THE EXTRACTION OF IRON(III) BY HIGH MOLECULAR WEIGHT ALKYLAMINES

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CONTENTS

SUMMARY

The Extraction of Iron(III)
by High Molecular Weight Alkylamines

The work described in this thesis has been divided into five chapters. In Chapter I a general review has been presented on the most recent applicationsof solvent extraction to inorganic chemistry.

The work described in the remaining four chapters is an investigation of the extraction of sulphuric acid and ferric iron from aqueous sulphate solutions by the secondary and tertiary amines di- and tri(3,5,5,trimethylhexyl)amines dissolved in various organic solvents.

In Chapter II the extraction of sulphuric acid by the secondary and tertiary amines dissolved in iso-amyl alcohol has been discussed, and it has been shown that in the absence of micelle formation of the amine salts in this solvent the extraction obeys a simple equilibrium law. Also high values for the equilibrium constants for the formation of the amine sulphate and bisulphate have been found, which is expected for a high dielectric constant solvent.

The extraction of Fe(III) from aqueous sulphate solutions by di(3,5,5,trimethylhexyl)amine dissolved in benzene and chloroform has been described in Chapter III and

it has been shown that when using solutions (chloroform) in which there is no micelle formation of the amine salts the extraction can be described by an equation based on the assumption that it is a partially hydrolysed species such as $FeOHSO_4$ or $(FeOHSO_4)_2$ which is extracted from the aqueous phase. However, when using benzene solutions, in which the amine sulphate forms micelles, systematic deviations from the predicted behaviour are obtained.

It has also been shown that the extraction occurs by adduct formation of the amine sulphate with the species $FeOHSO_4$ or $(FeOHSO_4)_2$ (or both) from the aqueous phase to give a complex in the organic phase which has the stoichiometric formula $(R_2NH_2)_2FeOH(SO_4)_2$, where R is 3,5,5,trimethylhexyl. The presence of the species $FeOH^{+2}$ and possibly $(FeOH)_2^{+4}$ have been identified in the isolated complex by ultra-violet spectroscopy, although infra-red spectroscopy failed to do this. Two possible structures have been proposed for the complex, firstly, a chain-like or linear structure, and, secondly, a cyclic trimeric structure. The former is preferred in view of certain spectroscopic evidence.

In Chapter IV the phenomenon of micelle formation of di(3,5,5,trimethylhexyl)ammonium sulphate has been studied in various organic solvents by the techniques of light scattering, isopiestic molecular weight measurements, and viscometry, in an attempt to relate this with the nature of the solvent for the amine sulphate. It has been shown that micelle formation occurs in non-polar or weakly polar solvents which have negligible hydrogen bonding ability. It has been suggested that the micellar particle is an inverted Hartley micelle with the non-polar alkyl chains on the outside and the polar groups and the associated water on the inside of a roughly spherical configuration, which is stabilized by inter-molecular hydrogen bonding.

The effect of the solvent for the amine on the extraction of Fe(III) has been discussed in Chapter V and has been shown to depend on several factors. Also an interface mechanism for the extraction has been proposed on the basis of the surface-active properties of the amine salts.

To the best of the author's knowledge this thesis contains no material which has been published by other persons or submitted for a degree in any University by the author or other persons, except where due reference is made in the text.

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Chapter I

GENERAL REVIEW

SOLVENT EXTRACTION IN INORGANIC CHEMISTRY

Solvent extraction has become increasingly important in recent years in inorganic chemistry, particularly in the analytical, and process chemistry fields. This application of solvent extraction to inorganic systems has been reviewed by several authors[1-6]. The classification of solvent extraction systems is purely arbitrary, however, some order can be given to a discussion of such systems by considering the reactions involved.

Diamond and Tuck[5], and Marcus[6] in the most recent reviews on solvent extraction in inorganic chemistry have classified extraction systems in this way. These authors point out that in any classification system there will be examples which will fit simultaneously into more than one category, and, in fact, there will probably be gradual transitions from one mode of behaviour to another.

Extraction systems can be divided into two very broad classes. The first of these describes the simplest of all solvent extraction systems in which a third substance distributes itself between two immiscible liquids without a chemical reaction occurring in either phase. Berthelot in

1872[7] first described this simplest type of extraction system by stating that when a third substance is present in a system of two immiscible liquids it distributes itself between them in a definite manner if it is soluble in both of them. This led to the simplest form of the Nernst distribution or partition law[8], which states that if c_1 and c_2 are the concentrations of the solute in phases 1 and 2 at equilibrium at constant temperature then

$$\frac{c_1}{c_2} = \text{constant (the distribution or partition coefficient)} \qquad (1.1)$$

It will be as well to distinguish here between the terms used in the study of solvent extraction systems. The derivation of the thermodynamic quantity, which is the distribution or partition coefficient or constant, has been described by Morrison and Freiser[3], and Diamond and Tuck[5]. It is necessary to repeat this derivation in order to understand the nature of the approximations involved in the distribution law, and the limitations of the experimentally determined quantity, which is termed the distribution ratio.

At equilibrium at constant temperature and pressure, the chemical potentials μ_1 and μ_2 (partial molal free energies) of the solute in each phase are equal, provided the chemical nature of the solute species is the same in both phases.

$$\mu_1 = \mu_2 \tag{1.2}$$

but $$\mu = \mu^{o} + R.T.\ln a \tag{1.3}$$

where μ^{o} is the chemical potential in the standard state (usually taken as a hypothetically ideal 1 molal solution), and "a" is the activity of the solute.

Thus $$\mu_1^{o} + R.T.\ln a_1 = \mu_2^{o} + R.T.\ln a_2 \tag{1.4}$$

and rearranging $$\frac{a_1}{a_2} = e^{-(\mu_2^{o} - \mu_1^{o})/R.T.} \tag{1.5}$$

but since $$\frac{a_1}{a_2} = \frac{m_1 \cdot \gamma_1}{m_2 \cdot \gamma_2} \tag{1.6}$$

where m_1 and m_2 are the molalities of the solute in phases 1 and 2 respectively, and γ_1 and γ_2 are the corresponding molal activity coefficients.

Hence $$\frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} \cdot e^{-(\mu_2^{o} - \mu_1^{o})/R.T.} \tag{1.7}$$

In equation (1.7) the exponential term is a constant provided the presence of the solute does not significantly affect the mutual solubilities of the two solvents.

Thus we can write K_D the distribution coefficient as

$$K_D = \frac{m_2}{m_1} = K' . \frac{\gamma_2}{\gamma_1} \qquad (1.8)$$

where K' is a constant for the system at constant temperature.

From equation (1.8) it can be seen that the distribution coefficient K_D is dependent on the activity coefficients of the solute in each of the phases, and as the activity coefficients approach unity, at low concentrations, the value of K_D becomes constant.

The quantity which is usually determined in extraction experiments is the distribution ratio D which is defined as

$$D = \frac{\text{Total concentration in the organic phase}}{\text{Total concentration in the aqueous phase}} \qquad (1.9)$$

The expression for D includes all species of the same component in the respective phases, including those which do not extract. If the conditions were ideal, with no interactions in either phase, then D would be equal to K_D, however, this is seldom encountered in the usual solvent extraction systems.

The usefulness of the experimentally determined distribution ratio is demonstrated in Chapter 3 of this thesis.

Probably the best known example of the first class of extraction systems, which describe a simple physical distribution based on relative solubilities, in inorganic chemistry is the distribution of molecular iodine between water and carbon tetrachloride[9-11]. The distributions of the other halogens and interhalogen complexes have also been widely studied[12-16].

Other examples of the distribution of inorganic molecules between water and an inert organic solvent are the distribution of mercuric halides between benzene and water[17], and the distribution of simple halides of arsenic and germanium between aqueous hydrohalic acid solutions and various inert organic solvents[18,19].

The extraction of osmium tetroxide into carbon tetrachloride has also been studied[20], and it was first considered by Anderson and Yost[20] that a tetramer was formed in the organic phase. Martin[21], however, found no evidence for polymeric osmium tetroxide species. This system can therefore be considered to belong to the first class of extraction systems.

A rather unique example of this class of extraction systems is the extraction of metallic mercury into non-polar solvents such as n-hexane and cyclohexane. Moser and Voigt[22] have studied the dismutation of the mercurous dimer in extremely dilute nitric acid solutions, into mercuric ions and free mercury, by the distribution method. Free mercury was found to be soluble to a limited extent in non-polar solvents, more soluble, in fact, than in aqueous solutions, and so the use of the distribution technique was possible.

The second very broad class of extraction systems in inorganic chemistry describes those in which there is a reaction, other than straight out physical solubility, of one form or another in one or both of the phases. This reaction may be merely solvation of a species from the aqueous phase by the organic solvent, or may be the reaction of a metal ion with a chelating agent to form a chelate complex. This class of extraction systems is by far the larger and more important of the two. Almost all examples of extraction systems in modern analytical or process chemistry will appear under this category. There are, of course, many ways in which reactions can occur in extraction systems, and so, this second class can be divided into several sub-classes.

In a discussion of these sub-classes it is proposed to mention each sub-class and give an example or two of each, and then to discuss in more detail the sub-class dealing with the basic extractants, the high molecular weight amines, with which this thesis is most concerned.

The first of these sub-classes describes the classical extraction systems in which organic chelating agents such as acetylacetone or 8-hydroxyquinoline dissolved in organic solvents are shaken with an aqueous solution of the metal to be extracted. A certain amount of the chelating agent passes into the aqueous phase and reacts with the metal ions, thus satisfying the coordination number of the metal, and gaining electrical neutrality. The neutral complex, being soluble in organic solvents, then distributes itself between the organic and aqueous phases. This type of chelate system is very important in analytical chemistry since it enables quantitative extraction of the metal, and by choosing the correct conditions for the aqueous phase, enables the separation of one metal from another depending on the relative stabilities of their complexes. Examples of this type of system are the extraction of ferric iron by chloroform solutions of acetylacetone[23], and 8-hydroxyquinoline[24]. A reagent which has acquired considerable importance recently is thenoyltrifluoroacetone, and has been used successfully for the extraction of zirconium[25].

The second sub-class of extraction systems includes those in which there is solvation, by the solvent, of a species from the aqueous phase. It is possibly necessary at this stage to point out the difference in the terms "solvent" and "diluent" used in the current literature on solvent extraction chemistry. The term "solvent" is applied to a liquid which actually reacts with a species contained initially in the aqueous phase. The "solvent" may thus be the organic phase itself or may be dissolved in an inert organic liquid to form the organic phase. The inert organic liquid is usually termed the "diluent". The use of the term "diluent" is readily accepted in the process chemistry field, but is not used as frequently in the literature dealing with the fundamental chemistry of solvent extraction systems. Throughout this thesis, therefore, where reference has been made to the "solvents" for the amine or amines, this means the "diluents" for the amine or amines in the sense used in the solvent extraction literature.

Probably the best known example of extraction occurring by solvation is the extraction of ferric iron from chloride solutions by ethers[26-28]. The species extracted is now accepted to be the solvated complex iron (III) acid $HFeCl_4$. In actual fact it is the proton in this type of complex acid which is solvated and possibly hydrated, and there is no primary solvation of the metal ion which is tetrahedrally surrounded by chloride ions. The species in the organic phase can probably be considered to be $(R_2OH^+)(FeCl_4^-)$. As well as their ability to extract complex metal acids like $HFeCl_4$ by solvation, this type of solvent can also extract strong mineral acids. Nitric acid is strongly extracted by ethers, probably as the complex $(R_2OH^+)(NO_3^-)$[29]. It is generally accepted that the actual mechanism of the solvation of the acidic proton involves hydrogen bonding.

It is interesting to note that sulphuric acid does not extract into ethers, ketones, or esters, but will extract into alcohols[30,31,32]. Sulphuric acid is known to have a strong primary hydration in aqueous solution arising from the presence of 2 oxy- and 2 hydroxyl-groups which can hydrogen bond water molecules very strongly. Extraction of sulphuric acid into alcohols, thus occurs not by solvation of the acid protons but by solvation of the anion.

Included in this class of solvating agents are the relatively new and extremely important neutral phosphorus compounds. Probably the most widely studied of these being tri-n-butyl phosphate. Tri-n-butyl phosphate was found to extract nitric acid as the complex ($TBP.HNO_3$)[33], with the proton of the acid strongly associated with the anion, and the whole molecule being solvated. The bonding mechanism is probably again a hydrogen bonding one between the phosphoryl oxygen atom and the acidic proton of the acid. In fact, the reaction to form the solvated complex is considered to occur by replacement of a molecule of water attached to the TBP molecule by a molecule of nitric acid from the aqueous phase. With very strong acids, such as perchloric, hydrochloric, and sulphuric acids, the extraction by TBP is thought to give complexes of the type $H(H_2O)_4^+.A^-.(TBP)$[33,34]. Other neutral phosphorus compounds, including the esters of phosphoric acid, phosphinic acid, and phosphonic acid, and the substituted phosphine oxides, have all been investigated in various extraction systems.

Another very important property of this class of solvating solvents is their ability to directly solvate metal ions. The extraction of salts by primary solvation of the cation does not necessitate the complexing of the metal by the anion as in the extraction of $HFeCl_4$. For example the perchlorate salts of metals such as cobalt and nickel[35] can be effectively extracted from aqueous solutions by long chain water insoluble alcohols.

The neutral phosphorus compounds are also well known for their ability to extract metal salts from aqueous solutions. Madigan and Cattrall[36] have studied the extraction of thorium (IV) from aqueous nitrate solutions by dibutylbutylphosphonate and have found evidence for the extraction of a tri-solvate of the type $\left[Th^{+4}(NO_3)_3.3DBP\right]^+NO_3^-$. Solvation of the metal ion is thought to occur by donation of the pair of electrons from the phosphoryl oxygen atom.

It is generally accepted that extraction of metal salts by the neutral phosphorus compounds occurs by direct coordination of the compounds to the metal ion by donation of the pair of electrons on the phosphoryl oxygen atom. It is, however, also possible that certain complex metal acids may be extracted by solvation of the proton of the acid by the neutral phosphorus compound. An example of this is the extraction of cobalt (II) from concentrated hydrochloric acid by tri-n-butyl phosphate[37], where the extracted complex is thought to be $(TBPH^{+1})_2.CoCl_4^{-2}$.

The third sub-class of extraction systems includes those compounds which are often referred to as the "liquid ion-exchangers", due to their similarity in behaviour to the ion-exchange resins. Probably the best known liquid cation exchangers are the acidic esters of phosphoric acid, an example of which is the di-ester, di(2-ethylhexyl) phosphoric acid. Compounds of this type are almost insoluble in water but quite soluble in organic solvents, and most important have the ability to extract metal ions from aqueous solutions. They are thus ideally suited to solvent extraction systems, and have been widely used in process chemistry, especially in the atomic energy field for the recovery of valuable constituents from irradiated fuel elements.

Di(2-ethylhexyl)phosphoric acid was found to be extremely useful for the extraction of beryllium from aqueous sulphate solutions obtained during the processing of the mineral beryl[38]. The extraction of metal ions from aqueous solutions is considered to occur by the release of a proton to the aqueous phase from the phosphoric acid ester, and by donation of the pair of electrons from the phosphoryl oxygen atom to the metal, to form neutral complexes of the type $(R_2PO_4)_2Be$. The term "liquid cation exchangers" was applied to this type of reagent since it was found possible to replace one metal ion by another depending on the stability of the complex formed with the alkylphosphoric acid. The order of replacement was found to be similar to that of cation exchange resins. This difference in stability of the complex formed in going from one metal to another was demonstrated by Madigan[39], who suggested that a separation of copper, cobalt, and nickel, from sulphate solutions, was possible using di(2-ethylhexyl) phosphoric acid by choosing the correct conditions for the aqueous phase.

The "liquid anion exchangers" have been investigated very extensively recently, and include compounds such as the primary, secondary, and tertiary long chain alkylamines, the arylamines, and the alkyl and aryl derivatives of the ammonium, phosphonium, and arsonium ions. The alkyl and aryl derivatives of the ammonium, phosphonium, and arsonium ions have been fully discussed by Diamond and Tuck[5]. Large cations such as the tetraphenyl-ammonium, phosphonium, and arsonium ions have the ability to extract large anions from aqueous solutions as coordinately unsolvated salts or ion pairs. Reagents of this type have been used to some extent in analytical chemistry. Tribalat[40,41] has extracted tetraphenylphosphonium chloride and perrhenate with chloroform. Ziegler[42] has extracted halide complexes of silver and copper by the addition of tributylammonium chloride to the aqueous phase, and by extracting the ion pair formed with an organic solvent. Ziegler[43-45] has also used several other large cations such as the tripropylammonium, hexadecyltrimethylammonium, and tetrabutylammonium ions for the extraction of anions such as chromates, permanganates, chloroplatinates, chloropalladates, rhenates, thiomolybdates, vanadates, and ferro- and ferricyanides.

The use of high molecular weight amines in solvent extraction systems has developed rapidly over the last decade and again, as with the organic phosphorus compounds, the majority of the work in this field has been done by process chemistry laboratories associated with the various atomic energy authorities.

The similarity of the organic amine salts to anion exchange resins was suggested initially by Smith and Page[46], who suggested the possibility of their use for the extraction of complex metal anions from aqueous solutions. Since this initial publication on the solvent extraction properties of organic amines, many papers have appeared in the literature describing the use of amines for the extraction of metals from aqueous solution, and the subject has been reviewed thoroughly by several authors[47-53].

The high molecular weight amines and their salts, generally, are almost insoluble in water and very soluble in organic solvents, and so lend themselves ideally to solvent extraction systems. The free amines themselves have been used extensively for the extraction of acids from aqueous solutions. However, whilst the free amines are usually added initially to extraction systems for the extraction of metal species, it is generally accepted that they are first converted to their salts, and that these species are responsible for the extraction of the metal. This type of system can, therefore, only operate in acid solutions.

It should be mentioned that the fully alkyl substituted quaternary ammonium salts $R_4N^+X^-$ have been investigated to some extent, and have the advantage that they can be used in high pH solutions in the region where the ordinary amine salts would hydrolyse.

Primary, secondary, and tertiary alkyl- and aryl-amines have all been used in extraction systems, and results have shown that the nature of the amine, and the organic "diluent" used for the amine, exert a profound influence on the extraction. Metals such as iron (III), vanadium (III), the rare earths, titanium, zirconium, thorium, and uranium (IV) are effectively extracted from sulphate solutions by primary amines, but the extraction decreases with change to secondary and tertiary amines. On the other hand the extraction of vanadium (V), molybdenum (VI), and uranium (VI) tends to increase from primary to secondary and to tertiary amines. With chloride and nitrate solutions, generally, tertiary amines show greater extractions than secondary or primary amines, and fluoride and phosphate solutions were found to behave more like sulphate solutions.

For the long chain alkylamines the length and nature of the alkyl chain appears to have a significant effect on the extraction by the amine. Generally a branched chain secondary amine behaves more like a straight chain tertiary than like a straight chain secondary amine, and a highly branched alkyl chain interferes seriously with the extraction possibly by a steric hindrance effect.

The "diluent" for the amine also has a great influence on the extraction, depending on the compatibility of the amine salts with the "diluent". Some amine salts are less soluble in certain solvents than in others, and show a decreasing solubility in the order sulphate, bisulphate, chloride, and nitrate, and in the order tertiary, secondary, and primary ammonium salt. The amine salts appear to be more soluble in long chain alcohols than in hydrocarbon type solvents, and so in cases where difficulty has been obtained in keeping the amine salts in solution, small quantities of a long chain alcohol have been added to the organic phase. The presence of this long chain alcohol, however, in the organic phase was found to decrease the extraction. In certain "diluents" the amine salts tend to form molecular aggregates or micelles, and this also has a detrimental effect on the extraction.

The extraction of metals from aqueous solutions by the high molecular weight amines is also very dependent on the nature of the aqueous phase, which must of course contain extractable metal species. The aqueous phase must also be acidic, as mentioned before, since it is assumed that initially acid is extracted to form simple amine salts which subsequently react with metal species from the aqueous phase. Since the amines are weak bases their salts are fairly readily hydrolysed, and can be converted back to the free amine form simply by shaking a solution of the salt with a high pH aqueous phase. This has been found to be very useful in process work for the recovery of the extracted metal from the organic phase, since by simply shaking an organic solution of the extracted metal compound with an aqueous solution of sodium hydroxide or sodium carbonate, the metal can be re-extracted from the organic phase. This re-extraction from the organic phase can also be accomplished by shaking the organic phase with an aqueous phase containing a high ionic strength of a simple anion. The complex metal anion is then replaced by the simple anion in an anion exchange reaction.

The reactions involved in the extractions by all three classes of amines are simply described by Coleman *et al.*[48]. The first reaction to occur is the extraction of acid from the aqueous phase.

$$R_3N_o + HX_A \rightleftharpoons R_3NHX_o \qquad (1.10)$$

where R_3N is any tertiary amine, and HX is a monobasic acid. Subscripts "o" and "A" refer to the organic and aqueous phases respectively.
With a dibasic acid such as sulphuric acid, the normal amine sulphate is formed together with the acidic amine bisulphate salt.

One anion is then readily exchanged for another from the aqueous phase as shown in equation (1.11)

$$R_3NHX_o + Y_A \rightleftharpoons R_3NHY_o + X_A \qquad (1.11)$$

where Y_A is another anion from the aqueous phase. For the simple anions the order of preference in the amine solutions is perchlorate > nitrate > chloride > bisulphate > fluoride, which is similar to that in anion exchange resins. The anion Y_A can also be a complex metal anion such as $UO_2(SO_4)_2^{-2}$. This reaction for the extraction of metals from the aqueous phase implies the transport of an anionic species across the interface.

Moore[47] suggests that the acid HX can also be a complex metal acid such as $HFeCl_4$, the species formed in the organic phase would then be $(R_3NH^+)(FeCl_4^-)$. This reaction, however, cannot be separated from the two stage reaction where hydrochloric acid is extracted initially to form the amine hydrochloride, followed by the ion exchange replacement of chloride for the complex metal anion $FeCl_4^{-1}$.

According to Coleman <u>et al</u>.[48,53] there is yet a further possible reaction for the extraction of metals from aqueous solutions by amines, that of adduct formation, which implies the transport of a neutral species across the interface. It is proposed at this stage to disregard the extraction of a complex metal acid, as suggested by Moore[47], as a separate reaction for metal extraction, since although it has some merit when dealing with the free amine in the organic phase, it seems unlikely that it would occur in the usual extraction systems where the amine is reacted with acid beforehand, and is actually introduced into the system as the amine salt.

There are thus two possible reactions to be discussed for metal extraction by amines, that of anion exchange, and that of adduct formation, which according to Coleman[53], although they may sound drastically different, represent only an arbitrary choice of description for equilibrium extractions, as the alternative equations are thermodynamically equivalent. There is, however, an important distinction between the two extraction reactions, which Coleman has overlooked, and this is the fact that extraction can occur in the absence of any complex metal anionic species in the aqueous phase, providing that the metal, in the form of the neutral species, is not fully coordinated in the aqueous phase. Previously it had been suggested that for an efficient extraction to occur it was necessary to choose the conditions of the aqueous phase so that there were extractable complex metal anionic species present.

In actual practice in any equilibrium study the two reactions would be indistinguishable, and would lead to the formation of the same metal complex in the organic phase.

Coleman *et al.*[48], as examples of the two reactions, have described the extraction of uranium (VI) from sulphate solutions as occurring by either the replacement of a sulphate ion from the organic phase by a complex anionic uranium species such as $UO_2(SO_4)_2^{-2}$ as mentioned before, or by the direct reaction of an amine sulphate species from the organic phase with a neutral uranyl sulphate species such as UO_2SO_4 from the aqueous phase. These two reactions are shown in the following equations.

$$UO^{+2}_{2_A} + SO^{-2}_{4_A} \rightleftharpoons UO_2SO_{4_A} \qquad (1.12)$$

Equation (1.12) describes the formation of undissociated uranyl sulphate in the aqueous phase.

$$UO_2SO_{4_A} + (R_3NH)_2SO_{4_o} \rightleftharpoons (R_3NH)_2UO_2\ (SO_4)_{2_o} \qquad (1.13)$$

Equation (1.13) describes the reaction of undissociated uranyl sulphate in the aqueous phase with amine sulphate in the organic phase.

The alternative reaction is shown in the following equations.

$$UO_{2_A}^{+2} + 2SO_{4_A}^{-2} \rightleftharpoons UO_2(SO_4)_{2_A}^{-2} \qquad (1.14)$$

Equation (1.14) describes the formation of the complex metal anion in the aqueous phase.

$$(R_3NH)_2SO_{4_o} + UO_2(SO_4)_{2_A}^{-2} \rightleftharpoons (R_3NH)_2\ UO_2(SO_4)_{2_o} + SO_{4_A}^{-2} \qquad (1.15)$$

The simple anion exchange reaction is shown in equation (1.15).

McDowell and Case[54] have attempted to determine whether or not the extraction is a simple anion exchange one by the introduction of labelled sulphate into the organic phase. These workers obtained no evidence for the transfer of an anionic uranium species across the interface, and have suggested that the extraction occurs via a neutral or even a cationic uranium species from the aqueous phase. It should be pointed out also that McDowell and Case postulated an interface mechanism for the extraction as opposed to the usually accepted extraction mechanism of the reaction actually occurring within one or other of the two phases, followed by transference of the complex across the interface. This interface mechanism has some merit in view of the surface-active properties of the long chain amines and their salts. It would be extremely difficult, however, to distinguish between the two mechanisms.

There is quite a large amount of evidence in the literature for the extraction of anionic species from aqueous solutions, but it should be borne in mind that it may still be possible, in many cases, to postulate the extraction of a neutral species as McDowell and Case have for uranium (VI), and obtain a complex in the organic phase identical to that obtained by any anion exchange reaction.

It is not proposed to make a complete survey of the literature on the extraction by amines, since this has been done very thoroughly in the several reviews[47-53], which adequately describe the work reported up until 1961. It is proposed, however, to discuss several papers which have been published recently, which give support to both extraction theories.

Good _et al._[55-59] have published an interesting series of papers in which they explain their results on the basis of the ion-exchange reaction. Good and Bryan[55,56] have studied the extraction of iron (III) and cobalt (II) from chloride solutions by various amines dissolved in various "diluents" and have examined, spectrophotometrically, the organic solutions obtained. The results of this work suggested the presence of the anionic species $FeCl_4^{-1}$ and $CoCl_4^{-2}$ in the organic solutions, and Good and Bryan concluded that these anionic species must be involved in the extraction process. The reactions are described by the following equations.

$$R_3NH^{+1}Cl^{-1}_{o} + FeCl^{-1}_{4_A} \rightleftharpoons R_3NH^{+1}FeCl^{-1}_{4_o} + Cl^{-1}_{A} \qquad (1.16)$$

$$2R_3NH^{+1}Cl^{-1}_{o} + CoCl^{-2}_{4_A} \rightleftharpoons (R_3NH^{+1})_2CoCl^{-2}_{4_o} + 2Cl^{-1}_{A} \qquad (1.17)$$

Good and Bryan also suggest that an alternative reaction for the extraction of iron(III) from chloride solutions could be written by assuming that the extracted species is actually the complex metal acid as shown in equation (1.18). This reaction can probably be disregarded, however, as has been discussed previously, since Good and Bryan converted their amines to the amine salts before the extraction of the metals.

$$R_3N_{o} + H^{+}_{A} + FeCl^{-1}_{4_A} \rightleftharpoons R_3NH^{+}FeCl^{-1}_{4_o} \qquad (1.18)$$

Good and Bryan[57] have also investigated the extraction of the oxalate complexes of iron(III), nickel (II), and cobalt (II), by various amines in chloroform as "diluent", and have found evidence for the presence of the complex anions

$[Fe^{+3}(C_2O_4)_3]^{-3}$, $[Co^{+3}(C_2O_4)_3]^{-3}$, $[Ni^{+2}(C_2O_4)_2]^{-2}$, and

$[Co^{+2}(C_2O_4)_2]^{-2}$

in the organic phase. The anion exchange reaction proposed by these workers is shown in equation (1.19).

$$nR_3NH^+A^-_o + \left[M^{+n}(C_2O_4)_n\right]^{-n}_A \rightleftharpoons \left[R_3NH^+\right]_n \left[M^{+n}(C_2O_4)_n\right]^{-n}_o + nA^-_A \qquad (1.19)$$

where n = 2 or 3, and A^- is the anion of the amine salt present in the organic phase prior to extraction, since the amine solutions were reacted with various acids before the extraction experiments.

In asimilar series of experiments, Good, Bryan and Maus[58] studied the extraction of the cyanide complexes of iron (II), iron (III), cobalt (III), and cobalt (II), and again found evidence for the presence of the anionic cyanide complexes in the organic phases. The proposed anion exchange reaction is shown in equation (1.20).

$$yR_3NH^+A^-_o + M(CN)^{-y}_{x_A} \rightleftharpoons \left[R_3NH^+\right]_y \left[M(CN)_x\right]^{-y}_o + yA^-_A \qquad (1.20)$$

The anion exchange reaction is also postulated by Good, Bryan and Juge[59] for the extraction of iron (III) from sulphate solutions by a primary amine, since there is spectral evidence for the presence of the species $Fe(SO_4)_2^{-1}$ in the organic phase.

The results obtained by Good and Bryan[54,55] for the extraction of the chloride complexes of iron(III) and cobalt (II) are further supported by an investigation carried out by Lindenbaum and Boyd[60] who studied the extraction of iron(III), cobalt (II), copper (II), manganese (II), and nickel (II), from aqueous chloride and bromide solutions by tri-*n*-octylamine and tri-iso-octylamine dissolved in toluene. A spectrophotometric study of the organic phases demonstrated the presence of the tetrahedrally coordinated species $(M^{+3}X_4)^{-1}$ and $(M^{+2}X_4)^{-2}$.

White, Kelly and Li[61] on the other hand suggest that for the extraction of iron(III), and indium (III) from chloride solutions by tri-*n*-octylamine dissolved in benzene the anionic species present in the organic phase are $FeCl_5^{-2}$ and $InCl_5^{-2}$. Their results, however, were not based on a spectrophotometric study, but were obtained from a study of the dependence of the distribution ratio on the amine hydrochloride concentration. They obtained a second power dependence of the distribution ratio on the amine hydrochloride concentration in the organic phase, and suggested that this was evidence for the presenceof a doubly charged anion in the organic phase such as MCl_5^{-2}.

The extraction of uranium (VI) has been studied extensively, and a recent series of papers by Sato[62-65] have shown that the extraction of this element from sulphate solutions by various amines in various "diluents" is not quite as simple as postulated by Coleman <u>et al.</u>[48]. Sato has found that for the several amines studied the species formed in the organic phase is generally the same, with two amine sulphate molecules associated with each uranium. The generalised extraction reaction, as suggested by Sato, is shown in the following equation.

$$2(R_3NH)_2SO_{4_o} + UO_2SO_{4_A} \rightleftharpoons (R_3NH)_4UO_2(SO_4)_{3_o} \qquad (1.21)$$

Equation (1.21) thus represents the adduct formation reaction, and agrees with the suggestion of McDowell and Case[54] that no anionic uranium species is transferred across the interface. It must not be overlooked, however, that an alternative anion exchange reaction could still be considered for the extraction.

The extraction of thorium (IV) from sulphate solutions by several primary amines in various "diluents" has been studied by Vdovenko <u>et al.</u>[66], who obtained evidence for complexes of the type $(RNH_3)_4\ Th(SO_4)_4$ in the organic phase. McDowell and Allen[67] have also investigated the extraction of thorium (IV) from sulphate solutions using di-n-decylamine dissolved in benzene, and have identified the extracted complex as

$(R_2NH_2)_nTh(SO_4)_{2+\frac{n}{2}}$. n can have various values up to a maximum of about 6 which occurs at high aqueous thorium concentrations. There are thus several possible complexes in the organic phase such as $(R_2NH_2)_2SO_4 \cdot Th(SO_4)_2$, $2(R_2NH_2)_2SO_4 \cdot Th(SO_4)_2$, and $3(R_2NH_2)_2SO_4 \cdot Th(SO_4)_2$. In other words adducts can be described containing one molecule of neutral thorium sulphate and 1,2 and 3 molecules of the amine sulphate. The species transferring across the interface in this case would be a neutral thorium sulphate molecule. On the other hand the anion exchange reaction would suggest the transfer of the anionic species $Th(SO_4)_3^{-2}$, $Th(SO_4)_4^{-4}$, and $Th(SO_4)_5^{-6}$ across the interface.

In a further study McDowell and Allen[68] have used the distribution method to obtain values for the formation constants of the thorium tri- and tetra- sulphate-complexes $Th(SO_4)_3^{-2}$, and $Th(SO_4)_4^{-4}$.

The extraction of uranium (IV) and (VI) from nitric acid solutions by various amines in various "diluents" has been suggested to occur by an anion exchange reaction, and the ionic species that are extracted have been identified as the $U(NO_3)_6^{-2}$, and $UO_2(NO_3)_3^{-1}$ complex anions respectively[69-71]. The identification of the anionic species was done spectrophotometrically, and the spectra of the organic phases were very nearly identical to the spectra of U(IV) and U(VI) in nitric acid solution. This is not absolute proof, however, of the transference of a complex anion across the interface, but since the complex anion is the predominant species in the aqueous phase the postulation of the anion exchange reaction seems reasonable.

Similar results have been obtained for other actinide-nitric acid systems, and for the trivalent actinides, Marcus, Givon and Choppin[72] have found a second order dependence of the distribution ratio on the amine nitrate concentration, indicative of the extraction of the anionic species, $M(NO_3)_5^{-2}$.

The extraction of tetra- and hexavalent actinides from hydrochloric acid solutions by tri-n-octylamine dissolved in xylene has been investigated by Keder[73], who describes the reaction as being an anion exchange one with the transference of the species MCl_6^{-2} and $MO_2Cl_4^{-2}$ across the interface.

A study of the extraction of thallium (III) also from hydrochloric acid solutions by trinonylamine in benzene[74] has confirmed the existence of the $TlCl_4^{-1}$ anion in the organic phase.

An extremely interesting example of the two possible extraction reactions is the extraction of plutonium (IV) from nitrate solutions by various tertiary amines which has been studied by Baroncelli, Scibona and Zifferero[75]. Their results show that only one complex is formed in the organic phase, this being $(R_3NH)_2Pu(NO_3)_6$, but according to Baroncelli *et al.* there are two possible reactions for the formation of this compound in the organic phase. Firstly there is the anion exchange reaction with the transfer of the species $Pu(NO_3)_6^{-2}$ across the interface as shown in equation (1.22). Aqueous nitrate solutions of plutonium (IV) are known to contain this anionic complex.

$$Pu(NO_3)_{6_A}^{-2} + 2R_3NHNO_{3_o} \rightleftharpoons (R_3NH)_2Pu(NO_3)_{6_o} + 2NO_{3_A}^- \qquad (1.22)$$

Alternatively, Baroncelli *et al.* have suggested that an adduct type reaction may occur as shown in equation (1.23) with the transfer of the neutral species $Pu(NO_3)_4$ across the interface, which is also known to exist in the aqueous phase.

$$Pu(NO_3)_{4_A} + 2R_3NHNO_{3_o} \rightleftharpoons (R_3NH)_2Pu(NO_3)_{6_o} \qquad (1.23)$$

Throughout this chapter it has been emphasized that the extraction of metals from aqueous solutions by high molecular weight amines is not as simple as first thought, and may occur by reactions other than the anion exchange one originally proposed. The reaction in any extraction system may occur by either simple anion exchange or by adduct formation or more probably by a combination of both, but regardless of whichever reaction does take place the complex or complexes which appear in the organic phase are always the same, and are determined by the coordination properties of the metal being extracted. The nature of the "diluent" for the amine will also have a large effect on the extracted complex, in such a way that for a "diluent" of low dielectric constant the complex will be largely undissociated, and unsolvated by the "diluent", whereas for a higher dielectric constant solvent, the complex may be partly dissociated, and solvated by the "diluent".

There is, however, a much more important aspect of the extraction which has received very little consideration from other workers in this field, and this is the mechanism for actual transference of the metal species across the interface.

There appear to be two schools of thought on this subject, firstly there is the consideration that complex formation occurs wholly within the aqueous phase, and the metal species is transferred across the interface as the amine salt-metal salt complex. The second mechanism considers that complex formation occurs at the aqueous-organic interface, with the amine salt never completely passing into the aqueous phase, but orientated in such a way that the hydrophilic groups penetrate into the aqueous layer, and complex or ion exchange with the metal species, on the aqueous side of the interface.

Van Ipenburg[49], in his discussion on the extraction of metal salts by amine salts, assumes that the complex is formed in the aqueous phase, or at least on the aqueous side of the boundary layer, and is then transferred across the interface to the organic phase. This worker bases his assumption on the fact that reactions and equilibration generally will be much faster in the aqueous phase than in the organic phase, due to the lower viscosity and higher dielectric constant of the aqueous layer. Van Ipenburg also suggests that it is quite plausible that a little of the polarizable amine should distribute into the aqueous phase to form, firstly, the amine salt, and then the metal complex. In fact, it is generally assumed that in solvent extraction systems the complexing reagent, if it is introduced into the system as a separate organic phase, will distribute itself between the aqueous and organic phases. Complex formation will then occur in the aqueous phase containing the metal to be extracted, and the neutral complex, which is soluble in the organic phase, will then distribute itself between the two phases.

Most quantitative treatments of extraction data[3,36,38,39,76] have been dealt with in this way, and the equilibria involved in the extraction are described on the basis of the complex formation occurring in the aqueous phase, The interface mechanism of McDowell and Case[54], as mentioned previously, has considerable merit when dealing with the extraction properties of the high molecular weight amines, since they and their salts are generally only very sparingly soluble in the aqueous phase, and have been shown to have surface-active properties. In any event, the interface mechanism suggested by McDowell and Case does suggest that the reaction occurs on the aqueous side of the interface, so there is very little difference between the two mechanisms, except that for the interface one it is not necessary for the organic part of the amine or amine sulphate to actually pass through the boundary into the aqueous phase.

The surface-active properties of the long chain amine salts are discussed in Chapter 5 of this thesis, however, it is reasonable to assume that the long chain amines and their salts will concentrate at the aqueous-organic interface with the hydrophobic parts immersed in the organic phase, and the hydrophilic parts penetrating into the aqueous phase.

McDowell and Case[54] have suggested that, for the extraction of uranium (VI) from sulphate solutions, the amine sulphate concentrates at the aqueous-organic interface with the sulphate groups immersed in the aqueous phase, and studies have shown that the sulphate part of the amine sulphate remains strongly associated with the organic amine and does not predominantly ionize, as would be expected. This is reasonable in view of the high sulphate concentration in the aqueous phase. The reaction of amine sulphate with a neutral uranyl sulphate molecule can thus occur at the interface.

It would be expected that some ionization of the amine sulphate would occur at the interface, and so the anion exchange reaction would also be feasible for the interface mechanism.

The final equilibrium is of course independent of the way in which it is reached, and so the consideration of either extraction mechanism will lead to the same result.

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Chapter II

THE EXTRACTION OF SULPHURIC ACID BY DI- AND TRI(3,5,5,TRIMETHYLHEXYL)AMINES.

I. INTRODUCTION

Long chain alkyl amines were first used in 1948 by Smith and Page[1] for the quantitative separation of strong acids from water soluble organic acids such as glycine and glutamic acid. The extraction of acids from aqueous solutions by the amines dissolved in organic solvents such as chloroform and nitrobenzene, relies on the property of the amine salts of being soluble in the organic phase and almost insoluble in water. Smith and Page found the extraction to be dependent on several factors such as the nature of the amine, the type of organic solvent used for the amine, and on the type of acid to be extracted from the aqueous phase. Tertiary amines were found to be more efficient acid binders than primary or secondary amines, and the chain length of the alkyl group attached to the nitrogen atom had an effect, in that the binding efficiency improved as the carbon chain was increased. Several solvents for the amine were investigated and chloroform and nitrobenzene were found to give the most satisfactory results. The solubilities of the amine salts in the organic phase were also found to be important and certain salts, such as those formed with sulphuric acid, were found to be less soluble in chloroform than the corresponding hydrochlorides, and separated out as third phases.

Since this initial application of amines to the extraction of mineral acids, a considerable amount of work has been carried out on the investigation of the suitability of many amines in many "diluents" for the extraction of acids from aqueous solutions. The results of this work have been reviewed by several authors[2-6].

However, it was not until 1956, when Allen[7,8] studied the equilibria between tri-n-octylamine in benzene, and di-n-decylamine in benzene, and sulphuric acid, that any real progress was made towards the elucidation of the physical chemistry of this type of system. The extraction of sulphuric acid can be considered to occur in two steps, firstly, the neutralization of the amine to form the normal amine sulphate, and secondly, the reaction of this normal amine sulphate with more acid to form the amine bisulphate, as shown in equations (2.1) and (2.2).

$$2R_o + H_2SO_{4_A} \overset{K_1}{\rightleftharpoons} R_2H_2SO_{4_o} \qquad (2.1)$$

$$R_2H_2SO_{4_o} + H_2SO_{4_A} \overset{K_2}{\rightleftharpoons} 2RH_2SO_{4_o} \qquad (2.2)$$

where R is the amine, $R_2H_2SO_4$ and RH_2SO_4 are the amine sulphate and bisulphate respectively, and the subscripts "o" and "A" refer to the organic and aqueous phases. K_1 and K_2 are the corresponding equilibrium constants.

Allen found that the extraction to form the amine sulphate did not obey a simple equilibrium law, as described in equation (2.3), over a large concentration range, as expected, and explained his results on the basis of the polymerization of the amine sulphate in benzene solution.

$$K_1 = \frac{\left[R_2H_2SO_4\right]_o}{\left[R\right]_o^2 \cdot a_{H_2SO_{4_A}}} \qquad (2.3)$$

where $\left[R_2H_2SO_4\right]_o$ and $\left[R\right]_o$ are the molar concentrations of the amine sulphate and free amine in the organic phase respectively, and $a_{H_2SO_{4_A}}$ is the activity of sulphuric acid in the aqueous phase.

For the formation of the tri-<u>n</u>-octylammonium sulphate the extraction was found to obey the equilibrium law, provided the concentration of the amine sulphate did not exceed a value of 0.02M. For values of the amine sulphate concentration in benzene which exceeded 0.02M, systematic departures from the expected behaviour were obtained. Allen explained these anomalies by referring to the withdrawal of the amine sulphate from the system as a micellar type colloid.

For the formation of the amine bisulphates of the amines, the simple equilibrium law as described in equation (2.4), was again found not to be obeyed.

$$K_2 = \frac{\left[RH_2SO_4\right]_o^2}{\left[R_2H_2SO_4\right]_o \cdot a_{H_2SO_{4_A}}} \qquad (2.4)$$

$\left[RH_2SO_4\right]_o$ is the molar concentration of the amine bisulphate in the organic phase. Allen explained his results by considering the formation of the amine bisulphate to be an anion exchange reaction in which sulphate ions were exchanged for bisulphate ions. This reaction is thermodynamically indistinguishable from the former one which suggested that amine bisulphate is formed by the reaction of the normal amine sulphate with more acid. In this treatment, Allen again suggested that the amine bisulphates, and the amine sulphates were bound up in a colloidal type micelle.

In an attempt to determine the actual size of the colloidal particles in these systems, Allen[9] carried out a light scattering study of various amine salts. The results of this work, however, did not substantiate his suggestion that the anomalies in the extraction behaviours could be explained by assuming aggregation of the amine salts in benzene solution. In fact, the only salt which was found to have a size large enough to be considered reasonable for consistency with the extraction behaviour, was the di-n-decylammonium sulphate. The tri-n-octylammonium sulphate proved to be monomeric in benzene solution. However, this result does not agree with work carried out by Fomin et al,[10] who studied the polymerization of tri-n-octylammonium sulphate in benzene by cryoscopic methods, and suggested that, even though at low acidities in the aqueous phase the amine sulphate is monomeric, polymerization does occur at higher aqueous acidities to form a trimer or possibly higher polymers.

Verstegen and Ketelaar[11,12] studied the distribution of sulphuric acid between water and solutions of tri-n-octylamine and tri-n-hexylamine in kerosene and benzene. These workers found that when using kerosene as solvent for the amines, the extractions did not obey the simple equilibrium law for any concentration of the amines, but found that the equilibrium law was obeyed for concentrations of the amines in benzene which were below certain values. The concentration values were 0.019 mole/l. for tri-n-octylamine, and 0.005 mole/l. for tri-n-hexylamine. The results obtained by Verstegen and Ketelaar were in agreement with those found by Allen[7].

Boirie[13], and Shevchenko and Zhdanov[14] investigated the extraction of sulphuric acid from aqueous solutions by tri-n-octylamine in benzene and carbon tetrachloride. Boirie suggested that the simple equilibrium law should be followed until an amine sulphate concentration of at least 0.48M is reached. However, her calculations were based on thermodynamically, rather insubstantial grounds, since she neglected to take into account the activity of sulphuric acid in the aqueous phase. Shevchenko and Zhdanov[14] obtained results which were in agreement with those found by Boirie, but also neglected activities in the aqueous phase.

Baes[15] studied the extraction of sulphuric acid from aqueous solutions which contained large amounts of sodium sulphate (0.50M), by the secondary amine di-n-decylamine in benzene. He also found that the equilibrium law was not obeyed, and assumed polymerization of the amine salts in benzene solution. This assumption has been found to be correct in view of Allen's light scattering studies[9].

The extraction of other mineral acids has been investigated by many workers. Newman and Klotz[16] studied the extraction of hydrochloric acid by tri-n-octylamine dissolved in benzene and showed that the reaction can be described by the simple equilibrium law with the formation of the amine hydrochloride in the organic phase. A similar study was made by Bizot and Tremillon[17] for the same amine dissolved in carbon tetrachloride.

Wilson and Wogman[18] studied the extraction of other hydrohalic acids by tri-n-octylamine dissolved in several solvents of varying dielectric constants and their results showed that the equilibrium constants for the formation of the amine hydrohalides increased as the dielectric constant of the solvent increased. Wilson and Wogman found that for aqueous solutions of hydrohalic acids below 2M in concentration the formation of the simple amine salts took place as expected, however, for higher concentrations of the acids, the extraction of excess acid occurred. Thus, at an aqueous concentration of hydrochloric acid of 10M, two moles of acid were found to be associated with one mole of amine. This had previously been noticed by Bertocci and Rolandi[19] for hydrohalic acids. A similar effect has been noticed by several workers for the extraction of nitric acid by amines, and Shevchenko et al[20] concluded that the species $(TOA.HNO_3).HNO_3$ was formed in the organic phase. TOA refers to tri-n-octylamine. Wilson and Wogman suggested that a similar species may be formed by the hydrohalic acids.

The extraction of nitric acid from aqueous solutions by amines dissolved in organic solvents has been investigated more extensively than any other mineral acid. This is due to the relatively high cost of nitric acid in process chemistry which makes its recovery for re-use economically possible.

Verstegen[21] studied the distribution of nitric acid between water and solutions of tri-n-octylamine in various solvents. In most cases this worker found the equilibrium law to be obeyed, but found that the equilibrium constant was strongly dependent upon the solvent used for the amine. The equilibrium constant was found to be greater for solvents with high dielectric constants, as was found for the extraction of hydrohalic acids by Wilson and Wogman[18].

Shevchenko *et al.*[20] studied the extraction of nitric acid by tri-*n*-octylamine in *o*-xylene and in carbon tetrachloride and found high partition coefficients provided the equilibrium concentration of acid in the organic phase was not greater than the initial amine concentration. These workers concluded that the simple amine nitrate salt $TOA.HNO_3$ was formed in the organic phase. However, at very high nitric acid concentrations in the aqueous phase, excess nitric acid was found to be extracted as mentioned previously. Shevchenko *et al* suggested that the species $(TOA.HNO_3).HNO_3$ was formed in the organic phase and were able to obtain equilibrium constants for the extraction into *o*-xylene and carbon tetrachloride. The values for the equilibrium constants were 0.09 and 0.13 respectively which compared favourably with values found for the extraction of nitric acid by tributyl phosphate and di-isopentylmethylphosphonate of 0.22 and 0.30 respectively for the formation of the species $(TBP.HNO_3)$ and $(DPMP.HNO_3)$[22, 23]. The values for the amine nitrates are, however, lower than these for the phosphorus compounds suggesting that the $(TOA.HNO_3).HNO_3$ species is less stable. It has been suggested that the extraction of nitric acid by tributyl phosphate is analogous to the extraction by amine nitrates.

This extraction of excess nitric acid by amines has been reported by several other workers[19, 24, 25, 26, 27]. Most of these are in agreement with the extraction of two moles of nitric acid for each mole of amine, but Vdovenko et al.[26] have suggested that a third mole of nitric acid can be extracted when the aqueous nitric acid concentration is 12M. It has also been suggested[26, 27], that there is evidence for polymerization of the amine nitrate species in certain organic solvents.

It can be seen from the above summary of the work already reported in the literature that a great amount has been done on the investigation of the extraction of mineral acids from aqueous solutions by long chain amines dissolved in various organic solvents. An attempt has been made to summarize the results of this work in table 2.1, by listing the values for the equilibrium constants for the extraction of various acids by various amines as reported in the literature.

It can be seen from the values for the equilibrium constants shown in table 2.1, that there are several factors influencing the extraction of mineral acids from aqueous solution by amines as suggested by Smith and Page[1]. The extraction order appears to be $H_2SO_4 > HNO_3 > HCl$. There is also dependence on the amine, and on the solvent for the amine. Amine salts are extracted to a greater extent by solvents of high dielectric constant. Polymerization of the amine salts in the organic phase also has an effect on the equilibrium constant for the extraction, and according to Allen[7,8], is responsible for the observed deviation from the expected simple equilibrium law behaviour.

The equilibrium studies described in this chapter were, therefore, carried out using a solvent for the amines, iso-amyl alcohol, in which it was known that no aggregation of the amine salts occurred. The aggregation properties of the amine salts are discussed in Chapter 4 of this thesis.

It was expected that the simple equilibrium law would be obeyed for the extraction of sulphuric acid by the secondary and tertiary amines, di(3,5,5,trimethylhexyl)amine, and tri(3,5,5,trimethylhexyl)amine, and that regular

Table 2.1

Equilibrium constants for the extraction of various acids by various amines

Amine	Acid	Solvent	Dielect. constant	Equilibrium constant	Units	Temp. °C	Ref.
Tri-n-hexyl amine	H_2SO_4	benzene	2.28	$K_1=0.45x10^7$	$(mole/1.)^{-4}$	25	(12)
Di-n-decyl amine	H_2SO_4	benzene	2.28	** $K_1=1.67x10^{17}$ *** $K_2=2.6\ x10^2$	$(mole/1.)^{-6}$ $(mole/1.)^{-3}$	25	(8)
Didecylamine	H_2SO_4	benzene	2.28	$K_1=0.25x10^{12}$	$(mole/1.)^{-4}$	ns.	(13)
Didecylamine	H_2SO_4	CCl_4	2.24	$K_1=0.32x10^{11}$	$(mole/1.)^{-4}$	ns.	(13)
Methyldioctyl amine	H_2SO_4	benzene	2.28	$K_1=0.20x10^9$	$(mole/1.)^{-4}$	ns.	(13)
Methyldioctyl amine	H_2SO_4	CCl_4	2.24	$K_1=0.32x10^8$	$(mole/1.)^{-4}$	ns.	(13)
Methyldidecyl amine	H_2SO_4	benzene	2.28	$K_1=0.25x10^{12}$	$(mole/1.)^{-4}$	ns.	(13)
Methyldidecyl amine	H_2SO_4	CCl_4	2.24	$K_1=0.13x10^{11}$	$(mole/1.)^{-4}$	ns.	(13)
Tridecylamine	H_2SO_4	benzene	2.28	$K_1=0.56x10^9$	$(mole/1.)^{-4}$	ns.	(13)

Table 2.1 contd.

Amine	Acid	Solvent	Dielect. constant	Equilibrium constant	Units	Temp. °C	Ref.
Tridecylamine	H_2SO_4	CCl	2.24	$K_1=0.89\times10^7$	$(\text{mole/l.})^{-4}$	ns.	(13)
Tridecylamine	H_2SO_4	white spirit	-	$K_1=0.50\times10^6$	$(\text{mole/l.})^{-4}$	ns.	(13)
Tri-*n*-octyl amine	H_2SO_4	benzene	2.28	$K_1=1.87\times10^8$	$(\text{mole/l.})^{-4}$	25	(12)
Tri-*n*-octyl amine	H_2SO_4	benzene	2.28	$K_1=1.90\times10^8$ * $K_2=1.49\times10^3$	$(\text{mole/l.})^{-4}$ $(\text{mole/l.})^{-3}$	25	(7)
Tri-*n*-octyl amine	H_2SO_4	benzene	2.28	$K_1=0.33\times10^9$ $K_2=0.25\times10^2$	$(\text{mole/l.})^{-4}$ $(\text{mole/l.})^{-1}$	ns. ns.	(13) (13)
Tri-*n*-octyl amine	H_2SO_4	CCl_4	2.24	$K_1=0.50\times10^7$	$(\text{mole/l.})^{-4}$	ns.	(13)
Tri-*n*-octyl amine	H_2SO_4	CCl_4	2.24	$K_1=0.24\times10^7$	$(\text{mole/l.})^{-4}$	ns.	(14)
Tri-*n*-octyl amine	HCl	benzene	2.28	$K=1.4\times10^4$	$(\text{mole/l.})^{-2}$	ns.	(16)
Tri-*n*-octyl amine	HCl	CCl_4	2.24	$K=1.0\times10^4$	$(\text{mole/l.})^{-2}$	ns.	(17)

Table 2.1 contd.

Amine	Acid	Solvent	Dielect. constant	Equilibrium constant	Units	Temp. °C	Ref.
Tri-n-octyl amine	HNO_3	nitro-benzene	29.8	$K = 50 \times 10^6$	$(mole/l.)^{-2}$	40	(21)
Tri-n-octyl amine	HNO_3	$CHCl_3$	4.5	$K = 6.2 \times 10^6$	$(mole/l.)^{-2}$	40	(21)
Tri-n-octyl amine	HNO_3	benzene	2.28	$K = 0.11 \times 10^6$	$(mole/l.)^{-2}$	40	(21)
Tri-n-octyl amine	HNO_3	benzene	2.28	$K = 0.38 \times 10^6$	$(mole/l.)^{-2}$	25	(21)
Tri-n-octyl amine	HNO_3	modified dodecane	2.0	$K = 0.084 \times 10^6$	$(mole/l.)^{-2}$	25	(21)

The equilibrium constants in this table were obtained assuming the equilibrium law to hold, except where otherwise stated.

N.S. Temp. not stated, but extraction work was done at Room Temp.

K_1 and K_2 refer to the formation of amine sulphate and bisulphate respectively.

Due to suggested polymerization of the amine salts in benzene, Allen[7,8] calculated his K values using the following equations.

* $K_2 = \dfrac{X^3_{RH_2SO_4}}{a_{H_2SO_4} \cdot X^{\frac{3}{2}}_{R_2H_2SO_4}}$ where X denotes mole fractions of amine sulphate and bisulphate

** $K_1 = \dfrac{1}{a_{H_2SO_4} \cdot [R]^3}$ An empirical relationship which explained the extraction results.

*** $K_2 = \dfrac{X^2_{RH_2SO_4}}{a_{H_2SO_4} \cdot X_{R_2H_2SO_4}}$ Where X again denotes mole fractions.

equilibrium constants K_1 and K_2 for the formation of amine sulphate and bisulphate respectively would be obtained for each amine. This was, in fact, found to be so for amine solutions in iso-amyl alcohol whose initial concentrations were in the range of 0.01M to 0.10M.

It was also expected that, due to the higher dielectric constant of the solvent iso-amyl alcohol for the amines, higher values for the equilibrium constants would be obtained than found by other workers for amine solutions in benzene. This again was found to be so.

II. EXPERIMENTAL

1. Reagents

Di- and Tri(3,5,5,trimethylhexyl)amines.

The samples of the secondary amine di(3,5,5,trimethylhexyl)amine and the tertiary amine tri(3,5,5,trimethylhexyl)amine used in this investigation were obtained from L. Light and Co. as very pale yellow almost colourless liquids. Micro-analysis of the secondary amine gave the following figures, (Found: C,80.58; H,14.23; N,5.64. Calcd. for $C_{18}H_{39}N$: C,80.22; H,14.59; N,5.20).

The equivalent weight of each amine was determined by titration in an aqueous ethanol solution using standard aqueous hydrochloric acid. The titration of the amine was followed using a direct reading pH meter (Philips PR9400), and a glass electrode. The aqueous ethanol solution was obtained by mixing 50ml of ethanol with 25ml of water, and then 50ml of this solution were used to dissolve the weighed amount of amine. It should be pointed out that the pH values measured in this solution are probably not absolute values, and since this determination only required a measurement of the sharp pH change at the end point, the recording of the pH values was permissible.

A typical titration curve for di(3,5,5,trimethylhexyl)amine is shown in figure 2.1, for the titration of 0.2976g of the amine with a 0.157N hydrochloric acid solution. The presence of only one inflection in this curve shows the absence of any appreciable amounts of primary or tertiary amines as impurities.

The equivalent weight of the tertiary amine was determined in the same way.

This type of pH titration in an aqueous ethanol medium has been used by Verstegen and Ketelaar[12], and by Beirie[13] for the estimation of tri-n-octylamine solutions in benzene

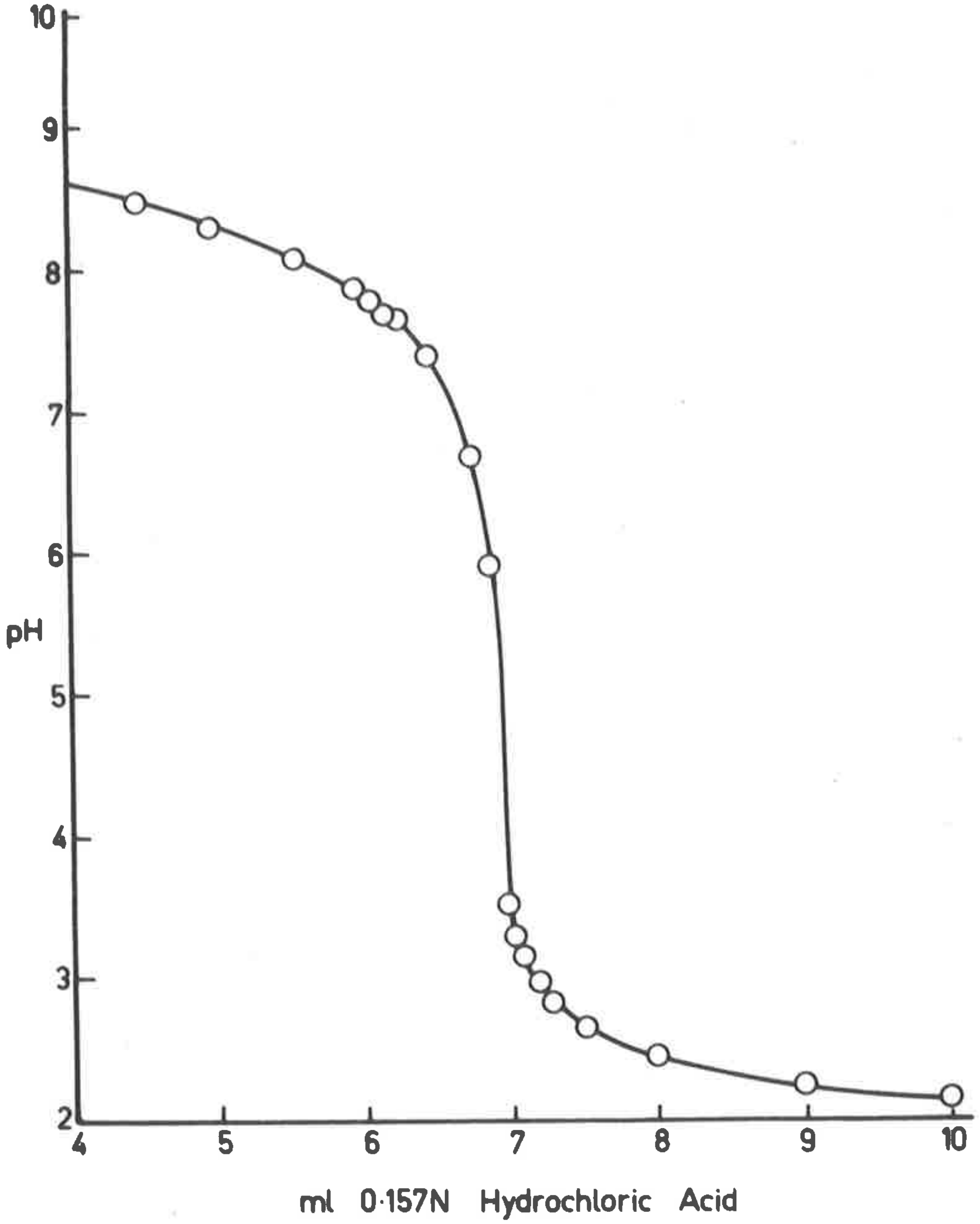

Figure 2.1 pH titration of di(3,5,5,trimethylhexyl)amine in an aqueous ethanol medium.

with standard aqueous perchloric acid. Beirie[13] also carried out titrations using standard sulphuric acid solution, and obtained two inflection points in the titration curve corresponding to the formation of the amine sulphate and the amine bisulphate.

Allen[7,8], previously, had determined concentrations of amines in organic solvents by potentiometric titrations in completely non-aqueous media, using perchloric acid dissolved in dioxan.

Bertocci and Rolandi[19] determined concentrations of amine solutions in xylene by titration with perchloric acid dissolved in glacial acetic acid, and crystal violet as indicator.

The values obtained for the equivalent weights of the two amines are given in table 2.2.

Table 2.2

The equivalent weights of di- and tri(3,5,5,trimethylhexyl)amines

	calcd.	found
Di(3,5,5,trimethylhexyl) amine	269.5	272.6
Tri(3,5,5,trimethylhexyl) amine	395.7	396.9

Relative values for the basicities of each of the amines were obtained from the pH titration curves by assuming that the pH values at the 50 per cent. neutralisation points were equal to the pKa values of the amines. It should be pointed out that these are probably not the absolute pKa values, since the pH titrations were done in an aqueous ethanol medium. It is, however, possible to compare the two values, as each pH titration was carried out under identical conditions. The values obtained were 8.72 for di(3,5,5,trimethylhexyl)amine, and 7.45 for tri(3,5,5,trimethylhexyl)amine.

The basicity of the secondary amine is, therefore, considerably greater than that of the tertiary amine.

Iso-amyl alcohol

B.D.H. reagent grade, which was specified to contain 3-methyl-butanol with 15-30% of 2-methyl-butanol (B.Pt.128-132°C), was fractionally distilled, and the fraction boiling at 130-132°C was collected.

Di(3,5,5,trimethylhexyl)amine solutions in iso-amyl alcohol

For the extraction experiments using di(3,5,5,trimethylhexyl)amine, solutions were made up at 25.0°C in the concentration range 0.01M to 0.10M by dilution of a standard 0.10M amine solution, which had previously been obtained by dissolving a known weight of the amine in iso-amyl alcohol at 25.0°C. The concentration of this standard 0.10M amine solution was checked by titration using the indicator method described in section 3.1. Prior to the extraction experiments, the amine solutions were saturated with water at 25.0°C. The water used for this had itself been previously saturated at 25.0°C with iso-amyl alcohol to prevent any volume change of the organic phase.

Tri(3,5,5,trimethylhexyl)amine solutions in iso-amyl alcohol.

Only one concentration, 0.10M, was used in the extraction experiments with the tertiary amine. However, the same pre-treatment was applied to this amine as for the secondary amine.

Aqueous sulphuric acid solutions.

Aqueous solutions were made up using "Analar" grade sulphuric acid in the concentration range of 0.001M to 0.50M, by dilution of a standardised 1.0M stock solution. The actual concentrations of these solutions, initially, were not important, and the solutions were used without further standardization, since only the aqueous sulphuric acid concentrations at equilibrium were required for calculation of the equilibrium constants.

These solutions were used in the equilibria studies for the two amines. The low concentration solutions were used for the study of the formation of the amine sulphates, and the higher acid concentrations were used for the study of the formation of the amine bisulphates.

For the investigation of the distribution of sulphuric acid between iso-amyl alcohol alone, and water, sulphuric acid solutions of concentration 0.10M to 5.0M were used.

All sulphuric acid solutions were saturated with iso-amyl alcohol at 25°C prior to the extraction experiments.

2. Extraction Procedure.

All extraction experiments were carried out at 25°C using a rapid stirring technique. No anomalous results were obtained using this technique as found by Allen and McDowell[28] for the extraction of uranium by amine sulphates (see Chapter 4).

Equal volumes (20ml) of aqueous and organic solutions were thoroughly mixed in the vessel shown in figure 2.2. This vessel was fitted with a stirrer A attached through a "Quickfit" stirrer gland B. This enabled several such vessels to be placed in a thermostat

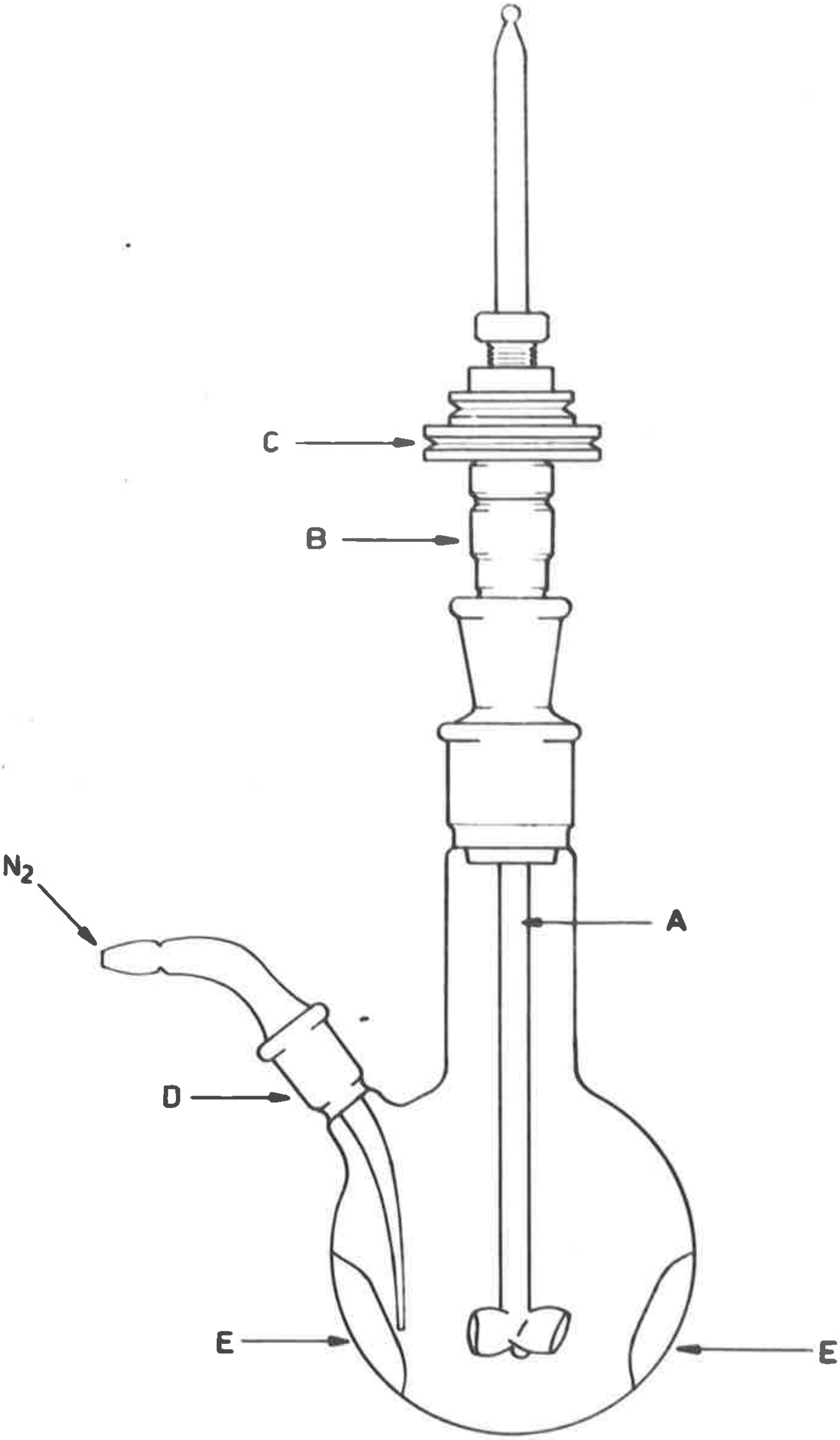

Figure 2.2 Vessel used for equilibration studies.

simultaneously, and enabled the stirrers to be driven by one motor using a system of pulleys C. The vessel contained an opening D in the side for introduction of solutions and had indentations in the sides E which acted as baffles to give more efficient mixing. For the study of the formation of the amine sulphates it was found necessary to bubble nitrogen through the vessel. This was done to prevent any absorption of carbon dioxide, since the concentrations of sulphuric acid at equilibrium in the aqueous phases were very low. The nitrogen stream was first bubbled through iso-amyl alcohol, and then through water to minimize the loss of either phase by evaporation. The nitrogen gas escaped from the vessel by diffusion through the felt gland sealing the stirrer.

Each equilibration was carried out for 60 min. This time was found adequate to enable equilibrium to be reached. When equilibrium had been reached the phases were separated in laboratory separatory funnels and filtered. The filtration removed any entrainment of either phase in the other. For the experiments mentioned previously where the equilibration was done under nitrogen, the separation was also done under nitrogen. The aqueous phases in these cases were immediately analysed by pH measurement under nitrogen.

3. Analyses of the Phases.

3.1 The organic phases.

The determination of free amine.

For the cases where there was insufficient sulphuric acid in the aqueous phase to completely form the amine salts, and equilibrium mixtures were obtained which contained a mixture of amine sulphate and free amine, the concentrations of free amine were determined by pH titration. The titrations were carried out on aliquots of the iso-amyl alcohol solutions dissolved in an aqueous ethanol mixture, using the procedure described in section 1 of this chapter. Similar titration curves to the one shown in figure 2.1 were obtained. This method enabled the determination of very small amounts of free amine in the organic phase to be made in the presence of amine sulphate. The presence of the amine sulphate did not have any effect on the titration results.

The concentrations of the original amine solutions before extraction were determined also.

It was also found possible to carry out the determination of free amine by the use of an indicator. The amine dissolved in ethanol was titrated with standard hydrochloric acid solution using the indicator bromo-phenol blue. The end point was determined by the very sharp colour change of bright blue to yellow.

The determination of the amine sulphate

The concentrations of the amine sulphate in the organic phase, for the solutions which contained a mixture of amine sulphate and free amine, were obtained by firstly determining the free amine concentration as above, and by subtracting this from the concentration of amine initially. This gave the concentration of amine combined as amine sulphate, and enabled the concentration of amine sulphate to be determined.

For the cases where there was a mixture of amine sulphate and amine bisulphate, the method of difference was also used. The concentration of amine bisulphate, determined as below, was subtracted from the concentration of amine initially, which gave the concentration of amine bound up as the amine sulphate.

To check the accuracy of this method, several of the di(3,5,5,trimethylhexyl)amine solutions containing sulphuric acid as amine sulphate or bisulphate were shaken with an aqueous solution of standard sodium carbonate. This procedure, due to the weak basicity of the amine, resulted in the back extraction of the sulphuric acid from the organic phase into the aqueous phase, with the conversion of the amine salts in the organic phase to the free amine.

To ensure complete re-extraction of sulphuric acid from the organic phase, a 5:1 ratio of sodium carbonate solution to the iso-amyl alcohol solution was used. The sodium carbonate solution had initially been saturated with iso-amyl alcohol to prevent any volume change of either phase. After this back extraction, the phases were separated and filtered. The amount of standard sodium carbonate solution used up was then determined by titration. The free amine concentrations of the organic phases were also determined in the usual way.

The results obtained from these check experiments were in excellent agreement with those obtained by the difference method.

<u>The determination of the amine bisulphate</u>.

The formation of amine bisulphate is considered to take place by the extraction of sulphuric acid, the amount of which is greater than required for complete formation of the normal amine sulphate. Therefore, it has been assumed that in solutions which contain amine bisulphate, the concentration of free amine is negligible.

Allen[8] determined the total concentration of sulphuric acid in the organic phase for extraction experiments using di-<u>n</u>-decylamine dissolved in benzene, by titration with standard sodium ethoxide as described by Fritz[29].

A similar estimation of the total sulphuric acid concentration in the organic phase was attempted in the present study, by pH titration with standard aqueous sodium hydroxide solution, in an aqueous ethanol medium. An inflection was obtained, in the pH titration curve, corresponding to the titration of the bisulphate ion, which enabled the direct determination of the amine bisulphate concentration in the organic phase.

Typical titration curves are shown in figure 2.3, for di(3,5,5,trimethylhexyl)amine salt solutions which were 0.021N, 0.057N, 0.076N, and 0.089N with respect to amine bisulphate, in iso-amyl alcohol. Aliquots (2ml) of these solutions which contained a mixture of amine sulphate and bisulphate were dissolved in 50ml of ethanol and 25 ml of water and were titrated with 0.097N sodium hydroxide solution using a direct reading pH meter.

It was found impossible, using the above conditions, to obtain a second inflection corresponding to the titration of the total amount of sulphuric acid in the organic phase. The reliability of the above method for the determination of the amine bisulphate concentration was tested by the determination of the total amount of sulphuric acid present in each of the above amine salt solutions using the re-extraction technique described above for the determination

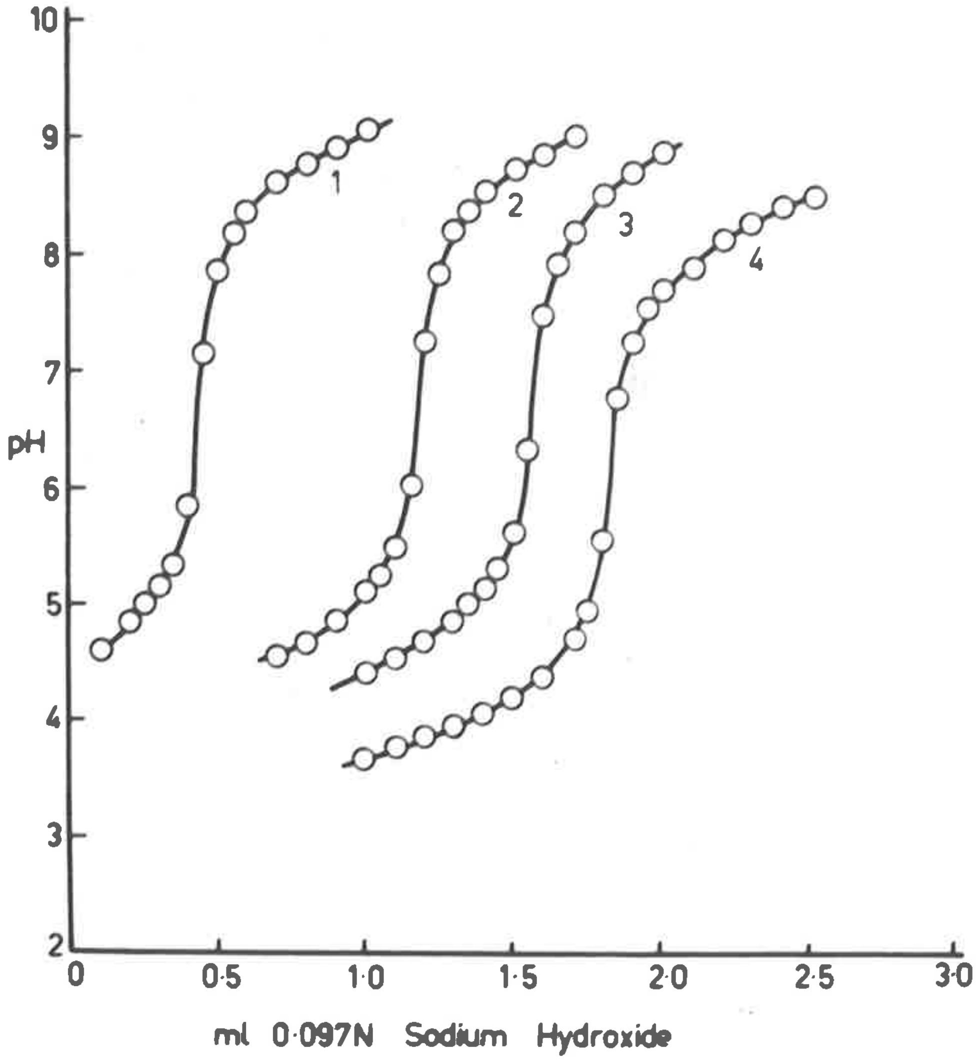

Figure 2.3 pH titration of the di(3,5,5,trimethylhexyl)ammonium bisulphate in the organic phases.

1. 0.021 N Amine bisulphate
2. 0.057 N " "
3. 0.076 N " "
4. 0.089 N " "

of the amine sulphate. The amounts of amine bisulphate which should have been present in the organic phases were calculated, and were found to be in excellent agreement with the values found by pH titration.

The determination of sulphuric acid dissolved in iso-amyl alcohol in the absence of amine.

During the equilibration experiments with iso-amyl alcohol solutions of the amine, it was found that at very high (greater than about 0.40M) aqueous concentrations of sulphuric acid, an appreciable amount of the acid was soluble in the alcohol itself. The amount of acid dissolved in the iso-amyl alcohol was determined in a series of experiments which were carried out in the absence of amine in the organic phase. This determination was done using the pH titration method described previously for the determination of bisulphate. In this case the inflection in the pH titration curve gave the total amount of sulphuric acid dissolved in the iso-amyl alcohol.

3.2 The aqueous phases.

The determination of sulphuric acid

(a) greater than 0.01M The aqueous phases containing sulphuric acid of concentrations greater than 0.01M, were analysed by titration with standard sodium hydroxide solution, using phenol phthalein as the indicator.

(b) <u>less than 0.01M</u>. The aqueous phase containing very small concentrations of sulphuric acid were analysed by pH measurement, using a direct reading pH meter, and a glass electrode. It was found necessary to carry out the pH measurements under an atmosphere of nitrogen to prevent the absorption of carbon dioxide. It was also necessary to prevent the diffusion of potassium chloride from the calomel electrode. In order to do this a special salt bridge was constructed. This consisted of a glass tube with a fine asbestos fibre sealed into one end. This end was then ground down until the fibre was exposed. The leakage of potassium chloride was found to be negligible using this salt bridge, and the pH measurements appeared to be unaffected.

The concentrations of sulphuric acid in the aqueous phases were then obtained from the pH measurements using a standard curve of pH against sulphuric acid concentration. The standard pH curve was obtained by the titration of 50ml of pure water with a 5.17×10^{-4}M sulphuric acid solution. The pH value of the water was measured after each small addition of acid. The determination was carried out under nitrogen to prevent interference by carbon dioxide. It was found exceedingly difficult to measure the pH value of pure water in such an unbuffered system, and obtain a value of 7.0. This was apparently due to the desorption of ions from the surface of the electrodes, and from the surface of the vessel used in the measurements. A plastic vessel was used for the measurements to minimize this effect.

Allen[8] used this procedure to obtain sulphuric acid concentrations from pH measurements, but the pH values measured by him were much lower than those obtained in the work with di(3,5,5,trimethylhexyl)amine. Thus Allen did not need to construct a calibration curve which extended to the low acidities experienced with the above amine.

Two calibration curves were constructed. The first using pure water, and the second using pure water which had been equilibrated, with an amine solution in iso-amyl alcohol. This equilibrated water phase was then shaken several times with iso-amyl alcohol to remove any amine which may have partitioned into the aqueous phase. The presence of the amine in the first organic phase was considered likely to remove any trace of hydrogen ions which may have been present in the aqueous phase. Water treated in this way was considered to be a close approximation to the aqueous phase obtained in the sulphuric acid distribution experiments.

However, the pH of this treated water was still not equal to 7.0, this again being due possibly to the presence of traces of ions desorbed from the glass-ware, and to the presence of iso-amyl alcohol.

The second curve was used for the actual computing of results from the extraction work involving the secondary amine since it most closely represented the conditions of the experiments.

It would be expected that the actual equilibrated aqueous phases from the extraction work with di(3,5,5,trimethylhexyl)amine would contain traces of the amine salts, even though they are practically insoluble in water. Thus the second type of calibration curve, even though it more closely approximates the system investigated than the first, still involves some error.

For the tertiary amine tri(3,5,5,trimethylhexyl) amine, this difficulty in pH measurement was not as great since the basicity of the amine was found to be less than that of the secondary amine, and so the equilibrium pH values were much lower, and were in the range investigated by Allen[8] for di-n-decylamine.

III. RESULTS AND DISCUSSION.

1. The Extraction of Sulphuric Acid by Di(3,5,5,trimethylhexyl)amine.

1.1 The formation of the amine sulphate.

The equilibrium* involved in the formation of the di(3,5,5,trimethylhexyl)ammonium sulphate can be written as

$$H_2SO_{4_A} + 2R_o \underset{}{\overset{K_1}{\rightleftharpoons}} R_2H_2SO_{4_o} \qquad (2.5)$$

where R is di(3,5,5,trimethylhexyl)amine, and for brevity and convenience, reacting sulphuric acid is written in the undissociated form. Subscripts "A" and "o" refer to the aqueous and organic phases respectively. The equilibrium constant K_1 can then be written using activities as

$$K_1 = \frac{a_{(R_2H_2SO_4)_o}}{a_{H_2SO_{4_A}} \cdot a^2_{R_o}} \qquad (2.6)$$

Making the assumption that the activity coefficients of the amine sulphate in the organic phase are unity, and also

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* The individual equilibrium reactions involved in the formation of amine sulphate and amine bisulphate are given in Appendix I.

assuming that the concentration of amine bisulphate is negligible as long as free amine is present in the organic phase, we can write the expression for K_1 as

$$K_1 = \frac{\left[R_2H_2SO_4\right]_o}{a_{H_2SO_{4_A}} \cdot \left[R\right]_o^2} \qquad (2.7)$$

where $\left[R_2H_2SO_4\right]_o$ and $\left[R\right]_o$ refer to the molar concentrations of amine sulphate and free amine in the organic phase respectively.

The activities of sulphuric acid in the aqueous phases were obtained using the equation used by Allen[7], and Verstegen[12].

$$a_{H_2SO_4} = \gamma_{\pm}^3 \cdot c_{\pm}^3 = 4\gamma_{\pm}^3 \cdot c^3 \qquad (2.8)$$

where $\gamma_{\pm}$ = mean molal activity coefficient.

$c_{\pm}$ = mean ionic molality.

c = molal concentration.

Values of the mean molal activity coefficient $\gamma_{\pm}$ are listed in Harned and Owen[30] for varying sulphuric acid molalities. Molalities were obtained from molarities using the solvent density as given in "Handbook of Chemistry and Physics"[31].

It should be pointed out that for this initial work on the formation of the amine sulphate, the concentrations of sulphuric acid in the aqueous phases were so low that molarities were equivalent to molalities and the values for $\gamma_\pm$ were taken as unity. However, for the following sections of this chapter it was necessary to convert molarities to molalities, and obtain the corresponding $\gamma_\pm$ values from Harned and Owen.

The results of the extraction experiments for the formation of the amine sulphate are shown in table 2.3. The concentrations of amine used in these experiments were in the range of 0.01M to 0.10M.

The values for the ratio $\dfrac{[R_2H_2SO_4]_o}{[R]_o^2}$, the aqueous pH values at equilibrium, the calculated values for the activities of the aqueous sulphuric acid solutions, and the calculated values for K_1, are shown in the table.

The values for K_1 given in table 2.3 show considerable variation even though they are of the same order. The reason for this is the inability to measure the pH value of the aqueous phases with the precision necessary to obtain very constant values for K_1. The aqueous solutions contained considerable amounts of iso-amyl alcohol, which

Table 2.3

The values of K_1 for the formation of di(3.5.5.trimethylhexyl)ammonium sulphate.

Initial amine concentration M	$\frac{[R_2H_2SO_4]_o}{[R]_o^2}$	Aqueous pH value at equilibrium	Molal concentrn. H_2SO_4 in aqu. ph. $C\times10^6$	$a_{H_2SO_{4_A}}\times10^{16}$	$K_1\times10^{-15}$
0.10	782	4.48	32.26	1343	5.8
0.10	395	4.96	24.49	587	6.7
0.10	103	5.36	17.52	215	4.8
0.10	77.8	5.45	16.18	169	4.6
0.10	30.7	5.63	12.68	81.5	3.8
0.10	23.4	5.60	13.41	96.4	2.4
0.02	23.0	5.53	14.85	131	1.8
0.01	21.0	5.61	13.09	89.5	2.4
0.01	19.4	5.76	10.73	49.3	3.9
0.02	9.64	5.68	11.96	68.4	1.4
0.02	8.81	5.76	10.73	49.3	1.8

Table 2.3 contd.

Initial amine concentration M.	$\frac{[R_2H_2SO_4]_o}{[R]^2_o}$	Aqueous pH value at equilibrium	Molal concentrn. H_2SO_4 in aqu. ph. $C \times 10^6$	$a_{H_2SO_{4_A}} \times 10^{16}$	$K_1 \times 10^{-15}$
0.02	8.81	5.77	11.35	58.5	1.5
0.10	7.80	5.74	10.83	50.8	1.5
0.04	4.65	5.92	7.64	17.8	2.6
0.06	3.11	5.92	7.64	17.8	1.8
0.05	2.69	6.02	5.68	7.33	3.7
0.10	2.29	6.08	4.44	3.50	6.5
0.10	1.92	6.02	5.68	7.33	2.6
0.10	1.92	5.96	6.81	12.62	1.5
0.10	1.72	6.05	5.36	6.15	2.8

appeared to have an effect on the glass electrode and caused some drift in the pH readings. This was possibly due to some kind of surface action, in view of the surface-active properties of iso-amyl alcohol. Also the amine salts themselves have been shown to be surface-active agents, and since the aqueous phases almost certainly contained traces of these salts, it might be expected that these also would have an effect on the glass electrode. This surface effect added to the usual difficulties in measuring pH values in unbuffered solutions of such low acidities, were probably responsible for the scattered K_1 values shown in table 2.3.

However, the systematic deviations as reported by Allen[7,8] for tri-n-octylamine, and for di-n-decylamine in benzene were not apparent. The values for K_1 found by Allen[7] for a 0.10M solution of tri-n-octylamine in benzene are shown, for the sake of comparison, in table 2.4. It can be seen that the values for K_1 vary systematically from about 70×10^8 (mole/l.)$^{-4}$ at the higher aqueous sulphuric acid activities to about 2×10^8 (mole/l.)$^{-4}$ for the lower sulphuric acid activities. It can also be seen that the values for the aqueous sulphuric acid activities at

Table 2.4

The values of K_1 for the formation of tri-*n*-octylammonium sulphate in benzene, as found by Allen[7]

*$a_{H_2SO_{4_A}} \times 10^9$	*$\frac{[R_2H_2SO_4]}{[R]^2}$	$K_1 \times 10^{-8}$
1000	7200	72
800	2800	35
680	1200	18
500	540	11
400	300	7.5
310	160	5.2
210	81	3.7
170	52	3.0
120	32	2.7
85	22	2.6
41	7.5	1.8
28	4.8	1.7
19	2.9	1.5
5.5	0.89	1.6
1.8	0.38	2.1

* The values in the above table were obtained from a graphical representation of Allen's results, and so are only approximate.

equilibrium as found by Allen, are considerably greater than those found in the present study. It should also be pointed out that, although the highest value obtained by Allen for the ratio $\frac{[R_2H_2SO_4]}{R^2}$, as shown in table 2.4, would seem to be about ten times greater than the highest value shown in table 2.3 for di(3,5,5,trimethylhexyl)amine, the actual difference in the compositions of the two phases involved is only small. This is because the concentrations of free amine are so small for the higher aqueous sulphuric acid activities that a very small change in the concentration of the former will cause a very large change in the value for the ratio $\frac{[R_2H_2SO_4]}{R^2}$. Thus the accuracy of this ratio is strongly dependent on the precision with which the concentration of free amine is determined.

The results shown in table 2.3 do, therefore, suggest that the formation of the amine sulphate for di(3,5,5,trimethylhexyl)amine dissolved in iso-amyl alcohol does obey the equilibrium law as described in equation (2.5), over the initial amine concentration range of 0.01M to 0.10M.

The value for K_1, obtained from table 2.3 is approximately $(4 \pm 3) \times 10^{15}$ (mole/l.)$^{-4}$.

The value for K_1 is quite large, and is somewhat greater than the value of $0.25 \times 10^{12} (\text{mole}/1.)^{-4}$ found by Beirie[13] for didecylamine in benzene. However, previous studies have shown that the value of the equilibrium constant is strongly dependent on the dielectric constant of the solvent for the amine, and so we might expect a value for K_1 for di(3,5,5,trimethylhexyl)amine dissolved in iso-amyl alcohol which is larger than that for didecylamine dissolved in benzene. It is also possible that the basicity of di(3,5,5,trimethylhexyl)amine may be greater than that of didecylamine, and this could also account for the larger value of K_1 for the former amine. This difference in basicities, however, between two somewhat similar amines, would seem to be insufficient to account for such a large difference between the K_1 values. This suggests that the solvent for the amine does have an important effect on the value for the overall equilibrium constant, as mentioned above.

The overall equilibrium for the extraction is composed of several individual equilibria, as shown in Appendix I, which are related to the various factors influencing the extraction such as the basicity of the amine, the nature of the solvent for the amine etc. The distribution of the amine salts between the aqueous and the organic phases is one of these individual equilibrium reactions, and, naturally enough, will be strongly dependent on the nature of the solvent for the amine. A solvent which is more compatible with the amine salts will be expected to give a higher value for the overall equilibrium constant than a solvent which is less compatible with the amine salts.

The long chain alkylammonium salts are essentially "soap-like" in nature, consisting of polar and non-polar sections. The behaviour of soaps in solutions with organic solvents is strongly dependent, according to Jirgensons[32], on the nature of the solvent. In alcohol, soaps are molecularly dissolved because the alcohol molecules have some affinity for the polar and non-polar sections of the soap molecules, and can solvate both. On the other hand in a non-polar solvent, such as benzene, there is strong solvation of the hydrocarbon chains, but no interaction of the polar "heads" with the solvent molecules. Consequently, the polar "heads" are pushed out of solution, and micelles are formed with the polar groups turned to the inside of the micelle.

A similar effect has been found with the long chain alkylammonium salts, as discussed in Chapter 4 of this thesis, and it has been shown that di(3,5,5,trimethylhexyl)ammonium sulphate is molecularly dissolved in iso-amyl alcohol, with perhaps some dissociation, but is highly aggregated in benzene.

It is not unreasonable, therefore, to expect that in a solvent such as iso-amyl alcohol, which is more compatible than benzene with the amine salts the value for the overall equilibrium constant might be larger than for benzene. In fact, the value obtained for K_1 for di(3,5,5,trimethylhexyl)amine dissolved in iso-amyl alcohol suggests that this is indeed so.

1.2 The formation of the amine bisulphate

The equilibrium involved in the formation of the di(3,5,5,trimethylhexyl)ammonium bisulphate can be written as

$$R_2H_2SO_{4_o} + H_2SO_{4_A} \overset{K_2}{\rightleftharpoons} 2RH_2SO_{4_o} \qquad (2.9)$$

where K_2 the equilibrium constant is given by

$$K_2 = \frac{a^2_{(RH_2SO_4)_o}}{a_{(R_2H_2SO_4)_o} \cdot a_{H_2SO_{4_A}}} \qquad (2.10)$$

By making the assumption as previously that the activity coefficients of the species in the organic phase are equal to unity, and by assuming that in the presence of amine bisulphate the amount of free amine is negligible, we can write the expression for K_2 as

$$K_2 = \frac{\left[RH_2SO_4\right]_o^2}{\left[R_2H_2SO_4\right]_o \cdot a_{H_2SO_{4_A}}} \qquad (2.11)$$

Where $\left[RH_2SO_4\right]_o$ and $\left[R_2H_2SO_4\right]_o$ refer to the molar concentrations of amine bisulphate and amine sulphate in the organic phase respectively.

Equation (2.11) can be written in the logarithmic form as

$$\log \frac{\left[RH_2SO_4\right]_o^2}{\left[R_2H_2SO_4\right]_o} = \log a_{H_2SO_{4_A}} + \log K_2 \qquad (2.12)$$

A plot of log $\frac{\left[RH_2SO_4\right]_o^2}{\left[R_2H_2SO_4\right]_o}$ against log.$a_{H_2SO_{4_a}}$ should give a straight line of slope one. The results of the extraction equilibria for the formation of the amine bisulphate, are shown in table 2.5. The concentrations of amine used in these experiments, as shown in the table were in the range of 0.01M to 0.10M. The values for the ratio $\frac{\left[RH_2SO_4\right]_o^2}{\left[R_2H_2SO_4\right]_o}$, the aqueous sulphuric acid molarities and the calculated molalities, the calculated activities of the aqueous acid solutions, and the values for

K_2 are also shown in the table. The aqueous sulphuric acid activities were calculated using equation (2.8). The molarities of sulphuric acid were converted to molalities using the values of the solution densities. The values for the mean molal activity coefficients were obtained using a graphical plot of values of $\gamma_{\pm}$ for various sulphuric acid solution molalities as given in Harned and Owen[30].

It can be seen from the table that the values for K_2 are reasonably constant over the concentration range studied. The average value for K_2 obtained from table 2.5 is $(1.18 \pm 0.2) \times 10^3$ (mole/l.)$^{-2}$.

The result of the log-log. plot is shown in figure 2.4. A straight line is certainly obtained as predicted by equation (2.12), and the slope of this line is 0.95, which is in excellent agreement with the expected value of one.

These results show that the equilibrium law as described by equation (2.9) is certainly obeyed over the amine concentration range studied.

Table 2:5

The values of K_2 for the formation of di(3,5,5,trimethylhexyl)ammonium bisulphate

Initial amine concentration M	$\frac{[RH_2SO_4]_o^2}{[R_2H_2SO_4]_o}$	Equilibrium aqueous H_2SO_4 molarity M	Equilibrium aqueous H_2SO_4 molality C	Mean molal activity coefficient $\gamma_\pm$	$a_{H_2SO_4{}_A} \times 10^6$	$K_2 \times 10^{-3}$
0.10	0.867	0.348	0.355	0.170	877	0.99
0.10	0.365	0.219	0.222	0.205	375	0.97
0.06	0.208	0.147	0.148	0.232	162	1.28
0.10	0.132	0.120	0.121	0.247	107	1.23
0.02	0.061	0.085	0.085	0.280	54.2	1.13
0.04	0.046	0.072	0.072	0.279	38.8	1.19
0.06	0.035	0.060	0.060	0.318	28.2	1.24
0.01	0.018	0.042	0.042	0.360	14.2	1.27
0.10	0.010	0.031	0.031	0.397	7.77	1.29

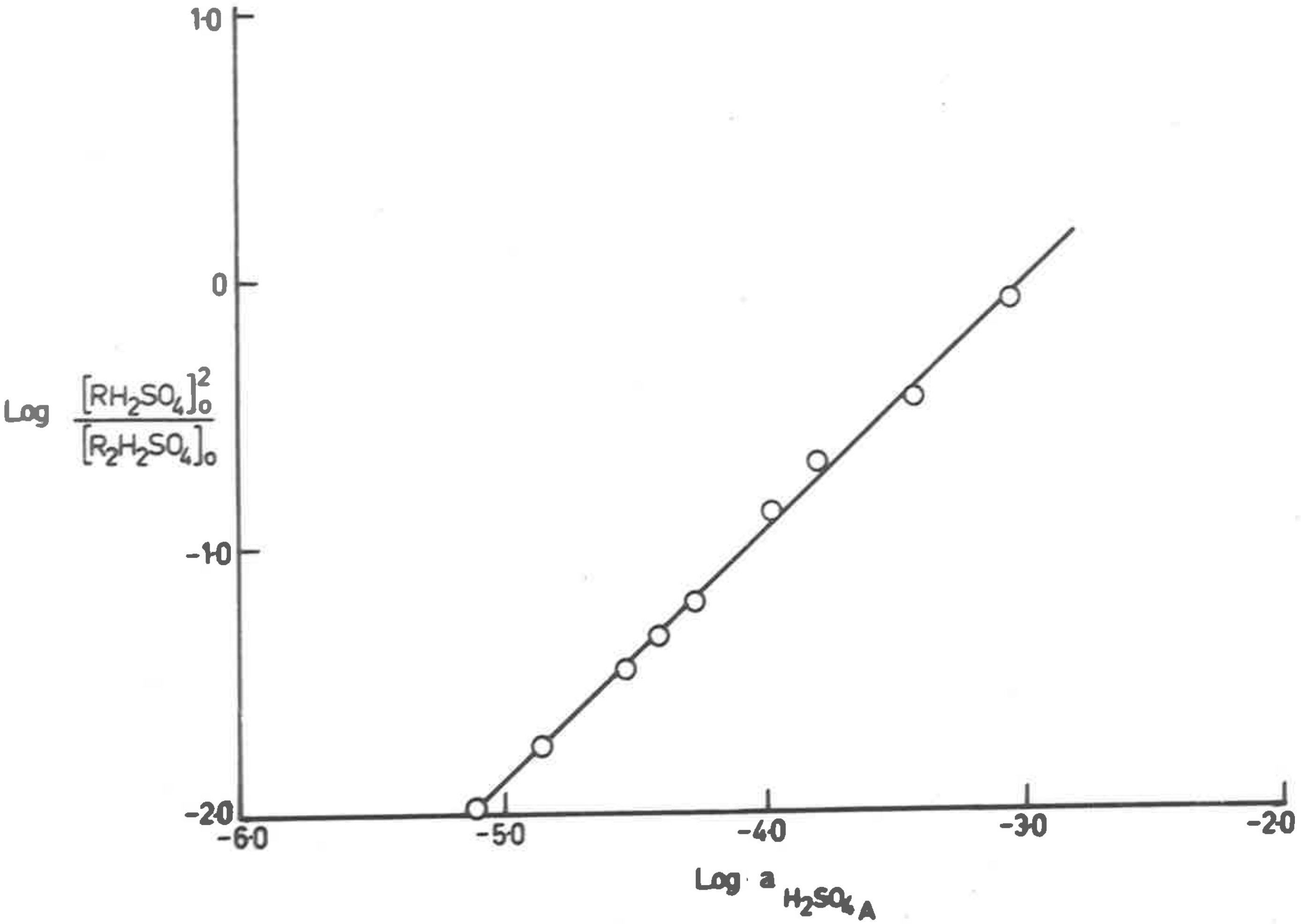


Figure 2.4 $\text{Log} \frac{[RH_2SO_4]_o^2}{[R_2H_2SO_4]_o}$ against log $a_{H_2SO_{4A}}$ for the formation of di(3,5,5,trimethylhexyl)-ammonium bisulphate.

2. The Extraction of Sulphuric Acid by Tri(3,5,5,trimethylhexyl)amine.

The extraction of sulphuric acid by the tertiary amine was much less extensively studied than the extraction by the secondary amine, since only a comparison of their relative extraction abilities was required. It was assumed that the extraction by the tertiary amine in iso-amyl alcohol would also follow the simple equilibrium law, since in this solvent there appears to be no tendency for the amine salts to aggregate. The comparison of the abilities of the two amines for the extraction of sulphuric acid was desirable since the secondary amine was found to be suitable for the extraction of ferric iron from aqueous sulphate solutions using solvents such as benzene, whereas the tertiary amine did not extract iron under any conditions.

2.1 The formation of the amine sulphate.

The equilibrium involved in the formation of the tri(3,5,5,trimethylhexyl)ammonium sulphate can be written as in equation (2.5). R. in this case is tri(3,5,5,trimethylhexyl)amine. The equilibrium constant is again given by equation (2.7).

The results of the extraction equilibria for the formation of the amine sulphate are shown in table 2.6.

For the investigation using the tertiary amine only one concentration of the amine in iso-amyl alcohol was used, this being 0.10M.

The values for K_1 given in table 2.6 do show some variation. However, this again may be due to the determination of the aqueous sulphuric acid concentrations, which as before were obtained by pH measurement. Even so, the values for K_1 are of the same order, and do once again give support to the equilibrium law for the formation of amine sulphate. The systematic variations found by Allen[7], for tri-n-octylamine are not apparent from the results shown in the table.
The value for K_1 is $(1.10 \pm 1) \times 10^{14}$ $(\mathrm{mole/l.})^{-4}$.

This value is somewhat lower than that obtained for the secondary amine, in fact, it is about one tenth lower. This is due to the lower basicity of the tertiary amine whose pKa value was found to be 7.45 compared to 8.72 for the secondary amine, as discussed in experimental section 1.

For a secondary and tertiary amine of comparable basicities, one might have expected a higher K_1 value for the tertiary amine than for the secondary amine simply on the grounds that the solvent, iso-amyl alcohol, would have a higher affinity for the tertiary amine sulphate due to the presence of the additional carbon chain. This would possibly tend to make the amine sulphate and iso-amyl alcohol more compatible.

Table 2.6

The values of K_1 for the formation of tri(3,5,5,trimethylhexyl)ammonium sulphate.

$\frac{[R_2H_2SO_4]_o}{[R]_o^2}$	Aqueous pH value at equilibrium	Molal concentrn. H_2SO_4 in aqu. ph. $C \times 10^5$	$a_{H_2SO_{4_A}} \times 10^{14}$	$K_1 \times 10^{-14}$
147.9	3.72	8.70	263.6	0.56
32.21	3.84	5.62	71.0	0.45
16.56	4.26	2.72	8.05	2.06
10.35	4.23	2.88	9.35	1.11
3.93	4.44	2.04	2.94	1.34

It is interesting to compare this value for K_1 with those found for tri-n-octylamine and tri-n-hexylamine dissolved in benzene, as determined by Verstegen and Ketelaar[12]. These workers obtained values of 1.87×10^8 $(\text{mole/l.})^{-4}$, and $0.45 \times 10^7 (\text{mole/l.})^{-4}$ respectively for the two amines.

It again seems unreasonable that this very large increase in K_1 for tri(3,5,5,trimethylhexyl)amine is due to a basicity difference alone, and, as has been suggested for the secondary amines in the discussion section 1.1, is more probably due to the greater compatibility of the amine salts with iso-amyl alcohol than with benzene.

2.2 The formation of the amine bisulphate

The equilibrium involved in the formation of the tri(3,5,5,trimethylhexyl)ammonium bisulphate can be written as in equation (2.9). R in this case is tri(3,5,5,trimethylhexyl)amine. The equilibrium constant is again given by equation (2.11).

Only two experiments were carried out to determine the equilibrium constant for the formation of the tertiary amine bisulphate. The initial amine concentration in each case was 0.10M. The results for these equilibria are shown in table 2.7.

Table 2.7

The values of K_2 for the formation of tri(3,5,5,trimethylhexyl)ammonium bisulphate

$\frac{[RH_2SO_4]_o^2}{[R_2H_2SO_4]_o}$	Equilibrium aqueous H_2SO_4 molarity M	Equilibrium aqueous H_2SO_4 molality C	Mean molal activity coefficient $\gamma_{\pm}$	$a_{H_2SO_{4_A}} \times 10^6$	$K_2 \times 10^{-3}$
0.013	0.024	0.024	0.430	4.58	2.84
0.062	0.056	0.056	0.325	23.6	2.63

The value for K_2 obtained from the table for the formation of the amine bisulphate is $(2.73 \pm 0.11) \times 10^3$ $(\text{mole/l.})^{-2}$. This value is greater than the corresponding K_2 value for the secondary amine by a factor of about two which would suggest that the affinity of iso-amyl alcohol for the tertiary amine salts is greater than that for the secondary amine salts, which, as discussed in section 2.1 above, is not unreasonable.

3. The Distribution of Sulphuric Acid Between Water and Iso-amyl Alcohol.

During the extraction work described previously using iso-amyl alcohol as the solvent for the amines, it was found necessary to determine the distribution, if any, of sulphuric acid between water and iso-amyl alcohol itself. It was found that generally in the concentration range of aqueous sulphuric acid solutions studied, in the previous work, the amount of acid soluble in iso-amyl alcohol alone was negligible. However, at much higher aqueous sulphuric acid concentrations (greater than about 0.4M), which were only used in one or two experiments with the amines, the distribution of sulphuric acid between iso-amyl alcohol and water became appreciable.

The distribution of sulphuric acid between water and iso-amyl alcohol should follow the form

$$(H_2SO_{4und.})_A \overset{K_D}{\rightleftharpoons} (H_2SO_4)_o \qquad (2.13)$$

where $(H_2SO_{4und.})_A$ and $(H_2SO_4)_o$ are the undissociated acid in the aqueous and organic phases respectively. K_D the distribution constant or distribution ratio is given by the following expression.

$$K_D = \frac{a_{H_2SO_{4_o}}}{a_{(H_2SO_{4und.})_A}} \qquad (2.14)$$

where $a_{H_2SO_{4_o}}$ and $a_{(H_2SO_{4und.})_A}$ are the activities of undissociated sulphuric acid in the organic and aqueous phases respectively.

If we assume that the activity coefficient of the sulphuric acid in the organic phase is unity, equation (2.14) can be written as

$$K_D = \frac{\left[H_2SO_4\right]_o}{a_{(H_2SO_{4und.})_A}} \qquad (2.15)$$

where $\left[H_2SO_4\right]_o$ is the molar concentration of sulphuric acid in the organic phase.

Table 2.8 shows values for the concentration of sulphuric acid in the organic phase for various molarities of sulphuric acid in the aqueous phase. The corresponding molalities and activities of the total sulphuric acid are also shown. It can be seen that the concentration of sulphuric acid in the organic phase increases with increasing concentration of acid in the aqueous phase. Zharovski and Mel'nik[33], and Whitehead and Geankoplis[34] had found this to be so for the extraction of sulphuric acid from aqueous solutions by several oxygen containing solvents, including iso-amyl alcohol.

Tuck[35] has studied the distribution of nitric acid between water and diethylene glycol dibutyl ether, and has determined the activity coefficients of undissociated nitric acid in the organic phase, by a knowledge of the activity coefficients of the acid in the aqueous phase. The thermodynamic extraction or distribution coefficient for nitric acid in this system is described by the relationship,

$$K_D = \frac{m_o.\gamma_o}{m_u.\gamma_u} \tag{2.16}$$

where $m_o\gamma_o$ is the activity of nitric acid in the organic phase, and $m_u\gamma_u$ is the activity of undissociated nitric acid in the aqueous phase. By knowing the ionization constant for nitric acid Tuck was able to calculate the activity of the undissociated nitric acid in the aqueous phase using the relationship,

$$m_u.\gamma_u = \frac{m_{\pm}^2.\gamma_{\pm}^2}{I} \tag{2.17}$$

Table 2.8

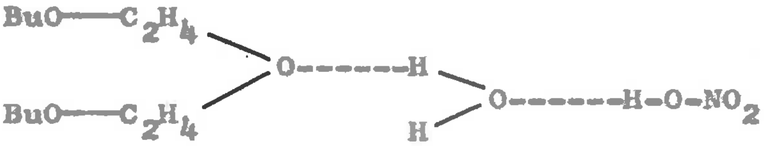
The Extraction of Sulphuric Acid by Iso-amyl Alcohol.

Equilibrium aqueous H_2SO_4 molarity M	Equilibrium aqueous H_2SO_4 molality C	Mean molal activity coefficient $\gamma_\pm$	$a_{H_2SO_4A}$ x10^4	Organic H_2SO_4 molarity M$\times10^3$
0.094	0.094	0.270	0.654	0.620
0.180	0.182	0.215	2.400	1.460
0.445	0.457	0.160	15.60	5.410
0.879	0.926	0.135	79.40	15.60
1.450	1.576	0.125	305.0	51.90
1.826	2.027	0.124	632.8	89.50
2.212	2.506	0.130	1383	160.6
3.662	4.464	0.190	24410	811.0

where I is the ionization constant for nitric acid, $m_{\pm}$ is the mean ionic molality of nitric acid in aqueous solution, and $\gamma_{\pm}$ is the mean molal activity coefficient.

This treatment can be applied to the extraction of sulphuric acid by iso-amyl alcohol, since it is necessary to obtain the activity of undissociated sulphuric acid in the aqueous phase as described in equation (2.11) to obtain K_D.

Tuck[35] has suggested that nitric acid is extracted by diethylene glycol dibutyl ether as a hydrate and suggests that a hydrogen bonded species is formed such as,



The extraction of a hydrate is also suggested for the extraction of sulphuric acid by tributyl phosphate, and Gignanov and Ponomarev[36] have found that up to 3M aqueous sulphuric acid the complex $H_2SO_4.TBP.2H_2O$ is formed. For higher concentrations of sulphuric acid there is evidence for the formation of the complex $H_2SO_4.TBP.H_2O$.

Sulphuric acid, however, does not extract into ketones, ethers, and esters, but does extract into alcohols, and according to Diamond and Tuck[37] these facts illustrate the competition between water and the organic solvent for the acid. Sulphuric acid is known to have a strong primary hydration in aqueous solution arising from the presence of 2 oxy- and 2 hydroxyl - groups which can hydrogen bond water molecules very strongly. Extraction into alcohols is possible, since such solvents can solvate the anion again by a hydrogen bonding mechanism. In non-hydroxylated solvents, however, there is no such competing hydrogen bonding reaction, and thus the sulphuric acid favours the aqueous phase.

This would suggest that in this case there is direct solvation of the undissociated sulphuric acid molecule in the organic phase by iso-amyl alcohol by extensive hydrogen bonding. It is almost certain that there will be some water in the organic phase and consequently the acid may be partly hydrated.

If we assume that the extraction of sulphuric acid by iso-amyl alcohol occurs by way of the undissociated molecule, the activity of the undissociated acid in the aqueous phase can be related to the activity of the dissociated sulphuric acid in the aqueous phase in the following way. It should be pointed out that the concentration of undissociated acid in aqueous solution only becomes appreciable at high concentrations, and hence the activity of the dissociated acid in the aqueous phase can be substituted by the activity of the total sulphuric acid.

$$a_{(H_2SO_{4\,und})_A} = \frac{(\gamma_{\pm}^{3} . c_{\pm}^{3})_{{H_2SO_4}_A}}{K_1 . K_2} \qquad (2.18)$$

where K_1 and K_2 are the first and second ionization constants for sulphuric acid, $\gamma_{\pm}$ is the mean molal activity coefficient, and $C_{\pm}$ the mean ionic molality. The activity of undissociated acid in the aqueous phase is thus,

$$a_{(H_2SO_{4\,und.})_A} = \frac{\text{activity of total } (H_2SO_4)_A}{K_1 . K_2} \qquad (2.19)$$

Expression (2.15) thus becomes,

$$K_D = \frac{\left[H_2SO_4\right]_o . K_1 . K_2}{a_{{H_2SO_4}_A}} \qquad (2.20)$$

Writing this equation in the logarithmic form gives,

$$\text{Log}\left[H_2SO_4\right]_o = \text{Log } a_{{H_2SO_4}_A} + K' \qquad (2.21)$$

where $$K' = \frac{K_D}{K_1.K_2} \qquad (2.22)$$

The result of plotting the logarithm of the sulphuric acid concentration in the organic phase against the logarithm of the activity of the total sulphuric acid in the aqueous phase is shown in figure 2.5. A straight line plot is certainly obtained, but the slope of this line is 0.72 instead of unity as predicted by equation (2.21). K' is obtained and is equal to 7.08×10^{-1}(mole/l.)$^{-2}$.

There must be, therefore, considerable error involved in neglecting the activities of sulphuric acid in the organic phase. The original assumption in obtaining expression (2.15), that the activity coefficients of sulphuric acid solutions in iso-amyl alcohol are unity, must be wrong. Low values obtained for the slopes of distribution ratio plots in other investigations[38,39] have been suggested to be due to the assumption that the activity coefficients of species in the organic phase are equal to unity. This was found not to be the case for the extraction of sulphuric acid by the amines in iso-amyl alcohol as described in this thesis. The assumption that the activity coefficients of the amine salts in the organic phase are unity was found to be a reasonable one. This is demonstrated in figure 2.4 where the slope of the straight line obtained for the log.-log. plot is very close to the predicted value.

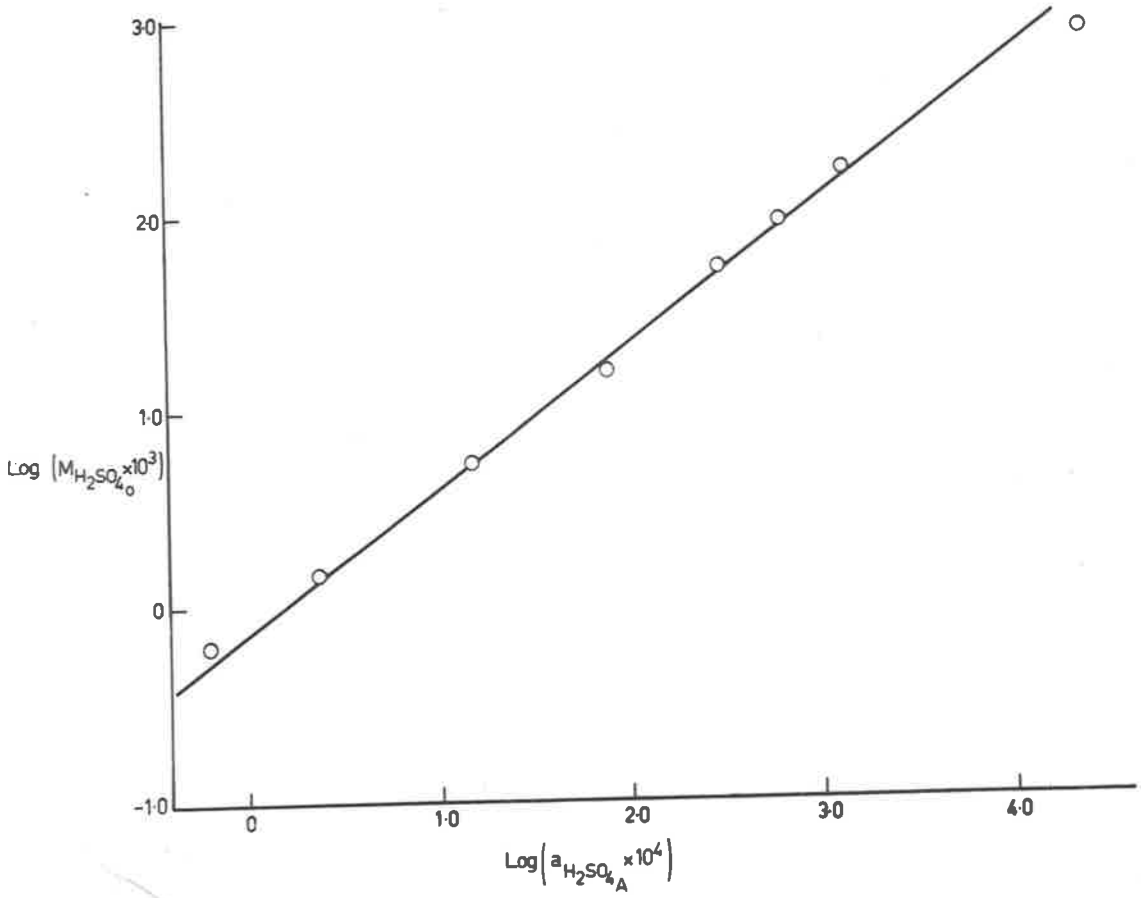


Figure 2.5 Log $(M_{H_2SO_{4_o}} \times 10^3)$ against Log $(a_{H_2SO_{4_A}} \times 10^4)$ for the extraction of sulphuric acid by iso-amyl alcohol.

It is desirable, therefore, to gain a knowledge of the activities of sulphuric acid in iso-amyl alcohol solution. However, this is not possible using the method of Tuck[34] due to the uncertainty of the first ionization constant of sulphuric acid.

IV CONCLUSIONS

The results presented in this chapter show that the extraction of sulphuric acid by the secondary and tertiary amines, di(3,5,5,trimethylhexyl)amine and tri(3,5,5,trimethylhexyl)amine dissolved in iso-amyl alcohol does obey a simple equilibrium law over the amine concentration ranges studied, and that high values for the equilibrium constants are obtained as expected.

The difference in the basicities for the two amines is reflected in a difference in the equilibrium constants for the formation of the amine sulphates, showing that the amine basicity is important in determining the acid extraction ability of the amine.

The large increase in the values for the equilibrium constants in going from a low dielectric constant solvent to a high dielectric constant solvent can be explained on the basis of a better compatibility of the high dielectric constant solvent for the amine salts. The ability of the amines to extract acids has, therefore, been shown to be strongly dependent on the solvent for the amine.

The values for the equilibrium constants are summarized in table 2.9.

Table 2.9

The values for the equilibrium constants for the formation of the amine sulphates and bisulphates.

Amine	pKa	K_1 (mole/l.)$^{-4}$	K_2 (mole/l.)$^{-2}$
di(3,5,5,trimethylhexyl)amine	8.72	$(4\pm3)\times10^{15}$	$(1.18\pm0.2)\times10^{3}$
tri(3,5,5,trimethylhexyl)amine	7.45	$(1.10\pm1)\times10^{14}$	$(2.73\pm0.11)\times10^{3}$

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Chapter III

THE EXTRACTION OF IRON(III) FROM AQUEOUS SULPHATE SOLUTIONS BY DI(3,5,5,TRIMETHYLHEXYL)AMINE.

I. INTRODUCTION

The extraction of iron(III) from aqueous sulphate solutions by high molecular weight amines has been investigated by two workers. Baes[1] in 1955 first published a fundamental study of the extraction of iron(III) from aqueous sulphate solutions by the secondary amine di-n-decylamine dissolved in benzene, and then in 1963 Good *et al.*[2] published a similar study using several amines dissolved in chloroform. The results reported in these two publications are somewhat at a variance with one another.

Baes[1] studied the dependence of the distribution ratio of iron(III) on the aqueous acid concentration, the aqueous sulphate concentration, the aqueous iron(III) concentration, and on the concentration of amine in the organic phase. Baes interpreted his results on the basis of the extraction of a partially hydrolysed species from the aqueous phase such as $FeOHSO_4$ to form an adduct in the organic phase of the type $(R_2NH_2)_2SO_4.FeOHSO_4$, where R is n-decyl.

Good, Bryan and Juge[2], on the other hand determined the stoichiometry of the extracted iron(III) species, for extraction by the commercial primary amine "Primene 81-R" dissolved in chloroform, by analysis of the aqueous solutions, before and after extraction, for H^+, total sulphate, and iron(III). The results of this study indicated a net gain in the organic phase of two iron(III) ions for every three sulphate ions, which can be explained, according to Good *et al.*, by assuming that the following ion exchange reaction occurred.

$$(RNH_3^{+1})_2SO_{4_o} + 2Fe(SO_4)^{-1}_{2_A} \rightleftharpoons 2RNH_3^{+1}Fe(SO_4)^{-1}_{2_o} + SO^{-2}_{4_A} \quad (3.1)$$

Good *et al.* thus suggested that the complex iron(III) anion $Fe(SO_4)_2^{-1}$ was extracted from the aqueous phase, and further supported their suggestion by measuring the spectrum of the extracted complex in the organic phase. This, they said, was similar to the spectrum obtained by Whiteker and Davidson[3] for aqueous iron(III) sulphate solutions containing the species $FeSO_4^{+1}$ and $Fe(SO_4)_2^{-1}$.

Good *et al.* point out that the spectral evidence while in agreement with the postulated existence of the $Fe(SO_4)_2^{-1}$ species in the organic phase does not provide final proof of its existence.

In each of these studies it would seem that insufficient work was done to prove, without any doubt, the existence of the suggested extracted species. This was especially true for the work done by Baes[1], who relied largely on extraction data to determine the nature of the species extracted.

The work described in this chapter was carried out in an attempt to determine the exact nature of the species extracted from aqueous iron(III) sulphate solutions by the secondary amine di(3,5,5,trimethylhexyl)amine.

The problem was approached in three ways.

(1) Firstly, an attempt was made to isolate the complex formed in the organic phase on extraction and to study its properties using spectroscopic and magnetochemical techniques. Neither Baes[1] nor Good et al.[2] in their studies of the extraction of iron(III) from aqueous sulphate solutions by high molecular weight amines attempted to isolate the extracted complex from the organic phase, and hence by analysis determine the stoichiometry. Alternatively the complex could be examined *in situ* in the organic phase without actually being isolated, by extracting enough of the metal to react fully with the complexing agent.

Subsequent analysis of the organic phase would enable its composition to be determined.

(2) Secondly, a purely physico-chemical study was made of the equilibria involved in the extraction, in which the dependence of the extraction on certain variables in the system was determined. This kind of study was made by Baes[1] for the extraction of iron(III) from sulphate solutions by di-*n*-decylamine, and whilst it lends suitable support to other evidence, does not alone enable the exact nature of the extracted species to be determined. On the other hand this type of study is extremely valuable for determining the equilibrium constants involved in the extraction.

(3) Thirdly, a spectroscopic examination was made of the solutions obtained in actual extraction experiments. This type of study has been used extensively by Good *et al.*[2,4-7] who have relied on ultra-violet spectroscopic studies of the organic phases after extraction experiments to identify the metal complex species present.

II. EXPERIMENTAL

1. General Reagents

Ferric Sulphate:

"Baker Analysed" reagent grade.

Di(3.5.5.trimethylhexyl)amine:

As in Chapter 2, experimental section 1.

Benzene:

"Analar" reagent grade extracted several times with conc. sulphuric acid then with water, dried over $CaCl_2$, fractionated, and fraction boiling at 80.0°C collected. (B.Pt.80.1°C).

Acetone:

"Analar" reagent grade, dried over $CaCl_2$, fractionated, and fraction boiling at 56-57°C collected. (B.Pt.56.5°C).

Chloroform:

"Analar" reagent grade purified to remove phosgene and HCl by 10 extractions with 0.5% sodium hydroxide solution followed by 10 extractions with distilled water. Dried over $CaCl_2$, fractionated under nitrogen, and fraction boiling at 61.0°C collected. (B.Pt.61.3°C). Stored under nitrogen away from light. Before use in the extraction experiments the chloroform was again extracted with water, and the aqueous extracts were tested for traces of chloride.

All other reagents were "Analar" grade.

2. The Preparation and Examination of the Iron(III) Complex and the amine Sulphate and Bisulphate.

2.1 Preparation

The di(3,5,5,trimethylhexyl)ammonium-Iron(III)-Sulphate Complex

The iron(III) complex was prepared by the general technique of extracting enough of the ferric iron species from the aqueous phase to react fully with the amine salts in the organic phase, and by subsequently evaporating the organic extract to dryness and collecting the solid remaining. There are several difficulties which immediately become evident in any proposal to carry out a preparation such as this. Firstly, the amine dissolved in an organic solvent upon equilibration with an acidic aqueous iron(III) sulphate solution will be converted to its salts and a mixture of the amine sulphate and bisulphate will be obtained. The second problem is in the choice of the acidity of the aqueous phase to ensure that, in fact, iron(III) does extract efficiently at a particular aqueous acid strength. If the acidity of the aqueous phase is too low (with a pH greater than about 2.5) then the amine will not be fully converted to its salts and a mixture of the amine sulphate and free amine will be obtained in the organic phase. On the other hand if the aqueous acidity is too high (with a pH value less than about 1.0) then the amount of amine bisulphate present in the organic phase becomes very large and the extraction of iron(III) will become very inefficient. The third difficulty which arises is in the choice of the iron(III) concentration in the aqueous phase. Since the iron(III) extraction ratios are only fairly small for extraction by di(3,5,5,trimethylhexyl)amine it is necessary to use a large excess of iron(III) in the aqueous phase over the amount necessary to react fully with the amine salts in the organic phase. Hence the concentration of iron(III) in the aqueous phase must be quite large, and this will cause the added complication that certain polymeric iron(III) species will be present in the aqueous phase in appreciable amounts which are normally absent or only present in trace amounts in very dilute aqueous iron solutions. Also at aqueous pH values of much greater than 2.0 it was found that highly concentrated iron(III) solutions tended to hydrolyse.

The actual preparation was carried out by extracting an aqueous solution containing about 1.0M ferric sulphate with an equal volume of a 0.1M amine solution in benzene. The same organic solution was shaken about five times with fresh samples of the aqueous phase until no more iron(III) was extracted. The extraction was carried out using aqueous solutions of different pH values viz. 0.15, 0.45, 0.60, 0.87, 1.12, 1.39, 1.85, and 2.32. The various pH values were obtained by adding sodium hydroxide to the aqueous ferric sulphate solution which was found initially to be very strongly acid (pH *ca* 0).

It has already been mentioned that immediately the organic amine solution is shaken with the first volume of the acidic iron(III) solution, the amine is converted to its salts, and hence in the above preparation it was not necessary to convert the amine to its salts prior to the iron(III) extraction experiments. However, in one or two experiments the amine was first converted to its salts by shaking with a 0.5M aqueous sulphuric acid solution.

When no more iron(III) would extract into the organic phase at the particular aqueous pH value, the organic solution was separated and filtered. The organic solvent was evaporated under reduced pressure and the product was dried by gentle heating under vacuum. In certain experiments the product was finally dried by heating at 110°C.

The material which was obtained was an orange-red, waxy, solid (M.Pt.204°C). On exposure to air it absorbed water and changed colour from red to yellow.

(a) Analysis for Iron(III) in the isolated material

The material isolated from the organic phase after extraction with the aqueous solutions at each pH value was analysed for ferric iron by two colorimetric methods using 8-hydroxyquinoline and *o*-phenanthroline. The analysis using 8-hydroxyquinoline was carried out on a weighed amount of the solid dissolved in ethanol using the procedure developed especially for analysis of organic phases obtained from actual extraction experiments. This is described in section 3.3.

The analysis using the *o*-phenanthroline method was carried out by decomposing a weighed amount of the solid with a sulphuric-nitric acid mixture. The resulting solution was evaporated to remove nitric acid, and after dilution with water was analysed as described by Vogel[8]. Optical densities were recorded at 510mμ (using a Unicam SP500 spectrophotometer).

(b) Analysis for Amine in the Isolated Material

The analysis for amine was carried out by dissolving a weighed amount of the material in a standard volume of benzene. This solution was then shaken with an aqueous sodium hydroxide solution (about 0.5N) which hydrolysed the amine salts to the free amine form. This procedure was similar to that described in Chapter 2, experimental section 3.1, using an aqueous sodium carbonate solution. The benzene solution containing the free amine was then filtered and analysed by pH titration as described in Chapter 2, experimental section 1. This gave the amount of amine present, as its salts, in the original weight of the solid.

(c) Microanalyses

Were carried out by the C.S.I.R.O. Micro-analytical Laboratories, Melbourne.

Di(3,5,5,trimethylhexyl)ammonium sulphate

The amine sulphate was prepared by dissolving a weighed amount of the amine in benzene and by shaking this solution with an aqueous phase containing an equivalent amount of sulphuric acid. The amount of sulphuric acid was calculated in order to convert the amine completely to the normal sulphate. However, it was usually found that the amount of acid present was a little greater than the amount necessary just to form the normal sulphate, and some amine bisulphate was also formed. This was removed by addition of an excess of free amine to the organic phase after separation which converted the amine bisulphate to the normal sulphate, and, gave a benzene solution which contained the amine sulphate and a small amount of the free amine.

The solvent was then evaporated under reduced pressure, and the solid was heated in an oil bath to about 120°C. A white sticky solid was obtained which became brittle on cooling. Recrystallization from acetone gave fine white crystals

(M.Pt.201°C), which absorbed water on exposure to air corresponding to a half a mole of water/mole.

(Found: C,66.81; H,12.57; S,5.03. Calcd. for $C_{36}H_{80}N_2SO_4\frac{1}{2}H_2O$:
C,66.92; H,12.63; S,4.96.)

Di(3,5,5,trimethylhexyl)ammonium Bisulphate

Di(3,5,5,trimethylhexyl)amine was dissolved in benzene and shaken with an approximately 5N aqueous sulphuric acid solution. This was done several times with fresh 5N acid solutions until no more acid would extract into the organic phase. The amine bisulphate, which formed, was found to be soluble to a limited extent in benzene and some precipitation occurred. The organic phase was then separated and poured into petroleum ether. The amine bisulphate immediately precipitated as a slightly pink crystalline solid. Recrystallization from an ethanol-petroleum ether mixture yielded white needles. The compound melted at about 108°C with some decomposition.

(Found: C,58.78; H,10.87. Calcd. for $C_{18}H_{41}NSO_4$:
C,58.81; H,11.24.)

2.2 Spectroscopic Study

Infra-Red

(a) Compounds: The amine sulphate, amine bisulphate and the iron(III) complex (anhydrous, and hydrated form) used in this study were as described above.

(b) Deuteration procedure: Two methods for deuteration were used, firstly, the red anhydrous iron(III) complex, described above, was stored in a dessicator over D_2O until it had been completely converted to the yellow form. The second method involved the preparation of the iron(III) complex, as described above, using an aqueous solution which was prepared by dissolving all the components in D_2O. The organic phase for this preparation was obtained by dissolving the amine sulphate in benzene.

(c) Techniques: Infra-red spectra were obtained with a Perkin-Elmer Model 21 double beam spectrophotometer, using the mulling technique. Hexachlorobutadiene and nujol were both used as mulling agents to enable the complete spectrum to be studied without interference from bands associated with the mulling agent. Hexachlorobutadiene was used in the frequency region 1900-4000 cm^{-1} to study bands associated with the N-H stretching vibrations, and nujol was used in the region 800-1900 cm^{-1} to study bands associated with the sulphate and bisulphate groups.

Ultra-violet

An ultra-violet spectroscopic examination of the iron(III) complex isolated from the organic phase after extraction with an aqueous phase at pH 2.32, as described in section 2.1, was carried out in benzene solution. Solutions of both the red anhydrous form and the yellow hydrated form (3.4×10^{-4}M, and 2.2×10^{-4}M respectively) of the iron(III) complex* were examined using pure benzene as blank. Spectra were recorded with a Unicam SP500 spectrophotometer.

The spectra of the above solutions were then recorded after addition of weighed amounts of di(3,5,5,trimethylhexyl) ammonium sulphate to make the solutions 0.030M with respect to uncomplexed amine sulphate. For this work a blank solution was used which contained 0.030M amine sulphate.

2.3 Molecular Weight Study

The molecular weight of complex (I) was determined in acetone, and benzene solutions using the isopiestic method of Signer[9,10]. The apparatus used for this determination was essentially the same as that described by Clark[10], except that a third bulb was added to act as a solvent reservoir. This enabled equilibrium to be reached faster since the distillation from the pure solvent reservoir was quite rapid. Weighed amounts of unknown and standard were introduced into the respective bulbs, solvent (2ml) was then added, and the apparatus was sealed under vacuum. The cell was then allowed

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* termed complex (I) and complex (II) respectively from here on.

to equilibrate for several days at 37.1°C.

When equilibrium had been reached the volumes of the unknown and standard solutions were measured by means of the calibrated tubes attached to each bulb. The molecular weight of the complex was then calculated using the following expression.

$$M_1 = \frac{g_1 \cdot v_2 \cdot M_2}{g_2 \cdot v_1} \tag{3.2}$$

Where M_1 and M_2 are the molecular weights of the unknown and the standard respectively, g_1 and g_2 are the weights of unknown and standard, and v_1 and v_2 are the volumes of the unknown and standard solutions respectively.

The standard used for the determinationswas azobenzene which was recrystallized twice from ethanol, and dried under vacuum.

It should be pointed out that there may be some inaccuracy introduced in this method by using azobenzene as the standard, because the molecular weight of the unknown was of the order of 20 times greater than that of the standard. Hence it was necessary to use a weight of unknown which was about 20 times that of the standard in order to obtain equilibrium volumes which were of about the same value.

Attempts to determine the molecular weight of complex (I) in ethanol solution failed owing to the difficulty of completely removing traces of water from this solvent which caused hydrolysis of the complex and the precipitation of ferric hydroxide.

It was also attempted to determine the molecular weight of the yellow hydrated complex (II) in acetone, but the yellow solution which was obtained initially gradually became dark red during equilibration. The molecular weight value obtained agreed reasonably well with that obtained for complex (I) and it was considered that complex (II) had been converted to complex (I) in solution.

2.4 Magnetic Study

The magnetic susceptibilities of complex (I) and complex (II) were measured at room temperature using the Gouy method. Special precautions were used to make sure that complex (I) did not absorb water during the experiments. In fact, the Gouy tube was packed with complex (I) and then heated at 100°C to remove any water which had been absorbed during the packing process. The tube was then stoppered and cooled in a dessicator. Measurements were made using this stoppered tube.

The temperature variation study was carried out by Professor R.L. Martin and Dr. C.R. Kanekar of the University of Melbourne. The sample of the Fe(III) complex (I) used for this study was prepared as in section 2.1 except that the final evaporation of the solvent benzene was carried out using a freeze drying technique so that the temperature was not raised above 20°C at a maximum at any time during the preparation. The product appeared to be partially hydrated.

3. Equilibrium Studies of the Extraction of Iron(III) from Aqueous Sulphate Solutions by Di(3,5,5,trimethylhexyl)amine.

3.1 Solutions

Di(3,5,5,trimethylhexyl)amine solutions in benzene and chloroform.

A stock amine solution (0.10M-0.12M) was made up at 25.0°C by dissolving a weighed amount of di(3,5,5,trimethylhexyl)amine in benzene (chloroform) which had previously been saturated with water. The stock amine solution was then standardized using the method described in Chapter 2, experimental section 3.1. Before use in the iron(III) extraction studies the stock amine solution was equilibrated at 25.0°C with aqueous solutions (previously saturated with solvent to prevent any volume change) identical in composition to those used in the extraction studies except that they contained no ferric iron.

This equilibration procedure gave mixtures of the amine sulphate and bisulphate in benzene (chloroform) solution which were in equilibrium with the aqueous phases of differing pH values to be used in the iron(III) extraction experiments. In this way it was possible to carry out the iron(III) extraction studies for dilute ferric iron solutions without any appreciable change in composition (except for iron(III)) of either phase during the actual experiments.

The equilibrated stock amine solution was diluted at 25.0°C with solvent saturated with water to obtain solutions, which were used in the iron(III) extraction studies, in the concentration range (with respect to total amine) of 0.004M to 0.12M.

Aqueous Sulphate Solutions

Aqueous solutions containing a constant molar strength of 0.50M total sulphate, and iron(III) concentrations of 0.001M, 0.005M and 0.01M in the pH range of about 1.0 to 2.0 were obtained by dissolving weighed amounts of ferric ammonium sulphate and anhydrous sodium sulphate in water, and adding a measured volume of a 1.788M standardized sulphuric acid solution. The compositions of these solutions are shown in table 3.1. The amount of sodium sulphate necessary to make the total molar strength of sulphate 0.50M in these solutions was adjusted, where necessary, to allow for the amount of

Table 3.1

Compositions of the aqueous sulphate solutions used in the iron(III) extraction experiments

	Iron(III) M	Na_2SO_4 M	H_2SO_4 M	Total Molarity of Sulphate M	Initial pH
A	0.001	0.47	0.03	0.50	2.03
B	0.005	0.46	0.03	0.50	2.03
C	0.01	0.45	0.03	0.50	2.03
D	0.001	0.31	0.19	0.50	1.00
E	0.005	0.30	0.19	0.50	1.00
F	0.01	0.29	0.19	0.50	1.00
G	0.001	0.40	0.10	0.50	1.46
H	0.001	0.43	0.07	0.50	1.65
I	0.001	0.43	0.05	0.50	1.82

ferric ammonium sulphate present. Thus for each solution $M\ H_2SO_4$ + $M\ Na_2SO_4$ + (molarity of the sulphate ion associated with the ferric ammonium sulphate) = 0.50M. In this way it was possible to keep the total ionic strengths of the aqueous solutions constant for each experiment.

A second series of solutions were made up identical in composition to those described in table 3.1 except that they did not contain iron(III). These solutions were used in the experiments, described above, for equilibration of the stock amine solution prior to the iron(III) extraction experiments.

All aqueous solutions were saturated at 25.0°C with either benzene or chloroform before use.

3.2 Extraction Procedure

All extraction experiments were carried out in a thermostat at 25.0°C by mixing equal volumes (20ml) of aqueous and organic phases in the reaction vessel shown in Chapter 2, figure 2.2. The extraction of iron(III) was found to be quite rapid with equilibrium being reached in under one minute. Baes[1] also found equilibrium to be reached in under one minute for the extraction of iron(III) from sulphate solutions by di-n-decylamine dissolved in benzene. The rapid extraction of iron(III) is demonstrated in table 3.2, which shows the percentage extraction after various extraction times from a 0.01 M iron(III) solution at pH 1.00 by two equilibrated solutions of di(3,5,5,trimethylhexyl)amine in benzene of initial concentration 0.01 M and 0.005 M respectively.

For the extraction experiments, therefore, a mixing time of 30 min was used, which was considered adequate to ensure that equilibrium was reached under all conditions.

After equilibration the phases were separated, filtered, and analysed.

The pH values of the aqueous phases after equilibration were recorded, and were found to vary by only ±0.02 of a pH unit from the values of the initial aqueous solutions. The values shown in table 3.1 were therefore taken as the pH values of the aqueous phases after the equilibration experiments.

3.3 Analysis of the Phases

Determination of Iron(III) in the aqueous phase

The o-phenanthroline colorimetric method was used as described in section 2.1 (a).

Table 3.2

The percentage extraction of iron(III) for various mixing times.

Initial Amine Concentration M	Percent, Extraction for Various Mixing times 1 min	5 min	30 min
0.10	22.4	22.4	22.3
0.005	3.4	3.3	3.4

Determination of Iron(III) in the organic phase

The concentration of iron(III) in the organic phase could be determined by the difference between the initial iron(III) concentration in the aqueous phase and the final concentration after extraction. This method, however, was found to have severe limitations when the concentration of iron(III) in the organic phase was very small, and led to considerable inaccuracy.

Baes[1] determined the concentration of iron(III) in the organic phase by re-extracting the metal into aqueous nitric acid and estimating the Fe(III) colorimetrically. This method, however, although giving satisfactory results, proved to be tedious when large numbers of analyses had to be done, and an alternative colorimetric procedure was used which enabled the determination to be carried out, directly, on the organic phase.

A method using 8-hydroxyquinoline was developed which was found to be most satisfactory, and enabled the determination of very small amounts of Fe(III) in the organic phase.

<u>The analytical method</u>: An aliquot of the organic phase containing iron(III) was dissolved in ethanol,

and glacial acetic acid (2ml), water (5ml) and a 2% solution of 8-hydroxyquinoline in ethanol (2ml) were added. The solution was then made to a volume of 50ml with ethanol, and the optical density was recorded at 460mμ.

A standard graph of concentration of Fe(III) against optical density was constructed, and a straight line was obtained in accordance with Beer's Law. Benzene-extract solutions, which had previously been analysed for Fe(III) by the back-extraction method of Baes[1] were used for the construction of this standard graph. These benzene-extract solutions were obtained from equilibration experiments with solution A, shown in table 3.1, and amine solutions in benzene of initial concentration 0.004M to 0.10M. A blank ethanol solution was prepared for the optical density measurementr containing all the reagents used in the analysis. The presence of amine salts and a small amount of the organic solvent, was found to have no effect on the optical density of the ferric 8-hydroxyquinolate solution.

The results obtained by this direct colorimetric analysis of the organic phase were in excellent agreement with the expected values obtained by a mass balance of iron(III) in the system.

Determination of the uncomplexed di(3,5,5,trimethylhexyl)ammonium sulphate concentration in the organic phase.

It should be pointed out, here, that for the conditions used in these extraction studies the amounts of free amine in the equilibrated organic phases were negligible, and the organic phases always contained mixtures of the amine bisulphate and sulphate.

The concentration of amine bisulphate was obtained by pH titration (as in Chapter 2, experimental section 3.1) and subtraction of this value from the total initial amine concentration gave the amount of amine as amine sulphate both free and complexed with Fe(III). The latter quantity was calculated from the Fe(III) concentration determined by analysis and assuming one mole of amine sulphate was attached to each Fe(III). At the low Fe(III) concentrations used in this study, the amount of amine sulphate complexed to Fe(III) in the organic phase was very small, and subsequent adjustment of the total amine concentration to allow for this generally made only a small difference to the values.

The presence of Fe(III) in the organic phases interfered with the determination of the amine bisulphate concentration by pH titration and therefore adjustments were made to the titration results to allow for this. The smallest adjustments were necessary for organic extract solutions obtained after equilibration experiments with 0.001M aqueous iron(III) solutions since only small amounts of Fe(III) were extracted. In fact, for equilibration experiments with the 0.001M aqueous iron(III) solution at pH 1.00 the amounts of Fe(III) in the organic extracts were so low that the effect on the pH titrations was negligible. Hence the determinations of amine bisulphate were carried out on the organic phases obtained after equilibration with 0.001M aqueous iron(III) solutions, and the values obtained (after adjustment for Fe(III) where necessary) were used to calculate the total amine sulphate concentrations. These values were used in subsequent work with more concentrated Fe(III) solutions, since the same amine solutions as used for the studies with 0.001M Fe(III) solutions were used for this work.

The adjustment to the titration results for the amounts of Fe(III) in the organic phases were made assuming that iron(III) was already present as the partially hydrolysed species $(FeOH)^{+2}$, and that this was converted to $Fe(OH)_3$ by reaction with sodium hydroxide.

4. Ultra-Violet Spectroscopic Examination of the Organic Phases after the Fe(III) Extraction Studies

An ultra-violet spectral examination was made of certain of the benzene solutions obtained after the Fe(III) extraction studies. Blank solutions were used which were identical in composition to the benzene extract solutions except that they contained no Fe(III).

Only a limited number of the organic phases obtained after extraction experiments with aqueous Fe(III) solutions at pH 2.03 were suitable for spectral studies since the optical densities were generally too high to be measured in the wavelength range of interest (270-400mμ).

The ultra-violet spectra of the aqueous sulphate solutions containing Fe(III) as described in table 3.1 were also recorded in the same wavelength region, using pure water as the blank. It was impossible to record the complete spectra of the solutions containing 0.01M Fe(III) due to their very high optical densities.

III. RESULTS AND DISCUSSION

A. Examination of the Isolated Iron(III) Complex.

1. Analysis

The results of the analyses of the solids isolated from the organic phases after extraction of Fe(III) from the aqueous phases at each pH value are shown in table 3.3. The percentages of Fe(III) together with the numbers of amine groups and sulphate groups per Fe(III) ion are shown for each solid. The numbers of sulphate groups per Fe(III) ion were determined using the micro-analytical figures for sulphur.

It should be mentioned that micro-analysis figures for nitrogen in compounds of the type reported in this thesis were generally found to be low, and hence reliance was placed only on the C, H, and S figures. Where necessary amine present in the compound was determined by titration as in experimental section 2.1 (b).

Complex (I) isolated from the organic phase as an orange-red, waxy, solid using the aqueous solution at pH 2.32 gave the following micro-analytical figures.

Table 3.3

The Compositions of the solids prepared using aqueous solutions of various pHs.

Aqueous pH	Fe(III) %	No. of Amine Gps/Fe(III)	No. of Sulphate Gps/Fe(III)
0.15	1.54	10.59	ND
0.45	4.09	3.73	3.21
0.60	4.34	3.30	ND
0.87	5.33	2.72	2.69
1.12	5.42	2.62	2.43
1.39	5.79	2.45	2.12
1.85	6.72	2.08	2.02
2.32	6.92	2.00	2.00

ND Not determined.

Calcd. for $C_{36}H_{81}N_2O_9S_2Fe$: C,53.7; H,10.1; S,7.96; Fe,6.93
Found C,53.0; H,9.74; S,7.89; Fe,6.92.

Complex (I) absorbed water on exposure to air and changed to the yellow complex (II), whose micro-analytical figures were as follows:

Calcd. for $C_{36}H_{81}N_2O_9S_2Fe.1H_2O$: C,52.5; H,10.2; S,7.78; Fe,6.78
Found: C,52.2; H,10.1; S,8.28; Fe,6.67

A sample of complex (II) lost 2.1% in weight on heating at 120°C. For the formula $C_{36}H_{81}N_2O_9S_2Fe.1H_2O$, loss of 1 water corresponds to 2.2%.

Complex (I) was found to be extremely soluble in all organic solvents to give orange-dark red solutions. In water the complex appeared to hydrolyse to give $Fe(OH)_3$. Complex (II) dissolved readily in all organic solvents to give initially yellow-orange solutions, which gradually changed to orange-dark red suggesting that it was converted to complex (I). Complex (II) also lost water on heating at 100°C to give complex (I).

The results shown in table 3.3 are represented graphically in figures 3.1 and 3.2. In figure 3.1 the

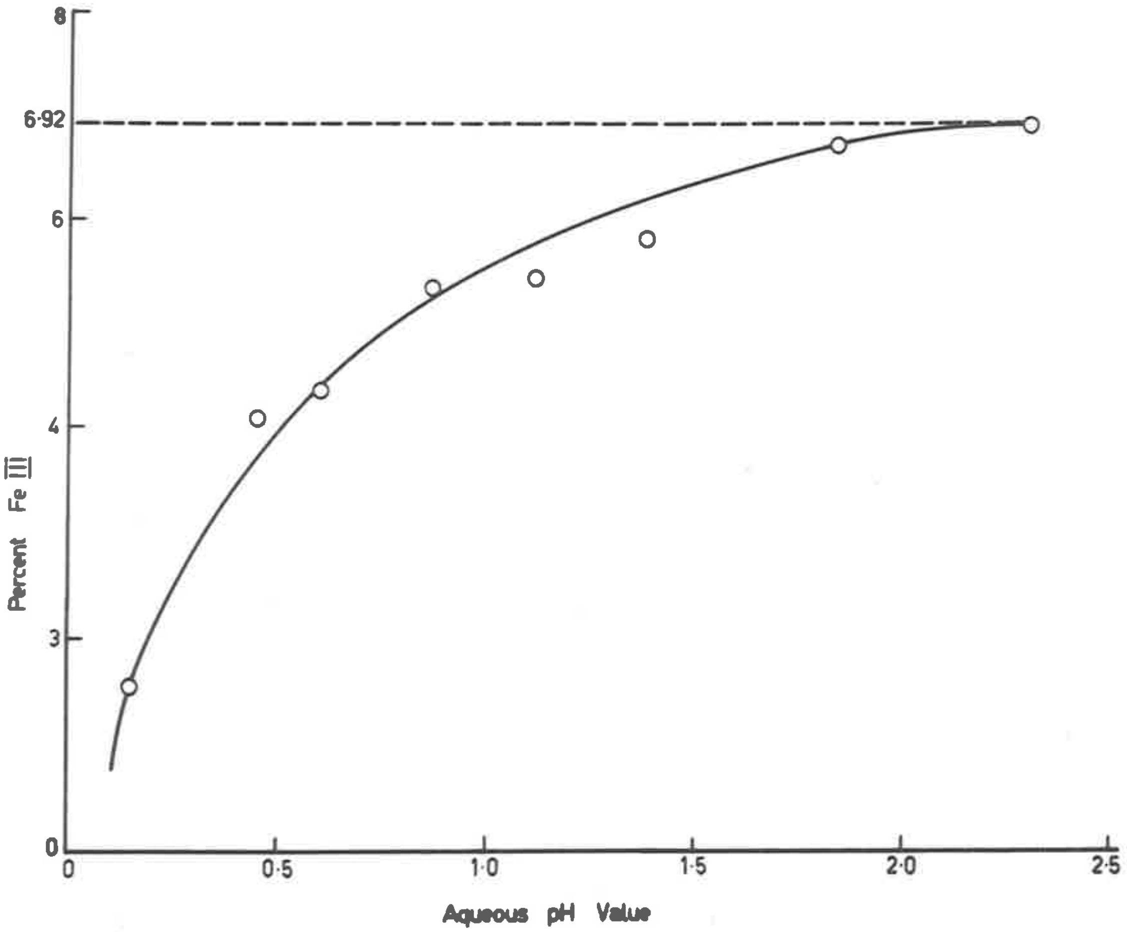


Figure 3.1 The iron(III) contents of the solids isolated from the organic phases.

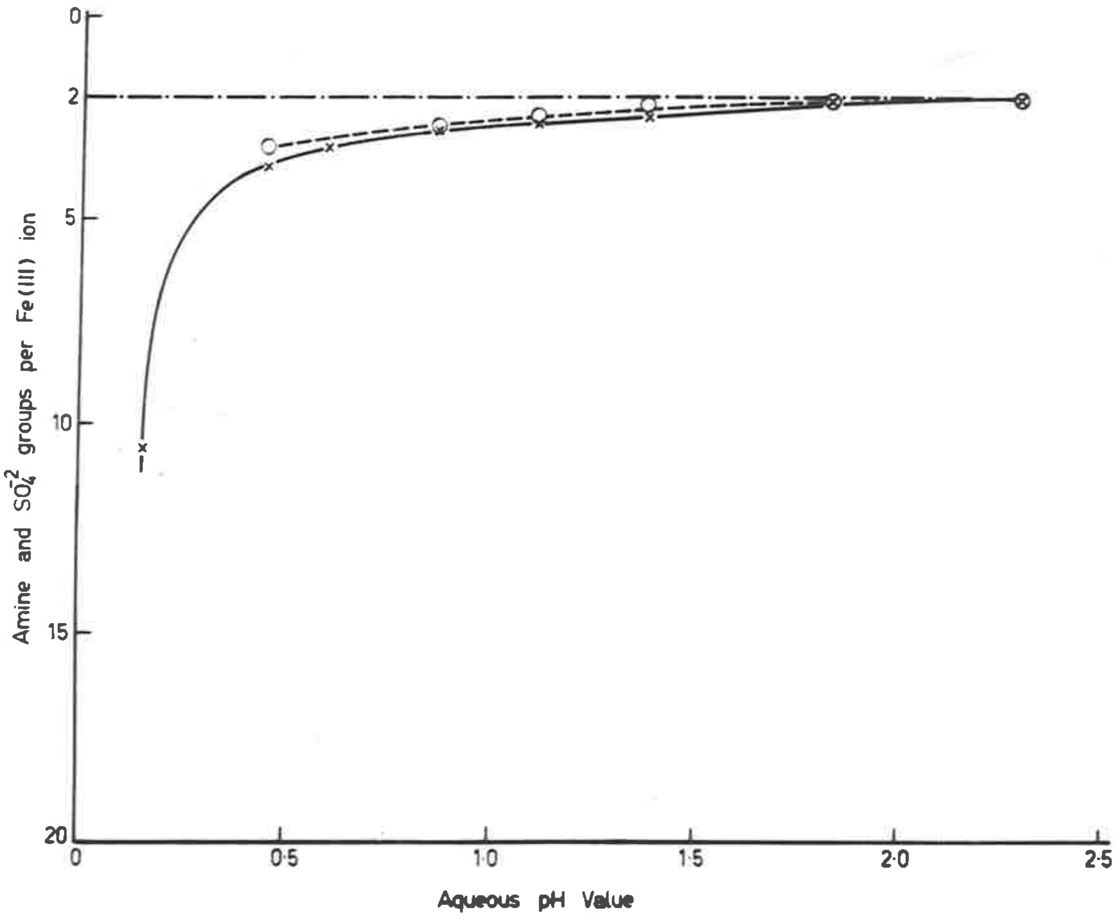


Figure 3.2 The number of amine and sulphate groups per Fe(III) ion in the solids isolated from the organic phases.

percentage of Fe(III) in the solids is plotted against the aqueous pH, and in figure 3.2 the numbers of amine groups and sulphate groups per Fe(III) ion in the solids are also plotted against pH.

It can be seen from the figures that the Fe(III) content of the solids increases with increase in pH of the aqueous phase, and appears to approach a constant value of 6.92 per cent. in the pH region of 2.1 to 2.3. The number of amine groups per Fe(III) ion is very large for the lower pHs but shows, along with the number of sulphate groups per Fe(III) ion, the same tendency as the Fe(III) content of approaching a constant value, and in the pH region of 2,1 to 2.3 both have the value of 2.

There is, therefore, a tendency for the solid separated from the organic phase to approach a limiting composition of 6.92 per cent. Fe(III) and 2 amine and 2 sulphate groups per Fe(III) ion in the aqueous pH region of about 2.1 to 2.3.

The micro-analysis of complex (I), which was prepared using an aqueous solution at pH 2.32, is consistent with the empirical formula $(R_2NH)_2FeOH(SO_4)_2$ where R is 3,5,5,trimethylhexyl, and this formula is also consistent with the above evidence since it contains 2 amine and 2 sulphate groups per Fe(III) ion and has a theoretical Fe(III) content of 6.93 per cent. The analysis of complex (II) is consistent with the formula $(R_2NH_2)_2FeOH(SO_4)_2.1H_2O$.

The formation of complex (I), in its simplest form, can be considered to occur by the reaction of an amine sulphate molecule from the organic phase with the iron(III) species $FeOHSO_4$ from the aqueous phase.

This would seem reasonable in view of the results of the study of the extraction of uranium (VI) from aqueous sulphate solutions by high molecular weight amines by Sato[11, 12] and others[13, 14, 15] who have found evidence for the fact that there appears to be no amine bisulphate complexed with uranium (VI) in the organic phase, and that it is the amine sulphate which is complexed with the uranium (VI) species from the aqueous phase. Similarly Baes[1] for the extraction of Fe(III) from sulphate solutions by di-n-decylamine has suggested that it is the amine sulphate which is complexed to the Fe(III) species from the aqueous phase.

Sato[11, 12] has also shown, by an infra-red spectroscopic study of the organic extracts, that at higher aqueous acidities mixtures of the amine bisulphate and the uranium (VI) sulphate-amine sulphate complex are obtained.

Hence it seems quite reasonable to assume that in the present study similar mixtures of amine bisulphate and the iron(III) hydroxy-sulphate-amine sulphate complex will be obtained in the organic phase when using aqueous solutions of higher acidities. It appears that the solids isolated from the organic solutions which had Fe(III) contents less than the theoretical value of 6.93 per cent. for complex (I), and which contained greater than 2 amine and 2 sulphate groups per Fe(III) ion, were merely such mixtures.

In fact, the analysis figures shown in table 3.3 are in excellent agreement with this, since a calculation of the amounts of Fe(III) expected in the isolated materials for mixtures of complex (I) and amine bisulphate which have the same number of amine groups per Fe(III) ion as shown in the table, give Fe(III) percentages which are very close to the experimental values.

2. Spectroscopic Study.

2.1 Infra-Red

(a) Spectra of di(3.5.5.trimethylhexyl)ammonium Sulphate and bisulphate

In order to understand the infra-red spectra of the iron(III) complexes (I) and (II) it is necessary to assign the bands found in the simple amine, and the amine salts.

<u>N-H stretching vibrations</u>: The infra-red spectra of the normal amine sulphate and bisulphate are shown in figure 3.3. In the region 1900-400cm^{-1}, as shown by curves (c) and (d), it can be seen that there are several fairly broad bands which are associated with the N-H and C-H stretching vibrations. The large bands occurring at about 2800-3000cm^{-1} can be disregarded as they are due to the C-H stretching vibrations, and, of course, appear unchanged in the pure amine, and in all the amine compounds. There are, however, several other bands appearing in curves (c) and (d) which are important.

Heacock and Marion[16] have studied the infra-red spectra of a large group of secondary amines and their nitrate, perchlorate and chloride salts, and have found that in most cases the normal N-H stretching band for the free bases occurs in the region 3380-3205cm^{-1}, and that with the formation of the amine salts considerable attenuation and displacement of the normal N-H stretching band towards lower frequencies occurs. In nearly all the cases studied by Heacock and Marion[16] a complex series of absorption bands was found in the region 2800-2000cm^{-1} which is associated with $-NH_2^+$ stretching vibrations.

Figure 3.3 Infra-red Spectra of

Di(3,5,5,trimethylhexyl)ammonium Sulphate and Bisulphate.

(a) amine sulphate in nujol.
(b) amine bisulphate in nujol.
(c) amine sulphate in hexachlorobutadiene.
(d) amine bisulphate in hexachlorobutadiene.

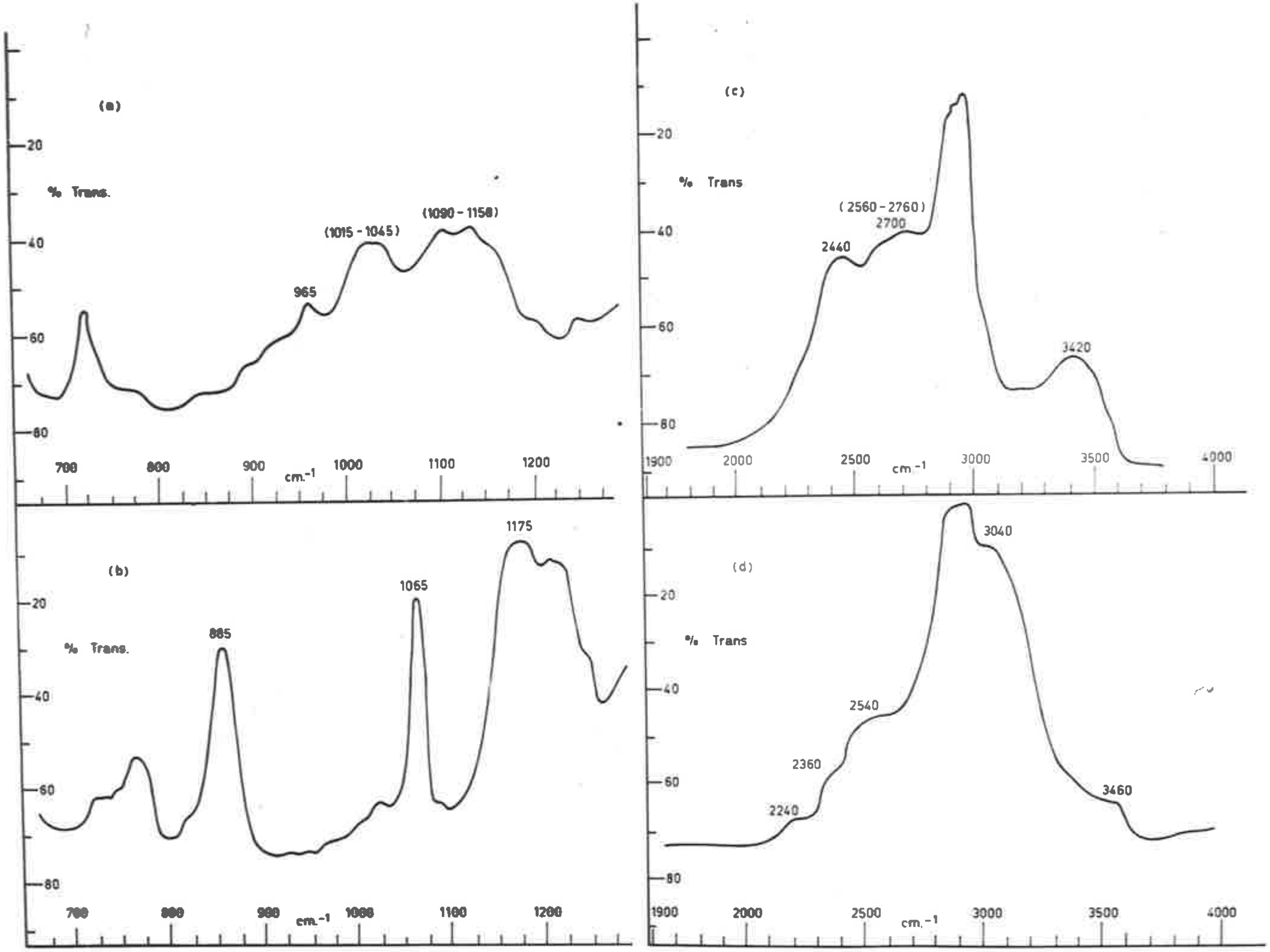

(a)
% Trans.
20
40
60
80
965
(1015 - 1045)
(1090 - 1150)
700
800
900
cm.-1
1000
1100
1200
(b)
% Trans.
20
40
60
80
885
1065
1175
700
800
900
cm.-1
1000
1100
1200
(c)
% Trans
20
40
60
80
(2560 - 2760)
2700
2440
3420
1900
2000
2500
cm.-1
3000
3500
4000
(d)
3040
20
% Trans
40
2540
2360
60
2240
3460
80
1900
2000
2500
cm.-1
3000
3500
4000

Figure 3.3

The bands, therefore, occurring in the spectrum of di(3,5,5,trimethylhexyl)ammonium sulphate, shown by curve (c) in figure 3.3, at about 2440cm^{-1}, and 2560-2760cm^{-1} are probably due to N-H stretching vibrations associated with the $-NH_2^+$ group.

The spectrum of the free amine di(3,5,5,trimethylhexyl)amine is shown in figure 3.4, and the characteristic absorption found by Heacock and Marion[16] for the normal N-H stretching band can be seen in the region 3200-3300cm^{-1}. This absorption band is quite broad and very weak for this particular amine which is possibly caused by the large alkyl chains surrounding the N-H group and holding it in a rigid configuration, and hence interfering with the N-H stretching vibration. In fact, Heacock and Marion[16] report actual cases where the N-H stretching vibration in the free amine is completely missing in the spectrum.

It should be mentioned, here, that Heacock and Marion[16] also observed a medium to strong absorption peak near 1600cm^{-1} for all the secondary amine salts studied, which was absent in spectra of the corresponding free bases. This band they said was due to deformation vibrations of the protonated secondary amino group. A band which occurred at 1620cm^{-1} (not shown in figures 3.3 and 3.5) was observed in the present study for all the compounds involving the

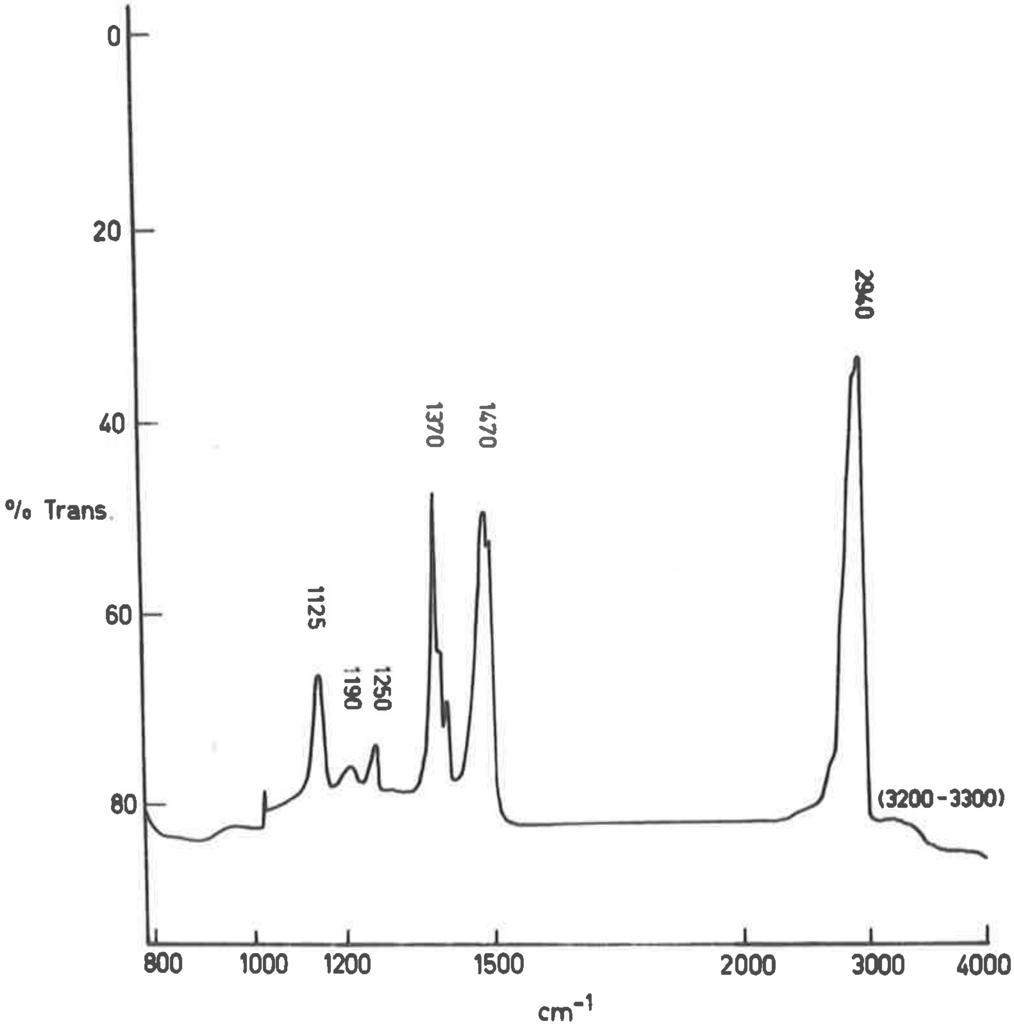


Figure 3.4 The infra-red spectrum of di(3,5,5,trimethylhexyl)amine.

quaternary ammonium species and is probably due to this deformation vibration of the $-NH_2^+$ group. This band was absent in the infra-red spectrum of the free base di(3,5,5,trimethylhexyl)amine shown in figure 3.4. A similar band is observed for the deformation vibration associated with the hydroxyl group in water[17], and hence in the hydrated quaternary ammonium compounds the band at $1620cm^{-1}$ is probably due to a combination of both deformation vibrations.

Keder, Wilson and Burger[18] have studied the nuclear magnetic resonance spectra of certain tri-n-octylammonium salts in several organic solvents, and by studying the position of the H-N resonances in the magnetic field for the alkylammonium salts, have found a strong down-field shift which appears to be dependent upon the anion associated with the alkylammonium ion. This, they said, was due to the formation of strong hydrogen bonds between the protonated amine and the anion associated with the alkylammonium ion, and that the strength of the hydrogen bond was dependent on the particular anion.

Keder *et al.*[18] have supported their N.M.R. Study with an infra-red spectroscopic study in the N-H stretching frequency region, and have found a shift in the N-H stretching frequency to lower values with increase in hydrogen bonding. This shift to lower frequency was again found to be strongly dependent on the anion associated with the alkylammonium cation.

The considerable attenuation and displacement of the normal N-H stretching band in the secondary amines towards lower frequencies on the formation of the amine salts, as found by Heacock and Marion[16], may, in fact, be due largely to the interaction between the protons attached to the quaternary nitrogen atom and the associated anion. This may result in the appearance of the complex series of absorption bands in the region 2800-2000cm^{-1}.

According to Chenon and Sandorfy[19] the free $-NH_2^+$ stretching frequency, if it were possible to determine this, may appear in the region 3200-3000cm^{-1}, however, hydrogen bonding of this group is responsible for the shift of several hundred wave numbers and the $-NH_2^+$ stretching frequency appears in the region 2000-2800cm^{-1}.

In view of the above evidence it seems quite probable that such interactions occur in di(3,5,5,trimethylhexyl) ammonium sulphate and that there is strong hydrogen bonding between the protons attached to the quaternary nitrogen atom and the associated sulphate group.

The spectrum of the amine bisulphate, as shown by curve (d) in figure 3.3 shows very much weaker bands in the region found for the normal sulphate, and shows a strong absorption band at about 3040cm^{-1}. This band is again probably due to N-H stretching vibrations associated with the $-NH_2^+$ group but occurs at a higher frequency due to much weaker hydrogen bonding between the protons associated with the alkylammonium ion and the bisulphate anion. According to Elsworth and Sheppard[20] under conditions of weak hydrogen bonding most stretching frequencies of the NH_2^+ group would lie in the region 3100-3000cm^{-1}, which is consistent with that found above for the amine bisulphate. It is interesting to note that in the normal amine sulphate two hydrogen bonds can form between the protons attached to the quaternary nitrogen atom and the sulphate group, whereas in the amine bisulphate it is more likely that only one such hydrogen bond will be formed. In the case of the normal amine sulphate this could lead to extensive inter-molecular hydrogen bonding by interaction between the protons associated with the alkylammonium ion and sulphate groups attached to adjacent amine sulphate molecules.

The difference between the spectra of the normal amine sulphate and the amine bisulphate is consistent with the evidence found by Keder *et al.*[18] that the strength of the hydrogen bonding, and hence the shift in the N-H stretching frequency, is dependent on the anion associated with the alkylammonium group.

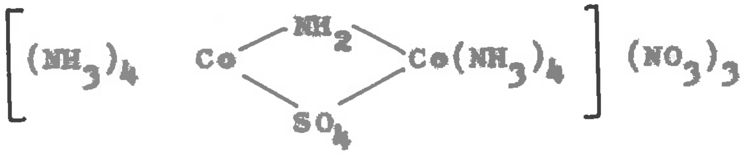
There is a further peak shown in curves (c) and (d) in figure 3.3 which merits some mention. This occurs at about 3400-3460cm^{-1}, and might be thought to be due to the stretching vibration associated with the hydroxyl group in free water. According to Bellamy[21] the free O-H stretching frequency should occur in the region 3650-3590cm^{-1}, but is considerably shifted to lower frequencies by hydrogen bonding. In the alkylammonium compounds described in the present work hydrogen bonding must certainly occur and it would be expected to find the O-H stretching frequency for water occurring in a region lower than 3650-3590cm^{-1}. However, the band at 3400-3460cm^{-1} persists in all the alkylammonium compounds studied even after dehydration, and hence is probably not due to the O-H stretching vibration, but alternatively is another absorption due to the N-H stretching vibration. In fact, this may be the stretching vibration band which is observed in the free amine as shown in figure 3.4, considerably strengthened due to the tetrahedral configuration of the quaternary nitrogen atom which decreases the shielding effect of the long chain alkyl groups.

It can be seen from this study that although the band associated with the N-H stretching vibration for the simple amines is usually well defined at a single frequency, the bands for the alkylammonium salts are quite complex, and the numbers, intensities, and positions of these bands are determined by the interactions of the protons associated with the $-NH_2^+$ group.

Absorptions due to the sulphate and bisulphate groups: The spectra of the amine sulphate and bisulphate in the region 800-1300cm^{-1} associated with the absorptions due to the sulphate and bisulphate groups are shown in figure 3.3 by curves (a) and (b). The vibrational frequencies associated with the sulphate groups are described fully by Nakamoto[17], who has shown the effect on the infra-red spectrum of the sulphate ion acting in a normal salt, and in a unidentate and bidentate complex. The free sulphate ion belongs to the high symmetry point group Td, and hence has four fundamental modes of vibration of which only v_3 and v_4 are infra-red active. The free sulphate ion has infra-red absorption bands occurring at 1104cm^{-1} and 613cm^{-1}. In certain sulphate salts and complexes, however, other absorption bands are observed in the infra-red spectrum. In this discussion only the v_1 and v_3 fundamental modes of vibration will be considered since they show vibrational frequencies in the region of 800-1300cm^{-1} which was investigated in the present study.

The spectrum of the salt $[Co(NH_3)_6]_2[SO_4]_3 \cdot 5H_2O$, described by Nakamoto[17], shows two absorption bands at 973cm^{-1}, and 1130-1140cm^{-1} corresponding to the v_1 and v_3 modes of vibration respectively.

On coordination of the sulphate ion to a metal, however, the symmetry is lowered with the appearance of new bands in the spectrum. The lowering of symmetry is different for sulphate acting as a unidentate rather than a bidentate group with the result that in the unidentate sulphate complex $[Co(NH_3)_5SO_4]Br$ v_3 splits into two bands at 1032-1044cm^{-1} and 1117-1143cm^{-1}, which appear in the spectrum in addition to the v_1 band at 970cm^{-1}. For a bidentate complex or a bridged bidentate complex such as



$$\left[(NH_3)_4Co\begin{matrix}NH_2\\SO_4\end{matrix}Co(NH_3)_4\right](NO_3)_3$$

v_3 splits into three bands and hence the spectrum in the region 800-1300cm^{-1} contains four absorption bands at 995cm^{-1}, 1050-1060cm^{-1}, 1105cm^{-1}, and 1170cm^{-1}.

The spectrum of di(3,5,5,trimethylhexyl)ammonium sulphate shown by curve (a) in figure 3.3, shows three absorption bands at frequencies of 965cm^{-1}, 1015-1045cm^{-1}, and 1090-1150cm^{-1} which are very close to the frequencies described above for sulphate acting as a unidentate group. The band at 965cm^{-1} can be assigned to the v_1 vibrational mode and is of moderate intensity as expected. The band at 1015-1045cm^{-1} is quite strong and broad while the band at 1090-1150cm^{-1} is also strong and broad and appears to be resolvable into two bands. One of these, however, is due to the C-N stretching vibration which appears in the spectrum of the free amine at 1125cm^{-1} as shown in figure 3.4.

The evidence gained from the infra-red spectrum of the amine sulphate supports the suggestion that there is strong hydrogen bonding occurring between the protons associated with the alkylammonium ion and the sulphate anion, since this might be expected to lower the symmetry of the sulphate ion sufficiently to give an infra-red spectrum similar to that of a unidentate complex.

The spectrum of the amine bisulphate, on the other hand, is less complex as shown by curve (b) in figure 3.3. Three bands are observed in the region 800-1300cm^{-1}, a sharp medium intensity peak at 885cm^{-1}, another sharp peak at 1065cm^{-1}, and a high intensity broad band at about 1175cm^{-1}. According to Cross[22] there are three bands associated with the bisulphate ion occurring at 1180-1160cm^{-1}, 1080-1000cm^{-1}, and 880-840cm^{-1}. Thus the absorption frequencies in the infra-red spectrum of di(3,5,5,trimethylhexyl)ammonium bisulphate are in excellent agreement with the literature values, which is consistent with the previous suggestion that the interaction between the alkylammonium ion and the bisulphate anion is much weaker than for the normal amine sulphate.

Sato[11] also obtained frequencies similar to those shown above for absorptions due to the bisulphate ion for several cyclohexyl- and benzyl-alkylammonium salts dissolved in chloroform.

(b) Spectra of the di(3,5,5,trimethylhexyl)ammonium-iron(III)-sulphate complexes.

N-H stretching vibrations: The infra-red spectra of complexes (I) and (II) in the region 1900-4000cm^{-1} are shown by curves (c) and (d) in figure 3.5. The most

Figure 3.5 Infra-red Spectra of Iron(III) Complexes (I) and (II).

(a) Complex (I) in nujol.

(b) Complex (II) in nujol.

(c) Complex (I) in hexachlorobutadiene.

(d) Complex (II) in hexachlorobutadiene.

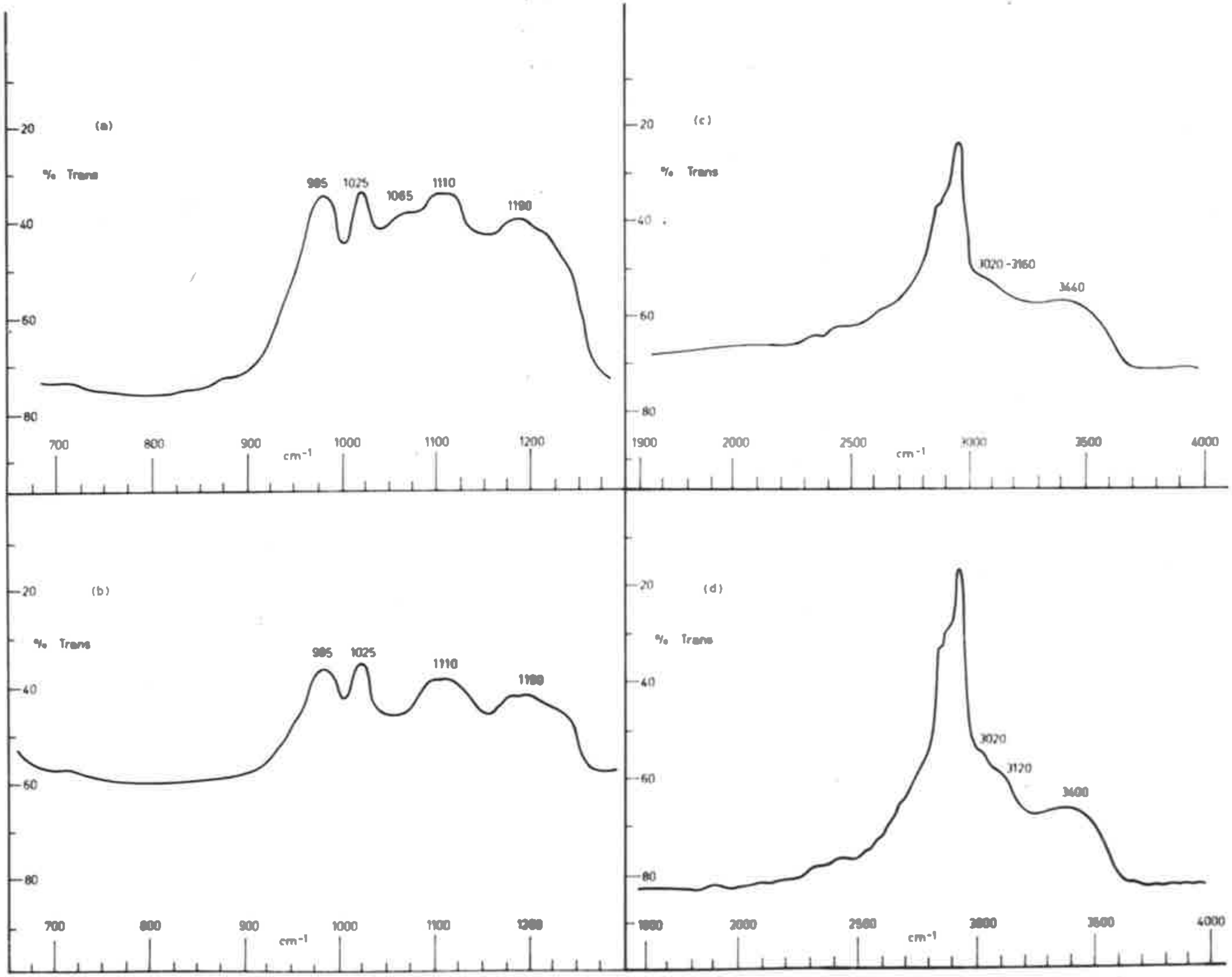

(a)
% Trans
20
40
60
80
985
1025
1065
1110
1190
700
800
900
1000
1100
1200
cm⁻¹
(b)
% Trans
20
40
60
80
985
1025
1110
1190
700
800
900
1000
1100
1200
cm⁻¹
(c)
% Trans
20
40
60
80
3020-3160
3440
1900
2000
2500
3000
3500
4000
cm⁻¹
(d)
% Trans
20
40
60
80
3020
3120
3400
1900
2000
2500
3000
3500
4000
cm⁻¹

Figure 3.5

significant difference between the spectra of the iron(III) complexes and that for the normal amine sulphate, shown by curve (c) in figure 3.3, is the absence of the broad N-H stretching bands associated with the $-NH_2^+$ group in the region of about 2400-2800cm^{-1}. It has already been suggested that the appearance of these bands in the normal amine sulphate spectrum may be due to extensive hydrogen bonding between the protons associated with the alkylammonium ion and the sulphate anion. The absence of these bands, therefore, in the spectra of the iron(III) complexes suggests that this hydrogen bonding becomes negligible or very weak once the sulphate anion associated with the alkylammonium cation is complexed to iron(III). This is consistent with the molecular weight studies described in Chapter 4 since it has been found that the amine sulphate forms large molecular aggregates (or micelles) in certain solvents. However, once the amine sulphate has been complexed with Fe(III) this tendency to form micelles becomes negligible. It is suggested in Chapter 4 that extensive inter-molecular hydrogen bonding between the protons attached to the quaternary nitrogen atoms and adjacent sulphate anions is responsible for the stabilization of the micelles.

There is further evidence for this, since in Chapter 4, results and discussion section 2 it is shown that the aggregation of the amine bisulphate in benzene solution is considerably less than that of the normal amine sulphate in the same solvent, which is consistent with the suggestion (section (a) above) that the interaction between the protons attached to the quaternary nitrogen atom and the bisulphate anion is considerably less than the interaction between these protons and the sulphate anion.

Much weaker interaction between alkylammonium cations and complex metal anions than between the cations and the anions of simple acids has also been suggested by Keder et al.[18] who obtained evidence for this from infra-red and N.M.R. spectroscopic studies. The reason for this is probably due to an electronic or stereochemical effect.

The absorption bands in the region 3020-3160cm^{-1}, as shown in figure 3.5 can probably be assigned to the N-H stretching vibrations. The large broad band which occurred in the region 3400-3460cm^{-1} for the amine sulphate is still evident in the spectra of the iron(III) complexes (figure 3.5), and as has been suggested already is probably another absorption due to the N-H stretching vibration.

There is no band or bands occurring in the spectrum of the iron(III) complex (I) which can be assigned with certainty to the O-H stretching vibration associated with the hydroxyl group believed to be complexed to Fe(III). This is to be expected in the 3400-3600cm^{-1} region since such a hydroxyl group would most certainly be hydrogen bonded and would thus give a broad, very low intensity, absorption band which would be hidden by the extensive N-H absorption. Hence, although infra-red evidence is lacking for the presence in the complex of the hydroxyl group, the possibility is not excluded because of the interference from N-H absorptions. It should be noted that complex (II) is simply the hydrated form of complex (I), and hence any attempt to identify the hydroxyl group complexed to Fe(III) in complex (II) would be fruitless due to the presence of water.

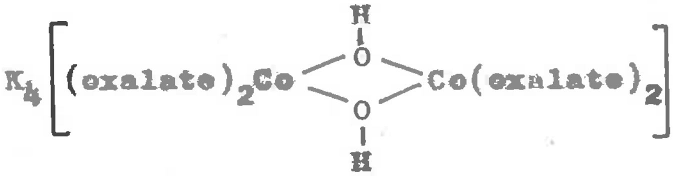
Deuteration: Due to the inability to detect any absorption which could be assigned to the hydroxyl group in complex (I), deuteration of the complex was carried out in the hope that this might bring about a change in the existing bands, or that new bands would appear in the spectrum. However, deuteration of complex (I) did not produce any observable change in the infra-red spectrum, and no new band appeared which could be assigned to the O-D stretching vibration. Similarly no new band appeared which could be assigned to the N-D stretching vibration.

The spectrum of complex (II) after absorption of D_2O was quite similar to that of the ordinary complex, except that two new bands were observed. These absorption bands which were broad and quite weak and which occurred in the regions 2100-2300cm^{-1} and 2400-2600cm^{-1} can probably be assigned to vibrations associated with D_2O itself or to N-H stretching vibrations which have been shifted to lower frequencies by hydrogen bonding to D_2O

Absorptions due to the sulphate and bisulphate groups: The spectra of the iron(III) complexes (I) and (II) in the region 800-1300cm^{-1} are shown by curves (a) and (b) in figure 3.5. Complex (I) shows four absorption bands at 985cm^{-1}, 1065cm^{-1}, 1110cm^{-1} and 1190cm^{-1} which are consistent with those expected for the sulphate ion acting as a bidentate ligand in a complex such as this. The band at 1065cm^{-1} is fairly weak but is detectable in the spectrum of complex (I). There is a further absorption which occurs at 1025cm^{-1} which has not been positively identified, but Sato[11] has reported this absorption band for amine sulphate-uranium VI sulphate complexes and hence it is possibly associated with the sulphate-group.

The spectrum of the yellow complex (II) is similar to that of complex (I) except that the absorption band at 1065cm^{-1} is absent. This is probably due to the fact that it is much weaker than that for complex (I) and becomes hidden by the broad band at 1110cm^{-1}.

There is considerable evidence[17] that hydroxo-metal complexes of the type M-O-H exhibit absorption due to bending modes in the region 850-1100cm^{-1}. In fact, the cobalt (III) complex[17]



$$K_4\left[(\text{oxalate})_2\text{Co}\begin{array}{c}\text{H}\\ \text{O}\\ \text{O}\\ \text{H}\end{array}\text{Co}(\text{oxalate})_2\right]$$

which contains hydroxyl ion bridging, has an absorption band occurring at about 1100cm^{-1} which is considered possibly due to O-H bending. It was thus thought initially that the band observed at 1025cm^{-1} for the iron(III) complexes (I) and (II) may be due to O-H bending of the hydroxyl group attached to iron(III), however, on deuteration of complex (I) this band remained unaffected and hence cannot be due to this. Deuteration of the cobalt (III) complex shown above results in complete disappearance of the band at 1100cm^{-1}.

This evidence does not rule out the possibility of the iron complexes (I) and (II) containing the hydroxyl group, since the absorption due to the O-H bending mode would be very weak and is probably hidden, if present, beneath the strong absorption bands associated with the sulphate groups.

It has been suggested in section 1 above on the constitution of the iron(III) complex that the solids isolated from the organic solutions, which had Fe(III) contents less than the theoretical value of 6.93 per cent., and which contained greater than 2 amine and 2 sulphate groups per Fe(III) ion, were mixtures of the complex (I) and amine bisulphate. Thus the infra-red spectra of such materials should show the characteristic bands associated with the bisulphate ion. However, the spectrum of the solid isolated from the organic phase using an aqueous solution at pH 0.87 did not show the characteristic absorption at 885cm^{-1} for the bisulphate ion as expected, but instead gave absorption bands very similar to those obtained for complex (I) except that the band at 1110cm^{-1} was shifted to about 1125cm^{-1} and was considerably increased in intensity. The reason for this is not clear but would suggest some interaction between the iron(III) complex and the amine bisulphate.

2.2 Ultra-violet

The spectra of complexes (I) and (II) in benzene solution are shown in figures 3.6 and 3.7. It should be remembered that analysis of complex(I) is consistent with the stoichiometric formula $(R_2NH_2)_2\ FeOH(SO_4)_2$ where R is 3,5,5,trimethylhexyl. The spectrum of complex (I) (shown in figure 3.6) has a peak occurring at 290mμ, and a broad band at about 335mμ .

Figure 3.6 Ultra-violet Spectrum of Complex (I)

●—●—● $(3.4x10^{-4})$M complex (I)

Δ—Δ—Δ $(3.4x10^{-4})$M complex (I) + 0.03M amine sulphate.

Figure 3.7 Ultra-violet Spectrum of Complex (II) in benzene.

○—○—○ $(2.2x10^{-4})$M complex (II).

■—■—■ $(2.2x10^{-4})$M complex (II) + 0.03M amine sulphate.

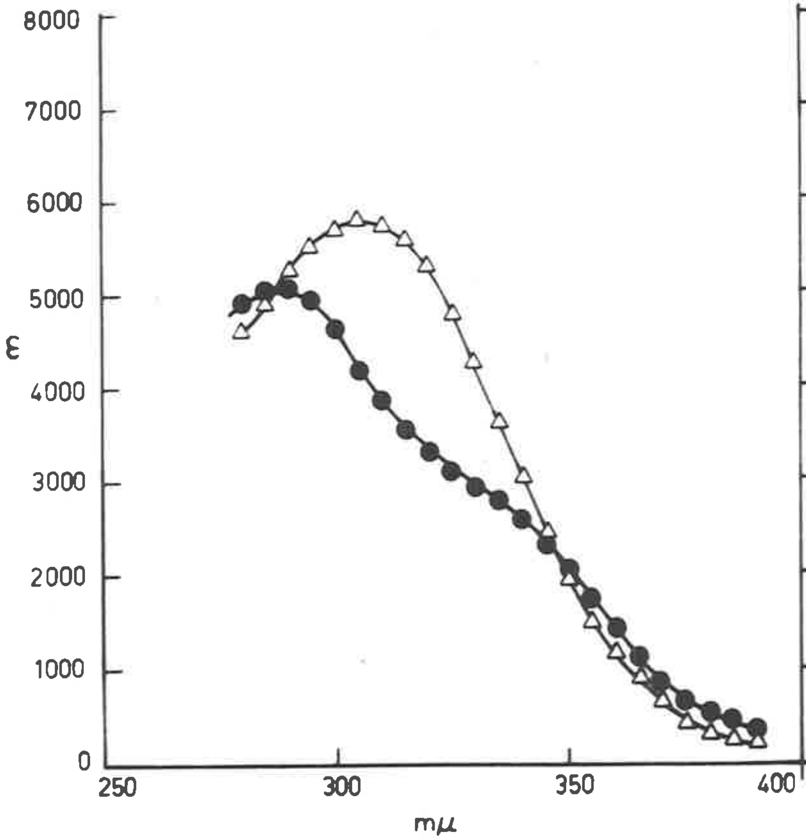


Figure 3.6

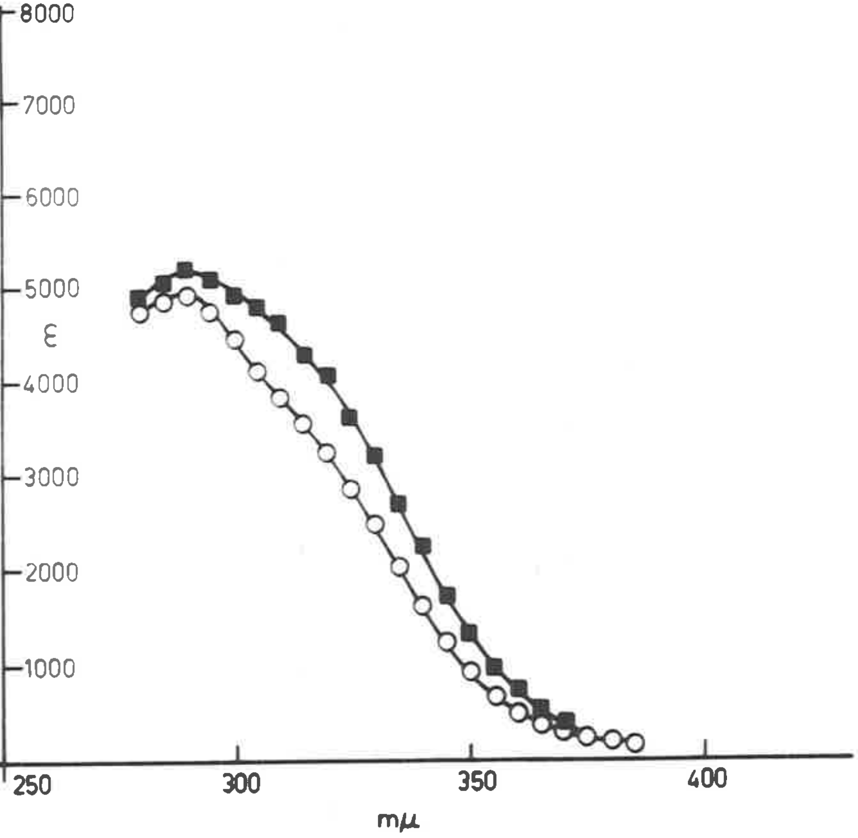


Figure 3.7

It has been suggested by several workers[3,23,24] that the partially hydrolysed Fe(III) species $FeOH^{+2}$ has an absorption peak at about 295mμ, with a molar extinction coefficient of about 2200. Also Mulay and Selwood[25] have found evidence for the dimerization of this species in aqueous solutions at high ($>10^{-3}$M) Fe(III) concentrations to form the species $(FeOH)_2^{+4}$ which according to them has an absorption peak at 335mμ. It would seem logical, therefore, to attribute the absorption peak at 290mμ to the partially hydrolysed Fe(III) species $FeOH^{+2}$, and the broad peak at 335mμ to the dimer $(FeOH)_2^{+4}$. The molar extinction coefficients, also shown in the figure, are about 5000 and 2700 respectively which are higher than found previously for aqueous solutions. Good *et al.*[2] have found that in chloroform-amine solutions the spectra of anionic transition-metal complexes have higher extinction coefficients than the same anions in aqueous solutions, particularly in the ultra-violet region, and suggest that this is due to the change in solvent and to solvent-metallic anion interactions. They have found, however, that the character and the positions of the absorption maxima remain constant.

The spectrum of complex (II), the hydrated form of complex (I), is shown in figure 3.7, and is somewhat similar to that of complex (I), with a maximum occurring at 290mμ.

The broad band at 335mμ, however, has greatly reduced in intensity.

It is interesting to study the effect on the spectrum of complex (I) of the introduction of a large excess of the amine sulphate into the benzene solution of the complex. The situation can now be considered to be essentially the same as that experienced in the iron(III) extraction studies described in section B, since in these studies the experimental conditions were chosen so that the amounts of Fe(III) extracted were almost negligible compared to the concentrations of the amine sulphate in the organic phases. Thus the organic extract solutions after the extraction of Fe(III) contained large excesses of uncomplexed amine sulphate.

The spectrum of complex (I) in a benzene solution containing 0.03M uncomplexed amine sulphate is shown in figure 3.6. It can be seen that the spectrum has undergone a very radical change, with the disappearance of the peak at 290mμ and the broad band at 335mμ, and with the appearance of a new absorption maximum at 305mμ. Whiteker and Davidson[3] in their investigation of iron(III)-sulphate-complex ions in aqueous solutions have attributed absorption in the region 300-310mμ to the species $FeSO_4^{+1}$ and $Fe(SO_4)_2^{-1}$.

The $Fe(SO_4)_2^{-1}$ species appears to have an absorption maximum at a slightly lower wavelength (300mμ) than the $FeSO_4^{+1}$ species which absorbs at about 305-310mμ. The respective extinction coefficients given by Whiteker and Davidson are 3000 and 2200. However, since there is such a small separation between the maximum for the $Fe(SO_4)_2^{-1}$ species and that for the $FeSO_4^{+1}$ species, it is difficult to assign the new absorption peak at 305mμ in figure 3.6 to one or other of these species. Nevertheless we can say that in the presence of excess amine sulphate the spectrum of complex (I) in benzene solution has a very pronounced contribution from iron(III)-sulphato-complex species such as $FeSO_4^{+1}$ or $Fe(SO_4)_2^{-1}$ (or both).

The effect on the spectrum of complex (II) of the presence of a large excess of the amine sulphate in the benzene solution, as shown in figure 3.7, is much less pronounced than for complex (I), and, in fact, the maximum at 290mμ appears to be almost unaffected. There is, however, a slight increase in absorption in the 310mμ region which is probably due to a small contribution from the species $FeSO_4^{+1}$ and $Fe(SO_4)_2^{-1}$.

3. Molecular Weight Study

The results of the molecular weight study are shown in table 3.4. The molecular weight is shown in the table

Table 3.4

Complex	Solvent	Concentration M	M.W.	No. Basic Units
(I)	Acetone	0.37	5,129	6.4
(I)	Benzene	0.25	2,930	3.6
(II)*	Acetone	0.22	4,828	6.0

* complex (II) reverts back to complex (I) in solution

together with the corresponding number of basic units. The basic unit is considered to have the stoichiometric formula $(R_2NH_2)_2FeOH(SO_4)_2$ which was found by analysis, where R is 3,5,5,trimethylhexyl.

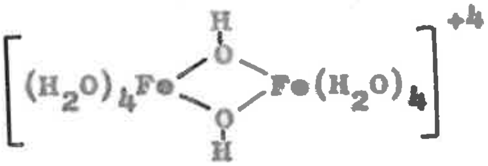
The molecular weight values shown in table 3.4 indicate some association of the basic molecular units in benzene and acetone solutions. However, this association is certainly not as extensive as that of the uncomplexed amine sulphate in benzene solution, since in this solvent the aggregate particle has a molecular weight of 31,230 (see Chapter 4). In fact, the association of complex (I) in benzene solution probably occurs by a different mechanism from that of the uncomplexed amine sulphate which has been suggested to occur by micelle formation stabilized by intermolecular hydrogen bonding, as described in Chapter 4.

4. Magnetic Study

The values obtained for the magnetic moments of complex (I) and its hydrated form complex (II) were 3.78 and 3.64 Bohr-magnetons respectively, which are anomalously low for ferric compounds[26].

Mulay and Selwood[25] have studied the hydrolysis of iron(III) perchlorate solutions, and have found that strongly acid solutions have a magnetic moment of 5.82 Bohr-magnetons. This, they said, was due to the $Fe^{+3}(H_2O)_6$ ion and was slightly lower than the spin-only value of 5.92. However, with increase in the pH of the iron(III) solutions the magnetic moment was found to decrease and the value obtained at pH 2.0 was about 3.8 Bohr-magnetons. For higher pH values (> 2.0) the magnetic moment appeared to reach a constant value of 3.6-3.7.

The decrease in magnetic moment with increase in aqueous pH was found to follow fairly closely the increase in the amount of the dimeric species $(FeOH)_2^{+4}$ present in the aqueous phase, and hence Mulay and Selwood[25] suggested that this dimer, which has the hydroxy-bridged structure shown below, was responsible for the decrease in the magnetic moment.



They also suggested that this binuclear complex was diamagnetic due to an exchange interaction between adjacent ferric irons, which destroyed all their paramagnetism.

A similar effect has been observed by Sommer and Pliska[27] who have studied the hydrolysis of iron(III) in acetate solutions. The magnetic moment of the solution (10^{-2}M iron(III)) at high acidity was found to be close to the expected value of 5.92, but with increase in pH value the magnetic moment decreased as found by Mulay and Selwood[25]. At pH 2.0 the value for the magnetic moment was about 3.8 Bohr-magnetons and reached a constant value of 3.3 at higher pHs. Sommer and Pliska[27], suggested that the decrease in magnetic moment could be attributed to the dimer $(FeOH)_2^{+4}$ as found by Mulay and Selwood[25], and to the acetate dimer $[Fe(CH_3COO)]_2^{+4}$ which they said was also present in aqueous solutions and could be expected to have similar anomalous magnetic properties to the hydroxy-bridged dimer.

The above evidence suggests that there is bridging of some kind, either hydroxy- or sulphato-bridging (or more probably both) between adjacent Fe(III) ions in complexes (I) and (II), which allows some exchange interaction to occur.

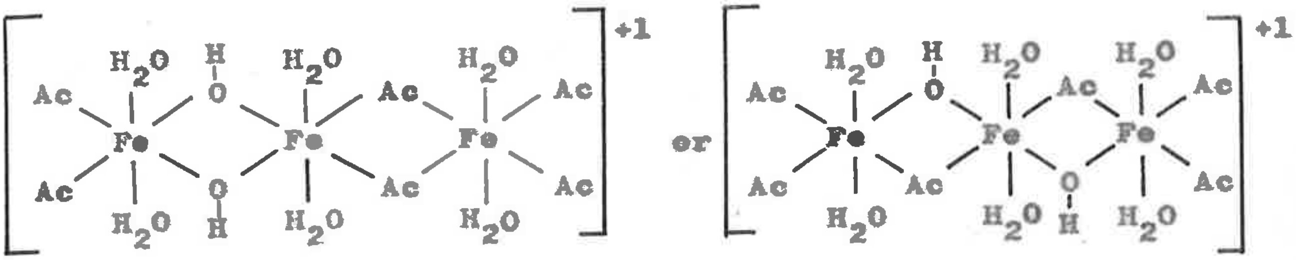
Martin and Kanekar[28] have studied the variation of the magnetic moment of the Fe(III) complex with temperature and have found that the change of magnetic susceptibility per Fe atom with temperature can be related to an exchange interaction term J if the complex is assumed to be trimeric.

The equation requires that the magnetic moment μ approaches 1 μ as T approaches 0°K and 5.9 μ as T approaches infinity. The magnetic behaviour can also be interpreted on the basis of the complex being a pentamer, heptamer, etc., but in view of the molecular weight evidence, discussed in section 3 above, the trimer seems more likely.

Martin and Kanekar found that a pre-treatment of the Fe(III) complex by heating _in vacuo_ at 90°C for various time intervals, which brought about dehydration of the sample, affected the magnetic behaviour to some extent. This may be due to the conversion of hydroxy-bridges to oxo-bridges, however, after making an adjustment to the quantity J to allow for this, the magnetic data obtained from the heated sample was found to agree moderately well with the trimer theory.

5. The Structure of Complex (I)

Sommer and Pliska[27], in their study of aqueous Fe(III) acetate solutions have isolated a complex cation as the chloroplatinate from an aqueous solution at about pH 1.5, and have suggested two possible structures as shown below.



Ac = CH_2COO^{-1}

By analogy with the structures suggested by Sommer and Pliska for the acetate complex we can postulate chain-like or linear structures for complex (I) as shown by A,B, and C in figure 3.8. The actual complex isolated in the preparation of complex (I) could probably be a mixture of A,B, and C.

The three structures shown in figure 3.8, which contain hydroxy-bridging and sulphato-bridging fit in quite well with the ultra-violet spectroscopic evidence given in section 2.2 above, since the presence of the $FeOH^{+2}$ species would give rise to the absorption maximum at 290mμ, and the broad peak at 335mμ would be due to the $(FeOH)_2^{+4}$ component in B and C. The absorption of water by complex (I) may be considered to occur by the rupture of the sulphato-bridges thus allowing water to be directly coordinated to iron.

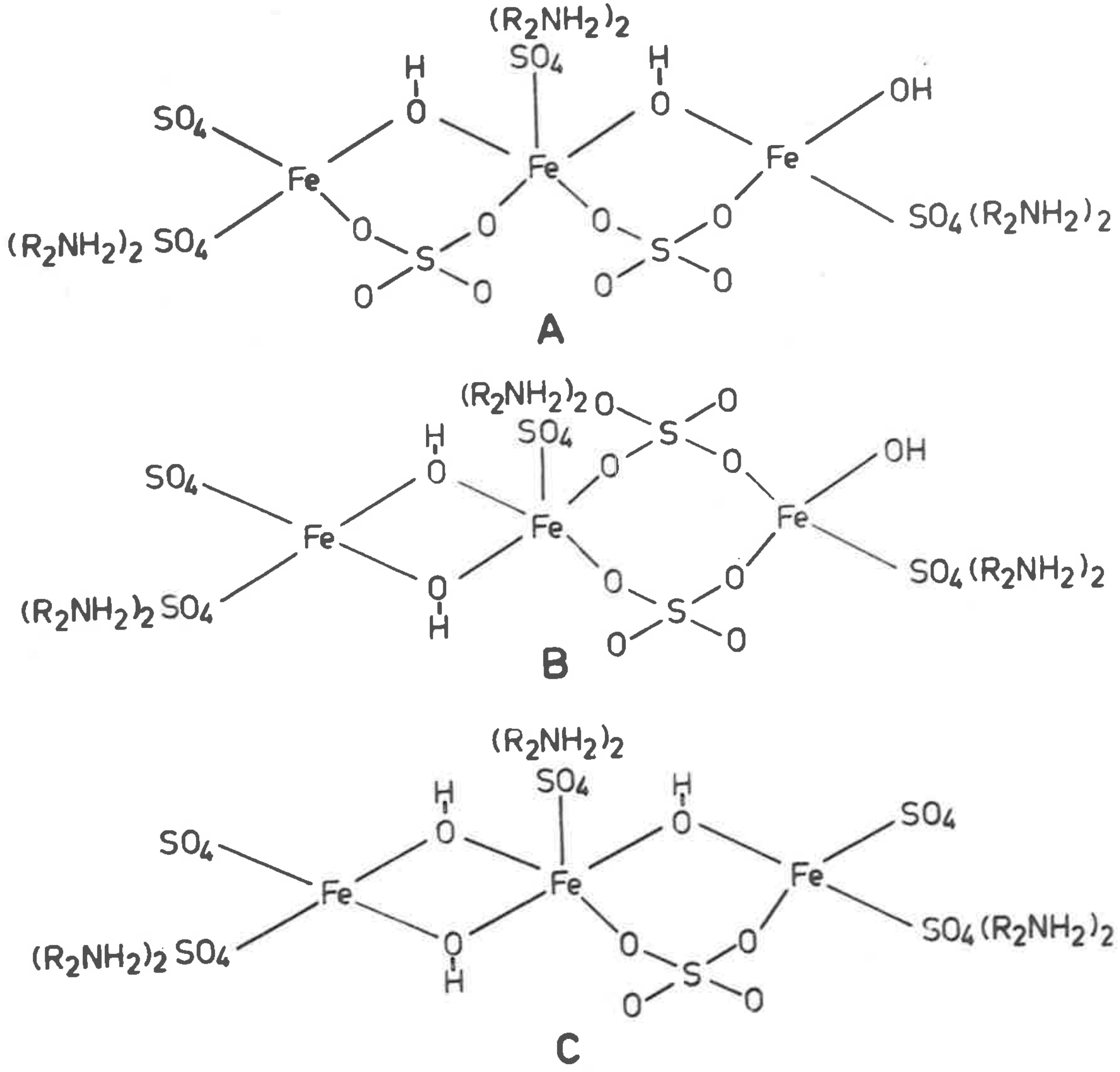


Figure 3.8 The linear structures for Complex (I).

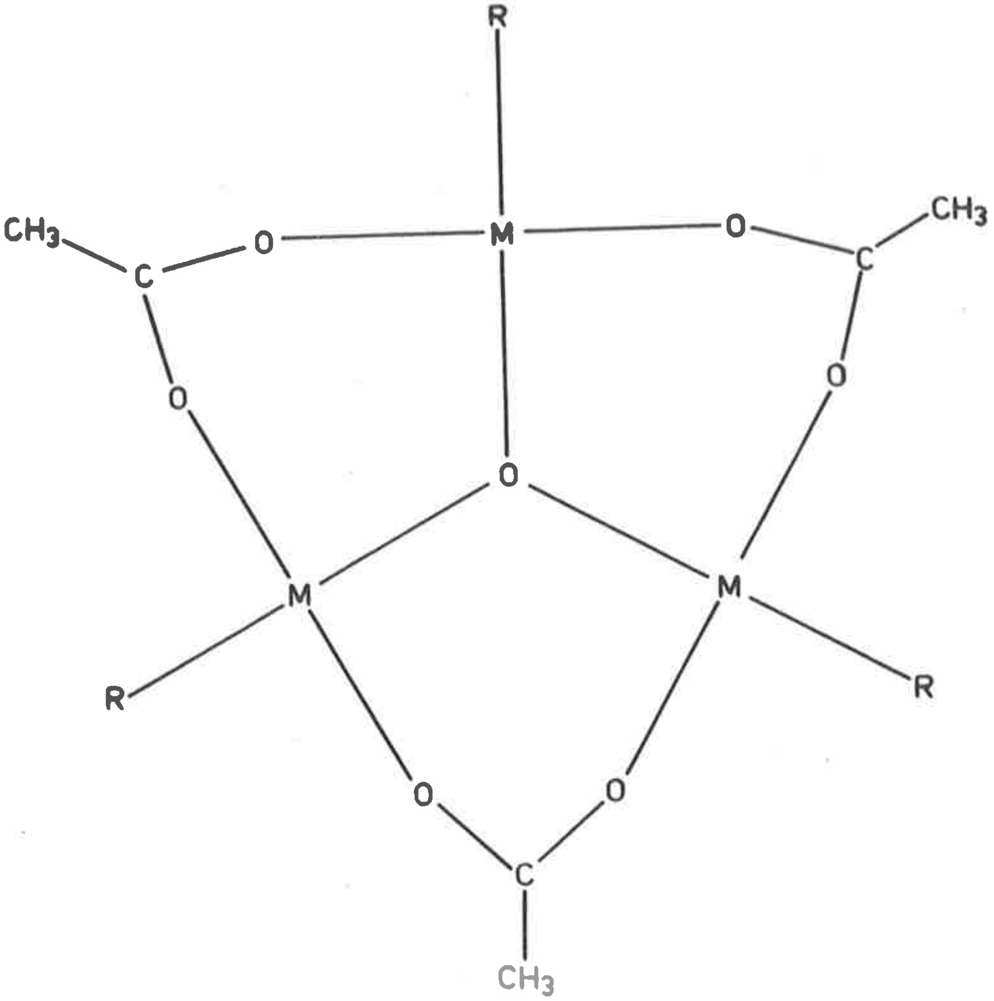
The effect on the spectrum of complex (I) of the addition of excess uncomplexed amine sulphate may be due to the replacement of the hydroxy-bridges by sulphato-bridges. This would, of course, give more Fe(III)-sulphate bonds and would give greater absorptions due to the species $FeSO_4^{+1}$ and $Fe(SO_4)_2^{-1}$. In complex (II), however, the very much smaller effect of excess uncomplexed amine sulphate on the spectrum of the hydrated complex is more difficult to explain unless one assumes that on the absorption of water by complex (I) the hydroxy-bridges as well as the sulphato-bridges are broken thus preventing attack by excess uncomplexed amine sulphate. This seems unlikely, however, in view of the low magnetic moment of complex (II) which suggests that there is still bridging of some kind between iron atoms.

The molecular weight evidence given in section 3, above, does not entirely disagree with the suggestion that complex (I) has a trimeric configuration, as shown in figure 3.8, since the molecular weight value in benzene solution indicates a high proportion of the trimer but higher units are not excluded. In acetone solution the molecular weight value corresponds to that of a hexamer, and this can be explained as being due to the linking of two trimeric units through sulphato-bridges.

An alternative configuration for complex (I) is obtained by analogy with a suggestion put forward by Orgel[29], who has proposed a cyclic structure for complex ions of the type $[M_3(Ac)_6(OH)_2]^+$, where M is Cr^{3+}, Fe^{3+}, or Al^{3+}, and Ac is CH_3COO^-, as opposed to the chain-like structure of Sommer and Pliska[27]. Orgel pictures the trinuclear basic acetates with the three metal atoms arranged in an equilateral triangle about a central O^{-2} ion, as shown in figure 3.9. The positions trans to the O^{-2} ion may be occupied by any of the ligands normally associating with trivalent transition-metal ions, e.g. water, amines, further acetate groups, and halide ions. The six acetate groups complete the octahedral coordination about the metal ions, each one lying completely to one side of the plane of the metal ions and linking a pair of them.

It is not possible to obtain a structure for complex (I) which is exactly analogous to that described by Orgel for the basic acetates, and retain the stoichiometry which has been found by analysis. However, a cyclic trimeric structure can be represented by considering that three octahedra can share corners, with the hydroxyl groups bridging at these points. Such a structure is shown in figure 3.10. In this representation the metal atoms are again arranged in an equilateral triangle, as suggested by Orgel, but instead of having a single O^{-2} ion at the centre of the triangle, the

(a) Projected onto the M_3O plane.



(b) Seen along an M-O direction, the dotted line indicating the M_3O plane.

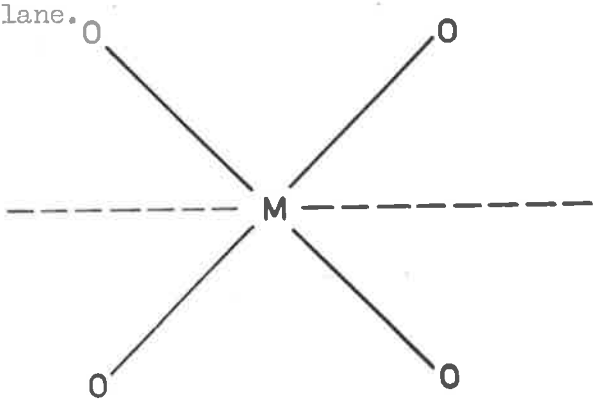
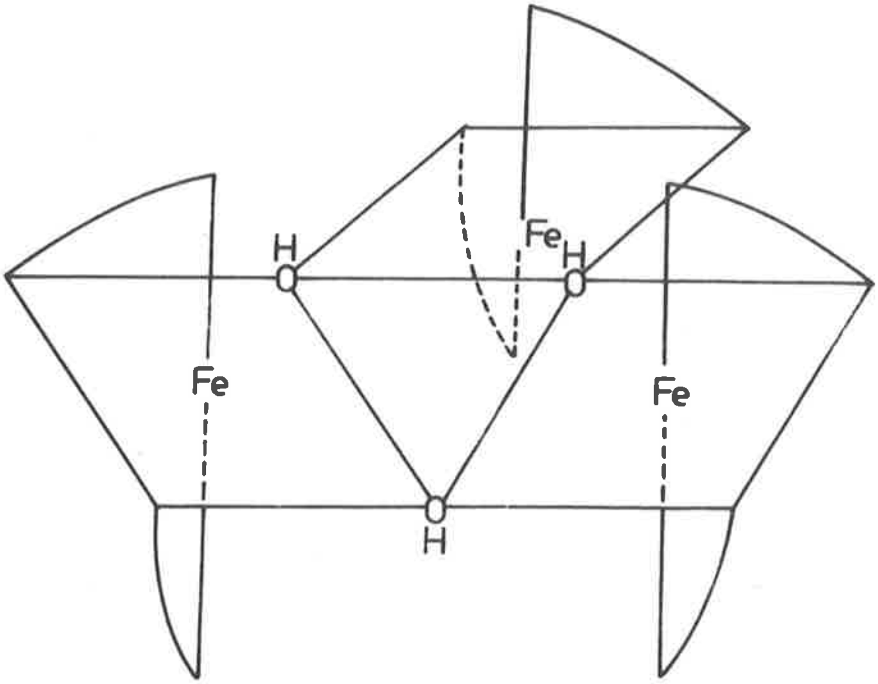


Figure 3.9 The trinuclear basic acetate structure of Orgel.

(a) Three octahedra linked by hydroxyl groups.



(b) Looking down on the $Fe_3(OH)_3$ plane.

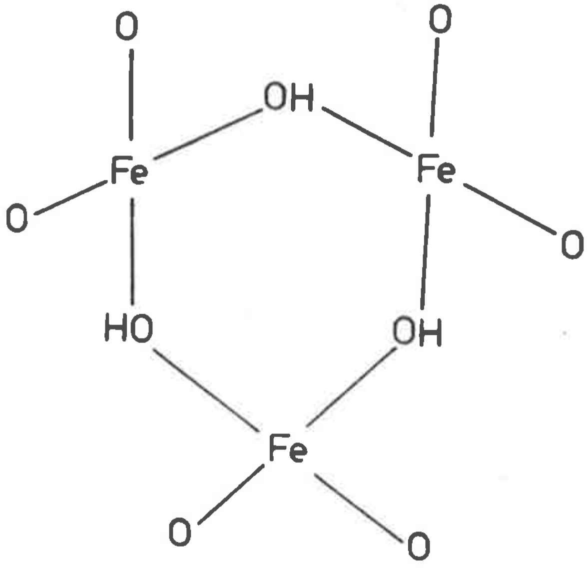


Figure 3.10 The cyclic structure for Complex(I).

three iron atoms are linked by hydroxyl groups which are themselves arranged in an equilateral triangle. The remaining coordination positions on the Fe(III) ions are taken up by sulphate groups. It is also possible to draw similar cyclic structures which contain sulphato-bridges as well as hydroxy-bridges.

The ultra-violet spectroscopic evidence, however, does not support the suggestion of a cyclic structure for complex (I) since it is not possible to include the dimeric $(FeOH)_2^{+4}$ species in such a structure. Also it is more difficult to explain the absorption of water by complex (I), and to explain the effect of an excess of uncomplexed amine sulphate on the spectrum of complex (I) on the basis of a cyclic structure. Thus the linear or chain-like configuration for complex (I) appears more favourable than the cyclic form.

B. Equilibrium Studies of the Extraction of Iron(III) from Aqueous Sulphate Solutions by Di(3,5,5,trimethylhexyl)amine.

If we assume that the extraction of iron(III) from aqueous sulphate solutions by the secondary amine di(3,5,5,trimethylhexyl)amine does involve a partially hydrolysed iron(III) species such as $FeOHSO_4$ or $(FeOHSO_4)_2$ in the aqueous phase and that the reacting species in the organic phase is the di(3,5,5,trimethylhexyl)ammonium sulphate, we can derive an expression to describe the extraction and see how well this expression explains the experimental results.

Two solvents for the amine were chosen, benzene and chloroform, since they were found to give suitable distribution ratios for Fe(III), and since in the former solvent the amine sulphate was found to form large molecular aggregates or micelles (see Chapter 4), and was non-aggregated in the latter solvent.

In Chapters 1 and 2 the possibility of having two extraction mechanisms for systems involving the long chain alkylamines is discussed. On the one hand there is the mechanism which considers that the reaction occurs within the aqueous phase, and on the other hand there is the interface mechanism. As pointed out in Chapter 2 consideration of either of these mechanisms will lead to the same result, and it is impossible to differentiate between the two in an extraction study as described in this thesis.

The individual equilibria involved in the extraction and the derivation of the extraction equations are shown in Appendix II. It can be seen from Appendix II that the extraction equation, for the extraction of the species $FeOHSO_4$ from the aqueous phase can be written as

$$D = \frac{K_1 \cdot \gamma_{SO_{4\,A}^{=}} \cdot \gamma_{Fe_A^{+3}}}{\gamma_{H_A^{+}}} \cdot \frac{[SO_4^{=}]_A [R_2H_2SO_4]_o}{[H^+]_A} \tag{3.3}$$

D is the distribution ratio defined as

$$D = \frac{\text{Total concentration of iron(III) in the organic phase}}{\text{Total concentration of iron(III) in the aqueous phase}} \tag{3.4}$$

and can easily be determined experimentally. γ refers to the molar activity coefficients and the brackets $[\quad]$ refer to the molar concentrations. The subscripts "o" and "A" refer to the organic and aqueous phases respectively and K_1 is the overall equilibrium constant for the extraction.

The expression for D, as shown by equation (3.3) thus predicts a first order dependence of the extraction on the concentration of uncomplexed amine sulphate in the organic phase, and on the sulphate ion activity in the aqueous phase, and an inverse first order dependence on the hydrogen ion activity in the aqueous phase.

For the extraction of the dimeric iron(III) species $(FeOHSO_4)_2$, as shown in Appendix II, the overall extraction equation can be written as

$$D = \frac{K_2 . \gamma^2_{Fe^{+3}_A} . \gamma^2_{SO^{=}_{4_A}}}{\gamma^2_{H^+_A}} . \frac{\left[SO_4^{=}\right]^2_A \left[R_2H_2SO_4\right]^2_o}{\left[H^+\right]^2_A} \qquad (3.5)$$

According to Milburn and Vosburgh[30] for aqueous iron (III) solutions up to a concentration of 10^{-4}M only the monomeric species $FeOH^{+2}$ is important. However, for iron (III) solutions of concentration 10^{-3}M to 10^{-2}M the amount of the dimeric species $(FeOH)_2^{+4}$ present becomes appreciable.

Equation (3.5) thus predicts a square dependence of D on the aqueous sulphate activity, and on the concentration of amine sulphate in the organic phase, and an inverse square dependence of D on the hydrogen ion activity in the aqueous phase.

1. Extraction Studies using di(3.5.5.trimethylhexyl)-amine solutions in benzene.

At a constant ionic strength and acidity in the aqueous phase, the activity of the sulphate ion, and the activity coefficient of Fe^{+3} will be essentially constant, and equation (3.3) can be written in the logarithmic form

$$\text{Log } D = \text{Log}\left[R_2H_2SO_4\right]_o + K' \qquad (3.6)$$

Equation (3.6) thus predicts that a log.-log. plot of the distribution ratio D against the molar concentration of uncomplexed amine sulphate in the organic phase should give a straight line of slope unity.

A study of the dependence of the distribution ratio on the concentration of uncomplexed amine sulphate in benzene solution was carried out by equilibrating the amine solutions described in experimental section 3.1 with six aqueous Fe(III) solutions which contained a constant molar strength of 0.50M total sulphate (see experimental section 3.1), and iron(III) concentrations of 0.001M, 0.005M, and 0.01M each at pH values of 1.00 and 2.03. The exact compositions of these solutions are given in table 3.1.

The results of this study are shown in tables3.5 to 3.10, where values for the distribution ratios and concentrations of uncomplexed amine sulphate at equilibrium are given. In tables 3.5 and 3.8 the values for the concentrations of amine sulphate and bisulphate in the organic solutions before the Fe(III) extraction experiments, and the corresponding ratios of amine bisulphate to amine sulphate are shown. These concentrations of amine sulphate and bisulphate were obtained from actual iron(III) extraction experiments by allowing for the amounts of Fe(III) extracted as described in experimental section 3.3, and can be

Table 3.5

The Extraction of iron(III) from aqueous solutions containing 0.001M iron(III) initially, at pH 1.00

*$[R]_o$ Initial M	$[R_2H_2SO_4]_o$ Initial M	$[RH_2SO_4]_o$ Initial M	$\frac{[RH_2SO_4]}{[R_2H_2SO_4]}$	$[Fe^{+3}]_A$ Equilibrium $M \times 10^4$	$[Fe^{+3}]_o$ Equilibrium $M \times 10^4$	D	$[R_2H_2SO_4]_o$ Uncomplexed at Equilibrium M
0.0040	0.0010	0.0020	2.00	9.85	0.287	0.029	0.00097
0.0050**	0.0013	0.0025	1.92	-	-	-	-
0.0080	0.0021	0.0039	1.86	9.67	0.573	0.059	0.0020
0.0100	0.0026	0.0049	1.88	9.53	0.645	0.068	0.0025
0.0150	0.0039	0.0072	1.85	9.38	0.860	0.092	0.0038
0.0200	0.0051	0.0098	1.92	9.18	1.07	0.117	0.0050
0.0300	0.0076	0.0148	1.95	8.73	1.22	0.140	0.0075
0.0500	0.0132	0.0237	1.80	8.73	1.58	0.181	0.0130
0.0600	0.0159	0.0282	1.77	8.50	1.65	0.194	0.0157
0.0800	0.0214	0.0371	1.73	8.33	1.86	0.223	0.0212
0.1000	0.0270	0.0461	1.71	8.24	2.08	0.252	0.0268

* The initial amine concentration refers to the concentration of amine in the original solutions before conversion to its salts.

** This solution was not used for extraction experiments with the 0.001M Fe(III) solution at pH 1.00.

Table 3.6

The Extraction of iron(III) from aqueous solutions containing 0.005M iron(III) initially, at pH 1.00

*$[R]_o$ Initial M	$[Fe^{+3}]_A$ Equilibrium $M\times10^3$	$[Fe^{+3}]_o$ Equilibrium $M\times10^3$	D	$[R_2H_2SO_4]_o$ Uncomplexed at Equilibrium M
0.0050	4.79	0.176	0.037	0.0011
0.0080	4.82	0.279	0.058	0.0018
0.0100	4.76	0.312	0.066	0.0022
0.0150	4.58	0.430	0.094	0.0035
0.0200	4.58	0.494	0.108	0.0046
0.0300	4.38	0.641	0.146	0.0070
0.0500	4.23	0.817	0.193	0.0124
0.0600	4.14	0.879	0.212	0.0150
0.0800	4.05	0.981	0.242	0.0204
0.1000	3.97	1.10	0.277	0.0259

* The initial amine concentration refers to the concentration of amine in the original solution before conversion to its salts. The initial concentrations of amine sulphate and bisulphate are shown in table 3.5.

Table 3.7

The Extraction of iron(III) from aqueous solutions containing 0.01M iron(III) initially, at pH 1.00

*$[R]_e$ Initial M	$[Fe^{+3}]_A$ Equilibrium $M\times10^3$	$[Fe^{+3}]_e$ Equilibrium $M\times10^3$	D	$[R_2H_2SO_4]_e$ Uncomplexed at Equilibrium M
0.0050	9.42	0.340	0.036	0.00096
0.0080	9.56	0.537	0.056	0.0016
0.0100	9.38	0.645	0.069	0.0020
0.0150	9.15	0.859	0.094	0.0030
0.0200	8.77	1.06	0.121	0.0040
0.0300	8.68	1.36	0.157	0.0062
0.0500	8.17	1.77	0.217	0.0114
0.0600	8.01	1.92	0.240	0.0140
0.0800	7.72	2.15	0.278	0.0191
0.1000	7.63	2.29	0.300	0.0247

* The initial amine concentration refers to the concentration in the original solution before conversion to its salts. The initial concentration of amine sulphate and bisulphate are shown in table 3.5.

Table 3.8

The Extraction of iron(III) from aqueous solutions containing 0.001M iron(III) initially, at pH 2.03

* $[R]_o$ Initial M	$[R_2H_2SO_4]_o$ Initial M	$[RH_2SO_4]_o$ Initial M	$\frac{[RH_2SO_4]}{[R_2H_2SO_4]}$	$[Fe^{+3}]_A$ Equilibrium $M\times10^3$	$[Fe^{+3}]_o$ Equilibrium $M\times10^3$	D	$[R_2H_2SO_4]_o$ Uncomplexed at Equilibrium M
0.0040	0.0016	0.00074	0.46	0.609	0.380	0.624	0.0012
0.0050	0.0020	0.00094	0.47	0.564	0.430	0.762	0.0016
0.0080	0.0032	0.0015	0.47	0.480	0.523	1.090	0.0027
0.0100	0.0040	0.0019	0.48	0.459	0.544	1.185	0.0035
0.0150	0.0062	0.0026	0.42	0.403	0.609	1.511	0.0056
0.0200	0.0084	0.0032	0.38	0.372	0.623	1.675	0.0078
0.0300	0.0124	0.0051	0.41	0.356	0.702	1.972	0.0117
0.0500	0.0214	0.0072	0.34	0.313	0.673	2.150	0.0207
0.0600	0.0260	0.0081	0.31	0.313	0.702	2.243	0.0253
0.0800	0.0350	0.0101	0.29	0.302	0.723	2.394	0.0343
0.1000	0.0440	0.0121	0.28	0.282	0.723	2.564	0.0433

* The initial amine concentration refers to the concentration in the original solution before conversion to its salts.

Table 3.9

The Extraction of iron(III) from aqueous solutions containing 0.005M iron(III) initially, at pH 2.03

*$[R]_o$ Initial M	$[Fe^{+3}]_A$ Equilibrium $M\times10^3$	$[Fe^{+3}]_o$ Equilibrium $M\times10^3$	D	$[R_2H_2SO_4]_o$ Uncomplexed at Equilibrium M
0.0050	4.00	1.11	0.278	0.00089
0.0080	3.27	1.72	0.526	0.0015
0.0100	2.91	2.08	0.715	0.0019
0.0150	2.22	2.81	1.266	0.0034
0.0200	1.84	3.19	1.734	0.0052
0.0300	1.50	3.58	2.387	0.0088
0.0500	1.30	3.74	2.877	0.0177
0.0600	1.24	3.92	3.161	0.0221
0.0800	1.19	3.85	3.235	0.0312
0.1000	1.15	3.94	3.426	0.0401

* The initial amine concentration refers to the concentration in the original solution before conversion to its salts. The initial concentrations of amine sulphate and bisulphate are shown in table 3.8.

Table 3.10

The Extraction of iron(III) from aqueous solutions containing 0.01M iron(III) initially, at pH 2.03

*$[R]_e$ Initial M	$[Fe^{+3}]_A$ Equilibrium $M\times10^3$	$[Fe^{+3}]_e$ Equilibrium $M\times10^3$	D	$[R_2H_2SO_4]_e$ Uncomplexed at Equilibrium M
0.0080	7.68	2.08	0.271	0.0011
0.0100	7.59	2.54	0.335	0.0015
0.0150	6.29	3.83	0.609	0.0024
0.0200	5.19	4.91	0.946	0.0035
0.0300	3.58	6.80	1.899	0.0056
0.0500	2.42	7.70	3.182	0.0137
0.0600	2.22	8.06	3.631	0.0179
0.0800	2.14	8.06	3.766	0.0269
0.1000	1.99	8.09	4.065	0.0359

* The initial amine concentration refers to the concentration in the original solution before conversion to its salts. The initial concentrations of amine sulphate and bisulphate are shown in table 3.8.

considered to be the concentrations of those salts in equilibrium with hypothetical aqueous solutions of the above compositions without Fe(III) being present.

The values for the ratios of amine bisulphate to amine sulphate present in the organic solutions before the iron extraction experiments, as shown in tables 3.5 and 3.8, appear to be reasonably constant for the lower concentration amine solutions. There is, however, some deviation from constancy for the more concentrated solutions, and this deviation appears to commence within a region of concentration of amine sulphate of about 0.004M to 0.008M. The decrease in the ratios of amine bisulphate to amine sulphate at the higher amine sulphate concentrations suggests that the equilibrium has shifted slightly to favour the formation of amine sulphate.

This might be expected in view of the high molecular association of the amine sulphate which occurs in the solvent benzene, as described in Chapter 4, since we might consider that a large molecular weight micelle as formed in an inert solvent such as benzene is a more stable configuration than say the un-associated amine bisulphate molecule, whose polar section is incompatible with the inert solvent molecules.

The formation of micelles in an organic solvent usually takes place at some critical concentration called the "critical micelle concentration" or CMC, and hence at concentrations of amine sulphate which are below the CMC no deviation of the ratio of amine bisulphate to amine sulphate from constancy would be expected. Hence it appears that the CMC for the amine sulphate in benzene solution occurs within the concentration range of 0.004M to 0.008M.

The amine sulphate micelle can be considered to have a constant composition in a particular solvent over a large concentration range, and therefore can be considered to have a constant activity.

This deviation from the expected behaviour, which appears to occur at amine sulphate concentrations above the "critical micelle concentration", and which is probably due to the approach of the activity of the amine sulphate micelle to a constant value, was again apparent in the iron(III) extraction results.

The plot of the logarithm of the distribution ratio for iron(III) against the logarithm of the concentration of uncomplexed amine sulphate in the organic phase is shown in figure 3.11. It can be seen that straight lines of slope unity, as predicted by equation (3.6) are not obtained over the complete concentration range of uncomplexed amine sulphate in the organic phase as expected. Straight

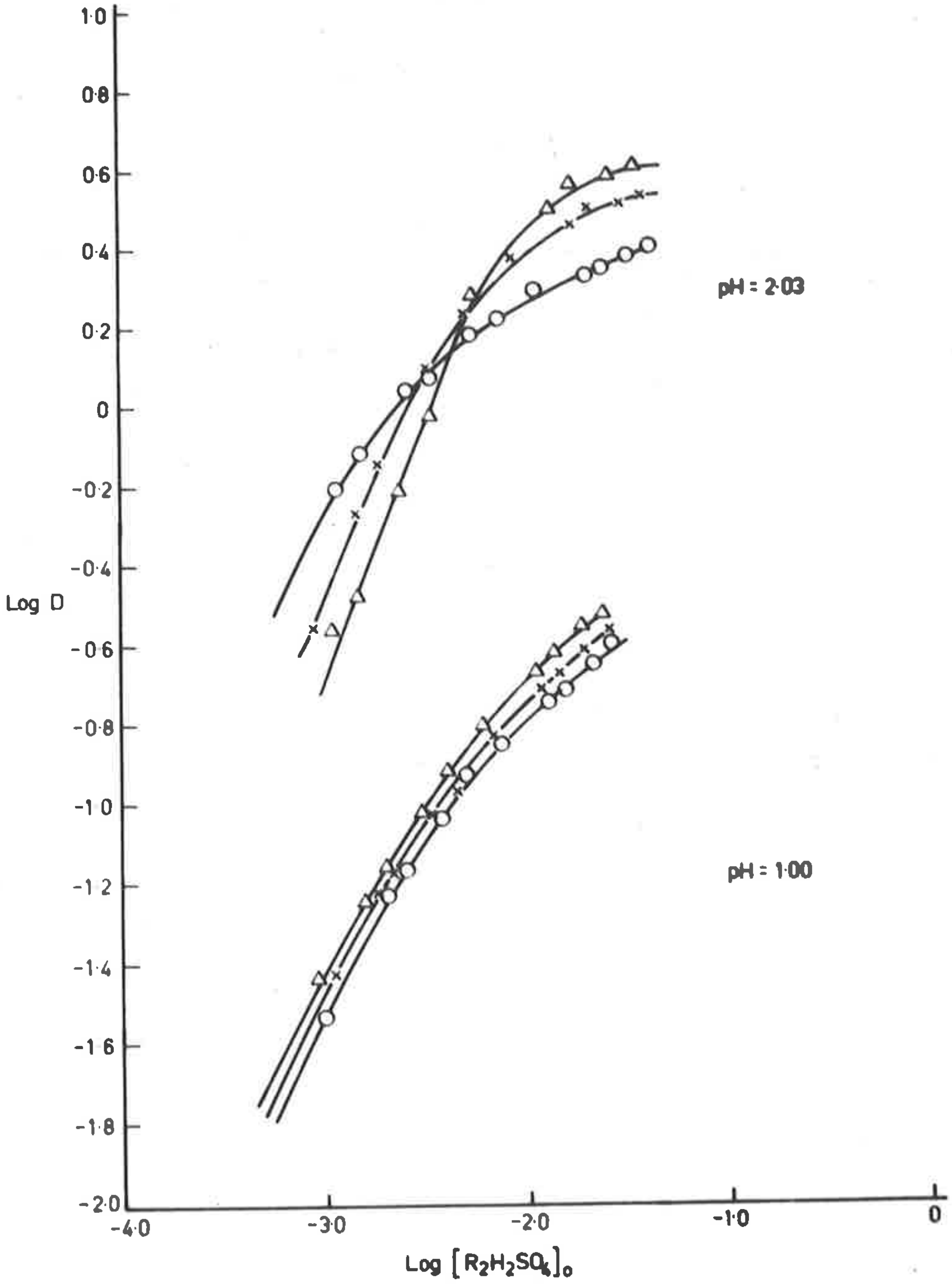


Figure 3.11 Log D against Log $[R_2H_2SO_4]_o$ for amine solutions in benzene.

o—o—o 0.001 M Fe(III)

×—×—× 0.005 M Fe(III)

Δ—Δ—Δ 0.010 M Fe(III)

lines of approximately unit slope are obtained, however, for the work with aqueous solutions at pH 1.00 in the lower amine sulphate concentration region. These straight lines show considerable deviation from the expected behaviour as the concentration of uncomplexed amine sulphate increases. This deviation appears to commense in about the same amine sulphate concentration region of 0.004M to 0.008M as was previously noted for the first appearance of the deviation of the ratio of amine bisulphate to amine sulphate from constancy, and, hence, is probably due to the same cause i.e. that of micelle formation of the amine sulphate.

Therefore the distribution ratio for Fe(III) should become independent of the concentration of uncomplexed amine sulphate in the organic phase as the concentration increases above the "critical micelle concentration", and, in fact, this appears to be so as shown in figure 3.11.

Equation (3.3) predicts that the distribution ratio for iron(III) should be independent of the total concentration of iron(III) present in the aqueous phase providing there are no polymeric species such as $(FeOH)_2^{+4}$ present. The log.-log. plots shown in figure 3.11 for aqueous iron(III) solutions containing 0.001M, 0.005M and 0.010M iron(III) initially, at pH 1,00 should, therefore, be superimposed. The curves, however, are not quite superimposed and there appears to be a slight increase in the distribution ratio with increase in aqueous iron(III) concentration . This may be due to the fact that the activity coefficients for aqueous iron(III) solutions are not constant at constant acidity and at constant ionic strength as has been assumed in obtaining equation (3.6), and that the activity coefficients actually increase slightly in going from a 0.001M to a 0.01M Fe(III) solution. Alternatively the effect may be simply an experimental one due to a slight difference in the aqueous acidities which is too small to alter the pH values significantly.

For the work with aqueous solutions at pH 2.03, the result of plotting the logarithm of the distribution ratio against the logarithm of the concentration of uncomplexed amine sulphate is even more interesting. The distribution ratios are much greater than those obtained for aqueous solutions at pH 1.00 as shown in figure 3.11, which alone suggests the extraction of a partially hydrolysed iron(III) species from the aqueous phase, since these species will be present in much greater amounts at the higher pH value. Straight lines are again obtained for low concentrations of uncomplexed amine sulphate, and the deviations observed for the study at pH 1.00 are also apparent and commence in about the same amine sulphate concentration range of 0.004M to 0.008M, as before. The slope of the straight line obtained when using the 0.001M concentration iron(III) solution again approaches a value of about unity for amine sulphate concentrations below the critical micelle value. However, the slopes of the lines obtained for 0.005M and 0.01M aqueous iron(III) solutions at amine sulphate concentrations which are below the "critical micelle concentration" are much greater than unity and have values of about 1.2 and 1.3 respectively.

Equation (3.5) which describes the extraction of the dimeric iron(III) species $(FeOHSO_4)_2$, can be written in the logarithmic form as shown by equation (3.7) for the extraction of iron(III) from aqueous solutions of constant acidity and aqueous sulphate ion activity.

$$\text{Log } D = 2 \text{ Log } \left[R_2H_2SO_4\right]_o + K'' \qquad (3.7)$$

Thus a log.-log. plot of the distribution ratio against the concentration of uncomplexed amine sulphate in the organic phase should give a straight line of slope 2.

The high values for the slopes of the lines obtained using 0.005M and 0.01M aqueous iron(III) solutions at pH 2.03, are therefore, due to the participation in the extraction of the dimeric species $(FeOHSO_4)_2$ whose concentration is known to become appreciable at high aqueous Fe(III) concentrations and at high aqueous pH values[30].

The results shown in tables 3.5 -3.10 have been obtained by examining the effect on the extraction of iron(III) of changing the concentration of amine sulphate present in the organic phase whilst keeping the composition of the aqueous phase essentially constant. This has been done, for aqueous solutions at two pH values. It has already been demonstrated that the extraction is strongly dependent on the aqueous pH value, and that extraction actually increases with increase in pH value, which is consistent with the extraction of a hydrolysed iron(III) species. It is useful, however, for comparison at a later stage to consider an equation which links the amine sulphate concentration and the aqueous pH value, and which describes the extraction of Fe(III) from aqueous sulphate solutions at a constant molar strength of 0.50M total sulphate over a range of amine sulphate concentrations and pH values.

At a constant ionic strength, and assuming that for very dilute iron(III) solutions the activity coefficient of iron(III) is unity, equation (3.3) can be written in the form

$$D = \frac{K''' . \left[R_2H_2SO_4\right]_o}{\left[H^+\right]_A} \qquad (3.8)$$

It should be pointed out that the activity of the sulphate ion will, of course, not be constant from one pH value to another, but will be directly proportional to the pH value. Hence the value for K''' for the extraction using amine sulphate dissolved in benzene, can be used for comparison with the value for the amine sulphate dissolved in chloroform providing that aqueous phases of identical composition are used.

Equation (3.8) can be written in the logarithmic form,

$$\text{Log } D = \text{pH} + \text{Log } \left[R_2H_2SO_4\right]_o + \text{ Log } K''' \qquad (3.9)$$

A plot of the logarithm of the distribution ratio against (pH + Log $\left[R_2H_2SO_4\right]_o$) is shown in figure 3.12 for cases shown in tables 3.5 - 3.8 where the log.-log. plot of the distribution ratio against the uncomplexed amine sulphate concentration showed a first order relationship below the "critical micelle concentration". The typical divergence from the expected behaviour, as shown previously in figure 3.11, can again be seen at amine sulphate concentrations above

Figure 3.12 Log D against pH + Log $[R_2H_2SO_4]_o$ for amine solutions in benzene.

1. 0.001M Fe(III), pH 2.03
2. 0.01 M Fe(III), pH 1.00
3. 0.005M Fe(III), pH 1.00
4. 0.001M Fe(III), pH 1.00

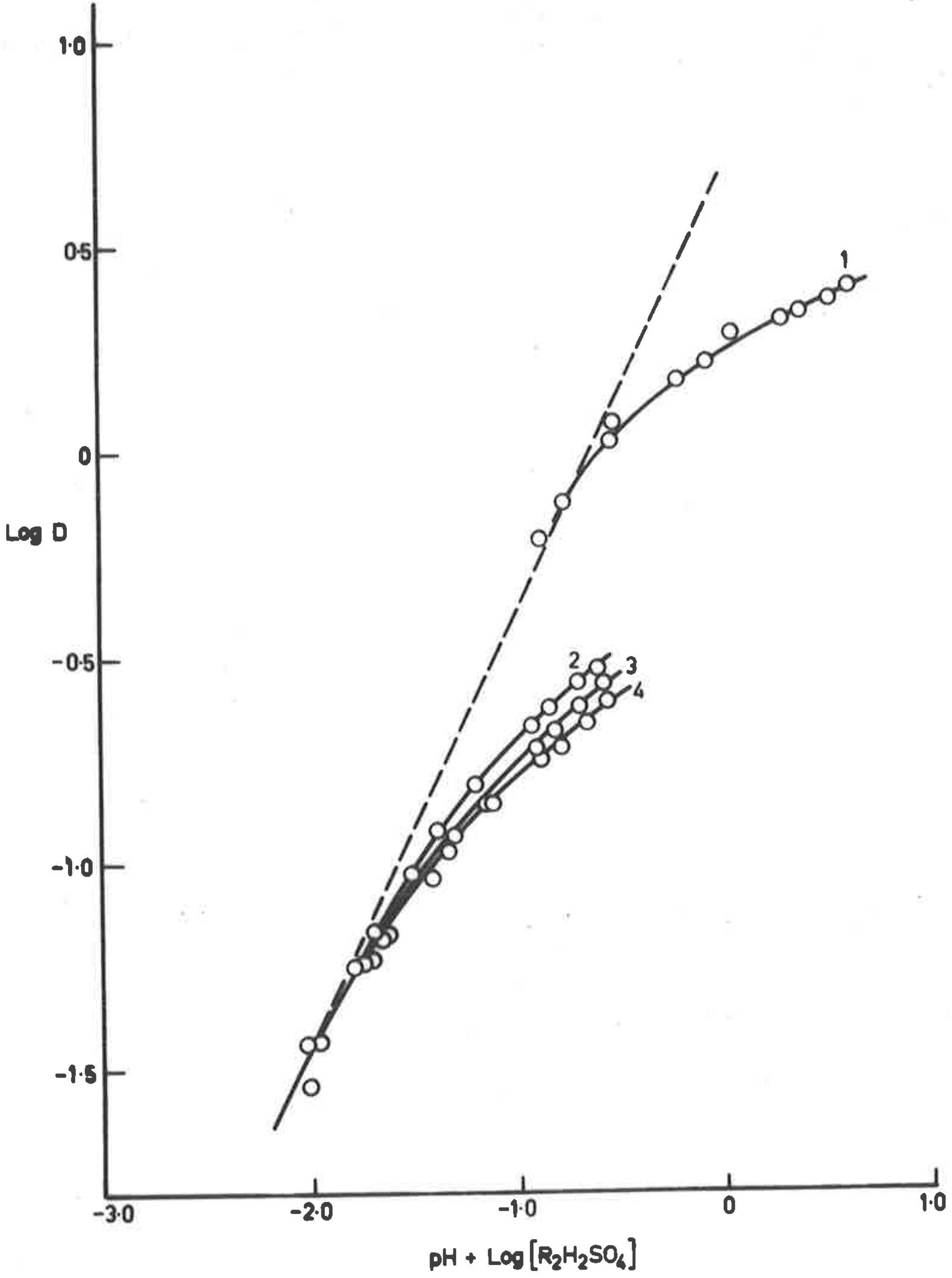


Figure 3.12

the "critical micelle concentration", however, the lines shown in figure 3.12 all appear to converge to a common straight line which is shown as a dotted line. It can be assumed, therefore, that the dotted line describes the extraction behaviour for amine sulphate concentrations which are below the "critical micelle concentration". The value obtained for log K''' from this dotted line is 0.71, and hence the extraction equation (3.9) can be written as,

$$\text{Log } D = pH + \text{Log } \left[R_2H_2SO_4\right]_o + 0.71 \qquad (3.10)$$

Equation (3.10) thus describes the extraction of the species $FeOHSO_4$ from aqueous sulphate solutions containing a constant molar strength of 0.50M total sulphate by di(3,5,5,trimethylhexyl)ammonium sulphate dissolved in benzene, providing the concentration of amine sulphate is below the "critical micelle concentration".

2. Extraction Studies Using di(3,5,5,trimethylhexyl)-amine solutions in chloroform.

A study of the dependence of the distribution ratio on the concentration of uncomplexed amine sulphate in chloroform solution was carried out by equilibration of the amine solutions described in experimental section 3.1 with seven Fe(III) solutions which contained a constant molar strength of 0.50M total sulphate (see experimental section 3.1). Four of these solutions contained Fe(III) concentrations of 0.001M and 0.01M each at pH values of 1.00 and 2.03, and the other three contained 0.001M Fe(III) at pH values of 1.46, 1.65, and 1.82. The exact compositions of these solutions are given in table 3.1.

Di(3,5,5,trimethylhexyl)ammonium sulphate was found to be non-aggregated in chloroform solution and did not form micelles. The aggregation properties of the amine sulphate in various organic solvents are fully discussed in Chapter 4. Since the amine sulphate does not form micelles in chloroform solution it was considered that in the iron(III) extraction studies the deviations from the expected behaviour as found with benzene as solvent for the amine sulphate would not occur. This was indeed found to be so, and gives considerable support to the assumption that the deviations from the expected behaviour which were found with benzene are, in fact, due to the molecular association of the amine sulphate in benzene.

The results obtained from the extraction studies are shown in tables 3.11 - 3.16. In tables 3.11 and 3.13 - 3.15 the values for the concentrations of amine sulphate and bisulphate in the chloroform solutions before the Fe(III) extraction experiments, and the corresponding ratios of amine bisulphate to amine sulphate are also shown. The initial

Table 3.11

The Extraction of Iron(III) from aqueous solutions containing 0.001M Fe(III) initially, at pH 1.00

*$[R]_o$ Initial	$[R_2H_2SO_4]_o$ Initial	$[RH_2SO_4]_o$ Initial	$\frac{[RH_2SO_4]}{[R_2H_2SO_4]}$	$[Fe^{+3}]_A$ Equilibrium	$[Fe^{+3}]_o$ Equilibrium	D	$[R_2H_2SO_4]_o$ Uncomplexed at Equilibrium
M	M	M		$M \times 10^4$	$M \times 10^4$		M
0.0105	0.0031	0.0044	1.42	10.09	0.439	0.044	0.0031
0.0211	0.0062	0.0087	1.40	9.71	1.00	0.103	0.0061
0.0422	0.0119	0.0185	1.55	8.77	1.99	0.227	0.0117
0.0632	0.0186	0.0260	1.40	8.01	2.67	0.333	0.0183
0.0843	0.0245	0.0354	1.44	7.41	3.13	0.422	0.0242
0.1054	0.0309	0.0437	1.41	6.89	3.69	0.536	0.0305

* The initial amine concentration refers to the concentration of amine in the original solution before conversion to its salts.

Table 3.12

The Extraction of iron(III) from aqueous solutions containing 0.010M Fe(III) initially, and at pH 1.00

*$[R]_o$ Initial M	$[Fe^{+3}]_A$ Equilibrium $M \times 10^3$	$[Fe^{+3}]_o$ Equilibrium $M \times 10^3$	D	$[R_2H_2SO_4]_o$ Uncomplexed at Equilibrium M
0.0105	10.09	0.297	0.029	0.0028
0.0211	9.67	0.645	0.067	0.0056
0.0422	9.15	1.36	0.149	0.0105
0.0632	8.39	2.00	0.239	0.0166
0.0843	7.83	2.59	0.331	0.0219
0.1054	7.27	3.10	0.426	0.0278

* The initial amine concentration refers to the concentration of amine in the original solution before conversion to its salts. The initial concentrations of amine sulphate and bisulphate are shown in table 3.11.

Table 3.13

The Extraction of Iron(III) from aqueous solutions containing 0.001M Fe(III) initially, at pH 1.46

$*[R]_e$ Initial M	$[R_2H_2SO_4]_e$ Initial M	$[RH_2SO_4]_e$ Initial M	$\frac{[RH_2SO_4]}{[R_2H_2SO_4]}$	$[Fe^{+3}]_A$ Equilibrium $M \times 10^4$	$[Fe^{+3}]_e$ Equilibrium $M \times 10^4$	D	$[R_2H_2SO_4]_e$ Uncomplexed at Equilibrium M
0.0211	0.0072	0.0068	0.94	8.46	2.15	0.254	0.0070
0.0422	0.0142	0.0137	0.96	6.74	3.99	0.592	0.0138
0.0632	0.0213	0.0206	0.97	5.57	5.28	0.948	0.0208
0.0843	0.0283	0.0277	0.98	4.88	6.20	1.270	0.0277
0.1054	0.0348	0.0358	1.03	4.12	6.97	1.692	0.0341

* The initial amine concentration refers to the concentration of the amine in the original solution before conversion to its salts.

Table 3.14

The Extraction of Iron(III) from aqueous solutions containing 0.001M Fe(III) initially, at pH 1.82.

*$[R]_o$ Initial M	$[R_2H_2SO_4]_o$ Initial M	$[RH_2SO_4]_o$ Initial M	$\frac{[RH_2SO_4]}{[R_2H_2SO_4]}$	$[Fe^{+3}]_A$ Equilibrium $M\times10^4$	$[Fe^{+3}]_o$ Equilibrium $M\times10^4$	D	$[R_2H_2SO_4]_o$ Uncomplexed at Equilibrium M
0.0234	0.0092	0.0050	0.54	5.89	4.73	0.803	0.0087
0.0467	0.0181	0.0104	0.57	4.14	6.78	1.638	0.0174
0.0701	0.0274	0.0154	0.56	3.27	7.63	2.333	0.0266
0.0928	0.0363	0.0203	0.56	2.75	8.24	2.996	0.0355
0.1168	0.0461	0.0246	0.53	2.60	8.63	3.319	0.0452

* The initial amine concentration refers to the concentration of amine in the original solution before conversion to its salts.

Table 3.15

The Extraction of Iron(III) from aqueous solutions containing 0.001M Fe(III) initially, at pH 2.03.

*$[R]_e$ Initial M	$[R_2H_2SO_4]_e$ Initial M	$[RH_2SO_4]_e$ Initial M	$\frac{[RH_2SO_4]}{[R_2H_2SO_4]}$	$[Fe^{+3}]_A$ Equilibrium $M\times10^4$	$[Fe^{+3}]_e$ Equilibrium $M\times10^4$	D	$[R_2H_2SO_4]_e$ Uncomplexed at Equilibrium M
0.0113	0.0046	0.0021	0.46	6.67	3.78	0.567	0.0042
0.0226	0.0093	0.0040	0.43	4.39	6.11	1.392	0.0087
0.0452	0.0185	0.0082	0.44	2.55	7.95	3.118	0.0177
0.0678	0.0280	0.0118	0.42	1.79	8.76	4.894	0.0271
0.0904	0.0373	0.0159	0.43	1.45	9.06	6.248	0.0364
0.1130	0.0466	0.0198	0.42	1.23	9.42	7.659	0.0457

* The initial amine concentration refers to the concentration of amine in the original solution before conversion to its salts.

Table 3.16

The Extraction of iron(III) from aqueous solutions containing 0.010M Fe(III) initially at pH 2.03.

*$[R]_o$ Initial M	$[Fe^{+3}]_A$ Equilibrium $M\times10^3$	$[Fe^{+3}]_o$ Equilibrium $M\times10^3$	D	$[R_2H_2SO_4]_o$ Uncomplexed at Equilibrium M
0.0113	9.74	1.52	0.156	0.0031
0.0226	8.10	3.12	0.385	0.0062
0.0452	5.39	5.87	1.089	0.0126
0.0678	3.56	7.59	2.132	0.0204
0.0904	2.55	8.63	3.384	0.0287
0.1130	2.08	9.38	4.510	0.0372

* The initial amine concentration refers to the concentration of amine in the original solution before conversion to its salts. The initial concentrations of amine sulphate and bisulphate are shown in table 3.15.

concentrations of amine sulphate and bisulphate were obtained as described in experimental section 3.3, and, as has already been mentioned in section 1, these concentrations can be considered to be the concentrations of amine sulphate and bisulphate in equilibrium with hypothetical aqueous solutions of the above compositions without Fe(III) being present.

The values for the ratios of amine bisulphate to amine sulphate, as shown in the tables, are very constant for each pH value and do not show the systematic variations found with benzene as solvent. The values for the ratios increase with decreasing pH showing that the amount of amine bisulphate present in the mixtures increases with increasing aqueous acidity.

A plot of the logarithm of the distribution ratio for iron(III) against the logarithm of the uncomplexed amine sulphate concentration is shown in figure 3.13. It can be seen that quite good straight lines are obtained for such a plot, and that the systematic deviations shown in figure 3.11 for benzene are not evident. The slopes of the lines obtained for the experiments using 0.001M aqueous iron(III) solutions at pH values of 2.03, 1.82, 1.46, and 1.00 are very close to unity as predicted by equation (3.6). The dotted line shown in the diagram for an aqueous solution at pH 1.63 has been

Figure 3.13 Log D against Log $[R_2H_2SO_4]_o$ for Amine Solutions in chloroform

◒—◒—◒ 0.001M Fe(III), pH 2.03
○—○—○ 0.001M Fe(III), pH 1.82
—·—□·— 0.001M Fe(III), pH 1.65
●—●—● 0.001M Fe(III), pH 1.46
◑—◑—◑ 0.001M Fe(III), pH 1.00
▲----▲----▲ 0.01 M Fe(III), pH 2.03
△----△----△ 0.01 M Fe(III), pH 1.00

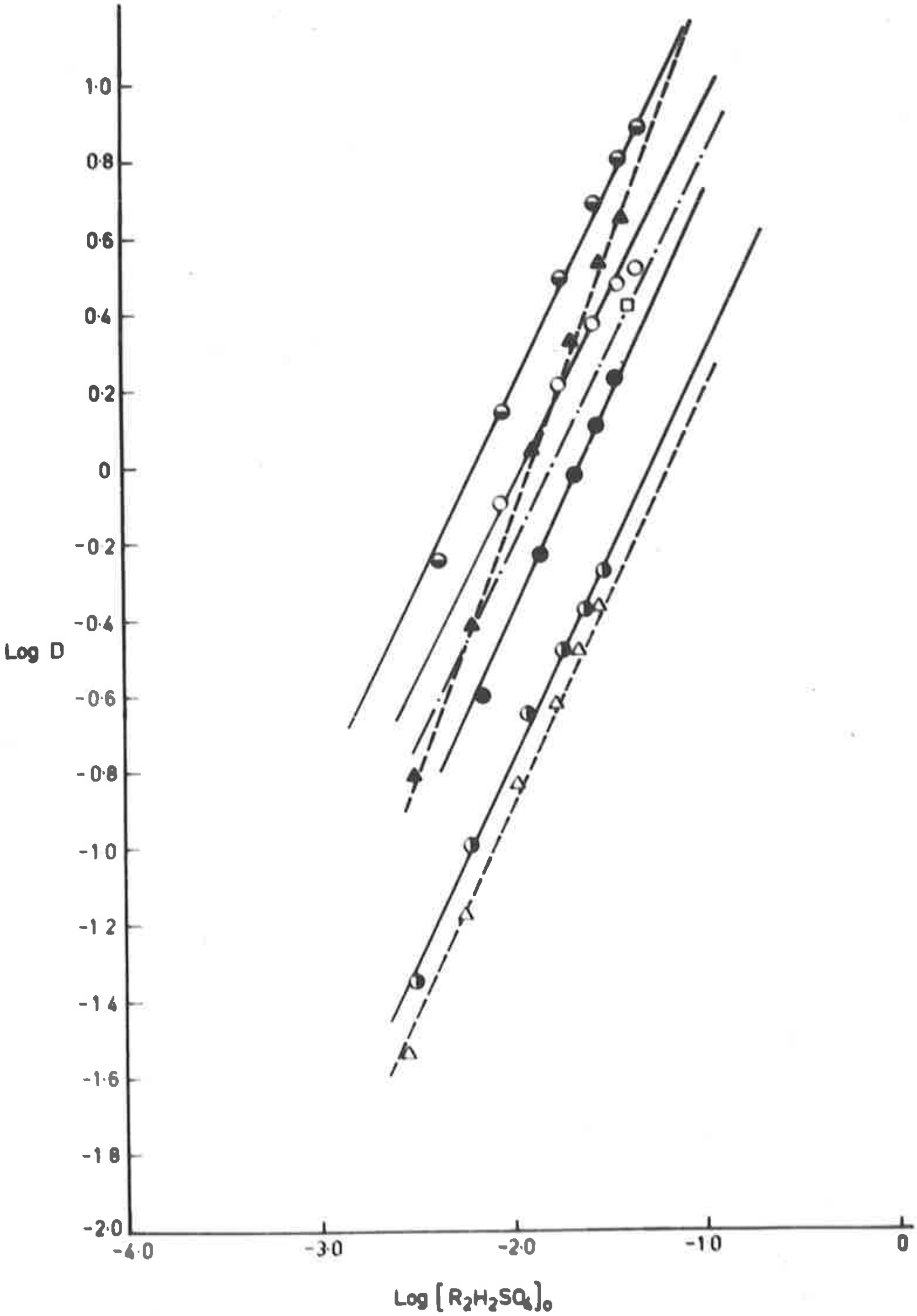

1·0
0·8
0·6
0·4
0·2
0
-0·2
-0·4
-0·6
-0·8
-1·0
-1·2
-1·4
-1·6
-1·8
-2·0
Log D
-4·0
-3·0
-2·0
-1·0
0
Log [R$_2$H$_2$SO$_4$]$_o$

Figure 3.13

drawn with a slope of one through the point obtained in one experiment using an aqueous solution at this pH value. The results obtained using 0.01M iron(III) solutions at pH values of 2.03 and 1.00 are also shown in figure 3.13, and again, as was observed with benzene as solvent for the amine, there appears to be a large increase in the slope of the line obtained at an aqueous pH of 2.03. The slope of the dotted line obtained for an aqueous 0.01M iron(III) solution at pH 2.03 is about 1.4 which is a much larger deviation from the predicted value of unity than can be accounted for by experimental error. This is again due to the extraction of the dimeric species $(FeOHSO_4)_2$, which, as has already been mentioned, is present in appreciable amounts in 0.01M Fe(III) solutions at pH 2.03.

The large increase in the extraction of Fe(III) with increase in aqueous pH value, as found in the work with benzene solutions, can again be seen in figure 3.13. Good _et al._[2] in their investigation of the extraction of Fe(III) from aqueous sulphate solutions by several amines suggest that the effect of pH can be explained as being due to the increased formation of the amine bisulphate at high acidities thus reducing the sulphate "sites" available for coordination to iron(III) in the organic phase. The results shown in figure 3.13, however, do not support this suggestion since the dependence of the distribution ratio for Fe(III) on the concentration of amine sulphate in the organic phase has been examined, and an increase in the iron(III) extraction is still found with increase in pH.

This increase in the extraction of iron(III) with increase in aqueous pH can be better demonstrated by selecting an arbitrary concentration of uncomplexed amine sulphate from figure 3.13, and by obtaining the corresponding distribution ratios for each aqueous pH value. If we choose an amine sulphate concentration of say 0.01M and plot the corresponding logarithms of the distribution ratios against the aqueous pH values a straight line is obtained of slope very close to unity as shown in figure 3.14. Equation (3.3) predicts that, for the extraction of the species $FeOHSO_4$ from the aqueous phase, the distribution ratio should show an inverse first order dependence on the aqueous hydrogen ion activity, or a direct first order dependence on the aqueous pH. The results shown in figure 3.14, therefore, clearly demonstrate the first order dependence of the distribution ratio on the aqueous pH, and hence give support to the extraction of a hydrolysed iron(III) species from the aqueous phase.

The suggestion, therefore, by Good <u>et al.</u>[2], that the decrease in extraction with increase in aqueous acidity is due to the formation of the amine bisulphate, whilst being

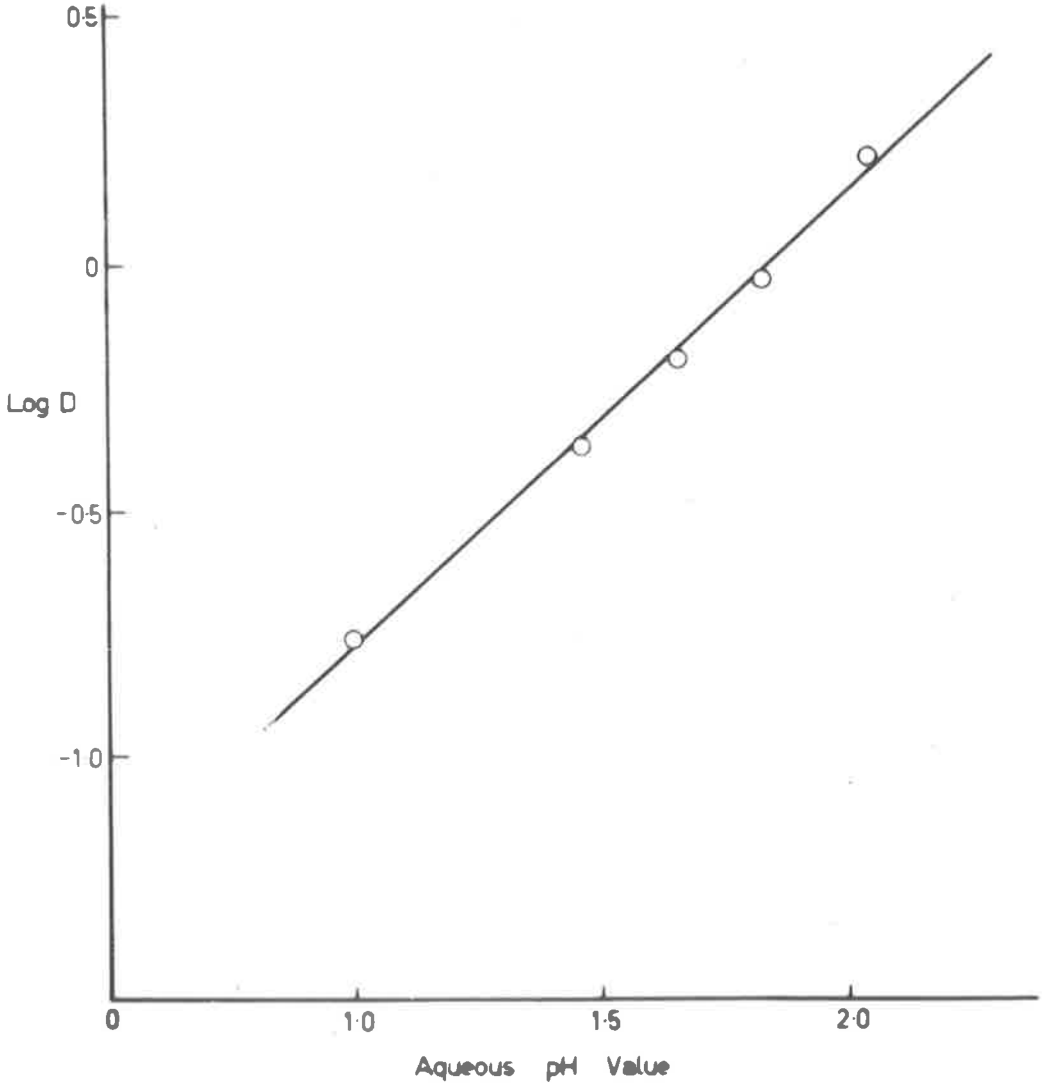


Figure 3.14 Log D against aqueous pH value for an uncomplexed amine sulphate concentration of 0.01M in chloroform.

partly true in that at high acidities the amount of amine sulphate present will be small and hence the extraction of iron(III) will be low, is not necessarily the complete explanation.

A plot of log D against (pH+Log$\left[R_2H_2SO_4\right]_o$) is shown in figure 3.15 for the cases shown in tables 3.11 - 3.15 where the log.-log. plot of D against $\left[R_2H_2SO_4\right]_o$ showed a first order relationship. The slope of the straight line obtained is unity and the value for log K''' is 0.18, hence the extraction equation, as described by equation (3.9), can be written as,

$$\text{Log } D = pH + \text{Log }\left[R_2H_2SO_4\right]_o + 0.18 \qquad (3.11)$$

It is interesting to compare the extraction equations for the amine dissolved in benzene as given by equation (3.10), and in chloroform as given by equation (3.11). It can be seen that the value for the distribution ratio obtained for iron(III) when using benzene as solvent should be about three times that obtained when using chloroform as solvent provided the amine sulphate concentration is below the "critical micelle concentration" for benzene. However, at high concentrations of amine sulphate in the organic phase (greater than the "critical micelle concentration") much lower values for the

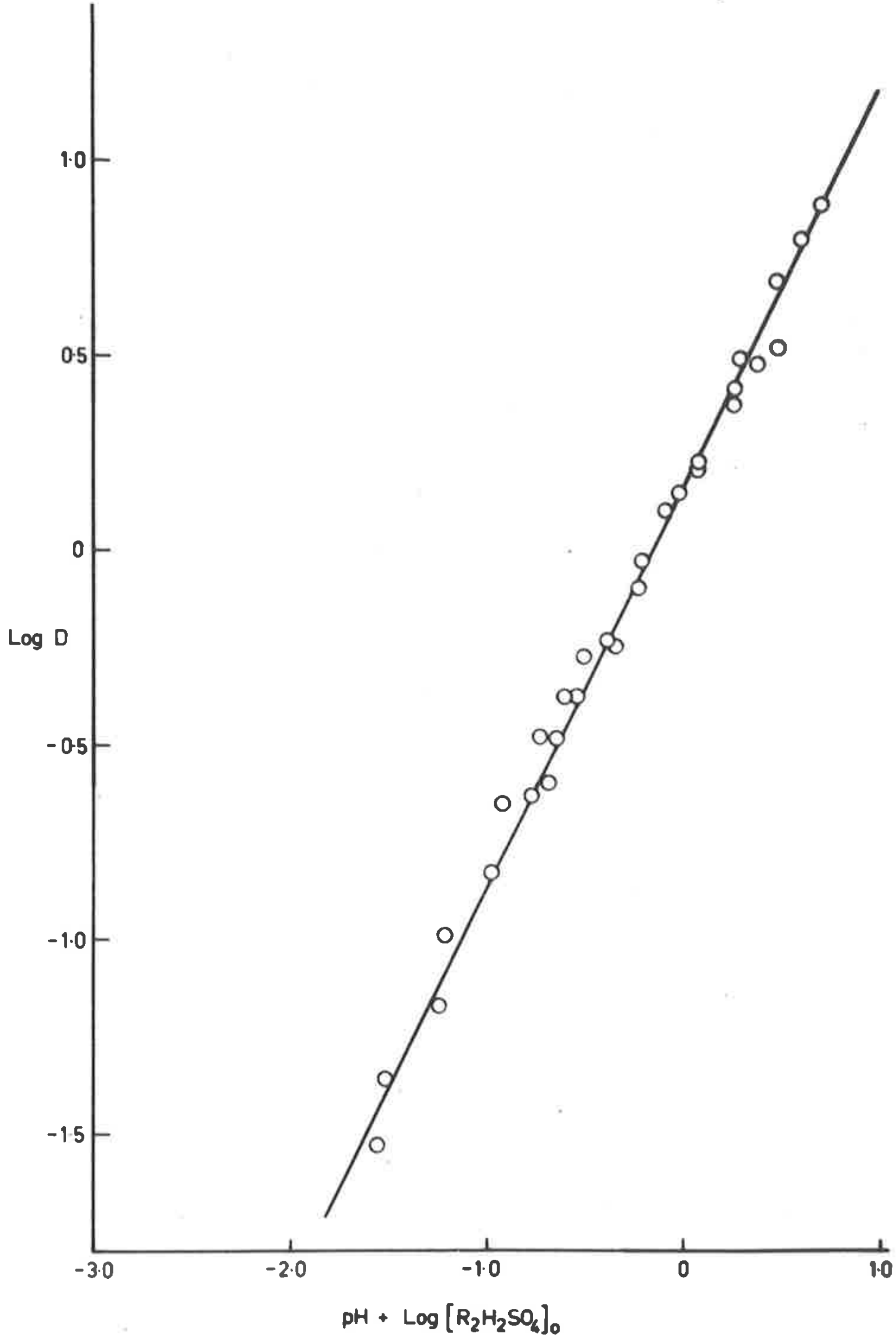


Figure 3.15 Log D against (pH + Log$[R_2H_2SO_4]_o$) for amine solutions in chloroform.

distribution ratio for iron(III) are obtained for the solvent benzene than for chloroform, due to the micelle formation of the amine sulphate in benzene. A study, therefore, of the effect of the solvent for the amine on the extraction can lead to misleading results if aggregation occurs in a particular solvent, and a concentration of amine sulphate is used which is above the "critical micelle concentration".

A more detailed study of the effect of micelle formation for several solvents for the amine is given in Chapter 5.

The results of the equilibrium studies, although they do not give absolute proof of the extraction of partially hydrolysed iron(III) species such as $FeOHSO_4$ and $(FeOHSO_4)_2$ from aqueous sulphate solutions by di(3,5,5,trimethylhexyl)-ammonium sulphate, can certainly be explained by an extraction theory which is based on the assumption that it is the partially hydrolysed iron(III) species which are extracted by reaction with the amine sulphate from the organic phase.

C. Ultra-violet Spectroscopic Examination of the Organic Phases After the Fe(III) Extraction Studies

The compositions of the benzene solutions obtained after the Fe(III) extraction experiments, as described in section B.1, which were used in the spectral studies are included in tables 3.5-3.10, however, for convenience these are given again in table 3.17.

Table 3.17

The Benzene solutions containing Fe(III) which were used for the Spectral Examination

Initial Fe(III) concn. in Aqu. Phase M	Aqu. pH	Initial Amine Concn. M	Concn. uncomplexed Amine Sulphate M	Fe(III) Concn. M	Curve No. in fig. 3.16
0.001	1.00	0.0040	0.00097	0.287×10^{-4}	6*
0.001	1.00	0.1000	0.0268	2.08×10^{-4}	7
0.005	1.00	0.0100	0.0022	0.312×10^{-3}	5
0.005	1.00	0.1000	0.0259	1.10×10^{-3}	9
0.01	1.00	0.0100	0.0020	0.645×10^{-3}	2
0.01	1.00	0.1000	0.0247	2.29×10^{-3}	8
0.001	2.03	0.0040	0.0012	0.38×10^{-3}	4
0.001	2.03	0.0050	0.0016	0.43×10^{-3}	3
0.001	2.03	0.1000	0.0433	0.723×10^{-3}	1

* The spectrum of this solution was measured in 1cm cells, all others were measured in 1mm cells.

The spectral curves of optical density against wavelength for the above solutions are shown in figure 3.16. It can be seen from the figure that an absorption peak occurs in the region 270-340mμ, and in nearly every case there appears to be a maximum at about 305-310mμ. There also appears to be a slight deformation of the smooth curves resulting in a shoulder at about 285-295mμ, but due to the limited number of experimental points in this region it is difficult to say whether this is a true effect or not. If it is, then the shoulder at 285-295mμ is most likely due to the absorption by the $FeOH^{+2}$ species, which, as has already been discussed in section A 2.2 has an absorption maximum at 295mμ[3, 23, 24].

The curves shown in figure 3.16 are very similar to that shown in figure 3.6 for a solution of complex (I) in benzene containing an excess of the uncomplexed amine sulphate which has a maximum at 305 mμ. This maximum has been suggested in section A 2.2 to be due to the species $FeSO_4^{+1}$, or $Fe(SO_4)_2^{-1}$ (or both). This similarity in the spectra is to be expected in view of the fact that the solutions, whose spectra are shown in figure 3.16, contained large excesses of uncomplexed amine sulphate as shown in table 3.17. These large excesses of uncomplexed amine sulphate were present simply because the experimental

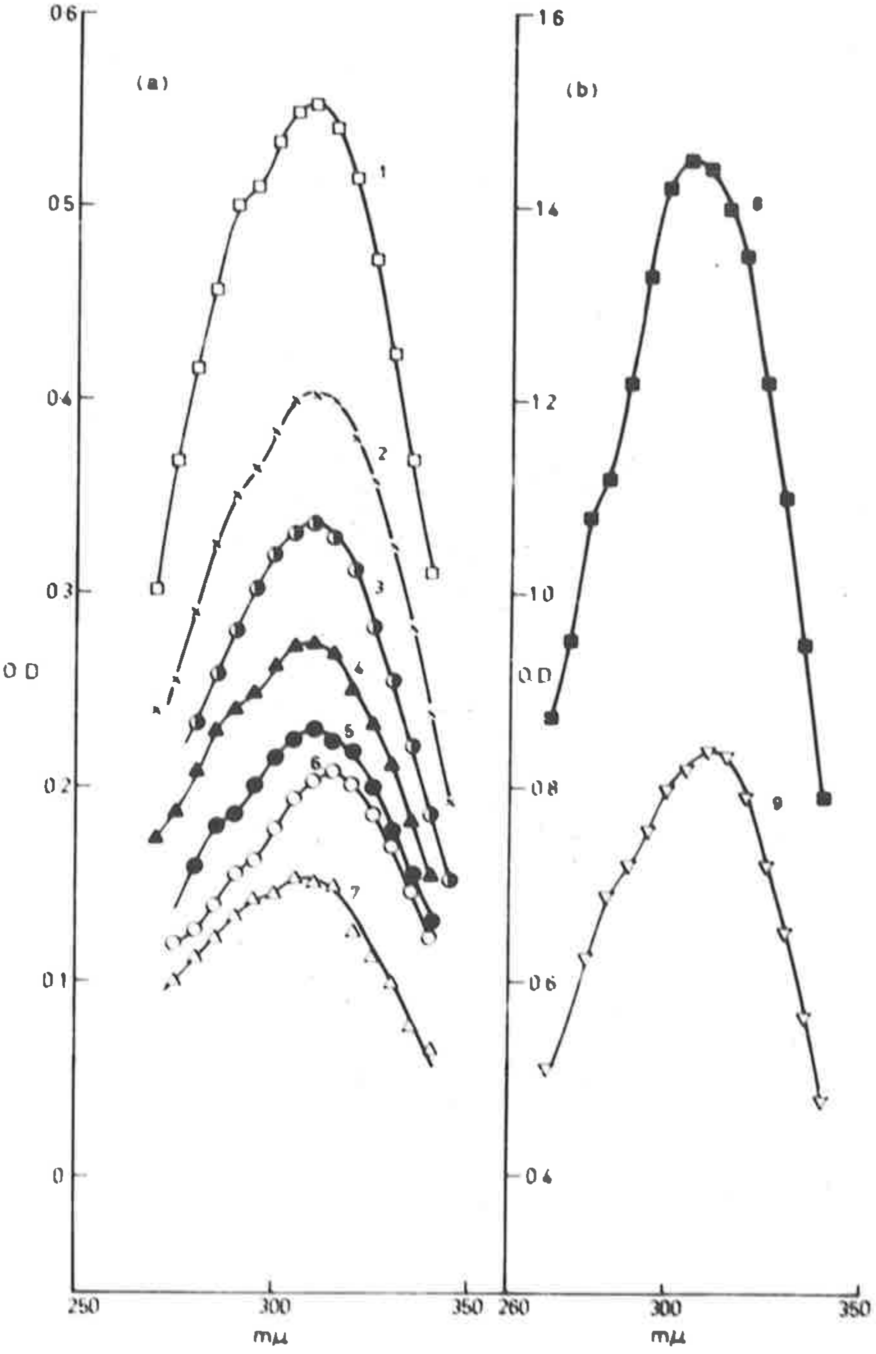


Figure 3.16 Ultra-violet spectra of the organic phases after the Fe(III) extraction experiments. The legend for the figure is given in table 3.17.

conditions for the equilibrium studies described in section B.1 were chosen so that the amounts of Fe(III) extracted were negligible compared to the concentrations of the amine sulphate. Hence, although the spectral examination of the organic phases obtained from the extraction experiments does not show the presence with any certainty of the partially hydrolysed species $FeOH^{+2}$ and $(FeOH)_2^{+4}$ in the organic extracts, this does not preclude the possibility that they are, in fact, present.

The results of the spectral examination of the organic phases after the Fe(III) extraction experiments do, however, fit in with the suggestion that it is complex (I) which is formed in the organic phase.

Good _et al_.[2], on the other hand, have examined the organic phases from their Fe(III) extraction studies with a primary amine dissolved in chloroform and have reported an absorption maximum at about 300mμ. The spectral curves obtained by them were quite similar to those shown in figure 3.16, except that the maximum appeared to occur at a slightly lower wavelength. Whiteker and Davidson[3], as discussed in section A 2.2, have found that the $Fe(SO_4)_2^{-1}$ species has an absorption maximum at about 300 mμ at a slightly lower wavelength than the $FeSO_4^{+1}$ species which has a maximum at 305-310mμ.

According to Good et al.[2] the appearance of a maximum at 300mμ in the spectra of their solutions is suggestive of the existence of the species $Fe(SO_4)_2^{-1}$ in the organic phases, which agrees with their original suggestion that it is this species which is extracted from the aqueous phase by primary amines. It should be pointed out that Good et al. have not investigated the effect, described above, of the presence of excess amine sulphate in the organic phase on the spectrum, however, the somewhat lower maximum (300mμ) obtained by them is probably sufficient evidence to say that the two systems are not strictly analogous.

The spectra of the aqueous Fe(III) solutions, which were used in the equilibrium studies, and which had the compositions given in table 3.1 in experimental section 3.1, are shown in figure 3.17. It can be seen that there is a large amount of absorption occurring in the region 270-340mμ with a maximum at about 305mμ. It is difficult to assign this absorption maximum to either the $FeSO_4^{+1}$ or $Fe(SO_4)_2^{-1}$ species, since, as has already been discussed in section A 2.2, the separation between the individual peaks is extremely small. It is probably sufficient to say that the maximum occurring at about 305mμ in the spectra of the

Figure 3.17 Ultra-violet Spectra of the Aqueous Iron(III) Solutions Used in the Extraction Experiments.

A.D.	×—×—×	0.001M Fe(III), pH 1.00 and 2.03
B.	○—○—○	0.005M Fe(III), pH 1.00
E.	△—△—△	0.005M Fe(III), pH 2.03
C.	●—●—●	0.01M Fe(III), pH 1.00
F.	◐—◐—◐	0.01M Fe(III), pH 2.03

pure water blank, 1mm cells.

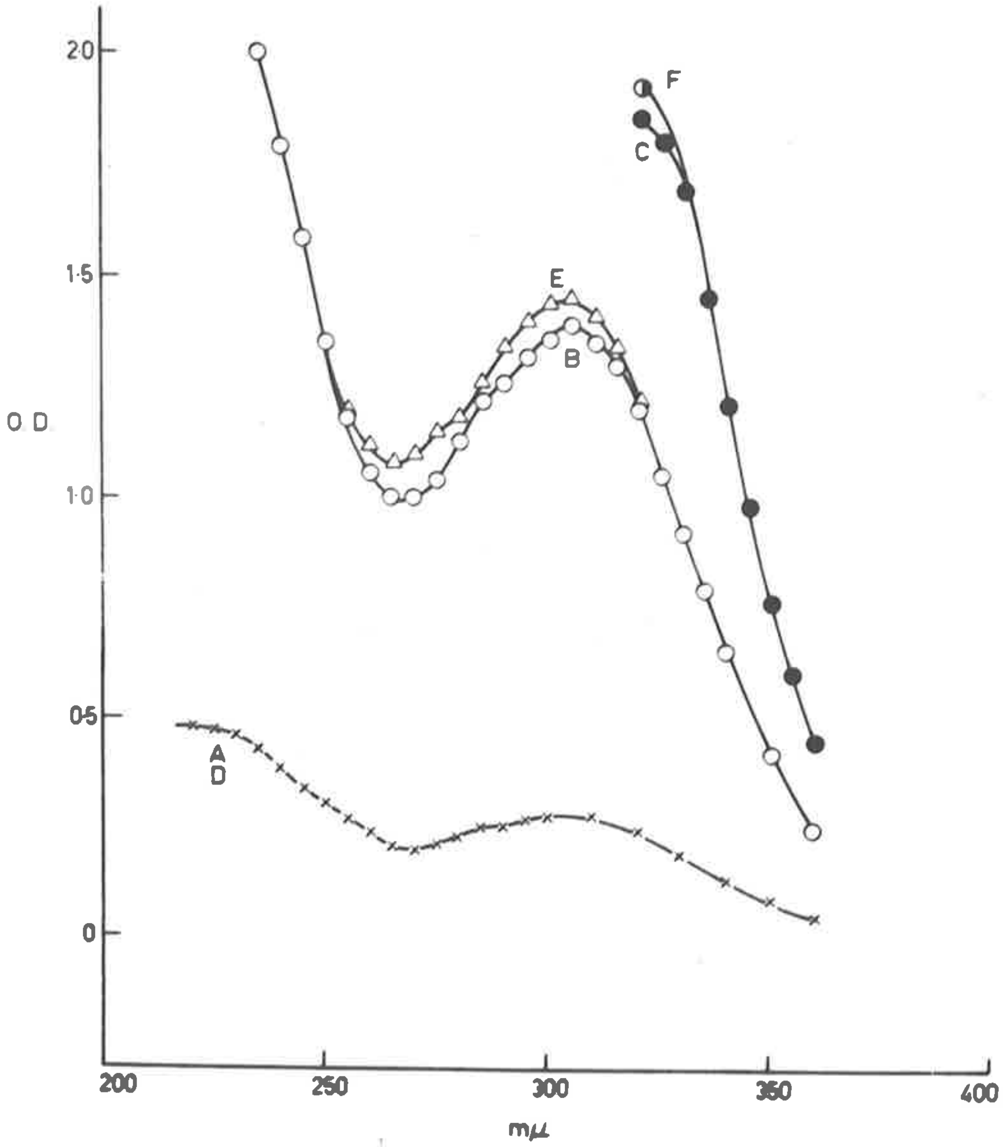


Figure 3.17

aqueous Fe(III) solutions is due to iron(III)-sulphate-complex species. The average extinction coefficient for solutions A,B,D, and E shown in figure 3.17 is 2800, which suggests that both the $FeSO_4^{+1}$ and $Fe(SO_4)_2^{-1}$ species are contributing to the spectrum since they have extinction coefficients of about 2200 and 3000 respectively.

The spectral curves for the 0.001M Fe(III) solutions at pH values of 1.00 and 2.03, shown in figure 3.17, are superimposed, whereas for the 0.005M Fe(III) solutions the curve for the pH 2.03 solution shows a slightly higher absorption in the region 260-320mμ than the pH 1.00 solution. Whiteker and Davidson[3] also found this in their studies and suggest that it is due to the increased amount of the $FeOH^{+2}$ species present in the pH 2.03 solution.

It is interesting to note that in the spectra of the aqueous Fe(III) solutions which are known to contain partially hydrolysed species such as $FeOH^{+2}$ and $(FeOH)_2^{+4}$ there is no characteristic peak or peaks associated with these species. This is due to the fact that they are hidden by the very strong absorptions associated with the larger amounts of the iron(III) sulphato-complex ions.

IV CONCLUSIONS

The results discussed in this chapter for the extraction of Fe(III) from aqueous sulphate solutions by the secondary amine di(3,5,5,trimethylhexyl)amine do give considerable support to the original suggestion of Baes[1] that the extraction of Fe(III) from aqueous sulphate solutions by a similar secondary amine, di-n-decylamine, involves a partially hydrolysed species from the aqueous phase.

The analysis of the complex isolated from the organic phase is certainly consistent with the stoichiometric formula $(R_2NH_2)_2FeOH(SO_4)_2$, where R is 3,5,5,trimethylhexyl, and the results of the extraction studies can be explained on the basis of the extraction of the partially hydrolysed species $FeOHSO_4$ and $(FeOHSO_4)_2$ from the aqueous phase.

An ultra-violet spectral examination of the complex isolated from the organic phase has established the presence of the species $FeOH^{+2}$ and $(FeOH)_2^{+4}$ in the complex, although infra-red spectroscopy failed to show the presence of the hydroxyl group. However, the limitations of the latter for identifying the metal-O-H vibrational frequencies in a system such as the one described here are also discussed in this chapter.

An ultra-violet spectral analysis of the organic phases obtained from the Fe(III) equilibrium studies demonstrates the possibility of drawing incorrect conclusions from such a study due to the effect on the spectrum of the extracted complex of the presence of large excesses of the uncomplexed amine sulphate in the organic extracts. Such a study provided evidence for the presence of iron(III)-sulphate-complex species in the organic phases whose absorptions interfered with those due to the $FeOH^{+2}$ and $(FeOH)_2^{+4}$ species.

A molecular weight study of the isolated complex in benzene and acetone solutions suggests some association in these solvents, and two structures for complex (I) have been proposed. Firstly, a chain-like structure similar to that suggested by Sommer and Pliska[27] for the basic ferric acetate cation has been considered, and, secondly, a cyclic trimer, as suggested by Orgel[29] for the basic ferric acetate cation has been proposed.

The former structure is favoured, however, since the ultra-violet spectroscopic evidence is easier to explain on the basis of a linear configuration for complex (I).

An infra-red spectroscopic study of di(3,5,5,trimethylhexyl)ammonium sulphate has shown that there is extensive hydrogen bonding between the protons attached to the quaternary nitrogen atoms and the sulphate groups of the amine sulphate molecules. This interaction is considerably less for the amine bisulphate and for the extracted Fe(III) complex.

Although the results presented in this chapter give support to the suggestion of the extraction of partially hydrolysed Fe(III) species by secondary amines such as di(3,5,5,trimethylhexyl)amine and di-_n_-decylamine, it is not impossible that the extraction involves a different species for a different amine type, and that the suggestion by Good _et al._[2] that the species $Fe(SO_4)_2^{-1}$ is extracted by a primary amine is, in fact, correct. This also gives considerable support to the suggestion that there are two reactions which are important in systems involving the high molecular weight amine salts. These are, firstly, the adduct formation reaction, which is proposed for the extraction of Fe(III) from sulphate solutions by di(3,5,5,trimethylhexyl)ammonium sulphate, as described in this thesis, and secondly, the anion exchange reaction as proposed by Good _et al._[2]

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Chapter IV.

THE AGGREGATION OF DI(3,5,5,TRIMETHYLHEXYL)AMMONIUM SULPHATE IN VARIOUS ORGANIC SOLVENTS.

I INTRODUCTION

The apparent constant activities of high molecular weight amine salts dissolved in certain inert solvents, which were first observed during the investigations of the extraction of uranium from aqueous solutions[1,2], have been assumed to be due to the molecular aggregation of the amine salts to form micelles. Similarly the unexpected deviations from the simple equilibrium law described in Chapter 2, for the extraction of sulphuric acid from aqueous solutions by tri-n-octylamine and di-n-decylamine dissolved in benzene, as found by Allen[3,4] have also been explained on the basis of constant activities of the amine salts due to micelle formation. The amine salt micelles were considered to have constant compositions in the inert solvents, and, hence, as such would have constant activities.

The phenomenon has also been observed in the present work and it has been shown (Chapter 3, results and discussion section B) for the extraction of iron (III) from aqueous sulphate solutions by di(3,5,5,trimethylhexyl)ammonium sulphate dissolved in benzene that the extraction appears to become independent of the amine sulphate concentration as the latter is increased, ie. the activity of the amine sulphate appears to be approaching a constant value. However, when chloroform is used as solvent for the amine sulphate the effect is not apparent and the extraction behaviour is as predicted by the theoretical equation.

It should be mentioned that the anomalous behaviours found by Allen and McDowell[5] for the extraction of uranium (VI) from sulphate solutions by tri-n-octyl- and di-n-decylammonium sulphates in benzene solution have been explained as being due to metastable conditions induced by the vigorous agitation customarily used in extraction procedures. The results of the studies described in this thesis, however, suggest that this is not so, since no anomalous results were obtained for the extraction of Fe (III) by di(3,5,5,trimethylhexyl)ammonium sulphate dissolved in chloroform using the same procedure for mixing the phases as was used for amine sulphate solutions in benzene.

The above evidence gives considerable support to the assumption that micelle formation is responsible for the apparent constant activities of the amine salts, since it has been found that the di(3,5,5,trimethylhexyl)ammonium sulphate is highly aggregated in benzene solution but not in chloroform solution. The high degree of aggregation of the amine sulphate in benzene and the non-aggregation in chloroform were determined by molecular weight measurements, as described in this chapter.

The molecular weight of the amine sulphate was also determined in iso-amyl alcohol solution and again no aggregation or micelle formation was found to occur in this solvent. Accordingly, as described in Chapter 2, the extraction of sulphuric acid from aqueous solutions by di(3,5,5,trimethylhexyl)amine dissolved in iso-amyl alcohol was found to obey a simple equilibrium law as predicted, and the systematic deviations found by Allen[3,4], for benzene solutions which he suggested were due to micelle formation, were not apparent.

In view of the vastly different aggregation properties of di(3,5,5,trimethylhexyl)ammonium sulphate in the above solvents and the apparent effect of such aggregation on the extraction of Fe(III) a study was made of the aggregation in various solvents in an attempt to determine the factors influencing the formation of micelles. The study is described in this chapter.

Allen[6] has investigated the aggregation of some amine salts in benzene solution using light scattering measurements, and has found evidence for high molecular aggregation of certain of these. Di-n-decylammonium sulphate was found to have a molecular weight of 28,000 corresponding to an aggregate containing 38 monomer units, whilst the tertiary amine salt tri-n-octylammonium sulphate appeared to be monomeric. However, it should be pointed out, as discussed in Chapter 2, that Fomin et al.[7] disagree with this latter result and suggest that tri-n-octylammonium sulphate is aggregated in benzene solution to some extent.

Another interesting observation made by Allen[6] was that the di-n-decylammonium sulphate- uranium (VI) sulphate complex appeared to be monomeric in benzene solution, or in other words the introduction of uranium (VI) into the benzene solution containing di-n-decylammonium sulphate broke up the amine sulphate micelles. A similar effect has been found in the present study, and, although the di(3,5,5,trimethylhexyl)-ammonium sulphate is highly aggregated in benzene solution, the amine sulphate-iron(III) sulphate complex has a much lower order of aggregation in the same solvent.

Allen[6] has also studied the viscosities of di-n-decyl-ammonium sulphate solutions in benzene containing either no uranium (VI), or varying amounts of uranium (VI) up to complete complex formation of all the amine sulphate. He has suggested that his results give additional evidence that the introduction of uranium (VI) into the amine sulphate solution causes de-aggregation. However, it may be suggested that this work does not give additional or independent evidence for aggregation and de-aggregation, but merely fits in with the other evidence obtained by light scattering. The limitations of viscometry as an independent evidence for aggregation and de-aggregation are discussed more fully in the results and discussion section 3.

The values for the molecular weight of di(3,5,5,trimethylhexyl)ammonium sulphate in several solvents were obtained using two methods, light scattering, and the Signer isopiestic method (Chapter 3, experimental section 2.3). The use of these two procedures for molecular weight determination was somewhat limited, and hence it was not possible to obtain molecular weight values in as many solvents as was desirable, however, the results which were obtained did show that the tendency of the amine sulphate to form micelles was strongly dependent on the solvent.

II EXPERIMENTAL

1. Reagents

Di(3,5,5,trimethylhexyl)ammonium sulphate

The amine sulphate was prepared as described in Chapter 3, experimental section 2.1, and was recrystallized twice from acetone. The material used for the investigations described in this chapter was the hydrated form $R_2H_2SO_4.\frac{1}{2}H_2O$, where R is di(3,5,5,trimethylhexyl)amine.

Di(3,5,5,trimethylhexyl)ammonium bisulphate

The amine bisulphate was prepared as in Chapter 3, experimental section 2.1.

Solvents

(1) **Benzene:**

"Analar" reagent grade purified as in Chapter 3, experimental section 1.

(2) **Toluene:**

"Univar" analytical reagent grade shaken several times with conc. sulphuric acid then with water, dried over calcium chloride, and fractionated. Fraction boiling at 110-111°C collected (B.Pt.110.6°C).

(3) **Carbon Tetra-chloride:**

"Univar" reagent grade, dried over calcium chloride, fractionated, and fraction boiling at 76.8°C collected (B.Pt.76.8°C).

(4) **Chlorobenzene:**

"May and Baker" reagent grade, shaken several times with conc. sulphuric acid, then with water, dried over calcium chloride, fractionated. Fraction boiling at 131.7°C collected (B.Pt.132.0°C).

(5) **Trichloroethylene:**

"Townson and Mercer" reagent grade, dried over calcium chloride, fractionated, and fraction boiling at 87.0°C collected (B.Pt.87.0°C).

(6) Chloroform:

"Univar" reagent grade, purified as in Chapter 3, experimental section 1. Immediately before use, dried over calcium chloride, fractionated under nitrogen, and fraction boiling at 61.0°C collected (B.Pt.61.3°C).

(7) Iso-Amyl Alcohol:

"B.D.H." reagent grade which was specified to contain 3-methyl-butanol with 15-30% of 2-methyl-butanol, dried over calcium chloride, fractionated, and fraction boiling at 130-132°C collected (B.Pt.128-132°C).

(8) Iso-Amyl Acetate:

"Analar" reagent grade, specified to contain 70-85% 3-methyl-butyl acetate and 15-30% 2-methyl-butyl acetate, dried over anhydrous sodium sulphate, fractionated, fraction boiling at 138-142°C collected (B.Pt.138-142°C).

(9) n-Decane:

"B.D.H.", reagent grade dried over calcium chloride, fractionated using a fraction splitting head, and fractions boiling at 174°C, 174-176°C, and 176-180°C collected (B.Pt.174°C).

(10) n-Octanol:

"Fluka puriss" specified to be >99% pure (B.Pt.193-195°C). Used as received.

(11) Di-isobutyl ketone:

"Union Carbide" sample, dried over calcium chloride, distilled under vacuum (B.Pt.169°C).

(12) Propylene dichloride:

"Union Carbide" sample, dried over calcium chloride, fractionated, fraction boiling at 96-97°C collected (B.Pt.96.8°C).

(13) 2-Ethylhexyl chloride:

"Union Carbide" sample, dried over calcium chloride, distilled under vacuum (B.Pt.173°C).

(14) Hexyl cellosolve $C_6H_{13}OCH_2CH_2OH$:

"Union Carbide" sample, distilled under vacuum (B.Pt.208°C).

(15) Methyl iso-amyl ketone:

"Union Carbide" sample, dried over calcium chloride, distilled under vacuum (B.Pt.143°C).

(16) 2-ethylhexyl aldehyde:

"Union Carbide" sample used as received.

(17) 2-ethylhexyl cellosolve:

"Union Carbide" sample, distilled under vacuum (B.Pt.-).

(18) Acetone:

"Analar" reagent grade purified as in Chapter 3, experimental section 1. Used for recrystallization of the di(3,5,5,trimethylhexyl)ammonium sulphate only.

(19) Ethyl alcohol:

Reagent grade was refluxed over sodium hydroxide and fractionated. The fraction boiling at 78-79°C was collected. (B.Pt.78.5°C).

The following solvents were also investigated but the amine salts were found to be insoluble in these.

Di-isopropyl ether
Di-ethyl ether
n-Hexane
n-Heptane
Cyclohexane
Iso-octane
Cyclohexene
Tetrahydrofuran
Petroleum ether
Nitrobenzene
Dioxan

2. Procedure

2.1 Light Scattering Measurements

Di(3.5.5.trimethylhexyl)ammonium sulphate solutions

Solutions of the amine sulphate in various solvents were obtained by weighing the solid directly into standard volumetric flasks, and by making the solutions to volume at 25.0°C. The solvents used for the light scattering studies were benzene, toluene, chlorobenzene, trichloroethylene, carbon tetrachloride, chloroform, and iso-amyl alcohol, and solutions were generally in the concentration range of 0.01-0.22 g/ml.

For the light scattering measurements it was necessary to remove as much dust as possible from the solutions since traces of dust can lead to misleading results. Two methods were used for this, firstly, high speed centrifugation with subsequent transference of the solutions to the light scattering cell by means of a dust free pipette, and, secondly, by forced filtration under a positive pressure of nitrogen of the solutions directly into the light scattering cell through a no. 5 porosity ultra-fine sintered glass filter.

All apparatus used for the above operations was rinsed many times with dust free solvent, and the light scattering cell itself was steamed for several hours before the light scattering measurements. The steaming procedure was carried out be directing a jet of steam through a fine tube into the upturned light scattering cell and allowing the condensed water to continuously rinse out the cell.

The dust free pipette was fitted with a ground glass joint which enabled the tip to be placed in a glass jacket to protect it from dust.

Refractive Index Increment

The refractive index increment $\frac{\partial n}{\partial c}$, where n is the refractive index and c is the concentration in g/ml, was measured for two solvents benzene and iso-amyl alcohol using a double prism differential refractometer of the type described by Darskus[8]. Allen[6] measured the refractive index increments for various alkylammonium salts, including di-n-decylammonium sulphate, in benzene solution and found a linear relationship between Δn and concentration, so that for various concentrations the refractive index increment $\frac{\partial n}{\partial c}$ was constant. In the present work only one concentration of di(3,5,5,trimethylhexyl)ammonium sulphate in each solvent was used and linearity was assumed.

It should be pointed out that $\frac{\partial n}{\partial c}$ for the amine sulphate in benzene solution was actually negative, a refractive index decrement being measured. This arose since the refractive index of the solution was less than that of the solvent itself. Allen[6] found similar negative values for his alkylammonium salts in benzene solution. Since $\frac{\partial n}{\partial c}$ appears as a squared term in the mathematical treatment of the results the negative value obtained for it did not affect the molecular weight calculations in any way.

The refractive index increments or decrements for the amine sulphate dissolved in the other solvents used for the light scattering studies were calculated using the Gladstone and Dale relationship[9]

$$\frac{\partial n}{\partial c} = K_2 - \frac{d_1}{d_2} . K_1 \qquad (4.1)$$

where $K_2 = \frac{n_2-1}{d_2}$ and $K_1 = \frac{n_1-1}{d_1}$

d = density, n = refractive index, and K is a constant. The subscripts 1 and 2 refer to the solvent and the polymer respectively. Hence by knowing $\frac{\partial n}{\delta c}$ for the amine sulphate dissolved in two solvents, and by knowing the refractive indices and densities of those solvents, equation (4.1) can be solved to obtain values for d_2, the density of the amine sulphate and K_2. Thus $\frac{\partial n}{\delta c}$ can be calculated for any other solvent provided the refractive index and the density of the solvent are known. Stacey[9] describes the use of the empirical Gladstone and Dale relationship and states that it may be used to calculate $\frac{\partial n}{\delta c}$ values provided the highest accuracy is not required.

The calculated values for $\frac{\partial n}{\delta c}$ are shown in table 4.1, and were obtained using the $\frac{\partial n}{\delta c}$ values measured for di(3,5,5,trimethylhexyl)ammonium sulphate solutions in benzene and iso-amyl alcohol, which are also shown in the table. Literature values[10] were used for the refractive indices and densities of the solvents.

Table 4.1

Values of $\frac{\partial n}{\partial c}$ for various di(3,5,5,trimethylhexyl)ammonium sulphate solutions.

Solvent	$\frac{\partial n}{\partial c}$
Benzene	-0.054*
Toluene	-0.048
Chlorobenzene	-0.092
Trichloro-ethylene	-0.016
Chloroform	0.029
Iso-amyl alcohol	0.094*
Carbon Tetrachloride	0.006

* measured values.

The value of -0.054 found for benzene is similar to the value of -0.0594 found by Allen[6] for di-*n*-decylammonium sulphate.

It should be pointed out that since the intensity of scattering from a particular polymer solution is a function of the square of the value for $\frac{\partial n}{\partial c}$, most accurate results are obtained when the value for $\frac{\partial n}{\partial c}$ is quite large irrespective of its sign. Hence, light scattering measurements cannot be used for molecular weight determinations for solutions with very small refractive index increments or decrements. Such was the case with amine sulphate solutions in carbon tetrachloride which had a $\frac{\partial n}{\partial c}$ value of 0.006, since, although it might be expected that the amine sulphate is highly aggregated in this solvent on the grounds of its low dielectric constant and dipole moment, the intensity of the scattered light was too small to be measured. Similarly little reliance could be placed on the light scattering results for chloroform, and trichloroethylene solutions of the amine sulphate since the refractive index increment value for the former solvent of 0.029, and the decrement value of 0.016 for the latter were too small, in view of the small particle size in these solvents, to give scattering intensities high enough to measure accurately. On the other hand solutions of the amine sulphate in iso-amyl alcohol, which also contained very small particles, had a high refractive index increment (0.094), and thus gave high scattering intensities.

The method was therefore severely limited to cases where large values for the refractive index increment or decrement were obtained.

Light scattering measurements and Molecular Weight Calculations

Measurements were made using a Peaker light scattering apparatus (Polymer Consultants Ltd.), and values for r_θ were obtained at angles of 140°, 135°, 120°, 105°, 90°, and 45°. r_θ is the ratio of the intensity of the scattered light to the intensity of the incident light, where θ is the measuring angle. The light scattering cell was the same as that described by Darskus[8].

In a system such as the one described here, where we are dealing with spherical particles of fairly small size, optical (45°/135°) symmetry is expected, however, although this was found to be the case for the pure solvents, high dissymmetry values were obtained for certain of the amine sulphate solutions due to the presence of traces of dust. The dissymmetry is equal to the ratio $\frac{r_{45}}{r_{135}}$.

In view of this, light scattering measurements were made at high angles (140°, 135°, 120°, and 105°), and values for r_{90} were calculated from each r_θ value using the expression

$$r_{90} = r_\theta \cdot \frac{\sin\theta}{1+\cos^2\theta} \qquad (4.2)$$

The limiting value for r_{90} was thus obtained and used in the molecular weight calculations. The r_θ values were corrected for each measuring angle to allow for scattering due to the solvent.

It should be pointed out that the presence of traces of dust in the solutions has an almost negligible effect at high measuring angles, since dust tends to scatter the light back in the direction of the incident beam, and hence has a very large effect at low measuring angles.

The Rayleigh ratio R_{90} was calculated using the expression,

$$R_{90} = C_c \; n^2 \; r_{90} \qquad (4.3)$$

where C_c is the calibration constant for the instrument and n is the refractive index of the solvent.

The calibration constant was obtained using pure benzene and a R_{90} value of 16×10^{-6} as given by Allen[6].

In actual fact the expression involving the molecular weight, as given by equation (4.4), contains the term $\left(\frac{c}{R_{90}}\right)_{o}$, which is the limiting ratio of $\frac{c}{R_{90}}$ as the concentration c in g/ml approaches zero. Therefore values were calculated for $\frac{c}{r_{90}}$ and were plotted against concentration and the resulting curve was extrapolated to zero concentration to give the limiting ratio $\left(\frac{c}{r_{90}}\right)_o$. This ratio was then used to calculate the value for $\left(\frac{c}{R_{90}}\right)_o$ with the aid of equation (4.3).

The molecular weight was then obtained using equation (4.4).

$$K \times \left(\frac{c}{R_{90}}\right)_o = \frac{1}{M} \qquad (4.4)$$

where M = molecular weight

and

$$K = \frac{2\pi^2 n^2}{Ne\lambda^4} \cdot \left(\frac{\partial n}{\partial c}\right)^2 \qquad (4.5)$$

n = the refractive index of the solvent obtained from the literature[10].

$\frac{\partial n}{\partial c}$ = refractive index increment or decrement.

Ne = Avogadro's Number.

λ = wavelength of the incident light.

It is assumed that in this simple system the solute viz. di(3,5,5,trimethylhexyl)ammonium sulphate is monodisperse, and that each aggregate particle or micelle has the same molecular weight M. In fact, Allen[6] has found evidence to suggest that this is indeed so, and hence the above assumption seems reasonable.

The Light scattering measurements were made using incident light of wavelength 546mμ, as used by Allen[6] who found that at 436mμ some of his compounds exhibited fluorescence.

In most of the light scattering experiments involving highly aggregated solutions the depolarization due to the solute was found to be very small, however, for iso-amyl alcohol solutions of the amine sulphate the depolarization was appreciable and corrections were made to the r values by using the following expression (4.6) for calculating r_{90} instead of equation (4.2).

$$r_{90} = r_{\theta} \cdot \frac{\sin\theta}{1 + \left(\frac{1-pu}{1+pu}\right)\cos^{2}\theta} \qquad (4.6)$$

The depolarization ratio p_u was obtained by measuring the scattered light at 90° using a sheet of polaroid in the horizontal and the vertical positions, and by calculating the ratio of the intensity of the horizontal component to the intensity of the vertical component.

For pure benzene the value obtained for p_u was 0.41, which is in excellent agreement with the literature value of 0.41 to 0.43 as given by Stacey[9].

It should be noted that the depolarization ratios for the amine sulphate solutions were corrected to allow for the depolarization due to the solvent, and hence were the depolarization ratios due to the solute.

2.2 Isopiestic Molecular Weight Determinations

The molecular weight of the di(3,5,5,trimethylhexyl)-ammonium sulphate in chloroform and ethanol solutions, and that of the amine bisulphate in benzene solution were determined by the Signer method described in Chapter 3, experimental section 2.3. This method for molecular weight determination although convenient to use is limited to cases where the molecular weight is of the order of a few thousand molecular weight units, and to solvents whose vapour pressures are quite large.

2.3 Viscosity Measurements

Viscometric studies for all the solvents except ethanol and acetone described in section 1 above in which the amine sulphate was found to be soluble were made using two Ubbelohde viscometers, one for low viscosity solvents and the other for very viscous solvents. The viscometry runs were carried out by firstly pipetting a known volume of the solvent into the viscometer, and by measuring the solvent flow time. Known volumes of an amine sulphate solution were then added to the pure solvent in the viscometer so as to give solutions which were generally in the range of 0.002-0.020 g/ml. The flow times of these solutions were measured to within 0.1 sec, and were generally in the range of 100-300 sec. The viscometer was thermostatted at 25.0°C. All solvents and solutions were filtered through ultra-fine filters, as described in section 2.1 to remove dust prior to the viscosity measurements.

Several concentrations of the amine sulphate in each solvent were used and the viscosity ratios $\frac{\eta}{\eta_o}$ were obtained be relating the flow time of the solution to the flow time of the solvent, η and η_o are the viscosities of the solution and solvent respectively. Specific viscosities η_{sp} were obtained using the expression

$$\eta_{sp} = \frac{(\eta - \eta_o)}{\eta_o} \qquad (4.7)$$

and viscosity numbers $\frac{\eta_{sp}}{c}$ were calculated by dividing the specific viscosities by the concentrations of the amine sulphate in g/ml. The limiting viscosity number, which is still often termed the intrinsic viscosity, is thus given by the expression,

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta - \eta_o}{\eta_o \cdot c} \right) = \lim_{c \to 0} \frac{\eta_{sp}}{c} \qquad (4.8)$$

It has been attempted in this chapter, as far as possible, to follow the most recently recommended terminology for viscosity relationships, as described by Onyon[11].

III RESULTS AND DISCUSSION

1. Light Scattering Studies

The values for $\frac{c}{r_{90}}$ for various concentrations of di(3,5,5,trimethylhexyl)ammonium sulphate in benzene, toluene, chlorobenzene, and iso-amyl alcohol are shown in figure 4.1, and by extrapolation to infinite dilution the values for $(\frac{c}{r_{90}})_o$ have been obtained. The values for the constant K, described by equation (4.5), and the molecular weight values were calculated, as in experimental section 2.1, and are shown in table 4.2. The Aggregation numbers N refer to the numbers of basic units associated with the micellar particles, and were calculated using the molecular weight value of 646 for the monomeric formula $R_2H_2SO_4.\frac{1}{2}H_2O$, where R is di(3,5,5,trimethylhexyl)amine.

The values for K and N of 2.426×10^{-8} and 48 respectively for the amine sulphate in benzene solution agree quite well with the values of 2.92×10^{-8} and 38 which were obtained by Allen[6] for benzene solutions of the fairly similar salt di-*n*-decylammonium sulphate, and show that these salts are highly aggregated in benzene solution. In fact, the solution of di(3,5,5,trimethylhexyl)ammonium sulphate consists of aggregates or micelles which contain 48 monomer units.

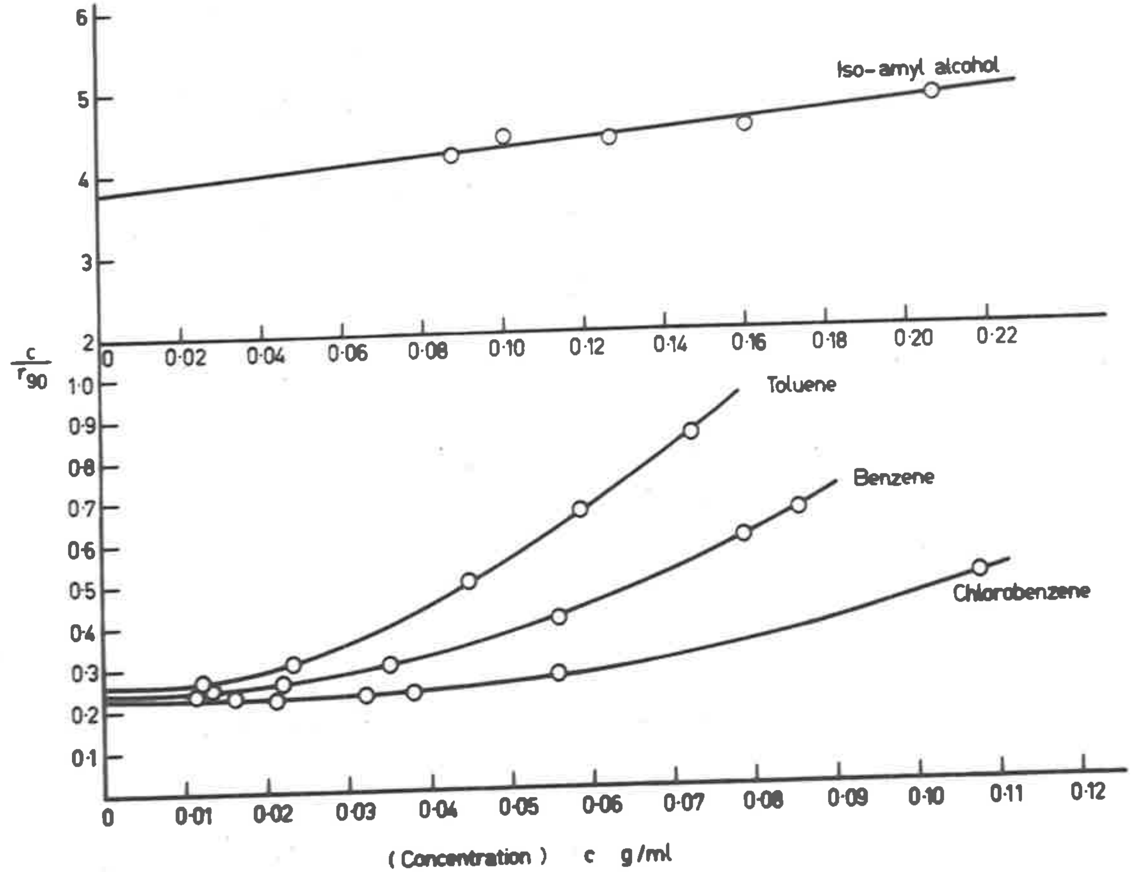

Figure 4.1 Light scattering data for various di(3,5,5,trimethylhexyl)-ammonium sulphate solutions.

Light scattering Data for di(3,5,5,trimethylhexyl)ammonium Sulphate solutions in various solvents

Solvent	Refractive Index[10]** n	$\left(\frac{c}{r_{90}}\right)_0$	Depolarization pu	K x10^8	M.W.	Aggreg. No. N	Dielect. Constant[12]	Dipole Moment[13,14]
Benzene	1.50112	0.220	<0.04	2.426	31,230	48	2.28	0
Chlorobenzene	1.52481	0.215	<0.03	7.268	11,010	17	5.71	1.6
Toluene	1.49693	0.230	<0.03	1.907	37,810	59	2.38	0.4
Iso-Amyl Alcohol	1.40853	3.80	≈ 0.30	6.467	598	1	15.30	1.7*

* This value is given by Le Fèvre[13] for a homologous series of aliphatic alcohols.

** These values are at 20°C except for Iso-Amyl Alcohol which is at 15°C.

It should be pointed out again at this stage that it has been assumed, in this work and supported experimentally by Allen[6], that the alkylammonium salts are monodisperse and that the aggregated particles, or micelles, are almost spherical in shape and are of uniform size throughout the solution.

The shapes of the $\frac{c}{r_{90}}$ against c plots for the amine sulphate dissolved in toluene, benzene, and to a lesser extent in chlorobenzene, suggest that the size of the micelle is increasing with concentration. This could be due to either an increase in the aggregation number N by the coalescence of individual micelles to form larger aggregates, or to the clumping together of individual micelles, with each retaining its initial size, as their number becomes greater with increase in amine sulphate concentration. However, the curves shown in figure 4.1 do appear to approach straight lines at low amine sulphate concentrations, and hence it has been assumed in this work that the micelles clump together rather than coalesce as the concentration increases, and that the size of the individual micelles remains the same.

It can be seen from table 4.2 that the size of the aggregate particle is very dependent on the solvent for the amine sulphate, and, in fact, in iso-amyl alcohol solution the amine sulphate is non-aggregated. The molecular weight value in iso-amyl alcohol is somewhat less than the monomeric value, which is probably due to some dissociation. In chlorobenzene the aggregate size is less than that for benzene showing that some de-aggregation has occurred, however in toluene the amine sulphate forms larger aggregates than in benzene.

The values for the depolarization ratio p_u, shown in table 4.2, are interesting, since there appears to be negligible depolarization occurring in solvents in which the amine sulphate forms aggregates, however, in iso-amyl alcohol in which the amine sulphate is non-aggregated the depolarization is quite large. A similar effect was found by Allen[6], and benzene solutions which contained large aggregates showed very little depolarization, whereas benzene solutions which contained non-aggregated or only slightly aggregated particles showed a very high depolarization. From this we can gain some knowledge as to the shapes of the particles present in solution. The low depolarization ratios obtained for solutions containing micelles suggests that they are in fact symmetrical and hence spherical, whereas the high depolarization ratio for iso-amyl alcohol solutions suggests that the non-aggregated amine sulphate molecule is extended linearly with the nitrogen atom at one end and the alkyl chains attached in a tail-like fashion.

The nature of the micellar particle

The nature of the micellar particle can be considered to be quite analogous to that described by Allen[6] for di-n-decylammonium sulphate. He pictures the micellar particle as an inverted Hartley micelle, with the non-polar alkyl chains on the outside and with the sulphate heads and the associated water on the inside of a roughly spherical configuration. The micelles are considered to be relatively stable, and this stability can be accounted for by hydrogen bonding between the protons attached to the quaternary nitrogen atoms and sulphate groups associated with neighbouring amine sulphate molecules. It should be pointed out that the bonding in a micellar particle may be quite non-specific, and that intermolecular hydrogen bond formation is not a necessary criterion for micelle formation, however, in the present case in view of the infra-red spectroscopic evidence for extensive hydrogen bonding in the amine sulphate, as described in Chapter 3, results and discussion section A.2.1, it seems highly probable that this is responsible for the stabilization of the micelle in non-polar solvents of negligible hydrogen bonding ability.

It has already been mentioned in Chapter 2, results and discussion section 1.1, that the alkylammonium salts are "soap-like" in nature, consisting of polar and non-polar sections, and that the behaviour of soaps in solutions with organic solvents is strongly dependent on the nature of the solvent. In alcohol, soaps are molecularly dissolved because the alcohol molecules have some affinity for the polar and non-polar sections of the soap molecules, and can solvate both. On the other hand in a non-polar solvent, such as benzene, there is strong solvation of the hydrocarbon chains, but no interaction of the polar "heads" with the solvent molecules. Consequently, the polar "heads" are pushed out of solution, and micelles are formed with the polar groups turned to the inside of the micelle.

In view of the similarity between soaps and the alkylammonium salts it is not surprising, therefore, to find that micelle formation occurs with di(3,5,5,trimethylhexyl)-ammonium sulphate in inert solvents such as benzene and toluene, since the polar sulphate groups are quite incompatible with the solvent. However, in iso-amyl alcohol solution which is a very polar solvent, the polar sulphate groups are solvated by the solvent, and hence micelle formation does not occur. Also the interaction of the alcohol molecules with the protons attached to the quaternary nitrogen atoms and with the associated sulphate groups prevents the formation of the micelle stabilising inter-molecular hydrogen bonds. In a solvent such as chlorobenzene which is a more polar solvent than benzene or toluene but which is less polar than iso-amyl alcohol it has been shown (table 4.2) that micelle formation does occur but the size of the micellar particle is less than those for benzene and toluene. In this case the polar sulphate groups of the amine sulphate are more compatible with the solvent chlorobenzene than with say benzene but are not compatible enough to prevent the sulphate groups from trying to "escape" from the solvent by forming micelles. Also the interaction between the solvent and the protons attached to the quaternary nitrogen atoms, although it brings about some de-aggregation, is not strong enough to prevent completely the stabilization of the micelles by inter-molecular hydrogen bonding between amine sulphate molecules.

2. Isopiestic Molecular Weight Determinations

The results of the Signer isopiestic molecular weight determinations for di(3,5,5,trimethylhexyl)ammonium sulphate dissolved in chloroform and ethanol are shown in figure 4.2, where the calculated molecular weight values (calculated as in Chapter 3, experimental section 2.3) are shown plotted against equilibration time. The approach of the systems to equilibrium can be seen, and the equilibrium molecular weight values obtained were 1030 and 505 respectively for chloroform and ethanol solutions. The value obtained for ethanol is

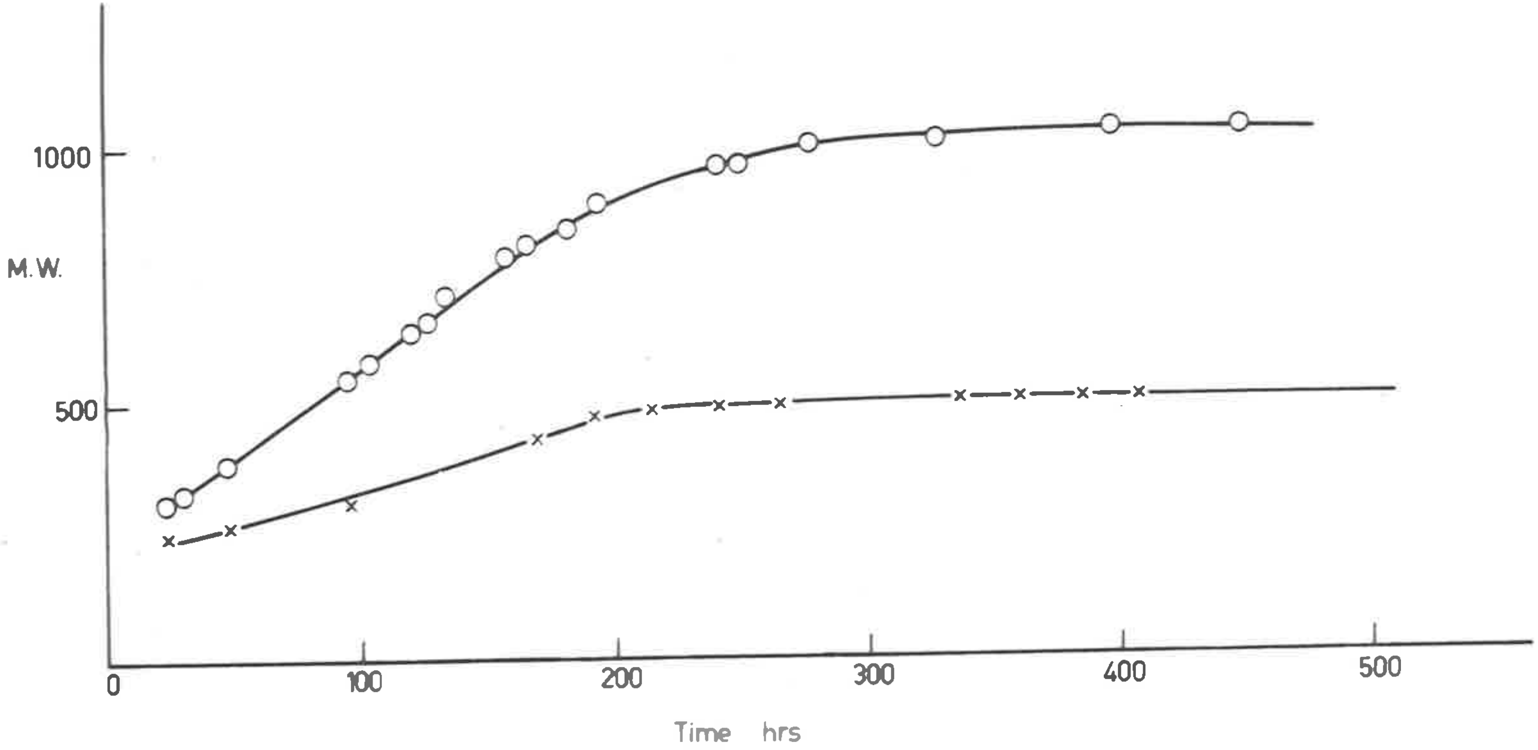

Figure 4.2 The determination of the molecular weight of di(3,5,5,trimethylhexyl)-ammonium sulphate by the Signer isopiestic method.

lower than that for the monomeric formula as was found previously with iso-amyl alcohol solutions, and hence again there is probably some dissociation of the amine sulphate occurring in this high dielectric constant solvent. The value for the amine sulphate in chloroform solution is greater than that for the monomeric formula and this indicates solvation of the amine sulphate molecule by the solvent. In fact, the solvated molecule contains about three molecules of solvent per amine sulphate molecule.

The most significant feature about the molecular weight value for the amine sulphate in chloroform solution is that it shows that there is no micelle formation in this solvent even though it is a slightly less polar solvent than chlorobenzene, having a dielectric constant[12] of 4.81 and a dipole moment[13,14] of 1.1 compared to those of 5.71 and 1.6 for the latter solvent. This is surprising since some aggregation has been shown to occur in chlorobenzene solution and hence we might expect some aggregation to occur in chloroform solution. There is evidence[15] that chloroform can form hydrogen bonds with certain basic groups and that the C-H group in the chloroform molecule can serve as a hydrogen bonding acid. Thus it can be suggested that chloroform can form fairly weak hydrogen bonds to the sulphate groups of the amine sulphate molecules. It can also be suggested that there is some interaction between chloroform via the chlorine atoms with the protons attached to the quaternary nitrogen atoms. The absence of micelle formation of the amine sulphate in chloroform solution is probably due to a combination of these two effects. The fairly weak interactions between chloroform and both the sulphate groups and the quaternary ammonium groups of the amine sulphate molecules are probably sufficient to offset the micelle stabilizing inter-molecular hydrogen bonding between the amine sulphate molecules.

The molecular weight value found for the amine sulphate in ethanol solution is analogous to the value found for iso-amyl alcohol as solvent, and shows that in these highly polar solvents, which have dielectric constants[12] of 24.30 and 15.30 respectively and dipole moments of 1.7*, there is strong solvation of the polar and non-polar groups of the amine sulphate molecule.

It has been shown in Chapter 3, results and discussion section A.3, that the Fe (III) complex(I)is not highly aggregated in benzene solution which is surprising

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* This value is given by Lè Fevre[13] for a homologous series of aliphatic alcohols.

in view of the high aggregation of the uncomplexed amine sulphate in this solvent. The reason for this is due to either much weaker, or the complete absence of, inter-molecular hydrogen bonding, resulting from an electronic or stereo-chemical effect, between the protons attached to the quaternary nitrogen atoms and sulphate groups associated with neighbouring amine sulphate molecules. In fact, this suggestion is supported by infra-red spectroscopic evidence as described in Chapter 3, results and discussion section A.2.1. In complex (I) the octahedral configuration of the Fe(III) ion prevents the amine sulphate molecules from approaching close enough to form inter-molecular hydrogen bonds, and hence stable micelles cannot exist.

The molecular weight value found for the amine bisulphate in benzene solution was 4,336, which is consistent with an aggregation number of about 12 monomeric amine bisulphate units. It can be seen that the extent of the aggregation of the amine bisulphate in benzene solution is considerably less than that of the amine sulphate in the same solvent (shown in table 4.2), and this must be due to the weaker interaction between the protons attached to the quaternary nitrogen atom and the bisulphate anion. In fact, the infra-red spectroscopic evidence (Chapter3, results and discussion section A 2.1(a)) supports this suggestion, and the weaker interaction must result in less extensive inter-molecular hydrogen bonding.

3. Viscosity Measurements

The Einstein hydrodynamic theory[16] for an infinitely dilute suspension of spheres predicts that the viscosity should obey the following equation.

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi \tag{4.9}$$

Where η and η_0 are the viscosities of the solution and pure solvent respectively, and ϕ is a hydrodynamic volume and is the volume fraction of the suspended spheres.

Since ϕ is a hydrodynamic volume it is independent of the particle size.

The Einstein theory is simplified by the assumption of infinite dilution since the particles of such a solution are separated by an infinite distance, and hence the disturbance of the flow pattern of the solvent by a given particle does not overlap with the disturbance of flow caused by the presence of a second suspended particle.

In the accessible range of concentration, however, there is always some interaction which increases the viscosity above its limiting value at infinite dilution. There are various types of interactions:

(1) Hydrodynamic interaction which arises from the overlap of flow patterns to two or more particles. Actual contacts between particles result in the temporary formation of doublets or higher aggregates.

(2) Electrostatic interactions[8] which lead to an electroviscous effect. In the present case where we are dealing with micelles of the type discussed above in section 1., in organic solvents, where the particles are considered to have an outer layer consisting of the long chain alkyl groups with the charged groups on the inside of the micelle, we can assume that the particles are essentially uncharged, and hence there is no electroviscous effect.

The viscosity can now be represented as a polynomial expression (equation 4.10), and as the concentration of the suspension increases, the degree of the polynomial must increase, to obtain a sufficient description of the experimental concentration behaviour.

$$\frac{\eta}{\eta_o} = 1 + a\phi + k_1(a\phi)^2 + k_2(a\phi)^3 + \ldots\ldots\ldots \qquad (4.10)$$

For spheres "a" has the value of 2.5, however, for non-spherical suspensions "a" has a greater value than this and depends on the shape of the particles, In terms of the specific viscosity and the limiting viscosity number or intrinsic viscosity based on volume fractions $[\eta]_\phi$, the expression becomes,

$$\frac{\eta_{sp}}{\phi} = [\eta]_\phi + k_1[\eta]_\phi^2.\phi + k_2[\eta]_\phi^3.\phi^2 + \dots\dots\dots\dots \qquad (4.11)$$

k_1, k_2......etc. are dimensionless interaction coefficients independent of ϕ, and their value depends on the shape and flexibility of the interacting particles and is made up of contributions from the various types of interactions which may be present in the system.

Allen[6] has made a viscometric study of di-n-decylammonium sulphate in several benzene solutions and has studied the effect on the viscosities of the introduction of uranium (VI) into these solutions. Allen plotted the viscosity numbers $\frac{\eta_{sp}}{c}$ against concentration and interpreted the decrease in the limiting viscosity number $[\eta]$ and the slope of the viscosity plot with increase in the amount of uranium (VI) present in the benzene solutions as being independent evidence for de-aggregation of the amine sulphate. However, this is not strictly correct since if we assume that the micelles are spherical, then, as we have seen above, the viscosity becomes independent of particle size. Hence, Allen's results cannot be interpreted directly as being independent evidence for de-aggregation, but can be explained on the basis of change in the hydrodynamic volume ϕ, or volume fraction of the particles, and hence be said to fit in with his results obtained from light scattering studies.

It has already been mentioned that for spheres the hydrodynamic volume is independent of particle size, but it is, naturally enough, dependent on the solvation of the particles. Solvation in this sense includes both chemically bound solvent, and entrapped solvent.

According to Allen[6], as has been discussed in section 1. above, the micellar particle can be best pictured as an inverted Hartley micelle with the non-polar alkyl chains on the outside and with the sulphate heads and the associated water on the inside of a roughly spherical configuration. In addition the present studies have given evidence for stabilization of the micellar particle by inter-molecular hydrogen bond formation between the protons attached to the quaternary nitrogen atoms and neighbouring sulphate groups, and hence the structure of the micelle can be considered to be fairly rigid. A structure for the micelle such as the one described above would therefore have the ability to entrap considerable quantities of the solvent within the nucleus of the particle itself, and the quantity of this entrapped solvent would almost certainly be dependent on the size of the micellar particle. The resulting effect is, of course, an increase in the hydrodynamic volume ϕ and consequently an increase in the viscosity.

It is not surprising, therefore, that Allen[6] obtained very high viscosities for di-n-decylammonium sulphate solutions in benzene, since he demonstrated by light scattering measurements that micelles were formed in this solvent. On the other hand he found, also by light scattering measurements, that introduction of uranium (VI) into the benzene solution of the amine sulphate caused de-aggregation of the amine sulphate, and that the pure amine sulphate-uranium (VI) sulphate complex was, in fact, monomeric.

Upon de-aggregation of the amine sulphate the large amounts of solvent which had previously been entrapped by the micellar particles would be released, and the resulting monomeric amine sulphate-uranium (VI) sulphate complex would possibly have only one or two solvent molecules bound to it. The net effect would be a decrease in the hydrodynamic volume ϕ and a subsequent decrease in the viscosity. Allen[6], indeed, found this to be so and observed a decrease in the viscosity upon de-aggregation of the amine sulphate.

This effect has also been observed in the present studies. The viscosity numbers for solutions of di(3,5,5, trimethylhexyl)ammonium sulphate dissolved in several solvents are plotted against the concentration in g/ml in figure 4.3. It can be seen from the figure that there is a very large increase in the viscosities in going from polar solvents such as iso-amyl alcohol and n-octanol for the amine sulphate to inert non-polar solvents such as carbon tetrachloride, toluene, and benzene. In fact, this increase in the viscosities appears to be in the order of aggregate size for solutions of the amine sulphate in the solvents used for light scattering studies, and the straight line obtained for the viscosity numbers against concentration for toluene solutions, which have been shown to contain the largest aggregates, has the largest slope and highest limiting viscosity number (or intrinsic viscosity). On the other hand the line obtained for iso-amyl alcohol solutions, which have been shown to contain non-aggregated particles, has a negligible slope and the lowest limiting viscosity number.

In view of the results obtained by Allen[6] the viscosity results shown in figure 4.3 are to be expected, and

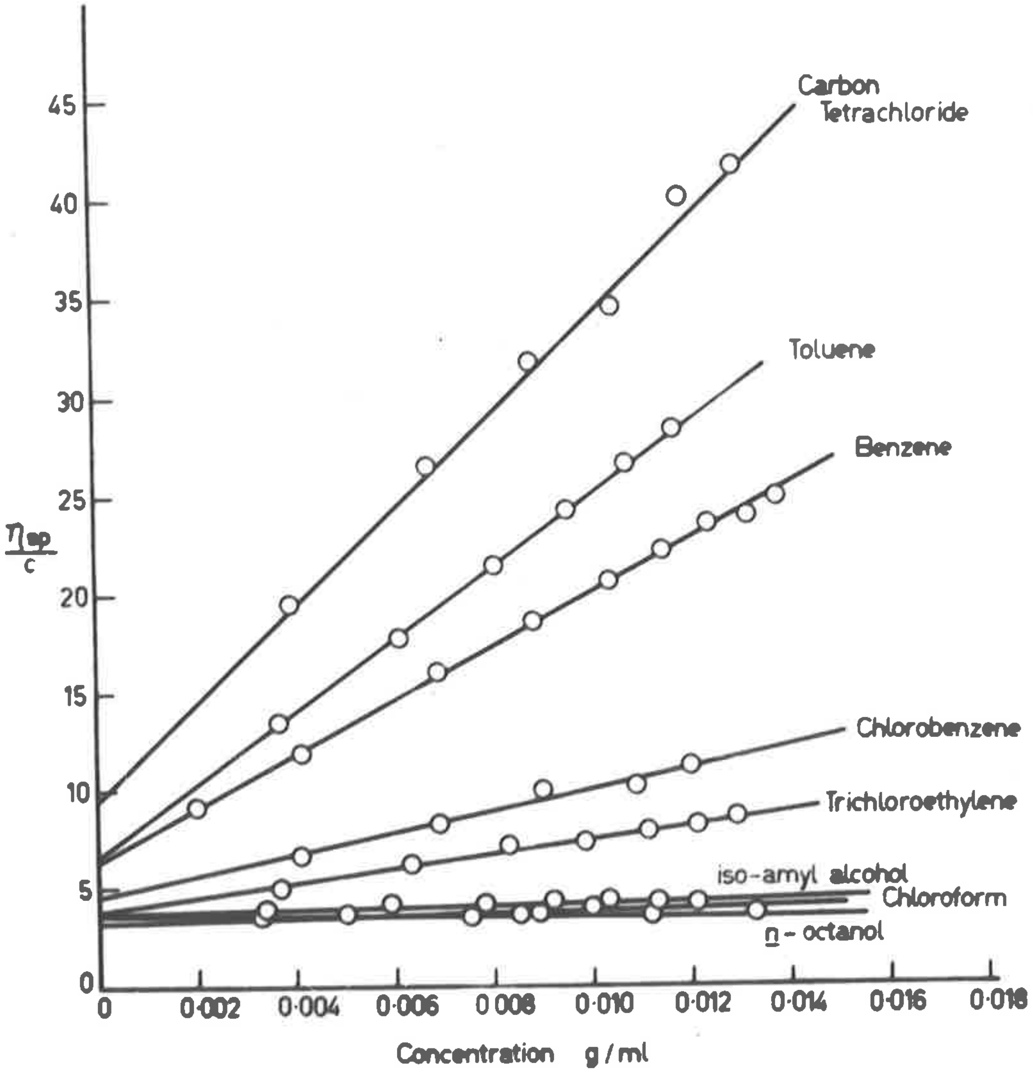

Figure 4.3 The viscosities of solutions of di(3,5,5,trimethylhexyl)ammonium sulphate in various solvents.

the same explanation as given above for his results can be used in the present case. The higher limiting viscosity numbers or intrinsic viscosities obtained for di(3,5,5,trimethylhexyl)ammonium sulphate solutions in which it is known that micellar particles exist, are due to the increase in the hydrodynamic volume ϕ of the particles and this is caused by the entrapping of large amounts of the solvent within the micelle. On the other hand the lower viscosities of the amine sulphate solutions containing non-aggregated particles are due to the much smaller hydrodynamic volume of the purely chemically solvated amine sulphate molecules.

It remains now to say something about the concentration dependence of the viscosity.

The viscosities of solutions in the experimental ranges of concentration are adequately described by equations (4.10) and (4.11), and it has already been pointed out that k_1, k_2.......etc. are interaction coefficients independent of the hydrodynamic volume ϕ . However, they can only be interpreted as interaction coefficients if the value of $a\phi$ in equation (4.10) does not change in the concentration region of measurements. We must assume, therefore, for the amine sulphate dissolved in any particular solvent in which aggregation is occurring, that the micellar particles are monodisperse and have the same hydrodynamic volume over the complete concentration range, and that the value for "a" is, in fact, constant in this concentration range. There will, of course, be a change in the value for "a", which depends on the shape of the particles, if there is any tendency for secondary aggregation of the micelles by the clumping together of individual micellar particles to form chain-like configurations. There is some evidence for this from the light scattering studies, as described in section 1., however, this effect appears to be serious only at much higher concentrations than were used in the viscosity studies. Thus we can assume that the value for "a" remains constant over the concentration range studied. Also we can assume that the hydrodynamic volume ϕ remains constant over this concentration range since from the light scattering studies and from Allen's results[6] the micellar particles appear to be monodisperse, and the size of the individual micelles does not appear to change with concentration within the range studied.

There is an additional factor which must be mentioned which is the critical micelle concentration (CMC) of the amine sulphate. This is the concentration at which micelle formation actually occurs. If the CMC occurs within the concentration range studied for the viscosity work then a discontinuity will occur in the viscosity curve of $\frac{\eta_{sp}}{c}$ against concentration. However, it has been suggested in Chapter 3, results and discussion section B.1 that the CMC for the amine sulphate in benzene solution is in the region of

0.004M to 0.008M, and since higher concentrations than this were used for the viscosity studies it was expected that the effect would not complicate the viscosity results in the concentration region of interest.

If we assume that $a\phi$ does not change in the concentration region studied, which is reasonable from the above discussion, then we can interpret the large slopes of the $\frac{\eta_{sp}}{c}$ against concentration plots, as shown in figure 4.3, for the cases in which aggregation does occur, as being due to the interactions between micelles, as characterised by the coefficients, k_1, k_2......etc.

It has been stressed throughout this section that for spherical particles the viscosity is independent of the particle size, and accordingly that measurements of viscosity are useless for molecular weight determination in systems involving spherical particles. However, it is interesting to compare the limiting viscosity numbers or intrinsic viscosities for di(3,5,5,trimethylhexyl)ammonium sulphate solutions in benzene and toluene. In these two solvents which have very similar dielectric constants and dipole moments, and in which it can be assumed that the solute-solvent interactions are very similar, the ratio of their limiting viscosity numbers, which from figure 4.3 are 6.1 and 6.5 respectively, is identical to the ratio of the molecular weight values for the amine sulphate in each solvent, as found by light scattering. The molecular weight value of the amine sulphate in toluene solution (37,810) was found to be greater than that in benzene solution (31,230). Thus in this case there seems to be a direct relationship between the limiting viscosity number and the particle size. This can be explained very simply since in similar solvents such as benzene and toluene the hydrodynamic volumes of the micelles are directly related to the particle size due to the rigidity of the micelle structure which results in a larger amount of solvent being entrapped by the larger micelles.

The above argument can be extended to the case of carbon tetrachloride which has a dielectric constant and dipole moment similar to those of benzene and toluene, and assuming that the solvent-solute interactions are again very similar, we can relate the limiting viscosity number for the amine sulphate in carbon tetrachloride solution (value 9.3 from figure 4.3) to that for the amine sulphate of known molecular weight in benzene solution, and obtain a relative value for the particle size of the amine sulphate in the former solvent. The molecular weight value obtained by this method is 47,610 which corresponds to an aggregation number of 74.

It should be pointed out that not all the viscosity results are shown in figure 4.3. Viscosity studies in the solvents methyl iso-amyl ketone, 2-ethylhexyl cellosolve, hexyl cellosolve, propylene dichloride, and iso-amyl acetate gave $\frac{\eta_{sp}}{c}$ against concentration plots similar to those shown for iso-amyl alcohol, chloroform, and n-octanol and hence are not shown in the figure. However, it can be said that in these solvents the viscosity behaviour was identical to that obtained using solutions in which the amine sulphate was non-aggregated. Similarly the results for the studies using the solvents 2-ethylhexyl chloride, and di-iso-butyl ketone are also not shown since the amine sulphate dissolved with great difficulty in these solvents and tended to settle out on standing. It was considered that unstable dispersions of the amine sulphate were obtained in these solvents and not true solutions. This is supported by the viscosity studies since the $\frac{\eta_{sp}}{c}$ against concentration plots gave slopes which were much greater than those obtained previously for solutions in other solvents in which aggregation occurred, but the corresponding limiting viscosity numbers were much smaller. This is just the situation one would expect for an unstable dispersion of the amine sulphate, since this would lead to very large solute-solute interactions resulting in large slopes for the viscosity plots, and would give low limiting viscosity numbers due to much smaller hydrodynamic volumes. The particles in the case of an unstable dispersion can be either aggregated or non-aggregated. With aggregated particles the smaller hydrodynamic volume can be explained as being due to much closer packing of the amine sulphate molecules in the micelles with the exclusion of the large amounts of entrapped solvent, and with the non-aggregated particles a smaller hydrodynamic volume is expected anyway.

The only other solvent not included in figure 4.3 is n-decane since this was found to be impure and contained traces of an alcohol, probably 2-butoxyethanol which is used in its separation from other hydrocarbons. The presence of this impurity was detected by measurement of the interfacial tension between n-decane and water, as described in Chapter 5 results and discussion section 2.

The results of the viscosity study of the iron(III) hydroxy-sulphate-amine sulphate complex (I), in benzene solution were analogous to those obtained by Allen[6] for the uranium (VI) sulphate-di-n-decylammonium sulphate complex, and are shown in figure 4.4. The results for the pure amine sulphate in benzene solution are shown again in figure 4.4 for comparison. The very marked decrease in the viscosity associated with the complexing of iron (III) to the amine sulphate can be seen from the figure, and agrees quite well with the previous evidence

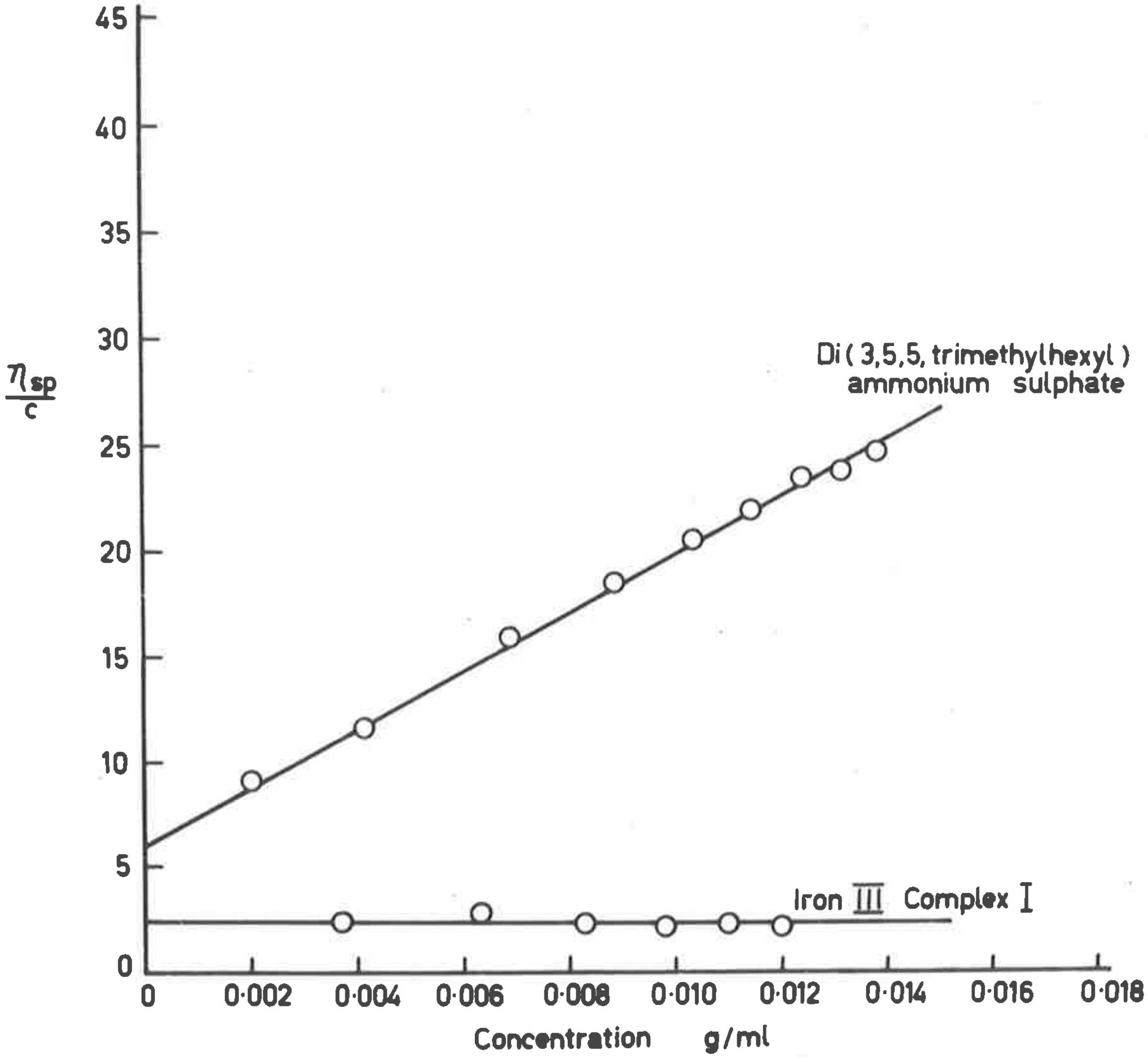

Figure 4.4 The viscosity of the iron(III) complex (I) in benzene solution.

that the iron (III) complex (I) is not highly aggregated in benzene solution (Chapter 3, results and discussion section A.3). The explanation for the change in viscosity behaviour in going from the pure amine sulphate to the iron (III) complex is, of course, exactly analogous to that given previously for Allen's work, which stated that there is a decrease in the hydrodynamic volume associated with the dissociation of the amine sulphate micelles.

The results shown in figure 4.4 for the iron (III) complex (I) in benzene solution are representative of the results of the viscosity studies for the complex in all the solvents in which the pure amine sulphate formed micelles, and hence the latter are not shown in the figure.

IV CONCLUSIONS

The results presented in this chapter demonstrate very well the phenomenon of aggregation of di(3,5,5,trimethylhexyl)ammonium sulphate in certain solvents, and lend support to the postulate that the observed deviations from the usual extraction behaviour are, in fact, due to the formation of micelles.

It has been shown that aggregation of the amine sulphate occurs in non-polar or weakly polar solvents of low or moderate dipole moments and dielectric constants which have negligible hydrogen bonding ability. In strongly polar solvents or in solvents such as chloroform, which can form hydrogen bonds by means of its acidic proton, no such aggregation occurs, and it seems fairly certain that this is due to the absence of the micelle stabilizing hydrogen bonds between the protons attached to the quaternary nitrogen atoms and sulphate groups associated with neighbouring amine sulphate molecules.

The results of a viscometric study also lend support to the formation of micelles, however, they can only be used in conjunction with other evidence obtained from light scattering and isopiestic molecular weight studies, and cannot be used as independent evidence for aggregation.

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Chapter V.

THE EFFECT ON THE EXTRACTION OF IRON(III) OF THE SOLVENT FOR THE AMINE

I. INTRODUCTION

It was recognized quite early in the study of the use of high molecular weight amines as solvent extraction agents that the role of the solvent for the amine or amine salts was an extremely important one. In fact, Coleman et al.[1] postulated that the amine (or amine salt)-organic solvent combination rather than the amine alone should be considered as the effective extractant.

Very few workers have investigated the effect of the solvent used for the amine or amine salt on the extraction of a single metal when all other factors which could influence the extraction efficiency are kept constant. Most of the discussions of the role of the solvent for the amine in the extraction process have been largely generalized descriptions of a vast array of amines and metals and often have led to misleading conclusions. As has already been pointed out in Chapter 3, the aggregation of the amine salts, in this case di(3,5,5,trimethylhexyl)ammonium sulphate, in certain solvents has a serious effect on the extraction of iron(III) at concentrations of the amine sulphate above the critical micelle concentration, and, in fact, a study of the role of the solvent for the amine sulphate in this extraction system suggests that the extraction is more efficient in chloroform than in benzene. This is, of course, true at concentrations above the critical micelle concentration, however, at concentrations of the amine sulphate which are below the critical micelle concentration the order of extraction efficiency is reversed, and the extraction becomes more efficient in benzene than in chloroform. An effect such as this can thus lead to incorrect conclusions when one is generalizing about a series of amines or amine salts in different "diluents", since some of the amine salts may aggregate and others may not.

Any satisfactory study, therefore, of the role of the "diluent" in an amine extraction system must be done with careful control of the other factors which are likely to influence the extraction.

According to Smulek and Siekierski[2] there are two important factors which must be taken into account in any extraction process.

(1) The solvation of the extractant by the solvent for the extractant in the organic phase.

(2) The solvation of the complex by the solvent for the extractant in the organic phase.

The third important factor which they do not mention is, of course, the extractant-extractant interaction which in the case of the di(3,5,5,trimethylhexyl)ammonium sulphate leads to aggregation in certain organic solvents.

Goble and Maddock[3] investigated the extraction of protactinium chloride from hydrochloric acid solutions by tri-n-butylamine in various organic solvents and found a correlation between the extraction efficiency and the dielectric constant of the solvent. Similarly Taube[4] studied the extraction of plutonium, neptunium, and uranium from sulphate and nitrate solutions by amines and other extractants, and suggested that the main factor influencing the extraction is a dipole-dipole interaction between the complex extracted and the molecules of the solvent for the extractant.

Good and Bryan[5], on the other hand, found that the extraction of cobalt(II) from hydrochloric acid solutions by tri-n-hexylamine in various solvents did not show any simple relationship between the extraction efficiency and the dielectric constant of the solvent, and, in fact, it appeared that except for certain halogenated solvents such as chloroform, the extraction of cobalt (II) was independent of the solvent for the amine.

Thus it can be seen that there is still a large amount of controversy as to the exact nature of the role of the solvent for the amine in an extraction system, since the effects of the solvent on the extraction appear to be many and quite diverse.

The work described in this chapter was carried out in an attempt to determine the effect of the solvent for di(3,5,5,trimethylhexyl)ammonium sulphate on the extraction of iron(III) from aqueous sulphate solutions, and it should be pointed out that such a study does not give a general behaviour for all systems.

In Chapter I of this thesis the postulate by McDowell and Case[6] of an interface mechanism for extraction systems involving high molecular weight amines and their salts has been discussed, and as has already been pointed out such a mechanism appears very attractive in the situation where the amine and its salts show very small solubilities in the aqueous layer, and have strong surface-active properties.

Thus the interfacial tensions were measured between solutions of the di(3,5,5,trimethylhexyl)ammonium sulphate in several organic solvents and aqueous solutions of identical compositions to those used in the iron(III) extraction studies described in Chapter 3. The lowering of the aqueous-organic solvent interfacial tension by the presence of the amine sulphate has been interpreted in terms of the concentration at the interface of the amine sulphate. This study is also described in the present chapter.

II. EXPERIMENTAL.

1. Reagents

Di(3,5,5,trimethylhexyl)ammonium sulphate

The amine sulphate was prepared as described in Chapter 3, experimental section 2.1, and was recrystallized twice from acetone. The hydrated form $R_2H_2SO_4.\frac{1}{2}H_2O$ where R is di(3,5,5,trimethylhexyl)amine was used.

Solvents

The solvents used for the work described in this chapter are given in Chapter 4, experimental section 1.

2. Procedure

2.1 The Extraction of Fe(III) by di(3,5,5,trimethylhexyl)ammonium sulphate in various solvents.

Solutions (0.050M) of the di(3,5,5,trimethylhexyl)-ammonium sulphate were made up in various organic solvents by weighing the solid directly into 25 ml volumetric flasks and making to volume at 25.0°C with the solvent which had previously been saturated with water. These solutions were then diluted at 25.0°C to obtain concentrations of 0.002M and 0.001M.

Extraction experiments were carried out using the solutions of the three concentrations described above for each organic solvent, by mixing equal volumes of these solutions, as described in Chapter 3, experimental section 3.2, with a 0.001 M aqueous iron(III) solution containing 0.50M total sulphate (see Chapter 3 experimental section, 3.1) at pH 2.10.

The aqueous iron solution had previously been saturated at 25.0°C with each organic solvent in turn.

Separation and analysis of the phases were carried out as described in Chapter 3, experimental section 3.3.

It should be pointed out that these studies were done using an aqueous iron (III) solution at pH 2.10 in order that the distribution ratios obtained would be as high as possible.

2.2. Measurement of the Interfacial Tensions

Interfacial tension measurements were made using the drop number technique described by Lewis[7]. The drop or Donnan pipette was of the type described by Reilly and Rae[8]. In fact, two pipettes, shown in figure 5.1, were used, the first which had a tip curved upwards was used for solvents whose densities were less than that of the aqueous phase, and the second with a straight tip was used for solvents whose densities were greater than that of the aqueous phase.

The technique consisted of filling the pipette with the organic phase A, immersing the pipette tip in the aqueous phase B, and determining for a known volume of the organic phase the number of drops which formed at the pipette tip C and which dropped upwards or downwards through the aqueous phase. The number of drops is dependent on the density difference between the aqueous and organic phases and on the interfacial tension. The diameter of the pipette tip is, of course, also important but this can be neglected if the same pipette is used in each experiment.

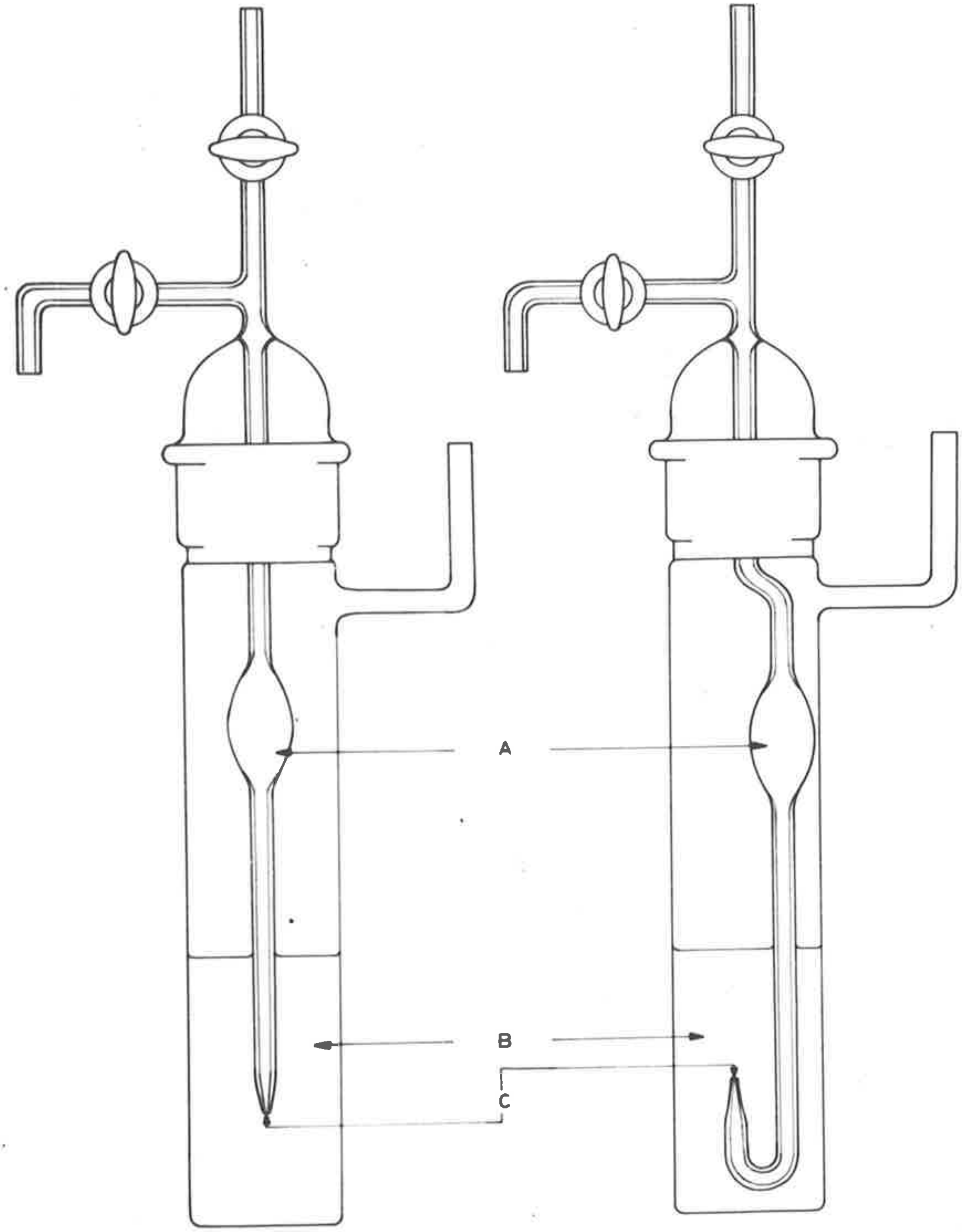

Figure 5.1 Drop pipettes used for interfacial tension measurements.

The drop number technique is very seldom used for absolute measurements of the interfacial tension, and is usually employed to compare the interfacial tension of one particular liquid with that of a liquid whose interfacial tension is known. For this reason benzene was used as the standard for experiments involving organic solvents and solutions whose densities were less than that of the aqueous phase, and carbon tetrachloride was used as the standard for cases where the densities of the organic phases were greater than that of the aqueous phase.

From the volume and the number of drops of the organic phase the apparent drop weight can be obtained and is given by the following expression

$$\text{Apparent drop weight} = \frac{V.\Delta\rho}{n} \qquad (5.1)$$

where V is the volume of the organic phase, n is the number of drops, and $\Delta\rho = (\rho_1 - \rho_2)$ where ρ_1 and ρ_2 are the densities of the aqueous and organic phases respectively.

Since the apparent drop weight is dependent on the interfacial tension a comparison of the apparent drop weight for the solvent of unknown interfacial tension with that of the standard solvent of known interfacial tension gives the interfacial tension for the former solvent.

Hence since V is constant,

$$\frac{\sigma}{\sigma_1} = \frac{n_1 \Delta\rho}{n\ \Delta\rho_1} \qquad (5.2)$$

where σ and σ_1 are the interfacial tensions for the standard solvent and the unknown respectively, n_1 and n are the numbers of drops of unknown and standard respectively and $\Delta\rho$ and $\Delta\rho_1$, are the density differences between the standard and the aqueous phase and between the unknown and the aqueous phase respectively.

There are several experimental factors which require special attention when using the above drop number technique and these are worth mentioning. The essential feature of the drop pipette is the tip which must be ground to give an opening which is almost perfectly round with very sharp edges and must be cleaned in chromic acid after every experiment. It is also essential to immerse the pipette to exactly the same depth below the surface of the aqueous phase in each experiment. The time taken to form the drop at the pipette tip is also critical and a long enough time must be allowed to ensure the formation of a nearly perfect drop. This was normally in the region of 10-20 sec. The temperature must be kept constant during the experiments and this was done by immersing the whole apparatus in a thermostat at 25.0°C. Finally special care must be taken to ensure that the drops form on the same edge (either the inside edge or outside edge) of the pipette tip in every experiment.

The counting of the drops was done mechanically using a simple hand counter. This, however, became very tedious when using certain systems due to the large number of drops formed. For example, when using iso-amyl alcohol the number of drops which formed was 1700. Consequently the use of an automatic counting system similar to that used by Edwards[9], was investigated which relied on the change in the conductivity of the aqueous phase when a drop of the very high resistance solvent passed between two electrodes. However, although this system worked for one particular solvent it was found necessary to rebuild it when this solvent was replaced by another of different dielectric constant and drop size, and hence became impracticable.

The aqueous solution used in the interfacial tension experiments was the same as that described above in section 2.1 for the iron(III) extraction experiments. The interfacial tensions were measured (by comparison with the standard solvents as mentioned before) between the above aqueous solution and 0.001M solutions of the di(3,5,5,trimethylhexyl)ammonium sulphate in various solvents, Similarly the interfacial tensions were obtained between the aqueous solution and the pure solvent.

The densities of all solvents and solutions were measured at 25.0°C.

III RESULTS AND DISCUSSION

1. The Extraction of Fe(III) by di(3,5,5,trimethylhexyl)ammonium sulphate in various solvents.

The results of the extraction of iron(III) from an aqueous sulphate solution containing 0.001M iron(III) at pH 2.10 by solutions (0.050M, 0.002M, and 0.001M) of the amine sulphate in various solvents are given in table 5.1, where the percentage extraction E is shown for the three amine sulphate concentrations in each solvent. The percentage extraction E, which is termed the extraction efficiency throughout this section, is defined as

$$E = \frac{\text{concentration of iron(III) in organic phase} \times 100}{\text{concn. iron(III) in org. phase + concn. iron(III) in aqu. phase}}$$

$$= \frac{100D}{1 + D}$$

where D is the distribution ratio defined as in Chapter 3, results and discussion section B.

Table 5.1.

Percentage Extraction of Iron(III) for Di(3,5,5,trimethylhexyl)ammonium sulphate Solutions in various Organic Solvents

Solvent	Percentage Extraction E			Dielectric[10] constant
	0.050M	0.002M	0.001M	
Benzene	72	37	24	2.28
Toluene	58	29	18	2.38
Chlorobenzene	79	34	18	5.71
Trichloroethylene	77	35	19	3.42
Carbon tetrachloride	42	20	15	2.24
Chloroform	88	16	10	4.81
Propylene dichloride	67	11	5.8	8.93
2-ethylhexyl chloride	21	7.1	4.7	5.05[i]
Di-isobutyl ketone	20	2.0	1.0	12.5[iii]
Methyl iso-amyl ketone	16	0.8	0.4	11.9[ii]
n-decane	3.8	0.2	0.08	1.99
Iso-amyl acetate	3.0	0.1	0.07	4.63
n-octanol	0	0	0	10.30
Iso-amyl alcohol	0	0	0	15.30
2-ethylhexyl cellosolve	0	0	0	16.0[v]
2-ethylhexyl aldehyde	0	0	0	9.07[iv]

i value for 1-chlorooctane

ii value for 2-heptanone

iii value for 4-heptanone

iv value for heptaldehyde

v value for methyl cellosolve

It should be pointed out that the use of the method described in experimental section 2.1 to obtain the results given in table 5.1 introduces a small inconsistency in that the concentration of the amine sulphate in the organic phase, which has been shown in Chapter 3 to be the species which reacts with iron(III), will not be the same for each organic solvent. This is because equilibration of the amine sulphate in a particular organic solvent with the aqueous phase will, as described previously in Chapters 2 and 3, produce an equilibrium mixture of the amine sulphate and bisulphate whose composition is dependent on the nature of the organic solvent. However, the differences will not be very large using aqueous solutions at pH 2.10 since the amounts of the amine bisulphate present in the organic phases will only be small.

The above effect will also have a small influence on the pH value of the aqueous phase since upon equilibration of the amine sulphate solution with the aqueous iron(III) solution at pH 2.10 some sulphuric acid will be extracted to form the amine bisulphate in the organic phase. Measurement of the pH values of the aqueous phases after equilibration experiments showed that the change in aqueous pH value in each case was only small, being in the range of

0.05 to 0.10 when using 0.050M amine sulphate solutions, and negligible when using the more dilute amine sulphate solutions.

In spite of the above limitations of the method it was decided that this was the most satisfactory and convenient way to investigate the effect of the solvent for the amine sulphate on the extraction of iron(III) since only a comparative study was required. It was considered that the small errors introduced by the above effect would not alter the order of extraction efficiency for the amine dissolved in various solvents.

Ratios of amine bisulphate/amine sulphate.

The variation in the amounts of the amine bisulphate and sulphate present in the organic phase after equilibration, as characterized by the ratios of the amine bisulphate to the amine sulphate, for solutions of the amine sulphate initially, in different solvents is demonstrated in table 5.2. The ratios of amine bisulphate/amine sulphate were determined as in Chapter 3, experimental section 3.3 for 0.010M di(3,5,5,trimethylhexyl)ammonium sulphate solutions initially, by equilibration with aqueous sulphate solutions containing 0.50M total sulphate at pH values of 1.00 and 2.10, and containing no iron(III).

Table 5.2

Ratios of Amine bisulphate/Amine sulphate for solutions in various solvents.

Solvent	Ratio of $\frac{\text{Amine bisulphate}}{\text{Amine sulphate}}$ pH 2.10	pH 1.00
Benzene	0.43	1.51
Toluene	0.17	1.39
Chlorobenzene	0.44	1.45
Trichloroethylene	0.39	1.43
Carbon tetrachloride	0.13	1.17
Chloroform	0.40	1.42
propylene dichloride	0.35	1.33
2-ethylhexyl chloride	0.10	0.86
Di-isobutyl ketone	0.23	1.48
Methyl iso-amyl ketone	0.45	6.00
n-decane	ND	ND
Iso-amyl acetate	ND	ND
n-octanol	0.14	3.33
Iso-amyl alcohol	0.54	6.25
2-ethylhexyl cellosolve	0.26	ND
2-ethylhexyl aldehyde	ND	ND

ND - not determined owing to practical difficulties.

It can be seen from table 5.2 that when using aqueous solutions at pH 2.10 there is quite a large variation in the ratio of amine bisulphate/amine sulphate for different solvents. It should be pointed out, however, that the actual variation in the concentration of amine sulphate is not as large as it would appear. A 0.10M amine solution which contains 0.020M amine bisulphate and 0.040M amine sulphate would have a ratio of amine bisulphate/amine sulphate of 0.50, whereas a solution which contains 0.004M amine bisulphate and 0.048M amine sulphate would have a ratio of 0.083. Thus from these two examples it can be seen that the very large change in the ratio of amine bisulphate/amine sulphate is associated with only a relatively small change in the concentration of amine sulphate (from 0.040M to 0.048M).

The variation in the ratio of amine bisulphate/amine sulphate is far less noticeable when using aqueous solutions at pH 1.00 except for three cases viz. methyl iso-amyl ketone, n-octanol, and iso-amyl alcohol. The ratios for these three solvents are very much greater than those for the remainder. The reason for this is not clear but may be due to a greater stability of the amine bisulphate in these high dielectric constant solvents arising from their greater solvating power.

Aggregation of the amine sulphate

The effect of the aggregation of the amine sulphate on the extraction of Fe(III) is clearly evident from the results shown in table 5.1. For those solvents in which aggregation is known to occur viz. benzene, toluene, chlorobenzene, carbon tetrachloride and to a small extent trichloroethylene it can be seen that at a concentration of the amine sulphate (0.050M) which is above the critical micelle concentration the order of the extraction efficiencies is carbon tetrachloride < toluene < benzene < chlorobenzene and trichloroethylene. The order of the aggregate sizes for the amine sulphate has been shown in Chapter 4 to be carbon tetrachloride > toluene > benzene > chlorobenzene and trichloroethylene and hence there is a definite correlation between the Fe(III) extraction efficiencies and the aggregate sizes. Those solvents in which the amine sulphate forms the largest aggregates have the lowest extraction efficiencies, and those solvents in which the amine sulphate forms the smallest aggregates have the highest extraction efficiencies.

At concentrations of the amine sulphate, however, such as 0.001M or 0.002M which are considered to be below the critical micelle concentration, the situation is somewhat different, and the iron(III) extraction efficiencies, except for a somewhat higher value for the 0.001M solution in benzene, all appear to be about the same. The slightly lower values for the carbon tetrachloride solutions are probably due to the fact that even at these low amine sulphate concentrations the critical micelle concentration is exceeded and the solutions still contain micelles.

It is interesting to note that the highest Fe(III) extraction efficiency shown in table 5.1 was obtained using a 0.050M amine sulphate solution in chloroform, and, as has already been discussed in Chapter 3, results and discussion section B, this is due to the fact that in this solvent there is no interference in the extraction of Fe(III) by the aggregation of the amine sulphate. However, for 0.001M and 0.002M amine sulphate solutions in chloroform the Fe(III) extraction efficiencies are less than those for solutions of the same concentration in the solvents in which aggregation normally occurs and whose concentrations are now below the critical micelle concentration.

Dielectric Constant of the Solvent.

The extraction efficiency falls remarkably as the dielectric constant of the solvent is increased above about 6.0, and there is negligible extraction for amine sulphate solutions in strongly polar solvents such as iso-amyl alcohol, and n-octanol, even after shaking for 24 hours. In these strongly polar solvents the solvent-amine sulphate interactions are very high, and this may be associated with the low Fe(III) extraction efficiencies.

There are several anomalies shown in table 5.1. Thus n-decane gives low iron(III)extraction efficiencies even though the pure solvent has a very low dielectric constant. This is most certainly due to the impure nature of the n-decane, as discussed in Chapter 4, and the presence of 2-butoxyethanol as impurity in this solvent would account for the low extraction efficiencies. Also the extraction efficiency of iso-amyl acetate as solvent for the amine sulphate would seem to be anomalously low in view of its dielectric constant which is about the same as chloroform. However, as will be seen later, the solubility of water in iso-amyl acetate is quite high and the solvent itself possesses some surface-active properties, both of which have been found to be associated with low iron(III)extractions. The third anomalous case is provided by 2-ethylhexyl chloride. The extraction results for this solvent must be disregarded however, in view of the uncertainty as to the solubility of the amine sulphate in 2-ethylhexyl chloride. It is considered that the amine sulphate is not truly dissolved in this solvent but only forms an unstable third phase dispersion. A similar effect was found for the solvent di-isobutyl ketone.

As has already been mentioned, for the solvents in which aggregation of the amine sulphate is known to occur there appears to be very little difference between the extraction efficiencies for amine sulphate concentrations which are below the critical micelle concentrations. In other words it appears that for these cases the extraction efficiencies are independent of the dielectric constant of the solvent. This is reasonable since for these solvents the solvent-amine sulphate interactions would be very small.

Hydrogen Bonding ability of the solvent.

The low extraction efficiency for the 0.001M amine sulphate solution in chloroform must be associated with the solvent-amine sulphate interactions. In Chapter 4 it has been suggested that hydrogen bond formation between the protons attached to the quaternary nitrogen atoms and the chlorine atoms of the solvent, and between the acidic protons attached to the chloroform molecules and the sulphate groups of the amine sulphate molecules prevents aggregation of the amine sulphate. This solvent-solute interaction may also interfere with the extraction of Fe(III) by affecting the ability of the sulphate group to complex with Fe(III). In a solvent such as trichloroethylene it appears that the solvent-amine sulphate interactions are less than in chloroform, since the results of the viscosity studies agree with the suggestion that there is some aggregation of the amine sulphate in trichloroethylene. Accordingly the Fe(III) extraction efficiencies are higher in trichloroethylene than in chloroform.

The Solubility of water in the solvent.

There is a further factor which may be important in determining the ability of a particular amine sulphate-solvent system for extracting iron(III). This is the amount of water associated with the organic phase. Table 5.3 gives the solubilities of water in the various pure solvents.

It can be seen from table 5.3 that these solvents in which there is negligible extraction of iron(III) have, generally, very large affinities for water, whereas the solubilities of water in the solvents in which there is good extraction of iron(III) are quite small. This suggests that the presence of appreciable amounts of water in the organic phase may have an effect on the amount of iron(III) extracted by the amine sulphate. This, of course, would be especially true if the iron(III) - amine sulphate complex

Table 5.3

The Solubility of Water in Various Organic Solvents

Solvent	Solubility of H_2O in[11,12,13] (per cent. by weight)	Temp. °C
Benzene[i]	0.057	25.0
Toluene[i]	0.040	25.0
Chlorobenzene[i]	0.034	25.0
Trichloroethylene	0,027	22.0
Carbon tetrachloride	0.010	24.0
Chloroform	0.084	24.5
Propylene dichloride	0.06	20.0
2-ethylhexyl chloride	0.04	20.0
Di-isobutyl ketone	0.75	20.0
Methyl iso-amyl ketone	1.5	20.0
n-decane	-	-
Iso-amyl acetate[ii]	0.90	20.0
n-octanol[iii]	3.45	20.0
Iso-amyl alcohol[ii]	9.2	20.0
2-ethylhexyl cellosolve	18.8	20.0
2-ethylhexyl aldehyde	0.4	20.0

[i] these values are given as per cent. by volume.

[ii] these values are actually for the primary amyl-compounds which contain mixed isomers.

[iii] this value is actually for iso-octanol which contains mixed isomers.

or the extracted species was unstable to water. In fact, it was found that the iron(III)complex (I), as described in Chapter 3, was soluble in dry iso-amyl alcohol giving a quite clear, stable solution, however, when dissolved in iso-amyl alcohol which had been saturated with water the solution became cloudy and ferric hydroxide was precipitated. It appears, therefore, that the complex (I) is readily hydrolysed in organic solvents containing appreciable amounts of water, and consequently this would lead to an instability of the extracted species in such solvents, and give low iron (III)extraction efficiencies.

The presence of appreciable amounts of water in the organic phase is probably a contributing factor towards low iron(III)extraction efficiencies.

The nature of the amine

It is quite well known[1] that the nature of the amine itself has a very strong influence on the extraction in a solvent extraction system, and it has been suggested[14] that the basicity of the amine is important in the extraction of a particular metal species from the aqueous phase.

It has been shown in Chapter 2 that the extraction of acids is strongly dependent on the basicity of the amine, and that higher equilibrium constants are obtained for the more basic secondary amine di(3,5,5,trimethylhexyl)amine than for the less basic tertiary amine tri(3,5,5,trimethylhexyl)amine. A similar effect has been observed in the iron(III) extraction work, although the decrease in the extraction efficiency using the tertiary amine in place of the secondary amine was found to be far greater than was observed in the sulphuric acid extraction studies. Negligible extraction of iron (III) occurred using identical conditions to those employed for the work with the secondary amine.

The decrease in the extraction of iron (III) in going from the more basic secondary amine to the less basic tertiary amine is probably not related in the same direct sense to the basicity as is the case for the extraction of acids, since the extraction of iron (III) occurs via the quaternary ammonium sulphate in which the basic nitrogen atom is already protonated. However, the effect can be explained by considering the inductive effect resulting from the alkyl chains attached to the nitrogen atom, which, if we assume that there is interaction between the sulphate group and the quaternary ammonium group, will affect the ability of the sulphate group to complex with iron(III).

It should be pointed out that it may not be so much an inductive as a stereochemical effect since it has been shown[14] that the inductive effect resulting from a change in size of the alkyl group attached to the nitrogen atom does not lead to stronger hydrogen bonds with ethanol in the direction predicted by the changes in electronegativity produced on the nitrogen.

It is interesting to note that in the case of the tertiary amine sulphate, since there is only one proton attached to each quaternary nitrogen atom, there can only be one hydrogen bond to a sulphate group. In the case of the secondary amine sulphate, however, there are two such protons, and this greatly increases the possibility for interaction between these and sulphate groups attached to neighbouring amine sulphate molecules. Hence this may explain why the secondary amine salts are usually more highly aggregated in certain solvents than the corresponding tertiary amine salts.

The importance of the interaction between the protons attached to the quaternary nitrogen atom of the quaternary cation and the associated sulphate group becomes more significant when we consider the extraction mechanism itself. To do this it is first necessary to discuss the surface-activity of the di(3,5,5,trimethylhexyl)ammonium sulphate.

2. The Surface-Activity of Di(3,5,5,trimethylhexyl)-ammonium Sulphate.

The interfacial tensions (dynes/cm) between various solvents and between 0.001M solutions of the amine sulphate in those solvents and aqueous sulphate solutions containing iron(III) at 25.0°C are given in table 5.4.

It is well known that[15] when water is placed in contact with an oil* the interface between the two liquids has a contractile tendency which is represented by the interfacial tension σ. For a liquid such as butanol which contains polar groups the value for the interfacial tension is only 1.8 dyne/cm since the butanol molecules concentrate at the oil-water interface where the repulsion between the packed and orientated molecules offsets somewhat the usual contractile tendency at the interface. This interfacial packing occurs because the polar hydroxyl groups can escape from the oil into the water layer leaving the non-polar alkyl chains immersed in the oil. The result is a state of low standard free energy.

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* means the organic phase.

Table 5.4

<u>Interfacial Tensions between some pure solvents and di(3,5,5,trimethylhexyl)ammonium sulphate solutions and an aqueous iron(III) solution</u>

	Pure solvent σ (dynes/cm)	0.001M amine Sulphate Solution σ (dynes/cm)	$\Delta\sigma$
Benzene	34.7*	12.3	22.4
Toluene	29.7	9.90	19.8
Chlorobenzene	43.0	12.8	30.2
Trichloroethylene	38.6	11.9	26.7
Carbon tetrachloride	43.7*	11.2	32.5
Chloroform	30.5	16.8	13.7
Propylene dichloride	34.9	14.9	20.0
2-ethylhexyl chloride	43.0	9.60	33.4
Di-isobutyl ketone	22.7	10.6	12.1
Methyl iso-amyl ketone	13.3	9.36	3.94
_n_-decane	23.5	10.6	12.9
Iso-amyl acetate	10.8	9.30	1.50
_n_-octanol	8.73	8.51	0.22
Iso-amyl alcohol	5.45	5.35	0.10
2-ethylhexyl cellosolve	3.58	3.61	negligible.
2-ethylhexyl aldehyde**	-	-	-

* literature values[15]; These are the values for the pure solvents against pure water, however, an experiment to determine the number of drops for the system pure benzene-pure water gave the same result as for the system pure benzene - aqueous iron(III) sulphate solution and hence it was concluded that the literature values for the systems using pure water could be used in the systems using the iron(III) sulphate solution.

** values for this solvent not determined.

For a three component system the situation is very similar, and for a solution of butanol dissolved in benzene adsorbing at the interface against water, the alcohol molecules again pack into the interface thus reducing the contractile tendency and hence reducing the value for the interfacial tension for pure benzene.

A substance which tends to pack into the oil-water interface thus reducing the interfacial tension is termed a surface-active agent.

From the results shown in table 5.4 it can be seen that di(3,5,5,trimethylhexyl)ammonium sulphate is a surface-active agent in certain solvents since it produces quite a large decrease in the interfacial tension $\Delta\sigma$ between the pure solvent and the aqueous iron(III)solution. There appears to be a correlation between the lowering of the interfacial tension and the extraction efficiency since solutions in those solvents in which the amine sulphate extracts iron(III)well show the largest values for $\Delta\sigma$. The one exception is 2-ethylhexyl chloride but, as has been mentioned in Chapter 4, little reliance can be placed on the results obtained for this solvent since it is suspected that in 2-ethylhexyl chloride the amine sulphate does not form a true solution.

There is also a correlation between the lowering of the interfacial tension and the tendency for the amine sulphate to form micelles, which would be expected since both are due to the tendency of the polar groups to "escape" from the non-polar solvent.

The lowering of the interfacial tensions for chloroform and propylene dichloride are larger than one would expect in view of the absence of micelle formation in these solvents, however, as can be seen from table 5.4, the final values for the interfacial tensions of 16.8 and 14.9 dynes/cm respectively for the amine sulphate solutions are somewhat higher than those obtained for solutions in the solvents in which the amine sulphate does aggregate. This suggests that the surface concentrations of the amine sulphate in chloroform and propylene dichloride are lower than for the other solvents. It is interesting to note that the interfacial tensions for the amine sulphate solutions in the solvents in which aggregation does occur are all about the same value of 10-12 dynes/cm which suggests that the surface concentrations are very similar for each solvent.

The values of the interfacial tensions for the other solvents, shown in table 5.4, in which there is negligible extraction of iron(III) and no aggregation of the amine sulphate, are generally quite low which demonstrates the tendency for the solvents themselves to concentrate at the oil-water interface, thus inhibiting the adsorption of the amine sulphate at the interface. The interfacial tension value for iso-amyl acetate is quite small and the lowering of the interfacial tension due to the presence of the amine sulphate in this solvent is also small which makes this solvent seem not such an anomaly as one would think from table 5.1, which shows an extremely low extraction for iron (III) by the amine sulphate in this solvent which has a dielectric constant very similar to chloroform.

The value (23.5 dynes/cm) shown in table 5.4 for the interfacial tension between n-decane and the aqueous iron(III) solution is much lower than the literature value[16] of 54 dynes/cm for the interfacial tension between this solvent and pure water, and hence must be due to the presence of the impurity 2-butoxyethanol which is used in the separation of n-decane from other hydrocarbons. It was found impossible to purify the solvent further by fractionation. The presence of this impurity in the n-decane, as has been mentioned already is probably the principal reason why low iron(III) extraction efficiencies were obtained for amine sulphate solutions in this solvent, and also why the aggregation of the amine sulphate in n-decane was found to be considerably less than expected for a solvent with such a low dielectric constant.

The interfacial mechanism for the extraction

From the above evidence for the surface-activity of the di(3,5,5,trimethylhexyl)ammonium sulphate in various organic solvents it seems fairly certain that the amine sulphate will be orientated at the interface in a manner such that the polar sulphate groups will penetrate into the aqueous phase leaving the long chain alkyl groups immersed in the organic phase and with the quaternary nitrogen atoms aligning the interface.

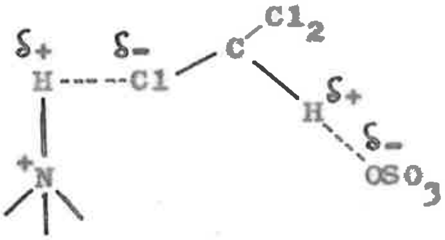
According to McDowell and Case[6] low values for the interfacial tensions between solutions of alkylammonium sulphates in certain solvents and aqueous sulphate solutions indicate that the sulphate part of the amine sulphate remains strongly associated with the organic quaternary ammonium group at the interface and is not predominantly ionized.

The reason for this is probably twofold. Firstly, the very high concentration of sulphate ions in the aqueous phase would simply by a mass action effect tend to oppose the ionization of the sulphate ions attached to the quaternary ammonium groups at the interface. The second and more important reason for the amine sulphate molecule remaining largely intact at the interface is the interaction (hydrogen bonding) between the protons attached to the quaternary nitrogen atoms and the associated sulphate group of the amine sulphate molecule. It has been demonstrated in Chapter 3 that this interaction is quite strong with di(3,5,5,trimethylhexyl)ammonium sulphate.

In view of this the interface mechanism for extraction of metal species by amine salts as suggested by McDowell and Case[6] becomes exceedingly attractive in the present system. The di(3,5,5,trimethylhexyl)ammonium sulphate molecules being orientated at the aqueous-organic interface in such a way that the sulphate groups can penetrate into the aqueous layer but still remain held at the interface by hydrogen bonding, as described above, provides for the formation of an interfacial complex between the sulphate groups held at the interface and iron(III) species from the aqueous phase. The transference of the complex to the organic phase then occurs by simple diffusion away from the interface.

The extraction behaviour in different solvents fits in quite well with the above theory since the most efficient systems employ solvents in which the hydrogen bonding between the protons attached to the quaternary nitrogens atoms and the associated sulphate groups is strongest, as characterized by micelle formation, and hence for these systems we would expect to have amine sulphate molecules concentrated at the aqueous-organic interface largely in the unionized form.

The solvent chloroform would seem to be an anomaly, since it has been suggested in Chapter 4 that the absence of amine sulphate micelles in this solvent is due to the replacement of the hydrogen bonding between the protons attached to the quaternary nitrogen atoms and the associated or neighbouring sulphate groups by hydrogen bonding to the solvent itself. However, it may be that the amine sulphate-chloroform interaction, although being strong enough to interfere with the intermolecular hydrogen bonding thus preventing micelle formation, is not strong enough to offset the intramolecular hydrogen bonding and there is still, in fact, some interaction between the protons attached to the quaternary nitrogen atoms and the associated sulphate group of the amine sulphate molecule. Alternatively the chloroform molecule can be pictured as acting in a bridging fashion since it is unique in that it can form hydrogen bonds to both the quaternary ammonium cation and to the associated sulphate group thus keeping the amine sulphate molecule intact at the interface.



For the very polar solvents such as iso-amyl alcohol and n-octanol the situation is probably very different since the amine sulphate molecules do not tend to concentrate preferentially at the interface. It is difficult to imagine, however, that the concentration of amine sulphate at the interface is zero, even though the lowering of the interfacial tensions of strongly polar solvents is very small. Hence the argument that the failure of the amine sulphate in these solvents to extract Fe(III) is due to the zero concentration of the amine sulphate at the interface seems unreasonable. In any event the ion-exchange reaction still occurs in iso-amyl alcohol which is shown by the fact that on shaking a solution of the amine sulphate in iso-amyl alcohol with an aqueous chloride solution, chloride ions are transferred to the organic phase.

Alternatively the few amine sulphate molecules which do appear at the interface may be predominantly ionized to give an ionized layer with the positively charged nitrogen atoms aligning the interface. This would set up an interfacial potential due to the phases on each side of the interface becoming electrically charged. Such a situation seems most favourable for systems involving organic solvents of high dielectric constant, since the strong interaction between the solvent molecules at the interface and the quaternary ammonium cations would assist the ionization of the sulphate ions, and hence would favour the ion-exchange reaction. On the other hand this situation would tend to oppose the alternative reaction suggested in this thesis of adduct formation which is the reaction of an undissociated amine sulphate molecule with an Fe(III) species from the aqueous phase.

The rate of extraction.

It might be thought at first sight that the large concentration of the di(3,5,5,trimethylhexyl)ammonium sulphate at the aqueous-organic interface in systems involving the organic solvents in which the amine sulphate displays a high surface-activity would tend to affect the total amount of iron(III)extracted, and hence a direct correlation between the concentration of the amine sulphate at the interface and the extraction efficiency might be expected. However, this does not appear to be so, as can be seen from the results given in tables 5.1 and 5.4, and the only influence the actual concentration of amine sulphate at the interface has on the extraction is, no doubt, to increase the rate of extraction. It has been shown in Chapter 3 that the rate of extraction of iron(III) by di(3,5,5,trimethylhexyl)ammonium sulphate is exceedingly rapid and this may be considered to be due to the large surface area and surface concentration of the amine sulphate in the extraction system itself.

It should be pointed out that the interfacial mechanism for the extraction, described above, is based on a static interfacial boundary, however, there is no reason why the same mechanism cannot be applied to the actual extraction experiments in which the two phases are agitated, and in which each droplet of the organic phase can be considered to have its own individual interfacial boundary identical to that proposed for the static system.

IV CONCLUSIONS

The results presented in this chapter demonstrate that there are many factors to be considered in assessing the part played by the solvent for the di(3,5,5,trimethylhexyl)ammonium sulphate in the extraction of Fe(III) from aqueous sulphate solutions. The properties of the organic phase for "good" and "bad" extraction are listed below, but it should be remembered that some of these, even though they are criteria for "good" or "bad" extractions, in themselves have an opposite effect on the extraction. For example one criterion for a "good" solvent is that micelle formation occurs in the solvent, however, the micelle formation itself strongly inhibits the extraction of iron (III).

<u>"Good" Extraction</u>	<u>"Bad" Extraction</u>
(a) Micelle formation of amine sulphate	(a) No micelle formation of amine sulphate
(b) Low solubility of water in	(b) High solubility of water in
(c) High surface-activity of amine sulphate	(c) Low surface-activity of amine sulphate
(d) Low surface-activity of solvent	(d) High surface-activity of solvent
(e) High critical micelle concentration of amine sulphate	(e) High hydrogen bond potential of solvent
(f) Strong intramolecular hydrogen bonding of the amine sulphate	(f) High dielectric constant of solvent.

"Good" Extraction contd.	"Bad" Extraction contd.
(g) Low hydrogen bond potential of solvent.	
(h) Low dielectric constant of solvent.	

The knowledge of only one or two of the above properties for a particular solvent system is insufficient to label it "good" or "bad" for extraction, for example as we have seen before iso-amyl acetate has a dielectric constant of about the same value as chloroform yet the extraction efficiency in the former solvent is much lower than in the latter. However, the surface-activities of the amine sulphate in each solvent are entirely different and in iso-amyl acetate there appears to be negligible surface-activity. Also the solubility of water in iso-amyl acetate is much greater than in chloroform leading to a much greater instability of the iron(III)sulphate-amine sulphate complex in the former solvent.

It is therefore necessary to have a complete knowledge of the properties of a particular solvent and of the behaviour of the amine sulphate in that solvent before any prediction can be made as to the iron(III)extraction efficiency.

The interfacial properties, described in this chapter, of the amine sulphate in the solvents in which the most efficient extractions of iron(III) are obtained give considerable support to the postulation of an interfacial mechanism for the extraction, and to the formation of an adduct as opposed to the usual ion-exchange reaction.

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Appendix I

The Equilibria involved in the Extraction of Sulphuric acid by di- and tri(3,5,5,trimethylhexyl)amines

The overall equilibrium constants K_1 and K_2 for the formation of amine bisulphate and amine sulphate as described in Chapter 2 of this thesis, are composed of the individual equilibria described in this appendix.

It should be pointed out that in solvent extraction studies involving the reaction of one species with another, it is generally assumed that this reaction occurs within one or other of the two phases. In the case of the neutralization of long chain alkylamines dissolved in organic solvents, it is assumed that this reaction occurs within the aqueous phase[1]. However, there is considerable evidence to suggest that the reaction occurs at the aqueous-organic interface[2]. The assumption that the reaction occurs within the aqueous phase is permissible, even though the long chain alkylamines are practically insoluble in water, since it is reasonable to assume that a trace of the amine would dissolve in water. The amine salts tend to be more soluble in water than the amine itself. The interface mechanism would also seem to be a reasonable one since it has been shown that the long chain alkylamines and their salts are generally surface-active,(see Chapter 5) and would yield an aqueous-organic interface with the nitrogen atoms orientated in a manner which would facilitate combination with a proton from the aqueous phase.

The consideration of either mechanism would give finally the overall equilibrium constants K_1 and K_2 as described by equations (2.7) and (2.11) in Chapter 2.

1. The Extraction Mechanism on the Basis of the Neutralization Occurring Within the Aqueous Phase

1.1 The formation of amine sulphate

The equilibria involved in this process are

(a) Distribution of the amine between organic and aqueous phases.

$$R_A \overset{k_1}{\rightleftharpoons} R_o \qquad (6.1)$$

$$\text{where} \quad k_1 = \frac{a_{R_A}}{a_{R_o}} \qquad (6.2)$$

where R refers to the amine, and subscripts "A" and "o" refer to the aqueous and organic phases respectively. a_{R_A} and a_{R_o} are the activities of the amine in the aqueous and organic phases.

(b) Neutralization of the amine in the aqueous phase.

$$2R_A + 2H^+_A + SO^=_{4_A} \overset{k_2}{\rightleftharpoons} 2RH^+_A + SO^=_{4_A} \qquad (6.3)$$

$$k_2 = \frac{a^2_{RH^+_A}}{a^2_{R_A} \cdot a^2_{H^+_A}} \tag{6.4}$$

(c) Association to form the amine sulphate

$$2RH^+_A + SO^=_{4_A} \overset{k_3}{\rightleftharpoons} R_2H_2SO_{4_A}{}^* \tag{6.5}$$

$$k_3 = \frac{a_{R_2H_2SO_{4_A}}}{a^2_{RH^+_A} \cdot a_{SO^=_{4_A}}} \tag{6.6}$$

(d) Distribution of the amine sulphate between the aqueous and organic phases.

$$R_2H_2SO_{4_A} \overset{k_4}{\rightleftharpoons} R_2H_2SO_{4_o} \tag{6.7}$$

$$k_4 = \frac{a_{R_2H_2SO_{4_o}}}{a_{R_2H_2SO_{4_A}}} \tag{6.8}$$

(e) Dissociation of the amine sulphate in the organic phase.

$$R_2H_2SO_{4_o} \overset{k_5}{\rightleftharpoons} 2RH^+_o + SO^=_{4_o} \tag{6.9}$$

$$k_5 = \frac{a^2_{RH^+_o} \cdot a_{SO^=_{4_o}}}{a_{R_2H_2SO_{4_o}}} \tag{6.10}$$

---

* Amine sulphate $(RH^{+1})_2SO_4^{-2}$

Equilibrium (e) can be neglected if it is assumed that the dissociation of the amine sulphate in the organic phase is negligible. A further equilibrium or equilibria must be added if the amine sulphate polymerises in the organic phase. However, in iso-amyl alcohol it has been found that no such polymerisation takes place.

By a combination of the expressions for the first four equilibrium constants the equation for the overall equilibrium constant can be obtained.

Rearranging the equation for k_3 we get

$$a^2_{RH^+_A} = \frac{a_{R_2H_2SO_{4_A}}}{a_{SO^=_{4_A}} \cdot k_3} \qquad (6.11)$$

which by substitution in the equation for k_2 gives

$$k_2 = \frac{a_{R_2H_2SO_{4_A}}}{a^2_{R_A} \cdot a^2_{H^+_A} \cdot a_{SO^=_{4_A}} \cdot k_3} \qquad (6.12)$$

but

$$a^2_{R_A} = k^2_1 \cdot a^2_{R_o} \qquad (6.13)$$

and

$$a_{R_2H_2SO_{4_A}} = \frac{a_{R_2H_2SO_{4_o}}}{k_4} \qquad (6.14)$$

which by substitution in equation (6.12) gives

$$k_2.k_3.k_1^2.k_4 = \frac{a_{R_2H_2SO_{4_o}}}{a_{R_o}^2 \cdot a_{H_A^+}^2 \cdot a_{SO_4^=}} \qquad (6.15)$$

but since

$$a_{H_2SO_4} = a_{H_A^+}^2 \cdot a_{SO_{4_A}^=} \qquad (6.16)$$

we get

$$k_2.k_3.k_1^2.k_4 = \frac{a_{R_2H_2SO_{4_o}}}{a_{H_2SO_{4_A}} \cdot a_{R_o}^2} \qquad (6.17)$$

the overall equilibrium constant K_1 given by equation (2.6) in Chapter 2 thus consists of several individual equilibrium constants.

$$K_1 \quad \text{the overall equilibrium constant} = k_2.k_3.k_1^2.k_4$$

1.2 The formation of the amine bisulphate.

In dealing with the individual equilibrium reactions involved in the formation of the amine bisulphate it is necessary to assume initially that in the presence of amine bisulphate in the organic phase the concentration of free amine is negligible. In other words the formation of amine bisulphate does not take place until all the free amine has been converted to the normal amine sulphate.

The following equilibria are involved.

(f) Distribution of the amine sulphate between the organic and aqueous phase.

$$R_2H_2SO_{4_o} \underset{}{\overset{k_6}{\rightleftharpoons}} R_2H_2SO_{4_A} \qquad (6.18)$$

$$k_6 = \frac{a_{R_2H_2SO_{4_A}}}{a_{R_2H_2SO_{4_o}}} \qquad (6.19)$$

(g) Dissociation of the amine sulphate in the aqueous phase.

$$R_2H_2SO_{4_A} \overset{k_7}{\rightleftharpoons} 2RH^+_A + SO^=_{4_A} \qquad (6.20)$$

$$k_7 = \frac{a^2_{RH^+_A} \cdot a_{SO^=_{4_A}}}{a_{R_2H_2SO_{4_A}}} \qquad (6.21)$$

(h) Association to form the amine bisulphate.

$$RH^+_A + HSO^-_{4_A} \overset{k_8}{\rightleftharpoons} RH_2SO_{4_A}{}^* \qquad (6.22)$$

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* Amine bisulphate $(RH)^+HSO_4^-$

$$k_8 = \frac{a_{RH_2SO_{4_A}}}{a_{RH^+_A} \cdot a_{HSO^-_{4_A}}} \qquad (6.23)$$

It should be pointed out that equilibria (g) and (h) when combined represent a simple anion exchange reaction as postulated by Allen[3].

(i) Distribution of the amine bisulphate between the aqueous and the organic phase.

$$RH_2SO_{4_A} \overset{k_9}{\rightleftharpoons} RH_2SO_{4_o} \qquad (6.24)$$

$$k_9 = \frac{a_{RH_2SO_{4_o}}}{a_{RH_2SO_{4_A}}} \qquad (6.25)$$

(j) Dissociation of the amine bisulphate in the organic phase.

$$RH_2SO_{4_o} \overset{k_{10}}{\rightleftharpoons} RH^+_o + HSO^-_{4_o} \qquad (6.26)$$

$$k_{10} = \frac{a_{RH^+_o} \cdot a_{HSO^-_{4_o}}}{a_{RH_2SO_{4_o}}} \qquad (6.27)$$

Again we can assume that the dissociation of the amine bisulphate in the organic phase is negligible, and that there is no polymerization in the organic phase. Rearranging equation (6.23) gives

$$a_{RH^+_A} = \frac{a_{RH_2SO_{4_A}}}{a_{HSO_{4_A}} \cdot k_8} \qquad (6.28)$$

and by substitution of this expression in equation (6.21) gives

$$k_7 = \frac{a^2_{RH_2SO_{4_A}} \cdot a_{SO^=_{4_A}}}{a_{R_2H_2SO_{4_A}} \cdot a^2_{HSO^-_{4_A}} \cdot k_8^2} \qquad (6.29)$$

but $$a^2_{RH_2SO_{4_A}} = \frac{a^2_{RH_2SO_{4_o}}}{k_9^2} \qquad (6.30)$$

and $$a_{R_2H_2SO_{4_A}} = k_6 \cdot a_{R_2H_2SO_{4_o}} \qquad (6.31)$$

thus by substitution of equations (6.30) and (6.31) in equation (6.29) we get

$$k_7 = \frac{a^2_{RH_2SO_{4_o}} \cdot a_{SO^=_{4_A}}}{a_{R_2H_2SO_{4_o}} \cdot a^2_{HSO^-_{4_A}} \cdot k_6 \cdot k_8^2 \cdot k_9^2} \qquad (6.32)$$

Equation (6.32) can be further simplified by introduction of the dissociation constants for sulphuric acid.

$$H_2SO_4 \xrightleftharpoons{k_{11}} H^+ + HSO_4^- \qquad (6.33)$$

$$k_{11} = \frac{a_{H^+} \cdot a_{HSO_4^-}}{a_{H_2SO_4}} \qquad (6.34)$$

and

$$HSO_4^- \xrightleftharpoons{k_{12}} H^+ + SO_4^= \qquad (6.35)$$

$$k_{12} = \frac{a_{H^+} \cdot a_{SO_4^=}}{a_{HSO_4^-}} \qquad (6.36)$$

a combination of equations (6.34) and (6.36) gives

$$k_{11} = \frac{k_{12} \cdot a^2_{HSO_4^-}}{a_{SO_4^=} \cdot a_{H_2SO_4}} \qquad (6.37)$$

and substitution for $\frac{a_{SO_4^=}}{a^2_{HSO_4^-}}$ in equation (6.32) gives

$$k_7 = \frac{a^2_{RH_2SO_{4_e}} \cdot k_{12}}{a_{R_2H_2SO_{4_e}} \cdot a_{H_2SO_{4_A}} \cdot k_6 \cdot k_8^2 \cdot k_9^2 \cdot k_{11}} \qquad (6.38)$$

By comparison of this expression with equation (2.10) in Chapter 2 it can be seen that

K_2 the overall equilibrium constant

$$= \frac{k_6 \cdot k_7 \cdot k_8^2 \cdot k_9^2 \cdot k_{11}}{k_{12}}$$

2. The Extraction Mechanism on the Basis of the Neutralization Occurring at the Aqueous-Organic Interface

For the postulation of the interface mechanism of the extraction it is assumed that neutralization actually occurs on the aqueous side of the interface. It is well known that certain long chain amines are surface-active[4] and tend to concentrate at the aqueous-organic interface with the basic nitrogens orientated towards the aqueous phase. For salts it is assumed that the water soluble parts penetrate into the aqueous layer. In fact for an amine salt a charged layer is obtained at the interface due to the penetration of the neutralizing anion into the aqueous phase and subsequent dissociation.

The equilibrium reactions which may be important in the neutralization of a long chain amine at the interface are shown below.

2.1 The formation of amine sulphate

(a) Distribution of the amine between the interface and the bulk of the organic phase.

(b) Neutralization of the amine at the interface.

(c) Association at the interface to form amine sulphate.

(d) Distribution of the amine sulphate between the interface and the bulk of the organic phase. This equilibrium will be dependent on the solubility of the amine sulphate in the organic phase.

The actual equilibria involved in the above reactions are indistinguishable from those for the alternative mechanism except that the equilibrium constants for (a) and (d) are slightly different to the corresponding constants for the other mechanism. The size of k_1 for the mechanism based on the reaction occurring within the aqueous phase would be very small, as would the k_1 for reaction (a) above, since the solubility of the amine in the aqueous phase would be very small, and the relative concentrations of amine at the interface to that in the bulk of the organic phase would also be very small. Similarly the size of k_4 in the alternate mechanism would be very large, as would the size of the equilibrium constant for reaction (d) above. Presumably, the equilibrium constants for reactions (b) and (c) above would be the same as the corresponding constants for the other mechanism.

The same arguments can be applied to the formation of the amine bisulphate, and the equilibrium reactions involved are as follows.

2.2 The formation of the amine bisulphate

(a) Distribution of the amine sulphate between the interface and the bulk of the organic phase.

(b) Dissociation of the amine sulphate at the interface.

(c) Association to form the amine bisulphate at the interface.

(d) Distribution of the amine bisulphate between the interface and the bulk of the organic phase.

The final expressions for the overall equilibrium constants K_1 and K_2 are identical for both the proposed mechanisms, and so, it is impossible to distinguish between the two processes using the equilibrium studies described in this thesis.

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Appendix II

The Equilibria involved in the extraction of Iron(III) from Aqueous sulphate solutions by di(3,5,5,trimethylhexyl)amine.

Extraction equations to describe the extraction of Fe(III) from aqueous sulphate solutions have been derived by considering the equilibria involved. It has been assumed for this purpose that the partially hydrolysed species $FeOHSO_4$ and $(FeOHSO_4)_2$ are extracted by reaction with the amine sulphate dissolved in the organic phase. It should be noted that the following treatment assumes that the reaction is occurring within the aqueous phase rather than at the aqueous-organic interface, however, as has been pointed out previously, consideration of either mechanism will lead to the same quantitative result.

Although this treatment is based on the reaction of the species $FeOHSO_4$ and $(FeOHSO_4)_2$ with amine sulphate in the aqueous phase, these species may not be involved as such. The reaction can be postulated as occurring between the amine sulphate and the ions $FeOH^{+2}$ and $(FeOH)_2^{+4}$ with subsequent reaction with another sulphate ion or ions in the aqueous phase to form the extracted complex. However, consideration of either reaction will lead to the same result and simply means a change in the order of the equilibria represented below.

The following equilibrium reactions can be written to describe the extraction.

(a) The Hydrolysis of Iron(III) in the Aqueous Phase

$$Fe^{+3}{}_A + H_2O_A \overset{k_1}{\rightleftharpoons} FeOH^{+2}{}_A + H^+{}_A \qquad (7.1)$$

where k_1 the first hydrolysis constant of iron(III) is represented by the equation

$$k_1 = \frac{a_{FeOH^{+2}{}_A} \cdot a_{H^+{}_A}}{a_{Fe^{+3}{}_A} \cdot a_{H_2O_A}} \qquad (7.2)$$

a represents the activities of the species and subscript "A" represents the aqueous phase. The subscript "o" in following expressions represents the organic phase.

By introducing activity coefficients

$$k_1 = \frac{\gamma_{(FeOH)^{+2}{}_A} \cdot \gamma_{H^+{}_A}}{\gamma_{Fe^{+3}{}_A} \cdot \gamma_{H_2O_A}} \cdot \frac{[FeOH^{+2}]_A[H^+]_A}{[Fe^{+3}]_A[H_2O]_A} \qquad (7.3)$$

where γ is the molar activity coefficient and the brackets $[\ \ ]$ refer to molar concentrations.

(b) The Formation of the Species $FeOHSO_4$ in the Aqueous Phase.

$$FeOH^{+2}{}_{A} + SO_4^{-2}{}_{A} \overset{k_2}{\rightleftharpoons} FeOHSO_{4A} \tag{7.4}$$

$$k_2 = \frac{a_{FeOHSO_{4A}}}{a_{FeOH^{+2}{}_{A}} \cdot a_{SO_4^{-2}{}_{A}}} \tag{7.5}$$

$$k_2 = \frac{\gamma_{FeOHSO_{4A}}}{\gamma_{FeOH^{+2}{}_{A}} \cdot \gamma_{SO_4^{-2}{}_{A}}} \cdot \frac{\left[FeOHSO_4\right]_A}{\left[FeOH^{+2}\right]_A \left[SO_4^{-2}\right]_A} \tag{7.6}$$

(c) The Distribution of Amine Sulphate Between the Aqueous and the Organic Phases.

$$R_2H_2SO_{4o} \overset{k_3}{\rightleftharpoons} R_2H_2SO_{4A} \tag{7.7}$$

where R is di(3,5,5,trimethylhexyl)amine.

$$k_3 = \frac{a_{R_2H_2SO_{4A}}}{a_{R_2H_2SO_{4o}}} \tag{7.8}$$

$$k_3 = \frac{\gamma_{R_2H_2SO_{4_A}}}{\gamma_{R_2H_2SO_{4_o}}} \cdot \frac{[R_2H_2SO_4]_A}{[R_2H_2SO_4]_o} \qquad (7.9)$$

(d) The Formation of the Complex in the Aqueous Phase.

$$FeOHSO_{4_A} + R_2H_2SO_{4_A} \xrightleftharpoons{k_4} R_2H_2SO_4.FeOHSO_{4_A} \qquad (7.10)$$

$$k_4 = \frac{a_{R_2H_2SO_4.FeOHSO_{4_A}}}{a_{FeOHSO_{4_A}} \cdot a_{R_2H_2SO_{4_A}}} \qquad (7.11)$$

$$k_4 = \frac{\gamma_{R_2H_2SO_4 \,.\, FeOHSO_{4_A}}}{\gamma_{FeOHSO_{4_A}} \cdot \gamma_{R_2H_2SO_{4_A}}} \cdot \frac{[R_2H_2SO_4.FeOHSO_4]_A}{[FeOHSO_4]_A [R_2H_2SO_4]_A} \qquad (7.12)$$

(e) The Distribution of the Complex between the Aqueous and Organic Phases.

$$R_2H_2SO_4.FeOHSO_{4_A} \xrightleftharpoons{k_5} R_2H_2SO_4.FeOHSO_{4_o} \qquad (7.13)$$

$$k_5 = \frac{a_{R_2H_2SO_4.FeOHSO_{4_o}}}{a_{R_2H_2SO_4.FeOHSO_{4_A}}} \tag{7.14}$$

$$k_5 = \frac{\gamma_{R_2H_2SO_4.FeOHSO_{4_o}}}{\gamma_{R_2H_2SO_4.FeOHSO_{4_A}}} \cdot \frac{\left[R_2H_2SO_4.FeOHSO_4\right]_o}{\left[R_2H_2SO_4.FeOHSO_4\right]_A} \tag{7.15}$$

Rearrangement of equation (7.3) gives

$$\gamma_{FeOH^{+2}_A} \cdot \left[FeOH^{+2}\right]_A = \frac{k_1 \cdot \gamma_{Fe_A^{+3}} \cdot \gamma_{H_2O_A}}{\gamma_{H^+_A}} \cdot \frac{\left[Fe^{+3}\right]_A \left[H_2O\right]_A}{\left[H^+\right]_A} \tag{7.16}$$

and by substituting for $\gamma_{FeOH^{+2}_A} \cdot \left[FeOH^{+2}\right]_A$ in equation (7.6) gives

$$k_2 = \frac{\gamma_{FeOHSO_{4_A}} \cdot \gamma_{H^+_A}}{k_1 \cdot \gamma_{SO^=_{4_A}} \cdot \gamma_{Fe^{+3}_A} \cdot \gamma_{H_2O_A}} \cdot \frac{\left[FeOHSO_4\right]_A \left[H^+\right]_A}{\left[Fe^{+3}\right]_A \left[H_2O\right]_A \left[SO_4^=\right]_A} \tag{7.17}$$

Rearranging equation (7.12) gives,

$$\gamma_{FeOHSO_4} \cdot \left[FeOHSO_4\right]_A = \frac{\gamma_{R_2H_2SO_4 \cdot FeOHSO_{4_A}}}{k_4 \cdot \gamma_{R_2H_2SO_{4_A}}} \cdot \frac{\left[R_2H_2SO_4 \cdot FeOHSO_4\right]_A}{\left[R_2H_2SO_4\right]_A}$$

(7.18)

and substitution in equation (7.17) gives

$$k_2 = \frac{\gamma_{R_2H_2SO_4 \cdot FeOHSO_{4_A}} \cdot \gamma_{H^+_A}}{k_1 \cdot k_4 \cdot \gamma_{SO^=_{4_A}} \cdot \gamma_{Fe^{+3}_A} \cdot \gamma_{H_2O_A} \cdot \gamma_{R_2H_2SO_{4_A}}} \cdot \frac{\left[R_2H_2SO_4 \cdot FeOHSO_4\right]_A \left[H^+\right]_A}{\left[Fe^{+3}\right]_A \left[SO^=_4\right]_A \left[R_2H_2SO_4\right]_A}$$

(7.19)

Introduction of k_3 and k_5 given by equations (7.9) and (7.15) which describe the distribution of the complexing agent and complex between the aqueous and organic phases, into equation (7.19) gives

$${}_2 = \frac{\gamma_{R_2H_2SO_4 \cdot FeOHSO_{4_o}} \cdot \gamma_{H^+_A}}{k_1 \cdot k_4 \cdot k_5 \cdot k_3 \cdot \gamma_{SO^=_{4_A}} \cdot \gamma_{Fe^{+3}_A} \cdot \gamma_{H_2O_A} \cdot \gamma_{R_2H_2SO_{4_o}}} \cdot \frac{\left[R_2H_2SO_4 \cdot FeOHSO_4\right]_o \left[H^+\right]_A}{\left[Fe^{+3}\right]_A \left[SO^=_4\right]_A \left[R_2H_2SO_4\right]_o}$$

(7.20)

The distribution ratio D is defined as

$$D = \frac{\text{The total concentration of iron(III) in the organic phase}}{\text{The total concentration of iron(III) in the aqueous phase}}. \qquad (7.21)$$

The total concentration of iron(III) includes all possible species present in the aqueous phase, but in the derivation of equation (7.20) only the species $FeOHSO_4$ is taken into account since it is this species which is considered to react with the amine sulphate. There are, of course, other iron(III) complex species present in the aqueous phase (neglecting for the moment the polymerized $(FeOH)_2^{4+}$ ion) such as $FeSO_4^{+1}$, $Fe(SO_4)_2^{-1}$, and perhaps higher sulphate complexes, and $Fe(OH)_2^{+1}$.

The distribution ratio, however, can be introduced into equation (7.20) by making the following assumptions:

(1) That the total amount of iron(III) in the organic phase is in the form of the complex $R_2H_2SO_4.FeOHSO_4$, i.e. there is only one Fe(III) complex present in the organic phase.

(2) That at equilibrium the concentration of the species $FeOHSO_4$ in an aqueous solution of constant ionic strength and fixed pH value is

directly proportional to the total concentration of iron(III) present.

Hence D is directly proportional to

$$\frac{\left[R_2H_2SO_4.FeOHSO_4\right]_A}{\left[Fe^{+3}\right]_A}$$

And since in the aqueous phase the activity of water can be considered to be constant, and if we assume that activity coefficients in the organic phase are unity, rearrangement of equation (7.20) and inclusion of D the distribution ratio gives,

$$D = \frac{k_1.\gamma_{SO_4^{=}{}_A}.\gamma_{Fe^{+3}{}_A}}{\gamma_{H^+{}_A}} \cdot \frac{\left[SO_4^{=}\right]_A\left[R_2H_2SO_4\right]_o}{\left[H^+\right]_A} \qquad (7.22)$$

Equation (7.22) describes the extraction derived on the basis of the extraction of the $FeOHSO_4$ species. If we now introduce the equilibrium constant for the formation of the dimeric iron(III) species $(FeOH)_2^{+4}$ we get a second extraction equation. The formation of the dimeric species can be written as

$$2FeOH^{+2}{}_A \xrightleftharpoons{k_6} (FeOH)_2^{+4}{}_A \qquad (7.23)$$

where
$$k_6 = \frac{a_{(FeOH)^{+4}_{2_A}}}{a^2_{FeOH^{+2}_A}} \qquad (7.24)$$

$$k_6 = \frac{\gamma_{(FeOH)^{+4}_{2_A}}}{\gamma^2_{FeOH^{+2}_A}} \cdot \frac{\left[(FeOH)^{+4}_2\right]_A}{\left[FeOH^{2+}\right]^2_A} \qquad (7.25)$$

Equation (7.24) now becomes,

$$(FeOH)^{+4}_2 + 2SO^{=}_{4_A} \overset{k_7}{\rightleftharpoons} (FeOHSO_4)_{2_A} \qquad (7.26)$$

$$k_7 = \frac{a_{(FeOHSO_4)_{2_A}}}{a_{(FeOH)^{+4}_{2_A}} \cdot a^2_{SO^{=}_{4_A}}} \qquad (7.27)$$

$$k_7 = \frac{\gamma_{(FeOHSO_4)_{2_A}}}{\gamma_{(FeOH)^{+4}_{2_A}} \gamma^2_{SO^{=}_{4_A}}} \cdot \frac{\left[(FeOHSO_4)_2\right]_A}{\left[(FeOH)^{+4}_2\right]_A \left[SO^{=}_4\right]^2_A} \qquad (7.28)$$

Equation (7.10) becomes,

$$(FeOHSO_4)_{2_A} + 2R_2H_2SO_{4_A} \overset{k_8}{\rightleftharpoons} (R_2H_2SO_4.FeOHSO_4)_{2_A} \qquad (7.29)$$

$$k_8 = \frac{a_{(R_2H_2SO_4\ .\ FeOHSO_4)_{2_A}}}{a_{(FeOHSO_4)_{2_A}} \cdot a^2_{R_2H_2SO_{4_A}}} \qquad (7.30)$$

$$k_8 = \frac{\gamma_{(R_2H_2SO_4.FeOHSO_4)_{2_A}}}{\gamma_{(FeOHSO_4)_{2_A}}\,\gamma^2_{R_2H_2SO_{4_A}}} \cdot \frac{\left[(R_2H_2SO_4.FeOHSO_4)_2\right]_A}{\left[(FeOHSO_4)_2\right]_A \left[R_2H_2SO_4\right]^2_A} \qquad (7.31)$$

And equation (7.13) becomes

$$(R_2H_2SO_4.FeOHSO_4)_{2_A} \overset{k_9}{\rightleftharpoons} (R_2H_2SO_4.FeOHSO_4)_{2_o} \qquad (7.32)$$

$$k_9 = \frac{a_{(R_2H_2SO_4.FeOHSO_4)_{2_o}}}{a_{(R_2H_2SO_4.FeOHSO_4)_{2_A}}} \qquad (7.33)$$

$$k_9 = \frac{\gamma_{(R_2H_2SO_4.FeOHSO_4)_{2_o}}}{\gamma_{(R_2H_2SO_4.FeOHSO_4)_{2_A}}} \cdot \frac{\left[(R_2H_2SO_4.FeOHSO_4)_2\right]_o}{\left[(R_2H_2SO_4.FeOHSO_4)_2\right]_A} \qquad (7.34)$$

Equation (7.16) can be written as

$$\gamma^2_{FeOH^{+2}_A} . \left[FeOH^{+2}\right]^2_A = \frac{k_1{}^2 . \gamma^2_{Fe^{+3}_A} . \gamma^2_{H_2O_A}}{\gamma^2_{H^+_A}} \cdot \frac{\left[Fe^{+3}\right]^2_A \left[H_2O\right]^2_A}{\left[H^+\right]^2_A} \qquad (7.35)$$

Substitution in equation (7.25) and rearrangement gives

$$\gamma_{(FeOH)^{+4}_{2_A}} . \left[(FeOH)^{+4}_2\right]_A = \frac{k_6 . k_1{}^2 . \gamma^2_{Fe^{+3}_A} . \gamma^2_{H_2O_A}}{\gamma^2_{H^+_A}} \cdot \frac{\left[Fe^{+3}\right]^2_A \left[H_2O\right]^2_A}{\left[H^+\right]^2_A} \qquad (7.36)$$

Substitution for $\gamma_{(FeOH)^{+4}_{2_A}} . \left[(FeOH)^{+4}_2\right]_A$ in equation (7.28) gives

$$k_7 = \frac{\gamma_{(FeOHSO_4)_A} . \gamma^2_{H^+_A}}{k_6 . k_1{}^2 . \gamma^2_{Fe^{+3}_A} . \gamma^2_{H_2O_A} . \gamma^2_{SO^=_{4_A}}} \cdot \frac{\left[(FeOHSO_4)_2\right]_A \left[H^+\right]^2_A}{\left[Fe^{+3}\right]^2_A \left[H_2O\right]^2_A \left[SO_4^=\right]^2_A} \qquad (7.37)$$

Rearrangement of equation (7.31) gives

$$(\mathrm{FeOHSO_4})_{2_A} \cdot \left[(\mathrm{FeOHSO_4})_2\right]_A = \frac{\gamma_{(\mathrm{R_2H_2SO_4 . FeOHSO_4})_{2_A}}}{k_8 . \gamma^2_{\mathrm{R_2H_2SO_4}_A}} . \frac{\left[(\mathrm{R_2H_2SO_4 . FeOHSO_4})_2\right]_A}{\left[\mathrm{R_2H_2SO_4}\right]^2_A}$$

(7.38)

Substitution of this expression in equation (7.37) and introduction of k_3 and k_9 as given by equations (7.9) and (7.34) to obtain the amine sulphate and the complex in the organic phase, gives equation (7.39)

$$k_7 = \frac{\gamma_{(\mathrm{R_2H_2SO_4 . FeOHSO_4})_{2_o}} . \gamma^2_{\mathrm{H^+}_A}}{k_1^2 . k_3^2 . k_6 . k_8 . k_9 . \gamma^2_{\mathrm{Fe^{+3}}_A} . \gamma^2_{\mathrm{H_2O}_A} . \gamma^2_{\mathrm{SO_4^=}_A}} . \frac{\left[(\mathrm{R_2H_2SO_4 . FeOHSO_4})_2\right]_o \left[\mathrm{H^+}\right]^2_A}{\left[\mathrm{Fe^{+3}}\right]^2_A \left[\mathrm{H_2O}\right]^2_A \left[\mathrm{SO_4^=}\right]^2_A \left[\mathrm{R_2H_2SO_4}\right]^2_o}$$

(7.39)

The definition for D, however, remains the same and can be introduced into equation (7.39) by making the following assumptions:

(1) That the total amount of iron(III) in the organic phase is in the form of the complex $(\mathrm{R_2H_2SO_4 . FeOHSO_4})_2$.

(2) That at equilibrium the concentration of the species $(FeOHSO_4)_2$ in an aqueous solution of constant ionic strength and fixed pH value is directly proportional to the total concentration of iron(III) present.

If we make the further assumption, as before, that activity coefficients of species in the organic phase are unity, equation (7.39) can be rearranged to give equation (7.40).

$$D = \frac{K_2 . \gamma^2_{Fe^{+3}_A} . \gamma^2_{SO_4^{=}{}_A}}{\gamma^2_{H^+_A}} \cdot \frac{[SO_4^{=}]^2_A [R_2H_2SO_4]^2_o}{[H^+]^2_A} \qquad (7.40)$$

Equation (7.40) describes the extraction derived on the basis of the $(FeOHSO_4)_2$ species in the aqueous phase reacting with amine sulphate.