THE SOLVENT EXTRACTION OF COPPER

WITH TRI-N-OCTYLAMINE

by

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ABSTRACT

The extraction of copper (11) by tri-n-octylamine from aqueous solutions containing LiCl, HCl and $CaCl_2$ has been studied.

Effects of aqueous phase chloride concentration, metal concentration and the presence of ferric and ferrous iron on extrability of copper were studied experimentally.

The first stability constant of copper-chloro complex K_1 in solutions of LiCl has been calculated from spectrophotometric data.

Molecular weight measurements were carried out to obtain information about aggregation of TOAHCl and extracted metal-amine complexes and the dimerization constant was calculated from experimental data.

The behaviour of water during the extraction of copper has been studied by the Karl Fischer titration method.

page	line	corrected
2	1 from above	chloride
12	7 from above	slope 1.6129
14	13 from above	a_w^h = activity of water
14	3 from below	at low concentrations $(S)^x$ can be taken as unity, then D_{Cu} becomes ...
18	4 from below	$\log D_{Cu} = \text{const.} + n \log \text{TOAHCl}$
21	15 from above	combine
43	3 from below	while the excess TOAHCl is unhydrous.
76	4 from below	curve
78	5 from above	$Cu^{2+} + Fe^{2+} + 2Cl^- + 3H_2O \quad CuCl_2^- + Fe(OH)_3 + 3H^+$
80	7 from above	TIOA
82	1 from below	aqueous

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CHAPTER 1

INTRODUCTION

This thesis is concerned with the extraction of copper from chloric solutions by tri-n-octylammonium hydrochloride. The chemistry of the solvent extraction of copper is of particular importance and the possibility of obtaining very pure copper from low grade ores or its separation from other metals has been studied by a number of workers. Solvent extraction methods of recovering copper are already in use commercially.

The first part of the present work involves experiments done to investigate the effect of aqueous chloride concentration on the distribution of copper. For this purpose LiCl, HCl and $CaCl_2$ were used as supporting electrolytes. The effects of metal concentration and amine concentration have also been studied.

Analysis of the experimental data indicated that the behaviour of the system was not simple. In order to get more information concerning the copper-chloride species present, spectrophotometric analysis was carried out for aqueous phases. Experiments showed that the system was very complicated. Only the first complexing constant could be calculated.

The behaviour of the amine in the organic phase was studied by measuring molecular weights. Aggregation of the amine salt and amine-copper complex was also studied using the technique of vapour pressure osmometry.

Experiments were also carried out to determine the behaviour of water during the extraction process. This was done by measuring the water contents of various organic solutions which were obtained by extraction of aqueous phases with different metal and chloride concentrations. Effects of other salts on water extraction were also shown.

Finally, the extraction behaviour of copper in the presence of ferric and ferrous ions was studied. Reverse effects of ferric and ferrous ions on the distribution of copper were observed.

Each chapter contains experimental technique, results and a discussion of results by comparing with literature data. Since a literature survey is included in each chapter for that particular part of the study, it was thought that presenting a literature survey as a whole was unnecessary.

CHAPTER 2

SOLVENT EXTRACTION OF COPPER FROM CHLORIDE SOLUTIONS

In the section below, the extraction of copper from three different aqueous chloride solutions, HCl, LiCl and $CaCl_2$ is described.

First of all, dependence of distribution of copper on the chloride concentration of the aqueous phase was examined in each case and compared.

Secondly, in LiCl aqueous solutions only, copper concentration was varied, and at the full loading of the organic phase, the copper:chloride ratio of the organic complex was determined.

In the third and last part of the experiment, LiCl was used as a supporting electrolyte once again, aqueous phase copper and chloride concentrations were kept constant and the amine concentration was varied in order to see the effect of organic phase concentration on the distribution of copper.

From all experimental results, the copper-amine complex formed in the organic phase was determined.

Materials

Lithium chloride

The stock solution of lithium chloride was prepared by dissolving

lithium carbonate in 10.0M HCl until the reaction was complete. Then the residue was filtered off and the LiCl solution was standardized. The chloride content of the solution was determined by Volhard's method. The lithium content was determined by Atomic Absorption Spectrometry (A.A.). The lithium content of the stock solution was 8.973M and the chloride content was 8.967M.

Cupric Chloride

The cupric chloride stock solution was prepared by dissolving hydrated $CuCl_2$($CuCl_2.2H_2O$ = 170.48) in distilled water. The concentrated cupric chloride solution was standardized by A.A. and was found to contain 124g/l Cu^{2+}.

Tri-n-octylamine

The purity of the tri-n-octylamine (TOA) was measured by potentiometric titration using standard HCl. The theoretical molecular weight of TOA is 353. Experimental results gave a value of 363.9 which indicated the presence of -small amounts of impurities.

0.1M stock solution of TOA in A.R. Benzene was prepared and standardized by potentiometric titration with standard HCl.

Calcium Chloride

To prepare 6M calcium chloride stock solution, the required amount of dried $CaCl_2$(M = 110.99, purity min.85%, 0.05% sulphate, 0.02% Fe) was dissolved in distilled water, filtered and standardized by A.A. The strength of the $CaCl_2$ solution was 5.925M.

Tri-n-octylamine Hydrochloride (TOAHCl)

0.1M tri-n-octylamine solution was equilibrated with 0.2M HCl by shaking equal volumes of TOA and HCl in a 1 litre separating

funnel for 5 minutes and separating the organic phase.

Experimental Technique

All distribution experiments were carried out batchwise in triplicate. In each case, 10ml of aqueous and 10ml or organic solution were shaken by an automatic shaker for two minutes in 50ml separating funnels. Experiments showed that equilibrium was reached in one or two minutes. When complete settling had been achieved the organic and aqueous phases were separated and the organic phase was stripped with an equal volume of distilled water.

Both organic phase strip and aqueous phase copper concentrations were analysed for copper by A.A.

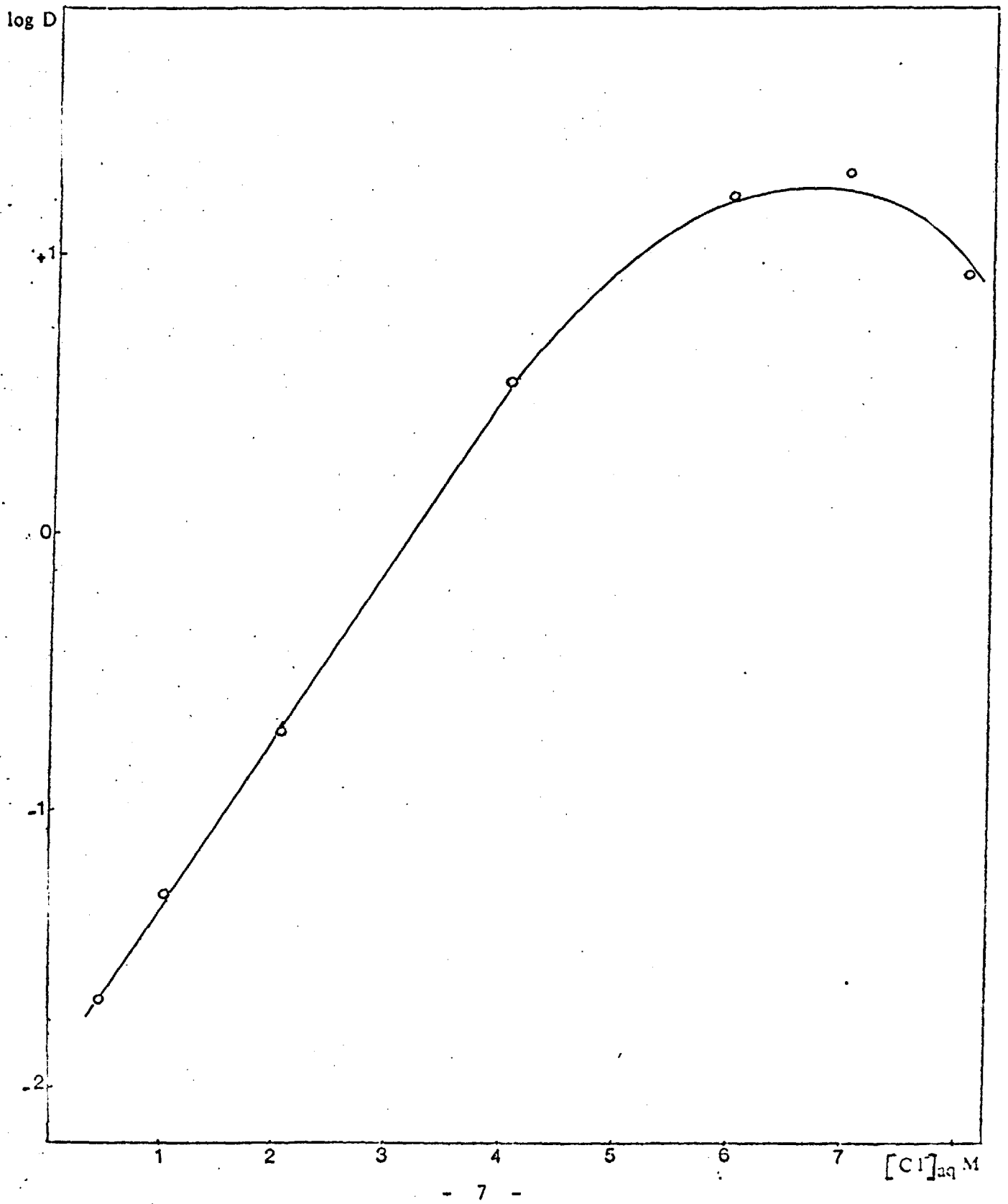
2.1a: Extraction of copper from HCl solutions

The extraction of trace copper from hydrochloric acid solutions by 0.103M TOAHCl in benzene was determined. To observe the effect of aqueous phase chloride concentrations on the distribution coefficient of copper, the copper concentration was kept constant, at 0.01g/l, while the chloride concentration was varied from 0.5 to 8.0M. Extraction results are presented in figures (Table 2.Ia) and as a graph of log of the distribution coefficient (D) of copper against chloride molarity (Figure 2.Ia). As shown in the graph, the distribution coefficient increases linearly from 0.5M up to 4.0M and then passes through a maximum at 7.0M HCl.

2.Ib: Extraction of copper from LiCl solutions

Further experiments were carried out using aqueous solutions containing various concentrations of lithium chloride.

Figure: 2.Ia



In this part of the study the copper concentration was 0.01g/l and the organic phase 0.103M amine. Experimental results are shown in Table(2.I.b) and again log D_{Cu} values were plotted against chloride concentrations. As can be seen from Figure 2.I.b, at small concentrations of LiCl, approximately up to 2M, log D_{Cu} increases smoothly but non-linearly. With a further increase of molarity, complete linearity in the working range is observed.

2.I.c: Extraction of copper from $CaCl_2$ solutions

Six aqueous solutions were prepared containing 0.0095g/l Cu^{2+}, 0.1M HCl and 0.45, 0.95, 1.45, 1.95, 2.45 and 2.95M $CaCl_2$. Organic phase strength, as in the previous experiments, were kept at 0.103M. Extraction results are shown in Table(2.I.c.)

The distribution coefficient of copper, as will be discussed later, is lower than in the HCl and LiCl systems. D_{Cu} increases linearly between 2M and 6M calcium chloride.

2.11. Variation of the copper concentration

In the previous experiments, it was observed that the extraction of copper from aqueous solutions containing LiCl gave the highest distribution coefficients, and phase separation was also quicker in the LiCl system. This led to the use LiCl as a supporting electrolyte in most subsequent work.

To investigate the influences of copper concentration in the aqueous solution on the extractive capacity of the organic phase, and to obtain the highest distribution conditions, aqueous solutions were prepared containing 5.9M LiCl and 0.1M HCl. Nine aqueous solutions were prepared containing copper between

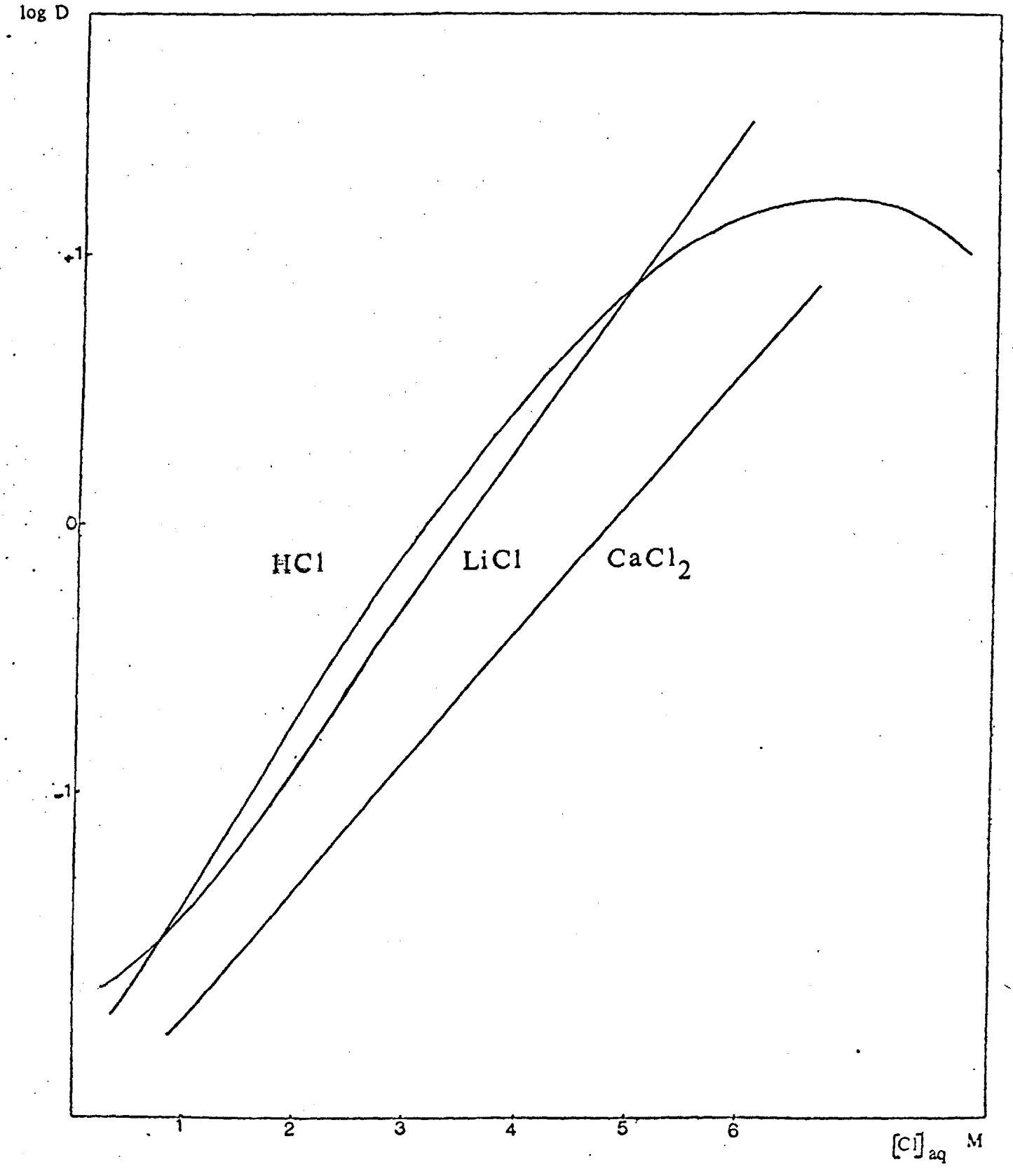


Figure: 2.Ib,c

1.2 - 23.6g/l, and copper was extracted by 0.103M TOAHCl in benzene in each case.

An extraction isotherm is presented in Figure 2 11, where organic phase Cu^{2+} concentrations are plotted against aqueous phase Cu^{2+} concentration. The results are given in Table 2 11. The horizontal part of the curve indicates that the organic phase is fully loaded with copper and this occurs at 2.6g/l or 0.0409M. Thus, the copper:amine molar ratio was obtained at full loading which is equal to 1:2.5207.

In order to determine what type of metal-amine organic complex was formed, the chloride content of the organic phase was analysed by Volhard's Method. 2ml portions of organic phase were stripped by dilute HNO_3 and 20ml portions of the aqueous solution obtained were titrated by NH_4CNS in the presence of 25ml of 0.103M $AgNO_3$, 5ml 6M HNO_3, 2ml nitrobenzene and 1ml ferric alum as an indicator.

Experimental results and calculations showed that the total chloride concentration in the organic phase is 7.97915g/l or 0.22502M. Therefore the Cu:chloride ratio is 1:4.7673 and as was calculated before the copper:amine ratio is 1:2.5207. Combining these two experimental results, the copper-amine complex formed in the organic phase is

$$\overline{(TOAH)_2\ CuCl_4 .\ 0.52(TOAHCl)}.$$

2.111. Variation of the amine concentration of the organic phase

The effect of amine concentration of the organic phase on the extraction of copper from LiCl solutions was investigated.

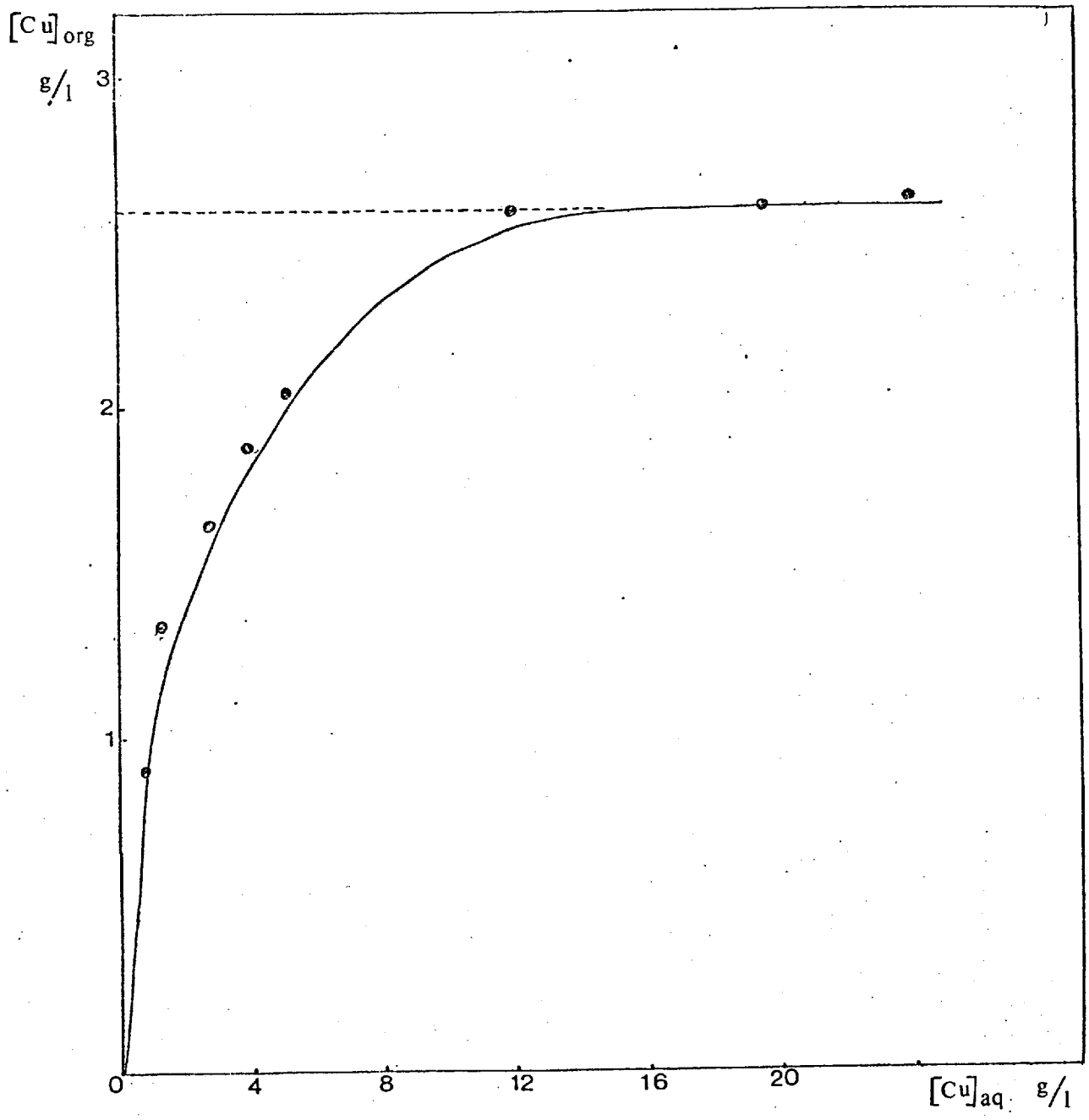


Figure: 2 II

For this purpose 7 different organic solutions were prepared containing 0.1, 0.075, 0.050, 0.025, 0.010, 0.0075 and 0.0050M amine, and an aqueous solution with 5.9M LiCl, 0.1MHCl and 0.010g/l copper. When log D_{Cu} values are plotted against log TOAHCl M, where TOAHCl is the total amine concentration of the organic phase, as is shown in Figure2.11, the results lie on a straight line with a slope 1.3064.

2. 1V. Discussion

In this chapter, the distribution coefficient of copper has been examined and the dependence of D_{Cu} on the type of supporting electrolyte and the ligand concentration of the aqueous phase, as well as the amine concentration or organic phase has been analysed.

In amine extraction systems, the distribution ratio generally depends on the composition of the aqueous phase and association of the amine salt.

General distribution coefficient functions have been put forward by Marcus and Kertes[1], Schmidt[2], Fomin[3], Ipenburg[4] and others. All of them are of the same opinion concerning dependence of D_M upon the aqueous phase metal concentration, ligand concentration, activity of the extractant, hydration of the organic complex, and the activity coefficient changes of the aqueous phase in the presence of various supporting electrolytes. D_M usually increases with increasing aqueous phase metal concentration. In some cases, however, the decrease of D_M is due to polymer formation in the aqueous phase[3].

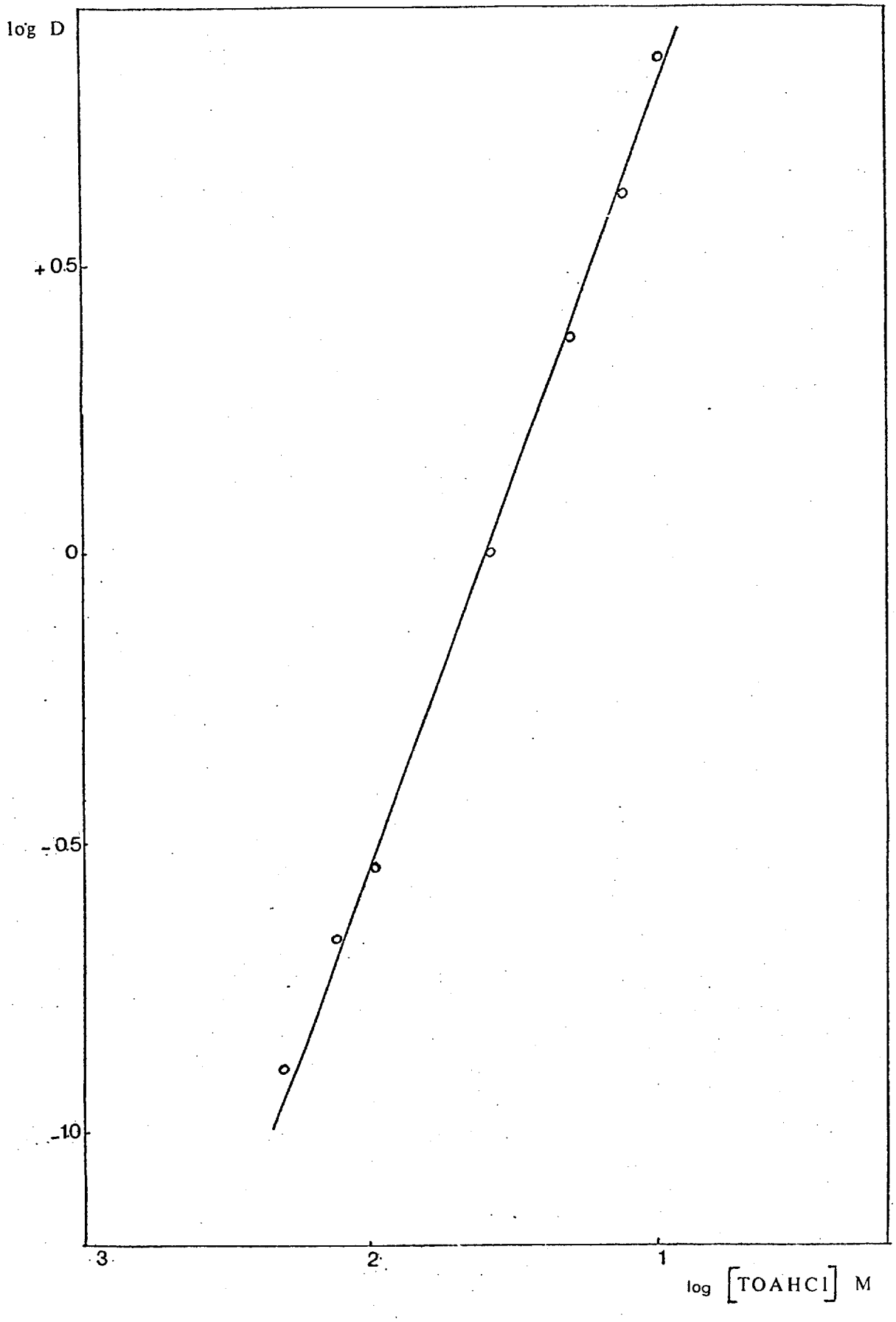


Figure: 2 III

In the section above, we only concentrated upon the effects of anion concentration of aqueous phase, different supporting electrolytes (HCl, LiCl, $CaCl_2$) and amine concentration on the change of distribution of copper.

The distribution coefficient is defined as

$$D = \frac{[\text{Metal}]_o}{[\text{Metal}]_{aq}}$$

In the simplest case when the aqueous phase contains only the metal salt MA_n, the extractant S and the organic complex formed $MA_m \times S$, then D_M can be written as [3]

$$D_M = K[A]^m(S) \times \frac{f^{m+1}}{fo} \quad a_w^h$$

where fo = activity coefficient of the organic complex

f^{m+1} = activity coefficient of the metal in the aqueous phase

a_w^h = activity coefficient of the water in the aqueous phase

K = equilibrium constant.

From this expression, it can be seen that D_M is directly proportional to the concentration of the anion raised to a power equal to the number of anions in the extracted species. It is also dependent on the activity of the extractant and on the activity coefficients of the metal in the aqueous and the organic phases. However, at tracer metal extractions, activity coefficients in both phases can be taken as unity. If the organic phase concentration is kept constant, D_M becomes[3]

$$D_M = K[A]^m[M]^m . \; f_{\pm}^{m+1} \; a_w^h .$$

In the presence of other salts or supporting electrolytes, this becomes

$$D_M = ([A_1][M_1] + [A_2][M_2])^m \gamma^{m+1} \cdot a_w^h$$

where M_2 is the concentration of supporting electrolyte. As will be seen, salting-out agents having the anion in common with the extractable metal salt increase the distribution ratio by increasing the concentration of anions in the aqueous phase. This might suggest that different supporting electrolytes at equivalent concentrations should have the same effect.

The reason for different effects of the salting-out agents lies in the activity coefficient changes entering into the D_M equation. Activity coefficients in the presence of other salts depend on the nature of the second salt, its ionic strength and also the total ionic strength. If the ionic strength of the added salt is I_n and γ_a and γ_b are the activity coefficients of metal in the presence of salting-out agent and the absence of salting-out agent, the relation $\frac{1}{2}(\log \gamma_a - \log \gamma_b) = \delta_n \cdot I_n$ holds δ_n = Harned coefficient.

Rozen[5] suggests that one of the reasons for variation of the activity coefficient in the aqueous phase is the varying hydration of the electrolyte which results in the variation of the water activity and the activity of the metal salt.

From experimental results, the plot of $\log D_{Cu}$ against $\log[Cl^-]$ shown in Figure 2.1V.1, the distribution of copper, when it is extracted from LiCl, HCl and $CaCl_2$ solutions, increases linearly with a positive slope up to 4M chloride concentration. The first thing to be noted is the decrease of D_{Cu} in the HCl system when chloride concentration is increased to 7-8M. When this is compared with Sato's results in which 0.1g/l Cu^{2+} was

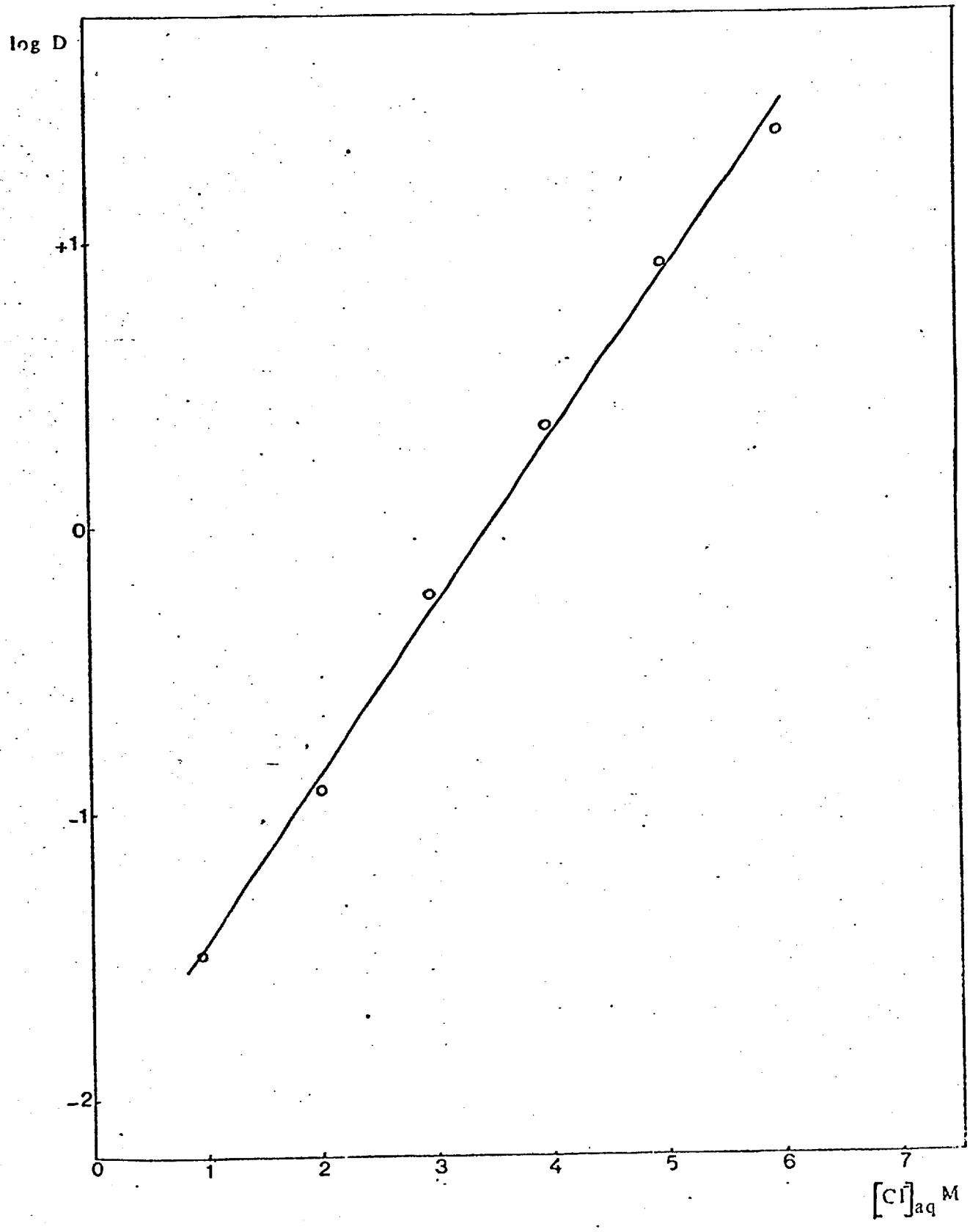


Figure: 2.1V 1

extracted from HCl and LiCl solutions by 0.1M TOA in benzene, the graphs are almost identical.

The "HCl effect" of the appearance of a maximum in the extraction isotherms, is usually attributed to the interaction of the co-extracted acid with the amine hydrochloride to form the HCl_2^- anion on the assumption that the latter is taken up preferentially by the ammonium cation. Another possibility would be the lack of dissociation of the protonoted anioic chloro-metalate in concentrated HCl solutions, in contrast to the alkali salt of the chlorometal acid.

In Figure 2.1V.2, the extraction percentage of Cu is plotted against aqueous phase chloride concentrations for each case in order to see clearly the effect of supporting electrolytes on extraction. A LiCl solution gives the highest extraction, 98% at 6-7M strengths.

Table 2.1V.1 shows the water activities in various aqueous solutions of HCl, LiCl and $CaCl_2$. (6)

M	HCl	LiCl	$CaCl_2$
0.5	0.9824	0.9826	0.9751
1.0	0.9625	0.9632	0.9430
2.0	0.9136	0.9168	0.8492
3.0	0.8524	0.8588	0.7131
4.0	0.7808	0.7888	0.5517
5.0	0.7000	0.7078	0.3936
6.0	0.614	0.6190	0.2790
7.0	0.524	0.526	0.2030
8.0	0.438	0.435	

Table 2.1V.1

In general, water activities at equal chloride concentrations are almost the same in HCl and LiCl solutions, but in $CaCl_2$ solutions they are relatively lower.

The third section of this chapter deals with the effect of

amine concentration on the distribution of copper. As was mentioned previously the distribution coefficient depends on the composition of the aqueous phase and the association of the extractant, the amine salt. There are three possibilities when amine salts are used as extractants.[2] The amine salt may not be associated at all; association is insignificant which means that each molecule reacts independently of others, or association occurs. If there is no association occurring, the extraction reaction can be expressed as

$$Cu^{2+} + 2\ Cl^{-} + n\ \overline{(TOAHCl)} \rightleftharpoons \overline{(TOAH)_n\ (CuCl_{2+n})}$$

assuming the ratio of activity coefficient of the metal complex to the activity coefficient of the amine salt remains constant, the equilibrium constant for this reaction

$$K_{Cu} = \frac{\left[(TOAH)_n\ (CuCl_{2+n})\right]_o}{\left[Cu^{2+}\right]_a \left[Cl^{-}\right]^2_{aq} \left[TOAHCl\right]^n_o \ (\gamma^{\pm}_{CuCl_2})^{2+1}}$$

and $$D_{Cu} = \frac{\left[(TOAH)_n\ (CuCl_{2+n})\right]_o}{\left[\sum Cu^{2+}\right]_{aq}}$$

where $\gamma^{\pm}_{CuCl_2}$ = average ionic activity coefficient of the metal salt in the aqueous solution.

$$D_{Cu} = K_{Cu} \left[Cl^{-}\right]^2_{aq} \left[TOAHCl\right]_o \ (\gamma^{\pm}_{CuCl_2})^{2+1}$$

If the composition of the aqueous phase is kept constant, this becomes

$$\log D_{Cu} = \text{const} + n \left[TOAHCl\right]_o$$

When $\log D_{Cu}$ is plotted as a function of amine hydrochloride concentration, the resulting graph should be linear with a slope equal to n. The n value from our experimental results as shown in

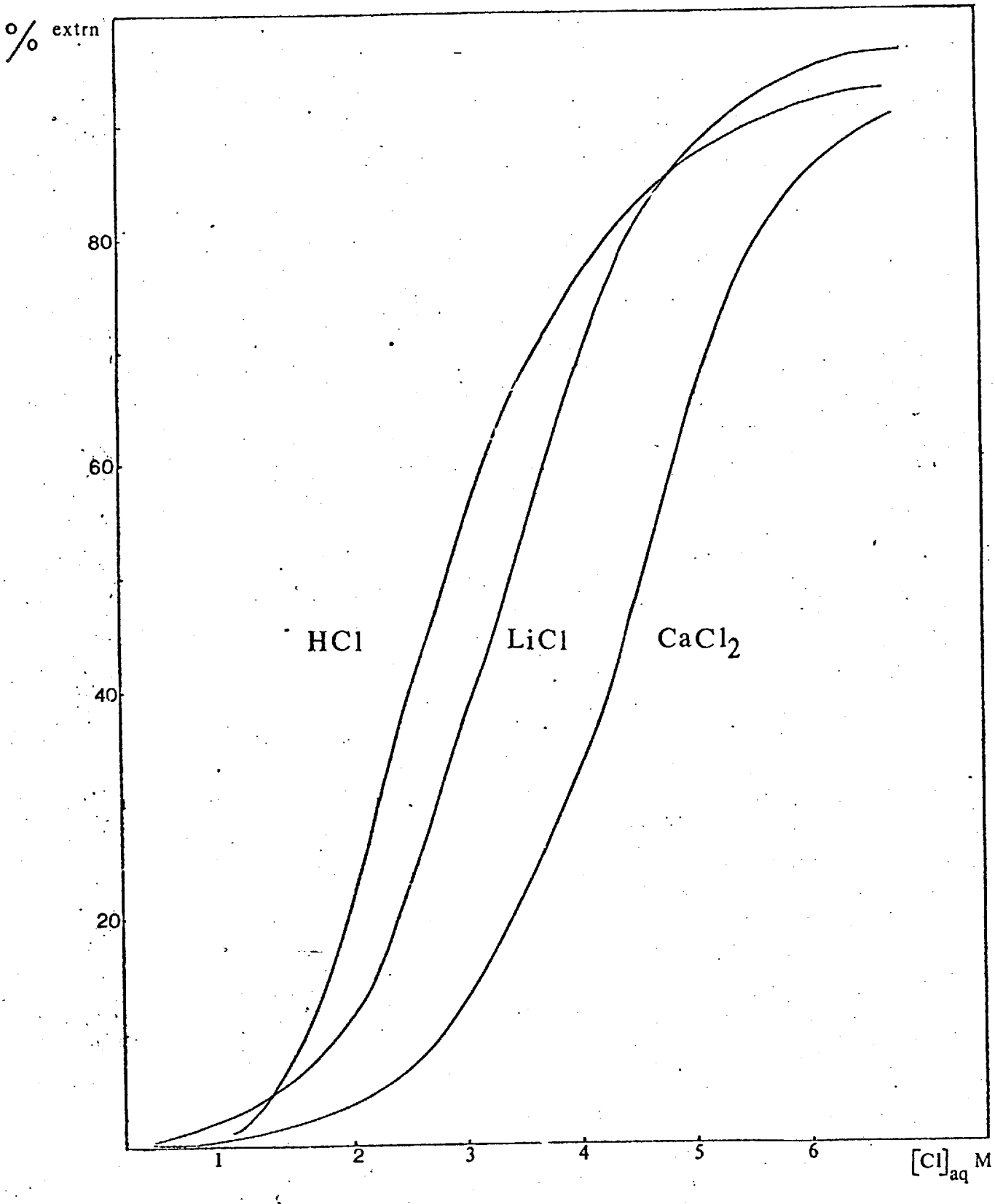


Figure 2.1V 2

Figure 111 is 1.3064.

The extraction reaction of copper from chloride solutions by TOAHCl is given by Sato[7] and Ramazanova[8] as

$$Cu^{2+} + 2Cl^- + 2\,\overline{TOAHCl} \rightleftharpoons \overline{(TOAH)_2\,CuCl_4}$$

It was also shown experimentally that the Cu:amine ratio of the organic complex was 1:2.5307 suggesting that at least two amine molecules are reacting with Cu^{2+}. Therefore the plot of log D_{Cu} against log TOAHCl should give a slope, or n value, equal to 2. This difference suggests association of the amine salt and this will be discussed in Chapter 5.

The above relationship changes if the amine salt is associated, because the equilibrium reaction will be

$$Cu^{2+} + 2Cl^- + n\,\overline{(TOAHCl)_p} \rightleftharpoons \overline{(TOAH(TOAHCl)_{p-1})_n(CuCl_{2+n})}$$

where p is the degree of association of the amine salt. The distribution coefficient for this reaction will be

$$D_{Cu} = K_{Cu}\,[Cl^-]^2\,[(TOAHCl)_p]^n\,(\gamma^{\pm}_{CuCl_2})^{2+1}$$

$$\log D_{Cu} = \text{const.} + n \log[(TOAHCl)_p]$$

Thus, the plot of log D_{Cu} against the logarithm of the analytical concentration of the amine salt does not denote the number of amine salt molecules but the number of associates of these molecules taking part in the extraction reaction.

In Section 11 the amine-copper complex formed was determined by calculating the metal:amine:chloride ratios and it was found to be 1:2.5207:4.7673 which suggests the formation of complex

$$\overline{(TOAH)_2\,CuCl_4 .\ 0.52(TOAHCl)}.$$

This result partially agrees with Ivanova's[9] and Lindenbaum's[10] work of extraction of Cu^{2+} from HCl solutions by TOA and TlOA. They probably did not take into account the association of the organic phase and reached the conclusion that the Cu-amine complex was in the form of $\overline{(TOAH)_2CuCl_4}$. Their spectrophotometric analysis of organic phases confirms the presence of $CuCl_4^-$ ions.

Sato[7], by spectrophotometric analysis found the Cu:amine:chloride in the molar ratio 1:2:4 i.e. $(TOAH)_2$ or $(TOAHCl)_2$ and he gave an equilibrium expression for the reaction of the organic species with a neutral cupric chloride molecule as

$$CuCl_2 + 2\ \overline{(TOAHCl)} \rightleftharpoons \overline{(TOAH)_2CuCl_4}.$$

On the other hand, Ramazanova[8], from his experimental results, and a rectilinear relationship between log D_{Cu} and log TOAHCl with a slope 2 suggests that two amine molecules combines with $CuCl_4^{-2}$ ion according to the reaction

$$CuCl_4^{2-} + 2\overline{(TOAHCl)} \rightleftharpoons \overline{(TOAH)_2CuCl_4} + 2\ Cl^-$$

From our experimental results and analysis, assuming that the only extractable species in the aqueous phase are $CuCl_4^{2-}$ ions, the extraction reaction can be expressed by the equation

$$CuCl_4^{2-} + 2.52\ \overline{(TOAHCl} \rightleftharpoons \overline{(TOAH)_2CuCl_4.0.52\ TOAHCl}$$

There are, of course other factors affecting the organic complex formation and the whole extraction process such as the possibility of co-extraction of water, association of the organic complex and the presence of other extractable anions in the aqueous phase which will be discussed in following chapters.

CHAPTER 3

SPECTROPHOTOMETRIC ANALYSIS OF THE AQUEOUS PHASE

The object of spectrophotometric analysis of the aqueous phase was to obtain further information on the various copper chloride complexes which existed in the solution. Absorption spectra of LiCl, HCl and $CaCl_2$ solutions were obtained. Then we calculated the extinction coefficients and attempted to calculate the complexing constants.

Materials

Experimental solutions were prepared from standardized cupric chloride, lithium chloride, calcium chloride and hydrochloric acid stock solutions in 25ml standard flasks. Chloride and copper contents of these series of solutions are shown in Table (3.1).

Experimental Technique

Optical density measurements were carried out on a Hilger and Watts Uvispec spectrophotometer. The solutions were held in 0.5cm path length silica cells. In all measurements, the reference solution contained the same LiCl or HCl concentrations as in the sample solution.

Optical densities were measured at 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300 and 310nm wavelengths.

Results

I) Spectra of cupric chloride solutions containing HCl, LiCl:

First of all, the spectrum of $CuCl_2$ solution containing 1 g/l Cu^{2+} was obtained. This was done by plotting wavelengths against optical densities. By the same method, spectra of cupric solutions containing 1.0 M HCl, 0.5 M LiCl and 1 g/l Cu^{2+} were plotted. The results are given in Table (3.1) and in Figure (3.I).

As shown in the Figure, the spectrum of $CuCl_2 - H_2O$ solution consists an absorption band at wavelengths greater than 225nm.

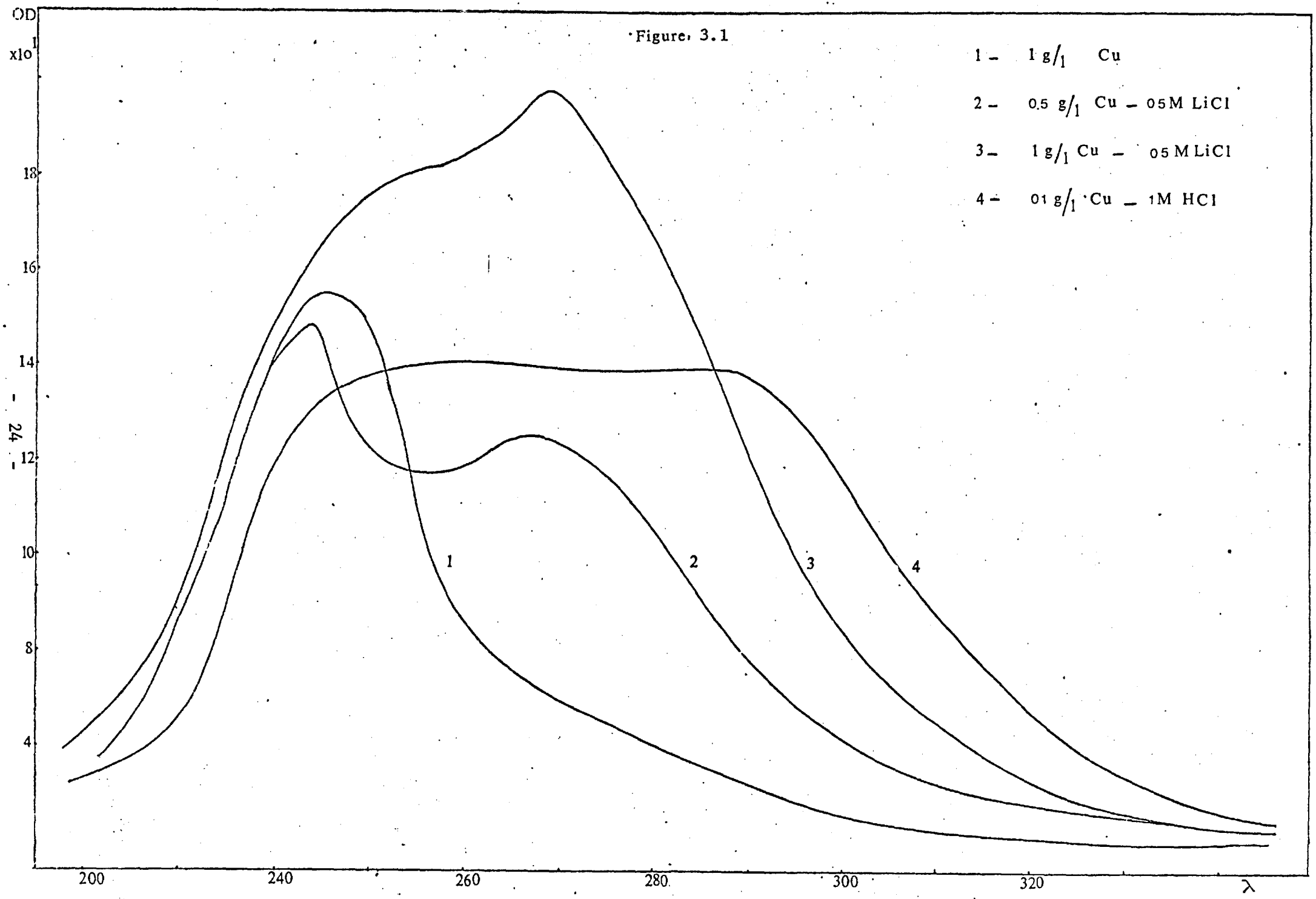
In the presence of additional chloride ions in the aqueous solution the absorption band (which is due to absorption of Cu-Chloride complexes) starting at the wavelength 250nm was also observed. This band is steeper than the previous one. In the spectrum of $CuCl_2 - HCl - H_2O$, it was difficult to identify this band.

The change of optical density with increasing chloride concentration of $CuCl_2 - LiCl - H_2O$ solution is shown in Figure (3.11) and Table (3.1). Spectra of solutions, containing 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0M LiCl all have absorption bands at 220nm and 250nm but maximum points increase with increasing chloride concentration of each solution.

II) Calculation of extinction coefficients:

It was assumed that the optical density of each solution is the sum of the individual optical densities of all the metal complexes in that solution and these optical densities are

Figure. 3.1


OD
x10
18
16
14
12
10
8
4
- 24 -
200
240
260
280
300
320
λ
1 – 1 g/l Cu
2 – 0.5 g/l Cu – 05M LiCl
3 – 1 g/l Cu – 05 M LiCl
4 – 01 g/l Cu – 1M HCl
1
2
3
4

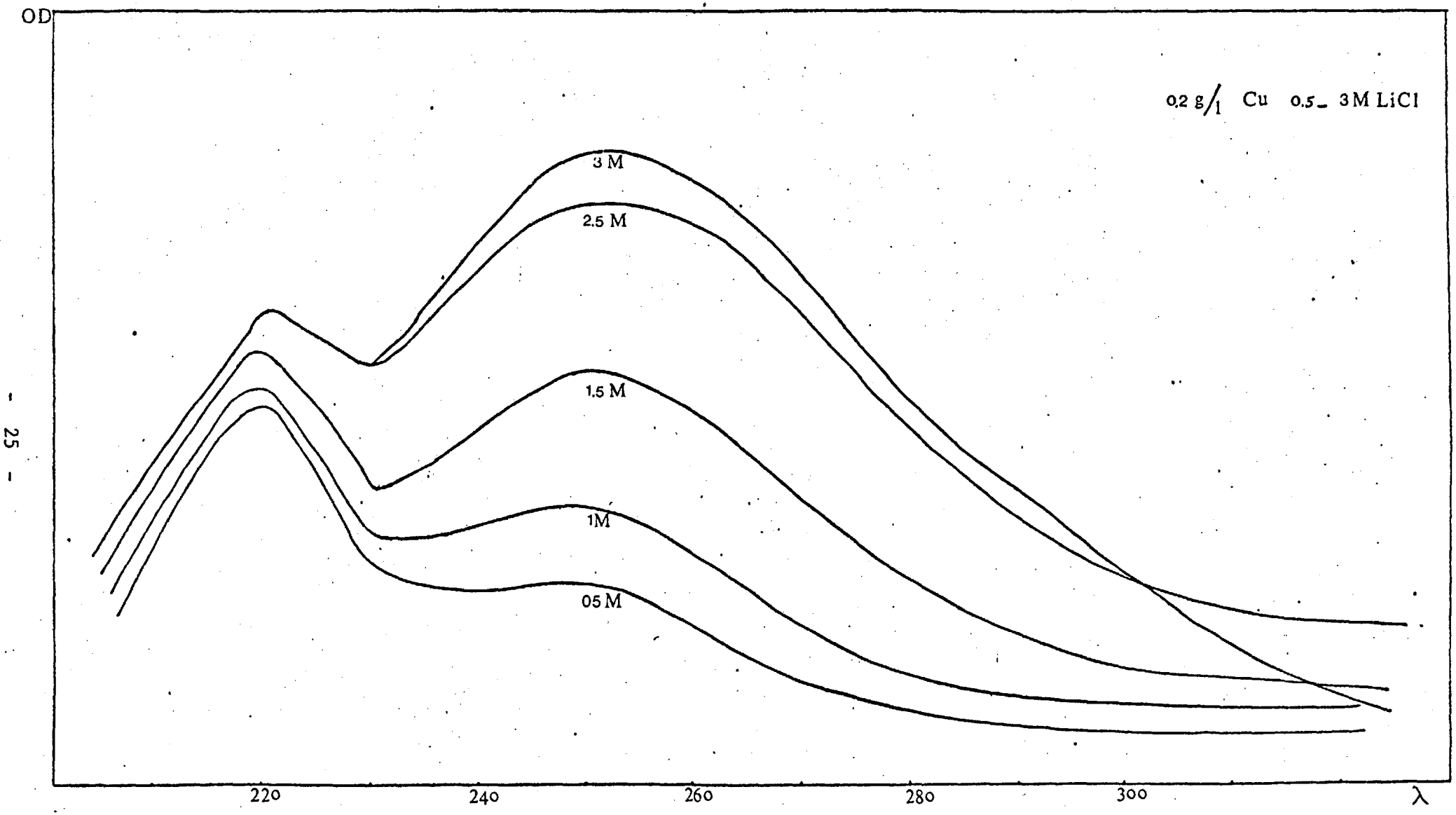


Figure: 3.11

directly proportional to the concentrations of these complexes. The overall molar extinction coefficient of a solution at a particular wavelength is defined as

$$\varepsilon^{\lambda} = \frac{\text{optical density}}{(\text{path length}).\ [Cu]_{total}}$$

ε^{λ} can be defined by the slope of the Beer's Law plot - i.e. optical density against metal concentration. Total optical density, therefore, can be written as follows

$$Cu_{tot}\varepsilon^{\lambda} = \varepsilon_{o}^{\lambda}\left[Cu^{2+}\right] + \varepsilon_{1}^{\lambda}\left[CuCl^{+}\right] + \varepsilon_{2}^{\lambda}\left[CuCl_{2}\right] + \ldots$$
$$= \sum_{0}^{n} \varepsilon^{\lambda}\left[CuCl_{n}^{2-n}\right] \qquad (A)$$

The extinction coefficients of solutions with chloride molarities 1.18 and 1.67 were calculated at the wavelengths between 200 - 310nm. They are shown at Table (3.11)

III) Calculation of the first complexing constant K_1:

The change of extinction coefficients with chloride concentration of aqueous solution is shown in Figure (3.111) for wavelengths 240, 250, 260 and 270nm.

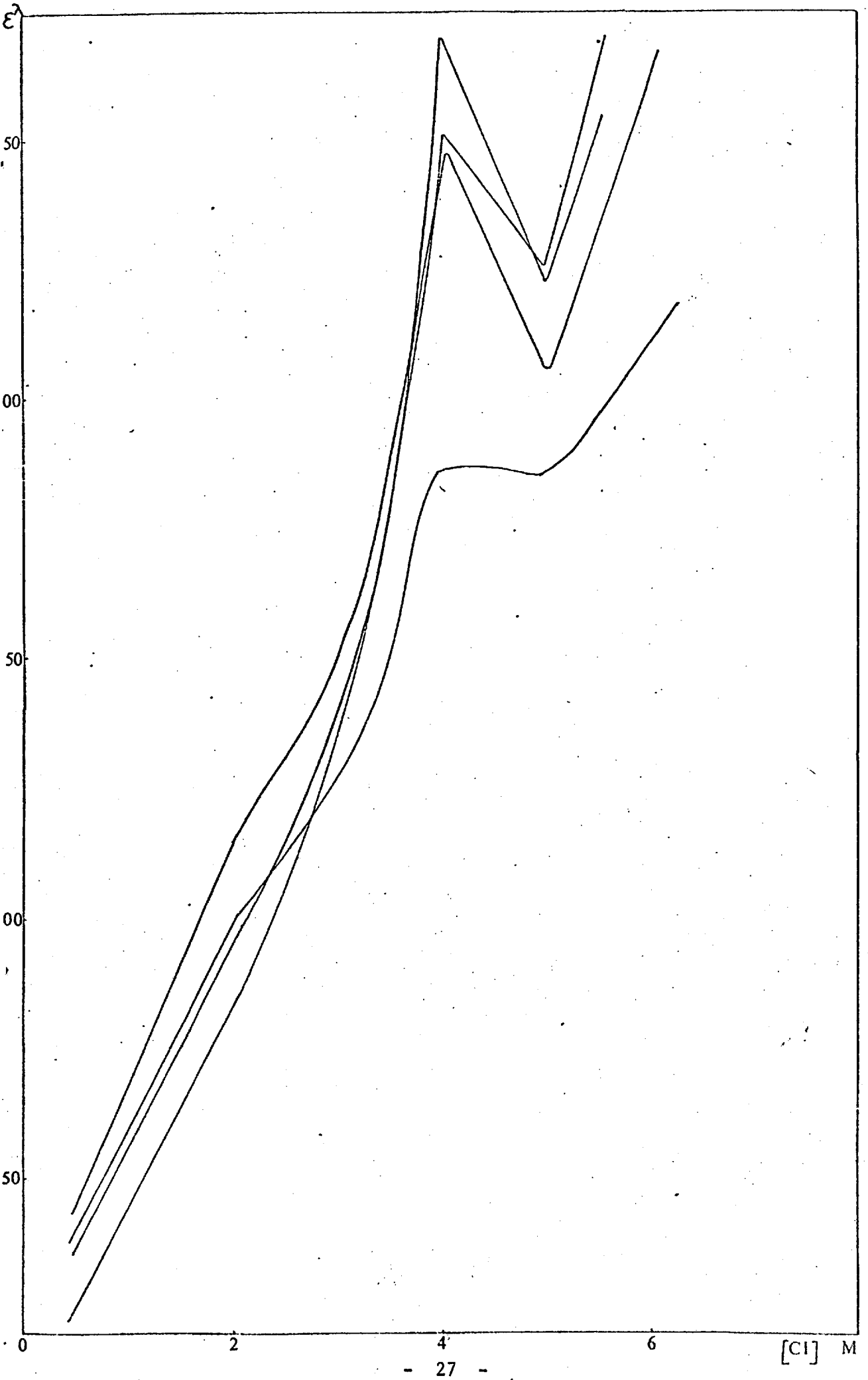
The graph shows linearity up to 2M chloride concentration: if we assumed that only Cu^{2+} and $CuCl^{+}$ ions exist in this region, then we can write an equation by dividing both sides of equation (A) by Cu_{tot}

$$\varepsilon^{\lambda} = \frac{\varepsilon_{o}^{\lambda}\left[Cu^{2+}\right]}{[Cu]_{tot}} + \frac{\varepsilon_{1}^{\lambda}\left[CuCl^{+}\right]}{[Cu]_{tot}}$$

or

$$\varepsilon^{\lambda} = \varepsilon_{o}^{\lambda}\alpha_{o} + \varepsilon_{1}^{\lambda}\alpha_{1} \qquad (B)$$

Figure: 3.111



on the other hand $\alpha_o + \alpha_1 = 1$ (C)

and first complexing constant is given by

$$K_1 = \frac{\alpha_1}{\alpha_o \, a_{Cl}} \quad (D)$$

from (B) and (C), the fraction of first complex is

$$\alpha_1 = \frac{\varepsilon^\lambda - \varepsilon_0^\lambda}{\varepsilon_1^\lambda - \varepsilon_0^\lambda} \quad (E)$$

from (C) and (D) $\alpha_1 = \left[\frac{1}{K_1 a_{Cl}} + 1\right]^{-1}$ (F)

from (E) and (F) $\frac{\varepsilon_1^\lambda - \varepsilon_0^\lambda}{\varepsilon^\lambda - \varepsilon_0^\lambda} = \frac{1}{K_1 a_{Cl}} + 1$

this can be written as a linear function

$$y = mx + n$$

where $y = \frac{1}{\varepsilon^\lambda - \varepsilon_0^\lambda}$, $m = \frac{1}{\varepsilon_1^\lambda - \varepsilon_0^\lambda} \cdot \frac{1}{K_1}$, $x = (a_{Cl})^{-1}$

$n = (\varepsilon_1^\lambda - \varepsilon_0^\lambda)^{-1}$

If y, the change of the extinction coefficient at one particular wavelength is plotted against x, recipical of chloride activity of the aqueous solution slope m and intercept n can be calculated. ε_o^λ was measured in previous experiments. This enables us to calculate ε_1^λ and K_1.

Calculated values of ε_1^λ and K_1 are given below ;

(Figure 3, 1V and V)

λ	ε_1^λ	K_1(mole)$^{-1}$
240	171.4301	0.62
250	180.8181	0.79
260	179.6576	0.64
270	131.0861	0.56

(K_1) average = 0.6525 ~0.65 mole

Figure: 1.V

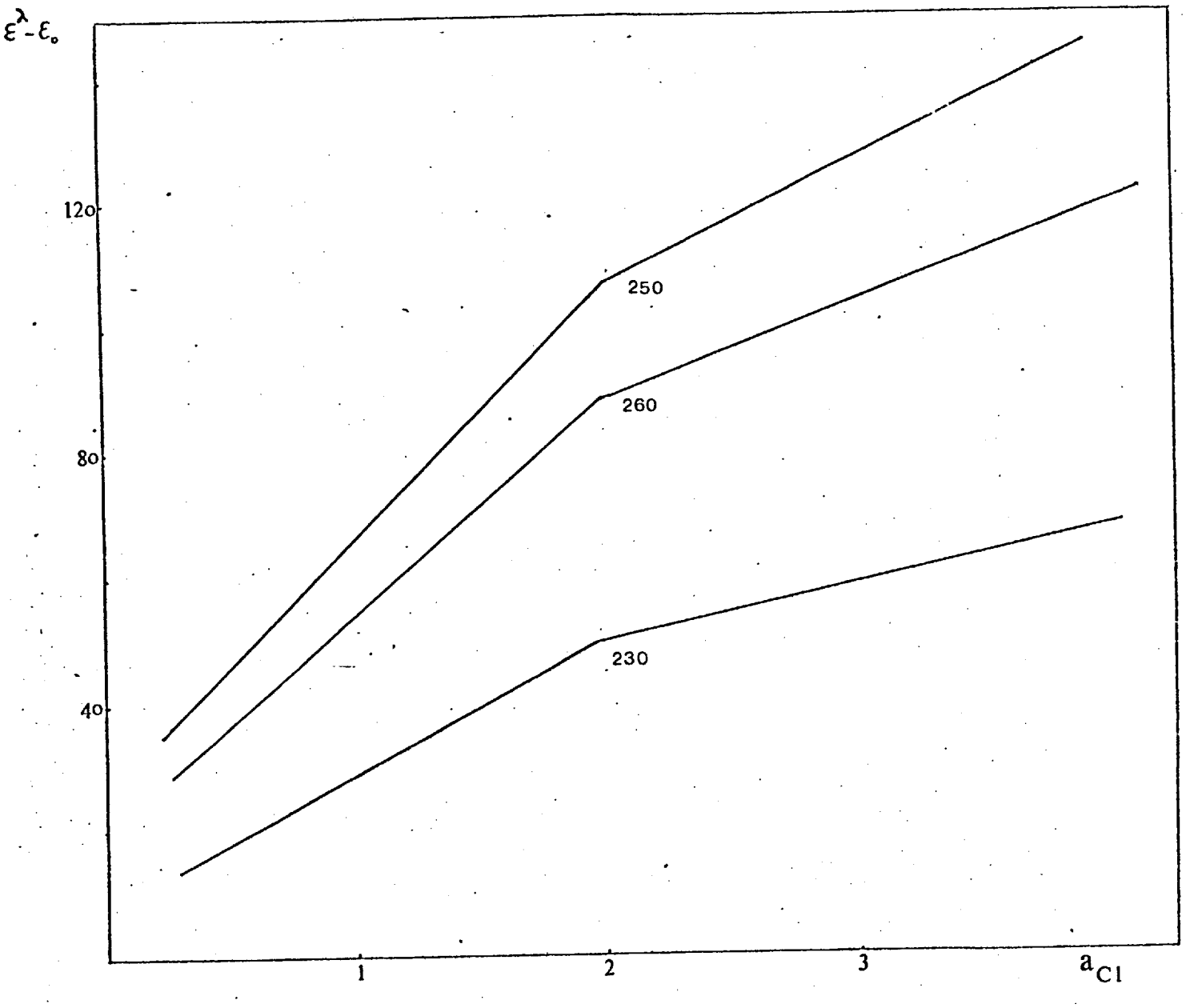
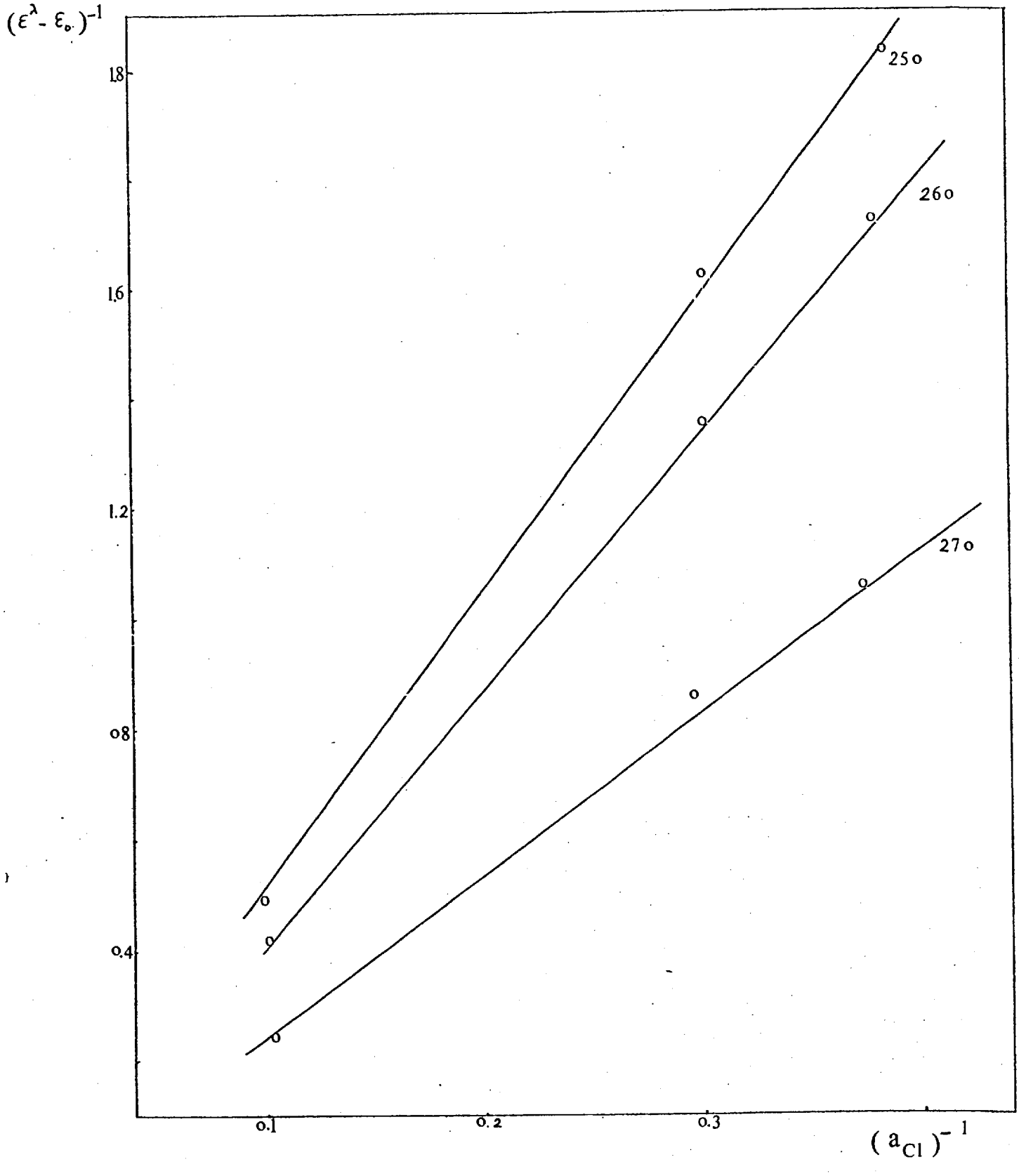

$\varepsilon^{\lambda}-\varepsilon_{\circ}$
120
80
40
250
260
230
1
2
3
a_{Cl}

Figure : 3.VI


$(\epsilon^{\lambda} - \epsilon_o)^{-1}$
1.8
1.6
1.2
0.8
0.4
0.1
0.2
0.3
$(a_{Cl})^{-1}$
25o
26o
27o

IV) Calculation of second complexing constant K_2:

We can again assume that in some range over 2M chloride concentration, the only species contributing the spectra are Cu^{2+}, $CuCl^{+}$ and $CuCl_2$. We can write a similar equation as we did for calculation of K_1

$$\alpha_0 + \alpha_1 + \alpha_2 = 1 \qquad \varepsilon_0^{\lambda} + \varepsilon_1^{\lambda}\alpha_1 + \varepsilon_2^{\lambda}\alpha_2 = \varepsilon^{\lambda}$$

$$K_1 = \frac{\alpha_1}{\alpha_0 a_{Cl}} \qquad K_2 = \frac{\alpha_2}{\alpha_1 a_{Cl}}$$

With combination of these equations, we end up with an expression as follows

$$\frac{\varepsilon^{\lambda} - \varepsilon_0^{\lambda}}{a_{Cl}^2} + \frac{K_1}{a_{Cl}}(\varepsilon^{\lambda} - \varepsilon_1^{\lambda}) = K_1K_2\varepsilon_2^{\lambda} - K_1K_2\varepsilon^{\lambda}$$

or $y = n - mx$

When this equation was used for wavelengths 240, 250 and 260nm and chloride concentrations 2 - 6M, it was observed that the experimental results do not comply with the above equation, and therefore, it was impossible to calculate K_2 and

In this situation either the assumption was wrong or the existence of Cu^{2+}, $CuCl^{+}$ and $CuCl_2$ ions was in such a small range that it was impossible to calculate K_2 with the experimental results.

Attempts were made to calculate K_3 by the same method but again they were unsuccessful.

Discussion

Optical investigation of cupric chloride solutions containing various chlorides were carried out previously by some other workers.

It is known that the colour of a $CuCl_2$ solution changes from blue to green with increasing concentration. Addition of other

chlorides turns the colour of $CuCl_2$ solution into yellow.

All previous workers agree that the complex formation in dilute $CuCl_2$ gives complexes which absorb the ultra violet region. Some workers assumed that the absorption band at about 250nm may be ascribed to tetra-or tri-chloro complexes and displacement of this band with increasing wavelength is probably due to formation of polynuclear complexes.

All investigators assumed the validity of the Mass Action Law.

Miranov[11] determined the stability constants of the inner sphere and outer sphere complexes of the ion $Cu(H_2O)_6^{2+}$ with chloride from the electronic spectra of these compounds. He stated that the change in intensity of the ultraviolet absorption band may result from reactions of two types.

$$\left[Cu(H_2O)_6\right]^{2+} + nCl^- \rightleftharpoons \left[CuCl_n(H_2O)_{6-n}\right]^{2-n} + n\ H_2O$$

$$\left[CuCl_n(H_2O)_{6-n}\right]^{2-n} + mCl^- \rightleftharpoons \left[CuCl_n(H_2O)_{6-n}\right]^{2-n-m}$$

where n and m are the numbers of chloride ions in the inner and outer co-ordination spheres.

Andreev[12] in his study of composition and structure of Cu^{2+} solutions compares the electronic absorption spectra of aqueous solutions with those of crystalline Cu^{2+} complexes of known composition and structure. His study led him to the conclusion that in the $CuCl_2$ - H_2O solution, complex formation takes place as follows:

$$\left[Cu(H_2O)_6\right]^{2+} \longrightarrow \left[CuCl_n(H_2O)_m\right] \longrightarrow \left[CuCl_4(H_2O)_2\right]^{2-}$$

In the case of $CuCl_2$ - HCl - H_2O solutions, formation of these complexes proceeds as

$$\left[Cu(H_2O)_6\right]^{2+} \rightarrow \left[CuCl_n(H_2O)_m\right] \rightarrow \left[CuCl_4(H_2O)_2\right]^{2-} \rightarrow \left[CuCl_6\right]^{4-}$$

The last two complexes have the structure of an orthorombically distorted octahedron and tetragonal bipyramid. He also states that the tetrahedral $CuCl_4^{2-}$ ions are absent from the $CuCl_2$ - HCl - H_2O systems even at limitingly high concentrations of $CuCl_2$ and HCl.

Saposhnikova[13] has also studied the complex formation in Cu^{2+} - HCl - H_2O system. From his observations, he concluded that at lower concentrations of HCl ($5X10^{-3}$ - 0.5M) the spectrum of the system shows an intense absorption band at 250nm due to the lower chloro-complex of copper. When the HCl concentration is increased from 0.5 to 4M, the intensity of optical density increases and the absorption band moves smoothly from 250nm to 275-280nm. This displacement of the absorption band can be explained by the absorption of $CuCl(H_2O)_5^+$, trans $\left[CuCl_4(H_2O)\right]^{2-}$ ions and also intermediate complexes. At high HCl concentrations (5-12M), absorption spectra of solutions show an additional band at 238nm and 385nm. He points out that in this range tetrahedral $CuCl_4^{2-}$ ions are formed. In the study of spectra of solutions containing $CuCl_2$ and 12.5-13M HCl, he observed a sharp decrease in the intensity of the absorption band at 238nm, characteristic of the complex $CuCl_4)^{2-}$.

Bjerrum[14] assumed that the co-ordination number of Cu^{2+} ions remains unchanged and is equal to four, and that the complex

formation takes place as follows:

$$[Cu(H_2O)]^{2+} \rightarrow [CuCl(H_2O)_3]^{+} \rightarrow [CuCl_2(H_2O)_2] \rightarrow [CuCl_3(H_2O)]^{-} \rightarrow [CuCl_4^{2-}]^{2-}$$

The above authors, in contrast to Bjerrum introduce a more complicated scheme of complex formation as given below:

$$[Cu(H_2O)_6]^{2+} \rightarrow [CuCl(H_2O)_5]^{+} \ldots\ldots\ldots \text{ trans-} [CuCl_4(H_2O)_2]^{2-} \rightarrow [CuCl_4]^{2-} \text{ (tetrahedral)} \rightarrow (\ldots CuCl_6 \ldots)$$

Above 4M HCl, the chemical composition of the system is determined by the co-ordination equilibria, undissociated HCl molecules begin to take a part in the complex formation process. As in the equation

$$[CuCl_4(H_2O)_2]^{2-} \rightleftharpoons [CuCl_4]^{2-} \quad \text{(tetrahedral)}$$

hydrogen chloride molecules act as dehydrating agent.

Sato[7] in his work on "complex formation in Cu - HCl - TOAHCl extraction system" shows that in the spectra of aqueous solutions, the absorption is due to the aquo-ion $[Cu(H_2O)_6]^{2+}$ at low acidity, and the tetrahedral species $CuCl_4^{2-}$, at high acidity.

Bjerrum's results for stability constants of copper-chloride complexes have been chosen as the most satisfactory by many investigators. By using spectrophotometric measurements and assuming that the co-ordination number of copper ions remains unchanged and is equal to four, and that the activity coefficients of Cu^{2+} and Cl^{-} are unity, Bjerrum calculated the stability constants at 22.5° C ($CuCl_2$ - HCl) as $K_1 \leq 1$, K_2 = 0.1-0.4,

K_3 = 0.02-0.06, K_4 = 0.003-0.01 1/mole.

McConnell and Davidson[15] have tried to calculate the stability constants in solutions containing Cu^{2+} perchlorate, HCl and perchloric acid at an ionic strength of unity. They could only detect $CuCl^+$ and $CuCl_2$ ions. Their measurements at wavelengths 260, 270, 280nm and at a temperature of 25.2°C gave average K_1 value 1.30 $\pm$ 0.03 and 0.23 0.15 1/mole for K_2.

After the re-examination of other authors' works we may return to our results and compare them with theirs. In the experimental range used firstly, the increase of the optical density with increasing chloride concentration and a peak at 250nm in the spectra of Cu^{2+}-chloride solutions were observed. However, in contrast to Andreev's statement, our method of examination of Cu-chloride aqueous solutions shows that Cu^{2+} and $CuCl^+$ ions exist only up to 2M Cl^- concentrations. This difference is probably due to the use of different electrolytes, LiCl instead of HCl.

The first stability constant was found to be 0.65 which is lower than the others as listed below:

Researcher	K_1	Solution
Miranov [11]	0.87	Mixture of LiCl and perchloride
Bjerrum [14]	1	HCl
McConnell [15]	1.30	Perchloric acid and HCl mixture
D'Amore [16]	1.18	$NaClO_4$
Simirous [17]	- 1	LiCl

Conclusion

In the analysis of aqueous $CuCl_2$ solutions and the attempt to calculate the stability constants the following conclusions were reached :

1- The coptical density of Cu-chloride solutions increase with increasing chloride concentration,

2- The spectrum consists a peak at 250nm in the range 0.5-6M Cl^- which corresponds to the absorption of the first copper complex $CuCl^+$

3- First complexing constant $K_1 = 0.69M^{-1}$

4- The method used for calculation of stability constants is not useable for the other constants K_2, K_3, K_4.

CHAPTER 4

HYDRATION OF ORGANIC PHASE

Some authors explain certain abnormalities in solvent extraction processes by suggesting that co-extraction of other species or water occurs from the aqueous phase.

In this chapter, hydration of the organic phase as a function of chloride concentration in the presence of different supporting electrolytes is examined. In each case the water content of the organic phase was measured by the Karl Fisher titration method. No attempt was made to measure the water content of diluent, benzene or TOAHCl but, whenever it was necessary, literature values were used. It was assumed that by keeping the organic phase concentration constant in each case, the solubility of water inTOAHCl in benzene would remain constant, and differences would be due to changes in the activity of water in the aqueous phase.

Materials

LiCl, HCl, $CaCl_2$ aqueous solutions

Stock solutions were prepared for distribution experiments (c.f. Chapter 2) containing 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 M Cl^- and 0.1 g/l of copper was used.

TOAHCl

0.1 M TOAHCl in benzene was prepared by the same method as is described in Chapter 2.

Karl Fisher (K.F.) reagent and water-methanol solution

They were both supplied by Hopkin and Williams.

Experimental Technique

The water contents of organic solutions were determined by using a Karl Fisher apparatus (Baird and Tablock). First, K.F. reagent was standardized. Then, 3mls of standard water solution was put into the titration beaker containing a small magnetic stirrer and was placed on a hot plate with a rotating magnet below. Small portions of K.F. reagent were introduced from the burette and titration was continued until the needle reached the point "excess Fisher". Water-methanol solution was then added until the needle swung back to the centre. Readings from both K.F. reagent and water-methanol solution burettes were taken and 1ml of the organic solution was introduced into the beaker. The titration repeated and the Burette readings were again recorded.

4.1. Standardization of K.F. reagent

Standardization of K.F. reagent with weighed amount of water showed that

1ml K.F. reagent = 0.00582 g. water

which is higher than the given value of 0.0050 g.

4.11. Water contents of organic solutions

Water contents of organic phases are presented in Table (4.11). The change of water content of the organic phase

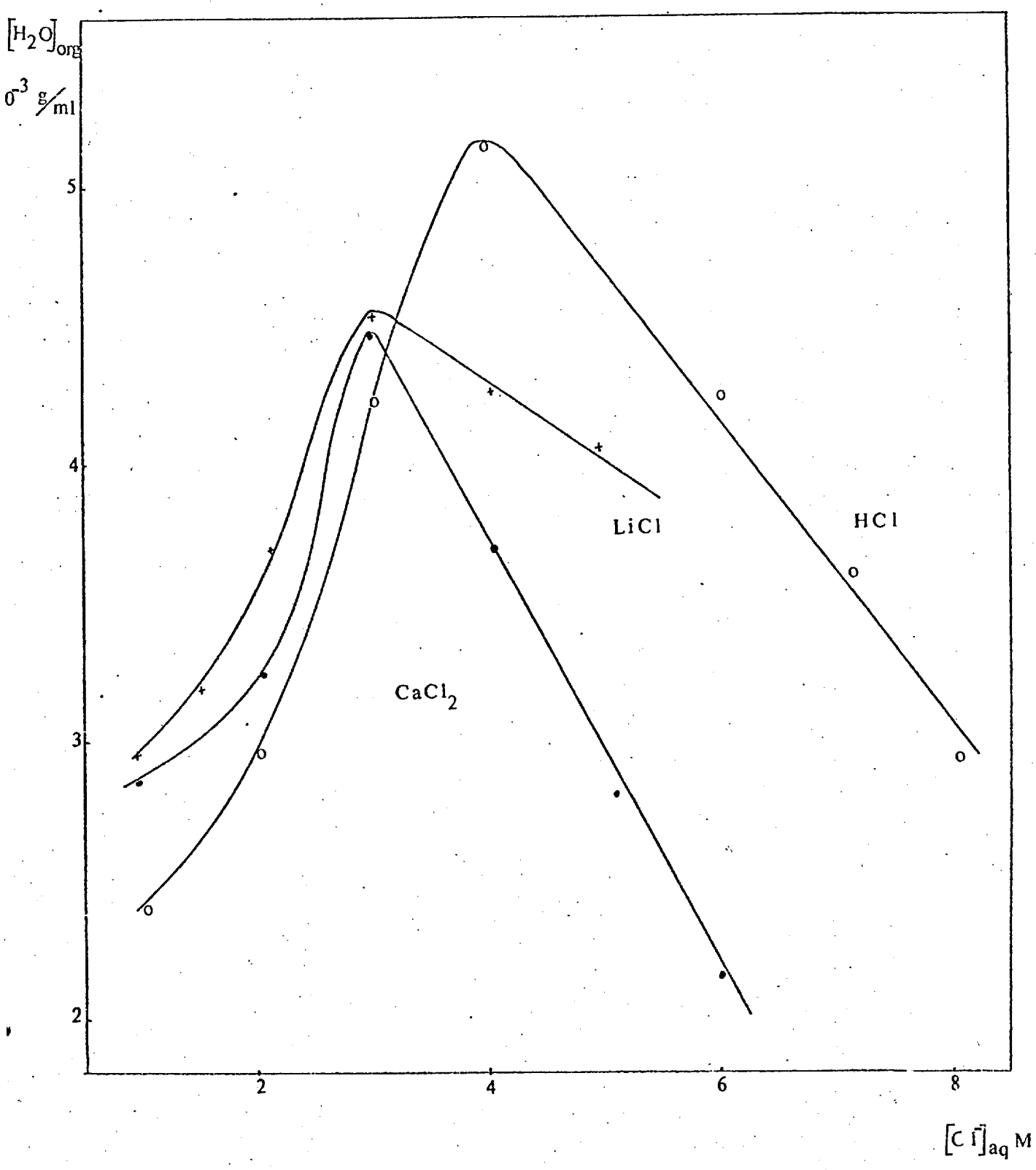
(after extraction of copper) with the chloride molarity in each system is shown in Figure (4.11). When copper is extracted from salt solutions i.e. LiCl and $CaCl_2$, the water content of the organic phases increases with increasing chloride molarity up to 3 M, then decreases sharply. The maximum point in HCl system was observed at 4 M Cl^- .

During titration, it was observed that some precipitates were forming in the case of organic phase obtained from the extraction of HCl aqueous solutions and that these were coating the electrode. The results obtained from these series of experiments may be described as being rather poor, mainly for this reason. On the other hand, there was no precipitate formation during K.F. titrations of LiCl and $CaCl_2$ solutions. Titration results of organic phases obtained from $CaCl_2$ solutions were the most reproducible.

As shown on Figure (4.11) maximum water contents of organic phases are

from HCl solutions	5.2 g/l	at 4 M Cl^-
from LiCl solutions	4.54 g/l	at 3 M Cl^-
from $CaCl_2$ solutions	4.46 g/l	at 3 M Cl^-

Series of experiments were carried out to see the effect of aqueous phase metal concentration on the hydration of the organic phase. Because of the relatively reproducible results obtained when $CaCl_2$ was used as the supporting electrolyte, seven aqueous solutions were prepared containing 1.95 M $CaCl_2$, 0.1 M HCl (totally 4 M Cl^-) and 0.0095, 0.180, 0.444, 1.000, 1287 and 1.485 g/l Cu^{2+}. The amine concentration in the organic phase was kept constant,



change of $[H_2O]_{org}$ with aqueus phase chloride molarity

Figure: 4.11a

0.103 M TOAHCl.

Water contents of organic phases are given in Table (4.11b) and the effect of Cu^{2+} concentration on the hydration of the organic phase is shown in Figure (4.11b).

As the metal concentration of the organic phase increased the water content of the organic phase decreased.

4.111. Discussion

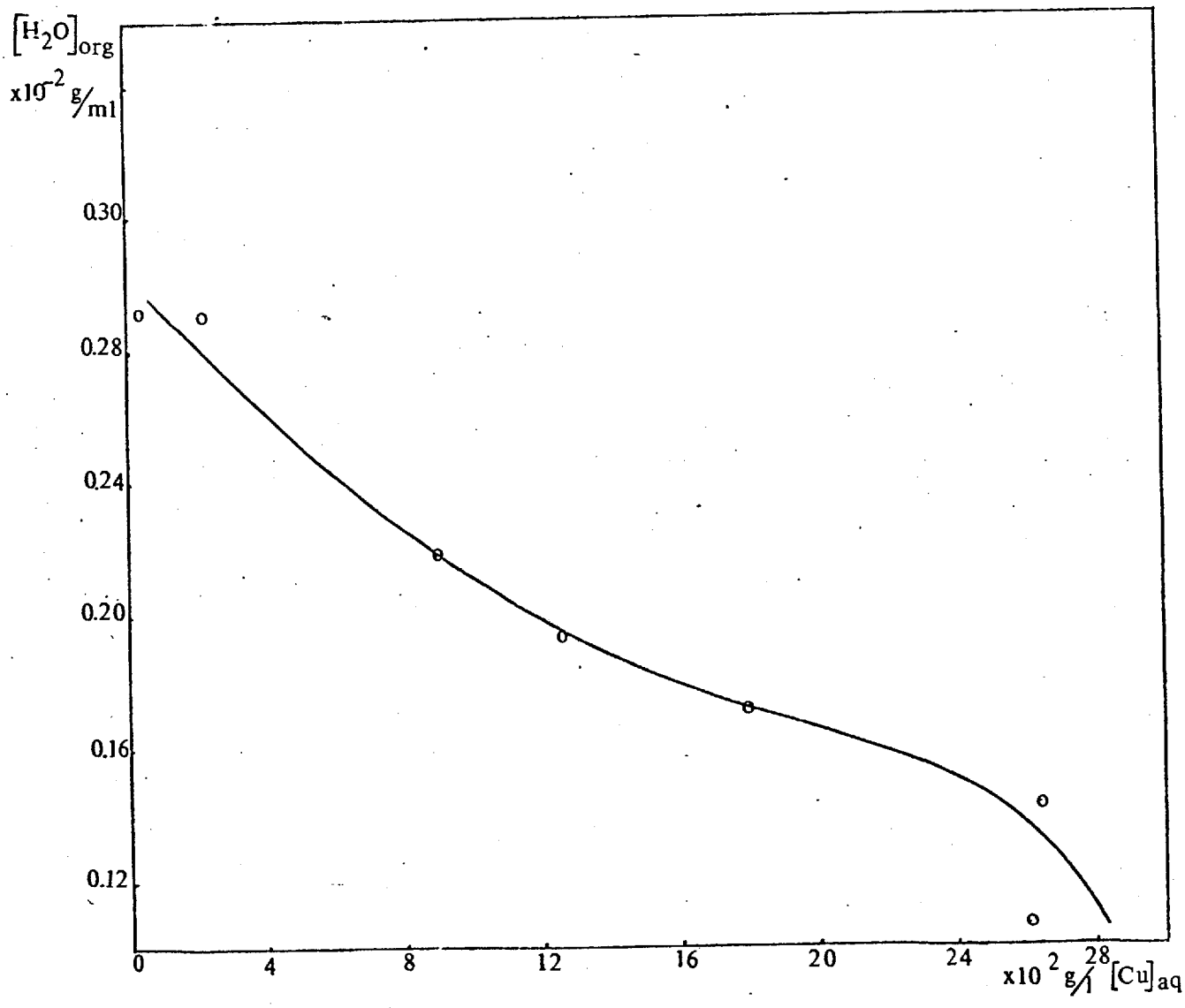
There has been a considerable amount of research carried on the co-extraction of water by TOA and its salts. There is general agreement that extraction of water is higher when TOA salts are used rather than TOA itself.

Coleman[50] states that co-extraction of water depends on the amine concentration, the type of diluent, the metal to be extracted and the activity of the aqueous phase. According to his work, the corrected water content (i.e. the increase in the solubility of water in the organic phase) varies linearly with amine concentration. At a given amine concentration water extraction is directly proportional to the water activity suggesting that not more than one H_2O molecule associates with each amine monomer. The molar ratio of water in 0.1 M TOAHCl is close to one.

The general expression for hydration of the organic phase is

$$1/_n(\overline{TOAHCl})_n + d\ H_2O \longrightarrow 1/_c(\overline{TOAHCl \cdot dH_2O})_c$$

Frolov[51] gives an expression for the dependence of the hydration of TOAHCl in toluene on salt concentration and water activity as follows



water content of the organic phase

Figure : 4.11b

$$c_w = c_{wo} \cdot a_w + h \cdot a_w \cdot c_s$$ where

c_{wo} = water solubility in pure solvent at $a_w = 1$
c_w = water solubility in TOAHCl
h = degree of hydration of TOAHCl
a_w = activity of water
c_s = salt concentration.

His infra-red spectra show evidence of hydrogen bond formation between molecules and the salt as well as between two water molecules.

The theory of hydration of amine salts is discussed by McMillan and Mayer[18].

Fukutomi[19] has calculated the water content of the free base TOA and found that it was not more than 0.0001 g/l/g of amine but, a relatively large of water was present in amine salts.

Rolandi[20], on the other hand, found no water in the organic phase when 0.100 M TOA was equilibrated with 0.4 M HCl and the molar ratio of water present to TOAHCl was one. Organic phase molar ratio does not change even if 0.1 M TOA is equilibrated with 1.7 M HCl but contains 0.095 M water. However, when HCl concentration is increased to 8.25 M, $[HCl]_{org}$ increases from 0.1 to 0.17 M and organic phase water content in each case is 0.1 M. At the aqueous concentrations higher than 3.5 M, HCl begins to dissolve in the amine salt. Each mole of TOAHCl is associated with one mole of water while the excess water is unhydrous.

The dependence between organic phase water and metal

concentrations is given by Gardener and McKey[21] with an expression

$$M_w = M_w^o - Am_m - {}^1/_2 B m_m^2$$

where

Mw = water concentration of organic phase

M_w^o = water content of the extractant at unit activity

m_m = metal concentration of organic phase

A = function of activity of water, $\lim_{m_m \to o} \frac{m_w - m_w^o}{m_m} = \lim A$

gives number of water molecules that hydrating the extracted salt.

The effect of water activity in solvent extraction process has been examined by Fomin[3]. He describes the concentration of the organic complex as follows:

$$\left[MA_n . hH_2O \times S\right] = K \left[MA_n\right]^{n+1} \gamma_{\pm}^{n+1} \quad a_w^h \quad (S)^x . \quad \frac{1}{\gamma^o}$$

where

M = metal concentration

A = ligand concentration

(S) = activity of the extractant

$\gamma_{\pm}$ = mean activity of salt in aqueous phase

γ_o = activity of salt in organic phase

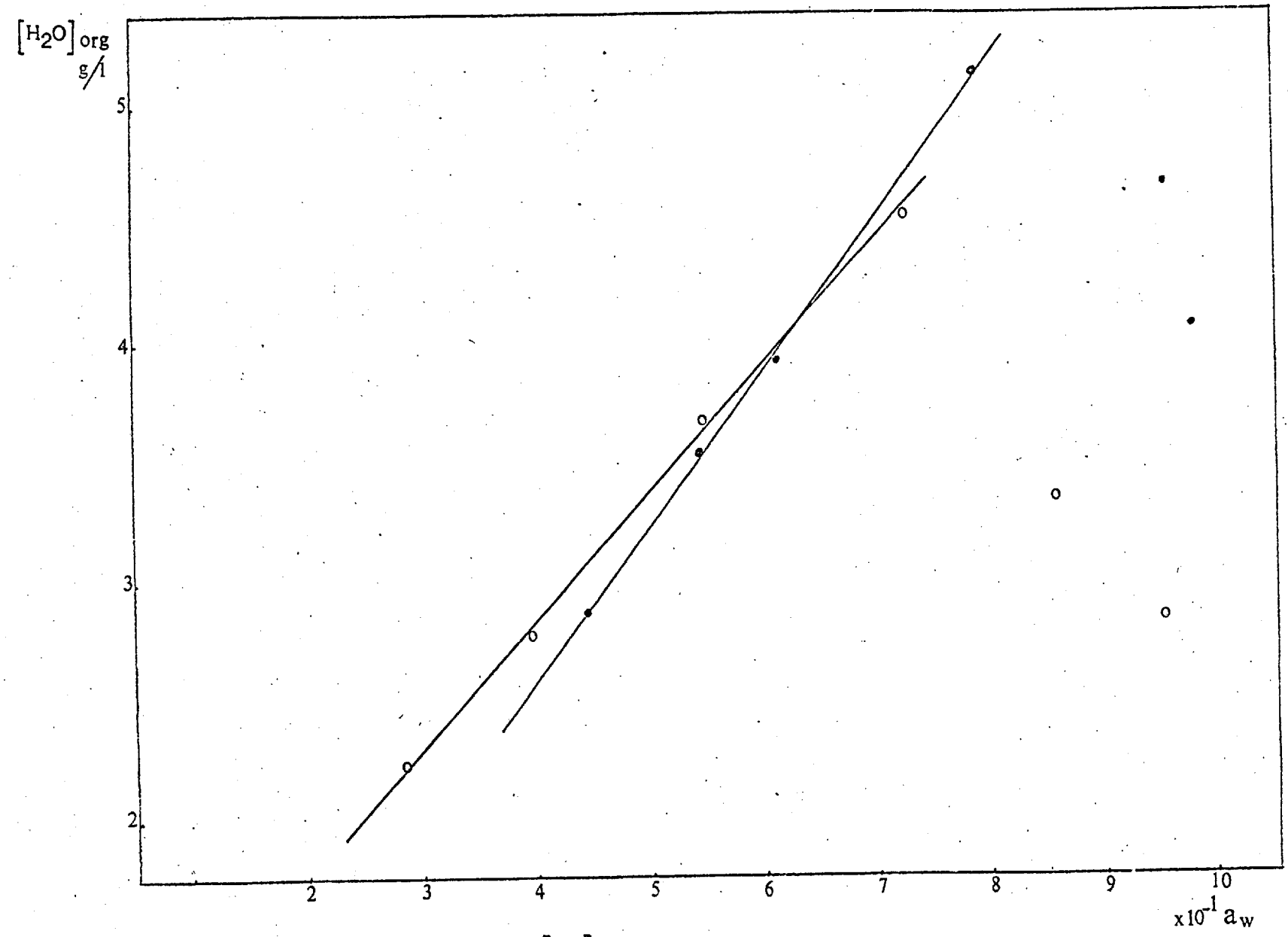
a = activity of water

h = hydration number

According to his expression, the concentration of metal in the organic phase must decrease with decreasing water activity in the aqueous phase if the activity coefficient of ligand and the activity coefficient of the organic complex remain constant.

Variations of concentrations and activities in the aqueous phase change the activity of water. First of all, different salting-out agents have different degrees of hydration. For this reason at equal concentrations of chloride and metal to be extracted, in the present work organic phase water contents differed. Table (2.1V.1) shows the water activities at various chloride concentrations of HCl, LiCl and $CaCl_2$ solutions. If water is being extracted into an organic phase there are two possibilities, either it is extracted independently, or it is solvating another species which is extracted. When the hydration of the extractable ions is taken into account, extractable copper chloride complexes present in the aqueous phase are $CuCl_3^-$, $CuCl_2$, $CuCl_4^{2-}$. There is a lack of data about activity coefficients of these hydrated ions and also it is not known in what range of aqueous chloride concentrations these ions are present, or which complexes take part in the extraction process.

When the present results are compared with those of other workers, in the range of 0.2-0.8 activity the results shown in Figure (4.111) fit very well into Frolov's expression showing linearity between water activity of the aqueous phase and the water content or the organic phase. However, when the water activity gets closer to one, in all cases non-linearity is observed. This behaviour can be seen more clearly when total water of the organic phase is plotted against aqueous chloride concentrations (Figure 4.11a). In three cases (LiCl, HCl, $CaCl_2$ aqueous solutions) when the chloride concentration is increased, which means decreasing water activity, and decreasing



change of $[H_2O]_{org}$ with activity of water

Figure: 4.111

organic phase water content, the experimental results show an increase of total water in the organic phase. Organic phases have maximum water when the aqueous chloride concentration is 3 M for the salts and 4 M for hydrochloric acid.

We know that complex formation in Cu^{2+} - Cl^- solutions takes place according to the equation

$$\left[Cu(H_2O)_6\right]^{2+} + nCl^- \rightleftharpoons \left[CuCl_n(H_2O)_{6-n}\right]^{2-n}$$

Andreev[12,3] stated in his spectra studies of $CuCl_2$-HCl-H_2O systems that at chloride concentrations greater than 4M $CuCl_4^{2-}$ complexes are dominant. Complex formation takes place by stepwise replacement of water molecules in the inner sphere of $\left[Cu(H_2O)_6\right]^{2+}$ ions by Cl^- ions

$$\ldots\ \left[(CuCl_3(H_2O)_3\right]^- \rightleftharpoons \text{trans}\left[CuCl_4(H_2O_2\right]^{2-} \rightleftharpoons \left[CuCl_4^{2-}\right]\text{tetrahedral} \rightleftharpoons (CuCl_6)$$

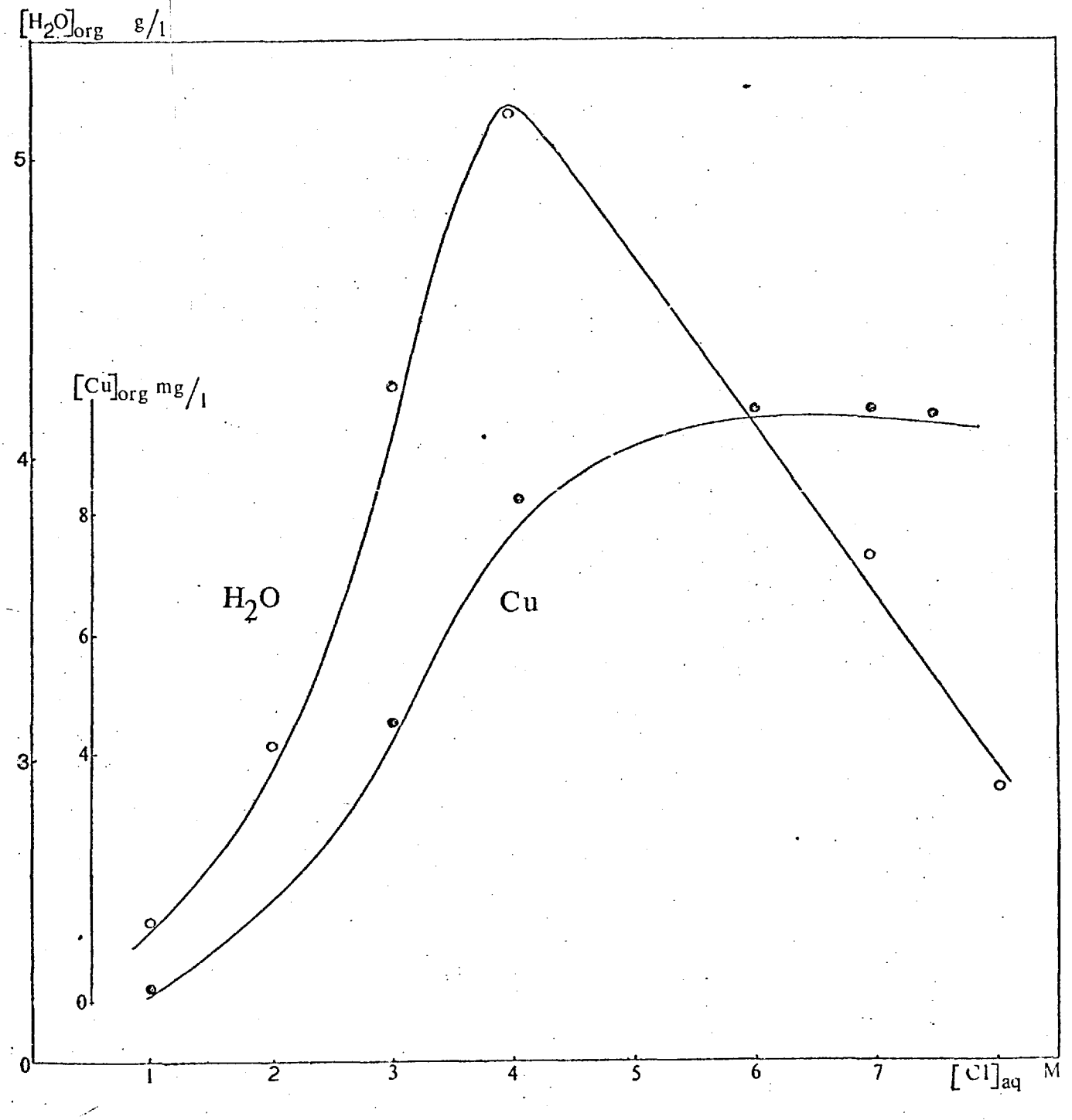
Starting from 4M HCl, the chemical composition of the Cu^{2+}-H_2O-HCl system is determined by these co-ordination equilibria, undissociated HCl molecules beginning to act as a dehydrating agent.

In the literature, no results have been found for the $CuCl_2$-H_2O-LiCl or $CuCl_2$-H_2O-$CaCl_2$ systems. From the present results, the phenomenon of hydration of the organic phase can only be explained by the presence of different chloride complexes in the aqueous phase. At lower concentrations of chloride, lower hydrated chloride complexes are dominant in the system and are being extracted. As the chloride concentration is increased, the concentration of these complexes increases and so does the extraction percentage. Obviously the water content of the organic

phase will increase. However, this increase is not linear with the chloride concentration. Probably the aqueous phase contains a mixture of these lower complexes. But, at higher chloride concentrations, $CuCl_4^{2-}$ will predominate in the system. Water activity will decrease linearly with increasing chloride concentration.

Comparison of the extraction of copper and the total water content of the organic phase, at varying aqueous chloride concentrations, is shown in Figure (4.1V). There is a noticeable change of slope in both lines in the ranges of 1-4 and 4-8 M chloride.

The dependence of water content of the organic phase on the metal concentration of the organic phase is given in Figure (4.11b). This shows the decrease of organic water with increasing copper concentration in the organic phase. When the copper content of the organic phase reaches 0.27-0.28 g/l, it is saturated and the water molarity of the organic phase at saturation is 0.0584 M. Experiments were not carried out, but by using literature values of water contents of benzene and of 0.1 M TOAHCl the water content of the extractant was calculated to be 0.019 M + 0.035 M = 0.054 M, which is close to the value obtained experimentally at the saturation point. This might suggest that at high metal concentrations of the aqueous phase water is not taking part in the extraction process. On the other hand, the curve does not fit Gardener's expression of relation between organic metal and water contents which is a parabolic curve obtained by treating experimental results by the method of least squares. (Extraction of uranyl nitrate by several extractants.)



Extraction from HCl solutions

Figure: 4.1V

It can be concluded that in the extraction of copper by TOAHCl, water is being extracted in considerable amounts. Hydration or the organic phase depends on the changes in activities and types of extractable ions in the aqueous phase when the amine concentration in the organic phase was kept constant.

CHAPTER 5

MOLECULAR WEIGHT DETERMINATIONS

It is known that aggregation of the extractant plays an important role in the extraction mechanism. Therefore, in this section of the work, molecular weights of TOA, TOAHCl and TOAHCl-Cu complex were determined by vapour pressure osmometry (v.p.o.). Monomer and dimer concentrations and dimerization constant were also calculated by using the experimental data.

Materials

Benzene:

Because of its almost ideal behaviour in v.p.o. measurements, GPR grade benzene was used as a solvent.

Benzil:

Seven Benzil solutions were prepared for calibration of v.p.o. Concentration of these solutions are listed in Table (5.1).

TOA:

Series of TOA solutions were prepared by diluting with Benzene Table (5.11).

TOAHCl:

Equal volumes of TOA-Benzene solution were equilibrated with 0.2M HCl. After separation of the two phases, it was found that the organic phase contained 128.3908g/kg TOAHCl. It was diluted

in order to obtain a series of solutions with different concentrations.

TOAHCl-Cu

Copper was extracted from an aqueous solution containing 5.9M LiCl, 0.1M HCl and 20.0g/l Cu^{2+}. The strength of TOAHCl was 0.1M. Loaded organic phase then diluted with benzene to obtain series of solutions with various molalities.

Experimental Technique

A Hewlitt-Packard Vapour Pressure Osmometer (v.p.o.) was used for the molecular weight determinations. In order to maintain thermal stability in v.p.o. it is necessary to operate the thermostatic chamber at a temperature some degrees above ambient. For this reason all measurements were carried out at $37^{o}C$.

The theory of operation is given in Appendix I.

First of all, the instrument was calibrated with Benzil and the calibration constant K was determined.

All measurements given in Tables are the average of four readings.

Calibration of v.p.o.

Molecular weights for ideal solutions are given by the formula

$$\left(\frac{V}{C}\right)_{C=0} = \frac{K}{M} \quad \text{----------} \quad (A)$$

where K = empirical constant, depending on temperature and properties of the solvent

V = v.p.o. bridge output in volts

C = Solute concentration in g/kg solvent

M = Molecular weight of solute

The intercept at C=O of a plot of V/C against C gives the

value of $(\frac{V}{C})C=0$ if the molecular weight of benzil is known we can calculate K.

The v.p.o. readings for Benzil are given below and the linear dependence of V and C is shown in Figure (5.1).

Table(5.1)

Benzil - Benzene g/kg	VmV	v/C
7.6838	0.52	0.06767
15.5405	1.12	0.07207
29.6893	2.16	0.07275
41.8143	3.01	0.07198
50.4700	3.52	0.06944
69.9411	5.14	0.07349

The intercept of $^{V}/_{C}$ against C as shown in Figure (5.11) is 0.0715mV and slope $0.00mV(g/kg)^2$.

The molecular weight of benzil is 210.2g and by substituting these into the above equation

$$K = 15.031 \text{ mV/molal.}$$

Molecular weight of TOA

For non-ideal solution, the above relationship becomes

$$\frac{V}{C} = (\frac{V}{C})_{C=0} (1 + AC + BC_2 + \ldots) \text{ ---------- (B)}$$

where A and B are the second, third etc virial coefficients. Generally only first two terms, (1 + AC) are used.

$$\therefore \frac{V}{C} = (\frac{V}{C})_{C=0} (1 + AC)$$

V.p.o. readings for TOA solutions are

Table(5.11)

C g/kg	VmV	v/C
19.3585	0.925	0.04778
34.6826	1.60	0.04613
36.4726	1.585	0.04346
48.5650	2.26	0.04653
53.8068	2.34	0.04386

The plot of $^{v}/_{C}$ against C as shown in Figure (5.11) is a straight line with negative slope. Its intercept, $(\frac{V}{C})C=0$ is at

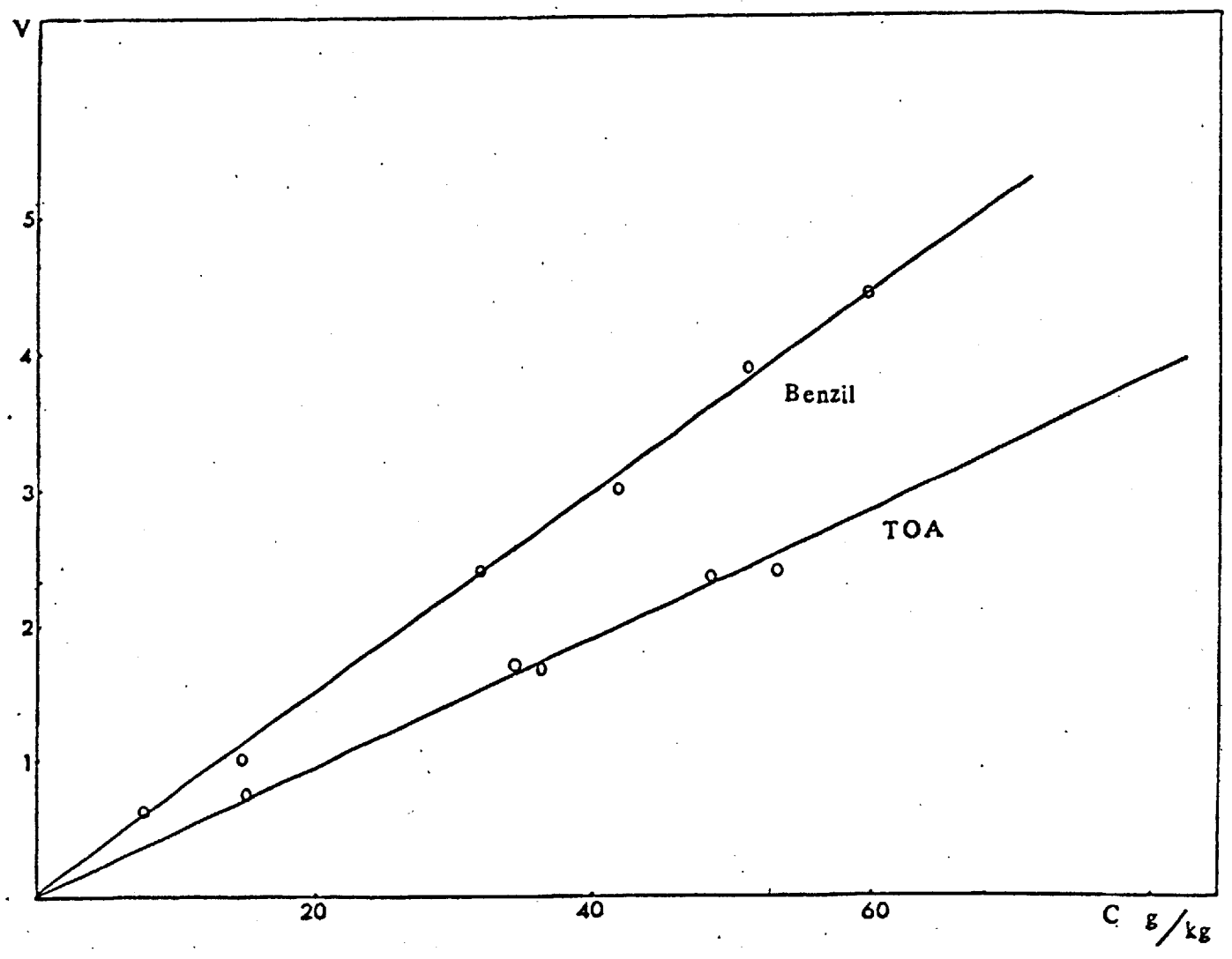


Figure: 5.1

0.046mV/g/kg. If this value and K which was calculated before are substituted into equation (A), the molecular weight of TOA is found to be 326.76g.

This is lower than the theoretical value of 353 which is probably due to the presence of impurities.

Trioctylamine hydrochloride

v.p.o. readings for TOAHCl solutions are given below

C g/kg	V mV	V/C
6.6392	0.185	0.02762
13.3339	0.305	0.02287
18.5126	0.445	0.02404
38.9045	0.800	0.02056
58.1918	1.120	0.01925
82.7818	1.530	0.01872

(Table (5.111)

The Figure (5.11) shows the change of C with $\frac{V}{C}$. As it is shown it behaves non-ideally. This is assumed to be due to aggregation of TOAHCl molecules in benzene.

Apparent molecular weights for each solution were calculated by using the relation $\frac{V}{C} = \frac{K}{M}$ in which K was calculated before and found to be 15.0314. Apparent molecular weights are reported in Table (5.1V).

The theoretical monomer molecular weight of TOAHCl is 389.5g. If apparent molecular weights are divided by the theoretical value, aggregation number $\bar{n}$ for each solution is obtained.

C g/kg	App.mole weight	n
6.6992	544.322	1.397
13.3391	657.141	1.687
18.5126	625.327	1.605
38.9045	731.101	1.877
58.1918	780.854	2.004
82.7818	802.961	2.061

Apparent molecular weights and aggregation numbers for TOAHCl solutions

Table (5 1V)

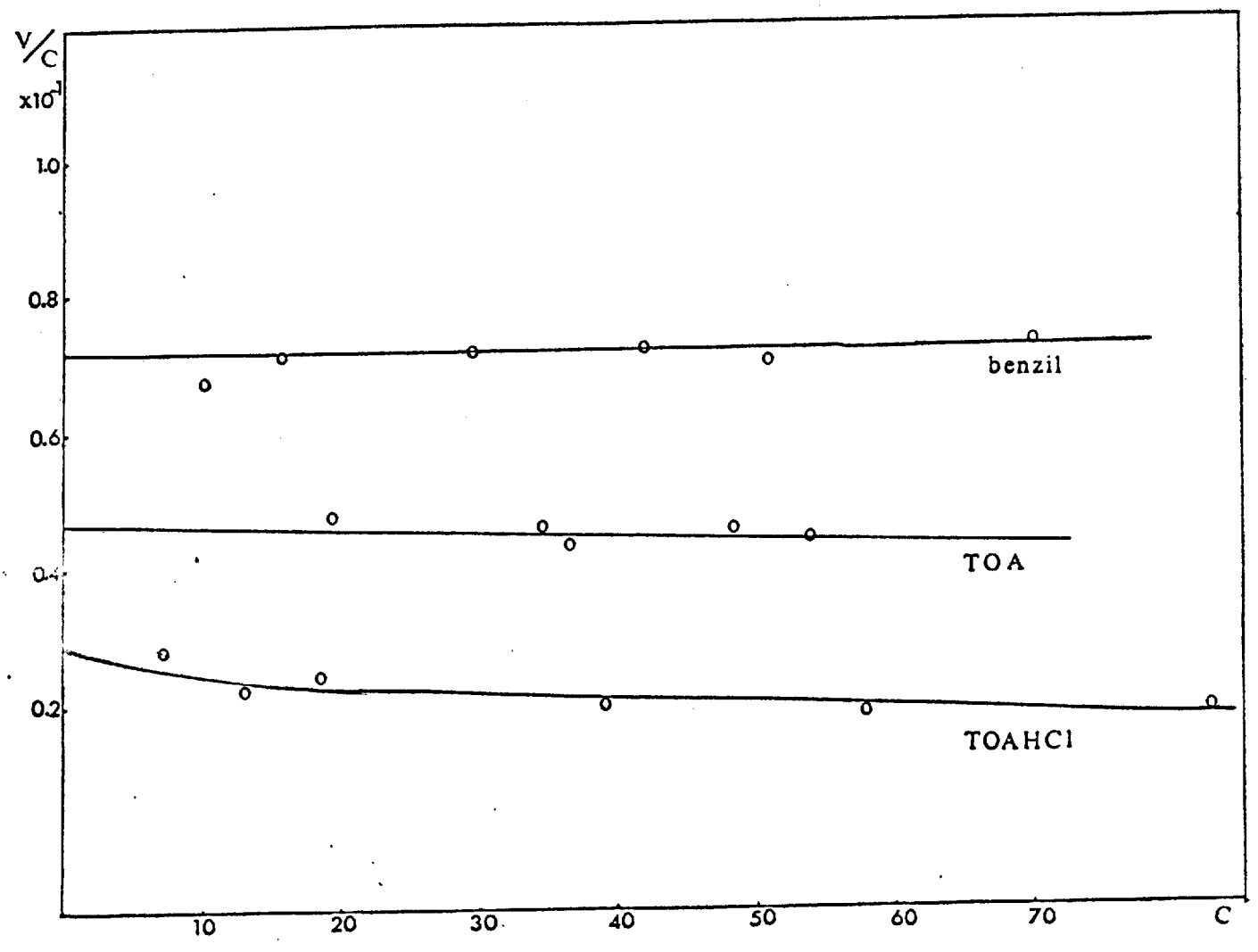


Figure: 5.11

The aggregation number varies between 1.39 and 2.06. The plot of aggregation numbers against molal concentrations shows the dependence of each other Figure (5.111). $\bar{n}$ increases with increasing concentration of TOAHCl up to 2 which suggests that TOAHCl in benzene forms only dimers but not any higher polymers.

Calculation of dimerization constant K_D

We may assume that TOAHCl solution contains only monomers and dimers. The equilibrium reaction is

$$2\ \text{TOAHCl} \underset{}{\overset{K_D}{\rightleftharpoons}} (\text{TOAHCl})_2$$

$$\therefore\ C_2 = K_D C_1^2$$

where C_1 = monomer concentration

C_2 = dimer concentration

K_D = dimerization constant.

The total molal concentration of monomers and dimers C_o is given by

$$C_o = C_1 + C_2 = C_1 + K_D C_1^2$$

The total stoichiometric molal concentration of TOAHCl is given by

$$C' = C_1 + 2C_2 = C_1 + 2K_D C_1^2$$

The average aggregation number $\bar{n}$ is defined as the total stoichiometric concentration divided by the total concentration of monomers and dimers

$$\bar{n} = \frac{C}{C_o}$$

$$\frac{\bar{n}}{C} = \frac{1}{C_1 + K_D C_1^2} = \frac{K_D}{C + K_D C_1} \quad \ldots\ldots\ldots\ldots \quad (A)$$

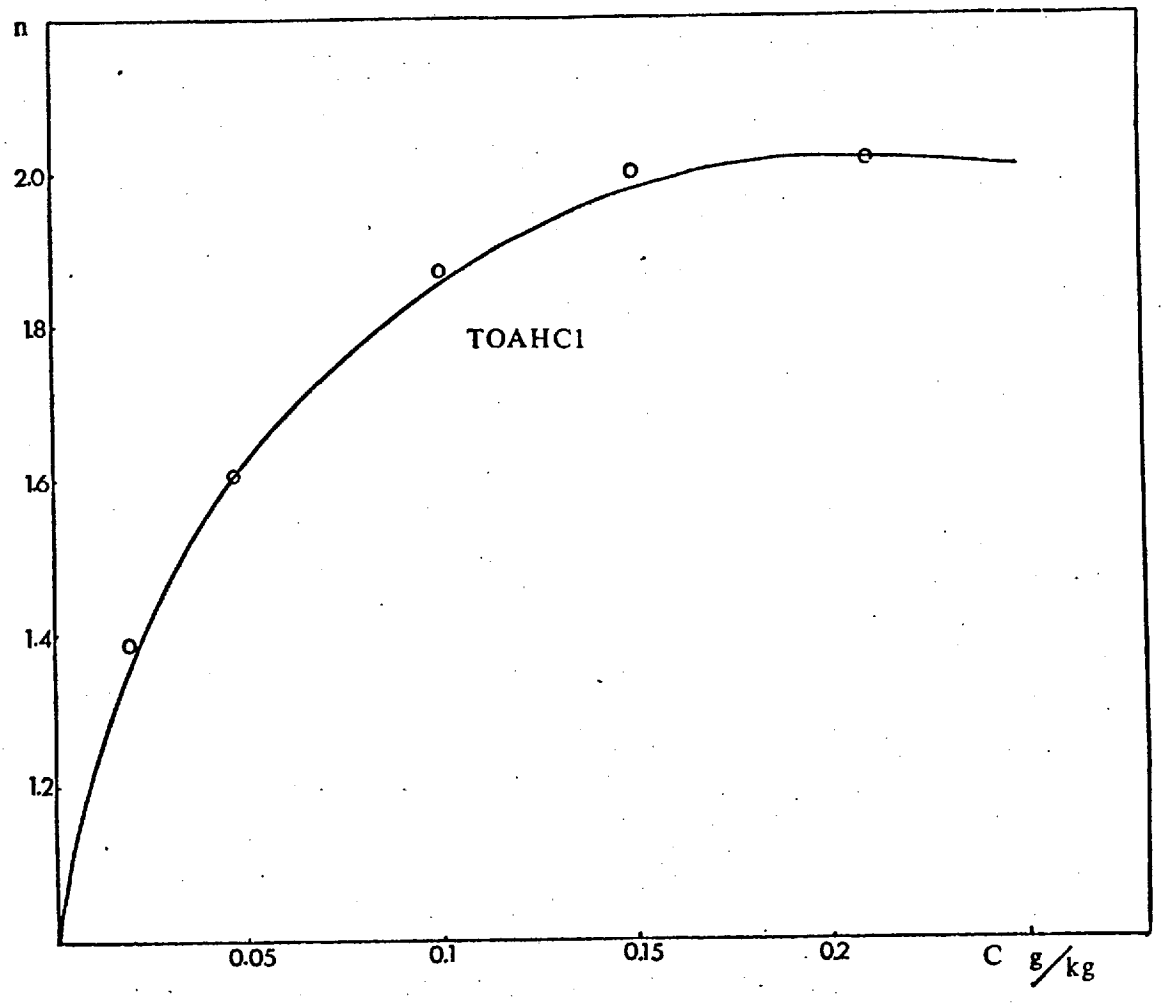


Figure: 5.111

but

$$C' = C_1 + 2K_D C_1$$

$$C_o = C_1 + K_D C_1^2$$

$$n = \frac{C'}{C_o}$$

If these are substituted into the equation (A)

$$C' \cdot K_D = \frac{\bar{n}(\bar{n}-1)}{(2-n)} = N$$

The plot of N against the total molal concentration of TOAHCl C gives the slope equal to K_D. K_D value was found to be equal to 8.18 which is lower than Kojima's value of (12.9 ± 0.5).

Calculations of monomer and dimer concentrations in TOAHCl solution

As it was shown in the previous paragraph

Total molal concentration $C' = C_1 + 2C_2$

monomer concentration $C_1 = C - 2C_2$

dimer concentration $C_2 = 1/2\ (C - C_1)$

But as $\bar{n} = \frac{C}{C_o}$ by substitution

$$n = \frac{C}{C-C_2} = \frac{2C}{C + C_1}$$

or $C_1 = C\ \frac{(2-n)}{n}$ $\qquad C_2 = C'\ (\frac{n-1}{n})$

$$\log C_1 = \log C' + \log \frac{(2-n)}{n} \qquad \ldots\ldots\ldots\ldots \text{(B)}$$

$$\log C_2 = \log C' + \log \frac{(n-1)}{n} \qquad \ldots\ldots\ldots\ldots \text{(C)}$$

Thus the monomer and dimer concentrations can be calculated from the total concentration of TOAHCl and the average aggregation number $\bar{n}$.

The Table below gives the monomer and dimer concentrations at given molal concentrations of TOAHCl.

C	Monomer	Dimer
0.0172	0.017	0.0048
0.0342	0.041	0.0179
0.0998	0.051	0.0466

Table (5.V)

The plot of equation (B) and (C) is shown in Figure (5.1V). It shows that log C_1 and log C_2 increase linearly with log C . The slope of monomer line is 0.658 and dimer line 1.29. Two lines intercept at TOAHCl molality 0.162. At this concentration monomer and dimer concentrations are equal.

Copper salt of trioctylamine hydrochloride

Apparent molecular weights of each TOAHCl-Cu solution was calculated and are tabulated in Table (5.V1). Average aggregation numbers were also calculated by dividing the apparent molecular weights by the theoretical average molecular weight.

As was shown in previous chapters the organic complex formed at full-loading is

$$(TOAH)_2\ CuCl_4 .\ 0.52\ TOAHCl$$

The theoretical average molecular weight is

$$M_{theor.} = X_1 m_1 + X_2\ m_2$$

where X_1, m_1 corresponds to the component of the above composition $(TOAH)_2\ CuCl_4$ and X_2, m_2 corresponds to 0.52 TOAHCl.

Mole fractions $X_1 = \frac{1}{1 + 0.52}$ $X_2 = \frac{0.52}{1 + 0.52}$

$$M_{theor.} = 732.989.$$

Figure (5.V) shows that as the molal concentration of the solution approaches to 0, n = 1 indicating the existence of of monomers only. Thus $M_{theor.}$ should be exhibited by the solution at zero concentration (Figure 5.V1).

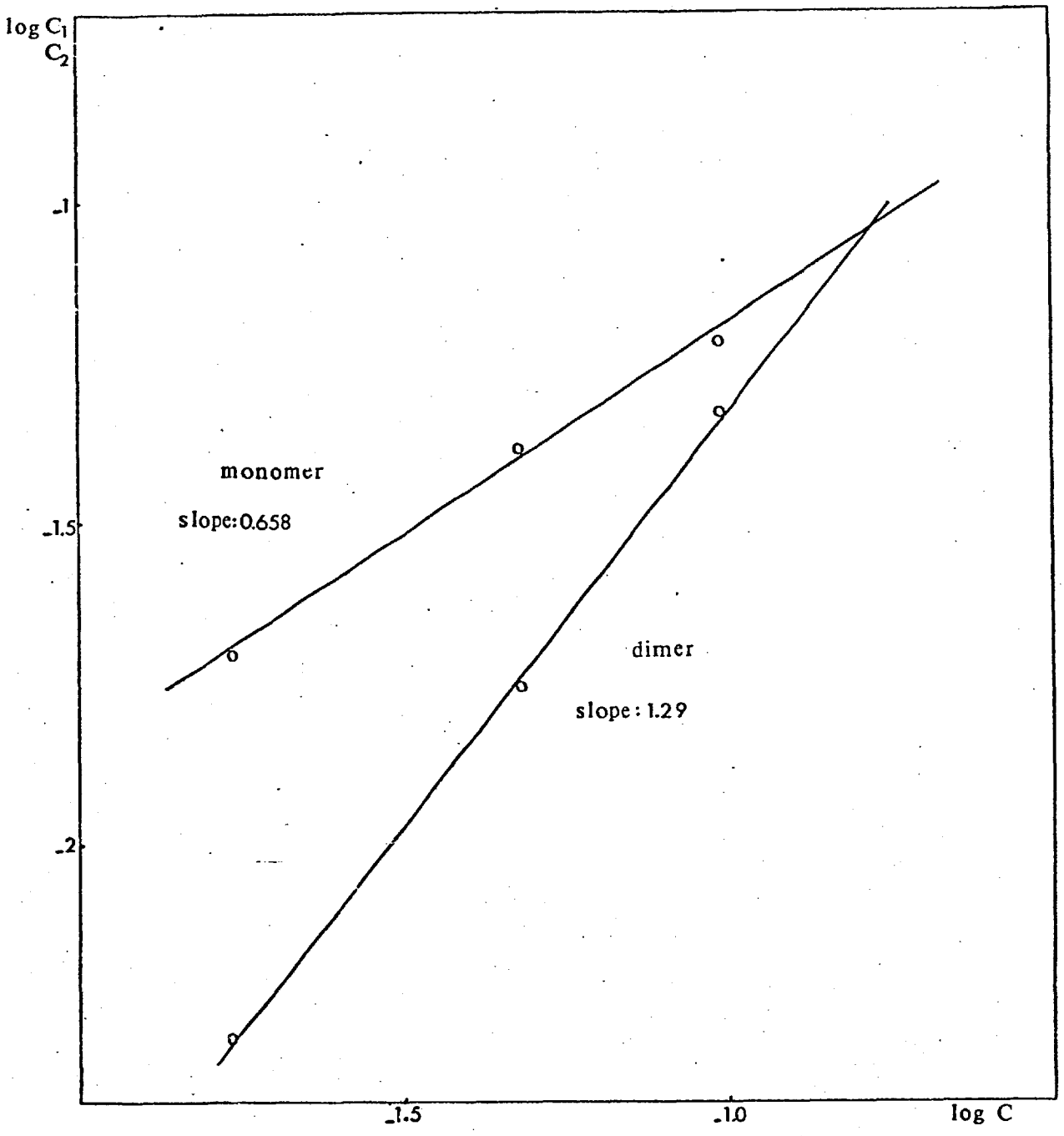


Figure: 5.1V

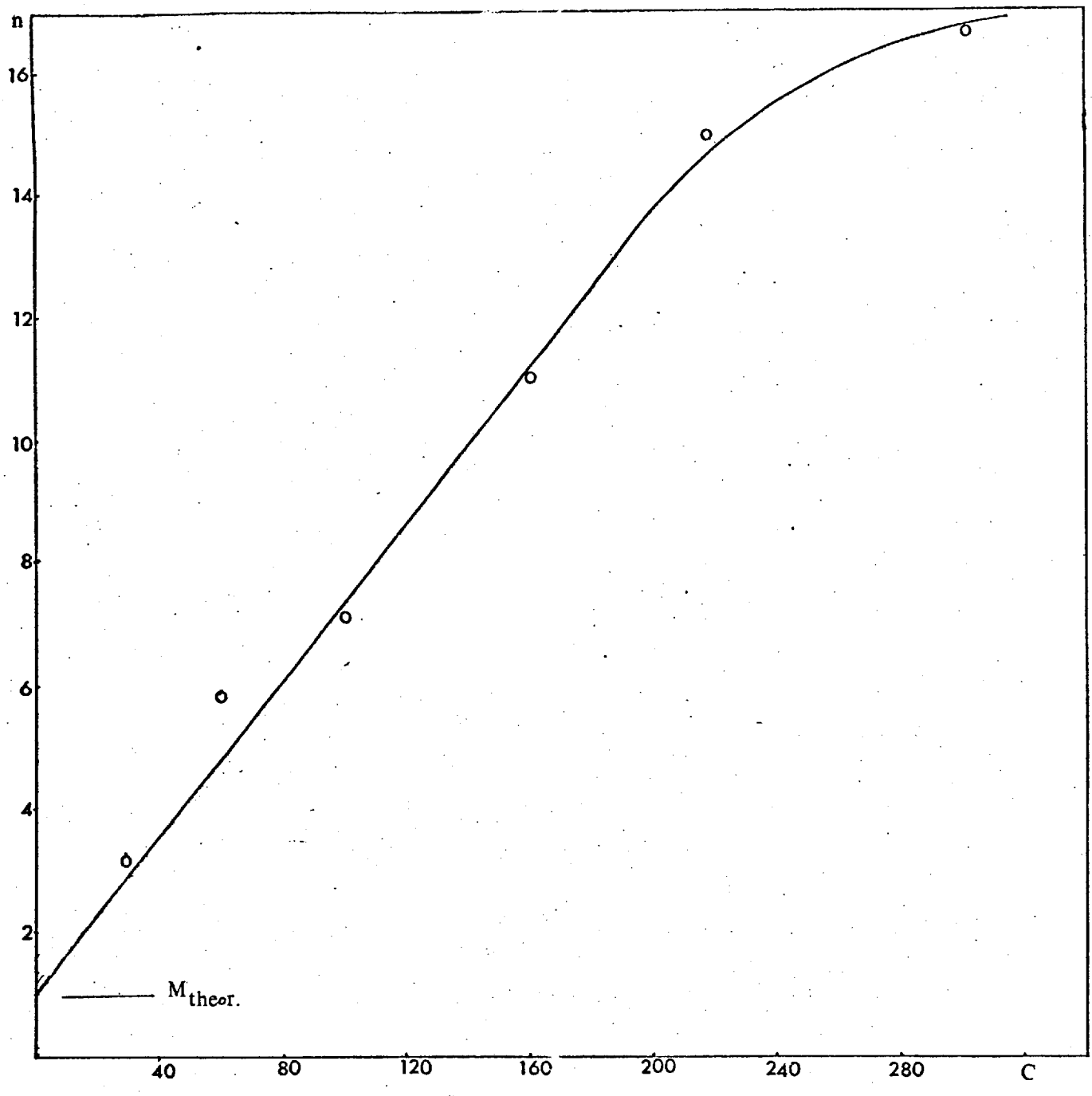


Figure: 5.V

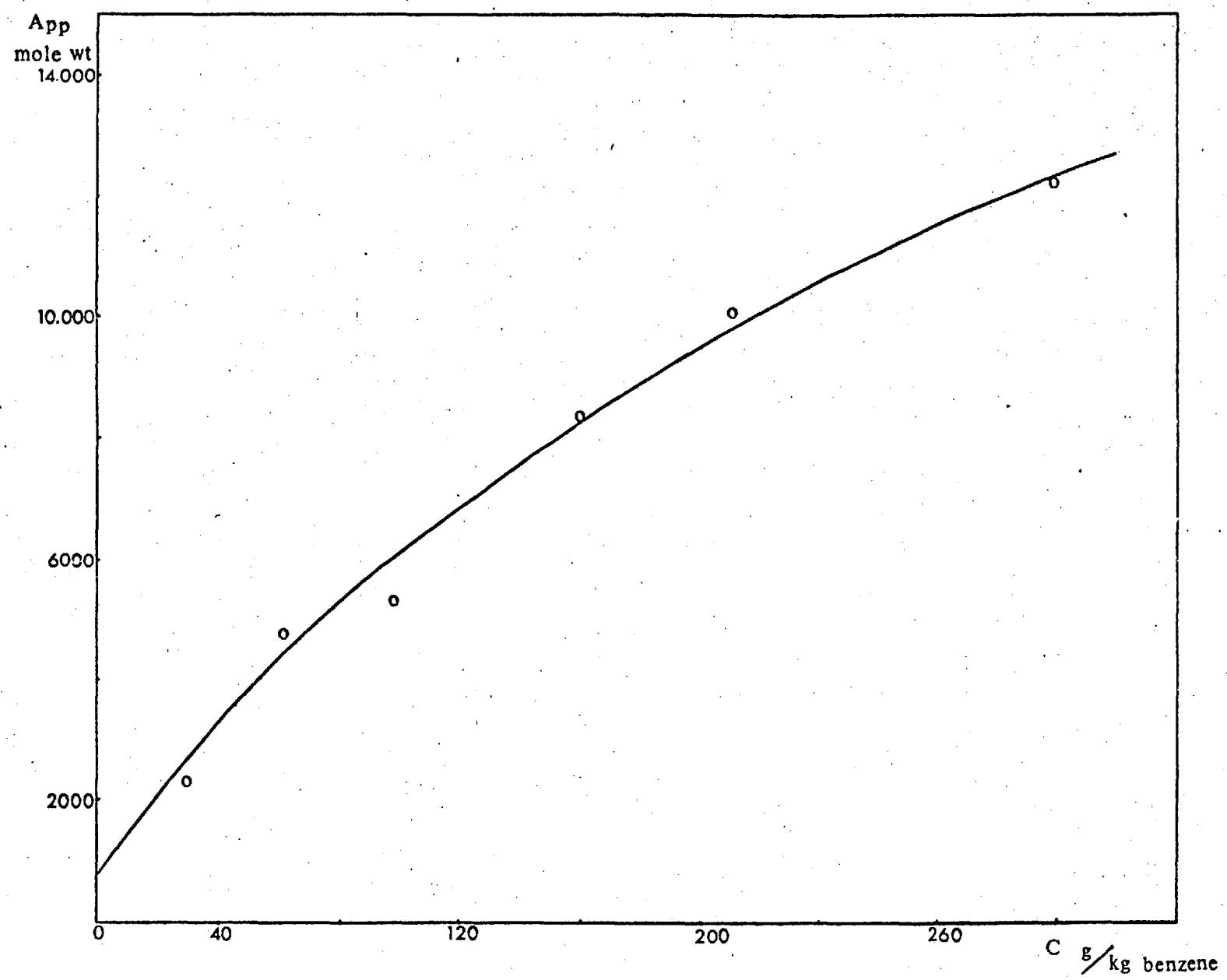

App
mole wt
14.000
10.000
6000
2000
0
40
120
200
260
C g/kg benzene

Figure: 5.V1

COPPER SALT OF TRIOCTYLAMINE HYDROCHLORIDE

C	VmV	V/C	App.mole wt	$\bar{n}$
30.0624	0.17	0.00565	2656.72	3.62
62.5027	0.195	0.003120	4817.99	6.57
99.5244	0.285	0.002884	5249.12	7.16
161.6311	0.290	0.001794	8377.90	11.42
212.0081	0.290	0.001368	10988.94	14.99
298.5600	o.365	0.001222	12295.36	16.77

Table (5.V1)

Experimental results indicate that polymerization is taking place.

Discussion

In this section, by determining molecular weights an attempt was made to get some information about association of the extractant TOAHCl and also the extracted compound. This was expected to provide some explanation for the composition of the extracted copper complex.

It is shown by many authors[2,22,23] that most of the amine salts can polymerize and associates of amine salts often enter the composition of the extracted compound without changing their degree of association.

The associative forces which are operative between one salt molecule and another can be described as the energy of attraction A between their dipoles

$$A = \frac{2\mu^4}{3r\ kT}$$

where μ = dipole moment of the pole molecule

r = distance between the molecules

k = Boltzmann constant.

Association increases with increasing dipole moment of the salt molecule and decreases with its size i.e. decrease in the number and the length of alkyl chains and temperature.

Association of amines and their salts also depends on the nature of diluent and its solvation power which would have an effect on the degree of association and the number of associates.

Aggregation of amines and their salts, their influence on the distribution coefficient have been studied by many workers.

The effect of polymerization of extractant on the distribution coefficient can be shown simply by writing the expression[3]

$$D = \frac{K}{f_o} (S)^p \quad \ldots\ldots \quad \text{(Chapter 2)}$$

or $\log D = \log K + p \log (S).$

In the simplest case, we can assume that only dimerization is occurring; then, equilibrium constant for dimerization is given by

$$K_2 = \frac{[C_2]}{[C_1]^2}$$

where $[C_1]$ and $[C_2]$ are the concentrations of monomers and dimers. If the initial concentration of the extractant is $[C_o]$

$$2[C_2] + [C_1] = [C_o]$$

or $$2 K_2 [C_1]^2 + [C_1] - [C_o] = 0$$

$$[C_1] = \frac{(1 + 8K_2 C_o)^{1/2} - 1}{4 K_2}$$

considering micro amounts of concentration; by substitution

$$\frac{d \log D}{d \log [C_o]} = \frac{4K_2 [C_o]}{1 + 8 K_2[C_o] - (1 + 8 K_2 [C_o])^{1/2}} \cdot p$$

As was mentioned in Chapter (2) and suggested by other workers, the slope of the plot of log D against $\log [C_o]$ was expected to give the number of extractant molecules associated with metal. However, as shown above, the slope varies with degree of dimerization.

Schmidt[22], to show the effect of polymerization, gives an expression for distribution coefficients in terms of concentrations and activity coefficients. If reaction is taking place according to the reaction below

$$M^{m+} + mA^{-} + n\ (\text{Amine HA})_p \rightleftharpoons \left[\text{Amine H}\ (\text{Amine HA})_{p-1}\right]_n \left[MA_{n+m}\right]$$

where p = degree of association of the amine salt

$$D = K\left[A^{-}\right]^{m}_{aq}\left[(\text{Amine HA})_p\right]^{n}_{o}\ \left(\gamma^{\pm}_{MA_m}\right)^{m+1}$$

Thus, D does not necessarily vary with p.

Schmidt states that for micro amounts of metals all relationships, for the extraction by monomers are valid. However, the extraction of high concentrations of metal salts may be accompanied by the disruption of the formation of associates of the type $\left\{(\text{Amine H})_n\ MA_{n+m}\right\}_y$ or $(\text{Amine HA})_x\ (MA_n)_y$.

The plot of log D against log TOAHCl suggests the formation of associates of TOAHCl during the extraction. In fact, molecular weight determinations showed that TOAHCl is benzene consists of dimers.

The TOA-HCl system in particular has been studied by Newman[23], Fukutomi[24], Duyckaerts and many other workers.

The equilibrium constant for the reaction of TOA with HCl

$$\text{TOA} + H^{+}\ Cl^{-} \overset{K}{\rightleftharpoons} \overline{(\text{TOAHCl})}$$

was given by Newman as $K = (1.4 \pm 0.4) \times 10^{-4}$ and he states that aggregation takes place at amine concentrations greater than 2×10^{-2}M.

Kojima's value for the equilibrium constant is $(1.51 \pm 0.02) \times 10^{-4}$ and for dimerization constant (12.9 ± 0.5)

and when HCl concentration is greater than 3M, more acid is extracted into amine than corresponds to the 1:1 composition. Therefore 5 possible amine-hydrochloride species will exist i.e. $(TOAHCl)_2HCl$, $(TOAHCl)_3HCl$, $(TOAHCL)_3(HCl)_3$ are major complexes and $(TOAHCl)_2(HCl)_2$, $(TOAHCl)_3HCl$ are minor complexes.

The theoretical methods for calculation of monomer and dimer concentrations are given by several authors[27,34].

The conclusion of our experimental results and other workers' reports is that TOAHCl in benzene forms associates of $(TOAHCl)_n$ where $0>n>2$. Considering this polymerization, the extraction of copper takes place according to the equation

$$Cu^{2+} + 2\ Cl^- + \frac{2}{n}\ \overline{(TOAHCl)}_n \rightleftharpoons \overline{(TOAH)_2CuCl_4} \quad \ldots\ldots \quad (A)$$

with metal:Amine ratio 1:2. Thus the slope of the log D - log (TOAHCl plot should be not 2 but $^2/_n$. Moreover, since n changes with the amine concentration, the above relation-should not be linear.

Our experimental data for the metal:amine ratio is 1:2.5207 and linear dependence of log D on log TOAHCl was found, with slope 1.6129.

Schmidt explains this mechanism by assuming that there is no change in the association of the molecules of the extractant agent on formation of the compounds and by the reaction below:

$$Cu^{2+} + 2Cl^- + 2\overline{(TOAHCl)_n} \rightleftharpoons \left[\overline{TOAH(TOAHCl)_{n-1}}\right]_2\ CuCl_4 \quad \ldots\ (B)$$

This is confirmed by the fact that the extractive capacity of

amine salts at saturation with metal salts is usually much less than the omplex being extracted[22]. That is the reaction of the type given in Equation (A). The ratio of metal:amine at saturation is usually greater. Because of lower dielectric constant of the medium, polymerization of the amine salt is greater.

It was reported that in the extraction of macro quantities of $CuCl_2$, depolymerization of the amine salt takes place, monomeric TOAHCl molecules combine with $CuCl_2$ and polynuclear components of the type $\left[(TOAH)_2CuCl_4\right]_n$ are formed in the organic phase [22], and Equation (B) only applicable at low concentrations of metal salt in the organic phase.

The present data confirms that polymerization of TOAHCl-Cu complexes occurs. By combination of experimental data obtained in previous chapters and association of the extractant the composition of the organic phase is

$$\left\{\left((TOAH)\ (TOAHCl)_n\right)_2\ \ Cu\ Cl_4\right\}_m$$

Conclusion

From molecular weight determinations we were able to show

1- TOAHCl forms aggregates in benzene and aggregation number increases with increasing molality of TOAHCl.
2- Dimerization constant $K_D = 8.18$.
3- TOAHCl-Cu forms polymers in the organic phase.

CHAPTER 6

EXTRACTION OF COPPER BY TOAHCl IN PRESENCE OF IRON

Many of the industrial solutions which contain copper also contain the salts of other metals. Some metals act as reducing agents and thus influence the extraction mechanism of copper.

In this section the influence of iron was determined. It was observed that bivalent and trivalent iron affect the distribution of copper in opposite ways.

Materials

TOAHCl: 0.1M TOA solution was made up by diluting with benzene. 100 mls parts of this solution was equilibrated with equal volumes of 0.2M HCl.

Ferric chloride (0.5M): 135.2g $FeCl_3.6H_2O$ was dissolved in water containing 20ml/l concentrated HCl and diluted to 1 litre.

Ferrous chloride (0.5M): 46.44g $FeCl_2.4H_2O$ was dissolved in water, filtered and diluted to 1 litre. However, because of hydrolysis, it was difficult to keep Fe^{2+} in the solution. Some iron wire was put into the solution to prevent formation of Fe^{3+}. This would continuously increase the concentration of Fe^{2+}. For this reason, concentration of the solution was checked by A.A each time it was used.

LiCl. The stock solution which was used in previous experiments

was diluted according to the required chloride concentrations.

Experimental Technique

Because of its speed and accuracy, a first series of experiments were carried out by Akufve[28-9]. However, it was difficult to obtain optimum conditions in order to determine the effect of varying metal concentrations of the aqueous phase on distribution coefficients. The rest of the experiments were carried out by shake-out tests.

Extraction of Fe^{3+} by TOAHCl

300 mls of aqueous solution containing 1.0M LiCl and 8.25 Fe^{3+} and 0.1M TOAHCl solution were put in contact in the Akufve system. Every other 15 min., 2 mls samples of each phase were taken out and more Fe^{3+} was added into the aqueous phase. After 8 samples more LiCl was added to increase the extraction capacity Organic phase samples were stripped with equal volumes of dilute HCl and the iron concentration of solutions were determined by A.A. (Table 6.I.)

There was no way of determining the aqueous phase metal concentration before each addition. The experimental results therefore, do not give much information. In addition, the phase ratio for each pair of measurements is different making it difficult to compare the distribution coefficients. It can only be stated that Fe^{3+} is easily extracted from chloride solutions at even low chloride molarity.

Extraction of copper in presence of ferric ions

In order to determine the effect of Fe^{3+} ions on the extraction of copper from chloride solutions, an aqueous solution

was prepared containing 5M LiCl and 10ppm Fe^{3+}. 285 mls of aqueous and of organic solutions were put in the Akufve. After taking the first samples, some $FeCl_3$ and $CuCl_2$ was introduced into the system. The experiment was carried out by taking 2 mls of samples of each phase and adding Fe^{3+} and Cu^{2+} to the aqueous phase.

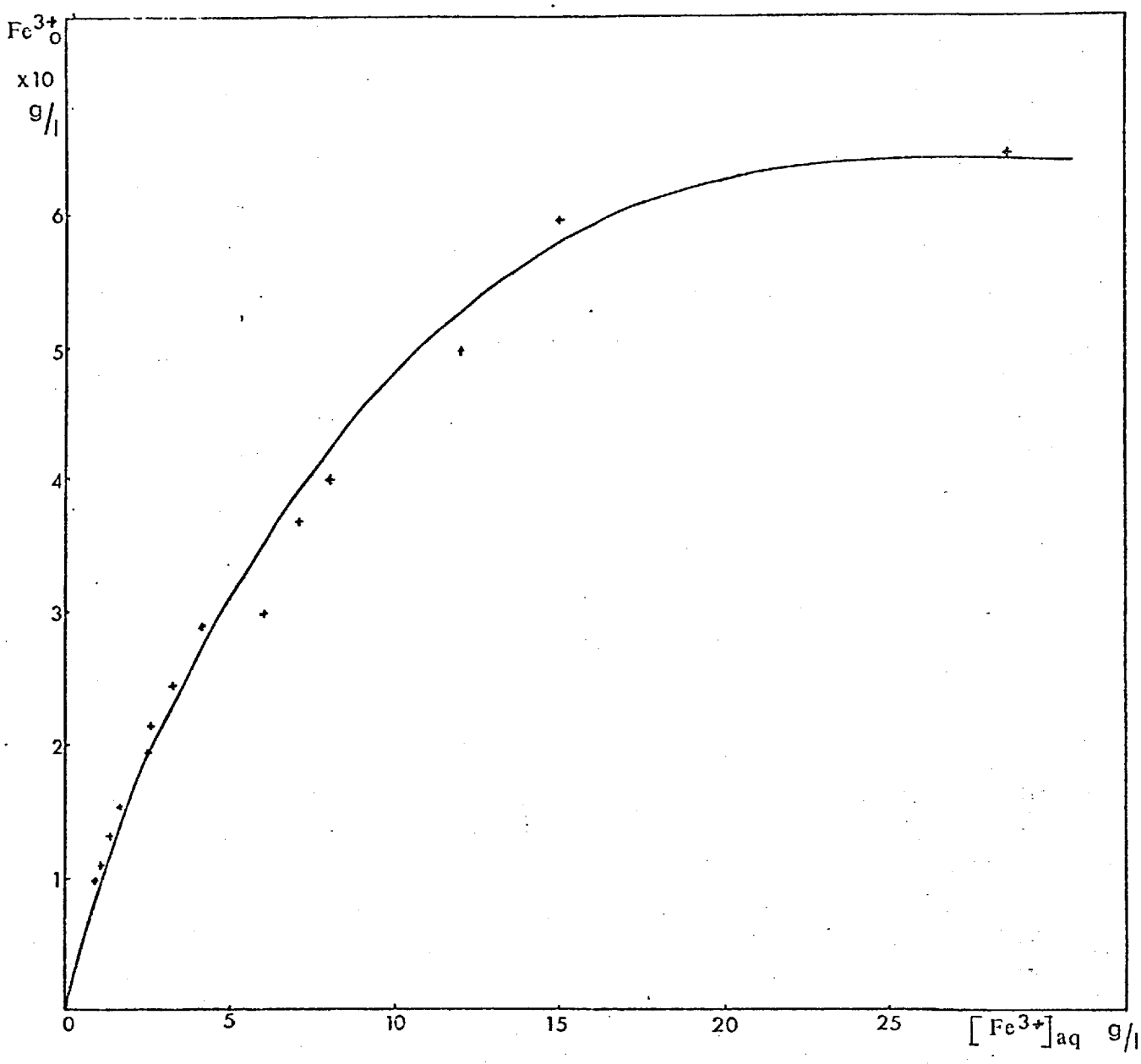
The same experiment was repeated by using shaking funnels. The aqueous phase LiCl concentration was 4M and Cu^{2+} concentration was kept constant, 100 ppm. Fe^{3+} concentration was varied from 32.5 to 262.5 ppm. Aqueous and organic phase Fe^{3+} and Cu^{2+} concentrations are shown in (Table 6.11). The average extraction percentage for iron was 92.2 whereas for copper it was 6-20%. This cata supports the possibility of separating iron and copper by this method.

A second series of aqueous solutions were prepared containing higher concentrations of both metals. Cu^{2+} concentration was again kept constant, 1g/l and Fe^{3+} was varied between 1 and 28.5 g/l.

At about equal concentrations of Fe^{3+} and Cu^{2+} almost 99% of iron was extracted and the extraction percentage of copper was 25-27%. When the Fe^{3+} concentration was doubled its extraction fell to 75-80% but Cu^{2+} also decreased to 5-10%.

As the Fe^{3+} concentration of the aqueous solution increased the organic phase became saturated and the molarity of Fe^{3+} in the organic phase reached 0.1M. The amine:metal ratio is 1:1 suggesting formation of Amine $HFeCl_4$ complexes (Figure 6.1).

At high concentration of Fe^{3+} very low copper extraction was observed (4-5%).



6.1

Extraction of copper in presence of Fe^{2+} ions.

The first sets of aqueous solutions were prepared containing 0.1MHCl, 2M LiCl, 100 ppm Cu^{2+} and various concentrations of Fe^{2+}. All concentrations are shown in Table (6.1V).

The second sets of solutions were prepared with higher chloride concentration, 4M LiCl and 0.1M HCl.

When the aqueous phase chloride concentration was increased, an increase in extraction of both metals was observed (Figure 6.11). As can be seen in Figure (6.11), increasing Fe^{2+} concentration results in increased copper extraction. The relationship between aqueous phase Fe^{2+} and extraction of copper is not linear.

At high concentrations of Fe^{2+} i.e. Fe^{2+} : Cu^{2+} is 3:1 extraction of copper is almost 99%. At equal concentrations of Fe^{2+} and Cu^{2+} (116 ppm), nearly all of the copper and 72% or iron was extracted. The experimental data shows that in the presence of the other, the extraction of both cupric copper and ferrous iron is increased due to changes of valency.

Discussion

Since the extraction of copper by TOAHCl, from chloride media was discussed in detail, it is interesting to see the influence of other metals which present in the aqueous solution. In this chapter, only the presence of Fe^{3+} and Fe^{2+} ions was studied and their effect on the extraction mechanism determined.

The possibility of extraction of iron in the ferric state by various amines has been shown previously by other workers. H.D. Mahlman and his co-workers[30], and Wilson[31] studied the

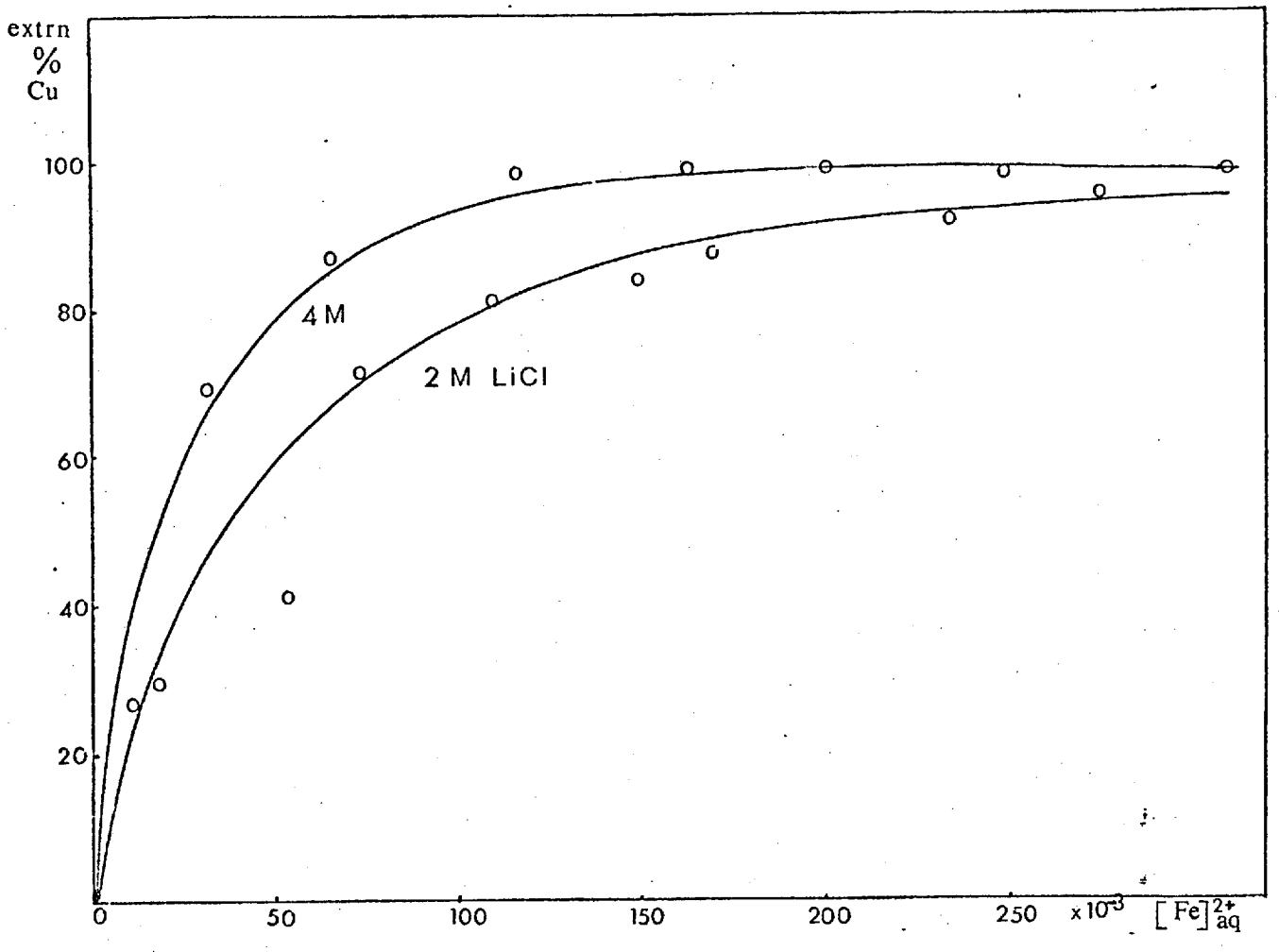

extrn
%
Cu
100
80
60
40
20
4 M
2 M LiCl
0
50
100
150
200
250
x10⁻³
[Fe]²⁺aq

Figure 6.11

effect of HCl concentration of the aqueous phase on distribution of Fe^{3+}. They observed nearly 95% extraction from 4M HCl aqueous solutions and stated that the extraction percentage increased with increasing HCl concentration. Muller[32] showed the extraction of Fe^{3+} by various amines and concluded that tertiary amines are the bext extractants. W. Smulek and S. Siekiereki[33] showed the effect of diluent on solvent extraction in general and in particular in case of Fe^{3+} extraction. Juznic[35] in his paper on "extraction of Fe^{3+} from HCl media with TOA in benzene" showed the co-extraction of water as a function of iron concentration in the organic phase.

Spectrophotometric studies of organic phases were carried out by M. Good[36], Nelson[37], Lindenbaum[38] and Duyckaerts[39]. According to their data, extracted metal exists as tetrachloroferrate. J.M. White[40] however, noted the existence of negatively charged $FeCl_5^-$ species and from his slope analysis, extraction takes place according to the equation:

$$Fe^{3+} + 3\ Cl^- + 2R_3NHCl \leftrightharpoons (R_3NH)_2\ FeCl_5$$

W. Muller and G. Duyckaerts[32] in their study of the extraction of Fe^{3+} from HCl solutions observed the dependence of distribution coefficient on aqueous phase chloride molarity. The distribution coefficient passes through a maximum at 10M HCl. In the increasing part of the durve when the aqueous phase HCl concentration is less than 10M, complexes formed in the organic phase have 2:1 amine: metal ratio and in the decreasing part, at high acidity, the amine: metal ratio is 1:1. They also observed excess acid in the organic

phase when the aqueous phase contained high concentrations of HCl.

Schmidt's statement[2] is that iron in the ferric state is readily extracted from HCl solutions even at low HCl concentrations so that by this way Fe^{3+} can be separated from many elements. His spectrometric analysis gives evidence of the existence of the $FeCl_4^-$ species in the organic phase with amine:metal ratio 1:1. Therefore, the organic complex is $(AmineH)(FeCl_4)$. If the extractant is associated then the reaction will take place according to the equation:

$$Fe^{3+} + Cl^- + 2(\overline{Amine\ HCl})_p \rightleftharpoons \overline{\{Amine\ H\ \ Amine\ HCl\}_{p-1}\ \ FeCl_4\{Amine\ HCl\}_p}.$$

From this review of the research which has been done in the extraction of ferric chloride, it can be concluded that Fe^{3+} extracted from HCl solutions is present in the organic phase as $FeCl_4^-$ ions and at high aqueous Cl^- concentrations, the amine: metal ratio is 1:1. On the other hand, extraction of Fe^{2+} is very much less[2], only at high chloride concentrations does it become significant. The Author's observation was that in the extraction of Fe^{2+} some of the iron was in ferric state.

In the solvent extraction of copper we determined the influence of ferric and ferrous ions in the aqueous phase. The presence of ferrous ions resulted on increase of copper extraction and conversely, the extraction of iron in the presence of Cu^{2+} ions was also increased. This phenomena can be explained by a reduction mechanism taking place in the aqueous phase. Between copper and iron ions in the solution we find the relationship

$$Fe^{2+} + Cu^{2+} \rightleftharpoons Fe^{3+} + Cu^{+}$$

A potential-pH diagram for chloride systems for iron and copper is given by Kametani[41].

$E^{o}Fe^{3+}/Fe^{2+} = 0.76$ V and $E^{o}Cu^{2+}/Cu^{+} = 0.17$ V

Cu^{2+} will be reduced to Cu^{+} by the reaction

$$Cu^{2+} + Fe^{2+} \times 2Cl^{-} + 3 + H_2O \rightleftharpoons CuCl_2^{-} + Fe(OH)_3 + 3H^{+}$$

When the aqueous solution is treated with the extractant, the anions formed pass into the organic phase and reaction shifts to the left. The presence of excess chloride in the aqueous phase shifts the reaction to the right.

The overall extraction process as suggested by Ramazanova[42] can be expressed as follows:

$$Fe^{2+} + Cu^{2+} + 4\ Cl^{-} + 2\ \overline{TOAHCl} \rightleftharpoons \overline{TOAHFeCl_4} + \overline{TOAHCu\ Cl_2}$$

Iron is extracted as ferric and copper as cuprous ions. As the extraction proceeds, aqueous Fe^{2+} and Cu^{2+} concentrations will decrease continuously but the concentration of Cu^{+} will increase. Ramazanova's[42] spectrometric analysis confirms the presence of $FeCl_4^{-}$ and $CuCl_2^{-}$ ions in the organic phase.

As has been reported and was observed in the present experiments, in the presence of Fe^{2+} one finds increased copper extraction (by Gunzler and Muhl; extraction by TBP and by Ramazanova's extraction by TOAHCl). Kametani however, states that if Versatic 911 is used as extractant copper is not extracted. He observes poor phase separability and co-extraction of Fe^{2+} by formation of double salts or complexes between Fe^{2+} and Fe^{3+}, probably formation of hydroxide complexes.

Extraction of monovalent copper by TOAHCl is much higher than extraction of bivalent copper[8]. The presence of Fe^{2+} ion in the aqueous phase increases the concentration of Cu^{+}. Thus the overall copper extraction in the presence of Fe^{2+} will be higher. The same relationship can be drawn for extraction of iron. Extraction of Fe^{2+} itself is weaker than Fe^{3+}. In the presence of Cu^{2+}, Fe^{3+} ions are formed and extracted. Thus if iron and copper in an aqueous solution are initially in the bivalent form it is possible to remove them at the same time by TOAHCl.

The presence of Fe^{3+} has a reverse effect on copper extraction. In the experiments it was observed that extraction of copper decreased in the presence of Fe^{3+}. Iron extracted to the extent of almost 95% whereas copper extraction was only 4-5%. Because Fe^{3+} can easily be extracted at low concentrations of supporting electrolytes, it is possible to separate iron from other metals such as Co, Ni, Cu, Pb and Mn. In fact, we can find the use of these methods in technology. Purification of Co[44] and Ni[43] are the most important ones of the rest.

In the case of purification of Co, the initial solution is treated with chloride in order to convert all the iron into extractable trivalent compound. Then the aqueous solution is brought into contact in a counter-current mixer settler with an equal volume of the organic phase (TAA). By this operation the concentration of iron is reduced by a factor of about 30,000. The chloride concentration of the residual aqueous solution is

then increased and it is treated with TAA in kerosine in order to extract Co.

In the Falconbridge process, the pregnant solution contains 120 g/L Ni; also some Fe, Co and Cu. The iron is oxidized to the ferric state and is removal is accomplished by TBP. The residual aqueous solution containing Ni, Co and Cu with a very little iron is extracted with TISOA leaving a pure nickel solution.

Conclusions

1- The presence of ferrous ions in the aqueous solution results in
   a) increased copper extraction
   b) increased iron extraction in the presence of Cu^{2+}
   c) iron is extracted as Fe^{3+} and Cu is in monovalent

2- In presence of ferric ions Cu^{2+} is not extracted at4M chloride concentration. It is possible to separate iron from copper by this process.

CHAPTER 7

GENERAL SUMMARY

The main object of solvent extraction processes is to obtain solutions of metals with high purity, ready for electrolytic or other methods of producing metals. By solvent extraction methods, it is also possible to recover metals from low grade ores and separate them from other metals.

This work involves extraction of copper from chloride solutions by TOAHCl. Solvent extraction of copper was studied by various researchers using different types of amines or their salts. (Aliquat 336[45], Methyltrioctyl ammonium chloride[46], dimethylbenzyl octa dectyl ammonium chloride[47], tetrahexyl ammonium chloride[48], TOA[46], TlOA[30], TBA[49], Alamine 336[49]. Adogen 364[49], Amherlite LA-1[45] and Primene JMT[45].

Because of its higher extractive capacity and high solubility TOA was chosen as an extractant. It is known that salts of amines are better extractants. For this reason, the hydrochloride salt of TOA was used not TOA itself.

Extraction of metals by amines or by their salts is expressed by the following reaction

$$M^{m+}_{aq} + m\,A^{-}_{aq} + n\,(\overline{\text{Amine HA}})_o \rightleftharpoons \overline{(\text{Amine H})_n\,MA_{m+n}}$$

and the equilibrium constant

$$K_m = \frac{\left[(\text{Amine H})_n\,MA_{m+n}\right]\gamma_o}{M_{aq}\left[A^-\right]^m_{aq}\left[\text{Amine HA}\right]^n \gamma_{\pm MA_m} \cdot \gamma^n \text{Amine HA}}$$

The distribution coefficient is given by

$$D_M = \frac{\left[(\text{Amine})_n\,MA_{m+n}\right]_o}{\left[MA_m\right]_{aq}}$$

In the case of strong electrolytes, the metal complex concentration in the aqueous phase may be taken as $\left[M^{m+}\right]_{aq}$. Then the distribution coefficient of the metal

$$D = K_M\left[A^-\right]^m_{aq}\left[\text{Amine HA}\right]^n \gamma_{MA_m} \cdot \gamma^n_{\text{amine HA}} \cdot \gamma^{-1}_{\text{org M}}$$

Distribution of metal depends on the concentration of the amine salt, aqueous phase anion concentration and activity coefficients of amine salt, amine-metal complex and metal in the aqueous phase. Therefore, distribution coefficient depends on the composition of aqueous phase and behaviour of the extractant.

In the following sections; first the effect of aqueous phase composition and effects of organic phase on distribution of copper will be discussed.

Effect of aqueous phase composition on distribution of copper

The composition of the aqueous phase determines the main parameters affecting the distribution coefficient. First of all, the influence of anion concentration was studied. As was shown above, the distribution coefficient increases in parallel with qqueous phase anion concentration. However, experimental

results in the first chapter indicated that different electrolytes at equivalent concentrations did not have equal effects. LiCl gave the highest distribution and D values for $CaCl_2$ were the lowest. On the other hand, when HCl was used as a supporting electrolyte, a maximum point was found, followed by an increase in the distribution coefficient. This is explained by the "HCl effect". The reason for the different effects of these supporting electrolytes with common anion is the change of activity coefficients due to the hydration of the electrolyte. This results in variation of the water activity and activity of the metal. To confirm this, water activities for LiCl, HCl and $CaCl_2$ solutions at equal chloride molarities are shown in Table (2.1V 1).

When the organic phase was saturated with copper by keeping organic phase amine concentration and aqueous phase Cl^- concentration constant and increasing the concentration of copper in the aqueous phase, the amine:metal:chloride ratio in the organic phase was 2.52:1:4.76. This suggests that 2 amine molecules combine with one molecule of copper. Spectrophotometric analysis has not been carried out on the organic phase but published data confirms the presence of $CuCl^-_4$ ions.

Spectrophotometric studies of the aqueous phase indicated that up to 2M chloride concentrations only Cu^{2+} and $CuCl^+$ ions existed and the first complexing constant was 0.69 M^{-1}. The same method of analyzing the data was, however not applicable for other stability constants k_2 k_3 k_4.

A graphical method was also applied to determine the extractable copper-chloride complexes in the aqueous phase. The theory of the method is given in Appendix II None of the literature values for stability constants (Giovanni, G. D'Amore, Bjerrum) could give a definite answer. Only the graph obtained by using Bjerrum's values for stability constants is shown in Figure (7.I). The D_{Cu} curve does not coincide with any α curves. Probably this is due to the presence of not one but several complexes.

Generally the solvent extraction technique is applied to the separation of elements rather than to their extraction from aqueous solutions. From this point of view, the influence of ferric and ferrous ions on the extraction mechanism was studied. According to the experimental work and literature data, if iron present in aqueous copper solutions is in ferric state, it is possible to separate them by solvent extraction method and separation is easier at higher chloride concentrations. If iron is in the ferrous state, a reduction mechanism occurs in the aqueous phase, Cu^{2+} is reduced to Cu^{+} and co-extracted. Two examples of the application in industry of such a process are given in Chapter 6.

Effect of organic phase composition

Extraction experiments were carried out to observe the effect of amine concentration on distribution of copper. Co-extraction of water and aggregation of amine salt are the two other factors one can expect to have an influence on the distribution of metal.

Application of the slope analysis method suggested that aggregation was occurring in the organic phase. Molecular weight determinations confirmed this assumption. Tri-n-octylamine hydrochloride forms dimers in benzene. On the other hand, copper-amine complexes exist in the organic phase as polynuclear species.

Some abnormalities in solvent extraction processes are caused by co-extraction of water. As was mentioned previously, hydration of the organic phase depends on the chloride concentration of the aqueous phase and the type of supporting electrolyte when other concentrations are kept constant.

Taking into account all the factors, the extraction mechanism of copper by TOAHCl in chloride media takes place according to the equation

$$m\mathrm{Cu}^{2+} + 4m\ \mathrm{Cl}^{-} + 2m\ (x+1)\ \overline{(\mathrm{TOAHCl})} \rightleftharpoons \left\{\overline{(\mathrm{TOAH})(\mathrm{TOAHCl})_x)_2\ \mathrm{Cu\ Cl_4}}\right\}_m$$

In the presence of ferrous ions

$$\mathrm{Fe}^{2+} + \mathrm{Cu}^{2+} + 4\mathrm{Cl} + 2\ \overline{\mathrm{TOAHCl}} \rightleftharpoons \overline{\mathrm{TOAH\ FeCl_4}} + \overline{\mathrm{TOAH\ CuCl_2}}.$$

APPENDIX 1

Theory of the V.P.O.

For a solution obeying Raoult's Law, the lower of the solvent vapour pressure (p) due to a solute of mole fraction concentration x_2 is given by

$$p = p_1^{o} x_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where p_1^{o} is the vapour pressure of the pure solvent.

If the solvent vapour is assumed to behave ideally

$$\frac{1}{p}\ \frac{dp}{dT} = \frac{\Delta H_v}{RT^2} \quad \text{Clausius-Clapeyron equation} \ldots\ldots (2)$$

where H_v = enthalpy of vapourization

R = gas constant

T = absolute temperature.

A v.p.o. operates on the principle of the solution drop temperature being raised by condensation of solvent vapour until the vapour pressure of the solution is equal to the vapour pressure of the pure solvent.

When temperature is increased from T_1 to T_2, integration of equation (2)

$$\int_{p_1}^{p_2} dp = \frac{\bar{p}\Delta\bar{H}_v}{R\bar{T}^2} \int_{T_1}^{T_2} dT$$

Therefore $$\Delta T = \frac{RT^2}{\bar{p}\ \bar{H}_v} \Delta p \quad \ldots\ldots\ldots\ldots (3)$$

by substitution of equation (1) into (3) $$\Delta T = \frac{R\,T^2}{\bar{p}\ \ \Delta H_v} p_1 x_2$$

or $$\Delta T = k_1 x_2$$

also $$\Delta T = k_2 V$$

by substitution $$x = \frac{k_1 V}{k_2}$$

In dilute solution $$x_2 = \frac{C}{M_2}\ \frac{M_1}{1000}$$

where C is the solute concentration in g/kg., M_1 is solvent molecular weight and M_2 is solute molecular weight

Combining last two equations

$$\frac{V}{C} = \frac{K}{M_2}$$ where K is a constant.

Hence for a particular solvent and operating temperature graph of V against C for a solute of known behaviour enables to determine K. This K value then is used to calculate the molecular weights of other solutes.

When solution is not ideal then,

$$\frac{V}{C} = \frac{V}{C}_{C=0} (1 + AC + BC^2 \ .....)$$

where A and B are the second and third coefficients.

Generally above equation is used in the form

$$\frac{V}{C} = \frac{V}{C}_{C=0} (1 + AC)$$

When V/C is plotted against C, the intercept gives the value of $\frac{V}{C} = \frac{V}{C}_{C=0}$. Since all solutions approach Raoultion behaviour at low concentrations, $\frac{V}{C}_{C=0}$ value can be substituted into the equation and M_2 is calculated.

APPENDIX II

Calculation of α_n values for Cu - Cl system :

Formation of four chlorocomplexes can be shown as :

$$Cu^{2+} + Cl^- \quad CuCl^+ \quad \ldots\ldots k_1$$
$$CuCl^+ + Cl^- \quad CuCl_2 \quad \ldots\ldots k_2$$
$$CuCl_2 + Cl^- \quad CuCl_3^- \quad \ldots\ldots k_3$$
$$CuCl_3^- + Cl^- \quad CuCl_4^{2-} \ldots\ldots k_4$$

In general,

$$k_n = \frac{CuCl_n^{2-n}}{CuCl_{n-1}^{3-n} \cdot Cl} \cdot \frac{1}{F}$$

where F = mean activity coefficient.

It was assumed that log $CuCl_n^{2-n}$ changes evenly from $\gamma_{Cu^{2+}}$ to γ_{CuCl_4} in concentrated solutions. For concentrated solutions, log F = A + B C_{ion} where C is the total normality of the ion. On the other hand, d log α_n / d log Cl = n-$\bar{n}$ where α_n = $CuCl_n^{2-n}$/Cu

or $n - \bar{n} = \frac{d \log \alpha_n}{d \log F + d \log Cl^-}$ but $C_{ion} = Cl^-$ (since Cu is low and Cl^- is high).

$\frac{d \log \alpha_n}{d\ Cl^-} = \frac{0.43}{Cl^-} + B\ (n - \bar{n})$ but α_n is proportional to $\frac{(\ )}{436}$.

$\frac{d \log \frac{436}{}}{d\ Cl^-} = \frac{0.43}{Cl^-} + B\ (n - \bar{n})$. According to Bjerrum's calculations for LiCl, B =0.23

It can also be written that $k_4 = \alpha_4 / (I-\alpha_n)\ F\ Cl^-$.

Bjerrum's k values are:

$k_1 \leq 1$, $k_2 = 0.1, 0.4$, $K_3 = 0.02, 0.06$, $k_4 = 0.003, 0.001$

These give α values

$$\alpha_c = \frac{1}{T}, \quad \alpha_1 = \frac{k_1 [Cl] F}{T}, \quad \alpha_2 = \frac{k_2 [Cl]^2 F^2}{T}$$

$$\alpha_3 = \frac{k_3 [Cl]^3 F^3}{T}, \quad \alpha_4 = \frac{k_4 [Cl]^4 F^4}{T}$$

where, $T = 1 + k_1[Cl]F + \beta_2[Cl]^2F^2 + \beta_3[Cl]^3F^3 + \beta_4[Cl]^4F^4$

Table given below shows the values calculated by using above equations

$\beta_2 = 0.04$, $\beta_3 = 8 \times 10^{-4}$, $\beta_4 = 2.4 \times 10^{-6}$.

$k_1 = 0.4$, $K_2 = 0.1$, $k_3 = 0.02$, $k_4 = 0.003$.

Cl	α_o	α_1	α_2	α_3	α_4
0.0	1	0	0	0	0
1.0	0.556	0.378	0.064	218×10^{-3}	1.11×10^{-5}
2.0	0.209	0.482	0.276	0.0318	5.53×10^{-4}
3.0	0.055	0.325	0.48	0.141	6.30×10^{-3}
4.0	0.011	0.148	0.448	0.332	0.0310
5.0	1.75×10^{-3}	0.049	0.349	0.496	0.105
6.0	2.29×10^{-4}	1.32×10^{-2}	0.191	0.555	0.241

$k_1 = 1$, $k_2 = 0.4$, $k_3 = 0.06$, $k_4 = 0.01$.

Cl	α_o	α_1	α_2	α_3	α_4
0.0	1	0	0	0	0
1.0	0.613	0.328	0.056	2.28×10^{-3}	1.23×10^{-5}
2.0	0.233	0.424	0.309	0.034	6.11×10^{-4}
3.0	0.059	0.275	0.516	0.144	6.76×10^{-3}
4.0	0.012	0.122	0.512	0.321	0.034
5.0	1.81×10^{-3}	0.041	0.362	0.487	0.109
6.0	2.47×10^{-4}	0.011	0.198	0.542	0.249

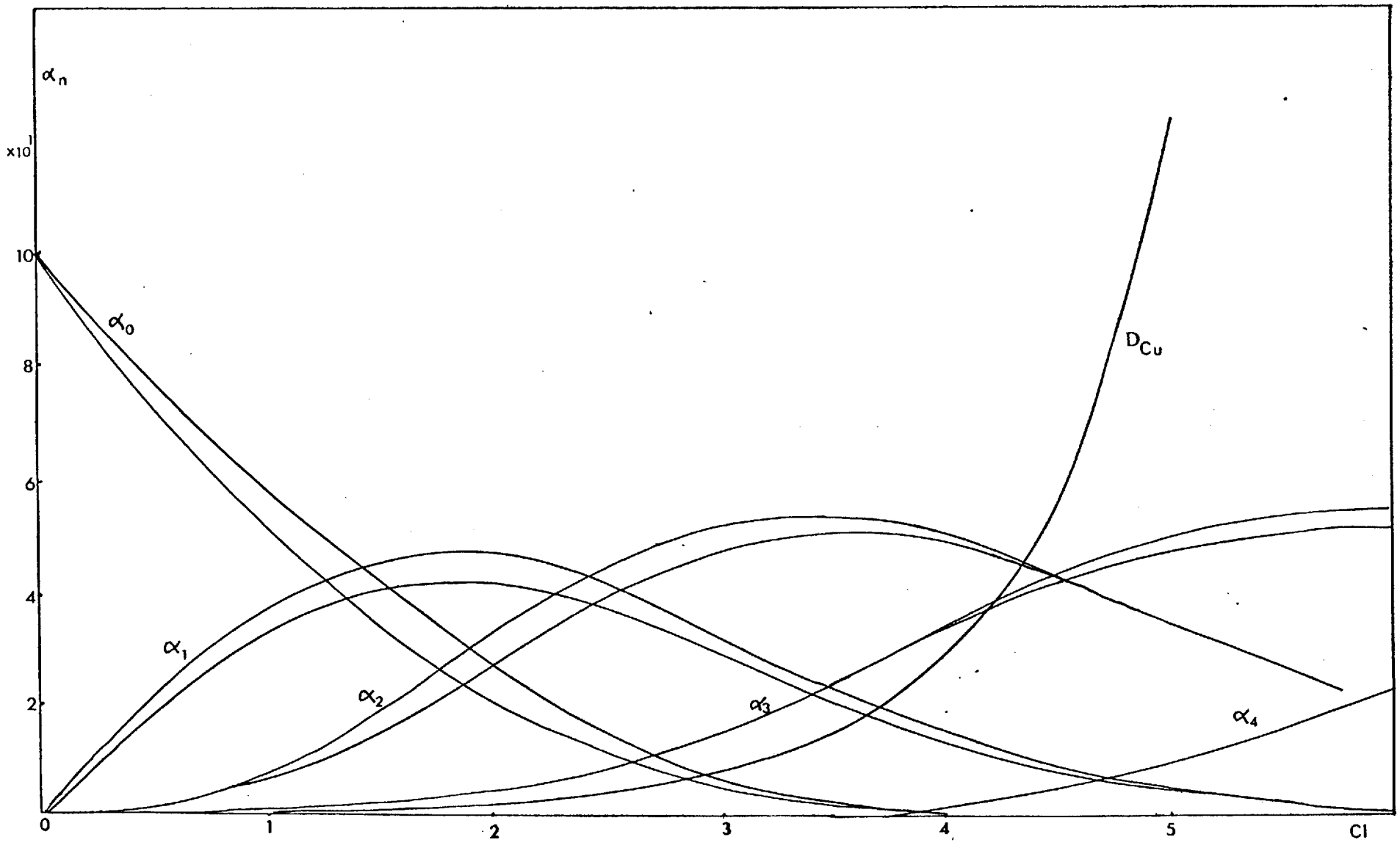

α_n
x10
10
8
6
4
2
0
1
2
3
4
5
Cl
α_0
α_1
α_2
α_3
α_4
D_{Cu}

figure: 7.1.

TABLES OF RESULTS

Table (2.1a) Extraction from HCl solutions

Total Cl^- M	Before extrn. g/l	After extrn. g/l		D_{Cu}	Log D_{Cu}
0.5	0.0105	0.010	0.0005	0.050	-1.6990
1.0	0.0115	0.0099	0.0016	0.161	-1.3197
2.0	0.0103	0.0088	0.0015	0.197	-0.7042
4.0	0.0108	0.0024	0.0084	3.500	0.5441
6.0	0.0105	0.0006	0.0099	16.500	1.2175
7.0	0.0105	0.0005	0.0100	20.000	1.3010
8.0	0.0105	0.0011	0.0094	8.545	0.9318

Table (3.1b) Extraction from LiCl solutions

Total Cl^- M	Before extrn. g/l	After extrn. g/l		D_{Cu}	Log D_{Cu}
1.0	0.0105	0.0100	0.0003	0.05	-1.30103
2.0	0.0101	0.0085	0.0014	0.188	-0.72538
3.0	0.0100	0.0060	0.0040	0.666	-0.17614
4.0	0.0097	0.0025	0.0070	2.920	0.46538
5.0	0.0095	0.0008	0.0081	11.000	1.04139
6.0	0.0095	0.0005	0.0090	18.000	1.25523

Table (3.1c) Extraction from $CaCl_2$ solutions

Total Cl^- M	Before extrn. g/l	After extrn. g/l		D_{Cu}	Log D_{Cu}
1.0	0.0095	0.0093	0.0002	0.00215	-1.6676
2.0	0.0096	0.0093	0.0003	0.00322	-1.4913
3.0	0.0095	0.0083	0.0011	0.18070	-0.7431
4.0	0.0096	0.0067	0.0024	0.50750	-0.2946
5.0	0.0096	0.0038	0.0051	1.6053	0.2054
6.0	0.0093	0.0022	0.0070	3.6360	0.5606

Table (2.11) Variation of the copper concentration

Initial aq.concn. g /l	After Extraction	
	Aqueus phase	Organic phase
1.2	0.295	0.905
1.35	0.260	1.090
2.70	1.160	1.640
3.92	2.020	1.900
4.90	2.780	2.120
9.90	7.500	2.400
12.10	9.600	2.500
19.50	16.950	2.650
23.60	21.000	2.600

Table (2.111) Variation of the amine concentration of the organic phase

$[TOAHCl]$ M	$[Cu^{2+}]_{aq}$ g/l	$[Cu^{2+}]_o$	D_{Cu}	Log D	Log$[TOAHCl]$
0.103	0.0016	0.0084	5.25	0.8651	-0.9872
0.07725	0.0019	0.0081	4.263	0.6297	-1.1121
0.05115	0.0030	0.0070	2.333	0.3679	-1.2914
0.02575	0.0050	0.0050	10.000	0.0000	-1.5892
0.0130	0.0078	0.0022	0.282	0.4179	-1.9872
0.007525	0.0082	0.0018	0.212	-0.6737	-2.1121
0.005115	0.0086	0.0014	0.123	-0.9101	-2.2914

OPTICAL DENSITIES. Table (3.1)

Cu^{2+}(g/l)	1.05	1.05	0.090	0.100	0.98	0.109	0.095	0.300	0.295
LiCl(M)	1.0	1.5	2.0	3.0	4.0	5.0	6.0	0.5	1.0
200	0.173	0.229	0.269	0.404	0.312	0.370	0.511	0.261	0.335
210	0.594	0.630	0.591	0.788	0.605	0.620	0.733	0.840	0.930
220	0.744	0.726	0.720	0.855	0.814	1.008	0.956	1.733	1.899
230	0.444	0.492	0.557	0.773	0.953	1.226	1.301	1.085	1.293
240	0.465	0.593	0.711	1.060	1.445	1.616	1.707	0.951	1.386
250	0.538	0.724	0.876	1.289	1.881	1.820	1.983	1.051	1.602
260	0.424	0.660	0.810	1.244	2.003	1.965	2.272	0.875	1.336
270	0.260	0.478	0.619	1.034	1.870	1.978	2.461	0.520	0.871
280	0.148	0.305	0.421	0.746	1.449	1.742	2.274	0.282	0.504
290	0.088	0.170	0.256	0.465	0.916	1.346	1.774	0.153	0.283
300	0.054	0.087	0.146	0.259	0.499	0.905	1.210	0.130	0.154
310	0.033	0.039	0.079	0.137	0.253	0.548	0.776	0.058	0.084

Cu^{2+}	0.310	0.310	0.400	0.405	0.405	0.018	0.00175	0.0165
LiCl	1.5	2.0	0.5	1.0	2.0	3.0	4.0	5.0
200	0.347	0.427	0.321	0.430	0.490	0.125	0.132	0.125
210	0.877	0.839	0.930	1.064	0.974	0.133	0.174	0.166
220	1.935	1.925	2.107	2.029	2.204	0.146	0.203	0.167
230	1.508	1.958	1.485	1.703	2.450	0.130	0.184	0.191
240	1.785	2.410	1.324	1.803	3.140	0.177	0.254	0.256
250	2.110	2.900	1.462	2.081		0.211	0.303	0.295
260	1.810	2.970	1.174	1.755	2.960	0.199	0.313	0.315
270	1.242	2.090	0.716	1.102	2.570	0.161	0.286	0.311
280	0.764	0.410	0.387	1.644	0.872	0.114	0.231	0.263
290	0.445	0.864	0.209	0.344	1.173	0.069	0.158	0.188
300	0.245	0.455	0.116	0.194	0.669	0.036	0.096	0.120
310	0.141	0.238	0.064	0.105	0.351	0.015	0.056	0.083

Cu^{2+}	0.0265	0.037	0.040	0.038	0.0059	0.056	0.056	0.068
LiCl	6.0	4.0	5.0	6.0	3.0	4.0	5.0	6.0
200	0.221	0.236	0.279	0.365	0.258	0.341	0.327	0.469
210	0.280	0.370	0.390	0.459	0.535	0.545	0.544	0.601
220	0.225	0.424	0.385	0.476	0.550	0.585	0.592	0.653
230	0.295	0.431	0.284	0.620	0.512	0.608	0.678	0.866
240	0.383	0.572	0.620	0.778	0.711	0.819	0.819	0.911
250	0.450	0.673	0.744	0.893	0.883	0.975	1.079	1.253
260	0.535	0.690	0.825	1.033	0.881	0.991	1.164	1.460
270	0.571	0.636	0.806	1.124	0.763	0.990	1.146	1.610
280	0.522	0.507	0.686	1.036	0.565	0.729	0.969	1.518
290	0.387	0.358	0.469	0.798	0.342	0.497	0.695	1.196
300	0.259	0.227	0.285	0.550	0.188	0.309	0.435	0.826
310	0.169	0.143	0.165	0.359	0.102	0.218	0.257	0.532

EXTINCTION COEFFICIENTS Table (3.11)

LiCl	1.18M $(a_{Cl})^-$ = 1.025			1.67M $(a_{Cl})^-$ = 0.65		
λ	ε^λ	$\varepsilon^\lambda - \varepsilon_o$	$(\varepsilon^\lambda - \varepsilon_o)^{-1}$	ε^λ	$\varepsilon^\lambda - \varepsilon_o$	$(\varepsilon^\lambda - \varepsilon_o)^{-1}$
200	4.28836	1.26951	0.7877			
210	6.80675	3.66344	0.2729			
220	35.9503	7.6192	0.13125			
230	61.0336	31.3835	0.03186	73.3916	43.7415	0.02286
240	70.2824	58.8523	0.01990	90.6315	79.2014	0.01263
250	77.8869	70.6799	0.01415	100.6447	93.4377	0.01070
260	74.4543	69.3867	0.01441	94.0892	90.1785	0.01109
270	52.70303	49.7714	0.02010	67.6587	65.7713	0.01520
280	31.58243	30.042	0.0042			
290	17.24021	8.9161	0.1121			
300	8.89326	3.6320	0.7753			
310	4.29305	0.8969	1.1150			

λ	ε_1^λ	K_1
230	124.7071	0.53
240	171.4301	0.62
250	180.8181	0.79
260	179.6576	0.64
270	131.0860	0.56

Average $K_1 = 0.63$

Total water contents of organic phases extracted from $LiCl$, HCl, $CaCl_2$ solutions

Cl^-	From HCl solutions		From LiCl solns.		From $CaCl_2$ solns.	
M	g/l	M	g/l	M	g/l	M
1.0	3.939	0.218	3.209	0.179	2.882	0.159
1.5	4.541	0.252				
2.0	3.019	0.167	3.646	0.215	3.233	0.179
3.0	4.254	0.236	4.545	0.252	4.489	0.249
4.0	5.138	0.286	4.250	0.236	4.250	0.206
5.0			4.063	0.225	2.826	0.157
6.0	3.786	0.210			2.218	0.123
7.0	3.681	0.202				
8.0	2.881	0.159				

Table (4.11a)

Change of organic phase water content with aqueous phase copper concentration

$Cu^{2+}{}_a$ initial	$Cu^{2+}{}_o$ equilib.	H_2O_o	H_2O_o	$Cu^{2+}{}_o / H_2O_o$
g/l	g/l	g/l	M	M
0.095	0.013	2.836	0.157	0.0013
0.180	0.036	2.814	0.156	0.0036
0.444	0.099	2.102	0.117	0.0133
0.700	0.135	1.896	0.105	0.0202
1.000	1.688	1.688	0.093	0,0319
1.287	1.420	1.420	0.103	0.0419
1.485	0.270	1.051	0.058	0.0728

Table (4.11b)

Extraction of Fe^{3+} by TOAHCl (AKUFVE)

	$[Fe^{3+}]_i$ ppm	$[Fe^{3+}]_{aq}$	$[Fe^{3+}]_o$	% Extrn.	Phase Ratio
1)	8.25	6.25	2.00	24	300/300
2)	10.49	6.00	4.87	43	293/292
3)	14.74	7.00	7.74	52	288/290
4)	19.05	6.00	13.05	68	286/288
5)	36.29	10.00	26.29	72	288/286
6)	57.48	18.00	39.47	69	291/284
7)	142.22	33.00	109.22	77	291/282
8)	33.00	20.00	3.00	39	291/280
9)	20.00	16.00	4.00	20	288/278

Table (6.1)

Extraction of Fe^{3+} and Cu^{2+} from 4M LiCl aqueous solutions

Table (6.11)

	$[Fe^{3+}]_i$	$[Cu^{2+}]_i$	$[Fe^{3+}]_{aq}$	$[Cu^{2+}]_{aq}$	$[Fe^{3+}]_o$	$[Cu^{2+}]_o$
1)	27.5	122.5	3.6	110	13.90	12.5
2)	32.5	-	4.4	-	28.10	-
3)	40.0	12.0	4.1	92	35.90	28.0
4)	75.0	115	5.75	108	69.25	7.0
5)	132.5	110	20.0	92	111.50	18.0
6)	187.5	122.5	5.45	96	182.05	26.5
7)	220.0	115.0	10	94	210.00	21.0
8)	262.5	127.5	12	102	250.50	25.5

	Extrn % Fe^{3+}	Cu^{2+}
1)	57.0	10.2
2)	97.5	-
3)	89.5	23.3
4)	92.4	6.1
5)	84.3	16.3
6)	97.2	10.2
7)	95.6	18.3
8)	95.4	20.0

All concentrations are in ppm.

Extraction of Fe^{3+} in presence of Cu^{2+}, from 4M LiCl solutions

	$[Fe^{3+}]_i$	$[Fe^{3+}]_{aq}$ g/l	$[Fe^{3+}]_o$ g/l	Mo	D_{Fe}^{3+}	Extrn %
1)	1.000	0.0095	0.991	0.0177	104.21	99.05
2)	1.100	0.0140	1.086	0.0195	77.57	98.70
3)	1.350	0.0245	1.326	0.0237	54.10	98.11
4)	1.600	0.0450	1.555	0.0274	34.56	97.20
5)	2.500	0.570	1.930	0.0346	3.39	77.20
6)	2.600	0.435	2.165	0.0388	4.98	83.30
7)	3.200	0.750	2.450	0.0439	3.27	76.60
8)	4.100	1.200	2.900	0.0519	2.42	70.70
9)	6.000	3.000	3.000	0.0537	1.00	50.00
10)	7.100	3.400	3.700	0.0663	1.09	52.11
11)	8.000	4.500	3.500	0.0627	0.78	43.75
12)	12.000	7.200	4.800	0.0859	0.67	40.00
13)	15.000	9.000	6.000	0.1075	0.66	40.00
14)	28.500	22.000	6.500	0.1164	0.30	22.81

Table (6.111a)

Extraction of Cu^{2+} in presence of Fe^{3+}, from 4M LiCl solutions

	$[Cu^{2+}]_i$ g/l	$[Cu^{2+}]_{aq}$ g/l	$[Cu^{2+}]_{org}$ g/l	Extraction %
1)	1.100	0.800	0.300	27.25
2)	1.200	0.900	0.300	25.00
3)	1.050	0.975	0.075	7.14
4)	1.150	1.075	0.075	6.52
5)	1.300	1.075	0.225	17.30
6)	1.100	1.075	0.025	2.27
7)	1.100	1.075	0.025	2.27
8)	1.225	1.075	0.150	12.20
9)	1.250	1.200	0.050	4.17
10)	1.000	0.950	0.050	5.00
11)	1.100	1.050	0.050	4.17
12)	1.250	1.200	0.050	4.00
13)	1.350	1.100	0.050	2.00
14)	1.160	1.000	0.110	13.79

Table (6.111.b)

Extraction of Cu^{2+} and Fe^{2+}

2M LiCl + 0.1M HCl

$[Fe^{2+}]_{aq}$ ppm	$[Cu^{2+}]_{aq}$ ppm	Extrn % Fe^{3+}	Extrn % Cu^{+}
10	110	60.0	27.2
19	112.5	81.5	28.8
54	105	48.0	40.9
74	108	87.0	72.2
110	110	77.0	81.8
150	125	66.6	84.0
170	125	83.5	79.2
200	115	77.0	82.6
235	125	53.2	92.
260	115	68.5	91.3
275	115	70.1	95.7
325	105	59.4	92.4

4M LiCl + 0.1 HCl

$[Fe^{2+}]_{aq}$ ppm	$[Cu^{2+}]_{aq}$ ppm	Extrn % Fe^{3+}	Extrn % Cu^{+}
31.25	115.0	36.	70.5
65.00	110.0	91.	88.2
116.25	116.3	72.5	99.5
130.00	-	30.8	-
162.50	115.0	66.5	99.5
200.00	115.0	55.0	99.5
250.00	120.0	49.0	99.5
290.00	120.0	46.5	99.5

(Table (6.1V)

LIST OF SYMBOLS

a_w = activity of water

A ligand concentration

aq = aqueous phase

A = function of activity of water (Chapter 4)

α = fraction of Cu Cl complexes

A,B = second, third virial coefficients (Chapter 5)

c_{w_o} = water solubility in pure solvent at $a_w = 1$

c_w = water solubility in TOAHCl

c_s = organic salt concentration

C = solute concentration in g/kg solvent (Chapter 5.1)

C_1 = monomer concentration (Chapter 5)

C_2 = dimer concentration (Chapter 5)

C_o = total molal concentration of monomers and dimers

C = total stoichiometric molal concentration

D = distribution coefficient of the metal

δ = Harned coefficient

ε = molar extinction coefficient

f = activity coefficient

I_n = ionic strength

h = degree of hydration

$K_{1,2}$ = first, second complexing constants

K = Boltzmann constant

K_D = dimerization constant

K = equilibrium constant

λ = wavelength

M = metal concentration

M_w = water concentration of organic phase (Chapter 4.III)

M^o_w = water content of the extractant at unit activity (Chapter 4.III)

m_m = metal concentration of organic phase (Chapter 4)

M = molecular weight (Chapter 5)

$\bar{n}$ = aggregation number

O.D = optical density

o = organic phase

p = degree of association of the amine salt (Chapter 2.IV)

r = distance between the molecules

(S) = activity of the extractant

TOA = tri-n-octylamine

V = v.p.o. bridge output in volts

γ_o = activity of the salt in the organic phase

$\gamma_{a,b}$ = activity coefficient of metal in the presence and absence of salting-out agent

$\gamma^{+}_{CuCl_2}$ = average ionic activity coefficient of the metal salt in the aqueous solution

$\overline{\quad}$ = organic species

$[\ ]$ = concentration

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