A study of the mechanism of the solvent extraction of metal ions by carboxylic acids

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A STUDY OF THE MECHANISM OF THE SOLVENT EXTRACTION
OF METAL IONS BY CARBOXYLIC ACIDS

BY

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Supervisor: Dr. M.J. Jaycock

A Thesis Submitted in Partial Fulfilment of the
Regulations for the Degree of Doctor of Philosophy
of Loughborough University of Technology.

September 1967
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The author would like to express his sincere thanks to Dr. M.J. Jaycock for his enthusiasm and encouragement during the supervision of the work, even through a period of personal bereavement.

The Ministry of Technology, Warren Spring Laboratory, are gratefully acknowledged for their financial support of the project, and Messrs. A. Fletcher and A. North, and Dr. D. Flett from the Laboratory are thanked for useful discussions regarding the work.

Professor R.F. Phillips is acknowledged for providing research facilities at the University, and Mr. T. Young (Glass-blower) is thanked for his assistance.

In addition, Miss Helen McLure is sincerely thanked for all her help in the preparation of this manuscript.
A study of the species involved in the extraction of metal ions from aqueous solutions into organic solvents with long-chain carboxylic acids has been made.

The theoretical analysis of the extraction data in terms of a single equilibrium approach and a multiple equilibria method has been made. The two approaches have been shown to be equivalent in the case of one extracted complex, and an extraction expression has been proposed to describe the extractions. The analysis of the data has been considered in terms of this expression by graphical and regression procedures.

Under the equilibrium extraction conditions studied, the extracted species in the case of copper (II), cobalt (II) and nickel (II) systems appear to be predominantly dimeric in nature and are usually solvated with carboxylic acid molecules in the organic phase.

Results obtained from the extraction of copper from an aqueous solution into free-falling drops of n-octoic acid dissolved in carbon tetrachloride indicate that the rate of extraction does not vary appreciably over the pH range studied. The measurement of the interfacial tensions in the same system suggests that no abrupt change in the nature of the interfacial region occurs as the pH of extraction increases.
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CHAPTER 1

Introduction
Solvent extraction, or liquid-liquid extraction as it is also known, involves the transfer of species from one of two essentially immiscible liquids into the other. In the present study, the solvent extraction of metal ions from aqueous phases into organic phases with carboxylic acids as extractants is considered.

The general method of solvent extraction has been used for the separation and purification of metals in analytical chemistry for a considerable time. The first references to the uses of the method were given in the nineteenth century. Thus, Péligot described the extraction of uranyl nitrate by ether in 1842 [1]; Vogel reported the extraction of cobalt thiocyanate into a mixture of amyl acetate and diethyl ether at about the same time [2]; and in 1892, Rothe described the extraction of ferric iron from chloride solution into diethyl ether [3]. These early experiments have been followed by the development of a variety of reagents for the extraction of a large number of metals in analytical chemistry. In turn, this has led to the application of solvent extraction techniques to the recovery and purification of metals on an industrial scale.

The present interest in the commercial application of solvent extraction to the recovery of metals results from the development of atomic energy programmes in many countries from about 1945 onwards. The demand for uranium in the nuclear energy fields led to a consideration of solvent extraction techniques for the recovery of the metal from its ores. It was found that solvent extraction could be used to recover the uranium more economically and efficiently than with the ion exchange methods which were used previously. Later, the method was developed for the purification of uranium for use in nuclear reactors, and also for the processing of irradiated nuclear fuels.

An important development from the work on the extraction of uranium has been the study made of the recovery of non-nuclear metals.
As a result of the research there are many plants in operation at the present time using solvent extraction techniques to separate and recover metals such as hafnium and zirconium, tantalum and niobium, and thorium and the rare earths. However, these techniques have been limited to the recovery of high-value metals in most cases. The application of solvent extraction methods to the recovery of the more common metals has been limited for a number of reasons, including the high cost of some extractants. However, expensive extractants can be used if the solution containing the metal to be extracted is available in a form which requires no other expensive chemical processing. Thus in the future there are three main areas of metal recovery where solvent extraction methods are likely to find increasing application [4]: (a) in the recovery of metals from waste solutions e.g. from waste-dump leachings; (b) in the production of ultra-pure metals by separating them from impurities; (c) in the treatment of complex ores containing a mixture of metals, some of which are lost or only partly recovered in conventional pyrometallurgy or chemical extraction e.g. Cu/Zn.

A wide variety of reagents have been developed for use as extractants. These reagents can be grouped into a number of categories: (a) amines and other nitrogen-containing compounds; (b) organophosphorus compounds; (c) alcohols; (d) ketones; (e) carboxylic acids; (f) miscellaneous reagents. The structures and typical uses of some examples of the commercially available extractants which fall into these classes are given in the Table 1.

The search for new extractants which could be used for the recovery of common metals led to a consideration of carboxylic acid systems. A number of carboxylic acids are commercially available as by-products from the petroleum industry. These include the versatic and naphthenic acids, and typical structures of these acids are given
in Table 1. The work described in this thesis was undertaken to provide more information about the mechanism of the extraction of metal ions with carboxylic acids. In comparison to the large number of qualitative studies which have been made on the system, there is very little information available on the mechanism of the extraction.

Table 1: The structures and uses of some commercially available Solvent extraction reagents.

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<th>Reagent and commercial Source</th>
<th>Structure</th>
<th>Typical uses</th>
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<td>(a) Amines and other nitrogen-containing reagents</td>
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<td>Primene J.M.T., (Rohm and Haas Co.)</td>
<td>Primary amine;</td>
<td>Extraction of ferric iron</td>
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<tr>
<td></td>
<td>(CH₃)₃CH - (CH₂ - CH₄)₄NH₂</td>
<td></td>
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<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>LA - 2, (Rohm and Haas Co.)</td>
<td>Secondary amine, R₂NH;</td>
<td>Uranium extraction from leach liquors.</td>
</tr>
<tr>
<td></td>
<td>N-lauryl trialkyl methylamine</td>
<td></td>
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<td>Alamine 336, (General Mills, Inc.)</td>
<td>Tertiary amine, R₃N;</td>
<td>Uranium extraction from leach liquors.</td>
</tr>
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<td></td>
<td>R = C₈ - C₁₀, with C₈ predominating</td>
<td>Co/Ni separation in chloride liquors</td>
</tr>
<tr>
<td>TIOA, tri-iso-octylamine, (Union Carbide Chem. Co.)</td>
<td>N - [-CH₂CH₂CH CH₂CH₃]₃CH₃</td>
<td>Extraction of metal chloride solutions.</td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>Aliquat 336, (General Mills, Inc.)</td>
<td>Trialkyl methyl ammonium salt; [CH₃ - N (R)₃]⁺Cl⁻</td>
<td>Vanadate and Chromate extraction.</td>
</tr>
<tr>
<td></td>
<td>R = C₈ - C₁₀, with C₈ predominating.</td>
<td></td>
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<td>LIX - 63, (General Mills, Inc.)</td>
<td>α - hydroxyoxime;</td>
<td>Cu extraction from ammoniacal solution</td>
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<td></td>
<td>RR⁺ C(OH) - C = NOH</td>
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</table>
Reagent and commercial source | Structure | Typical uses
---|---|---
LIX - 64, (General Mills, Inc.) | Mixture of 2-hydroxybenzophenoximes | Extraction of Cu, and its separation from ferric iron in acidic solutions from natural ore leachings.

(b) Organophosphorus compounds.
TBP, tri-n-butyl phosphate, (Albright and Wilson).

D2EHPA, di-(2-ethylhexyl) - phosphoric acid, (Union Carbide Chem. Co.)

TOPO, Tri-n-octylphosphine oxide, (Eastman Organic Co.)

(c) Alcohols
Capryl alcohol, 1-octanol

(d) Ketones
MIBK, methyl isobutyl ketone
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<td>Versatic acids, (Shell Chem. Co.)</td>
<td>Tertiary carboxylic acids;</td>
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<tr>
<td>α-bromo lauric acid, (Israel Mining Ind.)</td>
<td>CH₃(CH₂)₉CHBr COOH</td>
<td>Synergistic action with TBP or amines, especially in the extraction of the actinides.</td>
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<tr>
<td>(f) Miscellaneous reagents.</td>
<td>CH - CH</td>
<td></td>
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<tr>
<td>TTA, 2-thienyl trifluoroacetone.</td>
<td>(\text{O} \quad \text{O})</td>
<td></td>
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<tr>
<td></td>
<td>(\text{CH} \quad \text{C} \quad \text{CH}_2 \quad \text{C} \quad \text{CF}_3)</td>
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<td>(keto form)</td>
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The use of carboxylic acids for the solvent extraction of metal ions in analytical chemistry has been widely reported in the literature. One of the first workers to appreciate the potential of the acids as extractants of metals was Biffen, who described the extraction of calcium with stearic acid dissolved in trichlorobenzene [5]. He also suggested an extension of the method to more soluble metal stearates, such as aluminium and magnesium.

Later, a number of workers described the use of aromatic carboxylic acids as extractants. Thus, Johnson showed that the benzoates of Fe(III), Al, Be, Ga, In and Sc are extracted from aqueous solutions at a pH of 7 by ethyl acetate and butyl, or amyl, alcohol [6]. The extraction of
plutonium with anthranilic, salicylic and cinnamic acids in various organic solvents was studied by Harvey et al [7]. The same acids, together with 3, 5-dinitrobenzoic acid, when dissolved in chloroform or methyl isobutyl ketone were found to extract La, Th(IV) and U(VI) by Hök-Bernström [8]. It was found in this study that Th could easily be separated from La, but in order to separate Th and U(VI) a close control of the extraction conditions was necessary. In particular, methyl isobutyl ketone was found to be a very good solvent for the metal complexes.

It has been suggested that carboxylic acids could be involved in chelate complexes with the metal ions in the organic phase, since both oxygen atoms of the carboxylate groups could occupy positions in the first solvation shell of the metal ions [9]. Metal chelates in general represent a type of coordination compound in which a metal ion combines with a polyfunctional base capable of occupying two or more positions of the coordination sphere of the metal ion to form a cyclic compound. The chelating agents which possess "acidic" groups function as bases by the loss of a proton e.g. the carboxylate group [10].

Salicylic acid H₂A, where A represents the salicylate anion, is a dibasic acid which forms complexes with a number of metal ions. Since the ligand may be A²⁻ as well as HA⁻, it is possible for the acid to form chelate complexes with metal ions, as has been reported in the literature [11, 12]. However, in the case of methoxybenzoic acid HB, where B represents the methoxybenzoate anion, similar chelate compounds cannot be formed since there is no phenolic hydrogen present. Hök-Bernström compared the extraction of U(VI) with salicylic acid and methoxybenzoic acid [13]. The close similarity of the distribution curves for the two systems led her to suggest that the salicylate complexes are built up by HA⁻ ligands. The complexes in the organic phase were of the form UO₂(HA)₂ and UO₂(HA)₂H₂A and these are of a similar
form to those found in a study of the extraction of U(VI) with acetylacetone dissolved in chloroform [9]. In the case of the methoxybenzoate complexes of U(VI), the only complex in the organic phase was found to be UO₂B₂. This is probably because steric hindrance effects by the methoxy groups prevent an extra molecule from being associated with the complex. Further work by Hörk-Bernström on the extraction of Th(IV) with salicylic acid into methyl isobutyl ketone showed that only one complex of the form Th(HA)₄H₂A was present in the organic phase [14]. It was suggested that the distribution coefficient of Th(HA)₄ between the two phases was very low and that it was not detected in the organic phase.

The first reference to systems involving the extraction of metal ions by carboxylic acids which are similar to those used in the present study was made by West and co-workers [15]. They made a qualitative study of the extraction of a series of metal ions by aliphatic carboxylic acids in relation to their interference with the extraction of copper. With n-decapic acid dissolved in ethyl acetate it was found that for complete extraction of an aqueous solution containing copper and hydroxyl ions, it was necessary for the molar concentration of the acid to be at least twice the molar concentration of copper, after excess hydroxyl ions had been neutralised. The optimum extraction of copper was reported to take place over a range of pH from 6.3 to 10.3 of the aqueous solution. As well as copper, the metals Mn, Fe, Ni, Pd, Co and Ru could be extracted by the n-decanoic acid, although the Co and Ni precipitates did not dissolve in the organic phase, but they settled at the interface. By using n-butyric acid dissolved in benzene as the extractant, greater selectivity was obtained, and only Cu, Mn and Fe were extracted.

Sundaram et al extended the study to the extraction of beryllium with n-butyric acid dissolved in chloroform [16]. The maximum
extraction of beryllium occurred from aqueous solutions at a pH of 9.3 to 9.5. Later, the same extractant system was used for the separation of beryllium from ferric iron and aluminium [17]. Normally, aluminium is completely extracted from aqueous solutions above a pH of 3.4, and ferric iron above a pH of 4.20, by n-butyric acid dissolved in chloroform. By adding a complexing agent, such as sodium ethylenediaminetetraacetic acid, to the aqueous solution before extraction it was found that only the beryllium was subsequently extracted into the organic phase by the acid.

In addition to the use of unsubstituted carboxylic acids as extractants, a study has been reported of the extraction of metal ions into ethyl ether with perfluorocarboxylic acids [18]. Trivalent metals, such as Fe(III) Al(III) and Cr(III), and also U(VI) and Be(II), can be separated from monovalent and other divalent metals with perfluorobutyric acid (C\text{\textsubscript{3}}F\text{\textsubscript{7}}COOH). With perfluorooctanoic acid (C\text{\textsubscript{15}}F\text{\textsubscript{7}}COOH), Ca(II), Mg(II), Fe(II), Pb(II) and Zn(II) and other divalent metals can be separated from monovalent metals. The optimum extraction of a metal ion in these systems was found to occur at a pH of the aqueous solution just below that at which the cation of the metal would precipitate as the hydroxide. This is the same condition under which the optimum extraction of metal ions with unsubstituted carboxylic acids, such as naphthenic acids, occurs. The authors of the study on the use of the fluoroacids as extractants suggested that the extracted species were basic salts, except in the case of Ca(II), which appeared to extract as the normal salt. The evidence for the presence of basic salts was based on the analysis of the crystalline products which were obtained on evaporating the ether extracts. The analyses indicated formulae such as:

\[ M(OH)(C\text{\textsubscript{3}}F\text{\textsubscript{7}}COO)_{2}xH\text{\textsubscript{2}}O \] for Fe(III) and Al(III), where \( x = 2 \); and

\[ \text{Be(OH)}(C\text{\textsubscript{3}}F\text{\textsubscript{7}}COO)_{5}5H\text{\textsubscript{2}}O. \] The authors gave no other evidence for structures of these compositions. However, the analysis of a solid product obtained
from a solution does not prove conclusively that a species of the same composition is present in the solution. For instance, ether molecules may have been involved in the species in solution, and these would not have been detected by the analysis of the product from the solution. It would therefore seem desirable that further work should be carried out on this system to identify the species in solution.

The extraction of metal ions with commercially available carboxylic acids has been studied by a group of Russian workers. In a series of papers from 1960 onwards, Gindin and co-workers reported on studies made with a C_7 - C_9 fatty acid fraction as extractant [19, 20, 38]. It was reported that the extraction of a metal ion was largely dependent on the pH of the aqueous solution containing the metal ion. A series was presented showing the order in which metals are preferentially extracted from aqueous solution, viz:

\[
\begin{align*}
\text{Sn(IV)} & > \text{Bi(III)} > \text{Fe(III)} > \text{Sb(III)} > \text{Pb(II)} > \text{Al(III)} \\
\text{Cu(II)} & > \text{Ag(I)} > \text{Cd(II)} > \text{Zn(II)} > \text{Ni(II)} > \text{Co(II)} \\
\text{Mn(II)} & > \text{Ca(II)} > \text{Mg(II)} > \text{Na(I)}
\end{align*}
\]

The metals in this series are in the order of increasing basicity, and hence in the order in which the hydroxides of the metals are precipitated. It was suggested in these studies that the anion of the metal present had no significant effect on the extraction. However, the results obtained for this thesis, and also some published data [21], which will be discussed later, have shown that this is not correct.

Some further work reported by Shikheeva, who used a naphthenic acid to extract some metal ions from sulphate solutions, confirmed the selectivity scale for a mixture of metal ions which was given by Gindin et al [22]. The same acid was used by Efendiev et al to extract some less common and rare earth metals [23]. These workers established
the following selectivity scale for metal ions from their study, viz:

\[
\text{Zr(IV)} > \text{Th(IV)} > \text{In(III)} > \text{Ga(III)} > \text{Al(III)} > \text{U(IV)} > \\
\text{Sc(III)} > \text{Y(III)} > \text{La(III)}
\]

Naphthenic acid dissolved in ether or hexanol has been shown by Bauer and Lindstrom to be an effective extractant for the rare earth metals [24]. Although the separation obtained throughout the rare earth series is only moderate, the separation factors can be greatly increased if competitive complexing agents are added to the aqueous solution. Thus, ethylenediaminetetraacetic acid is suitable for use in the separation of the adjacent rare earths in the yttrium group, while diethylenetriaminepentaacetic acid is useful for separating those in the cerium group.

Fletcher et al in this country made a study of the use of naphthenic and versatic acids as extractants at about the same time as Gindin and co-workers published similar results in Russia [25, 26]. They found that although the naphthenic acids are less specific as extractants than the dialkyl phosphoric acids and long-chain amines, they could be used for the extraction of certain common metal ions from aqueous sulphate solutions [25]. Thus, Cu could be separated from Co, Ni, Fe(II), Mn and possibly Zn, but not from Fe(III). It was shown that the metal can be recovered from the organic phase by stripping the phase with the stoichiometric amount of mineral acid to produce solutions which are suitable for electrowinning of the metal.

Fletcher and Wilson confirmed that the extraction of a metal ion by a carboxylic acid is dependent on the pH value of the aqueous solution, and showed that the maximum extraction occurs just below the pH value for the precipitation of the metal hydroxide [25]. They also suggested that the stabilities of the metal naphthenates follow
the order: Mn < Fe < Co < Ni < Cu > Zn, since the pH values for 50 per cent extraction of the metals (pH_{0.5}) increased in the same order.

It was pointed out by Irving and Williams that the pH_{0.5} values of metal complexes, for a constant excess of reagent, are a measure of their relative stabilities [27]. This is a result of the competition between the metal ions M^{2+} and the hydrogen ions for the anions \( \text{X}^- \) of the reagent. The more stable the complex, the greater is the hydrogen ion concentration at which it will persist in appreciable amounts.

The results of numerous investigations of the first transition series of metals have shown that the so-called "natural order" of the stability of complexes of bivalent transition metals is the same as that given above for the metal naphthenates, regardless of the nature of the donor group [27 - 30]. Only in a very few cases have deviations from this order been observed [31], although sometimes the difference in stability for successive metals is small. There is sufficient experimental evidence on other divalent metals to extend the above series of relative stabilities as follows:

\[
\begin{align*}
\text{Pt} & > \text{Pd} > \text{Hg} > \text{Be} > \text{Cu} > \text{Ni} > \text{Co} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \\
\text{Ca} & > \text{Sr} > \text{Ba}
\end{align*}
\]

Univalent and trivalent metal ions have not been as extensively studied and a reliable order for stability with these ions is not available. The series for divalent metal ions is somewhat different from the one given by Gindin et al for extractions with carboxylic acids, but the effect of the anions present in the system and also hydrolysis effects may account for some of the discrepancies.

A recent extension of the work on extractions with carboxylic acids has been the development in Israel of \( \alpha \)-bromolauric acid \((\text{CH}_3\text{(CH}_2)_9\text{CHBrCOOH})\) as an extractant [32]. This reagent has the advantage that the decreased pK value of the acid in comparison to the
unsubstituted acid allows extraction of metals at lower pH values, and hence this reduces hydroxide formation. However, the acid suffers from the disadvantage that emulsions are often formed in the system, and in order to break these the process has to be operated at higher temperatures.

The separation of a metal ion from a mixture of metal ions in aqueous solution by extraction with a carboxylic acid is dependent largely on the difference in the pH values at which the hydroxides of the metals are precipitated. In the cases when there is a considerable difference in this pH value between the metal to be extracted and the other metals present, then a good separation can be achieved in a few extraction stages. This has been demonstrated with the following separations [25]:

\[
\text{Cu}^{2+}/\text{Ni}^{2+}; \text{Cu}^{2+}/\text{Co}^{2+}; \text{Cu}^{2+}/\text{Zn}^{2+}; \text{Fe}^{2+}/\text{Cu}^{2+}.
\]

However, when there is only a small difference in the pH values of hydroxide precipitation, e.g. with \(\text{Ni}^{2+}/\text{Co}^{2+}\), then separation is not possible in a few stages. In these cases, a separation can be achieved by using the metal carboxylates themselves as extractants to give an exchange reaction of the type:

\[
(\text{HCOO})_{\text{W}} + (\text{MR})_{\text{O}} \rightleftharpoons (\text{HCOO})_{\text{O}} + (\text{MR})_{\text{W}}
\]

The extraction takes place by the displacement of a metal ion in the aqueous solution with a metal present in the organic phase as the carboxylate. Gindin et al drew up a series of metals in the order of their decreasing ability to pass into the organic phase during the exchange reaction [35-37, 19, 20]:

\[
\text{Sn(IV), Bi(III), Fe(III), Pb(II), Al(III), Cu(II), Cd(II), Zn(II), Ni(II), Co(II), Mn(II), Mg(II), Na(I)}
\]
Any metal, present in the aqueous phase as a cation, will displace all those metals to the right of it in the above series from the corresponding metal carboxylate, dissolved in the organic phase. The metals in the series are in the order of increasing basicity and hence this is the same order as noted earlier for the extraction of metal ions from aqueous solution with carboxylic acids.

The work of Gindin et al on the exchange reaction of a cobalt soap (CoR₂₆) with aqueous solutions of various metal ions showed that for Sn(IV), Fe(III), Pb(II), Al(III) and Cu(II), the exchange proceeds almost to completion (i.e. > 99%) [36]. The reaction between the cobalt soap and aqueous nickel ion solutions gave a small value for the separation coefficient (\( \beta_{\text{Ni/Co}} = 1.8 - 1.9 \)) which remained essentially constant even under widely different operating conditions. The separation coefficient \( \beta_{A/B} \) is defined as \( D_A / D_B \), where \( D_A \) and \( D_B \) represent the distribution ratios of the two metals A and B. To separate pairs of metals which are similar in physical properties and which have small separation coefficients, such as Ni/Co, the exchange extraction process can be carried out in a countercurrent extraction column, which provides a large number of extraction stages [39].

The separation and recovery of metals from ores by extraction with carboxylic acids has been demonstrated on a pilot-plant scale in this country, and on an industrial scale in Russia. Thus a process for the treatment of a mixed copper-nickel sulphide concentrate, based on the use of a naphthenic acid to separate copper and nickel from the solution obtained by roasting and leaching the ore, has been operated on a pilot-plant scale [40]. The major disadvantages of the process proved to be the costs involved in the removal of iron from the system and in the alkali requirement of pH control. The iron has to be removed from the solution by precipitation before carrying out the solvent extraction steps, since naphthenic acid is not a suitable extractant for ferric
iron owing to the low solubility of the ferric naphthenate complex [26]. High-purity cobalt has been prepared on an industrial scale from cobalt contaminated with nickel, copper and iron by using the exchange extraction process [41]. A similar process has been operated by the Russian Severonickel Combine in order to purify nickel electrolyte [4, 42].

The range of metal ions which have been extracted with various carboxylic acids by a number of workers is indicated in the periodic table given in Fig. 1.1. The numbers which occur with the metals in the periodic table indicate that the extraction of these metals with carboxylic acids has been studied, and they refer to literature references. It is evident from Fig. 1.1 that a large group of divalent metals are extracted by carboxylic acids, together with certain trivalent and monovalent metals. The alkali metal ions form carboxylates quite readily, but these have a high aqueous solubility and tend to form emulsions in the aqueous phase [43].

The mechanisms of solvent extraction reactions in general have not been studied as intensively as qualitative aspects of the extractions. In order to consider the overall mechanism of an extraction it is necessary to take account of the processes taking place in the two phases and across the interface between the two phases. Thus the reactions in the aqueous phase, the diffusion of species to the interface, the transfer of species across the interface, the diffusion of species away from the interface, and possibly further reactions in the organic phase, must all be considered. If a reaction takes place during the passage of a species across the interface region there will be a resistance to the transfer of the species, unless the reaction is a very simple one. If the resistance is large, then this step may become the rate-determining step of the extraction. In a commercial process, the resistance may be a significant factor in the economics
Fig. 1.1 The extraction of metal ions with carboxylic acids. The source references are indicated in the square brackets.
of the process, and therefore information about the nature of the resistance would be desirable.

In the case of the carboxylic acids as extractants, the processes which take place in the interfacial region between the two phases should be important. The long-chain acids which are used as extractants are surface active since they are composed of a hydrophilic group, the carboxyl group, and a hydrophobic group, the alkyl chain. The interfacial region should therefore be saturated with carboxylic acid molecules arranged with the hydrophilic carboxyl groups extending into the aqueous phase and the hydrophobic alkyl chains in the organic phase. The extraction of a metal ion from an aqueous solution, through the interfacial region, and into the organic phase should lead to changes in the nature of the interfacial region. It should be possible to study these changes by measuring the interfacial tensions of the systems, and also by studying the mass transfer of the metal ions to and from drops containing the carboxylic acid.

The attempts that have been made to derive a general equation to describe the extraction of metal ions by carboxylic acids are based on two apparently different models. In one model, the extraction is considered to proceed by a cation exchange process, and a single equilibrium is postulated between the metal ions and hydrogen ions in the aqueous phase, and the metal complex and carboxylic acid in the organic phase [44,45]. In the second approach, the numerous equilibria which exist in both the organic and aqueous phases are considered. The series of equilibrium equations which can be formulated by assuming that only the undissociated acid and the undissociated, unsolvated, metal complex cross the interface, are then solved [46]. The extraction equations that are obtained from the two models have been compared, and used to analyse the experimental extraction data [47].
CHAPTER 2

Theory of the Distribution of Metal Ions between Aqueous Solutions and Organic Phases Containing Carboxylic Acids

"A solute will distribute itself between two essentially immiscible solvents in such a way that the ratio of the concentrations of the solute in the two phases after equilibration has been achieved at a particular temperature is a constant, provided the solute has the same molecular weight in each phase".

2.1 The Theoretical Consideration of Extraction with Carboxylic Acids by a Single Equilibrium Approach.

It has been pointed out by a number of workers that the solvent extraction of metal ions often proceeds in a manner formally analogous to the ion-exchange reaction of metal ions with resins [10, 44, 48]. Thus the extraction of a metal ion ($M^{2+}$) from an aqueous solution by a carboxylic acid (RH) dissolved in an organic phase may be considered to proceed in a manner similar to a cation exchange reaction. This exchange reaction may be represented in the simplest terms by a general equation of the form:

$$
(M^{2+})_w + z(RH)_O \rightleftharpoons (M_R)_z + z(H^+)_w,
$$

(2.1)

where the subscripts w and O refer to the aqueous phase and the organic phase respectively. This equilibrium assumes that only one metal complex of the form ($M_R$) and the carboxylic acid (RH) are present in the organic phase, and only ($M^{2+}$) and ($H^+$) are present in the aqueous phase.

The simple exchange reaction as indicated in equation (2.1) does not adequately describe the extraction that is obtained in practice because a number of other factors affect the equilibrium. The effects on the equilibrium of interactions in the organic phase and the nature of the metal ion in the aqueous phase need to be considered [43].

2.1.1. The association of carboxylic acids dissolved in organic solvents.

A number of workers have shown that carboxylic acids tend to associate in essentially non-polar organic solvents to give mainly dimers [49]. The extraction equation can be modified to take account of the dimerisation of the carboxylic acid in the organic phase as follows:
where \((\text{RH})_2\)_0 represents the dimeric acid in the organic phase.

2.1.2. **The Solvation of the extracted species in the organic phase.**

The solvation of metal complexes in organic phases has been reported in many cases. For instance, Baes reported that the dimeric alkyl phosphoric acids extract metal ions M^{z+} to give complexes of the type \(\text{MR}_z\text{H}\) (or \(\text{MR}_z\text{zRH}\)) at low loadings of the organic extractant [50]. Kimura studied the extraction of copper and cobalt from aqueous chloride solutions by di-(2-ethylhexyl) - phosphoric acid dissolved in toluene, and showed that the extracted complexes were di-solvated and monomeric [51]. In addition, alkali metal carboxylates and heavy metal carboxylates are not very soluble in organic solvents alone, but they are appreciably soluble when the solvents contain excess carboxylic acid [52, 53]. This suggests that solvation of the metal complexes with the carboxylic acid occurs in the organic phase.

If the metal complex, solvated with the carboxylic acid, in the organic phase is represented by \(((\text{MR}_z\text{RH})_x)_0\), then the extraction equilibrium becomes:

\[
(M^{z+})_w + (z + x)/2 ((\text{RH})_2)_0 \rightleftharpoons (\text{MR}_z\text{RH})_x)_0 + z (H^+)_w \quad (2.3)
\]

2.1.3. **The polymerisation of the extracted species in the organic phase.**

Baes et al found evidence for the polymerisation of metal complexes at high loadings of the organic phase during studies made on the extraction of uranium and ferric iron with dialkyl phosphoric acids [54, 55]. In the case of extraction with carboxylic acids, if \(x\) represents the number of molecules of carboxylic acid that are bound to the \(j\)'th polymer of the extracted species, then an extraction equation taking into account the possibility of polymerisation of the extracted species can be written, viz:

\[
(M^{z+})_w + (z + x)/2 ((\text{RH})_2)_0 \rightleftharpoons (\text{MR}_z)(\text{RH})_x)_0 + z (H^+)_w \quad (2.2)
\]
The thermodynamic equilibrium constant for the extraction, $K_T$, can be obtained by applying the Law of Mass Action to the equilibrium given in (2.4). Thus:

$$j(N^{z+})_w + (zj + x)/2 \ \left( (RH)_z \right)_0 \rightarrow (MR_z)_j (RH)_x)_0 + zj(H^+)_w \tag{2.4}$$

$$K_T = \left[ (MR_z)_j (RH)_x \right]_0 [H^+]_w^{zj} [N^{z+}]_w^{-j} \left[ (RH)_z \right]_0^{1-6j + x}/2 \tag{2.5}$$

In this expression the square brackets represent thermodynamic activities.

### 2.1.4. The nature of the metal ion in the aqueous phase.

The equilibrium given in equation (2.4) was obtained by assuming that interactions with the metal ion $M^{z+}$ in the aqueous phase, such as hydrolysis or the formation of anionic complexes in the aqueous phase, were negligible. However, if this is not the case there will be competing reactions for the metal ion in the aqueous phase. For instance, Baes reported that in a study of the extraction of metal ions with dialkyl phosphoric acids, the presence of anions and water in the organic phase at high loadings of the organic extractant indicated that competing reactions occurred in the aqueous phase [50].

The complexes formed between the metal ion $M^{z+}$ and the ligand $L$ in the aqueous phase may be considered to result from a stepwise formation process. The concept of the stepwise formation of metal complexes became generally accepted after the work of the Bjerrums [56-58], especially after the study of metal ammine formation in aqueous solutions made by J. Bjerrum [58].

In the general case, the aqueous phase will contain the uncharged species $ML_z$ together with a series of cationic species $ML_z - 1$, $ML_z - 2$, ..., $ML_z$, and also a series of anionic complexes $ML_z + 1$, $ML_z + 2$, ..., $ML_z$. The maximum number of ligands which can coordinate to the metal ion is represented by $Z$. The formation stages of the complexes are more strictly described as stages of substitution in the
solvated ion, but for a formal description the coordination of solvent molecules can be omitted. Rossotti points out that this omission is justified provided that the reactants are in such low concentrations that the amount of water remains essentially constant throughout the series of measurements [59]. If the charges on the species present are omitted for the sake of generality, then a typical series of stepwise equilibria can be postulated, together with the corresponding stability constants:

\[
\begin{align*}
M + L & \rightleftharpoons ML \\
ML + L & \rightleftharpoons ML_2 \\
\ldots & \\
ML_{Z-1} + L & \rightleftharpoons ML_Z
\end{align*}
\]

The \( K \) terms represent the stepwise stability constants. The total concentration of metal \( M \) in the aqueous phase, \( (C_M)_w \), is given by:

\[
(C_M)_w = ([M] + [ML] + [ML_2] + \ldots + [ML_{Z-1}] + [ML_Z])
\]

(2.6)

(2.7)

If the terms \([ML], [ML_2], \ldots, [ML_{Z-1}], [ML_Z]\) are replaced by the appropriate expressions obtained from the set of equations given in (2.6) then:

\[
(C_M)_w = ([M] + K_1[M][L] + K_1K_2[M][L]^2 + \ldots + K_1K_2 \ldots K_Z[M][L]^Z)
\]

(2.8)

Hence, on dividing equation (2.8) by \([M]\):

\[
(C_M)_w [M]^{-1} = (1 + K_1[L] + K_1K_2[L]^2 + \ldots + K_1K_2 \ldots K_Z[L]^Z) = \beta
\]

(2.9)

If \( \beta \) represents the overall stability constant for the reaction:

\[
M + iL \rightleftharpoons ML
\]

(2.10)

and \( K \) represents the stepwise stability constant for the reaction:
\[ ML_{i-1} + L \rightleftharpoons ML_i, \]  

then:

\[ \beta_i = (1 + \sum_{i=1}^{Z} K_i [L]^i) \]

The various species present in the system during the extraction of the metal ions with the carboxylic acid will distribute themselves between the organic and aqueous phases. The distribution of solutes between two phases was originally considered in 1872 by Berthelot and Jungfleisch [60]. Later, Nernst investigated the subject in more detail and stated the partition isotherm [61]. This states that for a solute A partitioning between two phases a and b, the following relationship holds:

\[ (A)_a (A)_b^{-1} = \text{constant} = E_A, \]  

where \( E_A \) is the extraction coefficient and \( (A)_a \) and \( (A)_b \) are the concentrations of the species A in the phases a and b.

However, equation (2.13) only rarely holds over a wide range of concentrations for the systems encountered in inorganic chemistry because the distributing species are often involved in chemical reactions, such as dissociation or association in either phase.

It can be shown by a thermodynamic analysis that the activity of any species in one phase bears a constant ratio to the activity of the same species in a second phase in equilibrium with it [62]. This ratio is called the thermodynamic partition coefficient, and is denoted by the symbol \( p \). Its relationship to the extraction coefficient \( E_A \) is given by:

\[ p_A = [A]_a [A]_b^{-1} = \gamma_a (A)_a \gamma_b^{-1} (A)_b^{-1} = E_A (\gamma_a \gamma_b^{-1}), \]  

where the square brackets represent the activity of the species A and \( \gamma \) its activity coefficient.

The Nernst partition isotherm holds rigorously for a single
species over any concentration range where \((\gamma_a, \gamma_b^{-1}) = 1\), and in practice where the total concentration of solute, \(C_A\), approaches zero and \(\gamma_a\) and \(\gamma_b\) approach unity. Thus Grahame and Seaborg, using radiochemical tracer techniques, found that the extraction coefficient of gallium chloride between ethyl ether and hydrochloric acid (6M) remains essentially constant (±5%) over a concentration range of \(10^{-12}\) to \(2 \times 10^{-3}\) M gallium chloride [63].

In general, at higher concentrations a constancy in the partition coefficient might be anticipated when the ratio of the activity coefficients remains constant. However, it is rather unlikely that this ratio will remain constant over extensive concentration ranges in two solvents so different from one another that they are essentially immiscible [10].

It is found in practice that the chemical interactions between the distributing species and the other components of each phase will significantly affect the concentrations of the species. Since the overall, or stoichiometric, distribution of the component is important when making measurements on the system, it is convenient to define a more practical quantity than the thermodynamic partition coefficient to describe the extraction. Therefore the distribution ratio of a species, \(D\), is defined as the ratio of the total concentrations of the species in the organic and aqueous phase, respectively. Thus for the distribution of a metal ion \(M^{2+}\) between an organic and an aqueous phase:

\[
D = \frac{(C_M)_0}{(C_M)_w} \left(\frac{C_M}{C_M^{-1}}\right)
\]

where \((C_M)_0\) is the total concentration of \(M^{2+}\) in the organic phase and \((C_M)_w\) is the total concentration of \(M^{2+}\) in the aqueous phase.

If it is assumed that only one metal complex of the form \((MR)_x(RH)_y\) is present in the organic phase, then:
On combining equations (2.15) and (2.16) and rearranging the resulting expression:

\[
[(MR)_{\text{j}}(RH)_{\text{x}}]_0 = D(C_M)_w j^{-1} \tag{2.17}
\]

Also, from equation (2.9):

\[
[M]^{-\text{j}} = (C_M)_w^{-\text{j}} \beta^{\text{j}} \tag{2.18}
\]

These expressions for \([(MR)_{\text{j}}(RH)_{\text{x}}]_0 \) and \([M]^{-\text{j}} \) may be substituted for the appropriate terms in equation (2.5) to give:

\[
K_T = D (C_M)_w j^{-1} [H^+]^{z_j}_w \beta^{j} (C_M)_w^{-j} [(RH)_2]_0^{-(z_j + x)/2} \tag{2.19}
\]

If the activity of the dimeric carboxylic acid is taken to be equal to the concentration of the dimer, then \((C_{\text{RH}})_0\), the total concentration of acid in the organic phase, may be related to the dimer concentration by the following approximate equation:

\[
(C_{\text{RH}})_0 = 2[(RH)_{\text{2}}]_0 \tag{2.20}
\]

Hence, on making this substitution into equation (2.19), and since by definition \(\log [H^+]^{z_j}_w = -z_j \text{pH}\), the following relationship is obtained on taking logarithms to the base 10:

\[
\log D = \log K + \log j - j \log \beta + z_j \text{pH} + (j - 1) \log (C_M)_w + (z_j + x)/2 \log (C_{\text{RH}})_0 - (z_j + x)/2 \log 2. \tag{2.21}
\]

The equilibrium constant \(K\) is different from the thermodynamic equilibrium constant \(K_T\) because of the approximations used in evaluating the activity terms.
The single equilibrium method has been applied by a number of workers to describe the extraction of metal ions with carboxylic acids. An equation basically similar to equation (2.21) for the case of \( j = 1 \) was derived by Fletcher and Flett [45], although they adopted a different nomenclature to that used above. Adamski et al also used a similar approach, but they did not consider the possibility of polymerisation of the complex in the organic phase [44].

The previous work on the single equilibrium method has been based on the assumption that only one complex is present in the organic phase in order to simplify the problem. However, in order to derive a general extraction equation, the presence of more than one complex must be considered. Thus from equation (2.21):

\[
D = K_j(C_M^j - 1) (C_RH_0)^{(zj + x)/2} \beta^{-j[H^+]^{-zj}} 2^{-(zj + x)/2} \tag{2.22}
\]

In the case when more than one complex is present in the organic phase, all the possible combinations of \( j \) and \( x \) in the extracted species must be considered, i.e:

\[
D = \left( \sum_{j=1}^{m} \sum_{x=1}^{n} K_j(C_M^j - 1) (C_RH_0)^{(zj + x)/2} \beta^{-j[H^+]^{-zj}} 2^{-(zj + x)/2} \right) \tag{2.23}
\]

Equation (2.23) is a general extraction expression for the case of one or more complexes in the organic phase.

2.2 The Theoretical Consideration of Extraction with Carboxylic Acids by a Multiple Equilibria Approach.

The first quantitative description of the use of complexes for the solvent extraction of metal ions was made by Kolthoff and Sandell in 1941 [64]. They derived a quantitative expression for the extraction of metal ions in the form of dithizonates from aqueous solutions, and used this to describe the extraction of zinc dithizinate...
into chloroform. A more comprehensive treatment of the solvent extraction of metal complexes was given by Irving et al [62, 65, 66], and this has subsequently been developed by Dyrssen [67], Stary [68], Ringbom [69], Morrison and Freiser [10] and other authors.

These theoretical approaches were used mainly to describe the extraction of metal ions by chelate complexes. Carboxylic acids may or may not form chelate complexes with metal ions, as discussed in Chapter 1. However, as Diamond and Tuck point out, the mechanism of extraction with carboxylic acids is closer to that of chelate systems than to that of the large unhydrated salts [9]. If the theory is applied to the carboxylic acid systems, a series of equilibria involving the distribution of both the carboxylic acid and the metal complex between the organic and aqueous phases can be postulated. It is convenient to consider the distribution of the acid between the two phases before considering the equilibria involved in the formation of the metal complex.

2.2.1 The nature of carboxylic acids in organic solvents.

It has been known for a long time that carboxylic acids tend to associate to dimers in non-polar organic solvents. Thus in 1891, Nernst reported on the distribution of acetic and benzoic acids between water and benzene, and he postulated that the acids were monomeric in the aqueous phase and dimeric in the organic phase [61, 70, 71]. Molecular weight studies and distribution measurements later confirmed that carboxylic acids are present mainly as dimers when in solution in non-polar solvents [72-74]. More exact measurements have shown that during the extraction of acetic acid with benzene, the organic phase contains measurable concentrations of monomeric molecules [75, 76]. Pohl et al [77, 78] and Maryott et al [79] determined the monomer-dimer equilibrium constants for dilute solutions of several carboxylic
acids in benzene by measuring the changes in the dielectric constants with concentration. In 1958, Goodman reported the dimerisation constants for a number of carboxylic acids dissolved in n-heptane [49]. The measurements were made by a distribution method, using $^{14}$C-labelled acids.

The existence of dimers in non-polar organic solvents is attributed to the formation of strong hydrogen bonds from the oxygen atoms of the carboxyl groups [80], as shown:

\[
\begin{array}{c}
\text{R} \quad \text{O} \quad \text{H} \quad \cdots \quad \text{O} \\
\text{C} \quad \text{O} \quad \text{H} \quad \cdots \quad \text{O} \\
\text{R}
\end{array}
\]

The broken lines indicate hydrogen bonds. The structural studies of Pauling and Brockway [80], and others [81], showed that the configuration of such dimers involves a symmetrical coplanar structure of the two carboxyl groups, connected by two hydrogen bonds.

In solvents, such as chloroform, which are weak donors for hydrogen bonds, the dimerisation constants for the acids are much smaller than in non-polar solvents [82]. In polar solvents, carboxylic acids exist in the monomeric form because the single molecules are stabilised by hydrogen-bond formation with the solvent. Thus benzoic acid exists in the monomeric form in solution in acetone, ethyl alcohol and phenol [83].

2.2.2 The nature of carboxylic acids in aqueous solutions.

The nature of carboxylic acids and long-chain amphipathic molecules in dilute aqueous solutions has been the subject of much argument. Thus in 1958, it was shown in a series of papers by Mukerjee et al [84-87] that a large number and variety of experimental results on solutions of electrolytes containing amphipathic ions are not
consistent with the view that these electrolytes are unassociated at concentrations below the critical micelle concentration. The anomalous results could be explained qualitatively, and in some cases quantitatively, by assuming a reversible dimerisation of the long-chain ions, accompanied by ion-pairing when the counterions are organic in nature. In contrast, some later work, involving a potentiometric study on dodecyl sulphonates, gave little evidence of dimerisation [88], and also some conductivity data on sodium dodecyl sulphate could be explained satisfactorily by postulating non-associated electrolytes [89]. Overall, however, the later data which has been published on this topic tends to support the association theory.

In 1965, Mukerjee [90] analysed in detail the extensive body of data, which has been published previously by Goodman [49], on the distribution of a series of carboxylic acids between n-heptane and aqueous phosphate buffers. The distribution coefficients of the acids were measured for concentrations as low as $10^{-8} \text{M}$ in water, and over a range of several orders of magnitude of concentration. For the acids from n-octoic to myristic, over about three orders of magnitude in concentration, the data could be explained by a simple theoretical scheme without postulating the association of carboxylic acid anions. As the concentration was increased, the data began to deviate from this scheme at concentrations in the aqueous phase of less than $3 \times 10^{-5} \text{M}$ (for n-decoic acid), $2 \times 10^{-4}$ (for dodecoic acid) and $10^{-5} \text{M}$ (for myristic acid), and at much lower concentrations for the higher acids studied (palmitic, stearic, oleic, and linoleic acids). A qualitative explanation, made by Goodman [49], was that the deviations were due to the association of carboxylic acid anions, since they were all in the direction which led to more acid being present in the aqueous phase than was expected. Mukerjee found that the data could only be interpreted quantitatively by postulating the self-association of two...
acid anions to give a dimer in the aqueous solution [90]. In addition, the formation of trimers, or higher aggregates, was found to be negligible, and reliable values of the dimerisation constants for the postulated equilibrium $2A^- \rightleftharpoons A^-_2$ were derived for the carboxylic acids studied.

The observed increase in the values of the dimerisation constants of the acids with chain length has been considered by a number of workers. Thus Schrier et al [91] suggest that it could be explained in terms of hydrophobic bond formation between the non-polar side chains of the dimerised acids according to the formula:

\[ R \cdot \cdot \cdot \cdot \cdot R \]
\[ \backslash \cdot O-H \cdot \cdot \cdot \cdot O-H \]

The term "hydrophobic bonding", or more correctly "hydrophobic interaction" describes the tendency of non-polar groups to associate in aqueous solution, thereby reducing the extent of contact with neighbouring water molecules [92]. Mukerjee considers that the hydrophobic chains entwine with each other, thus leaving the charged groups apart, and that with the increase in the chain length and flexibility, there is more hydrocarbon-water interface to be lost while the intercoiling of the chains is facilitated [84, 90].

2.2.3 The distribution of a carboxylic acid between an organic and an aqueous phase.

In the following equilibria, which can be postulated as contributing to the distribution of the carboxylic acid (RH) between the two phases, the subscripts O and w refer to the organic and aqueous phase respectively.
For the dissociation of the acid in the aqueous phase:

\[ (\text{RH})_w \leftrightarrow (H^+)_w + (\text{R}^-)_w, \quad K_{\text{RH}} = [H^+]_w [\text{R}^-]_w / [\text{RH}]_w, \]  

(2.24)

where \( K_{\text{RH}} \) is the dissociation constant (or ionisation constant) of the acid.

For the distribution of the undissociated monomer between the two phases:

\[ (\text{RH})_w \leftrightarrow (\text{RH})_0, \quad K_p = [\text{RH}]_0 [\text{RH}]_w^{-1}, \]  

(2.25)

where \( K_p \) is the partition coefficient of the monomeric acid, \( (\text{RH}) \).

For the association of acid anions in the aqueous phase:

\[ 2(\text{R}^-)_w \leftrightarrow (\text{R}_2^-)_w, \quad K_{\text{Dw}} = [\text{R}_2^-]_w [\text{R}^-]_w^{-2}, \]  

(2.26)

where \( K_{\text{Dw}} \) is the dimerisation constant of the acid anions in the aqueous phase.

For the monomer-dimer equilibrium in the organic phase:

\[ 2(\text{RH})_0 \leftrightarrow (\text{RH}_2)_0, \quad K_{\text{Do}} = [(\text{RH})_2]_0 [\text{RH}]_0^{-2}, \]  

(2.27)

where \( K_{\text{Do}} \) is the dimerisation constant of the acid in the organic phase.

In order to simplify the approach at this stage, the activity coefficients are assumed to remain constant throughout the various distributions, and the activity of any species is taken to be equal to the concentration of that species. Then, if \( (C_{\text{RH}})_O \) is the total concentration of acid in the organic phase:

\[ (C_{\text{RH}})_O = [\text{RH}]_0 + 2[(\text{RH})_2]_0 \]  

(2.28)

Also if \( (C_{\text{RH}})_w \) is the total concentration of acid in the aqueous phase:

\[ (C_{\text{RH}})_w = [\text{R}^-]_w + [\text{RH}]_w + 2[\text{R}_2^-]_w \]  

(2.29)
If the respective expressions for \([\text{RH}]_0\) from equation (2.25) and for \([(\text{RH})_2]_0\) from equations (2.27) and (2.25) are substituted into equation (2.28), then:

\[
(C_{\text{RH}})_0 = \left( K_p [\text{RH}]_w + 2(K_p)^2 K_Dc [\text{RH}]_w^2 \right) \tag{2.30}
\]

Also if the respective expressions for \([\text{R}^-]_w\) from equation (2.24) and \([\text{R}_2^-]_w\) from equations (2.26) and (2.24) are substituted into equation (2.29), then:

\[
(C_{\text{RH}})_w = \left( 2K_{Dw} (K_{\text{RH}})^2 [\text{H}^+]^{-2} [\text{RH}]_w^2 + [\text{RH}]_w + K_{\text{RH}} [\text{H}^+]^{-1} [\text{RH}]_w \right) \tag{2.31}
\]

If \(D_{\text{RH}}\), the distribution ratio of the carboxylic acid, is defined as:

\[
D_{\text{RH}} = \frac{\text{Total concentration of acid in organic phase}}{\text{Total concentration of acid in aqueous phase}}
\]

then:

\[
D_{\text{RH}} = \left( \frac{(C_{\text{RH}})_0}{(C_{\text{RH}})_w} \right)^{-1} \tag{2.32}
\]

Hence on substituting for \((C_{\text{RH}})_0\) from equation (2.30) and for \((C_{\text{RH}})_w\) from equation (2.31), into equation (2.32):

\[
D_{\text{RH}} = \left( K_p [\text{RH}]_w + 2(K_p)^2 K_Dc [\text{RH}]_w^2 \right)^{-1} \left( 2K_{Dw} (K_{\text{RH}})^2 [\text{H}^+]^{-2} [\text{RH}]_w^2 + [\text{RH}]_w + K_{\text{RH}} [\text{H}^+]^{-1} [\text{RH}]_w \right)^{-1} \tag{2.33}
\]

Now the total concentration of acid in the system, \((C_{\text{RH}})_T\), is given by:

\[
(C_{\text{RH}})_T = (C_{\text{RH}})_0 + (C_{\text{RH}})_w \tag{2.34}
\]

Thus if the expressions for \((C_{\text{RH}})_0\) from equation (2.30) and for \((C_{\text{RH}})_w\) from equation (2.31) are substituted into equation (2.34), and the resulting expression is rearranged:

\[
(2(K_p)^2 K_Dc + 2K_{Dw} (K_{\text{RH}})^2 [\text{H}^+]^{-2})[\text{RH}]_w^2 + (K_p + 1 + K_{\text{RH}} [\text{H}^+]^{-1})[\text{RH}]_w
- (C_{\text{RH}})_T = 0 \tag{2.35}
\]
This is a quadratic equation in \([RH]_w\) and the roots of the equation can be obtained in the normal way. The value of \([RH]_w\) that is obtained from the solution of the equation must be positive to have any real significance, and the only root which can have a positive value is given by:

\[
[RH]_w = -B + \frac{(B)^2 - 4AC}{2A},
\]

(2.36)

where

\[
A = (2(K_p)^2K_{DO} + 2K_{DW}(K_{RH})^2[H^+]^{-2}),
\]

\[
B = (K_p + 1 + K_{RH}[H^+]^{-1}),
\]

\[
C = (C_{RH})_T
\]

In order to calculate \([RH]_w\) in a particular system, the values of the constants \(K_{RH}\), \(K_p\), \(K_{DO}\), and \(K_{DW}\) are required. The values of these constants for the distribution of a number of carboxylic acids between n-heptane and an aqueous phosphate buffer have been given in the literature [49, 90]. The values for n-octoic acid and n-decoic acid are given in Table 2.1.

The value of the dissociation constant, \(K_{RH}\), of n-decoic acid could not be found in the literature. An approximate value was obtained by extrapolation of the plot of \(pK_{RH} = -\log K_{RH}\) as a function of the reciprocal of the number of carbon atoms in the acid \((n^{-1})\) for a series of carboxylic acids (Fig. 2.1). The values of \(pK_{RH}\) for acids from acetic to n-nonoic were obtained from Dippy [93] and from Kortüm et al [94]. A value of \(pK_{RH} = 4.91\) for n-decoic acid was obtained by extrapolating the plot to a value of \(n^{-1} = 0.1\), where \(n = 10\) for n-decoic acid.

Unfortunately, the values of \(pK_{RH}\) for the acids from acetic to n-nonoic do not lie on a smooth curve and the value obtained for n-decoic acid by this method can only be an approximate one. However, Tanaka et al have assumed a value of \(pK_{RH} = 4.90\) for n-decoic acid in a study of the extraction of some metal decoates [95].
<table>
<thead>
<tr>
<th>System</th>
<th>$K_{RH}^{25^\circ C}$</th>
<th>Reference</th>
<th>$K_{DO}^{23^\circ C}$</th>
<th>Reference</th>
<th>$K_{DW}^{23^\circ C}$</th>
<th>Reference</th>
<th>$K_{P}^{23^\circ C}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-octoic acid/n-heptane/aqueous phosphate buffer</td>
<td>$1.275 \times 10^{-5}$</td>
<td>[93]</td>
<td>$5.8 \times 10^{3}$</td>
<td>[49]</td>
<td>$&lt;10$</td>
<td>[90]</td>
<td>4.3</td>
<td>[90]</td>
</tr>
<tr>
<td>n-decoic acid/n-heptane/aqueous phosphate buffer</td>
<td>$1.230 \times 10^{-5}$</td>
<td>From Fig. 2.1</td>
<td>$6.9 \times 10^{3}$</td>
<td>[49]</td>
<td>40</td>
<td>[90]</td>
<td>75</td>
<td>[90]</td>
</tr>
</tbody>
</table>
Fig. 2.1 $pK_{RH}$ as a function of $n^{-1}$ for carboxylic acids
The values of $K_{Dw}$, $K_{DO}$ and $K_p$ for n-octoic acid and n-decoic acid dissolved in carbon tetrachloride have not been published, and in the case of the commercial acids, such as the naphthenic acids, none of the constants are known. The values of the constants given by Goodman were measured in a study of the distribution of carboxylic acids between n-heptane and aqueous phosphate buffers at pH 7.45, ionic strength 0.16 and 23°C [49]. Mukerjee adjusted the value of $K_{DO}$ for the n-decoic acid/n-heptane system, which was given by Goodman, so that the experimentally observed value of $K_p$ could be accounted for over a range of acid concentrations [90].

2.2.4 The equilibria involved in the formation and distribution of the metal complex.

The following equilibria can be formulated as contributing to the formation and distribution of the metal complex between the organic phase (o) and the aqueous phase (w).

For the formation of the metal complex $(MR_z)$ in the aqueous phase:

$$(M^{z+})_w + z(R^-)_w \rightleftharpoons (MR_z)_w, \quad K_{MR_z}^w = [MR_z]^w [R^-]^w [M^{z+}]^{-1}_w, \quad (2.37)$$

where $K_{MR_z}^w$ is the formation constant of the metal complex.

For the distribution of the metal complex between the phases:

$$(MR_z)_w \rightleftharpoons (MR_z)_o, \quad K_{D,MR_z}^w = [MR_z]^o [MR_z]^{-1}_w, \quad (2.38)$$

where $K_{D,MR_z}^w$ is the distribution constant of the complex.

For the polymerisation of the complex in the organic phase:

$$j(MR_z)_o \rightleftharpoons ((MR_z)_j)_o, \quad K_{P,MR_z} = [(MR_z)_j]_o [MR_z]^{-j}_o, \quad (2.39)$$

where $K_{P,MR_z}$ is the polymerisation constant of the complex.

For the solvation of the polymeric complex in the organic phase:
where $K_{(MR_{z})_{j}(RH)_{x}}$ is the solvation constant of the polymerised complex, and $x$ refers to the number of molecules of the carboxylic acid that are bound to the $j$'th polymer of metal complex.

Now if it is assumed that the activity coefficients remain constant throughout the various distributions, and that the activity of any species may be taken to be equal to the concentration of that species, then $(C_{M_{w}})^{T}$, the total concentration of metal $M$ in the organic phase, is given by:

$$
(C_{M})_{w} = \beta [M^{z+}]_{w},
$$

and the distribution ratio $(D)$ of the metal ion is defined in equation (2.15) as:

$$
D = (C_{M})^{-1}_{w} (C_{M})_{O},
$$

therefore if these two equation are combined:

$$
(C_{M})_{O} = D[M^{z+}]_{w} \beta.
$$

Hence if the expression for $(C_{M})_{O}$ from equation (2.42) is substituted into equation (2.41):

$$
D = \left( \sum_{j=1}^{m} \sum_{x=1}^{n} j\left( [MR_{z}]_{j}(RH)_{x} \right)_{0} + [MR_{z}]_{j} \right) [M^{z+}]_{w} \beta^{-1}.
$$

In order to simplify this expression for $D$, expressions for
[(MRz)j (RH)j]0 and [(MRz)j]0 are obtained from equations (2.40) and (2.39). Thus from equation (2.39):

\[(MRz)j]0 = K_{P,MR} [MRz]j 0 \quad (2.44)\]

and from equation (2.40):

\[[(MRz)j (RH)j]x0 = K_{MR} [(MRz)j (RH)xj] 0 \quad (2.45)\]

If equation (2.44) is substituted into equation (2.45):

\[[(MRz)j (RH)j]x0 = K_{MR} [(MRz)j (RH)xj] 0 \quad (2.46)\]

Hence if this expression for \([(MRz)j (RH)j]0\) is substituted into equation (2.43), together with the expression for \([(MRz)j]0\) from equation (2.44):

\[D = \left( \sum_{j=1}^{m} \sum_{x=1}^{n} j(K)_{zj} (RH)_{xj} [RH]xj 0 K_{P,MR} [MRz]j 0 + K_{P,MR} [MRz]j 0 \right) \quad (2.47)\]

This expression for D can be simplified by substituting for \([MRz]j 0\). Thus if the expression for \([MRz]w\) from equation (2.38) is substituted into equation (2.37), and the resulting expression is raised to the j'th power:

\[ [MRz]j 0 = (K_{MR})zj (K_{D,MRz})j [Mz+]j [R+]zj \quad (2.48)\]

If this expression is substituted into equation (2.47):

\[D = \left( \sum_{j=1}^{m} \sum_{x=1}^{n} j(K)_{zj} (RH)_{xj} [RH]xj 0 K_{P,MR} [MRz]j 0 + K_{P,MR} [MRz]j 0 \right) \quad (2.49)\]
Now if equation (2.24) is raised to the \( z_j \)'th power:

\[
[R^-]_{w}^{z_j} = (K_{RH})^{z_j} [H^+]_{w}^{z_j} [RH]_{w}^{z_j}
\]

This expression for \([R^-]_{w}^{z_j}\) can be substituted into equation (2.49) to give:

\[
D = \left( \sum_{j=1}^{m} \sum_{x=1}^{n} j (K_{P,D,M_z} (K_{D,M_z})^{j} (K_{MR_z})^{j} (K_{RH})^{z_j} [H^+]_{w}^{z_j} [RH]_{w}^{z_j})
\]

\[
(K_{MR_z})^{j} (RH)_x \left( [RH]_{O}^{x} + 1 \right) \left( [M^z_+]_{w} \beta \right)^{-1}
\]

Now if the expression for \([(RH)_2]_O\) from equation (2.27) is substituted into equation (2.28):

\[
2 K_{DO} [RH]_{O}^{2} + [RH]_{O} - (C_{RH})_{O} = 0
\]

This is a quadratic equation in \([RH]_{O}\) and since the value of \([RH]_{O}\) must be positive to have any real significance, the root of the equation is given by:

\[
[RH]_{O} = -1 + (1 + 8K_{DO} (C_{RH})_{O}^{2})^{1/2} (4K_{DO})^{-1}
\]

Equation (2.53) can be simplified when the value of \((C_{RH})_{O}\) is such that:

\[
8 K_{DO} (C_{RH})_{O} \gg 1 \text{ and } (8 K_{DO} (C_{RH})_{O})^{2} \gg -1,
\]

then equation (2.53) can be written in the following approximate form:

\[
[RH]_{O} = (C_{RH})_{O}^{2} \left( K_{DO} \right)^{-1/2} (2)^{-1/2}
\]

The percentage errors involved in using equation (2.55) rather than (2.53) have been calculated by using the computer program given in Appendix 1 for the n-octoic acid/n-heptane and n-decoic acid/n-heptane systems. The values of \([RH]_{O}\) obtained from the two equations have been calculated for different values of \((C_{RH})_{O}\). The plots of
Log \((c_{RH})_0\) as a function of Log (% Error) for the n-octoic acid and n-decocoic acid systems are given in Fig. 2.2. For both acids dissolved in n-heptane, the error involved in using equation (2.55) rather than the full equation (2.53) falls from about 4.8% for a value of \((c_{RH})_0 = 10^{-2}\)M to about 0.5% for \((c_{RH})_0 = 1\)M. Tanaka et al used the approximation given in (2.55) in a consideration of the distribution of n-decocoic acid between benzene and an aqueous phase [46]. Over the range of acid concentrations that were used in the study (0.2M to 2.0M) the error involved amounted to between about 4.0% to 1.3%, if the value of \(K_{DO} = 4.0 \times 10^2\) which is given in the paper is used. In a later study, Tanaka et al quote a value of \(K_{DO} = 2.5 \times 10^2\) for n-decocoic acid in benzene [95]. In this case the error was between 3.2% and 2.3% over the concentration range of acid used (0.5M to 1.0M).

If equation (2.25) is raised to the \(zj\)th power:

\[
[RH]_{w}^{zj} = [RH]_{0}^{zj} (K_p)^{-zj} \tag{2.56}
\]

Also if equation (2.55) is raised to the \(zj\)th power:

\[
[RH]_{0}^{zj} = (c_{RH})_{0}^{zj/2} (K_{DO})^{-zj/2} (2)^{-zj/2} \tag{2.57}
\]

Thus if this expression for \([RH]_{0}^{zj}\) is substituted into equation (2.56):

\[
[RH]_{w}^{zj} = (c_{RH})_{0}^{zj/2} (K_{DO})^{-zj/2} (2)^{-zj/2} (K_p)^{-zj} \tag{2.58}
\]

An expression for \([RH]_{0}^{x}\) can be obtained by raising equation (2.55) to the \(x\)th power:

\[
[RH]_{0}^{x} = (c_{RH})_{0}^{x/2} (K_{DO})^{-x/2} (2)^{-x/2} \tag{2.59}
\]

The value for \([RH]_{w}^{zj}\) from equation (2.58) and for \([RH]_{0}^{x}\) from equation (2.59) can be substituted into equation (2.51). In order to simplify the formulation of the resulting equation, let:
1. n-decoic acid/n-heptane
   \( K_{DO} = 8.2 \times 10^3 \)

2. n-octoic acid/n-heptane
   \( K_{DO} = 5.8 \times 10^3 \)

3. n-decoic acid/benzene
   \( K_{DO} = 4.0 \times 10^2 \) from [46]

4. n-decoic acid/benzene
   \( K_{DO} = 2.5 \times 10^2 \) from [95]

Fig. 2.2 \( \log (C_{RH0}) \) as a function of \( \log (\% \text{ error}) \)
and also:

$$K_{j,x} = K_{(MR\_z\_j(RH)\_x)} (K_{DO})^{-x/2} (2)^{-x/2}$$

Then on substituting equations (2.58) and (2.59) into equation (2.51), and using the above definitions of $K_j$ and $K_{j,x}$:

$$D = \left( \sum_{j=1}^{m} \sum_{x=1}^{n} K_j ([M^{z+}]_w^{j-1} [H^+]^{-z_j} (C_{RH}^{z_j/2}) (K_{j,x} (C_{RH}^{x/2} + 1))(\beta)^{-1} \right)$$

Now by raising equation (2.9) to the $(j - 1)$'th power:

$$[M^{z+}]_w^{j-1} = (C_M)_w^{j-1} / (\beta)^{j-1}$$

Hence on substituting $[M^{z+}]_w^{j-1}$ from equation (2.63) into equation (2.62):

$$D = \left( \sum_{j=1}^{m} \sum_{x=1}^{n} K_j (G_{M\_w}^{j-1} [H^+]^{-z_j} (C_{RH}^{z_j/2}) (K_{j,x} (C_{RH}^{x/2} + 1))(\beta)^{-1} \right)$$

Equation (2.64) is a general expression which can be used to describe the extraction of metal ions ($M^{z+}$) from aqueous solution by a carboxylic acid ($RH$) in the organic phase. However, it is difficult to apply directly to the analysis of experimental extraction data.

A simplified expression can be obtained if it is assumed that only one complex of the form ($K_{(MR\_z\_j(RH)\_x)}$) is present in the organic phase and also that:

$$K_{j,x} (C_{RH})^{x/2} \gg 1$$
If these assumptions are made, then:

\[ D = K_j \cdot K_{j,x} \cdot (C_{w})^{j-l} \cdot [H^+]^{-z_j} \cdot (C_{RH})^{(z_j+x)/2} \cdot p^j \]  

(2.66)

Hence, on taking logarithms to the base 10:

\[ \log D = \log K_j + \log K_{j,x} - j \log \beta + (j - l) \log (C_{w}) + z_j \cdot pH + \]

\[ \frac{(z_j + x)}{2} \log (C_{RH}) \]  

(2.67)

Tanaka and Niinomi used a similar multiple equilibria method to describe the extraction of copper by n-decoic acid dissolved in benzene [46]. Recently, Tanaka et al have extended their studies, and they have considered the extraction of Co (II) and Fe (III) by n-decoic acid in terms of the same theoretical approach [95].

2.2.5 A comparison of the single equilibrium approach and the multiple equilibria approach.

The extraction expressions given in equations (2.21) and (2.67) are derived from the two approaches, assuming that only one complex of the form \(((MR)^j \cdot (RH))_x\) is present in the organic phase. The two equations are similar in form, and they can be shown to be equivalent in the following manner [47]. By definition, from equations (2.60) and (2.61):

\[ (K_j)(K_{j,x}) = j \cdot K_{P,MR} \cdot (K_{D,MR})^j \cdot (K_{MR})^j \cdot (K_{RH})^z_j \cdot (K_{P})^{-z_j} \cdot (z_j+x)/2 \]

\[ (K_{D,0})^{-z_j} \cdot (z_j+x)/2 \cdot K_{(MR)_j} \cdot (RH)_x \]  

(2.68)

Now by substituting the expressions for: \(K_{P,MR}\) from (2.39); \(K_{D,MR}^j\) from (2.38); \(K_{MR}^j\) from (2.37); \(K_{RH}^z_j\) from (2.24); \(K_{P}^{-z_j}\) from (2.25); \(K_{D,0}^{-z_j} (z_j+x)/2\) from (2.27) and \(K_{(MR)_j} \cdot (RH)_x\) from (2.40) into equation (2.68):
\[ (K_j)(K_{j,x}) = j[H^+]^{z_j} w [(MR_z)_j] (RH)_x X_0 z^{-(z_j+x)/2} [(RH)_2]_0^{-(z_j+x)/2} [M^{z_+}]_w^{-j} \]

(2.69)

Hence for a constant value of \([H^+]^{z_j}\), the terms \([(RH)_2]_0^{-(z_j+x)/2}\), \([M^{z_+}]_w^{-j}\) and \([(MR_z)_j] (RH)_x X_0\) are also constant. If these terms are included in a constant \(K^1\), and if logarithms to the base 10 of equation (2.69) are taken:

\[ \log K_j + \log K_{j,x} = \log j - \left(\frac{(z_j + x)}{2}\right) \log 2 + \log K^1 \]

(2.70)

If this expression is substituted into equation (2.67):

\[ \log D = \log j - \left(\frac{(z_j + x)}{2}\right) \log 2 + \log K^1 - j \log \beta + (j - 1) \log (C_M)_w + z_j \text{pH} + \left(\frac{(z_j + x)}{2}\right) \log (C_{RH})_0 \]

(2.71)

This equation is equivalent to the extraction equation (2.21) which was derived by using the single equilibrium approach.

The two approaches give equivalent equations for the case of one extracted complex even though different assumptions are used to derive the equations in each case.

Thus, in the single equilibrium approach, the acid in the organic phase is assumed to be present as dimer only, and the concentration of the acid is taken to be equal to the dimer concentration. In the multiple equilibria method, however, the total concentration of acid present is related to both the monomer concentration and to the dimerisation constant of the acid by equation (2.55). In the case of n-octoic acid and n-decoic acid dissolved in n-heptane, the error involved in assuming that only dimer is present in the organic phase is small since the values of the dimerisation constants of the acids in the organic phase are large in both cases (ca. \(10^3\)).
A further difference between the two approaches is the simplification introduced in the multiple equilibria method in equation (2.65), viz:

\[ K_{j,x} \left( C_{RH} \right)^{x/2} \gg 1, \]

where \( K_{j,x} = K_{(MR)}_{j,(RH)} x \) \( K_{DO}^{-x/2} 2^{-x/2} \) from equation (2.61).

Unfortunately the order of magnitude of \( K_{(MR)}_{j,(RH)} \) is not known, but in the case of one complex of the form \( (MR)_x (RH)_x \) in the organic phase it should be large. Then, in the presence of an excess of acid in the organic phase, the term \( K_{j,x} \left( C_{RH} \right)^{x/2} \) should be greater than unity. Tanaka et al have shown that by using this approximation, an equation which describes the extraction of copper from aqueous solution into benzene with n-decoic acid can be obtained [46].

The simplification introduced in equation (2.65) appears to be largely responsible for destroying the distinction between the two extraction approaches.

2.3 The mathematical analysis of the extraction data by regression analysis methods.

The use of graphical methods for the analysis of data from systems containing metal complexes has been quite extensive. However, while it is true that the methods can be used on a wide variety of data, the values of the parameters that are obtained are not usually unique. In addition, there is generally no dependable measure of the reliability of the values that are determined. With statistical methods of analysis, however, it is possible to refine parameters and to select with confidence the "best fit" among a number of possibilities.

The use of electronic computers in the application of statistical methods to the analysis of data obtained from studies of complexes in solution has been pioneered by the Swedish school of workers, including
Sillen and Rydberg. At the present time, computer programs such as GAUSS [96] and LETAGROP [97] can be used to calculate equilibrium constants for polynuclear, for protonated, and for hydrolysed complexes, and also for the analysis of mixed species [98]. In contrast, however, the methods have not yet been widely applied to the analysis of data from systems of interest in solvent extraction processes.

2.3.1 Linear regression analysis of extraction data in the case of one extracted complex

Equation (2.67), which was derived from the multiple equilibria approach, describes the extraction with carboxylic acids when there is only one complex in the organic phase. It can be rearranged to the form:

\[ \log D = ((j-1) \log (C_M)_w + (zj + x)/2 \log (C_{RH})_O + zj \, \text{pH}) \]
\[ + (\log K_j + \log K_{j,x} - j \log \eta)(2.72) \]

This expression is then in the form of the equation of a straight line:

\[ Y = a + bX, \]

where:

\[ Y = \log D, \]
\[ X = ((j-1) \log (C_M)_w + (zj + x)/2 \log (C_{RH})_O + zj \, \text{pH}), \]
\[ a = (\log K_j + \log K_{j,x} - j \log \eta) \quad (2.73) \]

In order to calculate the parameters of the straight lines which give the best fits with the extraction data, the mathematical method of least squares has been used [99]. In the general method, it is assumed that a series of values of two variables, \( X \) and \( Y \), are related
by an expression of the form:

\[ Y = \alpha + \beta X + e, \]  

(2.74)

where \( \alpha \) and \( \beta \) are parameters, and \( e \) is a random error variable.

The form of the distribution of the error is not important if the errors are independent of each other. Expressions of this kind are called regression relationships, and \( \alpha \) and \( \beta \) are called regression coefficients. The values of \( \alpha \) and \( \beta \) are not usually known, but they can be estimated by the least squares method from \( n \) pairs of observations of \( X \) and \( Y \).

In order to measure the interdependence of the two variables, \( X \) and \( Y \), the correlation coefficient \( (r) \) is used. This is defined as:

\[ r = b \frac{\left( \sum X^2 - \sum X \sum X/n \right) \left( \sum Y^2 - \sum Y \sum Y/n \right)}{\left( \sum X^2 - \sum X \sum X/n \right)^{1/2} \left( \sum Y^2 - \sum Y \sum Y/n \right)^{1/2}} \]  

(2.75)

It can be shown that:

\[-1 \leq r \leq +1 \]  

(2.76)

In the case when \( r = 0 \), there is no linear relationship between \( X \) and \( Y \), and the two variables are said to be "uncorrelated". When \( r = +1 \), there is a perfect linear relationship between \( X \) and \( Y \), and both variables increase together. When \( r = -1 \), there is a perfect linear relationship between \( X \) and \( Y \), and \( Y \) decreases as \( X \) increases.

The least squares analysis of the extraction data has been carried out with the aid of an electronic computer, using the extraction expression derived from the multiple equilibria approach (equation 2.72). Three modifications to the amount of acid in the organic phase, \( (C_{RH})_0 \), have been introduced. These are: (a) when the amount of acid in the organic phase is so large that it can be considered to be a constant value in comparison to the amount present in the metal complex and in
the aqueous phase; (b) when an allowance for the amount of acid present in the metal complex is required; and (c) when an allowance for the amount of acid in the aqueous phase is required. The equilibria postulated in the multiple equilibria method to describe the distribution of the carboxylic acid can be used to calculate the amount of acid in the aqueous phase.

In case (a) when the amount of acid in the organic phase is considered to be constant, the term \((z_j + x)/2 \log \left( {C_{RH}}_O \right) \) in equation (2.72) can be combined with the constant term, and the extraction expression becomes:

\[
\log D = (\log K_j + \log K_{j,x} - j \log \beta + ((z_j + x)/2 \log \left( {C_{RH}}_O \right) )
+ ((j - 1) \log \left( {C_M}_w + z_j \text{pH} \right) )
\]

Then for the least squares analysis, assuming a linear equation of the form \(Y = a + bX\):

\[
Y = \log D,
\]

\[
X = ((j - 1) \log \left( {C_M}_w + z_j \text{pH} \right),
\]

\[
a = (\log K_j + \log K_{j,x} + ((z_j + x)/2 \log \left( {C_{RH}}_O \right) ),
\]

assuming \(\beta\) is unity. It is necessary to regard \(\beta\) as unity at this stage, since there is a lack of published data available on the values of stability constants for complexes formed between metal ions \((M^{z+})\) and the anions of long chain carboxylic acids \((R^-)\) in the aqueous phase. In the cases when the concentration of \((R^-)\) in the aqueous phase is low the assumption is probably well justified. Tanaka, for instance, has assumed \(\beta\) to be unity in a study of the extraction of copper by n-decoic acid [46].

When a significant amount of the metal complex is present in the
organic phase, the concentration of free acid in that phase (i.e. uncomplexed acid) can no longer be regarded as equal to \((C_{RH}^{\text{O}})\). The amount of acid present in the metal complex can be calculated as follows. For a single complex of the form \(((MR)_z(RH)_x\) in the organic phase, there are \((zj + x)\) moles of acid associated with \((j)\) moles of complex. Thus for \((C_{M}^{\text{O}})\) moles of complex there are \(((C_{M}^{\text{O}})(z + x/j))\) moles of acid used. If \((C_{RH}^{\text{O}})\) represents the amount of uncomplexed acid in the organic phase, then:

\[
(C_{RH}) = (C_{RH})_T - ((C_{M}^{\text{O}})(z + x/j)), \tag{2.79}
\]

where \((C_{RH})_T\) is the total amount of acid present in the system. Now from equation (2.15):

\[
D = (C_{M}^{\text{O}})(C_{M}^{\text{W}})^{-1}
\]

Thus if the expression for \((C_{M}^{\text{O}})\) from equation (2.15) is substituted into equation (2.79):

\[
(C_{RH}) = (C_{RH})_T - (D (C_{M}^{\text{W}})(z + x/j)) \tag{2.80}
\]

Hence if this expression for \((C_{RH})\) is substituted for \((C_{RH}^{\text{O}})\) in the general extraction equation (2.72):

\[
\log D = ((j - 1) \log (C_{M}^{\text{W}}) + zj \ p\text{H} + ((zj + x)/2 \log ((C_{RH})_T - (D (C_{M}^{\text{W}})(z + x/j)) + (\log K_{j} + \log K_{j,x} - j \log \beta)) \tag{2.81}
\]

Then for the least squares analysis, assuming a linear equation of the form

\[
Y = a + bX:
\]

\[
Y = \log D,
\]

\[
X = ((j - 1) \log (C_{M}^{\text{W}}) + zj \ p\text{H} + ((zj + x)/2 \log ((C_{RH})_T - (D (C_{M}^{\text{W}})(z + x/j)))))
\]
\[ a = (\log K_j + \log K_{j,x}), \text{ assuming } \beta \text{ is unity} \quad (2.82) \]

For case (c) it is necessary to take into account the fact that the solubility of a carboxylic acid in an aqueous solution increases with the pH of the solution. In order to calculate the amount of acid present in an aqueous solution at a given pH it is necessary to calculate the distribution ratio of the acid \( (D_{RH}) \) at that pH. Now from equation (2.36), the variation of \([RH]_w\) with pH can be obtained, and if the value of \([RH]_w\) at a given pH is substituted into equation (2.33) then the value of \( (D_{RH}) \) at that pH can be calculated. The variation of \( \log (D_{RH}) \) with pH for the distribution of n-octoic acid and n-decoic acid respectively between n-heptane and water has been calculated with the aid of the computer program given in Appendix 2, and the results are given in Fig. 2.3. The value of \( (D_{RH}) \) for n-decoic acid at any pH is considerably greater than the corresponding value for n-octoic acid. This is expected since the increase in the length of the alkyl chain from n-octoic to n-decoic acid favours the solubility of n-decoic acid in the organic phase.

In order to make allowance for the amount of acid in the aqueous phase, the term \( (C_{RH})_O \) in the extraction equation must be modified. Thus from equation (2.32):

\[ D_{RH} = (C_{RH})_O (C_{RH})_w^{-1}, \]

and from equation (2.34):

\[ (C_{RH})_T = (C_{RH})_O + (C_{RH})_w. \]

Thus if the expression for \( (C_{RH})_w \) from equation (2.32) is substituted into equation (2.34):

\[ (C_{RH})_O = (D_{RH})(C_{RH})_T (1 + D_{RH})^{-1} \quad (2.83) \]
Fig. 2.3 Distribution of carboxylic acids between n-heptane and water as a function of pH

1. n-octoic acid
2. n-decoic acid
If this expression is then substituted into the extraction equation (2.72):

\[
\log D = ((j - 1) \log (C_M)_w + zj \, \text{pH} + ((zj + x) / 2) \log (D_{RH} (C_{RH})_T (1 + D_{RH})^{-1})) + (\log K_j + \log K_{j,x} - j \log \beta)
\]

Then for the least squares analysis, assuming a linear equation of the form

\[ Y = a + bX \]

\[ Y = \log D \]

\[ X = ((zj + x) / 2 \log (D_{RH} (C_{RH})_T (1 + D_{RH})^{-1})) + zj \, \text{pH} + (j - 1) \log (C_M)_w, \]

\[ a = (\log K_j + \log K_{j,x}), \text{ assuming } \beta \text{ is unity} \] (2.85)

In the least squares computer program (Appendix 3), the analysis of the extraction data is carried out using the basic extraction equation (2.72), and three subroutines are introduced as required to take account of the modifications to the term \((C_{RH})_0\). The analysis of each set of data is carried out for various combinations of integral values of \(j\) and \(x\). A value of \(a\) (intercept), \(b\) (slope), and \(r\) (correlation coefficient) is obtained for each linear regression line, and hence for each \(j\) and \(x\) value used. An estimate of the error between the data and the linear regression line is also made. The error term is defined as the difference between the value of \(\log D\) as indicated by the linear regression line and the experimentally determined value of \(\log D\), for each value of pH. The mean absolute value of the error (average error) and the root mean square value are calculated.
The "perfect" fit between the extraction data and the proposed extraction equation (2.72) would be the case of zero average error and slope of the regression line (b) equal to unity. Therefore the value of the average error and the root mean square error are calculated, relative to a line of slope equal to unity, for each value of \( j \) and \( x \) used.

2.3.2 Multiple regression analysis of extraction data in the case of one extracted complex.

In the simple linear regression analysis, a part of the variability of one variable \( (Y) \) can be accounted for by means of a second variable \( (X_1) \), and in such a case \( (X_1) \) can be used as a predictor for \( (Y) \). In many cases, however, the residual variability which is not explained by the single predictor \( (X_1) \) can be reduced by some additional observed variables, \( (X_2, X_3, \ldots, X_p) \). In such a case, all the \( (p) \) variables are used to predict \( (Y) \). The simple linear regression equation can be generalised to take account of \( p \) variables, \( (X_1, X_2, \ldots, X_p) \), by the general linear model:

\[
Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_p X_p + e, \quad (2.86)
\]

where all the \( (X_i) \) values are fixed, and \( (e) \) is a random variable. The error distribution need not be known, but the errors must be independent of each other.

The values of the regression coefficients \( (\beta_0, \beta_1, \ldots, \beta_p) \) are estimated from \( (n) \) sets of observations of \( (Y, X_1, X_2, \ldots, X_p) \). The estimates \( (b_0, b_1, \ldots, b_p) \) of the parameters \( (\beta_0, \beta_1, \ldots, \beta_p) \) are obtained by minimising the sum of the squared residuals:

\[
S = \sum(Y - (b_0 + b_1 X_1 + \ldots + b_p X_p))^2 \quad (2.87)
\]

The \( (p + 1) \) values of \( (b) \) are given by solving the following \((p + 1)\)
equations:

\[ \frac{\partial S}{\partial b_0} = 0, \quad \frac{\partial S}{\partial b_1} = 0 \ldots \quad \frac{\partial S}{\partial p_1} = 0 \]

i.e., the equations:

\[-2 \sum (Y - (b_0 + b_1 X_1 + \ldots + b_p X_p)) = 0,\]

\[-2 \sum X_1 (Y - (b_0 + b_1 X_1 + \ldots + b_p X_p)) = 0,\]

\[-2 \sum X_p (Y - (b_0 + b_1 X_1 + \ldots + b_p X_p)) = 0\]

\[(2.88)\]

The \((p + 1)\) equations are called "normal equations", and they can be rewritten in the form:

\[ n_0 b_0 + \sum X_1 b_1 + \sum X_2 b_2 + \ldots + \sum X_p b_p = \sum Y \]

\[ \sum X_1 b_0 + \sum X_1^2 b_1 + \sum X_1 X_2 b_2 + \ldots + \sum X_1 X_p b_p = \sum X_1 Y \]

\[ \sum X_p b_0 + \sum X_p X_1 b_1 + \sum X_p X_2 b_2 + \ldots + \sum X_p^2 b_p = \sum X_p Y \]

\[(2.89)\]

There are \((p + 1)\) equations for the \((p + 1)\) estimators, and since the equations are linear they can be solved by standard mathematical methods.

The extraction equation for one complex in the organic phase can be rearranged from the form given in equation (2.67) to:

\[ (\log D' + \log (C_{Hi}^w)) = j(\log (C_{Hi}^w) + z \, pH + (z/2) \, \log (C_{RH})_0 - \log \beta) \]

\[ + x((1/2) \, \log (C_{RH})_0) + (\log K_j + \log K_j, x) \]

\[(2.90)\]
Now comparing this rearranged equation with a general linear equation of the form:

\[ Y = \beta_1 x_1 + \beta_2 x_2 + \text{Const.}, \quad (2.91) \]

then: \[ Y = (\log D + \log (C_M)^w), \]

\[ x_1 = ((1/2) \log (C_{RH})_0), \]

\[ x_2 = (\log (C_M)^w + z \cdot pH + (z/2) \log (C_{RH})_0), \]

if \( \beta \) is assumed to be unity,

\[ \text{Const.} = (\log K_j + \log K_{j,x}), \]

\[ \beta_1 = x, \]

\[ \beta_2 = j \quad (2.92) \]

The three corresponding normal equations are:

\[ n \cdot \text{Const.} + \sum x_1 \cdot x + \sum x_2 \cdot j = \sum Y \quad (2.93) \]

\[ \sum x_1 \cdot \text{Const.} + \sum x_1^2 \cdot x + \sum x_1 \cdot x_2 \cdot j = \sum x_1 \cdot Y \quad (2.94) \]

\[ \sum x_2 \cdot \text{Const.} + \sum x_1 \cdot x_2 \cdot x + \sum x_2^2 \cdot j = \sum x_2 \cdot Y \quad (2.95) \]

If equation (2.93) is divided by \( n \):

\[ \text{Const.} + \sum x_1 \cdot x/n + \sum x_2 \cdot j/n = \sum Y/n \quad (2.96) \]

If this expression is substituted for (Const.) in equations (2.94) and (2.95):

\[ \sum x_1 \cdot x/n - \sum x_1 \cdot x \cdot x/n - \sum x_1 \cdot x_2 \cdot j/n + \sum x_1^2 \cdot x + \]

\[ \sum x_1 \cdot x_2 \cdot j = \sum x_1 \cdot Y \quad (2.97) \]
Hence the values of \((x)\), \((j)\) and \((\text{Const.})\) can be obtained by solving the three equations (2.96)-(2.98).

The three normal equations which are given in equations (2.93)-(2.95) may also be solved by arranging them in the form of \((3 \times 3)\) matrices, and then calculating the determinants.

The multiple regression analysis of the extraction data has been carried out on an electronic computer using the program given in Appendix 4. The values of \((j)\), \((x)\), and \((\text{Const.})\), are calculated from the normal equations given in (2.93)-(2.95) by using the substitution procedure outlined in equations (2.93)-(2.98) above. The program contains three subroutines which are introduced as required to make modifications to \((C_{RH})_0\) in the extraction equation, in the same manner as described for the linear regression program. These modifications are for the cases: (a) when the concentration of acid in the organic phase is considered to be constant; (b) when an allowance is required for the acid in the complex; and (c) when an allowance is required for the acid in the aqueous phase.

A measure of the "fit" between the multiple regression line and the data is obtained from an error term, which is defined as:

\[
(\log D + \log (C_{H}^w)) - j(\log (C_{H}^w) + z \text{pH} + z/2 \log (C_{RH})_0) - x(1/2 \log (C_{RH})_0)
\]

(2.99)

For each analysis of the data, a value of the average error and the root mean square error is calculated from this error term.
2.3.3 The calculation of equilibrium constants for a mixture of metal complexes in the organic phase.

A group of workers in Sweden have been largely responsible for the development of computer methods as a supplement to graphical methods of analysis of data from complexes in solution. At the present time, interest is centred on the use of the methods in the case of systems containing mixed complexes.

A program (LETAGROP) has been designed by the Swedish workers to adjust a number of equilibrium constants simultaneously, once the formulae of the complexes and the approximate values of the equilibrium constants have been found by graphical methods [97, 193, 194]. It has been claimed that the program can be used in cases where the measured quantity cannot be expressed as a linear, or even an explicit, function of the unknown parameters.

The program LETAGROP suffers from a disadvantage that it has been written in Ferranti Mercury Autocode, which cannot be used directly with IBM or ICT computers. To use the program with the computer facilities available in this University it would have been necessary to translate the program into the Fortran code. However, it has been found by other workers that the translation of programs for use with different computers is often a difficult task due to incompatibility between the machines. In addition, the computer facilities available at the start of the work (IBM 1620 computer) could not have dealt with the size of the program.

Perrin and Sayce have very recently published a program which can be used to calculate the equilibrium concentrations in mixtures of metal ions and complexing species [98]. This program has been written in the Fortran code for use with an IBM 360/50 computer. Unfortunately, the program cannot be used in its present form to calculate equilibrium constants since the values of these constants are required.
in the procedure for calculating equilibrium concentrations.

In view of the lack of suitable published programs for the calculation of equilibrium constants for mixed complexes in solution, it was decided to program an ICT 1905 digital computer to analyse the data from carboxylic acid extractions.

In the case of metal–carboxylic acid complexes in the organic phase, a complex of the form \((\text{MR}_z)\) can be considered to be formed by the following equilibrium and the corresponding equilibrium constant \((k_1)\) can be written:

\[
\text{M} + z \text{R} & \rightleftharpoons (\text{MR}_z)_w \\
& \rightleftharpoons (\text{MR}_z)_0 \\
& k_1 = [\text{MR}_z]^w_0 [\text{R}]^{-z}[\text{M}]^{-1}_w \\
\tag{2.100}
\]

Also, the solvation of the complex \((\text{MR}_z)_0\) can be represented by the following equilibrium and equilibrium constant \((k_2)\):

\[
(\text{MR}_z)_0^j + x (\text{RH})_0 & \rightleftharpoons (\text{MR}_z)_0^j (\text{RH})_x^j \\
& k_2 = [(\text{MR}_z)_0^j (\text{RH})_x^j]_0 [\text{MR}]^{-j}_z [\text{RH}]^{-x}_0 \\
\tag{2.101}
\]

If the value of \([\text{MR}_z]_0^{-j}\), which can be obtained from equation (2.100), is substituted into equation (2.101), then:

\[
k_2 = [(\text{MR}_z)_0^j (\text{RH})_x^j]_0 k_1^{-j} [\text{R}]^{-zj}_w [\text{M}]^{-j}_w [\text{RH}]^{-x}_0 \\
\tag{2.102}
\]

Now the concentration of metal in the organic phase \((C_M)_0\) is given by:

\[
(C_M)_0 = \sum_{j=1}^{\alpha} \sum_{x=0}^{\beta} j [(\text{MR}_z)_0^j (\text{RH})_x^j]_0 \\
\tag{2.103}
\]

in the case of a mixture of metal complexes in the organic phase.

Hence if the expression for \([(\text{MR}_z)_0^j (\text{RH})_x^j]_0\) from equation (2.102) is substituted into equation (2.103):

\[
(C_M)_0 = \sum_{j=1}^{\alpha} \sum_{x=0}^{\beta} j k_2 k_1^{-j} [\text{R}]^{zj}_w [\text{M}]^{-j}_w [\text{RH}]^{-x}_0 \\
\tag{2.104}
\]
If all the constants for each complex in equation (2.104) are combined in a common constant $k^1$;

$$(C_M)_0 = \sum_{j=1}^{\alpha} \sum_{x=0}^{\beta} k^1 [R]^x_j [M]^j_w [RH]^0_w$$

(2.105)

Now, from the definition of the distribution ratio ($D$) of the metal ion given in equation (2.15):

$$D = \frac{(C_M)_O (C_M)_w}{(C_M)_w (C_M)_O}$$

Hence if the expression for $(C_M)_O$ from this equation is substituted into equation (2.105):

$$(C_M)_D = \sum_{j=1}^{\alpha} \sum_{x=0}^{\beta} k^1 [R]^x_j (C_M)_w [M]^j_w [RH]^0_w$$

(2.106)

If it is assumed that $[M]^j_w = (C_M)_w^j$, then equation (2.106) can be rearranged to the form:

$$D = \sum_{j=1}^{\alpha} \sum_{x=0}^{\beta} k^1 [R]^x_j (C_M)_w^{-1} [M]^j_w (C_M)_w^{j-1} [RH]^0_w$$

(2.107)

This equation is in fact a linear equation of the form:

$$y = a_1 b_1 + a_2 b_2 + \ldots$$

(2.108)

where:

$$y = D,$$

$$a_1 = k^1,$$

$$a_2 = k^2,$$

$$b_1 = [R]^x_j (C_M)_w^{j-1} (C_M)_w^{-1} [RH]^0_w,$$

$$b_2 = [R]^x_j (C_M)_w^{j-1} (C_M)_w^{-1} [RH]^0_w,$$

etc.
For (p) complexes, a series of (p) linear equations can be written, and can be solved by normal elimination and substitution procedures.

In order to use expression (2.107) for the analysis of extraction data, the terms \([R^j_w]\) and \([RH]^X\) must be obtained in terms of the concentrations \((C_{RH})_0\) and \((C_{RH})_w\), respectively. Thus equation (2.52) can be solved by using the normal formula for the solution of a quadratic equation, and since the root obtained must have a positive value:

\[
[RH]_0 = -1 + (1 + 8k_{D0}(C_{RH})_0)^{\frac{1}{2}} (4k_{D0})^{-1}
\]

Also by substituting the expression for \([RH]_w\) from equation (2.24) and \(2[R^2-]\) from equation (2.26) into equation (2.29), and by solving the quadratic equation as above;

\[
[R]_w = - (1 + [H]/k_{RH}) + ((1 + [H]/k_{RH})^2 + 4(2k_{Dw}(C_{RH})_w)^{\frac{1}{2}}(4k_{Dw})^{-1}
\]

Expressions for \([R]^j_w\) and \([RH]^X\) can then be obtained and substituted into equation (2.107).

As described in section (2.3.1), the term \((C_{RH})_0\) in the above equation can be modified to make allowance for the amount of acid present in the metal complexes and also for the acid in the aqueous phase.

The amount of acid present in the metal complexes in the organic phase is given by the expression:

\[
\sum_{j=1}^{\infty} \sum_{x=0}^{\infty} [(MR)^j_z (RH)^x] (zj + x)
\]  
(2.109)

Also, the amount of acid present in the aqueous phase can be obtained by using the procedure outlined in section (2.3.1). An expression for the term \((C_{RH})_0\) can be obtained in terms of the distribution ratio of the acid \((D_{RH})_0\) and the total amount of acid present \((C_{RH})_T\) as given in equation (2.83).

Equation (2.107) is a general expression which can be used to
describe \( p \) complexes in the organic phase. However, the calculation becomes lengthy as the number of complexes increases, and even with a large electronic computer the analysis takes a considerable time.

Initially it was decided to program the computer to consider \( p \) complexes. In order to do this, use was made of two standard ICT subroutines, \( \text{UTMI} \) and \( \text{F2LYNSYT} \), for solving a set of linear equations. Unfortunately, when these subroutines were used in the main program it was found impossible to obtain finite values for the equilibrium constants \( k^1 \). The reason for this could not be found, even with the help of the computer personnel, but a possible explanation is that the linear equations are badly valued, as will be discussed below.

Since the two subroutines mentioned above could not be used for the analysis, a program using a direct substitution procedure was written for the analysis of extraction data, assuming the presence of two and three complexes, respectively, in the organic phase.

In the case of two complexes, the two linear equations are:

\[
\begin{align*}
  a_1 b_{11} + a_2 b_{12} &= y_1 \\
  a_1 b_{12} + a_2 b_{22} &= y_2
\end{align*}
\]

where \( a_1 = k_1 = \text{value of } k^1 \text{ for the complex } (MR_z j_1) (RH) x_1, \text{ etc.}, \) and the other symbols are as defined in equation (2.108). By combining the two equations in (2.110) it can be shown that:

\[
a_2 = \frac{b_{11} y_2 - b_{12} y_1}{b_{11} b_{22} - b_{12} b_{12}}
\]

and

\[
a_1 = \frac{b_{22} y_1 - b_{12} y_2}{b_{11} b_{22} - b_{12} b_{12}}
\]

In order to obtain finite values for \( a \) i.e., \( k^1 \) from the solution of these equations, it is obviously necessary for the
denominator and numerator to have non-zero values in each case. This requirement will be satisfied if the differences between the product terms in both the numerator and denominator are also non-zero.

In the case of three complexes in the organic phase, the following three linear equations can be written:

\[ a_1 b_{11} + a_2 b_{12} + a_3 b_{13} = y_1 \]
\[ a_1 b_{12} + a_2 b_{22} + a_3 b_{23} = y_2 \]
\[ a_1 b_{13} + a_2 b_{23} + a_3 b_{33} = y_3 \]  

(2.112)

These equations can be solved by elimination and substitution procedures to give expressions for \( a_1 \), \( a_2 \) and \( a_3 \) in terms of \( b \) and \( y \). A similar limitation applies to the solution of these expressions as mentioned above for the two complex case, if finite values of \( a \) i.e. \( (k^1) \) are to be obtained.
CHAPTER 3

A Study of the Structures of some Metal Carboxylates in Solution by Physical Methods
3.1 The Copper (II) - Carboxylic Acid System.

A large amount of information has been published in the literature on the nature of copper (II) acetate and its homologues (i.e. the higher carboxylates), both in the solid state and in solution in various solvents. It has been shown by the use of a number of physical methods of study that these compounds can exist in a dimeric form, containing two copper (II) ions in a molecule, as shown in Fig. 3.1.

Although the compounds have been studied quite extensively, the actual nature of the copper-to-copper bond is still open to discussion. The evidence for the existence of the dimeric form from physical methods of study will be considered under the following headings: (a) magnetic measurements; (b) absorption spectra; (c) other physical methods.

3.1.1 Magnetic measurements.

The copper (II) ion \((3d^9)\) has one unpaired electron in the \((3d)\) shell, and originally its compounds were considered to have magnetic moments close to the spin-only value, 1.73 Bohr Magnetons (B.M.), irrespective of the bond type involved. The observed values of the magnetic moments are 1.9 - 2.2 B.M. for most copper (II) compounds with ionic or rather weak covalent bonds, and 1.72 - 1.82 B.M. for the compounds with strong covalent bonds. Recently, however, a large number of copper (II) compounds have been reported which have subnormal magnetic moments (i.e. less than 1.72 B.M.) at room temperature, and they are considered to possess in most cases rather weak covalent bonds \([100]\). The group of compounds including copper (II) acetate and its homologues are important examples of compounds with subnormal magnetic moments. Table 3.1 summarises the magnetic properties of some copper (II) carboxylates from the data given in a review by Kato et al \([100]\). In this table, \(\chi_\alpha\) is the magnetic susceptibility per copper (II) ion.
Fig. 3.1 Proposed dimeric structure for copper (II) carboxylates. R represents alkyl groups. L represents axial ligands.
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Formula of compounds</th>
<th>T(°K)</th>
<th>$\chi_a \times 10^6$ c.g.s., e.m.u.</th>
<th>$\chi_a \times 10^6$ c.g.s., e.m.u.</th>
<th>$\mu$ (B.M.)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>Cu(CH$_3$CO$_2$)$_2$</td>
<td>295</td>
<td>4.39</td>
<td>869</td>
<td>1.39</td>
<td>[102, 126]</td>
</tr>
<tr>
<td></td>
<td>Cu(CH$_3$CO$_2$)$_2$H$_2$O</td>
<td>290</td>
<td>3.99</td>
<td>875</td>
<td>1.43</td>
<td>[126, 127]</td>
</tr>
<tr>
<td>n-octoic acid</td>
<td>Cu(C$<em>7$H$</em>{15}$CO$_2$)$_2$</td>
<td>293</td>
<td>1.71</td>
<td>830</td>
<td>1.40</td>
<td>[126]</td>
</tr>
<tr>
<td>n-decoic acid</td>
<td>Cu(C$<em>9$H$</em>{19}$CO$_2$)$_2$</td>
<td>293</td>
<td>1.39</td>
<td>845</td>
<td>1.41</td>
<td>[126]</td>
</tr>
</tbody>
</table>
corrected for the diamagnetism of the other atoms in the compound, and \( \chi \) is the magnetic susceptibility per gram (i.e. specific susceptibility).

The study of the magnetic properties of copper (II) acetate and its homologues has been extensive. As early as 1915, Lifschitz and Rosenbohm recorded that the molar susceptibility of copper (II) acetate monohydrate at room temperature was much lower than the values for copper (II) compounds in general \([101]\). Many investigators have repeated these magnetic measurements, and the abnormally low magnetic moment has been confirmed \([102]\).

In 1956, exact measurements of the temperature variation of the magnetic susceptibilities of anhydrous and hydrated copper (II) acetates were made by Figgis and Martin \([102]\), and Perakis \([103]\), in order to obtain more information about the nature of the copper-to-copper bond in the acetates. Figgis and Martin proposed that lateral overlap of the \( 3d_{x^2-y^2} \) orbitals of the copper (II) ions occurred, since the metal atoms were close to one another. This type of metal-metal interaction was called "\( \delta \)-bonding", and the bond was considered to be so weak that the configuration of the dimeric molecule could only be maintained by means of the four bridging acetate groups.

If the magnetic interaction of the copper (II) carboxylates originates from the direct copper-copper linkage, then the interaction would be expected to be affected by the distance between the metal ions. The magnetic interaction between metal ions is assumed to increase as the distance between the ions decreases. Thus, the short distance between the two copper (II) ions in copper (II) acetate monohydrate (2.64Å) \([104]\), leads to a fairly large magnetic interaction in the compound (1.43 B.M.). Similarly, a large magnetic interaction between the metal ions is also present in chromium (II) acetate, which is isostructural with copper (II) acetate \([105]\). As a result, the four
unpaired electrons of each chromium (II) ion become fully paired, and
the substance is diamagnetic at room temperature [106].

3.1.2 Absorption spectra

The visible and ultraviolet spectra of a large number of copper
(II) carboxylates and their derivatives have been measured in organic
solvents and on single crystals of the salts by a number of workers
[108-114].

Graddon made a study of the absorption spectra for a series of
copper (II) carboxylates in non-donor solvents, with carboxylic acids,
pyridine, dioxan, or water as axial ligands, (L in Fig. 3.1), and he
found that the spectra were similar in each case [108]. When ligand
(L) was a carboxylic acid, a strong absorption band was observed at a
wavelength of about 680 m\(\mu\) (\(\varepsilon\) ca. 200), and a shoulder on the ultra­
violet high-intensity band was present at about 375 m\(\mu\) (\(\varepsilon\) ca. 60).
The spectra were similar when ligand (L) was water, but the molar
absorptivity of the 680 m\(\mu\) band was somewhat lower (ca. 170) and the
375 m\(\mu\) band appeared as an inflexion on the ultraviolet band (\(\varepsilon\) ca.
66).

Typical spectra obtained in the present study from organic
solutions containing copper extracted into carbon tetra-chloride or
n-heptane with n-octoic acid are given in Fig. 3.2. The spectra were
measured on a Unicam S.P. 800 Spectrophotometer using glass cells
(1 cm.) against a reference solution containing n-octoic acid dissolved
in carbon tetrachloride or n-heptane. Both spectra show a band at
375 m\(\mu\) (\(\varepsilon\) ca. 60) which appears as a shoulder on the ultra-violet
high-intensity band, and also a band at about 680 m\(\mu\). The molar
absorptivity of the 680 m\(\mu\) band was reduced on changing the solvent
from carbon tetrachloride (\(\varepsilon\) ca. 240) to n-heptane (\(\varepsilon\) ca. 170).

The absorption band at about 680 m\(\mu\) has been assigned to the
Fig. 3.2. Absorption spectra from copper (II) extraction system.

- CuCl/NaCl-Octoic acid/Heptane system.
  \([\text{Cu}]_{\text{org}} = 8.9 \times 10^{-3} \text{ M/l}\)

- CuSO₄/Na₂SO₄-Octoic acid/Carbon tetrachloride system
  \([\text{Cu}]_{\text{org}} = 4.6 \times 10^{-3} \text{ M/l}\)
normal metal-ligand interaction, and is the so-called "copper band" [115, 116]. Graddon attributed the high-intensity band in the region of 300 μm to a charge transfer reaction of the type:

\[ R \text{CO}O^- + Cu^{2+} = R \text{CO}O^+ + Cu^+, \]

since the position of the band is not affected by variation in the axial solvating ligands (L in Fig. 3.1), but it is sensitive to changes in the carboxylate anions [108].

The nature of the band at 375 μm has not been completely settled. Thus, Tsuchida et al assumed that it was due to the copper-to-copper bond, since the polarised absorption spectra showed that the absorption at 375 μm was much stronger along the copper-to-copper bond than in the plane of the complex [111]. In addition, the band was not observed for crystals of copper (II) formate tetrahydrate, in which no direct metal-to-metal bond exists [111, 117].

A correlation is also found between the magnetic moments of various solutions of the copper (II) carboxylates and the presence of the 375 μm band. Thus when the carboxylates with subnormal magnetic moments are dissolved in highly coordinating solvents, which would be expected to lead to a break-up of the dimeric structure, the band is not observed, and the magnetic moment is normal. If a weakly coordinating solvent is used, however, the magnetic moment remains at a subnormal value, and the 375 μm band is present [110, 111, 118].

At the present time, it is believed that the appearance of a band at 375 μm does not prove the existence of a direct copper-to-copper bond since a number of copper (II) compounds, which are considered to be monomeric, have a band in this region. Thus, Graddon observed a peak at 375 μm in copper (II) acetylacetonate [119]. However, the band is observed in all the copper (II) carboxylates which have subnormal magnetic moments, and which are believed to be dimeric in non-
coordinating solvents.

A number of workers have obtained indirect evidence for the nature of metal-to-metal bonding in species by considering the variation in the metal-ligand and ligand vibrations in the infrared spectra [120].

Tsuchida et al found that sodium acetate and copper (II) formate, which have no dimeric structure, show a broad and strong antisymmetric CO O\(^-\) stretching frequency between 1560 and 1600 cm\(^{-1}\) [113]. On the other hand, they reported that many of the copper (II) carboxylates show a rather sharp and well defined band at 1595 to 1600 cm\(^{-1}\). Tsuchida et al proposed that the different features in the infrared spectra are due to the difference in the state of the carboxylate ions, and they considered this difference to be evidence for a dimeric structure in these carboxylates.

Fig. 3.3 shows an infrared spectrum which is typical of those obtained in the present study from organic phases containing copper (II) extracted from aqueous solution by n-octoic acid dissolved in n-heptane or carbon tetrachloride. The region of the spectrum shown covers a range from about 1300 cm\(^{-1}\) to 1800 cm\(^{-1}\), which includes the carboxylate stretching frequencies. The spectrum of n-octoic acid dissolved in n-heptane over the same range is also shown. The spectra were determined on samples of the organic solutions in an infrared cell with potassium bromide windows by using a Unicam S.P. 200 Spectrophotometer. The positions of the peaks were checked against the spectrum of polystyrene which was run on the same chart as the sample spectrum. The spectra of organic solutions containing copper (II) were also run on a Unicam S.P. 100 Spectrophotometer. This is a high-resolution instrument, and it was possible to measure the peak positions accurately from the spectra obtained.

Table 3.2 shows that in all the spectra measured of solutions
1 = n-octoic acid (1.00M)/n-heptane

2 = Cu/n-octoic acid/ n-heptane.

\[ [\text{Cu}]_{\text{org}} = 2.96 \times 10^{-3} \text{ M/L}. \]

Fig. 3.3 Infrared spectra from copper (II) extraction system.
<table>
<thead>
<tr>
<th>Extraction System</th>
<th>Organic phase</th>
<th>$\nu_{\text{CO O}^-}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO$_4$(10.68mM)/Na$_2$SO$_4$ - C Cl$_4$/n-Octoic acid (1.00M)</td>
<td>Cu(1.02 x 10$^{-2}$M)/n-Octoic acid/C Cl$_4$</td>
<td>1620</td>
</tr>
<tr>
<td>CuSO$_4$(5.00mM)/NaNO$_3$ - Benzene/Naphthenic acid (0.898M)</td>
<td>Cu(4.98 x 10$^{-3}$M)/Naphthenic acid/Benzene</td>
<td>1616</td>
</tr>
<tr>
<td>CuCl$_2$(10.68mM)/NaCl - n-heptane/n-Octoic acid (1.00M)</td>
<td>Cu(1.03 x 10$^{-2}$M)/n-Octoic acid/n-heptane</td>
<td>1620</td>
</tr>
</tbody>
</table>
containing a copper (II) carboxylate complex a sharp peak was observed at a frequency of about 1620 cm\(^{-1}\). This peak was not observed in the reference organic solutions which did not contain copper, but no differences were found in the other regions of the spectra.

Kuroda has measured the infrared spectra of a number of copper (II) carboxylates in dioxan [121]. For copper (II) n-octoate she reported a band at 1620 cm\(^{-1}\) and assigned this to the antisymmetric stretching frequency of the carboxylate group (\(\nu_{as} COO^\cdot\)).

3.1.3 Other physical methods.

A number of workers, including Graddorn [122], Tanaka et al [46], and Fletcher et al [45], have obtained evidence for dimeric structures in copper (II) carboxylates from equilibrium distribution studies. This evidence will be considered in more detail in Chapter 4.

Martin and Whitley reported that copper (II) carboxylates are non-conductors of electricity in benzene and dioxan, and cryoscopic measurements of the carboxylates in dioxan indicated that they were dimeric in structure [110]. In contrast, the magnetic susceptibility, electrical conductivity, and cryoscopic and spectroscopic evidence, indicated that in water the dimeric structure was destroyed. Ebullioscopic measurements of some copper (II) carboxylates in benzene made by Rai et al supported a dimeric structure [123].

The crystal structure of copper (II) acetate monohydrate was determined by X-ray analysis in 1953 by Niekerk and Schoening [104]. The monohydrate was shown to be binuclear molecule, Cu\(_2\)(CH\(_3\)COO)\(_4\)2H\(_2\)O, in which the copper (II) ions are bridged in pairs by four acetate groups with two water molecules occupying the terminal positions (Fig. 3.1; L = H\(_2\)O, R = CH\(_3\)). The distance between the two copper (II) ions (2.64 Å) is only slightly greater than the interatomic distance in metallic copper (2.56 Å), and the copper (II) ion is 0.22 Å out of the
plane of the four oxygen atoms.

\[ \text{Cr}_2(\text{CH}_3\text{CO}_0)_4 \cdot 2\text{H}_2\text{O}, [105], \quad \text{and Mo}_2(\text{CH}_3\text{CO}_0)_4', [125], \]

have been shown to have similar structures to the copper complex, although in the molybdenum acetate the metal atoms are drawn inside the parallel plane of the oxygen atoms.

Cotton, in a recent review article on metal-to-metal bonds, has compared the metal-metal distances in copper (II), chromium (II), and molybdenum (II) acetates, and he has used them as a diagnostic test for the presence or absence of a metal-to-metal bond [125]. The extremely short molybdenum-molybdenum bond distance in \( \text{Mo}_2(\text{CH}_3\text{CO}_0)_4 \) (2.11 Å) is considered evidence of a structural metal-to-metal bond, whereas Cotton considers the copper-copper and chromium-chromium distances (both 2.64 Å) to indicate no such bond.

Although nuclear magnetic resonance measurements have been made by a number of workers to obtain information about the structures of coordination compounds, the technique does not appear to have been applied to the metal-carboxylate complexes. Since these contain hydrogen atoms, each kind of proton should show a resonance at a part of the proton magnetic resonance spectrum that is characteristic of its environment in the complex.

In the present study, proton magnetic resonance measurements were made on a series of organic solutions containing copper (II) extracted from various aqueous solutions with carboxylic acids dissolved in organic solvents. The measurements were made using a Perkin Elmer R10 Nuclear Magnetic Resonance Spectrometer, and the chemical shifts of the signals were measured relative to tetramethylsilane (TMS) contained in the solutions as an internal standard. The band widths of peaks were measured at half the peak heights in cycles per second (cps).

The results from the measurements are summarised in Table 3.3.
Table 3.3 Proton Magnetic Resonance data from copper (II)/carboxylic acid/organic solvent systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Acid Proton (T)</th>
<th>Peak Width (cps)</th>
<th>System</th>
<th>Acid Proton (T)</th>
<th>Peak Width (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Octoic acid/C Cl₄ (1.00M)</td>
<td>-2.06</td>
<td>2</td>
<td>n-Octoic acid/C Cl₄/2.06 x 10⁻³ M Copper</td>
<td>-2.10</td>
<td>4</td>
</tr>
<tr>
<td>n-Octoic acid/n-Heptane (1.00M)</td>
<td>-2.30</td>
<td>2</td>
<td>n-Octoic acid/n-Heptane/2.96 x 10⁻³ M Copper</td>
<td>-2.26</td>
<td>6</td>
</tr>
<tr>
<td>n-Octoic acid/n-Heptane (0.550M)</td>
<td>-2.37</td>
<td>1.5</td>
<td>n-Octoic acid/n-Heptane/2.46 x 10⁻³ M Copper</td>
<td>-2.48</td>
<td>2</td>
</tr>
<tr>
<td>Naphthenic acid/Benzene (0.898N)</td>
<td>-2.40</td>
<td>3</td>
<td>Naphthenic acid/Benzene/5.3 x 10⁻³ M Copper</td>
<td>-2.15</td>
<td>12</td>
</tr>
</tbody>
</table>
The signals observed in the region 7-9 (τ) for all solutions containing n-octoic acid were similar both in their positions and character. In the case of naphthenic acid in benzene, the signals in this region were rather broad due to the branched structure of the acid. The presence of metal ions in the organic solutions appeared to have little effect on the signals in this region. The peaks at ca. 9.1, 8.6, and 7.8 (τ) were attributed to the protons of the terminal methyl group, the methylene groups in the alkyl chain, and the methyl group in the α-position to the carboxyl group, respectively [128]. The signals in the region 7-9 (τ) are not included in Table 3.3.

The signals from the protons of the carboxyl groups of the carboxylic acids were observed in the range of -2.1 to -2.4 (τ). The differences in the positions of the acid proton signals were probably due to solvent effects. In the absence of any metal ions in the organic phase, the peaks were sharp (ca. 2 cps) and only a single signal was observed in the range of -2.1 to -2.4 (τ) for each solution examined. In the presence of copper, the acid proton peak broadened as the copper concentration increased, but again only a single peak was observed in each case. The single resonance observed may correspond to the average environment of the protons from the solvating acid molecules (L in Fig. 3.1) and those from the dimeric carboxylic acid in the organic phase.

3.1.4 The structures of copper (II) compounds.

The characteristic shape of the coordination shell of copper (II) is either an octahedron, which is distorted by stretching along one axis, or a square planar structure, which is in fact the limiting case of the distortion [106].

In copper sulphate pentahydrate (Cu SO₄ 5H₂ O), for example, each copper (II) ion is surrounded by four water molecules at the corners of
a square, and two oxygen atoms from the sulphate anions occupy each axial position to complete an elongated octahedron as shown in Fig. 3.4. The fifth water molecule is not coordinated to the copper (II) ion, but it is hydrogen bonded between a second sulphate oxygen and a bound water molecule in the plane [129].

In the case of the dimeric structure postulated for the copper (II) carboxylates (Fig. 3.1) the metal atoms are surrounded in a square plane by the four bridging oxygen atoms of the carboxylate groups. When the ligand (L) is water or some other molecule (e.g. carboxylic acid), each copper atom has a distorted octahedral coordination.

3.2 The nickel (II) - carboxylic acid system

In comparison to copper (II) acetate monohydrate, Niekerk and Schoening found that the crystal structure of the nickel (II) acetate complex, Ni(CH₃COO)₂ 4H₂O, indicated a monomeric structure [130]. The nickel atom was surrounded octahedrally by four water molecules and by two oxygen atoms which belonged to different acetate groups.

In general, the complexes of the nickel (II) ion (d⁸) can be classed into one of three structural types; octahedral, tetrahedral, or square planar. The visible absorption spectra for the first two structures are distinctive, and only a few complexes are known definitely to have the square planar structure [106].

The visible spectra of octahedral nickel (II) complexes have several distinguishing features. From a consideration of the energy level diagram for (d⁸) ions in an octahedral field, three spin-allowed transitions are expected, and bands in the ranges 8,000 - 11,000 cm⁻¹, 12,000 - 19,000 cm⁻¹ and 25,000 - 29,000 cm⁻¹ are generally observed. In addition, the molar absorptivities of the bands are at the low end of the range for octahedral complexes of the first transition series in general i.e. 1-10 [106]. Octahedral nickel (II) complexes should
Fig. 3.4. Crystal structure of CuSO$_4$·5H$_2$O. [129]
have two unpaired electrons from the orbital splitting diagrams, and this has been found to be the case, with magnetic moments from 2.9-3.4 B.M. [106].

The energy level diagram for a \((d^8)\) ion in a tetrahedral field shows that there should be an absorption band around \(15,000\text{cm}^{-1}\), and also one at \(7,000 - 8,000 \text{cm}^{-1}\). In addition, the bands in the spectra have relatively high molar absorptivities e.g. the visible band usually has a value of about 200. Most tetrahedral nickel (II) complexes are blue in colour, due to the presence of the absorption band in the red part of the visible spectrum. It is also found that for a \((d^8)\) ion in a tetrahedral field there are always two unpaired electrons, no matter how strong the ligand field [106].

Fig. 3.5 shows two absorption spectra which are typical of those measured in the present study from organic phases containing nickel (II) extracted from aqueous solution with n-octoic acid dissolved in n-heptane. The spectra were measured in an analogous manner to those in the copper (II) system. In these spectra, two main peaks are evident. The one at about \(400 \text{m} \mu\) (\(\varepsilon\) ca. 10) is sharp in comparison to the broad peak at about \(700 \text{m} \mu\) (\(\varepsilon\) ca. 4), which in fact appears to consist of two peaks. The spectrum is similar to the absorption spectrum of \([\text{Ni(H}_2\text{O)}_6]^{2+}\), which is octahedral in structure [106]. This consists of bands at \(1,175 \text{m} \mu\) (\(\varepsilon\) ca. 2.0), \(740 \text{m} \mu\) (\(\varepsilon\) ca. 1.8), \(650 \text{m} \mu\) (\(\varepsilon\) ca. 1.5) and \(396 \text{m} \mu\) (\(\varepsilon\) ca. 5.2). The band between \(650-740 \text{m} \mu\) appears as a broad peak with a small split due to spin-orbit coupling [106].

A number of nickel (II) complexes which were originally believed to have a square planar structure have now been shown to have more complicated structures. Thus bis (dimethylglyoximato) nickel (II) which exists in non-coordinating solvents as a square-planar structure and is diamagnetic, in the solid state has an octahedral structure.
Fig. 3.5 Absorption spectra from nickel (II) extraction system.

--- NiSO₄/KNO₃-Octoic acid/Heptane system. [Ni]ₜₐₐ = 1.08 x 10⁻² M/l.

--- NiSO₄/KNO₃-Octoic acid/Heptane system. [Ni]ₜₐₐ = 4.8 x 10⁻³ M/l.
Fig. 3.6 Absorption spectra from cobalt (II) extraction system.

--- CoSO₄/Na₂SO₄-Octoic acid/Heptane

[Co]₀rg = 7.52 x 10⁻³ M/ℓ

--- CoSO₄/Na₂SO₄-Octoic acid/Heptane

[Co]₀rg = 3.50 x 10⁻³ M/ℓ
This is because a nickel-to-nickel bond is formed \([106, 120]\). Also, nickel (II) acetylacetonate associates into trimers by the sharing of oxygen atoms both in the crystal state and in solution in non-coordinating solvents \([106]\).

Evidence for a dimeric structure in nickel (II) carboxylates of the form \([\text{Ni R}_2 2\text{RH}]_2\) has been found from equilibrium distribution studies by Fletcher et al \([45]\). These results will be considered in Chapter 4. Tappmeyer and Davidson also found evidence for nickel (II) acetate dimers in anhydrous acetic acid \([131]\).

3.3 The cobalt (II) - carboxylic acid system.

Niekerk and Schoening found that cobalt (II) acetate, \(\text{Co(CH}_3\text{CO O})_2 4\text{H}_2\text{O}\), was isostructural with the nickel complex, in which the metal atom is surrounded octahedrally by four water molecules and by two oxygen atoms which belong to different acetate groups \([130]\). They found no evidence for a dimeric structure in the complexes.

The cobalt (II) ion has a \((d^7)\) electronic configuration and it can form both octahedral and tetrahedral types of complexes. The normal state for a \((d^7)\) ion in an octahedral field should be with three unpaired electrons, but for ligands with high fields (e.g. \(\text{CN}\)) pairing of the electrons occurs to leave only one unpaired electron \([106]\).

An octahedrally coordinated cobalt (II) ion should have three spin-allowed d-d transitions. In \([\text{Co(H}_2\text{O})_6]^{2+}\) a peak appears at about 540 m\(\mu\) (\(\varepsilon\) ca. 10) and a shoulder on the peak appears at about 490 m\(\mu\) (\(\varepsilon\) ca. 5.). A third peak appears in the near infrared region. The visible absorption spectrum is rather weak, and is placed in the blue end of the spectrum: which accounts for the pale pink colour of \([\text{Co(H}_2\text{O})_6]^{2+}\).

From the orbital splitting diagram for a \((d^7)\) ion in a tetrahedral field, the complexes should have three unpaired electrons
irrespective of the strength of the ligand field, and from an energy level diagram, three spin-allowed transitions are expected [106]. The spectra of tetrahedrally coordinated cobalt (II) complexes have high molar absorbances in comparison to the octahedral complexes, and the absorption is towards the red part of the spectrum. This accounts for the deep blue colour of most tetrahedral cobalt (II) complexes.

Fig. 3.6 shows two absorption spectra which are typical of those measured in the present study from organic phases containing cobalt (II) extracted from aqueous solution with n-octoic acid dissolved in n-heptane. The organic phases containing small amounts of cobalt were pale yellow in colour, but as the loading increased, the solutions deepened in colour to give a straw colour. A broad peak was observed in these straw-coloured solutions at about 550 m\(\mu\) (\(E\) ca. 63), which probably consisted of two peaks at about 520 m\(\mu\) and 560 m\(\mu\). The spectra of the pale yellow solutions were less defined, and a plateau region was observed at about 550 m\(\mu\) (\(E\) ca. 63). The difference between the two spectra may indicate that more than one complex is present in the system.

Evidence for a dimeric structure in cobalt (II) carboxylates has been obtained by a number of workers. Thus Fletcher et al obtained evidence from equilibrium distribution studies for species of the form [Co \(R_2 2RH\)]\(_2\) in solution [45]. Tanaka et al reported that in the organic solutions from the extraction of cobalt (II) solutions with n-decoic acid, a dimeric complex was formed at the higher concentrations, while a monomer prevailed at lower concentrations [95]. The monomer was reported to contain hexacoordinated cobalt (II), while a structure involving cobalt-to-cobalt bonds was proposed for the dimer. Schweitzer et al, however, carried out radiochemical tracer studies of the solvent extraction of some cobalt (II) chelates, and they found that in organic phases containing n-octoic acid/1-octanol and n-hexoic
acid/l-hexanol, a monomeric species (Co $R_2$) predominated [132]. These results from equilibrium distribution studies will be considered in more detail in Chapter 4.

Further evidence for the existence of dimeric cobalt (II) carboxylates came from the work of Benson et al, who studied the reaction between cobalt (II) and lead (IV) acetates in acetic acid [133]. They found that the order of the reaction with respect to plumbic acetate is unity under all conditions, whereas with respect to cobaltous acetate the reaction is non-integral and can be varied by the addition of plumbous acetate. The authors accounted for these facts by postulating dimeric cobalt (II) species in the reaction mechanism. In a later study, Proll et al concluded that cobalt (II) exists to a slight extent in a polynuclear form in anhydrous acetic acid [134]. Tappmeyer et al also considered that cobalt (II) acetate dimers can be found in anhydrous acetic acid [131].

The results obtained from some proton magnetic resonance measurements made on organic phases containing cobalt (II) extracted from aqueous solutions with n-octoic acid dissolved in n-heptane are summarised in Table 3.4. The positions and band widths of the carboxyl proton peaks are noted. As found in the case of the copper (II) systems, the peaks broaden as the concentration of metal ions in the organic phase increases, but only a single peak is obtained. The other regions of the spectrum appear to be unchanged by the presence of the cobalt (II) ions.
Table 3.4: Proton magnetic resonance data from cobalt (II) – n-octoic acid/n-heptane systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Acid proton (ppm)</th>
<th>Peak width (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-octoic acid/n-heptane (1.00 M)</td>
<td>-2.4</td>
<td>2</td>
</tr>
<tr>
<td>n-octoic acid/n-heptane (1.00 M)/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.38 x 10⁻³ M cobalt</td>
<td>-2.35</td>
<td>9</td>
</tr>
<tr>
<td>n-octoic acid/n-heptane (1.00 M)/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.52 x 10⁻³ M cobalt.</td>
<td>-2.15</td>
<td>14</td>
</tr>
</tbody>
</table>

3.4 A consideration of the dimeric structure of some metal carboxylates in solution

The factors which control the formation of the dimeric structures of metal carboxylates in solutions are complex, but a number of general points can be made.

The dimeric structure of the copper (II) acetate type has been confirmed in compounds with copper (II) and chromium (II) ions, both of which have an odd number of electrons in the (dₓ) orbitals. This suggests that one of the conditions necessary for the formation of the dimeric structure is the easy removal of one of the ligands (L in Fig. 3.7) which are bound by weaker bonds in a distorted octahedral complex ion [100].

The formation of the dimeric structure is much more favourable in organic solvents than in water, in which it is destroyed to give monomeric, hydrated, ions [135]. If the formation of the dimeric structure takes place as indicated in Fig. 3.7, then the system will gain entropy on the right hand side of the equation, since the total number of molecules on this side is greater than on the left hand side [11]. This may be one of the reasons why the dimeric structure can be retained in organic solvents, even though the bonds between the
Fig. 3.7 Proposed system for formation of dimeric copper (II) carboxylates
metal ions and the carboxylate ions are considered to be rather weak [100].

In general, the solvents which strengthen the coordinate bonds in copper (II) carboxylates promote both the formation of dimeric molecules in solution and also the magnetic interaction between the copper (II) ions. The bonds between the carboxylate and copper (II) ions are strengthened as the dielectric constant of the solvent decreases. Solvent molecules with strong coordination power, such as water, may replace the oxygen bonds of the carboxylate and lead to a breakdown of the dimeric structure [100]. Whether the dimeric structure is maintained in a particular solvent, is determined by the bonding competition between the carboxylate ions and the solvent molecules.

3.5 A consideration of possible structures for metal carboxylates in solution.

In the case of the metal (II) - carboxylic acid system, a number of complexes can be formulated which may exist in solution depending on the conditions.

The structure of a monomeric metal (II) - carboxylic acid complex, (MR), could be formulated in two ways, viz:

![Diagram](image)

(I)  (II)
In structure (I), a four-membered ring is formed by using the two equivalent oxygen atoms of the carboxylate group to bond to the metal (M), unless another coordinating ligand, such as an alcohol or water, is present. In this case, structure (III) could be postulated:

![Structure III]

If the monomeric complex, (MR), is formed without chelation, as indicated in (II), then a C=O bond is exposed, which is rather unlikely in view of the preference of carboxylic acids for dimer formation whenever possible.

Complexes of the form (MR) may be present in only small amounts in non-polar organic solvents, since the dimeric structure of the acid is strongly favoured in these conditions. However, increasing amounts of the monomeric complex may be present as the solvent becomes more polar, and hence the proportion of monomeric acid increases. In addition, in the presence of a coordinating solvent, the monomeric complex will be stabilised to some extent as shown in (III).

If one of the acidic hydrogen atoms of the dimeric carboxylic acid is removed by ionisation, then the resulting singly-charged anion could be capable of chelation with a positively charged metal ion. Thus, if the remaining hydrogen bond is assumed to be unbroken, the M(H(RCOO))₂ complex that would be formed can be represented as in (IV):
Peppard et al have postulated a similar structure in the case of metal-alkylphosphoric acid complexes [195, 196]. The alkylphosphoric acids have also been shown to have a similar dimeric structure in some organic solvents to the carboxylic acids [195].

If the other hydrogen atom in structure (IV) is replaced by a metal atom, then an eight-membered ring (V) could be postulated:

Sidgwick suggested a similar structure in the case of the polynuclear ferric carboxylates, and considered that an unstrained ring was formed in the complex, presumably by the "puckering" of the ring [197].

Complexes of the form (MR₂) could be formed if two carboxylate groups are linked to the metal atom (M). Although this complex could have a structure based on either a square-plane or a tetrahedron, the latter form would probably be favoured as a result of steric strain in the planar structure. The tetrahedral complex could be postulated as in (VI):
However, the formation of complexes \((\text{MR}_2)(\text{RH})\) and \((\text{MR}_2)(\text{RH})_2\), where the \(\text{RH}\) represents a carboxylic acid molecule, could be formed by addition of the acid molecules to the square planar form of the \((\text{MR}_2)\) complex. The resulting octahedral complex in the case of \((\text{MR}_2)(\text{RH})_2\) could be formulated as in (VIII):

\[
\text{RH} \\
\text{R-C} \quad \text{M} \quad \text{C-R} \\
\text{RH} \\
(VII)
\]

In order for a dimeric structure of the copper (II) acetate type i.e. \((\text{MR}_2)_2(\text{RH})_2\) to be formed from structure (VII), it is necessary for one of the solvating ligands (RH) to be removed from the complex. Two molecules of the resulting \((\text{MR}_2)(\text{RH})\) complex can then be linked by carboxylate bridges to give the dimeric structure as indicated in Fig. 3.7.

For further units to be built-up from this basic dimeric structure, it would be necessary to postulate the formation of hydrogen-bonds between the solvating acid molecules (L in Fig. 3.7).
of two dimeric entities.

A number of studies have been reported in the literature on the cobalt (II) - carboxylic acid system. Tanaka et al obtained evidence for a complex of the form \((\text{CoR}_2)(\text{RH})_4\) at low loading of the organic phase, and \((\text{CoR}_2)_2(\text{RH})_4\) as the loading increased [95]. Fletcher et al also postulated cobalt (II) and nickel (II) complexes of the form \((\text{MR}_2)_2(\text{RH})_4\) from a study of the equilibrium distribution data [45], but they did not propose any structures for these complexes. In addition, Schweitzer et al reported that a monomeric species of the form \((\text{CoR}_2)\) was formed in solution [132].

The monomeric cobalt complex \((\text{CoR}_2)(\text{RH})_4\) is presumably based on an octahedral structure, which is quite common for Co(II) complexes. The two carboxylate groups occupy two coordination positions, respectively, in the structure, and the other solvating acid molecules (RH) may fill the other positions in the octahedral structure or be hydrogen-bonded to the complex.

If the dimeric cobalt complex, \((\text{CoR}_2)_2(\text{RH})_4\), is based on the copper (II) acetate structure, it would be necessary for the additional two carboxylic acid molecules to be associated with the solvating acid molecules (L in Fig. 3.7), presumably by hydrogen bonding. This would seem to be rather unlikely in view of the fact that a similar structure has not been reported for the copper (II) complex.

An alternative dimeric structure could be proposed if two carboxylate groups are used to bridge the \((\text{CoR})(\text{RH})_2\) units together, as indicated in (VIII):
A similar chain structure using carboxylate and hydroxyl groups as bridges to link-up the metal atoms has been proposed by Küntzel in the case of the chromium-carboxylic acid complexes [198, 199]; viz:

\[
\begin{align*}
\text{(IX)}
\end{align*}
\]

The action of the carboxylate group as a bridging group between metal atoms has been known for some time. Thus the acetate and formate groups often bridge two metal atoms together by using each oxygen atom of the group to form a bond to a different metal atom [198]:

\[
\begin{align*}
\text{(X)}
\end{align*}
\]

Thus in the beryllium carboxylate salts, \( \text{Be}_4\text{O(R.COO)}_6 \), a central
oxygen atom is surrounded tetrahedrally by four beryllium atoms, and each edge of the tetrahedron is composed of the grouping [198]:

\[
\text{Be} - \text{O} \quad \equiv \quad \text{C} \quad \equiv \quad \text{O} - \text{Be}
\]

(XI)

It has been confirmed by X-ray crystal structure determinations that the acetate anion, and presumably other carboxylate anions, can coordinate with a metal ion in one of the following ways:

(XII)

(XIII)

(XIV)

(XV)

Thus, sodium formate has been shown by X-ray analysis to have structure (XII), and to have two C-O bonds of equal length [200]. Structure (XIII) occurs in Li(CH₃COO)₂H₂O and the two C-O bonds are found to be of different lengths [201]. This structure has also been found quite frequently among the carboxylates of metals of higher valency. The bidentate structure (XIV) has been reported for Zn(CH₃COO)₂H₂O [202], and Na[UO₂(CH₃COO)₃] [203]. The bridged structure (XV) has been confirmed for Cu₂(CH₃COO)₄·2H₂O [104], Cr₂(CH₃COO)₄·2H₂O [105], and Mo₂(CH₃COO)₄ [125].

Table 3.5 contains a summary of the complexes which are considered most likely to exist in the organic phases resulting from the extraction of copper (II), cobalt (II), and nickel (II) ions by carboxylic acids. The list of complexes is intended to serve as a guide in the interpretation of the extraction data by graphical and statistical methods which is made in the following chapter.
<table>
<thead>
<tr>
<th>Copper (II) system</th>
<th>Cobalt (II) system</th>
<th>Nickel (II) system</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuR₂</td>
<td>CoR₂ [132]</td>
<td>NiR₂</td>
</tr>
<tr>
<td>CuR₂.2RH</td>
<td>CoR₂.2RH</td>
<td>NiR₂.2RH</td>
</tr>
<tr>
<td>CuR₂.4RH</td>
<td>CoR₂.4RH [95]</td>
<td>NiR₂.4RH</td>
</tr>
<tr>
<td>(CuR₂)₂</td>
<td>(CoR₂)₂</td>
<td>(NiR₂)₂</td>
</tr>
<tr>
<td>(CuR₂)₂(RH)₂ [45]</td>
<td>(CoR₂)₂(RH)₂</td>
<td>(NiR₂)₂(RH)₂</td>
</tr>
<tr>
<td>(CuR₂)₂(RH)₄</td>
<td>(CoR₂)₂(RH)₄ [45, 95]</td>
<td>(NiR₂)₂(RH)₄ [45]</td>
</tr>
</tbody>
</table>
CHAPTER 4

An Experimental Study of the Equilibrium Distribution of Metal Ions between Aqueous Solutions and Organic Phases containing Carboxylic Acids
4.1 An Experimental Study of the Equilibrium Distribution of Metal Ions

In order to obtain information about the structures of species involved in the extraction of various metal ions with carboxylic acids, a series of distribution studies has been carried out. The distribution of the metal ions between aqueous solutions and organic solvents containing the carboxylic acids has been studied at chemical and thermal equilibrium. The distribution has been measured as a function of the pH of the equilibrium aqueous phase and of the carboxylic acid and total metal ion concentrations. In addition, the nature of the organic phase has been varied, and the effect on the distribution of the metal ions of various anions and supporting electrolytes in the aqueous solutions has been measured.

4.1.1 Carboxylic acids.

The straight-chain carboxylic acids, n-octoiic acid (melting-point 15-16°C) and n-decoic acid (melting-point 29-30°C) were obtained from the Eastman Kodak Company and they were used without further purification. A sample of a naphthenic acid (N.A. 230(S.P.)) was obtained from the Shell Chemical Company, and it was used without further purification.

4.1.2 Organic solvents.

The organic solvents used in the study were benzene, n-heptane and carbon tetrachloride.

Benzene was purified by washing it with concentrated sulphuric acid to remove thiophene, then with distilled water and dilute sodium hydroxide solution, and finally with two portions of distilled water. It was dried by distilling it from phosphorus pentoxide [136].

n-Heptane (B.D.H., IP specification) was distilled from a five foot fractionation column (Todd Scientific Company) filled with Fenske rings, and the fraction which would distil at 98.4°C under standard pressure conditions was collected. Samples of the distillate were
tested for impurities by vapour phase chromatography, using a column containing a stationary phase of squalane, at a temperature of 70°C. No impurities were detected by this method in the samples of n-heptane that were examined.

The sample of carbon tetrachloride (B.D.H., Analar grade) was used without further purification, after checking its ultraviolet spectrum. The fact that no narrow absorption band was observed with a maximum at a wavelength of 318 m\(\mu\) (\(\varepsilon = 108\)) indicated that the concentration of any carbon disulphide present in the carbon tetrachloride was less than about 5 \(\times 10^{-5}\) M [137].

4.1.3 The preparation of solutions

The standard solutions of n-octoic acid and n-decoic acid were made up by weight in the required volumes of the organic solvents. The solution of naphthenic acid in benzene was made up to approximate strength by weight and it was then estimated by titration with standard sodium hydroxide solution to the phenolphthalein end-point using a standard procedure [138]. The acid value of the naphthenic acid, defined as the number of milligrams of potassium hydroxide required to neutralise the free acid in one gram of the sample, was found to be 346 by using this titration procedure. Hence the average molecular weight of the sample of naphthenic used was 162, which is equivalent to a carboxylic acid containing 9 carbon atoms.

In order to be able to compare directly the results obtained from the equilibrium distribution studies with those from the interfacial tension and extraction-column studies described later, considerable care was taken to avoid contamination of the solutions, especially by surface active impurities. All the aqueous solutions used throughout the work were prepared using water which was obtained by distilling deionised water twice from a quartz still. The conductivity of the
water was less than 1 \( \mu \text{mho cm}^{-1} \), and the surface tension was 71.8 dynes cm\(^{-1} \) at 25\(^\circ\)C by du Nouy tensiometer. The water from the still was stored in large glass flasks which had been thoroughly cleaned with chromic acid and then washed well with distilled water before use. All the other glassware used was cleaned prior to use by soaking it in chromic acid for a considerable time. It was then washed free of chromic acid with copious amounts of distilled water and dried in an oven.

The aqueous metal ion solutions were prepared as follows. Solutions of copper, cobalt, sodium and potassium salts were made up by weight in the required volumes of water from the respective salts (B.D.H., Analar grade). The aqueous solutions of nickel sulphate were made by dilution of a concentrated standard solution (prepared from Analar grade nickel sulphate, B.D.H.). This standard solution was analysed for its nickel concentration by a gravimetric determination of the nickel dimethylglyoxime complex [139]. Sodium or potassium salts (Analar grade, B.D.H.) were used to adjust the ionic strengths of the aqueous metal ion solutions as required.

4.1.4 Determination of the equilibrium distribution of the metal ions.

The distributions of the metal ions between equal volumes of aqueous solutions and organic solvents containing the carboxylic acids were carried out in clean, dry, glass tubes which were fitted with ground-glass stoppers. The pH of each aliquot of aqueous solution was adjusted with a small volume of concentrated sodium hydroxide solution (B.D.H., Analar grade) before it was contacted with an equal volume of the organic phase. The tube was then stoppered securely and sealed with a strip of "Parafilm" (a thermoplastic sealing tissue, Gallenkamp) around the ground-glass joint to prevent any leakage of the contents. It was then placed on a disc which could be rotated vertically to produce end-over-end shaking of the contents of the tube. The disc and
tube were placed in a thermostat tank, which was kept at a constant temperature of 25 ± 0.05°C, and rotated at a rate of about 15-20 revolutions per minute for one hour. Preliminary experiments showed that after this period of agitation the contents of the tube were in chemical and thermal equilibrium.

After one hour, the disc was stopped and the contents of the tube were allowed to separate. The phase separation was quite rapid and complete in most cases, especially where supporting electrolyte was present in the aqueous solution. In other cases, the separation of the phases was aided by centrifuging the tubes for a short time. No change in the phase volumes with the distribution of the metal ions was detected in the case of copper, cobalt and nickel extractions. In the case of sodium and potassium extractions, a change in the phase volume was observed at the higher range of extraction.

Aliquots of both equilibrium phases were removed from the tube as carefully as possible to prevent any back-mixing of the phases. The aliquots were then analysed for their respective metal ion concentrations, and the pH of the equilibrium aqueous phase was measured. In order to analyse the organic phases, they were stripped of metal ions by contacting them with known volumes of hydrochloric acid (0.2M) for one hour using the rotating disc. It was found that the metal ions were quantitatively back-extracted into the aqueous phase by this method. The metal ion concentrations of aliquots of the equilibrium aqueous phases and the acid-stripped equilibrium organic phases were determined by colorimetric analysis. The sodium and potassium ion concentrations of the acid-stripped equilibrium organic phases were determined by flame photometric analysis of aliquots of the phases.

4.1.5 The colorimetric determination of copper.

Copper forms a violet-coloured complex in aqueous solution with
bisacetaldehyde-oxalyldihydrazone in the pH range of 7-10, [140-143]. This complex is stable for at least one week if the solution is kept out of direct sunlight. The method was chosen for the colorimetric determination of copper because it had the advantage that all the reagents used and the coloured complex that was formed were in aqueous solution in comparison to some other colorimetric methods in which the copper complex has to be extracted into an organic solvent e.g. the copper-diethyldithiocarbamate complex. In addition, because of the high molar absorptivity (ca. 22,000) at the wavelength of maximum absorption, the method is very sensitive to small amounts of copper [141].

For the determination, the following reagents were prepared [140]:
a saturated aqueous solution of oxalyldihydrazide (B.D.H., Laboratory reagent), which is reported to be stable for one month [142]; a 40 per cent solution of acetaldehyde (B.D.H., Analar grade) in water; and ammonium hydroxide solution, made by diluting 30 mls 0.880 ammonia B.D.H., Analar grade) to 100 mls with water.

The following procedure was adopted for carrying out the determination [140]. An aliquot of the sample solution containing less than 50 \( \mu g \) copper was transferred to a 25 ml graduated flask. Ammonium hydroxide solution (1 ml), saturated oxalyldihydrazide solution (1 ml) and acetaldehyde solution (2 mls) were then added in this order and the volume was made up to 25 mls with water. A violet colour developed in the solution at once, and it reached its maximum intensity after two hours. The absorbance of the solution was measured, after at least three hours had been allowed for the colour to develop, at a wavelength of 536 m\( \mu \) against a blank solution prepared in a similar manner. A Unicam S.P.600 spectrophotometer was used to measure the absorbance of the solutions in 1cm matched-glass cells. A calibration plot of absorbance as a function of copper concentration was linear up to a concentration of 50 \( \mu g \) of copper and hence the Lambert-Beer law is
obeyed within this range of concentration. The aliquots of the equilibrium phases which contained copper were diluted to give absorbance readings within this range when they were complexed with oxalyldihydrazide. A value of 22,110 for the molar absorptivity at a wavelength of 536 m\(\mu\) was obtained from the slope of the graph of absorbance as a function of copper concentration. In comparison, Stevancevic obtained a value of 23,600 at a wavelength of 542 m\(\mu\) [141], and Irving et al obtained a value of 23,900 at a wavelength of 536 m\(\mu\) [140].

4.1.6 The colorimetric determination of nickel.

A convenient method for the colorimetric determination of nickel involves the formation of the complex between nickel and ammoniacal dimethylglyoxime after the nickel has been oxidised [139]. The reddish-brown coloration formed in the presence of an oxidising agent, such as iodine, is probably due to the soluble nickelic dimethylglyoxime complex. The interference produced by the presence of iron may be overcome by the use of ammonium citrate and ammonium hydroxide solutions.

For the determination the following reagents were prepared [144]: an aqueous ammonium citrate solution, made by adding citric acid (500g Analar grade, B.D.H.) to ammonia (500 mls 0.880 ammonia, Analar grade B.D.H.) and then diluting the mixture to one litre; a 0.1N iodine solution, made by dissolving iodine (12.692g Reagent grade, B.D.H.) and potassium iodide (25g Analar grade, B.D.H.) in water and diluting to one litre; ammoniacal dimethylglyoxime solution, made by dissolving dimethylglyoxime (1g Laboratory reagent, B.D.H.) in ammonia (500 mls 0.880 ammonia, Analar grade B.D.H.) and then diluting to one litre.

The following procedure was adopted for carrying out the determination [144]. An aliquot of the sample solution containing less than 420 \(\mu g\) nickel was added to a 100 mls graduated flask,
and ammonium citrate solution (10 mls) and iodine solution (5 mls) were added, shaking the flask after each addition. The flask was allowed to stand for two minutes, before the ammoniacal dimethylglyoxime solution (25 mls) was added while shaking the flask. The contents of the flask were then diluted to 100 mls with water, and the flask was allowed to stand for a further five minutes. The absorbance was measured within 5-20 minutes of preparation of the solution at a wavelength of 445 m\(\mu\) (\(\lambda_{\text{max}}\)) against a blank solution prepared in a similar way. A Unicam S.P. 600 spectrophotometer was used to measure the absorbance of solutions in 1 cm matched-glass cells. A calibration plot of absorbance as a function of nickel concentration was linear up to a concentration of 425 \(\mu\)g nickel and hence the Lambert-Beer law is obeyed within this concentration range. All aliquots of the equilibrium phases which contained nickel were diluted to give absorbance readings within this range when they were complexed with dimethylglyoxime. A value of 11,760 was obtained for the molar absorptivity at a wavelength of 445 m\(\mu\) from the slope of the graph of absorbance as a function of nickel concentration. No literature value of the molar absorptivity could be found for the determination of nickel under the same experimental conditions as described above.

4.1.7 **The colorimetric determination of cobalt.**

An excellent method for the colorimetric determination of cobalt is based on the soluble red complex that is formed when cobalt ions react with an aqueous solution of nitroso-R-salt (sodium 1-nitroso-2-hydroxynaphthalene-3, 6-disulphonate) [145]. The reaction proceeds only slowly in acid solution, but when the free acid is neutralised with sodium acetate the formation of the complex is rapid. The resulting colour is very slightly dependent on the pH of the solution, but by the use of a constant amount of sodium acetate the significance
of this effect is reduced. Although other metals produce coloured complexes with the nitroso-R-salt, these are destroyed by treatment with nitric acid. The cobalt complex is only slightly affected by prolonged boiling with nitric acid [145].

For the determination of the cobalt the following reagents were prepared [145]: a 50 per cent (w/v) solution of sodium acetate trihydrate (B.D.H. Analytical grade) in water; a 0.75 per cent (w/v) solution of nitroso-R-salt (Organic reagent, Hopkin and Williams, Ltd.) in water; a 1:2 nitric acid: water mixture (the nitric acid was a Micro-Analytical Reagent, B.D.H.).

The following procedure was adopted for carrying out the determination [145]. An aliquot of the sample solution containing less than 180 \( \mu g \) cobalt was added to a 50 mls graduated flask, and sodium acetate solution (5 mls) and nitroso-R-salt solution (5 mls) were added. The pH of the mixture was checked at this point and if necessary it was adjusted with sodium acetate solution to give a pH of 5.5 ± 0.5. The flask was then heated in boiling water for 6-10 minutes, before nitric acid solution (5 mls) was added and the heating continued for a further 2-4 minutes. The flask was then cooled to room temperature and the contents were diluted to 50 mls with water. The absorbance was measured as soon as possible after the preparation of the solution at a wavelength of 520 m\( \mu \) against a blank solution prepared in a similar way. A Unicam S.P. 600 spectrophotometer was used to measure the absorbance of solutions in 1 cm matched-glass cells. A calibration plot of absorbance as a function of cobalt concentration was linear up to a concentration of 180 \( \mu g \) cobalt, and hence the Lambert-Beer law is obeyed within this concentration range. All aliquots of the equilibrium phases which contained cobalt were diluted to give absorbance readings within this range when they were complexed with nitroso-R-salt. A value of 14,810 was obtained for the molar absorptivity at a wavelength of 520 m\( \mu \) from
the slope of the graph of absorbance as a function of cobalt concentration. No published value of the molar absorptivity could be found for the complex formed between cobalt and nitroso-R-salt under the experimental conditions described above.

4.1.8 The determination of sodium and potassium by flame photometry.

The sodium and potassium concentrations of the equilibrium organic phases were determined by flame photometric analysis of aliquots of the aqueous solutions obtained from stripping the organic phases with hydrochloric acid. A Unicam S.P. 900 Flame Spectrophotometer connected to an external recorder was used. By using a wavelength motor drive it was possible to scan automatically through the wavelength regions where the sodium or potassium ions had strong emission lines. The peak height could then be measured accurately from the trace on the chart of the recorder. Sodium was determined using the 589.0 μm emission line and potassium from the 766.5 μm line. Calibration solutions containing sodium and potassium within the range of 0-10 parts per million were prepared by dilution of standard sodium nitrate and potassium nitrate solutions, respectively. The flame photometer was adjusted to give a full-scale deflection on the recorder when solutions containing 10 parts per million of sodium or potassium were measured at the respective wavelength. A calibration plot of peak height as a function of sodium or potassium concentration was prepared each time the instrument was switched on because it was not possible to duplicate exactly the characteristics of the flame once it had been turned off. All the aqueous samples were diluted to give solutions containing 0-10 parts per million of sodium or potassium.

4.1.9 The measurement of pH.

All the pH measurements made in this study were carried out using a Pye Ingold electrode (Type 405) connected to a Pye Potentiometric pH...
Meter, which is graduated to 0.001 of a pH unit. This electrode has a single rod assembly, combining the functions of a glass electrode and a reference electrode, and it has the advantage that only a small volume of aqueous solution (approximately 3 mls) is required for a measurement to be made. The glass electrode portion consists of a pH sensitive membrane, which is fused on the inner of two concentric tubes, and is filled with a dilute acid solution. A silver chloride inner element is immersed in the acid, and this is connected to a central conductor of the coaxial cable lead. The cuter chamber, formed between the two concentric tubes, acts as the reference electrode section and is filled with a saturated potassium chloride solution. The silver chloride inner element is connected to the screening of the coaxial cable, and a small porous plug in the side of the cuter chamber forms a liquid junction with the test solution.

The pH equipment was standardised initially by using a series of standard buffer solutions chosen so that their pH values covered the range of pH used in the equilibrium distribution studies. A standard potassium hydrogen phthalate solution (0.05 M) was chosen as the main reference buffer solution and it was taken to have a pH value of 4.005 at 25°C. The solution was prepared by dissolving the required weight of potassium hydrogen phthalate crystals (B.D.H. pH standard) in deionised water distilled twice from the quartz still, after they had been dried in an oven at 110-120°C for two hours. A 0.1 M solution of potassium dihydrogen citrate (B.D.H., Analar grade) in distilled water gave a pH reading of 3.714 at 25°C in comparison to the literature value of 3.72 at 25°C [139]. A mixed phosphate buffer solution (0.025 M) was prepared by dissolving K$_2$HPO$_4$ (3.40 g Analar grade, B.D.H.) and Na$_2$HPO$_4$ (3.55 g Analar grade, B.D.H., dried at 110-130°C for 2 hours) in CO$_2$-free distilled water, and then diluting the mixture to one litre. This solution gave a pH reading of 6.82 at 25°C, compared to the
literature value of 6.86 at 25°C [139]. The buffer solutions were renewed every three weeks.

The first pH measurements that were made on equilibrium aqueous phases were not very reproducible because it was found that a drift occurred in the reading indicated on the pH meter. This drift was always in the direction of lower pH values, and took place over a period of time until a steady reading was eventually obtained. In Fig. 4.1 a typical series of measurements of pH that were made on the potassium hydrogen phthalate buffer solution and on an equilibrium aqueous phase are shown. In this graph, \( \Delta pH \), the difference between the final, steady, reading of the pH and the pH at time \( t \), is plotted as a function of time \( t \) in minutes. Although these results are typical of the variations of pH readings with time that were observed, the duration of the drift when measuring equilibrium aqueous phases was always considerably longer than in the case of the standard buffer solution. Thus it was found that the pH readings often drifted for up to 4 hours in the case of the equilibrium aqueous phases, whereas steady, reproducible, values for the buffer solutions were obtained within 30 minutes of the electrode being place in the solutions. One possible explanation for the prolonged drift in the case of the equilibrium aqueous phases is that the electrode may become contaminated with any organic phase present. In addition, Mattock suggests that after an electrode has been standardised in a buffer solution, it often takes an appreciable period of time to settle to the pH of the sample solution [146]. The reason is that desorption of buffer from the glass surface of the electrode takes a considerable time even when the electrode is agitated, and this is especially noticeable with weakly buffered solutions. A number of workers have reported similar difficulties to those experienced in this present study, when pH measurements are made in aqueous solutions containing soaps of the carboxylic acids [147, 148]. In
Fig. 4.1 △ pH as a function of time during pH measurement

- Equilibrium aqueous phase
- Potassium hydrogen phthalate buffer (0.05M)
particular, Tanaka has found that a similar drift in the pH readings is obtained with aqueous phases from the extraction of some metal decoates into benzene [147].

In order to remove any organic phase from the surface of the electrode, it was cleaned after each measurement on an equilibrium aqueous phase by soaking it in hydrochloric acid (10^{-2} M) for at least one hour. Before each new measurement was made, the electrode was removed from the acid, washed well with distilled water, and dried with a filter paper. It was then standardised in potassium hydrogen phthalate buffer (0.05 M), and usually it was found that no adjustment of the standardisation control was required. All the pH measurements in the study were carried out at a temperature of 25 ± 0.05°C. The pH reading that was obtained after the drift had ceased was taken to be equal to the pH value of the aqueous phase at equilibrium with the organic phase.

Another factor which has to be considered when measuring the pH of the aqueous phases is the effect of the supporting electrolyte, which is present to adjust the ionic strengths of the solutions. Bates has discussed some of the limitations involved in measuring the pH of aqueous solutions of high ionic strengths [149]. He considers that unless the test solution is a fairly dilute aqueous solution of simple solutes, and that its acidity closely matches that of the buffer solution, then the measured pH value cannot justifiably be regarded as an accurate measure of the hydrogen ion activity of the solution.

4.2 Experimental results from equilibrium distribution measurements

The data obtained from the carboxylic acid extractions are presented in the customary graphical form of log (D) as a function of the pH of the equilibrium aqueous phase, where (D) is the experimentally determined value of the distribution ratio of the metal ions. These
plots will be called "log D-pH" plots in the following discussion of the results.

In the present work, the extraction of the metal ions has been studied from aqueous solutions containing a large excess of an "inert" electrolyte, as well as the metal ions. The purpose of the electrolyte, was to study the extractions from aqueous media of constant ionic strengths.

In general, the constant ionic medium is usually obtained by using a cation (e.g. Na⁺) and an anion (e.g. ClO₄⁻ or NO₃⁻) which are presumed to be inert and so not to form complexes with the reacting species [204]. The extraction is then studied from solutions containing the reacting species and the inert ions in such concentrations that the activity coefficients for a certain ion are presumed to be the same in all the solutions studied. The fact that the activity coefficient terms can be neglected by using this procedure results in a considerable simplification when using the law of mass action with complicated equilibria. This simplification is necessary in view of the lack of comprehensive information on the values of activity coefficients for anything but the simplest systems.

The method suffers from the disadvantage that in practice it is often difficult to avoid complex formation between the reacting species and the ions of the electrolyte. For example, the reversal in the order of extraction of zinc and cadmium ions by carboxylic acids in the presence of excess chloride and sulphate ions has been attributed to the formation of metal-anion complexes of different strengths [21].

The results obtained from the carboxylic acid extractions will be considered in three main sections, viz: (i) copper (II) systems, (ii) nickel (II) systems, and (iii) cobalt (II) systems.
4.2.1 Results from the copper (II) extraction systems

Fig. 4.2 shows the log D-pH plot obtained from the extraction of an aqueous copper sulphate solution (5.0 m M) with a commercial carboxylic acid, naphthenic acid (0.898 N), dissolved in benzene. The ionic strength of the aqueous solution was 1.02 in the presence of potassium nitrate (0.995 M). In this system, the value of log D increases almost linearly with pH in the lower range of extraction, but with further increase in pH the plot becomes curved.

Fletcher and Flett have reported similar studies made on the extraction of some transition metals with naphthenic acid in benzene [45]. The acid used in the work had a molecular weight of 244 in comparison to 162 for the acid in the present study. The log D-pH plots given for the copper (II) system were obtained from the extraction of an aqueous copper sulphate solution (5.0 m M), containing sodium nitrate to adjust the ionic strength to unity, with various acid concentrations (0.09 N to 0.88 N).

From the extraction results, Fletcher et al reported that a linear relationship existed between log D and pH over a range of log D from about -1.0 to +1.0, and that the slopes of the straight lines varied from 2.3 to 2.5.

The almost linear portion of the log D-pH plot in Fig. 4.2 has a slope of about 2.7, and the final slope is about 1.5. The difference between the slopes in the present study and those in the Fletcher et al paper may be accounted for by the fact that different regions of the extraction curve were used in each case. In addition, the published data appear to be subject to a considerable amount of error. This may have arisen from two factors. Firstly, as indicated in section 4.1.9, the pH tends to drift over a period of time when measurements are made on equilibrium aqueous phases. This is probably due to contamination of the electrode with organic phase. However,
Fig. 4.2 $\text{CuSO}_4 (5.0 \text{ m M})/\text{NaNO}_3 (0.995 \text{ M}) - \text{naphthenic acid (0.898 M)}/\text{benzene}$
no indication of the methods adopted for the measurement of pH were
given in the paper.

In addition, the values of (D) used in the paper were obtained
from the experimentally determined value of the copper concentration in
the organic phase and from the aqueous concentration obtained by
difference from the total copper concentration. No information regarding
the errors involved by using this procedure rather than by actually
measuring the aqueous concentration of copper was given by the workers.

In the present study of the extraction of copper (II) ions, the
organic and aqueous phase copper concentrations at each pH were
determined experimentally, and the value of (D) was obtained from the
ratio of the two concentrations. The average error involved in the
determination of the two concentrations was found to be ±3% based on
an overall mass-balance before and after the extraction.

Unfortunately, it is not possible to test the extraction
expression proposed in equation (2.67) to any extent by using data
obtained from extractions with naphthenic acid because there are
insufficient thermodynamic and solubility data available in the litera-
ture. The values of the constants $K_{RH}$, $K_{DO}$, $K_{Dw}$, $K_P$ introduced in
section (2.2.3) are unknown for the system, and consequently this
limits the analysis of the data to the cases when the acid concen-
tration can be considered to be constant.

In view of these limitations in the case of extractions with
commercial acids such as naphthenic acid, it was decided to use the
straight-chain carboxylic acids as extractants. The acids chosen for
the study were n-octoic acid ($C_{15}H_{15}COOH$) and n-decoic acid ($C_{19}H_{19}COOH$)
since information has been published on the solubility of these acids
in aqueous solution, and also reliable values for the equilibrium
constants are also known [49, 90].

After the work was started, Tanaka and Niinomi published a paper
in which they considered the extraction of copper with n-decoic acid dissolved in benzene [46]. In the study, copper, (2.0 m M) was extracted from sulphate solutions by a range of acid concentrations (0.2 M to 2 M), but the ionic strengths of the aqueous solutions were not adjusted with any additional electrolyte. Although no log D-pH plots are given in the paper, Tanaka has indicated that curved plots were obtained from the data [147].

Fig. 4.3 shows a log D-pH plot obtained in the present study from the extraction of a copper sulphate solution (10.68 m M) containing sodium sulphate (0.326 M) by n-decoic acid (1.00 M) dissolved in n-heptane. In this system, it was found that above about 50% extraction of copper (ca. pH = 4.13) a pale-green precipitate formed in the organic phase, which tended to separate at the interface. Tanaka et al gave no indication that a similar effect was obtained in the system using benzene as a solvent for the acid, even at higher loadings of the organic phase. The precipitation is probably due to the decreased solubility of the copper (II) - n-decoic acid complex in n-heptane as compared to benzene, and in addition the effect of the sodium sulphate in the aqueous phase may also have a considerable modifying effect on the solubility of the complex.

Because of the limitations on the loading of the organic phases containing n-decoic acid dissolved in n-heptane, a study was made of the use of n-octoic acid in n-heptane as an extractant for copper (II) solutions. Fig. 4.4 contains the log D-pH plots obtained from the extraction of copper sulphate solutions (10.68 m M) containing potassium nitrate (0.99 M) with various concentrations of n-octoic acid in n-heptane. The plots are curved for each acid concentration, and are displaced towards higher pH values as the concentration of acid is decreased. Fig. 4.5 contains a similar log D-pH plot for the extraction of a copper sulphate solution (5.0 m M) containing
Fig. 4.3 Copper extraction system: 
\( \text{CuSO}_4 (10.68 \text{ m M})/\text{Na}_2\text{SO}_4 (0.328\text{ M}) - \text{ n-decoic acid} (1.00 \text{ M})/\text{n-heptane}. \)
Fig. 4.4 Copper extraction system:
\[ \text{CuSO}_4(10.68 \text{ m M})/\text{KNO}_3(0.998\text{ M}) - \text{n-octoic acid/n-heptane} \]
Fig. 4.5 Copper extraction system:
\( \text{CuSO}_4 (5.0 \text{ m M})/\text{NaNO}_3 (0.995 \text{ M}) - \text{n-octoic acid (0.550 M)/n-heptane}. \)
sodium nitrate (0.995 M) by n-octoic acid (0.550 M) in n-heptane.

The effect of changing the anions in the extraction system is shown in Fig. 4.6. For this study, n-octoic acid (1.000 M) dissolved in n-heptane was used to extract copper (II) from aqueous solutions containing chloride, nitrate or sulphate anions. The ionic strengths of the aqueous solutions were adjusted to unity in the case of the chloride and nitrate systems with the corresponding sodium salt, but in the case of the sulphate system, the ionic strength was found to be only 0.989 on checking the solution. The log D-pH plots were similar in shape, but were displaced in the order: nitrate < chloride < sulphate towards higher pH values.

The reason for the displacement of the curves appears to be due largely to the complexing of the copper (II) ions with the anions present in the aqueous phases. The literature values for stability constants indicate that only weak complexing of copper (II) occurs with the nitrate anion, but that the complexing with the chloride and sulphate anions is much stronger [205]. Unfortunately, there appears to be a good deal of disagreement between various published values of the constants and it is therefore only possible to use the values for a qualitative description of the complexing.

Flett observed a selectivity change in the extraction curves with a change in the anion during a study of the extraction of zinc and cadmium ions with naphthenic acid [21]. In the presence of sulphate anions, cadmium extracted before zinc, whereas when the anion was changed to chloride, zinc extracted first. It was suggested that strong complexing of the zinc took place with the sulphate anion, while in the case of the chloride anion cadmium formed the stronger complex. The published values for the association constants of zinc with chloride or sulphate support this, but in the case of cadmium, the constants vary widely, and are of little use.
Fig. 4.6 Effect of anion on extraction of copper (II) with n-octoic acid (1.00 M)/n-heptane.
In a later study, Flett used the data from the extraction of zinc with naphthenic acid to investigate the ion association complexes of the sulphate anion at a constant total ionic strength [206]. The equilibrium constants for the formation of $ZnSO_4$ and $Zn(SO_4)_2^-$ were found to $10^{0.3}$ and $10^{1.66}$, respectively, from the study.

The effect of changing the organic solvent from n-heptane to carbon tetrachloride on the extraction of copper from sulphate solution (10.68 mM) by n-octoic acid (1.000 M) is shown in Fig. 4.7. The log $D$-pH plot is again a smooth curve.

The analysis of the organic phases resulting from the extraction of copper in the various systems showed them to contain a ratio of sodium ions to copper ions of less than 0.01 over the range of pH used in the extractions. The effect of this small amount of sodium in the organic phase was neglected.

4.2.2 Analysis of data, and discussion of results from copper (II) extraction systems

The fact that the data obtained from the extraction of copper (II) systems (and also cobalt (II) and nickel (II) systems) with carboxylic acids give rise to curved log $D$ vs. pH plots can be explained by reference to the extraction equation (2.67), viz:

$$\log D = \log K_j + \log K_{j,x} - j \log \beta + (j - 1)\log (C_M)_w + z_j pH + ((z_j + x)/2)\log (C_\text{RH}_0)$$

From a consideration of this equation, a plot of log $D$ as a function of pH should only yield a straight line if: (i) $(C_\text{RH}_0)$ is constant and (ii) either $(C_M)_w$ is constant, or $j = 1$. Since in the distribution measurements usually carried $(C_M)_w$ is not constant, then a linear plot should only result if the following conditions are satisfied: $j = 1$, the carboxylic acid concentration is very much greater than the
Fig. 4.7 Copper extraction system:
$\text{CuSO}_4(10.68 \text{ M})/\text{Na}_2\text{SO}_4(0.326 \text{ M})$ - n-octoic acid (1.00 M)/CCl$_4$
metal ion concentration, and the pH is low (i.e. a negligible amount of acid is present in the aqueous phase).

Tanaka and Niinomi analysed some data from the extraction of copper (II) sulphate with n-decoic acid in benzene in terms of the equation (2.67), but they introduced a number of simplifications [46]. It was assumed that only one complex of the form \((MR_j)^n(RH)_x\) was in the organic phase, and that a large excess of the carboxylic acid was present, so that the term \((C_{RH})_0\) in the equation could be included in a constant term. Since \((\beta)\) was considered to be constant in the case of copper extractions, a plot of \((\log D - (j - 1) \log (C_{Cu}^w))\) as a function of pH should give a straight line of slope equal to \((zj)\). Hence, \((j)\), the number of \((MR_j)\) units in the complex should be obtained from the slope of the graph. It was reported in the paper that when the data were plotted in this manner a straight line plot was only obtained when \((j)\) was assumed to have a value of two. The results from the plots therefore suggested that the extracted species was of the form: \((CuR_2)^2(RH)_x\).

In order to obtain the number of solvating acid molecules in the complex i.e. \((x)\), Tanaka et al assumed a value of \((j)\) equal to two in equation (2.67) and then showed that the slope of the plots of \((\log D - \log (C_{Cu}^w) - 4\log (C_{RH}^w))\) as a function of \((\log (C_{RH})_0)\) should be equal to \((zj + x)/2\). Linear plots of slope equal to 3.0 were obtained from the extraction data, and hence the value of \((x)\) was assumed to be 2.0.

The analysis of the extraction data by graphical techniques appeared to show that a complex of the form \((CuR_2)^2(RH)_2\) was present in the organic phase, under the extraction conditions used in the study. However, no details were given in the paper as to the fit that was obtained between the extraction data and species of other structures.
The copper (II) extraction data obtained in the present work have been analysed graphically after the methods of Tanaka et al [46]. In each case it was assumed that an excess of the carboxylic acid was present, and that the \((\beta)\) term could be taken to be equal to unity.

Fig. 4.8 shows the \((\log D - \log (C_{Cu}^w))\) vs. pH plots using the data obtained from the extraction of copper sulphate solution \((10.68 \text{ m M})\) with n-octoic acid in n-heptane \((\log D \text{ vs. pH plot, Fig. 4.4})\). The fact that linear plots of slope equal to \((4.0)\) are obtained indicates that the extracted complex is dimeric i.e. \((\text{CuR}_2)_2(\text{RH})_x\). In order to calculate the value of \((x)\) in the complex, a plot of \((\log D - \log (C_{Cu}^w) - 4\text{pH})\) as a function of \(\log (C_{RH})_O\) was drawn (Fig. 4.9). The slope of this linear plot was found to be equal to \((3.0)\), and hence a value of \((x)\) equal to two was indicated. It would therefore appear from the graphical analyses of the extraction data that a complex of the form \((\text{CuR}_2)_2(\text{RH})_2\) was the predominating complex in the organic phase.

Figs. 4.10 to 4.14 contain the plots of \((\log D - \log (C_{Cu}^w))\) as a function of pH for the data from the following copper (II) extraction systems: (a) copper (II) sulphate \((5.0 \text{ m M})\) extracted with n-octoic acid \((0.550 \text{ M})\) in n-heptane (Fig. 4.10); (b) copper (II) nitrate, chloride and sulphate \((10.68 \text{ m M})\) extracted with n-octoic acid \((1.00 \text{ M})\) in n-heptane (Fig. 4.11); (c) copper (II) sulphate \((10.68 \text{ m M})\) extracted with n-decoic acid \((1.00 \text{ M})\) in n-heptane. (Fig. 4.12); (d) copper (II) sulphate \((10.68 \text{ m M})\) extracted with n-octoic acid \((1.00 \text{ M})\) in carbon tetrachloride, (Fig. 4.14). In all of these plots, a straight line of slope equal to \((4.0)\) was drawn through the experimental points and in all cases there is a close fit between the data and the line. The predominating complex in these systems would therefore appear to be a dimerised copper (II) carboxylate complex, \((\text{CuR}_2)_2(\text{RH})_x\).
Fig. 4.8 Copper extraction system: CuSO$_4$ (10.68 m M)/KNO$_3$ (0.998 M) - n-octoic acid/n-heptane.
Fig. 4.9 Copper extraction system: CuSO$_4$ (10.68 m M)/KNO$_3$ (0.99 M) - n-octoic acid/n-heptane.
Fig. 4.10 Copper extraction system:
\[
\text{CuSO}_4 (5.0 \text{ m M})/\text{NaNO}_3 (0.995 \text{ M}) - \text{n-octoic acid} (0.550 \text{ M})/\text{n-heptane}
\]
Fig. 4.11 Effect of anion on extraction of copper (II) with n-octoic acid (1.00 M)/n-heptane.
Fig. 4.12 Copper extraction system:
CuSO₄(10.68 m M)/Na₂SO₄(0.326 M) - n-decovic acid⁴(1.00 M)/n-heptane.
Fig. 4.13 Extraction system: CuSO₄ (10.68 m M)/Na₂SO₄ (0.326 M) - n-octoic acid (1.000 M)/CCL₄
Fig. 4.14 Copper extraction system: CuSO\textsubscript{4}(5.0 m M)/NaNO\textsubscript{3}(0.995 M) - naphthenic acid (0.898 N)/benzene
The graphical analysis of the extraction data by the methods described above has a number of disadvantages. In the first place, it is difficult to test the fit between the data and complexes of various structures. Secondly, the methods used above are based on the assumption that the acid is in sufficient excess over the metal ion concentration that it can be regarded as constant. However, this assumption is only justified at low loadings of the organic phase and in addition, since the amount of acid in the aqueous phase increases with the pH of extraction, allowance should also be made for this. In practice it is difficult to modify the present graphical methods to take account of variations in the acid concentration. Finally, it is difficult to represent graphically the cases in which more than one complex is present in the organic phase.

In order to overcome the limitations of the graphical methods, the mathematical analysis of the extraction data by regression analysis procedures was attempted. By using these methods it should be possible to obtain reliable estimates of the degree to which various structures fit the data.

The multiple regression procedure outlined in section (2.3.2) was used to calculate the least squares values of \( j \) and \( x \) in the complex \( (MR) \cdot (RH)^z \) assuming the presence of only one complex in the organic phase. A computer program was written for the analysis (Appendix 4), and as previously described three modifications to the term \( (\text{CRH})_0 \) in the extraction equation (2.90) were introduced. These were for (a) when the acid concentration was considered to be constant (constant-acid routine), (b) when an allowance for the acid present in the complex was made (complexed-acid routine), and (c) when an allowance for the solubility of the acid was made (solubility routine).
In the present program, it has been found necessary to use a successive approximation procedure in order to calculate \( (C_{RH})_0 \) from the initial acid concentration. Unfortunately, the analysis leads to inadmissible values of \( (j) \) and \( (x) \) e.g. (negative values) in the cases where the changes in the acid concentration due to complexing and solubility in the aqueous phase are small. When the analysis is carried out with data obtained from a range of extraction conditions, where the amount of acid complexed is not negligible, reasonable values for \( (j) \) and \( (x) \) are obtained as shown in Table 4.1.

In Table 4.1, the results obtained from the multiple regression analysis of data from the extraction of copper (II) sulphate with n-octoic acid in n-heptane are presented. The average error term is calculated from the expression given in equation (2.99), and the results from the constant-acid, complexed-acid and solubility routines are given. It is evident from the results that the effect of correcting for the solubility of the acid in the aqueous phase leads to only a small change in the values of \( (j) \) and \( (x) \) calculated by using the complexed-acid routine only. This is expected in view of the low solubility of the acid over the range of pH used in the copper (II) extractions.

The results from the analysis indicate that a value of \( (j) \) equal to 2 appears to satisfy the extraction equation, but the value of \( (x) \) appears to vary between 1 and 2. The multiple regression procedure used seems to be capable of calculating a value of \( (j) \) with a reasonable degree of accuracy, but the value of \( (x) \) obtained appears to be more susceptible to experimental errors in the data. In addition, the presence of a number of complexes in the organic phase may lead to considerable modifying effects on the analysis.

The reason for the regression analysis failing to work with some of the extraction data is probably due to the fact that the analysis in terms of equation (2.90) and the solution of the three normal
Table 4.1 Multiple regression analysis of copper (II) extraction data

<table>
<thead>
<tr>
<th>Extraction system</th>
<th>Constant-acid routine</th>
<th>Complexed-acid routine</th>
<th>Complexed-acid and Solubility routines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>j</td>
<td>x</td>
<td>Average error</td>
</tr>
<tr>
<td>1. CuSO₄ (10.68 m M)/KNO₃ (0.998 M) - n-octoic acid/heptane</td>
<td>2.058</td>
<td>1.545</td>
<td>0.1005</td>
</tr>
<tr>
<td>Acid concentrations:</td>
<td>1.414 M/0.550 M/0.318 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.324</td>
<td>1.622</td>
<td>0.05769</td>
<td>2.452</td>
</tr>
<tr>
<td>2. CuSO₄ (5.0 m M)/NaNO₃ (0.995 M) - n-octoic acid (0.549 M)/n-heptane and CuSO₄ (10.68 m M)/KNO₃ (0.998 M) - n-octoic acid (1.414 M, 0.550 M, 0.318 M)/n-heptane.</td>
<td>1.696</td>
<td>1.251</td>
<td>0.1203</td>
</tr>
</tbody>
</table>
equations in (2.96 - 2.98), leads to badly-valued equations. The
differences between the various products in equations (2.96) to (2.98)
may become so small that terms are eliminated with the result that
improbable values for (j) and (x) are obtained.

In order to obtain additional information about the fit between
the extraction data and species of various structures, a linear
regression analysis using the method of least squares was carried out.
The extraction expression in the form given in equation (2.72) was
used and the data were analysed for various combinations of integral
values of (j) and (x) with the aid of a computer program (Appendix 3).
The analyses were carried out assuming that only one complex of the
form \((MR_z^j)(RH)_x\) was present in the organic phase. For a given
structure, the "perfect fit" between the data and the extraction
expression (2.72) would be the case of zero average error with respect
to a line of slope equal to unity. The value of this average error
term has therefore been calculated for each analysis.

Tables 4.2 to 4.7 summarise the results obtained from the
analysis of the copper (II) extraction data by the linear regression
method. In these tables, the values of the average error terms are
given for a series of complexes. As discussed in Chapter 3 (Table
3.5) these complexes are considered the species most likely to be
present in the organic phase. The regression analysis was carried
out on the computer using the three subroutines mentioned above i.e.
constant-acid, complexed-acid, and solubility routines.

The constant-acid routine is limited in its usefulness and is
included mainly to act as a comparison with the other methods. It
is not possible to consider the effect on the analysis of variations
in (x) in the complex \((MR_z^j)(RH)_x\) by using this routine, since the
term \((zj + x)/2 \log (C_{RH})_0\) is included in a constant term in the
extraction equation (2.72).
Table 4.2 Linear regression analysis of data from extraction system:

CuSO$_4$(10.68 M)/KNO$_3$(0.99 M) - n-octoic acid/n-heptane

<table>
<thead>
<tr>
<th>Complex</th>
<th>Acid $1.414\text{ M/0.550 M}$</th>
<th>Acid $1.414\text{ M/0.550 M}$</th>
<th>Acid $0.550\text{ M/0.318 M}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average error</td>
<td>Average error</td>
<td>Average error</td>
</tr>
<tr>
<td>Constant-acid routine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuR$_2$</td>
<td>0.2475</td>
<td>0.2137</td>
<td>0.2538</td>
</tr>
<tr>
<td>(CuR$_2$)$_2$</td>
<td>0.1809</td>
<td>0.1655</td>
<td>0.1046</td>
</tr>
<tr>
<td>Complexed-acid routine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuR$_2$</td>
<td>0.2524</td>
<td>0.2166</td>
<td>0.2611</td>
</tr>
<tr>
<td>CuR$_2$·2RH</td>
<td>0.2970</td>
<td>0.2071</td>
<td>0.2997</td>
</tr>
<tr>
<td>CuR$_2$·4RH</td>
<td>0.4975</td>
<td>0.3587</td>
<td>0.3867</td>
</tr>
<tr>
<td>(CuR$_2$)$_2$</td>
<td>0.1780</td>
<td>0.1640</td>
<td>0.1057</td>
</tr>
<tr>
<td>(CuR$_2$)$_2$(RH)$_2$</td>
<td>0.1372</td>
<td>0.1035</td>
<td>0.1294</td>
</tr>
<tr>
<td>(CuR$_2$)$_2$(RH)$_4$</td>
<td>0.3287</td>
<td>0.2672</td>
<td>0.2200</td>
</tr>
<tr>
<td>Complexed-acid and solubility routines</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuR$_2$</td>
<td>0.2525</td>
<td>0.2166</td>
<td>0.2613</td>
</tr>
<tr>
<td>CuR$_2$·2RH</td>
<td>0.2974</td>
<td>0.2071</td>
<td>0.3002</td>
</tr>
<tr>
<td>CuR$_2$·4RH</td>
<td>0.4982</td>
<td>0.3587</td>
<td>0.3876</td>
</tr>
<tr>
<td>(CuR$_2$)$_2$</td>
<td>0.1777</td>
<td>0.1640</td>
<td>0.1059</td>
</tr>
<tr>
<td>(CuR$_2$)$_2$(RH)$_2$</td>
<td>0.1379</td>
<td>0.1035</td>
<td>0.1305</td>
</tr>
<tr>
<td>(CuR$_2$)$_2$(RH)$_4$</td>
<td>0.3295</td>
<td>0.2672</td>
<td>0.2214</td>
</tr>
</tbody>
</table>
Table 4.3  Linear regression analysis of data from extraction system: 
\( \text{CuSO}_4(5.0 \text{ m M})/\text{NaNO}_3(0.995 \text{ M}) - \text{n-octoic acid (0.5496 M)}\) 
n-heptane.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Constant-acid routine</th>
<th>Complexed-acid routine</th>
<th>Complexed-acid and solubility routines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average error</td>
<td>Average error</td>
<td>Average error</td>
</tr>
<tr>
<td>CuR₂</td>
<td>0.2265</td>
<td>0.2277</td>
<td>0.2277</td>
</tr>
<tr>
<td>CuR₂·2RH</td>
<td>-</td>
<td>0.2312</td>
<td>0.2312</td>
</tr>
<tr>
<td>CuR₂·4RH</td>
<td>-</td>
<td>0.2370</td>
<td>0.2370</td>
</tr>
<tr>
<td>(CuR₂)₂</td>
<td>0.06846</td>
<td>0.06881</td>
<td>0.06881</td>
</tr>
<tr>
<td>(CuR₂)₂(RH)₂</td>
<td>-</td>
<td>0.06925</td>
<td>0.06925</td>
</tr>
<tr>
<td>(CuR₂)₂(RH)₄</td>
<td>-</td>
<td>0.06987</td>
<td>0.06987</td>
</tr>
</tbody>
</table>
Table 4.4  Linear regression analysis of data from extraction of copper (II) (10.68 mM) with n-octoic acid (1.00 M)/n-heptane in the presence of sulphate, chloride and nitrate anions.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Sulphate system Average error</th>
<th>Chloride system Average error</th>
<th>Nitrate system Average error</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Constant-acid routine</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuR₂</td>
<td>0.1355</td>
<td>0.1655</td>
<td>0.1744</td>
</tr>
<tr>
<td>(CuR₂)₂</td>
<td>0.06237</td>
<td>0.05492</td>
<td>0.04719</td>
</tr>
<tr>
<td><strong>Complexed-acid routine</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuR₂</td>
<td>0.1372</td>
<td>0.1676</td>
<td>0.1766</td>
</tr>
<tr>
<td>CuR₂·2RH</td>
<td>0.1426</td>
<td>0.1739</td>
<td>0.1832</td>
</tr>
<tr>
<td>CuR₂·4RH</td>
<td>0.1517</td>
<td>0.1846</td>
<td>0.1943</td>
</tr>
<tr>
<td>(CuR₂)₂</td>
<td>0.06006</td>
<td>0.05595</td>
<td>0.04690</td>
</tr>
<tr>
<td>(CuR₂)₂(RH)₂</td>
<td>0.05715</td>
<td>0.05840</td>
<td>0.04654</td>
</tr>
<tr>
<td>(CuR₂)₂(RH)₄</td>
<td>0.05376</td>
<td>0.06216</td>
<td>0.04604</td>
</tr>
<tr>
<td><strong>Complexed-acid and solubility routines</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuR₂</td>
<td>0.1372</td>
<td>0.1676</td>
<td>0.1766</td>
</tr>
<tr>
<td>CuR₂·2RH</td>
<td>0.1426</td>
<td>0.1739</td>
<td>0.1832</td>
</tr>
<tr>
<td>CuR₂·4RH</td>
<td>0.1517</td>
<td>0.1846</td>
<td>0.1943</td>
</tr>
<tr>
<td>(CuR₂)₂</td>
<td>0.06006</td>
<td>0.05595</td>
<td>0.04690</td>
</tr>
<tr>
<td>(CuR₂)₂(RH)₂</td>
<td>0.05714</td>
<td>0.05840</td>
<td>0.04654</td>
</tr>
<tr>
<td>(CuR₂)₂(RH)₄</td>
<td>0.05375</td>
<td>0.06216</td>
<td>0.04604</td>
</tr>
</tbody>
</table>
Table 4.5  Linear regression analysis of data from extraction system: 
\[ \text{CuSO}_4(10.68 \text{ M})/\text{Na}_2\text{SO}_4(0.326 \text{ M}) - \text{n-decoic acid (1.00 M)}/\text{n-heptane}. \]

<table>
<thead>
<tr>
<th>Complex</th>
<th>Constant-acid routine</th>
<th>Complexed-acid routine</th>
<th>Complexed-acid and solubility routines</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuR$_2$</td>
<td>0.07507</td>
<td>0.07574</td>
<td>0.07574</td>
</tr>
<tr>
<td>CuR$_2$.2RH</td>
<td>-</td>
<td>0.07775</td>
<td>0.07775</td>
</tr>
<tr>
<td>CuR$_2$.4RH</td>
<td>-</td>
<td>0.08112</td>
<td>0.08112</td>
</tr>
<tr>
<td>(CuR$_2$)$_2$</td>
<td>0.03937</td>
<td>0.03896</td>
<td>0.03896</td>
</tr>
<tr>
<td>(CuR$_2$)$_2$(RH)$_2$</td>
<td>-</td>
<td>0.03845</td>
<td>0.03845</td>
</tr>
<tr>
<td>(CuR$_2$)$_2$(RH)$_4$</td>
<td>-</td>
<td>0.03772</td>
<td>0.03772</td>
</tr>
</tbody>
</table>
Table 4.6 Linear regression analysis of data from extraction system:
\[ \text{CuSO}_4 (10.68 \text{ m M})/\text{Na}_2\text{SO}_4 (0.326 \text{ M}) - \text{n-octoic acid (1.00 M)}/\text{CCl}_4 \]

<table>
<thead>
<tr>
<th>Complex</th>
<th>Constant-acid routine Average error</th>
<th>Complexed-acid routine Average error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CuR}_2 )</td>
<td>0.1904</td>
<td>0.1934</td>
</tr>
<tr>
<td>( \text{CuR}_2 \cdot 2\text{RH} )</td>
<td>-</td>
<td>0.2023</td>
</tr>
<tr>
<td>( \text{CuR}_2 \cdot 4\text{RH} )</td>
<td>-</td>
<td>0.2175</td>
</tr>
<tr>
<td>( \left( \text{CuR}_2 \right)_2 )</td>
<td>0.03637</td>
<td>0.03525</td>
</tr>
<tr>
<td>( \left( \text{CuR}_2 \right)_2 \left( \text{RH} \right)_2 )</td>
<td>-</td>
<td>0.03549</td>
</tr>
<tr>
<td>( \left( \text{CuR}_2 \right)_2 \left( \text{RH} \right)_4 )</td>
<td>-</td>
<td>0.03594</td>
</tr>
</tbody>
</table>
Table 4.7  Linear regression analysis of data from extraction system:
CuSO₄(5.0 M)/NaNO₂ (0.995 M) - naphthenic acid (0.898 N)/benzene

<table>
<thead>
<tr>
<th>Complex</th>
<th>Constant-acid routine</th>
<th>Complexed-acid routine</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuR₂</td>
<td>0.011889</td>
<td>0.011990</td>
</tr>
<tr>
<td>CuR₂ 2RH</td>
<td>-</td>
<td>0.012296</td>
</tr>
<tr>
<td>CuR₂ 4RH</td>
<td>-</td>
<td>0.012811</td>
</tr>
<tr>
<td>(CuR₂)₂</td>
<td>0.010968</td>
<td>0.010825</td>
</tr>
<tr>
<td>(CuR₂)₂(RH)₂</td>
<td>-</td>
<td>0.010645</td>
</tr>
<tr>
<td>(CuR₂)₂(RH)₄</td>
<td>-</td>
<td>0.010400</td>
</tr>
</tbody>
</table>
In order to obtain the value of (x) from the analysis, it is necessary to use the complexed-acid and solubility routines. The application of the solubility routine to the data has only a small effect on the values of the average error terms. This is to be expected since the solubility of the acid is low in the present systems.

In the case of the data from the extraction of copper (II) sulphate (10.68 m M) with various concentrations of n-octoic acid in n-heptane (log D vs. pH plot Fig. 4.4), the results from the linear regression analysis are given in Table 4.2. Over the complete range of acid concentrations used (1.414 M/0.550 M/0.318), the complex \((\text{CuR}_2)_2(\text{RH})_2\) leads to the lowest average error values, and this result is confirmed when the analysis is repeated with the higher acid concentrations (1.414 M/0.550 M). With the lower range of acid concentrations (0.550 M/0.318 M), however, the complex \((\text{CuR}_2)_2\) appears to be most favoured, although the average error value for the complex \((\text{CuR}_2)_2(\text{RH})_2\) is only slightly greater. The linear regression analysis of the data from the extraction of copper (II) sulphate solutions (5.0 m M) with n-octoic acid (Table 4.3) also indicates that an unsolvated dimeric complex of the form \((\text{CuR}_2)_2\) is the main extracted species. However, the average error terms for the complexes \((\text{CuR}_2)_2, (\text{CuR}_2)_2(\text{RH})_2, (\text{CuR}_2)_2(\text{RH})_4\) are similar to one another and it is difficult to choose with confidence between the structures.

The results in Table 4.4 were obtained from the linear regression analysis of data from the extraction of copper (II) with n-octoic acid (1.000 M) in the presence of excess sulphate, chloride, and nitrate ions in the aqueous phase (log D vs. pH plot Fig. 4.6). In the case of the sulphate and nitrate systems the average error terms indicate that the \((\text{CuR}_2)_2(\text{RH})_4\) complex gives the best fit, but with the chloride system, the unsolvated dimer \((\text{CuR}_2)_2\) is favoured.
In the case of the analysis of the copper (II) - n-decoic acid data (Table 4.5), the complexed-acid and solubility routines give the lowest average error in the case of the complex \((\text{CuR}_2)_2(\text{RH})_4\) although the differences between the values of the average errors for \((\text{CuR}_2)_2', (\text{CuR}_2)_2(\text{RH})_2\) and \((\text{CuR}_2)_2(\text{RH})_4\) are small. The results from this analysis illustrate the general observation that it is often difficult to choose between a number of structures of the form \((\text{MR})_x(\text{RH})_x\) when the value of \(x\) is changed using only the results from the regression analyses.

The difficulty of choosing between a series of complexes can be illustrated graphically for the copper (II) - n-decoic acid extraction data. For the linear regression analysis, the extraction expression given in equation (2.72) can be rearranged into the form of a linear equation:

\[ Y = a + bX, \]

where \(Y = \log D\)

\[ X = ((j - 1) \log (C_M)_w + (zj + x)/2 \log (C_{\text{RH}O}) + zj \text{ pH}), \]

\[ a = (\log K_{j.} + \log K_{j,x}), \] assuming that \(\beta\) is unity.

In the analysis of the data, the least squares method was used to test the equation with various combinations of integral values of \(j\) and \(x\), using the complexed-acid routine. In Figs. 4.15a and 4.15 b, \(\log D\) is plotted against the function \(X\) for a number of values of \(j\) and \(x\), and a line of slope equal to unity is drawn through the points, using the intercept obtained from the least squares analysis. From the plots, it would appear that the complexes in which \(j = 2\) give the best fit with the extraction data, but it is very difficult to choose between the complexes \((j = 2; x = 0, x = 2, \text{ and } x = 4)\) with any degree of confidence.
Fig. 4.15a log D-X plot for copper system: CuSO₄ (10.68 m M)/Na₂SO₄ (0.326 M) - n-decoic acid (1.00 M)/n-heptane
Fig. 4.15b log D-X plot for copper system:
CuSO₄ (10.68 m M)/Na₂SO₄ (0.326M) - n-decoic acid (1.00M)/n-heptane
From the linear regression analysis of the data from the extraction of copper (II) sulphate (10.68 m M) with n-octoic acid (1.00 M) dissolved in carbon tetrachloride, a complex of the form (CuR_2)_2 is indicated (Table 4.6). In the case of the copper (II) sulphate-naphthenic acid/benzene data (log D vs. pH plot Fig. 4.2), the complex (CuR_2)_2(RH)_4 gives the best fit. It is not possible to carry out the solubility routine with the data from these two systems because of insufficient published data on the constants for the distribution of the acids between the aqueous solutions and the organic phases.

The results from the analysis of the copper (II) extraction data by regression methods, using the basic extraction expression proposed in equation (2.67) and assuming only one complex in the organic phase, confirm the conclusions from graphical analyses and physical methods of study (Chapter 3) that the complexes are predominantly dimeric in structure viz. (CuR_2)_2(RH)_x. The fact that it appears to be difficult to obtain unambiguous values of (x) in the complexes by these methods may be due to the effects of other complexes in the system and also that the experimental data are not of sufficient accuracy.

In view of the tendency of copper (II) carboxylates to form a dimeric structure of the copper (II) acetate monohydrate type (Fig. 3.1), it appears likely that the complexes formed in the present extraction systems will be based on this structure. The unsolvated dimer, (CuR_2)_2, which was the favoured complex in some of the analyses, can be formed quite easily by the loss of solvating acid molecules from the copper (II) acetate structure without destroying the basic dimeric structure. The complex (CuR_2)_2(RH)_4 which was also indicated in the analyses is difficult to form from the copper (II) acetate structure unless the two further acid molecules are hydrogen-bonded
to the complex. A complex based on this structure appears to be rather improbable, however, and a basic change of structure from the copper (II) acetate type may be indicated, as reported for the cobalt (II) carboxylates [95].

It is obviously not possible to determine without some ambiguity the structures of the complexes by using the present regression methods unless the results are considered in conjunction with the evidence from graphical and physical methods of study. As mentioned above, part of the difficulty of using the regression methods may result from the presence of mixed complexes in the organic phase.

Haffenden et al in a recent paper also found evidence for modifying effects with mixed complexes when they used a least squares procedure to analyse the data obtained from the extraction of copper (II) ions by trimethyl acetic acid ((CH₃)₃C COOH) [207]. It was assumed by these workers that the average constitution of the metal species in each phase remained essentially constant over the ranges of pH, metal concentrations, and acid concentrations that were studied. A successive approximation procedure was used to obtain the equilibrium concentration of free acid in the organic phase and then to calculate average values for the number of metal ions, for the number of acid molecules in the extracted species, and for the number of acid molecules associated with the metal ions in the aqueous phase. Over the ranges of reactant concentration studied, the average constitution of the extracted complex was found to be (Cu₁.₉ R₃.₈ RH₂.₁), and it was suggested that this represented a polymeric species of the form (CuR₂)₂(RH)₂, together with a small amount of the monomer (10%). However, no attempt was made to extend the least squares procedure to take account of the presence of mixed species in the organic phase, or to calculate equilibrium constants for the formation of the complexes.
Tanaka et al. in a recent paper [95] used a graphical approach to derive values of the equilibrium constants for an extraction equilibrium of the form:

\[ j(M^{2+}) + (zj + x)/2((RH)_{2})_0 \rightleftharpoons ([MR]_{j}^{z}(RH)_{x})_0 + zj H^+ \]  (4.1)

A relationship between the distribution ratio of the metal ion (D) and the constant for this equilibrium \( K_{j,x}^{1} \) was derived by using the following procedure. From equation (2.41):

\[(C_M)_{0} = \left( \sum_{j=1}^{l} \sum_{x=0}^{x} j([MR]_{j}^{z}(RH)_{x})_0 \right),\]

and from equation (2.9):

\[(C_M)_{w} = \beta [M^{2+}]_{w}\]

Hence from the definition of (D) given in equation (2.15):

\[ D = \left( \sum_{j=1}^{l} \sum_{x=0}^{x} j([MR]_{j}^{z}(RH)_{x})_0 / \beta^{-1} [M^{2+}]^{-1}_{w} \right) \]  (4.2)

Now from equation (4.1):

\[ K_{j,x}^{1} = ([MR]_{j}^{z}(RH)_{x})_0 / [H^+]^{zj} ([RH]_{2})_0 \cdot [M^{2+}]^{-j} \]  (4.3)

If the expression for \([MR]_{j}^{z}(RH)_{x})_0 \) is substituted from equation (4.3) into equation (4.2), then:

\[ D = \left( \sum_{j=1}^{l} \sum_{x=0}^{x} j K_{j,x}^{1} [H^+]^{-zj} ([RH]_{2})_0 \cdot [M^{2+}]^{-j} \beta^{-1} \right) \]  (4.4)

Now, since from equation (2.63):
Equation (4.5) was then used by Tanaka et al. to obtain a value of $(K_{j,x}^1)$ for the formation of a dimeric complex $(\text{CuR}_2)_2(\text{RH})_2$ in the copper (II) - n-decenoic acid system. If it is assumed that only one complex of this form is present in the organic phase, then equation (4.1) becomes:

$$D = \sum_{j=1}^{2} \sum_{x=0}^{1} j \frac{K_{j,x}^1}{[\text{H}^+]^{-z}} \frac{[\text{RH}]_{2}^{-1}(z+x)/2}{[\text{Cu}]_{w}^{j-1} \beta^{-j}}$$

(4.5)

Equation (4.5) was then used by Tanaka et al. to obtain a value of $(K_{j,x}^1)$ for the formation of a dimeric complex $(\text{CuR}_2)_2(\text{RH})_2$ in the copper (II) - n-decenoic acid system. If it is assumed that only one complex of this form is present in the organic phase, then equation (4.1) becomes:

$$2 \text{Cu}^{2+} + 3(\text{RH})_2^0 \xrightarrow{K_{22}^{1}} (\text{CuR}_2)_2(\text{RH})_2^0 + 4\text{H}^+$$

(4.6)

For the same system, equation (4.5) simplifies to the form:

$$D = 2 K_{22}^{1} \frac{[\text{Cu}]_{w}^1}{[\text{RH}]_2^3} \frac{[\text{Cu}]_{w}^1}{[\text{H}]^{-4}},$$

(4.7)

if it is assumed that $\beta^{-j}$ is equal to unity.

A value for $(K_{22}^{1})$ can be obtained from the slope of a plot of $(\log D - 4\log \text{Cu})$ as a function of $\log ([\text{Cu}]_{w}^1)$. In the present work, the data from the extraction of copper (II) sulphate (10.68 m M) with n-octanoic acid in n-heptane (log D vs. pH plot Fig. 4.4) was analysed by this method, and the slopes of the least squares straight lines for the data were calculated. The values of the slopes and the corresponding values of the constant $(K_{22}^{1})$ are given in Table 4.8. The average value of $(K_{22}^{1})$ was found to be $(2.7 \pm 0.3) \times 10^{-13}$. 
Table 4.8  Values of constant \( \left( K_{e2} \right) \) for copper (II)-n-octoic acid systems.

<table>
<thead>
<tr>
<th>Acid concentration</th>
<th>Slope</th>
<th>( K_{e2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.414 M</td>
<td>( 0.225928 \times 10^{-12} )</td>
<td>( 3.196 \times 10^{-13} )</td>
</tr>
<tr>
<td>0.550 M</td>
<td>( 0.106790 \times 10^{-13} )</td>
<td>( 2.567 \times 10^{-13} )</td>
</tr>
<tr>
<td>0.318 M</td>
<td>( 0.181394 \times 10^{-14} )</td>
<td>( 2.256 \times 10^{-13} )</td>
</tr>
</tbody>
</table>

Tanaka et al obtained a value of \( K_{e2} = 1.58 \times 10^{-12} \) in the case of the copper (II) - n-decoic acid system. The procedure used by these workers to obtain values of the constants \( (K_{e2}^{1}) \) from equation (4.5) appears to be invalid, however, and will be discussed in more detail later.

4.2.3 Results obtained from the nickel (II) extraction systems

The log D vs. pH plots obtained from the extraction of nickel sulphate solutions (10.68 M) containing potassium nitrate (0.989 M) with various concentrations of n-octoic acid in n-heptane are presented in Figs. 4.16a and 4.16b.

The error involved in the determination of the nickel concentrations of the equilibrium organic and aqueous phases was normally less than \( \pm 3\% \) calculated on a mass-balance basis.

4.2.4 Analysis of data, and discussion of results from nickel (II) extraction systems

If the extraction data are plotted as \( (\log D - \log (C_{Ni}^{1})) \) vs. pH after the method of Tanaka et al [46], then the results are as shown in Figs. 4.17a and 4.17b. In the case of acid concentrations from 1.414 M to 0.318 M (Fig. 4.17a), linear plots of slope 4.0 are obtained, which suggests that a complex of the form \( (NiR_{2})_{2}(RH)_{x} \) is the main complex in the organic phase.
Fig. 4.16a Nickel extraction system:
$\text{NiSO}_4(10.68 \text{ m M})/\text{KNO}_3(0.998 \text{ M}) - \text{n-octoic acid/n-heptane}$
Fig. 4.16 Nickel extraction system:
NiSO₄(10.68 M)/KNO₃(0.989 M) - n-octoic acid/n-heptane
Fig. 4.17a Nickel extraction system: \(\text{NiSO}_4(10.68 \text{ m M})/\text{KNO}_3(0.989 \text{ M}) - \text{n-octoic acid/n-heptane}\)
Fig. 4.17b Nickel extraction system:

$\text{NiSO}_4(10.68 \text{ m M})/\text{KNO}_3(0.989 \text{ M}) - \text{n-octoic acid/n-heptane}$
The corresponding plots for the data from the 0.201 M and 0.100 M acid extractions, however, are curved (Fig. 4.17b), and it is not possible to obtain linear plots by using values of \( (j) \) other than 2 in equation (2.67). The reason for the non-linearity of the plots appears to be due, therefore, to the fact that the carboxylic acid concentrations in these systems can no longer be assumed to remain constant during the extractions. Evidence from infrared measurements on the organic phases after extraction indicated the presence of only a small amount of free carboxylic acid. The analysis of the organic phases for their sodium ion concentrations showed that the ratio of sodium to nickel in the phases increased to a maximum of about 0.06 over the pH range 5.6 to 6.8 used in the nickel extractions. A reduction in the acid concentrations of the organic phases probably occurs by the formation of sodium carboxylates, which are quite soluble in water in comparison to the heavy metal carboxylates.

To calculate the value of \( (x) \) in the extracted complex \((\text{NiR}_2)_2(\text{RH})_x\), a plot of \(\log D - \log (C_{\text{Ni}}) - 4\ \text{pH}\) as a function of \(\log (C_{\text{RH}})\) was drawn (Fig. 4.18). For the acid concentrations from 1.414 M to 0.318 M, a linear plot with slope equal to 4.0 was obtained. Hence a value of \( (x) \) equal to 4.0 in the complex \((\text{NiR}_2)_2(\text{RH})_x\) was indicated. In the case of the lower acid concentrations (0.201 M and 0.100 M) the data do not fall on the line of slope 4.0 probably because of the solubility of the acid in the aqueous phase.

The results obtained from the multiple regression analysis of the nickel (II) extraction data are given in Table 4.9. Over the complete range of acid concentrations used (1.414 M to 0.100 M) a value of \( (j) \) equal to 2 is indicated from the constant-acid, complexed-acid, and solubility routines, and the value of \( (x) \) is 4 when all corrections are made, including for the acid in the aqueous
Fig. 4.18 Nickel extraction system:
$\text{NiSO}_4(10.68 \text{ M})/\text{KNO}_3(0.989 \text{ M})$ - n-octoic acid/n-heptane
<table>
<thead>
<tr>
<th>Acid concentrations</th>
<th>Constant-acid routine</th>
<th>Complexed-acid routine</th>
<th>Complexed-acid and Solubility routines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>j x Average error</td>
<td>j x Average error</td>
<td>j x Average error</td>
</tr>
<tr>
<td>1.414 M/1.000 M/0.550 M/0.318 M/0.201 M/0.100 M</td>
<td>2.224 5.101 0.1515</td>
<td>2.456 5.019 0.1860</td>
<td>2.150 3.514 0.2672</td>
</tr>
<tr>
<td>1.414 M/1.000 M/0.550 M/0.318 M</td>
<td>2.383 5.906 0.1174</td>
<td>2.564 5.850 0.1480</td>
<td>2.572 5.482 0.1827</td>
</tr>
<tr>
<td>0.201 M/0.100 M</td>
<td>1.528 2.530 0.2326</td>
<td>1.824 1.749 0.2508</td>
<td>3.719 1.005 0.2268</td>
</tr>
</tbody>
</table>
phase. The solubility correction in the nickel (II) systems is important especially in the higher pH ranges of extraction since from Fig. 2.3 it is evident that the distribution ratio of n-octoic acid between n-heptane and water falls from about $6.3 \times 10^3$ to about $6.3 \times 10^{-1}$ over the pH range used in the extractions (5.0 to 7.0).

When the data from the higher acid concentrations used (1.414 M/1.000 M/0.550 M/0.318 M) and from the lower concentrations (0.201 M/0.100 M) are analysed by the multiple regression method, rather different results are obtained. In the former case, the value of $(j)$ is (3) and the $(x)$ value is (5) when corrections including the solubility correction are used. For the data obtained from the extractions with the lower acid concentrations (0.201 M/0.100 M), the values $(j = 4, x = 1)$ are obtained.

The reason for the variations in the $(j)$ and $(x)$ values calculated by the multiple regression method cannot be explained satisfactorily, although the data from the two lowest acid concentrations used (0.201 M and 0.100 M) must have a considerable modifying effect on the analysis.

The linear regression analysis of the extraction data leads to results which are much more self-consistent than in the case of the multiple regression procedure. With the data from the whole range of acid concentrations (1.414 M - 0.100 M) the complex $(\text{NiR}_2)_2(\text{RH})_4$ leads to the lowest average errors and hence is the best fit for the system (Table 4.10). A similar result is obtained with the data from the higher range of acid concentrations (1.414 M to 0.318 M), but for the lowest acid concentrations (0.201 M/0.100 M), the complex $(\text{NiR}_2)_2$ gave the lowest average error.

The results from the linear regression analysis therefore indicate that the predominating complex in the organic phase is $(\text{NiR}_2)_2(\text{RH})_4$ when the acid concentration used is high (1.414 M to
Table 4.10  Linear regression analysis of data from extraction system:

\[
\text{NiSO}_4 (10.68 \text{ m M})/\text{KNO}_3 (0.989 \text{ M}) - \text{n-octoic acid/n-heptane}
\]

<table>
<thead>
<tr>
<th>Complex</th>
<th>Unit slope</th>
<th>Unit slope</th>
<th>Unit slope</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>av. error</td>
<td>av. error</td>
<td>av. error</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiR\textsubscript{2}</td>
<td>0.4472</td>
<td>0.3771</td>
<td>0.2419</td>
</tr>
<tr>
<td>(NiR\textsubscript{2})\textsubscript{2}</td>
<td>0.7976</td>
<td>0.5863</td>
<td>0.3020</td>
</tr>
</tbody>
</table>

**Constant-acid routine**

| NiR\textsubscript{2} | 0.4324 | 0.3757 | 0.2495 |
| NiR\textsubscript{2}.2RH | 0.3098 | 0.2776 | 0.3064 |
| NiR\textsubscript{2}.4RH | 0.7378 | 0.3327 | 0.5651 |
| (NiR\textsubscript{2})\textsubscript{2} | 0.7617 | 0.5787 | 0.2918 |
| (NiR\textsubscript{2})\textsubscript{2}.(RH)\textsubscript{2} | 0.3546 | 0.3452 | 0.2562 |
| (NiR\textsubscript{2})\textsubscript{2}.(RH)\textsubscript{4} | 0.2992 | 0.1715 | 0.3294 |

**Complexed-acid routine**

| NiR\textsubscript{2} | 0.3925 | 0.3769 | 0.2873 |
| NiR\textsubscript{2}.2RH | 0.4179 | 0.2919 | 0.4785 |
| NiR\textsubscript{2}.4RH | 0.9527 | 0.3588 | 0.8550 |
| (NiR\textsubscript{2})\textsubscript{2} | 0.6626 | 0.5635 | 0.2237 |
| (NiR\textsubscript{2})\textsubscript{2}.(RH)\textsubscript{2} | 0.5675 | 0.3371 | 0.3676 |
| (NiR\textsubscript{2})\textsubscript{2}.(RH)\textsubscript{4} | 0.3507 | 0.1990 | 0.6407 |

**Complexed-acid and solubility routines**

| NiR\textsubscript{2} | 0.4472 | 0.3771 | 0.2419 |
| NiR\textsubscript{2}.2RH | 0.7976 | 0.5863 | 0.3020 |
| NiR\textsubscript{2}.4RH | 0.4324 | 0.5863 | 0.3020 |
0.318 M data), and hence the results from the graphical analysis described earlier are confirmed. Fletcher and Flett also postulated the existence of a complex of the form \((NiR_2)_2(RH)_4\) in the organic phases resulting from the extraction of nickel (II) sulphate solutions with naphthenic acid in benzene, by using graphical methods of analysis.

If it is assumed that the complex \((NiR_2)_2(RH)_4\) is the predominating complex in the case of the extractions with high acid concentrations, then equation (4.5) can be modified accordingly to calculate values of the equilibrium constant for the following equilibrium:

\[
2 \text{Ni}^{2+} + 4((\text{RH})_2)_0 \rightleftharpoons \frac{K_{24}^1}{(\text{NiR}_2)_2(\text{RH})_4}_0 + 4\text{H}^+ \quad (4.8)
\]

From equation (4.5):

\[
D = 2 \frac{K_{24}^1}{[H^+]^4} [(\text{RH})_2]_0^4 \frac{([\text{Ni}^2]^4)}{([\text{Ni}^2])^4}, \text{assuming } \beta \text{ is unity.} \quad (4.9)
\]

Values for \(K_{24}^1\) were calculated from the least squares slopes of the plots of \((\log D - 4\text{pH})\) vs. \((\log ([\text{Ni}^2])\), and they are given in Table 4.11. The average value of \(K_{24}^1\) was found to be \((7.34 \pm 3) \times 10^{-20}\).

<table>
<thead>
<tr>
<th>Acid</th>
<th>Slope</th>
<th>(K_{24}^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.414 M</td>
<td>0.6731 \times 10^{-19}</td>
<td>1.35 \times 10^{-19}</td>
</tr>
<tr>
<td>1.000 M</td>
<td>0.9278 \times 10^{-20}</td>
<td>7.42 \times 10^{-20}</td>
</tr>
<tr>
<td>0.550 M</td>
<td>0.4896 \times 10^{-21}</td>
<td>4.27 \times 10^{-20}</td>
</tr>
<tr>
<td>0.318 M</td>
<td>0.5297 \times 10^{-22}</td>
<td>4.15 \times 10^{-20}</td>
</tr>
</tbody>
</table>

In the case of a monomeric nickel complex, such as \((NiR_2)(\text{RH})_4\), in the organic phase in addition to the dimeric complex \((NiR_2)_2(\text{RH})_4\), then the corresponding equation to (4.5) can be used to obtain values
of $K_{14}^1$ and $K_{24}^1$. When this expression is applied, it is found that different values for $(K_{24}^1)$ are obtained as shown in Table 4.12.

Table 4.12 Values of $(K_{24}^1)$ for nickel (II) system from equation (4.5)

<table>
<thead>
<tr>
<th>Acid</th>
<th>Slope</th>
<th>$K_{24}^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.414 M</td>
<td>0.1744 x $10^{-20}$</td>
<td>2.468 x $10^{-21}$</td>
</tr>
<tr>
<td>1.000 M</td>
<td>0.2212 x $10^{-21}$</td>
<td>8.850 x $10^{-22}$</td>
</tr>
<tr>
<td>0.550 M</td>
<td>0.2078 x $10^{-22}$</td>
<td>4.995 x $10^{-22}$</td>
</tr>
<tr>
<td>0.318 M</td>
<td>0.2618 x $10^{-23}$</td>
<td>3.256 x $10^{-22}$</td>
</tr>
</tbody>
</table>

However, no satisfactory values for $(K_{14}^1)$ could be obtained by this method, which suggests that if these species represent the actual case in the system then only the dimeric species are important. The variations between the values of $(K_{24}^1)$ in Table 4.11 and in Table 4.12, however, illustrate the need for caution in interpreting the results. Unfortunately, there are no reported values in the literature for comparison.

4.2.5 Results from the cobalt (II) extraction systems

The log D vs. pH plots obtained from the extraction of cobalt sulphate solutions (10.0 m M) containing sodium sulphate (0.32 M) with various concentrations of n-octoic acid dissolved in n-heptane are given in Fig. 4.19. The plots are curved, as noted for the copper (II) and the nickel (II) extraction systems.

The error involved in the cobalt analysis of the equilibrium organic and aqueous phases was less than $\pm 3.5\%$, calculated on a mass-balance basis.

4.2.6 Analysis of data, and discussion of results from cobalt (II) extraction systems

The cobalt (II) extraction data are presented as
Fig. 4.19 Cobalt extraction system:

CoSO₄ (10.00 mM)/Na₂SO₄ (0.32 M) - n-octoic acid/n-heptane
(log D - log (C_{Co})_w) vs. pH plots in Fig. 4.20. The slope of the linear plots is equal to 4.0, and hence the extracted complex would appear to be dimeric, and of the form (CoR_2)_2(RH)_x.

Since the slope of the (log D - log (C_{Co})_w - 4pH) vs. log (C_{RH})_0 plot for the data (Fig. 4.21) is equal to 4.0, a value of 4.0 for x in the complex is indicated.

Thus the graphical analysis of the data after the methods of Tanaka et al [46] suggests that a complex of the form (CoR_2)_2(RH)_4 is the predominating complex in the organic phase under the given extraction conditions.

Tanaka et al in a recent paper analysed some data from the extraction of cobalt (II) with n-decoic acid in benzene [95]. The total cobalt concentrations extracted in the study ranged from 10^{-5} to 5 x 10^{-3} M, and an initial acid concentration of 1.00 M was used. Tanaka originally interpreted the extraction data in terms of the formation of a monomer of the form (CoR_2)(RH)_4 at low concentrations in the organic phase, and a dimer (CoR_2)_2(RH)_6 at higher concentrations [208]. Later, however, Tanaka et al appear to have reinterpreted the data [95], and to have discussed the results in terms of the following equilibria.

\[ 2 \text{Co}^{2+} + 4((\text{RH})_2)_0 \xrightleftharpoons{K_{24}^{1}} ((\text{CoR}_2)_2(\text{RH})_4)_0 + 4 \text{H}^+ \]

\[ \text{Co}^{2+} + 3 ((\text{RH})_2)_0 \xrightleftharpoons{K_{14}^{1}} ((\text{CoR}_2)(\text{RH})_4)_0 + 2 \text{H}^+ \quad (4.10) \]

Also, the dimerisation constant of the monomer in benzene was obtained from the equilibrium:

\[ 2((\text{CoR}_2)(\text{RH})_4)_0 \xrightleftharpoons{K_{\text{dim}}^{1}} ((\text{CoR}_2)_2(\text{RH})_4)_0 + 2((\text{RH})_2)_0 \quad (4.11) \]
Fig. 4.20 Cobalt extraction system:
\( \text{CoSO}_4 (10.00 \text{ m M})/\text{Na}_2\text{SO}_4 (0.32 \text{ M}) - \text{n-octoic acid/n-heptane} \)
Fig. 4.21 Cobalt extraction system: 
\( \text{CoSO}_4(10.00 \text{ m M})/\text{Na}_2\text{SO}_4(0.32 \text{ M}) - \) 
n-octoic acid/n-heptane.
In order to obtain values of \((K_{24}^1)\) and \((K_{14}^1)\) for the complexes 
\(\{(\text{CoR}_2)_2(\text{RH})_4\}\) and \(\{(\text{CoR}_2)(\text{RH})_4\}\) respectively, Tanaka et al modified equation (4.5) to the form:

\[
D = K_{14}^1 [(\text{RH})_2]_0^3 [\text{H}^+]^{-2} + 2 K_{24}^1 [(\text{RH})_2]_0^4 (\text{CoO})_w [\text{H}^+]^{-4} \tag{4.12}
\]

This equation can be rearranged to the form:

\[
D = K_{14}^1 [(\text{RH})_2]_0^3 [\text{H}^+]^{-2} (1 + 2 K_{24}^1 (K_{14}^1)^{-1} [(\text{RH})_2]_0 (\text{CoO})_w [\text{H}^+]^{-2}) \tag{4.13}
\]

In the paper, a plot of \((\log D - 2\text{pH})\) vs. \((\log (\text{CoO})_w + 2\text{pH})\) was compared with a normalised function \(y = \log (1 + x)\) in order to obtain the values of the constants \((K_{14}^1)\) and \((K_{24}^1)\). This procedure appears to be suspect, however, because it does not appear to be possible to arrange equation (4.13) into a form which can be used for calculating values of \((K_{14}^1)\) and \((K_{24}^1)\) independently by using the normalising technique.

In the present work a value for \((K_{24}^1)\) was obtained by rearranging equation (4.12) into the form:

\[
(D)[\text{H}^+]^2 = K_{14}^1 [(\text{RH})_2]_0^3 + 2 K_{24}^1 [(\text{RH})_2]_0^4 (\text{CoO})_w [\text{H}^+]^{-2} \tag{4.14}
\]

and from the slope of the plot of \((\log D - 2\text{pH})\) vs. \((\log (\text{CoO})_w + 2\text{pH})\), \((K_{24}^1)\) can be obtained. The values of \((K_{24}^1)\) obtained from the slopes of the least squares straight lines for the cobalt (II) extraction data are given in Table 4.13.

**Table 4.13 Values of \(K_{24}^1\) for cobalt (II) system.**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Slope</th>
<th>(K_{24}^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.414 M</td>
<td>0.2837 x 10^{-20}</td>
<td>4.47 x 10^{-21}</td>
</tr>
<tr>
<td>1.000 M</td>
<td>0.5589 x 10^{-21}</td>
<td>5.11 x 10^{-21}</td>
</tr>
<tr>
<td>0.706 M</td>
<td>0.1589 x 10^{-21}</td>
<td>5.68 x 10^{-21}</td>
</tr>
<tr>
<td>0.318 M</td>
<td>0.4754 x 10^{-23}</td>
<td>3.72 x 10^{-21}</td>
</tr>
</tbody>
</table>
The average value for \((K_{24}^1)\) was found to be \((4.75 \pm 0.58) \times 10^{-21}\) by this method. Tanaka et al quoted a value of \(K_{24}^1 = 2 \times 10^{-20}\) for the cobalt (II) - n-decoic acid/benzene system \([95]\), obtained by using the normalising procedure.

The intercept of the plot of \((\log D - 2pH)\) vs. \((\log (C_{Co}^0) + 2pH)\) should yield a value for \((K_{14}^1)\) if the complex \((CoR_2)(Rh)_4\) is present in the organic phase. However, since the measurement of the intercept leads to more error than the determination of the slope, equation (4.12) is better rearranged to the form:

\[
(D)[H^+]^4(C_{Co}^0)^{-1} = K_{14}^1 [(Rh)_2]^3 [H^+]^2 (C_{Co}^0)^{-1} + 2 K_{24}^1 [(Rh)_2]^0,
\]

and \((K_1^1)\) can then be evaluated from the slope of a plot of \((\log D - 4pH - \log (C_{Co}^0))\) vs. \((-2pH - \log (C_{Co}^0))\). In the present work, only the analysis of the data from the extraction of cobalt (II) with 0.318 M n-octoic acid gave a positive value for the slope, and hence a value for \((K_{14}^1)\). The value of \((K_{14}^1)\) obtained was \(9.04 \times 10^{-13}\) in comparison to a value of \(1.3 \times 10^{-10}\) reported by Tanaka et al \([95]\).

A value for the dimerisation constant \((K_{1 dim}^1)\) can be obtained from \((K_{14}^1)\) and \((K_{24}^1)\) since it can be shown by combining equations (4.10) and (4.11) that:

\[
K_{1 dim}^1 = (K_{24}^1)(K_{14}^1)^{-2}
\]

\((K_{1 dim}^1)\) in the present work for the 0.318 M acid system was found to be equal to \(5.86 \times 10^{-5}\). A value of \(K_{1 dim}^1 = 5.01 \times 10^{+2}\) was given by Tanaka et al for the n-decoic acid/benzene extraction system. It would appear from the order of magnitude of \((K_{1 dim}^1)\) that the dimeric complex is the predominating species in the organic phase.

The results from the multiple regression analysis of the cobalt (II) extraction data are given in Table 4.14. Over the whole range of
Table 4.14  Multiple regression analysis of data from extraction system:

${\text{CoSO}_4}(10.00 \text{ M})/{\text{Na}_2\text{SO}_4}(0.32 \text{ M}) - \text{n-octoic acid/n-heptane}$

<table>
<thead>
<tr>
<th>Acid concentrations</th>
<th>Constant-acid routine</th>
<th>Complexed-acid routine</th>
<th>Complexed-acid and Solubility routines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>j</td>
<td>x</td>
<td>Average error</td>
</tr>
<tr>
<td>1.414 M/1.000 M/0.7065 M/0.318</td>
<td>2.140</td>
<td>4.338</td>
<td>0.1625</td>
</tr>
<tr>
<td>1.414 M/1.000 M</td>
<td>2.098</td>
<td>7.072</td>
<td>0.1195</td>
</tr>
<tr>
<td>0.7065 M/0.318 M</td>
<td>1.958</td>
<td>2.205</td>
<td>0.2066</td>
</tr>
</tbody>
</table>
acid concentrations used (1.414 M to 0.32 M), the analysis gives values of (j) equal to (2) and (x) equal to (3). In the case of the higher acid concentrations (1.414 M/1.000 M) a value of (j) equal to (2) is again indicated, but the value of (x) has increased to (7) in all the routines. The analysis of the data from the lower acid concentrations (0.7065 M/0.318 M) confirms that the main complex is of the form \((\text{CoR}_2)_2(\text{RH})_x\)', but (x) falls to a value of (1).

In the case of the linear regression analysis of the extraction data from the complete range of acid concentrations, the complex \((\text{CoR}_2)_2(\text{RH})_4\) leads to the lowest average error (Table 4.15). A similar result is obtained from the analysis of the data from the extraction with the two higher acid concentrations (i.e. 1.414 M/1.000 M). With the two lower acid concentrations (0.7065 M/0.318 M) however, the complex \((\text{CoR}_2)_2(\text{RH})_2\) is favoured.

The results from the regression analyses and graphical methods confirm that the extracted cobalt (II) complex is dimeric and of the form \((\text{CoR}_2)_2(\text{RH})_x\)', but whereas the graphical methods and also the linear regression analysis for the complete range of data indicate a value of (x) equal to (4), the multiple regression analysis leads to variable results.

Fletcher and Flett also obtained evidence for a dimeric cobalt (II) complex of the form \((\text{CoR}_2)_2(\text{RH})_4\) from a graphical analysis of data obtained from the extraction of cobalt (II) sulphate with naphthenic acid in benzene [45].

4.2.7 Analysis of extraction data in the case of more than one complex in the organic phase

The results obtained from the analysis of the carboxylic acid extraction data in terms of equations (2.110) and (2.111) (Section...
Table 4.15  Linear regression analysis of data from extraction system:  
\[
\text{CoSO}_4(10.00 \text{ M})/\text{Na}_2\text{SO}_4(0.32 \text{ M}) - \text{n-octoic acid/n-heptane.}
\]

<table>
<thead>
<tr>
<th>Complex</th>
<th>Unit slope</th>
<th>Unit slope</th>
<th>Unit slope</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>av. error</td>
<td>av. error</td>
<td>av. error</td>
</tr>
<tr>
<td><strong>Constant-acid routine</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{CoR}_2)</td>
<td>0.3325</td>
<td>0.3170</td>
<td>0.3070</td>
</tr>
<tr>
<td>((\text{CoR}_2)_2)</td>
<td>0.4316</td>
<td>0.2442</td>
<td>0.3225</td>
</tr>
<tr>
<td><strong>Complexed-acid routine</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{CoR}_2)</td>
<td>0.3334</td>
<td>0.3191</td>
<td>0.3110</td>
</tr>
<tr>
<td>(\text{CoR}_2_2\text{RH} )</td>
<td>0.3035</td>
<td>0.2962</td>
<td>0.3153</td>
</tr>
<tr>
<td>(\text{CoR}_2_4\text{RH} )</td>
<td>0.3540</td>
<td>0.2777</td>
<td>0.3998</td>
</tr>
<tr>
<td>((\text{CoR}_2)_2)</td>
<td>0.4263</td>
<td>0.2462</td>
<td>0.3238</td>
</tr>
<tr>
<td>((\text{CoR}_2)_2_\text{RH}_2)</td>
<td>0.2706</td>
<td>0.1954</td>
<td>0.2288</td>
</tr>
<tr>
<td>((\text{CoR}_2)_2_\text{RH}_4)</td>
<td>0.2043</td>
<td>0.1591</td>
<td>0.2531</td>
</tr>
<tr>
<td><strong>Complexed-acid and solubility routines</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{CoR}_2)</td>
<td>0.3355</td>
<td>0.3228</td>
<td>0.3227</td>
</tr>
<tr>
<td>(\text{CoR}_2_2\text{RH} )</td>
<td>0.3236</td>
<td>0.3126</td>
<td>0.3490</td>
</tr>
<tr>
<td>(\text{CoR}_2_4\text{RH} )</td>
<td>0.3887</td>
<td>0.2887</td>
<td>0.4703</td>
</tr>
<tr>
<td>((\text{CoR}_2)_2)</td>
<td>0.4061</td>
<td>0.2501</td>
<td>0.3193</td>
</tr>
<tr>
<td>((\text{CoR}_2)_2_\text{RH}_2)</td>
<td>0.2739</td>
<td>0.2057</td>
<td>0.2676</td>
</tr>
<tr>
<td>((\text{CoR}_2)_2_\text{RH}_4)</td>
<td>0.2490</td>
<td>0.1739</td>
<td>0.3464</td>
</tr>
</tbody>
</table>
2.3.4) for the presence of two and three complexes, respectively, in the organic phase, were not encouraging. It was found impossible in most cases to obtain finite values for the equilibrium constants \((k_1)\) and in the cases for which values were obtained, these appeared to be of the wrong order of magnitude.

It would appear that the reason for the invalid results is that the linear equations which are used to describe the systems (2.110) and (2.112) are badly-valued. The result of this is that the terms in the equations often become zero and hence give infinite values when they are manipulated in the calculations.

In order to try and overcome some of these difficulties a successive approximation procedure was used in order to solve the equations and obtain values of the equilibrium constants for two extracted complexes. It had been hoped that the procedure could be modified for the general case of \((p)\) complexes in the organic phases, once the method had been proved for two complexes.

The procedure adopted involved the use of the equations (2.100) to (2.107) given previously in Section 2.3.4, for the case of two complexes. In the method, the error between the value of \((C_M)_0\) calculated from equations (2.103) and (2.105) was minimised by varying the values of the equilibrium constants \((k_1)\).

A computer program has been written to carry out the error-minimising procedure (Appendix 5). In the program, the value of \((k_1)\) is varied until a minimum error value is obtained. The procedure is then repeated with a value of \((k_1)\) until a minimum error is again obtained. When this has been completed, the value of \((k_1)\) is reduced by a factor \((F_1)\), such that \(F_1 = (F + 1)/2\), where \((F)\) is the old factor. When a minimum error has been obtained again, the value of \((k_2)\) is reduced by the factor \((F_1)\) and the procedure continued. By setting a limit to the factor \((F_1)\), the process can be continued until the changes
in \((k_1^1)\) and \((k_2^2)\) produce no significant changes in the error term.

Although the program functioned satisfactorily, the values of \((k_1^1)\) and \((k_2^2)\) which were obtained appear to be several orders of magnitude too high, and the values of the errors calculated are also high.

A set of results obtained from the analysis of copper (II) sulphate - n-octoic acid extraction data (\(\log D\) vs. \(pH\) plot Fig. 4.4) are given in Table 4.16.

Table 4.16 Calculation of equilibrium constants for two complexes in extraction system:

\[
\text{CuSO}_4 (10.68 \text{ M})/\text{KNO}_3 (0.99 \text{ M}) - \text{n-octoic acid (1.414 M/0.550 M/0.318 M)/n-heptane.}
\]

<table>
<thead>
<tr>
<th>Complex</th>
<th>(k_1^1)</th>
<th>Complex</th>
<th>(k_2^2)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CuR}_2))</td>
<td>0.126 (\times 10^{-5})</td>
<td>((\text{CuR}_2)(\text{RH})_4)</td>
<td>0.182 (\times 10^{+14})</td>
<td>0.1395</td>
</tr>
<tr>
<td>((\text{CuR}_2))</td>
<td>0.776 (\times 10^{+4})</td>
<td>((\text{CuR}_2)_2(\text{RH})_2)</td>
<td>0.781 (\times 10^{+4})</td>
<td>0.1567</td>
</tr>
<tr>
<td>((\text{CuR}_2)(\text{RH})_4)</td>
<td>0.182 (\times 10^{+14})</td>
<td>((\text{CuR}_2)_2(\text{RH})_2)</td>
<td>0.466 (\times 10^{+5})</td>
<td>0.1395</td>
</tr>
<tr>
<td>((\text{CuR}_2)_2)</td>
<td>0.709 (\times 10^{+10})</td>
<td>((\text{CuR}_2)_2(\text{RH})_2)</td>
<td>0.100 (\times 10^{+5})</td>
<td>0.1593</td>
</tr>
<tr>
<td>((\text{CuR}_2)(\text{RH})_2)</td>
<td>0.291 (\times 10^{+9})</td>
<td>((\text{CuR}_2)_2(\text{RH})_2)</td>
<td>0.862 (\times 10^{+4})</td>
<td>0.1544</td>
</tr>
</tbody>
</table>

The fact that the values of the error terms given in Table 4.16 are similar, and are often identical for different combinations of complexes, can be explained if the analysis takes place in an error "depression" from which it is difficult to escape. If the error "surface" is complicated, then a number of these depressions may exist which would make it difficult to decide on reliable values for the equilibrium constants.

Similar difficulties were evidently encountered by Schweitzer, who attempted to use a stepwise regression analysis to calculate
equilibrium constants in the case of mixed complexes [209]. The computer program used led to untenable values, and had to be abandoned.

In the present work, no satisfactory values for the equilibrium constants in the case of two extracted complexes for the nickel (II), cobalt (II) and copper (II) extraction data could be obtained. As a result, it was decided not to extend the approach to consider the general case of (p) complexes in the organic phase.
CHAPTER 5

A Study of Interfacial Effects on the Mass Transfer of Copper (II) Ions from Aqueous Solutions into Carbon Tetrachloride Solutions of n-Octoic Acid
5.1 Introduction

The long-chain carboxylic acids, which are used as extractants for metal ions are surface-active, since they contain a hydrophilic group, i.e. the carboxyl group, and a nonpolar, hydrophobic, alkyl chain. At an organic solvent-aqueous solution interface, the acid molecules will be arranged with the carboxyl groups in the water, and the alkyl chains penetrating into the organic phase.

If the pH of the aqueous substrate is changed, the nature of the interfacial film is altered. As the pH is increased, the acids become ionised, and as a result of the repulsion between the ions there is a decrease in the cohesive forces within the film.

The presence of electrolytes in the substrate may have considerable effects on the properties of the monolayer at the interface, especially if the ions are capable of forming insoluble compounds with the carboxylic acids. This interaction is marked if the pH of the substrate is such that basic metal ions are formed in the solution.

The interaction between metal ions and monolayers of long-chain carboxylic acids at the air-aqueous solution interface has been studied previously by a number of workers [152-155], but no significant work has been reported with reactions at the liquid-liquid interface.

If there is a change in the nature of the surface film with pH at the liquid-liquid interface, this might be expected to lead to changes in the rate of extraction of metal ions with carboxylic acids, if the transfer across the interface is the rate controlling step. The extractions with carboxylic acids are largely pH-dependent, with the maximum extraction of the metal ions taking place at pH values just below the point of precipitation of the metal hydroxides [25].

In order to obtain information about the nature of the interface as the pH of the aqueous solution is varied, a study of the extraction of copper into free-falling drops of carbon tetrachloride containing
n-octoic acid has been carried out. A series of interfacial tension measurements covering the same extraction system have also been made.

5.2 A study of the extraction of copper into free-falling drops of n-octoic acid in carbon tetrachloride.

5.2.1 Introduction

The general methods of studying mass transfer into liquids drops have been reported in the literature [156-159]. Although the methods have been of rather limited use in fundamental studies, mainly because of complications due to interfacial turbulence, they have been found useful for studying the effects of surface-active agents on mass transfer.

The early work showed that traces of surface active compounds in systems containing liquid drops reduced the extraction rates considerably. In systems involving extraction from rising or falling drops, e.g. in the case of extraction of acetic acid from water to benzene, it has been shown that, in the absence of surface active compounds, there is a marked movement inside the moving drop. The rate of mass transfer has been found to be dependent on the rate of movement in the drop. Although usually the hydrodynamic characteristics of the systems are not defined well enough for absolute values of the rates of mass transfer to be determined, it has been reported that surface active compounds almost eliminate motion within drops, and consequently the rates of mass transfer are reduced [160].

The falling drop possesses a natural circulation in addition to the high initial rate of circulation which is caused by the detachment of the drop from the tip or nozzle. The natural circulation occurs by a direct transfer of momentum across the interface, and the presence of a monolayer at the interface may affect it in two main ways [160]. Firstly, the surface viscosity of the monolayer may
cause a dissipation of energy and momentum at the surface so that the drop behaves rather more as a solid than as a liquid, and hence the internal circulation is reduced. Also, the flow of liquid around the drop will tend to push the film towards the rear of the drop, and as a result of the film's back-spreading pressure \( \Pi \) it will resist further compression. The result will be that the movement of the surface is damped, and hence the transfer of momentum across the drop is reduced. As well as reducing the circulation inside the drop, the rate of fall of the drop will also be reduced [161-165]. The circulation within a falling drop and the opposing effect of the surface pressure gradient can be shown schematically as follows (after Davies and Rideal [160]):

\[ \text{Circulation} \quad \text{Surface pressure gradient} \]

5.2.2 Description of the apparatus

The extraction column and reservoir used in the study are shown in Fig. 5.1. Two glass columns have been used of the same design, but of different dimensions. In preliminary experiments with the smaller column (dimensions: 4\( \frac{1}{2} \) feet long x 1\( \frac{1}{2} \) inches inside diameter), it was found that drops of the organic phase on their passage down the column often collided with the walls. In order to avoid this effect, a second larger column was made (dimensions: 5 feet long x 2\( \frac{3}{4} \) inches inside diameter) and the studies reported were carried out in this column.

The column (Fig. 5.1) consists essentially of an inner glass tube surrounded by a glass jacket through which water can be pumped
Fig. 5.1 Extraction column and reservoir.
from a thermostat tank to maintain a constant temperature in a solution contained in the column. It was found that a temperature of 25± 0.1°C could be maintained in the column after the water had been circulating through the jacket for at least one hour. The solution was added through a socket (B.19) at the top of the column and it was drained through the stopcock (C) (4 mm key bore) at the bottom.

The organic phase was added at the top of the column from a glass reservoir. This had a capacity of about 100 mls and was surrounded by a glass jacket through which water could be circulated. A burette (Grade A, 10 mls capacity) fitted on top of a side-arm which led into the reservoir.

The drops of the organic phase were formed at glass tips. These were made by drawing-out pieces of glass-tubing into jets, which were then ground until they were free from chips. The other ends of the tips fitted into a socket (B7) at the end of the reservoir. By using extension pieces made from glass capillary tubing, the height of the tip above the bottom of the column could be varied. In order to prevent the tips and extension pieces from falling down the column, they were attached to the reservoir by a nylon cord.

The volume of organic phase, which formed at the bottom of the column during an extraction run, was kept as small as possible by placing a glass filler rod in the section of the column leading to the stopcock (C). This rod fitted loosely into the section and was kept in a central position by three pips of glass fused on the side of the rod.

Before the column was first used, the taps (A), (B) and (C) were "ground-in" their sockets, by using a fine, wet, carborundum powder, in order to prevent leakage from the taps when the column was in use. No grease was used on any of the taps or joints in order to avoid the possibility of contaminating the system with components from the
grease. It was found that the taps could be operated smoothly and without any leakage of the solutions once they had been "ground-in" in their sockets.

The apparatus was cleaned with the aid of chromic acid, and it was then washed out with distilled water and acetone, before being dried with a current of air.

5.2.3 Preparation of solutions

The aqueous solutions containing copper (10.68m M) were prepared by dissolving copper (II) sulphate (Analar grade, B.D.H.) in water which had been deionised and distilled twice from a quartz still. The ionic strengths of the solutions were adjusted to unity with sodium sulphate (Analar grade, B.D.H). The solution of n-octoic acid in carbon tetrachloride (1.00 M) was prepared by weighing the acid (Eastman Kodak Company, melting point 15-16°C) into the required volume of carbon tetrachloride (B.D.H. Analar grade). The pH of the aqueous copper sulphate solution was adjusted with sodium hydroxide solution or dilute hydrochloric acid to the required value before it was placed in the extraction column.

Considerable care was taken when preparing and handling solutions to avoid contaminating the system with impurities. A number of studies have shown that even very small traces of impurities, especially when they are surface active, can have a very great effect on the transfer of material to and from liquid drops [160, 162].

5.2.4 Operation of the column

The reservoir was filled with the organic phase in the following manner. The tip and extension pieces were attached to the reservoir, and the tip was then dipped into a beaker containing the organic phase. The burette tap (A) was closed and the organic phase was sucked into the reservoir by opening tap (B) and applying suction to the capillary
tube with a pump. The tap (B) was closed when the reservoir was three parts full, and the organic phase was added through the burette up to the reference mark on the capillary tube. It was found necessary to fill the reservoir by sucking up the solution in order to displace the air bubbles which collected in the tip and extension pieces. However, the final adjustment of the liquid level up to the reference mark on the capillary tube could be controlled more accurately by adding the solution from a burette than by sucking up the solution.

The column was filled with the aqueous solution which was then allowed to reach a temperature of 25±0.1°C by circulating water through the jacket. The reservoir containing the organic phase was then placed in position on top of the column, taking care to ensure that all the air was expelled from the column. Water was then circulated round the reservoir until its contents were at a temperature of 25±0.1°C.

In order to release drops of the organic phase at a controlled rate from the tip, the following procedure was adopted. With the reservoir in position, tap (A) was closed and tap (B) was turned until it was fully open. Tap (C) was then carefully opened until drops were released from the tip at the required rate. Provided that no air was trapped in the column, the drop rate could be controlled by making adjustments on tap (C) only. A small volume of the organic phase (ca. 1 ml) collected continuously at the bottom of the column. After the column had been running for a short time (ca. 2 minutes) an organic phase containing copper could be collected from the bottom of the column without any entrainment of the bulk aqueous phase.

Preliminary experiments showed that for a constant drop rate the amount of copper extracted per unit time per unit volume of organic phase remained constant (±3% of mean value) after the column had been running for three minutes. The following standard operating procedure was therefore adopted. The column was set up and the drop rate was
adjusted to 20 drops per minute. After three minutes, the organic material was collected from the bottom of the column for a further ten minutes. Taps (B) of the reservoir and (C) of the column were then closed. The total volume of the organic phase which had passed through the column was then measured by opening tap (A) of the burette and adding more of the organic phase up to the reference mark on the capillary tube of the reservoir. By counting the total number of drops which had passed down the column, the volume per drop of the organic phase could then be calculated. In addition, the average time for the drops to fall from the tip to the interface at the bottom of the column was measured with a stopwatch. The samples of the organic phases which were collected from the bottom of the column were analysed for their copper concentrations by stripping aliquots of the phases with hydrochloric acid and then determining the copper in the stripped solutions by colorimetric analysis with oxalylldihydrazide as described for the equilibrium distribution studies (Chapter 4.).

The extraction of copper was measured as a function of the distance of fall of the drops (i.e. contact time) at a constant pH of the aqueous solution, and a range of pH values of the aqueous solutions were used. A tip of diameter 0.345 cms (outside) and 0.15 cms (inside) was used in the study. In order to carry out the series of measurements at a fixed pH, a large volume of the aqueous solution was prepared (18 litres), and the pH was adjusted with acid or alkali as required. The column was then filled with the solution, and the extraction at one fall height was measured. The column was then emptied, cleaned and dried as described above, and filled with a fresh sample of the aqueous solution. A measurement at a different fall height was then made. A similar procedure was used until all the measurements at a fixed pH had been completed. The solutions from the column were then combined, and the resulting solution was used for
a further two runs at different pH values before it was rejected. The copper concentration was checked between runs, and the effect of the copper extracted by the organic phases was found to be negligible.

5.2.5 The mass transfer coefficient

Consider a drop of organic phase falling through a continuous aqueous solution containing copper. Then a differential material balance on the dispersed-phase (i.e. organic phase) results in the following expression [156-159]:

\[ V \frac{dC}{dt} = k_d A \left( C - C_c \right) \]

(5.1)

where \( V \) is the volume of a drop (c.c.),

\( C \) is the average concentration of copper in the drop (g mole/l),
\( C_c \) is the copper concentration of the aqueous solution (g mole/l),
\( D \) is the equilibrium distribution ratio,
\( A \) is the interfacial area of the drop (sq. cm.),
\( k_d \) is the overall mass transfer coefficient based on the organic phase concentration (g mole/(sec.)(sq.cm.)(g mole/l)).

The boundary conditions on the drop concentration and time of contact were chosen as the average concentration in the drop \( C_{x_1} \) after a distance of fall \( (x_1) \) i.e. contact time of \( (t_1) \), and the average concentration \( C_{x_2} \) after a distance of fall \( (x_2) \) i.e. contact time of \( (t_2) \). With these boundary conditions, equation (5.1) was integrated as follows:

\[ \int_{x_1}^{x_2} \frac{dC}{C - C_c} = \int_{t_1}^{t_2} \frac{k_d A \ dt}{V} \]

(5.2)

Since the volume of the aqueous solution was large, the concentration of copper in it was assumed to be constant, and hence by carrying out the integration in equation (5.2):
\[
\ln \frac{C_{x_2} - DC_c}{C_{x_1} - DC_c} = \frac{k_d A}{V} (t_2 - t_1)
\]

If the velocity of fall is \( v \), then:

\[
k_d = \frac{Vv}{A(x_2 - x_1)} \ln \frac{C_{x_2} - DC_c}{C_{x_1} - DC_c}
\]

(5.4)

where \( v \) is in \((\text{cms. sec}^{-1})\).

In the paper by Garner and Hale [158], the integration of equation (5.2) appears to have been carried out incorrectly, since authors quote the result as:

\[
\ln \frac{C_{x_1} - DC_c}{C_{x_2} - DC_c} = \frac{k_d A}{V} (t_2 - t_1)
\]

The method described above has been used by a number of workers to study mass transfer in free-falling drops [156-159]. In the method it is not necessary to consider mass transfer which occurs during the formation and detachment of the drop, and thus leaves only the question of transfer during the withdrawal of the drops at the end of the column.

Since the object of the work was to study the mass transfer mechanism during the free-fall period of the drops, it was necessary to eliminate or minimise the effects of mass transfer during drop formation and coalescence.

At present, no reliable method exists in the literature for entirely eliminating end effects [159]. Thus the original graphical extrapolation procedure to zero column height that was given by Sherwood et al [166], and by Licht et al [167], using a plot of the log (solute fraction unextracted) as a function of drop-fall time, or column height, has been shown by Licht and Pansing to be invalid [168].
In the present study, in order to reduce the transfer to the coalesced drops at the bottom of the column, the interfacial area of the coalesced layer was kept very small. By using a filler rod, the volume of organic phase at the bottom of the column was kept to a minimum. Therefore the copper concentration in the samples collected should be approximately equal to the average concentration of the drops just before they land at the coalesced layer.

Transfer during withdrawal was assumed to be negligible by Calderbank et al in their work on droplet heat transfer, and their results agree well with theoretical predictions [169]. A similar method for considering end effects appears therefore to have been used by several workers before.

The interfacial areas of the drops (A) were calculated by assuming the drops to be spherical and of radius (r). Since the average volume of each drop (V) was known from the total number of drops formed from a known volume of the organic phase, the average radius of a drop (r) could be obtained from the standard formula for the volume of a sphere, viz:

\[ V = \frac{4}{3} \pi r^3 \]  

The average surface area of a drop was then calculated by substituting the value of (r) into the formula for the surface area of a sphere, viz:

\[ A = 4\pi r^2 \]  

The interfacial areas calculated by the above method were only approximate values, since the drops were not spherical in shape, but were elliptical. In free-fall, the drops tended to oscillate about their axes. A small spherical drop (Plateau's spherule) was formed behind the main drop as it fell from the tip, but the contribution of
this smaller drop to the total surface area and to the drop volume was ignored. In order to obtain information about the shape of the drops, and hence their apparent surface areas, it would be necessary to undertake a comprehensive study of the drops in free-fall by photographic techniques.

In addition to the difficulties of determining the effective surface areas of the drops, the general method of determining absolute rates of mass transfer to and from falling drops is complicated by a number of other factors. These mainly arise from interfacial turbulence, with the result that the measured transfer rates do not refer to absolutely quiescent interfaces [160].

5.2.6 The flux

In view of the difficulties in determining absolute values of the mass transfer coefficients by the present method, it was decided to use the flux (J) as an additional parameter in order to follow any changes in the transfer of copper to the falling drops as the pH of the aqueous extraction was changed. The flux (J) is defined as the amount of copper extracted per unit surface area of organic phase per unit contact time.

5.2.7 Results from extraction column experiments

The results obtained from a study of the extraction of copper (10.68 mM) from aqueous solutions containing sodium sulphate (0.319M) with falling drops of n-octoic acid (1.0OM) dissolved in carbon tetrachloride are given in Figs. 5.2-5.3.

Fig. 5.2 shows the average amount of copper extracted per unit surface area of the organic phase (M copper/litre/sq. cm) as a function of the distance of fall of the drops (cms), and of the pH of the aqueous solution.

The flux across unit surface area of the organic phase per unit
Fig. 5.2 Copper extraction as a function of distance of fall
Fig. 5.3 Flux (J) as a function of pH
contact time is plotted as a function of the pH of the aqueous solution in Fig. 5.3.

The values of the overall mass transfer coefficients based on the organic phase concentration \( k_d \) have been calculated from the extraction data given in Fig. 5.2 by using equation (5.4). The values of \( (C_{x_1}) \) and \( (C_{x_2}) \) were taken to be the average copper concentrations of drops after they had fallen distances of 30 cms. and 120 cms, respectively. The average velocity of the drops was 17.0 cms. per second. The values of the equilibrium distribution ratios (D) were obtained from the plot of \( \log D \) as a function of the equilibrium pH (Fig. 4.7, Chapter 4), which was determined from a series of equilibrium distribution measurements on the system. The values of (D) at pH = 3.556 and at pH = 5.240 were obtained by extrapolation of the plot.

Table 5.1 contains the values of the mass transfer coefficients, \( k_d \), expressed in \( \text{g. mole/(sec)(sq.cm)(g. mole/}) \) units.

<table>
<thead>
<tr>
<th>pH</th>
<th>D</th>
<th>V/A</th>
<th>( C_{30\text{cms}} ) (M/( l ))</th>
<th>( C_{120\text{cms}} ) (M/( l ))</th>
<th>( k_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.556</td>
<td>1.48 \times 10^{-2}</td>
<td>0.0551</td>
<td>6.342 \times 10^{-5}</td>
<td>1.057 \times 10^{-4}</td>
<td>0.07506</td>
</tr>
<tr>
<td>4.135</td>
<td>2.588</td>
<td>0.0552</td>
<td>3.838 \times 10^{-4}</td>
<td>1.036 \times 10^{-3}</td>
<td>0.0001753</td>
</tr>
<tr>
<td>4.510</td>
<td>9.441</td>
<td>0.0569</td>
<td>5.635 \times 10^{-4}</td>
<td>1.495 \times 10^{-3}</td>
<td>0.001235</td>
</tr>
<tr>
<td>4.868</td>
<td>14.52</td>
<td>0.0554</td>
<td>6.334 \times 10^{-4}</td>
<td>1.677 \times 10^{-3}</td>
<td>0.000909</td>
</tr>
<tr>
<td>4.945</td>
<td>14.96</td>
<td>0.0571</td>
<td>6.317 \times 10^{-4}</td>
<td>1.633 \times 10^{-3}</td>
<td>0.000846</td>
</tr>
<tr>
<td>4.965</td>
<td>15.07</td>
<td>0.0570</td>
<td>6.934 \times 10^{-4}</td>
<td>1.746 \times 10^{-3}</td>
<td>0.000875</td>
</tr>
<tr>
<td>5.103</td>
<td>15.56</td>
<td>0.0573</td>
<td>7.362 \times 10^{-4}</td>
<td>1.864 \times 10^{-3}</td>
<td>0.000910</td>
</tr>
<tr>
<td>5.240</td>
<td>161.4</td>
<td>0.0571</td>
<td>7.850 \times 10^{-4}</td>
<td>1.946 \times 10^{-5}</td>
<td>0.000060</td>
</tr>
</tbody>
</table>
5.2.8 Discussion of results

From Fig. 5.2, it is seen that a linear relationship exists between the amount of copper extracted per unit surface area of the organic phase and the distance of fall of the drops (i.e. contact time), at a fixed pH of the aqueous solution.

At a constant fall height, the amount of copper extracted increases with the pH of the aqueous solution. This would be expected, since the extraction of metal ions from aqueous solutions by carboxylic acids has been shown to depend largely on the pH of the aqueous solutions [25]. The maximum extraction is reported to take place at pH values just below the precipitation points of the metal hydroxides. Unfortunately, in the present extraction column it is only possible to study the extraction using aqueous solutions adjusted within a relatively small pH range, because of precipitation of the copper around pH 5.3 and the small amount extracted at low pH values.

The fact that a linear relationship exists between the amount of extraction and the contact time is rather surprising in view of the range of concentrations of copper than were extracted. Thus at the lowest pH value studied (3.556), the percentage extraction was less than 1% over the whole range of contact times, whereas at the highest pH (5.240) the extraction varied from 6.9% to 17.8% after contact times of 1.7 and 7.0 seconds, respectively.

The results would seem to indicate that some additional factor or factors are having compensating effects as the extraction of copper increases. The overall effect appears to be that a constant diffusion gradient or interfacial resistance is set up across the surface of the drop, and this leads to a linear relationship between extraction and contact times over a range of copper extraction.

The flux across the organic phase (J) is plotted as a function of the pH of the aqueous solution in Fig. 5.3. At low pH values, the
flux increases rapidly, but then levels off as the pH is increased. If the rate-determining step in the extraction involves a reaction at the interface, and if a radical change in the nature of the interfacial region had occurred with a change in the extraction conditions, then a corresponding change in the flux might be expected. Since in fact a continuous change in the flux is observed with increasing pH it appears that no radical change in the interfacial region has occurred.

At this point, it is interesting to consider the work of Spink and Sanders on the reaction between monolayers of stearic acid and copper (II) ions at the air-aqueous solution interface [153, 154]. The authors used a Langmuir surface balance to determine the force-area (Η-A) characteristics of the monolayers. It was found that as the pH of the aqueous substrate containing copper was increased, the nature of the surface film changed from liquid-condensed to solid-condensed, until the transformation was complete at a pH depending on the concentration of copper present. Immediately above this pH, the films were brittle, and they gave larger areas per molecule. The authors considered that the changes in the nature of the film were associated with the formation of a metallic soap in the monolayer over the lower range of pH, and then with basic soap formation at pH values close to the point of hydroxide formation.

The range of pH values over which Spink and Sanders observed the changes in the nature of the surface film varied with the concentration of copper (II) ions. It was found that the curves for different copper concentrations were similar in their characteristics, except that they were displaced 0.5 pH unit towards the lower pH values for each tenfold increase in copper concentration. By using this guide, the pH range over which a change in the surface film
should occur in the presence of 10 mM copper (II) ions should be pH 3.5 to 5.0. The extraction column studies were carried out with 10.68 mM copper (II) ions, and by analogy with Spink and Sander's work a change in the nature of the surface film might also be expected in this pH range. However, the present results from the extraction column do not give any evidence to support such a change.

Any direct comparison of the results from Spink et al with those from the extraction column is somewhat speculative, because a number of important differences are evident in the two studies. These factors may account for the apparently different nature of the interfacial films in the two cases.

Firstly, the fact that the column experiments were carried out by studying the liquid-liquid interface rather than the air-aqueous solution interface used by Spink et al, may have modifying effects on the film. In addition, as a result of the short alkyl chain of n-octoic acid \( \text{C}_{15} \text{H}_{31} \text{CO OH} \), the acid will not form very stable monolayers at either the air-aqueous solution, or organic solvent-aqueous solution interface. In comparison, the longer chain-length acids, such as stearic acid \( \text{C}_{17} \text{H}_{35} \text{CO OH} \), which are often used in monolayer studies at the air-aqueous solution interface, do form stable, insoluble, monolayers.

The interfacial region of the falling drops in the extraction column must also be considerably affected by the circulation within the drops, and also by the other hydrodynamic forces acting on them. The motion in the drops and also the motion of the drops themselves are complicated, as mentioned earlier. Thus, in comparison to the monolayer studies at the air-aqueous solution interface, which can be regarded as essentially equilibrium systems, the results from the extraction column were obtained under dynamic conditions.
The aqueous substrates used in Spink et al's work differed considerably from those used in the extraction column. The extraction of copper was studied from aqueous solutions containing sodium sulphate (0.319 M) to adjust the ionic strengths to unity. In comparison, the studies of Spink et al were carried out in the absence of ions other than copper (II). The presence of the large excess of electrolyte in the aqueous substrate must have a considerable modifying effect on the nature of the interface.

The fact that no radical change occurs in the nature of the interfacial region as the pH of extraction increases appears to be confirmed by the values of the mass transfer coefficients based on the organic phase concentration ($k_d$, Table 5.1). Over the range of pH from 4.0 to 5.1, the values of ($k_d$) are essentially constant ($\pm 8\%$ of mean value), which may indicate that no major change in the nature of the extraction occurs over this range. The values of $k_d$ at pH = 3.556 and pH = 5.240, however, differ considerably from the mean value of $k_d$ over the range of pH from 4.0 to 5.1. This is probably due in part to inaccuracies in estimating the values of the distribution ratio (D) by extrapolation of the log D-pH plot.

5.3 A study of the liquid-liquid interface by interfacial tension measurements

5.3.1 Introduction

A common method of studying adsorption at the liquid-liquid interface involves the measurement of interfacial tensions and then the application of the Gibbs adsorption equation to the data.

The Gibbs adsorption equation can be written in the following form [170]:

$$-d\gamma = \sum_i \Gamma_i \, d\mu_i = RT \sum_i \Gamma_i \, d \ln a_i,$$

(5.7)
where \( \gamma \) is the surface tension of a solution in which the chemical potential and activity of component \( (i) \) are \( \mu_i \) and \( a_i \), respectively, and \( \Gamma_i \) is the surface concentration of that component.

There has been considerable discussion in the literature as to whether the equation should be modified when applied to electrolytes, because each molecule can dissociate into two or more ions [170]. Thus, in the case of uni-univalent electrolytes, the equation is sometimes used with a factor 2, viz:

\[
\Gamma_2 = -\frac{1}{2RT} \frac{d\gamma}{d\ln a_2}
\]  

(5.8)

For example, in the absence of electrolyte, the adsorption of sodium alkyl sulphates at the heptane-water interface follows equation (5.8), whereas in the presence of added electrolyte, equation (5.8) without the added factor 2 is required [171].

However, small amounts of electrolyte may be sufficient to alter the behaviour of the systems so that the data agree with the equation omitting the factor 2, especially at low concentrations of the surface active agent [172].

In papers by Shinoda and Nakayama [173] and Lucassen-Reynders [174], the possibility of calculating the surface excesses of surface active ions and of gegenions separately at the air-water interface has been considered. The Gibbs adsorption equation has been used to interpret the surface tension data in the cases where either the surface active ion or gegenion concentration is held constant, while the other ionic concentration in each case is varied in a range below, but near to, the critical micelle concentration, or monolayer-completion concentration.

For a four-component mixture in a dilute solution, the adsorption equation at constant temperature is given by:
where component 1 refers to water, component 2 is the surface active ion, component 3 is the gegenion, and the simili-ion is component 4. Shinoda et al assume electroneutrality for the bulk of the solution, and then base their calculations on the assumption that the adsorption of the simili-ion is zero. However, as Lucassen-Reynders points out [174], the electroneutrality of the bulk of the solution also implies that the surface is also electrically neutral i.e:

$$\Gamma_2 + \Gamma_4 = \Gamma_3,$$  (5.10)

which requires a non-zero value for $\Gamma_4$, and is a contradiction of the other assumptions used by Shinoda et al. In addition, the known existence of quite high surface potentials under these conditions casts some doubt on the validity of the assumption of electrical neutrality of the surface.

In the case of the liquid-liquid systems resulting from the extraction of metal ions with carboxylic acids, it is not possible at the moment to analyse the interfacial tension data by the Gibbs adsorption equation owing to the complexity of the system. The equilibrium aqueous phase contains excess electrolyte (e.g. sodium sulphate), copper (II) ions, and anions of the carboxylic acid, and the organic phase consists of the copper and sodium complexes of the acid, together with excess of the carboxylic acid.

In addition, it would be very difficult to obtain a direct measure of the adsorption at the interface of the system by using the normal methods for the liquid-liquid interface i.e. the emulsion method [175], but it may be possible to obtain some additional information from surface potential [172] or radiotracer studies.

Even though a direct analysis of the interfacial tension data
by the Gibbs equation is not possible in the present system, the fact that the extraction is largely pH-dependent may lead to changes in the nature of the interfacial region as the extraction proceeds, and it may be possible to obtain qualitative information about the region from the measurements.

5.3.2 Measurement of interfacial tensions by drop-weight method

The drop-weight method provides a very convenient method for measuring surface and interfacial tensions. The use of the method for studying a variety of systems has been extensively reported in the literature [160, 176-8], and is well established.

The method is based on the fact that the weight (or volume) of a liquid drop which detaches itself from the tip of a vertical tube is determined largely by the surface tension of the liquid. If the drops are formed very slowly, they detach themselves completely from the tip when the gravitational pull just reaches the restraining force of surface tension:

\[ Mg = V d g = 2 \pi a \gamma \]

i.e. \( \gamma = \frac{Mg}{2 \pi a} = \frac{Vdg}{2 \pi a} \),

(5.11)

where \( (g) \) is the gravitational acceleration, \( (M) \) and \( (V) \) are the mass and volume of each drop that falls from the tip, \( (d) \) is the density of the liquid, and \( (a) \) is the radius of the tip of the tube.

However, it is necessary to correct these relations since the liquid forming the drop does not completely leave the tip and also the tip is seldom exactly vertical. The importance of the correction factors is indicated by the fact that drops can be as much as 40 per cent smaller than predicted by equations (5.11) [160]. Harkins and Brown made a very careful experimental study of drop sizes and they introduced a correction factor, \( (F) \) [176, 179]. They found that \( (F) \)
is a function of \(a\) and \(V\), where:

\[
\gamma = \frac{F \Delta g}{2 \pi a} = \frac{F V \Delta g}{2 \pi a}
\]  

(5.12)

The factor \(F\) can be obtained from the tables of Harkins and Brown [176, 179].

It has been reported that tips should be of such a size that the ratio \((a/V^2)\) lies between 0.75 and 0.95, since the factor \((F)\) is least sensitive to variations in \((a/V^2)\) in this range [160]. In the present measurements of the interfacial tensions of n-octoic acid/carbon tetrachloride-aqueous solution systems, the tip used gave a ratio of \((a/V^2)\) between 0.75 and 1.20 over the range of systems studied.

5.3.3 Experimental study

The drop-volume method is particularly suitable for measurement of interfacial tensions between two immiscible liquids [180]. In this case the drops that are obtained are much larger than those at the air/liquid interface, and the sizes of the drops can be measured volumetrically with considerable accuracy. The tip can be joined to an "Agla" micrometer syringe (Messrs. Burroughs Wellcome and Co., Ltd., London) by which the volume of the drop can be measured directly. The micrometer can be read down to a reading equivalent to 0.0001 ml.

The tips used in the measurements must be ground truly cylindrical and perpendicular, and the edges must be sharp and free from any imperfections (e.g. chips in the perimeter). The outside of the tip from which the drops are formed must either be completely wetted or completely non-wetted by the liquid, otherwise drops will be formed with an unknown value of \((a)\). However, the bore of the tip must not be too hydrophobic or the drops will break off inside the bore instead of right at the end of the tip. A very lightly siliconised stainless steel provides a good material for the tip. In the present study a
tip was turned on a lathe from a stainless steel (Firth-Vickers FM). One end of the tip was tapered to fit accurately into the end of the barrel of an Agla syringe. The other end of the tip from which drops were formed had a diameter of 0.9054 cms by cathetometer. This end of the tip was lightly siliconised by using "Repelcote" water repellent (Hopkin and Williams, Ltd.), which consists of a solution of dimethyldichlorosilane in carbon tetrachloride. The tip was recoated with "Repelcote" periodically.

It is important when making interfacial tension measurements that the syringe and tip are held securely in a vertical position and also free from any vibration. In addition, the measurements must be carried out at a constant temperature. In the present study, the micrometer syringe with the tip attached was fastened to a brass former which could be supported inside a glass cylinder (Fig. 5.4). A sample tube containing the aqueous solution was placed inside a larger tube, which was then secured in a large rubber bung and inserted in the bottom of the cylinder. The syringe was carefully filled with the organic phase by means of a small pipette and the tip was inserted. The syringe and tip were then mounted in the glass cylinder and adjusted so that the end of the tip was beneath the surface of the aqueous solution in the sample tube. The complete assembly was then supported in a thermostat tank and allowed to reach the temperature of the tank (25± 0.05°C) which took about one hour.

After having checked that the drop completely wetted the end of the tip, the drop was carefully expanded by rotating the micrometer. The initial formation of the drop was performed quite quickly, but the delivery of the final 10 per cent of the volume leading to detachment was carried out very slowly and carefully over a period of about 10 minutes. In the final stages of the drop formation it was necessary to operate the micrometer very carefully in order to prevent any vibration.
Fig 5.4 Diagram of drop-volume apparatus
from being transmitted to the syringe and tip, which would cause the drop to fall prematurely. After each drop had been detached, the volume of the drop was obtained from the reading on the micrometer. A number of drops were formed at the tip in the same way and the mean volume was calculated. In a series of measurements on each sample it was found that the volume of each drop was within ±0.5% of the mean volume.

After a series of volume measurements had been completed, the syringe was removed from the thermostat tank and was washed out with carbon tetrachloride. The glass syringe and glass sample tubes were soaked in clean chromic acid until they remained completely wetted when they were withdrawn from the acid. They were then washed with syrupy phosphoric acid to remove adsorbed chromate ions, as recommended by Davies and Rideal \[160\], followed by distilled water. All glassware was then "steamed-out" for 15 minutes using steam produced by boiling distilled water, before being washed with twice-distilled water, and dried in an oven. The stainless steel tip was thoroughly washed with carbon tetrachloride (Analar grade, B.D.H.) and then dried in an oven. The tip was not cleaned in the chromic acid, because stainless steel is attacked by the acid.

All the aqueous solutions were prepared from "Analar" grade reagents using deionised water which had been distilled twice from a quartz still. The organic solution was prepared by dissolving n-octoic acid (Kodak Chemical Co., Melting point 15-16°C) in carbon tetrachloride (B.D.H., Analar grade) as described for the equilibrium distribution studies. All the solutions were prepared and handled with care to ensure that no surface-active impurities contaminated the systems.

In order to apply equation (5.12) to the calculation of interfacial tensions, the density (d) has to be replaced by the effective density of the heavier liquid when suspended in the lighter one i.e.
the difference between their densities [180]. All the densities measured in the study were determined at a temperature of $25 \pm 0.1^\circ C$ with a pyknometer (10ml).

A series of interfacial tension measurements have been carried out on the extraction system studied previously by the falling-drop method in the column. The interfacial tensions of the following systems were determined as a function of the pH of the aqueous substrates:

(a) copper sulphate (10.68 M)/sodium sulphate (0.319 M)/water – n-octoic acid (1.000 M)/carbon tetrachloride.
(b) copper sulphate (10.68 M)/water – n-octoic acid (1.000 M)/carbon tetrachloride.
(c) sodium sulphate (0.319 M)/water – n-octoic acid (1.000 M)/carbon tetrachloride.
(d) water – n-octoic acid (1.000 M)/carbon tetrachloride.

For each system, aliquots of the two phases were shaken together for one hour at $25 \pm 0.05^\circ C$, after having adjusted the pH of the aqueous substrate with sodium hydroxide solution. The two phases were then allowed to separate, and aliquots of the phases were removed as described in the procedure for carrying out the equilibrium distribution studies (Chapter 4). The interfacial tensions of the systems were then measured by the drop-weight method at $25 \pm 0.05^\circ C$.

5.3.4 Results of interfacial tension measurements

The interfacial tensions of the systems (dynes/cm) are plotted as a function of the pH of the equilibrium aqueous substrates in Fig. 5.5.

In the case of systems containing sodium sulphate, the interfacial tension falls steadily as the pH of the aqueous substrate increases. The presence of copper (II) ions in the system does not appear to lead to any significant change in the variation of the
Fig. 5.5 Interfacial tensions at 25°C for Cu(II) extraction systems as a function of equilibrium pH.
interfacial tension with pH.

In the absence of any sodium sulphate in the system, the extraction of copper (II) ions leads to a much smaller reduction in the interfacial tensions as the equilibrium pH increases.

If a radical change in the nature of the interfacial region occurred over a definite range of pH, then it might be expected to lead to a marked change in the interfacial tension in this region. Since in the present study only a gradual decrease was observed as the pH increased, it would appear that no marked change in the structure of the interfacial region had occurred.

The presence of copper (II) ions in the system containing sodium sulphate had only a small effect on the interfacial tension. This may be due to the large excess of sodium sulphate present which may lead to an increasing concentration of sodium counter-ions near to the interface as the pH of the substrate, and hence the degree of ionisation of the carboxylic acid, increased. When copper ions are present in the system, an exchange process may take place between the sodium and copper ions and this may lead to only a small change in the interfacial tension. In addition, only a small number of copper ions may be present in the interfacial region as a result of the excess of sodium ions present in the system.

The presence of sodium sulphate in the system will also affect the mutual solubility of the n-octoic acid and water, and hence the distribution ratio of the acid, since the concentration of acid in the aqueous phase is decreased in the presence of the salt [181]. As far as the effect on the interfacial tension is concerned, it is found in general that the addition of a salt which enhances the mutual solubility of two components of a system will lower the interfacial tension, and vice versa [182]. However, the behaviour of systems containing four or more components is complex. For example, if sodium...
chloride is added to a water-sodium stearate-benzene system, the interfacial tension between the two phases is reduced, apparently because the sodium soap is "salted-out" by the sodium chloride either into the benzene phase or into the interface [183].

In addition, the ions in the aqueous solution will have a modifying effect on the structure of the water in the solution, and this in turn will have an effect on the structure of the interface.

In order to discuss these effects, it is necessary to consider the structure of liquid water.

A considerable number of models have been put forward in the literature in attempts to describe the structure of liquid water. The common feature of each of these models appears to be that the structure is based on a partial retention of the tetrahedrally-directed hydrogen-bonding involved in the structure of ice, but with the length of the O---H—O bond increased. Kavanau suggests that water can be regarded as a specific type of associated liquid in which the association is present in the whole volume of the liquid and gives rise to a three-dimensional network [184].

The presence of ions in water appears to modify the tetrahedral lattice of the water molecules, and tends to impose a new order on them. This seems to be largely due to the difference between the ion-water and the water-water interactions [184]. The effect of an ion on the water structure is approximately proportional to its polarising power i.e. the ratio of charge to radius. Thus, Everett has estimated the range of influence of alkylammonium and carboxylate ions on neighbouring water molecules to be 5 Å [185].

Anions and cations have different modifying effects on the structure of water [184]. Thus with anions, the predominating effect appears to be a lattice distortion due to steric factors which depend largely on the shape and size of the ions. As expected, the steric
disturbance increases with the volume of the dissolved ion, and hence the region in which hydrogen-bonds are being disturbed or broken also increases. In the case of cations, the interactions between the solute and the water lattice give rise to additional lattice distortions associated with changes in the ionic and molecular charge distributions [184].

The water structure is substantially distorted in the presence of transition-metal ions since these can form strong donor-acceptor bonds with the water molecules. The attraction between these ions and water is strong, with the result that complexes can often be identified in solution. Thus with $[\text{Cr(H}_2\text{O)}_6]^3+$, the exchange rate of the complexed water is known to be very slow (half-life ca. 40 hours) [184]. Nuclear magnetic resonance studies of paramagnetic cations in $^{17}$O-enriched water give mean lifetimes of water molecules in the first coordination sphere from $5 \times 10^{-7}$ seconds for the copper (II) ion to $3.7 \times 10^{-3}$ seconds for the nickel (II) ion [184].

At the interface between an organic phase and an aqueous solution, it has been suggested that some of the water molecules will be oriented by the adjacent methylene groups of surface-active molecules into an ice-like structure [160]. Part of this effect has been attributed to hydrogen-bonding, and similar interactions have been reported for the dissolution of both rare gases and hydrocarbon gases in water [160].

One widely-held explanation for the effect is that the water forms a "cage" around the non-polar substance, causing enthalpy and entropy to be lost and diminishing the total free volume of the solution [186]. This entropy loss in fact is mainly responsible for the increasing insolubility of homologous, long-chain, molecules in water. At a liquid-liquid interface, it appears that the dipoles of monolayer-forming molecules may orientate and hinder the rotation of the dipoles
of several layers of water molecules at the interface below the head-
groups [160].

In the case of an interface between an organic phase containing
carboxylic acids and an aqueous phase containing copper (II) and
sodium ions, it is possible that only those acid molecules which have
preferred orientations will be adsorbed at the interface, and only
these molecules may actually take part in the extraction of the copper
ions.

The idea of preferred orientations at interfaces was first put
forward to explain the relatively slow rate of adsorption of palmitic
acid at the water-hexane interface [170]. Although part of the
adsorption time may be attributed to a breakdown of the dimeric
structure of the acid in the organic phase to give monomers which may
then be adsorbed at the interface, this explanation does not completely
describe quantitative results which are obtained. It has therefore
been suggested that an entropy barrier exists at the interface, and
that it is necessary for the molecules to become ordered or lose some
of their degrees of freedom before they can be adsorbed [187].

The presence of an electric charge on the carboxylic acid
molecules at the interface, as a result of ionisation and the
adsorption of counter-ions, will lead to a change in the properties
of the interfacial film and also to a difference in the pH between
the bulk solution and the interface [160]. The electric charge
leads to a considerable loss of lateral adhesion between the acid
molecules as a result of the repulsion between the similar electric
charges developed on adjacent end-groups, where dissociation takes
place [188,189].

A further important effect of the charge on the acid molecules
at the interface is that the pH value at the surface is altered.
Thus, Peters measured the interfacial tensions of long-chain acids
at the benzene-water interface and found that the change of inter-
facial tension which is indicative of half-ionisation occurred at
about three pH units to the alkaline side of the point at which such
acids are half-ionised in solution [190,191]. As Davis and Rideal
point out, if the pK value of the head-group (-COOH) is assumed not
to change, then these interfacial tension measurements show that the
pH in the surface must be different from the measured value in the bulk
aqueous phase [160]. From the Boltzmann equation for the distribution
of a cation (e.g. H\(^+\)) in terms of a potential (\(\psi\)) near the positive
surface relative to the bulk of the liquid:

\[
S_{H^+}^C = C \cdot e^{-\psi/2kT},
\]

where (C) refers to ionic concentration, the subscript (S) refers to
the surface, (k) is the Boltzmann constant, (T) is the absolute
temperature, and (\(\psi\)) is the potential. Hence, since by definition
pH = -log \(C_{H^+}\):

\[
\text{pH}_S = \text{pH}_B + \psi / 2.3kT,
\]  

(5.14)

where pH\(_S\) and pH\(_B\) are the surface and bulk pH, respectively. Thus from
equation (5.14) it is evident that only when \(\psi = 0\) will the surface
and bulk pH values be equal, and if \(\psi\) is negative, pH\(_S\) will be less
than pH\(_B\) since the charge on the surface attracts hydrogen ions into
the vicinity of the surface.

The effect of the charged surface on the pK value of the head-
group appears to be relatively small, even in the case of weakly
ionised long-chain compounds. Thus Betts and Pethica found only a
small shift in pK (ca. 0.7 units) for stearic acid and nonadecylamine
adsorbed at the air-aqueous solution interface [192]. It is possible
that the effect may be more pronounced when the aqueous solution
contains a considerable excess of electrolyte. Davies and Rideal,
however, are of the opinion that any changes of pK at the surface will be small and that one may calculate with reasonable accuracy surface properties, including pH, using the normal bulk value of pK for the head-groups [160].

5.4 A general consideration of the nature of the interface in the extraction system.

It is evident from a consideration of the liquid-liquid system resulting from the extraction of metal ions from aqueous solutions by carboxylic acids in organic solvents that the interface will be affected by a considerable number of factors.

In the interfacial region, the acid will be present both in an unionised and an ionised form, with the relative proportions of each depending largely on the pH of the substrate. The orientation of these acid molecules will also depend on the pH as a result of the repulsion between the molecules as they become ionised. In addition, the dimeric structure of carboxylic acids in organic solvents is likely to have a considerable effect on the structure of the interfacial region. The dimeric structure will depend on the nature of the organic solvent since the dimerisation of the acid is reduced as the solvent becomes more polar. The presence of a charge on the interfacial region, resulting from the ionisation of the acid and adsorption of counter ions, will lead to a change in the properties of the interface, and to a difference between the interface and bulk pH values.

The water molecules in the vicinity of the interface will be oriented by the methylene groups of the long-chain carboxylic acids, and in the bulk aqueous phase the presence of the metal and electrolyte ions will have a considerable effect on the water structure. The net effect of the ions on the water structure will be either a
structure-breaking or a structure-making action depending on the size and charge of the ions. In addition to the simple anions and cations, the presence of hydrated and hydrolysed species and metal-carboxylic acid species in the aqueous phase will have a modifying effect on the water structure.

In order to obtain further information about the nature of the interface, a study of the variation of the surface potential with extraction conditions might be useful. Also, by the use of radio-tracer studies it might be possible to obtain further details about the transfer of species across the interface, provided that the extraction conditions are carefully controlled.
CHAPTER 6

General Conclusions
It is difficult to obtain direct evidence for the structures of species involved in the extraction of metal ions into organic solvents with carboxylic acids because of the nature of the systems. Since the heavy metal carboxylates are not very soluble in pure organic solvents alone, the extractions are usually carried out with an excess of the carboxylic acid in an organic solvent. The carboxylates are appreciably soluble in the presence of an excess of the acid, and this suggests that solvation of the complexes occurs in the organic phase. However, it does not appear to be possible to isolate the solvated complexes from solution, although a number of adducts, such as the urea derivatives have been isolated and analysed.

The fact that the organic phases contain excess of the carboxylic acid also makes the interpretation of absorption spectra from the systems more difficult. The excess acid leads to a swamping effect, and consequently any weak absorption bands will probably not be detected.

The accurate determination of the equilibrium distribution data is made difficult in the present system by the problems of pH measurement. As mentioned in Chapter 2, the solubility of the carboxylic acids used as extractants increases in the aqueous phase with the pH of extraction. The adsorption of these long-chain acids onto glass electrodes appears to be responsible for the drift in the pH with time that is observed when equilibrium aqueous phases are measured. Again, the accurate determination of pH is complicated by the presence of the excess "inert" electrolyte in the aqueous phase.

The extraction expression proposed in equation (2.67) can be used to describe the extraction of metal ions with carboxylic acids if only one complex predominates in the organic phase. If more than one complex is present in appreciable amounts than the general expression given in equation (2.64) must be used. This expression,
however, is difficult to apply directly to the analysis of experimental extraction data.

The analysis of the extraction data using graphical methods based on equation (2.67) is satisfactory if the acid concentration in the organic phase can be regarded as constant during extraction i.e. for low loading of the organic phase and low solubility of the acid in the aqueous phase. However, the graphical representation of the results for more than one extracted complex becomes difficult.

The use of regression methods of analysis for systems containing mainly one complex is convenient provided that experimental errors are not high. The most efficient procedure is to use the regression methods of analysis in conjunction with graphical methods. The latter can be used to reject data of high experimental error, and regression methods can then be used to obtain reliable estimates of the "fit" between the data and the proposed structures.

The analysis of data from systems containing mixed complexes is probably best tackled with the aid of regression procedures. However, the problem is complicated since with the methods based on the technique of minimising the errors between the data and the proposed structures, it is often difficult to decide if the results represent true situations. Obviously the problem has to be considered from a chemical as well as from a mathematical viewpoint.

The results obtained from the study of the extraction of copper by n-octoic acid in the column by the falling-drop method suggest little variation of the rate of extraction with pH. The range of pH conditions which can be used with the present extraction column, however, is rather limited. The problem of the precipitation of the metal hydroxide as the pH is raised, and the small amount extracted at low pH values limit the extent of the studies. It may be possible to extend the study of the lower range of extraction by using
radioactive tracers, but in a column of the same dimensions as the present one the problem of disposal of the radioactive waste would be considerable. A study of the mass transfer of metal ions from drops of the aqueous phase falling through the organic phase may yield additional information about the extraction at the higher pH values.

The presence of excess electrolyte in the aqueous phase will have a considerable modifying effect on the nature of the interfacial region in these extraction systems. As the pH of the aqueous phase is increased, the carboxylic acid molecules become ionised and the counter-ions of the electrolyte become adsorbed at the interface. The presence of the resulting electric charge at the interface leads to changes in the properties of the interfacial film, which may affect the extraction of the metal ions. On the other hand, the electrolyte may have a swamping effect on the system, and small changes in the interfacial tensions due to extraction of metal ions may not be detected.

As far as the use of carboxylic acids as commercial extractants of metal ions is concerned, two serious disadvantages appear to limit their widespread use. Firstly, the cost of the alkali required to adjust the pH of the aqueous solutions is regarded as being prohibitive. Although relatively cheap alkalies are available, such as calcium hydroxide, these have some undesirable effects on the extraction. Secondly, the loss of reagent through its solubility in the aqueous phase becomes important with the extraction of metals at high pH e.g. Co/Ni. This effect may be minimised by using longer-chain acids but these are more expensive reagents.
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APPENDIX 1. PROGRAM FOR ACID DIMER ERROR CALCULATION.

READ 1,ZKDO,N
1 FORMAT(E10.4,I12)
PUNCH 2,ZKDO
2 FORMAT(10HM-J.JAYCOCK/32HCALCULATION OF ACID DIMER ERROR./5HZKDO=,
1 E10.4//3X,3HCHR,11X,5HERRO,11X,5HRATIO/)
DO 4 M=1,N
READ 3,CHR
3 FORMAT(E10.4)
   AHRO=(-1.+SQRTF(1.+8.*ZKDO*CHR))/(4.*ZKDO)
   APRO=SRTF(CHR/(2.*ZKDO))
   ERROR=100.*(APRO-AHRO)/AHRO
   RATIO=APRO/AHRO
4 PUNCH 5,CHR,ERROR,RATIO
5 FORMAT(E10.4,5X,E10.4,5X,E10.4)
PUNCH 6
6 FORMAT(79X,1H-)
   CALL EXIT
END
C APPENDIX 2. PROGRAM FOR PARTITION OF ACID AS A FUNCTION OF PH.

READ 10,PH,R
10 FORMAT(2F7.4)
READ 11,ZKP,ZKHA,ZKDO,ZKDA
11 FORMAT(4E10.4)
PUNCH 12
12 FORMAT(11HM,J.JAYCOCK/38HPARTITION OF ACID AS A FUNCTION OF PH./
14X,2HPH,18X,1HR,17X,3HDHR17X,7HLOG DHR/)
PUNCH 13
13 FORMAT(3HKP=E10.4,8X,4HKHA=E10.4,8X,4HKDO=E10.4,8X,4HKDA=E10.4
1/
DO 40 K=1,50
H=EXPF(-PH*2.3025851)
AQ=2.*ZKDA*((ZKHA/H)**2)+2.*ZKDO*ZKP*ZKP
BQ=1.+ZKP+ZKHA/H
HR=(SQRTF(BQ*BQ+4.*AQ*R)-BQ)/2.*AQ
DHR=(ZKP*(1.+2.*ZKDO*ZKP*HR))/(1.+ZKHA/H+2.*ZKDA*((ZKHA/H)**2.)*HR
1)
RC=DHR*R/(1.+DHR)
XDHR=LOGF(DHR)/2.3025851
PUNCH 39,PH,RC,DHR,XDHR
39 FORMAT(El0.4,2(10X,El0.4),10X,F8.5)
40 PH=PH+.1
PUNCH 91
91 FORMAT(79X,1H-)
CALL EXITX
END
APPENDIX 3. LINEAR REGRESSION PROGRAM FOR ONE COMPLEX.

```plaintext
DIMENSION DZ(10,50), CMZ(10,50), PHZ(10,50), RHINTZ(10), CMINTZ(10), J1Z(10), XZ(10,50), AVERUZ(50), RMSRUZ(50), CONSTZ(50), RZ(50), MZ(50)
READ (1,101) I5
101 FORMAT(I2)
100 FORMAT(3I1)
READ(1,1) I1, I2, I3
READ(1,11) I1, I2, I3, J2, M1, M4
1 FORMAT(F4.0,12,F7.3,I2,I3)
DO 3 J1 = 1, J2
READ(1,110) RHINT, CMINT, J1
110 FORMAT(F7.4,F7.2,I2)
RHINTZ(JA) = RHINT
CMINTZ(JA) = CMINT
J1Z(JA) = J1
DO 3 J = 1, J1
READ(1,2) D, CM, PH
2 FORMAT(3F7.4)
DZ(JA, J) = D
IF (11) 21, 21, 22
21 CMZ(JA, J) = CM - (ALOG(ATWT))/2.3025851
GO TO 3
22 CMZ(JA, J) = CM
3 PHZ(JA, J) = PH
WRITE (2,30) ATWT
30 FORMAT(1X,11HM,J.JAYCOCK//1X,69HLEAST SQUARES ANALYSIS OF DISTRIBUTION DATA AS A FUNCTION OF J AND X./1X,11HATOMIC WT.=/,F8.3//)
```
350 CONTINUE  
   IF(I2+I3) 358, 358, 351  
358 WRITE (2, 359)  
359 FORMAT(1X, 15HRH UNCOrRECTED.//)  
351 IF(I2) 354, 354, 352  
352 WRITE (2, 353)  
353 FORMAT(1X, 33HRH CORRECTED FOR ACID IN COMPLEX.//)  
354 IF(I3) 131, 131, 355  
355 WRITE (2, 356)  
356 FORMAT(1X, 36HRH CORRECTED FOR AQUEOUS SOLUBILITY.//)  
   READ(1, 11) ZKP, ZKHA, ZKDO, ZKDA  
11 FORMAT(4E10.4)  
   WRITE (2, 12) ZKP, ZKHA, ZKDO, ZKDA  
12 FORMAT(1X, 3HKP=,E11.4, 7X, 4HKHA=,E11.4, 7X, 4HKDO=,E11.4, 7X, 4HKDA=,E11.4)  
131 DO 94 K=1, M1  
   PJ=K  
   IF(I2+I3) 361, 361, 121  
121 IF (K=6) 31, 34, 34  
31 IF (K=3) 32, 33, 33  
32 M2=4*K  
   GO TO 35  
33 M2=3*K  
   GO TO 35  
34 M2=2*K  
35 M2=M2+1  
   M5=M4  
   GO TO 360  
361 M2=1  
   M5=1
360 WRITE (2, 36)
36  FORMAT(//3X,1HJ, 5X,1HX,7X,5HSLOPE,9X,6HCONST.,7X,6HAV.ERROR,5X,9
1HRMS.ERROR,4X,10HCORR.COEF./)
    AVERZ=100.
    DO 7 L=1,M5
      XS=L-1
      I=XS
      DSUM=0.
      XSUM=0.
      X2SUM=0.
      XDSUM=0.
      JSUM=0
      IC=0
      DO 362 IM=1,50
        MZ(IM)=0
        DO 4 MA=1,J2
          RHINT=RHINTZ(MA)
          CMINT=CMINTZ(MA)
          J1=J1Z(MA)
          JSUM=JSUM+J1
          R=RHINT
          DO 4 M=1,J1
            D=DZ(MA,M)
            CM=CMZ(MA,M)
            PH=PHZ(MA,M)
            IF (12)365,365,364
        R=RHINT-(Z+XS/PJ)*(EXP(2.3025851*(CM+D)))
    364 IF (13)367,367,366
    365 H=EXP(-PH*2.3025851)
    366 AQ=2.*ZKDA*((ZKHA/H)**2)+2.*ZKDO*ZKP*ZKP
\[ BQ = 1. \times ZK + ZK + ZK \times H / H \]
\[ HR = \left( (BQ + 8Q + 4. \times AQ) \times AQ \right) + 5 - BQ / 2 \times AQ \]
\[ DHR = (ZK \times (1. + 2 \times ZDO \times ZKP \times HR)) / (1. + ZKHA / H + 2 \times ZKDA \times (ZKHA / H) \times 2) \times HR \]

\[ R = DHR \times R / (1. + DHR) \]
\[ IF(R)370, 370, 367 \]

\[ IC = IC + 1 \]
\[ RZ(IC) = R \]
\[ MZ(IC) = M \]
\[ GO TO 4 \]

\[ 367 \]
\[ X = (P \times J - 1) \times CM + Z \times P \times PH + (Z \times P \times X) \times ALOG(R) / 2.3025851) / 2. \]
\[ XZ(MA, M) = X \]
\[ X2 = X \times X \]
\[ XD = X \times D \]
\[ DSUM = D + DSUM \]
\[ XSUM = X + XSUM \]
\[ X2SUM = X2 + X2SUM \]
\[ XDSUM = XD + XDSUM \]
\[ SN = JSUM - IC \]
\[ SLOPE = (SN \times XDSUM - XSUM \times DSUM) / (SN \times X2SUM - XSUM \times XSUM) \]
\[ CONST = (X2SUM \times DSUM - XSUM \times XSUM) / (SN \times X2SUM - XSUM \times XSUM) \]
\[ ERSUM = 0 \]
\[ ER2SUM = 0 \]
\[ IF(IC)52, 52, 940 \]

\[ 52 \]
\[ DO 5 NA = 1, J2 \]
\[ J1 = J1 + (NA) \]
\[ DO 5 N = 1, J1 \]
\[ IF(MZ(NA))521, 521, 5 \]

\[ 521 \]
\[ D = DZ(NA, N) \]
\[ DC = SLOPE \times XZ(NA, N) + CONST \]
ERROR = \text{ABS}(D-DC)
ERROR2 = (D-DC)^2
ER2SUM = ER2SUM + ERROR2
ERSUM = ERROR + ERSUM
5 CONTINUE
AVER = ERSUM/SN
RMSERR = (ER2SUM/SN)^0.5
DXSUM = 0.
DDSUM = 0.
DO 51 MB = 1, J2
  J1 = J1Z(MB)
  DO 51 M3 = 1, J1
    DXXSUM = DXXSUM + (XZ(MB, M3) - XSUM/SN)^2
 51 DDDSUM = DDDSUM + (DZ(MB, M3) - DSUM/SN)^2
CORR = SLOPE * (DXSUM/DDSUM)^0.5
WRITE (2, 6) K, I, SLOPE, CONST, AVER, RMSERR, CORR
6 FORMAT (1X, I3, 3X, 13, 4(3X, E11.4), 4X, F10.7)
ERUSUM = 0.
R2USUM = 0.
DO 63 L3 = 1, J2
  J1 = J1Z(L3)
  DO 63 L2 = 1, J1
    DUX = XZ(L3, L2) + (DSUM - XSUM)/SN
    CONSTZ(L) = (DSUM - XSUM)/SN
    R2USUM = R2USUM + (DZ(L3, L2) - DU)^2
 63 ERUSUM = ERUSUM + ABS(DZ(L3, L2) - DU)
AVERUZ(L) = ERUSUM/SN
RMSRUZ(L) = (R2USUM/SN)^0.5
IF (L-M2) 62, 61, 61
61 IF (AVERZ - AVER) 9, 62, 62
62 AVERZ=AVER
7 CONTINUE
9 WRITE (2,92)
92 FORMAT(//32X,15HUNIT SLOPE FIT.,/3X,1HJ,5X,1HX,7X,8HAVERROR,7X,
19HRMSERROR,5X,6HCONST./)
I=I+1
DO 94 L1=1,I
  LX=L1-1
  WRITE (2,93) K,LX,AVERUZ(L1),RMSRUZ(L1),CONSTZ(L1)
93 FORMAT(1X,I3,3X,I3,5X,E10.4,2(4X,E10.4))
94 CONTINUE
940 IF(IC)98,98,95
95 WRITE(2,900)PJ,XS
900 FORMAT(1X,22HR NEGATIVE FOR POINTS=/1X,3HPJ=E11.4,5X,3HXS=E11.4)
DO 97 LC=1,IC
  WRITE(2,96)MZ(LC),RZ(LC)
96 FORMAT(1X,2HM=E11.4,7X,2HR=E11.4)
98 READ(1,194)14
194 FORMAT(I1)
  IF(I4)197,197,195
195 READ(1,196)I1,I2,I3
196 FORMAT(3I1)
  WRITE(2,198)
198 FORMAT(///)
  GO TO 350
197 WRITE (2,91)
91 FORMAT(1H1)
99 CONTINUE
END
FINISH
APPENDIX 4. MULTIPLE REGRESSION PROGRAM FOR A SINGLE COMPLEX:

```
DIMENSION DZ(10,50),CMZ(10,50),PHZ(10,50),RHINTZ(10),CMINTZ(10),J1Z(10),X1Z(10,50),X2Z(10,50)
READ(1,101)
101 FORMAT(12)
   DO 71 K=1,I5
      READ(1,100)I1,12,I'
100 FORMAT(C3I)
      READ(1,1)Z,J2,ATWT
      FORMAT(F4.0,I2,F7.4)
      71 JA=1,J2
      READ(1,110)RHINT,CMINT,J1
110 FORMAT(F7.4,F7.2,I2)
      RHINTZ(JA)=RHINT
      CMINTZ(JA)=CMINT
      J1Z(JA)=J1
      DO 3 JA=1,J2
         READ(1,11)D,CM,PH
      3 FORMAT(3F7.4)
      DZ(JA,J)=D
      IF(I1)21,21,22
      21 CMZ(JA,J)=CM-(ALOG(ATWT))/2.3025851
      GO TO 3
      22 CMZ(JA,J)=CM
      PHZ(JA,J)=PH
      READ(1,102)PJ,XS
102 FORMAT(2F4.1)
      PJ0LD=PJ
```
XSOLD=XS
WRITE(2,30) ATWT
30 FORMAT(1X,11HM,J,JAYCOCK//1X,41HREGRESSION ANALYSIS OF DISTRIBUTION
IN DATA./1X,11HATOMIC WT.=',F8.3//)
31 IF(12)303,303,301
301 WRITE(2,302)
302 FORMAT(1X,32HCORRECTED FOR ACID IN COMPLEX./)
303 IF(13)306,306,304
304 WRITE(2,305)
305 FORMAT(1X,35HCORRECTED FOR AQUEOUS SOLUBILITY./)
   READ(1,11)ZKP,ZKHA,ZKDO,ZKDA
11 FORMAT(4E10.4)
   WRITE(2,12) ZKP,ZKHA,ZKDO,ZKDA
12 FORMAT(1X,3HKP=',E11.4,5X,4HKHA=',E11.4,5X,4HKDO=',E11.4,5X,4HKDA=',E1
11.4/)
306 IF(12+13)307,307,309
307 WRITE(2,308)
308 FORMAT(1X,15HRH UNCORRECTED./)
309 CONTINUE.
   SY=0.
   SX1=0.
   SX2=0.
   SX1X2=0.
   SX1Y=0.
   SX2Y=0.
   SX12=0.
   SX22=0.
   JSUM=0.
   WRITE(2,500)PJ,XS
500 FORMAT(2F7.4)
DO 4 MA=1,J2  
RINT=RINTZ(MA)  
CMINT=CMINTZ(MA)  
J1=J1Z(MA)  
JSUM=JSUM+J1  
DO 4 M=1,J1  
R=RINT  
D=DZ(MA,M)  
CM=CMZ(MA,M)  
PH=PHZ(MA,M)  
IF(12)42,42,41  
41 R=RINT-(Z+XS/PJ)*(EXP(2.3025851*(CM+D)))  
42 IF(13)44,44,43  
43 H=EXP(-PH*2.3025851)  
AQ=2.*ZKDA*((ZKHA/H)**2)+2.*ZKDO*ZKP*ZKP  
BQ=1.+ZKP+ZKHA/H  
HR=((BQ*BQ+4.*AQ*R)**.5-BQ)/2.*AQ  
DHR=(ZKP*(1.+2.*ZKDO*ZKP*HR))/(1.+ZKHA/H+2.*ZKDA*((ZKHA/H)**2.)*HR**1)  
R=DHR*R/(1.+DHR)  
44 Y=CM+D  
IF(R)441,441,440  
441 WRITE(2,442)  
442 FORMAT(1X,29HR NEGATIVE, ANALYSIS INVALID.//)  
GO TO 52  
440 R=ALOG(R)/2.3025851  
X2=Z*PH+ZR/2.+CM  
X1=ZR/2.  
X1Z(MA,M)=X1  
X2Z(MA,M)=X2
SY=SY+Y
SX1=SX1+X1
SX2=SX2+X2
SX1X2=SX1X2+X1*X2
SX1Y=SX1Y+X1*Y
SX2Y=SX2Y+X2*Y
SX12=SX12+X1*X1
4 SX22=SX22+X2*X2
SN=JSUM
G=(SN*SX12-SX1*SX1)/(SN*SX12-SX1*SX2)**2
PJ=((SN*SX1Y-SX1*Y)*(SN*SX1X2-SX1*SX2)-(SN*SX12-SX1*SX1)*(SN*SX2Y
1-SX2*SY))/(-G)
XS=((SN*SX1Y-SX1*Y)*(SN*SX22-SX2*SX2)-(SN*SX1X2-SX1*SX2)*(SN*SX2Y
1-SX2*SY))/G
IF(12)49,49,45
45 IF(ABS(PJ-PJ0LD)-.001)46,46,47
46 IF(ABS(XS-XS0LD)-.001)49,48,48
47 PJ=(PJ+PJ0LD)/2.
PJ0LD=PJ
IF(10000.-PJ)471,471,470
470 IF(PJ)471,471,309
471 WRITE(2,472)
472 FORMAT(2X,19HJ ANALYSIS INVALID.)
GO TO 49
48 XS=(XS+XS0LD)/2.
XS0LD=XS
IF(10000.-XS)481,481,480
480 IF(XS+.5)481,481,309
481 WRITE(2,482)
482 FORMAT(2X,19HX ANALYSIS INVALID.)
GO TO 49
49 CONTINUE
  CONST=(SY-SX2*PJ-SX1*XS)/SN
  WRITE(2,5)PJ,XS,CONST
  5 FORMAT(6X,1HJ,12X,1HX,10X,6HCONST./3('1X,E11.4'))
  ERSUM=0.
  ER2SUM=0.
  DO 50 L1=1,J2
    J1=J1Z(L1)
    DO 50 L2=1,J1
      ERROR=ABS(CMZ(L1,L2)+DZ(L1,L2)-PJ*XZ(L1,L2)=XS*XZ(L1,L2)=CONST)
      ERSUM=ERSUM+ERROR
    50 ERROR=ERSUM+ERROR**2
    AVER=ERSUM/SN
    RMSERR=(ER2SUM/SN)**.5
    WRITE(2,51)AVER,RMSERR
  51 FORMAT(2X,10HAV. ERROR=,E11.4,9X,13HR,M,S,ERROR=,E11.4/)
  52 READ(1,61)I4
  51 FORMAT(1I1)
  IF(I4)64,64,62
  62 READ(1,63)I1,I2,I3
  63 FORMAT(3I1)
  GO TO 31
  64 WRITE(2,7)
    7 FORMAT(1H1)
  71 CONTINUE
END
FINISH
APPENDIX 5. APPROXIMATION PROCEDURE FOR ANALYSIS OF DISTRIBUTION DATA:

DIMENSION DZ(10,50), CMZ(10,50), PHZ(10,50), RHINTZ(10), CMINTZ(10), J1
   Z(10), JZ(10), IX(10), XK(10), A(5740,5), AT(5,40,5)
READ(1,201) I5
201 FORMAT(I2)
   DO 71 K=1,15
   READ(1,1)Z,J2, ATWT
   1 FORMAT(F4.0, I2, F7.3)
   IZ=Z
   DO 3 JA=1,J2
   READ(1,210) RHINT, CMINT, J1
   210 FORMAT(F7.4, F7.2, I2)
   RHINTZ(JA)=RHINT
   CMINTZ(JA)=CMINT
   J1Z(JA)=J1
   DO 3 J=1,J1
   READ(1,2) D, CM, PH
   2 FORMAT(3F7.4)
   DZ(JA,J)=D
   CMZ(JA,J)=CM-(ALOG(ATWT))/2.3025851
   3 PHZ(JA,J)=PH
   DO 32 N1=1,J2
   WRITE(2,31) J1Z(N1), CMINTZ(N1), RHINTZ(N1)
   31 FORMAT(1X, I3, 5X, F8.2, 5X, F8.4)
   DO 32 WRITE(2,33)( DZ(N1,N2), CMZ(N1,N2), PHZ(N1,N2), N2=1, J1Z(N1))
   32 FORMAT(1X, 3(F8.4, 5X))
   WRITE(2,30) ATWT
   30 FORMAT(1X, 11HM.J.JAYCOCK//1X, 3OHANALYSIS OF DISTRIBUTION DATA, /1X,
111 HATOMIC WT. =, F8.3//)
READ(1, 11) ZKP, ZKHA, ZKDO, ZKDA
11 FORMAT(4E10.4)
WRITE(2, 12) ZKP, ZKHA, ZKDO, ZKDA
12 FORMAT(1X, 3HKP=, E11.4, 5X, 4HKHA=, E11.4, 5X, 4HKDO=, E11.4, 5X, 4HKDA=, E11.4//)
READ(1, 120) N
120 FORMAT(12)
READ(1, 800) L1
800 FORMAT(12)
DO 71 L2 = 1, L1
READ(1, 121) (JZ(1T), IX(1T), IT = 1, N)
121 FORMAT(212)
WRITE(2, 122) (JZ(IS), IX(IS), IS = 1, N)
122 FORMAT(1X, I2, 2X, I2)
K(1) = +1.0 E+15
K(2) = +1.0 E+13
NC = 0
NT = 0
M1 = 0
MB = 0
M2 = 0
FACT = 10
ALIM = 1.0005
OLDER = +1.0 E+75
XKOLD1 = +1.0 E+75
XKOLD2 = +1.0 E+75
13 CONTINUE
DO 132 LC = 1, J2
DO 132 LD = 1, J1
DO 132 LE=1,N
132 AT(LC,LD,LE)=0.
   IF(M1.EQ.5)GO TO 400
   IF(M2.EQ.5)GO TO 401
   ERR=0.
34 DO 4 MA=1,J2
15 J1=J1Z(MA)
   DO 4 M=1,J1
16 COM=0.
   DO 18 I6=1,N
ZJ=JZ(I6)
   XI=IX(I6)
18 COM=COM+(Z*ZJ+XI)*AT(MA,M,16)*XK(I6)
   RHINT=RHINTZ(MA)-COM
180 IF(RHINT)<.184,184,183
184 WRITE(2,185)MA,M,RHINT,COM
185 FORMAT(1X,5HPOINT,tX,2I2,2I3HRHINT=,.E12.6)
181 RHINT=RHINTZ(MA)
   XK(1)=XK(1)/10.
   XK(2)=XK(2)/10.
   GO TO 13
183 CONTINUE
R=RHINT
17 H=EXP10(-PHZ(MA,M))
   AQ=2.*ZKDA*((ZKHA/H)**2)+2.*ZKDO*ZKP*ZKP
   BQ=1.+ZKP+ZKHA/H
   HR=(SQRT(BQ*BQ+4.*AQ*R)-BQ)/2.*AQ
   DHR=(ZKP*(1.+2.*ZKDO*ZKP*HR))/(1.+ZKHA/H+2.*ZKDA*((ZKHA/H)**2)+HR)
   R=DHR*R/(1.+DHR)
\[ RA = \left( \left( \sqrt{1 + \frac{H}{ZKHA}} \right)^2 + 8 \cdot ZKDA \cdot \left( \frac{RHINT - R}{1.4 \cdot H/ZKHA} \right) \right) = \frac{H}{ZKHA} / 4 \cdot ZKDA \]

\[ RO = \left( \sqrt{1 + \frac{H}{ZKDO}} \right) / (4 \cdot ZKDO) \]

\[ CMW = \text{EXP10}(CMZ(MA, M)) \]

\[ \text{DO } 20 \ I1 = 1, N \]

\[ A(MA, M, I1) = (CMW \cdot JZ(I1)) \cdot (RA \cdot (I2 \cdot JZ(I2)) \cdot (RO \cdot I2)) \]

\[ AT(MA, M, I1) = A(MA, M, I1) \]

\[ YS = CMW \cdot \text{EXP10}(DZ(MA, M)) \]

\[ NB = NB + 1 \]

\[ \text{IF}(NB, \text{EQ}, 1) \text{GO TO } 13 \]

\[ \text{RHS} = 0 \]

\[ \text{DO } 21 \ I2 = 1, N \]

\[ \text{RHS} = XK(I2) \cdot A(MA, M, I2) + \text{RHS} \]

\[ \text{ERR} = \text{ERR} + \text{ABS}(YS - \text{RHS}) \]

\[ \text{IF}(\text{NC}, \text{EQ}, 0) \text{GO TO } 99 \]

\[ \text{IF}(\text{OLDER} = \text{ERR}) = 22, 22, 23 \]

\[ NT = NT + 1 \]

\[ \text{IF}(NT, \text{EQ}, 1) \text{GO TO } 500 \]

\[ \text{IF}(NT, \text{EQ}, 2) \text{GO TO } 501 \]

\[ \text{IF}(NT, \text{EQ}, 3) \text{GO TO } 502 \]

\[ \text{IF}(NT, \text{EQ}, 4) \text{GO TO } 503 \]

\[ \text{GO TO } 23 \]

\[ 500 \ XK(1) = XK(1) \cdot \text{FACT} \]

\[ \text{GO TO } 23 \]

\[ 501 \ XK(1) = XK(1) / \text{FACT} \]

\[ \text{GO TO } 23 \]

\[ 502 \ XK(2) = XK(2) \cdot \text{FACT} \]

\[ \text{GO TO } 23 \]

\[ 503 \ XK(2) = XK(2) / \text{FACT} \]

\[ \text{IF}(NT, \text{EQ}, 0) \text{GO TO } 100 \]

\[ \text{IF}(NT, \text{EQ}, 1) \text{GO TO } 101 \]
IF (NT.EQ.2) GO TO 102
IF (NT.EQ.3) GO TO 103
IF (NT.EQ.4) GO TO 106
99 NC=1.
100  XK(1)=XK(1)/FACT
     M2=0
     M1=M1+1
     GO TO 104
101  XK(1)=XK(1)*FACT
     M2=0
     M1=M1+1
     GO TO 104
102  XK(2)=XK(2)/FACT
     M1=0
     M2=M2+1
     GO TO 104
103  XK(2)=XK(2)*FACT
     M1=0
     M2=M2+1
104  IF (OLDER-ERR).EQ.13,13,114
114  OLDER=ERR
     GO TO 13
106  IF (XK(1)-XKOLD1).EQ.110,107,110
107  IF (XK(2)-XKOLD2).EQ.110,105,110
110  XKOLD1=XK(1)
    XKOLD2=XK(2)
    NT=0
    GO TO 100
105  IF (FACT-ALIM).EQ.109,109,108
108  FACT=(1.+FACT)/2.
WRITE(2,301)XK(1),XK(2),FACT,ERR
301 FORMAT(1X,6H'XK(1)=',E10.4,5X,6H'XK(2)=',E10.4,5X,5H'FACT=',E10.4,5X,4H'ERR=',E17.11)
NT=0
M1=0
M2=0
GO TO 100
109 WRITE(2,200)XK(1),XK(2),ERR
200 FORMAT(1X,6H'XK(1)=',E10.4,5X,6H'XK(2)=',E10.4,5X,4H'ERR=',E17.11)
GO TO 71
400 IF(NT)402,402,403
402 XK(1)=XK(1)*FACT
GO TO 404
403 XK(1)=XK(1)/FACT
404 NT=2
GO TO 102
401 IF(NT-2)400,405,406
405 XK(2)=XK(2)*FACT
GO TO 407
406 XK(2)=XK(2)/FACT
407 NT=0
GO TO 100
71 CONTINUE
STOP
END
FINISH