THE EXTRACTION OF METAL IONS FROM AQUEOUS SULPHATE MEDIA BY ALKYLAMINES

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CONTENTS

A. INTRODUCTION

Over the last 25 years the use of high molecular weight alkylamines in inorganic solvent extraction systems has been extensively investigated. A great deal of the research has followed purely theoretical lines; however, considerable success has been achieved using these compounds and solvent extraction techniques in the nuclear fuel and mineral processing industries.

In 1948, Smith and Page[1] first reported that long-chain alkylamines could be used to extract strong acids from aqueous solutions into organic solvents. They found that the salts formed could act as "liquid anion exchangers". Subsequently, many reports of the use of these compounds to extract metals from aqueous solutions have appeared in the literature[2–20].

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TABLE 1

Results of studies of the extraction of metals from sulphate media

Metal oxidation state	Amine	Diluent	Proposed formula of extracted complex	Proposed mechanism	Ref.
U^{VI}	N-Cyclohexyl-n-octyl N-Cyclohexyl-n-dodecyl N-Cyclohexylstearyl N-Cyclohexyl-2-ethylhexyl N-Benzyl-2-ethylhexyl N-Benzyl-n-dodecyl N-Benzyldi-n-dodecyl N,N-Dibenzyl-n-dodecyl	Chloroform Benzene Various	$(RR'NH_2)_4UO_2(SO_4)_3$	Adduct formation	27, 30, 31
U^{VI}	Tri-n-dodecyl Di-n-dodecyl n-Dodecyl Dimethyl-n-dodecyl	Benzene Various	$(R_3NH)_4UO_2(SO_4)_3(H_2O)_3$ [a]	Adduct formation	28, 32, 34
U^{VI}	Tri-n-octyl Methyldioctyl [b] Didecyl Methyldidecyl Tridecyl	Carbon tetrachloride	$(R_3NH)_4UO_2(SO_4)_3$ $(R_2NH_2)_4UO_2(SO_4)_3$ $(R'R_2NH)_4UO_2(SO_4)_3$	Uncertain	25
U^{VI}	Tri-n-octyl	Benzene	$(R_3NH)_n UO_2(SO_4)_{(1/2)n+1}$ $n = 4$ or 5	Adduct formation	26
U^{VI}	Di-n-decyl	Benzene Carbon tetrachloride	$(R_2NH_2)_6UO_2(SO_4)_4(H_2O)_6$ [a]	Anion exchange	41
U^{VI}	Tri-n-octyl	Benzene Various	$(R_3NH)_4UO_2(SO_4)_3(H_2O)_3$ [a]	Adduct formation	29, 32, 35, 36

Metal ion	Amine	Solvent	Species	Mechanism	Ref.
U^{VI}	Di-n-octyl	Benzene Various	$(R_2NH_2)_4UO_2(SO_4)_3(H_2O)_3$	Adduct formation	32
U^{VI}	Trioctyl[b] Tridecyl Methyldioctyl Methyldidecyl	Benzene Carbon tetrachloride	$(R_3NH)_4UO_2(SO_4)_3$	Anion exchange	64
Fe^{III}	Di-n-decyl	Benzene	$(R_2NH_2)_2FeOH(SO_4)_2$	Adduct formation	50
Fe^{III}	Primene 81-R[c]	Chloroform	$(RNH_3)Fe(SO_4)_2$	Anion exchange	51
Fe^{III}	Di (3,5,5-trimethylhexyl)	Benzene Chloroform	$(R_2NH_2)_2FeOH(SO_4)_2$[a]	Adduct formation	37, 38
Fe^{III}	3,5,5-Trimethylhexyl n-Dodecyl	Isopentanol	$(RNH_3)_2FeOH(SO_4)_2$[a]	Adduct formation	39
Th^{IV}	Di-n-decyl	Benzene	$(R_2NH_2)_n Th(SO_4)_2 + (1/2)n$ $n = 2, 4, 6$	Adduct formation	44
Th^{IV}	Di-n-octyl Di-n-tridecyl	Toluene Xylene	$(R_2NH_2)_6 Th(SO_4)_5$	Adduct formation	46
Sc^{III}	Di(3,5,5-trimethylhexyl)	Chloroform	$(R_2NH_2)_4 ScOH(SO_4)_3$[a]	Adduct formation	40
Ru^{III}	Primene-JMT[d] Amberlite-LA-2[e] Tri-n-hexyl Tri-n-octyl Tri-isooctyl Tri-n-nonyl	Benzene Chloroform Carbon tetrachloride Nitrobenzene	$(RNH_3)Ru(SO_4)_2$	Anion exchange	62
Ln^{III}[f]	n-Dodecyl	Chloroform	$(RNH_3)_3 Ln(SO_4)_3$	Anion exchange	58
Hf^{IV}	Alamine-336[g]	Kerosene	$(R_3NH)_2Hf(OH)_2(SO_4)_2$ $(R_3NH)_2Hf(OH)_4SO_4$	Anion exchange	63

The footnotes to this Table are to be found at the top of the next page.

Footnotes to Table 1:

a A complex of this formula was actually isolated from the organic phase.

b Although the author has not specifically stated so, it can be assumed that these are straight-chain amines.

c A commercial straight-chain primary amine with 12—14 carbon atoms.

d A commercial highly branched-chain primary amine with 18—24 carbon atoms.

e A commercial highly branched-chain secondary amine with 24—27 carbon atoms.

f Ln^{III} represents the Sc^{III}, Y^{III} and La^{III} ions.

g A commercial tertiary amine, principally tri-n-octyl and tri-n-decyl.

In this review an attempt has been made to present a more specialised survey which concentrates on the extraction of metal ions from acidic aqueous sulphate media. Particular attention has been given to those systems where suggestions have been made regarding the stoichiometry of the complexes formed in the organic phase and the mechanism of extraction. The systems which have been studied in this way are summarised in Table 1. It becomes apparent when considering sulphate systems that examples can be found which demonstrate the possibility of there being two types of extraction mechanism, anion exchange and direct complexation (adduct formation). The proposed mechanisms for the systems reported in the literature are also given in Table 1.

B. THE AMINE SULPHATE AND BISULPHATE SALTS

When considering amine extraction systems, the amine salt should be regarded as the extracting agent, rather than the free amine itself. In fact, most metal extractions are performed from acidic aqueous media so that if the organic phase initially contains the free amine, it can be considered to be first converted to its salt before extraction occurs. When the amine salt is used in the initial organic phase, it is still necessary to keep the aqueous phase acidic to prevent the hydrolysis of the salt which results in the liberation of free amine. In fact, the amine salt can be reconverted to the free amine simply by shaking the organic phase with an aqueous solution of sodium hydroxide or sodium carbonate — a fact that has been made use of in many processes for the recovery of metals from the organic phase. This limitation on the aqueous phase conditions does not apply, however, when fully substituted quaternary ammonium salts are used as extractants. These compounds can be used to extract metals from neutral and slightly alkaline solutions as well as from acidic solutions.

The conversion of an amine to its salts in an acidic sulphate medium can be represented by the equations

$$2 \, \overline{R} + H_2SO_4 \rightleftharpoons \overline{R_2H_2SO_4} \tag{1}$$

$$\overline{R_2H_2SO_4} + H_2SO_4 \rightleftharpoons 2 \, \overline{RH_2SO_4} \tag{2}$$

where R is any primary, secondary or tertiary amine, and $R_2H_2SO_4$ and RH_2SO_4 refer to

the amine sulphate and bisulphate salts respectively. Species in the organic phase are denoted by a bar; other species not marked by a bar are in the aqueous phase.

Depending on the aqueous phase conditions the organic phase may contain at equilibrium the pure bisulphate salt (very high acidities), the pure sulphate salt (at one particular acidity value characteristic of the amine itself), a mixture of the amine bisulphate and sulphate salts (high acidities) or a mixture of the amine sulphate salt and the free amine (low acidities).

C. THE ANION EXCHANGE REACTION

Solutions of amine salts in organic diluents have been found to act as "liquid anion exchangers" in that the anion of the amine salt, in the present case the sulphate or bisulphate ion, can be exchanged for another anion from the aqueous phase.

$$\frac{n}{2} \overline{R_2 H_2 SO_4} + X^{n-} \rightleftharpoons \overline{(RH)_n X} + \frac{n}{2} SO_4{}^{2-} \tag{3}$$

where X^{n-} represents any anion, including such complex metal-containing anions as $UO_2(SO_4)_2{}^{2-}$ or $Fe(SO_4)_2{}^{-}$.

This reaction implies the transport of anionic species across the aqueous/organic interface, and also suggests that in the case of metal ion extraction it is essential to have the metal ion in an appropriate complexed anionic form in the aqueous phase in order to bring about transfer of the metal to the organic phase.
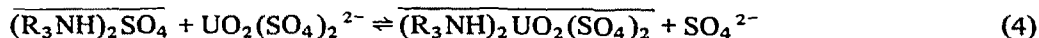
D. THE ADDUCT FORMATION REACTION

In their discussion of the extraction of uranium(VI) from sulphate solutions, Coleman et al.[4] propose that there is another possible mechanism for the extraction of metals from aqueous solutions by amines, viz. that of adduct formation. In this mechanism the transport of a neutral metal containing species across the interface is implied. Thus there are two possible reactions to be discussed which, according to Coleman[9], are thermodynamically equivalent since they both result in the formation of the same species in the organic phase and are therefore only an arbitrary choice of a description for the equilibrium processes. However, in making this point Coleman has overlooked a very important distinction between the two mechanisms.

Cattrall[21] has pointed out that extraction can occur even when there is no anionic metal-containing species in the aqueous phase, provided that the metal, in the form of the neutral species, is not fully coordinated (with ligands other than water) in the aqueous phase. Previous to this it had been suggested that it was necessary to have an extractable metal-containing anionic species in the aqueous phase in order to have efficient extraction. Of course, now it is generally accepted that both mechanisms are possible and the one which predominates depends largely on the composition of the aqueous phase and possibly on the amine type.

E. THE EXTRACTION OF URANIUM

Coleman et al.[4] have described the extraction of uranium(VI) from sulphate solutions as occurring by either one of the following mechanisms. First, there is the anion exchange mechanism

$$\overline{(R_3NH)_2SO_4} + UO_2(SO_4)_2{}^{2-} \rightleftharpoons \overline{(R_3NH)_2UO_2(SO_4)_2} + SO_4{}^{2-} \tag{4}$$

This reaction involves the transfer of an anionic metal-containing species across the aqueous/organic interface.

Secondly, there is the adduct formation (direct complexation) reaction

$$\overline{(R_3NH)_2SO_4} + UO_2SO_4 \rightleftharpoons \overline{(R_3NH)_2UO_2(SO_4)_2} \tag{5}$$
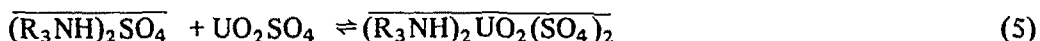
Equation (5) represents the direct reaction of a neutral uranyl sulphate species with the amine sulphate salt.

Since it is not possible to determine whether a neutral or anionic species is being transferred across the interface using the usual equilibrium studies, McDowell and Case[22] attempted to elucidate the mechanism of the uranium(VI) extraction by introducing labelled sulphate into the organic phase. They found no evidence for the transfer of an anionic uranium-bearing species and concluded that a neutral species is involved.

McDowell and Coleman[23], however, have carried out a more detailed study of this system for the extraction of uranium(VI). The aqueous phases in this study consisted of uranyl sulphate, sodium sulphate and sulphuric acid. The amount of sodium sulphate present was varied to produce conditions suitable for the preferential formation of the anionic species $UO_2(SO_4)_2{}^{2-}$ (high sulphate) or the neutral species UO_2SO_4 (low sulphate). The organic phase was di-n-decylammonium sulphate in benzene which contained sulphate radioactively tagged with ^{35}S to distinguish between sulphate which originated from the organic phase and that which originated from the aqueous phase. An interfacial mechanism was assumed for the extraction, which is highly likely in view of the high surface activity observed for the amine sulphate in this system.

This mechanism is similar to that proposed by Cattrall and West for the extraction of iron(III) from aqueous sulphate solutions by di(3,5,5-trimethylhexyl)ammonium sulphate in benzene[24]. In this case also, the amine sulphate was observed to be highly surface-active. In both these systems it is suggested that the amine sulphate concentrates at the aqueous/organic interface with the hydrophilic sulphates extending into the aqueous phase and the hydrophobic hydrocarbon chains extending into the organic phase. It is also suggested that the sulphate groups remain largely undissociated at the interface. The extraction of a metal-containing species then proceeds by direct complexation with the sulphate at the interface followed by diffusion of the complex away from the interface into the bulk organic layer. According to the elegant experiment of McDowell and Coleman[23] a difference in the rate of exchange of sulphate ions between the organic and aqueous phases should occur depending upon the mechanism for the extraction of uranium. Of course, the difference between the two mechanisms lies in the fact that for the ion-exchange process a

sulphate ion is transferred to the aqueous phase, which does not happen in the adduct formation reaction. McDowell and Coleman suggest that this should affect the rate of exchange of sulphate between the organic and aqueous phases and so differentiate between the two mechanisms.

The results of this work have shown that the transfer rate of $^{35}SO_4{}^{2-}$ to the aqueous phase is faster at higher concentrations of the sulphate ion in the aqueous phase ($\geqslant 0.05\,M$) and slower at lower sulphate ion concentrations ($< 0.01\,M$). This, according to McDowell and Coleman, suggests that both extraction mechanisms can occur simultaneously and that the one which is favoured is dependent on the concentration of the sulphate ion in the aqueous phase. At higher sulphate ion concentrations the uranium is present to a large extent as the complex disulphato anion and the anion exchange mechanism predominates, whereas at lower sulphate ion concentrations quite high amounts of the neutral or cationic uranium species exist and the adduct formation mechanism predominates.
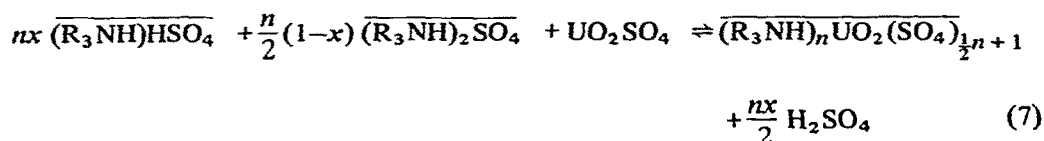
Several attempts have been made to determine the stoichiometry of the complex formed in the organic phase for the extraction of uranium from sulphate solutions.

Boirie[25] has investigated the extraction of uranium(VI) from sulphate media using a range of amines dissolved in carbon tetrachloride. Her findings are slightly different to the proposal of Coleman et al.[4] in that the species formed in the organic phase has an empirical formula in which two amine sulphate molecules are associated with each uranium. No mechanism has been proposed for this reaction but a process such as that outlined below could describe the extraction.

$$2\,\overline{(R_3NH)_2SO_4}\ +UO_2(SO_4)_2{}^{2-}\rightleftharpoons\overline{(R_3NH)_4UO_2(SO_4)_3}\ +SO_4{}^{2-}\tag{6}$$

Equation (6) represents, of course, the anion exchange mechanism but it would also be possible to postulate an adduct formation mechanism for the reaction, such as that given in eqn. (8).

In 1958, Allen[26] studied the extraction of uranium(VI) by benzene solutions of tri-n-octylamine. His results suggest that the extracted complex is monomeric with respect to uranium. From loading experiments and extraction isotherm analysis, Allen determined that between 4 and 5 amine groups per uranium are present in the extracted complex. He hypothesised that for each aqueous uranium activity, a given number of normal amine sulphates are combined with each mole of uranium in the complex. On this basis an equation has been proposed, as follows, for the reaction of an organic sulphate–bisulphate species with a neutral uranyl sulphate molecule.

$$nx\,\overline{(R_3NH)HSO_4}\ +\frac{n}{2}(1-x)\,\overline{(R_3NH)_2SO_4}\ +UO_2SO_4\rightleftharpoons\overline{(R_3NH)_nUO_2(SO_4)_{\frac{1}{2}n+1}}$$

$$+\frac{nx}{2}\,H_2SO_4\tag{7}$$

where n is the number of amine groups per uranium in the extracted complex and x is the "equivalent" fraction of amine bisulphate present in association with the uncomplexed amine sulphate. Equation (7) predicts that the transfer of each mole of uranium to the or-

ganic phase is accompanied by the transfer of $nx/2$ moles of H_2SO_4 to the aqueous phase. Accordingly, Allen carried out acid transfer measurements and was able to calculate values of n which are in good agreement with those obtained from the other techniques.

From the distribution data, Allen was also able to obtain estimates for the formation constants of the species UO_2SO_4 and $UO_2(SO_4)_2{}^{2-}$ which are in fair agreement with previously reported values. His evidence suggests that only very low or negligible proportions of the species $UO_2(SO_4)_3{}^{4-}$ are present at sulphate ion concentrations below $1.0\,M$.

Sato has extensively investigated uranium(VI) extraction using a large number of amines and a wide range of diluents[27-36]. This worker suggests, as had Boirie[25] previously, that two amine sulphate molecules are associated with each uranium in the organic phase. The following general equation is proposed, applicable at low acidities, to account for this.

$$2\,\overline{(R_3NH)_2SO_4} + UO_2SO_4 \rightleftharpoons \overline{(R_3NH)_4UO_2(SO_4)_3} \tag{8}$$

For the extraction at higher aqueous acidities, Sato has also proposed the following process which involves the amine bisulphate.

$$4\,\overline{(R_3NH)HSO_4} + UO_2SO_4 \rightleftharpoons \overline{(R_3NH)_4UO_2(SO_4)_3} + 2\,H_2SO_4 \tag{9}$$

This latter process, however, seems unlikely since it involves the conversion of amine bisulphate to amine sulphate, which is not favoured by high acidities.

It can be seen that eqn. (8) represents the adduct formation mechanism. In fact, Sato[30,31] has stated that the anionic species $UO_2(SO_4)_2{}^{2-}$ is not extractable and has reasoned that the formation of this species at higher acidities accounts for the observed lowering of uranium extraction under these conditions. However, in view of McDowell and Coleman's[23] evidence for the extraction of both neutral and anionic uranium species, this proposal of Sato is not convincing. In any case, the decreased extraction of uranium at higher acidities can be accounted for by the increased formation of the amine bisulphate, which does not extract uranium, a point which Sato has overlooked.

Sato has proposed additional evidence for the stoichiometry of the extracted uranium complex by analysing an organic phase which was saturated with uranium[28] and by analysing solid material recovered from the organic phase by removal of the solvent[34,35]. He suggests that the results of these studies further indicate that there are two amine sulphate molecules associated with each uranium, and that the uranium complex has the stoichiometric formula $(R_3NH)_4UO_2(SO_4)_3(H_2O)_3$. It should be pointed out, however, that in none of his studies has Sato attempted to establish the most favourable conditions for the formation of the pure uranium complex, as was done by Cattrall and West[37,38], Cattrall and Peverill[39] and Cattrall and Slater[40] for the preparation of iron(III) and scandium(III) complexes in similar systems. These workers show that the aqueous acidity range within which it is possible to prepare the pure complexes is extremely narrow and that preparations carried out outside these limits will yield mixtures of either the complex and the amine bisulphate (higher acidities) or the complex and the free amine (lower acidities). Hence Sato's conclusions must be looked upon with certain reservations.

A different stoichiometry for the complex extracted from sulphate solutions has been proposed by McDowell and Baes[41] using benzene solutions of di-n-decylammonium sulphate. Their evidence shows that the complex species present in the organic phase actually contains three amine sulphate units per extracted uranium. These workers have produced supporting evidence by isolating a species of this stoichiometry from the organic phase and showing that it can be recrystallised without a change in composition. They conclude that the most probable equation to describe the extraction process is
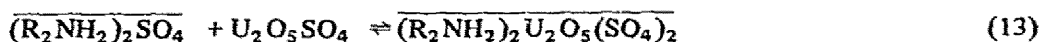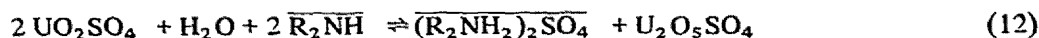
$$3 \overline{(R_2NH_2)_2SO_4} + UO_2(SO_4)_2{}^{2-} \rightleftharpoons \overline{(R_2NH_2)_6 UO_2(SO_4)_4} + SO_4{}^{2-} \qquad (10)$$
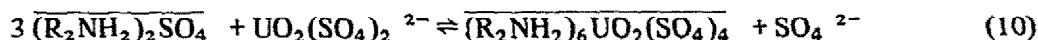
No evidence was found for the extraction of the complex ion $UO_2(SO_4)_3{}^{4-}$.

Equation (10) represents the anion exchange mechanism but it should be remembered that the subsequent study of McDowell and Coleman[23] indicates that, depending on the aqueous sulphate ion concentration, the adduct formation mechanism is also possible. This process would be represented by the equation

$$3 \overline{(R_2NH_2)_2SO_4} + UO_2SO_4 \rightleftharpoons \overline{(R_2NH_2)_6 UO_2(SO_4)_4} \qquad (11)$$
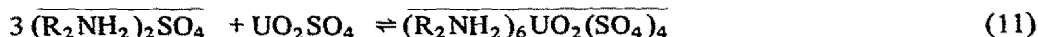
At pH values higher than 3, where the amount of acid is insufficient to convert all the amine to the sulphate salt, McDowell and Baes[41] found amine/uranium ratios of four and lower, and the aqueous phase contained hydrolysed uranium species. In addition the absorption spectra of the organic phases were consistent with the presence of hydrolysed uranium species. These workers propose the following reactions to explain this.
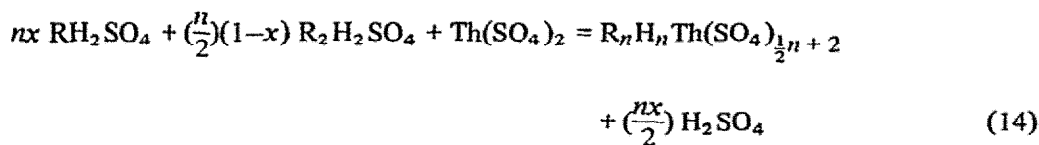
$$2 UO_2SO_4 + H_2O + 2 \overline{R_2NH} \rightleftharpoons \overline{(R_2NH_2)_2SO_4} + U_2O_5SO_4 \qquad (12)$$

$$\overline{(R_2NH_2)_2SO_4} + U_2O_5SO_4 \rightleftharpoons \overline{(R_2NH_2)_2 U_2O_5(SO_4)_2} \qquad (13)$$

The current state of knowledge of the extraction of uranium(VI) from sulphate media has been summarized by Coleman and Roddy[42]. Several different experimental methods indicate that when amines such as tri-n-octylamine in benzene are used, 2–2.5 moles of the amine sulphate are bound per uranium, and when di-n-decylamine in benzene is used, 3 moles of the amine sulphate are associated with each uranium. Neither of these results can be reconciled with the results of distribution studies, where the exponential dependence of the distribution ratio on the amine concentration is first-order. It was initially assumed that the obvious discrepancies were due to aggregation of the amine salts and complexes in the organic phase. Coleman and Roddy[42] point out that this explanation is unacceptable in view of the complete absence of aggregation for both the sulphate salt and the complex for the tri-n-octylamine case and in view of the fact that di-n-decylammonium sulphate forms a nearly 40-fold aggregate in benzene whilst the complex is monomeric. Coleman and Roddy[42] have attempted unsuccessfully to explain this anomalous behaviour on the basis of several other factors such as the change in the aggregation number of the reagent and the complex with changing water content of the organic phase, or the systematic error in measurement of the aggregation number or the distribution ratio. Also, the effect of changing water content on the exponential dependence of the distribution ratio on the

amine concentration has been considered, and the possibility of dissociation and solvation of species in the organic phase. However, these workers have finally concluded that the anomaly must be "a cumulative result of relatively small contributions from several effects, fortuitously acting together". Thus the situation is far from resolved.

F. THE EXTRACTION OF THORIUM

The extraction of thorium(IV) from sulphate media by long-chain alkylamines has also received much attention. Vdovenko et al.[43] have used several primary amines in a range of organic solvents and have obtained evidence for complexes of the type $(RNH_3)_4 Th(SO_4)_4$ in the organic phase. This complex can be envisaged as a neutral thorium(IV) sulphate species combined with two amine sulphate units.

McDowell and Allen[44] have also investigated the extraction of thorium(IV) using di-n-decylamine in benzene. Their extraction isotherms indicate an average of six amines per thorium in the organic phase and they suggest the following equilibrium expression for the extraction.

$$nx \, RH_2 SO_4 + (\tfrac{n}{2})(1-x) \, R_2 H_2 SO_4 + Th(SO_4)_2 = R_n H_n Th(SO_4)_{\frac{1}{2}n+2}$$

$$+ (\frac{nx}{2}) \, H_2 SO_4 \qquad\qquad (14)$$

where R is di-n-decylamine, n is the number of amines per thorium, and

$$x = \frac{[RH_2 SO_4]}{[RH_2 SO_4] + 2[R_2 H_2 SO_4]}$$

In writing eqn. (14) two assumptions have been made; first, that thorium complexes only with the amine sulphate and not with amine bisulphate, and secondly, that the fraction of the uncomplexed amine which is present as the amine bisulphate is not affected by the presence of the thorium complex in the organic phase. Both of these assumptions seem to be quite valid in view of the results of subsequent studies on the extraction of iron (III) and scandium(III) in similar systems[37-40]. McDowell and Allen have obtained additional evidence for the value of n by measuring the amount of acid transferred according to eqn. (14), and have obtained values for n in good agreement with the value of 6 found using the extraction isotherm method. A third check on the value for n was obtained using extraction data at a constant aqueous sulphate concentration and varying sulphuric acid activity. Once again reasonably good agreement was obtained.

In eqn. (14) it is implied that a neutral thorium sulphate species in transferred across the interface as a complex with three molecules of amine sulphate. However, on the basis of McDowell and Coleman's results for uranium[23] an anion exchange mechanism cannot be ruled out.

In a subsequent study Allen and McDowell[45] used a distribution method involving an organic phase containing di-n-decylammonium sulphate in benzene to obtain formation constants for the anionic species $[Th(SO_4)_3]^{2-}$ and $[Th(SO_4)_4]^{4-}$ in aqueous solution. However, there is certainly no evidence that these anions are involved in the transport of thorium to the organic phase.

More recently, Awwal and Carswell[46] have investigated the extraction of thorium(IV) by secondary amines. These workers have shown that for the two secondary amines studied high extraction is obtained at the lower acid concentrations and that the extraction decreases as the concentration of sulphuric acid is increased. They do not, however, comment on the fact that as the aqueous acid concentration increases the concentration of the amine bisulphate salt in the organic phase also increases. In fact this alone could be responsible for low thorium extraction since it can be assumed that only the amine sulphate salt complexes with the thorium. Awwal and Carswell's results do, of course, favour the adduct formation mechanism since the most favourable extraction occurs under aqueous phase conditions which are least favourable for the formation of anionic thorium species. Their results also suggest that the extracted complex contains three amine sulphate molecules per thorium.

Awwal and Carswell have discussed a possible structure for the complex as consisting of "a thorium atom surrounded by three sulphate groups and a total of six amine molecules". Such a structure is, of course, inconceivable and the complex must surely have the stoichiometric formula $(R_2NH_2)_6 Th(SO_4)_5$, and can be considered to be formed by the reaction of three amine sulphate molecules with the species $Th(SO_4)_2$ from the aqueous phase. Awwal and Carswell also suggest that hydrogen bonding plays a significant role in the attachment of the amine groups. It is well known, of course, that in amine salts (and complexes) there is considerable hydrogen bonding interaction between the protons attached to the quaternary ammonium ion and the associated anion[21,47-49] although the interaction for the complexes is smaller than for the simple amine sulphate and bisulphate salts[48].
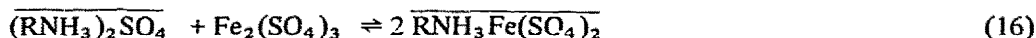
G. THE EXTRACTION OF IRON

The extraction of iron(III) from sulphate media by long-chain alkylamines has been investigated almost exhaustively and the nature of the extracted species seems to be well characterised. In 1955 Baes[50] was the first to investigate the extraction of iron(III) from aqueous sulphate solutions by di-n-decylamine in benzene. He studied the dependence of the distribution ratio for iron(III) on the aqueous iron(III) concentration, the aqueous sulphate concentration, the aqueous sulphuric acid concentration, and on the concentration of the amine in the organic phase. Baes has interpreted his results in terms of the extraction of a partially hydrolysed species, such as $FeOHSO_4$, from the aqueous phase resulting in an adduct of the type $(R_2NH_2)_2 SO_4 FeOHSO_4$ transferring to the organic phase.

Good et al.[51] have studied the extraction of iron(III) using the commercial primary amine Primene 81-R dissolved in chloroform. They have determined the stoichiometry of

the extracted iron(III) species by analysis of the aqueous phases, before and after extraction, for hydrogen ion, total sulphate and iron(III). These studies indicate a net gain in the organic phase of two iron(III) ions for every three sulphate ions, which Good et al. have explained by assuming that the following ion exchange reaction occurs.

$$\overline{(RNH_3)_2SO_4} + 2\ Fe(SO_4)_2^- \rightleftharpoons 2\ \overline{RNH_3Fe(SO_4)_2} + SO_4^{2-} \tag{15}$$
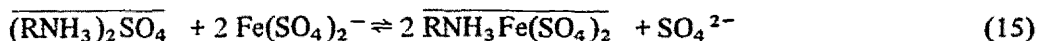
In support of their suggestion that the anionic species $Fe(SO_4)_2^-$ is extracted, Good et al. have measured the spectrum of the organic phase containing the extracted complex. They have shown that this spectrum is similar to that obtained by Whiteker and Davidson[52] for aqueous iron(III) sulphate solutions containing the species $FeSO_4^+$ and $Fe(SO_4)_2^-$. Good et al. point out, however, that although this spectral evidence is suggestive of the presence of the species $Fe(SO_4)_2^-$ in the organic phase, it cannot be taken as absolute proof of its existence. They suggest that the following adduct formation reaction would also be consistent with the extraction data.

$$\overline{(RNH_3)_2SO_4} + Fe_2(SO_4)_3 \rightleftharpoons 2\ \overline{RNH_3Fe(SO_4)_2} \tag{16}$$

In an attempt to resolve the obvious discrepancy between the results of Baes[50] and Good et al.[51], Cattrall and West[37,38] have studied the extraction of iron(III) from aqueous sulphate media by the secondary amine, di(3,5,5-trimethylhexyl)amine dissolved in benzene and chloroform. They approached the problem first by isolating the extracted complex from the organic phase and determining its composition[37]. The preparation of the complex was accomplished by establishing the aqueous phase conditions (pH 2.3) which give rise to the formation of only the amine sulphate salt in the organic phase. Then the organic phase was completely saturated with iron(III) using these aqueous phase conditions by continually extracting aqueous solutions of high iron(III) concentration until no more iron would extract. The solvent was then removed yielding a dark red solid which changed to a yellow colour by absorption of one mole of water on standing in air. This water could be removed by gentle heating. The complex was found to have the stoichiometric formula $(R_2NH_2)_2FeOH(SO_4)_2$, which is the same composition as that proposed by Baes (ref. 50) on the basis of his distribution studies. Cattrall and West suggest that this complex is formed by reaction of the partially hydrolysed species $FeOHSO_4$ or $(FeOHSO_4)_2$ from the aqueous phase with amine sulphate from the organic phase. To support this suggestion they have measured the spectrum of benzene phases containing the extracted complexes and have found some evidence for the presence of the species $FeOH^{2+}$ and $(FeOH)_2^{4+}$. The room-temperature magnetic moments of the isolated complexes ($\mu_{eff} = 3.6-3.8$ B.M.) were found to be anomalously low for Fe^{III} compounds and this has been attributed to magnetic coupling between Fe^{III} ions of a hydroxy-bridged polymer. Cattrall and West have proposed linear trimeric structures for the complex by analogy with Sommer and Pliska's[53] suggestions for the cationic Fe^{III}—acetato polymer. These are shown in Fig. 1. The trimeric formulation seems highly likely since Cattrall and West found that the molecular weight of the compound in benzene indicates a high proportion of a trimeric species.

An alternative configuration for the complex was proposed by Cattrall and West by analogy with the cyclic structures of the basic acetate complex ions of Fe^{3+} and Cr^{3+} which have the formula[54] $[M_3O(CH_3COO)_6L_3]^+$. The cyclic structure is shown in Fig.2.
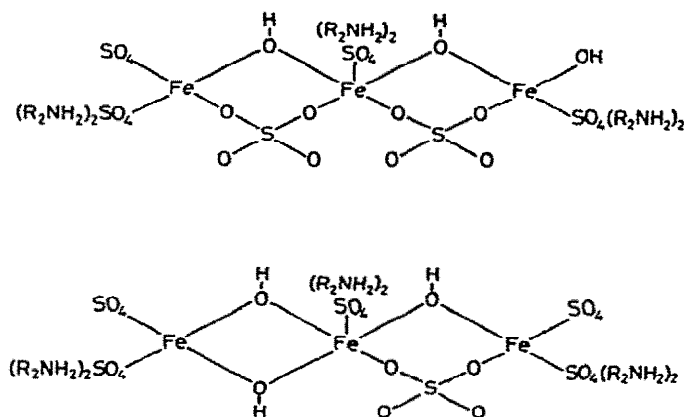
Fig.1. Linear trimeric structures for the iron (III) complex.
R = 3,5,5-trimethylhexyl- (reproduced by permission of the
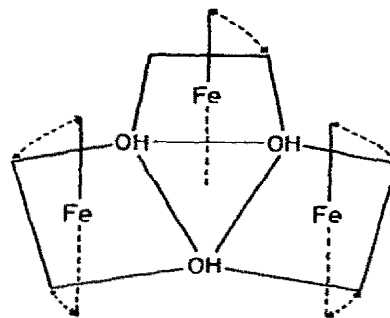Editor, *J. Inorg. Nucl. Chem.*).

Fig.2. A cyclic structure for the iron-
(III) complex (reproduced by per-
mission of the Editor, *J. Inorg. Nucl.
Chem.*).

Cattrall and West have supported their preparative studies by investigating the distri-
bution of iron(III) between aqueous sulphate solutions and solutions of di(3,5,5-trimethyl-
hexyl)ammonium sulphate in benzene and chloroform[38]. The results of these studies
have verified distribution equations which were derived using the assumption that the par-
tially hydrolysed species $FeOHSO_4$ and $(FeOHSO_4)_2$ are extracted. Additional evidence
for the extraction of these species has been obtained from the observation that the distri-
bution coefficient for iron(III) has a direct dependence on the pH of the aqueous phase.
These results, together with the even more convincing evidence of the isolated complex,
strongly suggest that, for the case of secondary amines, the extraction of iron(III) takes
place via an adduct formation reaction and the extracted complex has the general formula
$(R_2NH_2)_2SO_4 FeOHSO_4$.

In order to determine whether this conclusion could also be extended to the extraction
of iron(III) by primary amines, Cattrall and Peverill[39] have investigated the extraction of
iron(III) from aqueous sulphate solutions by 3,5,5-trimethylhexylamine and *n*-dodecyl-
amine dissolved in iso-amyl alcohol, using the same preparative technique as was used by
Cattrall and West for the preparation of the secondary amine complex[37].

Cattrall and Peverill have isolated from the organic phases dark red complexes of the
stoichiometric formula $(RNH_3)_2SO_4 FeOHSO_4$ which were recrystallisable from methanol
or ethanol without change in composition except for the addition of a mole of alcohol.
The magnetic moments, solution spectra, and infrared spectra of these complexes show
that they are completely analogous to the secondary amine sulphate adducts studied by
Cattrall and West[37,38]. In each case the physical measurements are in better agreement
with the existence in the complexes of the dihydroxy bridging unit, $Fe(OH)_2Fe$, than they
are with the existence of the oxo-bridged $Fe-O-Fe$ unit.

Cattrall et al.[55] have carried out temperature-variable magnetic susceptibility studies
on the primary amine sulphate adducts, and on $FeOHSO_4$ itself, in order to obtain more

information on the nature of the bonding within the complexes. They conclude that the basic unit in the adducts is most likely a trinuclear cluster (isosceles triangle) of interacting iron(III) ions which are bridged through hydroxy groups and not through oxy linkages. Thus the configuration shown in Fig.2 is favoured for all the complexes.

Prados and Good[56] have measured the Mössbauer spectra at several temperatures down to 4.2°K of the extracted iron(III) complexes obtained by Cattrall and West[37] using di-(3,5,5-trimethylhexyl)amine, and by Cattrall and Peverill[39] using 3,5,5-trimethylhexyl-amine and n-dodecylamine. The results of this study are consistent with the model proposed by Cattrall et al.[55] on the basis of magnetic measurements. Both the primary and secondary amine compounds give similar Mössbauer parameters and the spectra indicate that the iron(III) sites are equivalent. Consequently, Prados and Good conclude that the equilateral triangular trimer is the most likely structure for these compounds.

In all of the systems studied by Cattrall et al.[37-39], the extraction of iron(III) has been found to take place by an adduct formation mechanism involving the species $FeOHSO_4$ or $(FeOHSO_4)_2$. These workers have found no evidence for the extraction of the anionic species $Fe(SO_4)_2^-$ as proposed by Good et al.[51]. The aqueous phase conditions used by Good et al., however, were slightly different from those employed by Cattrall and Peverill[39] in that they contained a large excess of the sulphate ion. Cattrall and Peverill have suggested that this factor could account for the different stoichiometries determined for the extracted complexes in the two cases.

H. THE EXTRACTION OF SCANDIUM

Cattrall and Slater[40] have studied the extraction of scandium(III) from aqueous sulphate solutions by di(3,5,5-trimethylhexyl)amine in chloroform using similar techniques (aqueous pH 2.3) to those employed by Cattrall and West[37,38]. Preparative studies were carried out and a complex was obtained having the stoichiometric formula $(R_2NH_2)_4ScOH(SO_4)_3$ which absorbed 1 mole of water on exposure to air. This complex can be considered to be formed by reaction of the species $ScOHSO_4$ in the aqueous phase with two molecules of the amine sulphate. The mechanism, of course, would be the adduct formation one in this case. (The species $(ScOHSO_4)_2$ could also be involved in the extraction.) It is not surprising that a hydrolysed scandium species is involved in the extraction since scandium(III) shows considerable tendency (as does iron(III)) to hydrolyse in aqueous solution[57]. The scandium complex is, in fact, different from the iron(III) complexes in that it contains two molecules of amine sulphate per scandium compared with only one for the iron case. In addition the iron(III) complexes tend to associate in solution whereas Cattrall and Slater have found that the scandium complex is monomeric in chloroform solution.

Cattrall and Slater[40] have also carried out distribution studies in conjunction with the preparative studies and this system provides an excellent example of the dangers associated with relying on distribution studies (in particular, slope analysis studies) for determining the stoichiometry of extracted complexes without having a knowledge of such factors as the extent of the association of the reagent and complex in the organic phase.

Cattrall and Slater observed that the exponential dependence of the distribution ratio of scandium on the stoichiometric amine sulphate concentration was close to unity and hence this could lead to the conclusion that one amine sulphate molecule is bound per scandium.This would be, of course, in contradiction with the results of the preparative studies. The problem arises from the fact that the amine sulphate, in this particular case, in chloroform, is not monomeric as is required for a simple slope analysis interpretation. Slater[49] has found that di(3,5,5-trimethylhexyl)ammonium sulphate in chloroform solution follows a monomer—dimer—trimer equilibrium behaviour. The scandium complex on the other hand was found to be monomeric over the concentration range studied. Cattrall and Slater, on using the monomer concentrations of the amine sulphate in chloroform in their treatment of the distribution data, have found a second-order dependence of the distribution ratio on the amine sulphate monomer concentration, which agrees with the stoichiometry found for the complex. These workers also found a first-order dependence of the distribution ratio on the aqueous pH at a constant amine sulphate concentration in the organic phase, which also agrees with the extraction of the hydrolysed species $ScOHSO_4$ from the aqueous phase.

Slater[49] has proposed an interfacial mechanism for the extraction of scandium in this system and this mechanism is similar to the one proposed by McDowell and Coleman[23] for the uranium extraction system and to the one proposed by Cattrall and West[24] for the extraction of iron(III). The model for the mechanism is shown in Fig.3. In this model it is suggested that the highly surface-active amine sulphate salt is concentrated at the interface with the hydrophilic sulphates extending into the aqueous phase and the hydrophobic hydrocarbon chains extending into the organic phase. It is suggested that the sulphate groups remain largely undissociated at the interface and take part in direct complexation with metal-containing species in the aqueous phase. The resulting complex then diffuses away from the interface into the bulk organic phase (where it possibly reacts with a second amine sulphate molecule). This model seems most attractive for systems involving amine salts which are highly surface-active.
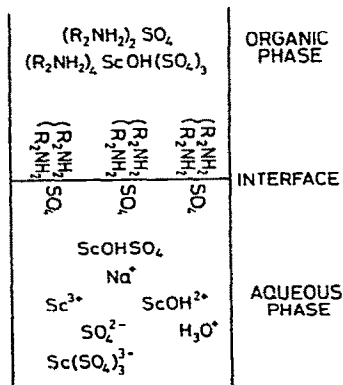

Fig.3. The proposed interfacial mechanism for the extraction of scandium(III). R = 3,5,5-trimethyl-hexyl.

The extraction of scandium from aqueous sulphate solutions has also been investigated by Shevchuk et al.[58], who studied the extraction of scandium by the primary amine, n-dodecylamine. These workers have proposed the following anion exchange reaction to account for their results.

$$\overline{(RNH_3)_2SO_4} + Sc(SO_4)_2{}^{3-} \rightleftharpoons \overline{(RNH_3)_3Sc(SO_4)_3} + 3\,SO_4{}^{2-} \tag{17}$$
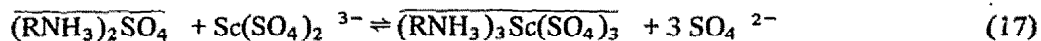
Complex anionic scandium species of the type shown in eqn. (17) are known to exist in aqueous solution[58-60]. However, most of the work done by these workers was on the extraction of lanthanum and it seems as if the scandium extraction mechanism was proposed mostly by analogy with the lanthanum system.

Slater[49] has made a preliminary study of the extraction of scandium with primary amines (n-dodecylamine and 3,5,5-trimethylhexyl-amine) and his results are more in agreement with the adduct formation mechanism proposed for the secondary amine system involving the species $ScOHSO_4$.

Another study on the extraction of scandium from aqueous sulphuric acid solutions has been carried out by Smirnov et al.[61], who used a series of amines dissolved in kerosene. Although these workers did not propose a mechanism for the extraction, they found that when scandium was extracted from a 1 M sulphuric acid solution, a complex was formed in the organic phase which contained six amine groups per scandium.

I. THE EXTRACTION OF RUTHENIUM

Shanker et al.[62] have studied the extraction of ruthenium(III) from aqueous sulphate solutions with a selection of primary, secondary and tertiary amines. However, the way in which these workers have interpreted their results does not contribute anything of significance to the understanding of the mechanism involved in the extraction. They have assumed at the outset that the extraction must occur according to the following equation without any regard to the possibility that an adduct formation mechanism may be involved.

$$\overline{(R_3NH)_2SO_4} + 2\,Ru(SO_4)_2{}^- \rightleftharpoons \overline{R_3NHRu(SO_4)_2} + SO_4{}^{2-} \tag{18}$$
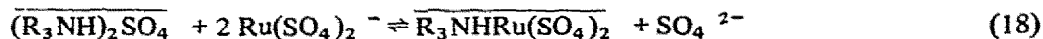
Consequently these workers have anticipated that the dependence of the distribution ratio on the amine concentration in the organic phase must be half-order. It should also be pointed out that they have neglected to take into account the amine bisulphate salt, which would undoubtedly be present in the organic phase under the conditions they used, and it has already been shown that this salt does not take place in the direct complexation reaction. In addition they have attempted to explain the high values for their slopes of 2 log D vs. the logarithm of the amine concentration curves as being due to aggregation in the organic phase and suggest that this "anomalous" behaviour is also observed in other systems such as the extraction of uranium from sulphate solutions. However, their results are the reverse of those observed in the uranium system, where lower values for the slopes are obtained for the distribution studies when loading studies predict higher values. The

results obtained for this ruthenium extraction system may well be better explained on the basis of an adduct formation mechanism (as for iron(III)) than by the anion exchange reaction proposed.

J. THE EXTRACTION OF HAFNIUM, YTTRIUM, LANTHANUM AND EUROPIUM

Limited studies have been carried out on the extraction of hafnium, yttrium, lanthanum and europium from sulphate solutions by amines.

· Aly et al.[63] have studied the extraction of hafnium(IV) from acidic aqueous sulphate solutions using the commercial tertiary amine, alamine-336 (principally tri-n-octyl and tri-n-decyl) in kerosene solution. These workers report a decrease in extraction of hafnium with increase in aqueous phase acidity and also report a second-order dependence of the distribution ratio on the amine concentration. From these results and from the results of varying the aqueous sulphate ion concentration they conclude that at low sulphate ion concentration the complex in the organic phase has the composition $(R_3NH)_2Hf(OH)_4SO_4$ and at high sulphate ion concentration the composition is $(R_3NH)_2Hf(OH)_2(SO_4)_2$. It should be pointed out, however, that from the limited number of experiments carried out in this work it is very difficult to agree categorically that the above complexes do actually form in the organic phase. These workers have not considered the presence of the amine bisulphate salt in the organic phase and the effect that this salt may have on the system, and they have not considered any aggregation reactions which may occur in the organic phase.

Slater[49] has carried out a preliminary study of the extraction of yttrium, lanthanum and europium from acidic aqueous sulphate solutions with n-dodecylamine and di(3,5,5-trimethylhexyl)amine in chloroform. He has found that these three elements are very poorly extracted by these two amines, which should be compared with the quite high extraction found for scandium for the same amines. In fact, negligible extraction occurred for yttrium, lanthanum and europium under identical conditions used for the extraction of scandium. This result, of course, suggests that these two amines, particularly di(3,5,5-trimethylhexyl)amine, may be very useful extractants for the separation of scandium from the rare earth elements. Additional work on the extraction of yttrium suggests that the complex formed is very similar to that found for scandium, viz. $(R_2NH_2)_4YOH(SO_4)_3$.

It can be seen from the systems discussed in this review that considerable work has been carried out on the elucidation of the mechanisms involved in the extraction of metal ions from aqueous sulphate media by amines. However, in many cases a number of uncertainties remain and it appears that this field of research can still provide a rewarding area for future work.

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