THE KINETICS OF LIQUID-LIQUID EXTRACTION OF METALS IN A ROTATING DIFFUSION CELL

A rotating diffusion cell is used to study the rates of extraction of divalent transition metals by di-(2-ethylhexyl)-phosphoric acid and a sulphur analogue. A chemical-diffusion model describes the rate curves.

A Thesis submitted for the degree of Doctor of Philosophy

by

Hamantkumar Vasudev PATEL, B.Eng., M.Eng.

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ABSTRACT

A rotating diffusion cell (RDC) has been used to study the kinetics of extraction of the transition metals cobalt (II), nickel (II), copper (II) and zinc (II) from sulphate solutions into either of two extractants held in n-heptane; di-(2-ethylhexyl) phosphoric acid (D2EHPA) or di-(2-ethylhexyl) dithiophosphoric acid (D2EHDTPA). The metal concentration was 10 mM and the aqueous pH was held at 4.5. The extractant concentration was varied between 0.015 to 0.4 M. In the case of cobalt extraction by D2EHPA, the metal concentration and the pH were varied. Different diluents and modifiers were also studied.

The rate of extraction by D2EHDTPA was found to be faster than D2EHPA.

A comprehensive mathematical model, based upon established two film theory, was developed and used to describe the above experimental results. The model was also used to predict values of the important parameters: (i) the grouped kinetic parameter $\Theta_1$ for D2EHPA and $\Theta_{L1}$ for D2EHDTPA,

$$\Theta_1 = k_R \cdot D_{(HR)} \cdot K_{2d} \cdot P_{2}^{2}$$

and

$$\Theta_{L1} = k_L \cdot D_{HL} \cdot K_{d} \cdot P_{HL}^{2}$$

and

(ii) the aqueous and organic film mass transfer coefficients.

Parameter (i) was used to predict values of the second order chemical rate constants:

For D2EHPA, $k_R$ ($m^3/kmol.s$) with various metals:

$Co^{2+} = 9.460 \times 10^7$;  $Ni^{2+} = 1.325 \times 10^7$;

$Cu^{2+} = 1.213 \times 10^8$;  $Zn^{2+} = 2.436 \times 10^9$.

For D2EHDTPA, $k_L$ ($m^3/kmol.s$) with various metals:

$Co^{2+} = 3.158 \times 10^9$;  $Ni^{2+} = 2.690 \times 10^9$;

$Cu^{2+} = 3.821 \times 10^9$;  $Zn^{2+} = 1.073 \times 10^{10}$.

These values compared well with those found by other authors but using quite different experimental techniques.

In the case of cobalt extraction by D2EHPA, the more polar diluents lowered the initial rate. The overall model predicts such behaviour where the rate is also dependent on the partition coefficients of the extractant.

Finally, the theory of the RDC allows the prediction of the diffusion layer thicknesses, this information together with the reaction zone thickness is used to explore the influences of diffusion and chemical reaction on the overall transfer process. The diffusion processes are calculated to be the most important of the two. This is especially so for the D2EHDTPA systems.
Dedicated to the Memory of

My Beloved Grandfather
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1.1 Liquid-Liquid Extraction

In liquid-liquid extraction, a solute is transferred from one liquid phase, known as the feed, to another partially miscible or immiscible liquid phase, known as the solvent. The remaining aqueous phase, after extraction, is called the raffinate. Liquid-liquid extraction is commonly and incorrectly\(^1\) referred to as 'Solvent Extraction'.

Liquid-liquid extraction processes can be broadly divided into two groups:

(i) Those involving physical interactions between the solute and the solvent, possibly involving polarity differences or hydrogen bonding. Many liquid-liquid extraction processes in the organic chemical industry belong to this group. Thus, the separation of aromatic from aliphatic hydrocarbons is an important unit operation in the petroleum refineries. In this last case the recovery of solute from the solvent is by physical means, usually distillation.

(ii) Those involving specific chemical interactions. All liquid-liquid extraction processes in the hydrometallurgical industry belong to this group. The metal ion forms a discrete metal-solvent complex thus, allowing extraction of a specific metal from a mixture of metal ions present in the raffinate phase. The solute recovery (stripping) involves chemical reversal of the
interaction. Typically, where extraction is pH dependent, the loaded organic phase can be stripped by an aqueous phase of much lower pH.

In this investigation an acidic organic extractant, HR, is used to extract divalent metals. The extraction-reaction equation is:

\[
\text{M}^{2+} + 2\text{HR}_{\text{(org)}} \rightleftharpoons \text{MR}_2\text{C}_{\text{(org)}} + 2\text{H}^+_{\text{(aq)}}
\]  

(1.1.1)

If one proceeds from left to right then this is known as forward extraction. Stripping is reversal of the reaction, where the organic phase is contacted with strong concentrated acid.

In many cases, especially those involving chemical interaction, extractants which selectively extract a given component cannot be used directly as a solvent due to their unsuitable physical properties, e.g. high viscosity. In this case the extractant is dissolved in an inert carrier solvent, known as the diluent, to make a solution of the extractant. If the diluent does not have adequate solvency for the solute-extractant complex so formed (this usually leads to a third phase formation in the form of a precipitate), then a further component, identified as the modifier, is added to the 'solvent'. The modifier improves the solvency but may have effects on the equilibria and the kinetics; it can also prevent emulsion formation.

A comprehensive book on the subject of liquid-liquid extraction is the 'Handbook of Solvent Extraction' \(^{(2)}\). Much of the chemistry of metal extraction is described by Kertes and Marcus \(^{(3)}\) and Sekine and Hasegawa \(^{(4)}\). For the basic chemical engineering principles on the subject, the textbook by Treybal \(^{(5)}\) and a book edited by Hanson \(^{(6)}\) is recommended. A publication on the subject, but related to transport
phenomena, is that by Laddha and Degaleesan\(^{(7)}\).

1.2 Application of Liquid-Liquid Extraction

The origin of liquid-liquid extraction is indebted to analytical chemistry, in which dilute aqueous solutions of metals were concentrated using an extractant reagent in the organic phase. The earliest industrial applications were found in the petroleum industry but use of the technology has been applied progressively in the organic chemical, petrochemical\(^{(8,9)}\), nuclear\(^{(10-12)}\), pharmaceutical and the general metals industries.

1.2.1 Extraction of non-metallics

The application of liquid-liquid extraction in the non-metallic industry can be divided into four general groups:

(a) Petroleum and petrochemical industry;
(b) Pharmaceutical industry;
(c) Coal tar industry\(^{(13,14)}\);
(d) Fertilizer industry\(^{(15)}\).

The first industrial use of liquid-liquid extraction was established in the petroleum industry with the Edeleanu process in 1911\(^{(9)}\). This process used liquid sulphur dioxide to selectively extract aromatic hydrocarbons from lamp kerosenes. Bailes and co-workers\(^{(16)}\) have described in detail some of the more important aromatic separation processes.

The pharmaceutical industry uses liquid-liquid extraction in most of their separation operations. The technique is used to extract 'drugs' and natural products (e.g. antibiotics), an important example being the extraction of penicillin and insulin. Few details have been published on these processes but an informative background has been set down by Ridgway and Thorpe\(^{(17)}\).
1.2.2 Extraction of metals

The industrial use of liquid-liquid extraction for the separation, purification and concentration of metal ions was pioneered by the nuclear industry \(^{(18)}\), where in 1942 diethylether was used to separate and purify uranium and plutonium from ores and/or fission products. Since then the technique has been applied to extract a wide range of metals \(^{(19,20)}\), which include chromium, cobalt, copper, molybdenum \(^{(21)}\), nickel, uranium, vanadium, rare earths \(^{(22)}\), platinum group metals \(^{(23)}\), tantalum/niobium, zirconium, hafnium and gold.

Recently, liquid-liquid extraction technology has been applied to recover metal from scrap and waste processings \(^{(24)}\) and from low grade materials \(^{(25)}\).

The development of metal extraction flowsheets and the variety of extractants used are discussed by Bailes et al. \(^{(16)}\). A comprehensive description of the various liquid-liquid extraction processes in the hydrometallurgy industry is to be found in the textbooks by Ritcey and Ashbrook \(^{(26)}\).

In the last two decades there has been an important expansion of interests and development in liquid-liquid extraction, with an increasing growth of its application in industry especially in the hydrometallurgical industry. Approximately 200,000 tonne of copper and 25,000 tonne of uranium per year \(^{(27)}\) are now being processed by this route. In 1977 the Nchanga Consolidated Copper Mines Ltd., Zambia, was reported to be producing 182 tonne of copper per day \(^{(20)}\) through liquid-liquid extraction.

To illustrate the role of liquid-liquid extraction in the hydrometallurgical industry, the process for the separation and production of cobalt and nickel \(^{(28)}\) will be considered. In principle, the process flowsheet would consist of leaching, forward extraction and electrowinning or a precipitation process to obtain a final product. The actual process is
as shown in Figure 1.2.1.

The aqueous feed solution (typically from a leaching process containing 10 g Co/l and 10 g Ni/l) at pH 5.0 to 5.5 is contacted with 20% D2EHPA (in kerosene with 5% tributyl phosphate modifier) previously equilibrated with ammonium hydroxide.

The loaded solvent is scrubbed with part of the strip liquor containing cobalt sulphate at a pH of 5.0 to 5.5 in order to remove nickel impurities. The cobalt displaces nickel from the organic phase. As the nickel content of the aqueous scrub is increased, a bleed of the scrub raffinate is returned to the extraction circuit. The scrubbed solvent is stripped by sulphuric acid to give a liquor rich in cobalt (ca. 100 g Co/l). The cobalt can be recovered by an electrowinning process or by reducing the cobalt sulphate solution by hydrogen to give metal. The nickel, in the raffinate, can be similarly recovered. Part of the cobalt sulphate liquor is returned to the scrub circuit to maintain the cobalt balance. The stripped solvent is equilibrated with ammonium hydroxide and recycled to the extraction circuit.

The process described above is different from most other processes for the following reasons:

1. the solvent is pre-equilibrated with an alkali to provide desired pH buffering during extraction. This maximises the amount of cobalt extracted;

2. nickel impurity is removed by scrubbing with a solution containing high concentration of cobalt;

3. differential column contactors are used. Often, mixer-settlers are used for metal extraction.
The present work is related to this important process for cobalt/nickel recovery. A commercially important extractant Di-(2-ethylhexyl) phosphoric acid, D2EHPA, and its sulphur analog will be investigated.

1.3 The Importance of Equilibria in Liquid-Liquid Extraction

Generally, when a single solute (s) is distributed between two phases, in which s is unaffected by other solutes in the system, then the distribution of the solute can be represented by:

\[ [s]_\beta = f([s]_\alpha) \]  \hspace{1cm} (1.3.1)

where, \([s]_\beta\) is the concentration of s in the organic phase (the 'solvent', \(\beta\)) and \([s]_\alpha\) is the concentration of s in the aqueous phase (the raffinate, \(\alpha\)). Equation (1.3.1) describes a single curve known as an isotherm.

Many of today's metal extraction systems involve the competitive distribution of two solutes, e.g. the extraction of cobalt by di-(2-ethylhexyl) phosphoric acid (HR) from acid medium:

\[
\text{Co}^{2+} \text{(aq)} + 2\text{(HR)} \rightarrow \text{CoR}_2 \text{(HR)}_2 \text{(org)} + 2\text{H}^+ \text{(aq)} \hspace{1cm} (1.3.2)
\]

The equilibrium position is now very much dependent on the concentration of hydrogen ions. In such cases the distribution of solutes, say \(s_1\) and \(s_2\), can be represented more properly by:

\[ [s_1]_\beta = f([s_1]_\alpha, [s_2]_\alpha) \]  \hspace{1cm} (1.3.3)

where \([s_1]\) is the concentration of solute \(s_1\) (e.g. cobalt) and \([s_2]\) the concentration of solute \(s_2\) (e.g. \(H^+\)). Equation (1.3.3) describes an equilibrium surface, see Figure 1.3.1, which will have the following axes
FIGURE 1.3.1: Equilibrium Surface Represented by Equation (1.3.3)
for the cobalt system (Equation (1.3.2)):

\[ [s_1]_B = [Co^{2+}]_{(org)} \]

\[ [s_1]_A = [Co^{2+}]_{(aq)} \]

and

\[ [s_2]_A = [H^+]_{(aq)} \]  \hspace{1cm} (1.3.4)

The properties of such equilibrium surfaces and mathematical models to represent them have been described by Hughes et al. \(^{(29-31)}\). If nickel was also present in the problem, then another dimension would have to be introduced since the nickel now affects the equilibrium position.

For any one transition metal extracted by an organic acid, HR, the dependence of the equilibrium position on pH can be shown as follows: the general metal extraction process can be represented by:

\[ M^{n+}_{(aq)} + nHR_{(org)} \rightleftharpoons MR_n_{(org)} + nH^+_{(aq)} \]  \hspace{1cm} (1.3.5)

where \( K \) is the extraction constant and is defined as:

\[ K = \frac{[MR]^n_{(org)} \cdot [H^+]^n_{(aq)}}{[M^{n+}]_{(aq)} \cdot [HR]^n_{(org)}} \]  \hspace{1cm} (1.3.6)

Note [] is concentration. If [] is replaced by activity{ } then K becomes a true thermodynamic constant. Here the water of hydration has been left out in order to simplify the presentation.

The metal distribution ratio is defined as:

\[ D = \frac{\text{Concentration of metal in organic phase}}{\text{Concentration of metal in aqueous phase}} \]  \hspace{1cm} (1.3.7)
If we assume that $MR_n$ is the only species of metal present in the organic phase and $M^{n+}$ the only species of metal in the aqueous phase, then Equation (1.3.7) can now be redefined as:

$$D = \frac{[MR_n]_{\text{org}}}{[M^{n+}]_{\text{aq}}} \quad (1.3.8)$$

Combining Equation (1.3.8) and Equation (1.3.6) and taking logarithms gives the following expression:

$$\log(D) = \log\left( K \cdot \frac{[HR]_n_{\text{org}}}{[H^{+}]_n_{\text{aq}}} \right)$$

$$= \log(K) + n \log([HR]_{\text{org}}) - n \log([H^+]_{\text{aq}})$$

$$\Rightarrow \log(D) = \log(K) + n \log([HR]_{\text{org}}) + n \cdot \text{pH} \quad (1.3.9)$$

$K$ may be treated as a constant and $[HR]_{\text{org}}$ will remain practically unchanged if trace metal is used in the extraction, then

$$Y = \text{constant} + m \cdot X \quad (1.3.9a)$$

Under constant extraction loading, a plot of $\log(D)$ ($Y$) against pH ($X$) should give a family of parallel lines for a number of equally charged cations, see Figure 1.3.2. If we assume that the free extractant concentration is unaltered (i.e. we have low metal concentration involved), then the slope of this plot gives $n$, hence, the stoichiometry of the reaction. For divalent transition metals $n$ should equal 2.

It can be shown that the relationship between the percentage of metal extracted ($\% E$) and the distribution ratio is:
FIGURE 1.3.2: Plot of log D against pH for Di(1-methylheptyl) phosphonic acid (DMHPA).

Source: Xu et al. (1979)

Aqueous phase: 0.01 M metal sulphate
Organic phase: 0.1 M DMHPA in heptane

Slope = 2
\[ \% E = \frac{100 \cdot D}{D + V/V_0} \]  \hspace{1cm} (1.3.10)

where \( V \) = the volume of the aqueous phase

\( V_0 \) = the volume of the organic phase.

An alternative way to show the dependence of extraction of metal on the pH of the aqueous phase is to plot \( \% E \) against pH. Such a plot is shown in Figure 1.3.3 for the extraction of transition metals by D2EHPA\(^{(32)}\).

The plot illustrates the role which pH plays in the selective extraction (i.e. separation) of a given metal from a solution containing many metals by a given extractant. Each metal occupies a position on the plot determined by the pH\(_0\) value, that is the pH at which 50% of the metal is extracted. It is the metals which form the strongest complexes which lie in positions of low pH\(_0\) values.

In the present work the kinetics of the process of forward extraction of first row transition metals (in particular cobalt, nickel, copper and zinc) will be investigated, that is the reaction will move left to right in Equation (1.1.1). Obviously the pH chosen for this reaction will be such that it encourages the reaction to proceed. However, as the metal loads into the organic phase the aqueous phase will tend to become more acidic because of liberated protons. In order to study the rate of reaction at a constant pH it is seen to be necessary to pH stat (see Section 2.4.4) the aqueous phase. The moment at which the concentration of metal in the aqueous and organic phase becomes constant will be the equilibrium point and it will be specific to the pH chosen for the experiments and the initial concentration of the extractant and the temperature.

1.4 The Importance of Kinetics in Liquid-Liquid Extraction

The rate of extraction is also important to commercial operations.
FIGURE 1.3.3: Plot of % Extraction Metals Against pH for D2EHPA

Source: Mobil Bulletin, Reference (32)
If the rate is slow then a long contact time is required and so larger mixer sections giving longer residence time. Mixer-settlers would be the first choice in this case of slow kinetics giving typically a three minute residence time in the mixer. If the rate is fast then column contactors might be a first choice.

In the past, the rates of liquid-liquid extraction processes were considered to be dependent on diffusional resistances only. This is probably true for processes where physical interactions are involved but many metal extraction processes are based on specific stoichiometric chemical interactions as mentioned in the previous section. These last processes, therefore, exhibit mass transfer with simultaneous chemical reaction; the rate depending upon:

(i) the diffusional resistances;

(ii) the kinetics of the chemical reaction steps.

It is difficult to distinguish by experiment the contribution of these steps in any one system.

The various processes in the mass transfer of a divalent metal and an acidic extractant, HR, are schematically depicted in Figure 1.4.1. The extractant HR may generate in the organic phase aggregates of the form \((HR)_n\); these are in equilibrium in that phase with the monomer HR. This monomer diffuses to the interface through an organic film and then partitions into the aqueous diffusion film and the aqueous phase. The acidic extractant dissociates in the aqueous reaction zone \(\delta_r\) and the anion \(R^-\) reacts with the divalent metal ion in this region. The reaction zone can vary in thickness even extending outward into the bulk aqueous phase. In the other limit when \(\delta_r \to 0\), the zone is infinitely thin and reaction is at the interface proper. A stepwise reaction leads to a \(MR_2\) complex which partitions and diffuses back through the organic film. The
FIGURE 1.4.1: Schematic Representation of the Extraction of a Divalent Metal Cation, $M^{2+}$, by an Acidic Extractant, HR, from an Aqueous Phase into the Organic Phase.
released protons $\text{H}^+_{(aq)}$ diffuse into the bulk aqueous phase.

The chemical reaction involving ionic species must be on the aqueous side of the interface. The diffusion films ($\delta$) incorporate molecular and eddy transport phenomena.

The term 'interface' refers to a thickness of molecular dimensions but $\delta$ may vary from several to one hundred $\mu$m. It is these diffusional films which change from one contacting technique to another as the hydrodynamics change.

Recently, a considerable amount of research has been reported on the kinetics of the liquid-liquid extraction of metals. In particular, the extraction of copper by hydroxyoximes (33-38), uranium by tributyl phosphate (TBP) (39) and various transition metals by di-(2-ethylhexyl) phosphoric acid (40-42,72). The listing is extensive and a good summary is to be found in the review by Danesi and Chiarizia (43).

1.5 Methods of Studying Kinetics

It is apparent that different kinetic results arise from various workers studying the same chemical systems. This can be attributed to the fact that the researchers have chosen different contacting techniques and different ranges of concentration of metals and extractant. The choice of a different technique leads to varying hydrodynamics which will affect the rate. For the moment it will be argued that a single technique gives either good mixing or poor mixing. The kinetic control depends upon this and the concentration and surface activity of the extractant, see Table 1.5.1.

The various techniques which have been used to study liquid-liquid extraction are:
### TABLE 1.5.1

**Qualitative Criteria to Identify the Probable Processes Which Control the Extraction Kinetics on the Basis of the Degree of Mixing, the Surface Activity of the Extractant and the Concentration of the Metal to be Extracted**

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<td>Low</td>
<td>High</td>
<td>Interfacial Chemical Reaction</td>
</tr>
<tr>
<td>Strong</td>
<td>High</td>
<td>High</td>
<td>Transport Processes</td>
</tr>
<tr>
<td>Weak</td>
<td>Low</td>
<td>High</td>
<td>Interfacial or Aqueous Chemical Reactions</td>
</tr>
<tr>
<td>Weak</td>
<td>High</td>
<td>High</td>
<td>Transport Processes</td>
</tr>
<tr>
<td>Strong or Weak</td>
<td>Low or High</td>
<td>Low</td>
<td>Transport Processes</td>
</tr>
</tbody>
</table>

Source: Danesi and Chiarizia\(^{(43)}\)
(i) The static constant interface cell
   (the Hahn cell)\(^{(44)}\).

(ii) The stirred constant interface cell
    (the Lewis cell)\(^{(45-47)}\).

(iii) The stirred tank-A.K.U.F.V.E. apparatus\(^{(48)}\).

(iv) The laminar jet\(^{(49)}\).

(v) The single drop (rising or falling)\(^{(50-52)}\).

(vi) The rotating diffusion cell\(^{(53-55)}\).

Although each technique exhibits different hydrodynamics a most important feature will be the knowledge (and measurement) of the interfacial area, since it is required to report a flux of metal or extractant measured in units of kmol/m\(^2\)/s and relating to the metal transferred from one phase to another. This requirement is met in all the experimental techniques listed above, except the stirred tank-A.K.U.F.V.E. apparatus.

Of course, in real contactors, the interfacial area is difficult (but not impossible) to measure and the hydrodynamics are complicated with the continuous break-up and reformation of drops. Thus for the present, a strategy might be adopted where the fundamental mass transfer phenomena can be measured in a system where the hydrodynamics are accounted for. It may then be possible in the future to build onto such fundamental data (e.g. mass transfer coefficients, diffusivities reaction rates, etc.) the hydrodynamics of a real contactor.

It is the rotating diffusion cell which of all the techniques listed above affords the possibility of accounting for the hydrodynamics. It also meets the important requirement of known interfacial area. The application of the RDC, the theory and the mode of operation will be discussed in Chapter Two. This technique is explored on the present work on the extraction of some first row transition metals.
1.6 Metal Extraction by D2EHPA

The use of D2EHPA to extract metals can be dated to the 1940's when it was used to recover uranium from ore leachants. Since then it has attracted the attention of many investigators both for its application in industrial separation processes and for its importance to the basic understanding of extraction processes.

The importance of D2EHPA can be judged from its commercial use to extract a wide variety of metals. It has been used to recover uranium\(^{(20)}\), vanadium\(^{(56)}\), beryllium\(^{(57)}\), zinc\(^{(58)}\), cobalt\(^{(59)}\), nickel\(^{(60)}\), molybdenum and lanthanides (rare earths). Some of the plants-processing using D2EHPA as an extractant are tabulated in Table 1.6.1.

**TABLE 1.6.1**

Plants Using D2EHPA to Extract Metals

<table>
<thead>
<tr>
<th>Aqueous Phase</th>
<th>Plant/Process</th>
<th>Metal Extracted</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{SO}_4)</td>
<td>Nippon Mining Co., Japan</td>
<td>Co-Ni, Zn</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>INCO, Copper Cliff, Canada</td>
<td>Co</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Pyrites Company, U.S.</td>
<td>Co</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Cotter</td>
<td>U</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Ranstad</td>
<td>U</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Dennison</td>
<td>(Y + (\text{RE})_2\text{O}_3)</td>
<td>+</td>
</tr>
<tr>
<td>(\text{HCl})</td>
<td>Molycrop</td>
<td>Eu</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Zincex</td>
<td>Zn</td>
<td>(58)</td>
</tr>
<tr>
<td></td>
<td>Espindesa</td>
<td>Zn</td>
<td>+</td>
</tr>
</tbody>
</table>

*Source Ritcey and Ashbrook\(^{(26)}\)*
1.6.1 Properties of D2EHPA

D2EHPA is commercially manufactured by Daihachi Chemical Industries and Mobil Chemical Company. It belongs to the class of acidic organophosphorus extractants, specifically to the alkyl phosphoric acid group. The general formula is:

```
O
<p>| |</p>
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
```

with both $R_1 = R_2$ and $R_1 \neq R_2$. $R_1$ and $R_2$ are alkyl chains. The functional group $= P(O)OH$ is common for all members of this class of extractants. The fundamental property of this group is the marked tendency towards the formation of an intermolecular hydrogen bonding and negligible tendency towards intramolecular hydrogen bonding.

The chemical structure of D2EHPA is shown in Figure 1.6.1. It is a weak mono-organic acid. Some of its properties are given in Table 1.6.2.

<table>
<thead>
<tr>
<th>Typish Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (monomeric), g</td>
<td>322.4</td>
</tr>
<tr>
<td>Appearance</td>
<td>Clear colourless liquid</td>
</tr>
<tr>
<td>Density, kg/m³ at 20°C</td>
<td>974</td>
</tr>
<tr>
<td>40°C</td>
<td>952</td>
</tr>
<tr>
<td>60°C</td>
<td>937</td>
</tr>
<tr>
<td>Refractive index, (25°C)</td>
<td>1.442</td>
</tr>
<tr>
<td>Purity - typically</td>
<td>95%</td>
</tr>
<tr>
<td>Viscosity, cP at 20°C</td>
<td>56</td>
</tr>
<tr>
<td>0°C</td>
<td>160</td>
</tr>
<tr>
<td>– 30°C</td>
<td>1710</td>
</tr>
<tr>
<td>Solubility at 20°C in water</td>
<td>0.01%</td>
</tr>
<tr>
<td>water in</td>
<td>2.4%</td>
</tr>
<tr>
<td>Flash point</td>
<td>171°C</td>
</tr>
</tbody>
</table>
Kolarik\(^{(61)}\) has compiled a list of the various work carried out on the physico-chemical properties of D2EHPA and other acidic organophosphorus extractants held in an organic phase. This review represents the single most important source of comprehensive information on the behaviour of organophosphoric acids.

One of the important properties of D2EHPA is its tendency to self-associate in all but the most polar diluents. Within the molecule of D2EHPA the hydrogen atom of the OH group can be an electron acceptor whilst the oxygen atom attached to the phosphorus atom can be an electron donator. The combination of these effects leads to strong hydrogen bonding between the P = O and P-O-H groups on adjacent molecules. It self-associates into a dimeric structure, see Figure 1.6.2. Using physical methods, such as the measurement of osmotic pressure, infra-red spectroscopy and the cryoscopic determination of molecular weight, many workers have confirmed that D2EHPA self-associates and is dimeric\(^{(62,63)}\) in non-polar solvents (like n-heptane). In polar solvents (like alcohols and carboxylic acids), it is monomeric\(^{(64)}\). It should be noted that a mixture of monomeric and dimeric forms have been reported by D2EHPA in acetone and chloroform\(^{(62)}\).
A possible explanation for the dimer species existing alone in the organic phase has been given by Kolarik (61). He explains that compared to higher self-associates the dimer is energetically favoured by the formation of an eight-membered ring, see Figure 1.6.2.

\[
\begin{align*}
R-O & \quad O-H \quad \textbf{-} \quad O \quad \textbf{-} \quad O-R \\
\text{P} & \quad \text{P} \\
R-O & \quad O \quad \textbf{-} \quad H-O \quad \textbf{-} \quad O-R
\end{align*}
\]

where \( R = 2\text{-ethylhexyl chain} \)

**FIGURE 1.6.2:** The Generally Accepted Dimeric Structure of D2EHPA Showing the 'Eight-Membered Ring'

As yet there is no evidence in the literature for the self-association of D2EHPA in the aqueous phase. However, it has been reported (65-69) that some acidic organophosphates do self-associate to a measurable extent in the aqueous phase. The self-association equilibrium constants, for the aqueous phase, reported in the literature are for differing ionic strengths and in the nature of the contributing electrolyte. There is also significant proof (68,62) that the acidic phosphates form the electrically charged species \( \text{HR}_2^- \) rather than the neutral \( (\text{HR})_2 \) associate. The exact mechanism which leads to the formation of either \( \text{HR}_2^- \) or \( (\text{HR})_2 \) in the aqueous phase has not been reported in the literature.

In recent years, new organophosphorus acid extractants have been developed, namely the alkyl phosphonic and phosphinic acids, see Figure 1.6.3 for their general structures. To the former group belongs PC88A* 

* Manufactured by Daihachi Chemical Company Limited, Japan.
(2-ethylhexyl-phosphonic acid, 2-ethylhexyl ester) also known as SME418 and to the latter CYANEX 272 (di-(2,2,4-trimethylpentyl) phosphinic acid). These extractants have better cobalt-nickel selectivity than D2EHPA, the order being:

\[
\text{PC88A} < \text{D2EHPA} < \text{SME418} < \text{CYANEX 272}
\]

CYANEX 272 also has the additional ability to co-extract whilst rejecting impurities, such as calcium. These reagents are now being fully investigated and they represent the most recent advances in cobalt-nickel separation.

![General Structure of (a) Alkyl Phosphonic Acid and (b) Alkyl Phosphinic Acids](image)

**FIGURE 1.6.3:** The General Structure of (a) Alkyl Phosphonic Acid and (b) Alkyl Phosphinic Acids

\[\text{Manufactured by Shell.}\]

\[\text{Manufactured by American Cyanamid.}\]
1.6.2 Previous studies on the kinetics of metal extraction by D2EHPA

Since the review of Coleman and Roddy\(^{(72)}\), a limited number of papers have been published on the kinetics of metal extraction by D2EHPA. These will now be commented upon. Only the most important papers are chosen for discussion.

The review by Coleman and Roddy on the kinetics of metal extraction by organophosphorus acids covers the majority of the contributions up to and including 1970. At the time, their work on the extraction of Iron(III) from perchlorate solutions by D2EHPA in n-octane\(^{(73,74)}\) was the only extensive piece of work in this area. They considered two experimental techniques, namely the quiescent interface cell and the stirred baffled tank and not surprisingly found different rate controlling mechanisms for the two techniques.

The results obtained for the quiescent interface cell showed that the initial extraction rate was proportional to the specific interfacial area and independent of the stirring speed. The high activation energy (estimated between 42 and 63 kJ/mole, depending on the D2EHPA concentration) together with the above observation, led these authors to conclude that the extraction rate was controlled by chemical reaction at the interface.

The authors proposed a mechanism consisting of two specific pathways of parallel interfacial reactions. The first path involves the formation of the 1:1 interfacial metal-complex with either the monomer (R\(^{-}\)) or the dimer (HR\(_2\)) ionised species of D2EHPA:

\[
\text{Fe(H}_2\text{O)}^{3+}_6 + R^- \xrightarrow{k_{1,m}} (\text{H}_2\text{O})_5\text{FeR}^{2+} + \text{H}_2\text{O} \quad (1.6.1)
\]

\[
\text{Fe(H}_2\text{O)}^{3+}_6 + \text{HR}_2 \xrightarrow{k_{1,d}} (\text{H}_2\text{O})_5\text{FeR}^{2+}.\text{HR} + \text{H}_2\text{O} \quad (1.6.2)
\]
The second path, in series with the first, considers the formation of the 1:2 interfacial metal-complex:

\[
\begin{align*}
\text{(H}_2\text{O)}_5\text{FeR}^{2+} \cdot \text{HR} & \xleftarrow{k_{2,s}} \text{(H}_2\text{O)}_5\text{FeR}^{2+} \cdot \text{H}^+ + \text{R}^- \\
\xrightarrow{k_{2,s}} \text{(H}_2\text{O})_4\text{FeR}_2^+ + \text{H}_2\text{O} + \text{H}^+ \\
\text{(H}_2\text{O})_5\text{FeR}^{2+} + \text{HR}_2 & \xrightarrow{k_{2,d}} \text{(H}_2\text{O})_4\text{FeR}_2^+ \cdot \text{HR} + \text{H}_2\text{O} \\
\xrightarrow{k_{2,d}'} \text{(H}_2\text{O})_5\text{FeR}^{2+} \cdot \text{HR} + \text{HR}_2 & \xrightarrow{k_{2,d}} \text{(H}_2\text{O})_4\text{FeR}_2^+ \cdot \text{HR} + \text{HR} + \text{H}_2\text{O}
\end{align*}
\]

In the above reactions subscripts \(m\) and \(d\) refer to the monomer and dimer species of D2EHPA respectively. Subscript \(s\) refers to the saturation of the interface with the mono-complexed iron. For simplicity the hydroxo-species proposed by the authors has been excluded.

The reaction steps (Equations (1.6.1) to (1.6.5)) together with the dimerisation and ionisation equilibria of D2EHPA (HR) were combined to formulate the overall reaction rate equations:

For the quiescent interface cell,

\[
-\frac{d[\text{Fe}]}{dt} \cdot \frac{1}{[\text{Fe}]} = \frac{(r_{1,m} + r_{1,d}) \cdot (r_{2,s} + r_{2,d} + r_{2,d}')}{r_{1,m} + r_{1,d} + r_{2,s} + r_{2,d} + r_{2,d}'}
\]

(1.6.6)

For the stirred tank,

\[
-\frac{d[\text{Fe}]}{dt} \cdot \frac{1}{[\text{Fe}]} = \frac{(r_{1,m} + r_{1,d}) \cdot r_{2}}{r_{1,m} + r_{1,d} + r_{2}}
\]

(1.6.7)

where the step rates are described by:
\[ r_{1,m} = 5.5 \times 10^{-4} \frac{[HR]^{0.5}}{[H^+]} \]

\[ r_{1,d} = 1.8 \times 10^{-3} \frac{[HR]}{[H^+]} \]

\[ r_{2,s} = \frac{1.5 \times 10^{-7}}{[Fe^{3+}] \cdot [H^+]} \]

\[ r_{2,d} = 9.0 \times 10^{-6} \frac{[HR]^{1.5}}{[H^+]^2} \]

\[ r_{2,d}' = 1.2 \times 10^{-5} \frac{[HR]^2}{[H^+]^2} \]

\[ r_2 = \frac{4 \times 10^{-4}}{[H^+]^2} \] (1.6.8)

It might be noted that any diffusion effects have been neglected in the above mechanism. This is surprising since we are considering the quiescent interface cell and stirred tank where diffusion is obviously an important parameter.

It is interesting to note that this system was studied by Karpacheva and Ilozheva\(^{(75)}\) and they report a different reaction mechanism. These workers studied the kinetics of iron (III) extraction by D2EHPA in synthine (a mixture of hydrocarbons) in a stirred mixer at 1500 rpm and 35° C. Their studies showed that the overall extraction rate was independent of the stirring speed above 800 rpm which led them to conclude that the rate is independent of the specific interface area. There is an error of assumption here, because at high speeds the diffusional layers are not absent; a 'slip' effect exists and this may mimic chemical control, i.e. independent of surface area.
The results led them to conclude that the rate was controlled by the slow reaction between Fe$^{3+}$ and ionised D2EHPA ($R^-$) in the aqueous phase:

$$\text{Fe}^{3+} + R^- \xrightarrow{\text{slow}} \text{FeR}^{2+}$$  \hspace{1cm} (1.6.9)

The following rate expression was assumed to be valid,

$$r_{Fe} = 5.9 \times 10^{-4} \frac{[\text{Fe}^{3+}][HR]^{0.5}}{[H^+]^{1.2}}$$  \hspace{1cm} (1.6.10)

at 25°C with a constant ionic strength of 1 kmol/m$^3$.

Coleman and Roddy\(^{(72)}\) have attributed the differing conclusions reached by themselves and Karpacheva and Ilozheva\(^{(75)}\), to an insufficient turbulent mixing in the system of Karpacheva and Ilozheva. Consequently, the specific interface area available for mass transfer approached an upper limit above 800 rpm. Despite some important differences, e.g. the effect of stirring speed on the rate of mass transfer, both groups of workers agree reasonably well. For instance they both have recorded high activation energies and within a certain range the same dependency of rate on the organic phase D2EHPA concentration.

From these pieces of work we can conclude that the rate of extraction of iron (III) from perchloric medium into an organic medium by D2EHPA is limited by a chemical reaction step. However, the site of reaction is not resolved, it may be in an aqueous interface zone or at a true interface. The important fact which does emerge from these studies is that hydrodynamics cannot be ignored in the analysis of the kinetics of metal extraction.

Biswas and Islam\(^{(76)}\) have recently reported the kinetics of iron-(III) extraction by D2EHPA in benzene from an acidic sulphate-acetate
media. They used mechanical shakers as mixers, hence the interfacial area was not measured. They found the rate of forward extraction to be directly proportional to \([\text{Fe}^{3+}]_{\text{aq}}\) and to the square root of \([\text{H}_2\text{R}_2]_{\text{org}}\). The order with respect to \([\text{H}^+]_{\text{aq}}\) varied from 0 to -1 depending on the acidity of the aqueous phase. At high acidities (pH less than 0.5) the order was -1 and at lower acidities (pH greater than 2.0) the rate was independent of \([\text{H}^+]_{\text{aq}}\). Thus,

\[
- \frac{d[\text{Fe}^{3+}]}{dt} = k_f \frac{[\text{Fe}^{3+}] \cdot [\text{H}_2\text{R}_2]^{0.5}}{[\text{H}^+]^c}
\]

(1.6.11)

where \(k_f\) is the forward rate constant and \(c\) varies from 0 to -1.

The rate determining step was stated to be the formation of the \(\text{Fe(OH)}_2\cdot\text{HA}\) complex through the interaction of aqueous HR with \(\text{Fe(OH)}_2^2+\). They concluded that the reaction occurred in the bulk aqueous phase.

Their results showed that at low concentrations the rate was unaffected by both sulphate and acetate ions. At higher concentrations of sulphate ions the rate decreased inversely (to the first order) where as for acetate ions (Ac) the rate was directly proportional to the acetate ion concentration. This was explained by the formation of iron-acetate complexes of the type \(\text{FeAc}^2+, \text{Fe}(\text{Ac})_2^+, \text{Fe}(\text{Ac})_3^+, \text{FeO}(\text{Ac})_6^+\) etc. which led to the following rate determining step being defined:

\[
\text{Fe}(\text{Ac})^2+ + \text{HR} \xrightarrow{\text{slow}} \text{Fe}(\text{Ac})\cdot\text{HR}^2+
\]

(1.6.12)

followed by the fast step:

\[
\text{Fe}(\text{Ac})\cdot\text{HA}^2+ \xrightarrow{\text{fast}} \text{FeR}^2+ + \text{AcH}
\]

(1.6.13)
These studies on the kinetics of Fe(III) extraction by D2EHPA illustrate the controversy often found in liquid-liquid extraction regarding the locale of the reaction site.

The extraction rate of copper and cobalt from aqueous sulphate medium by D2EHPA in kerosene was first studied by Brisk and McManamey(77). They used a crude form of stirred transfer cell (i.e. without an adequate baffling system) and an equilibrium extraction technique to follow the rate of transfer of radioactive $^{64}$Cu and $^{60}$Co between the phases, which were initially at equilibrium.

These last workers proposed that there was interfacial mass transfer resistance in addition to mass transfer resistance in the two phases. The Whitman two film relationship, which relates the overall mass transfer resistance to its constituent parts, was modified to include a term for the interfacial resistance:

$$\frac{1}{K_{aq}} = \frac{1}{k_{aq}} + \frac{1}{D_{aq} k_{org} + \frac{1}{k_{i,aq}}}$$  \hspace{1cm} (1.6.14)

and

$$\frac{1}{K_{org}} = \frac{1}{k_{org}} + \frac{D_{org} + \frac{1}{k_{aq}}}{k_{i,org}}$$  \hspace{1cm} (1.6.15)

where $K_{aq}$ and $K_{org}$ are the overall mass transfer coefficients, $D_{aq}$ and $D_{org}$ are the metal distribution coefficients adjusted for film theory. The values of $K_{aq}$ and $K_{org}$ were obtained experimentally using an integral relationship which assumes them to be time invariant. In order to calculate $k_{i,aq}$ and $k_{i,org}$, the values of $k_{aq}$ and $k_{org}$ were required and these were estimated using correlations developed for liquid-liquid mass transfer in stirred transfer cell(78).

$^\S$ Note! $D_{aq} \equiv H_w$ & $D_{org} \equiv H_o$ in reference (77)
They found the total mass transfer resistance to be greater than that estimated from the individual resistances in the two phases. This additional resistance was attributed to the interfacial resistance and was reported to be between 30 - 75% of the total resistance.

When the concentration of 'free' D2EHPA in the organic phase was greater than 0.01 M, the additional resistance was explained by considering the kinetics of the extraction reaction. The rate controlling step was the reaction of metal ion with a D2EHPA dimer to form a metal-D2EHPA complex and a proton. Thus,

$$M^{2+} \text{(aq)} + (HR)_2 \underset{\text{MHR}^{2+} + H^+ \text{(aq)}}{\rightleftharpoons}$$ (1.6.16)

where $M^{2+}$ is either $Cu^{2+}$ or $Co^{2+}$.

Although the authors assumed that the reaction took place at the interface, they did emphasise that it could also be in the aqueous phase close to the interface. Due to limitation with their technique, it is not possible to determine the exact location of the reaction zone. This arises from the fact that the interface hydrodynamics are not accounted for. In addition the data points were scattered and not detailed enough to draw any firm conclusions about the mechanism of the chemical reaction. The net chemical reaction can also be described by a reaction between:

(a) a metal ion and two molecules of monomeric D2EHPA;

or (b) a metal ion and two D2EHPA radicals from two ionised molecules of D2EHPA.

Since the work of Brisk and McManamey (77) several papers have been published on the extraction rate of metals and these will be discussed in chronological order. Since extraction of divalent transition metals is the subject of this thesis, the discussion will be restricted to divalent
metals, unless a specific case can be used to illustrate a point.

Vandegrift and Horwitz (79) have investigated the extraction kinetics of Ca\(^{2+}\) from nitric acid solution into a D2EHPA/dodecane, using a constant interface cell. They concluded that the overall rate of mass transfer was limited both by diffusion through a viscous water layer close to the interface and chemical reaction taking place at the interface.

The viscous aqueous layer was attributed to the presence of a structured 'ice-like' water layer. This idea may be very important for liquid-liquid kinetics since such a layer will affect the diffusivity of the species. The mechanism of the chemical reaction proposed was:

\[
\begin{align*}
\text{Ca}^{2+} \text{(aq)} + \text{(HR)}_2 \text{i} & \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} \text{CaR}_2 \text{i} + 2\text{H}^+ \text{(aq)} \\
\text{CaR}_2 \text{i} + 2\text{(HR)}_2 \text{(org)} & \overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}} \text{CaR}_2 \text{(HR)}_4 \text{(org)}
\end{align*}
\]  

(1.6.17)  (1.6.18)

The slow step is the transfer of calcium across the interface, i.e. Equation (1.6.17). Thus, the reaction must take place at the interface and not in the aqueous phase. The kinetic data were fitted by a pseudo first order rate law:

\[
r_{\text{Ca}} = A \left( k_{\text{aq}} [\text{Ca}^{2+}]_{\text{aq}} - k_{\text{org}} [\text{Ca}^{2+}]_{\text{org}} \right)
\]

(1.6.19)

where \( A \) = the interfacial area;

\( k_{\text{aq}} \) = aqueous to organic mass transfer coefficient;

\( k_{\text{org}} \) = organic to aqueous mass transfer coefficient.
The mechanism given above was used to derive expressions for the mass transfer coefficients in terms of concentrations and some stirring-dependent parameters:

\[
kaq = \frac{k_1[HMR]_1 \cdot k_2 \cdot [HR]^2_{org}}{k_2 \cdot [HR]^2_{org} + k_1 \cdot [H^+]^2} \tag{1.6.20}
\]

and

\[
kor = \frac{k_2 \cdot k_1 \cdot [H^+]^2_{aq}}{k_2 \cdot ([HR]^2_{org} + k_1 \cdot [H^+]^2} \tag{1.6.21}
\]

These mass transfer coefficients were referred to the pseudo first order rate law. It should be noted that \(k_2\) and \(k_2\) were independent of stirring and \(k_1\) and \(k_2\) are functions of the stirring speed.

The model fitted the experimental data well with the following numerical values at stirring speed of 60 rpm.

\[
kaq = 67 \times 10^{-5} \text{ cm/s}
\]

\[
korg = 18.5 \times 10^{-5} \text{ cm/s}
\]

and

\[
k_2/k_1 = 4.9 \times 10^{-3}
\]

The work of these authors on interfacial tension measurements\(^{(80)}\) showed that D2EHPA has surface active properties at the dodecane/nitric acid interface. By means of the Gibbs equation they established that the liquid-liquid interface was saturated at an extractant concentration of 0.0025 M at 25°C.
It should be noted that the concept of water having an 'ice-like' structure at the organic-aqueous interface has been proposed by other authors (81,82) and the result of Vandegrift and Horwitz (79) lends support to this hypothesis. Increase in temperature and stirring speeds would cause the breakage of the structure of water near the interface making it easier for Ca ions to enter the region near the interface.

In the above method of analysis the resistance due to diffusion or chemical reaction cannot be distinguished; pseudo chemical rate equations are likely to fit data well where the so called rate constant is an adjustable parameter.

Golding and Saleh (83) measured the mass transfer rates for cobalt and/or nickel in sulphate medium with 10% D2EHPA in kerosene and with 5% tri-butylphosphate as a modifier, in a modified Lewis cell. Three contacting regions, namely co-extraction, scrubbing and stripping, were considered. They reported that there was resistance to mass transfer in both phases and the rate of transfer was diffusion controlled. No kinetic mechanism was proposed. The mass transfer coefficient was reported to be dependent on the Reynolds number, organic phase loading and the contacting region.

Further work was reported on the above systems using a steady state stirred cell contactor (modified Lewis cell with vertical baffles to promote mixing in the individual phases), by Golding and Pushparajah (84). This study found that under the conditions studied there was no change in the extraction rate when the D2EHPA concentration was increased. Consequently, they concluded that the mass transfer for this system was controlled by diffusion processes rather than chemical reaction. Again, no mass transfer mechanism was proposed. Using correlations for the individual mass transfer coefficients given in the literature for the Lewis type cell (78,85) and comparing these calculated values to the
overall mass transfer coefficients (determined experimentally), the authors then concluded that there is evidence for an interfacial or chemical resistance.

The overall mass transfer coefficients were evaluated on the assumption of complete mixing within each of the cell compartments using:

\[
\text{Mass transfer rate} = K_{\text{org}} \cdot A \cdot (C^*_{\text{org}} - C_{\text{org}(2)})
\]  
(1.6.22)

where \( K_{\text{org}} \) = overall organic mass transfer coefficient;
\( C^*_{\text{org}} \) = organic phase metal concentration in equilibrium with aqueous phase metal concentration;
\( C_{\text{org}(2)} \) = outlet organic phase metal concentration;
\( A \) = interfacial area.

Komasawa and Otake (86) investigated the extraction and stripping rates of cobalt, copper and nickel in aqueous nitrate solution with D2EHPA in n-heptane, benzene and toluene in a stirred transfer cell. They proposed a two step reaction scheme in which the rate controlling step was the interfacial reaction:

\[
\begin{align*}
M^{2+}^{(aq)} + (HR)_2 &\rightleftharpoons \frac{k_1}{k_{-1}} RMR + 2H^{+}^{(aq)} \\
MR^{2+} + x(HR)_2 &\rightleftharpoons \frac{k_2}{k_{-2}} RMR .x(HR)_{2(\text{org})}
\end{align*}
\]  
(1.6.23)

where \( x = 2 \) for \( M = Ni^{2+} \) and \( 1 \) for \( M = Co^{2+} \) and \( Cu^{2+} \).

For simplicity the co-ordinated water has been neglected from the above reaction steps. The rate controlling step is Equation (1.6.24). Thus,
the rate expression is:

\[ r = \frac{k_2 K_1 [M^{2+}][HR]_2^{x+1}}{[H^+]^2} - k_{-2}[MR_2 \cdot x(HR)]_{(org)} \]  

(1.6.25)

where \( K_1 = k_1 / k_{-1} \).

According to the rate expression the extraction rate is first order with respect to the metal ion concentration and inverse second order with respect to the hydrogen ion. The dependency of the D2EHPA concentration is second order for cobalt and copper and third order for nickel. The rate equation for extraction was confirmed by the experimental data.

For the stripping rate Equation (1.6.25) predicted that it is dependent only on the concentration of the metal-extraction complex, (i.e. first order). The authors illustrated that this was the case for all the metals involved.

The extraction rate was improved when the diluent was changed from aromatic to aliphatic. The stripping rate was reported to be the same for the three metals and the diluents used.

From the data reported we can derive the order for the rate of extraction as:

\[ Cu^{2+} > Co^{2+} > Ni^{2+} \]

It is worth noting that the simple reaction scheme proposed by Komasawa and Otake \(^{(86)}\) is based on the mechanism proposed by Eigan and Tamm \(^{(87)}\) for the complex formation in the aqueous phase. This mechanism is for a homogeneous reaction.

A comprehensive investigation with regards to kinetics and mechanism of the interfacial mass transfer has been carried out by Cianetti
and Danesi (88). Using a 'forced convective constant interface area stirred cell' these authors studied the mass transfer of Zn(II), Co(II) and Ni(II) from aqueous nitrate solution into an n-dodecane solution of D2EHPA at 25°C.

The kinetic data were analysed in terms of pseudo first-order rate constants of the pseudo first-order reversible extraction reaction:

\[
M^{2+}_{(aq)} + 2(RR) \rightarrow MR + 2H^+_{(aq)}
\]  

\[
M^{2+}_{(aq)} \xrightleftharpoons[k_{aq}^{-1}]{k_{aq}} M^{2+}_{(org)}
\]  

(1.6.26)

Two models were considered to interpret the results:

(i) mass transfer rate controlled by interfacial chemical reactions;
and (ii) mass transfer rate controlled by interfacial film diffusion.

The two chemical equations describing the extraction mechanism are:

\[
M^{2+} + 2(HR) \xrightleftharpoons[k_k^1]{k_k^{-1}} MR_2 + 2H^+_{(aq)}
\]  

(1.6.27)

and

\[
MR_2 + v(HR) \xrightleftharpoons[k_k^2]{k_k^{-2}} MR_2 \cdot (HR)_{2v-2} + 2(HR)_{v}
\]  

(1.6.28)

The pseudo first order 'rate constants' are:

**Model (I)**

\[
k_{aq} = \frac{k_k^1 \cdot a^v_D}{a^v_D + k_k \cdot [H^+]^2_{(aq)}}
\]  

(1.6.29)
where $k_1 = k_1^* \cdot [(HR)_1]^2$

$k_{-2} = k_{-2}^* \cdot [(HR)_1]^2$

$k_R = k_{-1}/k_2$

$v = 2$ (Zn$^{2+}$), 3 (Co$^{2+}$) and 4 (Ni$^{2+}$)

$a_D = \text{dimer activity of D2EHPA in dodecane.}$

Model (II)

$$k_{aq} = \frac{(1/\Delta_{aq}) \cdot a_D^v}{a_D^v + \Delta_{org}^a \cdot [H^+]^2}$$

$$k_{org} = \frac{(1/\Delta_{org}) \cdot [H^+]^2}{\Delta_{aq} \cdot a_D + [H^+]^2}$$

where $\Delta_{org} = \frac{\delta_{org}}{D_{org}} = \text{the ratio between thickness of the diffusion film and the diffusion coefficient};$

$\Delta_{aq} = \frac{\delta_{aq}}{D_{aq}}$

Both models fitted the experimental data. For forward and reverse extraction the rate constants were very similar for zinc, cobalt and nickel. Hence, the authors concluded that the kinetics of the mass transfer process is diffusion controlled. Again it is suggested that the microscopic diffusional control is due to the presence of a viscous
and structured layer of interfacial water adjacent to the liquid-liquid interface.

It is interesting to note that the same extraction mechanism was proposed by Komasawa and Otake (86) for the extraction of cobalt and nickel and the same conclusions were drawn.

Ajawin and co-workers (89-91) have studied the extraction of zinc from sulphuric acid by D2EHPA in n-heptane, using a stirred cell of known interfacial area. Their initial work involved the extraction of the metal under a 'chemical control regime' at 25°C and at an ionic concentration of 1.0 kmol/m^3. They proposed that the controlling reaction occurred at the interface. The rate was reported to be:

\[
 r = k_1 \cdot \frac{[Zn^{2+}] \cdot [HR]}{[H^+]} \quad (1.6.33)
\]

and the estimated rate constant was 5.1 x 10^{-6} s^{-1}.

In further work (90) the above authors proposed a mechanism of extraction taking place at the interface. The dimer molecule of D2EHPA diffuses to the interface where it ionises and dissociates. The species HR^2- and HR are adsorbed at the interface and reacts according to:

\[
 Zn^{2+} + HR^2- \rightleftharpoons ZnR_2 + H^+ \quad (1.6.34)
\]

and \[ ZnR_2 + HR \rightleftharpoons ZnR_2.HR \quad (1.6.35) \]

The rate determining step is Equation (1.6.34). However, in their analysis of the rate data the bulk phase values were used rather than the interfacial concentrations of the interfacially adsorbed species.
The rate of reaction was found to decrease with ionic strength and increase with temperature. By relating the reaction rate constant to temperature (the Arrhenius equation) and the ionic strength, these workers estimated the rate constant to be $4.25 \times 10^{-7}$ m/s at $25^\circ$C and an ionic strength of 1.0 kmol/m$^3$. The activation energy was estimated to be 41.5 kJ/kmol which is said to be appropriate for an interfacial reaction.

It should be pointed out that their use of Debye-Huckel equation to explain the effect of ionic strength on the rate of reaction is strictly non-applicable, since it only applies to ionic strengths of less than 0.1 kmol/m$^3$. At the extraction concentrations they were studying (i.e. 0.01 M) the liquid-liquid interface will be saturated, thus, some account must be taken of the D2EHPA partitioning into the aqueous phase, in the overall analysis of the extraction mechanism.

The most recent work on the extraction of zinc by D2EHPA in n-heptane is that by Ajawin et al.\textsuperscript{(91)}. The investigation was carried out in a mixed regime where the rate was affected by diffusion as well as chemical reaction. They proposed a model for the initial extraction rate which included a term for film mass transfer coefficients. The equipment used was identical to that used in their earlier work\textsuperscript{(90)}. The rate controlling step was proposed to be the formation of ZnR$_2$ complex at the interface. The mass transfer coefficients were found to be dependent on the stirring speed to the power 1.0. The mass transfer resistance was found to be in the organic film.

Once again the analysis of the extraction mechanism ignores the partitioning of the D2EHPA. This latter work indicates the current trend towards the analysis of extraction data, where mass transfer with chemical reaction at the interface is accounted for.

Hughes and Zhu\textsuperscript{(92)} have proposed a comprehensive model for the
rate of extraction of cobalt from an aqueous phase into n-heptane containing D2EHPA using a growing drop cell. The model is based on the rate of mass transfer with chemical reaction and takes into account the hydrodynamics of the growing drop. The extraction mechanism considers the behaviour of D2EHPA in the organic phase as well as the aqueous phase. They proposed that the reaction took place in an aqueous film adjacent to the liquid-liquid interface. The rate controlling step was assumed to be:

\[
\text{Co}^{2+}(\text{aq}) + R^- (\text{aq}) \xrightleftharpoons[k_f]{k_f} \text{CoR}^+ (\text{aq})
\]

(1.6.36)

where \( k_f \) is pseudo first order forward rate constant.

The model fitted the experimental data well considering the difficulty involved in representing the hydrodynamics of a growing drop. This work is of great importance to the author of the present work because the model takes into account the physical properties of the extractant as well as the effect of the hydrodynamics. However, these authors neglected to mention the nature of the aqueous phase so meaningful comparison with other published work cannot be made.

Takahashi and Takeuchi (93) have studied the reaction kinetics for the extraction of cadmium from aqueous chloride solution with D2EHPA in n-heptane solution using a stirred vessel. The rate controlling step was reported to be:

\[
\text{Cd}^{2+} + 2HR^- \xrightleftharpoons[k_f]{k_f} \text{CdR}_2^+ + H^+
\]

(1.6.37)

occurring at the interface. The rate of extraction was found to be:

\[
\frac{r}{\text{Cd}^+} = k \cdot \frac{[\text{Cd}^{2+}] \cdot [HR]}{[H^+]} \quad \text{(1.6.38)}
\]
This result is in agreement with the rate expression reported in the literature and discussed earlier, for other divalent transition metals. The analysis of the data was not explained and the assumptions that the rate controlling step took place at the interface were not justified. No details were given of how the rate constant was evaluated. The extraction mechanism proposed has interfacial species involved but from the little information given, it is not clear whether the interfacial concentration of these species or the bulk concentration were used in the data analysis.

1.7 Conclusions

The kinetics of metal extraction by organophosphorus compounds is seen to be of commercial importance and presents a challenge in so far as the mechanism is not yet understood. Previous workers have used a number of experimental techniques to pursue the study, each study is open to criticism. It is now intended to study the extraction of certain transition metals using the rotating diffusion cell method. This is a technique which allows an understanding of the hydrodynamics. It is also intended to model the data through an approach based on Whitman's two-film theory but including a partition coefficient to express the concentration of D2EHPA near to the interface but in the aqueous reaction zone.
CHAPTER TWO

EXPERIMENTAL WORK
CHAPTER 2

EXPERIMENTAL WORK

2.1 Introduction

In this chapter the experimental aspect of the kinetic work is considered. The theory and the hydrodynamics of the rotating disc is extensively discussed in order to present the background which leads to the design of the rotating diffusion cell (RDC). The other equipment, which together with the RDC constitutes the apparatus required for the study is also described. The comprehensive experimental procedure is described under Section 2.4.

2.2 The Rotating Diffusion Cell

The rotating diffusion cell (RDC), for studying liquid-liquid systems was developed by Albery et al.\(^\text{(94)}\). The RDC is based on the rotating disc electrode used by electrochemists to study reactions at an electrode surface. It was developed from a modified Stokes cell to study two phase interfacial transfer.

Albery and co-workers\(^\text{(94)}\) used the RDC to investigate mass transfer in a number of systems, amongst which were carboxylic acids transferring between water and isopropyl myristate. Using the RDC, Sagert et al.\(^\text{(95)}\) have extended the work on the transfer of carboxylic acids. Hadgraft\(^\text{(96)}\) and Guy\(^\text{(97)}\) have measured interfacial transfer rates of drugs in a RDC, to elucidate the mechanism of precutaneous absorption of drugs.

In the field of solvent extraction kinetics, Fisk\(^\text{(98)}\) used the RDC to study the kinetics of forward extraction of copper (II) by 'ACORGA P50' extractant. He also investigated the nitration of toluene
The study on copper (II) by Fisk has been extended by Albery and co-workers \(^{(54)}\) to the stripping reaction. Recently, Lawson \(^{(99)}\) has used the RDC to study the kinetics of nitric acid and uranium extraction by tri-butylphosphate.

The RDC provides the foundation for a very useful experimental technique for measurement of mass (and heat) transfer. The technique has the means of precise hydrodynamic control of the transferring material to and from a reactive interface. It is one of the relatively few cases in which the interface is 'uniformly accessible' i.e. the thickness of the diffusion boundary layer (and the local mass transfer coefficient), is the same at all points on the interface, provided that the fluid motion over the interface is laminar. The transport to the interface is both well defined and calculable; exact solution to the Navier-Stokes equation can be obtained for laminar motion, as shown by Levich \(^{(100)}\).

The interfacial area through which mass transfer can occur, is known and is variable (between 40 mm\(^2\) to 300 mm\(^2\)). This facilitates the study of fast or slow rates of transfer. Also, the mass transfer can be conveniently controlled by altering the rotational speed of the cell.

### 2.2.1 The physical aspects of the rotating diffusion cell

The main components of the rotating diffusion cell were assembled after a design according to Albery et al. \(^{(94)}\). Slight modifications were made to improve the design and these will be described in this section where appropriate. The rotating diffusion cell is shown in Figure 2.2.1 and Plate 2.2.1. It consists of a rotating chamber (henceforth known as the rotating cell), containing one phase, which is immersed in a second quiescent phase. Two types of rotating cell were used, one made
KEY:
A = Aqueous phase
B = Organic phase
C = P.T.F.E. baffle
E = Calomel electrode
F = Membrane
G = Glass electrode
H = Titrant delivery tube
L = Perspex lid
N = Nitrogen purge tube
P = P.T.F.E. plug
S = Stainless steel hollow shaft
T = The rotating chamber
V = Thermostatted glass vessel (the stationary chamber)

FIGURE 2.2.1. Diagram of The Rotating Diffusion Cell
PLATE 2.2.1: The Rotating Diffusion Cell
from a perspex tube and the other from a glass reinforced P.T.F.E.

Perspex cell

The original rotating cell was fabricated from perspex and had a lower detachable section to facilitate easy exchange of the prepared filter. In a previous study, the author (101) had discovered that this design was prone to phase leakage through the threads of the detachable section and also the cell was susceptible to breakages due to the residual stresses incurred during the machining and tapping of the unit. Thus, the cell was redesigned as a whole tube. For a uniformly surfaced cell, the external and internal surfaces of the original perspex tube were first machined then smoothed down with a fine emery paper. Finally, the surfaces were polished using 'Brasso'.

'FLUOROSINT' cell

In order to investigate systems which would 'attack' a perspex cell as well as the 'Millipore filter', Fisk (98) used a rotating cell made from P.T.F.E. with a polyethylene membrane, 'Celgard 2500'. Since thin flat pieces of P.T.F.E. tend to bend, the cell had a bevelled construction, see Figure 2.2.2. This type of design must influence the hydrodynamics and, therefore, the application of Levich's theory to the rotating cell is questionable. In order to overcome the last uncertainty, the P.T.F.E. filter unit was completely redesigned at Bradford. The new cell was fabricated from glass reinforced P.T.F.E. ('FLUOROSINT' supplied by POLYPENCO), which is much stronger than P.T.F.E. but still possesses the chemical resistive property of normal P.T.F.E. The greater strength of the new material made it possible to produce a planer base; see Figure 2.2.3 for a schematic diagram of the design.
FIGURE 2.2.2. The P.T.F.E. Cell Used by Fisk Showing The Bevelled Construction

FIGURE 2.2.3. The new 'FLUOROSINT' Cell Showing The Planer Base
The most important component of the RDC is the specially treated 'Millipore' filter (F), which 'divides' the RDC into two chambers. The filter is treated so that only a central circular area between 100 mm\(^2\) to 200 mm\(^2\), shown as a dotted line, remains permeable, see Section 2.4.1. The filter is 'attached' to the rotating cell (T), which can be either the perspex cell or the 'FLUOROSINT' cell and which contains one of the liquid phases (B). In this work it is always the organic phase which is held inside the cell.

The rotating cell is surrounded by a thermostatted glass vessel (V) (the stationary chamber), which contains the second phase (A) (the aqueous phase). The liquid-liquid interface can be set up on either surface of the filter, but in this study it was always sited on the outer surface, that is, the one in direct contact with the aqueous phase.

The rotating cell is designed to rotate when it is driven by a belt attached to a Velodyne motor. The cell is mounted on a stainless steel pulley and a bearing unit. In previous work, the design suggested a pulley shrunk onto a P.T.F.E. centre sited on a central hollow shaft thus making the cell very light and easy to dismantle for cleaning. However, with usage, the P.T.F.E. centre deformed and introduced a wobble in the motion of the rotating cell. In the present work it was decided to replace the last design with a stainless steel pulley and sealed ball-race bearings. The new feature is similar to the design used by Hadgraft\(^{(96)}\) and Fisk\(^{(98)}\) but has incorporated in it a stainless steel cap and a P.T.F.E. plug to protect the sealed bearings against solvents. See Figure 2.2.4 for the cross section diagram. The new system is much steadier and appears to run successfully.

The rotating cell contains a stationary P.T.F.E. baffle (C) (see Section 2.2.2). The baffle is attached to a stainless steel hollow
FIGURE 2.2.4.1 The New Stainless Steel Pulley System.
shaft (S) which allows the rotating chamber to be filled with the organic phase and permits any subsequent material to be added to the organic phase, e.g. by a syringe or pipette. During an experiment the opening to the shaft is plugged with a P.T.F.E. stopper (P) which has a very fine central hole in order to reduce any evaporation that might occur.

The glass vessel (V) is covered by a perspex lid (L) to reduce evaporation losses to a minimum and also reduce the ingress of atmospheric carbon dioxide, see Section 2.4.4. The lid has holes for electrodes, a nitrogen purge tube, the titrant delivery tube and the rotating cell. In the original design, the lid was fixed to the pulley making the manipulation of the rotating cell rather cumbersome. In the present work the lid is free, which allows easy access to the RDC when cleaning is required.

2.2.2 The hydrodynamics of the rotating diffusion cell

The hydrodynamics of the rotating diffusion cell are based on the hydrodynamics of a rotating disc, see Section 2.2.3. The turning motion of the rotating cell, with the stationary P.T.F.E. baffle inside and the filter membrane attached to one end, imposes a defined flow of the liquid inside the cylinder and outside it, see Figure 2.2.5. The flow-field is only true for a laminar flow. Hadgraft (96) has examined experimentally the hydrodynamics by introducing some dye into the rotating cell when it is rotating. The flow patterns he reports are those shown in Figure 2.2.5.

As the cell is rotated, the ambient fluid is drawn towards the planer membrane and then forced away radially over the surface by the centrifugal force developed by the surface drag; it occurs on both sides of the membrane. Inside the rotating cell the stationary baffle prevents the radial convective transport, created by the rotating inner cylindrical
(b) Patterns in the rotating chamber

(c) Patterns below the membrane (102)

Figure 2.2.5: Diagrammatic representation of the fluid flow pattern near the Rotating Diffusion Cell

The inner rotating chamber

Z = 0
wall, being transferred to the central core of the liquid. Axial convective transport towards and normal to the filter surface is thus assured.

The liquid which is ejected from the centre of the membrane surface towards the inner walls of the rotating cell is compensated for by the liquid sucked in through the three slots in the baffle. In the outer chamber the distance to the inner wall is relatively large and is sufficient so as not to interfere with the flow patterns of the central core of the liquid. The flow of the solutions towards the membrane surface removes products formed at the interface and brings fresh reagents towards it. Also it should mix the solution in the main bulk of the chambers to give a reasonably uniform concentration of the non-reacted and reacted components.

2.2.3 The theory of the hydrodynamics of a rotating disc

Several assumptions are made when deriving the general equation of convective diffusion from the equations of continuity and motion. These assumptions are:

(i) the temperature of the liquid is constant;
(ii) the pressure gradient is relatively small;
(iii) the liquid motion is steady and laminar;
(iv) the liquid is incompressible.

The general equation of convective diffusion in cartesian coordinates \((x, y, z)\) is \((103)\):

\[
\frac{\partial C}{\partial t} + \nu_x \frac{\partial C}{\partial x} + \nu_y \frac{\partial C}{\partial y} + \nu_z \frac{\partial C}{\partial z} = D \left[ \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right] \quad (2.2.1)
\]
For a rotating disc it is best to use cylindrical co-ordinates \((r, z, \phi)\), see Figure 2.2.6, thus Equation (2.2.1) becomes:

\[
\frac{\partial C}{\partial t} + V_r \frac{\partial C}{\partial r} + V_z \frac{\partial C}{\partial z} + V_\phi \frac{\partial C}{\partial \phi} = D \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 C}{\partial \phi^2} + \frac{\partial^2 C}{\partial z^2} \right]
\]  

(2.2.2)

where \(V_r, V_z\) and \(V_\phi\) are the radial, axial and tangential velocity components respectively, (see Figure 2.2.7), \(C\) is the concentration and \(D\) the diffusivity coefficient.

The following treatment is for the rotating disc but applies to both sides of the membrane in the rotating diffusion cell. At the surface of the disc the following boundary conditions must be satisfied:

At \(z = 0\)
\[
V_r = 0 \\
V_z = 0 \\
V_\phi = rw
\]

(2.2.3)

where \(\omega\) (rad/s) is the angular velocity of the rotating disc. The variations of the component velocities have been described\(^{100}\) in terms of functions of a dimensionless distance \(\xi\):

\[
V_r = r.\omega.F(\xi) \\
V_z = \sqrt{v.\omega.H(\xi)} \\
V_\phi = r.\omega.G(\xi)
\]

(2.2.4)

where \(\xi = \sqrt{(\omega/v).z}\)  

(2.2.5)

There is also a function for pressure, \(p = p(z) = p.v.\omega.P(\xi)\) but is not considered here since the pressure is assumed to be constant. For details
FIGURE 2.2.6: The Cylindrical Coordinates for the Rotating Disc System

FIGURE 2.2.7: The Velocity Components of the Rotating Disc
see Reference (100). The functions F, G, and H are obtained by substituting Equation (2.2.4) into the Navier-Stokes and continuity equations and the resulting differential equations solved numerically. For the mathematics the reader should consult Levich (100). The functions are illustrated in Figure 2.2.8.

Considering the z axis, at the membrane surface (z = 0) the liquid rotates with the membrane. As z increases the centrifugal force imposed on the liquid produces shearing which forces the liquid outward. The function G describes how the tangential velocity varies in the solution, being a maximum at the disc surface and decreases exponentially to zero as z → ∞. The function F describes the radial velocity of the liquid and is zero at z = 0 rising rapidly to a maximum at z' = 0.1 mm and falling exponentially to zero as z → ∞. The function H describes the velocity of the liquid (shown as -H in Figure 2.2.8 because it is towards the disc) which 'replaces' the liquid propelled outward near the disc. It is zero at z = 0 as the solution rotates with the disc but increases from z = 0 to z → ∞. At values less than z = 0.1 z' there is convection in the solution. This secondary flow is due to the centrifugal force in the thin layer and is directed radially outward, because for z < 0.1 z' F(ξ) > H(ξ).

If we assume that concentrations in both chambers are only a function of distance from the membrane surface and the concentration distribution is independent of time (i.e. ∂C/∂t = 0) then we can simplify Equation (2.2.2). Also, due to the symmetry of the system, all derivatives containing ξ can be eliminated. The simplification leads to a second order one dimensional differential equation:

\[ V_z(z) \frac{dc}{dz} = D \frac{d^2c}{dz^2} \] (2.2.6)
FIGURE 2.2.8: Graph of Functions F, G and H
Levich has solved Equation (2.2.6) to give a solution which relates the boundary conditions on the surface of the disc \((C_0, C'_0; \text{see Figure 2.2.9})\), to the bulk concentration \((C_\infty)\):

\[
J = -D \left[ \frac{\partial C}{\partial z} \right]_{z=0} = D C'_0 = D \left[ \frac{C_\infty - C_0}{\delta} \right]
\]  \tag{2.2.7}

where \(\delta = \text{thickness of the diffusion layer}\)

\[
= 1.6117 \cdot D^{1/3} \cdot \nu^{1/6} \cdot \omega^{-1/2}
\]  \tag{2.2.8}

\(D = \text{diffusivity coefficient.}\)

Also,

\[
V_z = 0.510 \sqrt[3]{\omega^3/\nu} \cdot z^2 \text{ for } z << \sqrt{\nu/\omega}
\]  \tag{2.2.9}

The solution describing the concentration profile is not given here and the reader is referred to Reference (100) for details. Figure 2.2.9 shows, in a schematic form, how the concentration varies with \(z\) close to the disc surface.

It is more convenient to have the angular velocity defined in units of Hz, thus Equation (2.2.8) can be expressed as:

\[
\delta = 0.643 D^{1/3} \cdot \nu^{1/6} \cdot \Omega^{-1/2}
\]  \tag{2.2.10}

where \(\Omega\) is the angular velocity in Hz. Equation (2.2.9) demonstrates that \(V_z\) is independent of \(r\) and \(\varphi\), implying that the flux is even over the whole disc, see Figure 2.2.10. The eveness of the flux on the area for mass transfer is one of the main advantages of the rotating diffusion cell. In other experimental methods for studying kinetics, it is not possible to describe the flux with such confidence.
**FIGURE 2.2.9:** A Typical Concentration Profile for the Rotating Disc System

**FIGURE 2.2.10:** Schematic Diagram Showing the Even Flux on the Surface of the Disc
2.2.4 The theory of interfacial transfer in a RDC

Consider the transfer of a solute from an organic phase into an aqueous phase. The transfer process will consist of the diffusion of the solute to the membrane surface, interfacial transfer followed by the diffusion of the solute from the interface. If a chemical reaction is involved then it is assumed that the interfacial transfer is diffusional in nature with a chemical reaction contribution.

Using Fick's Law and Equation (2.2.10), to describe the aqueous and organic diffusion layer thicknesses, it is possible to mathematically represent the interfacial transfer. Such an analysis has been carried out by several workers (95, 101, 106), for the diffusional transfer of a solute and has led to the following expression:

\[
\frac{C_{\beta,\infty}}{J} = 0.643 \Omega \left[ \frac{v_\alpha^{1/6}}{P \cdot D_\alpha^{2/3}} + \frac{v_\beta^{1/6}}{D_\beta^{2/3}} + \frac{L}{a_0 \cdot D_\beta} + \frac{1}{a_0 \cdot k_{i,1}} \right]
\]

where \(C_{\beta,\infty}\) = bulk organic phase concentration of the solute; kmol/m\(^3\)

\(J = F / a_0 \cdot A\) = transfer flux; kmol/m\(^2\)s

\(\Omega = \) rotational speed of the rotating cell, Hz

\(F = \) transfer rate of solute; kmol/s

\(A = \) area of the interface (i.e. the membrane); m\(^2\)

\(a_0 = \) surface porosity of the membrane

\(v = \) kinematic viscosity; m\(^2\)/s

\(P = \) partition coefficient of the solute

\(D = \) diffusion coefficient; m\(^2\)/s

\(L = \) membrane thickness; m

\(k_{i,1} = \) forward interfacial transfer rate constant; m/s

Subscript

\(a = \) aqueous phase

\(\beta = \) organic phase.
For the derivation of Equation (2.2.11) the reader is referred to Reference (101).

The above relationship relates the transfer flux to the rotational speed. As $\Omega^{-1} \rightarrow 0$, i.e. infinite rotational speed, the resistance in the diffusion layers tends to zero. Therefore, the transport of solute from one phase to another becomes a function of both the resistance in the membrane and interfacial transfer term.

Equation (2.2.11) is linear in nature, hence, it is possible to construct a graph of $\Omega^{-1}$ as the abscissa and $1/J$ as the ordinate, with calculable slope and intercept. A plot of this kind is known as the 'Levich Plot'. The slope of the plot refers to the diffusion of solute to and away from the interface. The intercept, which corresponds to an infinite rotational speed, gives an indication of the interfacial transfer rate and diffusion in the membrane. A typical 'Levich Plot' is shown in Figure 2.4.2 and will be further discussed in Section 3.3.

For interfacial transfer with chemical reaction at the interface or in a thin reaction zone adjacent to the interface, the transfer process will be much more complex. However, we can generally describe the process by the following expression:

$$\frac{1}{J} = \left[ \text{Term due to diffusion in diffusion layer} \right] \cdot \Omega^{-1} + \left[ \text{Term due to transfer} \right] + \left[ \text{Term due to diffusion in the membrane} \right]$$

(2.2.12)

where $J =$ transfer flux; kmol/m$^2$s

$\Omega =$ rotational speed; Hz.

In this study the 'Levich Plot' is used to validate the metal extraction rate data using the result of Equation (2.2.11) that $1/J$ is a linear function of $\Omega^{-1}$. This linear relationship is then used to predict the experimental flux for a given rotational speed.
2.3 The Detailed Description of the Apparatus for Kinetic Studies

The apparatus for kinetic experiments consisted of the pH-stat apparatus and the RDC fitted with a 'Millipore' filter. The RDC has already been described in detail under Section 2.2.1. The remaining apparatus is described in the following sections.

2.3.1 The pH-stat apparatus

The pH-stat apparatus is an integral part of the 'Recording Titration System', RTS822, manufactured by Radiometer. The system, together with the RDC, is shown in Plate 2.3.1, and it consists of the following main items:

(a) a titrator (TTT80)
(b) an autoburette (ABU80)
(c) a servograph (REC80)
(d) a standard pH meter (PHM82).

The minor instruments are the pH probes, the titrigraph module (REA160) and the derivation unit (REA260). Also available is an optional pH-stat unit (REA260) for continuous pH-stat work of more than 70 minutes. The pH probes used in this study were the glass electrode (G2040C) and the calomel reference electrode (K4040).

The TTT80 titrator is an automatic titration control unit especially designed for use in conjunction with a pH meter (in this case the PHM82 unit). It monitors the ABU80 autoburette and permits the performance of many kinds of end-point titrations, titration curve recordings and pH-stat work with or without recordings. Another feature of the unit is that the titrant delivery rate is controlled and will be proportionally slowed down near the set pH-stat value, or the end point. The accuracy of pH-stat setting is ± 0.01 pH.
PLATE 2.3.1: The Complete Apparatus

- Motor Controller
- Velodyne Motor
- Rotating Diffusion Cell
- Titrant Reservoir
- pH meter
- Titrator
- Autoburette
- Recorder
The ABUBO autoburette is a fully automatic, computerised burette with digital display. It can be operated manually or remotely by the automatic titrator. The unit can deliver up to 25 cm$^3$, (or 2.5 cm$^3$), of the titrant with an accuracy of ± 0.5%. It can also deliver very small volumes (0.002 cm$^3$). The maximum delivery rate can be manually controlled between 5% to 160% of the full burette content per minute. If the above is used in conjunction with the proportional band control on the titrator a sensitive means for producing smooth pH-stat curves is obtained. In this work the delivery rate was between 5% - 15% per minute and the proportional band was always set to 0.05 as recommended by the manufacturer for pH-stat work$^{(104)}$.

The servograph is a high-performance instrument which is electronically linked to the autoburette. It has many different applications in conjunction with interchangeable plug-in modules. For pH-stat work the horizontal scale is the time scale and this can be varied from a minimum of 2.8 min. to a maximum of 70 min. on full scale deflection. The vertical scale gives the amount of titrant delivered; normally 1 cm = 1 cm$^3$ of titrant which can be expanded by two-fold. All experiments were carried out with the expanded mode option and for the time scale the setting was between 7 to 28 min.

The PHM82 standard pH meter is a digital precision laboratory instrument which satisfies all normal requirements for pH and other potentiometric measurements. It has an accuracy of ± 0.01 pH at 25°C. The unit is electronically linked to the titrator.

For detailed information on these units and other ancillary equipment available the reader is referred to the Radiometer reference manual for the RTS822 system$^{(104)}$. The mode of operation of this equipment was as prescribed by the manual.
2.3.2 The 'Millipore' filter

The MF 'Millipore' filter is composed of mixtures of cellulose acetate and cellulose nitrates. It is compatible with dilute acids and bases, aliphatic and aromatic hydrocarbons. The filters are made by uniformly spreading the liquid polymer across a bed. The side contacting the bed is shiny and therefore there is the possibility of the surface porosities being different on both sides. For consistency the filters were always used with the shiny surface presented outward to the aqueous phase. The surface structure of a typical 'Millipore' filter is shown in Plate 2.3.2.

Four different types of 'Millipore' filters were used, the difference being the pore size, i.e. 0.05, 0.22, 1.2 and 3.0 μm. These filters were hydrophobic in character. From practical experience it was found that the best filter to use for this work was the 0.22 μm pore size. Fisk (98) has reported this, but it is very much dependent upon the system being studied; other solvents and other aqueous phases may require the use of different filters.

The characteristics of the 0.22 μm filter (105) are given in Table 2.3.1. Fisk (98) has studied the properties of this filter and where appropriate his results are used.

| TABLE 2.3.1 |
| The Characteristics of the 'Millipore' Filter Used |

<table>
<thead>
<tr>
<th>Type</th>
<th>GSWP 047 00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter diameter</td>
<td>47 mm</td>
</tr>
<tr>
<td>Pore size</td>
<td>0.22 μm ± 0.02 μm</td>
</tr>
<tr>
<td>Mean thickness, L</td>
<td>150 μm</td>
</tr>
<tr>
<td>Void porosity</td>
<td>75%</td>
</tr>
<tr>
<td>Surface porosity, a₀</td>
<td>0.68 ± 0.01*</td>
</tr>
</tbody>
</table>

*From reference (98) for a treated filter; note the error quoted is the standard error of the mean.
Scanning Electron Micrograph of the Surface Structure of a 0.8 μm Pore Size 'Millipore' Filter
2.4 Experimental Procedure

2.4.1 Preparation of the filter

The 'Millipore' filter is treated to leave a central circular permeable region through which solute transfer is possible. The area appropriate to these studies is about 100 - 200 mm$^2$. The process for preparation of the holder and filter can be broken-down as follows:

(i) Preparation and cleaning of the perspex tube.
(ii) Fixing the 'Millipore' filter onto the tube.
(iii) Rendering the outer annulus region impermeable using a polymerising solution.
(iv) Washing and drying the treated filter, (henceforth known as the membrane).

The remaining old membrane and perspex cement from the bottom of the tube are removed by using a coarse and fine emery cloth (not necessary when a new perspex tube is used). The best method was found to be the use of coarse cloth to remove the bulk of the old remains and then the fine cloth to obtain a smooth surface. A circular motion on the emery cloth ensured an even surface of the tube. The perspex tube is then cleaned according to the procedure given in Section 2.4.3 to remove all traces of grease. This is very important when a new perspex tube is used since the surface is covered with lubricating oil and 'Brasso', (see Section 2.2.1).

In order to mate the filter to the tube, a thin layer of perspex cement ('Tensol') is first applied to the rim of the tube using a thin glass rod. The filter is then placed on the tube using a pair of philately forceps, with the correct surface facing outward (see Section 2.3.2). To ensure an even seal it is pressed down using a P.T.F.E. tube of same diameter and thickness. To complete the seal, further cement is applied onto the filter (up to 2 mm inward from the outer edge of the filter) and
it is then left to dry for approximately thirty minutes in a fume cupboard.

Rendering the outer annulus region of the filter impermeable is one of the most important stages. The filter's central circular region, the area required for mass transfer, has to be protected from the polymerising solution. Hadgraft (96) has investigated several different methods. The best method he found was the use of glycerol to protect the filter. However, Fisk (98) has reported that the presence of any trace of glycerol in the membrane can slow the rate by 30%. Thus, a new method was developed where no protective reagent is required. This method involves applying the polymerising solution whilst the prepared filter is rotating.

The rotation was achieved by attaching the perspex tube to the bearing unit and clamping it upside down on the motor stand. The rotation must be sufficiently fast to allow the solution to be absorbed evenly by the filter to begin the polymerising process. The optimal speed of rotation was found to be between 3 - 5 Hz.

The polymerising solution is applied with a flat artist's brush, beginning at the edge of the tube wall and working inward to the required circular area. The solution is applied sparingly and uniformly. As the solution evaporates the polymerised filter material becomes transparent and taut.

The composition of the polymerising solution (96) (by volume) is:

- 33% dioxan
- 33% hexane
- 33% 1,2 dichloroethane
- 1% distilled water.
The dioxan dissolves and polymerises the cellulose esters in the filter causing the pores to collapse. The other components dilute the dioxan and cause it to evaporate rapidly. The dilution is necessary since too much dioxan would dissolve the esters violently causing the filter to rupture. Another cause of rupture is the presence of peroxides\(^{(106)}\) in the polymerising solution. The presence of air in the storing vessel favours the formation of peroxides. To prevent the formation of peroxides the solution was always stored under nitrogen. Also, the individual components used to make the polymerising solution were first deoxygenated by bubbling nitrogen through them.

The final stage is to wash the filter with double distilled water. The best method was to fill the chamber with distilled water (approximately 25 cm\(^3\)) and allowed to permeate through the membrane several times. The treated filter (henceforth the membrane) is then dried and stored under vacuum in a desiccater until required for further use.

2.4.2 Determination of the membrane area

Several methods are available for determining the membrane area ranging from simplest to the most complex. Some of these are listed below:

1. Tracing the membrane area onto a translucent graph paper and counting the squares to determine the area.

2. The tracing and weighing method. This method involves tracing the area on a tracing paper and carefully cutting out and weighing it on a chemical balance. The area is determined by weighing the same piece of tracing paper of known area to determine the specific area (mm\(^2\)/s).
(3) The optical method. A low focal point travelling microscope with vernier scale is used to determine the average diameter by measuring several diameters, (the membrane area is approximately circular).

(4) The photographic method. This method involves taking an enlarged photograph of the membrane and a reference length to find the average diameter.

(5) Application of an image analyser system. This complex equipment uses a video camera in conjunction with an optical microscope to produce a digital image which can be analysed by a microcomputer.

In an earlier work (101) the author had investigated methods (1) and (2) and had found them to be effective. However, these methods involved separation of the membrane from the perspex tube as a planer surface is required to trace the area. Also, in the process of tracing the area the membrane is invariably damaged, thus it could not be used again.

Methods (4) and (5) are very accurate but both are uneconomical since the former involves developing and processing the film and the latter involves the use of very expensive and complex equipment.

The optical method (Method (3)) was therefore seen as the best alternative. This method is completely inexpensive and offers an opportunity to accurately determine the membrane area after it has just been made or after some of the complete set of experiments have been conducted.

The outer rim of the perspex tube was marked in thirty-two equally spaced positions, then the travelling microscope was used to measure the diameter of the permeable disc in the section of the membrane, thus, sixteen diameters were measured with an accuracy of \( \pm 0.001 \) cm. The average
diameter was then calculated and hence the permeable membrane was found. It is estimated that the standard mean error (2 σ\text{\textsubscript{n-1}}) on the area (typically = 2 cm\textsuperscript{2}) found this way is < ± 0.1% on a typical membrane.

### 2.4.3 Cleaning procedure

In kinetic studies it is important to use very clean equipment so as to minimise, if not to eradicate, the influence of contaminants. In liquid-liquid extraction work it is essential to remove all traces of surfactants as they have disastrous effects on mass transfer. Therefore, among the various methods available \textsuperscript{(107)}, any method involving detergents could not be used. The routine adopted used one or more of the following three methods:

(a) cleaning with a de-greasing agent \textsuperscript{(108)};
(b) use of the ultrasonic bath;
(c) cleaning with chromic acid.

The de-greasing agent was prepared by dissolving 100 g of potassium hydroxide in 50 cm\textsuperscript{3} of distilled water and after cooling made up to one litre with industrial methylated spirit. The chromic acid was prepared according to the procedure given in Vogel \textsuperscript{(107)}.

In general any 'equipment' to be used was first cleaned with the de-greasing agent followed by copious amounts of distilled water. All glassware and P.T.F.E. equipment was then carefully cleaned with chromic acid followed by a thorough rinsing with water then by distilled water and acetone. Whenever possible the glassware was dried in an oven and all other equipment was allowed to dry in the open laboratory. The above technique was followed when the glassware was used for the first time, or it proved to be dirty, and more importantly when the chemical system was changed. When handling the chromic acid utmost care was taken.
since it is an extremely corrosive acid and is known to form an explosive mixture in the presence of organic materials.

Because chromic acid attacks perspex, the perspex tubes were first cleaned with de-greasing agent followed by a thorough rinsing with distilled water. Further cleaning was achieved by immersing the tube in some distilled water in an ultrasonic bath for half an hour. Finally, it was rinsed several times with distilled water and allowed to dry naturally.

2.4.4 Experimental procedure

The experimental procedure is now generally described with detailed comments where appropriate. The procedure consists of preliminary preparation and the main method.

**Preliminary Preparation**

To ensure that the membrane is completely organic wetted, it is necessary to make sure that there is no moisture present in the membrane, see Section 3.2. To achieve this, the clean rotating cell with the membrane attached to it was stored overnight in a desiccator under vacuum. Prior to the commencement of the experiment, the rotating cell was removed from the desiccator and the membrane was immediately impregnated with a few drops of the pure diluent. Further 25 cm$^3$ of the diluent was placed inside the cell and allowed to percolate through the membrane, hence, ensuring an organic wetted membrane.

To prevent or minimise 'mass transfer' due to non-equilibrium of passive components the aqueous phase was saturated with the pure diluent at least eight hours before the commencement of the experiment. The saturation was accomplished by vigorously shaking approximately 250 cm$^3$ of the metal sulphate solution with 5 cm$^3$ of the diluent, in a clean 500 cm$^3$ capacity separating funnel, for one minute. The resulting mixture was allowed to separate into the two phases for a minimum period of eight
hours. Normally, the mixture was allowed to separate overnight.

All electrical equipment was switched on at least half an hour before the experiment was started. Also the stationary chamber, the aqueous phase (the metal sulphate solution saturated with the pure diluent), the diluent and the extractant concentrate (extractant held in the pure diluent) was thermostatted to $25 \pm 0.1^\circ\text{C}$. In addition, the stationary chamber was cleaned, with double distilled water followed by acetone and dried. Before the experiment was undertaken, the pH meter's calibration was checked and if required, recalibrated.

The pH-stat technique involves maintaining a preselected pH of a solution by adding either acid of alkali to it. In this work the pH of the aqueous phase was kept constant by the addition of sodium hydroxide (as $\text{H}^+$ ions are 'generated' at the interface or in the thin reaction zone on the aqueous side of the interface). The sodium hydroxide solution (the titrant) was prepared by the dilution of volumetric solution and re-standardised using standard sulphuric acid, before the experiment was undertaken. This precaution was deemed necessary because sodium hydroxide solution is sensitive to the atmospheric carbon dioxide and moisture content which causes it to deteriorate with time.

For this work the concentration of the titrant was in the range of 5.0 to 7.5 mM. This range permitted the extraction reaction to be 'followed' optimally and minimised the imminent formation of the metal hydroxide at the tip of the titrant delivery tube. This is due to the existence of a localised high pH in the region of the tip. It must be noted that no metal hydroxide was found in the bulk of the aqueous phase and the amount formed at the tip was very small.
Method

(i) A clean 250 cm\(^3\) graduated burette was filled with the aqueous phase and a specially made 50 cm\(^3\) graduated burette with the pure diluent. These two burettes constituted the 'filling apparatus', see Plate 2.3.1. This apparatus is used to place 190 ± 1 cm\(^3\) of the aqueous phase in the stationary chamber and 40 ± 0.1 cm\(^3\), less the volume of extractant concentrate to be injected at a later stage, of the pure diluent into the rotating cell. The specific volumes of the aqueous and organic phase are necessary to ensure a small, if any, pressure difference at the interface to minimise mass flow. Normally the interfacial tension is sufficient to withstand any pressure differences that might occur during the filling process. Initially, the stationary chamber was filled with 100 cm\(^3\) of the aqueous phase.

(ii) The next step involved preparing the rotating cell to be lowered into the aqueous phase. The excess diluent remaining in the rotating cell, from the preliminary preparation, was absorbed away with a clean tissue paper. Care was taken not to touch the membrane surface and that it was still covered with a film of the diluent.

The rotating cell was then filled with a few cm\(^3\) of the diluent from an 'accurately known volume', to ensure that the membrane remained wet whilst the cell was fixed to the stainless steel pulley system. The rotating cell was then lowered into the stationary chamber, with a drive belt on the pulley, until the aqueous phase surface just touched the membrane, thus, forming the aqueous–organic interface. Care was taken
(ii) continued .......

to ensure that no air bubbles were trapped beneath the membrane when the rotating cell was lowered into the aqueous phase. Once the interface was established the rotating cell was firmly fixed to the stand and the velodyne motor switched on at a low speed (typically 1 Hz). The remainder of the aqueous and the organic phase was then simultaneously added to the stationary chamber and the rotating cell, respectively.

The few cm$^3$ of the diluent, together with the remaining amount of the 'accurately known volume' constitutes the volume of the diluent to be placed into the rotating cell.

Once the rotating cell was filled, the central shaft opening was plugged using a P.T.F.E. stopper. In the case of experiments where the effect of modifiers on the extraction rate was investigated, the required amount of the modifier, held in the pure diluent, was first injected into the rotating cell, using a stainless steel needle and a glass syringe through the central opening before plugging it.

(iii) Then the nitrogen purge tube, the glass electrode, the calomel electrode and the titrant delivery tube were inserted into the aqueous phase through the perspex lid. The latter three items were all connected to the pH-stat apparatus. The pH-stat setting was set typically to pH 4.50 ± 0.01 pH.

The nitrogen purge was switched on. Then using concentrated sulphuric acid (10 M) and/or 2 M sodium hydroxide solution the aqueous phase pH was adjusted to pH 4.5. Having adjusted the pH, the rotating cell was left running, at the speed of 3.5 Hz, for twenty to thirty minutes to allow the system to equilibrate.
The nitrogen purge is required because during an experiment the flux can be very small and consequently it is necessary to reduce the amount of carbon dioxide entering the system to a minimum; Hadgraft (48) has reported that the carbon dioxide effects are particularly noticeable when the solution is being pH stated at high pH. This conclusion was confirmed in a controlled experiment in which the rotating cell was filled with pure n-heptane only, so any titrant added would correspond to the influx of carbon dioxide. The carbon dioxide effect at the pH-stat of 4.5 pH was found to be marginally significant.

The experiment was started when the extractant concentrate was injected into the rotating cell. At this stage the organic phase volume will be 40 cm$^3$. To accurately determine the amount of extractant concentrate added, the syringe was weighed before and after the injection.

During the experiment the rotational speed of the rotating cell was varied between 1 and 5 Hz, to give a number of linear traces, see Figure 2.4.1. The rotational speed was measured using a tachometer (model TM2011, RS Components Ltd). It is normal, when studying several rotational speeds, to alter the speeds so that first a 'high' then a 'low' speed is studied.

For each rotational speed considered, the apparatus was left running long enough to ensure that a consistent flux was being obtained; this is confirmed by a steady continuous pH-stat trace on the recorder.

The main idea behind pH-stat curve is to record the amount of titrant used to maintain a pre-selected pH as a function of
time. When titrant is added to maintain the pre-selected pH, the chart paper moves by an increment that corresponds to the titrant delivered. The recorder pen moves at a constant speed selected on the REC. In this way a curve is produced giving the titrant consumption needed to maintain the pre-selected pH as a function of time, hence, the flux of metal extraction.

Finally, at the end of the experiment, the electrodes, the nitrogen purge tube and the titrant delivery tube were removed and cleaned with distilled water. The rotating cell was also removed and cleaned with the pure diluent. Some diluent was allowed to percolate through the membrane to remove all traces of the extractant and the metal-extractant complex. The stationary chamber was also cleaned with distilled water.

2.4.5 Calculation of the experimental flux

The use of experimental data to calculate the experimental flux is now illustrated. A typical result is taken from experiment number HD11. The experimental conditions and the related information are given in Table 2.4.1.

In this experiment, 10.3209 ± 0.0001 g of 2 M D2EHPA/n-heptane concentrate was injected into the rotating cell containing 28 cm³ of n-heptane. Knowing the density of the concentrate, (measured at 25°C using a density bottle), the organic phase molarity, M_o, is simply calculated by mass balance:

\[ M_o = \frac{W_c \cdot M_c}{\rho_c \cdot V_o} \]  

(2.4.1)

where \( W_c \) = weight of the concentrate injected; (10.3209 g)
**TABLE 2.4.1**
The Experimental Conditions

RUN NUMBER: HD11

SYSTEM: D2EHPA/n-heptane/cobalt(II) sulphate

ORGANIC PHASE: 40 cm$^3$ of 0.592 M D2EHPA/n-heptane

AQUEOUS PHASE: 190 cm$^3$ of 0.04 M cobalt(II) sulphate

TITRANT: 5.0 mM sodium hydroxide

TEMPERATURE: 25.0 $\pm$ 0.1°C

pH-STAT: 4.50 $\pm$ 0.01 pH

MEMBRANE AREA, A = 1.865 cm$^2$

The initial aqueous phase metal concentration was assumed to be equal to the concentration calculated from the weighed amounts of metal sulphate used. The assumption was validated when no significant difference was found between metal added and metal determined by atomic absorption spectroscopy.

The complete results for the experiment are listed in Table 2.4.2. The rate of addition of titrant, $T$ (cm$^3$/min) for a given rotational speed is calculated by determining the slope of the corresponding trace on the pH-stat curve; a typical pH-stat curve is shown in Figure 2.4.1. The rate of liberation of H$^+$ ions, $F_H$, is related to the rate of extraction.
**TABLE 2.4.2**

Complete Results for Experiment No.: HD11

<table>
<thead>
<tr>
<th>Point Number</th>
<th>$f_1$, Hz</th>
<th>$T$, ml/min</th>
<th>$F_m$, kmol/s (10^{-11})</th>
<th>$F_m/\alpha_0 A$, kmol/m² s</th>
<th>$\dot{V}_T$, ml</th>
<th>$[H^+]_m$, mmol/dm³</th>
<th>$\gamma^2_0 A$, 10⁷ m² s³/kmol</th>
<th>$\omega_0$, Hz⁻¹</th>
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<tbody>
<tr>
<td>1</td>
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<td>6.544</td>
<td>1.51</td>
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<td>5</td>
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<td>1.151</td>
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<td>4.10</td>
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<td>9.73</td>
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<td>0.5903</td>
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Frequency

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<th>Calculated Flux, kmol/m² s</th>
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<td>8.815E-08</td>
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<tr>
<td>5.0</td>
<td>9.375E-08</td>
</tr>
</tbody>
</table>

Covariance = 1.567E + 05
Correlation Coefficient = 0.992
Slope = 1.284E + 07 m² s⁻¹/kmol
Intercept = 4.926E + 06 m² s/kmol
of $M^{2+}$, $F_M$, by the stoichiometry of the reaction, i.e. $F_H = -2x_F M'$ (for divalent metals only, see Section 1.3). The rate of release of $H^+_{(aq)}$ can be calculated from:

$$F_H = \frac{T \cdot M_{\text{NaOH}}}{60 \times 1000} \text{ kmol/s} \quad (2.4.2)$$

where $M_{\text{NaOH}}$ = molarity of the sodium hydroxide (the titrant).

Thus, the flux based on the metal is calculated from:

$$\text{Flux, } J = \frac{F_M}{a_0 A_t} \text{ kmol/m}^2\text{s} \quad (2.4.3)$$

where $a_0 = 0.68$ for the 'Millipore' filter used, see Section 2.3.2.

It is estimated that the standard mean error of a flux determination is $\pm 0.2\%$.

The quantity $V_T$ in the table refers to the amount of titrant added at the middle of the particular flux determination. It is required to calculate the average depletion of the extractant and the metal in the bulk organic and aqueous phases, respectively. Therefore, from mass balance:

$$[HR]_\infty = M_{HR,I} - \left[ \frac{M_{\text{NaOH}} \cdot V_T}{V_B} \right] \quad (2.4.4)$$

and

$$[M^{2+}]_\infty = \left[ \frac{V_\alpha}{V_\alpha + V_T} \cdot M_{M,I} \right] - \left[ \frac{M_{\text{NaOH}} \cdot V_T}{2V_\alpha} \right] \quad (2.4.5)$$

where $[HR]_\infty = \text{extractant concentration in the bulk organic phase}$

$[M^{2+}]_\infty = \text{metal concentration in the bulk aqueous phase}$

$M_{HR,I} = \text{initial molarity of the extractant, mol/dm}^3$
\[ V_a \] = the initial volume of the aqueous phase, cm\(^3\)
\[ V_b \] = the volume of the organic phase, cm\(^3\).

The value of \( (\alpha_0 A/F) \) and \( \Omega^{-2} \) is given in the table because they are the important variables concerning the transport of reactants see Section 2.2.4. Using these quantities the 'Levich Plot' can be constructed, i.e. a plot of \( (1/J) \) as the ordinate and \( \Omega^{-2} \) as the abscissa. The plot is shown in Figure 2.4.2. Linear regression analysis gives:

- the slope, \( m \) = \( 1.284 \times 10^7 \), m\(^2\)s\(^{-1}\)/kmol
- the intercept, \( c \) = \( 4.926 \times 10^6 \), m\(^2\)s/kmol
- the correlation coefficient, \( r \) = 0.992

For sixteen data points, the value of \( r \) should be \( > 0.742 \) for a 99.9% probability of a linear relationship\(^{(110)}\), thus, we have a 'good' experimental run. The linear relationship obtained was then used to calculate the fluxes at \( \Omega = 2, 3, 4 \) and 5 Hz. For further kinetic analysis the calculated flux at \( \Omega = 3 \) Hz was used.

The experimental fluxes for the various systems investigated are presented in Chapter Three.

A computer program (in FORTRAN 77) was written to calculate the experimental flux; the program, together with a typical input and the corresponding output can be found in Appendix (A).

2.5 Associated Experiments

2.5.1 The equilibrium curve of metals for D2EHPA

The pH at which to conduct the kinetic work was based on published metal distribution equilibria data for D2EHPA\(^{(32)}\). A single experiment was conducted to confirm one of the equilibria curves.
Figure 2.4.2: The 'Levich Plot' for Experiment No.: HD11

\[ \text{Slope} = 1.284 \times 10^7 \text{ mol}^{-1} \text{ms}^{-2} \text{kmol}^{-1} \]

\[ \text{Intercept} = 4.926 \times 10^6 \text{ kmol}^{-1} \text{ms}^{-2} \]

\[ \text{Correlation Coefficient} = 0.992 \]
The system considered was D2EHPA/n-heptane/copper(II) sulphate. The technique involved contacting 200 cm$^3$ of 0.6 M D2EHPA/n-heptane (the organic phase) with 200 cm$^3$ of 10 mM copper(II) sulphate (the aqueous phase), by vigorous mechanical mixing in a thermostatted glass vessel. The temperature was controlled at 25 ± 0.1°C and the pH of the dispersion was monitored by means of a combined glass electrode and a standard pH meter.

The pH was regulated by the addition of concentrated sulphuric acid and/or sodium hydroxide pellets. Following pH adjustment, the dispersion was allowed to equilibrate for five minutes; stable pH readings were achieved within 2 - 3 minutes of vigorous mixing. Samples of 5 cm$^3$ of the dispersion were taken and allowed to separate into the two phases. The aqueous phase was analysed for the metal concentration using atomic absorption spectroscopy. The organic phase concentration was assumed to be equal to the value determined by mass balance. To confirm this assumption the organic phase of one of the samples was stripped with sulphuric acid and the resulting aqueous phase (the strip liquor) was analysed for its metal content. The metal concentration found was in close agreement with the value calculated by mass balance. Consequently, the metal concentration in the organic phase was calculated by mass balance. The data are given in Section 3.8.1.

2.5.2 Measurement of interfacial tension

There are several methods available for determining the surface and interfacial tension of liquids, such as the platinum ring method, the drop-weight method, the pendant drop method, etc., see Davis and Rideal$^{(111)}$ for details. In this study it was convenient to use a platinum ring coupled with a Cambridge tensiometer, collectively known as the Du Nouy tensiometer, (Cambridge Instrument Company Limited). The mode of operation was as des-
cribed by Findlay (112). To check the accuracy of the procedure, the surface tension of double distilled water was measured. The surface tension was found to be 72.9 mN/m at 20°C, which compares well with the value of 72.75 mN/m at 20°C reported in the literature (113).

The Du Nouy tensiometer was used to measure the interfacial tension of 0.1 M D2EHPA in various diluents against double distilled water. The two phases were vigorously shaken for one minute and allowed to settle for at least 30 minutes before any measurements were made. The average of several readings was taken for each diluent. The reproducibility was found to be within + 2%. The results are presented in Section 3.8.2.

2.6 Chemical Reagents

2.6.1 Purification of D2EHPA

The commercially available D2EHPA invariably contains impurities. Such impurities may include alcohols, tri-alkyl phosphates, the mono form of the acid, polyphosphorus and metal contaminates.

The D2EHPA used in this work was obtained from British Drug House Chemical Limited (B.D.H.) and was of 96% purity (General Purpose Reagent grade), as received and determined by potentiometric method. This was confirmed by titration with standard sodium hydroxide (carbonate free), using step titration method (104).

There are several purification methods reported in the literature (114-117). A comprehensive method, involving many steps is presented by Schmitt and Blake (117). However, all of these methods have a serious draw-back: there is always a considerable loss of D2EHPA, during its purification. Sometimes as much as 50%.
In any case, a previous worker in laboratories at Bradford University has shown that the purification of D2EHPA (from B.D.H.) has not lead to markedly different kinetic results when such material was used to extract cobalt \(^{(92)}\).

The D2EHPA was purified by passing it through a 2 cm diameter chromatographic column, containing activated charcoal and basic and neutral aluminium oxide. The first 2 cm\(^3\) collected was discarded. The purified D2EHPA was then filtered using a 0.22 \(\mu\)m MF 'Millipore' filter to remove fine charcoal and aluminium oxide particles. Potentiometric titration with standard sodium hydroxide gave the acid content to be 97%.

Of course such a titration of total acid does not prove 'purity'. The method would detect the other acid impurities. One main impurity is the mono-di-2-ethylhexyl phosphoric acid, which should show two inflection points on the curve. When purified D2EHPA was titrated only one inflection point was found.

Finally, \(^{31}\)P n.m.r. spectra on this compound did not show any other phosphorus derived species. Of course, this technique will have a lower limit of detection and it is estimated that the limit of detection of any impurity applicable to the above was < 1%.

### 2.6.2 Purification of D2EHDTTPA

The sample of D2EHDTTPA was provided by Albright and Wilson Ltd. and was of 81.3% purity, as determined by potentiometric method. The impurities present can comprise sulphur, traces of alkylsulphides and the mono acids because D2EHDTTPA is usually synthesised by the direct interaction of the 2-ethylhexyl alcohol with phosphorus pentasulphide.

It was attempted to purify D2EHDTTPA in the same manner as D2EHPA but this proved to be inadequate. Consequently, the method of Levin and
co-workers (118) was adopted.

Procedure

A sample of 50 cm$^3$ of D2EHDTPA was diluted with 75 cm$^3$ of n-heptane and poured into a one litre separating funnel. To this 100 cm$^3$ of 4.5 M sodium hydroxide was slowly added and the mixture was gently shaken. The resulting emulsion was allowed to settle for 30 minutes and the aqueous phase (the bottom layer) was then rejected. The remaining organic phase was washed in succession with 100 cm$^3$ of 1 M sulphuric acid and 100 cm$^3$ of distilled water, again the aqueous phase was discarded.

The next step involved adding equal amounts (in this case 125 cm$^3$) of a mixture containing two thirds by volume of ethanol saturated with potassium hydroxide (approximately 25 g of potassium hydroxide in 200 cm$^3$ of ethanol) and one third by volume of distilled water. The resulting mixture was vigorously shaken for one minute and allowed to separate into the two phases for 30 minutes.

The potassium hydroxide reacts with the D2EHDTPA forming its potassium salt, which is soluble in the alcoholic solution, i.e. the aqueous phase. Thus, the acid has been transferred from the organic to the aqueous phase leaving the impurities in the organic phase. After discarding the organic phase the aqueous phase was washed several times with 75 cm$^3$ of n-heptane, retaining the n-heptane in the separating funnel on the last wash. To recover the D2EHDTPA the aqueous phase was acidified with 50 cm$^3$ of 2 M sulphuric acid and shaken. The acidification produces the D2EHDTPA, which transfers into the organic phase. After discarding the aqueous phase, the organic phase was washed several times in succession with 100 cm$^3$ of 0.25 M sulphuric acid and 100 cm$^3$ distilled water. Finally, the n-heptane was distilled off under vacuum (pressure of 25 mbar abs.) at 38 - 50°C to give the purified D2EHDTPA.
From potentiometric titration the purity was determined to be 96%; only a single end point was observed, indicating that no appreciable quantities of the mono ester are present. For greater purity Levin (118) recommends repeating the above procedure 2 - 3 times. However, owing to the limited amount of D2EHDTPA available to the author and a loss of approximately 10% every time the D2EHDTPA was purified, the procedure was carried out only once.

2.6.3 Other reagents

All chemicals used were of B.D.H. origin and of AnalR grade unless stated otherwise. The inorganic chemicals were used without further purification.

The metal sulphate solutions were prepared by dissolving the calculated quantities of the hydrated metal sulphate salts in double distilled water. The various metal sulphate salts used are listed in Table 2.6.1, with their hydrated structure formula and purity. Other aqueous solutions were also prepared using double distilled water.

The organic chemicals (modifiers) and the diluents used in this work are listed in Table 2.6.2 indicating their source, grade and purity (as quoted by the manufacturers). The diluents were simply passed through a column containing activated aluminium oxide and used without further purification. The modifiers were used as supplied.
### TABLE 2.6.1
The Metal Sulphate Salts Used

<table>
<thead>
<tr>
<th>Metal Sulphate</th>
<th>Formula</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt(II) sulphate</td>
<td>CoSO$_4$.7H$_2$O</td>
<td>99%</td>
</tr>
<tr>
<td>Nickel(II) sulphate</td>
<td>NiSO$_4$.7H$_2$O</td>
<td>99 - 104%</td>
</tr>
<tr>
<td>Copper(II) sulphate</td>
<td>CuSO$_4$.7H$_2$O</td>
<td>99%</td>
</tr>
<tr>
<td>Zinc(II) sulphate</td>
<td>ZnSO$_4$.7H$_2$O</td>
<td>&gt; 99.5%</td>
</tr>
</tbody>
</table>

### TABLE 2.6.2
The Organic Modifiers and Diluents Used

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
<th>Grade</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-methyl-1-butanol (isoamyl alcohol)</td>
<td>Aldrich</td>
<td>-</td>
<td>98%</td>
</tr>
<tr>
<td>Iso-decanol</td>
<td>B.D.H.</td>
<td>-</td>
<td>99.9%</td>
</tr>
<tr>
<td>2-ethylhexan-1-ol</td>
<td>B.D.H.</td>
<td>G.P.R.</td>
<td>99%</td>
</tr>
<tr>
<td>Tri-n-butylphosphate</td>
<td>B.D.H.</td>
<td>G.P.R.</td>
<td>98%</td>
</tr>
<tr>
<td>Tri-n-octylphosphine oxide</td>
<td>B.D.H.</td>
<td>G.P.R.</td>
<td>-</td>
</tr>
<tr>
<td>n-heptane</td>
<td>B.D.H.</td>
<td>AnalAr</td>
<td>99.5%</td>
</tr>
<tr>
<td>2,2,4-trimethylpentane (iso-octane)</td>
<td>B.D.H.</td>
<td>AnalAr</td>
<td>99.5%</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>B.D.H.</td>
<td>AnalAr</td>
<td>99.5%</td>
</tr>
<tr>
<td>Toluene</td>
<td>B.D.H.</td>
<td>AnalAr</td>
<td>99.5%</td>
</tr>
<tr>
<td>Octan-1-ol (n-octanol)</td>
<td>B.D.H.</td>
<td>G.P.R.</td>
<td>95%</td>
</tr>
</tbody>
</table>
CHAPTER THREE

RESULTS AND MEASUREMENTS
CHAPTER THREE

RESULTS AND MEASUREMENTS

3.1 Introduction

It was now necessary to test the modified rotating cells and the experimental technique by reproducing previous kinetic work carried out by Fisk (98) on a copper hydroxyoxime system. This last worker had also used a RDC in the original work on liquid-liquid extraction of metals studied by this technique. The comparison is described in Section 3.2.

The kinetics of extraction of various transition metals (i.e. Co(II), Ni(II), Cu(II) and Zn(II)) by D2EHPA and D2EHDTPA was then studied.

It should be noted here that in all experiments involving the RDC, the rate of extraction was studied as a function of the rotational speed (Ω, Hz). The speeds chosen were between 1.5 Hz and 5.0 Hz. For convenience, the rates corresponding to Ω = 3 Hz only were presented when comparison between various metals and any one extractant were made. This form of presentation was also chosen for subsequent modelling.

3.2 A Check on the Technique-Comparison with Fisk's Work

Fisk (98) studied the kinetics of the extraction of copper (II) by 5-nonylisalicylaldoxime (the commercial extractant 'P5000', manufactured by Acorga), held in n-heptane and toluene.

The results of the present author, which are of particular interest, are those which correspond to the measurement of flux when the 'P5000' concentration is varied; a constant stirring speed is used. Other experimental conditions are given below:
\[ \text{[Cu}^{2+}] = 10 \text{ mM} \]
\[ \text{pH} = 4.1 \]
\[ \text{temperature} = 25^\circ \text{C} \]
\[ \text{frequency} = 3 \text{ Hz} \]

'Millipore' filter pore size = 0.22 μm.

No attempt was made to cover all the conditions of the extensive work carried out by Fisk.

Initially, an attempt was made to reproduce the experiment corresponding to 'P5000' concentration of 49.1 mM. However, a discrepancy of approximately ten fold was obtained between the results; the flux obtained by the present worker was lower than Fisk's. A difference of ± 10% only is considered to be normal, since in different laboratories it is difficult to reproduce the interface identically\(^{(119)}\). In order to determine the source of error(s) several experiments were carried out, these were designed in order to consider the influence of various parameters of the RDC and the reagents. The following changes were made in experiments with the standard chemical system described above:

(a) different batches of 'Millipore' filters and 'P5000' were used;
(b) the method of preparing the membrane was varied;
(c) the height of the slots in the P.T.F.E. baffle were set at 15 mm as opposed to 25 mm;
(d) the gap between the membrane surface and the baffle's free edge was increased (the normal being 2 mm);
(e) use of double distilled water was introduced.
The use of double distilled water reduced the difference in flux slightly but the most significant reduction was attributed to the washing and subsequent drying of the prepared 'Millipore' filter. The filter is hydrophobic in nature but any moisture trapped in the pores can reduce the rate of reaction. On the basis of these observations, it was decided that in all future work double distilled water would be used and the membrane would be dried for at least eight hours in a vacuum desiccator prior to use. For short periods the membrane was stored, fully wetted, in the organic diluent (in this case n-heptane) and for longer periods it was stored in the desiccator.

Having eradicated the most likely source of discrepancy, several experiments were conducted with varying 'P5000' concentrations. These results and the results of Fisk\(^{(98)}\) are illustrated in Figure 3.2.1. The results at Bradford show consistently low fluxes compared with those of Fisk and this is of great concern. However, at Bradford a similar trend was obtained by another worker\(^{(120)}\) on this system. It was decided, after visits to Imperial College, that there was no obvious differences in technique between the two laboratories. One possibility is that the particular sample of 'P5000' used at Bradford contains some unknown impurity which is responsible for the consistently lower rate of extraction.

The greatest source of error with this technique is associated with the establishment of the interface on the membrane. The slightest carelessness leads to spurious results. The scatter obtained by Fisk, as shown in Figure 3.2.1, serves to illustrate the point. Unfortunately, there is no single test available to test the validity of a given result, only the reproduction of the results may be checked for.
\[ [\text{Cu}^{2+}] = 10 \text{ mM}; \ \text{pH} = 4.1; \ T = 25 \degree \text{C}; \ \Omega = 3 \text{ Hz} \]

**FIGURE 3.2.1:** Comparison of Fisk's Results with the Author's Work for 'P5000'
In an earlier work \cite{101}, the author has demonstrated the mastery of the technique and feels confident that the interface can be accurately 'constructed'. Incidentally, in this work the rate for extraction of copper by 'P5000' was faster than that for extraction by 'LIX64N' (commercial extractant manufactured by General Mills Inc.). This is an expected result.

3.3 Extraction of Cobalt(II) by D2EHPA

Three sets of experiments were undertaken in order to study the effect of varying the D2EHPA concentration, the aqueous pH and the cobalt (II) concentration on the rate of extraction of cobalt (II) by D2EHPA. The cumulative results are tabulated in Table 3.3.1 and the corresponding graphs are shown in Figures 3.3.1 to 3.3.3.

In these figures the influence of rotational speed on the rate of extraction is clearly illustrated; as the rotational speed increases the flux also increases. This observation can be explained using Fick's first law and the relationship between the diffusion layer thickness and the rotational speed (i.e. Equation (2.2.10)); the layer decreases with increasing speed:

\[
\text{Flux, } J_i = -D_{ij} \left[ \frac{\partial C_i}{\partial z} \right] z = 0 \tag{3.3.1}
\]

and

\[
\delta_j = 0.643 D_{ij}^{1/3} \cdot \nu^{1/6} \cdot \Omega^{1/2} \tag{2.2.10}
\]

Equation (3.3.1) can be approximated to:

\[
J_i = -D_{ij} \cdot \frac{\Delta C_i}{\delta_j} \tag{3.3.2}
\]
The Effect of [D2EHPA] on the Rate of Extraction of Cobalt.

FLUX/10-8 kmol/m²s

[Co²⁺] = 0.1 M, pH = 4.5; T = 25 °C

A = 2 Hz
B = 3 Hz
C = 4 Hz
D = 5 Hz

FIGURE 3.3.1
FIGURE 3.3.3: The Effect of pH on the Rate of Extraction of Cobalt
<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>([HR]) mol/dm(^3)</th>
<th>([Co^{2+}]) mol/dm(^3)</th>
<th>(pH)</th>
<th>Flux/10(^{-8}) kmol/m(^2)s</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDO1A</td>
<td>0.598</td>
<td>0.1</td>
<td>4.50</td>
<td>9.671</td>
</tr>
<tr>
<td>HDO2A</td>
<td>0.793</td>
<td>0.1</td>
<td>4.50</td>
<td>11.06</td>
</tr>
<tr>
<td>HDO3A</td>
<td>0.991</td>
<td>0.1</td>
<td>4.50</td>
<td>11.66</td>
</tr>
<tr>
<td>HDO4A</td>
<td>0.397</td>
<td>0.1</td>
<td>4.50</td>
<td>7.954</td>
</tr>
<tr>
<td>HDO5A</td>
<td>0.200</td>
<td>0.1</td>
<td>4.50</td>
<td>5.401</td>
</tr>
<tr>
<td>HDO6</td>
<td>0.586</td>
<td>0.1</td>
<td>4.00</td>
<td>9.376</td>
</tr>
<tr>
<td>HDO7</td>
<td>0.591</td>
<td>0.1</td>
<td>3.50</td>
<td>7.419</td>
</tr>
<tr>
<td>HDO8</td>
<td>0.594</td>
<td>0.1</td>
<td>3.00</td>
<td>4.022</td>
</tr>
<tr>
<td>HD10</td>
<td>0.597</td>
<td>0.06</td>
<td>4.50</td>
<td>9.048</td>
</tr>
<tr>
<td>HD11</td>
<td>0.592</td>
<td>0.04</td>
<td>4.50</td>
<td>8.105</td>
</tr>
<tr>
<td>HD12</td>
<td>0.589</td>
<td>0.02</td>
<td>4.50</td>
<td>6.397</td>
</tr>
<tr>
<td>HD13</td>
<td>0.589</td>
<td>0.08</td>
<td>4.50</td>
<td>9.706</td>
</tr>
<tr>
<td>HD14</td>
<td>0.592</td>
<td>0.1</td>
<td>5.50</td>
<td>9.973</td>
</tr>
<tr>
<td>HD15</td>
<td>0.594</td>
<td>0.01</td>
<td>4.50</td>
<td>5.339</td>
</tr>
<tr>
<td>HD16</td>
<td>0.595</td>
<td>0.12</td>
<td>4.50</td>
<td>9.845</td>
</tr>
</tbody>
</table>
Combining Equation (3.3.2) and (2.2.10) gives:

\[ J_1 = -\frac{1}{0.643} \frac{D_{ij}}{0.643} \frac{2/3}{v} \frac{1/6}{\Omega} \frac{1/2}{\Delta C_1} \]  

(3.3.3)

Thus, for a constant concentration driving force and assuming that the diffusivity of the metal and the viscosity of the solution remains constant, the transfer flux is proportional to the rotational speed (i.e. to the decreasing diffusional resistance), as observed in the flux plots.

i.e. \[ J_1 \propto \Omega^{1/2} (\alpha 1/\delta_j) \]  

(3.3.4)

The assumptions made above are reasonable because in this work the initial transfer rates were studied, hence, the concentration of various species can be regarded as approximately constant. In a typical experiment the extractant bulk organic concentration changes by less than 0.2% and the metal bulk aqueous concentration by less than 5%.

It should be noted that the transfer flux will approach a limiting value as \( \delta_j \to 0 \) (i.e. as \( \Omega \to \infty \)). As indicated in Section 2.2.4 this condition corresponds to:

(a) the removal of diffusional resistances in the two diffusional films;

leaving (b) any residual resistances due to chemical reaction at the interface plus any diffusional resistance in the interface (membrane ?). Such a condition is reflected by the height of the intercept on the ordinate axis of the Levich plot.
In Figure 3.3.1 it is noticed that the rate of cobalt extraction increases as the D2EHPA concentration was increased. This is as expected because the driving force has been increased. A similar, but less pronounced effect is observed in Figure 3.3.2 for varying aqueous cobalt concentration. This suggests that the rate is influenced more by the $[\text{D2EHPA}]$ than $[\text{Co}^{2+}]$. Both graphs also show that as the concentration of D2EHPA or cobalt is increased the flux approaches a limiting value.

The dependence of flux on the aqueous pH is shown in Figure 3.3.3. There is a distinct increase in flux with increasing pH up to pH 4. Thereafter the flux approaches a limiting value which is attained above the pH of 4.5. When studying the influence of pH on the rate of extraction the pH variation was restricted to pH $\geq 3.0$ because the sensitivity of the pH-stat technique is greatly reduced at lower pH values. Naturally, the upper pH limit is determined by the formation of the first metal-hydroxide precipitate; for cobalt (II) this occurs above the pH of 6.8\(^{(121)}\). However, the flux reached a limiting value well before this last pH.

The above observations imply that there is a considerable degree of diffusion control involved in the extraction mechanism. The extent of diffusional control with respect to the concentration (say of $[\text{Co}^{2+}]$) can be qualitatively deduced from a series of Levich plots on a single graph, see Figure 3.3.4. The graph shows that as the $[\text{Co}^{2+}]$ is increased the influence of rotational speed decreases (i.e. the slope of the Levich plot decreases). This implies that the degree of diffusional control is diminishing; the limiting value being a horizontal line (i.e. slope = 0). At the limiting condition the decreasing diffusion layer thickness has little influence on the transfer rate and the extraction process can be said to be chemical reaction controlled. More often than not there is diffusion and chemical control involved. In this situation the slope of the Levich plot does not decrease to zero but instead approaches a constant
FIGURE 3.3.4: The Levich Plot Showing the Effect of [Co²⁺]

\[ \text{Current} (\text{mA}) = \frac{zF}{2.303} \cdot \frac{\text{A} \cdot \text{S}}{\text{V} \cdot \text{m} \cdot \text{Kmolg}} \]
value and does not change with the increase in the concentration.

It can be seen that when the RDC is used, the Levich plot is a
convenient way of obtaining a general understanding of the mass transfer
rates in an extraction process.

From the inspection of Figures 3.3.1 to 3.3.3 the general rate of
extraction can be expressed as:

\[
\text{Rate} = \frac{\left[D2EHPA\right]^a \cdot \left[Co^{2+}\right]^b}{\left[H^+\right]^\gamma}
\]  (3.3.5)

where \(a\), \(b\) and \(\gamma\) are constants, their values will now be evaluated. The
rate \((r)\) is related to flux \((J)\) by the following relationship:

\[
\text{Rate} = \text{Flux} \times \frac{\text{Interface area (A)}}{\text{Phase volume (V)}}
\]  (3.3.6)

In the above series of experiments the interface area and the organic and
aqueous phase volumes were virtually constant, therefore, the flux is
directly proportional to the rate:

\[
\text{Flux} \propto \text{Rate} \propto \frac{\left[D2EHPA\right]^a \cdot \left[Co^{2+}\right]^b}{\left[H^+\right]^\gamma}
\]  (3.3.7)

\[
\therefore \quad J_{M^{2+}} = k \frac{\left[D2EHPA\right]^a \cdot \left[Co^{2+}\right]^b}{\left[H^+\right]^\gamma}
\]  (3.3.8)

where \(k\) is the proportionality constant.

Thus:

\[
\log(J) = \log(k) + a\log\left[D2EHPA\right] + b\log\left[Co^{2+}\right] - \gamma\log\left[H^+\right]
\]  (3.3.9)
For constant \([H^+]\) (i.e. pH) and \([Co^{2+}]\) we can simplify Equation (3.3.9) to:

\[
\log(J) = \alpha \log[D2EHPA] + (\log(k) + \beta \log[Co^{2+}] + \gamma pH) \quad (3.3.10)
\]

Therefore, a plot of \(\log(J)\) against \(\log[D2EHPA]\) should be linear.

The above approach can also be applied to the case when \([D2EHPA]\) and pH are constant (i.e. varying \([Co^{2+}]\)) or when \([D2EHPA]\) and \([Co^{2+}]\) are constant (i.e. varying pH). For initial rates, when only a limited extent of reaction has occurred concentrations can be assumed to be constant, if significant concentration of cobalt (II) and D2EHPA are initially used.

The plots are given in Figures 3.3.5 to 3.3.7. These graphs show that for varying \([D2EHPA]\) or \([Co^{2+}]\) the curve is linear within a limited range of concentrations. Applying linear regression analysis on the linear section of the curves, we can estimate the value of \(\alpha\) and \(\beta\), (i.e. \(\alpha = 0.5\) and \(\beta = 0.3\)). These values of \(\alpha\) and \(\beta\) confirm the conclusion reached earlier, that the dependence of the transfer rate is greater for D2EHPA than for cobalt (II). The curve for varying \([H^+]\) is non-linear except when higher pH is approached, therefore, the value of \(\gamma\) is not estimated.

Due to the fact that \(\alpha\), \(\beta\) and \(\gamma\) are not constant for all concentrations, no attempt was made to estimate the value of \(k\) (which can be related to the reaction rate constant). As indicated in Section 1.6.2 this general dependency on extractant, metal and proton concentrations is commonly found for the extraction of transition metals by acidic or chelating extractants.
\[ [\text{Co}^{2+}] = 0.1 \text{ M}; \quad \text{pH} = 4.5; \quad T = 25 \degree \text{C}; \quad \Omega = 3 \text{ Hz} \]

Slope \( = \alpha = 0.492 \)

**FIGURE 3.3.5:** Plot of \( \log(\text{FLUX}) \) against \( \log(\text{D2EHPA}) \)
FIGURE 3.3.6: Plot of log(FLUX) against log[Co^{2+}]

slope = \beta = 0.295

[DEHFA] = 0.6 M, pH = 4.5, T = 25 °C, \Omega = 3 Hz

log [Co^{2+}]
\[ [\text{D2EHPA}] = 0.6 \text{ M}; \quad [\text{Co}^{2+}] = 0.1 \text{ M}; \quad T = 25 \, ^\circ\text{C}; \quad \Omega = 3 \text{ Hz} \]

**Figure 3.3.7**: Plot of log(FLUX) against pH
3.4 Extraction of a Series of Transition Metals by D2EHPA

The four metals considered for the kinetic work were cobalt (II), nickel (II), copper (II) and zinc (II). Only the influence of organic phase concentration of D2EHPA was investigated, the pH being held constant at 4.5. At this pH most of the metals considered extract 100% with this extractant, see Figure 1.3.3, with the exception of nickel (II).

It must be noted that in the series of divalent metals investigated, copper (II) forms a metal hydroxide precipitate well before the other metals. From copper electrode study \(^{(122)}\) it is known that at the pH of 4.5 the maximum concentration of copper (II) ions is limited to 0.1 M, which is higher than the aqueous phase metal concentration of 0.01 M used in the present study. This implies that there is maximum concentration of metal ions 'available' for extraction.

The range of D2EHPA concentration chosen was such that a constant flux at the higher concentration of D2EHPA was reached for the most metals. This range for experimental work was:

\[
15 \text{ mM} \ < \ [\text{D2EHPA}] \ < \ 0.4 \text{ M}
\]

The other experimental conditions are listed in Table 3.4.1.

The results are tabulated in Tables 3.4.2 to 3.4.5 and graphically summarised in Figure 3.4.1. It should be realised that extensive data tabulation were required to generate the results in the tables and for the sake of brevity procedures of tabulation are not included in this thesis.

The reproducibility of the results was tested by conducting an experiment on each metal in the D2EHPA concentration range used, but several months later. In all cases the new measurements were found to agree with previous results in as far as the new single experimental point
FIGURE 3.4.1: The Extraction of Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ by D2EHPA.

- COBALT
- NICKEL
- COPPER
- ZINC

20.00 [M $^2+$] = 10 mM, pH = 4.5, T = 25 °C, $\Omega = 3$ Hz

FLUX/10^-8 Kmol/m²s
### TABLE 3.4.1

The Experimental Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>AQUEOUS PHASE:</td>
<td>10 mM of $M^{2+}$</td>
</tr>
<tr>
<td>ORGANIC PHASE:</td>
<td>$15 \text{ mM} \leq [D2EHPA] \geq 0.4 \text{ M}$</td>
</tr>
<tr>
<td>TEMPERATURE:</td>
<td>$25^\circ\text{C} \pm 0.1$</td>
</tr>
<tr>
<td>pH:</td>
<td>$4.50 \pm 0.01$</td>
</tr>
<tr>
<td>FREQUENCY:</td>
<td>$1.5 \text{ Hz} \leq \Omega \geq 5.0 \text{ Hz}$</td>
</tr>
</tbody>
</table>
### TABLE 3.4.2

Extraction of Cobalt by D2EHPA; for $\Omega = 3$ Hz

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>$[HR]$ (mol/dm$^3$)</th>
<th>$J/10^{-8}$ (kmol/m$^2$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDCO01</td>
<td>0.0997</td>
<td>1.905</td>
</tr>
<tr>
<td>HDCO02</td>
<td>0.0502</td>
<td>1.186</td>
</tr>
<tr>
<td>HDCO03</td>
<td>0.200</td>
<td>3.074</td>
</tr>
<tr>
<td>HDCO04</td>
<td>0.3972</td>
<td>4.763</td>
</tr>
<tr>
<td>HDCO05</td>
<td>0.026</td>
<td>0.6902</td>
</tr>
<tr>
<td>HDCO06</td>
<td>0.015</td>
<td>0.5192</td>
</tr>
<tr>
<td>HHDCO01</td>
<td>0.1</td>
<td>2.110</td>
</tr>
</tbody>
</table>

### TABLE 3.4.3

Extraction of Copper by D2EHPA; for $\Omega = 3$ Hz

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>$[HR]$ (mol/dm$^3$)</th>
<th>$J/10^{-8}$ (kmol/m$^2$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDCU01</td>
<td>0.0502</td>
<td>3.203</td>
</tr>
<tr>
<td>HDCU02</td>
<td>0.1012</td>
<td>4.936</td>
</tr>
<tr>
<td>HDCU03</td>
<td>0.200</td>
<td>7.670</td>
</tr>
<tr>
<td>HDCU04</td>
<td>0.0256</td>
<td>2.059</td>
</tr>
<tr>
<td>HDCU05</td>
<td>0.0147</td>
<td>1.352</td>
</tr>
<tr>
<td>HDCU06</td>
<td>0.393</td>
<td>9.007</td>
</tr>
</tbody>
</table>
### TABLE 3.4.4

Extraction of Nickel by D2EHPA; for $\Omega = 3$ Hz

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>$[H_{R}]$ $mol/dm^3$</th>
<th>$J/10^{-8}$ $kmol/m^2s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDNIO1</td>
<td>0.393</td>
<td>2.935</td>
</tr>
<tr>
<td>HDNIO2</td>
<td>0.201</td>
<td>1.719</td>
</tr>
<tr>
<td>HDNIO3</td>
<td>0.101</td>
<td>0.9674</td>
</tr>
<tr>
<td>HDNIO4</td>
<td>0.0507</td>
<td>0.4940</td>
</tr>
<tr>
<td>HDNIO5</td>
<td>0.0272</td>
<td>0.3041</td>
</tr>
<tr>
<td>HDNIO6</td>
<td>0.300</td>
<td>2.490</td>
</tr>
</tbody>
</table>

### TABLE 3.4.5

Extraction of Zinc by D2EHPA; for $\Omega = 3$ Hz

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>$[H_{R}]$ $mol/dm^3$</th>
<th>$J/10^{-8}$ $kmol/m^2s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDZNO1</td>
<td>0.101</td>
<td>12.47</td>
</tr>
<tr>
<td>HDZNO2</td>
<td>0.0505</td>
<td>7.240</td>
</tr>
<tr>
<td>HDZNO3</td>
<td>0.200</td>
<td>19.49</td>
</tr>
<tr>
<td>HDZNO4</td>
<td>0.0250</td>
<td>4.062</td>
</tr>
<tr>
<td>HDZNO6</td>
<td>0.150</td>
<td>17.00</td>
</tr>
<tr>
<td>HDZNO7</td>
<td>0.0761</td>
<td>10.64</td>
</tr>
</tbody>
</table>
fitted smoothly onto the overall curve found initially.

From Figure 3.4.1 the rate of extraction order can be established as:

\[ \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} \]

Some indication of the relative rates may be obtained if that rate for the extraction of nickel (II) by 0.1 M D2EHPA at 3 Hz is taken as unity and other rates at this extractant concentration and speed are ratioed accordingly, see Table 3.4.6.

**TABLE 3.4.6**

The Relative Rates for Co(II), Ni(II), Cu(II) and Zn(II) at \([HR] = 0.1 \text{ M and } [M^{2+}] = 10 \text{ mM, } \Omega = 3 \text{ Hz}\)

<table>
<thead>
<tr>
<th>Metal</th>
<th>(J/10^{-8} \text{ kmol/m}^2\text{s})</th>
<th>(J_{Ni^{2+}}/J_{M^{2+}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>0.9674</td>
<td>1.0</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1.905</td>
<td>2.0</td>
</tr>
<tr>
<td>Copper</td>
<td>4.936</td>
<td>5.1</td>
</tr>
<tr>
<td>Zinc</td>
<td>12.47</td>
<td>12.9</td>
</tr>
</tbody>
</table>

It is interesting to note that this order corresponds to the order obtained from reported equilibrium extraction curves. The same equilibrium order has been reported by Grimm and Kolarik\(^{123}\) for the extraction of these metals by D2EHPA in n-dodecane but from nitrate and chloride medium. These workers studied such equilibria in crude shake out experiments. Sato et al.\(^{124}\) also reports this equilibrium
order for D2EHPA and divalent metals. The significance of this order will be discussed in the concluding chapter.

3.5 Extraction of Metals by D2EHDTPA

The experimental conditions are those given in Table 3.4.1, except that D2EHDTPA was now used instead of D2EHPA. The results, for the rotational speed of $\Omega = 3$ Hz, are tabulated in Tables 3.5.1 to 3.5.4 and the corresponding plots of flux against D2EHDTPA concentration are given in Figures 3.5.1 to 3.5.4.

The order of the rate of extraction of the different metals was the same as that for D2EHPA. However, the differences in rates between these metals is not as marked as those found for D2EHPA, especially between copper and cobalt. For D2EHDTPA, up to a concentration of about 0.1 M, the rates are rather similar. In general, for D2EHDTPA concentrations greater than 0.1 M, the fluxes were approximately 15 times greater than those obtained for D2EHPA. Unlike the D2EHPA system, all the extraction 'curves' approached a limiting flux situation. There is very limited information in the literature on the extraction of divalent transition metals by D2EHDTPA, hence, comparison with published work is not possible. However, it is well known that this sulphur analogue of D2EHPA extracts metals more strongly than does D2EHPA (125), i.e. it shows a better pH functionality. Thus, the faster rates shown by D2EHDTPA fall in with the fact that the equilibrium extraction is stronger with the former extractant.

3.6 Effect of Diluents on the Rate of Cobalt (II) Extraction by D2EHPA

Five diluents were considered in all and the majority of them were representative of the main components of commercial diluents; the n-heptane represented a straight chain hydrocarbon, iso-octane a branched chain hydro-
Figure 3.5.1: The Extraction of Cobalt by D2EHPA.
Figure 3.5.2: The Extraction of Nickel by D2EHPA

\[ [\text{Ni}^{2+}] = 10 \text{ mM; pH} = 4.5; T = 25 ^\circ \text{C}; \Omega = 3 \text{ Hz} \]

FLUX/10 kmol/m²s
\[ [Cu^{2+}] = 10 \text{ mM}; \quad pH = 4.5; \quad T = 25 \degree C; \quad \Omega = 3 \text{ Hz} \]

**FIGURE 3.5.3: The Extraction of Copper by D2EHDTPA**
FIGURE 3.5.4: The Extraction of Zinc by D2EHDTPA
### TABLE 3.5.1

**Extraction of Cobalt by D2EHDTPA; for \( \Omega = 3 \text{ Hz} \)**

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>( [HR] ) mol/dm(^3)</th>
<th>( J/10^{-8} ) kmol/m(^2)s</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTCO01</td>
<td>1.101</td>
<td>20.61</td>
</tr>
<tr>
<td>HTCO02</td>
<td>0.0511</td>
<td>11.27</td>
</tr>
<tr>
<td>HTCO03</td>
<td>0.0268</td>
<td>7.473</td>
</tr>
<tr>
<td>HTCO05</td>
<td>0.399</td>
<td>30.06</td>
</tr>
<tr>
<td>HTCO06</td>
<td>0.124</td>
<td>20.95</td>
</tr>
<tr>
<td>HTCO07</td>
<td>0.103</td>
<td>21.24</td>
</tr>
<tr>
<td>HTCO08</td>
<td>0.053</td>
<td>13.70</td>
</tr>
<tr>
<td>HTCO09</td>
<td>0.202</td>
<td>30.56</td>
</tr>
</tbody>
</table>

### TABLE 3.5.2

**Extraction of Copper by D2EHDTPA; for \( \Omega = 3 \text{ Hz} \)**

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>( [HR] ) mol/dm(^3)</th>
<th>( J/10^{-8} ) kmol/m(^2)s</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTC0U01</td>
<td>0.0977</td>
<td>24.20</td>
</tr>
<tr>
<td>HTC0U02</td>
<td>0.050</td>
<td>14.96</td>
</tr>
<tr>
<td>HTC0U04</td>
<td>0.0266</td>
<td>8.411</td>
</tr>
<tr>
<td>HTC0U05</td>
<td>0.0165</td>
<td>5.090</td>
</tr>
<tr>
<td>HTC0U06</td>
<td>0.150</td>
<td>28.96</td>
</tr>
<tr>
<td>HTC0U07</td>
<td>0.0758</td>
<td>22.19</td>
</tr>
<tr>
<td>HTC0U08</td>
<td>0.299</td>
<td>32.23</td>
</tr>
</tbody>
</table>
### TABLE 3.5.3

Extraction of Nickel by D2EHDTPA; for $\Omega = 3$ Hz

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>$[I/R]_{mol/dm^3}$</th>
<th>$J/10^{-8}$ $kmol/m^2 s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTNIO1</td>
<td>0.0991</td>
<td>19.46</td>
</tr>
<tr>
<td>HTNIO2</td>
<td>0.197</td>
<td>22.64</td>
</tr>
<tr>
<td>HTNIO3</td>
<td>0.0515</td>
<td>13.12</td>
</tr>
<tr>
<td>HTNIO4</td>
<td>0.296</td>
<td>21.12</td>
</tr>
<tr>
<td>HTNIO5</td>
<td>0.0247</td>
<td>7.175</td>
</tr>
<tr>
<td>HTNIO6</td>
<td>0.148</td>
<td>18.74</td>
</tr>
</tbody>
</table>

### TABLE 3.5.4

Extraction of Zinc by D2EHDTPA; for $\Omega = 3$ Hz

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>$[I/R]_{mol/dm^3}$</th>
<th>$J/10^{-8}$ $kmol/m^2 s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTZN01</td>
<td>0.0989</td>
<td>26.19</td>
</tr>
<tr>
<td>HTZN02</td>
<td>0.051</td>
<td>14.79</td>
</tr>
<tr>
<td>HTZN03</td>
<td>0.0248</td>
<td>7.761</td>
</tr>
<tr>
<td>HTZN04</td>
<td>0.297</td>
<td>35.62</td>
</tr>
<tr>
<td>HTZN06</td>
<td>0.0732</td>
<td>21.18</td>
</tr>
<tr>
<td>HTZN07</td>
<td>0.199</td>
<td>34.59</td>
</tr>
</tbody>
</table>
carbon, cyclohexane a cyclic-hydrocarbon and toluene an aromatic
hydrocarbon. The n-octanol was chosen entirely for its low miscibility
with the aqueous phase and to introduce high polarity into the solvent
type.

The results, together with some of the physical properties of the
diluent, are tabulated in Table 3.6.1. The experimental conditions were
as given in the table. In general the extraction rates for different
diluents were slower than that observed for n-heptane (the datum point);
the extraction rate order being:

\[
\text{n-heptane} > \text{toluene} > \text{iso-octane} > \text{cyclohexane} > \text{n-octanol}
\]

This order is the same as that found for copper extraction by hydroxy-
oximes.

The main objective here was to try to correlate the metal extraction
rate with either some property of the diluent or D2EHPA in diluent.

One obvious influence of the diluent will be the way it alters the
amount of D2EHPA which partitions across the interface into the aqueous
phase. Also, the diluent will influence the degree of aggregation of
the extractant in the organic phase (for instance in polar diluents the
D2EHPA dimerises to a lesser extent than when it is held in non-polar
diluents). This will be discussed further in the concluding chapter of
this thesis.

3.7 Effect of Modifier on the Rate of Cobalt (II) Extraction by D2EHPA

Modifiers are sometimes added to D2EHPA systems in order to prevent
third phase precipitation.

Five additives were considered. Some of these chemicals are used
in industrial liquid-liquid processes as modifiers.
### TABLE 3.6.1

**Effect of Diluent on the Rate of Cobalt Extraction by D2EHPA**

Conditions: \([\text{D2EHPA}] = 0.1 \text{ M}; \ [\text{Co}^{2+}] = 10 \text{ mM}; \ \text{pH} = 4.5;\)

Temperature = 25°C; \(\Omega = 3 \text{ Hz}\)

<table>
<thead>
<tr>
<th>Diluent</th>
<th>(\frac{J}{10^{-8} \text{ kmol}/\text{m}^2\text{s}})</th>
<th>(\frac{J_{\text{diluent}}}{J_{n-\text{Heptane}}})</th>
<th>(\varepsilon) (\text{(158)})</th>
<th>Density (\rho) (\text{(kg/m}^3)</th>
<th>Dynamic Viscosity (\eta/10^{-3}) (\text{kg/m s})</th>
<th>Solubility Parameter (\delta) (\text{(128)})</th>
<th>Solubility in Water; % (\text{W}/10^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Heptane</td>
<td>2.008</td>
<td>1.00</td>
<td>1.924</td>
<td>679.46</td>
<td>0.3967</td>
<td>15.20</td>
<td>0.357</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>1.445</td>
<td>0.72</td>
<td>1.933</td>
<td>687.81</td>
<td>0.504^b</td>
<td>14.01</td>
<td>0.24</td>
</tr>
<tr>
<td>n-Octanol</td>
<td>0.934</td>
<td>0.47</td>
<td>9.86</td>
<td>821.57</td>
<td>7.363</td>
<td>21.1</td>
<td>53.8</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.059</td>
<td>0.53</td>
<td>2.015</td>
<td>773.89</td>
<td>0.898</td>
<td>16.78</td>
<td>10.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.534</td>
<td>0.76</td>
<td>2.379</td>
<td>862.19</td>
<td>0.5525</td>
<td>18.23</td>
<td>51.5</td>
</tr>
</tbody>
</table>

**NOTE:**

- a Average flux of two experiments except for toluene
- b At 20°C
- c All physical properties data are at 25°C
Most of these modifiers exhibit some degree of interfacial activity because the reagent molecule possesses both hydrophilic and hydrophobic properties. Therefore, the addition of these chemicals to the system will modify the interfacial properties; for instance they may lower the interfacial tension. Their effects will be important where commercial solvents include them as part of the solvent mixture.

The experimental results together with the experimental conditions are presented in Table 3.7.1. Whenever possible, two experiments were carried out and the average flux calculated. From the relative rates (with respect to the experiment with no additive), we can deduce that the addition of the modifier leads to a reduction of the metal extraction rate. The greatest reduction is observed with the addition of TOPO, which is known to be a very surface-active reagent (126).

3.8 Associated Experiments

3.8.1 Equilibrium extraction curve for copper (II)/D2EHPA

As mentioned in Section 2.5.1, a single experiment was conducted to obtain an equilibrium extraction curve for one of the metals considered in this work. The metal considered was copper (II). The results are plotted as % metal extracted (% E) against pH of the aqueous phase, see Figure 3.8.1. Comparison of the experimentally derived curve with a reported result from Mobil Co., U.S.A., Figure 1.3.3, shows that at pH 4.5 the extractant D2EHPA should fully extract the metal.

It should be noted that comparison of the % extraction against pH curves are useful only as an indication of the pH range over which metal extraction occurs. These curves shift with the metal and extractant concentrations and with the anion of the aqueous medium. This therefore explains why the authors result, Figure 3.8.1, does not match that reported by Mobil Co. (32).
FIGURE 3.8.1: The Percentage Extraction of Copper (II) as a Function of pH

[Graph showing % Extraction on the y-axis and pH on the x-axis, with data points at specific pH values and % extraction values.]
TABLE 3.7.1
Effect of Modifiers on the Rate of Cobalt Extraction;
Conditions: pH = 4.5; [Co$^{2+}$] = 10 mM; [D2EHPA] = 0.1 M;

$[\text{Modifier}] = 0.1 \text{ M}$; $\Omega = 3 \text{ Hz}$; Temperature = 25$^\circ\text{C}$

<table>
<thead>
<tr>
<th>MODIFIER</th>
<th>$\bar{J}/10^{-8} \text{ kmol/m}^2\text{s}$</th>
<th>$\frac{J_{\text{modifier}}}{J_{\text{n-heptane}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Datum - no additive</td>
<td>2.008</td>
<td>1.00</td>
</tr>
<tr>
<td>Iso-amyl alcohol</td>
<td>1.609</td>
<td>0.80</td>
</tr>
<tr>
<td>2-ethyl hexanol</td>
<td>1.471</td>
<td>0.73</td>
</tr>
<tr>
<td>Iso-decanol; 0.02 M</td>
<td>$1.816^2$</td>
<td>0.90</td>
</tr>
<tr>
<td>Iso-decanol; 0.1 M</td>
<td>$1.706^2$</td>
<td>0.85</td>
</tr>
<tr>
<td>Tri(n-butyl) phosphate</td>
<td>1.828</td>
<td>0.91</td>
</tr>
<tr>
<td>TOPO</td>
<td>1.230</td>
<td>0.61</td>
</tr>
</tbody>
</table>

NOTE: 1 Except for Iso-decanol
2 Single experiment
The results tabulated in Table 3.8.1 can be further analysed to derive the stoichiometry of the extraction reaction and the equilibrium extraction constant, $K_{ex}$. From the analysis presented in Section 1.3, we have the following relationship between the percentage of metal extracted and the distribution ratio ($D$):

\[
\% E = \frac{100D}{D + V/V_0} \quad (1.3.10)
\]

which gives:

\[
D = \frac{\% E \cdot V/V_0}{(100 - \% E)} \quad (3.8.1)
\]

where $V$ = the aqueous phase volume; 200 cm$^3$

$V_0$ = the organic phase volume; 200 cm$^3$.

Thus, a plot of $\log(D)$ against pH (according to Equation (1.3.9)) should give us a straight line. In Figure 3.8.2 we see that this is the case.

From the graph we have:

- Slope, $n = 2.078$ i.e. stoichiometry = 2
- and intercept, $c = -5.189$

but the intercept is also equal to:

\[
c = \log(K_{ex}) + n \cdot \log[D2EHPA] \quad (3.8.2)
\]
i.e.

\[
\log(K_{ex}) = c - n \cdot \log[D2EHPA] \quad (3.8.3)
\]

thus,

\[
K_{ex} = 1.871 \times 10^{-7}
\]

If we assume that the stoichiometry is 2 (rather than 2.078) then we can recalculate the equilibrium extraction constant as:

\[
K_{ex} = 1.80 \times 10^{-7}
\]
$[\text{D2EHPA}] = 0.6 \text{ M}$; $[\text{Cu}^{2+}] = 10 \text{ mM}$; $T = 25 \degree \text{C}$

Slope = 2.078

Intercept = -5.189

Correlation Coefficient = 0.996

FIGURE 3.8.2: Graph of log D Against pH for Cu$^{2+}$/D2EHPA/n-Heptane
TABLE 3.8.1

Result for the Equilibrium Extraction Curve;

\([\text{D2EHPA}] = 0.6 \text{ M}; [\text{CuSO}_4] = 10 \text{ mM}; \text{Temperature} = 25^\circ\text{C}\)

and Phase Ratio = 1.

<table>
<thead>
<tr>
<th>pH</th>
<th>% E</th>
<th>D = (\frac{(%E, \frac{V^-}{V_o})}{(100-% E)})</th>
<th>log D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.49</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>1.77</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>1.96</td>
<td>4.8</td>
<td>0.0504</td>
<td>-1.297</td>
</tr>
<tr>
<td>2.24</td>
<td>27.2</td>
<td>0.3736</td>
<td>-0.428</td>
</tr>
<tr>
<td>2.52</td>
<td>58.4</td>
<td>1.4038</td>
<td>0.147</td>
</tr>
<tr>
<td>2.73</td>
<td>78.4</td>
<td>3.6296</td>
<td>0.560</td>
</tr>
<tr>
<td>3.05</td>
<td>93.2</td>
<td>13.706</td>
<td>1.137</td>
</tr>
<tr>
<td>3.21</td>
<td>96.8</td>
<td>30.250</td>
<td>1.481</td>
</tr>
<tr>
<td>3.46</td>
<td>98.8</td>
<td>82.333</td>
<td>1.916</td>
</tr>
<tr>
<td>4.00</td>
<td>100.0</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>
3.8.2 Interfacial tension measurements

The interfacial tension measurements were carried out to supplement the rate results obtained for different diluents. The results are presented in Table 3.8.2.

<table>
<thead>
<tr>
<th>Diluent</th>
<th>Interfacial Tension, ( \gamma_i ) mN/m</th>
<th>Surface Tension, ( \gamma_d ) mN/m</th>
<th>Surface Pressure, ( (\gamma_d - \gamma_i) ) mN/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-heptane</td>
<td>14.1</td>
<td>50.4</td>
<td>36.3</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>7.7</td>
<td>49.3</td>
<td>41.6</td>
</tr>
<tr>
<td>n-octanol</td>
<td>1.0</td>
<td>8.6</td>
<td>7.6</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>8.0</td>
<td>50.1</td>
<td>42.1</td>
</tr>
<tr>
<td>Toluene</td>
<td>10.1</td>
<td>36.0</td>
<td>25.9</td>
</tr>
</tbody>
</table>

*Source: Whewell et al. (Reference 127).

No obvious relationship between rates and interfacial pressure is observed in Figure 3.8.3, unlike the work for copper/hydroxyoximes (127).
FIGURE 3.8.3: Plot of Initial Flux against Surface Pressure

\[ [\text{D2EHPA}] = 1 \text{ M}; \quad [\text{Co}^{2+}] = 10 \text{ mM}; \quad \text{pH} = 4.5; \quad T = 25 \degree \text{C}; \quad \Omega = 3 \text{ Hz} \]
CHAPTER FOUR

A MODEL AND A COMPUTER PROGRAM FOR THE

RATE OF METAL EXTRACTION
4.1 Introduction

In the simplest form, the process of mass transfer accompanied by a chemical reaction at a liquid-liquid interface consists of the diffusion of the reactants to the 'interface' which exists between the two phases where a reaction takes place, followed by the diffusion of the products away from the interface. The process of diffusion involves molecular diffusion and eddy diffusion in hydrodynamic layers. The site of the chemical reaction is open to much discussion but for a reaction involving ions and with a non-polar diluent, the reaction must be on the aqueous side of the interface.

The rate of extraction will be controlled by the slowest step. The process is said to be chemically controlled when the reaction is slow compared to the specific rate of diffusion, otherwise it is diffusion controlled. Often, the process of extraction takes place under the condition of mixed regime, i.e. when both chemical reaction and diffusion have to be considered. Any proposed model must be able to accommodate all possible regimes of control.

The phenomenon of simultaneous diffusion and chemical reaction in a liquid phase can be best represented by the continuum equation, thus, for jth species in kth phase:

\[ D_{jk} \nabla^2 C_j = \mathbf{U} \nabla C_j + \frac{\partial C_j}{\partial t} + r(C_j) \]

(4.1.1)

\[
\begin{bmatrix}
\text{Molecular Transport}
\end{bmatrix}
= \begin{bmatrix}
\text{Convection}
\end{bmatrix} + \begin{bmatrix}
\text{Accumulation}
\end{bmatrix} + \begin{bmatrix}
\text{Reaction Rate}
\end{bmatrix}
\]
where $D_{jk}$ = diffusivity of the $j$th reacting species in $k$th phase;

$C_j$ = concentration of the $j$th reacting species in $k$th phase;

$v^2$ = Laplacian operator;

$\nabla$ = 'nabla' or 'del';

$U$ = velocity vector;

$r(C_j)$ = reaction rate with respect to species $j$.

The continuum equation can be considerably simplified to the most commonly used three models to describe mass transfer at the interface, namely the stagnant-film model\(^{(130)}\), the penetration model\(^{(131)}\) and the turbulent-boundary layer model\(^{(132)}\).

For liquid-liquid systems it is necessary to modify the stagnant-film model, applied to gas-liquid systems, to include two stagnant-films, one on each side of the interface. The modified model is generally known as the Whitman two-film theory\(^{(133)}\).

For the two-film theory $U = 0$ and $\frac{3C_j}{3t} = 0$, thus, Equation (4.1.1) reduces to:

$$D_{jk} \frac{dC_j}{dv^2} = r(C_j)$$  \hspace{1cm} (4.1.2)

Astarita\(^{(134)}\) has solved the differential Equation (4.1.2) for a fast, diffusion controlled reaction to give:

$$N_j = \left[ \frac{2D_{jk}}{C_j^i} \right]^{\frac{1}{2}} \left[ \frac{C_j^i}{C_j^\infty} r(C_j) dC_j \right]$$  \hspace{1cm} (4.1.3)

where $N_j$ = flux of component $j$;

$C_j^\infty$ = the bulk concentration of species $j$ in the $k$th phase in which the reaction takes place;

$C_j^i$ = the interfacial concentration of species $j$. 
The Astarita 'solution' is now used in conjunction with a chemical reaction mechanism to formulate mass transfer models to describe the forward extraction of divalent metals by D2EHPA and D2EHDTTPA from sulphate medium. These models will include both diffusion terms and chemical kinetics.

Once the models were derived, a computer program incorporating an optimisation algorithm was written to optimise the various parameters in the models, using the experimental rate data reported in Chapter Three.

4.2 A Model of the Rate of Extraction of Divalent Transition Metals by D2EHPA

The model which is proposed in this section is one based on the theory developed by Rod et al.\footnote{135,136} for the extraction of metals with organic acids in liquid-liquid extraction systems. It is, in turn, based on the Whitman two-film theory and uses the solution of Astarita (i.e. Equation (4.1.3)). The model of Rod et al. was originally used to explain the extraction of copper (II) by hydroxyoximes in a fixed area transfer cell. Hughes and Rod\footnote{137} have described this model in detail and showed how it could be generally applied to liquid-liquid kinetics of extraction of metals by organic acids. Hughes and Zhu\footnote{92} have successfully modified this model to describe the rate of extraction of cobalt (II) by D2EHPA in a growing drop cell.

4.2.1 The proposed reaction mechanism

The chemical reaction mechanism for the extraction of metal ion by D2EHPA, involving complex formation is not simple and in some cases not yet fully understood, as was noted in Section 1.6. Therefore, certain assumptions must be made.
There is limited information in the literature regarding the mechanism and species involved, however, there is general agreement that the ionised species \( HR_2^- \) is involved in the reaction route. It has also been suggested in the literature\(^{(151,170,171)}\) that the neutral metal-complex product is of the form, \( MR_2.(HR)_2^* \). As D2EHPA predominantly behaves as a dimer in n-heptane, it is proposed that the dimer species is involved in the reaction path rather than the monomer. Also, species in the aqueous phase will be hydrated, e.g. \( \text{Co(H}_2\text{O)}_6^{2+} \) but the water of hydration is neglected in the following analysis for the sake of clarity.

The mass transfer situation is shown schematically in Figure 4.2.1. It is assumed that the concentration profiles are linear.

The organic extractant is transported from the bulk organic phase through the diffusion layer \( (\delta_B) \), to the inner membrane surface and then to the interface \( (i) \) on the aqueous side.

In this work, it was assumed that the membrane plays an insignificant role in the extraction process. The porosity of the treated membrane is some 69% with pore diameter of 0.22 \( \mu \text{m} \). The organic diffusion layer may be located within the membrane itself depending on the relative thickness \( \delta_B \) and \( L \).

The concentrations shown at the interface are arbitrary; high concentration may exist for surface active extractants and D2EHPA is known to be surface active\(^{(80)}\) but more so in alkali conditions. It is also assumed that the reaction takes place at the interface and/or extending out into the reaction zone, \( (\text{thickness } \delta_r) \) within the aqueous diffusion film, \( \delta_a \). It should be noted that, the possibility of the reaction zone extending into the bulk aqueous phase is not entirely neglected (i.e. true bulk aqueous phase reaction).

The extractant is slightly solubilised on the aqueous side of the interface, i.e. in the reaction zone \( (\delta_r) \) where it reacts with the divalent
metal ion. The metal ions are transported from the bulk aqueous phase through the aqueous diffusion layer into the reaction zone. The $H^+$ ions generated by the extraction reaction diffuses into the bulk aqueous phase. The metal complex so formed, $MR_2 \cdot (HR)_2$, transfers through the interface, the membrane and/or the organic diffusion layer into the bulk organic phase. By stoichiometry, the total flux of the metal is equal to half the total flux of the extractant.

In the reaction scheme given below and throughout this chapter, $C$ will represent the concentration. The superscript bar will denote the organic phase and its absence, the aqueous phase. The subscript $i$ will denote the 'interface', (here the term 'interface' is used in the broadest sense to represent the liquid-liquid phase boundary).

The extraction of divalent metal by D2EHPA (HR), may be described by the following:

1. partition of the extractant from the organic phase into the aqueous phase:

   $$\frac{P_{(HR)_2}}{(HR)_2} \rightleftharpoons \frac{(HR)_2}{(HR)_2}$$

   (4.2.1)

   with the partition coefficient,

   $$P_{(HR)_2} = \frac{C_{(HR)_2}}{C_{(HR)_2}}$$

2. the dissociation of the extractant in the aqueous phase,

   $$K_{2d} \quad (HR)_2 \rightleftharpoons HR_2^- + H^+$$

   (4.2.2)

   where $K_{2d} = \frac{C_{HR_2^-} \cdot C_{H^+}}{C_{(HR)_2}}$
(3) the intermediate complex formation,

\[
M^{2+} + HR_2 \rightleftharpoons \frac{k_R}{k'_{R}} \quad MR^+ \cdot HR
\]  
(4.2.3)

where \( \frac{k_R}{k'_{R}} = \frac{K_{MR^+ \cdot HR}}{K_{MR^+ \cdot HR}} = \frac{C_{MR^+ \cdot HR}}{C_{M^{2+}} \cdot C_{HR_2}} \)

(4) the final complex formation,

\[
MR^+ \cdot HR + HR_2 \rightleftharpoons \frac{k_{R2}}{k'_{R2}} \quad MR_2 \cdot (HR)_2
\]  
(4.2.4)

where \( \frac{k_{R2}}{k'_{R2}} = \frac{K_{MR_2 (HR)_2}}{K_{MR_2 (HR)_2}} = \frac{C_{MR_2 (HR)_2}}{C_{MR_2 (HR)_2} \cdot C_{MR_2 (HR)_2}} \)

(5) the partition of the metal complex into the organic phase,

\[
MR_2 \cdot (HR)_2 \rightleftharpoons \frac{P_{MR_2 (HR)_2}}{P_{MR_2 (HR)_2}} \quad MR_2 \cdot (HR)_2
\]  
(4.2.5)

with the partition coefficient,

\[
P_{MR_2 (HR)_2} = \frac{C_{MR_2 (HR)_2}}{C_{MR_2 (HR)_2}}
\]

Equations (4.2.1) to (4.2.5) can be combined to give the overall extraction equation:

\[
M^{2+} + 2(HR) + \frac{K_{ex}}{2} \quad MR_2 \cdot (HR)_2 + 2H^+
\]

with the equilibrium extraction constant,

\[
K_{ex} = \frac{C_{MR_2 (HR)_2} \cdot C_{H^+}^2}{C_{M^{2+}} \cdot C_{(HR)_2}^2}
\]  
(4.2.6)
4.2.2 Derivation of the rate and flux equations

In principle, all the reaction steps which represent the overall reaction mechanism, occurring in the bulk phases (homogeneous reaction) or at the liquid-liquid interface (heterogeneous reaction), can be slow enough to determine the rate of liquid-liquid extraction.

In this work, it is proposed that the rate limiting step is the addition of the first ligand, \( HR_2^- \), to the metal ion, i.e.

\[
M^{2+} + HR_2^- \rightleftharpoons MR^+ . HR
\]

(4.2.3)

where \( K_{MR^+ . HR} = \frac{k_R}{k_R'} \)

The addition of the first ligand to the metal ion as the rate determining step has been suggested for many metals\(^{52,92,72,172}\).

In the following derivation it is assumed that all other reaction steps are very fast and at equilibrium.

The rate of reaction, \( r \), according to the rate law can be represented by,

\[
-r = k_R C_{M^{2+}} C_{HR_2^-} - k_R' C_{MR^+ . HR}
\]

(4.2.7)

where \( k_R \) is the forward and \( k_R' \) is the reverse second order rate constant.

Substituting for \( k_R' \) in Equation (4.2.7) using Equation (4.2.3) gives the rate expression as:

\[
-r = \left[ k_R C_{M^{2+}} C_{HR_2^-} - \frac{k_R}{K_{MR^+ . HR}} C_{MR^+ . HR} \right]
\]

(4.2.8)

continued .......
It is virtually impossible to determine analytically the concentration of the intermediate chemical species such as \( \text{HR}_2^- \) and \( \text{M}^+ \cdot \text{HR} \), in any case, for a fast reaction, these concentrations approach zero. They can be eliminated from the rate expression by substitution using Equations (4.2.1) to (4.2.4). With further simplification the rate expression reduces to the final form:

\[
-r = k_R \cdot k_{2d} \cdot \frac{C_{M^{2+}} \cdot C_{(HR)_2}}{C_{H^+}} \left( 1 - \frac{1}{K_{ex}} \cdot \frac{C_{MR^+ \cdot HR} \cdot C_{(HR)_2}^2}{C_{M^{2+}} \cdot C_{HR_2^-}} \right) \quad (4.2.10)
\]

The flux of the extractant, \( \text{(HR)}_2 \), at the interface, \( N_{(HR)_2,1} \), can be derived by substituting the rate equation, Equation (4.2.10), into the Astarita solution, Equation (4.1.3), then integrating between the limits of the interfacial and bulk extractant concentration to give:

\[
N_{(HR)_2,1} = \left\{ \Theta_1 \cdot \frac{C_{M^{2+},1}}{C_{H^+,1}} \cdot \left[ 1 - \frac{1}{K_{ex}} \cdot \frac{C_{MR^+ \cdot HR} \cdot C_{(HR)_2} \cdot C_{H^+,1}^2}{C_{(HR)_2} \cdot C_{M^{2+},1}^2} \right] \right\}^{1/2}
\quad (4.2.11)
\]

where the group parameter \( \Theta_1 = \frac{D_{(HR)_2} \cdot k_R \cdot k_{2d}}{F_{(HR)_2}^2} (\text{m/s})^2 \) \quad (4.2.12)

In subsequent treatment the interfacial concentrations have been substituted by terms in bulk concentration and interfacial flux. At present, interfacial concentrations are not amenable to direct measurements.
4.2.3 Derivation of the aqueous and organic phase concentration equations

The concentration profiles of the reaction components (see Figure 4.2.1) in the aqueous and organic phase diffusion films can be represented by the following differential equations.

For the aqueous phase

\[
D_{H^+} \left[ \frac{dC_{M^2+}}{dz} \right] + 2D_{M^2+} \left[ \frac{dC_{M^2+}}{dz} \right] = 0 \tag{4.2.13}
\]

\[
D_{(HR)} \left[ \frac{dC_{(HR)}^2}{dz} \right] + 2D_{MR_{2}(HR)} \left[ \frac{dC_{MR_{2}(HR)}^2}{dz} \right] = 0 \tag{4.2.14}
\]

\[
D_{(HR)} \left[ \frac{dC_{(HR)}^2}{dz} \right] - 2D_{M^2+} \left[ \frac{dC_{M^2+}}{dz} \right] = -N_{(HR)} \tag{4.2.15}
\]

With the following boundary conditions:

when \( z = 0 \)

\[
C_{(HR)}^2 = C_{(HR)}^2,1
\]

\[
C_{MR_{2}(HR)}^2 = C_{MR_{2}(HR)}^2,1
\]

\[
\left[ \frac{dC_{M^2+}}{dz} \right] = 0 \quad \text{i.e. no partition} \tag{4.2.16}
\]

and when \( z = \delta_a \)

\[
C_{M^2+} = C_{M^2+},\infty
\]

\[
C_{H^+} = C_{H^+},\infty
\]

\[
\left[ \frac{dC_{(HR)}^2}{dz} \right] = 0 \quad \text{i.e. diffusion limit} \tag{4.2.17}
\]
where \( L \) = membrane thickness

\( \delta_r \) = reaction zone thickness

\( \delta_a \) = aqueous diffusion layer thickness

\( \delta_\beta \) = organic diffusion layer thickness

**FIGURE 4.2.1: Arbitrary Concentration Profile for the Model**
It can be shown that the integration of the above differential equations, with the boundary conditions given, leads to the following equations:

\[ C_{(HR)}_{2,\infty} = \frac{1}{P_{(HR)}_2} \left[ \frac{-\theta_2 \frac{C_{H^+}}{C_{M^{2+}}}}{4 \text{kex} \frac{C_{M^{2+}}}{C_{H^+}}} \right] \times \left[ \left( \frac{\theta_2 \frac{C_{H^+}}{C_{M^{2+}}} \frac{C_{H^+}}{C_{M^{2+}}}}{4 \text{kex} \frac{C_{M^{2+}}}{C_{H^+}}} \right)^2 + \frac{C_{H^+}}{\text{kex} \frac{C_{M^{2+}}}{C_{H^+}}} \right] \times \left[ \frac{C_{MR_2(HR)}_{2,1}}{\frac{C_{MR_2(HR)}_{2,1}}{2}} \right] \]  

(4.2.18)

where the grouped parameter, \( \theta_2 = \frac{D_{(HR)}_2 P_{MR_2(HR)}_2}{D_{MR_2(HR)}_2 P_{(HR)}_2} \)  

(4.2.19)

\[ C_{MR_2(HR)}_{2,\infty} = \text{kex} \frac{P_{(HR)}_2}{P_{MR_2(HR)}_2} \frac{C_{M^{2+},\infty}}{C_{H^+}} \frac{C_{(HR)}_{2,\infty}}{C_{H^+}} \]  

(4.2.20)

\[ C_{M^{2+},i} = C_{M^{2+},\infty} - \frac{N_{(HR)}_{2,i}}{2 \text{k}_{M^{2+}}} \]  

(4.2.21)

and \( C_{H^+,i} = C_{H^+,\infty} + \frac{N_{(HR)}_{2,i}}{\text{k}_{H^+}} \)  

(4.2.22)

For the organic phase:

\[ \frac{d\overline{C_{(HR)}_2}}{dz} + 2\frac{d\overline{C_{MR_2(HR)}_2}}{dz} = 0 \]  

(4.2.23)

\[ \frac{d\overline{C_{(HR)}_2}}{dz} = N_{(HR)}_{2,i} \]  

(4.2.24)
With the following boundary conditions:

\[
\text{when } z = 0 \quad c_{(HR) 2} = c_{(HR) 2,1} \\
\bar{c}_{MR_2(HR) 2} = \bar{c}_{MR_2(HR) 2,1}
\]

(4.2.25)

and when \( z = -\delta \) \( c_{(HR) 2} = c_{(HR) 2,\infty} \)

\[
\bar{c}_{MR_2(HR) 2} = \bar{c}_{MR_2(HR) 2,\infty}
\]

(4.2.26)

As for the aqueous phase, it can be shown that the solution of the above differential equations leads to the following equations:

\[
\bar{c}_{(HR) 2,1} = \bar{c}_{(HR) 2,\infty} - \frac{N_{(HR) 2,1}}{k_{(HR) 2}}
\]

(4.2.27)

\[
\bar{c}_{MR_2(HR) 2,1} = \bar{c}_{MR_2(HR) 2,\infty} + \frac{N_{(HR) 2,1}}{2k_{MR_2(HR) 2}}
\]

(4.2.28)

4.2.4 Important parameters of the model

The key parameters in the model are the film mass transfer coefficients (i.e. \( k_{H_2^+} \) and \( k_{(HR)} \)) and the grouped parameter \( \theta_1 \). The other parameters of some importance are the grouped parameter \( \theta_2 \) and the extraction constant \( K_{ex} \). All other parameters, such as the diffusion coefficients, the dimerization constant and other equilibrium constants, can be experimentally measured or obtained from the literature or estimated.

Within \( \theta_1 \), the important parameters are the second order rate constant \( (k_R) \) and the extractant partition coefficient \( (P_{(HR) 2}) \). The value of \( \theta_1 \) is
readily estimated by fitting the model to the experimental data, hence $k_R$ can be estimated, since $P_{(HR)^2}$, $K_{D}$ and $D_{(HR)^2}$ are known. Also, when $\theta_1$ is known it is possible to predict the extraction fluxes for a range of aqueous and organic concentrations. It should be noted that the other parameters within $\theta_1$ (i.e. $K_{D}$ and $D_{(HR)^2}$) are not affected by the choice of contacting technique, they are only affected by the choice of extractant and diluent.

4.3 Determination of the 'Free' Metal and 'Free' Extractant Concentration

In the bulk of the aqueous and organic phases the total amount of metal and extractant present, respectively, is not all 'available' for reaction.

In the aqueous phase the divalent metal sulphate is not completely dissociated and so the metal species exist as simple hydrated cation and ion-pair complexes. Here, the reference to the term metal sulphate and/or metal refers to the sulphate salt of cobalt (II), nickel (II), copper (II) and zinc (II). The degree of dissociation is dependent on the ionic strength and the sulphate ion concentration; increase in either or both suppresses the dissociation of the metal sulphate. In the present study the ionic strength can be assumed to be very low. Also, the pH chosen (viz. 4.5) for the kinetic work was such that the hydrolysis of the metal could be assumed to be insignificant$^{(138,139)}$.

In the case of the organic phase, the nature of the extractant is very much dependent on its chemical composition. Organic extractants containing donor atoms, exhibit interactions between molecules when in diluents of low dielectric constant and low hydrogen bonding ability (as in aliphatic diluents). These interactions between molecules lead to aggregation; this is well known in systems such as carboxylic acids$^{(140)}$, oxime solutions$^{(141,142)}$ and di-alkylphosphoric acids$^{(61)}$. In all such systems the aggregate species are in dynamic equilibrium with the monomer
species.

Whewell and Hughes\(^{(143)}\) have described three simple models of aggregation based on their work on, 'The Modelling of Equilibrium Data for Liquid-Liquid Extraction of Metals', i.e.:

(i) Dimer model
(ii) Tetramer model
(iii) Series model

Each of these models has a single parameter and each allows the estimation of the monomer concentration.

Since D2EHPA shows predominantly a dimer aggregation in n-heptane, only the dimer model will be considered here. For detailed information on the other models, the reader is referred to reference \(^{(143)}\).

4.3.1 The 'free' metal in the aqueous phase

The major species present in the aqueous phase are \(\text{M}^{2+}, \text{MSO}_4^-, \text{H}^+, \text{HSO}_4^-\) and \(\text{SO}_4^{2-}\). The other species, such as \(\text{M(}\text{SO}_4)_2\) and \(\text{M(OH)}^+\), are present in such a low concentration that they are considered to be negligible. The major species are related by the following equations:

\[
H^+_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{HSO}_4^-_{(aq)} \quad \text{(4.3.1)}
\]

where the association constant \(K_1^H = \frac{C_{\text{HSO}_4^-}}{C_{H^+} C_{\text{SO}_4^-}}\)

and

\[
\text{M}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{MSO}_4_{(aq)} \quad \text{(4.3.2)}
\]

where the association constant, \(\beta_1 = \frac{C_{\text{MSO}_4}}{C_{\text{M}^{2+}} C_{\text{SO}_4^-}}\)
Calculations using stability constants\(^{(139)}\) show that the concentration of the second complex involving the sulphate ligand (i.e. \(H_2SO_4\)) appears to be negligible. This is to be expected since a very small amount of sulphuric acid is added to the metal sulphate solution to initially adjust the pH of the aqueous phase to 4.5.

From simplified mass balances, based on:

(a) the sulphate ligand;
(b) the metal;
and (c) the hydrogen ion (proton);

we can describe the aqueous phase by the following three expressions:

\[
L = 1 + C_{\text{MSO}_4} + C_{\text{HSO}_4^-} \tag{4.3.3}
\]

\[
B = b + C_{\text{MSO}_4} \tag{4.3.4}
\]

\[
H = h + C_{\text{HSO}_4^-} \tag{4.3.5}
\]

where \(L\), \(B\), \(H\) are the total aqueous concentration of sulphate ligand, metal and the analytical proton respectively. The respective 'free' concentrations in the aqueous phase are described by the lower case letters. Although the amount of sulphate ligand present in the aqueous phase is conserved throughout the extraction process, the magnitude of \(B\) and \(H\) varies as the extraction proceeds. The above three equations are related by:

\[
L = B + 0.5 H \tag{4.3.6}
\]
For the mass transfer model described in Section 4.2, we need to know the values of \( h \) and \( b \). These can be obtained by solving Equations (4.3.3) to (4.3.6) simultaneously as follows:

Substitution of Equations (4.3.1) and (4.3.2) in Equation (4.3.3) gives:

\[
L = 1 + \beta_1 b l + K_1^H h l \quad (4.3.7)
\]

Similarly Equation (4.3.2) into Equations (4.3.4) and (4.3.1) then into Equation (4.3.5) gives:

\[
B = b + \beta_1 b l \quad (4.3.8)
\]

and \( H = h + K_1^H h l \quad (4.3.9) \)

Defining \( X_M = b/B \quad (4.3.10) \)

\[
X_H = h/H \quad (4.3.11)
\]

where \( X_M \) and \( X_H \) represents the fraction of the free metal ion and proton concentration, respectively.

By combining Equations (4.3.8) to (4.3.11) we derive the following expression for the fraction of free metal ion:

\[
X_M = \frac{K_1^H X_H}{K_1^H X_H + \beta_1 (1 - X_H)} \quad (4.3.12)
\]

Also, combining Equations (4.3.6), (4.3.8), (4.3.10) and (4.3.11) we derive another expression involving \( X_M \) and \( X_H \) together with the association constants and the analytical concentrations:
When Equation (4.3.12) is substituted into Equation (4.3.13) it leads to an expression which is cubic in $X_H$. This expression can be readily solved for $X_H$ using the Newton Raphson algorithm, when the pH (i.e. total proton concentration) and the metal concentration of the solution are known. Then $X_M$ can be calculated by substituting $X_H$ into Equation (4.3.12).

4.3.2 The 'free' extractant in the organic phase

The major species present in the organic phase are the aggregate of the extractant, the metal complex (and its polymers) and the monomer extractant. Thus, a simplified mass balance of the extractant in the organic phase gives:

\[
\begin{bmatrix}
\text{Total extractant} \\
\text{extractant}
\end{bmatrix} = \begin{bmatrix}
\text{Monomer extractant} \\
\text{metal complex}
\end{bmatrix} + \begin{bmatrix}
\text{Aggregate of the extractant}
\end{bmatrix}
\]

i.e.

\[
R = c_{HR} + 4. c_{MR_2(HR)_2} + n. c_{(HR)_n}
\]

It should be noted that in the above mass balance the charged species $HR_2^-$ and $MR^+HR$, existing at 'low concentration' in the aqueous diffusion layer, have been neglected.

Since D2EHPA primarily forms dimeric species in the organic phase, the above generalised statement (Equation (4.3.15)) can be simplified to:

\[
R = c_{HR} + 4. c_{MR_2(HR)_2} + 2. c_{(HR)_2}
\]
The equilibrium relationship between the monomeric form and the dimeric form of the extractant can be described by:

\[
K_{22} = \frac{C_{(HR)}^2}{C_{HR}}
\]  

(4.3.17)

where \( K_{22} \) = the dimerisation constant.

Thus, the monomer extractant concentration is:

\[
\overline{C}_{HR} = \left[ \frac{C_{(HR)}^2}{K_{22}} \right]^{\frac{1}{2}}
\]  

(4.3.18)

Substituting Equation (4.3.18) into Equation (4.3.16) gives:

\[
R = \left[ \frac{C_{(HR)}^2}{K_{22}} \right]^{\frac{1}{2}} + 4C_{MR_2(HR)}^2 + 2C_{(HR)}^2
\]  

(4.3.19)

Defining \( X_{HR,T} \) as the total free extractant in the organic phase, then,

\[
X_{HR,T} = \left[ \text{The total extractant} \right] - \left[ \text{The extractant complexed with the metal} \right]
\]

i.e. \( X_{HR,T} = R - 4C_{MR_2(HR)}^2 \)  

(4.3.20)

Combining Equations (4.3.19) and (4.3.20) gives:

\[
\left[ R - 4C_{MR_2(HR)}^2 \right] = X_{HR,T} = \left[ \frac{C_{(HR)}^2}{K_{22}} \right]^{\frac{1}{2}} + 2C_{(HR)}^2
\]  

(4.3.21)
Defining $X_{(HR)}^2 = \frac{C_{(HR)}^2}{R}$ \hfill (4.3.22)

where $X_{(HR)}^2$ is the fraction of the free dimeric extractant; substitution of Equation (4.3.22) into Equation (4.3.21) leads to the following expression:

$$X_{HR,T} = \left[ \frac{X_{(HR)}^2 \cdot R}{K_{22}} \right]^{\frac{1}{2}} - 2X_{(HR)}^2 \cdot R$$ \hfill (4.3.23)

$$O = 2 \cdot R \cdot X_{(HR)}^2 + \left[ \frac{X_{(HR)}^2 \cdot R}{K_{22}} \right]^{\frac{1}{2}} - X_{HR,T}$$

i.e. 

$$O = a \cdot y^2 + b \cdot y + c$$ \hfill (4.3.24)

where 

$$a = 2 \cdot R$$

$$b = \left[ \frac{R}{K_{22}} \right]^{\frac{1}{2}}$$

$$c = - X_{HR,T}$$

and 

$$y = \sqrt{X_{(HR)}^2}$$ \hfill (4.3.25)

The solution of the above 'quadratic' equation leads to the 'free' dimeric extractant concentration:

$$X_{(HR)}^2 = \left[ \frac{- \left( \frac{R}{K_{22}} \right)^{\frac{1}{2}} + \sqrt{\frac{R + 8 \cdot K_{22} \cdot R \cdot X_{HR,T}}{K_{22}}}}{4 \cdot R} \right]^2$$ \hfill (4.3.26)
Thus, knowing $R$, $X_{HR,T}$ and $K_{22}$, the amount of 'free' dimeric extractant in the organic phase can be calculated using Equations (4.3.26) and (4.3.22).

4.4 A Model of the Rate of Extraction of Divalent Transition Metals by D2EHDPDA

In Section 4.2 the model for mass transfer with chemical reaction was developed for the extraction of divalent metals by D2EHPA. In this section the model is appropriately modified so that it can be applied to the case of divalent metal extraction by the thio acid, D2EHDTPA.

4.4.1 The proposed reaction mechanism

The extraction chemistry with a thio analogue must be similar to that involving D2EHPA; the difference can be attributed to the nature of D2EHDTDA in the organic phase. The D2EHPA forms dimeric species in all but the most polar diluents, because of the strong hydrogen bonding between the $P = O$ and $P - O - H$ groups on adjacent molecules. The same phenomenon occurs to a much lesser extent with D2EHDTDA in all organic diluents, due to the D2EHDTDA weak hydrogen bonding between the $P = S$ and $P - S - H$ groups on adjacent molecules. Consequently the D2EHDTDA predominantly exists as a monomer species in the organic phase. Other workers support this last view (129).

The reaction route given below is analogous to that of D2EHPA, but for the D2EHDTDA the monomeric species (as opposed to the dimeric species for D2EHPA) is involved in the various steps of the overall extraction process. The notation used here is the same as that described in Section 4.2.1 with the exception of $HR$ which is used to represent the extractant molecule. For clarity $HL$ will represent the molecule of D2EHDTDA. Using Figure 4.2.1 (but with monomer replacing dimer) then,
(1) partition of the extractant,

\[
\begin{align*}
\text{HL} & \rightleftharpoons \text{HL}^+ \quad P_{\text{HL}} = \frac{C_{\text{HL}^-}}{C_{\text{HL}}} \\
\end{align*}
\]

(2) dissociation of the extractant,

\[
\begin{align*}
\text{HL} & \rightleftharpoons \text{L}^- + \text{H}^+ \quad K_d = \frac{C_{\text{L}^-} C_{\text{H}^+}}{C_{\text{HL}}} \\
\end{align*}
\]

(3) the intermediate complex formation,

\[
\begin{align*}
\text{M}^{2+} + \text{L}^- & \rightleftharpoons \text{ML}^+ \quad k_L = \frac{k_{L}'}{k_L'} = K_{\text{ML}^+} = \frac{C_{\text{ML}^+}}{C_{\text{M}^{2+}} C_{\text{L}^-}} \\
\end{align*}
\]

(4) the final complex formation,

\[
\begin{align*}
\text{ML}^+ + \text{L}^- & \rightleftharpoons \text{ML}_2 \quad k_{L2} = \frac{k_{L2}'}{k_{L2}'} = K_{\text{ML}_2} = \frac{C_{\text{ML}_2}}{C_{\text{ML}^+} C_{\text{L}^-}} \\
\end{align*}
\]

(5) the partition of the metal complex,

\[
\begin{align*}
\text{ML}_2 & \rightleftharpoons \text{ML}_2 \quad P_{\text{ML}_2} = \frac{C_{\text{ML}_2}}{C_{\text{ML}_2}} \\
\end{align*}
\]

Thus, the overall extraction process can be represented by:
where $K_{ex} = \frac{C_{ML2}C_{H^+}}{C_{HL}C_{M^{2+}}}$

4.4.2 Derivation of the rate, flux and concentration equations

Assuming the rate determining step is the addition of the D2EHDTPA anion, $L^-$, to the metal ion, (as for D2EHPA in Section 4.2.2, then the rate of reaction of $M^{2+}$ according to the rate law is:

$$-r = k_L C_{M^{2+}}C_L - k'_L C_{ML^+}$$

(4.4.7)

where $k_L$ and $k'_L$ are the forward and reverse second order rate constants respectively.

We can apply the modus operandi used for D2EHPA in Section 4.2.2 and 4.2.3 to derive:

(i) the interfacial flux expression for D2EHDTPA using the Astarita solution:

$$N_{HL,i} = \left[ \frac{\theta_{L1}}{C_{HL,i}} \cdot \frac{C_{ML2,i}}{C_{H^+}} \right] \times [1 - \frac{1}{K_{ex}} \cdot \frac{C_{ML2,i} \cdot C_{H^+}}{C_{HL,i} \cdot C_{M^{2+}}}] (C_{HL,i} - C_{HL,\infty})$$

where the grouped parameter $\theta_{L1} = \frac{D_{HL} k_L K_d}{p_{HL}^2}$

(4.4.8)

(ii) the concentration expression for the organic phase:

$$\overline{C_{ML2,i}} = \overline{C_{ML2,\infty}} + \frac{N_{HL,i}}{2 \overline{k_{ML2}}}$$

(4.4.9)

$$\overline{C_{HL,i}} = \overline{C_{HL,\infty}} - \frac{N_{HL,i}}{\overline{k_{HL}}}$$

(4.4.10)
and (iii) the concentration expression for the aqueous phase,

\[
C_{HL,\infty} = \frac{1}{p_{ML}} \left[ -\frac{\theta L2 \cdot C_{H^+,\infty}}{4Kex \cdot C_{M^{2+},\infty}} + \left( \frac{\theta L2 \cdot C_{H^+,\infty}}{4Kex \cdot C_{M^{2+},\infty}} \right)^2 \frac{C_{H^+,\infty}}{Kex \cdot C_{M^{2+},\infty}} \right] \times \left[ \frac{1}{C_{ML^2,1}} + \frac{\theta L2 \cdot C_{HL,1}}{2} \right]^{1/2} \tag{4.4.11}
\]

where the grouped parameter \( \theta L2 = \frac{D_{HL} \cdot p_{ML^2}}{D_{ML^2} \cdot p_{HL}} \) \tag{4.4.12}

\[
C_{ML^2,\infty} = Kex \cdot \frac{p_{HL}}{p_{ML^2}} \cdot \frac{C_{M^{2+},\infty} \cdot C_{HL,\infty}^2}{C_{H^+}} \tag{4.4.13}
\]

\[
C_{M^{2+},1} = C_{M^{2+},\infty} - \frac{N_{HL,i}}{2k_M^{2+}} \tag{4.4.14}
\]

and \( C_{H^+,1} = C_{H^+,\infty} + \frac{N_{HL,i}}{k_H^+} \) \tag{4.4.15}

The set of Equations (4.4.7) to (4.4.15) is now the overall model for the extraction of divalent metal by D2EHDTPA. The important parameters are similar to those of the D2EHPA model, see Section 4.2.4.

### 4.4.3 Determination of the 'free' metal and extractant concentration

The analysis of the aqueous and organic phase is as described in Section 4.3. The state of the aqueous phase is identical to that of the D2EHPA system, hence, the fraction of the 'free' metal ion \( (X_{M^{2+}}) \) and proton concentration \( (X_{H^+}) \) is determined using Equations (4.3.12) and (4.3.13).
The result of the analysis of the organic phase for the D2EHPA system (see Section 4.3.2), cannot be applied to the D2EHDTTPA system, because the molecules of D2EHDTTPA exist primarily as a monomeric species in the organic phase. This phenomenon simplifies the treatment of the organic phase. We do not require any extractant aggregation model to calculate the 'free' extractant; it can be assumed to be equal to the analytical amount of the uncomplexed D2EHDTTPA in the organic phase. As we are studying initial rates, the bulk concentrations can be assumed to be constant. Therefore, the fraction of the 'free' D2EHDTTPA in the organic phase is:

\[ x_{HL} = \frac{c_{HL}}{R} \]  

(4.4.16)

where

\[ R = c_{HL} + c_{ML_2} \]  

(4.4.17)

4.5 Sensitivity Analysis of the Models

Before allowing the two models to the experimental results, it is useful to know the sensitivity of the models with respect to the individual parameters. It is also useful to follow the behaviour of the model as changes are made to the concentrations of the "active" species. It is therefore proposed to test the sensitivity of the models using assumed value of the parameters and selected concentrations for the aqueous metal ion, the aqueous proton and the organic extractant.

4.5.1 The sensitivity of the D2EHPA model

The initial values chosen for the parameters and the concentrations in the D2EHPA model were:
The values of the above parameters are typical of those reported in the literature for the D2EHPA/n-heptane/cobalt (II) sulphate system. The concentrations of the various species are typical of the experimental conditions used in the present work. The dimer partition coefficient, \( P_{(HR)_{2}} \), was estimated using distribution data reported in the literature.
and the diffusion coefficient, \( D_{(HR)} \) was calculated using the Wilke-Chang\(^{(156)} \) correlation, see Section 5.2. The second order rate constant, \( k_R \), was assumed to be equal to the water replacement rate constant for cobalt (II).

Each 'variable' was varied in turn between feasible boundary values. The influence which each parameter had on the predicted flux is presented graphically in Appendix (B); for the sake of brevity, only those parameters having significant effect on the predicted flux, are reported.

The sensitivity analysis of the model indicated that:

(a) The model is very sensitive to the value of the aqueous phase film mass transfer coefficient, \( k_{M2+} \), in the range 0.1 to 1.0 \( \mu m/s \). Above 10 \( \mu m/s \) the model is insensitive to this parameter. For the organic phase film mass transfer coefficient, \( k_{(HR)} \), the predicted flux increases in the range 0.1 to 2 \( \mu m/s \). Above 10 \( \mu m/s \) the predicted flux remains constant.

(b) When the second order rate constant, \( k_R \), is increased from \( 10^3 \) to \( 10^6 \) m\(^3\)/kmol.s the predicted flux steadily increases by ten fold. When \( k_R \) is greater than \( 10^7 \) m\(^3\)/kmol.s (i.e. fast chemical reaction), the flux levels off to a maximum limiting value.

(c) As expected the flux increases as the extractant diffusion coefficient for the dimer form is increased.

(d) As the extractant dissociation constant \( K_{2d} \) is increased from \( 10^{-6} \) to \( 10^{-4} \) kmol/m\(^3\) the flux increases by a factor of three. The increase is as expected, because increasing
(d) continued ... 
the \( K_{2d} \) value leads to a greater amount of the \( HR_2^- \) species being present in the aqueous phase. Above \( 10^{-4} \) kmol/m\(^3\), the flux approaches a maximum value which corresponds to the maximum amount of the \( HR_2^- \) species in the aqueous phase.

(e) The model is extremely sensitive to the extractant partition coefficient. As the value of \( P_{(HR)_2} \) is increased the predicted flux decreases. This is to be expected since increase in \( P_{(HR)_2} \) leads to a lower concentration of the extractant in the aqueous phase.

(f) The model is sensitive to the extractant equilibrium constant. As the value of \( K_{ex} \) is increased from \( 10^{-7} \) to \( 10^{-4} \) the predicted flux also increases, thereafter the model is insensitive to the value of \( K_{ex} \).

(g) Changes in the metal sulphate formation constant, \( \beta_1 \) results in an insignificant change in the predicted flux. Also, the model is virtually insensitive to changes in \( K_H^1 \) and \( K_{22} \) value.

(h) When the physical property parameter \( \theta_2 \) was varied there was no change in the predicted flux provided \( \theta_2 \) was below 10.

The behaviour of the model with respect to the concentration of the metal ion, the extractant and the aqueous proton is as expected and as observed experimentally. The predicted flux increases with increases in either the metal or the extractant concentrations. With respect to the
aqueous proton concentration the predicted flux is constant up to the concentration of $1 \times 10^{-4}$ kmol/m$^3$ (i.e. pH of 4.0), thereafter the flux decreases with increasing concentration of the aqueous proton.

4.5.2 The sensitivity of the D2EHDTMPA model

The following initial values of the parameters and concentrations were chosen for the D2EHDTMPA model:

\[
\begin{align*}
    k_{M^{2+}, H^+} &= 50 \text{ nm/s} \\
    k_{HL, ML_2} &= 10 \text{ nm/s} \\
    k_L &= 3.3 \times 10^5 \text{ m}^3 \text{ kmol/s} \\
    D_{HL} &= 4.280 \times 10^{-10} \\
    P_{HL} &= 1560 \\
    K_d &= 1.738 \times 10^{-3} \text{ kmol/m}^3 \\
    \Theta_{L2} &= 1.0 \\
    K_{ex} &= 457.1 \\
    K_H &= 100 \text{ m}^3/\text{kmol} \\
    \beta_1 &= 229 \text{ m}^3/\text{kmol} \\
    C_{M^{2+}} &= 0.01 \text{ kmol/m}^3 \\
    C_{HL} &= 0.1 \text{ kmol/m}^3 \\
    C_{H^+} &= 3.162 \times 10^{-5} \text{ kmol/m}^3 \\
    C_{ML_2} &= 0.0 \text{ kmol/m}^3
\end{align*}
\]
As with the D2EHPA model the initial values of the parameters are typical of those reported in the literature for the D2EHDTPA/n-heptane/cobalt (II) sulphate system. The concentrations under consideration correspond to those studied in the present work. The partition coefficient, $P_{HL}$, and the diffusion coefficient, $D_{HL}$, was estimated as shown in Section 5.2. As with the sensitivity analysis of the D2EHPA model, Section 4.5.1, the second order rate constant, $k_L$, was once again assumed to be equal to the water replacement rate constant for cobalt (II).

The sensitivity of the D2EHDTPA model to changes in the parameter values, is similar to that of the D2EHPA model. Some typical results of the sensitivity analysis are presented graphically in Appendix (B).

Among the points revealed by the sensitivity analysis are:

(a) The model is very sensitive to film mass transfer coefficients ($k_{M2+}$ and $k_{HL}$), below 10 $\mu$m/s. Above 10 $\mu$m/s, the model is insensitive to these parameters.

The aqueous phase film mass transfer coefficient $k_{M2+}$ showed a greater sensitivity than the organic phase film mass transfer coefficient $k_{HL}$. In general, the flux increased with increase in $k_{M2+}$ or $k_{HL}$ value.

(b) When the second order rate constant, $k_L$, is increased from $10^3$ to $10^9$ m$^3$/kmol.s the calculated flux also increased.

(c) As anticipated the predicted flux increases as the extractant diffusion coefficient is increased.

(d) The flux increased by a factor of nine when the extractant dissociation constant $K_d$ was increased from $10^{-5}$ to $10^{-2}$ kmol/m$^3$. 
(e) The model is extremely sensitive to the extractant partition coefficient. As the value of $P_{HL}$ is increased the flux decreases. This behaviour is to be expected since increasing the $P_{HL}$ leads to a lower concentration of the extractant in the aqueous phase.

(f) Within the sensible range of $10^1$ to $10^3$ of the extractant equilibrium constant, $K_{ex}$, the predicted flux remained constant.

(g) The model was found to be slightly sensitive to the metal sulphate formation constant.

(h) The predicted flux is insensitive to the values of the parameters $K_{1}^H$ or $\theta_{L2}$.

The behaviour of the model with respect to the concentrations of the "active species" is as anticipated. Increase in either the metal ion or the Extractant concentration leads to increase in the predicted flux. With increase in the aqueous proton concentration the flux remained constant up to the value of $1 \times 10^{-4}$ kmol/m$^3$, (i.e. pH of 4.0) thereafter the flux decreased.

4.6 A Computer Program for the Optimisation of the Model's Parameters

After the model had been formulated the next step was to solve the corresponding mathematical equations (some of them non-linear in nature). In principle, the general form of the model was applied to the experimental data and by numerical methods parameter optimisation was achieved. A method of least squares was used, i.e. the minimisation
of the function $\phi$ defined by:

$$\phi = \sum_{i=1}^{n} (N_{ob} - N_{p})^2$$  \hspace{1cm} (4.6.1)  

where $n =$ number of observed data points;

$N_{ob} =$ observed quantity;

$N_{p} =$ predicted quantity.

Two methods for least-square optimisation were considered; the Gauss-Newton method\(^{(145)}\) and the Steepest-Descent method\(^{(146)}\). Other optimisation methods are given in references\(^{(147,148)}\). The Gauss-Newton method converges rapidly but the convergence is not reliable for 'poor' initial estimates of the parameters. The steepest-descent method works well for 'poor' estimates but convergence is very slow. Ideally one requires a method which takes advantage of the best features of both methods. Such an algorithm was developed by Marquardt\(^{(149)}\) and is generally known as Marquardt's method (sometimes referred to as the Levenberg-Marquardt method).

Marquardt's method performs an optimal interpolation between the two methods. The steepest-descent method is used to obtain a direction towards the 'minimum' and the Gauss-Newton method steps towards it.

The models derived in Section 4.2 and 4.4, were adapted for digital computer solution via a FORTRAN program called by the author FLUXM. The algorithm illustrating the structure of the program is shown in Figure 4.6.1 and the listing of the program, together with a description of the various 'units', in Appendix (C).

The program FLUXM uses the Marquardt's method in the form of subroutine BSOLVE, computer coded in FORTRAN IV by Ball\(^{(150)}\) to optimise the important parameters of the models, see Section 4.2.4. In the program, the BSOLVE coding was slightly modified to conform to FORTRAN 77.
SELECT THE MODEL REQUIRED THE PARAMETERS TO BE OPTIMISED AND READ RELATED DATA

CALL FMODEL TO READ EXPERIMENTAL DATA

CALL BSOLVE TO CALCULATE FLUX USING FUNCTION FJA AND THROUGH SUBROUTINE FMODEL HENCE OPTIMISE PARAMETERS

IS OPTIMISATION ACHIEVED

PRINT STATISTICAL INFORMATION

IS STATISTICAL INFORMATION REQUIRED

PRINT OPTIMISED PARAMETERS EXPERIMENTAL RESULTS AND CALCULATED FLUX

RE-RUN REQUIRED

PRINT ERROR MESSAGE

HAS AN ERROR OCCURRED

FIGURE 4.6.1: Flowdiagram of Program FLUXM
The program and the experimental data exist as files on the Bradford University mainframe computer (CYBER 180-830). The program is run interactively under the Network Operating System (NOS). The data required to run the program and the optimised results produced is described in Appendix (C).

Essentially the INPUT to the program consists of the experimental data, including the measured flux and the estimates of the parameters to be optimised. The OUTPUT from the program consists of the input data, the optimised parameters and the predicted flux. The reader is referred to Appendix (C) for detailed information on the input and output from the program.
CHAPTER FIVE

APPLICATION OF THE MODELS TO EXPERIMENTAL DATA
CHAPTER FIVE

APPLICATION OF THE MODELS TO EXPERIMENTAL DATA

5.1 Introduction

The optimisation program incorporating the two extraction models, derived in Chapter Four, is now applied to the experimental data in order to optimise the aqueous and organic film mass transfer coefficients $k_{M^{2+}}$ and $\overline{k}_{(HR)}$ (and $\overline{k}_{HL}$), respectively and the grouped kinetic parameter $\theta_1$ (and $\theta_{L1}$). Prior to optimisation it was necessary to specify values for the parameters not being optimised. The procedures for estimating or calculating some of these parameters are described in Section 5.2.

The following starting values were assumed for the three parameters to be optimised and the choice was based upon some values found in Reference (137) where a completely different metal extraction system ($Cu^{2+}$/LIX64N) had been studied.

\[
\overline{k}_{(HR)} = 10.0 \text{ \mu m/s (or } \overline{k}_{HL})
\]
\[
k_{M^{2+}} = 50.0 \text{ \mu m/s}
\]
\[
\theta_1 = 10.0 \times 10^{-12} \text{ (m/s)}^2 \text{ (or } \theta_{L1})
\]

A measure of how well the model fits the experimental data is indicated by the least square objective function $\phi$, defined in Chapter Four; the smaller the magnitude of $\phi$ the better the fit. It might be noted that the value of the least square objective function could be converted to a standard deviation provided we had a minimum of ten experimental data points per parameter to be optimised. The paucity of experimental data points in the present work dictates that such an
analysis would not be meaningful.

5.2 Specification of the Models Parameters

The parameters that need to be specified are the partition coefficients, the diffusion coefficients, the equilibrium extraction constants, $K_{ex}$, and various other 'equilibrium' constants. The method used to estimate/calculate the partition and the diffusion coefficients are described in Sections 5.2.2 and 5.2.3 respectively. The remaining parameters were obtained from the literature and some of these will be commented upon below. The values of all the specified parameters are summarised in Table 5.2.1.

The dissociation constant, $K_{2d}$, for the dimer species of D2EHPA in the water/kerosene system has been reported by Sato et al.\(^{(153)}\) to be $10^{-5}$ kmol/m\(^3\). For the dissociation of D2EHDTTPA in the same aqueous-organic system, Shibata and Nishimura\(^{(125)}\) have reported a value of $K_d$ to be $1.73 \times 10^{-3}$ kmol/m\(^3\). Since the aqueous-organic system studied by these workers is similar to the water/n-heptane system in the present work, these values of the dissociation constants will be used.

The dimerization constant, $K_{22}$, reported by Komasawa et al.\(^{(152)}\) and as listed in Table 5.2.1 is for the dimerization of D2EHPA in n-heptane.

The metal sulphate association constants, $\beta_1$, reported in Table 5.2.1 are for zero ionic strength and a temperature of 25°C\(^{(139)}\). In this present work the ionic strength of the aqueous phase can be regarded as negligible. The sulphuric acid association constant, $K_1^H$, is also for zero ionic strength and 25°C\(^{(139)}\).
### TABLE 5.2.1

Specification of the Models Unoptimised Parameters

(a) Parameters for the D2EHPA Model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimerization constant, $K_{22}$</td>
<td>$31000 \text{ m}^3/\text{kmol}$</td>
<td>(152)</td>
</tr>
<tr>
<td>Dissociation constant, $K_{2d}$</td>
<td>$10^{-5} \text{ kmol/m}^3$</td>
<td>(153)</td>
</tr>
<tr>
<td>Equilibrium extraction constant, $K_{ex}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>$4.0 \times 10^{-5}$</td>
<td>(151)</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>Not found in literature</td>
<td>-</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>$9.0 \times 10^{-4}$</td>
<td>(151)</td>
</tr>
<tr>
<td>Zinc (II)</td>
<td>0.955</td>
<td>(88)</td>
</tr>
<tr>
<td>Partition coefficient, $P(\text{HR})_2$</td>
<td>264</td>
<td>-</td>
</tr>
<tr>
<td>Diffusivity of the extractant, $D(\text{HR})_2$</td>
<td>$2.944 \times 10^{-10} \text{ m}^2/\text{s}$</td>
<td>-</td>
</tr>
<tr>
<td>Grouped physical property parameter, $\theta_2$</td>
<td>1.0</td>
<td>-</td>
</tr>
</tbody>
</table>

NOTE: The definition of the above parameters can be found in Chapter Four.
### (b) Parameter for the D2EHDTPA Model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation constant, ( K_d )</td>
<td>( 1.738 \times 10^{-3} ) ( \text{kmol/m}^3 )</td>
<td>(125)</td>
</tr>
<tr>
<td>Equilibrium extraction constant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_{ex} ) - Cobalt (II)</td>
<td>601.2</td>
<td>-</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>1380.4</td>
<td>(154)</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>( 1.995 \times 10^{12} )</td>
<td>(154)</td>
</tr>
<tr>
<td>Zinc (II)</td>
<td>177.8</td>
<td>(154)</td>
</tr>
<tr>
<td>Partition coefficient, ( P_{HL} )</td>
<td>1560</td>
<td>-</td>
</tr>
<tr>
<td>Diffusivity of D2EHDTPA, ( D_{HL} )</td>
<td>( 4.280 \times 10^{-10} ) ( \text{m}^2/\text{s} )</td>
<td>-</td>
</tr>
<tr>
<td>Grouped physical property parameter, ( \theta_{L2} )</td>
<td>1.0</td>
<td>-</td>
</tr>
</tbody>
</table>

### (c) Parameters Common to Both Models

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Association constant, ( K^H_1 )</td>
<td>100 ( \text{m}^3/\text{kmol} )</td>
<td>(139)</td>
</tr>
<tr>
<td>Metal sulphate association constant, ( \beta_1 ) - Cobalt (II)</td>
<td>229 ( \text{m}^3/\text{kmol} )</td>
<td>(139)</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>209 ( \text{m}^3/\text{kmol} )</td>
<td>(139)</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>224 ( \text{m}^3/\text{kmol} )</td>
<td>(139)</td>
</tr>
<tr>
<td>Zinc (II)</td>
<td>240 ( \text{m}^3/\text{kmol} )</td>
<td>(139)</td>
</tr>
</tbody>
</table>
It should be noted that the grouped physical property parameter \( \theta_2 \), defined by Equation (4.2.19), (or \( \theta_{L2} \) for the D2EHDTMPA system defined by Equation (4.4.12)) was assumed to be equal to 1.0 for all optimisation runs. This is a reasonable value for the parameter\(^{(137)}\) and in any case the predicted flux is insensitive to the value of the grouped physical property parameter, see Section 4.5.

5.2.1 The equilibrium extraction constants

The \( \text{M}^{2+}/\text{D2EHPA} \) systems

The equilibrium extraction constant, \( K_{ex} \), for the \( \text{M}^{2+}/\text{D2EHPA}/n\)-heptane systems, was defined in Section 4.2.1 as:

\[
K_{ex} = \frac{C_{\text{MR}_2\text{CHR}}^2 \cdot C_{\text{H}^+}^2}{C_{M^{2+}} \cdot C_{(\text{HR})^2}}
\] (4.2.6)

The \( K_{ex} \) value, as defined above, for cobalt and copper has been reported by Komasawa et al.\(^{(151)}\) to be:

\[
K_{ex}^{\text{Co}} = 4.0 \times 10^{-5}
\]

and

\[
K_{ex}^{\text{Cu}} = 9.0 \times 10^{-4}
\]

where the metal was extracted from a sulphate medium by D2EHPA in n-heptane at 25°C.

For the aqueous-organic systems studied by the author, the \( K_{ex} \) value for zinc was not found in the literature. However, Cianetti and Danesi\(^{(88)}\) reported a \( K_{ex} \) value of 0.955 for the extraction of zinc from nitrate solution by D2EHPA in n-dodecane at 25°C. Consequently, a value of 0.955 for zinc will be used.

As for zinc, a value of \( K_{ex} \) for nickel was not found in the literature.
However, in contrast to the zinc system no comparable literature values for $K_{ex}$ were found, therefore, for this system alone the $K_{ex}$ value was optimised together with the film mass transfer coefficients and the grouped kinetic parameter.

The $M^{2+}/D2EHDTPA$ systems

As for the D2EHPA systems the equilibrium extraction constants for $M^{2+}/D2EHDTPA/n$-heptane were acquired from the literature. In Section 4.4.1 $K_{ex}$ was defined as:

$$K_{ex} = \frac{C_{ML2} \cdot C_{H2}^2}{C_{M^{2+}} \cdot C_{H2}^2} \quad (4.4.6)$$

The $K_{ex}$ value, as defined by Equation (4.4.6), for nickel, copper and zinc has been reported by Levin and co-workers (154):

$$K_{ex_{Ni}} = 1380.4$$

$$K_{ex_{Cu}} = 1.995 \times 10^{12}$$

and

$$K_{ex_{Zn}} = 177.8$$

The D2EHDTPA was in octane diluent, which is comparable to the present work.

Unfortunately, a $K_{ex}$ value for cobalt extraction in either the present system or a comparable system was not found in the literature. Under these circumstances the equilibrium extraction constant was estimated using the following procedure.

Using Equation (4.4.1) to (4.4.6), in Section 4.4.1, it can be shown that the equilibrium extraction constant is related to the other 'equilibrium' constants of the system by the following expression:
where $\beta_2$ = the overall stability constant for the 1:2 metal complex;

$K_d$ = dissociation constant, Equation (4.4.2);

$P_{ML2}$ = partition coefficient of the metal complex, Equation (4.4.5);

$P_{HL}$ = partition coefficient of D2EHDTPA, Equation (4.4.1).

In Equation (5.2.1), the following variables are known:

$K_d = 1.738 \times 10^{-3} \text{ kmol/m}^3$;

and $P_{HL} = 1560$, estimated in Section 5.2.2.

Therefore, the unknown variables are $\beta_2$, $P_{ML2}$ and $Kex$. To calculate $Kex$ we need a value for $\beta_2$ and $P_{ML2}$. Shibata and Nishimura (125) have reported an overall stability constant, $\beta_2$, for $M^{2+}$/D2EHDTPA/kerosene systems. These values in conjunction with the $Kex$ value of nickel and zinc, mentioned earlier, can be used to estimate $P_{ML2}$, using Equation (5.2.1):

i.e. $P_{ML2} = \frac{Kex \cdot P_{HL}^2}{\beta_2 \cdot K_d^2}$  

(5.2.2)

Thus, for the Ni$^{2+}$/D2EHDTPA system, where

$Kex = 1380.4$

and $\beta_2 = 10^{5.24} \text{ (m}^3/\text{kmol})^2$ - from Reference (125)

$\therefore P_{ML2} = \frac{1380.4 \times (1560)^2}{10^{5.24} \times (1.738 \times 10^{-3})^2}$

$= 6.400 \times 10^9$
Similarly, for the Zn$^{2+}$/D2EHDTPA system, where

\[ K_{\text{ex}} = 177.8 \]

and

\[ \beta_2 = 10^{4.89} \text{ (m}^3/\text{kmol})^2 \text{ - from Reference (125)} \]

\[ \therefore \quad P_{ML2} = 1.845 \times 10^9 \]

Therefore, the average value of \( P_{ML2} = 4.122 \times 10^9 \). It should be noted that the \( K_{\text{ex}} \) value of copper was not used to calculate a third value of \( P_{ML2} \), because copper has an unusually high \( K_{\text{ex}} \) value.

The average calculated value of the metal-complex partition coefficient can now be inserted into Equation (5.2.1), together with the other variables, to calculate the equilibrium extraction constant for cobalt:

\[ K_{\text{ex}} = \frac{\beta_2 \cdot K_d^2 \cdot P_{ML2}}{P_{HL}^2} \]

where \( \beta_2 = 10^{5.07} \) (for cobalt from Reference (125)).

\[ \therefore \quad K_{\text{ex}}^{\text{Co}} = \frac{10^{5.07} \times (1.738 \times 10^{-3})^2 \times 4.122 \times 10^9}{(1560)^2} \]

\[ = 601.2 \]

5.2.2 The partition coefficients

The Partition Coefficient of D2EHPA

The partition coefficient of the dimer species of D2EHPA, \( P(\text{HR})_2' \), can be estimated using the monomer species partition coefficient, \( P_{\text{HR}}' \), and the distribution coefficient of D2EHPA, \( D \). These coefficients are
defined as follows:

\[ P_{HR} = \frac{C_{HR}}{C_{HR}^2} \]  (4.2.1)

\[ P_{HR} = \frac{C_{HR}}{C_{HR}^2} \]  (5.2.3)

and

\[ D = \frac{\text{total concentration of D2EHPA in the organic phase}}{\text{total concentration of D2EHPA in the aqueous phase}} \]

\[ = \frac{C_{HR,T}}{C_{HR,T}} \]  (5.2.4)

where \( C \) is the organic phase concentration; mol/dm\(^3\);

and \( C \) is the aqueous phase concentration; mol/dm\(^3\).

In the aqueous and organic phase, the total amount of the extractant will consist of the monomer and the dimer species of D2EHPA. Therefore,

\[ C_{HR,T} = C_{HR} + 2C_{(HR)_2} \]  (5.2.5)

and

\[ \overline{C}_{HR,T} = \overline{C}_{HR} + 2\overline{C}_{(HR)_2} \]  (5.2.6)

In the organic phase the monomer species is related to the dimer species by the following reversible reaction:

\[ \begin{align*}
2 (HR) & \rightleftharpoons (HR)_2 \\
& \quad \quad \frac{K_{22}}{2}
\end{align*} \]  (4.3.17)

where \( K_{22} = \frac{\overline{C}_{(HR)_2}}{\overline{C}_{HR}^2} \), the dimerization constant.

Substitution of Equation (5.2.5) into Equation (5.2.4) gives:

\[ \frac{\overline{C}_{HR,T}}{D} = \frac{C_{HR}}{2} + \overline{C}_{(HR)_2} \]
In Equation (5.2.7) we can eliminate $C_{HR}$ using the monomer partition coefficient, Equation (5.2.3). Thus,

$$
C_{HR} = \frac{1}{2} \left[ \frac{C_{HR,T}}{D} - \frac{C_{HR}}{P_{HR}} \right] \tag{5.2.8}
$$

The concentration of the monomer species in the organic phase, in the above equation, can be replaced by the dimer species concentration using the dimerization constant $K_{22}$, to give an expression for the concentration of the dimer species of D2EHPA in the aqueous phase:

$$
C_{HR} = \frac{1}{2} \left[ \frac{C_{HR,T}}{D} - \left( \frac{C_{HR}}{K_{22}} \right) \frac{1}{P_{HR}} \right] \tag{5.2.9}
$$

In Section 4.3.2 two equations were derived, Equation (4.3.22) and (4.3.26), which together allowed the concentration of the dimer species in the organic phase to be calculated. Combining these two equations and simplifying, gives the following relationship:

$$
\overline{C}_{HR} = \left[ \frac{-\left(\frac{1}{K_{22}}\right)^2 + \left(\frac{1}{K_{22}} + 8 \overline{C}_{HR,T}\right)^2}{4} \right]^2 \tag{5.2.10}
$$

Hence, the substitution of Equation (5.2.9) and (5.2.10) into Equation (4.2.1) gives an expression for the partition coefficient of the dimer species of D2EHPA:

$$
P_{HR} = \frac{\overline{C}_{HR}}{C_{HR}} = \left[ \frac{-\left(\frac{1}{K_{22}}\right)^2 + \left(\frac{1}{K_{22}} + 8 \overline{C}_{HR,T}\right)^2}{4} \right]^2 \tag{5.2.11}
$$
Therefore, $P(HR)_2$ is now expressed in terms which are either capable of measurement or can be estimated from other workers' results.

The distribution coefficient of D2EHPA, (required for the estimation of $P(HR)_2$) at an aqueous pH of 4.5, was estimated from the distribution data reported by Ul'yanov and Sviridova (155) for D2EHPA between octane and 0.1 M NaClO₄ solution. The distribution coefficient is estimated to be 266.1, corresponding to a D2EHPA concentration of 0.3 M.

When the following values,

$$K_{22} = 3.1 \times 10^4 \text{ m}^3/\text{kmol}$$
$$C_{HR,T} = 0.3 \text{ M}$$
$$D = 266.1$$

and
$$P_{HR} = 3160$$

are substituted into Equation (5.2.11), the dimer species partition coefficient of D2EHPA is calculated to be:

$$P(HR)_2 = 264.3$$

The partition coefficient of D2EHDTPA

The partition coefficient of D2EHDTPA, $P_{HL}$, was estimated from the data reported by Levin and co-workers (118). Their results are reproduced in Figure 5.2.1, from which the partition coefficient is estimated to be 1560 at an aqueous pH of 4.5. Although this value is for octane diluent, it is not expected to be significantly different for n-heptane.
FIGURE 5.2.1: Effect of pH on the Partition Coefficient of D2EHDTPA; 25°C
5.2.3 The diffusion coefficients

The diffusivity of D2EHPA and D2EHDTPA in the aqueous phase can be calculated using the Wilke-Chang correlation \(^{156}\), Equation (5.2.12). The author notes that this correlation applies only to dilute solutions, which is the case in the present work.

\[
D_{jk} = 7.4 \times 10^{-9} \left[ \frac{(\phi_K \cdot M_K)^{0.5} \cdot T}{\mu_K \cdot V_j^{0.6}} \right]
\]  

\(5.2.12\)

where \(D_{jk}\) is the diffusivity of the \(j\)th species in the \(k\)th solvent; \(m^2/s\)

\(\phi_K\) = the association parameter of the solvent

\(M_K\) = the molecular weight of the solvent

\(T\) = the absolute temperature; K

\(\mu_K\) = the viscosity of the solvent; kg/m.s

\(V_j\) = the molar volume of the \(j\)th species; cm\(^3\)/mol.

The molar volume of the dimer form of D2EHPA and D2EHDTPA has been calculated to be 856.8 and 459.3 cm\(^3\)/mol, respectively, using the additive-volume increments of Le Bas \(^{157}\).

The properties of the aqueous phase are assumed to be those of purified water, hence, we have the following values:

\(\phi = 2.6;\)

\(M = 18;\)

\(T = 298 K;\)

and \(\mu = 8.91 \times 10^{-4} \text{ kg/m.s} \) \(^{158}\).

Substitution of the above values into Equation (5.2.12) and calculating, gives the following value of the diffusivities of the dimer form of D2EHPA, \(D_{(HR)}\)\(^2\), and D2EHDTPA, \(D_{HL}\), in the aqueous phase:
D_{(HR)} = 2.944 \times 10^{-10} \text{ m}^2/\text{s}

and

D_{HL} = 4.280 \times 10^{-10} \text{ m}^2/\text{s}

5.3 The Cobalt (II) D2EHPA/n-Heptane System

The main body of results were concerned with the Co^{2+}/D2EHPA/n-
heptane system. A measurement of the flux against the following variables
had been made:

(i) D2EHPA concentration;
(ii) cobalt (II) concentration;
and (iii) aqueous phase pH.

The experimental approach was to vary one variable, whilst keeping others
constant, see Chapter Three. The D2EHPA model was first applied to the
three individual sets of experimental data and then to the collective
data.

5.3.1 Varying D2EHPA concentration

The result of fitting the D2EHPA model to the experimental data
is shown in Figure 5.3.1. The values of the optimised parameters were
as follows:

\bar{k}_{(HR)} = 13.94 \ \mu \text{m/s}

k_{M2+} = 64.09 \ \mu \text{m/s}

G_{1} = 3.403 \times 10^{-12} \ (\text{m/s})^2

\phi = 3.461 \times 10^{-16}

where \phi is the least square objective function.
$[\text{Co}^{2+}] = 0.1 \text{ M}$; $\text{pH} = 4.5$; $T = 25 \degree \text{C}$; $\Omega = 3 \text{ Hz}$

**FIGURE 5.3.1**: Fit of the D2EHPA Model to Varying [D2EHPA] Data
5.3.2 Varying cobalt (II) concentration

Again the three important parameters were optimised but using the experimental data for varying cobalt concentration. The result of optimisation is shown in Figure 5.3.2 and the values of the optimised parameter were:

\[
\begin{align*}
\overline{k_{(HR)}^2} &= 14.37 \, \mu \text{m/s} \\
k_{M^{2+}} &= 67.92 \, \mu \text{m/s} \\
\Theta_1 &= 4.288 \times 10^{-12} \, (\text{m/s})^2 \\
\phi &= 0.9427 \times 10^{-16}
\end{align*}
\]

5.3.3 Varying the aqueous phase pH

The data obtained by varying the aqueous phase pH was not successfully fitted by the model although convergence was achieved. This is clearly seen in Figure 5.3.3. However, the optimised values of the parameters were reasonable, insofar as they were similar to the values obtained for varying D2EHPA and cobalt (II) concentration. The optimised parameter values were:

\[
\begin{align*}
\overline{k_{(HR)}^2} &= 12.29 \, \mu \text{m/s} \\
k_{M^{2+}} &= 58.77 \, \mu \text{m/s} \\
\Theta_1 &= 4.689 \times 10^{-12} \, (\text{m/s})^2 \\
\phi &= 19.98 \times 10^{-16}
\end{align*}
\]

It is interesting to note that when one of the experimental data points was neglected (i.e. for pH = 3.0) from the optimisation the degree of fit improved dramatically. The optimised parameters were similar to the previous case but with a much smaller value of \(\phi\):
FIGURE 5.3.2: Fit of the D2EHPA Model to Varying [Co^{2+}] Data
Figure 5.3.3: Fit of the D2EHPA Model to Varying pH data.
The above result is as expected, because, as noted in Section 3.3, the pH-stat technique used to measure the flux is not very sensitive at low aqueous phase pH values (pH < 3). Consequently, the experimental data measured at pH 3 is excluded from the collective data.

5.3.4 Optimisation with all the cobalt (II)/D2EHPA/n-heptane experimental data

After fitting the D2EHPA model individually to the three sets of experimental data the next step was to fit the model to the collective cobalt data.

As several experimental variables are involved the results of parameter optimisation can be best illustrated by plotting the predicted flux against the measured flux, as shown in Figure (5.3.4). The closer the points are to the line of slope 1, the better the fit of the model. The plot shows that the model fits the experimental data well, as is also indicated by the $\bar{\phi}$ value. The optimised parameter values were:

\[
\begin{align*}
\bar{k}_{(HR)2} &= 14.50 \, \mu m/s \\
k_{M^{2+}} &= 64.28 \, \mu m/s \\
\theta_1 &= 4.762 \times 10^{-12} \, (m/s)^2 \\
\bar{\phi} &= 8.576 \times 10^{-16}
\end{align*}
\]
FIGURE 5.3.4: Comparison of Calculated and Measured Flux for Cobalt (II) Extraction Data
5.4 The Cobalt, Nickel, Copper, Zinc/D2EHPA/n-Heptane Systems

The D2EHPA model was then applied individually to the cobalt (II), nickel (II), copper (II) and zinc (II) data. Initially the three important parameters were optimised. The fit of the model to the experimental data is presented in Figure 5.4.1 and the optimised parameter values are summarised in Table 5.4.1.

When fitting the model to the experimental data corresponding to nickel (II)/D2EHPA system, four parameters were optimised; the fourth parameter being the equilibrium extraction constant. The optimised value was:

$$K_{\text{ex}} \text{Ni} = 8.207 \times 10^{-6}$$

The optimised values of the film mass transfer coefficients, $k_{M^{2+}}$ and $k_{(HR)2}$ for each metal are similar. This is to be expected since the hydrodynamic conditions are virtually identical in all the experiments. The only difference between the metals is the second order rate constant. This is clearly reflected in the optimised value of the grouped kinetic parameter $\theta_1$, in which the other constants ($P_{(HR)2}$, $K_{2d}$ and $D_{(HR)2}$) are expected to be the same for each system; the constants being reflected in the properties of the extractant and not the metal. Therefore, it was decided to refit the D2EHPA model to the experimental data assuming the values of $k_{M^{2+}}$ and $k_{(HR)2}$ to be the same as those obtained for the collective cobalt data and optimising $\theta_1$ only. The result of such an optimisation is shown in Figure 5.4.2 and the optimised $\theta_1$ value together with the least square objective function in Table 5.4.2. The fit of the model to the experimental data under these circumstances is reasonable. The values of the optimised parameters will be discussed further in Chapter Six.
TABLE 5.4.1
A Summary of the Optimised Values of the Aqueous and Organic Film Mass Transfer Coefficients and the Grouped Kinetic Parameter for the Co, Ni, Cu and Zn/D2EHPA/n-Heptane Systems

<table>
<thead>
<tr>
<th>Metal</th>
<th>$k_{M^{2+}}$ $\mu$m/s</th>
<th>$\bar{k}_{(HR)}$ $\mu$m/s</th>
<th>$\Theta_1/10^{-12}$ (m/s)$^2$</th>
<th>Least Square Objective Function $\phi/10^{-16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt (II)</td>
<td>71.16</td>
<td>15.62</td>
<td>4.425</td>
<td>0.0425</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>70.61</td>
<td>14.96</td>
<td>0.2758</td>
<td>0.1072</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>58.37</td>
<td>15.87</td>
<td>10.38</td>
<td>3.021</td>
</tr>
<tr>
<td>Zinc (II)</td>
<td>69.46</td>
<td>12.27</td>
<td>104.5</td>
<td>0.7427</td>
</tr>
</tbody>
</table>

TABLE 5.4.2
A Summary of the Final Optimised Values of the Kinetic Parameter $\Theta_1$, with $k_{M^{2+}} = 64.28$ and $\bar{k}_{(HR)} = 14.50$ $\mu$m/s Kept Constant for the Co, Ni, Cu and Zn/D2EHPA/n-Heptane Systems

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Theta_1/10^{-12}$ (m/s)$^2$</th>
<th>Least Square Objective Function $\phi/10^{-16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt (II)</td>
<td>3.996</td>
<td>0.3680</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>0.5598</td>
<td>0.1785</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>5.124</td>
<td>3.281</td>
</tr>
<tr>
<td>Zinc (II)</td>
<td>102.9</td>
<td>1.534</td>
</tr>
</tbody>
</table>
5.5 The Cobalt, Nickel, Copper, Zinc/D2EHDTTPA/n-Heptane Systems

The D2EHDTTPA model was now applied individually to the experimental data for the extraction of cobalt (II), nickel (II), copper (II) and zinc (II) by D2EHDTTPA. As with the D2EHPA system the aqueous and organic film mass transfer coefficients and the grouped kinetic parameter $\theta_{LL}$ were optimised. Figures 5.5.1 to 5.5.4 show the fit of the model to the experimental data and the optimised values of the parameters are tabulated in Table 5.5.1.

The optimised values of the aqueous film mass transfer coefficients were similar to those obtained for the D2EHPA system. However, the organic film mass transfer coefficients were approximately half the magnitude of those found for the D2EHPA systems. The value of the least square objective function for cobalt and nickel was high because of scatter in the experimental data and not due to any difficulties encountered during optimisation. The optimised parameters will be discussed further in Chapter Six.
Figure 5.5.1: Fit of the D2EHDTPA Model to the Cobalt Data.
\[ [\text{Ni}^{2+}] = 10 \text{ mM}; \quad \text{pH} = 4.5; \quad T = 25 \degree \text{C}; \quad \Omega = 3 \text{ Hz} \]

**Figure 5.5.2:** Fit of the D2EHDTPA Model to the Nickel Data
$[Cu^{2+}] = 1.0 \text{ mM}$, pH = 4.5, $T = 25^\circ C$, $\Omega = 3$ Hz

**Figure 5.5.3:** Fit of the D2EHPA Model to the Copper Data
FIGURE 5.5.4: Fit of the D2EHDTPA to the Zinc Data
TABLE 5.5.1
A Summary of the Optimised Values of the Aqueous and Organic Film Mass Transfer Coefficients and the Grouped Kinetic Parameter for the Co, Ni, Cu and Zn/D2EHDTPA/n-Heptane Systems

<table>
<thead>
<tr>
<th>Metal</th>
<th>Parameter</th>
<th>Least Square Objective Function</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{M2+}$</td>
<td>$k_{HL}$</td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>64.90</td>
<td>5.498</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>43.77</td>
<td>7.468</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>67.40</td>
<td>7.921</td>
</tr>
<tr>
<td>Zinc (II)</td>
<td>76.25</td>
<td>6.813</td>
</tr>
</tbody>
</table>
CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK
CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 The Rotating Diffusion Cell (RDC)

Previous contacting techniques, such as the Lewis cell (or its derivatives), the rising and falling drop technique, the growing drop cell etc., have introduced hydrodynamic uncertainties into the analysis of the experimental data. In other techniques such as the A.K.U.F.V.E. the interfacial area is indeterminate. The RDC technique on the other hand has many advantages including the ability to control the interfacial area in addition to which the hydrodynamics are well defined and understood. This technique has been used for both, metal extraction and other mass transfer studies, such as precutaneous absorption of drugs (159). Much of the recent work has been reviewed by Hanna and Nobel (160) and the use of the technique is likely to grow in the future.

6.2 The Membrane

There are still some questions to be answered about the role of the membrane in the overall extraction process. Several of these important questions will be dealt with in turn. In this work, it is assumed that the membrane merely serves as a support to the interface and does not interfere with the extraction process.

The membrane either offers resistance to transfer, due to porosity and tortuosity of the pores, or it plays no part other than to act as a physical support. On this last point some workers believe that the interface is outside the pore body and develops as liquid is drawn down through the pores and spun out by centrifugal action to give a layer covering of the mouths of pores.
The 'Millipore' membrane, used in the present work, has a pore size of 0.22 μm. In Chapter Two, a Scanning Electron Micrograph (S.E.M.) of a typical 'Millipore' filter, of 0.8 μm pore size, was shown in Plate 2.3.2. The very open surface structure of the membrane shown, is very similar to the 'Millipore' membrane, with a measured porosity of 69%, used in this study. The pore size of 0.22 μm is much greater than any molecular dimension of any species in the problem under investigation. However, it is possible that the eddies generated near an interface might be interfered within the pore itself. A typical eddy might be of 16 μm dimension, this is larger than the present pore size. Therefore, such eddies are expected to be dampened out by the presence of the pores. Eddies will be important if Marangoni effects are present and such effects would certainly manifest themselves, in the present D2EHPA and D2EHDTPA systems, but only at high pH e.g. > 6 pH units. Marangoni effects were not seen in the present work where the pH was 4.5.

Ageing of the membrane was not observed, for consistent results were obtained when experiments were carried out with a given membrane which had been previously used several months before.

6.3 The Extraction of Cobalt (II) by D2EHPA

6.3.1 The effect of diluent on the flux

The fastest rates are found for cobalt extraction by D2EHPA when the most non-polar diluent is used. This is also true for other extraction systems, e.g. extraction of copper by hydroxyoximes. Certainly, the standing concentration of D2EHPA in the aqueous film is predicted to be highest when the value of the partition coefficient, P(HR)₂, is lowest and like other extractants the P(HR)₂ is the lowest in the most non-polar solvents. The kinetic model used in this work, see Section 4.2, already predicts that lower P(HR)₂ values increase the rate of extraction, all
other things being equal, see sensitivity analysis, Section 4.5.1.

Independent work by Hareda and Miyake\textsuperscript{(161)}, on the extraction of copper by hydroxyoximes also suggests that the value of the partition coefficients has an important role in dictating the rate.

6.3.2 The effect of modifiers on the flux

The modifiers, explored in this work, all lowered the rate of extraction when added to a n-heptane/D2EHPA phase. They all are more polar than n-heptane and so the same arguments as above might be applied. Of course, more detailed data on the values of the partition coefficients under these conditions would be required to be certain of the argument.

6.4 The Modelling of the Experimental Data

The two models derived in Chapter Four were based on the Whitman two-film theory. The use of this theory is justified because efficient bulk mixing occurs in the cell used by the author. Both models have within them terms for diffusion and chemical reaction. The D2EHPA model is based on the dimer species of D2EHPA and the D2EHDTPA model uses the monomer species in the organic phase. This assumption is based on previously well established work which has identified such species as the predominant ones.

The importance of diffusion in the process is indicated by the film mass transfer coefficients and the importance of chemical reaction by the grouped kinetic parameter $\theta_1$ for the D2EHPA model and $\theta_{LL}$ for the D2EHDTPA model.

Thus, the modelling has accommodated mass transfer with chemical reaction, recognising the importance of the two controlling influences; the models allow identification of the two extreme situations of control by either mass transfer or the chemical reaction as well as allowing for mixed control.
6.4.1 The fit of the models to the experimental data

An illustration of how well the models fit the experimental data is shown in Figure 6.4.1 for the D2EHPA model and in Figure 6.4.2 for the D2EHDTTPA model. As was mentioned in Section 5.1, statistical analysis of the limited data is meaningless, however, the + 10% error bands on the flux comparison graphs give an indication of the fit of the models. The degree of fit is considered to be satisfactory.

6.4.2 The influence of pH on flux

There is one case for concern in that the model did not fit the extraction of cobalt by D2EHPA when the aqueous phase pH was varied, see Figure 5.2.3, Section 5.2, (the variation of flux with pH was only studied for the cobalt system). However, a sensitivity analysis of the D2EHPA model indicates that the predicted flux for varying aqueous phase pH (equivalent to hydrogen ion concentration) does follow a similar curve to the experimental curve. For details of the sensitivity analysis, refer to Section 4.5 and Appendix (C).

The precise reasoning behind this observation is not clear, however, it is postulated that the mass transfer coefficient for the hydrogen ion does play a part. This mass transfer coefficient was assumed to be the same as that for the cobalt metal ion but the present results indicate its potential importance.

One interesting feature of Figure 5.2.3 is the shape of the experimental curve. It is similar to that observed for equilibria in the cobalt (II) sulphate/D2EHPA system when per cent extraction is plotted against pH. This similarity is shown again in Figure 6.4.3 where the conditions of the equilibria curve are attached to the diagram. This last graph was taken from work in the laboratory at Bradford University(162). The equilibria curve does not lie exactly on the flux points but then the
FIGURE 6.4.1: Comparison of Calculated and Measured Flux for the D2EHPA Model
FIGURE 6.4.3: Influence of pH on the Kinetic Flux and Equilibrium
chemical conditions were slightly different, e.g. the flux experiments did not include isodecanol as a modifier and the cobalt was at a higher concentration (0.1 M).

The above observation suggests that there may be a relationship between initial rate of extraction and equilibrium position. The $K_{ex}$ or the $pH_{50}$ value (the pH at which 50% metal extraction takes place and read from equilibrium curves, as in Figure 1.3.3), may be regarded as a measure of the thermodynamic equilibrium position and metals giving higher $K_{ex}$ or lower $pH_{50}$ values are seen to form the strongest complexes with extractants ligands. It is of interest to explore the measured data to see if the fastest rate of extraction corresponds to the strongest complex forming situations.

For cobalt, the proposed relationship between the kinetics and the equilibrium is substantiated when flux is plotted against pH, as in Figure 6.4.3. The plot indicates that as the pH increases the percentage of metal extracted increases which also gives rise to an increased mass transfer driving force and this, in turn, leads to an increased metal transfer flux.

This observation may be further tested by its application to the extraction of a series of metals by D2EHPA (at a single pH of 4.5). In this instance the driving force for extraction may be taken as the difference between the operating pH of 4.5 and the $pH_{50}$ value for a particular metal, as read from Figure 1.3.3,

\[
\text{Flux} = f (pH - pH_{50})
\]

As seen from Figure 6.4.4, there is a relationship but more data are needed on other metals before a strict mathematical form of the link can be expressed. Indeed, the flux for a metal with $pH_{50} = 4.5$ will not
\[ [\text{D2EHPA}] = 0.2 \text{ M}; \quad [\text{M}^{2+}] = 10 \text{ mM}; \quad \text{pH} = 4.5; \quad T = 25 \, ^\circ\text{C} \]

![Graph showing the relationship between FLUX/10^-8 (Kmol/m^2 s) and (pH - pH) for Cobalt, Nickel, Copper, and Zinc.](image)

**FIGURE 6.4.4:** Plot of Initial Flux against (pH - pH)
be zero so it is uncertain where the curve or straight line would intercept the ordinate.

6.4.3 The second order rate constants found from the models

A test of the two models is to use them to predict the forward second order chemical rate constants $k_R$ and $k_L$. These are estimated using the group kinetic parameter $\theta_1$ and $\theta_{LL}$, for the D2EHPA and D2EHDTTPA systems, respectively, where the values of the aqueous phase diffusion coefficients ($D_{HR}$ and $D_{HL}$), the dissociation constants, ($K_{2d}$ and $K_d$) and the partition coefficients ($P_{HR}$ and $P_{HL}$) of the two extractants are known.

The $M^{2+}/$D2EHPA/n-heptane systems

In Section 4.2.2 the grouped kinetic parameter $\theta_1$ was defined as:

$$\theta_1 = \frac{k_R D_{HR} K_{2d}}{P_{HR}^2}$$  \hspace{1cm} (4.2.12)

.....

$$k_R = \frac{\theta_1 P_{HR}}{D_{HR} K_{2d}}$$  \hspace{1cm} (6.4.1)

The following values can be inserted into Equation (6.4.1) in order to calculate $k_R$:

$$P_{HR} = 264;$$

$$D_{HR} = 2.944 \times 10^{-10} \text{ m}^2/\text{s};$$

and

$$K_{2d} = 10^{-5} \text{ kmol/m}^3.$$
The values of $\theta_1$ used in the calculation of $k_{R'}$ were those corresponding to the case when only $\theta_1$ was optimised, that is when $k_{M^{2+}} = 64.28 \text{ \mu m}$ and $R_{(HR)} = 14.50 \text{ \mu m}$, for all metals, see Section 5.4.

The partition coefficient of the dimer species of D2EHPA was estimated using the monomer species partition coefficient and the distribution coefficient of D2EHPA, for details refer to Section 5.2.2. The diffusivity of the dimer species of D2EHPA in the aqueous phase was calculated using the Wilke-Chang\(^{(156)}\) correlation; the calculation is presented in Section 5.2.3.

The predicted values of $k_{R'}$ for the metals studied are summarised in Table 6.4.1. The values of Table 6.4.1 are compared with literature results in Table 6.4.3.

### TABLE 6.4.1

The Predicted Values of the Second Order Rate Constant, $k_{R'}$ for Extraction with D2EHPA

<table>
<thead>
<tr>
<th>Metal</th>
<th>$k_{R'}$ from $\theta_1$, $\text{m}^3/(\text{kmol.s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>$9.460 \times 10^7$</td>
</tr>
<tr>
<td>Nickel</td>
<td>$1.325 \times 10^7$</td>
</tr>
<tr>
<td>Copper</td>
<td>$1.213 \times 10^8$</td>
</tr>
<tr>
<td>Zinc</td>
<td>$2.436 \times 10^9$</td>
</tr>
</tbody>
</table>

The $M^{2+}$/D2EHDTTPA/n-heptane systems

The group kinetic parameter $\theta_L$ for the D2EHDTTPA systems, was defined in Section 4.4.2 as:
The following values can be substituted into Equation (6.4.2) in order to calculate $k_L$:

$$P_{HL} = 1560;$$

$$D_{HL} = 4.280 \times 10^{-10} \text{ m}^2/\text{s}$$

and

$$K_d = 1.738 \times 10^{-3} \text{ kmol/m}^3$$

These values were specified in Section 5.2.

Thus, $k_L$ can be predicted for different metals using the optimised value of $\theta_{L1}$ obtained, for the metals studied, in Section 5.5. The rate constants calculated are tabulated in Table 6.4.2.

**TABLE 6.4.2**

<table>
<thead>
<tr>
<th>Metal</th>
<th>$k_L$ from $\theta_{L1}$ m$^3$/kmol.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>$3.158 \times 10^9$</td>
</tr>
<tr>
<td>Nickel</td>
<td>$2.690 \times 10^9$</td>
</tr>
<tr>
<td>Copper</td>
<td>$3.821 \times 10^9$</td>
</tr>
<tr>
<td>Zinc</td>
<td>$1.073 \times 10^{10}$</td>
</tr>
</tbody>
</table>
The values of Table 6.4.2 are compared with literature values in Table 6.4.3.

The values of $k_R$ and $k_L$ reported here are of the correct order for a fast ligand replacement reaction in bulk phases. Danesi et al. (166) using the same test, on the extraction kinetics of Pu (NO$_3$)$_4$ with tri-laurylammonium nitrate (TLAHNO$_3$) and TcO$_4^-$ with alkylammonium nitrate, found values as low as $10^4$ and $10^3$ m$^3$/kmol.s). They point to their results as being too low, since the representative rates of bulk aqueous phase ion exchange or addition reaction, should be $10^8$ to $10^9$ m$^3$/kmol.s). Such rate constants can be even higher depending upon the species involved and the solvent used, thus, for H$^+$ + OH$^-$, the second order rate constant is found as $1.3 \times 10^{11}$ m$^3$/kmol.s) (167). It should be noted here that the diffusion limit second order rate constant is $10^9$ m$^3$/kmol.s) (168).

Freiser's (164) observations support the values of $k_R$ and $k_L$ found here. He worked on the extraction of Zn$^{2+}$ and Ni$^{2+}$ by 8-mercaptoquinoline and 2-methyl-8-mercaptoquinoline, finding values of second order rate constants as $3.4 \times 10^9$ and $1.1 \times 10^9$ m$^3$/kmol.s for zinc and $7.2 \times 10^6$ and $4.8 \times 10^6$ m$^3$/kmol.s) for nickel, respectively.

Further confidence can be placed on the present models, since, the rate constants are in an expected order, that is:

$$Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$$

Such an order is often found, for example, in the formation of complexes such as dithiozone 1:1 metal chelates. Freiser (164) reported the following order:

$$Zn^{2+} > Co^{2+} > Ni^{2+}$$

Therefore, the calculation of $k_R$ and $k_L$ is a sensitive test of the models.
### TABLE 6.4.3

#### Second Order Rate Constants

<table>
<thead>
<tr>
<th>System</th>
<th>2nd Order Rate Constant; m³/(kmol.s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A - Water replacement rates</strong></td>
<td></td>
<td>(163)</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>3.3 x 10⁵</td>
<td></td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>5.5 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>6.6 x 10⁸</td>
<td></td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>6.6 x 10⁷</td>
<td></td>
</tr>
<tr>
<td><strong>B - Ligand substitution reaction</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) Involving dithizone</td>
<td></td>
<td>(164)</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>&gt; 10⁷</td>
<td></td>
</tr>
<tr>
<td>Co²⁺</td>
<td>6.7 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>1.3 x 10³</td>
<td></td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>6.1 x 10⁶</td>
<td></td>
</tr>
<tr>
<td>(ii) Involving 8-mercaptoquinoline</td>
<td></td>
<td>(164)</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>7.2 x 10⁶</td>
<td></td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>3.4 x 10⁹</td>
<td></td>
</tr>
<tr>
<td>(iii) Involving 2-methyl-8-mercaptoquinoline</td>
<td></td>
<td>(164)</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>4.8 x 10⁶</td>
<td></td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>1.1 x 10⁹</td>
<td></td>
</tr>
<tr>
<td>(iv) Involving 1, 10-phenanthroline</td>
<td></td>
<td>(165)</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>1.2 x 10⁵</td>
<td></td>
</tr>
<tr>
<td>Co²⁺</td>
<td>1.2 x 10⁵</td>
<td></td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>1.5 x 10³</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>2 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>9.5 x 10⁵</td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>5 x 10⁶</td>
<td></td>
</tr>
<tr>
<td>Ag⁺</td>
<td>5 x 10⁶</td>
<td></td>
</tr>
</tbody>
</table>
6.4.4 An investigation of the rate controlling mechanism

At this point, the main feature of the models, that is mass transfer with chemical reaction is reinforced when the relative contribution of the diffusion and chemical reaction are estimated.

Hughes and Rod (137) have shown that for a given liquid-liquid extraction system, the aqueous and organic diffusion limits can be calculated for a set of measured flux data. For the present systems, where the extractant concentration in the organic phase is varying, the diffusion limits in the two films are defined as follows:

The $M^{2+}$/D2EHPA systems

\[
\text{Aqueous limit, } L_{aq} = 2k_{M^{2+}}C_{M^{2+}} \quad (6.4.3)
\]

and

\[
\text{Organic limit, } L_{org} = \overline{k(\text{HR})_2} \overline{C(\text{HR})_2} \quad (6.4.4)
\]

where

\[
k_{M^{2+}} = 64.28 \text{ pm/s}
\]

\[
\overline{k(\text{HR})_2} = 14.50 \text{ pm/s}
\]

and

\[
C_{M^{2+}} = 0.01 \text{ M.}
\]

The $M^{2+}$/D2EHDTPA systems

\[
\text{Aqueous limit, } L_{L,aq} = 2k_{M^{2+}}C_{M^{2+}} \quad (6.4.5)
\]

and

\[
\text{Organic limit, } L_{L,org} = \overline{k_{HL}} \overline{C_{HL}} \quad (6.4.6)
\]

where

\[
k_{M^{2+}} = 63.08 \text{ um/s}
\]

\[
\overline{k_{HL}} = 6.925 \text{ um/s}
\]

and

\[
C_{M^{2+}} = 0.01 \text{ M.}
\]
In Figures 6.4.5 and 6.4.6 for D2EHPA and D2EHDTTPA, respectively, the calculated diffusion limits in the two films are shown by curve (A). These curves represent the limit of flux when an instantaneous chemical reaction takes place, i.e. the maximum fluxes obtainable under complete diffusion control in either phase.

The experimental fluxes for a given set of conditions (listed in Table 3.4.1, but $\Omega = 3$ Hz), when all things are constant except the metal selected, are also shown in Figures 6.4.5 and 6.4.6. Obviously, the effect of the chemical reaction is to lower the flux, but this lowering is not very significant, that is the models are predicting a reaction which is mainly controlled by diffusion. It is of interest to note that in the case of D2EHPA the chemical influence on the flux is greater than that observed for D2EHDTTPA.

In both figures, it seems that the chemical reaction has increasing effect, lowering the overall flux in an order:

$$\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$$

Once again the order is as expected, since Freiser\textsuperscript{(164)} found such an order for the rate of formation of 1:1 dithizone complexes in bulk aqueous phases. Indeed, Cianetti and Danesi\textsuperscript{(88)} studied the extraction of cobalt, nickel and zinc in the system D2EHPA/n-dodecane - KNO\textsubscript{3}, water and found the same order, suggesting that at the interface a slow diffusion controlled formation of an outer sphere complex is rate controlling. However, these last workers report pseudo chemical kinetics without flux measurements, since, in their experiments, the interfacial area is not known. Consequently, the mathematical analysis employed by these last workers is quite different from that reported in the present work.
FIGURE 6.4.5: The Calculated Diffusion Limits for D2EHPA
6.4.5 The film mass transfer coefficients found from the models

Each mass transfer coefficient relates to the contacting equipment used and the conditions, such as the rotational speed. In the present work one would not expect the aqueous film mass transfer coefficients to change with metals, since, the hydrodynamic conditions are the same and it is reasonable to assume that the diffusion coefficients of the first row transition metals studied will be the same. The organic film mass transfer coefficients for a given extractant are also expected to be the same. Any difference between extractants will be due to different diffusivity and physical properties of the extractants. According to Tables 5.4.1 and 5.5.1, the film mass transfer coefficients show the expected trend.

Previously, Hughes and Rod(137) had reported mass transfer coefficients for the RDC used on the extraction of Cu$^{2+}$ by 'P5000', see Table 6.4.4. The present results give mass transfer coefficient values of the same order.

<table>
<thead>
<tr>
<th>System</th>
<th>$k_{aq}$ μm/s</th>
<th>$k_{org}$ μm/s</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$ + 'P5000'</td>
<td>21.8</td>
<td>10.4</td>
<td>(137)</td>
</tr>
<tr>
<td>M$^{2+}$ + D2EHPA</td>
<td>64.28</td>
<td>14.50</td>
<td>Present Work</td>
</tr>
<tr>
<td>M$^{2+}$ + D2EHDTTPA</td>
<td>63.08</td>
<td>6.925</td>
<td>Present Work</td>
</tr>
</tbody>
</table>

TABLE 6.4.4

Mass Transfer Coefficients for the RDC
6.4.6 The site of the chemical reaction

Some comment is now necessary on the site of the extraction reaction. The models used here have a feature which accommodates a reaction in a film on the aqueous side of the interface; this film may have variable thickness and in one limit it is a true surface involving a layer of molecular dimension. Because ionic species are involved in the reaction, it is unlikely for the reaction site to be in the organic phase (dielectric constant of n-heptane is 1.924 whilst for water it is 78.39\textsuperscript{158}).

It is now of interest to estimate the thickness of the reaction zone in the present problem. The theoretical treatment developed by Hughes and Rod\textsuperscript{137} can be used here.

Considering the D2EHPA system, then from mass transfer equations, the interfacial transfer flux of D2EHPA, \( N(HR)_{2,i} \), can be described by:

\[
N(HR)_{2,i} = \frac{k(HR)}{} \left[ C_{(HR)}_{2,\infty} - C_{(HR)}_{2,i} \right] \quad (6.4.7)
\]

see Figure 6.4.7.

Also, from Fick's law,

\[
N(HR)_{2,i} = -D(HR) \left[ \frac{d C_{(HR)}_{2}}{dx} \right]_{x=0} \quad (6.4.8)
\]

\[
= -\frac{D(HR)}{P(HR)} \cdot \frac{C_{(HR)}_{2,i}}{\lambda'} \quad \text{for a linear concentration profile} \quad (6.4.9)
\]

Elimination of the interfacial concentration of the extractant from Equation (6.4.7) and (6.4.9), via substitution, leads to the following expression for \( \lambda' \):

\[
i.e. \quad \lambda' = \frac{D(HR)}{P(HR)} \left[ \frac{C_{(HR)}_{2,\infty}}{N(HR)_{2,i}} - \frac{1}{k(HR)} \right] \quad (6.4.10)
\]
where $C_{(HR)2,\infty} = \text{free dimeric concentration of the extractant in the bulk organic}$

$C_{(HR)2,\infty} = \text{free dimeric concentration of the extractant in the bulk aqueous}$

$C_{(HR)2,i} = \text{organic interfacial concentration of the extractant}$

$C_{(HR)2,i} = \text{aqueous interfacial concentration of the extractant}$

$= C_{(HR)2,i}/P_{(HR)2} \quad \text{assumed}$

$\delta = \text{diffusion layer thickness}$

$\delta_r = \text{reaction zone thickness}$

FIGURE 6.4.7: The Interfacial Region
Hughes and Rod (137) estimated the reaction zone thickness as $\delta r = 3\lambda'$, therefore:

$$
\delta r = 3\lambda' = 3 \frac{D_{(HR)}}{P_{(HR)}} \left[ \frac{C_{(HR)}_{2,\infty}}{N_{(HR)}_{2,i}} - \frac{1}{k_{(HR)_2}} \right] \tag{6.4.11}
$$

Within Equation (6.4.11), $C_{(HR)}_{2,\infty}$, the free dimeric species of the extractant in the bulk phase, is calculated according to Equations (4.3.22) and (4.3.26), (see Section 4.3.2), and the flux based on the extractant can be related to the flux based on the metal via the stoichiometry, i.e. $N_{(HR)}_{2,i} = -2N_{M^{2+},i}$. Thus, the final form of Equation (6.4.11) is:

$$
\delta r = 3 \frac{D_{(HR)}}{P_{(HR)}} \left[ \frac{C_{(HR)}_{2,\infty}}{2\cdot N_{M^{2+},i}} - \frac{1}{k_{(HR)_2}} \right] \tag{6.4.12}
$$

A similar expression can be derived for the D2EHPA system:

$$
\delta r_{HL} = 3 \frac{D_{HL}}{P_{HL}} \left[ \frac{C_{HL}}{2\cdot N_{H^{2+},i}} - \frac{1}{k_{HL}} \right] \tag{6.4.13}
$$

For the purpose of calculating $\delta r$ and $\delta r_{HL}$ an extractant concentration of 0.1 M has been chosen. The organic film mass transfer coefficient required for the calculation is assumed to be the same for all four metals, hence, for the D2EHPA systems $k_{(HR)_2} = 14.50 \mu m/s$ and for the D2EHDTPA systems an average value of $k_{HL} = 6.925 \mu m/s$. The results for both systems, together with the other parameters required for the calculation, have been summarised in Table 6.4.5.
The Calculated Thickness of the Reaction Zone

(a) The $M^{2+}$/D2EHPA Systems

Extractant concentration = 0.1 M

\[ \bar{C}_{(HR)_2,\infty} = 0.04937 \text{ M} \]

\[ P_{(HR)_2} = 264 \]

\[ D_{(HR)_2} = 2.944 \times 10^{-10} \text{ m}^2/\text{s} \]

\[ \overline{K}_{(HR)_2} = 14.50 \text{ \mu m/s} \]

<table>
<thead>
<tr>
<th>Metal</th>
<th>$N_{M2+}, i/10^{-8}$, kmol/m² s</th>
<th>$\delta r$, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>2.110</td>
<td>3.56</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.9674</td>
<td>8.02</td>
</tr>
<tr>
<td>Copper</td>
<td>4.936</td>
<td>1.39</td>
</tr>
<tr>
<td>Zinc</td>
<td>12.47</td>
<td>0.42</td>
</tr>
</tbody>
</table>
(b) The $\text{M}^{2+}/\text{D2EHDTPA}$ Systems

$$C_{\text{HL},\infty} = 0.1 \text{ M}$$

$$P_{\text{HL}} = 1560$$

$$D_{\text{HL}} = 4.280 \times 10^{-10} \text{ m}^2/\text{s}$$

$$K_{\text{HL}} = 6.925 \mu\text{m}/\text{s}$$

<table>
<thead>
<tr>
<th>Metal</th>
<th>$N_{\text{M}^{2+},i}/10^{-8}$</th>
<th>$\delta r_{\text{HL}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>21.24</td>
<td>0.075</td>
</tr>
<tr>
<td>Nickel</td>
<td>19.46</td>
<td>0.093</td>
</tr>
<tr>
<td>Copper</td>
<td>24.20</td>
<td>0.051</td>
</tr>
<tr>
<td>Zinc</td>
<td>26.19</td>
<td>0.038</td>
</tr>
</tbody>
</table>

It is apparent that the reaction involving D2EHDTPA is 'nearer' to the molecular dimension interface than that involving D2EHPA; this is expected because the partition coefficient for the former chemical is about six times higher than for D2EHPA.

Also, with both reagents the metals show decreasing fluxes (rates), in the order:

$$\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$$
This fact also fits in with the order of increasing reaction zone thickness. Slower rates imply that the extractant penetrates the aqueous phase to a larger extent, before being consumed in the reaction with the metal.

The thickness of the aqueous diffusion layer in the rotating diffusion cell can be calculated from the Levich equation, (see Section 2.2.3);

\[
\delta_a = 0.643 \, D^{1/3} \, \nu^{1/6} \, \Omega^{-1/2} \tag{2.2.10}
\]

where \(\delta_a\) = aqueous diffusion layer thickness, m;
\(D\) = diffusion coefficient, m\(^2\)/s;
\(\nu\) = kinematic viscosity, m\(^2\)/s;
(for water \(\nu = 8.930 \times 10^{-7} \, m^2/s\) (158));
\(\Omega\) = rotational speed, Hz (= 3 Hz).

The diffusion coefficients of the metals studied, in the aqueous phase were calculated using the Nernst equation (169); these values will be the limiting value of \(D\) and an average value of \(7.16 \times 10^{-10} \, m^2/s\) is taken for the metals.

Thus,

\[
\delta_a = 0.643 \, (7.16 \times 10^{-10})^{1/3} \, (8.93 \times 10^{-7})^{1/6} \, 3^{-1/2}
\]

\[
= 32.59 \times 10^{-6} \, m
\]

\[
\therefore \delta_a = 32.59 \, \mu m
\]

This value will be the same for the D2EHPA and D2EHDTPA systems because the aqueous phase conditions are the same.
The thickness of the reaction zone calculated above may be compared with a value of 3 and 8 μm calculated for a diffusion film thickness by Danesi et al. (166) for kinetic experiments with a Lewis cell stirred at 1 Hz (60 r.p.m.). Also, the diffusion film thickness calculated from Levich theory for the RDC is greater than those values of Danesi and co-workers. In conclusion, the reaction zone is well within the diffusion layer.

6.5 Recommendations for Future Work

There are many useful measurements that could be made on systems which are studied using the RDC technique. The following may be suitable areas for further investigation:

(i) A continuation of the present work should involve the collection of more experimental data for the systems studied and for other divalent transition metal systems. The optimisation exercise could then be repeated, with all the mass transfer coefficients being optimised. This would lead to a better establishment of the pH dependency in the model. It would also be interesting to confirm trends in rates related to transition metal type.

(ii) The effect of temperature on the initial rate of extraction should be explored, thus leading to an estimation of the activation energy.

(iii) The degree of metal-complex polymerisation in the organic phase should also be studied. It is likely that this is an important point when studying extraction at higher metal loadings.
(iv) The rate of co-extraction of metals should be looked at using the RDC. This is an important feature of industrial metal separation processes since separation can be achieved based on the relative rates of extraction of metals.

(v) The RDC could also be used to measure the rate of stripping of metals. The technique used by Albery et al.\(^{(54)}\) could be employed, i.e. electro-chemical techniques to follow the metal or the use of ion-selective electrodes.

However, the most interesting area of future research would be the use of acid phosphates with different side chains to that of D2EHPA. The rate of extraction would be compared under otherwise identical conditions. Altering the molecular weights, by increasing the chain length, will change the partition coefficient, e.g. smaller molecules will be more soluble in the aqueous phase, hence, a lower partition coefficient value will result. In consequence, the rate should increase according to the proposed model, see \(\theta_1\) in Section 4.2.2. Also, for the same molecular weight but with different substituted groups in the side chains, both \(P(HR)_2\) and \(K_{2d}\) values would alter. The model should also respond in a predicative manner to these variations.

Finally, this work is supported by Harada and Miyake\(^{(161)}\), who reported in 1986 that the use of the partition coefficient in modelling liquid-liquid reactions is particularly important. The observation of the above workers together with the work of Preston\(^{(37)}\), who studied the extraction of \(\text{Cu}^{2+}\) by hydroxyoximes, reinforces the fundamental importance of partition coefficients as used in the development of the model in the present study.
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APPENDIX (A)

THE PROGRAM LEVICH
APPENDIX (A)

THE PROGRAM LEVICH

A.1 Introduction

The procedure described in Section 2.4.5. for calculating the experimental flux was adapted for digital computer solution via the FORTRAN program LEVICH presented in Table A.1.1. A typical input and output of the program is shown in Table A.1.2. and Table A.1.3. respectively.
TABLE A.1.1.

Listing of Program LEVICH

1 C **********************
2 C * PROGRAM LEVICH *
3 C **********************
4 C PROGRAM LEVICH
5 C VARIABLES ARE DECLARED
6 C DIMENSION COMEGA(20), F(20), FLUX(20), FREQ(4), OMEGA(20), RJ(20),
7 1TU(20), VT(20), X(2), Y(2)
8 REAL ALFAO, AREA, FS, J(4), M, MT, STO, TEMP
9 INTEGER I, K, N, PT(20)
10 CHARACTER *72, AQUEOUS, DATE*10, FILE*7, ORGANIC, PFN*7, SYSTEM,
11 TITLE1, TITLE2, TITRANT, UNIT1*10, UNIT2*16, UNIT3*16, UNIT4*2,
12 UNIT5*18, USNUM*7
13 DATA K/7/
14 UNIT1='mol/s'
15 UNIT2='kmol/m s'
16 UNIT3='l m s/lanol'
17 UNIT4='ls'
18 UNIT5='m s /kmol'
19 C USER NUMBER FROM WHICH DATA TO BE OBTAINED READ.
20 C PRINT*, 'USER NUMBER = ?'
21 READ*, USNUM
22 C PERMANENT DATA FILE NAME READ.
23 C PRINT*, 'PERMANENT DATA FILE NAME = ?'
24 READ*, PFN
25 IF (PFN.EQ.'STOP') GOTO 999
26 IF (PFN(7:7).NE. ' ') THEN
27 K=7
28 GOTO 60
29 ENDIF
30 CALL CHECK(PFN, K)
31 INTRC = 0
32 CALL PF('GET', 'DATA', PFN(: K), 'UN', USNUM, 'RC', INTRC, 'NA', NAT)
33 IF (INTRC.NE.0) THEN
34 PRINT *, 'ERROR: PERMANENT FILE', PFN, ' NOT ACCESSED.'
35 GOTO 50
36 ENDIF
37 C INPUT/OUTPUT CHANNELS ARE DEFINED
38 OPEN (UNIT=1, FILE='DATA', STATUS='OLD', IOSTAT=10)
TABLE A.1.1.: Continued . . .

52 IF (IO.NE.0) THEN
53 PRINT*, ' INPUT FILE ERROR '
54 STOP
55 ENDIF
56 REWIND (1)
57 OPEN (UNIT=2,FILE='RESULTS',STATUS='UNKNOWN', IOSTAT=IO)
58 IF (IO.NE.0) THEN
59 PRINT*, ' OUTPUT FILE ERROR '
60 STOP
61 ENDIF
62 REWIND (2)
63 C
64 C DATA READ IN
65 C
66 READ (1,*) FILE,DATE,SYS TEM,ORG ANIC,AQUEOUS,TITRANT,
67 1T ILE1, TIT LE2
68 READ (1,*) ALFAO,AREA,TEMP,FS,MT,STO,N
69 READ (1,*) (OMEGA(I),VT(I),TU(I),I-1,N)
70 REWIND (1)
71 C
72 C CALCULATIONS BEGUN
73 C
74 DO 100 I = 1,N
75 COMEGA(I) = (1.0/SQRT(OMEGA(I)))
76 F(I) = ((VT(I)*14.0/(TU(I)*FS))*MT/(STO*6.0E4))
77 FLUX(I) = F(I)/(ALFAO*AREA*1.0E3)
78 RJ(I) = (1.0/FLUX(I))
79 PT(I) = I
80 100 CONTINUE
81 C
82 C CALL SUBROUTINE FOR LINEAR REGRESSION CALCULATIONS
83 C
84 CALL LINREG(COMEGA,RJ,N,CC,M,C,V)
85 C
86 C FLUX FOR VARIOUS FREQUENCIES IS CALCULATED
87 C
88 DO 200 I = 1,4
89 FREQ(I) = I + 1.0
90 J(I) = (1.0/(M*SQRT(1.0/FREQ(I)) + C))
91 200 CONTINUE
92 C
93 C CALCULATED RESULTS ARE WRITTEN TO FILE 'RESULTS'
94 C
95 WRITE (2,300) FILE,DATE,SYSTEM,ORGANIC,AQUEOUS,TITRANT,
96 1TITLE1,TITLE2
97 300 FORMAT (1H1/18X,'RUN NUMBER: ',A7,26X,'DATE: ',A10/
98 16/(18X,A72)/)
99 WRITE (2,400) UNIT1,UNIT2,UNIT3,UNIT4,
100 1(PT(I),F(I),FLUX(I),RJ(I),COMEGA(I),I-1,N)
101 400 FORMAT (1H /19X,'POINT ',5X,'F',7X,'FLUX,(Jm)',3X,
102 1'(1/ (Jm))',3X,'(1/ FREQ.)'/20X,'NO.'/28X,A10,5X,A16,2X,
103 2A16,5X,A2///(21X,I2,3X,3(1PE9.3,3X),' 0',0PF4.3))
104 WRITE (2,500) (FREQ(I),J(I),I=1,4)
TABLE A.1.: Continued...

105 500 FORMAT (1HO//32X,'FREQUENCY',6X,'FLUX (Jc)'/35X,
106 1/s,11X,'kmol/m s'/4(35X,0PF3.1,9X,1PE9.3/))
107 WRITE (2,600) V,CC,M,UNIT5,C,UNIT3
108 600 FORMAT (1HO/18X,'COVARIANCE = ',1PE9.3//18X,
109 'CORRELATION COEFFICIENT = ',0,0PF4.3//18X,'SLOPE = ',
110 21PE9.3,3X,A18//18X,'INTERCEPT = ',1PE9.3,3X,A16/)
111 PRINT *,''
112 PRINT *,'RUN COMPLETE'
113 PRINT *,'TO RERUN TYPE IN THE NEW DATA FILE NAME'
114 PRINT *,'OR TYPE "STOP" TO STOP'
115 GOTO 50
116 999 WRITE (2, '(1H1)')
117 CLOSE (1)
118 CLOSE (2)
119 STOP
120 END

1 C
2 C SUBROUTINE LINREG
3 C
4 SUBROUTINE LINREG (COMEGA,RJ,N,CC,M,C,V)
5 REAL COMEGA(20),RJ(20),CC,M,C,V
6 INTEGER I,N
7 C
8 C VARIABLES ARE INITIALISED
9 C
10 SUMX = 0
11 SUMY = 0
12 SUMSQX = 0
13 SUMXY = 0
14 SUMSQY = 0
15 C
16 C CALCULATIONS BEGIN
17 C
18 DO 100 I = 1,N
19 SUMX = SUMX + COMEGA(I)
20 SUMY = SUMY + RJ(I)
21 SUMSQX = SUMSQX + COMEGA(I)**2
22 SUMXY = SUMXY + (COMEGA(I)*RJ(I))
23 SUMSQY = SUMSQY + RJ(I)**2
24 100 CONTINUE
25 SXX = SUMSQX - N*(SUMX/N)**2
26 SXY = SUMXY - N*(SUMX/N)*(SUMY/N)
27 SYY = SUMSQY - N*(SUMY/N)**2
28 V = SXY/SXX
29 CC = SXY/(SQR(SXX*SYY))
30 M = SXY/SXX
31 C = (SUMY/N) - M*(SUMX/N)
32 RETURN
33 END
TABLE A.1.1.: Continued

1 C
2 C SUBROUTINE CHECK
3 C
4 SUBROUTINE CHECK (PFN, K)
5 CHARACTER PFN*7
6 INTEGER I, K
7 I = 1
8 IF (PFN(I: I).NE. ' ') THEN
9 I = I + 1
10 GOTO 100
11 ELSE
12 K = I - 1
13 ENDIF
14 RETURN
15 END

TABLE A.1.2.: An Input File for Program LEVICH

'HD11'
'27-4-1984'
'SYSTEM: D2EHPA/n-HEPTANE/COBALT(II) SULPHATE'
'ORGANIC PHASE: 0.592 M D2EHPA/n-Heptane.'
'AQUEOUS PHASE: 0.04 M Cobalt(II) sulphate.'
'TITRANT: 5.0 mM Sodium hydroxide.'
'TEMPERATURE: 25.0 C. pH STAT: 4.50 pH.'
'MEMBRANE AREA, A = 1.865E-04 Sq.m.'

<table>
<thead>
<tr>
<th>pH</th>
<th>pHeq</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.50</td>
<td>3.40</td>
<td>13.3</td>
</tr>
<tr>
<td>1.50</td>
<td>2.41</td>
<td>12.1</td>
</tr>
<tr>
<td>4.00</td>
<td>3.30</td>
<td>12.3</td>
</tr>
<tr>
<td>1.98</td>
<td>2.58</td>
<td>11.9</td>
</tr>
<tr>
<td>4.50</td>
<td>3.26</td>
<td>11.8</td>
</tr>
<tr>
<td>2.48</td>
<td>2.90</td>
<td>12.4</td>
</tr>
<tr>
<td>5.00</td>
<td>3.55</td>
<td>12.5</td>
</tr>
<tr>
<td>3.00</td>
<td>2.93</td>
<td>11.9</td>
</tr>
<tr>
<td>4.00</td>
<td>3.66</td>
<td>13.5</td>
</tr>
<tr>
<td>1.98</td>
<td>2.95</td>
<td>13.4</td>
</tr>
<tr>
<td>5.00</td>
<td>2.80</td>
<td>9.79</td>
</tr>
<tr>
<td>3.00</td>
<td>3.43</td>
<td>13.8</td>
</tr>
<tr>
<td>3.00</td>
<td>3.53</td>
<td>14.0</td>
</tr>
<tr>
<td>5.00</td>
<td>3.25</td>
<td>11.3</td>
</tr>
<tr>
<td>1.98</td>
<td>2.50</td>
<td>12.0</td>
</tr>
<tr>
<td>4.00</td>
<td>3.50</td>
<td>13.3</td>
</tr>
</tbody>
</table>
TABLE A.1.3:
An Output File From Program LEVICH

RUN NUMBER: HD11
DATE: 27-4-1984

SYSTEM: D2EHPA/n-HEPTANE/COBALT(II) SULPHATE

ORGANIC PHASE: 0.592 M D2EHPA/n-Heptane.
AQUEOUS PHASE: 0.04 M Cobalt(II) sulphate.
TITRANT: 5.0 mM Sodium hydroxide.
TEMPERATURE: 25.0 °C.
pH STAT: 4.50 pH.
MEMBRANE AREA, A = 1.865E-04 Sq.m.

<table>
<thead>
<tr>
<th>POINT NO.</th>
<th>F (mol/s)</th>
<th>FLUX, (Jm) (kmol/m s)</th>
<th>(1/ (Jm)) (m s/kmol)</th>
<th>(1/FREQ.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.065E-08</td>
<td>8.399E-08</td>
<td>1.191E+07</td>
<td>0.535</td>
</tr>
<tr>
<td>2</td>
<td>8.299E-09</td>
<td>6.544E-08</td>
<td>1.528E+07</td>
<td>0.816</td>
</tr>
<tr>
<td>3</td>
<td>1.118E-08</td>
<td>8.815E-08</td>
<td>1.134E+07</td>
<td>0.500</td>
</tr>
<tr>
<td>4</td>
<td>9.034E-09</td>
<td>7.123E-08</td>
<td>1.404E+07</td>
<td>0.711</td>
</tr>
<tr>
<td>5</td>
<td>1.151E-08</td>
<td>9.077E-08</td>
<td>1.102E+07</td>
<td>0.471</td>
</tr>
<tr>
<td>6</td>
<td>9.745E-09</td>
<td>7.684E-08</td>
<td>1.301E+07</td>
<td>0.635</td>
</tr>
<tr>
<td>7</td>
<td>1.183E-08</td>
<td>9.331E-08</td>
<td>1.072E+07</td>
<td>0.447</td>
</tr>
<tr>
<td>8</td>
<td>1.026E-08</td>
<td>8.089E-08</td>
<td>1.236E+07</td>
<td>0.577</td>
</tr>
<tr>
<td>9</td>
<td>1.130E-08</td>
<td>8.907E-08</td>
<td>1.123E+07</td>
<td>0.500</td>
</tr>
<tr>
<td>10</td>
<td>9.173E-09</td>
<td>7.233E-08</td>
<td>1.383E+07</td>
<td>0.711</td>
</tr>
<tr>
<td>11</td>
<td>1.192E-08</td>
<td>9.397E-08</td>
<td>1.064E+07</td>
<td>0.447</td>
</tr>
<tr>
<td>12</td>
<td>1.036E-08</td>
<td>8.166E-08</td>
<td>1.225E+07</td>
<td>0.577</td>
</tr>
<tr>
<td>13</td>
<td>1.051E-08</td>
<td>8.284E-08</td>
<td>1.207E+07</td>
<td>0.577</td>
</tr>
<tr>
<td>14</td>
<td>1.198E-08</td>
<td>9.449E-08</td>
<td>1.058E+07</td>
<td>0.447</td>
</tr>
<tr>
<td>15</td>
<td>8.681E-09</td>
<td>6.845E-08</td>
<td>1.461E+07</td>
<td>0.711</td>
</tr>
<tr>
<td>16</td>
<td>1.096E-08</td>
<td>8.646E-08</td>
<td>1.157E+07</td>
<td>0.500</td>
</tr>
</tbody>
</table>

FREQUENCY /s

<table>
<thead>
<tr>
<th>FLUX (Jc) (kmol/m s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
</tr>
<tr>
<td>3.0</td>
</tr>
<tr>
<td>4.0</td>
</tr>
<tr>
<td>5.0</td>
</tr>
</tbody>
</table>

COVARIANCE = 1.567E+05
CORRELATION COEFFICIENT = 0.992
SLOPE = 1.284E+07 m s/kmol
INTERCEPT = 4.926E+06 m s/kmol
APPENDIX (B)

SENSITIVITY ANALYSIS OF THE MODELS
APPENDIX (B)

SENSITIVITY ANALYSIS OF THE MODELS

B.1 Sensitivity Analysis of the D2EHPA Model

The reader is referred to Section 4.5.1. for details of the parameters analysed; only those parameters showing a significant effect on the predicted flux are presented here:

Figure B.1.1.: Effect of $k_{M^2+} (= k_{H^+})$ on the Predicted Transfer Flux

Figure B.1.2.: Effect of $\kappa_{(HR)_2} (= \kappa_{MR_2(HR)_2})$ on the Predicted Transfer flux

Figure B.1.3.: Effect of $k_R$ on the Predicted Transfer Flux

Figure B.1.4.: Effect of $D_{(HR)_2}$ on the Predicted Transfer Flux

Figure B.1.5.: Effect of $K_{2d}$ on the Predicted Transfer Flux

Figure B.1.6.: Effect of $P_{(HR)_2}$ on the Predicted Transfer Flux

Figure B.1.7.: Effect of $K_{ex}$ on the Predicted Transfer Flux

Figure B.1.8.: Effect of $C_{(HR)_2}$ on the Predicted Transfer Flux

Figure B.1.9.: Effect of $C_{M^2+}$ on the Predicted Transfer Flux

Figure B.1.10.: Effect of $C_{H^+}$ on the Predicted Transfer Flux

Figure B.1.11.: Effect of $C_{MR_2(HR)_2}$ on the Predicted Transfer Flux
\[ k_{\text{H}^+} = k_{\text{H}^+} : \text{m/s} \]

**FIGURE B.1.1:** Effect of \( k_{\text{H}^+} \) (\( = k_{\text{H}^+} \)) on the Predicted Transfer Flux
FIGURE B.1.2.1  
Effect of $K_{\text{O}_2}$ on the Predicted Transfer Flux

$\Phi_{\text{O}_2} = \frac{K_{\text{O}_2} \varphi_{\text{O}_2}}{\text{mol/m}^2 \cdot \text{sec}}$
FIGURE B.1.3: Effect of $k_R$ on the Predicted Transfer Flux
Figure B.1.4.1. Effect of \( D_{\text{oxygen}} \)

on the Predicted Transfer Flux

Predicted Flux: \( \text{Kmol/m}^2 \cdot \text{s} \)
FIGURE B.1.5: Effect of $K_{2d}$ on the Predicted Transfer Flux
FIGURE B.1.6: Effect of $P_{\text{O}_2}$ on the Predicted Transfer Flux

Predicted Flux: $\text{kmol}/m^2\cdot s$
FIGURE B.1.7.1  Effect of $K_{ex}$ on the Predicted Transfer Flux
FIGURE B.1.8: Effect of $\overline{C}_{\text{OR}_2}$ on the Predicted Transfer Flux
FIGURE B.1.9.1: Effect of $C_{M^{2+}}$ on the Predicted Transfer Flux

Predicted Flux: Kmol/m².s
FIGURE B.1.10: Effect of $C_{H^+}$ on the Predicted Transfer Flux

$C_{H^+}$: kmol/m$^3$

PREDICTED FLUX, kmol/m$^2$e

$10^{-8}$

$10^{-9}$

$10^{-10}$

$10^{-5}$ $10^{-4}$ $10^{-3}$ $10^{-2}$
B.2 Sensitivity Analysis of the D2EHDTPA Model

The reader is referred to Section 4.5.2. for details of the parameters analysed; only those parameters having a significant effect on the predicted flux are presented here:

Figure B.2.1.: Effect of $k_{M2^+} (= k_{H^+})$ on the Predicted Transfer Flux

Figure B.2.2.: Effect of $\tilde{k}_{HL} (= \tilde{k}_{ML_2})$ on the Predicted Transfer Flux

Figure B.2.3.: Effect of $k_L$ on the Predicted Transfer Flux

Figure B.2.4.: Effect of $D_{HL}$ on the Predicted Transfer Flux

Figure B.2.5.: Effect of $K_d$ on the Predicted Transfer Flux

Figure B.2.6.: Effect of $P_{HL}$ on the Predicted Transfer Flux
FIGURE B.2.1: Effect of $K_{\text{H}_2^+}$ on the Predicted Transfer Flux

$K_{\text{H}_2^+}$ (eq. $K_{\text{H}_+}$) m/s

Predicted Flux: kmol/m$^2$.s
FIGURE B.2.2: Effect of $\bar{K}_{HL}$ ($= \bar{K}_{ML2}$) on the Predicted Transfer Flux
FIGURE B.2.3: Effect of $k_L$ on the Predicted Transfer Flux
FIGURE B.2.4: Effect of $D_{HL}$ on the Predicted Transfer Flux
FIGURE B.2.5: Effect of $K_d$ on the Predicted Transfer Flux
FIGURE B.2.6: Effect of $P_{HL}$ on the Predicted Transfer Flux
APPENDIX (C)

THE OPTIMISATION PROGRAM FLUXM
C.1 Introduction

The two models described in Chapter Four were adapted for digital computer solution via the FORTRAN program FLUXM presented below. The algorithm illustrating the structure of the program was shown in Figure 4.5.1. The listing of the program together with the input and the output are presented in Table C.1.1.

The subprograms (SUBROUTINES and FUNCTIONS), which constitute the program are tabulated in Table C.1.2. together with brief comments on their purpose. The various arrays declared in the program are dimensioned to allow up to ten parameters to be optimised and process up to eighty sets of experimental data. However, the program is coded to optimise a minimum of three and a maximum of six parameters of the mass transfer model. The program is written to allow optimisation of parameters belonging to the D2EHPA or the D2EHDTPA model. The model required can be selected by typing the appropriate extractant name when running the program.

The various variables used in the computer program, related to the models variables, are identified in Table C.1.3.

C.1.1 Running the program

The program and the experimental data exist as files on the Bradford University mainframe computer. The program FLUXM, was compiled and interactively run on the 'Control Data Corporation' CYBER 180-830 digital computer (the mainframe) at the University of
Bradford Computer Centre. The CYBER 180-830 runs under the Network Operating System (NOS), which was used for file manipulation, editing, compilation and running of the program.

C.1.2 Data required to run the program

The information needed to run the program can be divided into two groups:

(i) the data required for directing optimisation
(ii) the experimental data

The input of the optimisation information, see Table C.1.3., is controlled by the main program FLUXM and is asked for at the terminal. The input of experimental data, see Table C.1.4., is through a file called 'DATA' and is via the subroutine FMODEL.

C.1.3 Output from the computer program

As with the data input, the output from the program can be divided into two groups:

(i) information needed to interactively run the program and information related to the optimisation.
(ii) the result of the optimisation.

The information needed to direct the interactive running of the program, displayed at the V.D.U. terminal, is self explanatory. The other information displayed at the terminal shows the progress of the optimisation. It consists of the number of optimisation iterations performed so far, the number of parameters still to be optimised, the current value of the parameters and the least square function.
The initial conditions of the optimisation, the progress of the optimisation run is written to a file called 'RESULT'. When requested, the statistical information on the optimised parameters is also written to the RESULT file, i.e. when IST = 1. For an example of a typical RESULT file see Table C.1.1.
TABLE C.1.1:
(a) The listing of program FLUXM

1 C
2 C ***************************************************************
3 C * PROGRAM FLUXM: THIS PROGRAM OPTIMISES THE PARAMETERS
4 C * IN THE MASS TRANSFER MODEL FOR THE EXTRACTION OF DIVALENT
5 C * TRANSITION METALS BY AN ACIDIC EXTRACTANT IN A ROTATING
6 C * DIFFUSION CELL.
7 C *
8 C *
9 C * THE PARAMETERS THAT CAN BE OPTIMISED ARE:
10 C *
11 C * (1) KA1 - ORGANIC PHASE FILM MASS TRANSFER COEFFICIENT.
12 C * ( = KE1 )
13 C * (2) KB2 - AQUEOUS PHASE FILM MASS TRANSFER COEFFICIENT.
14 C * ( = KH2 )
15 C * (3) TH1 - GROUPED KINETIC PARAMETER.
16 C * (4) TH2 - GROUPED PHYSICAL PROPERTY PARAMETER.
17 C * (5) KEX - EQUILIBRIUM EXTRACTION CONSTANT.
18 C * ( = BET2 )
19 C * (6) K22 - DIMERIZATION CONSTANT.
20 C *
21 C ***************************************************************
22 C
23 PROGRAM FLUXM
24 C
25 VARIABLES ARE DECLARED.
26 C
27 DIMENSION Z(150), P(1700), B(10), BMIN(10), BMAX(10), BV(10),
28 1Y(150), A(10,12), H(10,12)
29 INTEGER FV(2), MODV
30 REAL KA1, KB2, KEX, BET1, BET2, NE, KH, K22, XM, XH, XHR
31 CHARACTER ITEXT*72, MOD*10
32 EXTERNAL FMODEL
33 C
34 COMMON BLOCKS ARE DEFINED.
35 C
36 COMMON ICC, NP, MODV
37 COMMON/FLUX/KA1, KB2, KEX, BET1, BET2, NE, KH, K22, KE1, KH2
38 COMMON/EQ/HT, BT, ST, HRT, BET1, BET2, KH, K22, XM, XH, XHR
39 C
40 INITIALISATION OF VARIABLES.
41 C
42 DATA Y, P, B, BMIN, BV, A, H, Z, FV, K22/150*0.0, 1700*0.0, 10*0.0,
43 110*0.0, 10*0.0, 120*0.0, 120*0.0, 150*0.0, 2*0.0, 0.0/
44 DATA KH/100.0/
45 C
46 INPUT/OUTPUT CHANNELS ARE DEFINED:
47 C
48 1 = READ FROM A FILE.
49 5 = READ AT THE TERMINAL.
50 6 = WRITE INTO A FILE.
TABLE C.1.1.: Continued . . .

52 OPEN (UNIT=1, FILE='DATA', STATUS='OLD', IOSTAT=IO)
53 IF (IO.NE.0) THEN
54 PRINT*, ' INPUT FILE ERROR '
55 STOP
56 ENDIF
57 REWIND (1)
58 OPEN (UNIT=5, FILE='INPUT', STATUS='UNKNOWN', IOSTAT=IO)
59 IF (IO.NE.0) THEN
60 PRINT*, ' INPUT FILE ERROR '
61 STOP
62 ENDIF
63 OPEN (UNIT=6, FILE='RESULT', STATUS='UNKNOWN', IOSTAT=IO)
64 IF (IO.NE.0) THEN
65 PRINT*, ' INPUT FILE ERROR '
66 STOP
67 ENDIF
68 REWIND (6)
69 C
70 C GUESSES OF PARAMETERS AND RELATED DATA READ IN.
71 C
72 100 NP = 1
73 PRINT *, 'TITLE OF PROBLEM ?'
74 READ (5,*) ITXT
75 PRINT *, 'DATA POINTS(N), PARAMETERS(KK) & STAT. CONTROL(1/0) ?'
76 READ (5,*) N, KK, IST
77 PRINT *, 'FORMATION CONSTANT OF THE METAL SULPHATE (BET1) ?'
78 READ (5,*) BET1
79 110 PRINT *, 'THE MODEL REQUIRED (D2EHPA/D2EHDTPA) ?'
80 READ (5,*) MOD
81 IF (MOD.EQ.'D2EHDTPA') THEN
82 MODV = 1
83 ELSE
84 IF (MOD.EQ.'D2EHPA') THEN
85 PRINT *, 'DIMERIZATION CONSTANT = ?'
86 READ (5,*) K22
87 MODV = 2
88 ELSE
89 PRINT *, 'ERROR IN THE SELECTION OF THE MODEL'
90 GOTO 110
91 ENDIF
92 ENDIF
93 IF (KK.LT.5) THEN
94 PRINT *, 'EXTRACTION CONSTANT = ?'
95 READ (5,*) BET2
96 ENDIF
97 PRINT 300, KK
98 READ (5,*) (B(I), I=1, KK)
99 PRINT *, 'LOWER BOUNDS OF PARAMETERS ?'
100 READ (5,*) (BMIN(I), I=1, KK)
TABLE C.1.1.: Continued...

101 PRINT *, 'UPPER BOUNDS OF PARAMETERS ?'
102 READ (5,*) (BMAX(I), I=1, KK)
103 PRINT 310
104 READ (5,*) (BV(I), I=1, KK)
105 PRINT *, 'OPTIMISATION BOUNDS (FNU, FLA, TAU, EPS & PHMIN) ?'
106 READ (5,*) FNU, FLA, TAU, EPS, PHMIN
107 C
108 C FMODEL CALLED TO READ EXPERIMENTAL DATA.
109 C
110 ICC = -1
111 CALL FMODEL(KK, B, N, Z, FV)
112 C
113 C OPTIMISATION PROCEDURE BEGINS.
114 C
115 200 WRITE (6,320) NP
116 WRITE (6,330) ITEXT, (J, BMIN(J), B(J), BMAX(J), BV(J), J=1, KK)
117 WRITE (6,340) (BV(J), J=1,6)
118 ICC = 0
119 KD = KK
120 IC = 0
121 ICON = KK
122 FV(1) = 0
123 GAMM = 0.0
124 210 CALL BSOLVE(KK, B, N, Z, Y, PH, FNU, FLA, TAU, EPS, PHMIN, IC, ICON, FV,
125 LDLV, BV, BMIN, BMAX, P, FMODEL, DERIV, KD, A, H, GAMM)
126 WRITE (6,350) FV(1), ICON, (B(J), J=1,6), PH
127 PRINT 360, FV(I), ICON, (B(J), J=1,6), PH
128 IF (FV(1).GT.200) GOTO 250
129 IF (ICON. GT. 0) GOTO 210
130 C
131 C ERROR IN THE OPTIMISATION ROUTINE ANALYSED AND PRINTED.
132 C
133 PRINT *, '
134 IF (ICON.EQ.(-1)) PRINT*, 'NO FUNCTION IMPROVEMENT POSSIBLE'
135 IF (ICON.EQ.(-2)) PRINT*, 'MORE UNKNOWNS THEN FUNCTIONS'
136 IF (ICON.EQ.(-3)) PRINT*, 'TOTAL VARIABLES (BV(I)) ARE ZERO'
137 IF (ICON.EQ.(-4)) PRINT 370
138 222 WRITE (6,380) ICON, (B(I), I=1,6), PH
139 C
140 C SUBROUTINE STAT CALLED WHEN IST = 1 AND ICON = 0 TO
141 C CALCULATE STATISTICAL INFORMATION ON OPTIMISED PARAMETERS.
142 C
143 IF (IST.EQ.1.AND.ICON.EQ.0) CALL STAT(KK, B, N, PH, H)
144 C
145 C FMODEL CALLED TO WRITE THE RESULTS.
146 C
147 WRITE (6,390) NP, ITEXT
148 ICC = 1
149 CALL FMODEL(KK, B, N, Z, FV)
150 224 PRINT 400, ICON
TABLE C.1.1.: Continued . . .

151 READ *, FV(1)
152 NP = NP + 1
153 IF (FV(1)) 100, 9999, 225
154 225 FLA = 0.0
155 PRINT 300, KK
156 READ (5, *) (B(I), I=1, KK)
157 PRINT 310
158 READ (5, *) (BV(I), I=1, KK)
159 GOTO 200
160 250 WRITE (6, 410)
161 WRITE (6, 380) ICON, (B(I), I=1,6), PH
162 PRINT 410
163 PRINT 380, ICON, (B(I), I=1,6), PH
164 PRINT 420
165 READ (5, *) FV(2)
166 NP = NP + 1
167 IF (FV(2)) 100, 260, 225
168 260 FV(1) = 0
169 WRITE (6, 430)
170 NP = NP - 1
171 GOTO 210
172 300 FORMAT (1H 'GUESSES OF PARAMETERS ? ', I2)
173 310 FORMAT (1H 'SELECT THE PARAMETERS TO BE OPTIMISED ? ')
174 320 FORMAT (1H1, 'OPTIMISATION NO. ', I4/)
175 330 FORMAT (1H1, 'PARAMETER LOWER LIMIT GUESS',
176 15X, 'UPPER LIMIT BV CARD/4X,' NO. '/(4X, I2, 6X,
177 23(1PE11.3, 2X), 3X, OPF3.1))
178 340 FORMAT (1H0, 'CALCULATIONS'/45X, 'PARAMETERS'/ BV CARD: ', 7X,
179 16(F2.0,9X)'/ FV(1) ICON', 4X, 'B(1)', 7X, 'B(2)', 7X, 'B(3)', 7X,
180 2'B(4)', 7X, 'B(5)', 7X, 'B(6)', 8X, 'PH'
181 350 FORMAT (1H1, 'CALCULATION NOT TERMINATED IN 200 ITERATIONS, ')  
182 360 FORMAT (1H1, 'PLEASE CHOOSE ONE OF THE FOLLOWING ',  
183 370 FORMAT (1H0/1X, 'CORRECTION SATISFY CONVERGENCE REQUIREMENTS'/  
184 11X, 'BUT LAMBDA FACTOR (FLA) STILL LARGE')
185 380 FORMAT (1H0, 'FINAL RESULTS'/8X, I2, 7(1PE11.3))
186 390 FORMAT (1H1, 'OPTIMISATION NO.', I4/'1X, A60/)
187 400 FORMAT (1H0, I4, 5X, 'PLEASE CHOOSE ONE OF THE FOLLOWING ',
188 1'OPTIONS BY ENTERING: '/15X, "0" TO TERMINATE PROGRAM'/
189 410 FORMAT (1H0, 'CALCULATION NOT TERMINATED IN 200 ITERATIONS')
189 420 FORMAT (1H0, 'PLEASE CHOOSE ONE OF THE FOLLOWING OPTIONS'/
190 430 FORMAT (1H1, 'OPTIMISATION CONTINUED'/)
191 440 FORMAT (1H0, I4, 5X, 'PLEASE CHOOSE ONE OF THE FOLLOWING ',
192 450 FORMAT (1X, 'AND SELECT THE PARAMETERS TO BE OPTIMISED'/)
193 460 FORMAT (1X, 'AND SELECT THE PARAMETERS TO BE OPTIMISED'/)
194 470 FORMAT (1X, 'AND SELECT THE PARAMETERS TO BE OPTIMISED'/)
195 480 FORMAT (1H1, 'OPTIMISATION CONTINUED'/)
196 9999 WRITE (6,'(1H1)')
200 STOP
201 END
TABLE C.1.1.: Continued . . .

1 C
2 C *********************************************************
3 C * SUBROUTINE BSOLVE: - MARQUARDT'S METHOD FOR OPTIMISATION *
4 C * *********************************************************
5 C *********************************************************
6 C SUBROUTINE BSOLVE (KK, B, NN, Z, Y, PH, FNU, FLA, TAU, EPS, PHMIN, I,
7 C 1ICON, FV, DV, BV, BMIN, BMAX, P, FUNC, DERIV, KD, A, H, GAMM)
8 C DIMENSION B(10), Z(150), Y(150), BV(10), BMIN(10), BMAX(10),
9 C IP(1700), A(10,12), AC(10,12), H(10,12)
10 C INTEGER FV(2)
11 C COMMON ICC
12 C K = KK
13 C N = NN
14 C KP1 = K + 1
15 C KP2 = KP1 + 1
16 C KBI1 = K*N
17 C KBI2 = KBI1 + K
18 C KZI = KBI2 + K
19 C DEFAULT PRECISION VALUES ASSIGNED.
20 C IF (FNU.LE.0.0) FNU = 10.0
21 C IF (FLA.LE.0.0) FLA = 0.01
22 C IF (TAU.LE.0.0) TAU = 0.001
23 C IF (EPS.LE.0.0) EPS = 0.00002
24 C IF (PHMIN.LE.0.0) PHMIN = 0.0
25 C KE = 0
26 C TEST FOR NO OPTIMISATION REQUIRED.
27 C 130 DO 160 I1 - 1, K
28 C 160 IF (BV(I1).NE.0.0) KE = KE + 1
29 C IF (KE.GT.0) GOTO 170
30 C 162 ICON = -3
31 C 163 GOTO 2120
32 C TEST FOR UNKNOWN > EQUATIONS ?.
33 C 170 IF (N.GE.KE) GOTO 500
34 C 180 ICON = -2
35 C 190 GOTO 2120
36 C 500 I1 = 1
37 C 530 IF (I.GT.0) GOTO 1530
38 C 550 DO 560 J1 - 1, K
39 C J2 = KBI1 + J1
40 C P(J2) = B(J1)
41 C J3 = KBI2 + J1
42 C P(J3) = ABS(B(J1)) + 1.0E-02
43 C 560 CONTINUE
TABLE C.1.1.: Continued ... 

52  GOTO 1030
53  590 IF (PHMIN.GT.PH.AND.I.GT.1) GOTO 625
54  DO 620 J1 = 1,K
55  N1 = (J1 - 1)*N
56  IF (BV(J1)) 601,620,605
57  601 CALL DERIV(K,B,N,Z,P(N1+1),FV,DV,J1,JTEST)
58  IF (JTEST.NE.(-1)) GOTO 620
59  BV(J1) = 1.0
60  DO 605 J2 = 1,K
61     J3 = KB11 + J2
62     P(J3) = B(J2)
63  CONTINUE
64  J3 = KB11 + J1
65  J4 = KB12 + J1
66  DEN = 0.001*AMAX1(P(J4),ABS(P(J3)))
67  IF ((P(J3) + DEN).LE.BMAX(J1)) GOTO 55
68  P(J3) = P(J3) - DEN
69  DEN = -DEN
70  GOTO 56
71  55 P(J3) = P(J3) + DEN
72  CALL FUNC(K,P(KB11+1),N,P(N1+1),FV)
73  FV(1) = FV(1) + 1
74  DO 610 J2 = 1,N
75     JB = J2 + N1
76     P(JB) = (P(JB) - Z(J2))/DEN
77  CONTINUE
78  CONTINUE
79  C
80  C SET UP CORRECTION EQUATIONS.
81  C
82  625 DO 725 J1 = 1,K
83     N1 = (J1 - 1)*N
84     A(J1,KP1) = 0.0
85     IF (BV(J1)) 630,692,630
86  630 DO 640 J2 = 1,N
87     N2 = N1 + J2
88     A(J1,KP1) = A(J1,KP1) + P(N2)*(Y(J2) - Z(J2))
89  CONTINUE
90  650 DO 685 J2 = 1,K
91     A(J1,J2) = 0.0
92     N2 = (J2 - 1)*N
93  670 DO 680 J3 = 1,N
94  672 N3 = N1 + J3
95  674 N4 = N2 + J3
96     A(J1,J2) = A(J1,J2) + P(N3)*P(N4)
97     H(J1,J2) = A(J1,J2)*2.0
98  CONTINUE
99  CONTINUE
100 IF (A(J1,J1).GT.1.0E-20) GOTO 725
```
TABLE C.1.1.: Continued

101 692 DO 694 J2 = 1,KP1
102 694 A(J1,J2) = 0.0
103 695 A(J1,J1) = 1.0
104 725 CONTINUE
105 GN = 0.0
106 DO 729 J1 = 1,K
107 729 GN = GN + A(J1,KP1)**2
108 C
109 C SCALE CORRECTION EQUATIONS.
110 C
111 DO 726 J1 = 1,K
112 726 A(J1,KP2) = SQRT(A(J1,J1))
113 DO 727 J1 = 1,K
114 A(J1,KP1) = A(J1,KP1)/A(J1,KP2)
115 DO 727 J2 = 1,K
116 727 A(J1,J2) = A(J1,J2)/(A(J1,KP2)*A(J2,KP2))
117 730 FL = FLA/FNU
118 GOTO 810
119 800 FL = FNU*FL
120 810 DO 840 J1 = 1,K
121 820 DO 830 J2 = 1,KP1
122 830 AC(J1,J2) = A(J1,J2)
123 840 AC(J1,J1) = AC(J1,J1) + FL
124 C
125 C SOLVE CORRECTION EQUATIONS.
126 C
127 DO 930 L1 = 1,K
128 L2 = L1 + 1
129 DO 910 L3 = L2,KP1
130 910 AC(L1,L3) = AC(L1,L3)/AC(L1,L1)
131 DO 930 L3 = 1,K
132 IF (L1 - L3) 920,930,920
133 920 DO 925 L4 = L2,KP1
134 925 AC(L3,L4) = AC(L3,L4) - AC(L1,L4)*AC(L3,L1)
135 930 CONTINUE
136 DN = 0.0
137 DG = 0.0
138 DO 1028 J1 = 1,K
139 AC(J1,KP2) = AC(J1,KP1)/A(J1,KP2)
140 J2 = KB11 + J1
141 P(J2) = AMAX1(BMIN(J1),AMIN1(BMAX(J1),B(J1)+AC(J1,KP2)))
142 DG = DG + AC(J1,KP2)*A(J1,KP1)*A(J1,KP2)
143 DN = DN + AC(J1,KP2)*AC(J1,KP2)
144 AC(J1,KP2) = P(J2) - B(J1)
145 1028 CONTINUE
146 COSG = DG/SQRT(DN*GN + 1.E-30)
147 JGAM = 0
148 IF (COSG) 1100,1110,1110
149 1100 JGAM = 2
150 COSG = -COSG
151 1110 CONTINUE
152 COSG = AMIN1(COSG,1.0)
```
TABLE C.1.1.1 Continued...

153  \[ \text{GAMM} = \text{ACOS(COSG)} \times 180.0/(3.14159265) \]
154  IF (JGAM.GT.0) \[ \text{GAMM} = 180.0 - \text{GAMM} \]
155  \[ \text{CALL FUNC(K,P(KBI1+1),N,P(KZI+1),FV)} \]
156  \[ \text{FV(1)} = \text{FV(1)} + 1 \]
157  1500 PHI = 0.0
158  DO 1520 J1 = 1,N
159      J2 = KZI + J1
160  PHI = PHI + (P(J2) - Y(J1))**2
161  1520 CONTINUE
162  IF (PHI.LT.PHMIN) GOTO 3000
163  IF (I.GT.0) GOTO 1540
164  1521 IF (ICON.NE.(-3)) ICON = K
165  GOTO 2110
166  1540 IF (PHI.GE.PH) GOTO 1530
167  C
168  C \text{EPSILON TEST.}
169  C
170  1200 ICON = 0
171  DO 1220 J1 = 1,K
172      J2 = KBI1 + J1
173  1220 IF (ABS(AC(J1,KP2))/(TAU+ABS(P(J2))).GT.EPS) ICON = ICON + 1
174  IF (ICON.EQ.0) GOTO 1400
175  C
176  C \text{GAMMA LAMBDA TEST.}
177  C
178  IF (FL.GT.1.0.AND.GAMM.GT.90.0) ICON = -1
179  GOTO 2105
180  C
181  C \text{GAMMA EPSILON TEST.}
182  C
183  1400 IF (FL.GT.1.0.AND.GAMM.LE.45.0) ICON = -4
184  GOTO 2105
185  1530 IF (I1 - 2) 1531,1531,2310
186  1531 I1 = I1 + 1
187  GOTO (530,590,800),I1
188  2310 IF (FL.LT.1.0E+5) GOTO 800
189  1320 ICON = -1
190  2105 FLA = FL
191  DO 2091 J2 = 1,K
192      J3 = KBI1 + J2
193      B(J2) = P(J3)
194  2091 CONTINUE
195  2110 DO 2050 J2 = 1,N
196      J3 = KZI + J2
197      Z(J2) = P(J3)
198  2050 CONTINUE
199  PH = PHI
200  I = I + 1
201  2120 RETURN
202  3000 ICON = 0
203  GOTO 2105
204  END
TABLE C.1.1. Continued ...

1 C
2 C  ************************************************************************************
3 C  *  
4 C  * SUBROUTINE FMODEL: THIS SUBROUTINE HAS THREE OBJECTIVES:  *  
5 C  *  
6 C  * (1) TO READ IN THE EXPERIMENTAL DATA FROM FILE 'DATA'.  *  
7 C  * (2) TO CALCULATE THE RESIDUALS; (FL(I)-FL(I)).  *  
8 C  * (3) TO PRINT THE OPTIMISED PARAMETERS.  *  
9 C  *  
10 C  *  
11 C  ************************************************************************************
12 C
13 SUBROUTINE FMODEL(KK,B,N,Z,FV)
14 DIMENSION CAP(80),CBP(80),CEP(80),CHP(80),Z(150),B(10),
15 1AKEX(80),S(80),FLM(80),FL(80)
16 INTEGER FV(2),MODV
17 REAL KA1,KB2,KEX,NE,KH,K22,KE1,KH2,R
18 CHARACTER MOD*10
19 C
20 C COMMON BLOCKS DECLARED.
21 C
22 COMMON ICC, NP, MODV
23 COMMON/EQ/HT, BT, ST, HRT, BET1, BET2, KH, K22, XM, XH,XHR
24 COMMON/FLUX/KA1, KB2, KEX, TH1, TH2, NE, KE1, KH2
25 EXTERNAL FCE
26 IF (ICC) 100,200,300
27 C
28 C EXPERIMENTAL DATA READ IN FROM FILE 'DATA'.
29 C
30 100 CONTINUE
31   READ (1,*) NS
32   DO 110 I = 1,NS
33     READ (1,*) CAP(I),CBP(I),CHP(I),CEP(I),FLM(I)
34     S(I) = 1.0E-08
35 110 CONTINUE
36   REWIND (1)
37   RETURN
38 C
39 C SET PARAMETERS.
40 C
TABLE C.1.1.1 Continued . . .

41 200 CONTINUE
42 KA1 = B(1) * 1.0E-06
43 KB2 = B(2) * 1.0E-06
44 TH1 = B(3) * 1.0E-12
45 TH2 = 1.0
46 IF (KK . GE. 4) TH2 = B(4)
47 IF (KK . GE. 5) BET2 = B(5)
48 IF (KK . GE. 6) K22 = B(6)
49 KE1 = KA1
50 IF (KK . GE. 7) KE1 = KA1 * B(7)
51 KH2 = KB2
52 IF (KK . GE. 8) KH2 = KB2 * B(8)
53 C
54 C CALCULATE RESIDUALS.
55 C
56 DO 220 I = 1, NS
57 C
58 C CALCULATE THE FRACTIONS OF ACTIVE COMPONENTS IN THE AQUEOUS PHASE.
59 C
60 C
61 HT = CHP(I)
62 BT = CBP(I)
63 ST = HT/2.0
64 X = 0.8
65 CALL XSOLV1(FCE, X, 0.0, 1.0, 0.005, 0.0, IER)
66 XH = X
67 HRT = CAP(I)
68 R = CAP(I) + CEP(I)
69 C
70 C CALCULATE FREE 'HR' IN THE ORGANIC PHASE.
71 C
72 CALL ORGMOD(R)
73 C
74 C VARIABLES FOR FLUX CALCULATION ARE ASSIGNED VALUES.
75 C
76 A0 = R * XHR
77 B0 = CBP(I) * XM
78 E0 = CEP(I)
79 H0 = CHP(I) * XH
80 KEX = BET2
81 IF (BET2 . LE. ((H0/A0)**2 * E0/B0)) THEN
82 FL(I) = 1.0E-20
83 GOTO 210
84 ENDIF
85 FL(I) = FJA(A0, B0, E0, H0) / 2.0
86 210 AKEX(I) = BET2 * XM * (XHR/XH)**2
87 Z(I) = (FLM(I) - FL(I)) / S(I)
88 220 CONTINUE
89 RETURN
TABLE C.1.1.: Continued...

90 C
91 C THE OPTIMISED PARAMETERS AND THE ASSOCIATED DATA ARE PRINTED.
92 C
93 300 CONTINUE
94 KA1 = B(1)*1.0E-06
95 KB2 = B(2)*1.0E-06
96 TH1 = B(3)*1.0E-12
97 IF (MODV.EQ.1) THEN
98 WRITE (6,320) KA1, KB2, TH1, TH2, BET2, KE1, KH2
99 ELSE
100 WRITE (6,330) KA1, KB2, TH1, TH2, BET2, K22, KE1, KH2
101 ENDIF
102 WRITE (6,340)
103 DO 310 I = 1, NS
104 WRITE (6,350) I, CAP(I), CBP(I), CHP(I), CEP(I), AKEX(I),
105 FLM(I), FL(I), (FLM(I)-FL(I))
106 310 CONTINUE
107 320 FORMAT (1HO//' OPTIMISED PARAMETERS ARE: '//
108 1' KA1 = ',1PE10.3,2X,' KB2 = ',E10.3,2X,' TH1 = ',
109 2E10.3,2X,' TH2 = ',E10.3//' BT2 = ',E10.3,2X,' KE1 = ',
110 3E10.3,2X,' KH2 = ',E10.3,//)
111 330 FORMAT (1HO,' OPTIMISED PARAMETERS ARE: '//
112 1' KA1 = ',1PE10.3,2X,' KB2 = ',E10.3,2X,' TH1 = ',
113 2E10.3,2X,' TH2 = ',E10.3//' BT2 = ',E10.3,2X,' K22 = ',
114 3E10.3,2X,' KE1 = ',E10.3,2X,' KH2 = ',E10.3,//)
115 340 FORMAT (1HO//4X,'K',6X,'CAC',8X,'CBC',8X,'CHC',8X,'CEC',8X,'KEX',8X,'FLM',8X,'FLC',8X,'DF'//)
116 350 FORMAT (3X,12,1X,8(1PE11.3)//)
118 RETURN
119 END
TABLE C.1.1.: Continued . . .

```plaintext
1 C
2 C  **************************************************************************************************
3 C  *
4 C  * SUBROUTINE STAT: - CALCULATES THE STATISTICAL INFORMATION. *
5 C  *
6 C  **************************************************************************************************
7 C
8 SUBROUTINE STAT(KK, B, N, PH, H)
9 DIMENSION B(10),H(10,12),C(10,10),V(10,10),SB(10),
10 1BN(10),BX(10)
11 S2Y = PH/(N - KK)
12 SY = SQRT(ABS(S2Y))
13 WRITE (6,100)
14 DO 10 I = 1,KK
15 10 WRITE (6,110) (H(I,L), L=1,KK)
16 CALL INVR(H,KK,B,0,DETERM,10,10)
17 WRITE (6,120)
18 DO 30 I = 1,KK
19 DO 20 J = 1,KK
20 20 V(I,J) = 2.0*S2Y*H(I,J)
21 SB(I) = SQRT(ABS(V(I,I)))
22 WRITE (6,110)(V(I,L), L=1,KK)
23 30 CONTINUE
24 WRITE (6,170)
25 DO 50 I = 1,KK
26 DO 40 J = 1,KK
27 40 C(I,J) = V(I,J)/SQRT(ABS(V(I,I)*V(J,J)))
28 WRITE (6,180) (C(I,L), L=1,KK)
29 50 CONTINUE
30 WRITE (6,130)SY,(I, SB(I), I=1,KK)
31 WRITE (6,150)
32 DO 60 I = 1,KK
33 BN(I) = B(I) - 1.796*SB(I)
34 BX(I) = B(I) + 1.796*SB(I)
35 WRITE(6,160) I, BN(I), B(I), BX(I)
36 60 CONTINUE
37 100 FORMAT (1H1,'STATISTICAL INFORMATION ON THE OPTIMISED',
38 1 ' PARAMETERS: '///, 4X, 'INFORMATION MATRIX'/)
39 110 FORMAT (4X,6(1PE12.3))
40 120 FORMAT (1H0/4X,'COVARIANCE MATRIX'/)
41 130 FORMAT (1H0/4X,'STAND.DEV. OF Y :',1PE12.3//
42 1(7X,'STAND.DEV. OF B(',I1,'):',1PE12.3))
43 150 FORMAT (1H0/4X,'90% CONFIDENCE INTERVALS'///14X,'BMIN',
44 19X,'B',10X,'BMAX')/
45 160 FORMAT ((3X,I5,3(1PE12.3)))
46 170 FORMAT (1H0/4X,'CORRELATION MATRIX'/)
47 180 FORMAT (4X,6(1PE12.3))
48 RETURN
49 END
```
```plaintext
TABLE C.1.1.: Continued ...

<table>
<thead>
<tr>
<th>1</th>
<th>C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>SUBROUTINE INVR:- CALLED BY SUBROUTINE STAT.</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>IF M = 0 THE SUBROUTINE CALCULATES THE INVERSE OF AN N X N MATRIX [A] AND STORES IT IN [A].</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>IF M = 1 IT SOLVES THE N LINEAR EQUATIONS AX = B M TIMES, WHERE EACH NEW B VECTOR IS</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>STORED IN B(N,M). THE SOLUTION IS STORED IN B. IN THE CALLING ROUTINE THE MATRICES ARE</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>DIMENSIONED A(ISIZE,JSIZE), B(ISIZE,M) M &lt;= ISIZE LIMITED TO M &lt;= 100.</td>
</tr>
</tbody>
</table>

SUBROUTINE INVR(A,N,B,M,DETERM,ISIZE,JSIZE)
DIMENSION IPIVOT(100),A(ISIZE,JSIZE),B(ISIZE,M),INDEX(100,2), IPIVOT(100)
EQUIVALENCE (IROW, JROW), (ICOLUM, JCOLUM), (AMAX, T, SWAP)

DO 10 J 1, N
10 IPIVOT(J) = 0

DO 105 I 1, N
SEARCH FOR PIVOT ELEMENT.

AMAX = 0.0
DO 35 J = 1, N

IF (IPIVOT(J) - 1) 15,35,15

DO 30 K = 1, N

IF (IPIVOT(K) - 1) 20,30,125

IF (ABS(AMAX) - ABS(A(J,K))) 25,30,30

IROW = J
ICOLUM = K
AMAX = A(J,K)
CONTINUE

IPIVOT(ICOLUM) = IPIVOT(ICOLUM) + 1
INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL.

IF (IROW - ICOLUM) 40,60,40
DETERM = -DETERM
DO 45 L = 1, N
SWAP = A(IROW,L)
A(IROW,L) = A(ICOLUM,L)
A(ICOLUM,L) = SWAP
IF (M) 60,60,50
```

TABLE C.1.1.: Continued...

49      50      DO 55 L=1,M
50      51      SWAP = B(IROW,L)
51      52      B(IROW,L) = B(ICOLUM,L)
52      53  55      B(ICOLUM,L) = SWAP
53      54  60      INDEX(I,1) = IROW
54      55  60      INDEX(I,2) = ICOLUM
55      56      PIVOT(I) = A(ICOLUM,ICOLUM)
56      57      DETERM = DETERM*PIVOT(I)
57      58      DIVIDE PIVOT ROW BY PIVOT ELEMENT.
58      59      A(ICOLUM,ICOLUM) = 1.0
59      60      DO 65 L = 1,N
60      61  65      A(ICOLUM,L) = A(ICOLUM,L)/PIVOT(I)
61      62  70      IF (M) 80,80,70
62      63  70      DO 75 L = 1,M
63      64  75      B(ICOLUM,L) = B(ICOLUM,L)/PIVOT(I)
64      65      REDUCE NON-PIVOT ROWS
65      66      DO 105 L1 = 1,N
66      67  85      IF (L1 - ICOLUM) 85,105,85
67      68  85      T = A(L1,ICOLUM)
68      69  85      A(L1,ICOLUM) = 0.0
69      70      DO 90 L = 1,N
70      71  90      A(L1,L) = A(L1,L) - A(ICOLUM,L)*T
71      72      IF (M) 105,105,95
72      73  95      DO 100 L = 1,M
73      74  100     B(L1,L) = B(L1,L) - B(ICOLUM,L)*T
74      75  105     CONTINUE
75      76  105     CONTINUE
76      77  105     CONTINUE
77      78  105     RETURN
78      79     END

<table>
<thead>
<tr>
<th>L</th>
<th>M</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>
TABLE C.1.1.: Continued...

```c
1 C
2 C **********************************************************************
3 C * SUBROUTINE XSOLVE1: SOLVES THE EQUATION FC(X) = 0 *
4 C * DEFINED BY FUNCTION FC(X) *
5 C * **********************************************************************
6 C
7 C SUBROUTINE XSOLVE1(FC,X,XMIN,XMAX,EPS,PHMIN,IER)
8 C
9 FL = 0.01
10 IT = 0
11 IER = 0
12 X0 = AMAX1(AMIN1(XMAX,X),XMIN)
13 FCX0 = FC(X0)
14 F02 = FCX0**2
15
16 IF (1.001*X0.LE.XMAX.AND.1.001*X0.GE.XMIN) THEN
17     DX = - 0.001*X0/(FC(1.001*X0)/FCX0 - 1.0)
18 ELSE
19     DX = 0.001*X0/(FC(0.999*X0)/FCX0 - 1.0)
20 ENDIF
21 20 X = X0 + DX/(1.0 + FL)
22 X = AMAX1(AMIN1(XMAX,X),XMIN)
23 IT = IT + 1
24 IF (IT.GT.20) GOTO 30
25 FCX = FC(X)
26 F2 = FCX**2
27 IF (F2.LT.F02) THEN
28     IF(ABS((X0-X)/(X0+0.01)).LT.EPS.OR.F2.LT.PHMIN) GOTO 40
29     X0 = X
30     FCX0 = FCX
31     F02 = F2
32     FL = FL/10.0
33     GOTO 10
34 ELSE
35     FL = FL*10.0
36     GOTO 20
37 ENDIF
38 30 PRINT *,,’ CONVERGENCE NOT REACHED IN 20 ITERATIONS’
39 IER = 1
40 40 RETURN
41 END
```
TABLE C.1.1.: Continued . . .

1 C
2 C ***********************************************************************************************************************
3 C * SUBROUTINE ORGMOD: - CALCULATES THE FRACTION OF * 
4 C * THE 'FREE' EXTRACTANT IN THE ORGANIC PHASE USING * 
5 C * THE APPROPRIATE AGGREGATE MODEL. * 
6 C * ***********************************************************************************************************************
7 C SUBROUTINE ORGMOD(R)
8 C REAL KH,K22,HRT,R
9 C INTEGER MODV
10 C COMMON ICC,NP,MODV
11 C COMMON/EQ/HT,BT,ST,HRT,BET1,BET2,KH,K22,XM,XH,XHR
12 C IF (MODV.EQ.1) THEN
13 C XHR = HRT/R
14 C ELSE
15 C XHR = DMODEL(R,HRT,K22)
16 C ENDIF
17 C RETURN
18 C END

1 C ***********************************************************************************************************************
2 C * FUNCTION FCE:- CALCULATES THE FRACTION OF THE ACTIVE * 
3 C * COMPONENTS IN THE AQUEOUS PHASE (I.E. XH AND XM.) * 
4 C * ***********************************************************************************************************************
5 C FUNCTION FCE(X)
6 C REAL KH,K22
7 C COMMON/EQ/HT,BT,ST,HRT,BET1,BET2,KH,K22,XM,XH,XHR
8 C XM = KH*XH/(KH*XH + BET1*(1.0 - XH))
9 C XH = X
10 C FCE = ST+BT - (1.0-XM)*(1.0 + BET1*BT*XM + KH*HT*XH)/(BET1*XM)
11 C RETURN
12 C END
TABLE C.1.1.: Continued ...

1 C 2 C 3 C 4 C
5 C 6 C 7 C 8 C
9 C 10 C
11 C
12 C
13 C
14 C
15 C
16 C
17 C
18 C
19 C
20 C
21 C
22 C
23 C
24 C
25 C
26 C
27 C
28 C
29 C
30 C
31 C
32 C
33 C
34 C
35 C
36 C
37 C
38 C
39 C
40 C
41 C
42 C
43 C
44 C
45 C
46 C
47 C
48 C
49 C
50 C
51 C
52 C

FUNCTION FJA(AO, BO, EO, HO)
REAL JA1, JA2, KA1, KB2, KE1, KH2, KEX, NE
COMMON/FLUX/KA1, KB2, KEX, TH1, TH2, NE, KE1, KH2

INITIAL VALUE OF 'AI' ESTIMATED USING 'KEX AND A0'.

AX = AO
AN = HO*SQRT(EO/BO/KEX)
IF (AN.GT.AO) THEN
   FJA = 0.0
   GOTO 30
ENDIF
AI = 0.5*(AX + AN)
DO 20 K = 1, 25

THE ORGANIC PHASE.

JA1 = KA1*(AO - AI)
EI = EO + 0.5*JA1/KE1

THE AQUEOUS PHASE.

P1 = TH2*HO*HO/(4.0*KEX*BO)
P2 = HO*HO*(EI + TH2*AI/2.0)/(KEX*BO)
P3 = P1*P1 + P2
AE = - P1 + SIGN(SQRT(ABS(P3)),P3)
IF (AE.GE.AI) GOTO 10
BI = BO - 0.5*JA1/KB2
IF (BI.LE.0.0) GOTO 10
HI = HO + JA1/KH2

THE FLUX IS CALCULATED ACCORDING TO THE ASTARITA'S METHOD.

PA = HI*HI*EI/(KEX*AI*AI*BI)
IF (PA.GE.1.0) GOTO 10
D = TH1*BI*(1.0 - PA)*(AI*AI - AE*AE)/HI
JA2 = SQRT(D)

CORRECTION ROUTINE.

IF ((ABS(JA1-JA2)/1.0E-8).LT.1E-5) GOTO 25
IF (JA1.GT.JA2) GOTO 10
AX = AI
AI = AI - (AI - AN)/2.0
GOTO 20
TABLE C.1.1.: Continued...

53   10  AN = AI
54       AI = AI + (AX - AI)/2.0
55  20 CONTINUE
56  25 FJA = (JA1 + JA2)/2.0
57  30 RETURN
58  END

1 C
2 C  *********************************************************************
3 C  *                     *  
4 C  *  FUNCTION DMODEL:- CALCULATES THE FRACTION OF FREE DIMERIC   *  
5 C  *  EXTRACTANT IN THE ORGANIC PHASE USING THE DIMER MODEL.       *  
6 C  *                     *  
7 C  *********************************************************************
8 C
9
10 REAL R,HRT,K22,AA,BB,CC,DIS
11   AA = 2.0*R
12   BB = SQRT(R/K22)
13   CC = - HRT
14   DIS = ((R/K22) - 4.0*AA*CC)
15   DMODEL = ((-BB + SQRT(DIS))/(2.0*AA))**2.0
16  RETURN
17  END

TABLE C.1.1.:  

(b) A Typical DATA (zinc/D2EHDTPA data) File for Program FLUXM

6
2.48E-02 0.01 3.162E-05 0.0 7.761E-08
5.10E-02 0.01 3.162E-05 0.0 1.479E-07
7.32E-02 0.01 3.162E-05 0.0 2.118E-07
9.89E-02 0.01 3.162E-05 0.0 2.619E-07
1.99E-01 0.01 3.162E-05 0.0 3.459E-07
2.97E-01 0.01 3.162E-05 0.0 3.562E-07
TABLE C.1.1.: (c) A Typical RESULT File of Program FLUXM

OPTIMISATION NO. 1

ZINC/D2EHDTPA DATA

<table>
<thead>
<tr>
<th>PARAMETER NO.</th>
<th>LOWER LIMIT</th>
<th>GUESS</th>
<th>UPPER LIMIT</th>
<th>BV CARD</th>
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<tbody>
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<td>1.000E+01</td>
<td>1.000E+02</td>
<td>1.0</td>
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<tr>
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<td>1.000E+00</td>
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<td>1.000E+00</td>
<td>5.000E+02</td>
<td>1.000E+06</td>
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</table>

CALCULATIONS

<table>
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<th>1.</th>
<th>1.</th>
<th>0.</th>
<th>0.</th>
<th>0.</th>
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</thead>
<tbody>
<tr>
<td>FV(1) ICON</td>
<td>B(1)</td>
<td>B(2)</td>
<td>B(3)</td>
<td>B(4)</td>
<td>B(5)</td>
<td>B(6)</td>
</tr>
<tr>
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<tr>
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<tr>
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<td>7.613E+01</td>
<td>2.114E+03</td>
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<tr>
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<td>6.806E+00</td>
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<td>3.309E+03</td>
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</tr>
<tr>
<td>29</td>
<td>0</td>
<td>6.813E+00</td>
<td>7.625E+01</td>
<td>3.280E+03</td>
<td>.000E+00</td>
<td>.000E+00</td>
</tr>
</tbody>
</table>

FINAL RESULTS

|   | 6.813E+00 | 7.625E+01 | 3.280E+03 | .000E+00 | .000E+00 | .000E+00 | 3.312E-01 |
TABLE C.1.1.: Continued

STATISTICAL INFORMATION ON THE OPTIMISED PARAMETERS:

INFORMATION MATRIX

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<th>9.719E-01</th>
<th>5.711E-03</th>
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</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.719E-01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.711E-03</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

COVARIANCE MATRIX

<table>
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<tr>
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<th>7.914E-02</th>
<th>9.804E-02</th>
<th>-3.440E+02</th>
</tr>
</thead>
<tbody>
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<td></td>
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</tr>
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<td>9.804E-02</td>
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</tr>
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<td>-3.440E+02</td>
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CORRELATION MATRIX

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<th>5.070E-01</th>
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</thead>
<tbody>
<tr>
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<td></td>
</tr>
<tr>
<td>5.070E-01</td>
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</tr>
<tr>
<td>-9.430E-01</td>
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<td></td>
</tr>
</tbody>
</table>

STAND.DEV. OF Y: 3.323E-01

STAND.DEV. OF B(1): 2.813E-01
STAND.DEV. OF B(2): 6.873E-01
STAND.DEV. OF B(3): 1.297E+03

90% CONFIDENCE INTERVALS

<table>
<thead>
<tr>
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<th>BMIN</th>
<th>B</th>
<th>EMAX</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>6.307E+00</td>
<td>6.813E+00</td>
<td>7.318E+00</td>
</tr>
<tr>
<td>2</td>
<td>7.501E+01</td>
<td>7.625E+01</td>
<td>7.748E+01</td>
</tr>
<tr>
<td>3</td>
<td>9.517E+02</td>
<td>3.280E+03</td>
<td>5.609E+03</td>
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</tbody>
</table>
**TABLE C.1.1.:** Continued...

**OPTIMISATION NO. 1**

**ZINC/D2EHDTBA DATA**

**OPTIMISED PARAMETERS ARE:**

\[
\begin{align*}
KA1 &= 6.813 \times 10^{-6} & KB2 &= 7.625 \times 10^{-5} & TH1 &= 3.280 \times 10^{-9} & TH2 &= 1.000 \times 10^{0} \\
BT2 &= 1.778 \times 10^{2} & KE1 &= 6.813 \times 10^{-6} & KH2 &= 7.625 \times 10^{-5}
\end{align*}
\]

<table>
<thead>
<tr>
<th>K</th>
<th>CAC</th>
<th>CBC</th>
<th>CHC</th>
<th>CEC</th>
<th>KEX</th>
<th>FLM</th>
<th>FLC</th>
<th>DF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.480 \times 10^{-2}</td>
<td>1.000 \times 10^{-2}</td>
<td>3.162 \times 10^{-5}</td>
<td>.000 \times 10^{+0}</td>
<td>1.806 \times 10^{+2}</td>
<td>7.761 \times 10^{-8}</td>
<td>7.752 \times 10^{-8}</td>
<td>8.569 \times 10^{-11}</td>
</tr>
<tr>
<td>2</td>
<td>5.100 \times 10^{-2}</td>
<td>1.000 \times 10^{-2}</td>
<td>3.162 \times 10^{-5}</td>
<td>.000 \times 10^{+0}</td>
<td>1.806 \times 10^{+2}</td>
<td>1.479 \times 10^{-7}</td>
<td>1.516 \times 10^{-7}</td>
<td>-3.716 \times 10^{-9}</td>
</tr>
<tr>
<td>3</td>
<td>7.320 \times 10^{-2}</td>
<td>1.000 \times 10^{-2}</td>
<td>3.162 \times 10^{-5}</td>
<td>.000 \times 10^{+0}</td>
<td>1.806 \times 10^{+2}</td>
<td>2.118 \times 10^{-7}</td>
<td>2.078 \times 10^{-7}</td>
<td>3.999 \times 10^{-9}</td>
</tr>
<tr>
<td>4</td>
<td>9.890 \times 10^{-2}</td>
<td>1.000 \times 10^{-2}</td>
<td>3.162 \times 10^{-5}</td>
<td>.000 \times 10^{+0}</td>
<td>1.806 \times 10^{+2}</td>
<td>2.619 \times 10^{-7}</td>
<td>2.628 \times 10^{-7}</td>
<td>-8.617 \times 10^{-10}</td>
</tr>
<tr>
<td>5</td>
<td>1.990 \times 10^{-1}</td>
<td>1.000 \times 10^{-2}</td>
<td>3.162 \times 10^{-5}</td>
<td>.000 \times 10^{+0}</td>
<td>1.806 \times 10^{+2}</td>
<td>3.459 \times 10^{-7}</td>
<td>3.471 \times 10^{-7}</td>
<td>-1.223 \times 10^{-9}</td>
</tr>
<tr>
<td>6</td>
<td>2.970 \times 10^{-1}</td>
<td>1.000 \times 10^{-2}</td>
<td>3.162 \times 10^{-5}</td>
<td>.000 \times 10^{+0}</td>
<td>1.806 \times 10^{+2}</td>
<td>3.562 \times 10^{-7}</td>
<td>3.552 \times 10^{-7}</td>
<td>1.038 \times 10^{-9}</td>
</tr>
</tbody>
</table>
### TABLE C.1.2:
The Various 'Units' of The Computer Program FLUXM.

<table>
<thead>
<tr>
<th>UNIT</th>
<th>COMMENTS</th>
</tr>
</thead>
</table>
| FLUXM | - This is the main program unit. It coordinates subroutines:  
  FMODEL - to read from and write to files,  
  BSOLVE - to perform optimisation calculations,  
  STAT  - to perform statistical calculations on the optimised parameters.  
  All input and output at the terminal is through this unit. |

**SUBPROGRAMS:**

| BSOLVE | - Called by the main program FLUXM to perform primary optimisation calculations and coordinate FMODEL (FUNC in BSOLVE) and DERIV (not required in our case). FMODEL is called to calculate the theoretical flux. |

| FMODEL | - Called by BSOLVE (when ICC = 0) to calculate the flux via function FJA. All input (when ICC = -1) and output (when ICC = 1), except for statistical information, is through this subprogram. |

<p>| STAT   | - Called by main program, when IST = 1, to perform statistical calculations on the optimised parameters. Writes the results to a file. It calls subroutine INVR. |</p>
<table>
<thead>
<tr>
<th>UNIT</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>INVR</td>
<td>Primary function to find the inverse of a $N \times N$ matrix. Called by subroutine STAT.</td>
</tr>
<tr>
<td>ORGMOD</td>
<td>Calculates the fraction of 'free' extractant $XHR$ in the organic phase; for D2EHDTDA when $MODV = 1$ and for D2EHPA when $MODV = 2$. It is called by FMODEL.</td>
</tr>
<tr>
<td>XSOLVE1</td>
<td>Called by FMODEL to solve the equation $FCE(x) = 0$; that is to solve the equations describing the fraction of the active metal ions and the protons in the aqueous phase.</td>
</tr>
<tr>
<td>FJA</td>
<td>This function describes the mass transfer models. It is used by FMODEL to calculate the flux, $FL(I)$, once the active components $A0$, $B0$, $E0$ and $H0$ are determined.</td>
</tr>
<tr>
<td>FCE</td>
<td>This function describes the equations needed to calculate the fraction of active components $XH$ and $XM$ in the aqueous phase.</td>
</tr>
<tr>
<td>DMODEL</td>
<td>When $MODV = 2$, this function calculates the fraction of 'free' dimeric extractant in the organic phase, using the dimer model. Requires $R$, $HRT$ and $K22$.</td>
</tr>
</tbody>
</table>
### TABLE C.1.3:
The Information Required to Run the Program Interactively

<table>
<thead>
<tr>
<th>Order of DATA Input</th>
<th>Variable</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ITEXT</td>
<td>A character variable of length 60. Used to give a title to the optimisation run, for identification purpose.</td>
</tr>
<tr>
<td>2 (i)</td>
<td>N</td>
<td>Number of experimental data points; must be equal to or be less than 80.</td>
</tr>
<tr>
<td>2 (ii)</td>
<td>KK</td>
<td>Number of parameters to be optimised. Its range of values is $2 &lt; KK &lt; 7$.</td>
</tr>
</tbody>
</table>
| 2 (iii)             | IST     | A flag for statistical calculations:  
|                     |         | 1 for statistical calculations to be performed on the optimised parameters.  
|                     |         | 0 when no statistical calculations required. |
| 3                   | BET1    | Formation constant of the metal sulphate. |
| 4                   | MOD     | A character variable of length 10. Used to select the mode required. It can have the 'value' of 'D2EHPA' or 'D2EHDTDA' only:  
|                     |         | 'D2EHPA' - when D2EHPA model required; then MODV = 2.  
|                     |         | 'D2EHDTDA' - when D2EHDTDA model required; then MODV = 1. |
| 4a                  | K22     | The dimerization constant in the organic phase model. Only asked for when MOD = 'D2EHPA'. |
### TABLE C.1.3.: Continued...

<table>
<thead>
<tr>
<th>Order of DATA Input</th>
<th>Variable</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>BET2</td>
<td>The extraction constant.</td>
</tr>
<tr>
<td>6</td>
<td>B(I)</td>
<td>The parameter values; KK long. On 1st. entry contains initial guesses and on final exit contains optimised parameters.</td>
</tr>
<tr>
<td>7</td>
<td>BMN(I)</td>
<td>Lower bounds of parameters; KK long.</td>
</tr>
<tr>
<td>8</td>
<td>BMAX(I)</td>
<td>Upper bounds of parameters; KK long.</td>
</tr>
<tr>
<td>9</td>
<td>BV(I)</td>
<td>Code for parameter type; KK long.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>= 0 if B(I) is not variable,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>= 1 if B(I) is variable and numerical derivatives are to be used.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>= -1 if B(I) is variable and analytical derivatives are to be used, (subroutine DERIV is required).</td>
</tr>
<tr>
<td>10 (i)</td>
<td>FNU</td>
<td>(Nu) factor (set to 10.0 if 0).</td>
</tr>
<tr>
<td>10 (ii)</td>
<td>FLA</td>
<td>(lambda) factor (set to 0.01 if 0).</td>
</tr>
<tr>
<td>10 (iii)</td>
<td>TAU</td>
<td>(tau) factor (set to 0.001 if 0).</td>
</tr>
<tr>
<td>10 (iv)</td>
<td>EPS</td>
<td>(eta) factor (set to 0.00002 if 0).</td>
</tr>
<tr>
<td>10 (v)</td>
<td>PHMIN</td>
<td>Cut off point for recalculating Jacobian matrix, usually set to 0.</td>
</tr>
</tbody>
</table>

**Note:** The variables 10 (i) to 10 (v) are factors in the Marquardt's optimisation method and are usually assigned the value of zero so that the default values in subroutine BSOLVE are used.
### TABLE C.1.4.:

The Information Acquired Through the File 'DATA' by the Program FLUXM.

<table>
<thead>
<tr>
<th>Order of DATA Input</th>
<th>Variable</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NS</td>
<td>- The number of experimental points to be read. Must be less than 80.</td>
</tr>
<tr>
<td>2 (i)</td>
<td>CAP(I)</td>
<td>- The concentration of the extractant in the organic phase.</td>
</tr>
<tr>
<td>2 (ii)</td>
<td>CBP(I)</td>
<td>- The concentration of the metal in the aqueous phase.</td>
</tr>
<tr>
<td>2 (iii)</td>
<td>CHP(I)</td>
<td>- The concentration of the $H^+_{(aq)}$ ions in the aqueous phase.</td>
</tr>
<tr>
<td>2 (iv)</td>
<td>CEP(I)</td>
<td>- The initial concentration of the metal-complex.</td>
</tr>
<tr>
<td>2 (v)</td>
<td>FLM(I)</td>
<td>- The measured flux based on the metal; in kmol/m²s.</td>
</tr>
</tbody>
</table>

**Note:** The variables 2(i) to 2(v) are read in NS times. Thus, for a given value of I the variables corresponds to a given experimental run. All concentrations are in kmol/m³.