S (XI-XIV). Silver extraction increases with an increase in the number of sulphur atoms in the ring from one to three. For macrocyclic Schiff bases an increase in the number of oxygen atoms (in going from II to III) increases the silver extraction constants (see below).

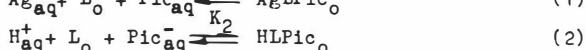
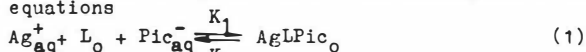
It specifically follows from the cited data that a decrease in the number of donor centres (heteroatom replacement with CH_2 group) lowers the extraction of the above elements.

Composition of extracted compounds

Metals are extracted with the macrocycles in question as complexes containing counterions. The most efficient of these are picrate, dipicrylamine, anions of some sulphophthalein dyes (the exceptions have been given above).

The metal:reagent:counterion ratio in the extracted complexes is usually equal to 1:1:1. In the extracted complexes of Hg (II), Cu (II), and Ag (I) with compounds IV and V and of Hg (II), Cu (II), Ag (I), and Co (II) with VI the metal: reagent ratio is equal to 1:1. For reagents X-XIV the metal: reagent:picrate ratio amounts to 1:1:1, both for silver and mercury. This is probably indicative of the proton splitting off from one of the reagent aminogroups when mercury is being extracted.

In the presence of counterions the reagents are capable of extracting not only the metal but also the hydrogen ion. For instance, the extraction of silver and picric acid with macrocycles I-III is described by equations



Equilibrium (2) has been studied spectrophotometrically. The obtained K_2 constants have been taken into account in calculating the K_1 constants from the data on silver distribution (pH is optimal for each macrocycle, see also Fig.2):

Reagent	K_1	K_2
I	7.60 ± 0.04	3.89 ± 0.04
II	5.86 ± 0.03	2.27 ± 0.03
III	6.88 ± 0.05	3.27 ± 0.06

Extractive-spectrophotometric determination of metals

Reagent II, selectively extracting silver, and reagent X, selectively extracting mercury, have been used. Determinations were performed using the method of two reagents. The reagents studied were 1-(2-pyridyl)-azo-2-naphthol, diphenylcarbazone, dithizone, 5-(n-dimethylaminobenzylidene)rhodanine (rhodanine), sulphochlorophenolazorhodanine and sulphochlorophenolazothiopropiorhodanine (tyrodine) - in the case of II and 1-(2-pyridylazo)-2-naphthol, diphenylcarbazone and dithizone - in the case of compound X. The best second reagents and the characteristics of developed procedures are shown below.

Characteristics of the methods for silver and mercury extractive-photometric determination

Metal	Macro-cycle	Second reagent	Wave-length, nm	Molar absorption coefficient	Detection limit, $\mu\text{g/ml}$	Determination not hindered by $C_M/C_{\text{Ag, Hg}}$
Ag	II	Rhodanine	490	$7.0 \cdot 10^4$	0.04	$\text{NO}_3^- (1 \cdot 10^5)$; $\text{Cd}, \text{Co}, \text{Mn}$ ($7 \cdot 10^4$); $\text{Tl}^I (2 \cdot 10^4)$; $\text{Ni}, \text{Pb}, \text{Zn} (1 \cdot 10^4)$; SO_4^{2-} , $\text{Cu}^{II} (3 \cdot 10^3)$; $\text{Hg} (200)$; $\text{Pd} (100)$; $\text{Fe}^{III} (50)$; $\text{Cl}^- (25)$.
		Tyrodine	580	$9.0 \cdot 10^5$	0.004	
Hg	X	Dithizone	490	$6.8 \cdot 10^4$	0.04	$\text{V}^V, \text{Ti}^{IV}, \text{Co}, \text{Ni}, \text{Mn}, \text{Cd}, \text{Zn}, \text{Sb}^{III}, \text{Sn}^{II}, \text{Mo}^{VI}, \text{Cr}^{III}, \text{F}^-, \text{Cl}^- (1 \cdot 10^3)$; $\text{Pb}, \text{SO}_4^{2-} (100)$; $\text{Cu}^{II}, \text{Bi}^{III}, \text{Fe}^{4II}$, $\text{Ag} (10)$

The procedures are distinguished by selectivity: silver determination is not interfered with by high quantities of Hg, Cu, Pd and other metals, although chloride does interfere with it; mercury determination is noticeably affected only by Cu, Bi, Ag and Fe (III). These procedures have been applied to determine small quantities of silver and mercury in compounds of complex composition.

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New Synergistic Extraction System for Removal of Fe(III) in Sulfate Solutions*

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ABSTRACT

Iron is always present as impurity in acid leaching solutions in hydrometallurgy and can be removed by precipitation of iron oxides or complex salts, or otherwise by solvent extraction or ion exchange. Studies reported so far on solvent extraction of iron from sulfuric acid leaching solutions have a common problem of stripping the iron extracted into the organic phase, and high concentration of sulfuric acid are often required. A new synergistic extraction system of primary amine with one of the several types of modifiers, such as alcohols and neutral phosphorus esters has been developed in the present work for the removal of iron in sulfate solutions. Stripping of iron from the loaded organic phase can be accomplished satisfactorily by dilute sulfuric acid solutions. Application of the new solvent system to the separation of Fe(III) in leaching solutions in zinc hydrometallurgy has been studied and reported.

INTRODUCTION

In hydrometallurgy and the inorganic chemicals industry, sulfuric acid is the most common reagent used for leaching or decomposition of solid raw materials such as ore, concentrate, roasted calcine or flue dust. Iron is always present in these raw materials as an impurity and thus often has to be removed from the leaching solutions. The leaching of zinc calcine and the recently developed direct high pressure leaching of zinc sulfide concentrate in zinc hydrometallurgy are typical examples. The methods used for iron removal from solutions can be generally divided into two categories, namely precipitation of iron oxides or complex salts and solvent extraction or ion exchange. Many processes have been developed to remove iron in solid form as jarosite, goethite and hematite^(1,2). They all suffer from similar problems of solid and liquid separation, the incorporation of metal values in the iron precipitate, the utilization of the solids and pollution problems arising from long term storage of the precipitates.

* Patent applied for, China Patent office.

Application of solvent extraction to remove iron from sulfuric acid solutions have been widely studied⁽³⁾. A number of solvents such as primary amines, secondary amines, alkyl phosphoric acid and carboxylic acids have been studied as solvents for iron removal. The problems associated with solvent extraction of Fe(III) are usually the slow rate of extraction, the occurrence of precipitates in the settlers and, in particular, difficulties in stripping the iron from the organic phase back into the aqueous phase. Either very high concentrations of sulfuric acid, such as 5-10 N, or more sophisticated methods have to be used for stripping. Different methods have been tested to improve the stripping operation such as reduction stripping, in which Fe(III) is reduced to Fe(II) during stripping, and hydrolytic stripping, where Fe(III) in the organic phase is hydrolyzed and precipitated as an oxide such as hematite^(4,5). These methods still suffer from problems such as expensive, high pressure operation and slow reaction rate.

In the present work, combinations of different extractants have been used to extract Fe(III) from zinc sulfate solutions with the objective being that the Fe(III) in the organic phase can be stripped by dilute sulfuric acid solutions. Zinc sulfate solutions from direct leaching of zinc sulfide concentrate under oxygen pressure were tested. Studies on the problems associated with the application of the developed solvent system in zinc hydrometallurgy and the chemistry of the extraction reactions involved are in progress.

EXPERIMENTAL

A mechanical agitator or electric shaker was used to carry out the extraction and stripping experiments. For temperature studies, the experiments were performed in a thermostat. Preliminary experimental results indicated that the extraction equilibrium was approached within three minutes. Most experiments were then carried out with five minutes as reaction time. The concentrations of metallic values in the aqueous phase after phase separation were analyzed and the concentrations of metals in the organic phase were calculated by difference. Iron was analyzed either by titration with potassium dichromate, by colorimetry with the addition of sulfosalicylic acid or by atomic absorption spectrometry. Zinc was also determined by atomic absorption spectrometry.

Primary amine N-1923, with formula $RR'CHNH_2$ and with a total number of carbon atoms 19-23, was supplied by the Institute of Organic Chemistry, Academia Sinica, Shanghai, China. Octanol-2 used was

chemical pure and the other chemicals used were analytical grade. The diluent used was commercial kerosene without any additional purification. The solutions used for initial tests were prepared from zinc sulfate and ferric sulfate with deionized water. The solutions obtained from high pressure leaching of zinc sulfide concentrate under oxygen atmosphere were used in the final tests. The Fe(II) in the leaching solution was oxidized by the addition of hydrogen peroxide.

RESULTS AND DISCUSSIONS

Screening of solvents for synergistic extraction of Fe(III) with primary amine Different solvents were tested for their combined effect on the solvent extraction of Fe(III) from solutions containing zinc sulfate and ferric sulfate with primary amine N-1923 as shown in Fig. 1. It can be seen that electron donor solvents enhance the extraction of iron by the primary amine while those with electron acceptor hydrogen atoms will decrease the extraction. The synergistic effect is increased with increasing of the electron donor property of oxygen atoms in the solvents. The synergistic effect of electron donor solvents does not increase continuously with the increasing of their concentration in the solvent mixture.

Fig. 2 shows the effect of different extractants with primary amine N-1923 as solvents on the stripping of iron from the organic phase by dilute sulfuric acid solutions. It can be found that by the addition of neutral esters or alcohols to the primary amine, the stripping of iron from the organic phase by dilute sulfuric acid is greatly improved. The results of these screening tests show that the combination of primary amine with alcohol or neutral phosphorus ester can be used for the extraction of Fe(III) from sulfate solutions and the Fe extracted can be stripped with dilute sulfuric acid. Zinc is practically not extracted into the organic phase. As octanol-2 is much cheaper than neutral phosphorus esters, experiments on the extraction of ferric iron from zinc sulfate solutions were carried out with mixtures of primary amine and octanol-2.

Extraction of Fe(III) with primary amine and octanol-2 Fig. 3 shows the effect of initial pH of solution on the extraction of Fe(III) as a function of octanol-2 added into the organic phase. It can be considered that the optimum pH value of solution for Fe(III) extraction is about 1.5 with no relation to the amount of alcohol in the organic phase. At low pH (as 0.5), the iron extracted decreases with increasing of the concentration of alcohol in the organic phase, while with

solution pH above 1.0 the iron extracted increases. The effect of the concentration of primary amine in the organic phase on the extraction of Fe(III) is shown in Fig. 4. The temperature of extraction has rather small effect on the extraction of iron within the temperature range studied 15-50°C.

Stripping of Fe(III) from the organic phase by dilute sulfuric acid

The effect of the amount of sulfuric acid used on the stripping of iron from the organic phase is shown in Fig. 5. With the ratio of the number of gram equivalents of H^+ added to the number of gram atoms of iron in the organic phase equals to five (equilibrium pH about 0.8), the percent of iron stripped is about 60%. Without addition of octanol-2 in the organic phase, the percent of iron stripped under the same conditions will be very low. At constant ratio of the amount of acid used for stripping to the amount of iron present in the organic phase, the concentration of acid used will be increased by increasing the organic to aqueous phase ratio resulting in higher percent of stripping.

Fig. 6 shows the isotherm of stripping with equilibrium pH value of about 0.85. It can be seen that the countercurrent stripping of iron in the organic phase studied can be carried out and the percent of iron stripped increases with the increasing of iron concentration in the organic phase.

Separation of Fe(III) from zinc in sulfate solutions The two-stage cross-flow extraction of Fe(III) from solutions with pH 1.45 containing Zn(II) 75 and Fe(III) 5 g/l with a solvent containing primary amine N-1923 12% and octanol-2 50% was carried out in the laboratory. The iron content in the raffinate was lower than 30 mg/l. Fig. 7 shows the amount of zinc extracted into the organic phase and the separation factor β of Fe to Zn as a function of concentration of octanol-2 in the organic phase. The concentration of zinc in the organic phase was lower than 10 mg/l and the separation factor of Fe to Zn can be as high as 10^6 order of magnitude.

The extraction of Fe(III) from solution obtained by high pressure leaching of zinc sulfide concentrate under oxygen was also studied. Fig. 8 shows the typical results of iron extraction as a function of initial pH of the leaching solutions. Results of iron and zinc extraction were practically the same as those obtained from solutions prepared with pure chemicals and deionized water. The concentration of zinc in the organic phase was lower than 10 mg/l. The results of stripping of iron extracted into the organic phase from leaching solutions

by dilute sulfuric acid as shown in Fig. 5 also indicated no difference from the iron extracted from solutions prepared with pure chemicals.

For leaching solution containing iron 11.05 g/l, the iron content in the raffinate of three-stage cross-flow extraction with the solvent system studied was lower than 10 mg/l as shown in Table 1. The separation of other impurities in the high pressure leaching solutions such as As and Sb is still under study.

Table 1. Results of cross-flow extraction of Fe(III) from high pressure zinc sulfide leaching solutions.
aq.: Zn(II) 75, Fe(III) 11.05 g/l.; 29°C., 5 min.
Org.: N-1923 12%, octanol-2 50% in kerosene.

No. of stages	1	2	3	3	3	3	3
O/A	1	0.67	0.6	0.6	0.6	0.6	0.4
pH _i	1.37	1.36	1.06	1.37	1.62	1.74	1.64
pH _e	2.62	2.25	1.27	2.57	4.14	4.92	3.74
raffinate Fe mg/l	3340	721	27	10	4.3	5.0	20

CONCLUSIONS

Solvent systems with combinations of extractants were found for the extraction of Fe(III) from sulfate solutions containing zinc or some other metals. The solvents used were secondary carbon primary amine with alcohols, such as octanol-2, or neutral phosphorus esters, such as TBP. The iron extracted into the organic phase can be stripped with dilute sulfuric acid as 0.5 N and the pH of the solution after stripping was equal to or lower than 0.8. The acid used for stripping was much less than those used for stripping from the solvents reported before. Preliminary results of separation of Fe(III) in the solutions obtained by high pressure leaching of zinc sulfide concentrate under oxygen are very encouraging. Work are still in progress.

NOMENCLATURE

A	Aqueous phase,
C _A	Conc. of alcohol or additional agent,
C _N	Conc. of amines,
C _O	Conc. in the organic phase,
E	Extraction,

f_{Fe}	Number of formula weight of Fe,
N_{H^+}	Number of gram equivalents of H^+ ,
O	Organic phase,
pH_i	Solution pH at start of experiment,
pH_e	Solution pH at equilibrium,
p-350	di-1-methyl-heptyl methylphosphonate,
S	Stripping,
t	Time,
TBP	Tributyl phosphate,
TRPO	Trialkyl phosphine oxide (alkyl group No. of C atoms = 8),
β	Separation factor,

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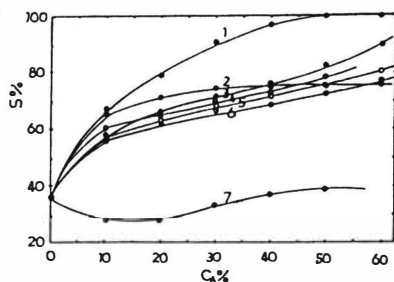
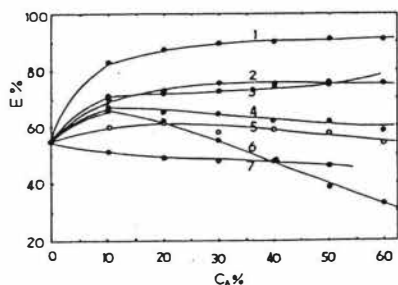


Fig. 1 Effect of the conc. of additional agents in organic phase on the extraction of Fe(III) by primary amine N-1923.
aq.: Zn 77, Fe 4.995 g/l, pH 1.50
Org.: 6% N-1923 in kerosene, additional agent (%)
1-TRPO, 2-p-350, 3-TBP, 4-octanol-2, 5-2-ethylhexanol,
6-n-octanol, 7-CHCl₃.
O/A = 1, 25°C 5min.

Fig. 2 Effect of the conc. of additional agents mixed with N-1923 on the stripping of iron by dilute sulfuric acid.
stripping agent: 0.50 N H₂SO₄;
Org.: 6% N-1923,
1-n-octanol, 2-TRPO, 3-octanol-2, 4-TBP, 5-2-ethylhexanol,
6-p-350, 7-CHCl₃.
25°C., 5 min., O/A = 1

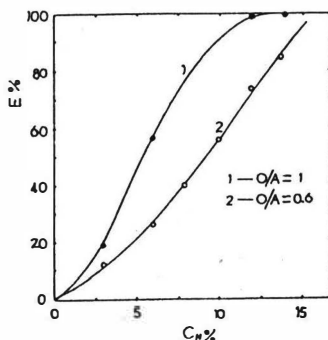
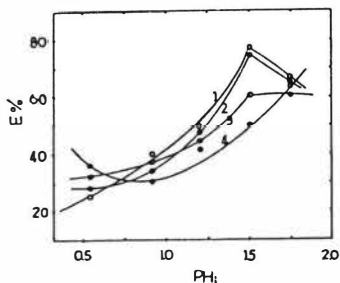


Fig. 3 Effect of solution initial pH on the extraction of Fe.
aq.: Zn 42, Fe 4.7 g/l.;
Org.: 1. N-1923 7.5%; octanol-2 30%
2. 6.0% 20%
3. 6.0% 10%
4. 6.0% 0%
28°C., 5 min., O/A = 1.

Fig. 4 Effect of the conc. of primary amine N-1923 in the organic phase on the extraction of Fe(III).
aq.: Zn 75, Fe 5.00 g/l; pH 1.48;
Org.: octanol-2 50%
1. O/A = 1 2. O/A = 0.6.
27°C., 5 min.

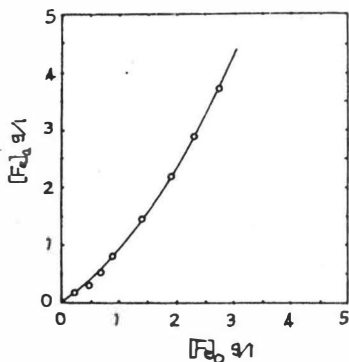
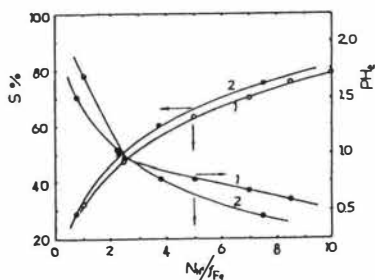


Fig. 5 Effect of the amount of sulfuric acid used on the stripping of Fe(III) from the organic phase.

Org.: 12% N-1923, 50% octanol-2;

Fe in org., phase: 1. 6.00 g/l extracted from solutions prepared with pure chemicals,

2. 7.45 g/l extracted from zinc sulfide high pressure leaching solution.

29°C., 5 min., O/A=1

Fig. 6 Stripping isotherm

aq.: Zn 75 g/l,

Org.: N-1923 12%, octanol-2 50% with different amount of Fe.

pHe = 0.8 0.9

28°C., 5 min., O/A=1

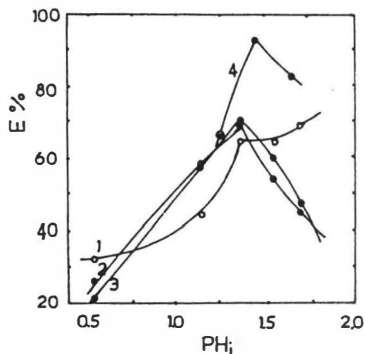
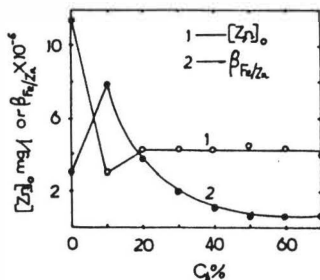


Fig. 7 Effect of the conc. of octanol-2 in the organic phase on the extraction of Zn and the separation factor of Fe to Zn by primary amine N-1923 respectively.

aq.: Zn 75, Fe 5.25 g/l, pH 1.20; Org.: N-1923 15% in kerosene

27°C., 5 min., O/A=1.

Fig. 8 Effect of solution initial pH on the extraction of Fe from high pressure leaching of zinc sulfide concentrate solutions.

aq.: Zn 75, Fe 11.05 g/l; Org.: N-1923 12%; octanol-2: 1. 0, 2. 30%, 3. 50%, 5. 50% and final results of two stage cross-flow extraction

29°C., 5 min., O/A=1.

Separation of Tungsten(VI) in Molybdate Solution by Synergistic Extraction with Primary Amine and Neutral Donor Extractants*

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ABSTRACT

Separation of molybdenum and tungsten is always a difficult problem. More work have been done on the removal of molybdenum in tungstate solutions while not much work has been reported on the separation of tungsten in molybdate solutions. It has been found by the present work that tungsten in molybdate solutions can be separated satisfactorily by the synergistic extraction with a mixture of primary amine and neutral donor extractants. The one stage extraction of W(VI) can be higher than 99%. The separation factor of W(VI) to Mo(VI) can be better than 10^3 and the synergistic factor can be higher than 100. Low concentration sodium hydroxide solutions can be used to strip the tungsten from the organic phase. Mechanism of extraction has been studied and proposed.

INTRODUCTION

Molybdenum and tungsten are very similar in chemical properties and they are often associated with each other in mineral deposits and in scraps from material processing industry. Both metals of higher purity and better quality are important to the development of modern technology. Methods of separation of tungsten and molybdenum have been investigated by many research workers. More work have been done on the removal of Mo(VI) in tungstate solutions while not much work has been reported on the separation of tungsten in molybdate solutions. Our previous work⁽¹⁾ have found that primary amines can be used to separate W(VI) from Mo(VI) in neutral or weakly alkaline solutions with preferential extraction of W(VI). However, the separation factor of W to Mo can only reach to about 150 under the experimental conditions investigated. Following our work on the synergistic extraction of Re(VII) by primary amine and neutral phosphorus ester⁽²⁾, studies on the extraction and separation of W(VI) in molybdate solutions were carried out. Much better results were obtained in comparison with those found by using primary amine only as the solvent.

* Patent Applied for, China Patent Office.

EXPERIMENTAL

A mechanical agitator or electric shaker was used to carry out the extraction and stripping experiments. Primary amine N-1923, with the formula of $RR'CHNH_2$ and with a total number of carbon atoms 19-23, was supplied by the Institute of Organic Chemistry, Academia Sinica, Shanghai, China. Primary amine 7101 with formula R_2CHNH_2 (R with C_8-C_{10}) and secondary amines 7201 and 7203 with formula $(R_2CH)_2NH$ (R with C_7-C_9 and with C_6-C_7 respectively) were supplied by the Institute of Uranium Ore Processing, Beijing, China. The other reagents and extractants used were analytical or chemical pure grade.

Solutions were prepared with analytical grade sodium tungstate and sodium molybdate. The concentrations of W(VI) and Mo(VI) were analyzed by thiocyanate colorimetry respectively. The presence of large amount of Mo(VI) in the aqueous phase interfered with the analysis of W(VI), therefore, the concentrations of W and Mo in the loaded organic phase were analyzed by quantitative stripping into the aqueous phase first. To prevent the possible interference from organic degradation products and Mo to the analysis of W in the organic phase, a parallel extraction test was made in each experiment under the same conditions from a solution containing Mo only, and the organic phase thus obtained was treated in the same manner and used as blank in the colorimetry.

RESULTS AND DISCUSSIONS

Studies on the extraction and separation of W(VI) from molybdate solutions. The amount of acid added into the alkaline molybdate solution has a very important effect on the extraction of W(VI) as given in Fig.1. The extraction of W(VI) and the Separation of W from Mo were found to be influenced by the time of contact as shown in Fig.2. It seems that the amount of Mo extracted increases with the increase of contact time. The pH value of aqueous phase at equilibrium was about equal to 7.

Fig.3 shows the effect of the concentration of a primary amine in the organic phase on the separation of W from Mo. It can be seen that the optimum concentration of primary amine to give the best separation increases with the increasing of the concentration of Mo in the aqueous phase. The results of extraction of W and Mo by the combinations of primary amine N-1923 with different neutral donor extractants are given in Table 1. Different neutral extractants were found to provide different degrees of enhancement to the extraction of W(VI) by primary

amine. Among the neutral extractants studied, best results of extraction were given by trialkyl phosphine oxide (TRPO). Work were then concentrated on the extraction of W(VI) with TRPO as the synergistic solvent and the typical results were given in Table 2. The one-stage extraction of W can be higher than 99% and the separation factor of W to Mo can be up to the order of 10^4 . Table 3 gives the effect of different classes of amines in combination with n-octanol in the organic phase on the extraction of W. From neutral or weakly alkaline solutions, the mechanism of extraction of W(VI), Mo(VI) and V(V) by amines has been found to be by solvation and not by anion exchange as reported in our earlier work⁽³⁾. The number of active hydrogen atoms attached to the nitrogen atom in an amine is very important to the solvation mechanism. The presence of two active hydrogen atoms in each molecule of primary amine gives the best results in solvation extraction among the three classes of amines, where as tertiary amine without active hydrogen atom attached will only give poor results.

The stripping of W(VI) from the organic phase with primary amine and neutral donor solvents such as TRPO as solvent can be carried out by using very dilute sodium hydroxide solution (as 0.1-0.2%). As long as the equilibrium pH value is above 7.5, the stripping is quantitative. The mole ratio of Mo to W in the stripping solution can be decreased by carrying one more extraction with very low concentrations of extractants (as 0.1-0.2% primary amine and neutral donor extractants respectively) in the organic phase. With four stages of contact all together, W in Mo can be separated and recovered by the solvent systems developed in the present work.

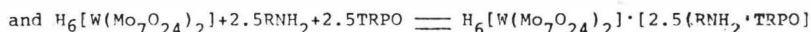
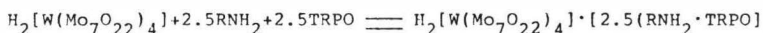
Discussion of the extraction mechanism

Fig. 4 gives the effect of the amount of acid added on the extraction of W and Mo from the solutions with different compositions. Fig. 5 shows the effect of the additional agent on the extraction of W from solutions containing W and solution containing W and Mo as well. Different results obtained under the same extraction conditions from the solutions of different compositions may be considered as due to the species extracted into the organic phase having different compositions and structures. The W extracted into the organic phase could be tungstate, different isopolyacids of tungsten or heteropolyacids of W and Mo from the aqueous solutions containing both W and Mo. In solutions with high concentration of Mo, the tendency for Mo to form isopolyacids is increased. It may be considered the species extracted into the organic phase could be heteropolyacids of Mo and W from solutions containing low concentration of W and high concentration of Mo. Table 4 gives the atomic

ratio of Mo to W in the organic phase taken at the point of maximum separation factor of W to Mo expressed as a function of the compositions of aqueous phase and organic phase.

It has been reported⁽⁴⁾ that with low concentration of W(VI) in the aqueous phase, the tungsten is in the form of monotungstate even in acidic solution. The degree of aggregation of Mo(VI) in aqueous solution will decrease with the decreasing of the concentration of Mo in the solution. The isopolyanions of Mo(VI) in the aqueous solution could be $\text{Mo}_7\text{O}_{24}^{6-}$, $\text{Mo}_4\text{O}_{14}^{4-}$, $\text{Mo}_3\text{O}_{10}^{2-}$ and $\text{Mo}_2\text{O}_7^{2-}$. The species extracted into the organic phase could be one or two heteropolyacids such as $\text{H}_2[\text{W}(\text{Mo}_7\text{O}_{22})_4]$ with Mo/W ratio of 28 and $\text{H}_6[\text{W}(\text{Mo}_7\text{O}_{24})_2]$ with Mo/W ratio of 14. The deviation of Mo/W ratio in the organic phase from the ideal value mentioned above as 28 or 14 may be arising from a small amount of other species extracted into the organic phase at the same time.

Studies were made on the extraction of W as a function of the concentration of primary amine and alcohol respectively with the other conditions being kept constant. Results were plotted on the logarithm-logarithm scale and the slopes of both straight lines obtained were found to be 2.5. The reactions of extraction can be suggested with examples as:



The above reactions will be reversed to the left side during stripping with equilibrium pH above 7.5.

CONCLUSIONS

Tungsten in weakly alkaline molybdate solutions can be synergistically extracted by solvation mechanism into the organic phase with a mixture of primary amine and neutral donor extractants, such as alcohol and neutral phosphorus ester, as solvent. Tungsten in the organic phase can be stripped by dilute sodium hydroxide solution. It has been proposed that the species extracted into the organic phase are possibly molybdotungstic acids such as $\text{H}_2[\text{W}(\text{Mo}_7\text{O}_{22})_4]$ and $\text{H}_6[\text{W}(\text{Mo}_7\text{O}_{24})_2]$.

NOMENCLATURE

A	Aqueous phase or its volume
C _A	conc. of alcohol or additional agent
C _N	conc. of amine
D	Distribution ratio
D	Extraction
f _w	Number of gram formula weight of tungsten
N _{H⁺}	Number of gram equivalents of H ⁺
O	organic phase or its volume
pHe	Aqueous phase pH at equilibrium
n-OA	n-octyl alcohol
DACHP	Di-isoamyl cyclohexylphosphonate
TBP	Tri-butyl phosphate
TRPO	Tri-alkyl phosphine oxide (alkyl group number of carbon=8)
TOA	Tri-octyl amine
TDA	Tri-decyl amine
α	synergistic factor
β	separation factor

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Table 1. Effect of different neutral extractants added to the organic phase on the separation of W(VI) from Mo(VI) by primary amine N-1923.

org.: 3% primary amine N-1923 with different neutral extractants in kerosene; O/A=1, 20°C., 5 min.
aq.: W(VI) 0.365, Mo(VI) 51 g/l; acid added: $N_H^+/f_W=30$.

org. phase			org. phase at equili.		E_W %	$\beta_{W/Mo}$
RNH ₂ %	neutral name	ext. M	W g/l	Mo g/l		
3	n-OA	0.32	0.306	2.77	83.3	90
3	DACHP	0.32	0.281	2.75	77.0	59
3	TBP	0.32	0.281	2.75	77.0	59
3	TRPO	0.188	0.325	2.68	89.0	147
0	n-OA	0.32	~0	~0		
0	DACHP	0.32	~0	~0		
0	TBP	0.32	~0	~0		
0	TRPO	0.188	~0	~0		

Table 2. Separation of tungsten from molybdenum by the mixture of primary amine N-1923 and TRPO as solvent.

aq.: composition same as given in Table 1.
O/A=1; t=5 min.; T 20°C.

org. phase		N_H^+/f_W		org. at equi.		D_W	D_{Mo}	$\beta_{W/Mo}$	α
RNH ₂ M	TRPO M			W g/l	Mo g/l				
0.066	0.188	25	7.0	0.301	2.21	4.70	0.0452	104	3.3
0.066	0.188	30	7.1	0.327	2.68	8.61	0.0560	155	5.6
0.066	0.188	50	7.1	0.364	4.49	364	0.0966	3768	141
0.066	0.094	35	7.1	0.344	3.38	16.4	0.071	231	6.36
0.066	0.047	35	7.25	0.301	3.32	4.70	0.0696	67.5	
0.066	0.39	35	7.15	0.3647	3.32	1216	0.0674	18000	471
0.066	0	35		0.263	3.15	2.58	0.0658	39.2	
0.01	0.094	35		0.029	1.89	0.086	0.039	2.2	
0.132	0.094	35		0.320	3.05	7.11	0.064	112	
0.066	0	30		0.222	2.81				
0	0.32	35		~0	~0				
0	0.094	35		~0	~0				

Table 3 Extraction of W(VI) by different classes of amines from weakly alkaline solutions
aq: W(VI) 89.2 mg/l, Mo(VI) 91.89 g/l, pH 9.30, $N_H/f_W=30$.
org.: 0.05 M amine & 1% n-octanol in kerosene
O/A=1, 20°C., t=5 min.

amine	aqueous at equili.		org. at equili.		$E_W \%$
	pH _e	W mg/l	W mg/l	Mo mg/l	
N-1923	7.30	47.6	41.6	712	46.0
7101	7.30	44.4	44.8	600	50.2
7203	7.15	81.3	7.2	16.3	8.9
7201	7.20	88.3	9.9	208	11.0
TOA	7.15	89.2	~0	0.40	~0
TDA	7.15	89.2	~0	~0	~0

Table 4 Atomic ratio of Mo to W in the organic phase as a function of the concentrations of Mo in the aqueous phase.
experimental conditions as given in Fig. 3.

aqueous phase			conditions for maximum of B_W/Mo			Mo/W in org.
W mg/l	Mo g/l	N_H/f_W	N-1923 %	additional extractant	B_W/Mo	Mo/W(atomic)
91.2	96.9	45	1.5	n-OA	203	29.0
91.2	76.5	35	1.25	n-OA	165	25.5
91.2	51.0	40	1.0	n-OA	185	24.5
365	51.0	50	3.0	TRPO	3768	24.0
91.2	25.5	30	0.5	n-OA	184	16.4
91.2	12.8	30	0.5	n-OA	315	14.0
91.2	5.10	10	0.125	n-OA	136	5.2

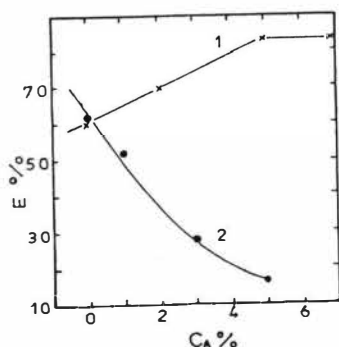


Fig.5 Effect of the amount of n-octanol added into the organic phase on the extraction of W(VI) from solutions with different compositions.
curve 1. aq.: W 365 mg/l, Mo 51 g/l, pH 9.0, $N_H/f_W=35$
org. 3% N-1923 and different amount of n-octanol in kerosene
curve 2. aq.: W 184 mg/l, $N_H/f_W=1.5$, org.: N-1923 1% and different amount of n-octanol in kerosene.
The other conditions were the same as given in Fig.1.

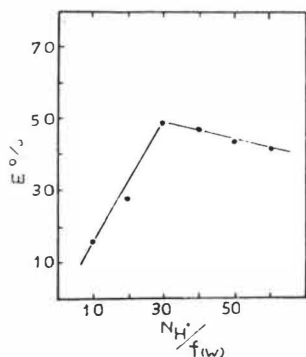


Fig. 1 Effect of the amount of acid added on the extraction of W(VI)
aq.: W 0.089 g/l, Mo 91.9 g/l; pH 9.30.
org.: 1% N-1923 and 1% n-octanol in kerosene
O/A=1, 20°C., 20 min.

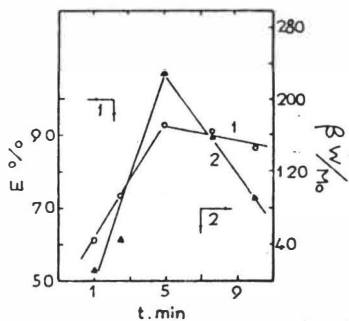


Fig. 2 Effect of the time of contact on the extraction of W and the separation of W from Mo.
aq.: W 365 mg/l, Mo 51 g/l, acid added $N_{H^+}/f_w=35$
org.: 3% N-1923 and 4.8% TRPO in kerosene, O/A=1, 20°C.

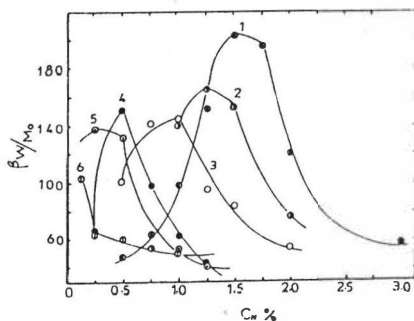


Fig. 3 Effect of the concentration of primary amine N-1923 on the separation factor of W to Mo.
aq.: W 91 mg/l and curve 1. Mo 96.9 g/l, $N_{H^+}/f_W=45$,
2. Mo 76.5 g/l, $N_{H^+}/f_W=35$, 3. Mo 51.0 g/l, $N_{H^+}/f_W=35$.
4. Mo 25.5 g/l, $N_{H^+}/f_W=25$, 5. Mo 12.8 g/l, $N_{H^+}/f_W=20$
6. Mo 5.1 g/l, $N_{H^+}/f_W=5$
The other conditions were the same as given in Fig. 1

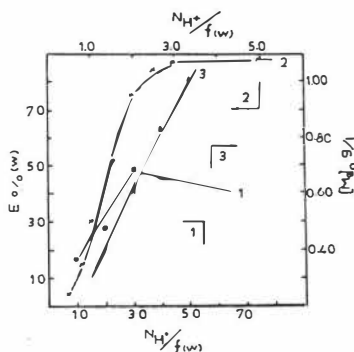


Fig. 4 Effect of the compositions of aqueous phase on the extraction of W(VI) by primary amine N-1923 as a function of the amount of acid added.
curve 1 and 3 aq.: W 89.2 mg/l, Mo 91.87 g/l 2. aq.: W 184 mg/l, no Mo added
org.: 1% N-1923 and 1% n-octanol in kerosene.
The other conditions were the same as given in Fig. 1.

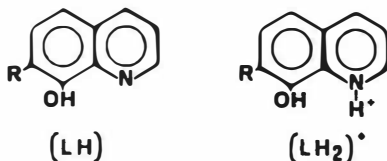
A NOVEL SOLVENT EXTRACTION SYSTEM FOR THE REFINING OF PRECIOUS METALS

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Solvent extraction based refining processes for precious metals undoubtedly offer several advantages over the traditional precipitation techniques and their usage by the industry is expected to become standard practice. In this paper a recently developed refining process for which patents are pending in a number of countries (1) is described. The process uses commercially available alkylated derivatives of 8-hydroxyquinoline (Kelex 100 or LIX 26) as the basis for the separation of precious metals. Data on the extraction and stripping characteristics of gold (III), platinum (IV), and palladium (II) as well as an integrated circuit employing the new extraction system are presented.

EXTRACTION

(a) Organic Solvent: The unique property of 8-hydroxyquinoline (8-HQ) derivatives to act as chelating agents and as anion exchange agents, when in protonated form, is the key factor for the success of this solvent extraction system. The simple and protonated forms of these reagents are shown below:



Kelex 100 (registered trade name of Sherex Chemical Co.) has been extensively used in the past by several investigators and its structure and composition has also been well defined. (2). However no details are available concerning the structure of LIX 26 (registered trade name of Henkel Corporation). Analytical work performed at McGill University involving gas liquid chromatography and mass spectrometry of LIX 26 samples has indicated the latter reagent to be 7-substituted 8-HQ consisting of a complex mixture of branched alkyl isomers with one or two unsaturations in the alkyl side chain. $C_{11}H_{22}$ and $C_{12}H_{24}$ are the most abundant alkylates of 8-HQ found in LIX 26.

In the earlier stages of the present development work, where Kelex 100 was used for the extraction of Au(III), Pt(IV) and Pd(II) from chloride media (3), difficulties were encountered due to the need to operate at high temperatures ($\sim 65^\circ\text{C}$) to avoid the precipitation of the relatively insoluble Kelex-Pt(IV) complex. This early

work had also indicated that aromatic rather than aliphatic diluents are preferred for better extraction performance. However, with the use of LIX 26 it was found Pt(IV) to be extracted at very high loadings at room temperature (20 - 25°C) without any precipitation problems. Thus mixtures of LIX 26, isodecanol and Solvesso 150 were adopted actually as the preferred organic solvent for the separation of Au(III), Pt(IV), and Pd(II). This solvent has to be purified prior to its use by acidification using 3N HCl and several H₂O washings in order to remove soluble impurities found in the as-received extractant which interfere with the metal extraction process. The LIX 26-isodecanol-Solvesso 150 system exhibits very fast metal extraction kinetics (<3 min) thus outperforming other reagents such as alkyl sulphides and oximes currently used in some refineries. Also phase separation characteristics are excellent with very short disengagement times and no emulsion problems. These characteristics have been confirmed on pilot-plant scale trials (4).

(b) Metal Distribution: The distribution of Au(III), Pt(IV), Pd(II) and several base metals in LIX 26 as a function of the equilibrium HCl concentration of the aqueous phase is shown in Fig. 1. Each curve on this figure was constructed by conducting separate tests for each metal. In the range of 2.0 to 3.0 M HCl Ni, As, and Te were found to be not extractable. The Au(III) and Pt(IV) extraction is favored at high acid levels while Pd(II) extraction is favored at low acid levels.

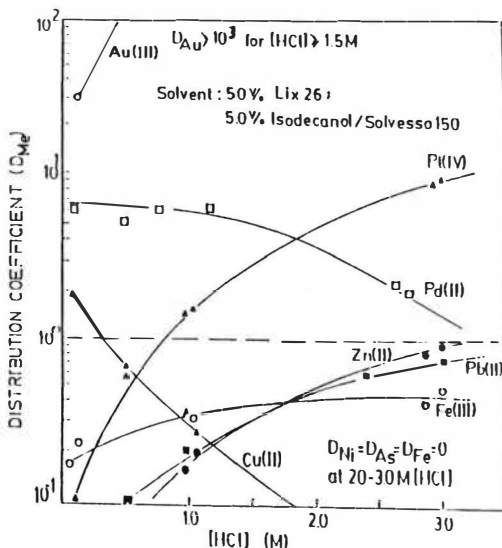
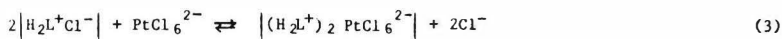
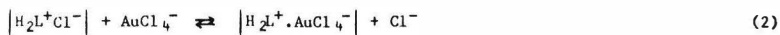


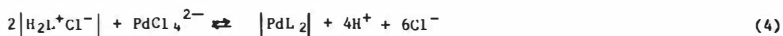
Fig. 1. Distribution coefficients of Au, Pt, Pd and several base metals in LIX 26 as a function of equilibrium HCl concentration (20°C; 3 min)

The marked difference in the extraction of Pd(II) and Au(III)/Pt(IV) is indicative of the different extraction mechanisms. At high acid concentrations LIX 26 (and equivalently Kelex 100) is protonated and therefore acts as an anionic exchanger for Au(III) and Pt(IV):



From individual loading tests the composition of $|H_2L^+.AuCl_4^-|$ has been confirmed, while the composition of the Pt(IV) complex was found to be: $|(H_2L^+)_2PtCl_6^{2-}|$. $2H_2L^+Cl^-$. The synthesis of Au(III) chelates with 8-HQ, the parent compound of LIX 26 and Kelex 100, has been reported in the literature (5). Formation of Au chelates was not observed with the C_{11}/C_{12} alkylated derivatives of 8-HQ provided that the extractant was purified prior to its use. Another important observation is the fact that aging (>1 week storage) of the Pt(IV) loaded organic results in complex transformation (ion-pair to chelate) which no longer can be stripped by water. A C_8H_{16} alkyl derivative of 8-HQ (not commercially available) that was used instead of LIX 26 resulted also in very strong Pt(IV) complex formation not strippable by H_2O . Therefore successful application of alkylated derivatives to precious metals extraction depends on the length and the structure of the alkyl substitutions ($C_{11}H_{22}$ and $C_{12}H_{24}$ are the preferred alkylates).

In contrast to Au(III) and Pt(IV), Pd(II) is extracted via chelate formation with alkylated derivatives of 8-HQ:



The mechanism of reaction (4) where HL is Kelex 100 has been studied by Ha and Freiser (6).

Plots of the distribution coefficients of Au(III), Pt(IV), and Pd(II), as a function of LIX 26 concentration are shown in Fig. 2. The solvent used consisted of equal concentrations (in v/o) of LIX 26 and isodecanol in Solvesso 150. When a concentrated solvent (20 to 25 v/o LIX 26) is employed longer disengagements times of the order of 5 to 6 minutes are required.

(c) **Selectivity:** Depending upon the relative abundance of precious metals and impurity elements in the chloride feed liquor different extraction procedures can be adopted. Gold, if present, is extracted first, at very high loadings (0.12 M Au/5 v/o LIX 26) as long as no excess extractant is employed. This can be

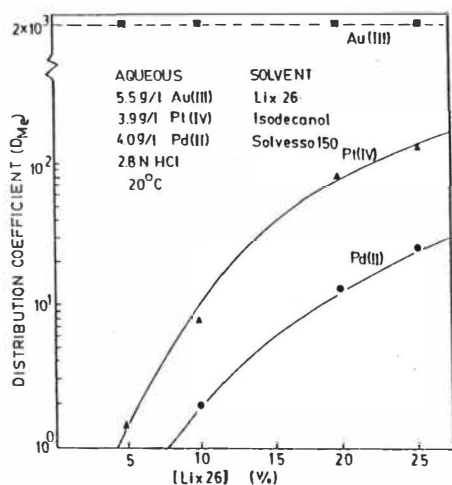


Fig. 2. Plots of $D_{Au(III)}$, $D_{Pt(IV)}$, and $D_{Pd(II)}$ versus initial LIX 26 concentration (20°C; 3 min)

controlled by using either a low strength solvent or a large A/O ratio. Table 1 demonstrates in fact that with A/O ratio equal to 3/1 Au is preferentially extracted from a real feed liquor (2.8 N HCl). The selectivity increases even further when a multi-stage counter current circuit is employed. Metals loaded in the organic phase during the contact of fresh organic with the partially depleted aqueous feed are exchanged with Au(III) in the consecutive stages thus improving selectivity. This is exemplified with the results of Table 2 where the composition of the organic and aqueous phases is given for consecutive contacts of the solvent with fresh aqueous feed liquor.

Table 1: The effect of A/O ratio on preferential extraction of Au(III) with LIX 26 (ORG: 10 v/o LIX 26 - 10 v/o isodecanol in Solvesso 150; AQ: 2.8 N HCl; 20°C; 3 min)

		Metal concentration in Raffinate (ppm)								
		Au	Pd	Pt	Ag	Cu	Fe	Pb	Ni	Zn
Feed Liquor	+	10007	460	190	98	5000	1060	1640	1150	1070
A/O	% Au Extr.									
1/5	> 99.9	1	2	5	5	3790	320	240	1150	24
1/3	> 99.9	1	1	5	10	4380	320	390	1140	47
1/1	> 99.9	3	100	10	48	4900	700	1080	1160	340
3/1	99.5	50	420	140	92	4960	1040	1600	1160	1000
5/1	89.0	1100	460	190	96	4970	1060	1640	1150	1060

Table 2: Back-extraction of Pt(IV) and Pd(II) with increasing Au loading of LIX 26. (ORG: 5 v/o LIX 26 - 5 v/o isodecanol in Solvesso 150; AQ: 2.8 N HCl - 1.0 N H₂SO₄; A/O = 1; 20°C; 3 min)

Contact No.	ORGANIC PHASE				AQUEOUS PHASE				
	Au	Pt	Pd	(g/L)	Au	Pt	Pd	Cu	Fe
				Feed					
1	7.86	1.09	1.05		7.89	1.66	4.33	11.30	0.22
2	15.81	0.47	0.40		0.034	0.57	3.28	11.40	0.23
3	21.38	0.09	0.01		0.34	2.28	4.98	11.30	0.22
4	23.51	0.04	<0.01		1.92	2.04	4.72	11.30	0.21
5	23.90	0.03	<0.01		5.76	1.71	4.35	11.30	0.21
					7.50	1.67	4.40	11.40	0.21

The Pt(IV) and Pd(II) are co-extracted with mixtures of LIX 26-isodecanol-Solvesso 150 at room temperature after Au(III) has been removed from the aqueous feed liquor. Depending on the relative concentrations of Pt and Pd in the feed liquor, adjustment of the acid strength might be required to increase the loading of the organic solvent for the most abundant of the two metals. Extraction isotherms for Pt(IV) and Pd(II) at two different acid levels are given in Fig. 3.

Total metal (Pt + Pd) loading of about 12 g/L with a 10 v/o LIX 26 solvent is obtained. Metal loading can be doubled by employing a 20 v/o LIX 26 solvent. Data demonstrating the selective extraction of Pt and Pd with LIX 26 employing different O/A ratios are given in Table 3. With the exception of Bi very good selectivity is obtained. Secondary PGM metals were not considered in the present work. However, based on solution chemistry considerations, it can be assumed that reduction of Ir(IV) to Ir(III) prior to Pt/Pd co-extraction will result in the retention of all the secondary PGM in the raffinate.

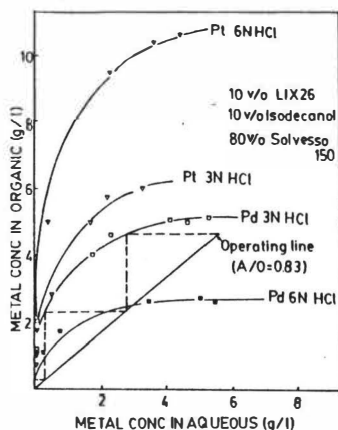


Fig. 3. Extraction isotherms for Pt(IV) and Pd(II) at 3.0 and 6.0 N HCl concentrations (20°C; 3 min)

Table 3: Effect of O/A ratio on Pt/Pd extraction and selectivity (ORG:10 v/o LIX 26; 10 v/o isodecanol; Solvesso 150, Aq (ppm): 6070 Pd; 3350 Pt; 10500 Cu; 740 Fe; 270 Pb; 1120 Zn; 470 Bi; 570 As; 330 Te; 2.5 N HCl, 3 min CT)

O/A	D _{Pt}	D _{Pd}		Cu	Fe	Pb	Zn	Bi	As	Te
1/3	3.1	1.23	S _{Pt} /Me	31	>2000	8.4	4.3	2.1	>2000	>2000
			S _{Pd} /Me	12.3	>2000	3.3	1.7	0.8	>2000	>2000
1/1	5.2	2.6	S _{Pt} /Me	43	17.4	7.8	2.7	0.7	117	>2000
			S _{Pd} /Me	24	10.4	9.7	1.6	0.4	70	>2000
3/1	5.5	33	S _{Pt} /Me	458	153	47	5.1	1.1	380	>2000
			S _{Pd} /Me	330	91.6	28.2	3.1	0.65	825	>2000

STRIPPING

(a) Gold

Gold is recovered directly from the loaded organic solvent by hydrolytic stripping. This method involves heating the organic phase in contact with H₂O at a ratio 10 to 1. With the action of H₂O at elevated temperatures (60 to 90°C) the complex $[H_2L^+.AuCl_4^-]$ is dissociated resulting in the regeneration of the extractant and the precipitation of high purity Au grains. The mechanism of this novel precipitation reaction is the subject of current investigations at McGill University. Hydrolytic stripping of Au is a selective process as it is exemplified with the results of Fig. 4. Carbon, the only major impurity found in the Au powder product can be easily removed by heating in an oxidizing atmosphere to give a product purity of at least 99.9% Au.

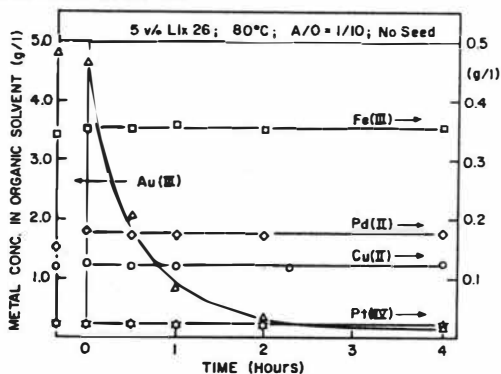


Fig. 4: Direct Au precipitation by hydrolytic stripping as a function of time

(b) Platinum/Palladium Separation

Due to the different nature of the Pt(IV) and Pd(II) complexes (ion-pair vs chelate) formed with alkylated derivatives of 8-HQ, selective stripping and separation of the two metals is easily accomplished; in contrast, amine extractants do not render themselves to selective stripping. Thus Pt is stripped first with H_2O followed by Pd stripping using a strong HCl solution (6 to 8 N). Reversal of the stripping sequence results in loss of selectivity and operation difficulties. Owing to co-extraction of HCl into the organic phase during metal loading, it is necessary to adjust the pH between 1.5 to 2 to optimize the selective stripping of Pt while maintaining good phase separation characteristics. The effect of equilibrium pH on the Pt stripping and Pt/Pd separation is shown in Fig. 5. Also in Fig. 5 it can be seen that Pt selectivity is adversely affected by maintaining a high free Cl^- concentration in the strip liquor. An increase in temperature has a marked beneficial effect on Pt stripping but no effect on Pd stripping. Stripping isotherms for Pt and Pd are shown in Fig. 6. Finally stripping and phase separation kinetics are very fast for both metals.

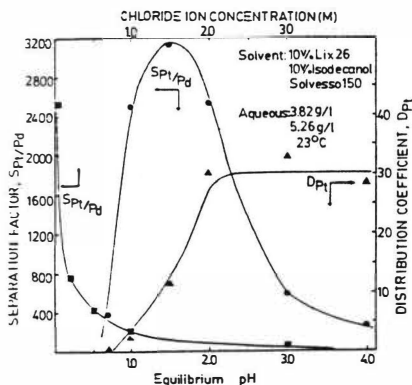
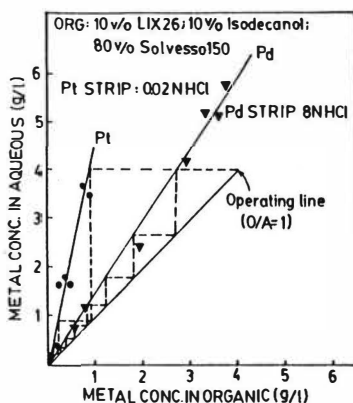


Fig. 5. The effects of equilibrium pH and free Cl^- concentration on selective stripping of Pt(IV) with water ($20^\circ C$; 3 min)

Fig. 6. Stripping isotherms for Pt/ H_2O and Pd/HCl ($20^\circ C$; 3 min)



PROPOSED FLOWSHEET

Based on the findings of this work, the flowsheet of Fig. 7 is proposed for the separation and recovery of Au, Pt, and Pd from contaminated

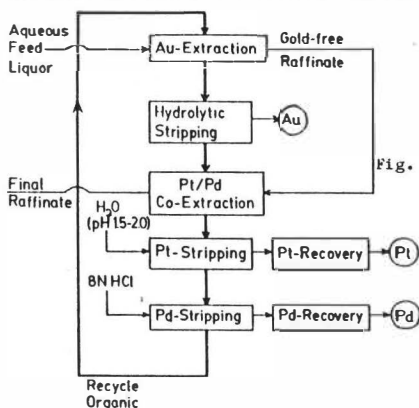


Fig. 7. The integrated circuit for the separation of Au(III), Pt(IV), and Pd(II) with LIX 26-isodecanol-Solvesso 150 system

aqueous chloride solutions using mixtures of LIX 26, isodecanol and Solvesso 150 as the preferred solvent extraction system. Other refining processes have to use different extractants to achieve the same task thus resulting in large complicated flowsheets. First, by controlling the A/O ratio, selective extraction of Au is achieved (<5 ppm Au in raffinate) followed by direct recovery of Au from the organic phase by hydrolytic stripping. The latter is the only batch operation in an otherwise continuous circuit. Presently mechanistic and reactor design studies are in progress to improve the efficiency of this recovery stage. This stripped organic is then contacted with the Au free raffinate to co-extract Pt and Pd. Selective stripping of Pt under controlled pH and free Cl⁻ concentration conditions follows and finally Pd stripping with strong (6 to 8N) HCl solutions completes this process. Eventual metal recovery from the two purified strip liquors can be effected by either conventional ammoniacal salt precipitation followed by calcination or alternatively by hydrogen reduction.

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1. Introduction

The use of solvent extraction combined with electrowinning as a means to recover specific metals from aqueous streams, such as low tenor leach liquors, has found application at large scale in a number of installations; the greatest tonnage of material so won being for copper. An increasing number of highly selective extractants is available for such purposes. In a typical installation, Figure 1a), an aqueous feed of complex and perhaps variable composition is contacted with a solvent (usually an extractant plus a hydrocarbon diluent) in two or three counter-current stages of mixer-settlers and the desired metal preferentially extracted. The loaded solvent passes to further mixer-settlers where the metal is stripped into a second aqueous phase, from which it is recovered electrolytically. The conventional electrowinning tankhouse, in which metal is deposited in massive form onto starter sheets, has the disadvantage of batch-wise operation, and the metal concentration fed from the stripping section to the tankhouse must be relatively high, e.g. 30-40 g l^{-1} for copper.

The cathode contactor developed and demonstrated at laboratory scale at Harwell Laboratory replaces by a single unit both the strip mixer-settler(s) and tankhouse, (Figure 1b)) and produces a powder product. The cell itself consists of a vessel, rectangular in the laboratory rig but cylindrical at larger scales, in which a cylindrical cathode rotates at such a speed as to induce intense turbulence and phase dispersion in two immiscible liquids, a solvent and a strip/electrodeposition liquor. Anodes are arranged around the vessel walls and are separated from contact with the organic phase by a cation exchange membrane. In a circuit such as that of Figure 1, loaded organic phase is fed to the contactor cell, where the metal is stripped under intense agitation and deposited as a fine dendritic powder on the cathode. The powder may be scraped from the cathode continuously and collected in the most appropriate manner. In the laboratory rig powder was carried away in a mixed aqueous/organic stream and filtered, but in an industrial process it could be removed in a concentrated slurry. Under laboratory conditions of mixing and deposition, the metal powder carries with it some of the solvent phase which preferentially wets it; an industrial installation would be engineered in such a way that no solvent became associated with the metal, or that the solvent was subsequently recovered.

The advantages of a cathode contactor process over conventional hydrometallurgy/electrowinning are:

- i) The ability selectively to extract a minor component from, e.g., a waste stream.
- ii) The capacity of the 'Eco-cell' from which the cathode contactor design is derived, to electrodeposit from very low concentration (a few ppm) feeds.
- iii) The resulting capacity, when a loaded solvent is also present in the same vessel, for very efficient stripping, due to the high concentration driving force so obtained.
- iv) Because the cathode does not have to be periodically replaced, as in a tankhouse, the contactor cells can be enclosed and hence more concentrated stripping acid used. This in turn enables the use of stronger extractants (e.g. Acorga P50 instead of P5100) which can treat more concentrated feeds. A case in point is the bleed stream from copper electrowinning.
- v) The product is removed continuously, rather than batchwise.
- vi) The product is of similar purity to bulk cathode material, and, for copper at least, of appropriate structure for pressing to 'green' powder metallurgical components.

This paper describes first the essential features of the experimental process development to date, and this is followed by consideration of the prospects for a practical industrial installation, including conceptual flowsheets for copper recovery.

2. Laboratory Development

The concept of the cathode contactor was first defined from laboratory bench experiments in which copper was deposited onto a stationary cathode in a stirred beaker. To an agitated aqueous phase was added a loaded organic solvent; copper transferred from this solvent to the aqueous phase and a solid product formed electrolytically on the cathode. The logical development of this was to employ a moving cathode, which would not only agitate the two-phase mixture, but facilitate automatic removal of the solid product, by, e.g., a fixed blade skimming the moving electrode surface.

Cells featuring rotating electrodes have been in existence for many years⁽¹⁾ and their ability to aid by turbulence the removal of metal from low concentrations long known. The present device is based on the cylindrical geometry of the Eco-cell (marketed by Ecological Engineering, now owned by Steetley Engineering).

A continuous flow laboratory trial was set up based on a 30A Eco-cell modified to function as a cathode contactor. A simulated electrowinning bleed stream of $25 \text{ g l}^{-1} \text{ Cu}^{2+}$ in $150 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$ was extracted in a single stage mixer-settler to give a $5 \text{ g l}^{-1} \text{ Cu}^{2+}$ loading of the 15 vol% ACORGA P50/Escaid extractant. In the Eco-cell the copper was stripped by $340 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$, and deposited on the cathode at a rate of 30 g h^{-1} . The friable deposit broke away intermittently from the cathode and was carried out of the process vessel with a solvent/acid dispersion; the powder was collected on a laboratory filter while the liquids were separated and recycled. Examination of the product showed highly dendritic particles of $1\text{--}5 \mu\text{m}$ diameter; the material could be die-pressed into complex shapes of adequate mechanical integrity ready for sintering.

3. Theoretical and Practical Considerations for Chemical Engineering Development

If the cathode contactor concept is to be used industrially a more sophisticated contactor cell than that used in the laboratory must be developed. In developing such a unit the aim must be to achieve better segregation of the three phases, with continuous product recovery, and to be aware of the principles of scale-up.

3.1 Phase segregation and product recovery

In the experimental contactor, the process vessel contained a fairly uniform dispersion of solvent and aqueous phases (solvent dispersed), and circulation patterns were ill-defined. In a larger-scale device, however, this could not be tolerated. In particular, there is a need for the inter-electrode annulus to operate free of solvent to prevent;

- a) 'burning' (carbon deposition) of organic phase onto the anodes (a phenomenon prevented in the laboratory by use of a proprietary cation-exchange membrane to shield the anodes)
- b) an unacceptable increase in the inter-electrode resistance due to the presence of the non-conducting organic droplets
- c) solvent wetting of the solid product, necessitating complex and expensive recovery steps.

This can be achieved by a refinement of the principle illustrated in Figure 2, and already demonstrated in the laboratory, in which the contactor vessel is segregated by calming baffles into two zones - an upper mixing zone and a lower essentially solvent-free electrodeposition zone. The product is recovered as an aqueous slurry from the conical base of the vessel and can then be filtered and washed.

3.2 Scale-up

In the cathode contactor two functions are combined: the stripping function is scaled up on the basis of constant residence time, i.e. volume proportional to volumetric throughput, while the electrodeposition function requires cathode area proportional to metal mass throughput. Consequently, as a segregated unit of the type shown in Figure 2 is scaled up the linear dimensions of the electrodeposition zone increase relative to those of the mixing zone.

On scaling up, the cathode peripheral velocity is kept constant, to maintain the same bulk-cathode mass transfer coefficient; it is on this coefficient that the current density (expressed in units of $A\ cm^{-2}$) at the cathode surface depends. If peripheral velocity is kept constant, the rotational power requirement increases linearly with cathode area.

4. Example: Flowsheet for Copper Recovery at 1030 te a⁻¹

In Figure 4 are shown two flowsheets for copper recovery at 1030 te a⁻¹. Two typical feed liquors have been selected, viz. a mine water at 0.5 g Cu²⁺ l⁻¹ and an electrowin bleed stream at 25 g Cu²⁺ l⁻¹; the latter flowsheet corresponds to the laboratory continuous flow experiment (cf. 2 above). The extractant for the mine water flowsheet is 5 vol% ACORGA P5100 (isotherms used are those of Tumilty et al.⁽³⁾) and for the electrowin bleed stream 10 vol% ACORGA P50 (isotherms measured in the laboratory).

The flowschemes are identical, except that three stages of extraction are used for the more concentrated feedstock but only one for the more dilute. The loaded organic phase is fed to a bank of seven cathode contactors in parallel; depending on the current density achievable, the cathode diameter would lie between 1 and 1.8 m. McCabe-Thiele constructions, Figure 3, compare the operation of a cathode contactor flowsheet with a conventional flowsheet incorporating two conventional strip stages.

The powder/aqueous slurry product removed from the contactor is first filtered, then washed and leached to remove residual acid, before being filtered again and dried.

An approximate comparison of unit product cost showed that the cathode contactor gave a significant advantage over a conventional scheme provided the premium grade powder product could be sold as such, i.e. for powder metallurgy, though not otherwise.

5. Conclusion

The cathode contactor has been demonstrated for the recovery from mixed

wastewaters of specific metal products in a potentially valuable form; moreover, the method can handle high-tenor liquors which are not readily treatable by conventional means. Though the cost comparison of cathode contactor and conventional products showed that for copper economies depended on the state of the market for powder, there could be more significant advantages for other materials - and the cathode contactor is in any case an attractive technique where effluent clean-up is mandatory. Some applications suggested have been the separation of Co/Ni/Cd, separation of Cu/Ni after co-extraction, iron removal in zinc processing and recovery of Ni from chloride processes. For a compact modular plant there is an optimum size based on a single 20,000 A contactor of ca. 150 te a⁻¹, and it is possible to envisage a skid-mounted transportable unit.

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FIG. 1a . Conventional

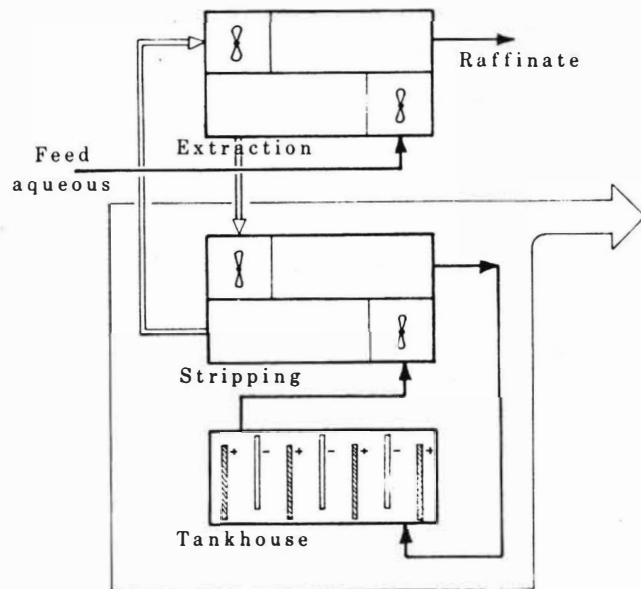


FIG. 1b . Cathode contactor

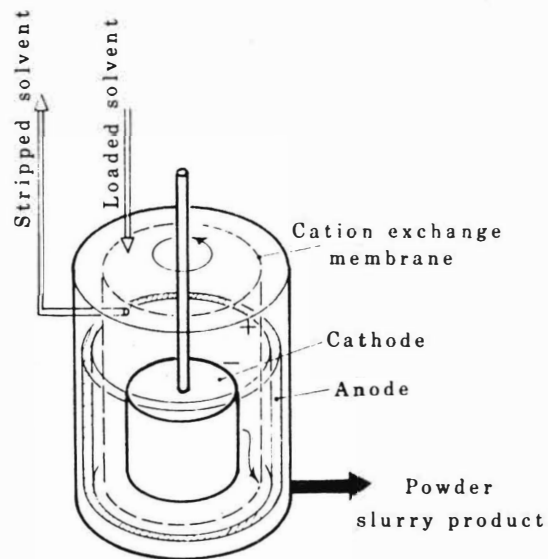


FIGURE 1. SOLVENT EXTRACTION/ELECTROWINNING USING CONVENTIONAL TANKHOUSE
AND CATHODE CONTACTOR

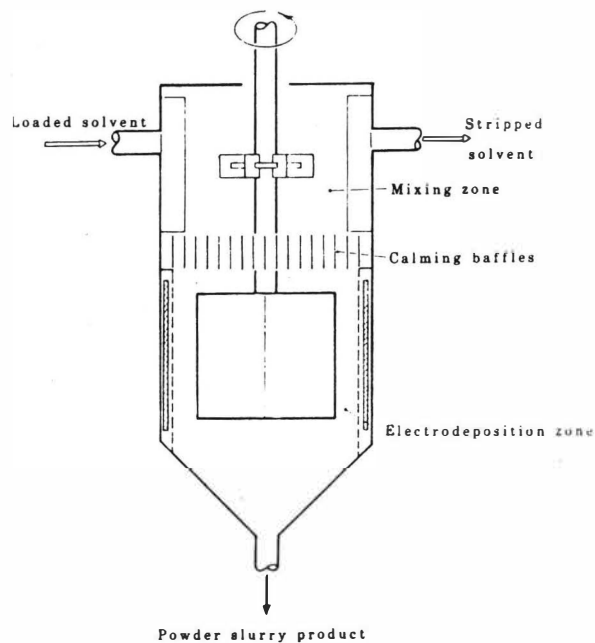


FIGURE 2. BAFFLED 2-ZONE CATHODE CONTACTOR

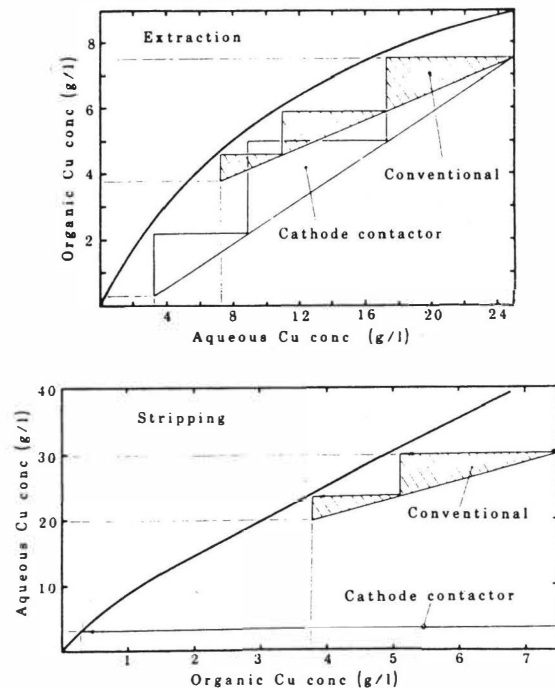


FIGURE 3. MCCABE-THIELE CONSTRUCTIONS FOR CATHODE CONTACTOR AND CONVENTIONAL FLOWSHEETS: ELECTROWIN BLEED STREAM

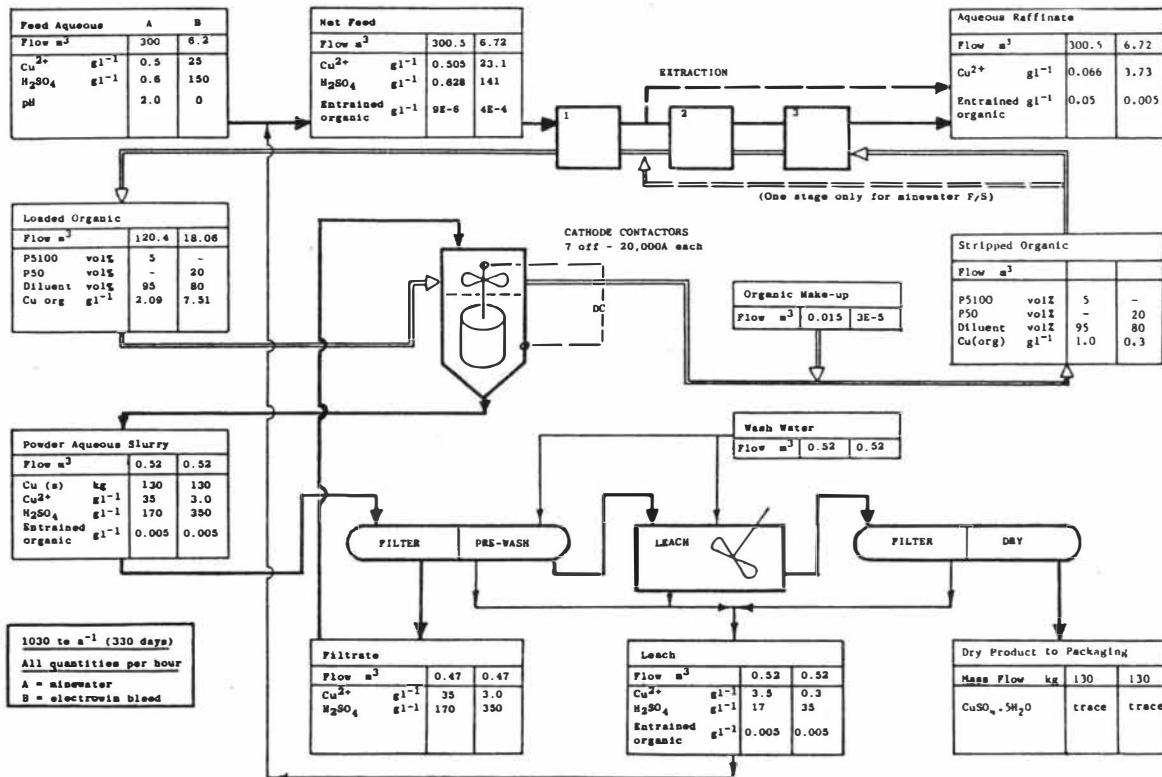


FIGURE 4. FLOWSHEETS FOR COPPER RECOVERY FROM MINEWATER AND ELECTROWIN BLEED STREAM

Recovery of Cobalt and Nickel from Electronic Alloy by Using Solvent Extraction

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Some electronic alloys such as Kovar contain high content of cobalt, nickel and other metals. It is considerably important to recover valuable metals from the waste electronic alloys by hydrometallurgical processes and there are some processes reported in the literatures. [1,2]

A new process has been developed and operated in a pilot plant to recover cobalt and nickel from alloy scraps by using solvent extraction, first with di-2-ethylhexyl phosphoric acid (DEHPA) to remove impurities and then with quaternary ammonium chloride (QAC) to separate cobalt from nickel.

Leaching and Iron Removal

Scraps were leached in a chloric-sulphuric mixed acid solution and with some nitric acid as oxidant. Iron in solution was removed by forming precipitation of jerosite, then the solution contained about 15 g dm^{-3} of Co, 27 g dm^{-3} of Ni and some other impurities. The compositions of the solution is shown in Table 1.

Removal of Impurities with DEHPA Cobalt Salt

Impurities in the feed solution such as Cu^{2+} , Fe^{3+} and so on can be extracted with quaternary ammonium chloride, but it is usually difficult to reduce their concentration to lower than, say, 0.005 g dm^{-3} [3].

DEHPA had been chosen to separate impurities from the leaching solution. The flow diagram is shown in Figure 1. Instead of sodium salt of DEHPA cobalt salt of DEHPA was used. DEHPA solution in concentration of 10% (V/V) in kerosene first contacted with sodium hydroxide solution to make sodium salt of DEHPA, then the sodium salt exchanged with cobalt chloride solution from scrubbing stage to make cobalt salt solution. If sodium salt of DEHPA had been used, part of cobalt in feed solution would have been coextracted with impurities into the organic phase.

Extraction by using the cobalt salt of DEHPA caused no loss of cobalt in the aqueous phase. The cobalt in the organic phase was scrubbed with a HCl solution of 0.4 Mol. The flow ratio of loaded organic phase and HCl solution was controlled to ensure that only minute amount of

impurities such as Cu, Mn was scrubbed to the aqueous solution. In this case about 10% of cobalt still remained in the organic phase, which would be stripped together with impurities and recovered later. The scrubbed solution, mainly cobalt chloride containing most of magnesium extracted was exchanged with sodium salt of DEHPA to produce cobalt salt. Magnesium in cobalt chloride solution would remain in aqueous, which drained to the treating center of waste water. No accumulation of impurities in the system was observed by using the recycling cobalt salt procedure as shown in Table 2. And it has following advantages;

- The cobalt in the scrubbed liquer can be directly recycled to the process stream.
- The concentration of cobalt in raffinate almost the same as that in the feed solution
- Of cause, it reduced the sodium content in the final nickel chloride solution.

The stripping of divalent metal ions were relatively easy but the trivalent ferric ion had to be stripped with 5 to 6 moles of hydrochloric acid and which deteriorated the working condition. Ferric ion trended to hydrolysis when the pH value of the feed solution suddenly rose in the entrance stage of solvent extraction because of the slow kinetics of ferric ion extraction. It is reasonable to reduce the iron content in feed solution as low as possible during the precipitation of jarosite.

Separation of Co from Ni with QAC

Alkylbenzyl QAC was adopted by Ivanov^[4] to purify nickel electrolyte and the process was carried out in a pilot plant. In this work a methyltrioctyl QAC (Trade Mark 7401 of Daling Fat Chemicals Manufactory) was used, and the concentration of QAC solution was 0.7 mole in kerosene. Figure 2. is the diagram of the process.

As other anion exchangers used in chloride solution the distribution coefficient of cobalt extracted by QAC increases with the concentration of chloride ion and the concentration of QAC. The distribution coefficient of cobalt extracted with alkyl QAC is greater than that with trialkyl tertiary amine at the same molar concentration. Extraction isothermal of cobalt and McCabe-Thiele construction is shown in Figure 3.

Small amount of nickel was entrained in the loaded organic phase and it could be scrubbed with a concentrated sodium chloride solution.

Cobalt was stripped with water and the isothermal and the McCabe-Thiele construction of stripping is shown in Figure 4. No harmful effects of DEHPA on the extraction and stripping of QAC have been observed both in bench and pilot experiments.

Pilot Plant Performance

Mixer-settlers with the mixer chamber of $17 \times 17 \times 22 \text{ cm}^3$ and the settler of $17 \times 68 \times 28 \text{ cm}^3$ were assembled in the pilot plant.

The DEHPA extraction of impurities worked very well. One problem was the precipitation of ferric hydroxide in the first two stages of extraction; because probably hydrolysis of ferric ion and the agglomeration happened there.

Although the viscosity of 0.7 mole of QAC solution was high it was no any problem in flowing through pipe line. And the phase separation was quick enough because of the big density difference between the two phases. High aqueous solution entrainment in the organic phase was observed when operated in organic as the continuous phase, particularly in the stripping stage, there high phase ratio of organic to aqueous was used. The cobalt chloride solution as concentrated as 70 to 80 g Co dm^{-3} and also a pure nickel chloride solution as listed in Table 4 were obtained. Both of the solutions were suitable to produce technical grade cobalt chloride and nickel chloride or other products. In the experiments the feed solution contained only about 160 g dm^{-3} of chloride ion, resulting in 350 to 1 of the ratio of Co to Ni in the nickel chloride solution. If higher concentration chloride ion was adopted, higher ratio of Co to Ni would be obtained.

Temperature was an important factor in operation since the solution became more viscous at lower temperature, usually the ambient temperature was kept not lower than 293 K. But even the ambient temperature dropped to 283 K it could still operate properly.

As anion exchange extractants for separation of cobalt from nickel, QAC are found to be a kind of good reagent, in some cases, even better than tertiary amines. QAC have high selectivity for cobalt, good stability. It can tolerate a wide range of variation of impurities and cobalt concentration in the feed solution and render the process flexible and low operation cost. But the low loading capacity of QAC makes them not suitable for the feed solution containing very high concentration cobalt.

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Table 1. Leaching Solution

No	Composition g dm ⁻³								Cl ⁻
	Ni	Co	Cu	Fe	Mn	Zn	Ca	Mg	
3	14.35	6.90	0.048	0.025	0.141	0.0089	0.065	0.106	165
5	18.20	7.99	0.052	0.059	0.184	0.013	0.045	0.123	169

Table 2. Composition Change of Organic Phase in Scrubbing Stag

Run	Composition of Organic Phase g dm ⁻³							
	Co	Cu	Fe	Mn	Zn	Ca	Mg	
3	entrance.	4.63	0.105	0.216	0.378	0.034	0.100	0.028
	exit	0.414	0.123	0.214	0.378	0.032	0.089	0.0046
	scrub eff.%	91.1	0	0.92	0	5.88	11	83.6
5	entrance	3.55	0.085		0.89	0.024	0.077	0.027
	exit	0.509	0.087		1.02	0.034		
	scrub eff%	86	0		0	0		

Table 3. Solution after Impurities Removal

No	Composition g dm ⁻³										pH
	Ni	Co	Cu	Fe	Mn	Zn	Ca	Mg	Cl ⁻		
A-1-5	18.20	8.84	0.0016	0.00078	0.0055	0.0036	0.005	0.144	164		4.20
A-1-10	18.74	9.66	0.0040	0.0005	0.0060	0.003	0.013	0.50	162		

Table 4. Compositions of Cobalt chloride and Nickel Chloride Solution

	Composition g dm ⁻³								Na
	Ni	Co	Cu	Fe	Mn	Zn	Ca	Mg	
NiCl ₂	16.88	0.041	0.002	0.0005	0.004	0.003	0.004	0.110	
	16.64	0.012	0.001	0.0005	0.004	0.003			
CoCl ₂	0.13	74.57	0.004	0.0008	0.004	0.004	0.001	0.003	4.51
	0.021	70.62	0.004	0.0008	0.006	0.003			1.05

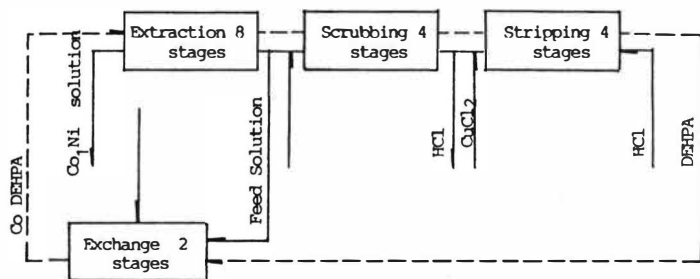


Fig. 1. Flow Diagram of Impurities Extraction with DEHPA

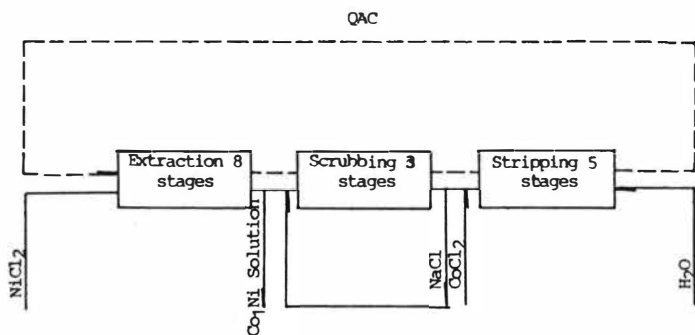


Fig. 2. Flow Diagram of Cobalt and Nickel Separation with QAC

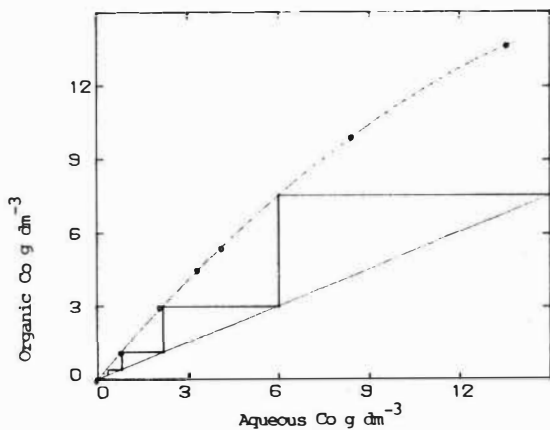


Fig. 3 Isotekernal of Cobalt Extraction with QAC and McCabe-Thiele Construction

Feed Solution Co 18.1, Ni 29.86, Cl^- 159 g dm^{-3} QAC 0.7 mole

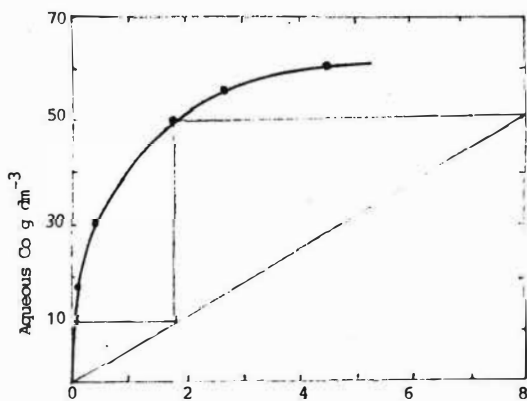


Fig. 4 Isothermal of Stripping of Cobalt and McCabe-Thiele Construction

Loaded Organic Phase Co 9.94, Ni 0.34 g dm^{-3}

The Refining of Silver by Solvent Extraction

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As known, silver is one of the most important metals in national economy and industry. Only a small portion of its production is from pure silver mineral, most pure silver is obtained as a byproduct of refining copper, lead and gold, and some silver is recovered from various industry wastage, such as photowastage, used catalysts and others. The traditional method of refining silver is considered to be a pyrometallurgical-smelting-electrolytical method which is inherent in complexity of technology, relatively high cost and long production period. Although this method has been proved to be suitable for large-scale production, its rather low recovery of silver and poor operation condition made it less meaningful.

In order to overcome a series of shortcomings mentioned above it is naturally to think of the solvent extraction. Recently, it has been widely used in refining and purification of rare elements as well as in the hydrometallurgy process of nickel, cobalt, copper and other coloured metals and proved to be an efficient new technology. There are a lot of reports on the solvent extraction, but none of them concerned its application in refining of silver, the reason of that probably is related to the chemical properties of silver. In the chromic medium silver exists mainly in the form of precipitate, which solubility in sulfuric acid is rather poor but is quite good in nitric acid medium. But nitric acid solution is possessed of rather strong oxidation characteristic, so from it the silver could be bled off in the form of black precipitate in sunlight. Consequently, the organic solvent contacted with nitric silver solution should be chemically stable, besides strong extraction ability and selectivity. These requirements could hardly be met by using oxygen extractant, phosphorus extractant and amine extractant which are usually used in practice.

Silver possesses an affinity to sulfur, so the sulfur solvent is suitable for refining silver. In fact, 20 years ago the soviet scholar (1,2) already discovered that thioether possesses a good extraction ability to silver. Later they discovered that extraction and complex may occur when dialkyl thioether is contacted with silver in nitric acid solution (3,4). Unfortunately, this thioether is a rather strong oxidant, so its use is limited only in the area of analytical and radioactive chemistry.

In order to develop a new extractant for refining of silver a series of research works have been carried out. We made up S304 which is a thioether with side chain. It seems that the side chain has some protection effect on sulfur atoms and may enhance the resistance of the solvent to oxidation.

On the basis of the selected extractant we formulated a small-scale technological scheme, studied apparatus, accomplished the expanded test and finally proposed a new technological scheme. This scheme has been put into practical test for more 2 years. It is shown that the proposed technology, equipment, operation conditions and the reused properties of the organic solvent are very satisfactory. Up to now the total amount of produced silver is about 1 ton. The purity of this metal is higher than 99.95%. The direct recovery is near to 99%.

Solvent Characteristic

The extractant S304 is made up in the factory by using industry feed-stock. Here the solvent kerosene is used as a diluent. S304 is light-

yellow oiled liquid with small viscosity. Its boiling point at atmosphere is about 300 c, and its mixture with kerosene smells just like kerosene. The animal test identifies that the extractant is not poison

During the technological research a purification of the extractant is carried out by using low pressure distillation. The purified extractant is colourless and without any special smell. It should be mentioned that there is not any purification of the extractant when the expanded test and practical test proceed.

Figure.1 illustrates the equilibrium curve of a 40% S304-kerosene mixture with nitrate silver at 30 c in a nitrate acid medium.

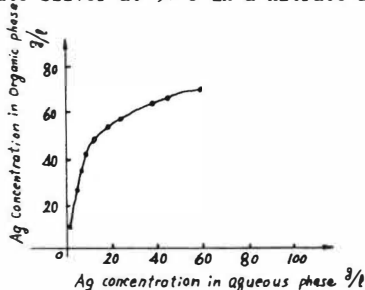


Figure 1 Isotherm for extraction of Ag

From figure 1 it can be seen that the operation capacity of the organic phase reaches 70g/l which fully satisfies the technological requirement. Such high Ag content in organic phase is rarely obtained when thioether is used in analytical chemistry.

The influence of the extractant concentration upon the extraction rate is illustrated in figure 2. It is shown that if the extractant concentration is higher than 30% the extraction rate will keep high. Consequently, it is not necessary to control extractant concentration rigorously in technology. According to the apparatus operation characteristics we increased the extractant concentration from original 40% to 60% in the expanded test, meanwhile increased the operation capacity from 70g/l to 90g/l.

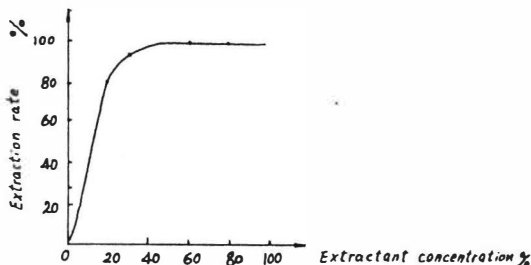


Figure 2 Influence of the extractant concentration on the extraction rate

It should be noticed that if extraction is not carried out in time after the organic phase extracts silver, a reduction of silver may occur. As a

result, the organic phase is getting dark brown due to appearance of black precipitates, meanwhile its viscosity is greatly increased. In the normal performance the colour of organic phase sometimes also could be changed from light yellow to brown because of the reduction of some residual silver. Experiments indicate that the residual Ag in organic phase should be controlled to below 1g/l so that its effect on the physical properties of organic phase will be insignificant and the extractant could be reused. Up to now the organic phase has been put into the practical test in the factory for more 2 years, the reuse number exceeds 150 and the loss solvent is less than 30g per 1 Kg pure silver.

Technological Scheme

Silver feedstock is solved by using nitric acid, which is an exothermal reaction. When the reaction occurs violently, system boils automatically. The filtrated solution is blended according to the silver concentration. The effect of the solution acidity on the extraction is insignificant, but too high acidity is not considered to be beneficial on extractant.

The extraction speed is very high. It is easy to separate phases and there is no interfacial substance produced. After extracting silver, the organic phase becomes light brown, whereas its volume and viscosity increase a little. The silver content usually is adjusted at about 15 mg/l, so that the extraction rate could be near to 99.99%.

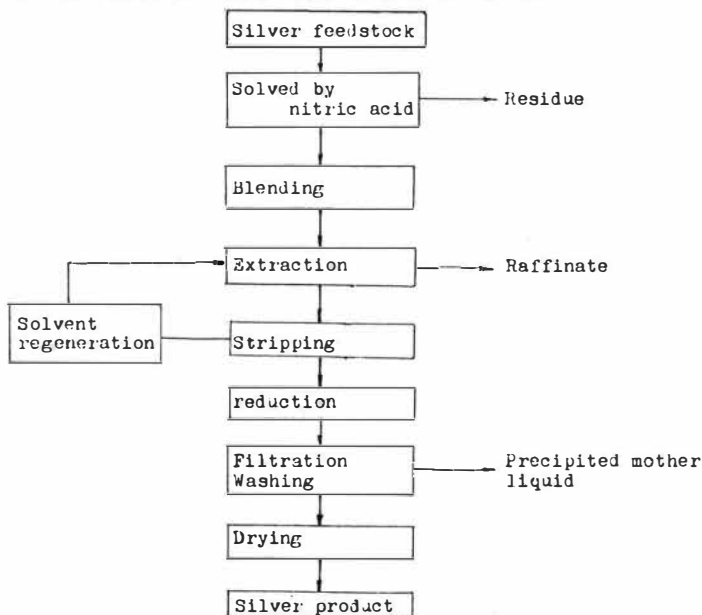


Figure 3 The technological scheme diagram of the refining of silver by using solvent extraction

The organic phase at first is washed by using dilute nitric acid with the aim to remove the entrained hydrous phase, and then is stripped with

aqueous ammonia. In stripping there are some brown membrane interfacial substances formulated and the phase separation is related to the silver content in the organic phase as well as the concentration of the aqueous ammonia. If these two factors matches properly, the phase separation take places quickly, otherwise, a emulsification occurs easily.

Silver strip solution is reduced by using hydrosulfide. The colour and particle size of silver product is related to the settling extent of the solution, silver concentration, aqueous ammonia concentration, hydrosulfide concentration, temperature, agitation intensity and other factors, but all these factors have not significant effect on the reduction reaction, so it is quite easy to control the reduction. The precipitated silver then undergoes filtration, washing, drying and finally becomes pure silver product. The silver content of the mother liquid is less than 0.1mg/l, so the liquid could be bled off or used to recover ammonia from it.

The purity of silver product is identified by using spectrographic method (table 1). It can be seen that the purity of silver obtained here is as high as that of silver made up by using electrolytic method.

Table 1 Spectrographic identification data

Impurity elements	Sb	Pt	Au	Mg	Pb	Sn	Cu
Impurity content	<10	<5	3.2	4	<5	<5	83
ppm	Fe	Ni	Bi	Al	Ir	Pd	Rh
	3.5	<5	<2	5	<10	<2	<5

Main equipment

Extraction of Ag by using S304, similar to the extraction of UO_2^{+} by using tributylphosphate, is a neutral coordination. This process is characterized by relatively high speed, so it is possible to select a centrifugal extractor as a main equipment. Centrifugal extractor has a series of advantages: high extraction efficiency, complete phase separation, small holdup, high operation adaptability and short time phase contact. Definitely, such extractor is more suitable for valuable metals having small throughput.

Centrifugal extractor is consisted of a stainless steel concentric cylinder and an organic glasses shell. There are some single stages which are connected each other by using polychloroethene. The whole equipment is moved by an adjusted electric motor with rotating speed about 300 rotation per minute.

In the experimental test with 5 Kg pure silver dairy throughput a cascade of centrifugal extractors equipped with 20mm diameter rotating cylinder is used. Such a cascade permits of a rather large change in rotation speed as well as in flowrates of two phases. The single stage extraction efficiency has been determined to be 96% and the separation between two phases is very satisfied without any entrainment, whereas the outlet aqueous phase is clean and transparent. In the production test with 15Kg pure silver dairy throughput a cascade of centrifugal extractors with a 34mm diameter rotating cylinder is applied. This equipment requires rather low rotating speed and permits of relatively large throughput. Its maximum total throughput may reach 50-60 liters per hour.

It should be mentioned that in the case of using centrifugal extractor it is necessary to filtrate two phase solution carefully as well as to bleed off suspended solid particles completely, otherwise, it will easily accumulated on the internal wall and leads to a plugging of equipment. In

fact, the key problem is how to ensure the reused organic phase be completely desilvered and well settled before stripping.

Stripping occurs in sodium medium that easily leads to a formulation of interfacial membranes. Therefore, centrifugal extractors are not suitable in this case. Here mixer-settlers combined with pumps are applied. From experiments it can be seen that mixing of two phases occurs sufficiently, backmixing among stages is small and stage efficiency is high. Meanwhile, the flow is more stable that is very useful for operations. In stripping it is more important to properly arrange aqueous ammonia concentration and silver concentration for each stage so that the phase separation occurs rapidly and emulsion could be avoided. Figure 4 illustrates a diagram for refining of silver by solvent extraction.

Table 2 illustrates the distribution of silver among stages in the case of using a cascade of 5 centrifugal extractors.

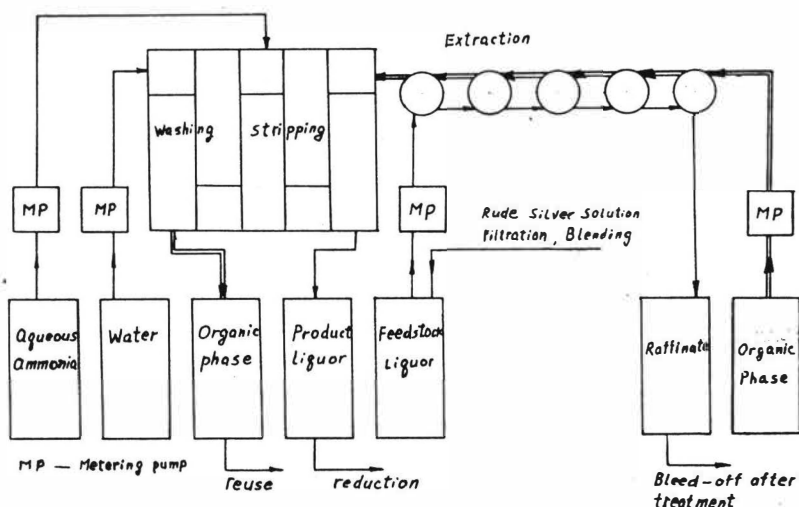


Figure 4 Diagram for refining of Ag by solvent extraction

Table 2 Distribution of silver between two phases in extraction section

F 132.12g/l
X 60% S304
F:X 1:1.56

extraction stage	Ag_a g/l	Ag_o g/l
E1	25.54	79.30
E2	7.08	33.54
E3	0.32	8.20
E4	0.065	3.00
E5	0.035	1.55

Under normal operation conditions at interfaces in the settler stages sometimes appears dark color membrane, which formulation is more obvious while using fresh organic phase. The speed of producing membrane is getting slow when the reuse number of organic phase increases. These membranes are gradually accumulated but hav'nt any significant effect on the normal operation during a long period, meanwhile, it is easily removed if necessary.

conclusions

The proposed scheme of the refining of silver by solvent extraction has been put into practical test for more 2 years. Results are very satisfied. As shown, silver recovery is 99.9%, direct recovery is near to 99% and purity of obtained silver is higher than 99.95% which is equivalent to the purity of silver made up by using electrolytic method. The proposed scheme is not only simple in technology, but also characterized by high efficiency and high purity. Based on the determined data consumption for making up 1 Kg pure silver at the chinese price system costs 2.2% output value.

It should be noticed that solvent extraction also could be used in the refining of silver from copper and lead anode slime as well as from silver catalysts.

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Zinc recovery from geothermal brine

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The Imperial Valley of California is rich in geothermal resources. A highly saline (hypersaline) brine containing 20-25 wt.% dissolved solids lies under the area near the Salton Sea. This brine can be exploited for both electric power production and for metal recovery. A 50 MWe flash-steam power plant can generate about 27000 cubic meters per day of waste brine. And the zinc contained in the brine has a yearly market value of about 10 million dollars. This paper reports the development of a solvent extraction formulation capable of selective recovery of zinc from the Imperial Valley hypersaline brine resource. The extraction, stripping, and scrubbing behavior of this formulation are described for both real and synthetic Imperial Valley brine. The equilibrium isotherms and selectivity data are discussed along with the implications on process flowsheet selection.

The use of our reagent formulation in a practical process for recovery of a marketable zinc product is also described. Several alternate process flowsheets are considered along with the relevant economic factors. We present data from operation of a lab-scale solvent extraction pilot plant. A mathematical model has been developed to predict the behavior of the solvent extraction plant. Another model has been developed to calculate the capital and operating costs for alternate process flowsheets. The process simulator and economic models have been tied together so that optimization of the zinc recovery process was possible. We show that solvent extraction is a viable technology for this application from both technical and economic viewpoints.

Zinc Recovery from Hydrometallurgical Zinc Processing Residues by Solvent Extraction.

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Abstract

Conventional hydrometallurgical zinc processing results in the production of iron residues during solution purification. These residue have been considered uneconomic to further processing for iron making as they contain remarkable quantities of zinc. Usually this zinc is regarded to be lost.

Espanola del Zinc S.A. have developed a process to recover the zinc from the iron residues obtained in their Cartagena facilities. The process consists of the main steps

- weak acid leaching
- solvent extraction
- electrolysis.

The present paper refers to the results of a six months lasting pilot-plant test campaign of the solvent extraction system. A mixture of di-(2-ethylhexyl)phosphoric acid (D2EHPA) and kerosene has been applied as extractant, resulting in an overall extraction efficiency greater than 98 % under carefully controlled pH-conditions.

Electrolyte grade purity of the strip solutions is achieved by intermediate wash and scrub stages of the zinc loaden solvent phase. In a second solvent extraction circuit the iron is removed from the organic phase and concentrated in order to minimize aqueous plant effluents.

Process alternatives and modifications will be discussed in detail, block diagrams and design parameters determined in the Lurgi Research and Development Centre, will be given.

Introduction

In early summer 1987 a new solvent extraction plant will come on stream in cartagena, Spain for the recovery of zinc from dilute aqueous leach liquors. It will be the first commercial plant in the world using the Di-(2-ethylhexyl)phosphoric acid (D2EHPA) extractant for zinc extraction in a single step from a sulphate system.

Although known in principle for some twenty years (1,2) said extractant so far has been applied in large scale production units for zinc only once, at Metalquímica, Spain. However, this process known as the Espindesa Zinc Process (3,4) works in a chloride system and uses the D2EHPA extractant in a second circuit for electrolyte purification.

The process to be applied in the new plant (see figure 1) consists of the steps:

- residue leaching with dilute sulphuric acid,
- solvent extraction and
- zinc electrowinning,

and might be regarded as a complement to the well known combination of the hot-acid-leaching/jarosite-precipitation-route or the hot-acid-leaching/hematite-precipitation-route respectively.

The basic process parameters have been developed by Espanola del Zinc S.A., only spanish zinc cathode producer. The results of their work have already been reported in a previous paper (5).

Lurgi and Espanola del Zinc in a joint laboratory and pilot plant test programme have established the necessary data to allow the design and construction of an industrial scale plant.

Residue Leaching

Basic sulphate residues obtained from solution purification at Espanola del Zinc's zinc plant have a zinc sulphate content of 7.0 to 7.5 % and represent the major loss in their electrowinning zinc process.

Leaching tests with dilute sulphuric acid showed that > 96 % of the zinc can be removed from the residues. Contact times of only 10 minutes and, according to the McCabe-Thiele plot given in figure 2,

two leaching stages are sufficient to achieve the desired low zinc sulphate level of 0.5 % in the remaining residues. Countercurrent decantation will be applied for leaching and solids separation. This technique provides excellent settling properties of the solids, in particular when the leach liquors are foreseen for further treatment in a solvent extraction process.

Flocculants have to be added to the suspension in order to improve the settling characteristics. Although they can have detrimental effects on phase separation in the solvent extraction circuit, no influence on the system has been observed with a flocculant addition of 30 to 50 g per tonne of jarosite residue during a six months' continuous pilot plant operation.

The final leach liquor of pH 2.0 - 2.5 has

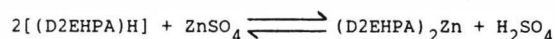
8.0 g/l zinc
0.09 g/l copper
0.06 g/l cadmium
0.08 g/l ferric iron

and a maximum suspended solids content of 10 mg/l.

Solvent Extraction

The extraction of zinc from sulphate solutions with D2EHPA is pH-dependent, ranging from 1.5 to 5.0. In the low range the solvent loading is relatively low compared to that at pH 5. Nevertheless the presence of iron and other extractable cations in the leach liquor does not allow to operate at the high pH level due to precipitation of hydroxides which would have detrimental effects on phase separation.

The most characteristic item of the extraction system is the changing of the pH with ongoing zinc extraction according to the simplified equation



In order to achieve maximum solvent loading it is mandatory to maintain the pH level at 2.5. Thus the sulphuric acid produced by the reaction has to be neutralized by means of sodium hydroxide or ammonia addition. Ammonia will be used in this plant. The use of the sodium or ammonia salt of D2EHPA instead of the free acid would serve

the same purposes, however has not been considered in this case due to process reasons.

Extraction of zinc from the leach liquor is achieved to greater than 98 % in two stages operated countercurrently with a solvent consisting of 12 vol.% of D2EHPA and 88 vol.% of kerosene. The McCabe-Thiele plot given in figure 3 shows that an overall organic to aqueous phase ratio of 1.5 will meet the requirements with an organic loading of approximately 6 g/l of zinc.

The raffinate is recycled to the leaching stage. A bleed-off has to be taken from the system in order to avoid ammonium sulphate built-up, meaning that the leaching process is operated at a nearly constant ammonium sulphate concentration.

As the solvent extraction process is associated with Espanola del Zinc's main electrowinning process, the strip liquors from solvent extraction have to meet the purity standards to be further processed in the electrowinning stage. Some impurities like copper, nickel, cobalt and cadmium can affect the electrolysis of zinc, in particular nickel can be quite detrimental. Consequently, a scrubbing stage using solutions from solution purification is introduced prior to stripping in order to remove impurities from the organic phase.

Stripping of the loaded solvent is carried out in two stages with spent electrolyte at an organic to aqueous phase ratio of 3.5. To prevent solvent from entering the electrolyte circuit, two adsorption columns will be operated. The adsorbants tested were activated carbon of different sizes and also inorganic material of large surface area. With this posttreatment of the electrolyte, no problems have been observed during the test runs, neither in electrolysis nor with the quality of the zinc cathodes produced.

Coextracted iron is not removed from the solvent with the stripping reagent. In order to avoid its built-up what finally would result in a reduced zinc extraction efficiency, a part of the barren solvent stream is taken out of the system for regeneration.

5 to 6 molar hydrochloric acid that removes the iron as a chlorocomplex is used for regeneration in a single stage. Washing of the regenerated solvent with water prior to recycle is mandatory in order to prevent chlorides from entering the sulphate circuit and the electrolyte.

The specific settling rates for all stages of the extraction process described have been determined in an continuously operated apparatus shown in figure 4. The separation area of the test equipment is 0.25 m^2 . The following operating parameters have been varied:

- agitator speed (mixing intensity)
- organic to aqueous phase ratio
- temperature.

For each operating condition, several throughputs have been adjusted and the corresponding heights of dispersion and the foreign phase content have been measured. The dependency of the height of dispersion layer on the separators load of total phase is plotted for different agitator speeds in figure 5. The temperature was kept at 25°C in all tests and the phase ratio was set to 1.5:1 organic to aqueous. The settling rate in the extraction stage thus was determined to be $4.3 \text{ m}^3/\text{m}^2\text{h}$ at a dispersion height of 50 mm.

The settling rates of the other extraction process stages are:

- $4.5 \text{ m}^3/\text{m}^2\text{h}$ for scrubbing
- $5.0 \text{ m}^3/\text{m}^2\text{h}$ for stripping
- $5.2 \text{ m}^3/\text{m}^2\text{h}$ for solvent regeneration and
- $5.0 \text{ m}^3/\text{m}^2\text{h}$ for solvent washing

all operated at an internal mixer phase ratio of 2:1 organic to aqueous.

The influence of the mixing intensity on phase separation is of minor importance. As expected, the separation is accelerated at reduced agitator speed, but variations in $\pm 100 \%$ would only result in changes of $\pm 10 \%$ in separation velocity. Accordingly it can be expected that no major changes of the separation behaviour will occur when applying the test results regarding mixing intensity observed in the test equipment to the unknown mixing intensity of the mixing pump in the industrial plant.

The aqueous FeCl_3 solution obtained from solvent regeneration represents a waste stream of the system. Further treatment of this process stream is required for two reasons:

1. its quantity, although only 7 % of the initial aqueous feed to solvent extraction at the very beginning, still is too high for discharge,
2. the still high concentration of free hydrochloric acid cannot be regarded as a loss due to cost reasons.

Therefore a second solvent extraction circuit is introduced into the overall process to recover the ferric chloride from the hydrochloric acid and to recover most of the hydrochloric acid at the same time that, after make-up, can be recycled to the regeneration stage. This second extraction circuit uses mixtures of a secondary, long-chain alkylamine, isodecanole and kerosene. The isodecanole, used in concentrations in the same order of magnitude than the extractant acts like a modifier in order to prevent formation of a third liquid phase. The system is well described in the literature (6) and is applied in a few industrial large scale operations.

Ferric chloride removal is achieved in a single stage extraction. Due to the slow extraction kinetics the average retention time in the mixer is kept at 10 to 15 minutes to achieve equilibrium.

The ferric chloride complex is stripped from the organic phase with water in a single stage. The resulting ferric chloride solution with 6 g/l iron and 1.5 g/l zinc could be a source for the production of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ used in water treatment, but has not been considered for this purpose.

Based on the results of the pilot plant test work referred to in this paper, a commercial scale plant is now under design. Start-up is scheduled for May 1987.

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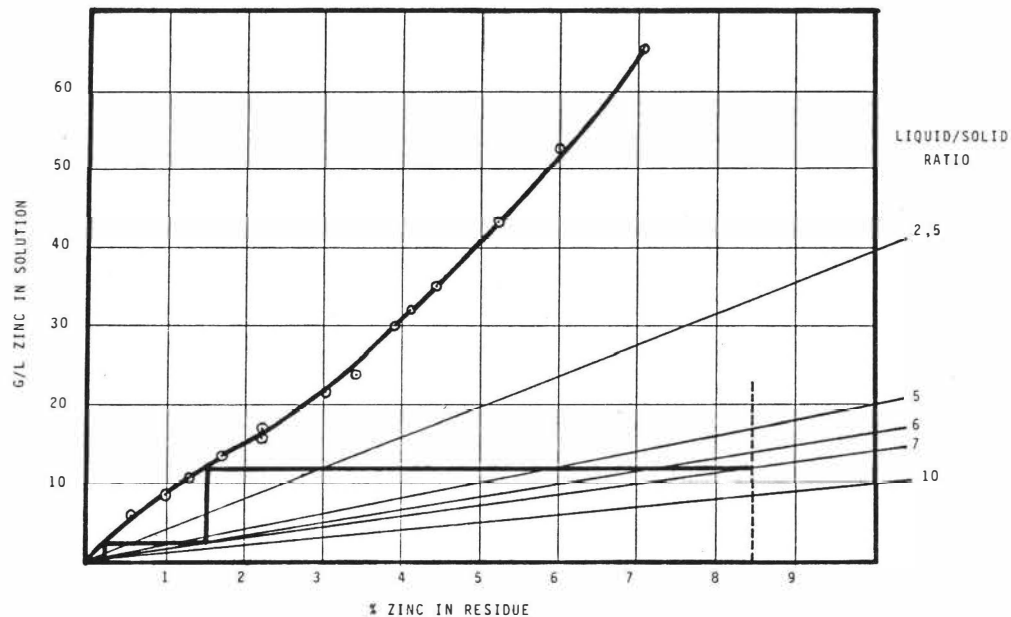


FIG. 2: MCCABE-THIELE PLOT FOR VARIOUS INITIAL ZnSO_4 CONCENTRATIONS IN THE RESIDUES AND DIFFERENT SOLID/LIQUID RATIOS.

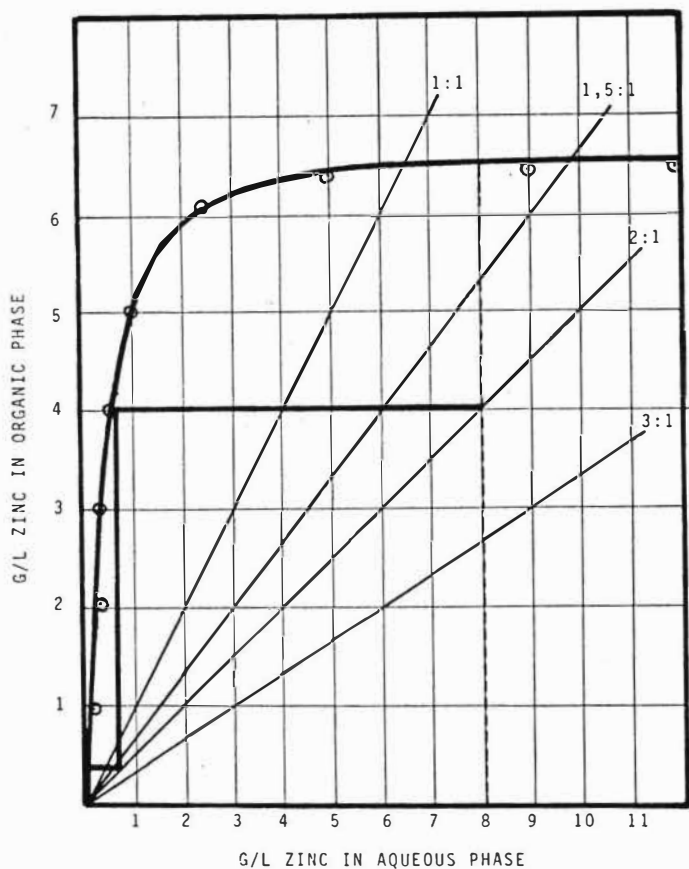


FIG. 3: MCCABE-THIELE PLOT AT PH 2,3 FOR THE
EXTRACTION OF ZINC.
SOLVENT: 12 VOL.% D2EHPA IN KEROSENE.

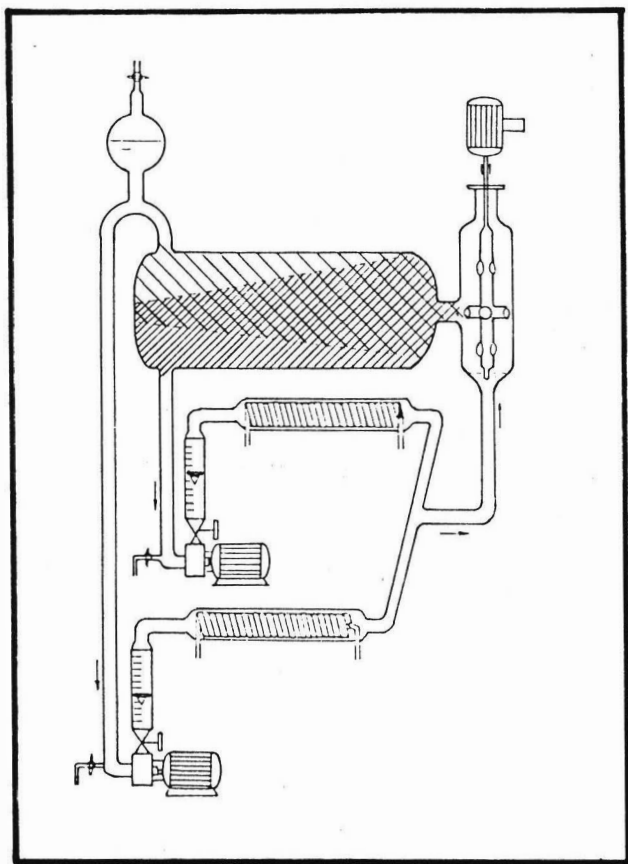


FIG. 4: SINGLE STAGE CONTINUOUS SETTLER
(PRINCIPAL LAYOUT)

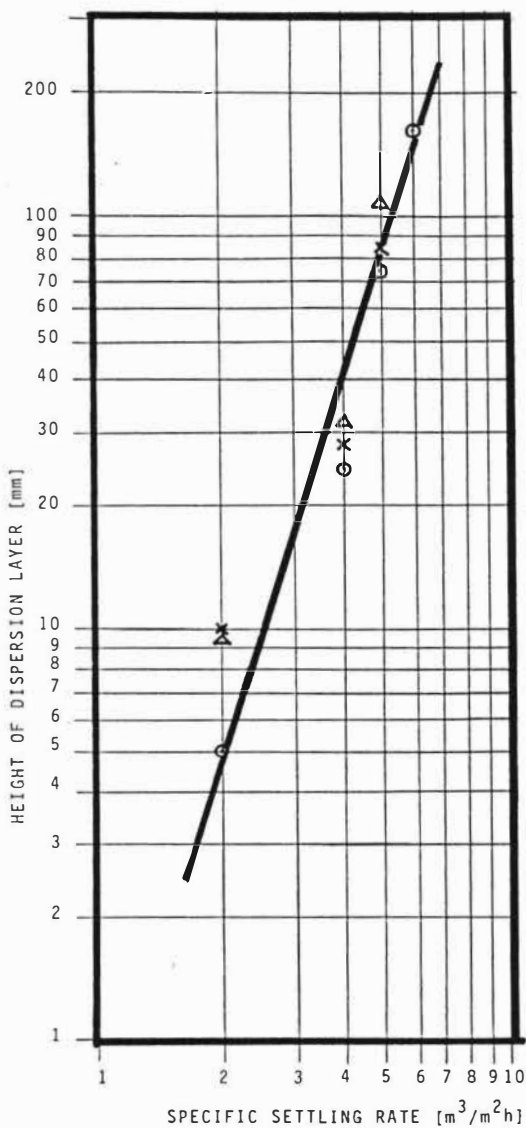


FIG. 5: DEPENDENCY OF THE SPECIFIC SETTLING RATES ON THE HEIGHT OF DISPERSION.

Extraction of zinc from ammoniacal-ammonium sulphate solutions using Di-2-ethyl hexyl phosphoric acid

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Introduction

Solvent extraction technique is not widely used in zinc metallurgy. In fact, there is only one plant based on a direct solvent extraction process for the production of zinc as the main product on a commercial scale. That is the Bilbao plant of Metal Quinica del Nervion in Spain, based on the Espindesa process^{1,2} developed by Technical Reunidas of Spain and came on stream in August 1976 with a design capacity of 8000 tons per annum of slab zinc. A second plant has been reported to be under construction in Portugal³. However, there is considerable interest and activity on the use of liquid-liquid extraction for separation and recovery of zinc.

Developments in zinc extraction from sulphate, chloride and other media have been extensively covered by Ritcey and Ashbrook⁴ and Lo, Baird and Hanson⁵. In general, it may be said that the organo phosphoric acid, Di-2-ethyl hexyl phosphoric acid (D2EHPA) is by far the most useful and widespread extractant for zinc. Majority of the processes described are concerned with sulphate or chloride based feed solutions and there are very few references on alkaline solutions. The possibility of zinc coextraction with copper/nickel from ammoniacal medium by LIX64N has been reported by Merigold⁶ and Eliassen^{7,8}. Kelrex 100^{9,10} has been mentioned to extract zinc from ammoniacal medium. The ratio of Cu/Zn in the loaded solvent could be increased from 5 to 80 by increasing the ammonium sulphate concentration and equilibrium pH. Shell Metal Extractant, SME529^{11,12}, Hostarex DK-16¹³ and LIX34¹⁴ were also reported to extract zinc from ammoniacal-ammonium sulphate or ammoniacal-ammonium carbonate media.

At Regional Research Laboratory, Bhubaneswar, an ammoniacal pressure leaching process was developed to extract metals from complex sulphide concentrates containing copper, zinc and lead.

Leach solutions arising out of this process contain copper and zinc as their ammine complexes and attempts were made to separate and recover these metals by solvent extraction and electrowinning techniques. Copper could be successfully extracted using LIX64N as solvent. From the copper free raffinate zinc extraction has been attempted using D2EHPA as solvent and was found feasible. A detailed investigation was carried out on this Zn-ammonia-D2EHPA system and the results are described in this paper.

Experimental

Actual leach liquors or synthetic solutions have been used. Di-2-ethyl hexyl phosphoric acid (D2EHPA), obtained from K&K Laboratories (USA) has been used without any further purification. Different volume percent solutions of the solvent in kerosene diluent have been prepared using tri-n-butyl phosphate as third phase inhibitor. All other chemicals used were of reagent grade.

Chemical analysis has been carried out using an atomic absorption spectrophotometer or by conventional methods.

All the experiments have been carried out in shake flasks except the continuous tests which were carried out in mixer-settler units.

Effect of pH:- The influence of pH on zinc extraction has been studied at three different ammonium sulphate concentrations of the aqueous phase. 5.0ml of zinc sulphate solution containing 262.9mg of zinc was mixed with 5.0ml of ammonium sulphate solution of 80/160/320 gpl concentration and the pH of the solution was adjusted to the desired value using 1:1 ammonia solution. After making up the volume of the aqueous phase to 20ml, it was contacted for 5 minutes with 20ml of 30% D2EHPA. Zinc content of the raffinate has been determined after separating it from the organic phase. Results of these tests were shown in Figure 1.

Effect of ammonium sulphate concentration:- Dependence of zinc extraction on the aqueous phase ammonium sulphate concentration has been studied at pH 9.5. 5.0ml of zinc sulphate solution was mixed with different volumes of 200/400 gpl ammonium sulphate solution so as to get the desired final concentration with respect

to ammonium sulphate and the pH of the solution was adjusted to 9.6 using 1:1 ammonia solution. After making up the volume to 20ml, 20ml of 20% D2EHPA was added and the phases were contacted for 5 minutes. Zinc content of the raffinate was estimated and the results were shown in Figure 2.

Processing of actual leach liquors:- From the actual leach liquor, copper has been separated using LIX64N as solvent. The resulting raffinate with a pH of about 9.6 has been used to obtain extraction and stripping isotherms.

Extraction isotherm:- Zinc raffinate containing 9.8 gpl zinc and 30% D2EHPA were contacted at different volume ratios. After phase separation, zinc content of both the phases was determined and a plot of zinc concentration of the aqueous phase versus the zinc concentration of the organic phase was obtained as shown in Figure 3.

Stripping isotherm:- A loaded organic containing 9 gpl zinc was equilibrated with a spent electrolyte containing 90 gpl zinc and 130 gpl sulphuric acid at different volume ratios. Zinc content of both the phases was estimated and a McCabe-Thiele construction was shown in Figure 4.

Continuous extraction and stripping experiments:- Using mixer-settler units, continuous extraction and stripping experiments were carried out using zinc raffinate, 30% D2EHPA and spent electrolyte as feed solutions.

Results and Discussion

Zinc extraction using Di-2-ethyl hexyl phosphoric acid as solvent was found to decrease with increasing pH, as can be seen from Figure 1. As is evident, the decrease in extraction is more with increasing ammonium sulphate concentration of the aqueous phase. Similar observations were made by some earlier investigators. Ritcey and Lucas⁹ reported that when Kelex 100 was used as solvent, an increase in both the pH and ammonium sulphate content resulted in decreased zinc extraction. When Hostarex DK-16 was used as solvent, Przeszlakowski and Wydra¹³ observed that increase of pH and ammonia concentration in the aqueous phase decreases zinc extraction. The results were confirmed by carrying out zinc

extraction over a wide range of aqueous ammonium sulphate concentration. The results obtained by carrying out the extraction at pH 9.6 (pH of actual leach liquor) with 20% solvent were shown in Figure 2, which shows that zinc extraction comes down from a value of about 75% to 25% when aqueous ammonium sulphate concentration was increased from 10 to 160 gpl. These experiments helped to regulate the use of ammonium sulphate in the leaching step. Having established the possibility of extracting zinc using D2EHPA, attempts have been made to use this solvent for actual leach liquors. McCabe-Thiele construction shown in Figure 3 indicates that almost complete zinc extraction can be achieved in 3 stages at equal flow rates of both phases. A similar plot (Figure 4) for stripping using a spent electrolyte and loaded organic with 9 gpl zinc shows that complete zinc stripping is possible at equal flow rates in three stages of contact. On the basis of these results, continuous extraction and stripping tests were conducted in mixer-settler units. It has been observed that the pH of the aqueous phase decreases to a critical region resulting in hydrolysis and crud formation. The solvent also gets converted to its ammonium salt resulting in stripping and formation of double salts in the stripping units.

Conclusions

Zinc can be extracted from ammoniacal ammonium sulphate solutions using Di-2-ethyl hexyl phosphoric acid as solvent. The extraction is sensitive to pH as well as ammonium sulphate concentration of the aqueous phase. A 20% solvent can load about 8 gpl zinc. Attempts to use this system for continuous extraction in mixer-settler units were not successful.

Acknowledgement

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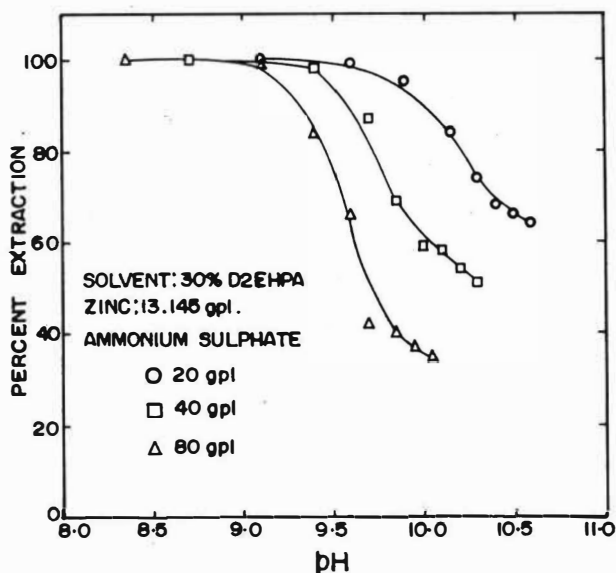


FIG.1: EFFECT OF pH ON ZINC EXTRACTION:

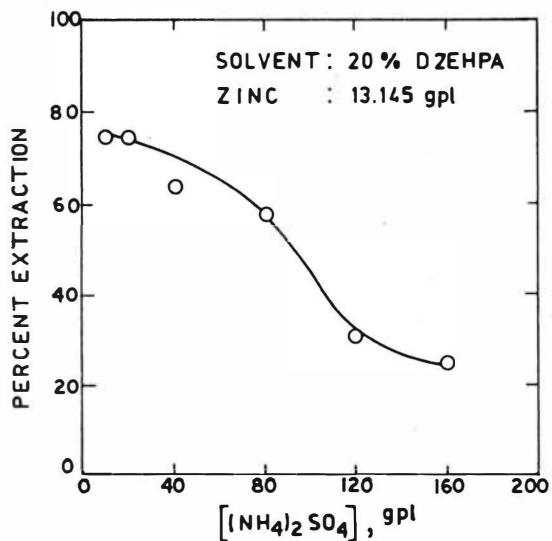


FIG.2: EFFECT OF AMMONIUM SULPHATE ON ZINC EXTRACTION

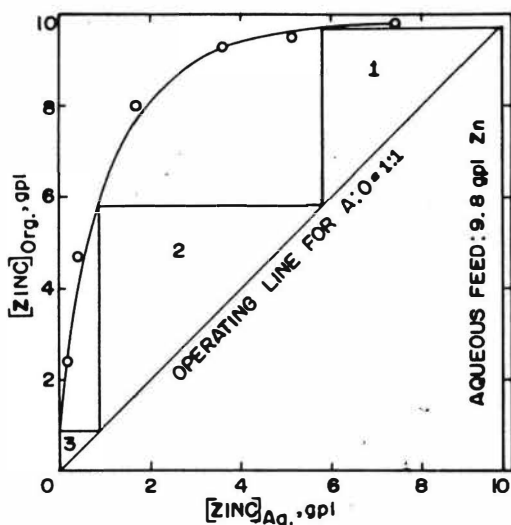


FIG.3: EXTRACTION ISOTHERM.

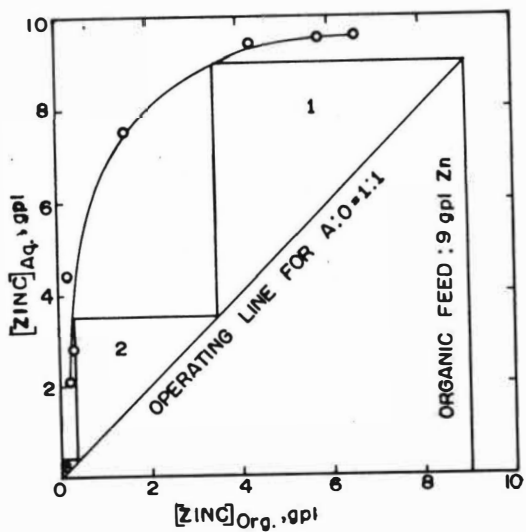


FIG.4. STRIPPING ISOTHERM.

THE RECOVERY OF NICKEL FROM CHLORIDE LEACH LIQUORS WITH ALKYL
PHOSPHORIC ACID/ALIPHATIC OXIME MIXTURES

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ABSTRACT: Mixtures of Di-2-ethylhexylphosphoric acid and other acidic alkyl phosphorus extractants with non-chelating alkyl oximes in xylene have been used to recover nickel from chloride leach liquors containing 5-10 g/L Ni in the presence of high concentrations of magnesium and chloride ions at pH values of less than about 3. The organic phase can be stripped with 10% sulphuric acid to provide a solution containing 30 g/L Ni. Both extraction and stripping equilibria were established within 30 seconds.

INTRODUCTION

The major proportion of the world's exploitable reserves of nickel comprise lateritic ores and many methods of processing have been proposed (1). Most of the commercial processes now in use are rather energy intensive (2) and this has led to the investigation of a method which is potentially less energy intensive with also the ability to cope with the wide variety of lateritic nickel ores (3) in a single process. The method does not involve expensive thermal pre-treatment or high pressure technology (4) with its problems of solid-liquid separation and difficulties in the handling of large quantities of material.

Process Development: Hydrochloric acid is used as leaching agent at 70 to 90°C on concentrations between 4 and 6 mol/L (preferably the azeotropic mixture of 21% w/w or 6.5 mol/L HCl (5,6,7,8,9)). Recoveries of nickel are over 90% but the selectivity is poor. The use of a chloride medium facilitates the use of solvent extraction for separating the various metals present, e.g. Fe(III) and Co(II) (11,12). Table 1 shows the composition of a typical leach liquor.

The nickel concentration (5-10 g/L) is too low for recovery by electro winning or reduction with hydrogen (even after adjustment to a suitable pH, e.g. the Derry Process (13)) and direct recycling of leach liquors results in lower recoveries, not only of nickel but also of other metals, e.g. Fe and Mg, with increasing metal concentration (6,9,14) due to the formation of a layer of insoluble metal chlorides just inside the outer surfaces of the ore particles - probably owing to the rapidity of the leaching reaction compared with the rate of diffusion of the metal ions out of the particles against a concentration gradient with accumulation of metal chlorides to beyond their solubility limit. This can be overcome by counter-current washing but any reasonably practical system would only give a maximum Ni concentration of 15 g/L or so in 6 stages (14). Iron can be removed from

the leach liquors (11) both by precipitation as FeOOH or solvent extraction. The normal precipitate, $\beta\text{-FeOOH}$, is unsuitable as it contains chloride ions within its structure, is easily peptized and difficult to wash. Other forms of FeOOH require higher pH with high metal losses due to co-precipitation especially onto particles of MgO used to control pH. Exchange extraction between iron(III) and the magnesium salt of Versatic acid (15) was impracticable owing to separation of a second organic phase from the magnesium Versate medium after a few hours but Fe(III) can be extracted in three stages with tributyl phosphate (11,12) as in the Falconbridge Matte Leach Process (16). Cobalt can be recovered by extraction with an anion exchanger such as Alamine 336 or Aliquat 336 giving a solution containing about 5-10 g/L nickel, about 40 g/L magnesium and up to about 5 g/L manganese at a pH of about 2 to 3 or less.

Nickel Extraction: Economic extraction of nickel from this solution requires a highly selective extractant that should work efficiently at fairly low pH, e.g. mixtures of LIX-63 with various carboxylic acids (17), but although these displayed favourable equilibrium behaviour, up to 3 hours were required for equilibrium for Ni(II) due to interfacial effects of the carboxylic acid (18,19). The extracted species was identified as $\text{Ni(Oxime)}_2(\text{RCOO})_2$ (18). Ni can be extracted preferentially from Co in sulphate media by mixtures of carboxylic acids and various oximes especially LIX-70 in the pH range 2.5 - 5 (20). Slow Ni extraction was observed except when dinonylnaphthalene sulphonic acid (DNNS) was present in small amounts. With LIX-63 and DNNS (21,22,23) Ni could be extracted in about 5 min. from solutions containing about 20 g/L free acid 50°C and stripped with 4M acids (21) but the stability of the extractant mixture to hydrolysis is suspect (22). Nickel can be extracted before Fe(III) at pH 1 with mixtures of DNNS and amines (24,25) but the stability of the amines used (based on alkylpicolylamines) is suspect and the reagents are not generally available. Nickel selective resins based on similar groups (XFS 4195 and XFS 43084) have also been developed and found to absorb Ni very strongly from chloride media at pH 2 to 3 (26). Mixtures of D2EHPA and LIX-63 have been used to extract Cu and Co ahead of nickel from sulphate media at about pH 2 to 2.5 (41). D2EHPA has been used commercially for separating Ni and Co from weakly acidic sulphate media (27, 28, 29, 30) at pH 4 to 6 and the chemistry of this extraction system has been investigated (31 to 36). Recently other alkyl-phosphorus reagents have been found to give better separation of Co from Ni by suppressing Ni extraction at pH values from about 4.5 up whilst enhancing that of cobalt by promoting the formation of tetrahedrally coordinated Co(II) species in the organic phase (37,38,39,40). A further problem associated with D2EHPA is its tendency to coextract magnesium and calcium at fairly low pH (42,43),

which would be an obvious problem with laterite leach liquors. Cyanex 272 is said not to coextract Mg (39).

None of the above extractant systems have the required characteristics, however, work by Preston (44,45,46) has indicated that mixtures of acidic alkylphosphorus extractants and non-chelating alkyl oximes have suitable properties although his data refer to sulphate media.

EXPERIMENTAL

Extractants included Di-2-ethylhexyl Phosphoric acid (D2EHPA) (Albright and Wilson), the phosphonic acid, SME 418 (Shell Chemicals) and the phosphinic acid, CYANEX 272 (Cyanamid). Oximes were prepared (27) from the corresponding aldehydes by reaction with hydroxylamine in the presence of soda-ash and purified by recrystallization from hexane. They were characterized by infrared spectroscopy. Table 2 shows structures of the alkylphosphorus extractants used in this work.

Solvent phases were prepared by dilution of the appropriate quantities of extractants in xylene and contacted with an aqueous phase containing initially 5 g/L Ni (as chloride) in 24 g/L magnesium chloride in separating funnels. The pH of the aqueous phase was adjusted using NaOH solution. In each case the sodium salt of the extractant was used to avoid large pH shifts. Aqueous phases were analysed for Ni and Mg by Atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

During initial studies the alkylphosphorus extractants alone did not extract any nickel at all owing to the extraction of large quantities of Mg. Figure 1 shows the results of tests at similar chloride concentrations using NaCl rather than $MgCl_2$. Figure 2 shows the effects of adding either of the two non-chelating oximes to each of the extractants under the same conditions. As can be seen the addition of the oximes has a dramatic effect on the extraction of nickel. The $pH_{0.5}$ of 0.75 for nickel for the 0.5 M D2EHPA - 0.5 M Octanal oxime mixture permitted all the nickel to be removed before magnesium extraction commenced at the same pH as for D2EHPA alone. The results for SME 418 and CYANEX 272 showed similar trends but higher $pH_{0.5}$ values as might be anticipated from their designated purpose for the improved preferential extraction of Co over Ni in comparison with D2EHPA.

Only 40 to 50% of the available nickel was extracted when the oximes were used on their own in xylene diluent under the same aqueous conditions, which shows both their inherent extraction capability and the degree of synergism of the mixtures. For the extraction of Ni(II) from 0.2M NaCl by mixtures containing 0.08 - 0.04 M D2EHPA and 0.03 - 0.08 M Octanal oxime in xylene, the nickel distribution dependence on pH was second order (see Fig. 3), whilst it was fourth order on the concentration of oxime (see Fig.

4.). Figure 3 also shows that nickel distribution was independent of nickel concentration indicating that the extracted species is probably monomeric. The nature of this species is now being studied by spectrophotometry.

When chloride concentration was varied using either NaCl or LiCl, it was found that increasing concentrations of Cl^- had no effect on the extraction of nickel by 0.5 M D2EHPA - 0.5 M Octanal oxime and 0.5 M SME 418 - 0.5 M Octanal oxime mixtures as to be expected for Ni(II), but that increasing amounts of alkali metal ions, Na^+ or Li^+ shifted the extraction isotherms to lower pH values (see Fig. 5). This is probably due to the removal of water from around outer co-ordination sphere of the nickel ion making it more acceptable to the extractant ligands at lower pH as the effect is comparable in magnitude to the increase in hydration energy of the metal ion present.

Loading and stripping isotherms for 0.5 M D2EHPA - 0.5 M Octanal oxime and 0.5 M SME 418 - 0.5 M Octanal oxime are shown in figures 6 and 7 and figures 8 and 9 respectively. 100 g/L Sulphuric acid can be used to strip nickel from the loaded organic phase to give a product containing about 30 g/L Ni. Both loading and stripping kinetics are rapid. Equilibrium was established within 30 seconds.

The effect of 5 g/L Mn(II) chloride (0.09 M) in the aqueous phase on the extraction of Ni(II) with 0.5 M D2EHPA - 0.5 M Octanal oxime was studied and showed that up to 30% of the manganese was co-extracted with the nickel but could possibly be removed along with any co-extracted magnesium by scrubbing with a 10 g/L nickel solution.

ACKNOWLEDGEMENTS

The authors wish to thank BP Minerals PLC and the SERC for the provision of a CASE studentship for DCS and also to thank Shell Chemicals and Dr W Rickelton of CYANAMID, Canada for the provision of samples of extractants. Mr R Wilson assisted with the preparation of the oxime samples.

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TABLE 1 Composition of typical Leach Liquors (11)

(2 hour Leach at 90°C in 5.1 mol/L HCl)

Major Elements Present (as chloride)	Fe g/L	Mg ²⁺ g/L	Mn ²⁺ g/L	Ni ²⁺ g/L	Co ²⁺ g/L	Cl ⁻ g/L
High Magnesia Laterite	37	40	0.8	3.3	0.2	180
High Iron Laterite	65	3	0.4	2.0	0.15	180

Also minor amounts of Cr(III), Al³⁺, Ca²⁺ and virtually no Si.

TABLE 2 Structures of Alkyl Phosphorus Extractants (40)

Extractant	Chemical Name	Structure	
D2EHPA	Di(2-ethylhexyl)phosphonic Acid	RO	O
		P	
		RO	OH R =
			C ₄ H ₉ CH(C ₂ H ₅)CH ₂ -
SME 418	2-Ethylhexylphosphoric acid Mono-2-ethylhexyl ester	RO	O
		P	
		R	OH
Cyanex 272	Di(2,4,4-trimethylpentyl) phosphinic acid	R	O
		P	
		R	OH R =
			CH ₃ CH(CH ₃)(CHC -
			(CH ₃) ₂ CH ₃ -

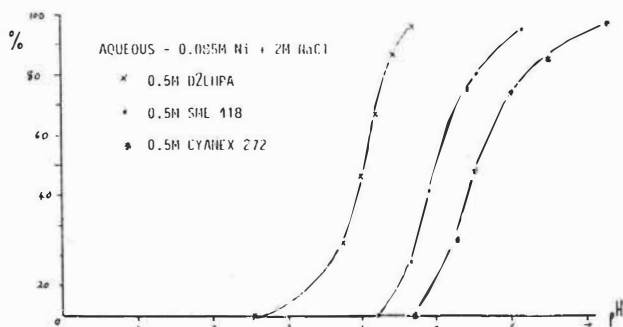


FIG. 1 - Extraction of Nickel (II) by each Extractant in Xylene.

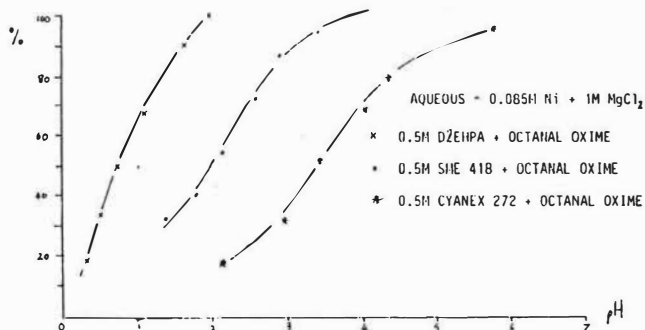


FIG. 2 - Extraction of Nickel (II) by Extractant - Oxime Mixtures.

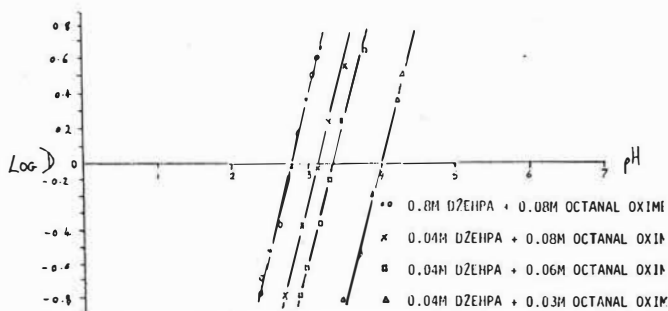


FIG. 3 - Extraction of Nickel (II) by Mixtures of D2EHPA and Octanal Oxime.

Aqueous - 0.02M NiCl₂ + 0.2M NaCl • • • 0.002M NiCl₂ + 0.2M NaCl

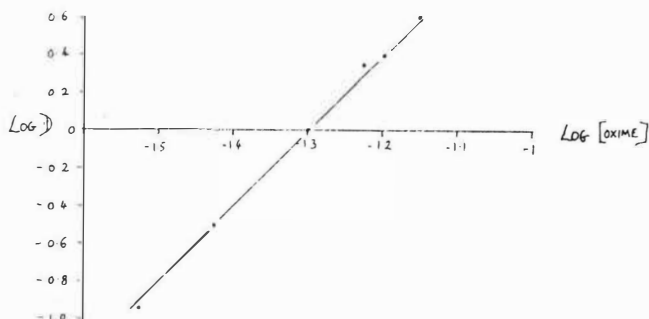


FIG. 4 - Effect of Oxime Concentration at Constant D2EHPA Concentration (0.04M) and Constant pH (i.e. 3.5)

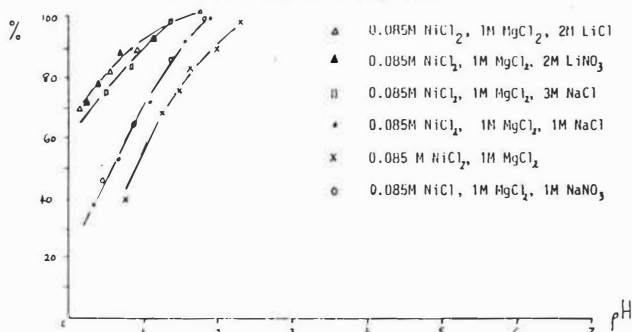


FIG. 5 - Effect of Different Metal Chlorides and Nitrates on Nickel (II) Extraction using 0.5M D2EHPA - 0.5M Octanal Oxime

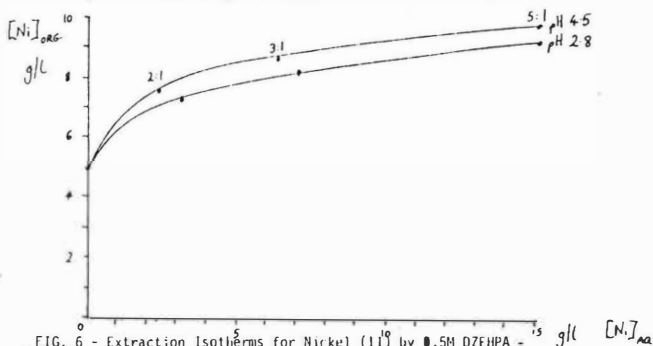


FIG. 6 - Extraction Isotherms for Nickel (II) by 0.5M D2EHPA - 0.5M Octanal Oxime

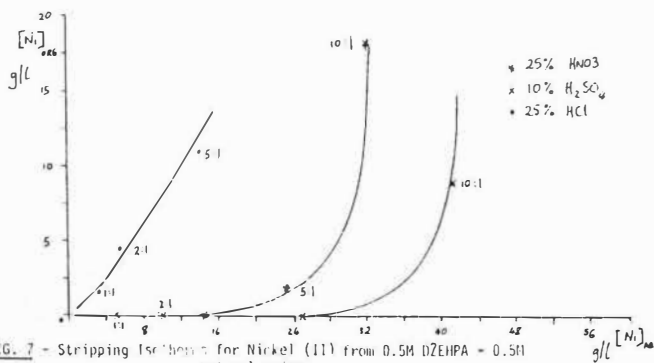


FIG. 7 - Stripping Isotherms for Nickel (II) from 0.5M D2EHPA - 0.5M Octanal Oxime

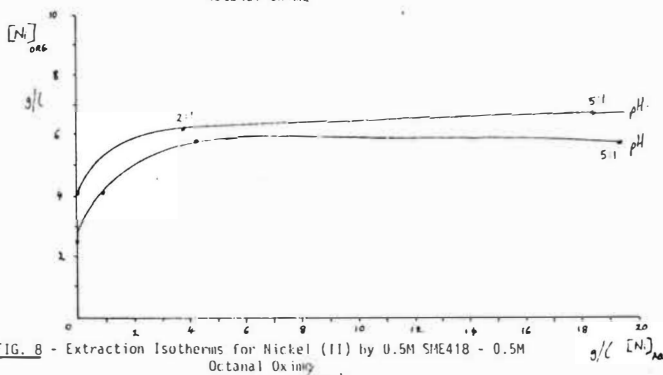


FIG. 8 - Extraction Isotherms for Nickel (II) by 0.5M SME418 - 0.5M Octanal Oxime

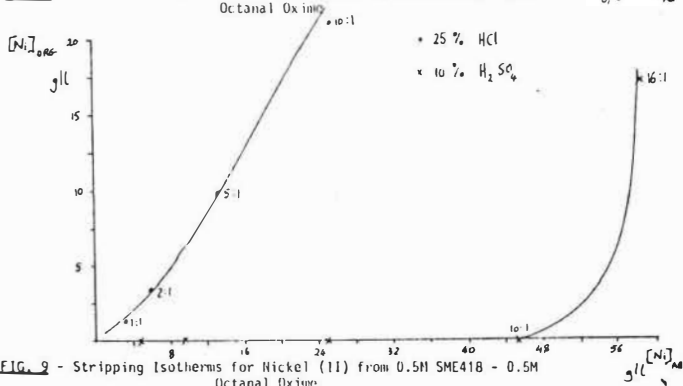


FIG. 9 - Stripping Isotherms for Nickel (II) from 0.5M SME418 - 0.5M Octanal Oxime

Extraction of Copper out of a Silver Nitrate Electrolyte

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A.Prior, Gerolfingen-Biel/Switzerland

Introduction

Silver refinement is an electrolytical process, carried out in Moebius or Balbach-Thum electrolysis cells, where an anode cast of scrap silver dissolves in the silver nitrate electrolyte and fine silver precipitates on the cathode. Some of the impurities coming into the system by anodic dissolution of silver scrap are themselves insoluble in the refinement electrolyte, the major proportion, however, is soluble and is not reduced cathodically due to low standard potential and/or low concentration. Naturally, this means that the concentration of these impurities in the refinement electrolyte must not exceed a certain value to keep them in solution and prevent their cathodic precipitation.

Being the main component in silver alloys (besides silver itself), especially copper is enriched in the refinement electrolyte, thus making it necessary to remove the whole volume of electrolyte after a certain critical level (about 60 g copper per liter) has been reached. Processing this spent electrolyte takes three major steps: cementation of silver on copper wire, cementation of copper on iron scrap and finally neutralization of the solution and its disposal.

The main disadvantages of this conventional process are the following:

- * cementation is not a very favourable operation because of its costs and complicated handling
- * neutralization of the remaining nitric acid solution and the following disposal cause serious environmental problems
- * cementation does not yield saleable products
- * when the proportion of silver in the anode materials is below 95 %, it is necessary to admix pure silver nitrate in order not to exceed the critical copper concentration.

Copper removal by solvent extraction

To overcome the above mentioned problems it is obvious to keep the silver refinement electrolyte's copper level low by means of a continuous solvent extraction process /1/. However, instead of simple copper extraction/electrowinning (as it is known from hydrometallurgical copper mining) a combined solvent extraction/membrane electrolysis process was developed /2,3/. The flow sheet of this process is shown in fig. 1.

Silver refinement electrolyte (E1) out of the refinement electrolysis cell (1) goes to the anode compartment (2) of a membrane cell where a scrap silver anode is dissolved. Through the buffer tank (3) this enriched electrolyte goes to a two-stage counter current solvent extraction unit (mixer-settlers 4 and 5) where copper is removed so that the depleted electrolyte can go back to the refinement cell.

The copper loaded organic phase (0) may undergo a scrubbing step (6), depending on the amount of coextracted silver. In the reextraction mixer-settler (7) the organic phase is stripped with acidic spent catholyte and goes back to extraction. The copper rich electrolyte E2 is sent to the cathode compartment of the membrane electrolysis (8) where pure copper is won by cathodic reduction, so that the depleted electrolyte is suitable as a stripping agent once more. The two compartments of this electrolysis are separated by an anion-selective membrane which holds back cations like copper and silver and lets pass only the nitrate ions to close the electric circuit.

This process offers several advantages over the conventional treatment of spent silver refinement electrolyte:

- * the process is continuous, thus granting constant electrolyte properties
- * there is no need to treat large quantities of acidic heavy-metal solutions for safe and non-polluting disposal
- * dissolution of scrap silver in the membrane cell makes admixture of silver nitrate unnecessary
- * end products are fine silver and pure copper

The extractant is a conventional chelating agent like LIX 64 N, SME 529 and the Acorga P 5000 series. Extraction selectivity over silver is good, with slight variation depending on which chemical is actually used. Further variables are reaction kinetics, acidity

of the extractant, copper transfer capacity and long-term stability of the chelating agent. Considering these boundary conditions one has the opportunity to select the best fitting extractant, according to the wide spectrum of possibilities offered by the chemical manufacturers.

The problem of nitric acid attack

Silver nitrate being the only readily soluble silver salt it is important not to contaminate the refinement electrolyte with anions like chloride or sulfate. Therefore nitric acid was chosen as stripping agent. Now nitric acid as an oxidizing chemical is much more harmful to copper extracting agents than the widely used sulfuric acid, thus stressing the importance of an extractant's stability against hydrolysis.

Fig. 2 shows the degradation of an organic phase (20 % PT 5050 in kerosene) in continuous contact with 2.0 molar nitric acid. Copper loading capacity decreases significantly, on the other hand the equilibrium copper concentration after stripping decreases at almost the same rate so that the net copper transfer capacity remains practically constant over several months.

In fig. 3 one can see a comparison of the remaining copper loading (as percentage of the initial copper loading) of various copper extractants after continuous contact with 2.0 m nitric acid over a period of 2 months (it is to be noted, though, that different extractants also require different concentrations of nitric acid for satisfactory stripping; therefore a statement concerning the practical suitability of certain extractants must not be derived directly from this figure).

Extractant degradation as well as stripping efficiency are essentially linked to the acid content, so the main incentive is to find an optimum between these contradictory parameters. To achieve this goal a computer program was developed which enables the planning engineer to predict the results of the stripping process, depending on boundary conditions like initial acid and copper concentration, phase ratio and number of (counter current) extraction stages.

Fig. 4 and 5 show computer plots comparing single stage and two stage counter current stripping. As phase ratio and copper concentration of the strip solution in both cases are identical the difference lies in the acid concentration required to achieve a copper transfer of 10 g/l strip solution. For single stage stripping you need 1,8 molar nitric acid, leading to a reextract acid concentration of 1,5 molar; for two stage counter current stripping an acid concentration of 1,3 molar is sufficient, leading to an acid concentration of 1,0 molar in the reextract phase (mind that the computer plots are not to read as common two-dimensional equilibrium isotherms but in fact represent a sectional view of a three-dimensional equilibrium plane).

Besides the installation of multistage stripping (which means more apparatus and thus higher costs) there is the possibility to reduce the strip solution's initial copper content in order to reduce the necessary acid concentration.

Here an optimum has to be found considering the premises given by the membrane electrolysis unit, where the (regarding reextraction) contradicting circumstances of high copper and low acid concentration both are favourable for the performance of the membrane cell.

Conclusion

As a combination of two processes which are rather novel developments themselves this concept offers new possibilities for the comparatively simple yet flexible and ecologically favourable treatment of (spent) silver refinement electrolyte. Showing a lot of significant advantages over existing technologies, the problems lie in the damaging influence of nitric acid on the organic inventory, thus emphasizing the importance of careful optimization of the process parameters.

Literature

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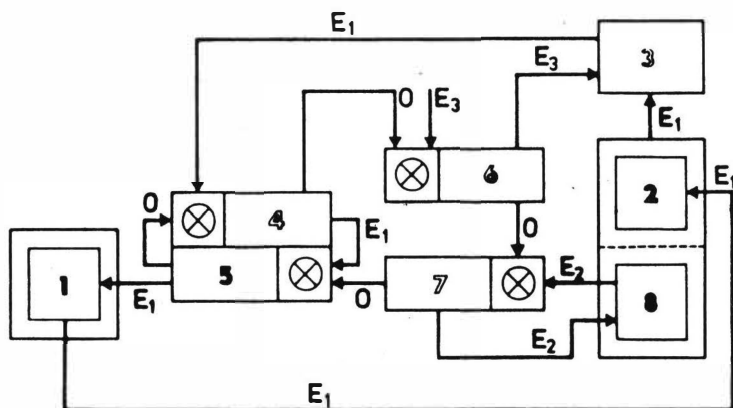


Fig. 1: Flow sheet of Cu/Ag separation plant

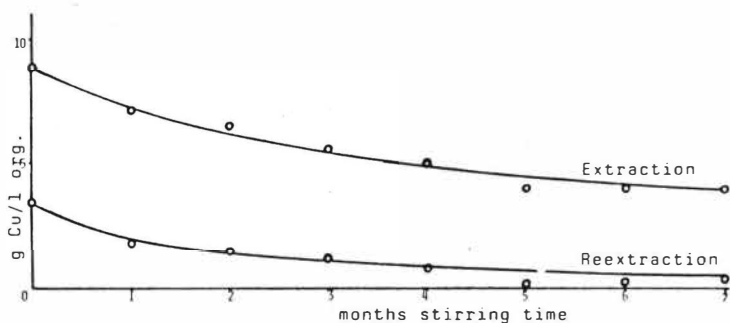


Fig. 2: Transfer capacity of 20 % PT 5050 in contact with 2.0 molar HNO_3

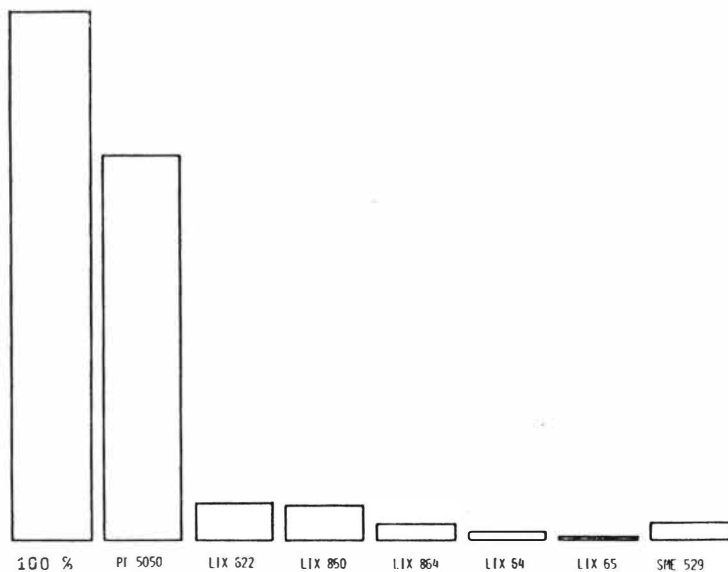


Fig. 3: Copper loading capacity of different extractants after 2 month's contact with 2.0 molar HNO_3

EQUILIBRIUM COPPER/NITRIC ACID/PT 5050

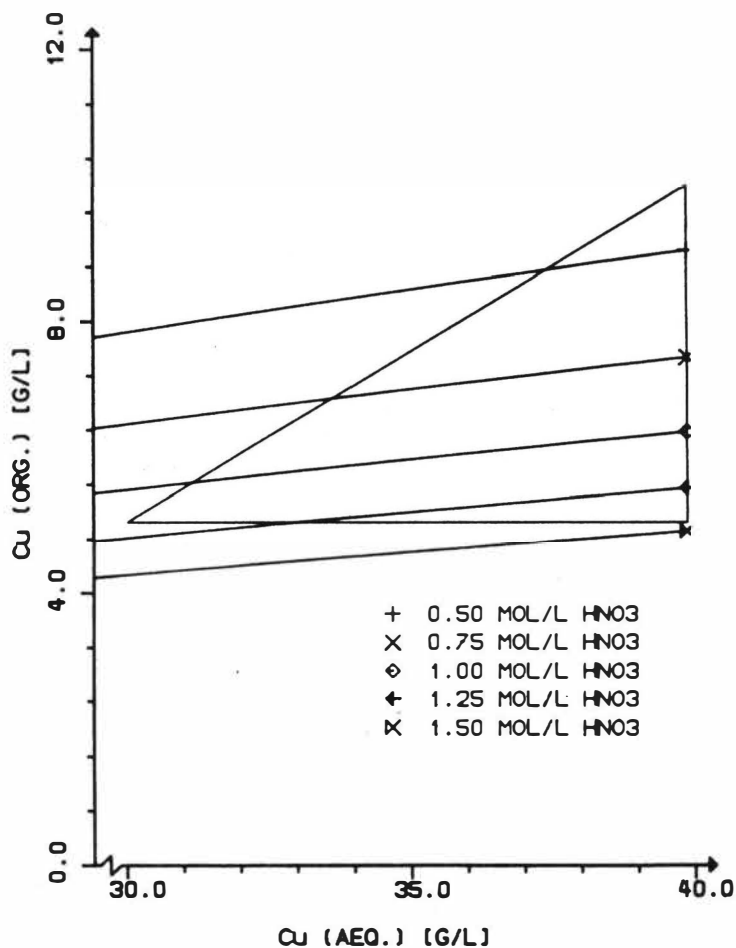


Fig. 4: Computer plot, single stage stripping

EQUILIBRIUM COPPER/NITRIC ACID/PT 5050

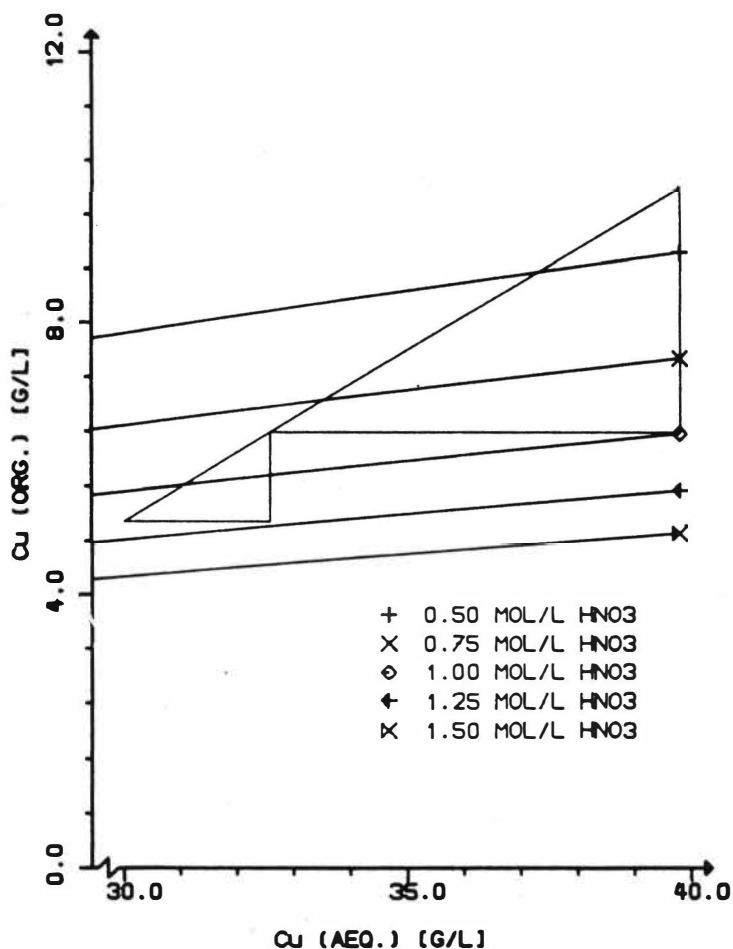


Fig. 5: Computer plot, two stage counter current stripping

The Study on The Mathematical Model of Fractional Counter Current Extraction for Rare Earth Separation with Acidic Phosphates and Noval Technology for Solvent Extraction-Simultaneous Separation of A, B, C-

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The Study on the Mathematical Model of Fractional Counter Current Extraction for Rare Earth Separation With Acidic Phosphates

By the use of modified counter current extraction model and the computer program proposed by the authors(1), the system of HEH(EHP)-Kerosene-HNO₃-(Ho-Er)(NO₃)₃ at different technological conditions and the system D2EHPA-Amsco-HCl-(Tm-Yb)Cl₃ are studied.

HEDH(EHP)-Kerosene-HNO₃-(Ho-Er)(NO₃)₃ system

For 1.0MHEH(EHP), (Mono(2-ethyl hexyl phosphonate), total rare earth concentration 0.2M, initial acidity 0.1-1.5N, 30 experiments are carried out and the extraction equilibrium model is obtained by least square method as

$$\begin{aligned} \text{extraction stage} \quad D_{Ho} &= 2.95912^{1.0955} H^{-0.76787} \\ D_{Er} &= 9.19682^{1.324} H^{-1.1193} \\ \text{wash stage} \quad D_{Ho} &= 0.412842^{0.0391} H^{0.12505} \\ D_{Er} &= 1.19132^{-0.06899} H^{0.07965} \end{aligned} \quad (1)$$

D-distribution ratio, Z-extractant conc., H-acidity.

Equation (1) is substituted into modified counter current extraction model and the system given above is calculated.

Technological condition 1:

N=12, NF=6, FE=20.0ml, $FX_{Ho}=0.0865M$, $FX_{Er}=0.0759M$,
FH=0.0813N, SC=10.0ml, SCH=1.12N, Zo=1.0M, SOL=30.0ml.

The calculated and experimental results are given in Fig. 1-4. The influences on the separation effect by the change of technology parameters are further considered. It shows that the calculated and experimental results are in good agreement.

For the purpose of realizing computer aided design and experiment progressively another experiment is carried out.

Technological condition 2:

$N=12$, $NF=6$, $FE=7.0\text{ml}$, $FX_{Ho}=0.0841M$, $FX_{Er}=0.0777M$,
 $FH=0.0908M$, $SC=3.5\text{ml}$, $SCH=1.13N$, $Zo=1.0M$, $SOL=10.0\text{ml}$.

By the use of the same model as in condition 1, the calculation for condition 2 is carried out. The result shows that, although the condition is changed, the model is valid.

D2EHFA-Amsco-HCl-(Tm-Yb)Cl₃ system

The calculation of 1M D2EHFA (Di(2-ethyl hexyl) orthophosphoric acid) -Amsco-HCl-(Tm-Yb)Cl₃ system (2) is carried out. The results are shown in equation (2) and Fig. 5-8.

$$\begin{aligned} D_{Tm} &= 18.568Z^{2.031}_H - 0.4139 \\ D_{Yb} &= 17.82Z^{2.247}_H - 0.5684 \end{aligned} \quad (2)$$

For all of the above systems the maximum number of iteration is 6.

Calculations show that, the modified model proposed by the authors in paper (1) is more satisfied and the computer aided design and experiment may be expected.

Novel Technology for Solvent Extraction-Simultaneous Separation of A, B, C-

The method of fractional counter current extraction is widely used in the technology for the separation of rare earths. It has the advantage that, we can get two products simultaneously. But for complicated system in which containing a lot of components, they must be divided into groups and separated individually. As for three components (A, B, C) system, two processes must be made.

Authors have designed a novel technology, there are three products simultaneously in one process and the feed is either organically or inorganically.

As for HEH (EHP)-Kerosene-(Gd-Tb-Dy) Cl₃-HCl system (La₂O₃-Gd₂O₃ 59.5% Tb₄O₇ 4.5%, Dy₂O₃ 36%). By the use of the method given above, there are three products, in the first exit is (La-Gd) Cl₃ (>99%), TbCl₃ is in the second (-65%) and DyCl₃ is in the third((Gd-Tb)Cl₃ -0.1%).

For Sm-Eu-Gd system the result is the same.

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- (1) Li Han, Chen Zhichuan, Zhou Jiaju, New Frontiers in Rare Earth Science and Applications Vol. 1 446-450.
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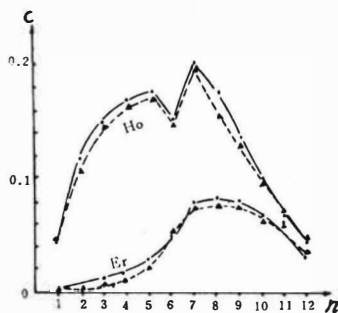


Fig. 1 Rare earth Conc. (C(M/L)) of Ho and Er in aqueous phase vs. no. of stage (n)
 --- Experimental value
 --- calculated value

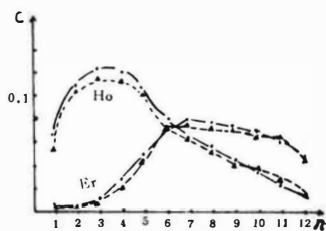


Fig. 2 Rare earth conc. (C(M/L)) Of Ho and Er inorganic phase vs. no. of stage

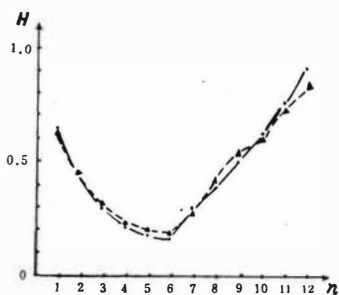


Fig. 3 Acidity (H) vs. no. of stage

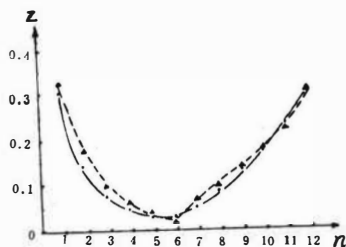


Fig. 4. Extractant conc. (Z) vs. no. of stage

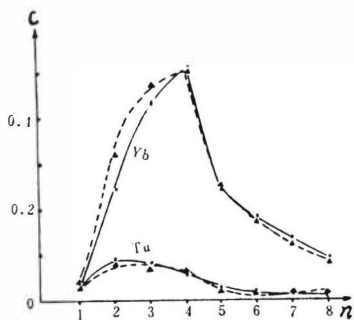


Fig. 5 Rare earth conc. of Tm and Yb in aqueous phase vs. no. of stage

--- Experimental value
 --- Calculated value

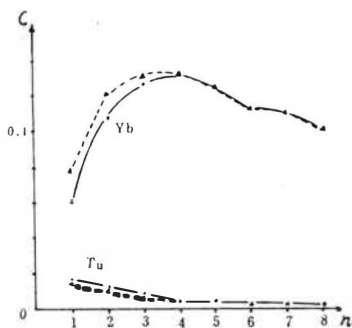


Fig. 6 Rare earth conc. of Tm and Yb in organic phase vs. no. of stage

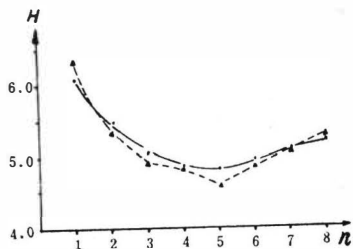


Fig. 7. Acidity vs. no. of stage

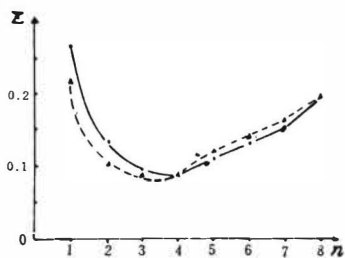


Fig. 8 Extractant conc. vs. no. of stage

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