

THE SOLVENT EXTRACTION OF COBALT

WITH TERTIARY AMINES

by

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A Thesis submitted for the Degree of
Doctor of Philosophy of the University of London.

March 1972.

ABSTRACT

The extraction of cobalt(II) from solutions containing either lithium chloride, hydrochloric acid, calcium chloride, mixed lithium chloride - lithium nitrate, or mixed hydrochloric acid - lithium sulphate by solutions of tri-n-octylamine in benzene has been studied.

The stability constants of the cobalt(II) chlorocomplexes occurring in solutions of LiCl up to 6M concentration have been calculated from spectrophotometric data.

The dimerisation constants of the chloride and nitrate salts of tri-n-octylamine have been calculated from data obtained by vapour pressure osmometry.

Karl Fischer titrations have been used to obtain information about the interphase transfer of water during the extraction of cobalt.

The organic cobalt complex is solvated by excess amine hydrochloride and its composition may be represented as $(\text{TOAH})_2\text{CoCl}_4 \cdot 0.3\text{TOAHCl}$. Slopes of 1.60 obtained for $\log D_{\text{Co}}$ against $\log$ amine salt concentration have been explained in terms of the aggregation of the amine salt in the organic phase. Extraction is believed to take place by transfer of CoCl_3^- from the aqueous to the organic phase. Slopes of $\log D_{\text{Co}}$ against $\log$ chloride activity indicate that the aqueous activity coefficient of the extractable complex increases very rapidly with the bulk chloride concentration. The decrease in extraction observed in concentrated hydrochloric acid solutions has been quantitatively explained in terms of preferential formation of the amine hydrogen dichloride, TOAH_2Cl_2 .

Extraction from mixed lithium chloride - lithium nitrate solutions indicated that cobalt extraction could be increased by the presence of a suitable second electrolyte in the aqueous phase. This effect has been demonstrated by extractions from mixed chloride - sulphate solutions.

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C H A P T E R 1

INTRODUCTION

The work described in this thesis is part of a study of the solvent extraction of metals that has been carried out in the Hydrometallurgy Group at the Royal School of Mines. The overall object of the study is to attempt to quantify extraction reactions in terms of the physico-chemical parameters of the system, such as the activities of components, stability constants and extraction constants. Previous theses have been concerned with the extraction of various metals by tertiary amines¹ and by alkyl phosphoric acids².

The extraction of cobalt from chloride solutions by trioctylamine was chosen for this study because it is a system of industrial importance. Cobalt can be readily separated from nickel by selectively extracting the former with organic solutions of tertiary amines from chloride liquors containing a mixture of the two metals. The separation of cobalt and nickel has always been one of the major problems in extractive metallurgy. The relative ease with which the separation can be made by amine extraction resulted in this system being one of the first solvent extraction processes that was given serious consideration by the traditionally technologically-conservative base-metal extraction industry. At least two commercial-scale processes utilising amine extractions of cobalt are in operation at the present time. Since the problems associated with handling highly corrosive chloride liquors have been largely overcome with the increasing use of plastics, further applications of this separation method are likely in the future.

The work that was carried out during the course of this investigation may be divided into several parts, each of which is briefly described below.

The extraction of cobalt(II) by solutions of tri-n-octylamine in benzene was studied. Extraction was carried out from aqueous solutions

containing either lithium chloride, hydrochloric acid, calcium chloride, or mixtures of lithium chloride and lithium nitrate. A few experiments were carried out using mixed sulphate-chloride solutions. Variables investigated included chloride concentration, metal concentration, and amine concentration. The extraction data were collected by the simple batch shake-up method, in which equal volumes of organic and aqueous phases were shaken together in separating funnels. The distribution of cobalt was measured by radio-tracer techniques using crystal scintillation counting of the gamma emission of ^{60}Co isotope. In some experiments the distribution of chloride was determined by liquid scintillation counting of the beta emission of ^{36}Cl isotope.

Preliminary analysis of the extraction data indicated that the behaviour of this system was far from simple. In the hope of clarifying the situation, the scope of the work was broadened, to include investigations of both the complexing of cobalt in the aqueous phase and the behaviour of the amine salts in the organic phase.

Much controversy surrounds the identification of the complexes formed by cobalt in the presence of chloride ions. It is generally agreed that the highest complex is the tetrahedral tetrachlorocobaltous ion, although it is not certain whether this ion is formed in aqueous solutions. Some workers maintain that cobalt is present as $\text{CoCl}_3 \cdot \text{H}_2\text{O}^-$ even in very high chloride solutions such as concentrated hydrochloric acid or saturated lithium chloride solutions. There is also uncertainty about the point at which the co-ordination of the central cobalt ion changes from an octahedral to a tetrahedral configuration. These uncertainties are reflected in the data available for the stability constants of the complexes. Published values for the constants above K_1 are very few and far between. One of the main difficulties in obtaining numerical values of stability constants for this system is that the complexing is very weak. This fact necessitates the use of high chloride concentrations and renders inapplicable the constant ionic strength method to maintain constant the activity coefficients of the ions. With some trepidation, therefore, a spectrophotometric study of the cobaltous chloride - lithium chloride system was undertaken, in an attempt to obtain a set of stability constants which could be used to help to elucidate the extraction behaviour. It is believed that partial success was achieved in this endeavour.

In addition to the complexities of the aqueous phase, the behaviour

of the amine in the organic phase is less than straightforward. Amine salts, which are polar ion-pairs, tend to form aggregates when dissolved in non-polar organic solvents. Aggregation of the extractant is known to have profound effects on the extraction behaviour exhibited by this type of system. Very few data were available on the aggregation of trioctylamine salts and so a study of the aggregation of the chloride and nitrate salts and the cobalt-amine complex was carried out, using the technique of vapour pressure osmometry.

In view of the high chloride salt concentrations used in this study and the resulting large differences in water activity between various aqueous phases, some work was also carried out to determine the behaviour of water during extraction of cobalt. This was done by measuring the water contents of various types of organic solutions, representative of those encountered in the extraction experiments, by Karl Fischer titrations.

The organisation of this thesis is slightly unusual in that certain parts of the work are presented as self-contained units. Thus Chapters 4, 5 and 6 are concerned respectively with spectrophotometry, vapour pressure osmometry, and water determinations. These chapters each contain experimental details, results and a discussion of the results. Chapter 3 contains the experimental details and the results of the solvent extraction work, but the discussion of these results is left until Chapter 7, which is a general discussion that attempts to draw together the preceding chapters. In other words, it is a discussion of the solvent extraction results into which numerical data derived in earlier chapters are introduced where applicable.

Wherever possible, the results and derived data are presented graphically in the text of this thesis. Only numerical data which do not lend themselves to graphical presentation are tabulated in the text. All other numerical data are collected together in Appendix 2. A table number followed by the letter X indicates that the table can be found in the appendix.

CHAPTER 2

LITERATURE SURVEY

2.A. Stability Constants of the cobaltous chlorocomplexes

The complexing that occurs between cobaltous ions and chloride ions in aqueous solutions is the subject of much controversy. The determination of the stability constants of these complexes is complicated by several factors. Cobalt(II) commonly has two co-ordination states, octahedral and tetrahedral. The uncomplexed aqueous cobaltous ion is octahedrally co-ordinated with six water molecules whereas the highest chlorocomplex is the tetrahedrally co-ordinated tetrachlorocobaltous ion, CoCl_4^{2-} . However it is not clear which of the intermediate complexes are octahedral and which are tetrahedral. The result is that the number of complexes that have to be considered is uncertain, since the possibility exists of pairs of intermediate complexes which have the same number of chloride ligands but different numbers of water molecules due to different co-ordination states of the central ion, e.g. $\text{CoCl}_2(\text{H}_2\text{O})_4$ (oct.) and $\text{CoCl}_2(\text{H}_2\text{O})_2$ (tet.). Katzin and Gerbert³ identified both the octahedral and tetrahedral forms of the dichlorocomplexes in alcoholic solutions by the method of continuous variations. Fine⁴ also detected tetrahedral CoCl_2 in acetone solutions.

In addition to the uncertainty concerning the number of chlorocomplexes that occur, the fact that the stabilities of these complexes in aqueous solutions are low, leads to difficulties in the interpretation of experimental data. The constant ionic strength method cannot be used in the determination of the higher stability constants since high ligand concentrations are required. Thus various assumptions have to be made about the activity coefficients of the ions in the system and the validity of the stability constants becomes very dependent on the validity of the assumptions.

Spectrophotometry has been the most widely used method of investigating the complexing in this system. Aqueous solutions containing uncomplexed cobaltous ions are pink. A broad weak absorption peak is exhibited by such solutions. The maximum of this peak occurs

at a wavelength of about 515 nm. In the presence of chloride at 3M and above, cobaltous solutions develop an intense blue colour. This strong absorption has three peaks in the 600 to 700 nm. wavelength range. The pink colour is generally attributed to cobalt(II) in octahedral co-ordination and the blue colour to cobalt(II) in tetrahedral co-ordination.

The first attempt to obtain numerical values of the stability constants was by Job⁵. He investigated the Co^{2+} - HCl system by spectrophotometry and concluded that only three complexes occurred, i.e. Co^{2+} , CoCl^+ and CoCl_3^- . All three complexes absorbed in the 500 nm. region, but only the latter absorbed in the so-called tetrahedral region, 600 to 700 nm. Values of the stability constants of these complexes were: $K_1 = 4 \times 10^{-3}$ and $\beta_3 = 1.2 \times 10^{-6}$.

The value found for K_1 by Job is considerably lower than the majority of values obtained in more modern investigations. These generally lie within the range 0.1 to 1.0 for a variety of media. A compilation of the stability constants quoted in the literature is given in Table 2.1. It will be seen that there are very few numerical values given for the stability constants of complexes higher than CoCl^+ . The paucity of data is a reflection of the inherent difficulty of the system.

Many workers have assumed that the spectra exhibited by cobalt(II) in concentrated hydrochloric acid solutions or saturated lithium chloride solutions are due to the CoCl_4^{2-} ion. For example, Mizutani and Sone⁶ attributed the absorption in the 600 to 700 nm. region to CoCl_4^{2-} and then calculated values of β_4 from extinction coefficient data. Smithson and Williams⁷ made the same assumption and used extinction coefficient data from this region to correct data obtained in the octahedral region for absorption due to CoCl_4^{2-} . The corrected octahedral data was then used to calculate a value for K_1 . Gill and Nyholm⁸, in a paper which discussed factors likely to favour the formation of tetrahedral complex halides of bivalent transition metals, implicitly assumed the formation of CoCl_4^{2-} in aqueous solutions. They presented a theoretical argument to show why both cobalt and copper do form the tetrachlorocomplex ion whereas nickel does not.

While there is ample experimental evidence to show that cobalt(II) does form anionic complexes in high chloride solutions⁹⁻¹³, it is less

Table 2,1 Stability constants of aqueous cobaltous chlorocomplexes

Method	T°C	Medium	Log values				Reference
			K_1	β_2	β_3	β_4	
Spect.	18	HCl various	-2.40	-	-5.92	-	5
Spect., p_{H_2O}		0 corrected	-	-3.95	-	-	18
Anion ex.		0 corrected	-	-1.28	-	-	19
Spect.	20	7M (ClO_4)	-0.43	-	-	-	7
Cation ex.		1.5M (Ni, NO_3)	-0.60	-	-	-	20
Cation ex.	20	0.69M ($HClO_4$)	0.69	0.51	-	-	21
Polarography		1.5M ($NaClO_4$)	-0.3	-	-	-	22
Spect.		1.5M ($NaClO_4$)	-0.4	-	-	-	22
n.m.r.	27	HCl various	-0.77	-3.54	-6.05	-8.11	17
Transport		0 corrected	$K_2 K_3 = -6.72$				16
Calorimetry	25	2M ($NaClO_4$)	-0.14	-	-	-	23
Spect.		3M ($NaClO_4$)	-0.28	-	-	-2.15	6
Spect.		6M ($NaClO_4$)	-0.43	-	-	-2.82	6
Spect.		7.3M ($NaClO_4$)	-1	-	-	<-3	6
Ag/AgCl elect.	25	2M ($NaClO_4$)	-0.18	-	-	-	24

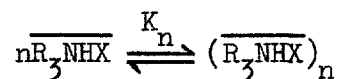
certain whether complete conversion to $CoCl_4^{2-}$ occurs even in saturated aqueous solutions of chloride salts. Cotton and co-workers¹⁴

studied the spectral and magnetic properties of several organic compounds containing CoX_4^{2-} ions, where $\text{X} = \text{Cl}^-$, Br^- or I^- . The spectra of solutions of these compounds in organic solvents were significantly different from the spectra of cobalt in concentrated aqueous solutions of HX or LiX and they concluded that "...there is no doubt that the spectra observed for the solutions in concentrated HX or LiX are largely, if not entirely, those of some tetrahedral species other than CoX_4^{2-} most probably $\text{CoX}_3\cdot\text{H}_2\text{O}^-$." Other workers have assumed that the dominant anionic complex is CoCl_3^- . Scaife and Wood¹⁵ assumed this to be the case in a study of the influence of temperature on the octahedral-tetrahedral equilibrium. Venkateswarlu and co-workers¹⁶ made the same assumption in order to calculate values of K_2K_3 from electrophoresis measurements. They found that for cobalt in HCl solutions, migration of the metal towards the cathode occurred up to 8.17M HCl . At higher acid concentrations, the metal migrated towards the anode. They assumed that only two metal species were involved, CoCl^+ and CoCl_3^- , and that at the neutral point, the concentrations of these two species were equal. The data from a recent nuclear magnetic resonance study¹⁷ of cobalt(II) in hydrochloric acid solutions indicated the presence of up to five metal complexes: $\text{Co}(\text{H}_2\text{O})_6^{2+}$, $\text{CoCl}(\text{H}_2\text{O})_5^+$, $\text{CoCl}_2(\text{H}_2\text{O})_2$, $\text{CoCl}_3(\text{H}_2\text{O})^-$ and CoCl_4^{2-} . A full set of stability constants were calculated from the data. These constants involved the activity of water. This interpretation of the data, particularly the proposed tetrahedral dichloro-complex, $\text{CoCl}_2(\text{H}_2\text{O})_2$ is thrown into some doubt by a statement in the paper which says that the data could also be described by a somewhat different set of stability constants which did not involve the activity of water. The authors maintain that their interpretation of the species present in solution is not altered by doing this. However it is not possible to distinguish between octahedral and tetrahedral CoCl_2 without involving water in the equilibria. This point is developed more fully in Chapter 4.

2.B. Aggregation and hydration of tertiary amine salts

Much work has been done to elucidate the aggregation of amine salts which occurs when they are dissolved in organic diluents. Aggregation into dimers is a general phenomenon in all but highly polar organic solvents. Dimerisation is generally attributed to ion-quadrupole formation which reduces the polarity of the monomeric ion-pairs of the amine salt. Aggregation into polymers higher than the dimer is observed in most amine salt-diluent systems as the concentration of the salt is increased. Amine nitrates appear to form trimers quite readily in many diluents, whereas for most other amine salts, trimer formation is rather unusual, and the dimer appears to be the basic unit from which higher aggregates are formed³⁰. Quite large aggregates have been observed. For example the formation of a 90-mer by trioctylamine nitrate in o-xylene has been reported³³. However the exact number of monomers involved in these large aggregates is uncertain.

The experimental techniques that have been employed to study aggregation include vapour pressure osmometry, light-scattering measurements, cryoscopy, and two-phase e.m.f. titrations. A comprehensive review of the work up to 1968 is given by Marcus and Kertes in their excellent monograph³⁵. In view of this compilation, the present survey is restricted to previous work on the chloride and nitrate salts of tertiary amines, since this is directly relevant to the present investigation. Table 2.2 lists the reported values of the aggregation constants K_n of these salts, where K_n refers to the reaction:



The K_n values for large aggregates are enclosed within parentheses to indicate that there is uncertainty about their exact composition. These large aggregates have been detected almost exclusively by the two-phase e.m.f. titration technique. The analysis of results obtained by this technique is done by computer. It is reported that the uncertainty in the analysis increases with the size of the polymer and that the number of monomers n in the large polymers should be regarded as some kind of average³³.

From Table 2.2 it is evident that the diluent has a major effect on the degree of aggregation of the amine salt. For example $TLAHNO_3$

Table 2.2 Aggregation constants of tertiary amine hydrochlorides and nitrates at 25°C.

Salt	Diluent	$\log K_n$	Reference
TLAHCl	o-xylene	$K_3=3.18, (K_{50}=73.6)$	33
TLAHCl	benzene	$K_2=1.27$	34
TLAHCl	benzene	$K_2=1.70$	25
TLAHCl	benzene	$K_2=1.48^*$	25
TLAHCl	benzene	$K_2=1.30$	26
TOAHCl	benzene	$K_2=1.11$	36
TLAHNO ₃	octane	$K_8=19.9, (K_{30}=80.0)$	33
TLAHNO ₃	dodecane	$(K_8=20.3), (K_{60}=108.3)$	33
TLAHNO ₃	o-xylene	$K_2=1.46, K_3=3.22, (K_{30}=45.2)$	33
TLAHNO ₃	m-xylene	$K_2=1.70, K_3=3.36, (K_{30}=49.5)$	33
TLAHNO ₃	t-butylbenzene	$K_2=1.89, K_3=3.92, (K_{30}=54.7)$	33
TLAHNO ₃	toluene	$K_2=1.66, K_3=3.16, (K_{50}=80.3)$	33
TLAHNO ₃	benzene	$K_2=0.90, K_3=2.28$	30
TLAHNO ₃	benzene	$K_2=1.82, K_3=2.60$	25, 30
TLAHNO ₃	carbon tetra-chloride	$K_2=1.34, K_3=3.43, K_4=5.64$	30
TOAHNO ₃	o-xylene	$K_2=1.51, K_3=3.36, (K_{90}=153.4)$	33

* Temperature = 37°C.

in octane and dodecane forms octamers, whereas, in aromatic solvents, dimers and trimers predominate. This type of behaviour is generally attributed to differences in the solvating power of the various diluents. Solvation of the amine salt by the solvent shields the high dipole moment of the ion-pair and reduces aggregation. In aliphatic hydrocarbons which are largely non-solvating, the greatest degree of aggregation is observed. In highly polar solvents such as

nitrobenzene and alcohols aggregation has not been observed and the amine salt can even dissociate²⁷. The degree of aggregation is also related to the nature of the anion of the amine salt^{26,27}. The stronger the interaction between the anion and cation of the salt, the less is the tendency to aggregate since the "solvation requirement" of the ion-pair is decreased.

The solvation requirement of the ion-pair is also thought to be the cause of the co-extraction of water into the organic phase, which is exhibited by all amine salts in varying degrees. Müller and Diamond²⁶ showed that, for the hydrohalide salts of TLA, the ratio of water to amine salt in the organic phase depended on both the anion of the salt and the diluent. For a given diluent, the ratio of water to amine salt decreased with the anion in the order, $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{SCN}^-$. For a given salt, the ratio decreased with the diluent in the order, cyclohexane > benzene or toluene > carbon tetrachloride > chloroform. They were able to qualitatively explain these effects in terms of the solvation requirements of the anions and the solvating ability of the diluents. The infra-red spectra of the hydrated salts showed that the water was bound in the amine salt. However they were not able to distinguish whether the water acted as a bridge between the anion and cation or whether it was hydrogen-bonded solely to the anion. Some recent work by Roddy and Coleman³¹ favours the latter conclusion.

The work of Roddy and Coleman³¹ together with that of Frolov³², has demonstrated further complexities in the behaviour of water in amine extraction systems. It has been shown that the concentration of water in the organic phase is a function of the water activity in the equilibrium aqueous phase. For example, both TLAHCl ²⁶ and TOAHCl ³¹ at a concentration of 0.1M in benzene have a water to salt ratio of approximately unity when in equilibrium with dilute aqueous phases, where the water activity is close to unity. However there is a linear decrease in the concentration of water in the organic phase as the water activity of the aqueous phase is decreased by increasing the electrolyte concentration.

In spite of the rather complex behaviour of water in these systems, it is generally agreed that the presence of water in the organic phase has very little effect on the aggregation of the amine salts. This has often been demonstrated by the similarity of results of aggregation measurements using both anhydrous and hydrated amine salts^{26,28,30,33}.

2.C. The extraction of cobalt by tertiary amines and quaternary ammonium salts.

As stated in the Introduction the solvent extraction separation of cobalt from nickel in chloride liquors by tertiary amines was one of the first applications of the technique that was given serious consideration by the base-metal extraction industry. Several early papers described processes which involved an amine solvent extraction step.

In 1961, Magner³⁷ outlined a process for the treatment of a complex sulphate leach liquor containing Co, Ni, Cu and Fe. The process, which at that time had been run at laboratory scale only, involved treatment of the liquor with H_2S to precipitate the copper as CuS , and simultaneously to reduce ferric iron to the ferrous state. Nickel and cobalt were then extracted together from the sulphate liquor by dinonylnaphthalene sulphonc acid in kerosene. The loaded extract was back-extracted with 6M HCl to remove both metals. The resulting chloride liquor was then suitable as a feed to a cobalt extraction circuit using tri-iso-octylamine in toluene. Virtually complete separation of cobalt from nickel was achieved in this step. Nickel metal was recovered by electrolysis of the raffinate from the amine extraction, while cobalt was also recovered by electrolysis after back-extraction of the loaded amine solution with water.

Tri-iso-octylamine was also chosen as the extractant in a process³⁸ developed at the U.S. Bureau of Mines, and reported in 1963, for the treatment of an impure nickel oxide, produced by ammonia leaching of a lateritic nickel ore. The oxide was smelted with carbon to produce a crude nickel metal which was cast into anodes. The anodes were electrolytically dissolved in diaphragm cells. The electrolyte was a mixed chloride-sulphate liquor. The purification of this liquor leaving the anode compartment involved solvent extraction with 0.6M TIOA in xylene. This removed Co, Cu, Fe and Zn from the solution, from which nickel was recovered by electrodeposition in the cathode compartment of the cell. Cobalt was selectively removed from the loaded amine by back-extraction with water to produce a solution suitable for recovery of cobalt by electrolysis.

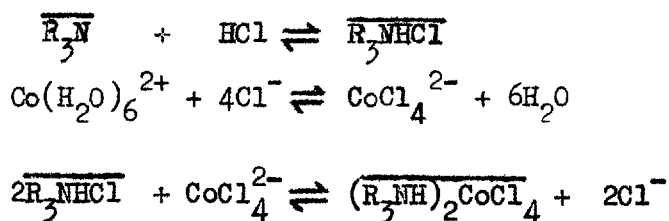
Russian interest in this type of process is evident in a paper by Ioffe and Dushkina³⁹ who proposed a process for the extraction of cobalt

from nickel by a 0.1M solution of a tertiary amine (C_{7-9}) in kerosene. The process involved the use of calcium chloride as the source of chloride ions instead of hydrochloric acid. This was done to take advantage of the improved extraction of cobalt which occurs in the presence of alkali or alkaline earth metal cations.

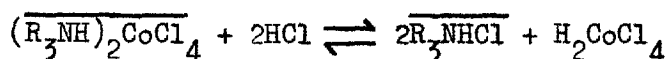
The early interest in these processes has culminated with the introduction of industrial amine extraction of cobalt. At least two commercial-scale processes are known to be in operation at this time in the Western world. A description of one of them, operated by Falconbridge Nickel at their Kristiansand refinery, has recently been published⁴⁰.

Concurrently with the development work described above, fundamental studies were being carried out to investigate the chemistry of the extraction of cobalt by tertiary amines and quaternary ammonium salts.

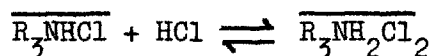
Good and co-workers undertook a lengthy investigation into the extraction of various transition metals by amines and quaternary ammonium salts, and the results were reported in a series of papers published between 1960 and 1965. The extraction of cobalt from hydrochloric acid solutions by various primary, secondary and tertiary amines was studied⁴¹. Tertiary amines were shown to be the most efficient extractants and it was also shown that the type of diluent used had a marked effect on the extraction. With all the amine-diluent systems studied, the extraction of cobalt increased with increasing aqueous hydrochloric acid concentration to a maximum in the region 8 to 10M HCl. At higher acid concentrations, the extraction decreased. The visible absorption spectra of the loaded organic phases indicated that cobalt was present as the $CoCl_4^{2-}$ ion, and it was suggested that the extraction was due to an anion exchange mechanism, represented by the following equations:



The decrease in extraction observed at high acid concentrations was attributed to the formation of non-extractable undissociated acidio chlorocomplexes:



This latter explanation was modified by the authors in a later paper⁴². They showed that the decrease in the extraction of cobalt did not occur when LiCl was used as a source of chloride ions instead of HCl. They observed that excess HCl was extracted by the amine from concentrated acid solutions, and the infra-red spectra of amine solutions containing excess acid indicated the presence of HCl_2^- ions. In view of these results, they suggested that the decrease in extraction of cobalt at high acid concentrations was due to competition between formation of the organic metal complex and formation of the amine dichloride:



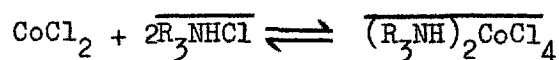
Another paper⁴³ in the series concerned the extraction of various transition metals, including cobalt, from both HCl and LiCl solutions by long chain quaternary ammonium halides. The chloride and bromide salts were shown to be good extractants. The extraction characteristics of the quaternary salts were similar to those of the tertiary amine salts, although the former were rather more efficient extractants. These results were similar to those reported by Wilson and co-workers in an earlier paper⁴⁴. This concerned the effects of the structure of quaternary ammonium halides on the extraction of Co^{2+} , Fe^{3+} , Zn^{2+} , and Tl^{3+} . It was shown that the extractant molecule should contain at least 24 carbon atoms in order to obtain high metal distribution coefficients.

Good and Srivastava⁴⁵ returned to the problem of the nature of the metal chloride complex existing in solutions of tertiary amine and quaternary ammonium salts. They investigated the extraction of Fe^{3+} , Co^{2+} , Ga^{3+} and In^{3+} . The techniques used to establish the composition of the organic metal complexes included slope analysis of distribution data, loading ratios, direct analysis of the loaded organic phases, infra-red spectra, and vapour pressure osmometry. They concluded that, for all the metals and extractants examined, the metal existed in the organic phase as the tetrachlorocomplex. Vapour pressure osmometry indicated that, except for indium, the organic metal complexes formed by both tri-n-hexylamine and Aliquat 336 (commercial trioctylmethylammonium chloride) in toluene were associated, and existed as trimers

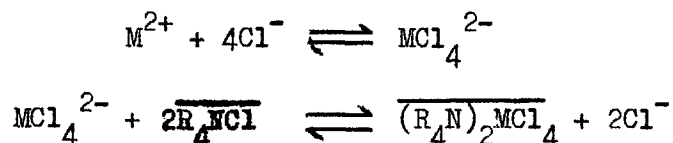
over a fairly wide concentration range. The authors noted that the slopes of log distribution coefficient against log extractant concentration led to several anomalies when compared with the theoretical slopes expected from the law of mass action. This type of inconsistency is not uncommon in amine extraction systems⁴⁶ and it is now generally attributed to aggregation of the amine salts into dimers and higher polymers.

The extraction of cobalt from hydrochloric acid solutions by tri-n-nonylamine in benzene was investigated by Venkateswarlu and Lal⁴⁷. They reported slopes of 3 and 1.5 for plots of log distribution coefficient against log chloride activity and log amine concentration respectively. They stated, without any attempt to justify their conclusions, that the results indicated the extraction of CoCl_3^- , HCoCl_4^- , and CoCl_4^{2-} , and that the fractional slope observed for $\log D_{\text{Co}}$ against log amine concentration could only be explained on the basis that at least two species are extracted, one being uninegative. Similar results were obtained in the present investigation and it will be shown that the fractional slopes can be satisfactorily interpreted by taking into account the aggregation of the amine salt.

The extraction of cobalt from hydrochloric acid by tri-n-octylamine was studied by Sato. The results were reported by him in two virtually identical papers^{48,49} published simultaneously in different Journals. Fractional slopes for $\log D_{\text{Co}}$ against log amine concentration were again observed. The slopes varied between 1.30 at 4M HCl and 1.75 at 8M HCl. The cobalt to amine molar ratio at full loading was approximately 0.5, and the ratio of cobalt in the organic phase to chloride in excess of that required for the stoichiometric amine hydrochloride was found to be 2. The visible absorption spectrum of the loaded organic phase indicated that the metal was present as CoCl_4^{2-} , in agreement with the work discussed above. The infra-red spectrum of the organic phase showed that the organic metal complex was unhydrated and this was confirmed by Karl Fischer titration. Analysis of the organic complex gave a molar ratio of Co : Cl : TOA equal to 1 : 4 : 2. Sato proposed that the extraction reaction should be represented as:



Two recent Russian papers have also been concerned with the mechanism of the extraction of cobalt. Ivanov and co-workers⁵⁰ studied the extraction of cobalt and nickel with several quaternary ammonium chlorides and also trioctylamine hydrochloride. They concluded that the mechanism of extraction was the same for both metals, involving the formation of the tetrachlorocomplex in the aqueous phase, followed by extraction of this complex into the organic phase:

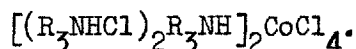


The extraction constants, k , were calculated using the following equation:

$$\frac{[\overline{(R_4N)_2MCl_4}]}{[M^{2+}]} = k[Cl]^{-2}\gamma_{\pm}[R_4NCl]^2$$

where $\gamma_{\pm}$ is the mean activity coefficient of the metal salt in the aqueous phase. For cobalt, $\log k = 1.74$ and for nickel, $\log k = -4.06$. These constants applied to all the extractants studied. It was found necessary to incorporate the aqueous activity coefficient of the metal in order to obtain constant values for k .

Shmidt and Mezhev⁵¹ used a cryoscopic technique to examine the organic metal complexes formed by extraction of cobalt with both tridecylamine and trilaurylamine hydrochlorides in p-xylene. They concluded that in both cases the organic metal complex was solvated by four extra amine salt molecules, and could be represented as:



It may be concluded that there is a considerable amount of evidence to show that cobalt exists in organic phases containing either tertiary amine hydrochlorides or quaternary ammonium chlorides as the tetrachlorocomplex ion, $CoCl_4^{2-}$. Most previous investigations have been of a largely qualitative nature, and except for one Russian paper⁵⁰, no attempts have been made to quantify the extraction reactions in terms of the physico-chemical parameters of the systems. As in the case of

most amine extraction systems, it is not clear whether cobalt extraction involves an anion exchange mechanism or whether it is a solvation reaction involving the extraction of neutral CoCl_2 into the organic phase. The fractional slopes obtained for $\log D_{\text{Co}}$ against $\log$ amine concentration indicate that aggregation of the amine salts affects the extraction of cobalt, but this has not been investigated in detail.

CHAPTER 3

SOLVENT EXTRACTION RESULTS

3.A. Experimental

3.A(1) Materials

Trioctylamine

Technical grade tri-n-octylamine was obtained from B. Newton-Maine Ltd. The molecular weight of this material, measured by vapour pressure osmometry was 349 (Section 6.D(iii)), which is within 1.2% of the theoretical value - 353, whereas potentiometric titration with standard HCl gave a value of 410, indicating the presence of a non-basic impurity. Analysis of the amine gave results in good agreement with the theoretical values: C = 81.53, H = 14.47, N = 4.16%; calculated: C = 81.60, H = 14.43, N = 3.97%.

Attempts to purify the amine by vacuum distillation, in order to improve its potentiometric molecular weight, were unsuccessful and the material was used without further treatment.

Solutions of trioctylamine in A.R. benzene were prepared as required and standardised by potentiometric titration with standard HCl.

Lithium Chloride

Concentrated stock solutions of lithium chloride were prepared by dissolving G.P.R. lithium carbonate in 10M A.R. hydrochloric acid until the reaction was complete. Unreacted solid was filtered off and the lithium chloride solution was then standardised. The chloride content was determined by Volhard's method and the lithium content was determined gravimetrically as lithium sulphate. Two stock solutions were prepared during the course of the work, and their analyses are given below:

	<u>Li content</u>	<u>Cl content</u>
1st LiCl stock solution	9.87M	9.84M
2nd LiCl stock solution	10.09M	10.08M

Lithium Nitrate

A stock solution of lithium nitrate was prepared in a similar manner to the lithium chloride solutions. 6.5M A.R. nitric acid was neutralised with G.P.R. lithium carbonate. Excess solid was filtered off and the solution standardised. Lithium was determined as above and nitrate was determined gravimetrically using Nitron reagent.

	<u>Li content</u>	<u>NO₃ content</u>
LiNO ₃ stock solution	6.54M	6.53M

⁶⁰Co isotope

1 mCi of ⁶⁰Co as CoCl₂ solution was obtained from the Radiochemical Centre, Amersham. This was mixed with a solution containing 500 ml. 0.973M HCl and 10 ml. 0.1M CoCl₂. The volume was made up to 1 l. with distilled water, and the resulting ⁶⁰Co stock solution had the following composition:

$$[\text{HCl}] = 0.487\text{M}, [\text{CoCl}_2] = 0.001\text{M}, \text{Activity} = 1 \mu\text{Ci } ^{60}\text{Co per ml.}$$

Suitable count rates for cobalt distribution measurements were obtained by adding the ⁶⁰Co stock solution to the initial aqueous phases in the proportion 2 ml. isotope solution per 100 ml. aqueous phase.

³⁶Cl isotope

100 $\mu\text{Ci } ^{36}\text{Cl}$ contained in 5.4 ml. of 3.9M HCl was obtained from the Radiochemical Centre, Amersham. The isotope solution was diluted to 500 ml. with distilled water, to give a stock solution with an acidity of 0.042M HCl and an activity of 0.2 $\mu\text{Ci } ^{36}\text{Cl}$ per ml. This stock solution was used in the proportion 2 ml. per 100 ml. of aqueous phase.

Other Reagents

All other reagents used were standard A.R. grade reagents.

3.A(ii) Distribution Experiments

All distribution experiments were carried out batchwise in quadruplicate. 20 ml. aliquots of the organic and aqueous phase were shaken together in 100 ml. separating funnels for 5 mins. at ambient temperature - 18 to 25°C. Within these limits a change in temperature had no detectable effect on the distribution coefficients.

Preliminary experiments had shown that equilibrium was achieved within the first minute of shaking. After settling, the phases were separated and 10 ml. samples were taken for radioactive counting to determine the concentration of the distributing element (either Co or Cl) in each phase. The counting techniques are described below. Prior to the distribution experiments, the amine solution in benzene was converted to amine hydrochloride, by shaking it with a two-fold excess of aqueous hydrochloric acid. In the cobalt distribution experiments, the amine hydrochloride solutions were then pre-equilibrated by shaking with an aqueous solution with the same composition as the test solution, but containing no cobalt.

3.A(iii) γ - counting.

The distribution of cobalt was determined by scintillation counting of the gamma emission of ^{60}Co .

An Ekco N664B counter equipped with a thallium activated sodium iodide scintillation crystal, coupled with an Ekco N530G scaler was used. The performance of the equipment had to be optimised for the isotope in use by preliminary experiments to find the control settings at which the least variation in count rate occurred with changes in the high tension voltage (E.H.T.). The settings established for ^{60}Co were: E.H.T. = 850V, discriminator bias = 15V and amplifier gain = 100X.

Counting was carried out by pipetting 10 ml. samples of solution into N552 polythene annular containers. Each container was then placed in the scintillation counter and counted for at least 100 seconds. Background count rates were obtained using empty containers.

The distribution coefficients of cobalt, D_{Co} , were calculated from the expression:

$$D_{\text{Co}} = \frac{R_O - R_B}{R_A - R_B}$$

where R_O , R_A and R_B are the organic, aqueous and background count rates, respectively. The percentage "mass balance" of counts was calculated after each determination of D_{Co} :

$$\text{Mass balance} = \frac{(R_O - R_B) + (R_A - R_B)}{(R_T - R_B)} \times 100\%$$

where R_T is the count rate of the initial aqueous solution prior to

equilibration. The ^{60}Co stock solution was added to the initial aqueous solutions in the proportion 2 ml. stock solution per 100 ml. aqueous solution. Thus the ^{60}Co concentration in a 10 ml. aliquot of initial aqueous solution was $0.2 \mu\text{Ci}$. This gave an R_T value of the order of 600-700 counts per second. Mass balances obtained in the cobalt distribution experiments were generally better than $100 \pm 3\%$.

3.A(iv) β - counting.

The distribution of chloride was determined by liquid scintillation counting of the beta emission of ^{36}Cl .

The equipment used was an Ekco N612 liquid scintillation counter, coupled with an Ekco N530G scaler. The counter was refrigerated to -20°C to reduce thermal noise and all samples were equilibrated to this temperature before counting. Optimum instrument settings for ^{36}Cl were found to be: E.H.T. = 1200V, discriminator bias = 20V and amplifier gain = 500X.

The scintillation solution consisted of 8 gm. 2,5-diphenyloxazole (P.P.O.) and 0.36 gm. 1,4-bis-(2-(5-phenyloxazole))-benzene (P.O.P.O.P.) dissolved in 1 l. sulphur-free toluene. An organic reference solution was prepared by dissolving 1 ml. aqueous stock ^{36}Cl solution in 100 ml. absolute alcohol.

The counting solutions were made up as follows:

Aqueous background: 10 ml. scintillation solution,
10 ml. absolute alcohol, 1 ml. water.

Aqueous reference: 10 ml. scintillation solution,
10 ml. absolute alcohol, 1 ml. aqueous phase before
extraction.

Aqueous samples: 10 ml. scintillation solution, 10
ml. absolute alcohol, 1 ml. aqueous phase after
extraction.

Organic background: 10 ml. scintillation solution,
10 ml. absolute alcohol containing 1% water, 10 ml.
amine hydrochloride solution.

Organic reference: 10 ml. scintillation solution, 10
ml. organic reference solution, 10 ml. amine hydro-
chloride solution.

Organic samples: 10 ml. scintillation solution, 10 ml. absolute alcohol containing 1% water, 10 ml. organic phase after extraction.

The counting solutions were made up in this fashion so that the background, reference and sample solutions of each phase were of identical compositions. In the case of the organic background, reference and sample solutions, it was found necessary to strictly adhere to the order of addition of the ingredients given above. Addition of the scintillation solution after the amine solution tended to lower the count rate. Typical count rates obtained for the various solutions were as follows:

Aqueous and organic backgrounds	: 1-2 c.p.s.
Aqueous reference	: 65-85 c.p.s.
Aqueous samples	: 65-85 c.p.s.
Organic reference	: 460-480 c.p.s.
Organic samples	: 2-10 c.p.s.

In spite of the very low count rates in the organic samples, satisfactory results for the chloride concentrations of the organic phases were obtained. The mass balances were not quite as good as those obtained for γ -counting since they varied between $100 \pm 4\%$. This was thought to be mainly due to inaccuracies in the count rates of the aqueous samples, as these all contained 5% water, which is known to have a quenching effect on β -counting.

3.B. Results

3.B(i) Extraction of chloride

Two series of experiments were carried out to determine the behaviour of chloride during contact of trioctylamine solutions with aqueous solutions containing chloride ions.

a) Chloride extraction from lithium chloride solutions

These experiments were carried out to determine whether there was any "invasion" of the organic phase by lithium chloride. That is, to determine whether any excess lithium chloride was extracted. Amine hydrochloride solutions in benzene (0.0983M) were shaken with lithium chloride solutions containing ^{36}Cl tracer, and the chloride concentration of the organic and

aqueous phases (Y_{Cl} and X_{Cl} , respectively) were measured after equilibration. The results are presented in Table 3.1, and it is evident that, over the lithium chloride concentration range examined (3.0 to 7.0M), the measured organic chloride concentrations do not differ significantly from the concentration of amine in the organic phase. This indicates that the organic phase contains stoichiometric amine hydrochloride only, and it is concluded that there is no invasion of the organic phase by lithium chloride.

b) Chloride extraction from mixed lithium chloride-lithium nitrate solutions.

The chloride contents of amine hydrochloride solutions were considerably reduced after equilibration with aqueous solutions containing mixtures of lithium chloride and lithium nitrate. The results obtained for organic chloride concentration after equilibrations of 0.0983M TOAHCl solutions with aqueous phases containing various ratios of lithium chloride and lithium nitrate are given in Table 3.2. In all cases the equilibrium organic chloride concentration was less than 50% of the total amine concentration. Thus part of the amine hydrochloride was being converted to amine nitrate during equilibration. Inspection of the results shows that nitrate ions are more strongly extracted than chloride ions by TOA. These results are analysed to obtain the chloride-nitrate exchange constant in Section 7.A(ii).

3.B(ii). Extraction of cobalt from chloride solutions

The extraction of trace cobalt ($2 \times 10^{-5}M$) from lithium chloride solutions by 0.0983M trioctylamine hydrochloride in benzene was determined and the results are plotted as the log of the distribution coefficient of cobalt ($\log D_{Co}$) against chloride molarity in Figure 3.1 (Table 3.1.X.). The chloride concentration range investigated was 3.0 - 7.5M. The limits of this range were set by the distribution coefficients of cobalt which varied from 10^{-2} to 10^2 . These are the minimum and maximum values respectively that can be determined accurately. Across this chloride concentration range, $\log D_{Co}$ values increase linearly with chloride concentration. Also plotted on Figure 3.1 (Table 3.1.X.) are results obtained for the extraction of trace cobalt from calcium chloride and hydrochloric acid solutions. The distribution coefficients from calcium chloride solutions, plotted against chloride

Table 3.1. Chloride extraction from LiCl solutions.

$$[\overline{\text{TOAHCl}}] = 0.0983\text{M}$$

$[\text{LiCl}]_{\text{M}}$	$[\text{Cl}]_{\text{total}}$	$X_{\text{Cl}}(\text{M})$	$Y_{\text{Cl}}(\text{M})$	% Mass Balance
7.00	7.0983	7.0727	0.0954	101.0
6.00	6.0983	5.9441	0.1004	99.7
5.00	5.0983	4.9167	0.0989	98.4
4.00	4.0983	3.9905	0.0984	99.8
3.00	3.0983	2.9496	0.0991	98.4

$$[\text{Cl}]_{\text{total}} = ([\text{LiCl}] + [\overline{\text{TOAHCl}}]) = \text{Total molar concentration of chloride in the system.}$$

Table 3.2. Chloride extraction from LiCl - LiNO₃ solutions.

$$[\overline{\text{TOAHCl}}] = 0.0983\text{M}$$

$[\text{LiCl}]_{\text{M}}$	$[\text{LiNO}_3]_{\text{M}}$	$[\text{Cl}]_{\text{total}}$	$X_{\text{Cl}}(\text{M})$	$Y_{\text{Cl}}(\text{M})$	% Mass Balance
4.00	3.50	4.0983	3.9878	0.0059	97.4
5.00	2.50	5.0983	5.0129	0.0115	98.6
6.00	1.50	6.0983	6.2073	0.0185	102.1
6.50	1.00	6.5983	6.8360	0.0285	104.0
7.00	0.50	7.0983	7.0953	0.0462	100.6
4.00	2.50	4.0983	4.1176	0.0079	100.7
5.00	1.50	5.0983	5.0010	0.0147	98.6
6.00	0.50	6.0983	6.0862	0.0371	100.4

$$[\text{Cl}]_{\text{total}} = ([\text{LiCl}] + [\overline{\text{TOAHCl}}]) = \text{Total molar concentration of chloride in the system.}$$

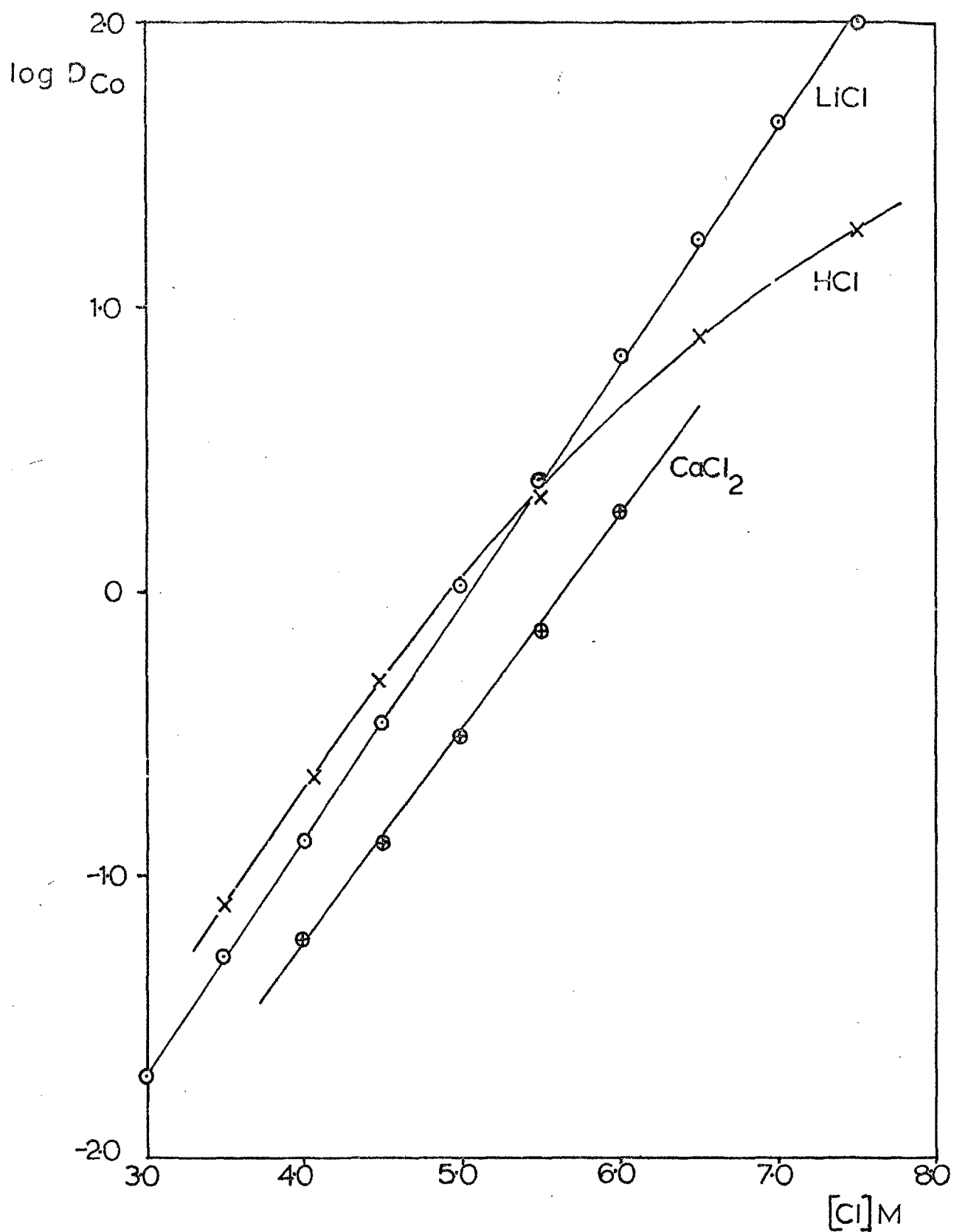


FIGURE 3.1 EXTRACTION OF TRACE COBALT FROM CHLORIDE SOLUTIONS.

$$[Co]_{total} = 2 \times 10^{-5} M \quad [\overline{TOAHCl}] = 9.83 \times 10^{-2} M$$

Data from Table 3.1.X.

concentration, where $[Cl] = 2[CaCl_2]$, lie on a line roughly parallel to the lithium chloride results. The distribution coefficients from hydrochloric acid solutions behave similarly at low acid concentrations, but they decrease relative to lithium chloride at higher acid concentrations.

The pH values of the aqueous phases before and after extraction from lithium chloride solutions were recorded and the results are presented in Table 3.1.X. There was a small amount of free hydrochloric acid (0.01M) in all these solutions, derived from the ^{60}Co stock solution. The pH of the solutions decreased as the lithium chloride concentration increased. This was thought to be due to the effect of the ionic strength of the solutions on the activity coefficients of the hydrogen ions. During extraction there was a small but almost constant increase in the pH of the aqueous phase. This effect was ascribed to the fact that the pre-equilibration solutions used contained no acid. Thus during pre-equilibration, some HCl could have been back-extracted from the organic into the aqueous phase, thereby converting some of the amine hydrochloride to free amine. During equilibration with solutions containing ^{60}Co , this free amine would react with HCl to re-form amine hydrochloride, and this could account for the small rise in pH of the aqueous phase. Further evidence for this explanation is presented below. (Section 3.B(v)).

3.B(iii) Extraction of cobalt from lithium chloride-lithium nitrate solutions

In order to study the influence of a second electrolyte in the aqueous phase on the extraction behaviour of cobalt, distribution experiments were carried out from aqueous solutions containing various proportions of lithium chloride and lithium nitrate. Lithium nitrate was chosen as the second electrolyte because data⁵⁵ were available which enabled the activities of the individual salts in the mixture to be calculated. In these experiments, macro amounts of cobalt ranging between $9.6 \times 10^{-4}M$ and $1.4 \times 10^{-2}M$ were extracted into 0.0983M trioctylamine hydrochloride in benzene. The aqueous phases contained various proportions of LiCl and $LiNO_3$ with constant total molarities of either 6.5M or 7.5M. The results of these experiments are fully recorded in Table 3.2.X. In Figure 3.2, $\log D_{Co}$ values for $[Co]_{total} = 9.6 \times 10^{-4}M$ are plotted against the chloride concentrations of the mixed solutions. For a given total molarity of lithium salts the results lie on smooth

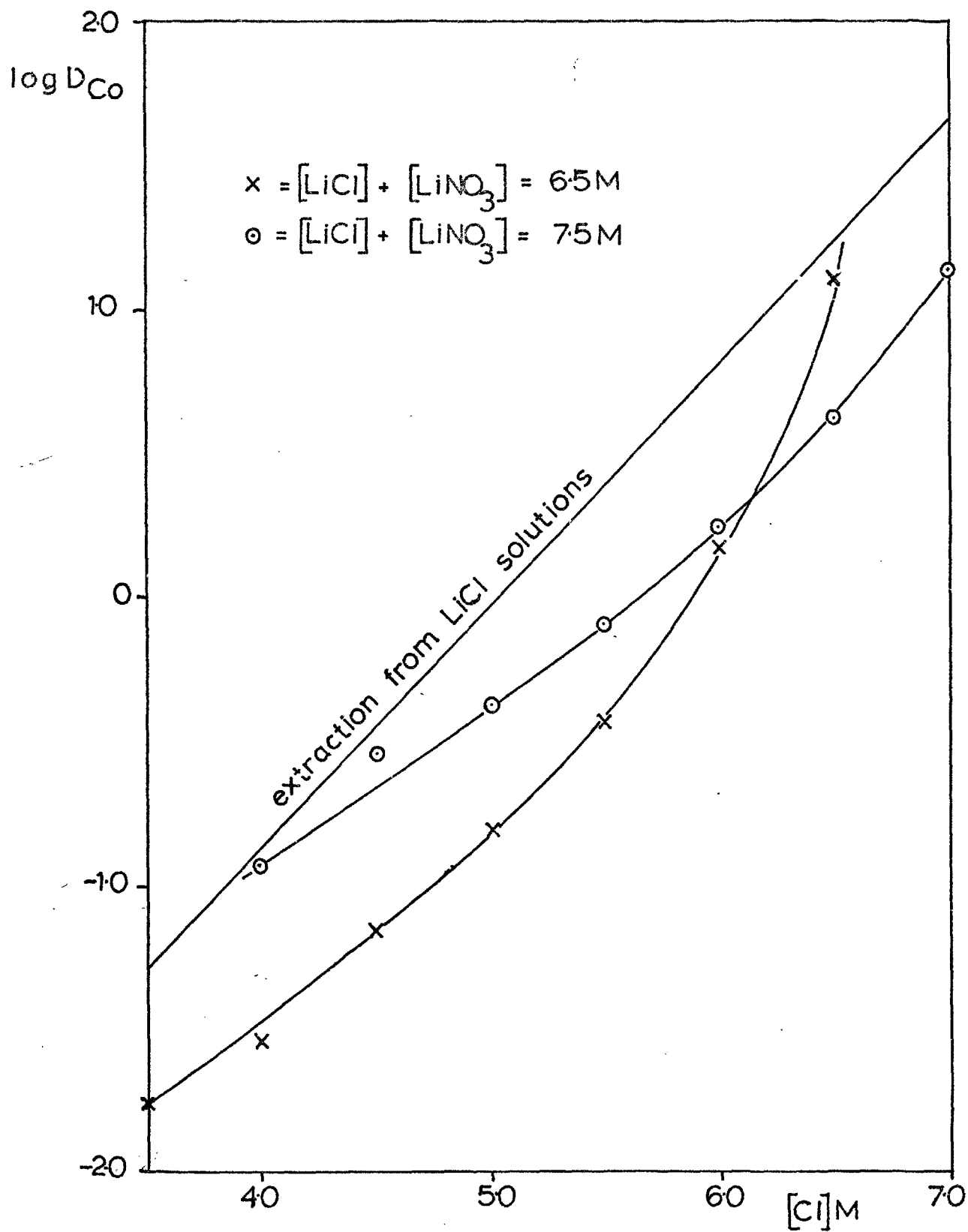


FIGURE 3.2 EXTRACTION FROM LiCl - LiNO₃ SOLUTIONS.

$$[\text{Co}]_{\text{total}} = 9.60 \times 10^{-4} \text{M} \quad [\text{TOAHX}] = 9.83 \times 10^{-2} \text{M}$$

Data from Table 3.2.X.

curves, which lie below the $\log D_{Co}$ values measured in solutions containing lithium chloride only which are also shown on the diagram. Thus the extraction of cobalt is hindered by the presence of lithium nitrate in the aqueous phase.

3.B(iv) Variation of the amine concentration of the organic phase

The effect of varying the amine concentration of the organic phase on the extraction of cobalt from both lithium chloride and mixed lithium chloride-lithium nitrate solutions was investigated. Amine concentrations from $4.9 \times 10^{-2} M$ to $1.0 M$ and a constant cobalt concentration of $1.92 \times 10^{-3} M$ were used. The results are tabulated in Table 3.3.X and displayed in Figure 3.3 as graphs of $\log D_{Co}$ against $\log [TOAHX]$ where $[TOAHX]$ is the total amine concentration in the organic phase. For amine concentrations of approximately $0.2 M$ and below ($\log [TOAHX] \leq 0.7$) the results lie on straight lines of slope 1.6 for extraction from both lithium chloride only and lithium chloride-lithium nitrate solutions. For amine concentrations greater than $0.2 M$, the results deviate upwards from linearity.

3.B(v) Variation of the cobalt concentration

The results of varying the cobalt concentration of the aqueous phase for extraction from lithium chloride - lithium nitrate solutions have already been reported (Table 3.2.X). The distribution coefficients of cobalt are independent of cobalt concentration in the range $10^{-3} M$ to $1.4 \times 10^{-2} M$ for solutions containing up to $5 M$ chloride. Above this value, the D_{Co} values decrease with metal concentration. A similar effect is observed during extraction from solutions containing lithium chloride only at chloride concentration above $6 M$ - Table 3.4.X.

An extraction isotherm was determined for the extraction of cobalt from $6.5 M$ $LiCl$ by $0.0983 M$ $TOAHCl$. This was done by varying the cobalt concentration of the aqueous phase from $10^{-4} M$ to $0.4 M$ and determining the equilibrium aqueous and organic metal concentrations - X_{Co} and Y_{Co} respectively. The results are presented in Table 3.5.X. and the extraction isotherm - Y_{Co} against X_{Co} - is given in Figure 3.4. The horizontal portion of the curve indicates that the organic phase is saturated with cobalt and this occurs at $Y_{Co} = 0.0428 M$. Thus the amine: metal molar ratio at full loading is equal to $1:2.29$.

In the extraction isotherm experiments an amount of hydrochloric

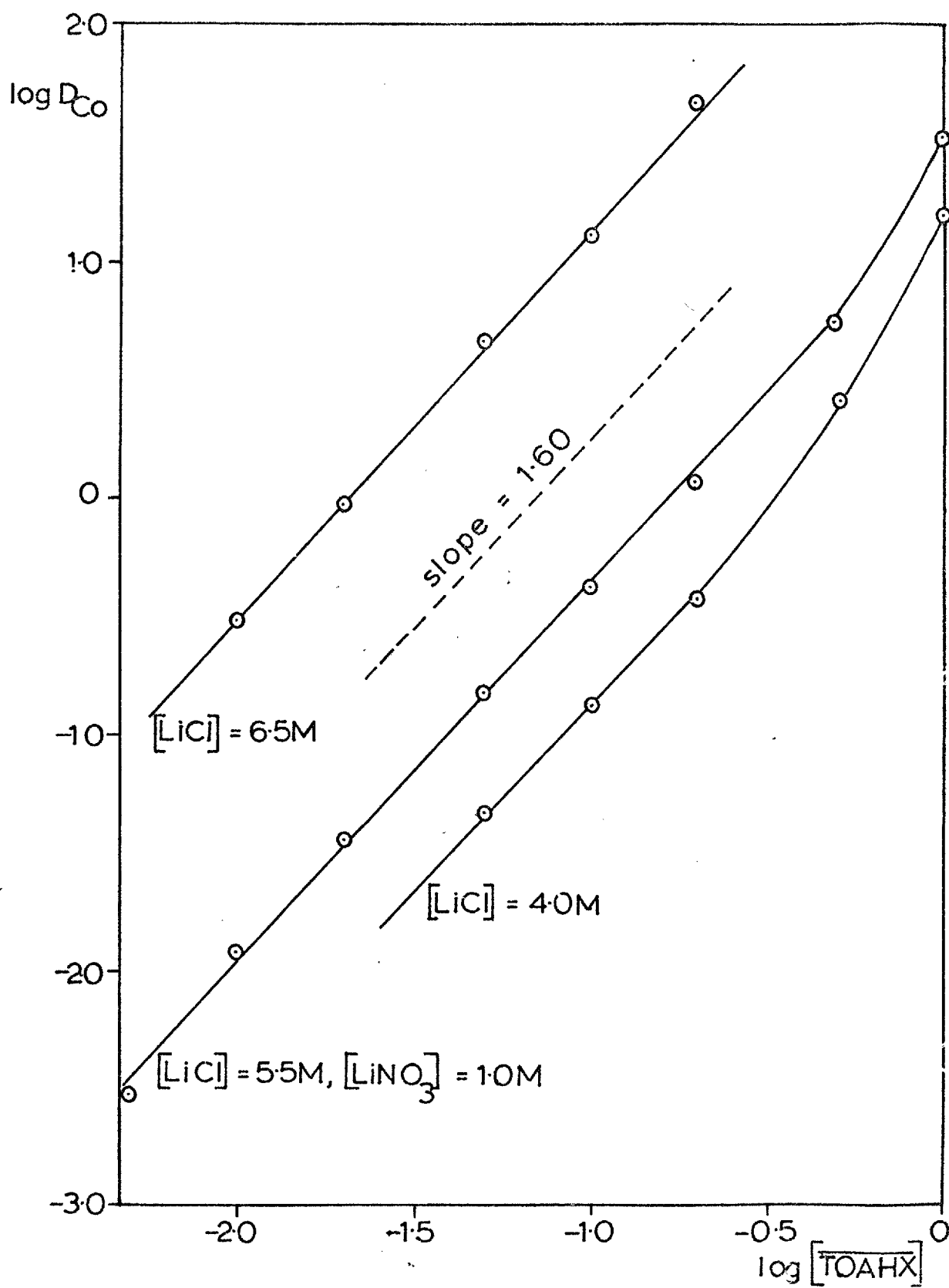


FIGURE 3.3 VARIATION OF ALIENE SALT CONCENTRATION.

$$[Co]_{total} = 1.92 \times 10^{-2} M$$

Data from Table 3.3.X.

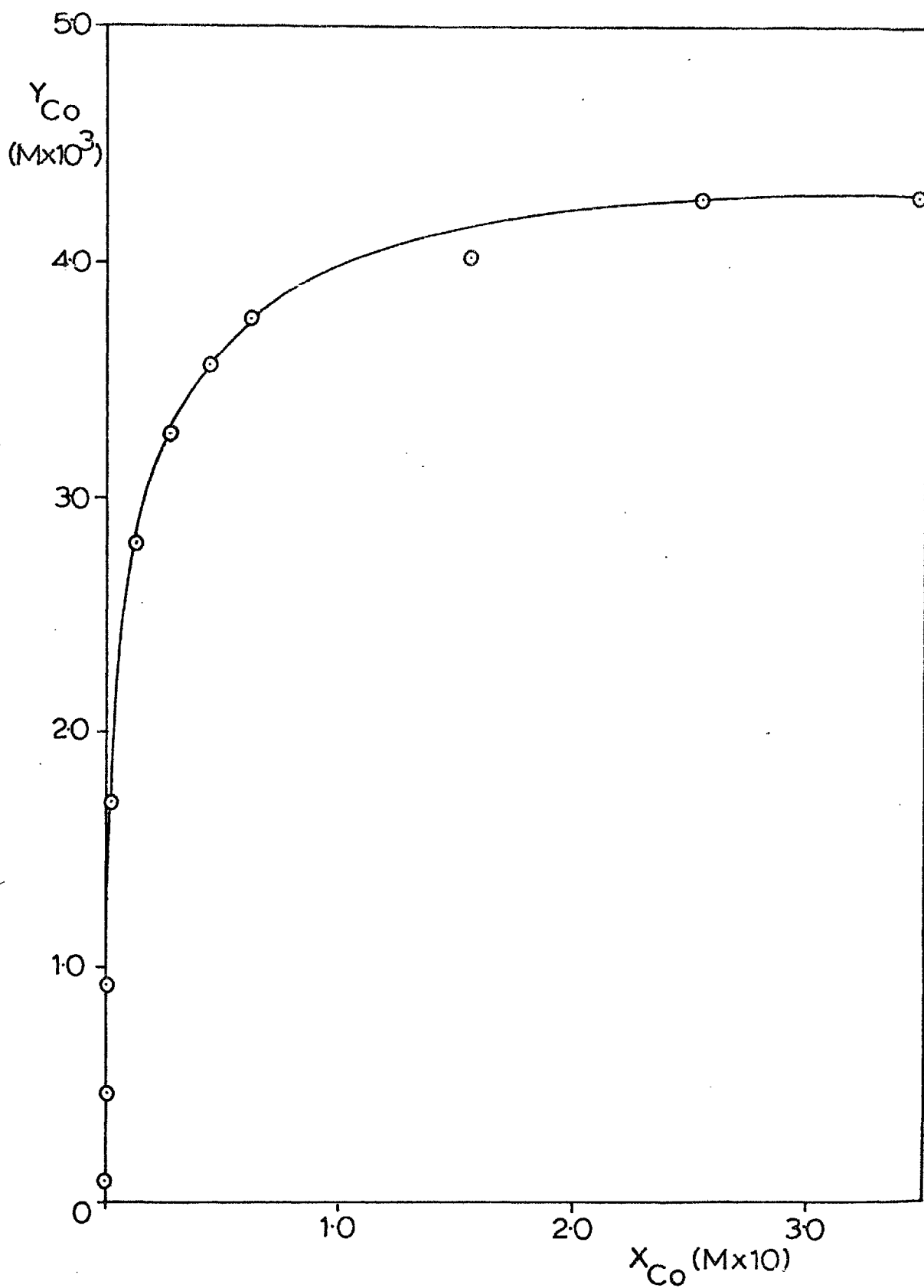


FIGURE 3.4 EXTRACTION ISOTHERM

$$[LiCl] = 6.5M \quad [TOAHCl] = 9.83 \times 10^{-2}M$$

Data from Table 3.5.X.

acid, equal to that present in the metal-containing solutions, was added to the pre-equilibration solutions. There was no significant change in the pH of the aqueous phases during extraction. This finding supports the argument put forward to explain the pH changes noted in other experiments (Section 3.B(ii)).

3.B(vi) Co-extraction of other cations

The possibility of co-extraction of lithium with cobalt was investigated by carrying out extractions of $10^{-2}M$ cobalt from various lithium chloride and lithium chloride - lithium nitrate solutions, representative of those used in previous experiments. The organic phases were then back-extracted to remove the metal by equilibration with dilute hydrochloric acid. Counting of the organic phases after back-extraction showed that all the cobalt had been transferred to the aqueous back-extraction solutions, and thus any co-extracted lithium should also have been transferred. The aqueous back-extraction solutions were examined for lithium content by atomic absorption spectrophotometry. In no case was any significant amount of lithium found, and it was concluded that lithium is not co-extracted with cobalt. The other cation present in these solutions which could have possibly been co-extracted with the cobalt was hydrogen ion. Rather than attempting a direct determination of co-extracted hydrogen ion by back-extraction, an indirect method was used. The distribution of trace cobalt ($2 \times 10^{-5}M$) was determined from a series of solutions in which lithium chloride was systematically replaced by hydrochloric acid while the total chloride molality was kept constant at 6m. If hydrogen ion was involved in the extraction reaction an increase in the distribution coefficient of cobalt would be expected under these conditions. This is fully explained in Chapter 7. A constant molality rather than a molarity was chosen because data⁵⁴ available for the activity coefficients of hydrochloric acid in lithium chloride solutions were expressed in molal units rather than molar units. However this choice of concentration units resulted in difficulties in making up solutions of constant total molality from molar stock solutions. This should have been done by weighing out aliquots of the stock solutions and diluting them on a weight basis. At the time, it was done instead by calculating the molal concentrations of the stock solutions from density data and then diluting by volume. This leads

to inaccuracies in the total molality of the mixed solutions, which in fact does not remain constant. The actual total chloride molalities of the mixed solutions ranged from 6.0m at the lowest acid concentration to 6.35m when half the lithium chloride was replaced by hydrochloric acid. These inaccuracies are reflected in the results obtained - Table 3.3. A slight increase in D_{Co} is observed as the hydrochloric acid concentration of the solution is increased. However this increase is attributed to the increase in total chloride molality of the solutions, rather than an effect due to the co-extraction of hydrogen ions. The actual molar concentrations used of LiCl and HCl are shown in Table 3.3.

Table 3.3 Distribution of trace cobalt from LiCl - HCl solutions.

$$[TOAHCl] = 0.0983M, \quad [Co]_{total} = 2 \times 10^{-5}M.$$

Total molal chloride concentration - nominally 6m (see text)

$[LiCl]_M$	$[HCl]_M$	D_{Co}
5.30	0.02	2.42
5.27	0.05	2.40
5.23	0.10	2.35
5.15	0.20	2.35
4.92	0.50	2.63
4.52	0.95	2.69
3.68	1.90	3.11
2.82	2.82	3.17

3.B(vii) Extraction from chloride-sulphate solutions

As a result of the analyses of the extraction of cobalt from lithium chloride - lithium nitrate solutions, it was decided to carry out some preliminary experiments on the extraction of cobalt into 0.0983M TOAHCl solutions from aqueous solutions containing mixtures of chloride and sulphate ions. The significance of these experiments is explained in Chapter 7.

In the first series of experiments, the extraction of trace quantities of cobalt ($2 \times 10^{-5} \text{M}$) from 4.0M HCl solutions containing various concentrations of lithium sulphate was studied. The lithium sulphate concentrations used ranged from zero to 1.415M . Across this range the distribution coefficient of cobalt increased from 0.220 to 2.02 . This is equivalent to an increase in the percentage extraction of cobalt from 17.8% at zero added sulphate to 66.7% at 1.415M added sulphate. The results of these experiments are recorded in Table 3.6.X, and graphically displayed as a plot of $\log D_{\text{Co}}$ against sulphate concentration in Figure 7.8. There is a linear increase in $\log D_{\text{Co}}$ with lithium sulphate concentration.

In a second series of experiments, solutions were prepared to simulate purified nickel - cobalt leach liquors. Varying amounts of hydrochloric acid were added to these solutions and extractions were carried out. The solutions contained 0.933M NiSO_4 (55gm./l.Ni) and 0.0678M CoSO_4 (4gm./l.Co) giving a total sulphate concentration of 1.0M . The added hydrochloric acid concentration range was zero to 5.75M . In order to demonstrate the effect of the nickel sulphate on the extraction of cobalt, a similar series of experiments were carried out on solutions containing 0.0678M CoSO_4 only, to which hydrochloric acid was added. The results are presented in Figure 7.9. (Table 3.7.X). It is evident that the presence of 0.993M nickel sulphate increases the distribution coefficient of cobalt from hydrochloric acid solutions.

3.B(viii) Spectrum of the organic phase

A typical spectrum of the organic phase containing cobalt is given in Figure 3.5. The characteristic blue colour of such solutions is due to the strong absorption occurring in the 600 to 700 nm. wavelength range. This absorption band has three peaks at 626 , 662 and 693 nm. respectively.

The overall extinction coefficients at these three peaks, calculated from the slopes of plots of optical density against organic cobalt concentration, were found to be : $\epsilon^{626} = 422$, $\epsilon^{662} = 572$, $\epsilon^{693} = 635$.

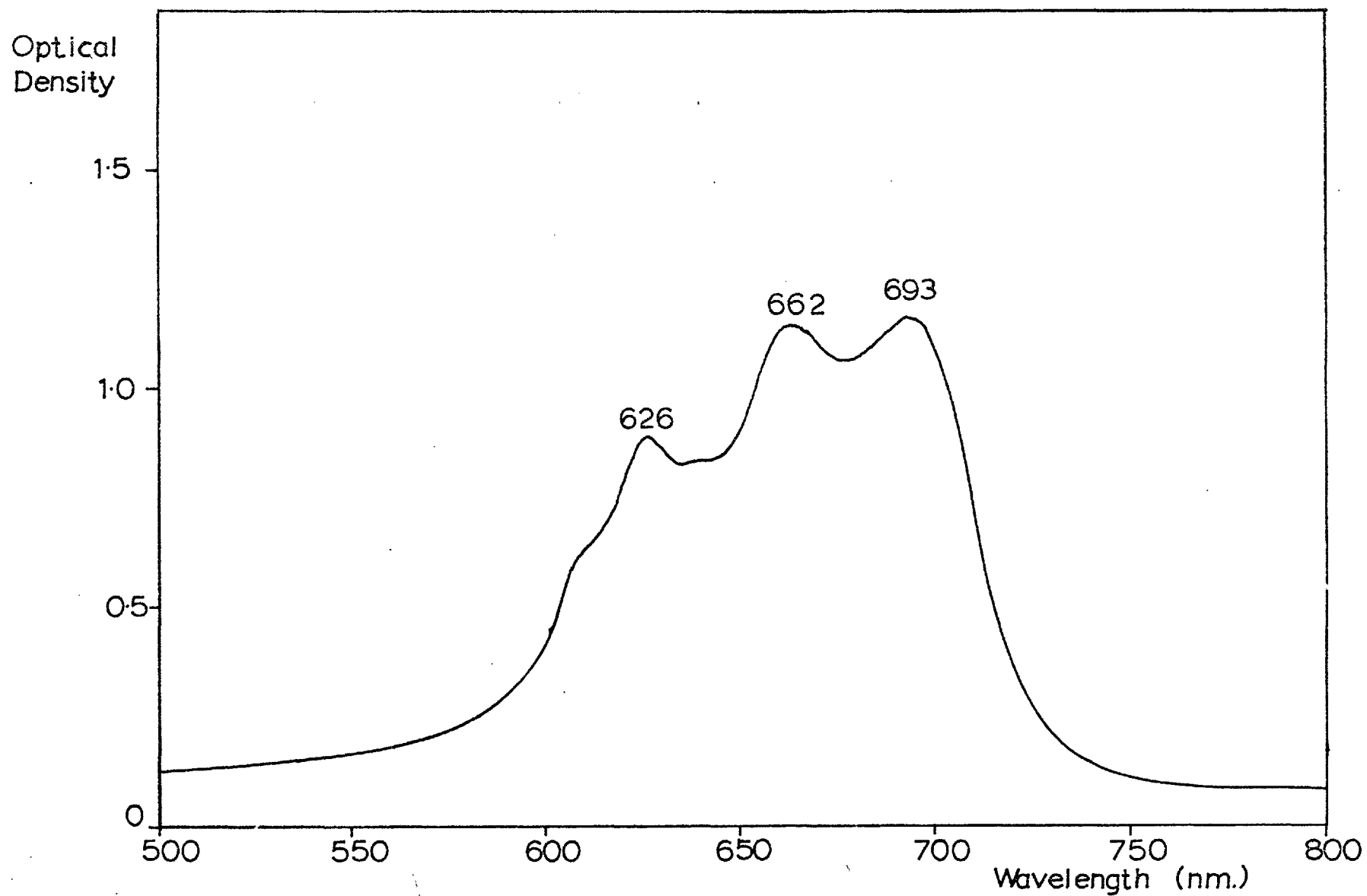


FIGURE 3.5 TYPICAL SPECTRUM OF THE ORGANIC PHASE - EXTRACTION FROM 7.5M LiCl

$$[\text{TOAHCl}] = 9.85 \times 10^{-2} \text{M} \quad [\text{Co}] = 1.952 \times 10^{-3} \text{M}$$

CHAPTER 4

SPECTROPHOTOMETRIC INVESTIGATION OF COBALT COMPLEXING IN LITHIUM CHLORIDE SOLUTIONS.

4.A. Introduction

In order to attempt to establish the stability regions of the various chlorocomplexes of cobalt(II), a spectrophotometric investigation of the absorption of aqueous solutions containing cobaltous chloride and lithium chloride was undertaken.

The main absorption peaks of solutions containing cobaltous and chloride ions occur in two parts of the visible region. The wavelength region 450 - 550 nm. is occupied by a broad weak absorption peak characteristic of the pink cobaltous solutions. The peak wavelength at low chloride concentrations is 510 nm, but this gradually rises to 530 nm, as the chloride concentration is increased. The overall molar extinction coefficient of this peak increases with chloride concentration, reaching a maximum value of 12 at about 9M chloride. At chloride concentrations greater than 3.5M, a second set of three peaks of invariant wavelength appear in the region 600 - 700 nm., in addition to the broad peak mentioned above. The overall molar extinction coefficients of these peaks rise very rapidly with chloride concentration, reaching maximum values of the order of 600 at approximately 12M chloride. Cobaltous solutions exhibiting this spectrum have a blue colour. These two distinct regions of absorption are generally correlated with two types of co-ordination exhibited by the cobaltous ion - the broad peak in the 450 - 550 nm. region is attributed to octahedral co-ordination, whilst the set of peaks in the 600 - 700 nm. region is attributed to tetrahedral co-ordination. For ease of reference in the following discussions, these two regions of the absorption spectrum, i.e. 450 - 550 nm. and 600 - 700 nm. will often be referred to as the octahedral and tetrahedral regions respectively. In addition full details of the nomenclature used throughout this

chapter are given below.

The tetrahedral peaks were found to be very temperature sensitive and absorption in this region increased rapidly with increasing temperature. For this reason, all spectrophotometric measurements were made with the sample cells held in a thermostatically controlled cell-holder set at 25°C.

Nomenclature

a_{Cl}	Effective chloride activity.
a_x	Activity of species x.
F	Activity coefficient function - Equation (4B4).
K_n, β_n	Thermodynamic equilibrium constants.
K_n^*, β_n^*	Apparent equilibrium constants - Equation (4B9).
K_n^{**}, β_n^{**}	Apparent equilibrium constants involving water activities.
m_A	Anion concentration - Equation (4B7).
$\bar{n}$	Average ligand number - Equation (4E23).
O.D.	Optical density.
P.L.	Path length in cm.
$[Co]_{total}$	Total cobalt concentration
α_n	Fraction of metal present as nth complex.
γ_n	Activity coefficient of nth complex.
γ_{Cl}	Activity coefficient of chloride ions.
ϵ^λ	Overall extinction coefficient at wavelength λ .
ϵ_n^λ	Extinction coefficient of nth complex at wavelength λ .

4.B. Basic Theory

A considerable amount of evidence has been amassed which indicates that the highest chlorocomplex of cobalt (II) is the tetrachlorocobaltous ion, $CoCl_4^{2-}$. In this ion the central cobalt ion is co-ordinated tetrahedrally to the four chloride ligands, whereas the uncomplexed cobaltous ion is known to have six water molecules in its primary hydration sheath

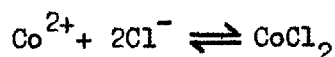
in octahedral co-ordination. There is uncertainty where the change from octahedral to tetrahedral co-ordination takes place in the series of chlorocomplexes of cobalt. It is generally assumed that CoCl_4^{2-} and $\text{CoCl}_3\cdot\text{H}_2\text{O}$ are tetrahedrally co-ordinated and that the lower complexes, CoCl_2 and CoCl^+ are octahedrally co-ordinated, with water occupying the unfilled co-ordination positions. However, there is evidence of the existence of two dichlorocobaltous complexes in organic solvents³, one with octahedral co-ordination and the other with tetrahedral co-ordination. These may be written as $\text{CoCl}_2\cdot 4\text{S}$ and $\text{CoCl}_2\cdot 2\text{S}$, respectively, where S represents a solvent molecule. In a recent n.m.r. investigation of cobalt complexing in hydrochloric acid solutions¹⁷, the data was best fitted by postulating the tetrahedral dichlorocomplex $\text{CoCl}_2\cdot(\text{H}_2\text{O})_2$ rather than the octahedral complex $\text{CoCl}_2(\text{H}_2\text{O})_4$.

The possibility of the existence of these two complexes is important because it relates to the way in which the equilibrium constants for complex formation are expressed. It is conventional, when writing equilibrium reactions in aqueous solutions, to ignore the hydration of the ions. Thus the equilibrium constant for the reaction:

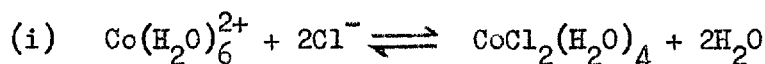


is written:
$$K = \frac{a_{\text{MA}^+}}{a_{\text{M}^{2+}} \cdot a_{\text{A}^-}}$$

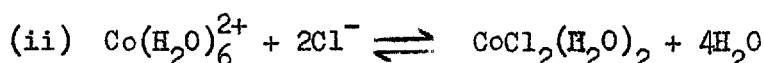
K involves only the activities of the metal species and the ligand. This convention is equivalent to assuming that the activity of the water molecules occupying the unfilled co-ordination positions of the metal species is the same as the water activity in the bulk of the solution. Using this convention, it is not possible to distinguish between the formation of the octahedral species $\text{CoCl}_2(\text{H}_2\text{O})_4$ and the tetrahedral species $\text{CoCl}_2(\text{H}_2\text{O})_2$ since the formation of both these ions would be written as:



If it is postulated that these two forms of dichlorocobaltous ion can exist, then the water molecules occupying the unfilled co-ordination positions must be considered to be as much an integral part of the complex ion as the chloride ligands themselves. Thus the formation reactions must involve the activity of water as well as the ligand activity. The formation reactions for the octahedral and tetrahedral forms of the dichlorocobaltous ion become, respectively:



$$\beta_{2(\text{oct})} = \frac{a_{\text{CoCl}_2}^2 a_{\text{H}_2\text{O}}^2}{a_{\text{Co}}^2 a_{\text{Cl}}^2}$$



$$\beta_{2(\text{tet})} = \frac{a_{\text{CoCl}_2}^4 a_{\text{H}_2\text{O}}^4}{a_{\text{Co}}^2 a_{\text{Cl}}^2}$$

If this type of convention is adopted, then it must be used throughout the series of possible stepwise complex formation reactions, since each addition of a ligand to the central metal ion will generally involve the displacement of a water molecule from a co-ordination position.

In this investigation, the data was analysed using both conventions outlined above. It was found that the best overall fit to the data was obtained using equilibrium reactions which did not involve water activity, i.e. using the normal convention. The derivations of the basic equations used for the analysis of the data are given below. To avoid complications, these equations are derived using equilibrium reactions written in the normal convention only. The results of the analysis using equations in which water activities are taken into account, and which were found to be less satisfactory, are discussed in Section 4.F.

Thus in the derivation of the basic equations and the analyses that follow, the possibility of the existence of at least five cobalt containing species is considered. Ignoring the hydration of the ions, these may be written as Co^{2+} , CoCl^+ , CoCl_2 , CoCl_3^- , CoCl_4^{2-} . No assumptions are made about the type of co-ordination exhibited by these ions.

One of the basic assumptions of a spectrophotometric investigation of this type, where numerical values of equilibrium constants are being sought, is that the extinction coefficients of the individual complexes remain constant as the compositions of the solutions being examined are changed.

Since the complexing occurring in the cobalt - chloride system is very weak, it was necessary to examine the total available ligand concentration range, that is from zero chloride to just below the saturation concentration of LiCl at 25°C, which is approximately 13M. For this reason it was not possible to control the ionic strength of the solutions by the use of a swamping inert electrolyte, as is usually done in systems where the complexing is strong. The effective "swamping electrolyte" in this system was the chloride salt itself since the metal concentrations used were very low. As chloride concentration was the main variable under investigation, the result was gross changes in the ionic strengths of the various solutions. The assumption of the constancy of extinction coefficients is difficult to justify under these conditions, since direct experimental evidence is not available. This assumption has been used implicitly several times before in spectrophotometric investigations of similar weakly complexing systems, e.g. References 56 and 57. The validity of the assumption could be tested by comparison of equilibrium constants obtained in this manner with those obtained by other experimental techniques. Unfortunately the paucity of numerical data make such comparisons difficult. However, it will be shown that the K_1 value obtained in this study is in reasonable agreement with those of previous investigations, some of which employed methods other than spectrophotometry.

Thus the initial assumption of the analysis of the spectrophotometric data is that the measured optical density of each solution is the sum of the individual optical densities of all the metal-containing species in that solution, and that these individual optical densities are directly proportional to the concentrations of each species, i.e.

$$\begin{aligned}\epsilon^\lambda[\text{Co}]_{\text{total}} &= \epsilon_0^\lambda[\text{Co}^{2+}] + \epsilon_1^\lambda[\text{CoCl}^+] + \epsilon_2^\lambda[\text{CoCl}_2] + \dots \\ &= \sum_0^n \epsilon_n^\lambda[\text{CoCl}_n^{2-n}] \quad (4B1)\end{aligned}$$

where: ϵ^λ = Overall molar extinction coefficient of the solution at wavelength λ

ϵ_n^λ = Molar extinction coefficient of the nth complex at wavelength λ

$n = 0$ to 4 for the Co-Cl system

$[\text{Co}]_{\text{total}}$ = Total molar concentration of cobalt in the solution.

The overall molar extinction coefficient ϵ^λ can be obtained from the measured optical density (O.D.) of the solution at wavelength λ by the use of the expression:

$$\epsilon^\lambda = \frac{\text{O.D.}}{\text{P.L.} \times [\text{Co}]_{\text{total}}}$$

where: P.L. = Solution path length in cm.

More accurately, ϵ^λ is given by the slope of the Beer's Law plot - O.D. against metal concentration - since ϵ^λ is then derived from several separate measurements rather than one measurement only. This latter method was used in the present work.

By dividing both sides of Equation (4B1) by $[\text{Co}]_{\text{total}}$, the following expression is obtained:

$$\epsilon^\lambda = \epsilon_0^\lambda \alpha_0 + \epsilon_1^\lambda \alpha_1 + \epsilon_2^\lambda \alpha_2 + \dots = \sum_0^n \epsilon_n^\lambda \alpha_n \quad (4B2)$$

where α_n is the fraction of cobalt present as the nth complex:

$$\alpha_n = \frac{[\text{CoCl}_n^{2-n}]}{[\text{Co}]_{\text{total}}}$$

Equation (4B2) is the general expression for the measured overall extinction coefficient at any wavelength and it states that it is a function of the individual extinction coefficients and concentrations of all the cobalt species that absorb at that wavelength.

The concentrations of the cobalt species are related by the stepwise equilibrium constants K_n :

$$K_n = \frac{[\text{CoCl}_n^{2-n}]}{[\text{CoCl}_{n-1}^{3-n}][\text{Cl}^-]} \frac{\gamma_n}{\gamma_{n-1}\gamma_{\text{Cl}}} \quad (4B3)$$

where γ_n and γ_{n-1} are the activity coefficients of the n th and $(n-1)$ th complexes, respectively, and γ_{Cl} is the activity coefficient of the chloride ions. Since none of these activity coefficients is known, it is necessary to make assumptions about them. The approximation generally used in such cases is that a single activity coefficient, F , can be used to replace the activity coefficient term in Equation (4B3), where:

$$\frac{1}{F} = \frac{\gamma_n}{\gamma_{n-1}\gamma_{\text{Cl}}} \quad (4B4)$$

This concept was first introduced by Bjerrum⁵⁷ and it is equivalent to assuming that the activity coefficients of adjacent complexes remain in a constant ratio as the ionic strength of the solutions are varied, i.e.

$$\frac{\gamma_n}{\gamma_{n-1}} = C \quad (4B5)$$

Bjerrum⁵⁷ states that this assumption is "not unreasonable in the case of concentrated solutions, where chemical similarity between ions, rather than the charge of the ions, determines the activity coefficients." He was able to show that, for the complexing of copper in concentrated chloride solutions, F was related to the bulk chloride concentration by:

$$\log F = A + B[\text{Cl}^-] \quad (4B6)$$

The constant B was found to depend on the particular chloride salt employed and had the values 0.20 in HCl, 0.23 in LiCl, 0.18 in MgCl_2 and 0.21 in CaCl_2 . This expression is similar to the empirical equation which describes the behaviour of the mean activity coefficients of many electrolytes at high concentrations:

$$\log \gamma_{\pm} = P + Qm_A \quad (4B7)$$

where: m_A is the concentration of the anion.

For concentrations greater than 3N, Q values are 0.18 for HCl and 0.20 for CaCl_2 . These values are in good agreement with the values given above of the constant B for these two electrolytes found by Bjerrum.

The fact that equations of the type given in (4B6) and (4B7) can describe the behaviour of activity coefficients in concentrated electrolytes follows quite logically from an examination of the extended forms of the Debye-Hückel equation, such as that proposed by Guggenheim⁵⁸.

$$\log \gamma_{\pm} = \frac{-A \cdot z_+ z_- I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + bI \quad (4B8)$$

At high ionic strengths, the first term on the right-hand side of this equation tends towards a constant value and the equation assumes the form of those given above.

The agreement between the B values in the expression for $\log F$ found by Bjerrum for Cu in HCl and CaCl_2 with the Q values in the expression for $\log \gamma_{\pm}$ for these two electrolytes shows that the term F is largely controlled by the mean activity coefficient of the electrolyte. Since it is conventional to equate the activity coefficients of the anion and cation with the mean activity coefficient, this is equivalent to saying that the term F in Equation (4B4) varies in proportion to variations in γ_{Cl} . This is the expected behaviour of F if the assumption concerning the activity coefficients of the metal complexes (Equation (4B5)) is valid, i.e. that they remain in a constant ratio. Thus Equation (4B5) is

evidently a reasonable assumption. This problem has been further examined by Marcus⁶⁰ and he has shown from theoretical considerations that the function he calls the "effective activity quotient", which is closely related to C in Equation (4B5), remains almost constant across the concentration range 2 to 12M in electrolytes of various valency types.

Thus the ratio of the activity coefficients of the metal complexes in the equilibrium expression, Equation (4B3), can be incorporated in the thermodynamic equilibrium constant K_n to give an apparent equilibrium constant K_n^* :

$$K_n^* = \frac{[\text{CoCl}_n^{2-n}]}{[\text{CoCl}_{n-1}^{3-n}]} \cdot \frac{1}{[\text{Cl}]\gamma_{\text{Cl}}} \quad (4B9)$$

Since $K_n^* = K_n \cdot \gamma_{n-1}/\gamma_n$, then if assumption (4B5) is valid, K_n^* should be a constant, independent of the bulk electrolyte concentration.

The term $[\text{Cl}]\gamma_{\text{Cl}}$ in the above equation is equal to the activity of the chloride ion in the bulk electrolyte. As it is not possible to measure individual ionic activity coefficients, it is conventional to use the "effective ligand activity", a , which is given by:

$$a = m\gamma_{\pm} \quad (\text{for a 1:1 electrolyte})$$

where: m is the concentration of the anion and $\gamma_{\pm}$ is the mean activity coefficient of the electrolyte. For lithium chloride, the effective chloride activity is given by:

$$a_{\text{Cl}} = m_{\text{LiCl}} \gamma_{\pm\text{LiCl}}$$

Equation (4B9) may thus be written:

$$K_n^* = \frac{[\text{CoCl}_n^{2-n}]}{[\text{CoCl}_{n-1}^{3-n}]a_{\text{Cl}}} \quad (4B10)$$

It should be noted that a_{Cl} in the above equation strictly refers to the activity of free chloride ions in the solution. Since in this investigation the ligand concentrations were always in large excess compared with the metal ion concentrations, the total chloride ion activity can be used as a good approximation. Dividing top and bottom of Equation (4B10) by $[\text{Co}]_{\text{total}}$ gives:

$$K_n^* = \frac{\alpha_n}{\alpha_{n-1}a_{\text{Cl}}} \quad (4B11)$$

Suitable combinations of the general expression derived for the overall extinction coefficients (Equation (4B2)) and the above expression for the apparent equilibrium constants, can be used to analyse the **spectrophotometric** data to obtain numerical values of these constants. However in view of the complexity of the system, with the possibility of the existence of at least five cobalt species, a qualitative examination of the spectra and changes in the spectra with chloride concentration is necessary in order that simplifications can be made before a numerical analysis is attempted.

4.C. Experimental

Experimental solutions were prepared from standardised stock solutions of cobaltous chloride and lithium chloride, and were acidified with perchloric acid to pH 2, to prevent hydrolysis. The LiCl used was G.P.R. grade, all other reagents were A.R. grade. Solutions were made up in 25 ml. standard flasks.

Optical density measurements were carried out on a Hilger and Watts Uvispec spectrophotometer, fitted with a thermostatically controlled cell-holder, which maintained the solutions at $25 \pm 0.1^\circ\text{C}$ during measurements. The solutions were held in matched 2 cm. path length silica cells. The reference solution contained the same LiCl concentration as the sample solution.

Optical densities were measured at the following wavelengths: 500, 505, 510, 515, 520, 525, 530, 535, 624, 662 and 690 nm. Generally measurements were made on solutions containing four different metal concentrations at each chloride concentration examined. In the 500 nm. range, the metal concentrations used were $(1,2,4,6) \times 10^{-2}\text{M}$, whereas in the 600 nm. range, because of the much stronger absorption in this region, metal concentrations were $(2,4,6,8) \times 10^{-4}\text{M}$. The LiCl concentrations used ranged between 1 and 13 molar.

Overall extinction coefficients were obtained from the optical density data by measuring the slopes of the Beer's Law plots, i.e. optical density against molar metal concentration. In order to obtain unbiased values of the extinction coefficients, the slopes were calculated by a linear regression programme on a desk computer. Good linear correlations were obtained showing that Beer's Law was obeyed under all conditions. Values of the overall extinction coefficients are given in Table 4.1. Extinction coefficients for the uncomplexed cobaltous ion were obtained from measurements made in cobaltous perchlorate solutions.

4.D. Qualitative Description of Results

The general shape of the absorption spectrum is shown in Figure 4.1. This is the spectrum of a cobalt chloride solution containing 7.0M LiCl. The broad weak peak in the 450-550 nm. region is the one assigned to the cobaltous ion with octahedral co-ordination. It is present when

Table 4.1 Experimental values of the overall molar extinction coefficients. $\lambda = 500 - 535 \text{ nm.}$

$[Cl]_M$	0	1.0	1.5	2.0	2.5	3.0	3.5	4.0
ϵ^{500}	4.595	4.963	5.098	5.269	5.464	5.646	5.886	6.210
ϵ^{505}	4.766	5.152	5.333	5.514	5.622	5.857	6.108	6.450
ϵ^{510}	4.816	5.224	5.414	5.567	5.762	5.942	6.258	6.631
ϵ^{515}	4.725	5.127	5.361	5.549	5.731	5.917	6.257	6.639
ϵ^{520}	4.547	4.980	5.175	5.393	5.587	5.817	6.119	6.511
ϵ^{525}	4.239	4.702	4.920	5.065	5.241	5.521	5.891	6.318
ϵ^{530}	3.825	4.319	4.476	4.642	4.807	5.071	5.450	5.890
ϵ^{535}	3.368	3.852	3.983	4.161	4.373	4.625	4.995	5.378

$[Cl]_M$	4.5	5.0	6.0	7.0	8.0	9.0	10.1	11.0
ϵ^{500}	6.584	6.961	7.730	8.350	8.563	7.708	5.805	5.476
ϵ^{505}	6.839	7.287	8.149	8.838	9.175	8.325	6.366	6.024
ϵ^{510}	7.053	7.500	8.428	9.263	9.700	8.890	6.842	6.354
ϵ^{515}	7.070	7.588	8.742	9.725	10.275	9.567	7.610	7.084
ϵ^{520}	6.994	7.547	8.721	9.963	10.825	10.399	8.646	8.146
ϵ^{525}	6.784	7.355	8.700	10.075	11.475	11.669	10.573	10.159
ϵ^{530}	6.427	6.941	8.371	9.938	11.588	12.021	11.122	10.756
ϵ^{535}	5.876	6.445	7.898	9.375	11.163	11.606	10.598	10.098

 $\lambda = 624, 662, 690 \text{ nm.}$

$[Cl]_M$	4.0	4.5	5.0	6.0	7.1	8.1	9.2	10.5
ϵ^{624}	0.509	0.942	1.234	3.863	40.00	111.25	230.00	332.25
ϵ^{662}	0.448	0.948	1.314	5.100	57.50	145.00	335.63	357.50
ϵ^{690}	0.353	0.763	1.248	5.100	61.25	149.38	357.50	530.00

$[Cl]_M$	10.7	11.3	11.7	12.1	12.5	12.9	13.0
ϵ^{624}	342.50	342.50	355.50	368.25	355.50	344.00	340.00
ϵ^{662}	500.50	504.25	522.25	540.50	519.50	509.00	503.00
ϵ^{690}	545.25	547.00	570.25	590.25	570.00	557.50	550.00

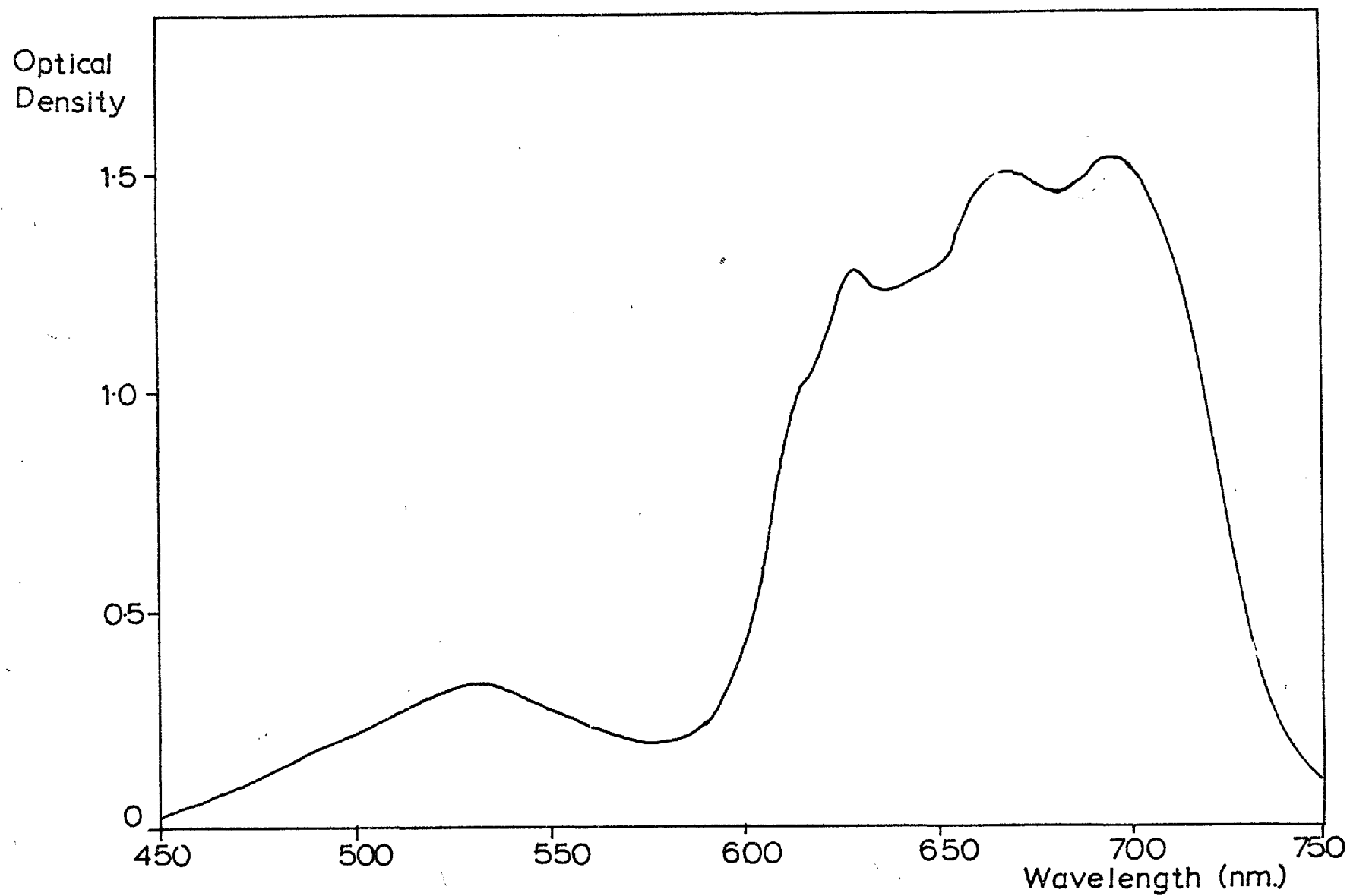


FIGURE 4.1 TYPICAL SPECTRUM OF THE Co - LiCl SYSTEM

$[\text{LiCl}] = 7.0\text{M}$ $[\text{Co}] = 1.948 \times 10^{-2}\text{M}$

there are no chloride ions in solution, due presumably to the co-ordination of water molecules around the cobaltous ion. As chloride is added to the solution, the peak wavelength gradually increases from its initial wavelength of 510 nm. to 530 nm. at 8M chloride and above. The absorbance also increases with increasing chloride, reaching a maximum at about 9M. Figure 4.2. is a plot of the overall extinction coefficients at three wavelengths lying within this broad peak with respect to the chloride concentration of the solution. It may be seen that there is a gradual linear rise in the extinction coefficients up to 3M chloride. At higher concentrations there is a steep rise to a maximum at 8 - 9M chloride. At the same time the peak wavelength rises from 510 nm. to 530 nm. The overall extinction coefficients for zero chloride were obtained from measurements on cobaltous perchlorate solutions.

The three strong peaks which appear in the 600 - 700 nm. region are assigned to cobalt in tetrahedral co-ordination. The peaks occur at 690, 662 and 624 nm. respectively and these wavelengths are invariant with chloride concentration. The overall extinction coefficients at these three wavelengths are plotted, on a semi-log basis, versus chloride concentration in Figure 4.3. They first become detectable between 3.5 - 4.0M chloride, at which point, they are about 0.1% of their maximum values. At 6.0M chloride they are about 1% of their maximum values which are reached at 12.1M chloride. At higher chloride concentrations (up to 13.0M) they decrease slightly. The ratios of the extinction coefficients of these peaks are plotted in Figure 4.4. Up to about 7M chloride these ratios vary, but at higher concentrations they remain constant. This is an indication that above 7M chloride the absorption in this wavelength region is probably due to one species only, whereas at lower concentrations the absorption is caused by at least two species.

The next section details the quantitative analyses from which the stability constants and individual extinction coefficients of the complexes were obtained. The octahedral wavelength region, i.e. 500 - 535 nm., was found to be most amenable to analysis and all the quantitative work is carried out on data obtained in this region. The number of complexes present in solution when significant absorption is exhibited in the 600 - 700 nm. region is such that quantitative analysis is not possible, and this data is used only for qualitative discussion in Section 4.G.

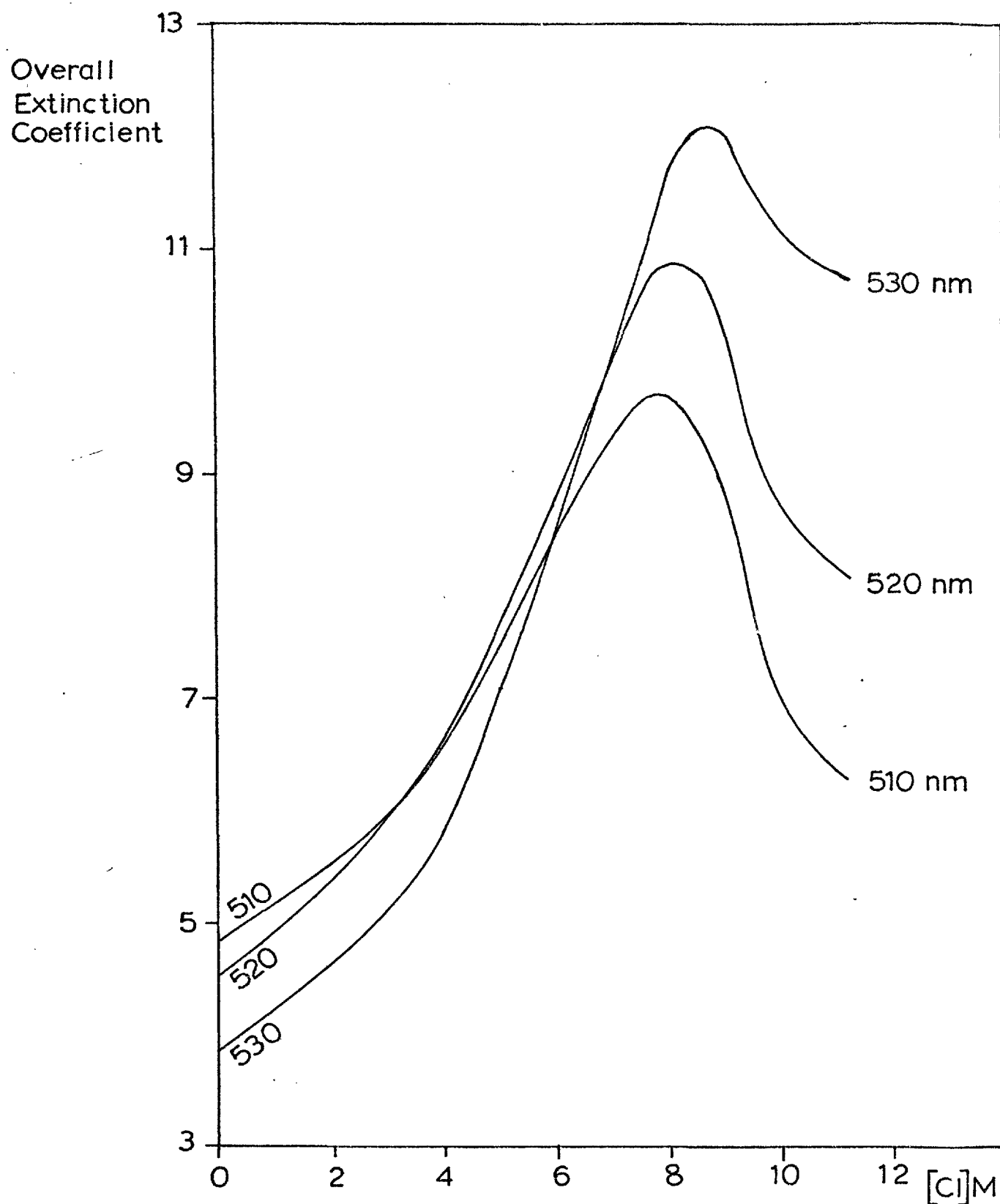


FIGURE 4.2 VARIATION OF THE OVERALL EXTINCTION COEFFICIENTS IN THE OCTAHEDRAL REGION.

Data from Table 4.1

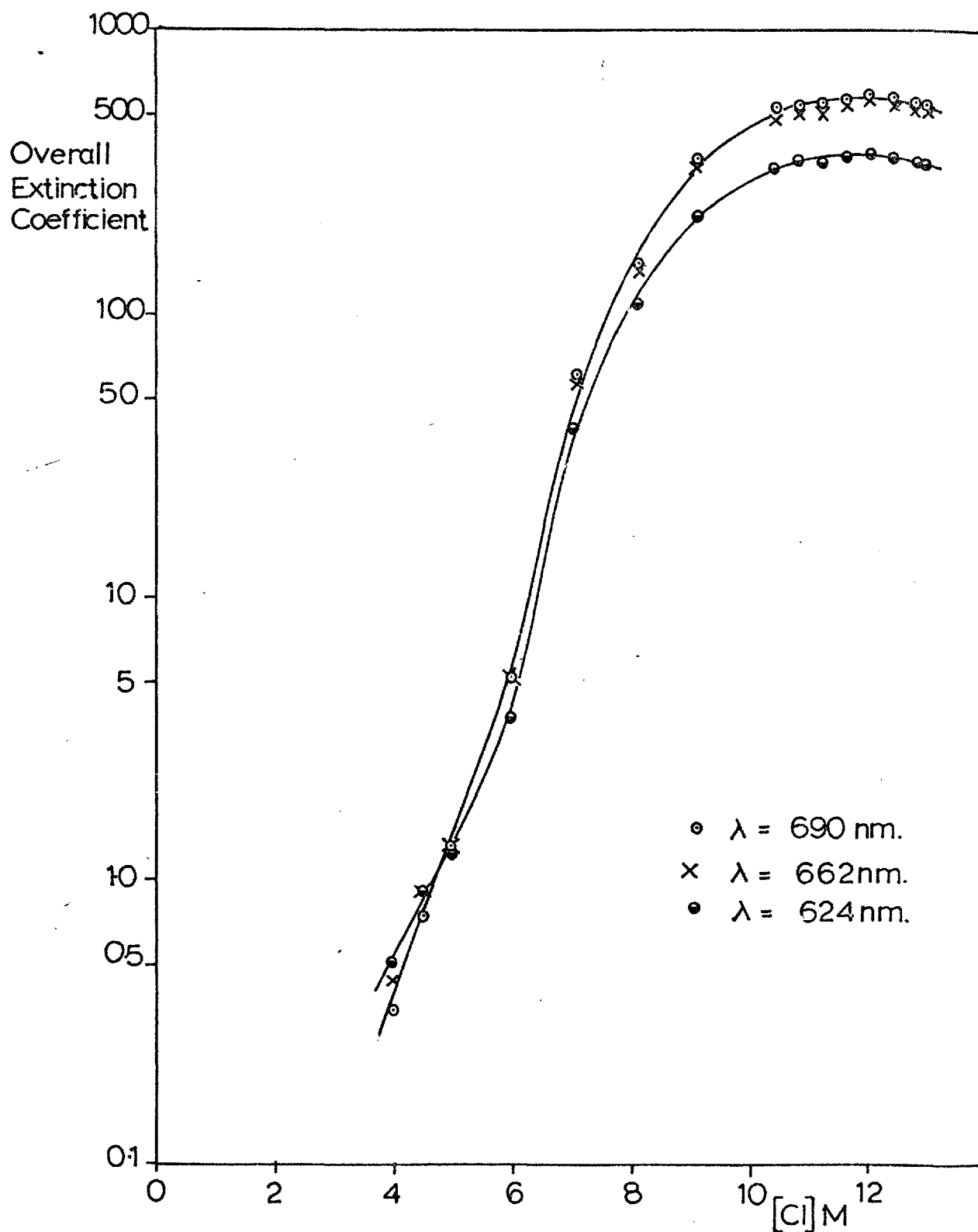


FIGURE 4.3 VARIATION OF THE OVERALL EXTINCTION COEFFICIENTS IN THE TETRAHEDRAL REGION.

Data from Table 4.1

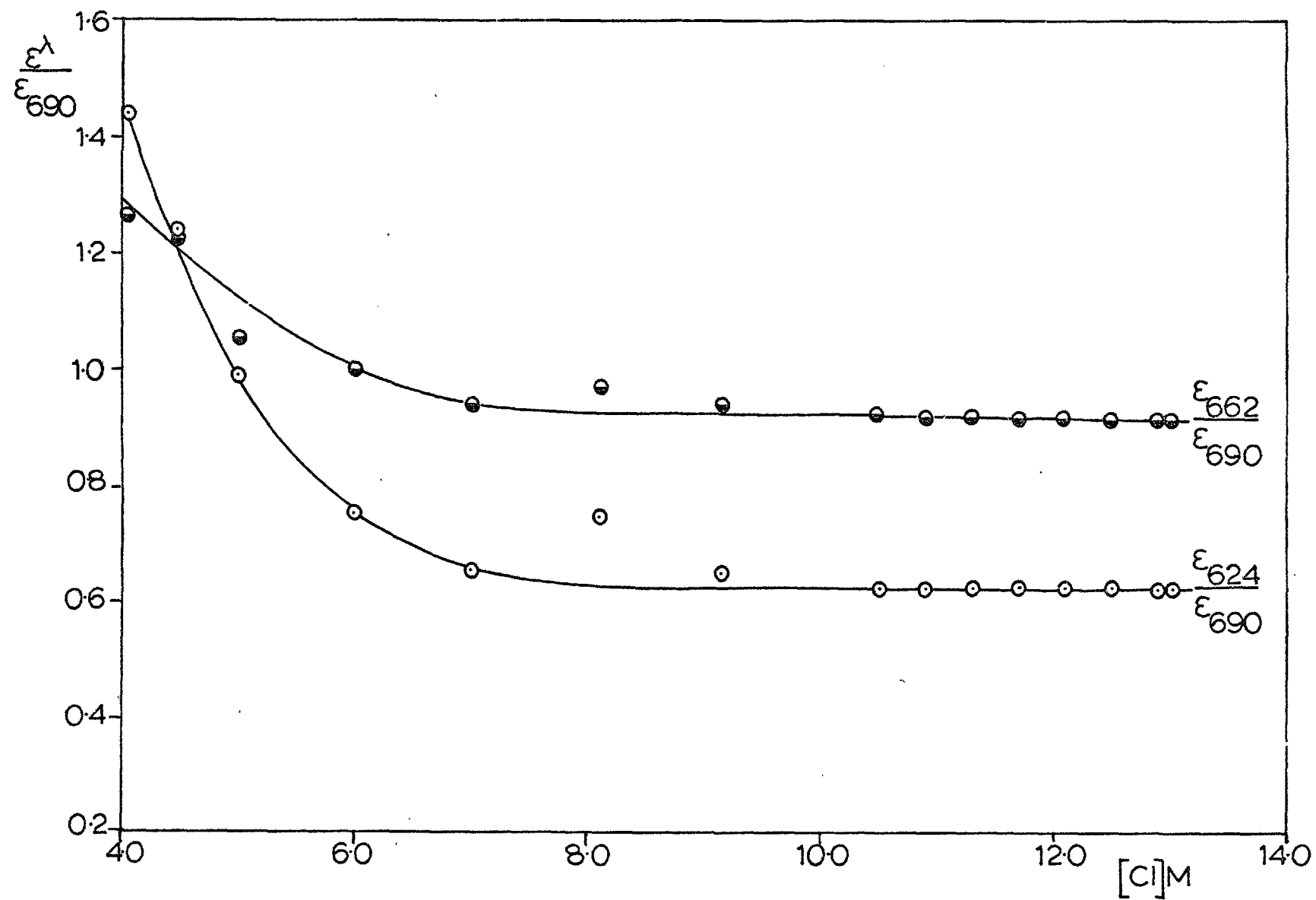


FIGURE 4.4 VARIATION OF THE RATIOS OF THE OVERALL EXTINCTION COEFFICIENTS
IN THE TETRAHEDRAL REGION. Data from Table 4.1

4.E. Quantitative Analysis of the Results.

4.E(i) Calculation of K_1^* and ϵ_1^λ

Examination of Figure 4.2. shows that, in the chloride concentration range 0 - 3M, the overall molar extinction coefficients in the octahedral region exhibit a gradual linear rise from their initial values at zero chloride. Above 3M chloride, the extinction coefficients rise fairly rapidly.

If the simple assumption is made that at low chloride concentrations only the two lowest cobalt complexes are present in detectable quantities, i.e. Co^{2+} and CoCl^+ , then the extinction coefficient data may be analysed to obtain K_1^* in the following manner:

$$\text{Initial assumption : } \alpha_0 + \alpha_1 = 1 \quad (4E1)$$

$$\text{From Equation (4B2) : } \epsilon^\lambda = \epsilon_0^\lambda \alpha_0 + \epsilon_1^\lambda \alpha_1 \quad (4E2)$$

$$\text{From Equation (4B11) : } K_1^* = \frac{\alpha_1}{\alpha_0 a_{\text{Cl}}} \quad (4E3)$$

From Equations (4E1) and (4E2) :

$$\epsilon^\lambda = \epsilon_0^\lambda (1 - \alpha_1) + \epsilon_1^\lambda \alpha_1$$

$$\therefore \epsilon^\lambda = \epsilon_0^\lambda - \epsilon_0^\lambda \alpha_1 + \epsilon_1^\lambda \alpha_1$$

$$\alpha_1 = \frac{\epsilon_1^\lambda - \epsilon_0^\lambda}{\epsilon_1^\lambda - \epsilon_0^\lambda} \quad (4E4)$$

From Equations (4E1) and (4E3) :

$$\frac{\alpha_1}{K_1^* a_{C1}} + \alpha_1 = 1$$

$$\therefore \alpha_1 = \left[\frac{1}{K_1^* a_{C1}} + 1 \right]^{-1} \quad (4E5)$$

From Equations (4E4) and (4E5) :

$$\frac{\epsilon_1^\lambda - \epsilon_0^\lambda}{\epsilon_1^\lambda - \epsilon_0^\lambda} = \left[\frac{1}{K_1^* a_{C1}} + 1 \right]^{-1}$$

$$\therefore \frac{\epsilon_1^\lambda - \epsilon_0^\lambda}{\epsilon_1^\lambda - \epsilon_0^\lambda} = \frac{1}{K_1^* a_{C1}} + 1 \quad (4E6)$$

$$\therefore (\epsilon_1^\lambda - \epsilon_0^\lambda)^{-1} = (a_{C1})^{-1} (K_1^* (\epsilon_1^\lambda - \epsilon_0^\lambda))^{-1} + (\epsilon_1^\lambda - \epsilon_0^\lambda)^{-1} \quad (4E7)$$

Thus in the region where Equation (4E1) is valid, a plot of $(\epsilon_1^\lambda - \epsilon_0^\lambda)^{-1}$ against $(a_{C1})^{-1}$ for each wavelength λ should give a straight line with a slope of $(K_1^* (\epsilon_1^\lambda - \epsilon_0^\lambda))^{-1}$ and an intercept of $(\epsilon_1^\lambda - \epsilon_0^\lambda)^{-1}$.

When these plots were drawn, it was found that for all wavelengths measured in the 500 - 535 nm. region, the data gave good straight line correlations for chloride concentrations ranging between 1.0 and 3.0M. At higher chloride concentrations the lines deviated from linearity, indicating that Equation (4E1) is no longer valid and thus species other than Co^{2+} and CoCl^+ are contributing to the spectra. A typical plot, for one wavelength (510 nm.) is given in Figure 4.5. The data from which the plots were made is tabulated in Appendix 2 (Table 4.1.X), together with the results for the best slopes, intercepts and correlation coefficients calculated by linear regression analysis. The derived K_1^* and ϵ_1^λ values are given in Table 4.2. The values of K_1^* are reasonably constant, ranging between 0.28 and 0.35 mole^{-1} with an average value of 0.32 mole^{-1} . The calculated values of ϵ_1^λ , the molar extinction coefficient of CoCl^+ , are plotted against wavelength in Figure 4.6. It may be seen that the absorption spectrum of CoCl^+ is similar in shape to that of Co^{2+} but that the absorption is stronger and the peak wavelength has risen to 515 nm.

Table 4.2 Calculated values of K_1^* and ϵ_1^λ

λ nm.	ϵ_1^λ	$K_1^*(\text{mole}^{-1})$
500	6.455	0.30
505	6.686	0.32
510	6.799	0.33
515	6.845	0.33
520	6.914	0.28
525	6.344	0.35
530	5.915	0.34
535	5.556	0.30
		Average 0.32

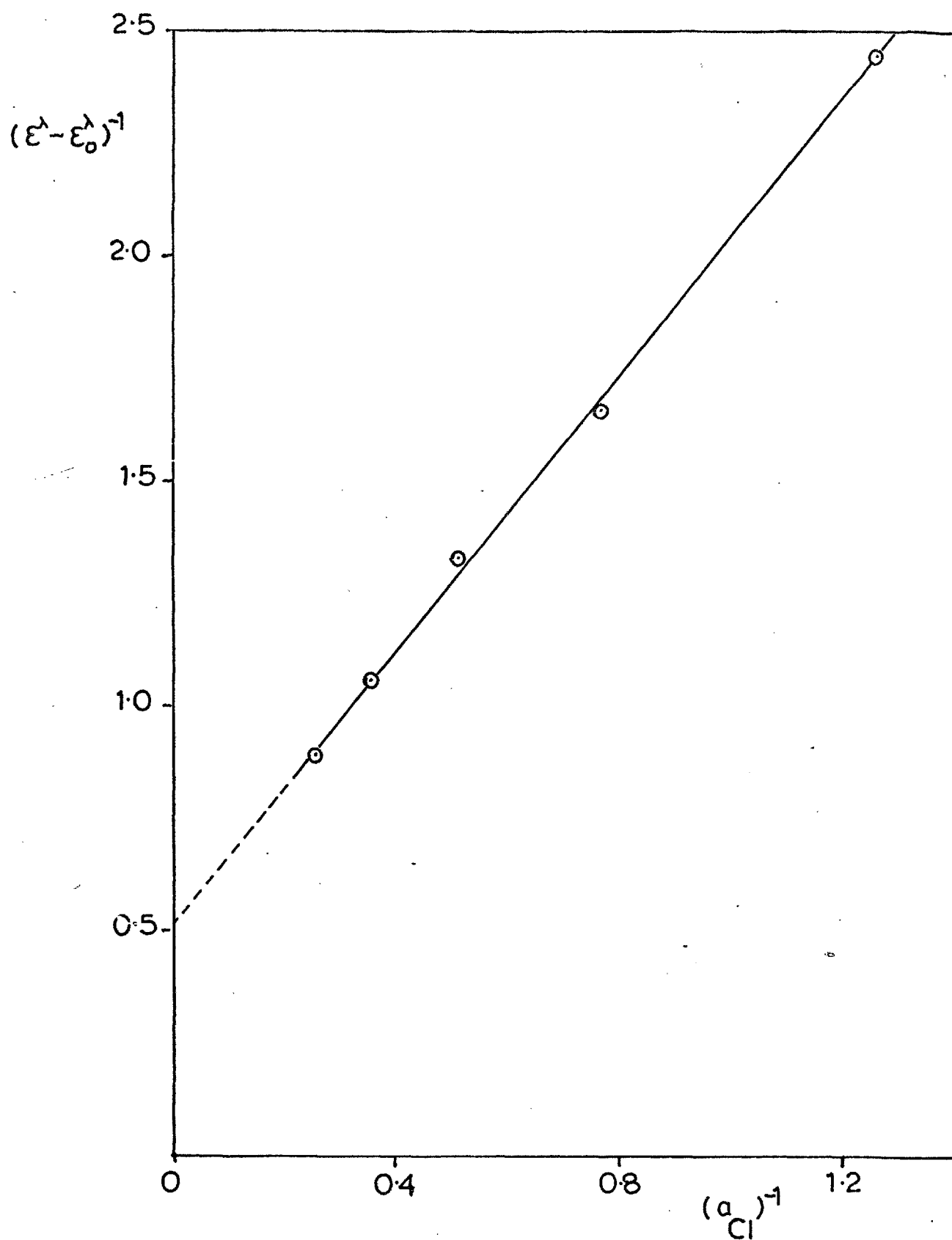


FIGURE 4.5

TYPICAL PLOT OF EQUATION (4E7).

Wavelength = 510 nm.

Chloride concentration range = 1.0 to 3.0M.

Data from Table 4.1.X.

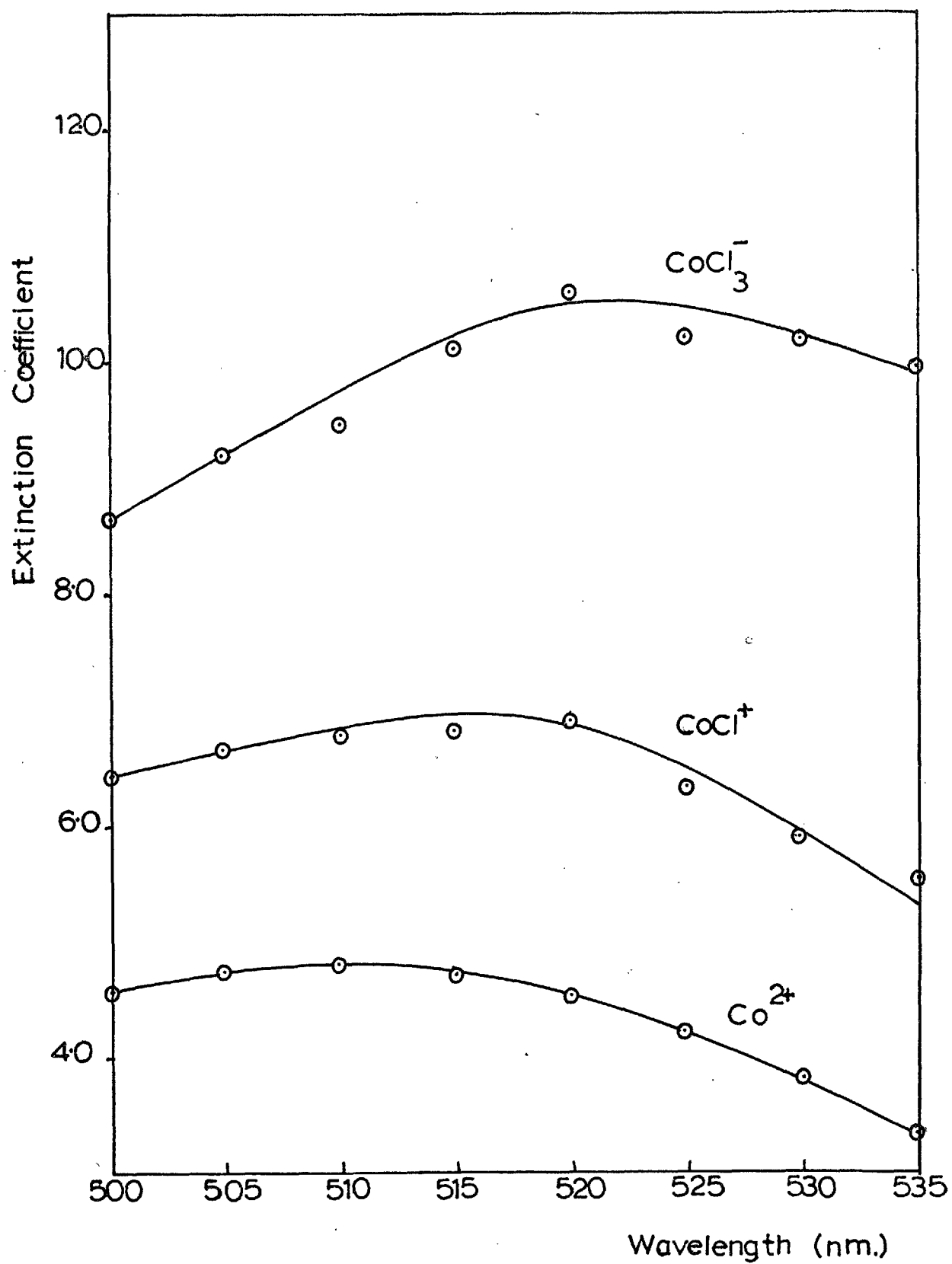


FIGURE 4.6 EXTINCTION COEFFICIENTS OF Co^{2+} , CoCl^+ , AND CoCl_3^-

Data from Tables 4.1, 4.2, and 4.3

4.E(ii) Combined Method for K_1^*

Having obtained values of ϵ_1^λ , it is possible to combine the data for all wavelengths to give a more accurate value of K_1^* by the use of Equation (4E6). The function on the left-hand side of this equation should be independent of wavelength and depend only on the chloride activity of the system. The functions $(\epsilon_1^\lambda - \epsilon_0^\lambda)(\epsilon^\lambda - \epsilon_0^\lambda)^{-1}$ were calculated for each value of λ at each value of a_{Cl} and then averaged. Examination of Equation (4E6) shows that a plot of $[(\epsilon_1^\lambda - \epsilon_0^\lambda)(\epsilon^\lambda - \epsilon_0^\lambda)^{-1}]_{av}^*$ against $(a_{Cl})^{-1}$ should have an intercept of unity and a slope of $(K_1^*)^{-1}$. This plot is given in Figure 4.7 and the relevant data is presented in Table 4.2.X. A good straight line with an intercept very close to 1.0 is obtained. The value of K_1^* derived from this plot is 0.33 mole⁻¹, and this is the value used in subsequent calculations.

4.E(iii) Calculation of K_2^* and ϵ_2^λ

A knowledge of the numerical values of ϵ_0^λ , ϵ_1^λ and K_1^* makes possible an analysis of the data for higher complexes.

The next logical assumption is that over some region of chloride concentration, greater than 3.0M, the species contributing to the spectra are Co^{2+} , $CoCl^+$, $CoCl_2$. By using this assumption, the data may be analysed to obtain values of K_2^* and ϵ_2^λ :

$$\text{Initial assumption: } \alpha_0 + \alpha_1 + \alpha_2 = 1 \quad (4E8)$$

Then from Equation (4B2):

$$\epsilon^\lambda = \epsilon_0^\lambda \alpha_0 + \epsilon_1^\lambda \alpha_1 + \epsilon_2^\lambda \alpha_2 \quad (4E9)$$

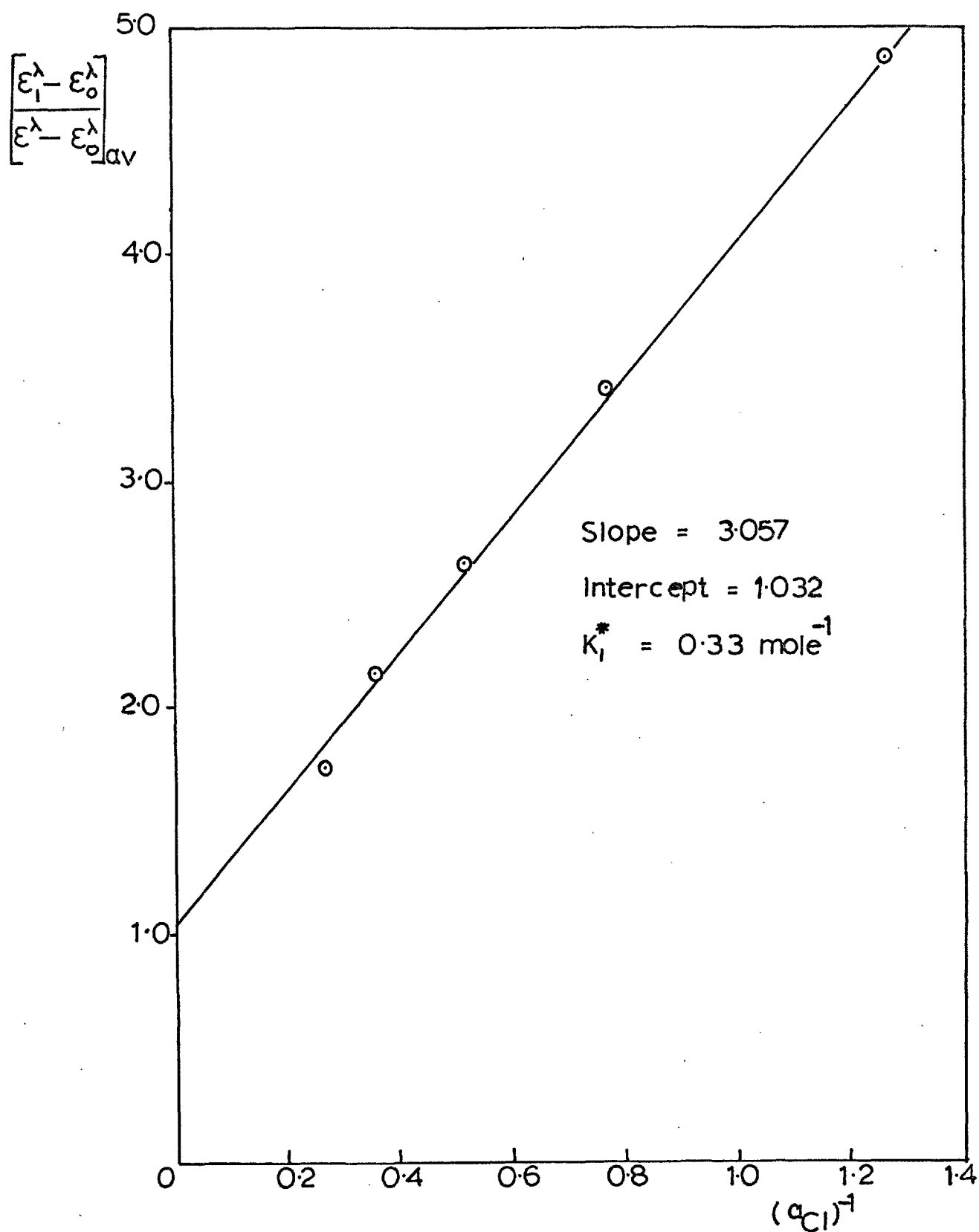


FIGURE 4.7 PLOT OF EQUATION (4E6) - THE COMBINED METHOD FOR K_1^*

Data from Table 4.2.X.

From Equation (4E11):

$$K_1^* = \frac{\alpha_1}{\alpha_0 a_{C1}} \quad \therefore \alpha_1 = \alpha_0 K_1^* a_{C1} \quad (4E10)$$

$$K_2^* = \frac{\alpha_2}{\alpha_1 a_{C1}} \quad \therefore \alpha_2 = \alpha_0 K_1^* K_2^* a_{C1}^2 \quad (4E11)$$

From (4E9), (4E10) and (4E11):

$$\epsilon^\lambda = \epsilon_0^\lambda \alpha_0 + \epsilon_1^\lambda \alpha_0 K_1^* a_{C1} + \epsilon_2^\lambda \alpha_0 K_1^* K_2^* a_{C1}^2$$

$$\therefore \alpha_0 = \epsilon^\lambda (\epsilon_0^\lambda + \epsilon_1^\lambda K_1^* a_{C1} + \epsilon_2^\lambda K_1^* K_2^* a_{C1}^2)^{-1} \quad (4E12)$$

From (4E8), (4E10) and (4E11):

$$\alpha_0 + \alpha_0 K_1^* a_{C1} + \alpha_0 K_1^* K_2^* a_{C1}^2 = 1$$

$$\therefore \alpha_0 = (1 + K_1^* a_{C1} + K_1^* K_2^* a_{C1}^2)^{-1} \quad (4E13)$$

From (4E12) and (4E13):

$$\epsilon^\lambda + \epsilon_1^\lambda K_1^* a_{C1} + \epsilon_2^\lambda K_1^* K_2^* a_{C1}^2 = \epsilon_0^\lambda + \epsilon_1^\lambda K_1^* a_{C1} + \epsilon_2^\lambda K_1^* K_2^* a_{C1}^2$$

$$\therefore (\epsilon^\lambda - \epsilon_0^\lambda) + K_1^* a_{C1} (\epsilon^\lambda - \epsilon_1^\lambda) = K_1^* K_2^* a_{C1}^2 (\epsilon_2^\lambda - \epsilon^\lambda)$$

$$\therefore (a_{C1})^{-2} (\epsilon^\lambda - \epsilon_0^\lambda) + K_1^* (a_{C1})^{-1} (\epsilon^\lambda - \epsilon_1^\lambda) = K_1^* K_2^* \epsilon_2^\lambda - K_1^* K_2^* \epsilon^\lambda \quad (4E14)$$

Thus from Equation (4E14), a plot of the function on the left-hand side against ϵ^λ should be a straight line with a negative slope. The slope will be equal to $-K_1^* K_2^*$ and the intercept equal to $K_1^* K_2^* \epsilon_2^\lambda$.

These calculations were carried out and the data plotted for all wavelengths measured between 500 and 535 nm. The results were somewhat scattered but in all cases the general shape of the plot was a parabolic curve with a maximum at the ϵ^λ value corresponding to 4.5M chloride. A typical plot is given in Figure 4.8.

From these results it was concluded that the initial assumption of the analysis - Equation (4E8) - is invalid. That is, there is apparently no chloride concentration region where the only species existing in solution are Co^{2+} , CoCl^+ and CoCl_2 .

4.E(iv) Calculation of β_3^* and ϵ_3^λ

The next simplifying assumption made was that there is a region of chloride concentration where the major species are Co^{2+} , CoCl^+ and CoCl_2^- with CoCl_2 existing only in negligible quantities. The analysis for this state of affairs is as follows:

$$\text{Initial assumption: } \alpha_0 + \alpha_1 + \alpha_3 = 1 \quad (4E15)$$

Then from Equation (4B2) :

$$\epsilon^\lambda = \epsilon_0^\lambda \alpha_0 + \epsilon_1^\lambda \alpha_1 + \epsilon_3^\lambda \alpha_3 \quad (4E16)$$

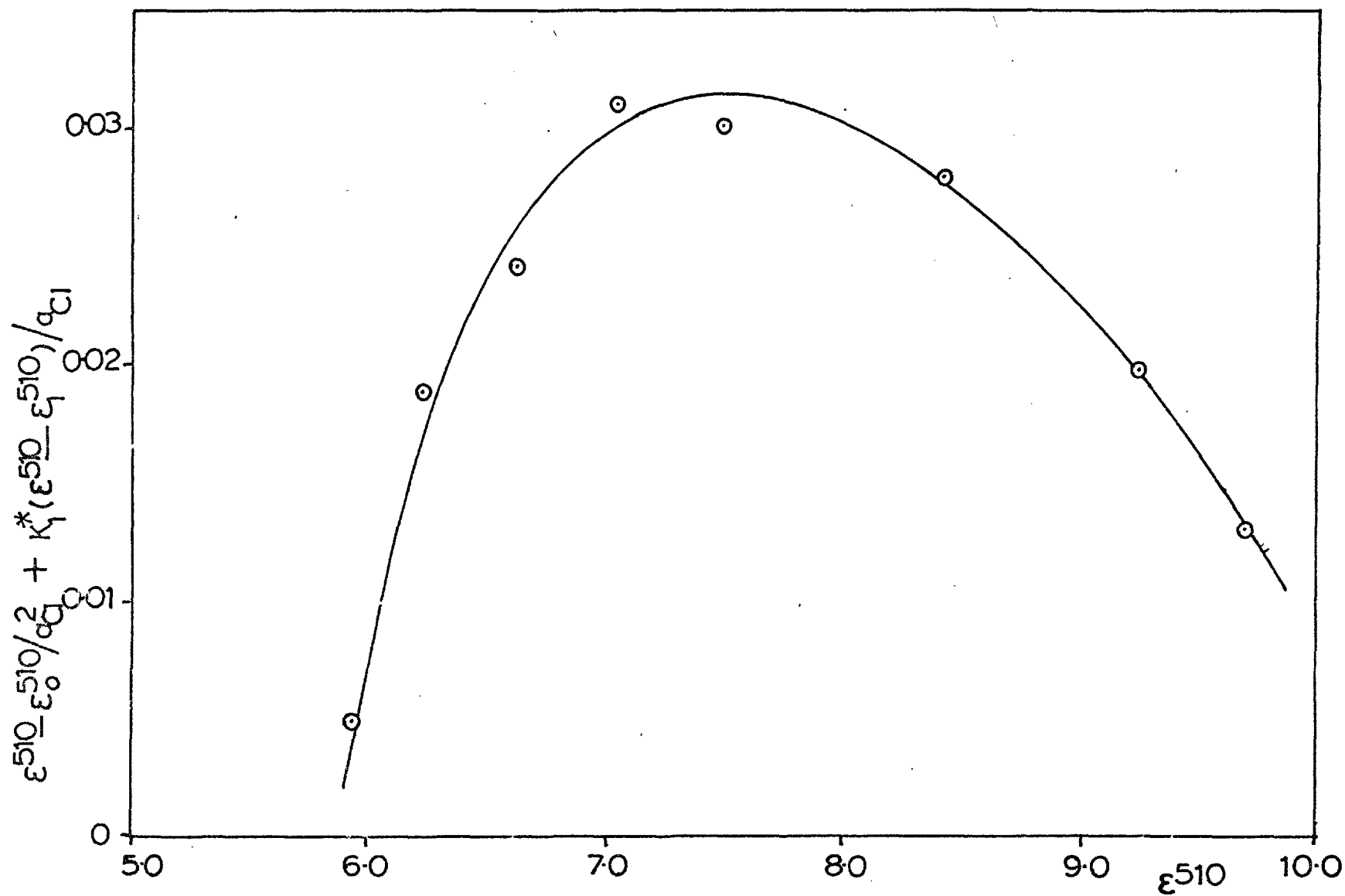


FIGURE 4.8 TYPICAL PLOT OF EQUATION (4E14)

Wavelength = 510 nm.

Chloride concentration range = 3.0 to 8.0M

From Equation (4B11):

$$K_1^* = \frac{\alpha_1}{\alpha_0 a_{Cl}} \quad \therefore \alpha_1 = \alpha_0 K_1^* a_{Cl} \quad (4E17)$$

$$\beta_3^* = \frac{\alpha_3}{\alpha_0 a_{Cl}^3} \quad \therefore \alpha_3 = \alpha_0 \beta_3^* a_{Cl}^3 \quad (4E18)$$

Following reasoning similar to that in the preceding section, the following equation may be derived:

$$(a_{Cl})^{-3}(\epsilon^\lambda - \epsilon_0^\lambda) + (a_{Cl})^{-2}K_1^*(\epsilon^\lambda - \epsilon_1^\lambda) = \beta_3^* \epsilon_3^\lambda - \beta_3^* \epsilon^\lambda \quad (4E19)$$

Thus a plot of the left-hand side of Equation (4E19) against ϵ^λ at a given wavelength should be a straight line with a negative slope. The slope of the line will be equal to $-\beta_3^*$, and the intercept at $\epsilon^\lambda = 0$ will be $\beta_3^* \epsilon_3^\lambda$.

When the data were calculated, the plots for all wavelengths in the 500 - 535 nm. range gave good straight lines with negative slopes over the chloride range 4.0 to 6.0M. At higher chloride concentrations the plots deviated from linearity, indicating that Equation (4E15) is no longer valid. A typical plot is given in Figure 4.9 and all the calculated data is tabulated in Table 4.3.X, together with the results of linear regression analyses for the best slopes, intercepts and correlation coefficients. The derived values of β_3^* and ϵ_3^λ are presented in Table 4.3. The numerical values of β_3^* range between $(0.75 - 1.27) \times 10^{-3}$ moles⁻³, with an average value of 1.07×10^{-3} moles⁻³. The ϵ_3^λ values are plotted versus wavelength in Figure 4.6 and this shows that $CoCl_3$

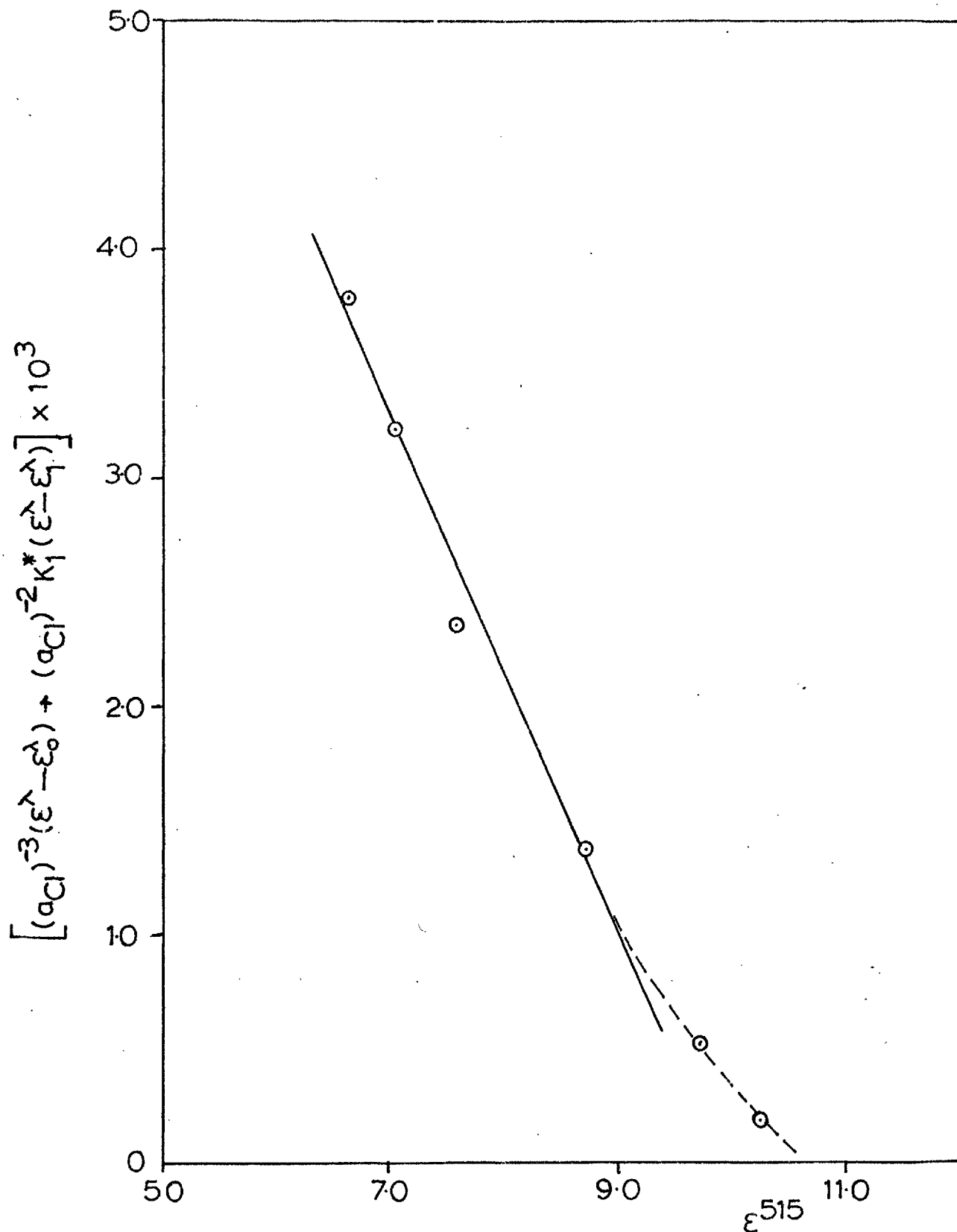


FIGURE 4.9 TYPICAL PLOT OF EQUATION (4E19).

Wavelength = 515 nm.

Chloride concentration range = 4.0 to 8.0M

Data from Table 4.3.X.

Table 4.3 Calculated values of β_3^* and ϵ_3^λ

λ nm.	ϵ_3^λ	$\beta_3^* \times 10^3$ (mole ⁻³)
500	8.633	1.14
505	9.222	1.09
510	9.485	1.27
515	10.126	1.04
520	10.628	0.75
525	10.271	1.25
530	10.221	1.14
535	9.979	0.87
Average		1.07

has an absorption spectrum in the wavelength range considered which resembles that of Co^{2+} and CoCl^+ . The absorption is stronger and the peak wavelength is at a higher value. This is consistent with the behaviour of the measured overall extinction coefficients with increasing chloride concentration as shown in Figure 4.2.

4.E(v) Combined Method for β_3^*

Having calculated values of ϵ_3^λ it is possible to combine the data for all wavelengths to get a more accurate value of β_3^* by a method similar to that used for K_1^* (See Section 4.E(ii)).

From Equation (4E19):

$$\frac{(\epsilon^\lambda - \epsilon_0^\lambda) + K_1^* a_{Cl} (\epsilon^\lambda - \epsilon_1^\lambda)}{(\epsilon_3^\lambda - \epsilon^\lambda)} = \beta_3^* a_{Cl}^3 \quad (4E20)$$

The function F' on the left-hand side of the above equation should be independent of wavelength and dependent only on the chloride activity of the system. Thus it is possible to calculate the function for each wavelength and obtain the average value for each chloride activity. A plot of the average value of the function versus a_{Cl}^3 should be linear with a slope equal to β_3^* . Alternatively, taking logs of Equation (4E20):

$$\log F' = \log \beta_3^* + 3 \log a_{Cl} \quad (4E21)$$

Thus a plot of $\log F'$ against $\log a_{Cl}$ should be linear with a slope of 3 and an intercept at $\log a_{Cl} = 0$ equal to $\log \beta_3^*$.

The calculated values of the function F' , using the previously determined values of ϵ_3^λ , are given in Table 4.4.X. There is a reasonable constancy of the F' values at each chloride concentration except for those at 7M chloride.

The log-log plot of the average value of the function, F'_{av} against chloride activity is given in Figure 4.10. A line of slope 3 is a good fit to the data except for the point corresponding to 7M chloride. This is an indication that the original assumption of this analysis, that only three species are present, i.e. Co^{2+} , $CoCl^+$ and $CoCl_3^-$, is invalid at chloride concentrations above 6M. In other words a higher complex or complexes are contributing to the spectrum. The results of a linear regression analysis of the data $\log F'_{av}$ versus $\log a_{Cl}$ up to 6M chloride is given in Table 4.4, together with the results of a similar analysis for F'_{av} versus a_{Cl}^3 . A plot of these latter data is not presented since the values range across several orders of magnitude. In both cases the correlation coefficients are close to unity indicating good linearity. The values of β_3^* obtained

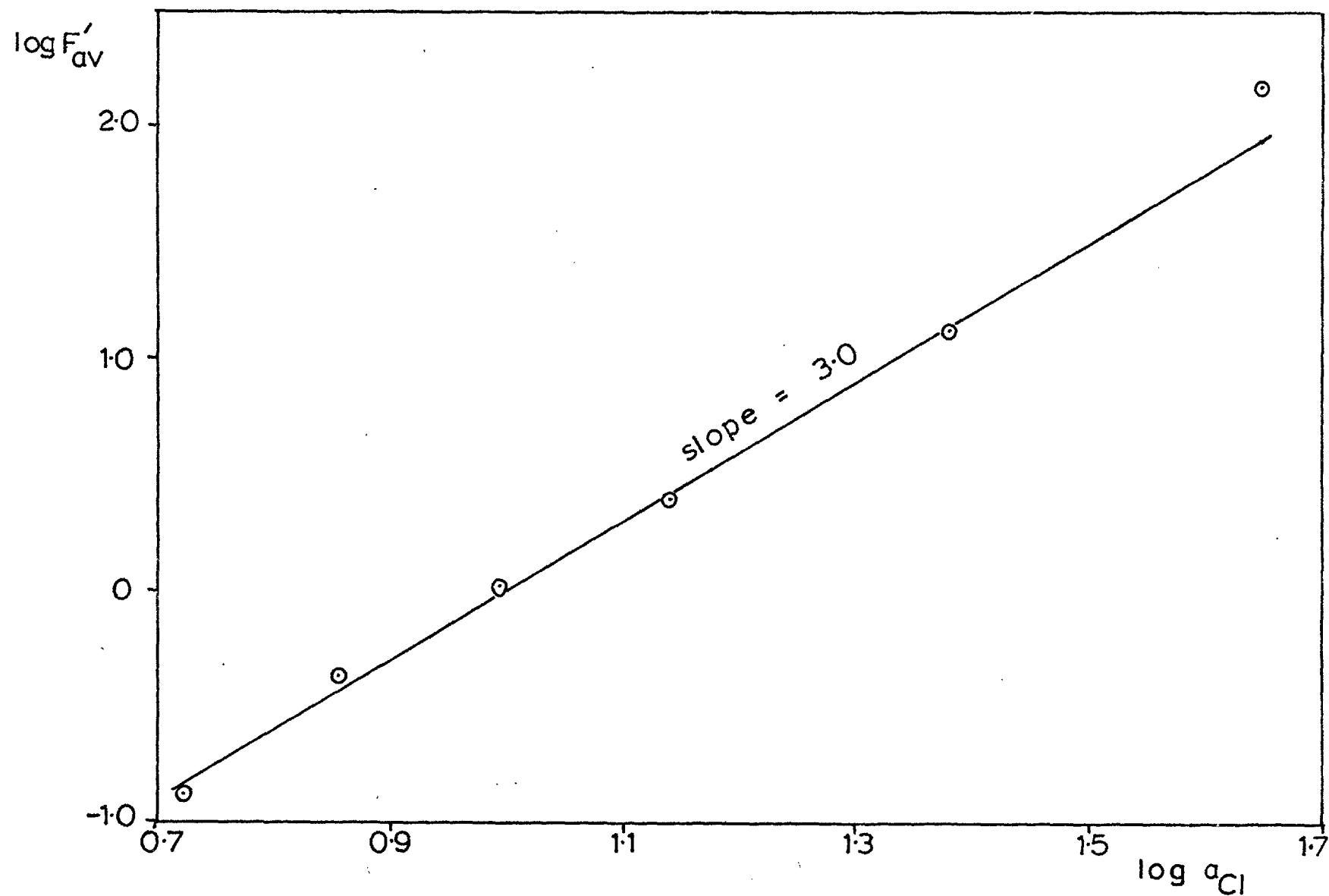


FIGURE 4.10 PLOT OF EQUATION (4E21) - THE COMBINED METHOD FOR β_3^*

Data from Table 4.5.X.

from the intercept and the slope respectively (Equations (4E21) and (4E20)) are in good agreement and they are both in reasonable agreement with the average value of $\beta_3^* = 1.07 \times 10^{-3}$ calculated in the preceding section.

Table 4.4. Linear Regression Analyses

Equation	Data	Corr.Coeff.	Intercept	Slope	β_3^* moles ⁻³
(4E21)	$\log F'_{av}$ vs. $\log a_{Cl}$	0.9984	-3.0086	3.0046	0.98×10^{-3}
(4E20)	F'_{av} vs. a_{Cl}^3	0.9999	0.0424	0.00096	0.96×10^{-3}

Since this combined method for β_3^* is expected to yield a more accurate value than the method used in the preceding section, the mean of the two values given in Table 4.4. is used for subsequent calculations, i.e.

$$\beta_3^* = 0.97 \times 10^{-3} \text{ moles}^{-3}$$

4.E(vi) Calculation of α_n and $\bar{n}$ values

The values of K_1^* and β_3^* obtained in the preceding sections may be used to calculate the distribution of cobalt amongst its various complexes as a function of chloride concentration. The stability

constants were obtained by assuming the existence of three cobalt containing species in solution - Co^{2+} , CoCl^+ and CoCl_3^- , with CoCl_2 present in negligible quantities. This assumption appears to be valid for chloride concentrations of up to 6M, and thus the fractions α_n of each species may be calculated up to this concentration, where:

$$\alpha_n = \frac{[\text{CoCl}_n^{2-n}]}{[\text{Co}]_{\text{total}}} \quad (4E22)$$

It may be simply shown that if,

$$\alpha_0 + \alpha_1 + \alpha_3 = 1 \quad \text{and} \quad [\text{Co}]_{\text{total}} \ll [\text{Cl}]$$

then :

$$\alpha_0 = \frac{1}{1 + K_1^* a_{\text{Cl}} + \beta_3^* a_{\text{Cl}}^3} \quad \alpha_1 = \frac{K_1^* a_{\text{Cl}}}{1 + K_1^* a_{\text{Cl}} + \beta_3^* a_{\text{Cl}}^3} \quad \alpha_3 = \frac{\beta_3^* a_{\text{Cl}}^3}{1 + K_1^* a_{\text{Cl}} + \beta_3^* a_{\text{Cl}}^3}$$

Also the average ligand number $\bar{n}$ is given by:

$$\bar{n} = \frac{K_1^* a_{\text{Cl}} + 3\beta_3^* a_{\text{Cl}}^3}{1 + K_1^* a_{\text{Cl}} + \beta_3^* a_{\text{Cl}}^3} \quad (4E23)$$

Calculated values of α_n and $\bar{n}$ are given in Table 4.6.X and plotted in Figure 4.11.

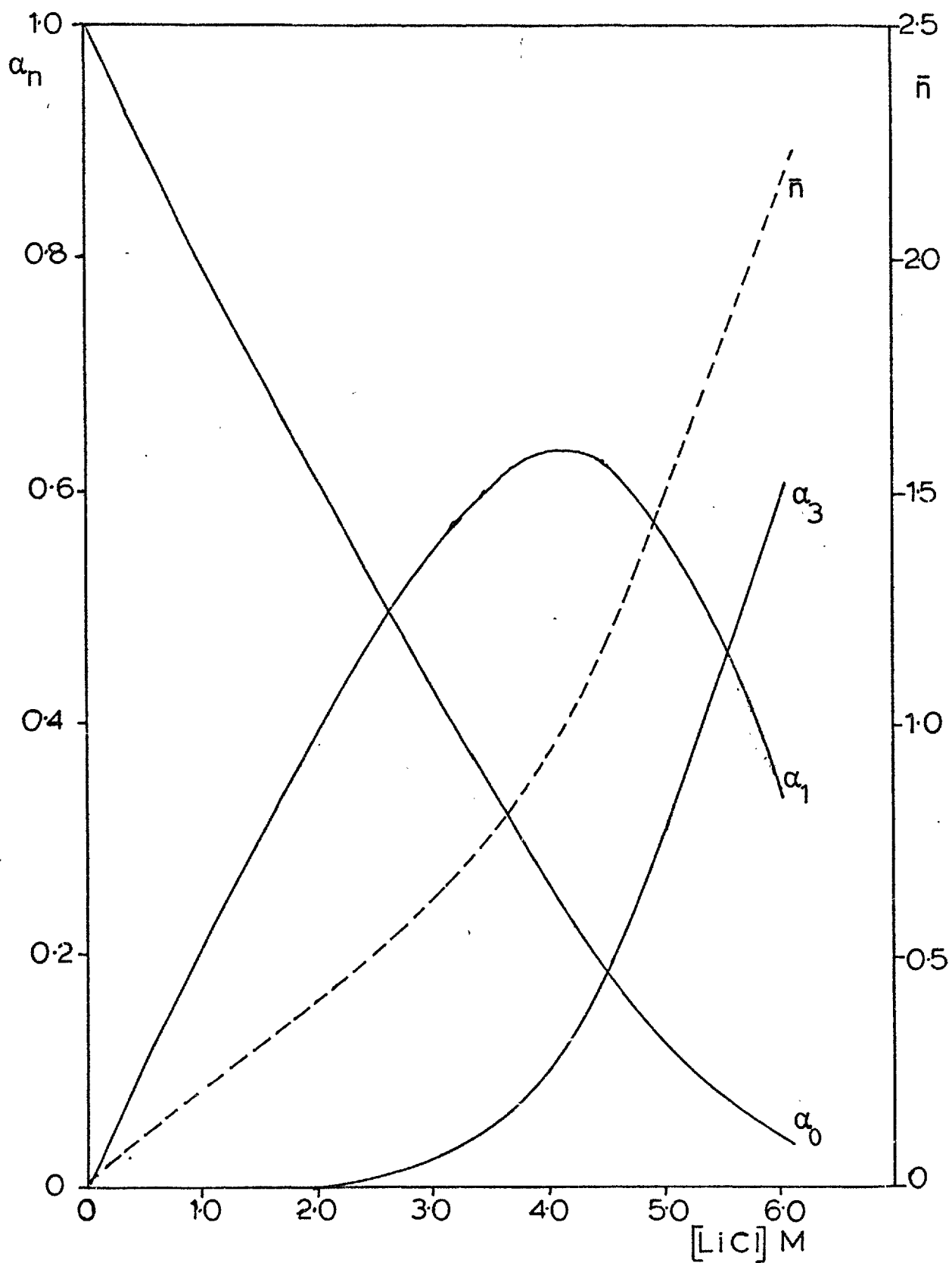


FIGURE 4.11 VARIATION OF α_n AND $\bar{n}$ VALUES WITH CHLORIDE CONCENTRATION

Data from Table 4.6.X.

4.E(vii) Comparison of the Theoretical and Measured overall extinction coefficients.

In order to demonstrate how well the measured data are described by the calculated stability constants, the theoretical overall extinction coefficients have been calculated by introducing values of α_n and ϵ_n^λ into Equation (4B2):

$$\epsilon^\lambda = \sum_{n=0}^{n=3} \epsilon_n^\lambda \alpha_n \quad (4B2)$$

The results for two values of λ , 500 and 530 nm., are tabulated in Table 4.7.X, and plotted in Figure 4.12, where the solid lines represent the theoretical values of the overall extinction coefficients and the circles are the measured values. It may be seen that there is very good agreement between the two sets of data.

4.F. Alternative analyses involving water activities

In Section 4.B. it was pointed out that it can be argued that water molecules occupying unfilled co-ordination positions of the central metal ion should be considered as an integral part of the complex ion. If this is the case, then, when writing the complex equilibria, water should be treated in exactly the same manner as the complexing ligand. Thus for a divalent metal ion, M^{2+} , with a co-ordination number, n , which forms complexes with the anion, A^- , the stepwise equilibria would

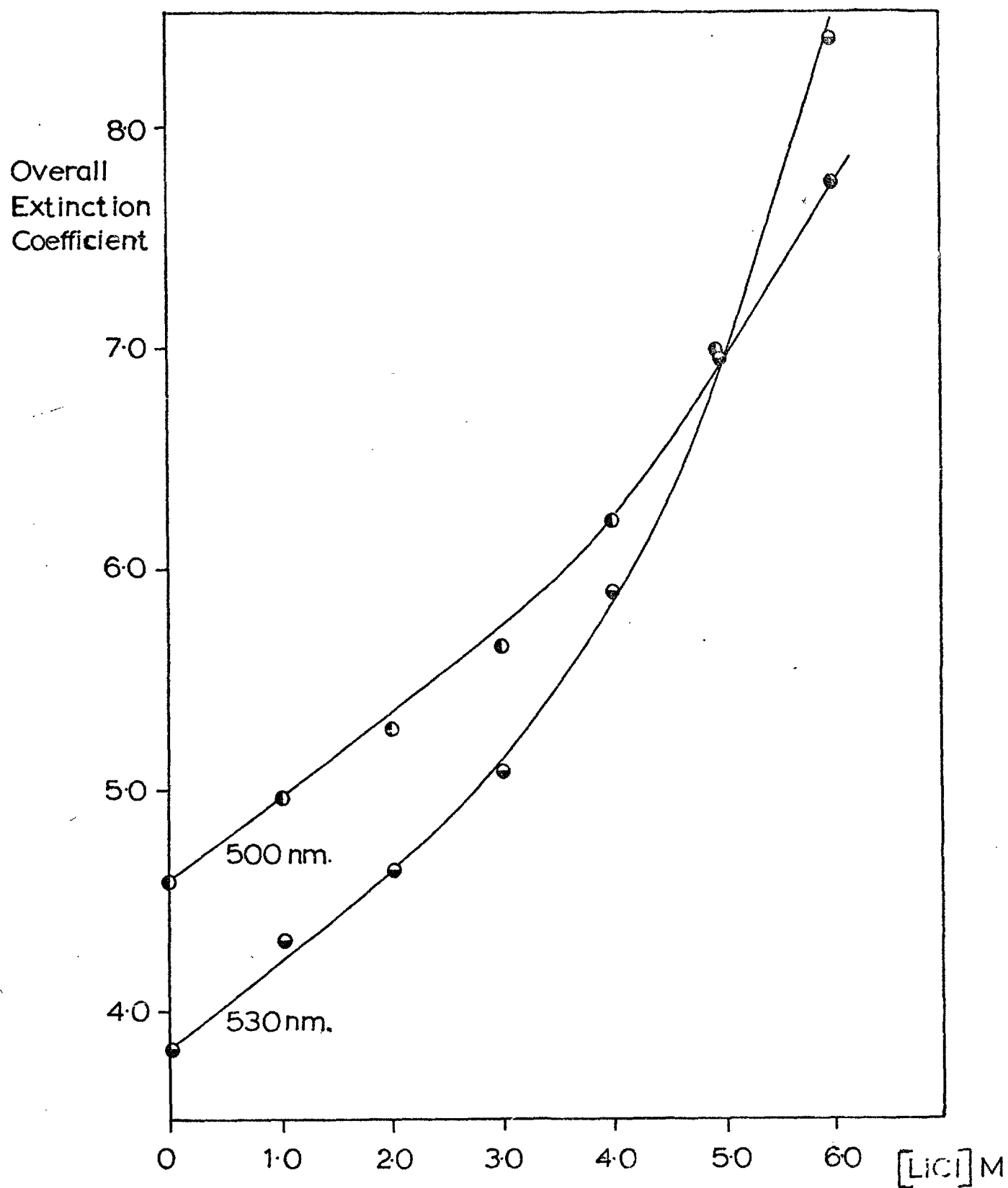


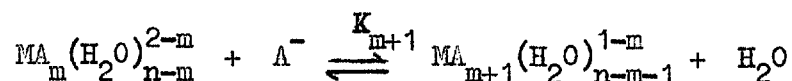
FIGURE 4.12 COMPARISON OF THE THEORETICAL AND MEASURED OVERALL EXTINCTION COEFFICIENTS.

Lines = Theoretical values

Circles = Measured values

Data from Table 4.7.X.

be written:



$$K_{m+1} = \frac{a_{MA_{m+1}} a_{H_2O}}{a_{MA_m} a_A}$$

Hence the equilibrium constant includes the activity of water in the system as well as the ligand activity.

In the chloro-cobaltous system the situation is complicated by the possibility of a change in the co-ordination number of the metal ion. If it is assumed that Co^{2+} and $CoCl^+$ are both octahedral complexes, then the equilibrium is of the type given above and K_1 is given by:

$$K_1 = \frac{a_{CoCl^+} \cdot a_{H_2O}}{a_{Co^{2+}} \cdot a_{Cl}}$$

Following the arguments given in Section 4.B, the apparent equilibrium constant involving water activity K_1^{**} becomes:

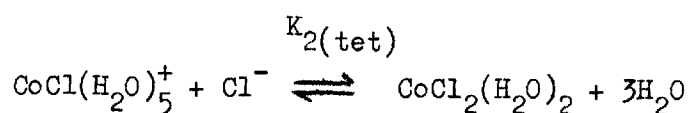
$$K_1^{**} = \frac{\alpha_1 \cdot a_{H_2O}}{\alpha_0 \cdot a_{Cl}}$$

where a_{Cl} is the effective chloride activity and a_{H_2O} is the water activity of the bulk solution, which can be obtained from published data for lithium chloride solutions.

Similarly if $CoCl_2$ is also an octahedral complex then:

$$K_{2(\text{oct})}^{**} = \frac{\alpha_2 a_{\text{H}_2\text{O}}}{\alpha_1 a_{\text{Cl}}}$$

However if the change to tetrahedral co-ordination takes place during the formation of CoCl_2 , then the equilibrium is:



and $K_{2(\text{tet})}^{**}$ becomes:

$$K_{2(\text{tet})}^{**} = \frac{\alpha_2 a_{\text{H}_2\text{O}}^3}{\alpha_1 a_{\text{Cl}}}$$

These modified forms of the apparent equilibrium constants can be combined with the general equation for the overall extinction coefficient (Equation (4B2)) to obtain equations from which the constants can be evaluated using exactly the same reasoning as before - Section 4.E, parts (i) to (v). Analogous equations are obtained; thus Equation (4E7) becomes:

$$(\epsilon^\lambda - \epsilon_0^\lambda)^{-1} = a_{\text{H}_2\text{O}} a_{\text{Cl}}^{-1} (K_1^* (\epsilon_1^\lambda - \epsilon_0^\lambda))^{-1} + (\epsilon_1^\lambda - \epsilon_0^\lambda)^{-1} \quad (4F1)$$

This equation applies where the only species in solution are Co^{2+} and CoCl^+ .

Where the absorbing species are Co^{2+} , CoCl^+ and octahedral CoCl_2 , an equation analogous to Equation (4E14) is obtained:

$$\begin{aligned}
& (a_{\text{H}_2\text{O}})^2 (a_{\text{Cl}})^{-2} (\epsilon^\lambda - \epsilon_0^\lambda) + K_1^{**} a_{\text{H}_2\text{O}} (a_{\text{Cl}})^{-1} (\epsilon^\lambda - \epsilon_1^\lambda) \\
& = K_1^{**} K_{2(\text{oct})}^{**} \epsilon_2^\lambda - K_1^{**} K_{2(\text{oct})}^{**} \epsilon^\lambda \quad (4\text{F}2)
\end{aligned}$$

If on the other hand the absorbing species are Co^{2+} , CoCl^+ and tetrahedral CoCl_2 , the above equation is slightly modified and becomes:

$$\begin{aligned}
& (a_{\text{H}_2\text{O}})^4 (a_{\text{Cl}})^{-2} (\epsilon^\lambda - \epsilon_0^\lambda) + K_1^{**} (a_{\text{H}_2\text{O}})^3 (a_{\text{Cl}})^{-1} (\epsilon^\lambda - \epsilon_1^\lambda) \\
& = K_1^{**} K_{2(\text{tet})}^{**} \epsilon_2^\lambda - K_1^{**} K_{2(\text{tet})}^{**} \epsilon^\lambda \quad (4\text{F}3)
\end{aligned}$$

Finally for the case where the absorbing species are Co^{2+} , CoCl^+ and tetrahedral CoCl_2^- , a modified form of Equation (4E19) is obtained:

$$(a_{\text{H}_2\text{O}})^5 (a_{\text{Cl}})^{-3} (\epsilon^\lambda - \epsilon_0^\lambda) + (a_{\text{H}_2\text{O}})^4 (a_{\text{Cl}})^{-2} (\epsilon^\lambda - \epsilon_1^\lambda) = \beta_3^{**} \epsilon_3^\lambda - \beta_3^{**} \epsilon^\lambda \quad (4\text{F}4)$$

The extinction coefficient data, effective chloride activities, and water activities obtained from data for lithium chloride solutions, were introduced into the above equations. A summary of the results obtained is given below.

K_1^{**} and ϵ_1^λ The extinction coefficient data in the range 1.0 to 3.0M chloride were described by Equation (4F1) with a success equal to that obtained using Equation (4E7). The correlation coefficients for the lines obtained at a given wavelength using each equation were almost identical. The values of K_1^{**} were about 10% higher than the values of

K_1^* , ranging between 0.28 and 0.39 mole⁻¹, with an average value of 0.36 mole⁻¹. The values of ϵ_1^λ obtained using Equation (4F1) were about 5% lower than those obtained using Equation (4E7). Thus over the chloride concentration range 1.0 to 3.0M the data are fitted equally well by equations derived both with and without water in the equilibria,

K_2^{**} and ϵ_2^λ Equations (4F2) and (4F3) are of the same form. They apply respectively to solutions which contain only either Co^{2+} , CoCl^+ and octahedral CoCl_2 or Co^{2+} , CoCl^+ and tetrahedral CoCl_2 . If either of these sets of conditions apply then plots of the left-hand side of the relevant equation against the overall extinction coefficient ϵ^λ , at various wavelengths λ , should give straight lines with negative slopes equal to $-K_1^{**}K_2^{**}$. When these plots were made results were obtained for both equations which resembled those shown in Figure 4.8., i.e. instead of straight lines with negative slopes, parabolic curves were obtained. Thus in this case, the fit to the data was not improved by introducing water activity into the equilibria, nor was it improved by postulating the existence of the tetrahedrally co-ordinated dichlorocobaltous ion, $\text{CoCl}_2(\text{H}_2\text{O})_2$.

β_3^{**} and ϵ_3^λ In this case the introduction of water activity into the equilibria proved positively disadvantageous. When the data were introduced to Equation (4F4) plots of the left-hand side of the equation against ϵ^λ gave points lying on continuous curves rather than straight lines, as the theory predicts. On the other hand straight lines and reasonably constant values of β_3^* were obtained using Equation (4E19), in which water activities had not been considered.

Thus since no positive improvements had been demonstrated in the fit to the data by the use of Equations (4F1), (4F2) and (4F3) and in the case of Equation (4F4), the fit was definitely not as good, it was concluded that there is no mathematical case for including water activities in the complex-forming equilibria in the cobalt chloride - lithium chloride system. This conclusion is in contrast to that of Zeltmann¹⁷ who found that the best fit to data obtained from an n.m.r. study of complexing in the cobalt chloride - hydrochloric acid system was achieved

by using equilibria involving water activities. Zeltmann states that his data could be described without the use of water activities, although less accurately, by using different values of the equilibrium constants. He also states that doing this does not alter the interpretation of the data. This latter statement is difficult to understand since one of the species he proposes in his interpretation is tetrahedral $\text{CoCl}_2(\text{H}_2\text{O})_2$ and this species cannot be distinguished from $\text{CoCl}_2(\text{H}_2\text{O})_4$ in a curve fitting exercise, unless water is involved in the equilibria.

However the data obtained in the present investigation are best interpreted by assuming that CoCl_2 , whether in octahedral or tetrahedral co-ordination, exists in negligible quantities, and that up to 6M lithium chloride the detectable cobalt species existing in solution are Co^{2+} , CoCl^+ and CoCl_3^- .

4.G. Complexing in solutions containing more than 6M chloride

In the preceding sections it has been shown that the experimental extinction coefficient data up to 6M chloride can be adequately described by postulating the existence of three cobalt species: Co^{2+} , CoCl^+ and CoCl_3^- . At higher chloride concentrations, the situation is complicated by the presence of appreciable absorption in the tetrahedral region (600 - 700 nm.). Absorption in this region first becomes detectable at approximately 4M chloride. Examination of Figure 4.11 shows that, below 4M chloride, the majority of the metal is present as Co^{2+} and CoCl^+ . It is thus concluded that these two species do not absorb in the tetrahedral region.

From Figure 4.3 it may be seen that at 6M chloride the tetrahedral absorption is about 1% of its maximum value. From 7 to 10M chloride,

this absorption rises very rapidly and attains a maximum value at 12.1M chloride. Beyond the maximum the absorption decreases by about 8% to 13M chloride. At 6M chloride, 60% of the cobalt is present as CoCl_3^- , whereas the tetrahedral absorption is only 1% of its maximum value. Thus if CoCl_3^- absorbs in the tetrahedral region, its absorption must be very weak.

The absorption in the tetrahedral region consists of three peaks with maxima at the wavelengths 624, 662 and 690 nm. In Figure 4.4, the ratios of the extinction coefficients of these three peaks are plotted against chloride concentration. The ratios vary up to about 7M chloride. Thereafter they remain reasonably constant up to the maximum chloride concentration examined. The most probable reason for the constancy of these ratios is that the absorption at all three wavelengths is due to one species only. Below 7M chloride, where the ratios vary, the absorption is due to at least two species. Examination of the overall extinction coefficients in the tetrahedral region, given in Table 4.1, shows that, at 7M chloride, the extinction coefficients are about 10% of their maximum values, attained at 12.1M chloride. Thus the variation in the ratios of these extinction coefficients, shown in Figure 4.4, takes place when the overall absorption is relatively low. This effect could be due to weak absorption in this region due to CoCl_3^- , which is of comparable magnitude to that due to the second species, when the concentration of the latter species is low. Because the absorption shown by the second species is very strong, as its concentration becomes appreciable, the weak absorption due to CoCl_3^- will become a negligible proportion of the overall absorption. Thus the overall extinction coefficients will become effectively equal to those of the second species, and the ratios of the extinction coefficients will become constant.

The identity of this second species is uncertain, although it is most probably CoCl_4^{2-} . The general shape of the absorption spectrum at high chloride concentrations and the peak wavelengths are similar to those reported for the CoCl_4^{2-} ion in various organic compounds. Literature values of the peak wavelengths are compared with those obtained in this study in Table 7.1. The maximum extinction coefficients observed at 12M LiCl are approximately 10% lower than those observed for CoCl_4^{2-} in $(\text{Ph}_3\text{MeAs})_2\text{CoCl}_4$ ³⁵, TBP³⁶ and TOA (this study). However, the ratios of the extinction coefficients for each of the

above cases agree to within 5%, indicating that the absorption could be due to the same species in each case. The fact that the maximum extinction coefficients are lower in the aqueous system suggests that not all the metal is converted to CoCl_4^{2-} in concentrated LiCl solutions.

Although the behaviour of the tetrahedral absorption can be qualitatively explained by the above argument, the behaviour of the octahedral absorption above 6M chloride presents some difficulties. Examination of Figure 4.2 shows that the extinction coefficients in this region rise to a maximum at a chloride concentration of approximately 8.5M. Thereafter they decrease, but even at 11M chloride, they are still about 90% of their maximum values in the wavelength region, 525 to 535 nm. However at 11M chloride, the tetrahedral absorption has also risen to over 90% of its maximum, indicating that much of the cobalt is present as the species assumed to be CoCl_4^{2-} . Thus this species must make a large contribution to the octahedral absorption.

The maximum values of the overall extinction coefficients in the octahedral region are approximately 20% larger than the calculated extinction coefficients of CoCl_3^- (c.f. Tables 4.1 and 4.3). Therefore there must be another species absorbing in the octahedral region, in order to account for the rise in the extinction coefficients to the maximum at 8.5M chloride. Although the species assumed to be CoCl_4^{2-} absorbs in this region, it cannot be responsible for the observed maximum, since, at 8.5M chloride, its absorption in the tetrahedral region, and thus its concentration, is still rising rapidly. In order to account for the observed behaviour of the octahedral spectrum, it is necessary to postulate the existence of a species intermediate between CoCl_3^- and CoCl_4^{2-} . This species absorbs in the octahedral region but probably does not absorb, or has only very weak absorption, in the tetrahedral region, since, above 7M chloride, the tetrahedral absorption is apparently due to one species only - CoCl_4^{2-} .

Two possible assignments for this intermediate complex are suggested below. However, it is emphasised that both these suggestions are entirely speculative, since the situation is too complicated, and there are too many unknown factors, to allow a sensible numerical analysis to be made of the data obtained above 6M chloride.

The first possibility is that the unknown intermediate complex

could be a polymeric metal species such as $\text{Co}_2\text{Cl}_6^{2-}$. Although this complex has not been postulated before, similar halide-bridged copper complexes such as $\text{Cu}_2\text{Cl}_6^{2-}$ and $\text{Cu}_2\text{Br}_6^{2-}$ have been reported^{59,92}. However this suggestion suffers from one main disadvantage. This is that solutions containing polymeric metal species are not expected to obey Beer's Law, since the proportion of polymeric species will alter as the concentration of metal in solution is changed. In this investigation, Beer's Law was obeyed at all chloride concentrations. Nevertheless, if the extinction coefficients of the polymeric species are similar to those of the monomeric species, then the effect of changes in the proportion of the polymeric species on the overall extinction coefficients could be negligible. In these circumstances, the solutions would appear to obey Beer's Law.

An alternative possibility, which avoids this difficulty, relies on the fact that no assumptions were made about the co-ordination of the various ions in the numerical analyses which established the existence of CoCl_3^- . It is thus possible that this ion could have two co-ordination states, i.e. octahedral $\text{CoCl}_3(\text{H}_2\text{O})_3^-$ and tetrahedral $\text{CoCl}_3\cdot\text{H}_2\text{O}^-$. The latter form would be favoured by increases in the concentration of LiCl due to the resulting lowering of the water activities of the solutions. In this situation, the CoCl_3^- species existing below 6M chloride would be the octahedral form and the unknown intermediate species, accounting for the maximum in the octahedral extinction coefficients, would be the tetrahedral form.

As pointed out above, it is not possible to justify either of these suggestions by a quantitative numerical analysis. The qualitative argument shows that there are apparently at least two species higher than CoCl_3^- occurring in solutions containing more than 6M chloride. The highest complex is probably CoCl_4^{2-} , but the evidence is not conclusive.

4.H. General Discussion

It was pointed out in Section 2.A. that the chlorocomplexes of cobalt are the subject of much controversy. Rather than helping to resolve the situation, the present study creates further complications.

The K_1 value obtained in this work agrees reasonably well with the values obtained in previous investigations. A compilation of the numerical values of the stability constants for the cobalt - chloride system reported in the literature has been given in Table 2.1.

The majority of the K_1 values given in this table, which were obtained in a variety of media, lie in the range, $\log K_1 = -(0.5 \pm 0.4)$. The value of $\log K_1^* = -0.48$, obtained in this work, lies well within this range.

It could be argued that this agreement is evidence of the validity of the basic assumption of this investigation, i.e. that the extinction coefficients of the individual complexes are independent of ionic strength. However it should be emphasised that K_1^* was calculated from data obtained in the LiCl concentration range 1 to 3M, which is quite restricted compared with the total range examined. Furthermore, evidence to the contrary is furnished by the behaviour of the extinction coefficients in the tetrahedral wavelength region. After reaching a maximum at 12.1M LiCl, these decrease by about 8% as the lithium chloride concentration is increased to 13M. Since the major absorption in this region has been attributed to CoCl_4^{2-} , the decrease in extinction coefficients can be explained either by postulating the appearance of a higher complex, such as CoCl_5^{3-} , which seems unlikely, or alternatively by assuming a decrease in the extinction coefficients of CoCl_4^{2-} . However a similar effect was noted by Bjerrum⁵⁷ for the absorption of copper in concentrated calcium chloride solutions. He explained the apparent decrease in the extinction coefficients at given wavelengths in very concentrated solutions by assuming that the whole absorption spectrum was shifted, due to the formation of ion-pairs between tetrachlorocupric ions and calcium ions. A similar argument could be put forward for the present system.

Nevertheless the constancy, or otherwise, of extinction coefficients remains unresolved. Because of this difficulty, the numerical results obtained in this work, and in others of a similar type, must

be treated with caution.

The fact that the data obtained up to 6M LiCl can be adequately described by postulating the existence of the three species Co^{2+} , CoCl^+ and CoCl_3^- , raises the problem of the apparent absence, or the presence in undetectable quantities, of CoCl_2 in these solutions. The reason for this remains obscure. Both the octahedral and tetrahedral forms of CoCl_2 have been detected by the method of continuous variations in non-aqueous solvents³, and the work of Zeltman¹⁷ on the cobalt - hydrochloric acid system, in which $\text{CoCl}_2(\text{H}_2\text{O})_2$ was postulated, has already been discussed.

However in spite of these, and other, theoretical difficulties, it will be shown that the stability region of CoCl_3^- , calculated from the results of this spectrophotometric investigation, correlates well with the behaviour of cobalt in the solvent extraction experiments. Thus although the equilibrium constants obtained here are merely the result of an exercise in curve-fitting, the fact that the results of this exercise correlate well with a completely independent technique, lends confidence to the view that these equilibrium constants have both physical significance and numerical validity.

4.J. Conclusions

1. Analysis of extinction coefficient data obtained from solutions containing cobaltous ions and lithium chloride indicates that three cobalt species, i.e. Co^{2+} , CoCl^+ and CoCl_3^- exist in the lithium chloride concentration range 0 to 6 molar.
2. The apparent equilibrium constants of these complexes, which relate their concentrations to the effective chloride activity of the solutions, are:

$$K_1^* = 0.33 \text{ mole}^{-1} \text{ and } \beta_3^* = 0.97 \times 10^{-3} \text{ mole}^{-3}.$$

3. The extinction coefficients of the two complex species have been calculated for the wavelength region 500 to 535 nm. and these are presented in Figure 4.6.
4. No evidence was found to support the existence of CoCl_2 in these solutions.
5. Solutions containing more than 6M LiCl show strong absorption in the wavelength region 600 to 700 nm. It is thought that the major source of this strong absorption is the CoCl_4^{2-} ion, although the evidence is not conclusive.
6. In order to account for the behaviour of the extinction coefficients in the wavelength region 500 to 535 nm. at chloride concentrations above 6M, it is necessary to postulate the existence of a complex intermediate between CoCl_3^- and CoCl_4^{2-} . Speculative suggestions concerning the nature of this intermediate complex have been made.

CHAPTER 5

HYDRATION IN THE ORGANIC PHASE

5.A. Introduction

In order to determine the extent of transfer of water into the organic phase during extraction with amine solutions, various types of organic phases were prepared and their water contents were determined by Karl Fischer titrations. The compositions of the organic phases investigated were typical of those encountered during extraction experiments. They may be classified into the following five series.

- Series 1 : Solutions of TOA in benzene saturated with water.
- Series 2 : Solutions of TOAHCl in benzene formed by shaking amine solutions with dilute HCl.
- Series 3 : Solutions of TOAHCl in benzene formed by shaking amine solutions with aqueous solutions containing dilute HCl plus various amounts of LiCl.
- Series 4 & 5: Solutions of TOAHCl in benzene fully loaded with cobalt, prepared by equilibration with aqueous phases of various compositions.

Full details of these solutions are given in Section 5.B(i). Water determinations were carried out in triplicate using 5 ml. aliquots of each solution. The results are reported in Section 5.C. and discussed in Section 5.D.

5.B. Experimental

5.B(i) Preparation of solutions

Five series of organic solutions were prepared for water analysis. The solutions were made up by shaking together, for 30 minutes at ambient temperature, 20 ml. of the required concentration of TOA in benzene with an equal volume of the appropriate aqueous phase.

Series 1 : Solutions B - E

Solutions of TOA in benzene ranging between 0.0099 and 0.1480M equilibrated with water.

Series 2 : Solutions F - I

Solutions of TOAHCl in benzene ranging between 0.0099 and 0.1480M formed by equilibrating TOA solutions with 0.23M HCl.

Series 3 : Solutions J - N

Solutions containing 0.0985M TOAHCl formed by equilibrating 0.0985M TOA solutions with aqueous phases containing 0.23M HCl plus various concentrations of LiCl ranging between 3.0-7.0M.

Series 4 : Solutions O - Q

Solutions of TOAHCl in benzene ranging between 0.0490 and 0.1480M, all fully loaded with cobalt, formed by equilibrating TOA solutions with aqueous solutions containing 0.23M HCl, 0.30M CoCl_2 and 6.0M LiCl.

Series 5 : Solutions P,R,S

Solutions containing 0.0985M TOAHCl fully loaded with cobalt, formed by equilibrating 0.0985M TOA with aqueous solutions containing 0.23M HCl, 0.30M CoCl_2 and 5.0-7.0M HCl.

Table 5.1. contains details of each organic solution and the corresponding aqueous phase with which it was equilibrated.

5.B(ii) Experimental procedure

Water determinations were carried out on three 5 ml. samples of each solution, using a B.T.L. Karl Fischer apparatus. The Karl Fischer (K.F.) reagent and water-methanol solution were both supplied by Hopkin and Williams. The nominal water equivalent of the K.F. reagent was given as 5.0 mg. H_2O /ml. The actual water equivalent was found to be 5.7 ± 0.1 mg. H_2O /ml., by standardisation of the reagent against weighed samples of water.

A back titration technique, detailed below, was used, in which a small excess of K.F. reagent was added to the sample and then the excess reagent was titrated with the water-methanol solution.

Titration technique: The titration beaker, the electrode and the magnetic follower were washed with acetone and dried in an air blast. Approximately 10 ml. of water-methanol solution were introduced from the burette. K.F. reagent was then titrated into the beaker in small portions - approximately 0.5 ml. per time. As each portion of reagent was introduced, the indicator needle swung over to "excess Fischer" and then rapidly swung back to "excess water". As the end point was approached the swing back to "excess

Table 5.1. Compositions of the organic and corresponding
aqueous phases used to prepare the experimental
solutions

Solution	Organic Phase	Aqueous Phase		
	[TOA] M	[HCl] M	[LiCl] M	[CoCl ₂] M
A	Benzene only		Water only	
B	0.0099		Water only	
C	0.0490		Water only	
D	0.0985		Water only	
E	0.1480		Water only	
F	0.0099	0.23	-	-
G	0.0490	0.23	-	-
H	0.0985	0.23	-	-
I	0.1480	0.23	-	-
J	0.0985	0.23	3.0	-
K	0.0985	0.23	4.0	-
L	0.0985	0.23	5.0	-
M	0.0985	0.23	6.0	-
N	0.0985	0.23	7.0	-
O	0.0490	0.23	6.0	0.30
P*	0.0985	0.23	6.0	0.30
Q*	0.1480	0.23	6.0	0.30
R*	0.0985	0.23	5.0	0.30
S*	0.0985	0.23	7.0	0.30

* 40 ml. of aqueous phase equilibrated with 20 ml. of organic phase to ensure full loading.

water" became slower. When the needle stayed on "excess Fischer" for 10-12 seconds, one further small addition of reagent was made (0.1 ml.) and then immediately water-methanol solution was added, dropwise, until the needle swung back to the centre of the indicator scale. Readings were then taken from both burettes. A 5 ml. sample of the unknown organic solution was then introduced into this balanced solution in the beaker and the titration repeated - i.e. K.F. reagent was added until a small excess was present and then water-methanol was added to bring the solution to balance. Burette readings were again recorded. A second sample was then introduced and titrated, followed by a third sample.

The titration beaker was then emptied, washed and dried, ready for the next set of determinations.

The reproducibility of the end points was found to be rather poor. This was mainly due to the inherent instability of Karl Fischer reagent which decomposes quite rapidly in the absence of water and thus causes the meter needle to show "excess water".

5.C. Results

5.C(i) Standardisation of Karl Fischer Reagent

Standardisation of K.F. reagent with weighed amounts of water gave the following results:

1 ml. K.F. reagent = 5.7, 5.8, 5.6, 5.6, 5.8 mg. H₂O.

Average value = 5.7 ± 0.1 mg. H₂O/ml. K.F. reagent

5.C(ii) Water contents of organic phases

The results of the water determinations are reported in Table 5.2. The second column of this table gives the solute concentrations of the organic phases - further details may be found in Table 5.1. The third column contains the results of the three separate determinations carried out on each solution. The fourth column contains the average value of the water concentration and this is expressed as a molarity in the fifth column.

5.D. Discussion

As stated in Section 5.B., the reproducibility of the results was rather poor. This can be seen on examination of the third column of Table 5.2. which contains the measured values of the water contents of the three samples taken from each solution. However, the averaged values, given in the fourth column have a reasonable internal consistency and they are also in general in fairly good agreement with published data. The major discrepancy with published work is for the solubility of water in benzene - Solution A. The value obtained in this work was 0.019M which does not compare well with the literature value of 0.035M⁶¹.

The presence of TOA in benzene does not appreciably increase the

Table 5.2 Water contents of Solutions A - S

Solution	Composition	Water content (mg/5 ml)	Average water content (mg/5 ml)	(M)
A	Benzene only	1.4, 2.0, 1.6	1.7	0.019
B	0.0099M TOA	1.7, 1.8, 2.7	2.1	0.023
C	0.0490M TOA	2.3, 3.2, 1.8	2.4	0.027
D	0.0985M TOA	1.6, 2.6, 2.2	2.1	0.023
E	0.1480M TOA	2.2, 2.4	2.3	0.026
F	0.0099M TOAHCl	2.8, 2.7, 2.3	2.6	0.029
G	0.0490M TOAHCl	6.0, 4.7, 6.4	5.7	0.063
H	0.0985M TOAHCl	9.2, 11.7, 8.9	9.9	0.110
I	0.1480M TOAHCl	16.5, 14.2, 16.5	15.7	0.174
J	0.0985M TOAHCl	8.9, 9.0, 8.4	8.8	0.098
K	0.0985M TOAHCl	8.2, 7.3, 9.3	8.3	0.092
L	0.0985M TOAHCl	7.7, 5.1, 8.0	6.9	0.077
M	0.0985M TOAHCl	7.3, 4.8, 6.8	6.3	0.070
N	0.0985M TOAHCl	5.2, 5.3, 5.6	5.4	0.060
O	0.0490M TOAHCl*	1.4, 1.1	1.3	0.014
P	0.0985M TOAHCl*	1.1, 2.4, 1.0	1.5	0.017
Q	0.1480M TOAHCl*	3.2, 1.8, 1.4	2.1	0.023
R	0.0985M TOAHCl*	2.6, 1.9, 2.2	2.2	0.024
S	0.0985M TOAHCl*	1.7, 0.6, 0.7	1.0	0.011

* Solutions fully loaded with cobalt.

water content of the organic phase. Solutions B to E are water saturated solutions containing concentrations of amine ranging from 0.0099M to 0.1480M. In all cases, the water contents are slightly higher - up to 0.008M - than that of pure benzene. However considering the accuracy of the results, and the fact that there is no correlation between the water contents and the amine concentrations of the solutions, these slight discrepancies are considered to be negligible. It is concluded that TOA in benzene is essentially unhydrated.

On the other hand, the hydrochloride salt of the amine shows definite evidence of hydration. Solutions F to I contain various concentrations of

TOAHCl ranging from 0.0099M to 0.1480M, formed by shaking amine solutions of the appropriate concentrations with 0.23M HCl. It is evident that as the amine salt concentration increases, so does the water content of the organic phase. Within experimental error, the ratio $[\overline{\text{H}_2\text{O}}]:[\overline{\text{TOAHCl}}]$ is 1 : 1. This is demonstrated in Figure 5.1. in which the average molar concentration of water in the organic phase is plotted against the molar concentration of TOAHCl. The results are adequately fitted by a straight line with a slope of unity and an intercept equal to the measured value of the solubility of water in pure benzene (Solution A). Thus it is concluded that TOAHCl in benzene, when formed by equilibration of the amine solution with dilute HCl, is associated with an equal molar concentration of water. This water is presumably held in the organic phase due to the formation of the monohydrate of the amine salt. This result is in agreement with the work of Bertocci and Rolandi⁶² on TOAHCl dissolved in xylene. They also found that each mole of amine hydrochloride was associated with one mole of water. Similar results were reported by Müller and Diamond²⁶ for solutions of trilaurylamine hydrochloride in benzene.

Although amine hydrochlorides may be monohydrated when in equilibrium with dilute aqueous solutions where the water activity is close to unity, some recent work by Frolov and co-workers³² has shown that the degree of hydration varies with the water activity of the equilibrium aqueous phase. They were able to express the solubility of water in solutions of various amine salts in a variety of diluents by the expression:

$$C_w = a_{\text{H}_2\text{O}}(C_{w0} + h.C_s) \quad (5D1)$$

where: C_w = Total molar concentration of water in the organic phase.

C_{w0} = Water solubility in the pure solvent at $a_{\text{H}_2\text{O}} = 1$.

C_s = Molar concentration of amine salt.

$a_{\text{H}_2\text{O}}$ = Activity of water in the equilibrium aqueous phase.

$h = \frac{C_w - C_{w0}}{C_s}$ = Degree of hydration of the salt at $a_{\text{H}_2\text{O}} = 1$.

The results obtained in this work for Solutions H and J to N demonstrate the effect of water activity. In these solutions, the amine hydrochloride concentration was kept constant, but the aqueous phases from which the amine salt solutions were formed contained varying amounts of LiCl ranging from 0 to 7.0M. Thus the water activities of the aqueous

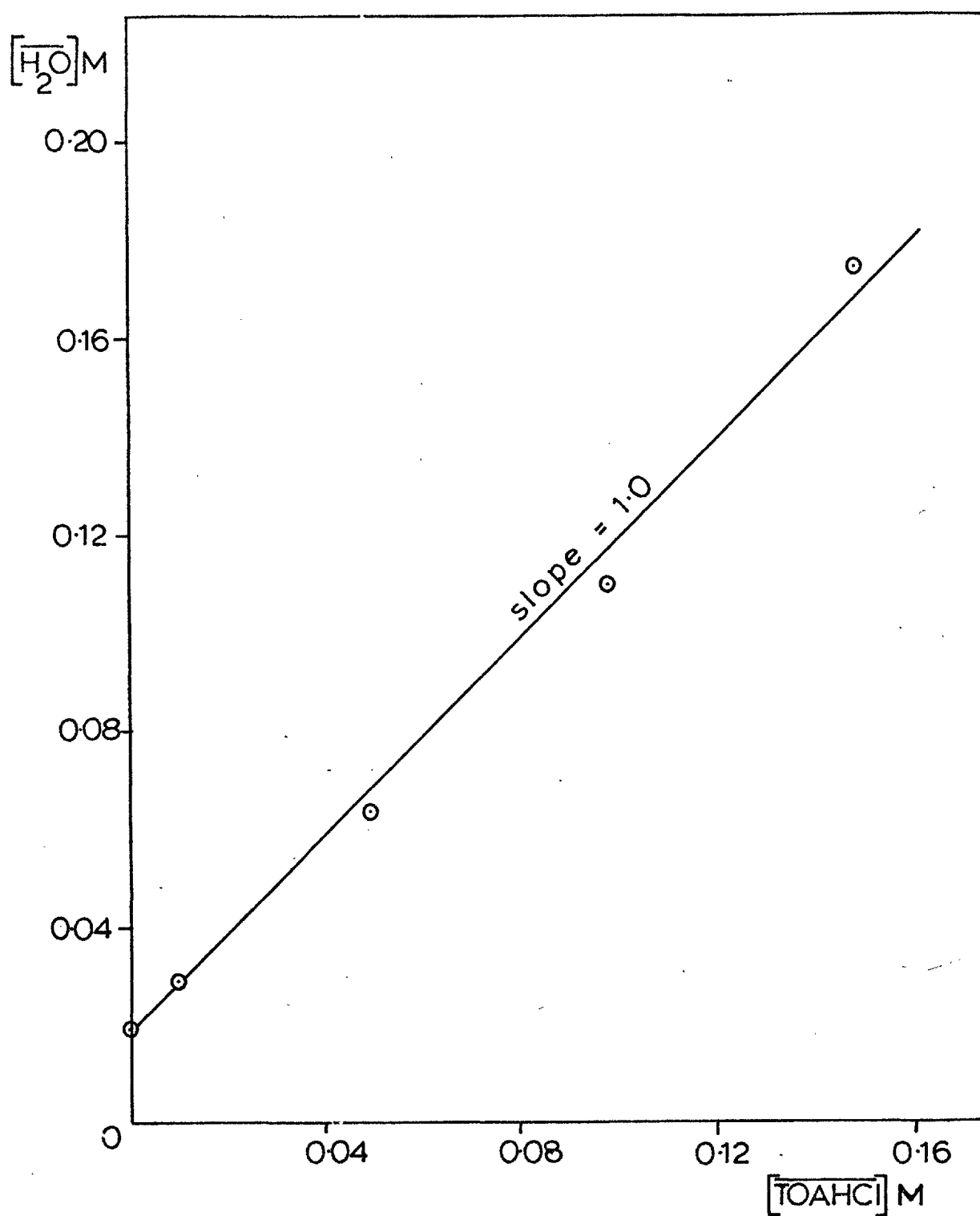


FIGURE 5.1 VARIATION OF ORGANIC PHASE WATER CONCENTRATION WITH TOAHCl CONCENTRATION.

Data from Table 5.2.

phases decrease from Solution J to Solution N. Examination of Table 5.2. shows that the water contents of the organic phases also decrease in this order. The decrease in total organic water content is directly proportional to the water activity of the equilibrium aqueous phase, as illustrated in Figure 5.2. This is a graph of total organic water content versus aqueous phase water activity. The water activities were calculated from published data for LiCl, assuming that the effect of the small concentration of HCl (0.23M) present in these solutions could be neglected. The results obtained by Frolov³² for TOAHCl in benzene are also plotted in Figure 5.2. These results were calculated from Equation (5D1) by introducing values of the parameters in this equation quoted by Frolov for this system, i.e. $h = 0.70$ and $C_{wo} = 0.035$. It may be seen that there is quite good agreement between the two sets of data.

So far in this discussion only the total water contents of the organic phases have been considered. In order to be able to calculate the amount of water associated with the amine hydrochloride, it is necessary to know how the solubility of water in benzene varies with aqueous phase water activity. Frolov states that there is a linear dependence of water solubility with water activity in many organic solvents. If this assumption is held to be true in this case, then the excess water in the organic phase, associated with the amine hydrochloride, can be calculated using the following expression:

$$C_H = C_w - a_{H_2O} \cdot C_{wo} \quad (5D2)$$

where: C_H = Molar concentration of water associated with TOAHCl.

The composition of the organic phase may be represented as $\text{TOAHCl} \cdot x\text{H}_2\text{O}$, where x is the degree of hydration, and is given by:

$$x = C_H / C_s \quad (5D3)$$

Since the water activity varies with the chloride concentration of the equilibrium aqueous phase, x may be related empirically to the chloride concentration. Values of x calculated from the experimental results for Solutions J-N are given in Table 5.3. x is plotted against aqueous chloride concentration in Figure 5.3. A straight line passing through $x = 1$ at zero chloride adequately describes these results, indicating that the degree of hydration of the amine hydrochloride decreases linearly as the molar chloride concentration of the aqueous phase increases. This information is utilised in Chapter 7,

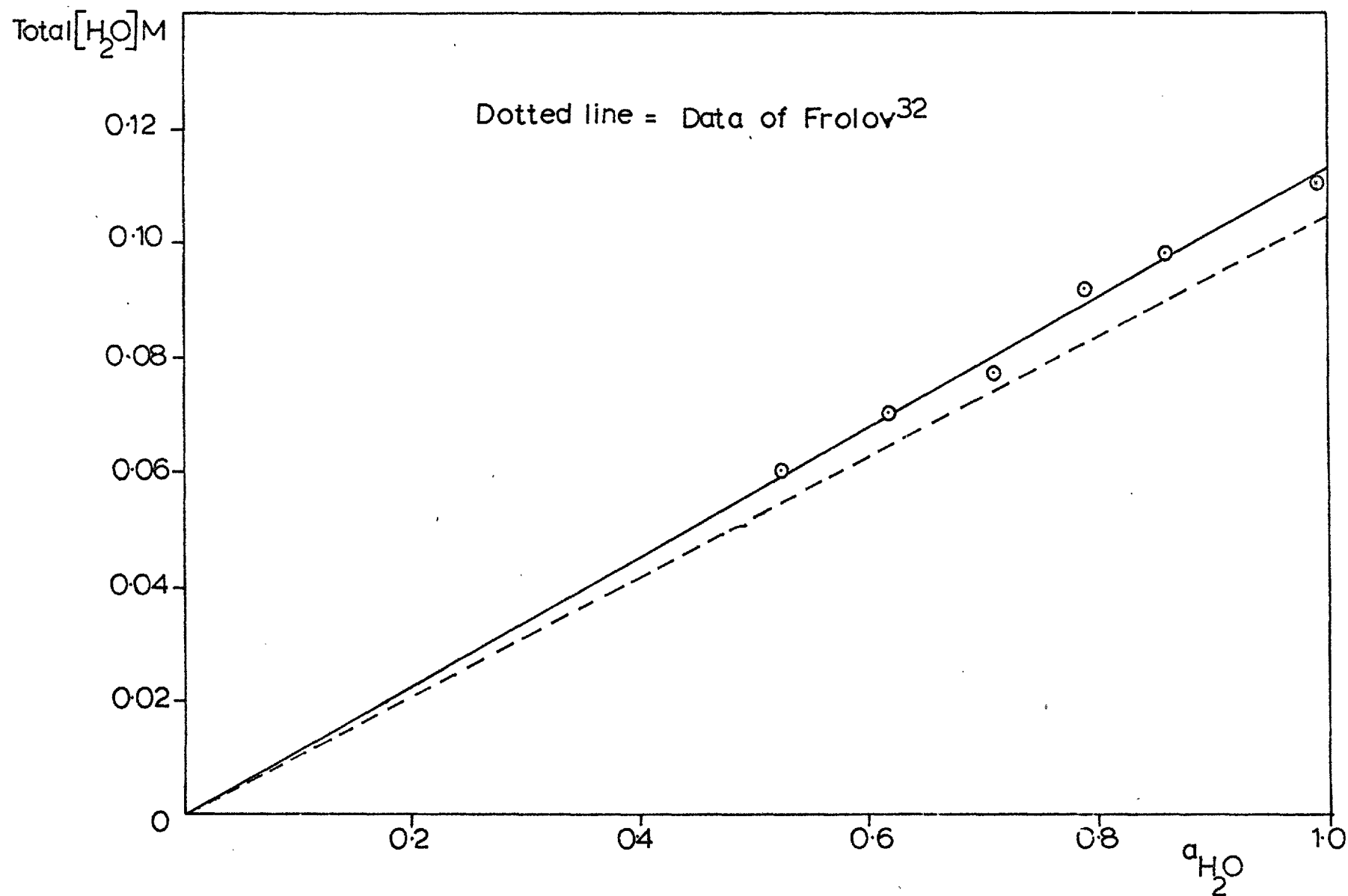


FIGURE 5.2 THE VARIATION OF TOTAL ORGANIC PHASE WATER CONCENTRATION WITH THE WATER ACTIVITY OF THE EQUILIBRIUM AQUEOUS PHASE.

$$[TOAHCl] = 9.85 \times 10^{-2} M$$

Data from Table 5.2

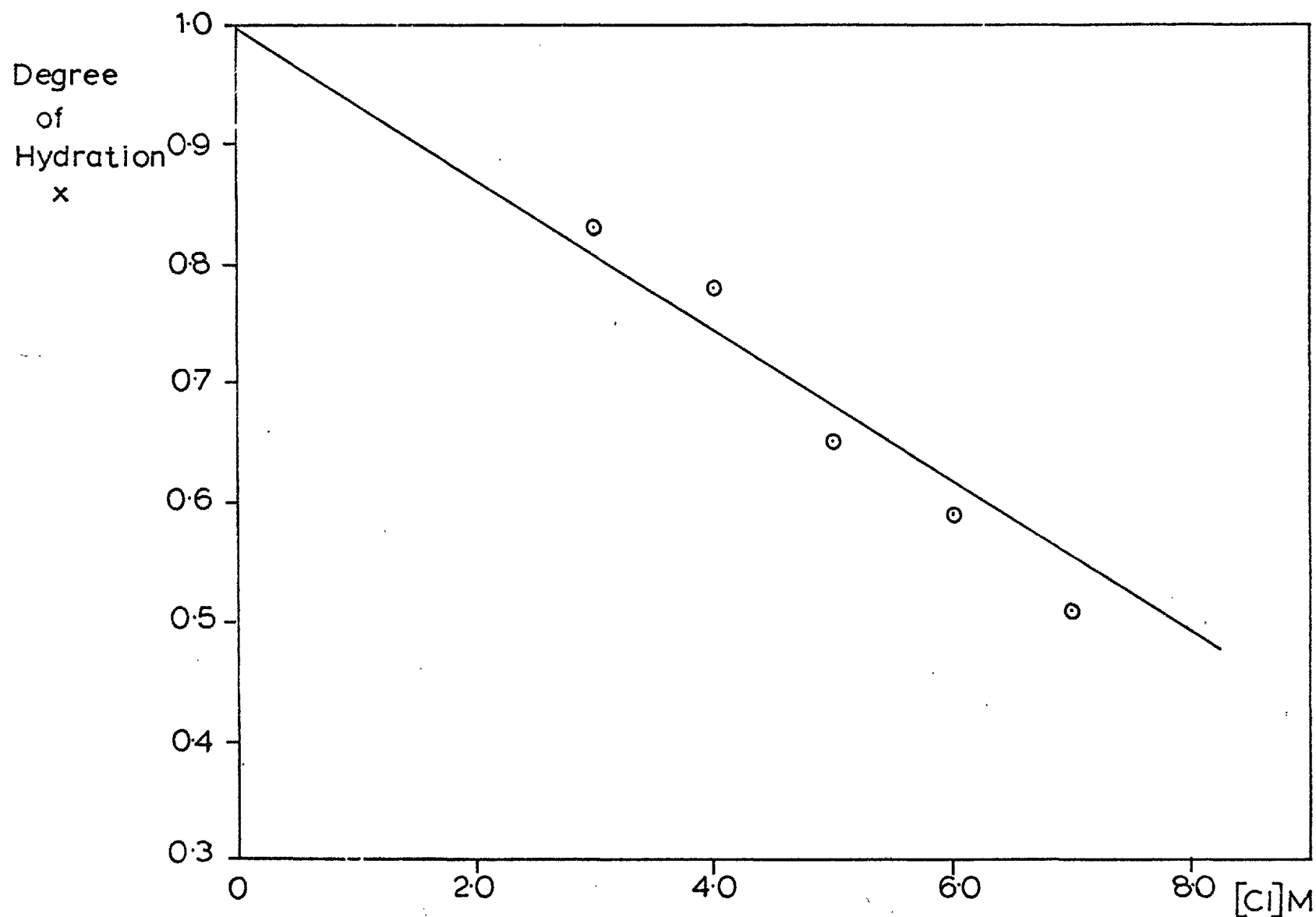


FIGURE 5.3 CHANGE IN THE DEGREE OF HYDRATION OF THE ORGANIC PHASE WITH AQUEOUS CHLORIDE CONCENTRATION.

$[TOAHCl] = 9.85 \times 10^{-2} M$

Data from Table 5.3

Table 5.3. The change in amine hydrochloride hydration with aqueous chloride concentration.

$$C_{wo} = 0.019M \quad C_s = [TOAHCl] = 0.0985M$$

Solution	$[Cl]_{aq}$ (M)	C_w (M)	$a_{H_2O} C_{wo}$ (M)	C_H (M)	x
J	3.0	0.098	0.016	0.082	0.83
K	4.0	0.092	0.015	0.077	0.78
L	5.0	0.077	0.013	0.064	0.65
M	6.0	0.070	0.012	0.058	0.59
N	7.0	0.060	0.010	0.050	0.51

The results for the amine hydrochloride solutions loaded with cobalt - Solutions O to S - can be analysed in a similar manner. The associated water is calculated by subtracting the solubility of water in benzene, corrected for aqueous phase water activity, from the measured total organic water concentration. The results of these calculations are given in Table 5.4. The calculated values of the concentration of water associated with the cobalt species in the organic phase are given in the right hand column of this table. In general, these values are very low and they are comparable with the concentrations of excess water found in benzene solutions containing trioctylamine only. Thus within experimental error, it is concluded that the extracted cobalt species in the organic phase is essentially unhydrated.

5.E. Conclusions.

This study of hydration in the organic phase when solutions of trioctylamine in benzene are contacted with various types of aqueous phase has resulted in the following conclusions:

- i) Trioctylamine in benzene, and the cobalt species extracted by trioctylamine hydrochloride in benzene are both essentially unhydrated.

Table 5.4. Association of water with the extracted cobalt species.

Solution	$[\overline{\text{TOAHCl}}]$ (M)	Total $[\overline{\text{H}_2\text{O}}]_{\text{M}}$	$a_{\text{H}_2\text{O}}^{\text{C wo}}$	Associated $[\overline{\text{H}_2\text{O}}]_{\text{M}}$
O	0.0490*	0.014	0.012	0.002
P	0.0985*	0.017	0.012	0.005
Q	0.1480*	0.023	0.012	0.011
R	0.0985*	0.024	0.013	0.011
S	0.0985*	0.011	0.010	0.001

*Organic phase fully loaded with cobalt

ii) Solutions of trioctylamine hydrochloride in benzene contain water when formed by equilibration with aqueous solutions. When the aqueous phase water activity is close to unity, the molar ratio of $\overline{\text{H}_2\text{O}} : \overline{\text{TOAHCl}}$ is 1:1. The organic water concentration decreases linearly with the equilibrium aqueous phase water activity.

CHAPTER 6

VAPOUR PRESSURE OSMOMETRY

6.A. Introduction

Previous work on amine extraction has repeatedly shown the important effects which the behaviour of amine salts and metal complexes in the organic phase has on the observed extraction properties. Solutions of long-chain amine salts, which are polar ion-pairs, in non-polar solvents such as benzene, readily form aggregates due to dipole-dipole interactions. An understanding of this type of non-ideal behaviour in the organic phase is necessary in order to make a proper interpretation of the solvent extraction data. With this objective, work was carried out to determine the apparent molecular weights of solutes dissolved in benzene, by vapour pressure osmometry. The change in apparent molecular weight with concentration was determined for the various types of solute encountered in the solvent extraction work described in Chapter 3. Where appropriate the results were analysed to give aggregation constants.

6.B. Materials

6.B(i) Benzil

Benzil (m.p. $94.0 - 94.8^{\circ}\text{C}$) was prepared from benzoin by a standard method⁶³. 1.976 gm. of benzil were dissolved in 20.418 gm. of A.R. benzene to form a stock solution with a concentration of 96.769 gm. benzil/kg. benzene.

6.B(ii) Trioctylamine

A "dry" stock solution of trioctylamine was prepared by dissolving 1.418 gm. TOA in 20.481 gm. A.R. benzene to give a solution of concentration 69.211 gm. TOA/kg. benzene. A "wet" stock solution of trioctyl-

amine was prepared by dissolving 1.244 gm. TOA in 20.428 gm. A.R. benzene and then shaking this solution with 25 ml. water. The concentration of the "wet" stock solution was 60.891 gm. TOA/kg. benzene.

6.B(iii) Trioctylamine Hydrochloride - "Pure"

Solid trioctylamine hydrochloride was prepared from trioctylamine by shaking a solution of 40 ml. TOA dissolved in 40 ml. benzene with three separate 80 ml. volumes of 1.5M HCl. After separation of the phases, the benzene was evaporated off, leaving an oily brown residue. The residue was dissolved in petroleum ether (b.p. 40 - 60°C) and the solution was cooled to -20°C. A precipitate was formed which was filtered off. The precipitate was then redissolved in fresh petroleum ether and the solution cooled again. The recrystallisation procedure was repeated twelve times. The final product was a waxy white solid with a melting point of 55 - 56°C. Analysis of this solid gave results in good agreement with those calculated for anhydrous trioctylamine hydrochloride: C = 74.13, H = 13.25, N = 3.52%; calculated, C = 73.94, H = 13.35, N = 3.59%.

1.507 gm. of this material was dissolved in 20.356 gm. A.R. benzene to form a stock solution containing 74.008 gm. TOAHCl/kg. benzene.

6.B(iv) Trioctylamine Hydrochloride - "Practical"

In order to be able to compare the behaviour of TOAHCl as used in the distribution experiments with that of the purified salt, a stock solution of "practical" TOAHCl was prepared by shaking an amine solution with HCl. This method of preparation necessitated calculation, rather than direct determination, of the weight concentration of TOAHCl in the solution. This was done by determining the equivalent weight of the trioctylamine by potentiometric titration with standard HCl. Assuming that the monohydrate of TOAHCl was formed during the equilibration with aqueous HCl (see Section 5.D), the weight gain of the organic solution could be calculated. The procedure was as follows:

4.033 gm. TOA were dissolved in 39.329 gm. A.R. benzene to give a solution containing 102.535 gm. TOA/kg. benzene. This solution was shaken with two equal volumes of 1.1M HCl. The equivalent weight of

the TOA was found to be 419.6 gm. Hence x gm. TOA would form $x(474.1/419.6)$ gm. solute by reaction with HCl, assuming the formation of $\text{TOAHCl} \cdot \text{H}_2\text{O}$.

Thus the stock solution of "practical" TOAHCl contained:

$$\left(102.535 \times \frac{474.1}{419.6} \right) = 115.853 \text{ gm./kg. benzene.}$$

6.B(v) Trioctylamine Nitrate

A stock solution of trioctylamine nitrate was prepared by shaking a solution of pure TOAHCl in benzene with 6M HNO_3 . The equilibrium constant for the nitrate-chloride exchange reaction for TOA is such that effectively complete conversion to the nitrate form occurs under these conditions. In view of the unknown state of hydration of the nitrate salt, the concentration of the TOAHNO_3 solution was expressed as a molality rather than a weight-weight concentration, by assuming that the molal concentration of the nitrate salt solution was equal to that of the original chloride salt solution. This avoided having to make assumptions about the total molecular weight of the nitrate salt.

Thus 1.394 gm. of solid TOAHCl were dissolved in 20.560 gm. A.R. benzene giving a solution of concentration 0.1740 molal. This solution (25 ml.) was shaken with 50 ml. 6M HNO_3 to give a stock solution of 0.1740m TOAHNO_3 .

6.B(vi) Cobalt salt of trioctylamine hydrochloride

Several attempts were made to obtain the cobalt salt of TOAHCl as a pure solid. This was done by preparing the salt in benzene solution by shaking a solution of TOAHCl with an aqueous phase containing sufficient cobalt ions and chloride ions to ensure full metal loading of the organic phase. After phase separation the benzene was evaporated off leaving a dark blue oily residue. A recrystallisation procedure similar to that used for the preparation of pure TOAHCl was carried out on the residue. A number of different solvents and solvent mixtures were used but in no case could a solid precipitate be made to form, and the attempt was abandoned.

Samples for molecular weight determinations were instead prepared in solution in the following manner:

2.977 gm. pure TOAHCl were dissolved in 40.608 gm. A.R. benzene. This solution was shaken with three 50 ml. portions of an aqueous solution containing 0.5M CoCl_2 and 6.0M LiCl . The equilibrium cobalt concentration of the organic phase was found by taking a 5 ml. sample of the organic solution and back extracting the cobalt into 25 ml. of water for subsequent analysis by atomic absorption spectrophotometry. The weight of cobalt extracted was found to be 0.195 gm. Assuming extraction of cobalt as CoCl_2 , the total weight gain of the organic phase due to metal loading was 0.430 gm. The concentration of the stock solution of the cobalt salt in benzene was calculated as 83.91 gm./kg. benzene.

The molar ratio of cobalt to TOAHCl at full loading calculated from these results was:

$$[\text{Co}] : [\text{TOAHCl}] = 1 : 2.31$$

This result was in good agreement with the value of 1:2.29 obtained from the extraction isotherm experiments (Section 3.B(v)).

An analysis of the molar ratio of cobalt to chloride was also carried out on this stock solution. A sample of the cobalt salt solution was back-extracted with 6M HNO_3 to ensure total removal of the chloride as well as cobalt from the organic phase. The aqueous back-extraction solution was then analysed for cobalt by atomic absorption and for chloride by Volhard's method. The molar ratio obtained was:

$$[\text{Co}] : [\text{Cl}] = 1 : 3.90$$

In order to check that all the chloride had been removed from the organic phase, it was recontacted with fresh 6M HNO_3 . This second aqueous solution gave a negative result when tested for chloride.

6.C. Procedure and Results

A Hewlett-Packard Vapour Pressure Osmometer (V.P.O.) was used for the molecular weight determinations. The bridge output from the V.P.O. was recorded on a Honeywell Electronik 19 recorder, set to give 1 mV full-scale deflection with up to 10 mV back-off available.

In order to maintain thermal stability within the V.P.O., it is necessary to operate the thermostatic chamber of the instrument at a temperature a few degrees above ambient. For this reason all measurements were carried out at 32.5°C.

The instrument has to be calibrated with a solute of known behaviour to determine the calibration constant K , which depends on the temperature and the solvent. Solutions of benzil in benzene were used for the calibration.

Molecular weight determinations were carried out on solutions derived from all the stock solutions described in the preceding section. Concentration series were prepared from these stock solutions by diluting weighed amounts of the stock solutions with weighed amounts of benzene.

The results obtained are presented graphically as plots of the bridge output from the V.P.O. (V) in millivolts, against solution concentrations (C) in gm. solute per kg. benzene in Figures 6.1 and 6.2. Numerical values of the results are contained in Tables 6.1.X to 6.7.X in Appendix 2. All results reported are the average of at least three, and in some cases many more, determinations on each solution.

6.D. Discussion

6.D(i) Theory

For a solution that obeys Raoult's law, it may be shown⁶⁴ that the bridge output of a V.P.O. is related to solute concentration by:

$$\frac{V}{C} = \frac{K}{M} \quad (6D1)$$

where V = V.P.O. bridge output in volts
 C = Solute concentration in gm./kg. solvent
 M = Molecular weight of solute
 K = Empirical constant dependent on the temperature, solvent, and instrument characteristics.

For non-Raoultian solutions a power series may be used to correlate the data:

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

where A, B , etc. are the second, third, etc., virial coefficients. Generally an expression involving the first and second terms only of the above expression is sufficient:

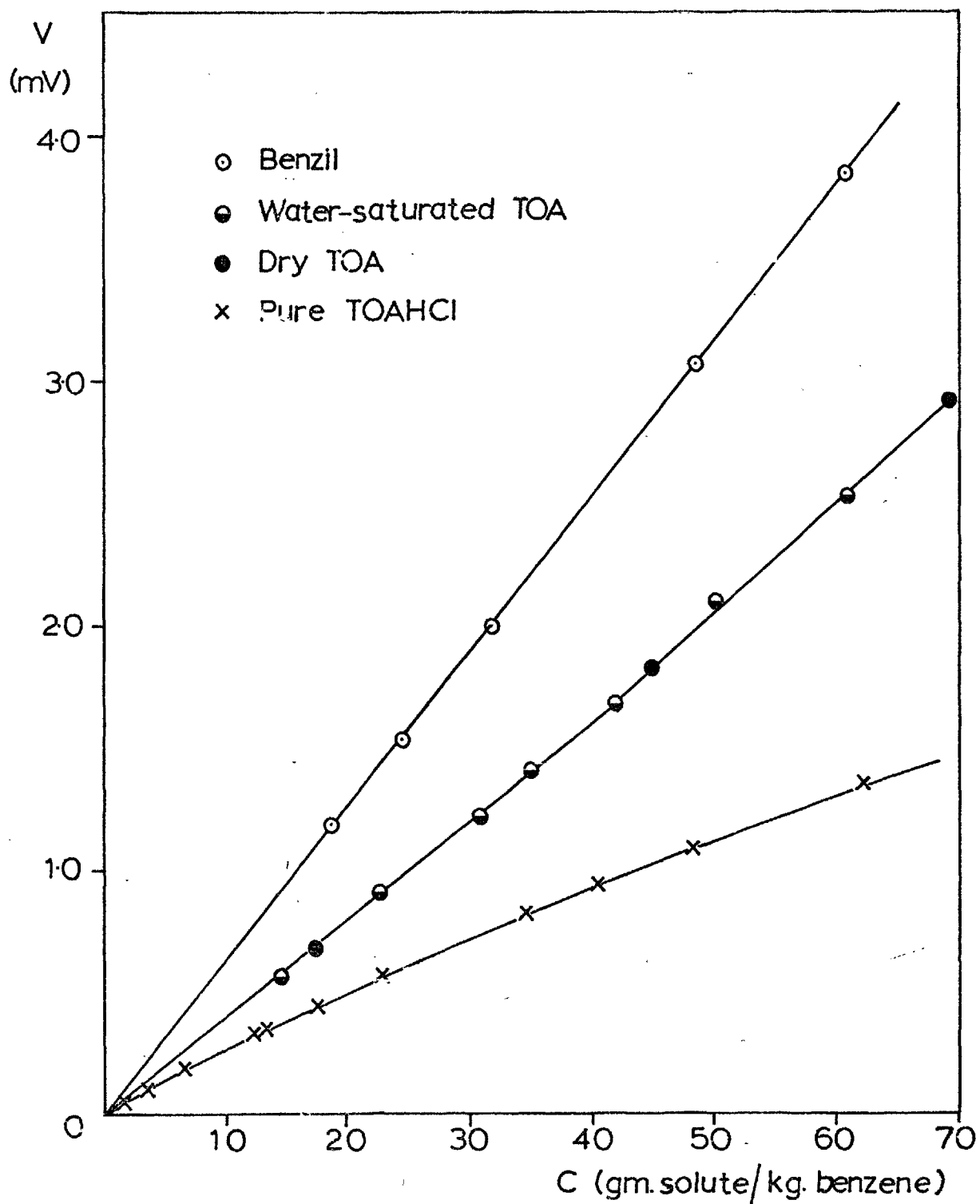


FIGURE 6.1 V.P.O. BRIDGE OUTPUT AGAINST SOLUTE CONCENTRATION.

Data from Tables 6.1.X to 6.3.X.

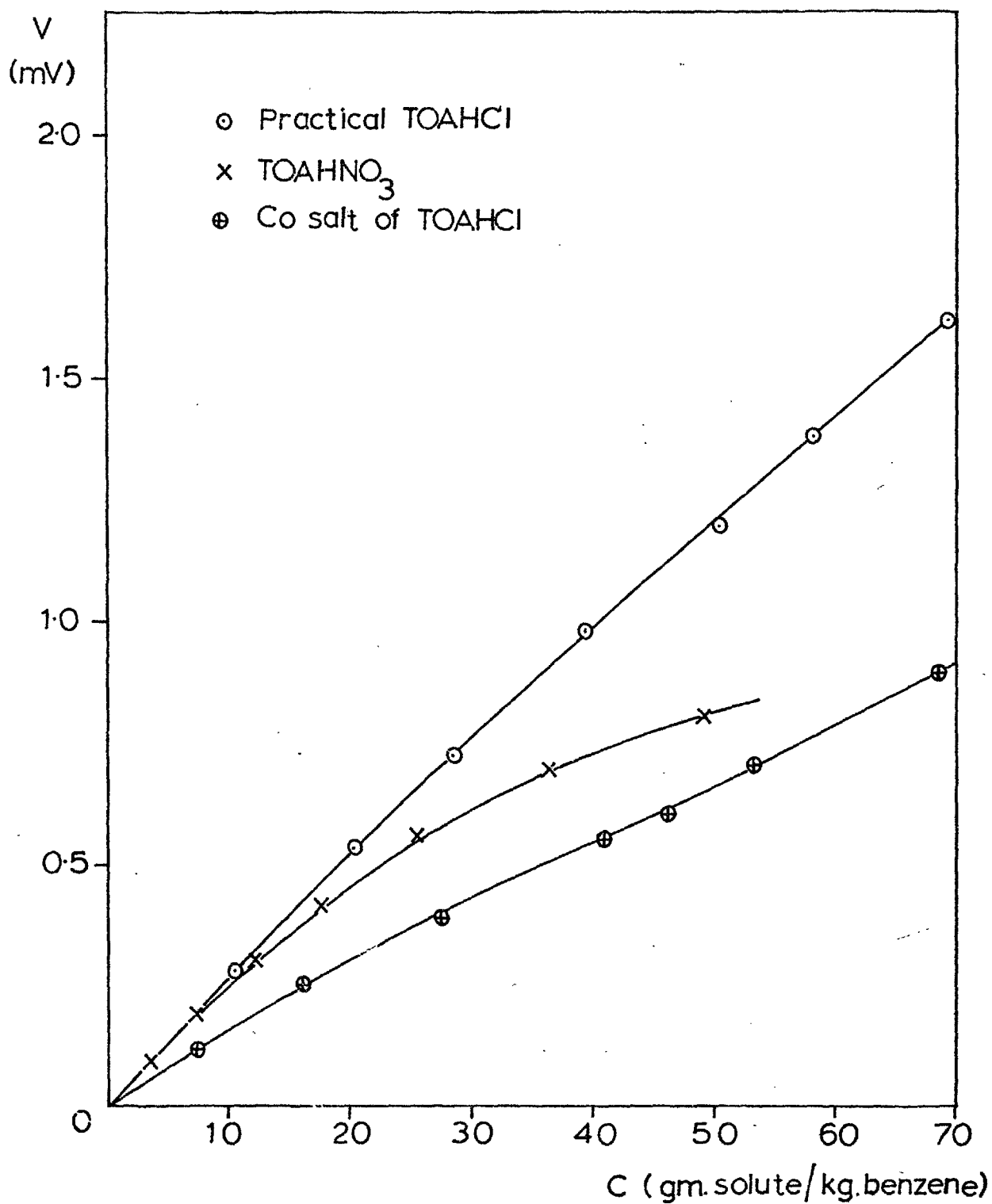


FIGURE 6.2 V.P.O. BRIDGE OUTPUT AGAINST SOLUTE CONCENTRATION.

Data from Tables 6.5.X to 6.7.X.

$$\frac{V}{C} = \left(\frac{V}{C}\right)_{C=0} (1 + AC) \quad (6D2)$$

The intercept at $C=0$ of a plot of V/C against C gives the value of $(V/C)_{C=0}$, and the slope gives the second virial coefficient A . Since all solutions approach Raoultian behaviour at low solute concentrations, the value of $(V/C)_{C=0}$ may be used in Equation (6D1) to give a value of K/M .

K is an empirical constant, and it must be determined by calibrating the instrument. This is done by determining $(V/C)_{C=0}$ for a solute which behaves ideally in the chosen solvent. The calibration is carried out at the same temperature as that to be used for the unknown determinations. The value of K is then given by:

$$K = \left(\frac{V}{C}\right)_{C=0} \cdot M_s \quad (6D3)$$

where M_s is the molecular weight of the "standard" solute.

6.D(ii) Calibration

Benzil was chosen as the solute for calibration in this investigation, since it is expected to behave ideally in benzene solution.

A plot of V/C versus C for benzil in benzene at 32.5°C is given in Figure 6.3. Linear regression analysis of the data gave the following results:

$$\text{Slope} = 0.0000 \text{ mV}/(\text{gm.}/\text{kg.})^2$$

$$\text{Intercept at } C=0 = 0.0635 \text{ mV}/(\text{gm.}/\text{kg.})$$

$$\text{Correlation coefficient} = -0.1902$$

The slope of the best line through the data is equal to zero. Thus the second virial coefficient, A , in Equation (6D2) is equal to zero, indicating that benzil does behave ideally in benzene. The intercept obtained is the value of $(V/C)_{C=0}$ and this may be combined with the molecular weight of benzil (210.2) to give the value of K from Equation (6D3).

$$\underline{K = 13.353 \text{ mV/molal}}$$

6.D(iii) Trioctylamine

A plot of V/C versus C for TOA in benzene is given in Figure 6.3. The results lie on a straight line with a small positive slope. These

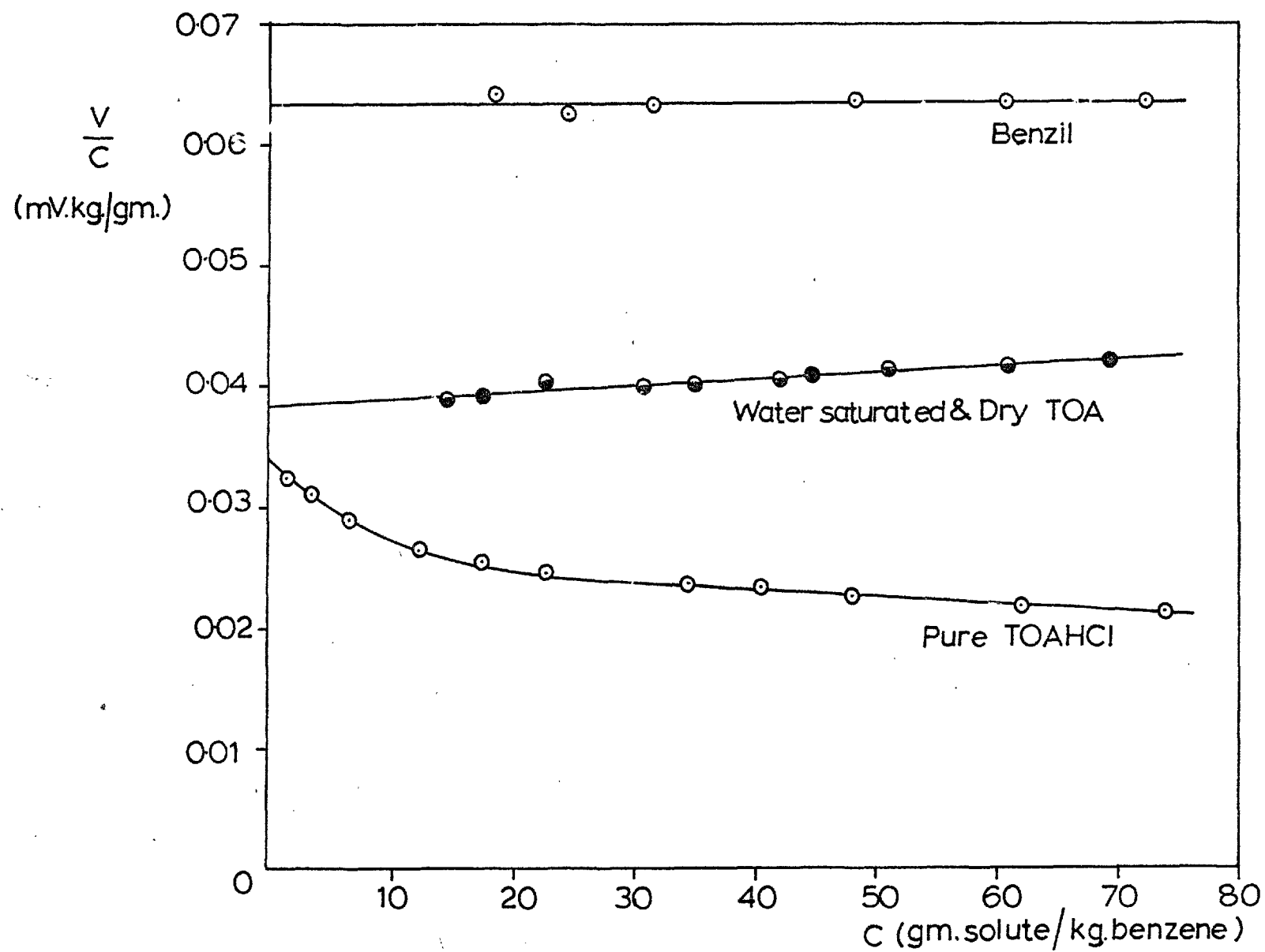


FIGURE 6.3 V/C AGAINST C FOR VARIOUS SOLUTES.

Data from Tables 6.1.X to 6.3.X.

results include both dry and water saturated solutions. Linear regression analysis gave the following results:

$$\text{Slope} = 5 \times 10^{-5} \text{ mV}/(\text{gm.}/\text{kg.})^2$$

$$\text{Intercept at } C=0 = 0.0383 \text{ mV}/(\text{gm.}/\text{kg.})$$

$$\text{Correlation coefficient} = 0.9642$$

The intercept and the value of K determined above were introduced into Equation (6D1) to obtain the molecular weight of TOA;

$$\underline{M.W. \text{ of TOA} = 349}$$

This value is 1.2% less than the theoretical value of 353. The small positive slope of the line in Figure 6.3 indicates a positive deviation from ideal behaviour of TOA in benzene over the concentration range studied.

The molecular weight of the TOA determined by potentiometric titration with standard HCl was found to be 419.6 (Section 6.B(iv)). This discrepancy was assumed to be due to the presence of a non-basic impurity. If this is the case, then the weight fraction of the impurity is given by:

$$\text{Wt. fraction} = \frac{M_p - M_t}{M_p}$$

where M_p = Apparent molecular wt. by potentiometric titration.

M_t = Theoretical molecular wt. of TOA.

Substitution of the values $M_p = 419.6$ and $M_t = 353$ gives a value for the weight fraction of the impurity of 0.159 and thus a weight fraction of 0.841 for the pure amine.

The apparent molecular weight M_v of a mixture of two substances in solution measured by vapour pressure osmometry is given by:

$$M_v = X_1 \cdot M_1 + X_2 \cdot M_2 \quad (6D4)$$

where X_1 = mole fraction of substance 1 of mol. wt. M_1

X_2 = mole fraction of substance 2 of mol. wt. M_2

If the solution contains x gm. of substance 1, and y gm. of substance 2, then:

$$X_1 = \frac{x/M_1}{x/M_1 + y/M_2} = \frac{xM_2}{xM_2 + yM_1}$$

Similarly
$$X_2 = \frac{yM_1}{xM_2 + yM_1}$$

Substituting for X_1 and X_2 in equation (6D4) gives:

$$M_V = \frac{M_1 M_2 (x + y)}{xM_2 + yM_1} \quad (6D5)$$

Considering 1 gm. of TOA, the following values may be substituted into Equation (6D5) to obtain the molecular weight M_2 of the impurity - $M_V = 349$, $M_1 = 353$, $x = 0.841$ and $y = 0.159$

$$\therefore 349 = \frac{353M_2}{0.841M_2 + 353 \times 0.159}$$

$$\therefore \underline{M_2 = 332}$$

Thus the molecular weight of the impurity in the trioctylamine is 332, providing the assumption of non-basicity of the impurity is correct. However it should be noted that the accuracy of this calculation is rather low, since an error of $\pm 1\%$ in M_V produces an uncertainty of $\pm 6\%$ in M_2 .

6.D(iv) Trioctylamine hydrochloride - Pure

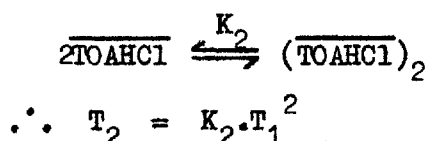
The V/C versus C plot for solutions of solid TOAHCl in benzene is shown in Figure 6.3. The points lie on a curve which approaches linearity as the solute concentration increases. This type of plot is indicative of highly non-ideal behaviour, and it is typical of the results obtained for all the amine salts investigated in this work. Non-ideal behaviour of long-chain amine salts in non-polar solvents is generally attributed to aggregation of the salts into dimers and higher polymers. Previous work on these types of systems has been discussed in Section 2.B.

The data obtained for TOAHCl were analysed on the assumption that the non-ideal behaviour was due to aggregation. The apparent molecular weight of the solute at each concentration was calculated by introducing each measured V/C value into Equation (6D1). Dividing the apparent

molecular weight by the monomer molecular weight of TOAHCl (389.5) gave the average aggregation number $\bar{n}$ for each solution. The apparent molecular weights and $\bar{n}$ values for TOAHCl in benzene are tabulated in Table 6.3.X, and a plot of $\bar{n}$ versus the molal concentration of TOAHCl is given in Figure 6.4.

It should be noted that this derivation of $\bar{n}$ values implicitly assumes that all the various species in solution behave ideally; that is, that the observed non-ideality of the solution is due to polymerisation of the solute, but that the individual polymeric species behave ideally. This is obviously questionable, especially in the light of the results for trioctylamine itself, which does not undergo aggregation, but nevertheless shows slight deviations from ideal behaviour. However in order that an analysis of the data can be attempted, this simplifying assumption is made.

The $\bar{n}$ values for the concentration range examined lie between 1.0 and 1.7. In order to calculate the dimerisation constant, it is assumed that the major species existing in solution are monomers and dimers. The validity of this assumption is demonstrated by the analysis that follows. Thus the equilibrium reaction is:



where T_2 = molal concentration of dimer
 T_1 = molal concentration of monomer
 K_2 = dimerisation constant

The total molal concentration of monomers and dimers, M , is given by:

$$M = T_1 + T_2 = T_1 + K_2 \cdot T_1^2 \quad (6D6)$$

The total stoichiometric molal concentration of TOAHCl, S , is given by:

$$S = T_1 + 2T_2 = T_1 + 2K_2 \cdot T_1^2 \quad (6D7)$$

By definition, the average aggregation number, $\bar{n}$, is equal to the total stoichiometric concentration divided by the total concentration of monomers and dimers:

$$\bar{n} = \frac{S}{M} \quad (6D8)$$

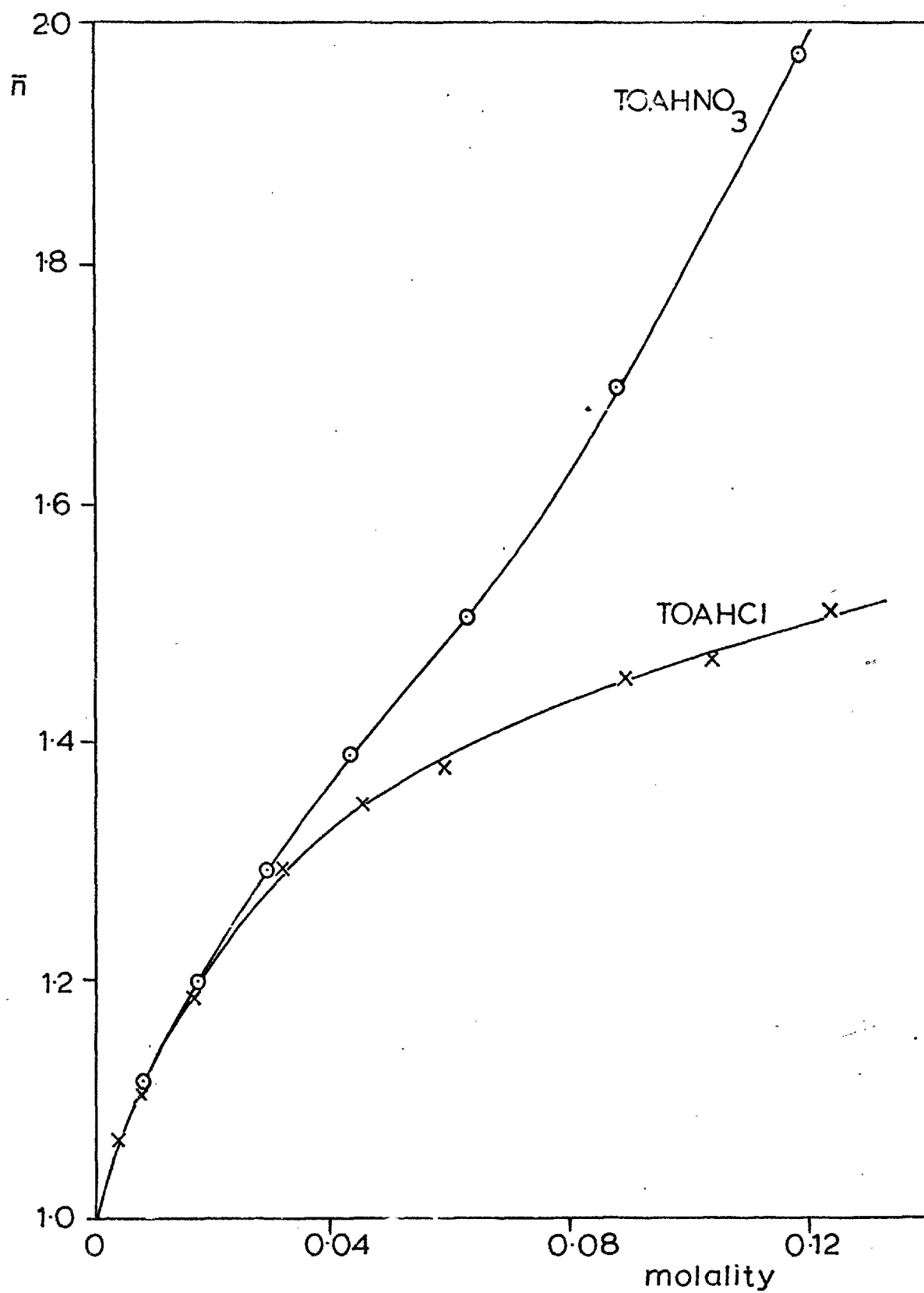


FIGURE 6.4 COMPARISON OF $\bar{n}$ VALUES FOR TOAHCl AND TOAHNO₃

Data from Tables 6.3.X and 6.6.X.

Elimination of M and T_1 from Equations (6D6), (6D7) and (6D8) gives the expression:

$$\frac{\bar{n}(\bar{n} - 1)}{(2 - \bar{n})^2} = K_2 \cdot S \quad (6D9)$$

Thus a plot of the function on the L.H.S. of Equation (6D9) against the stoichiometric molal concentration of TOAHCl should give a straight line passing through the origin, with a slope equal to K_2 . This plot is given in Figure 6.5. and the numerical data are contained in Table 6.3.X. The results lie on a straight line, indicating a monomer-dimer equilibrium, up to approximately 0.1m TOAHCl. At higher concentrations, the line deviates upwards from linearity, indicating the presence of higher polymers. Linear regression analysis of the data gave the following results:

Correlation coefficient = 0.9990

Intercept = -0.0326

Slope = 24.4326

The slope of the line is equal to the dimerisation constant, K_2 , of TOAHCl, thus:

$$\underline{K_2 = 24.4 \text{ mole}^{-1}} \quad \text{at } 32.5^\circ\text{C}$$

The only reported value for the dimerisation constant of TOAHCl in benzene is $K_2 = 12.9$ at 25°C , by Kojima et al.³⁶ who used a distribution method. The agreement with the present work is not good, but the discrepancy is comparable with the discrepancies between reported values of K_2 for TLAHCl in benzene, i.e. $K_2 = 18.6$ ³⁴, 20 ²⁶, 50 ²⁵, at 25°C and $K_2 = 30$ ²⁵ at 37°C .

Having established the concentration range over which only monomers and dimers exist, the concentrations of these two species may be calculated from the $\bar{n}$ values: From Equations (6D8) and (6D6):

$$\bar{n} = \frac{S}{T_1 + T_2}$$

From Equation (6D7):

$$T_2 = \frac{1}{2}(S - T_1) \quad \text{and} \quad T_1 = S - 2T_2$$

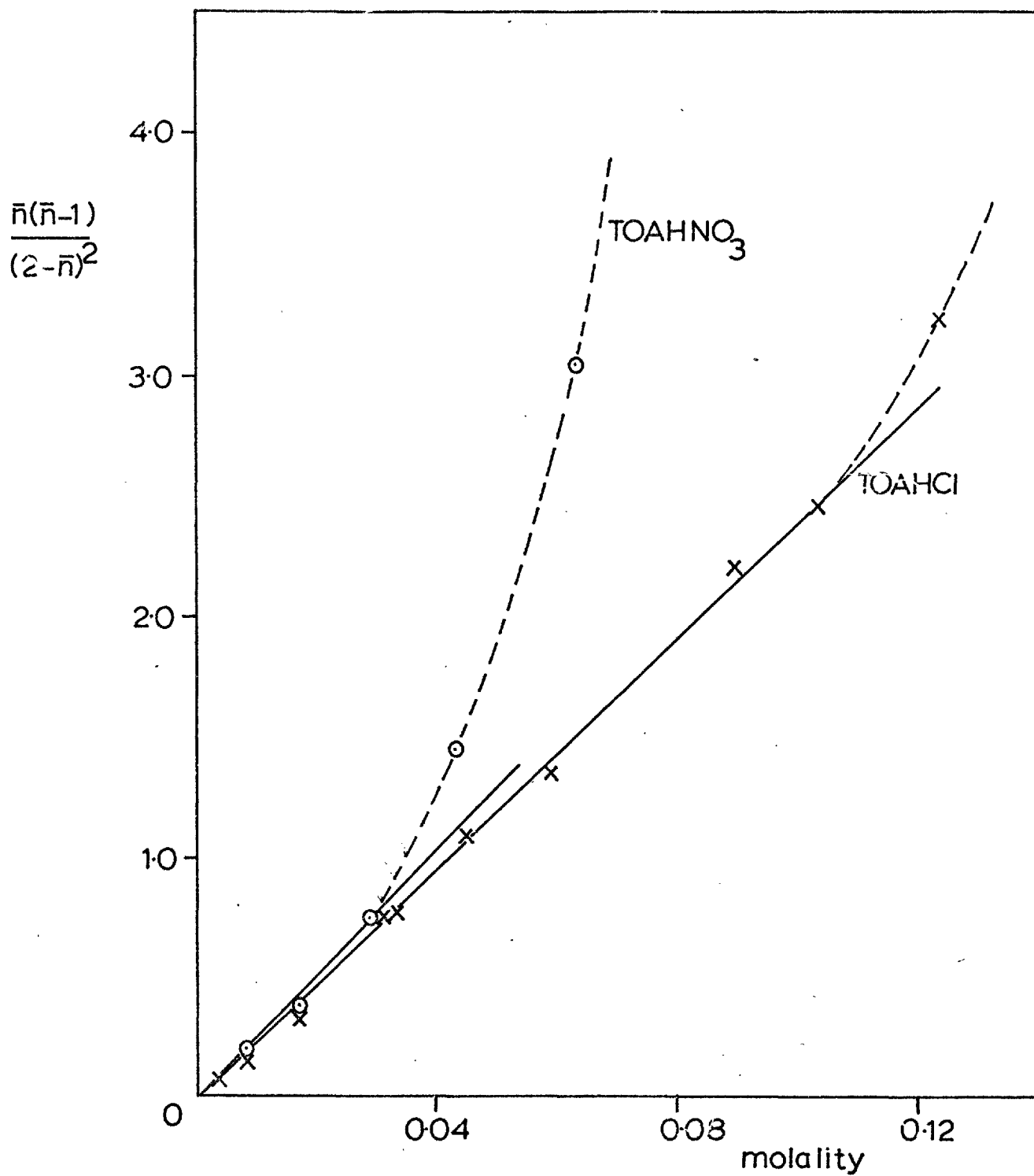


FIGURE 6.5 CALCULATION OF THE DIMERISATION CONSTANTS OF
TOAHCl AND TOAHNO₃

Data from Tables 6.3.X and 6.6.X.

$$\therefore \bar{n} = \frac{2S}{S - T_1} = \frac{S}{S - T_2}$$

$$\therefore T_1 = S \left(\frac{2 - \bar{n}}{\bar{n}} \right) \quad \text{and} \quad T_2 = S \left(\frac{\bar{n} - 1}{\bar{n}} \right) \quad (6D10)$$

Thus the monomer and dimer concentrations, T_1 and T_2 respectively, can be calculated from the total stoichiometric concentration of TOAHCl, S , and the $\bar{n}$ value. Equation (6D10) is valid for concentrations where only monomers and dimers are present. Calculated monomer and dimer concentrations are given in Table 6.4.X and the results are plotted as log concentration ($\log T_1$ or T_2) against log total stoichiometric amine hydrochloride concentration ($\log S$) in Figure 6.6. The concentrations have been changed from molal to molar so that they are compatible with the solvent extraction results discussed in Chapter 7. This conversion was done by using an empirical relationship relating molal and molar concentrations, which was determined for solutions of trioctylamine in benzene: $m = 1.29M$. It was assumed that this relationship could also be applied to solutions of TOAHCl in benzene.

Examination of Figure 6.6. shows that up to $S = 0.08M$, the log of the monomer concentration, $\log T_1$, increases linearly with $\log S$, the slope of the line being 0.67. $\log T_2$, the dimer concentration, also increases linearly with $\log S$. The slope of the dimer line is 1.45, approximately double that of the monomer line.

It is interesting to note that the two lines intercept at a $\log S$ value of -1.0. This is equivalent to a molal concentration of TOAHCl of 0.13m, which is slightly greater than the concentration at which deviation was observed in the monomer-dimer equilibrium for this salt - Figure 6.5. At the interception of the lines in Figure 6.6, the monomer and dimer concentrations in solution are equal. Thus it appears that higher polymers are not formed until the dimer concentration is approximately equal to the monomer concentration.

6.D(v) Trioctylamine hydrochloride - Practical

The apparent molecular weights of practical trioctylamine hydrochloride, calculated by introducing V/C values into Equation (6D1), are given in Table 6.5.X. In Figure 6.7, they are compared with the apparent molecular weights obtained for pure TOAHCl by plotting both

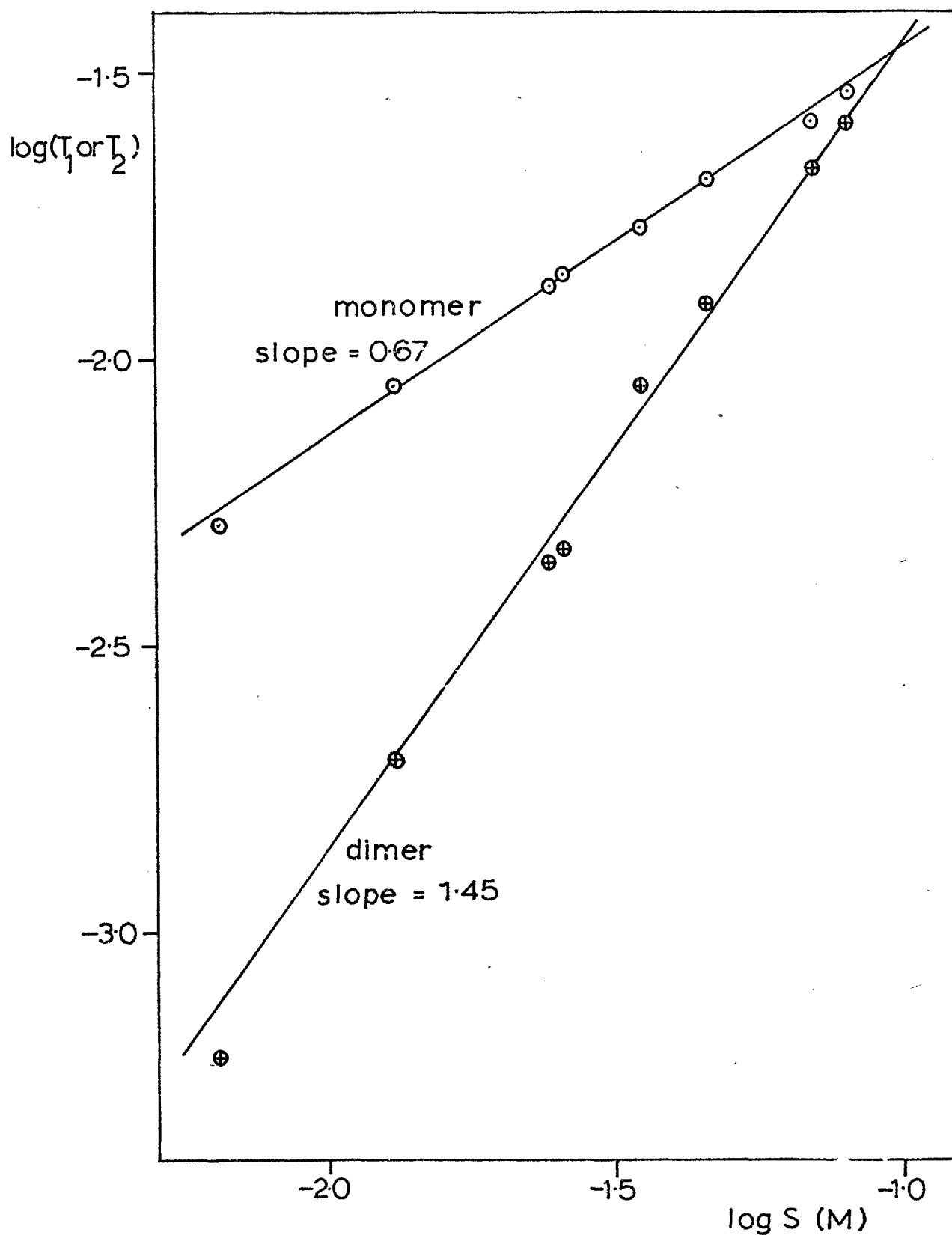


FIGURE 6.6 VARIATION OF THE CONCENTRATIONS OF MONOMERS AND DIMERS IN TOAHCl SOLUTIONS.

Data from Table 6.4.X.

sets of results against the molal concentrations of the solutions. The results for practical TOAHCl are somewhat scattered but in general they follow those of the pure material. The compositions of solutions of practical TOAHCl differ from those of the pure material in two respects. Firstly solutions of the practical material contain water of hydration, since they were prepared by equilibration with aqueous HCl, and secondly they contain the impurity which is present in the amine itself. It has been shown^{26,65,66} that the state of aggregation of amine salts is affected to a very minor extent by the presence of water in the organic phase. The presence of the impurity, which has a molecular weight of 332 (Section 6.D(iii)), will tend to lower the apparent molecular weight of the amine salt. In view of these uncertainties, the agreement between the results for the practical and pure TOAHCl solutions is considered to be reasonable. In the general discussion - Chapter 7 - V.P.O. data are used to explain the extraction behaviour of the amine hydrochloride, and it is assumed that the numerical results obtained for the pure amine hydrochloride can be used to describe the behaviour of the salt in the practical extraction systems.

6.D(vi) Trioctylamine Nitrate

In Section 6.B(v), it was stated that in view of the unknown state of hydration of the nitrate salt, the concentrations of the solutions of this salt were calculated as molalities, rather than weight-weight concentrations. This necessitates expressing the V.P.O. results as V/m instead of V/C , where m is the molality of the solution. When values of V/m are introduced into Equation (6D1), the average aggregation number $\bar{n}$ is obtained directly instead of the apparent molecular weight. This may be shown as follows:

$$m = C/M_o$$

where C = concentration in gm. solute/kg. solvent

M_o = monomer molecular weight of solute

$$\therefore \frac{V}{m} = \frac{V.M_o}{C}$$

From Equation (6D1) $\frac{V}{C} = \frac{K}{M}$

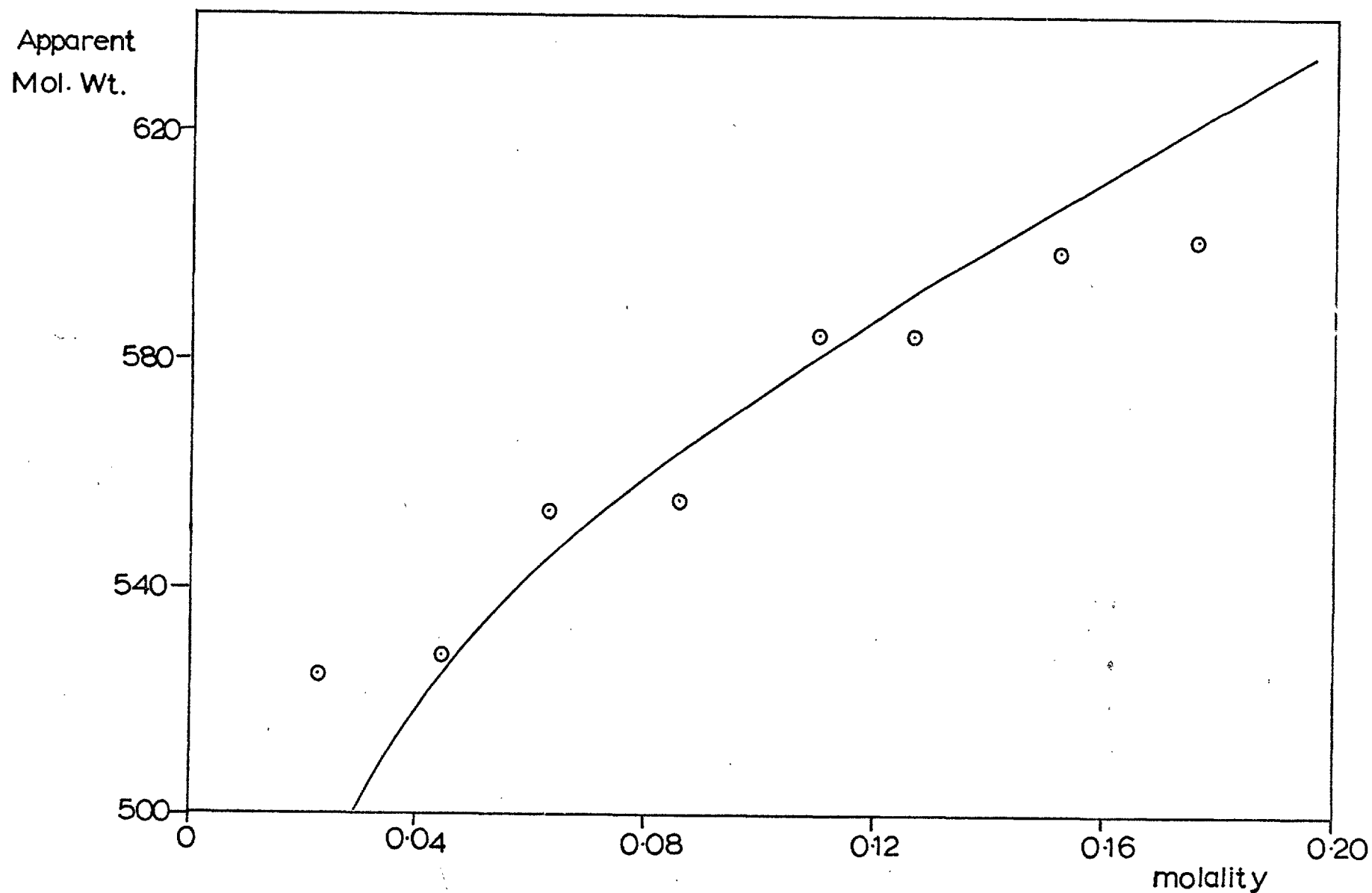


FIGURE 6.7 COMPARISON OF THE APPARENT MOLECULAR WEIGHTS OF PURE AND PRACTICAL TOAHCl SOLUTIONS.

Line = Pure TOAHCl Points = Practical TOAHCl Data from Tables 6.3.X and 6.5.X

$$\therefore \frac{V}{m} = \frac{K \cdot M_o}{M} = \frac{K}{\bar{n}}$$

$\bar{n}$ values for TOAHNO_3 are given in Table 6.6.X and they are compared with $\bar{n}$ values obtained for pure TOAHCl in Figure 6.4. The $\bar{n}$ values for the two salts are similar for concentrations up to 0.03m . At higher concentrations, the $\bar{n}$ values for the nitrate salt are much higher than those of the chloride salt, indicating greater aggregation of the former salt.

Equation (6D9) may be used to obtain the dimerisation constant of TOAHNO_3 . The function on the L.H.S. of Equation (6D9) is plotted against the molality of TOAHNO_3 in Figure 6.5. The linear behaviour expected for a monomer-dimer equilibrium extends only to a concentration of 0.03m . Above this concentration there is an upward deviation of the points, indicating the presence of higher polymers. The value of the dimerisation constant is given by the slope of the linear portion of the graph and is equal to:

$$\underline{K_2 = 25 \text{ mole}^{-1}} \quad \text{at } 32.5^\circ\text{C}$$

The concentration range over which the monomer-dimer equilibrium is obeyed by TOAHNO_3 found in this work is similar to that reported for tridodecylamine nitrate by Scibona and co-workers²⁵. They found that the monomer-dimer equilibrium was followed by solutions of this salt in benzene up to concentrations of 0.04m . At higher concentrations, the data indicated the formation of trimeric species.

6.D(vii) Cobalt salt of trioctylamine hydrochloride

The apparent molecular weights of the cobalt salt of TOAHCl are given in Table 6.7.X. In Figure 6.8 the results are plotted as a function of solute concentration, expressed as both a weight-weight concentration and also as the equivalent molar concentrations of cobalt in the organic phase. The apparent molecular weight of the solute increases by about 30% over the concentration range examined, indicating that association is occurring.

The molar ratio of cobalt to TOAHCl in these solutions is $1:2.31$. The theoretical ratio required for electrical neutrality, assuming cobalt is present as the tetrachlorocomplex, is $1:2.0$. The excess amine salt presumably solvates the metal complex. The composition of

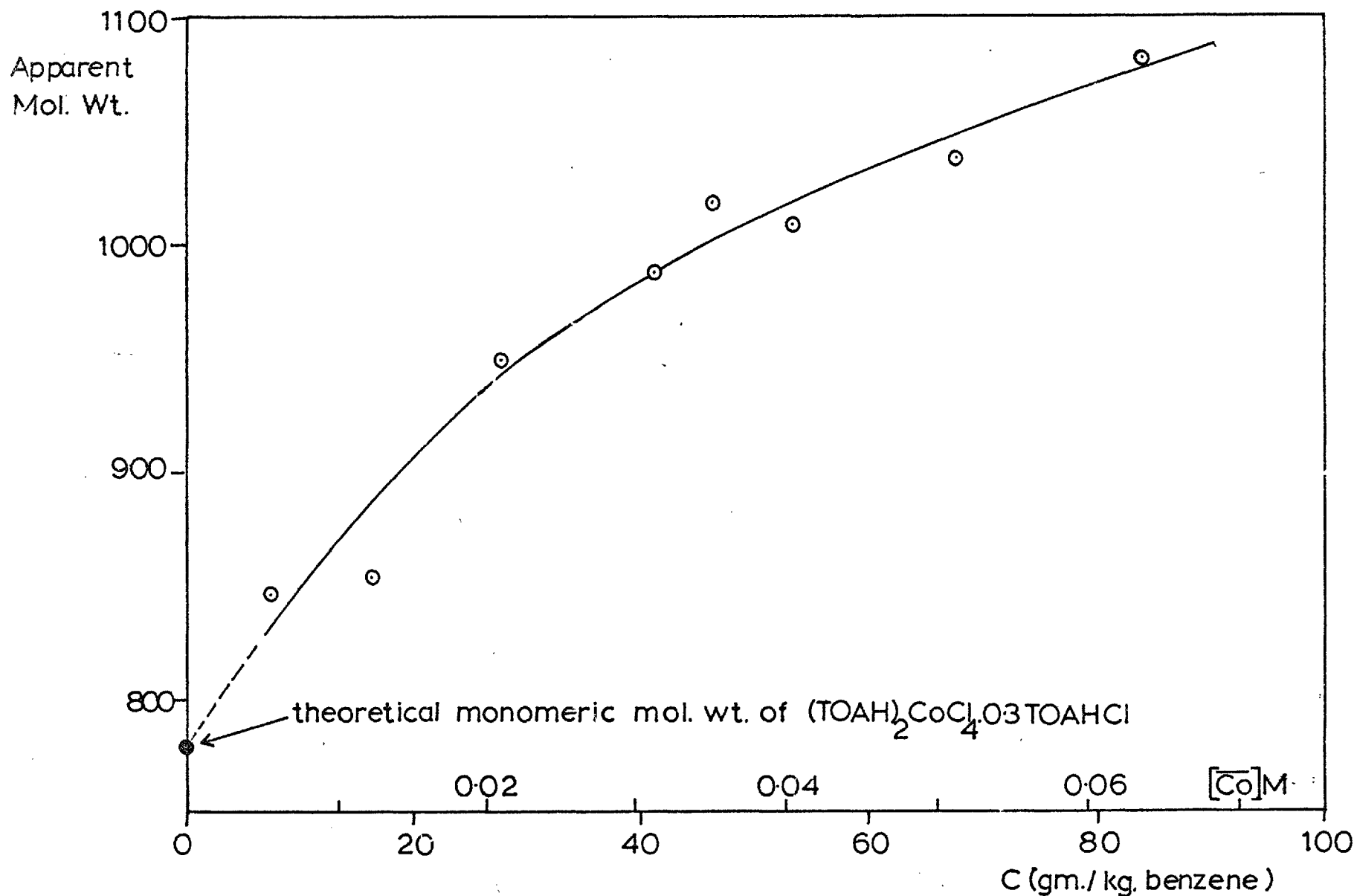
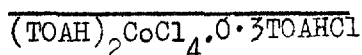


FIGURE 6.8 APPARENT MOLECULAR WEIGHT AGAINST CONCENTRATION FOR THE COBALT SALT OF TOAHCl

Data from Table 6.7.X.

the organic phase at full-loading is assumed to be:



This composition has the required metal to amine ratio and indicates that each mole of metal complex is solvated by 0.3 mole of amine salt. The theoretical average molecular weight in a solution of this composition, where both components of the solute exist as monomers, may be calculated from Equation (6D4):

$$M_v = X_1 M_1 + X_2 M_2$$

where component 1 = $(\text{TOAH})_2\text{CoCl}_4$, mol. wt. = 909
 component 2 = TOAHCl , mol. wt. = 389.5

The mole fractions of the two components, X_1 and X_2 , for the composition given above are:

$$X_1 = \frac{1}{1 + 0.3} = 0.77 \quad \text{and} \quad X_2 = \frac{0.3}{1 + 0.3} = 0.23$$

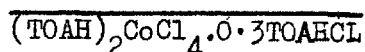
$$\text{Thus } M_v = 0.77 \times 909 + 0.23 \times 389.5 = \underline{789.5}$$

Since the results indicate that association of the solute occurs in this system, the solute components will only exist as monomers as the solute concentration approaches zero. Thus the theoretical molecular weight calculated above should be exhibited by the solution at zero solute concentration. The theoretical value is plotted at zero concentration in Figure 6.8, and it may be seen that a smooth curve through the majority of the experimental points may be extrapolated back to the theoretical point. It is considered that this agreement is satisfactory and that the V.P.O. data support the assumed composition of the organic species given above. Since this species is effectively a mixture of the metal complex and the solvating amine salt, it is not possible to analyse the association which occurs at finite solute concentrations in terms of equilibrium constants, because the behaviour of the individual components is not known. "Overall" apparent aggregation numbers ($\bar{n}^*$) can be calculated by dividing the measured apparent molecular weights by the theoretical monomeric average molecular weight calculated above. Values of $\bar{n}^*$ are given in Table 6.7.X. These increase with solute concentration, the maximum value being 1.392. These results contrast with those of

Good and Srivastava⁴⁵ who found that the apparent aggregation number of the cobalt species extracted by trihexylamine hydrochloride in toluene was close to 3 over the concentration range 0.02 to 0.1M.

6.E. Conclusions

1. The molecular weight of trioctylamine was found to be 349, compared with a theoretical value of 353. The impurity in the amine, indicated by the potentiometric molecular weight (419.6), was assumed to be non-basic, and its molecular weight was calculated - 332.
2. Pure trioctylamine hydrochloride forms aggregates when dissolved in benzene. The aggregation was found to follow a monomer-dimer equilibrium up to solute concentrations of approximately 0.1m, with a dimerisation constant, $K_2 = 24.4 \text{ mole}^{-1}$ at 32.5°C .
3. Practical trioctylamine hydrochloride, formed by direct equilibration of amine solutions with aqueous HCl, was found to behave similarly to the pure salt.
4. Trioctylamine nitrate solutions in benzene show a greater degree of aggregation than the chloride salt. The monomer-dimer equilibrium was obeyed only up to 0.03m, higher polymers being formed at higher solute concentrations. K_2 was found to be 25 mole^{-1} at 32.5°C .
5. The cobalt salt of trioctylamine hydrochloride forms aggregates when dissolved in benzene. As the solute concentration approached zero, the apparent molecular weight of the solute approached the theoretical molecular weight calculated for a monomeric solute of the following composition:



C H A P T E R 7

GENERAL DISCUSSION

7.A. The chloride and nitrate salts of trioctylamine

7.A(i) General

Measurements of the chloride concentrations of trioctylamine hydrochloride solutions equilibrated with both dilute HCl solutions and concentrated LiCl solutions (3.0 - 7.0M) have shown that, under these conditions, the stoichiometric amount of chloride is present in the organic phase. Thus there is no invasion of the organic phase by LiCl as is found in the case of quaternary ammonium chlorides⁵³. This is in agreement with the work of Sato^{49,52} on TOAHCl and of Good⁴² on several tertiary amine hydrochlorides.

The amine hydrochloride was found to extract water into the organic phase. At low aqueous chloride concentrations, where the water activity was close to one, the molar ratio in the organic phase of water to amine hydrochloride was approximately unity. As the chloride concentration of the aqueous phase was increased and thus the water activity decreased, the water content of the organic phase also decreased, in direct proportion to the water activity. Solutions of trioctylamine hydrochloride in equilibrium with aqueous lithium chloride may be represented as, $\text{TOAHCl} \cdot x\text{H}_2\text{O}$, where x is less than or equal to one, and depends on the water activity of the equilibrium aqueous phase. The change in x as a function of the chloride concentrations of the equilibrium aqueous lithium chloride solutions is given in Figure 5.3.

Water measurements were not carried out on trioctylamine nitrate solutions, but previous work has shown that solutions of amine nitrates generally have much lower water contents than the corresponding chlorides. Bertocci and Rolandi⁶² showed that solutions of trioctylamine nitrate in xylene extracted both water and excess acid from nitric acid solutions. The organic phase water concentration was related to the organic phase acid concentration with a molar ratio for water to nitric acid of one to approximately five. In addition,

the organic nitric acid concentration was proportional to the aqueous acid concentration. Thus the behaviour of water in amine nitrate solutions is apparently more complex than in amine chloride solutions.

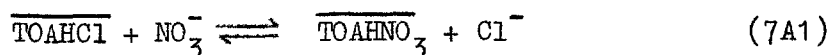
V.P.O. measurements carried out in this study indicated non-ideal behaviour of both TOAHCl and TOAHNO_3 in benzene. This was attributed to aggregation of the solutes. The chloride salt was less aggregated than the nitrate salt. The average aggregation numbers, $\bar{n}$, of the two salts were very similar up to a concentration of 0.03m , but thereafter, the $\bar{n}$ values of the nitrate salt were higher than those of the chloride salt, e.g. at 0.12m , $\bar{n}$ was 1.5 for TOAHCl and 2.0 for TOAHNO_3 .

The aggregation of the chloride salt was satisfactorily explained in terms of a monomer-dimer equilibrium for concentrations up to 0.1m , with evidence of higher polymers at higher concentrations. The dimerisation constant for TOAHCl in benzene was calculated and found to be $K_2 = 24.4 \text{ mole}^{-1}$ at 32.5°C . In the case of the nitrate salt, the monomer-dimer equilibrium was obeyed only up to a concentration of 0.03m , with $K_2 = 25 \text{ mole}^{-1}$ at 32.5°C . The formation of higher polymers was indicated at concentrations greater than 0.03m . Similar results have been reported by Scibona²⁵ for solutions of trilaurylamine nitrate in benzene which were shown to follow a monomer-dimer equilibrium up to 0.04m , with the formation of trimers at higher concentrations.

The influence of water in the organic phase on the aggregation of the amine salts was not investigated, but previous work has shown that there is little or no effect^{26,27,66,81}.

7.A(ii) The chloride-nitrate exchange constant

The results given in Section 3.C(i) for the organic chloride concentrations after equilibrations of TOAHCl solutions with aqueous solutions containing lithium chloride and lithium nitrate, indicate that nitrate is extracted into the organic phase. These results were found to be consistent with the following extraction equation:



The equilibrium constant for this reaction is:

$$K_x = \frac{[\overline{\text{TOAHNO}_3}] \cdot \bar{\gamma}_{\text{NO}_3} \cdot a_{\text{Cl}}}{[\overline{\text{TOAHCl}}] \cdot \bar{\gamma}_{\text{Cl}} \cdot a_{\text{NO}_3}} \quad (7A2)$$

where $\bar{\gamma}_{\text{NO}_3}$ and $\bar{\gamma}_{\text{Cl}}$ are the organic activity coefficients of the amine nitrate and chloride, respectively. a_{NO_3} and a_{Cl} are the aqueous activities of the ions.

It is assumed initially that the activity coefficients of the amine chloride and amine nitrate are equal. This assumption is discussed later. Secondly it is assumed that the equilibrium concentration of $\overline{\text{TOAHNO}_3}$ is equal to the initial concentration of $\overline{\text{TOAHCl}}$ in the organic phase minus the equilibrium concentration of $\overline{\text{TOAHCl}}$, i.e.

$$[\overline{\text{TOAHNO}_3}] = [\overline{\text{TOAHCl}}]_i - [\overline{\text{TOAHCl}}] \quad (7A3)$$

where $[\overline{\text{TOAHCl}}]_i$ = initial concentration of $\overline{\text{TOAHCl}}$

Using these two assumptions, Equation (7A2) becomes:

$$K_x = \frac{([\overline{\text{TOAHCl}}]_i - [\overline{\text{TOAHCl}}]) \cdot a_{\text{Cl}}}{[\overline{\text{TOAHCl}}] \cdot a_{\text{NO}_3}}$$

$$\therefore \frac{a_{\text{Cl}}}{a_{\text{NO}_3}} = \frac{K_x [\overline{\text{TOAHCl}}]}{[\overline{\text{TOAHCl}}]_i - [\overline{\text{TOAHCl}}]} \quad (7A4)$$

Thus a plot of $a_{\text{Cl}}/a_{\text{NO}_3}$ against $[\overline{\text{TOAHCl}}]/([\overline{\text{TOAHCl}}]_i - [\overline{\text{TOAHCl}}])$ should give a straight line passing through the origin, with a slope equal to the exchange constant, K_x . The aqueous chloride and nitrate ion activities for the mixed salt solutions, a_{Cl} and a_{NO_3} , were calculated from data published by Robinson and Lim⁵⁵. Details of these calculations are given in Appendix 1. The plot of equation (7A4) is given in Figure 7.1 and the numerical data is given in Table 7.1.X. Examination of Figure 7.1. shows that the theory

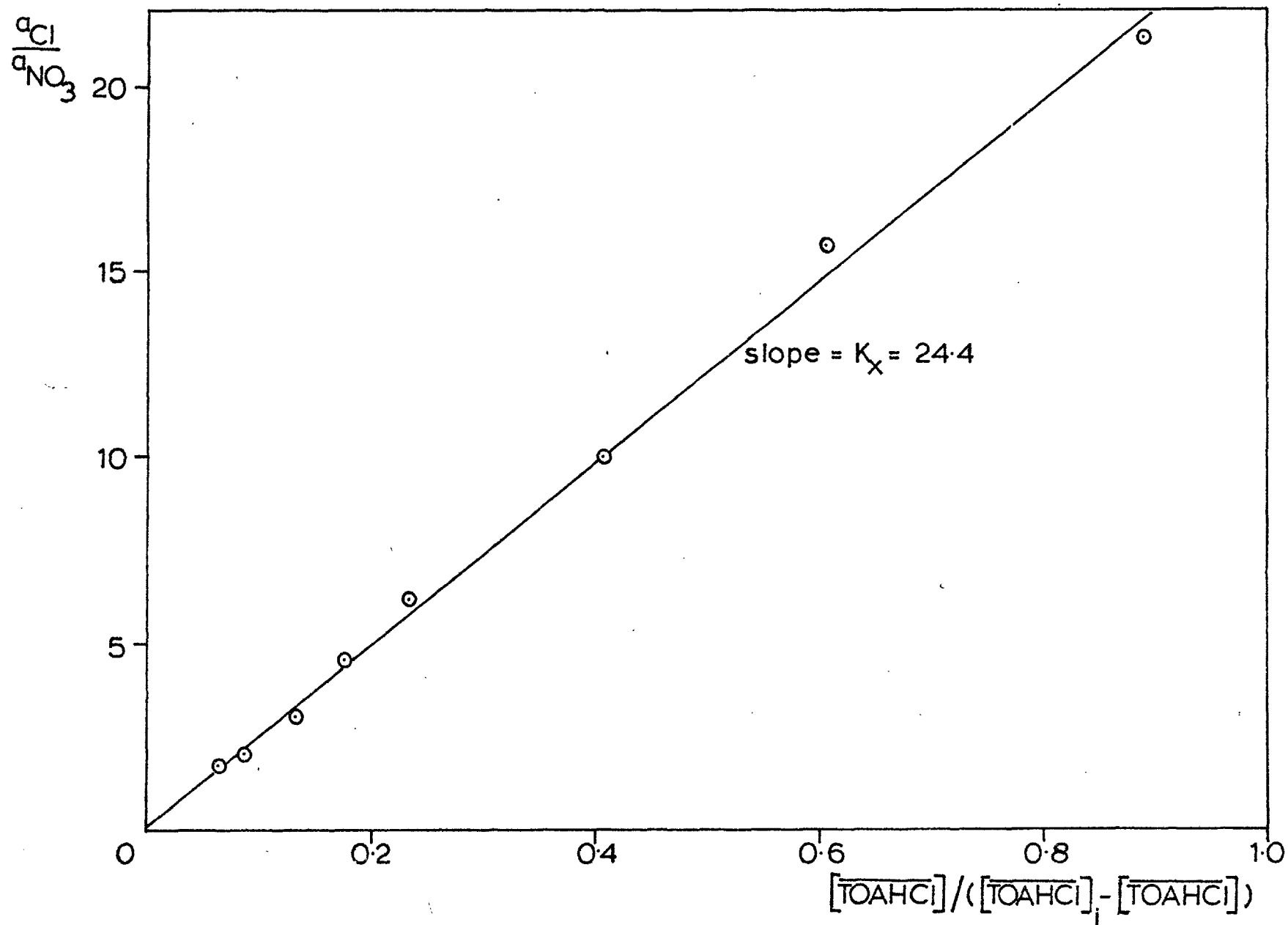


FIGURE 7.1 PLOT OF EQUATION (7A4)

Data from Table 7.1.X.

describes the experimental behaviour satisfactorily, with $K_x = 24.4$, calculated by linear regression analysis. The values of $[\text{TOAHCl}]$ calculated using this value of K_x are given in Table 7.2.X, and it may be seen that the calculated and experimental figures are in good agreement.

The chloride-nitrate exchange constant for TOA in benzene has not been previously reported. However the association constants K_{11} for extraction of the acids themselves by TOA in benzene are available, where K_{11} is given by:

$$K_{11} = \frac{[\text{R}_3\text{NHX}]}{[\text{R}_3\text{N}] a_{\text{H}^+} \cdot a_{\text{X}^-}} \quad (7A5)$$

For TOA in benzene, K_{11} values are 3.8×10^5 for $\text{X} = \text{NO}_3^-$ ⁶⁸, and 0.15×10^5 for $\text{X} = \text{Cl}^-$ ³⁶. From equations (7A2) and (7A5) the relationship between K_x and K_{11} is given by:

$$\frac{K_{11}(\text{NO}_3)}{K_{11}(\text{Cl})} = K_x = \frac{3.8 \times 10^5}{0.15 \times 10^5} = 25.3$$

This value is in good agreement with the value 24.4 calculated above.

It is concluded that the reaction given by Equation (7A1) adequately describes the extraction behaviour of trioctylamine in benzene when it is in equilibrium with aqueous solutions containing mixtures of lithium chloride and lithium nitrate, and that the nitrate ion is strongly extracted by TOA compared with the chloride ion.

One of the two assumptions made in the preceding analysis was that of equality of the activity coefficients of the two amine salts when in the presence of each other. It has been shown that the aggregation behaviour of the individual chloride and nitrate salts of the amine in benzene differ considerably for concentrations above 0.03M. The success achieved using the assumption of equal activity coefficients in the mixed solutions indicates that the aggregation behaviour in such solutions may be different. It is probable that the two salts will interact and this may lead to an "averaging" effect on the non-ideality of the mixed solute. Furthermore it will be shown subsequently that the extraction behaviour, with respect to cobalt, of mixed amine chloride-

amine nitrate solutions, is, in many respects, similar to that of solutions containing only the amine chloride. This suggests that the aggregation behaviour of the mixed solutions resembles that of the chloride salt rather than the nitrate salt.

7.B. The nature of the extracted cobalt species

There is much evidence in the literature which suggests that cobalt exists in organic solutions containing either tertiary amine hydrochlorides or quaternary ammonium chlorides as a complex which contains the tetrahedral CoCl_4^{2-} ion^{41,42,45,48,49,82}. The results of this study also support this conclusion.

The spectrum of the organic cobalt complex, shown in Figure 3.5, resembles the spectrum of aqueous solutions of cobalt containing high concentrations of chloride ions. The overall extinction coefficients of the organic complex are higher than the maximum values obtained for cobalt in LiCl solutions, which occurred at 12.1M LiCl (See Table 4.1). They are also higher than the extinction coefficients reported by Good and co-workers^{41,42} for cobalt in tri-iso-octylamine and tri-n-hexylamine. However they are close to the values reported by Gill and Nyholm⁸ for CoCl_4^{2-} in bis(triphenylmethylarsonium) tetrachlorocobaltate and also close to the values for CoCl_4^{2-} in TBP given by Morris and co-workers⁸³. Numerical values of all these results are given in Table 7.1.

Table 7.1 Comparison of peak wavelengths and overall extinction coefficients for CoCl_4^{2-} in various media.

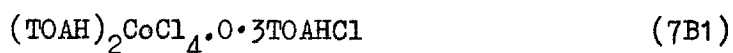
Medium	λ_{max}	ϵ^λ	λ'_{max}	$\epsilon^{\lambda'}$	λ''_{max}	$\epsilon^{\lambda''}$	Reference
THA in C_6H_6	700nm	583	665nm	571	630nm	408	41,42
TIOA in C_2HCl_3	695nm	542	665nm	506	625nm	365	41
TBP	693nm	640	660nm	?	630nm	?	83
$(\text{Ph}_3\text{MeAs})_2(\text{CoCl}_4)$	693nm	653	668nm	580	635nm	419	8
TOA in C_6H_6	693nm	635	662nm	572	626nm	422	This work
12.1M LiCl	690nm	590	662nm	540	624nm	368	This work

The cobalt to chloride molar ratio in the TOA complex obtained by direct analysis of the complex was 1:3.9, which is close to the theoretical value of 1:4 for CoCl_4^{2-} .

Analysis of the organic complex for lithium after extraction of cobalt from LiCl solutions gave negative results, indicating that lithium is not co-extracted with the cobalt.

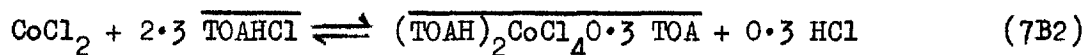
When part of the LiCl in the aqueous phase was replaced by HCl there was no appreciable change in the distribution coefficient of cobalt. This indicates that hydrogen ions are not co-extracted with the cobalt. If hydrogen ions were co-extracted with the metal, an increase in D_{Co} with the hydrogen ion content of the aqueous phase would be expected.

The cobalt to amine molar ratio in the organic phase at full loading was found to be 1 : 2.3. This result was obtained both from the extraction isotherm and from an analysis of purified TOAHCl loaded with cobalt. An identical loading ratio for cobalt in THAHCl in toluene has been reported⁴⁵. Assuming the metal species in the organic phase is CoCl_4^{2-} , then two R_3NH^+ ions would be required to maintain electrical neutrality. Thus the theoretical cobalt to amine molar ratio should be 1 : 2. In order to account for the observed ratio, it is necessary to postulate that the organic metal complex is solvated by 0.3 molecules of amine hydrochloride, and the extracted species may be represented as:



This formulation, however, gives a theoretical metal to chloride ratio in the complex of 1 : 4.3, whereas the measured ratio was 1 : 3.9. An alternative explanation which satisfies both measured ratios is that the metal complex is solvated by free amine rather than amine hydrochloride, i.e. $(\text{TOAH})_2\text{CoCl}_4 \cdot 0.3\text{TOA}$. This species has a metal to chloride to amine molar ratio of 1 : 4 : 2.3, in agreement with the experimental values. However the formation of this species requires the conversion of part of the amine hydrochloride to the free base during contact with aqueous solutions of pH less than 2 and which contain high chloride ion concentrations. This seems improbable. Furthermore, with the formation of free amine during the extraction, the reaction should become dependent on the hydrochloric acid concentration of the aqueous phase,

since the reaction would involve transfer of the acid from the organic to the aqueous phase as shown in the following equation:



A reaction of this type should show a decrease in D_{Co} as lithium chloride in the aqueous phase is replaced by hydrochloric acid. This effect was not observed. Similarly, extraction of cobalt from pure HCl solutions would be expected to be lower than from pure LiCl solutions. It is shown in Section 7.E. that identical cobalt distribution coefficients are obtained for HCl and LiCl solutions of equal chloride ion activity, providing the extraction of excess acid, which occurs with the former solutions, is taken into account.

The reason for the discrepancy between the theoretical and measured metal to chloride ratios is not understood, since it is thought unlikely to be accounted for by experimental error. However in view of the arguments presented above, it is assumed in the following discussions that the metal complex is solvated by amine hydrochloride rather than free amine, and that its composition is given by Equation (7B1). The solvation number of 0.3 was obtained for amine solutions which were fully loaded with cobalt. The solvation of the organic complex at low metal loadings is not known, but evidence will be presented which shows that the number of solvating molecules is probably independent of the organic phase metal concentration.

Water determinations on cobalt-saturated amine hydrochloride solutions, discussed in Section 5.D., showed that the organic metal complex is essentially unhydrated. This is in agreement with the work of Sato⁴⁸ on the cobalt - TOA system.

The molecular weight determinations, discussed in Section 6.D(vii), have shown that the apparent molecular weight of the organic metal complex in solution in benzene increases as its concentration increases. As the concentration of the complex approaches zero, the apparent molecular weight approaches the theoretical value calculated for a solution containing a monomeric mixture of 1.0 mole of $(\overline{\text{TOAH}})_2\text{CoCl}_4$ and 0.3 mole of $\overline{\text{TOAHCl}}$. The overall $\bar{n}$ values of the solute, calculated from the theoretical apparent molecular weight, increase quite slowly

with concentration, reaching a value of 1.39 at a concentration of 84 gm. solute/kg. benzene. This solution contains approximately 0.19M TOAHCl. The $\bar{n}$ value of a pure TOAHCl solution at 0.19M is 1.62. Thus the aggregation of the metal complex is less than that of the amine hydrochloride.

7.C. Variation of amine concentration

The variation of D_{Co} with total amine salt concentration is shown on a log-log scale in Figure 3.3. Each line on this diagram represents extraction from an aqueous phase of constant composition. Extraction from both lithium chloride and mixed lithium chloride-lithium nitrate solutions is represented. For amine salt concentrations of up to 0.2M ($\log[TOAHX] = -0.7$) the results lie on a series of parallel lines with slopes of 1.60. At amine salt concentrations greater than 0.2M, the lines deviate upwards from linearity. Because of the low total metal concentrations used ($1.92 \times 10^{-3}M$), the slopes of these lines are not significantly altered if the concentrations of free amine salt are plotted, rather than the total salt concentrations, by correcting for the concentration of amine salt bound to the metal complex.

Similar amine dependencies for cobalt extraction by tertiary amine hydrochlorides have been reported previously. Venkateswarlu and Lal⁴⁷ found slopes of 1.5 for the extraction of cobalt from HCl by tri-n-nonylamine, and Sato^{48,49} reported slopes varying between 1.30 and 1.75 for cobalt extraction by TOA from 4 to 10M HCl solutions.

It is conventional to regard a p th power dependence of the distribution coefficient on the amine salt concentration as indicating the participation of p amine salt molecules in the extracted metal complex. However, in general, the situation is more complicated than this due to the aggregation of amine salts, which occurs in many diluents. Failure to appreciate the effects of aggregation led to the proposals of erroneous extraction mechanisms in some of the early investigations of amine extraction systems, as pointed out by Kertes⁴⁶. Nevertheless it has frequently been observed that the distribution coefficient of a complex MA_{m+p}^{p-} varies with the p th power of the amine salt concentration, in spite of the fact that the amine salt is

aggregated. To account for this, Marcus⁷⁰ has suggested that aggregated amine salts may be monoionised and thus exchange only one anion:

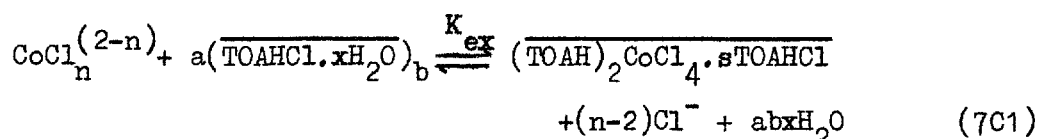


Providing the aggregation number q only varies slightly with the total amine salt concentration, then the concentration of the q -mer will be directly proportional to the total amine salt concentration and the required p th power dependency will be observed. This concept, however, does not explain non-integral power dependencies which are also frequently observed and generally attributed to amine salt aggregation. Very little quantitative work on this aspect of the extraction of metals by amines has been reported and the situation is not really understood.

In this investigation it has been found possible to calculate the monomer and dimer concentrations in TOAHCl solutions of up to 0.08M. This information can be utilised to analyse the observed amine salt concentration dependencies in terms of reactions involving extraction of the metal complex by either the monomer or the dimer of the amine salt. In order to do this, a generalised extraction equation is written, utilising the following experimentally observed information:

- i) The organic metal complex contains the $CoCl_4^{2-}$ ion.
- ii) The amine hydrochloride is hydrated by x water molecules. x is generally less than one, and depends on the aqueous water activity.
- iii) The organic metal complex is unhydrated, but is solvated by s amine salt molecules. s may be variable.
- iv) At low concentrations, the organic metal complex is unaggregated.

The generalised extraction equation is:



In this equation, a and b are related variables, where b is the aggregation number of the amine salt species involved in the extraction. The relationship between a and b depends on s , the number of amine salt molecules which solvate the organic metal complex, and s itself may be variable. The equation relating a , b and s is:

$$s = a \cdot b - 2 \quad (7C2)$$

K_{ex} , the extraction equilibrium constant is given by:

$$K_{ex} = \frac{\{(\overline{TOAH})_2 CoCl_4 \cdot s \overline{TOAHCl}\} \{Cl^-\}^{(n-2)} \{H_2O\}^{abx}}{\{CoCl_n^{(2-n)}\} \{(\overline{TOAHCl})_b\}^a} \quad (7C3)$$

In the case of low organic metal loadings, the activity coefficient of the organic metal complex may be assumed constant, and can be incorporated into K_{ex} .

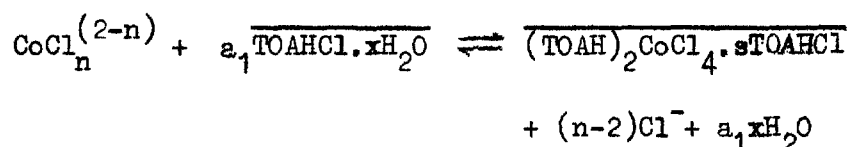
For the results under consideration, where the amine salt concentration was varied, while the aqueous phase composition was kept constant, the expression for K_{ex} may be further simplified. For constant aqueous phase conditions, the water activity, the aqueous chloride ion activity, and the indices x and n will be constant, and the activity of the extractable metal complex $CoCl_n^{(2-n)}$ will be proportional to the total aqueous metal concentration, X_{Co} . Thus, from equation (7C3):

$$\frac{[(\overline{TOAH})_2 CoCl_4 \cdot s \overline{TOAHCl}]}{X_{Co} \cdot \{(\overline{TOAHCl})_b\}^a} = \text{constant} = \frac{D_{Co}}{\{(\overline{TOAHCl})_b\}^a} \quad (7C4)$$

$$\therefore \frac{d \log D_{Co}}{d \log \{(\overline{TOAHCl})_b\}} = a \quad (7C5)$$

Equation (7C5) shows that the change in $\log D_{Co}$ with the log of the activity of the extracting amine salt species will be equal to the number of molecules of this species which are involved in the extraction reaction.

If it is assumed that the extraction of cobalt takes place via the monomer of TOAHCl, then the extraction reaction, Equation (7C1), becomes:



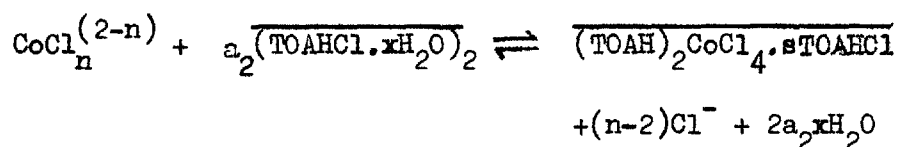
If it is further assumed that the monomer behaves as an ideal solute in benzene, and its concentration is represented by T_1 , then from Equation (7C5):

$$\frac{d \log D_{Co}}{d \log T_1} = a_1 \quad (7C6)$$

Thus if the change in $\log D_{Co}$ with the log of the monomer concentration can be determined, the slope of the line will be equal to a_1 , the number of monomer molecules involved in the extraction. A knowledge of a_1 enables s , the number of amine salt molecules solvating the organic metal complex, to be calculated from Equation (7C2), since, for extraction by the monomer, b is equal to one. Therefore:

$$s = a_1 - 2 \quad (7C7)$$

If, on the other hand, extraction is assumed to take place via the dimer only, and the dimer is assumed to be an ideal solute in benzene, an analogous set of equations is obtained. The extraction reaction becomes:



$$\frac{d \log D_{Co}}{d \log T_2} = a_2 \quad (7C8)$$

where T_2 = concentration of dimer

$$s = 2a_2 - 2 \quad (709)$$

Experimentally it is only possible to determine the change in the distribution coefficient of the metal as a function of the total amine salt concentration. Figure 3.3 shows that D_{Co} varies with the 1.6th power of the total amine salt concentration for extraction from various aqueous phases, i.e.

$$\frac{d \log D_{Co}}{d \log [\overline{TOAHX}]_{total}} = 1.60$$

In order to show the dependency of D_{Co} on the monomer or dimer concentrations, it is necessary to know how the concentrations of these species change with the total amine hydrochloride concentration in the organic phase, since:

$$\begin{aligned} \frac{d \log D_{Co}}{d \log(T_1 \text{ or } T_2)} &= \frac{d \log D_{Co}}{d \log[\overline{TOAHCl}]_{total}} \times \frac{d \log[\overline{TOAHCl}]_{total}}{d \log(T_1 \text{ or } T_2)} \\ &= 1.6 \times \frac{d \log[\overline{TOAHCl}]_{total}}{d \log(T_1 \text{ or } T_2)} \quad (7010) \end{aligned}$$

The calculations of the monomer and dimer concentrations as functions of the total amine hydrochloride concentration, up to 0.08M, were made in Section 6.D(iv). Figure 6.6 shows that the log of both the monomer and the dimer concentration varies linearly with the log of the total amine hydrochloride concentration, and that for the monomer:

$$\frac{d \log T_1}{d \log[\overline{TOAHCl}]_{total}} = 0.67 \quad (7011)$$

and for the dimer :

$$\frac{d \log T_2}{d \log[\overline{TOAHCl}]_{total}} = 1.45 \quad (7012)$$

These results were obtained for solutions of pure TOAHCl in benzene, but it is assumed that they can be applied to the impure practical TOAHCl solutions used in the extraction experiments.

Thus for the case where extraction is assumed to take place via the monomer only, from Equations (7C6), (7C10) and (7C11):

$$\frac{d \log D_{Co}}{d \log T_1} = a_1 = \frac{1.60}{0.67} = 2.39$$

s, the number of solvating amine salt molecules is then given by Equation (7C7):

$$s = a_1 - 2 = 0.39$$

For the case of extraction via the dimer only:

$$\frac{d \log D_{Co}}{d \log T_2} = a_2 = \frac{1.60}{1.45} = 1.105$$

$$s = 2a_2 - 2 = 0.21$$

Both the values of s obtained above are in reasonable agreement with the value 0.3, which is the number of molecules of excess amine salt associated with the organic metal complex at full loading, determined both by analysis of the organic phase (Section 6.B(vi)), and also from the extraction isotherm experiment (Section 3.C(v)). This agreement leads to two conclusions -

- i) A knowledge of the concentrations of the monomeric and dimeric forms of TOAHCl enables the observed slopes of $\log D_{Co}$ against $\log [\text{TOAHCl}]_{\text{total}}$ to be rationalised. This could not be done quantitatively if only the $\bar{n}$ values were known. However it is not possible to distinguish, by this method of analysis, which of the two species existing in TOAHCl solutions up to 0.08M is responsible for the extraction of the metal complex. This is because extraction by the monomer or the dimer of the amine salt, or a combination of both, will result in the observed change in D_{Co} with the total amine salt concentration.
- ii) The values of s calculated above were obtained using solutions of

low organic metal concentrations. The agreement of these values with the number of solvating amine salt molecules found at full loading indicates that the solvation of the organic metal complex is probably independent of the organic metal concentration. In other words s is not a variable quantity.

It should be noted that, in calculating the monomer and dimer concentrations from the V.P.O. data, it was assumed that these species behave as ideal solutes in benzene (see Section 6.D(iv)). Since these V.P.O. data were used in the analysis given above it is justifiable to use the same assumption again. This was done in order to derive Equations (706) and (708).

The use of the V.P.O. data limits the applicability of the analysis to amine salt concentrations up to 0.08M. Above this concentration higher polymers exist in the organic phase, and the monomer and dimer concentrations are unknown. However the slopes of $\log D_{Co}$ against $\log [\overline{TOAHX}]_{total}$ shown in Figure 3.3 remain constant up to 0.2M. This indicates that the extraction reaction is unchanged up to this concentration. At amine salt concentrations greater than 0.2M, the slopes of the lines in Figure 3.3 increase. This phenomenon requires comment. The slopes of the lines approach 2.3 although the data are rather limited. If the slopes in fact remain constant at 2.3 at high amine salt concentrations, this could be due to the amine salt exhibiting the behaviour postulated by Marcus⁷⁰, i.e. monoionisation of the higher amine salt aggregates. An alternative explanation is a change in the nature of the organic phase due to the presence of high concentrations of the polar amine salt. Müller and Diamond²⁶ have shown that the dielectric constant of solutions of tridodecylamine hydrobromide in benzene begins to rise when the amine salt concentration is greater than 0.1M. A similar effect occurring in the TOAHCl solutions could account for the enhanced extraction observed at high concentrations, since an increase in the dielectric constant would facilitate the accommodation of the ionic metal complex in the organic phase.

Finally attention is drawn to the fact that the change in D_{Co} with amine salt concentration is the same for extraction from mixed lithium chloride - lithium nitrate aqueous solutions as it is from solutions containing only lithium chloride. The organic phases in contact with the former solutions will have much of the amine in the nitrate form due to the preferential extraction of nitrate by TOA. This indicates

that the behaviour of organic solutions containing mixtures of amine hydrochloride and amine nitrate is very similar to solutions containing only amine hydrochloride. Thus the assumption of similar activity coefficients for the two salts when in the presence of each other, which was used in the calculation of the Cl-NO_3 exchange constant (Section 7.A(ii)), appears to be reasonable.

7.D. Variation of total metal concentration

7.D(i) Extraction from lithium chloride solutions

It was found that for extraction from lithium chloride solutions the relationship between D_{Co} and the total metal concentration depended on the metal concentration in the organic phase. When the molar ratio of organic cobalt to the total amine concentration was less than approximately 0.03:1.00, D_{Co} was independent of metal concentration. Assuming a metal to amine ratio in the organic complex of 1:2.3, D_{Co} remained independent of metal concentration until approximately 7% of the amine salt was bound in the metal complex. The range of metal concentrations used in this investigation, which were generally up to a maximum of $1.44 \times 10^{-2} \text{M Co}$, were such that the organic metal concentrations were greater than the above limiting ratio only when the aqueous solutions contained more than 6M chloride. At lower aqueous chloride concentrations, the distribution coefficients were low so that the metal to amine ratio was always below the limit. Thus D_{Co} was independent of total metal concentration, up to $1.44 \times 10^{-2} \text{M Co}$, for aqueous chloride concentrations below about 6M.

Where variations of D_{Co} with total metal concentration were observed, the equilibrium concentrations of free amine salt were calculated from the following expression:

$$[\overline{\text{TOAHCl}}]_{\text{free}} = [\overline{\text{TOAHCl}}]_{\text{total}} - 2.3Y_{\text{Co}} \quad (7D1)$$

where Y_{Co} is the metal concentration in the organic phase and the metal to amine salt ratio in the organic complex is assumed constant at 1:2.3.

The numerical results are given in Table 7.3.X and they are plotted as $\log D_{Co}$ against $\log [\overline{TOAHCl}]_{free}$ in Figure 7.2. Each series of points on this diagram represents extraction from an aqueous phase where the bulk electrolyte concentration was kept constant while the cobalt concentration was varied. The results lie on a series of parallel straight lines with slopes of 2.3. These results represent up to about 30% of the total amine hydrochloride bound in the metal complex. In one series of experiments, at $[Cl]_{aq} = 6.5M$, the metal concentration of the aqueous phase was increased until full metal loading of the organic phase was achieved, and it was found that the slope of the line remained constant at 2.3 until about 50% of the amine salt was bound in the metal complex. At higher organic metal concentrations, the slope decreased and became zero at full loading.

From these results it is concluded that at low metal loadings the distribution coefficient of the metal is proportional to the free amine salt concentration to the power 2.3:

$$D_{Co} = k [\overline{TOAHCl}]_{free}^{2.3} \quad (7D2)$$

The power dependency 2.3 is equal to the amine salt to metal ratio in the organic complex, which was observed at high metal loadings and deduced for low metal loadings in Section 7.C, and it indicates that the amine salt behaves in a pseudo-ideal fashion under the conditions of these experiments. This is because if the amine salt behaved ideally and did not form aggregates, an equation similar to (7D2) would describe the relationship between D_{Co} and the total amine salt concentration. This pseudo-ideality must be due to the fact that the aggregation of the amine salt remains constant in each series of experiments shown in Figure 7.2. The aggregation is thus dependent only on the total concentration of amine salt and is independent of the free amine salt concentration. It is also apparently unaffected by the presence of the organic metal complex. If this was not the case, and the aggregation was a function of the free amine salt concentration, as might be expected, then the degree of aggregation would vary as the amount of metal entering the organic phase increased. This would lead to a lowering of the slopes of the lines in Figure 7.2, in the same way that a slope lower than the theoretical value is observed for the change in D_{Co} with the total amine salt concentration - Section 7.C

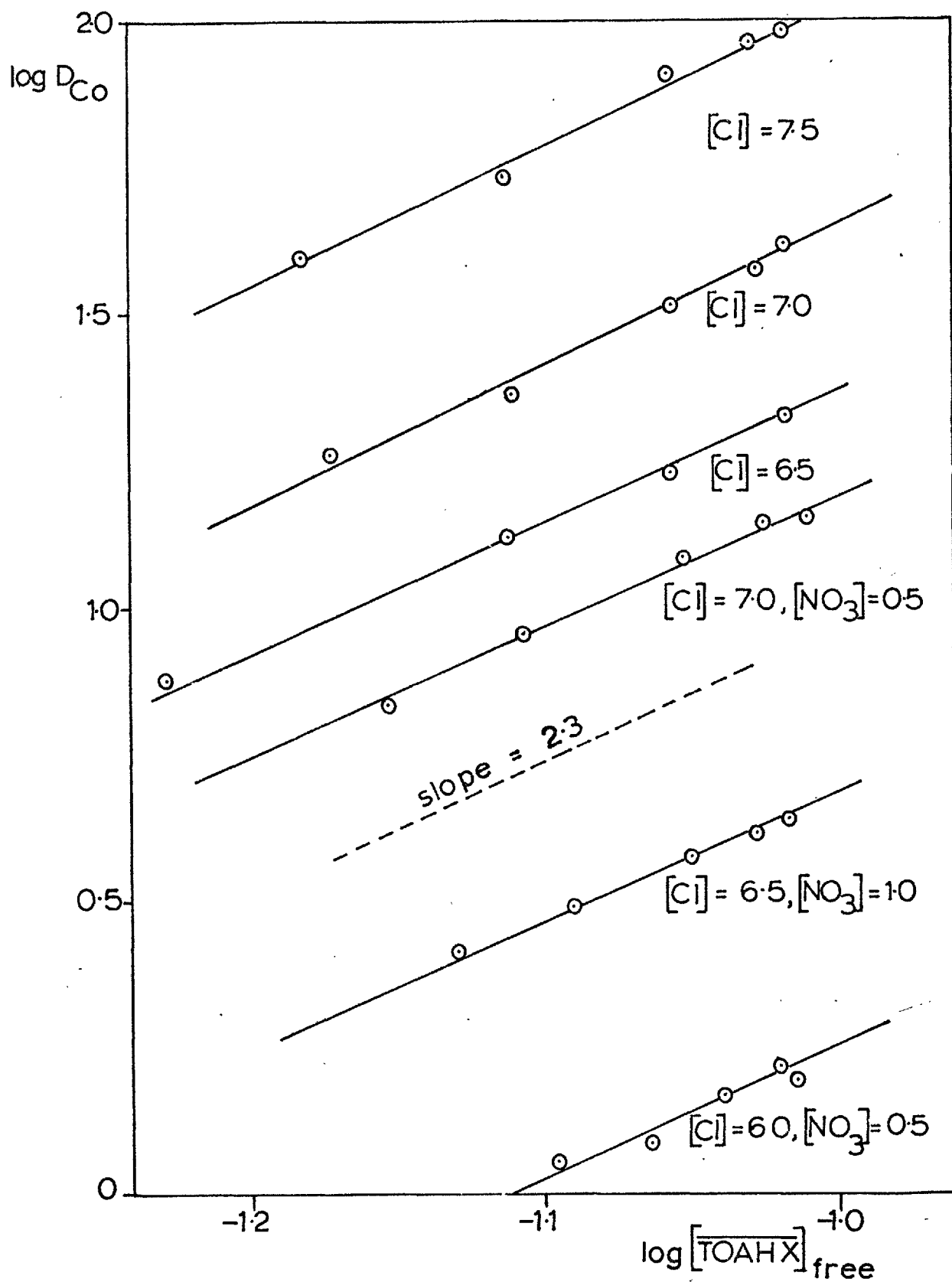


FIGURE 7.2 VARIATION OF D_{Co} WITH FREE AMINE SALT CONCENTRATION.

$$[\text{TOAHX}]_{\text{total}} = (9.76 \text{ to } 9.85) \times 10^{-2} \text{ M}$$

Data from Table 7.3.X.

and Figure 3.3. It is concluded that up to about 50% of full metal loading, the aggregation of the amine salt in the organic phase is independent of the organic metal concentration.

7.D(ii) Extraction from lithium chloride - lithium nitrate solutions

The effects of varying the total metal concentration on extraction from aqueous solutions containing mixtures of lithium chloride and lithium nitrate were very similar to those observed for extraction from chloride only solutions. This is in spite of the fact that the presence of nitrate in the aqueous phase leads to a large proportion of the amine in the equilibrium organic phase being present as the nitrate salt. Where variations of D_{Co} with metal concentration were observed, the free amine salt concentrations were calculated by an equation analogous to Equation (7D1):

$$[\text{TOAHX}]_{\text{free}} = [\text{TOAHX}]_{\text{total}} - 2.3 Y_{Co} \quad (7D3)$$

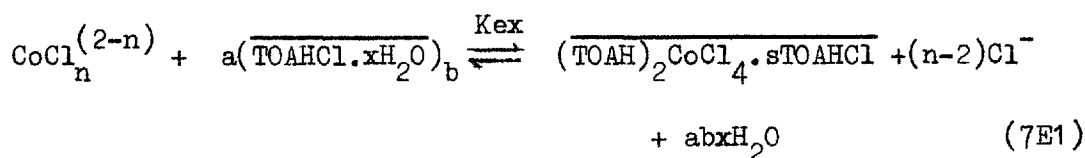
The use of X in the above equation indicates that the amine salt is a mixture of chloride and nitrate.

The results of these calculations are given in Table 7.3.X and plotted as $\log D_{Co}$ against $\log [\text{TOAHX}]_{\text{free}}$ in Figure 7.2. The results lie on a series of straight lines which are parallel to those obtained for extraction from aqueous solutions containing lithium chloride only. This similarity of slope again suggests that the extraction behaviour of mixed amine nitrate - amine hydrochloride solutions is similar to solutions containing only amine hydrochloride. Furthermore, the fact that all the lines plotted in Figure 7.2 have the same slope indicates that in the chloride - nitrate systems, $\log D_{Co}$ is proportional to the log of the total free amine salt concentration and it appears to be virtually independent of the proportion of the free amine salt which is in the chloride form. This is because the chloride to nitrate ratio in the organic phase is controlled by the chloride to nitrate ratio of the equilibrium aqueous phase and this aqueous phase ratio is different for each of the sets of results plotted on the diagram. Thus the proportion of amine salt present as the chloride differs for each set of results.

7.E. Variation of chloride concentration

7.E(i) Extraction from lithium chloride solutions

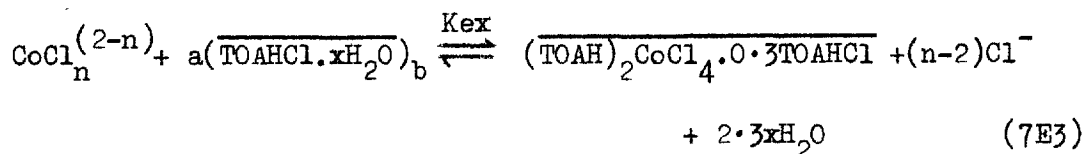
The generalised extraction equation for the extraction of cobalt by TOAHCl, which was developed in Section 7.C, is:



In the above equation, a , the number of molecules of the amine salt species involved in the extraction is related to b , the aggregation number of this species. The relationship between a and b depends on s , the number of amine salt molecules which solvate the organic metal complex, since:

$$s = a \cdot b - 2 \quad (7\text{E}2)$$

In Section 7.C it was shown that s is probably not variable and has a value of 0.3, which is independent of the organic metal concentration. Introducing this value of s into Equation (7E2) shows that the product of a and b has a value of 2.3. This information may be utilised in rewriting the extraction equation:



The **extractable** aqueous cobalt species has been written as $\text{CoCl}_n^{(2-n)}$, where n can take any value between 0 and 4, and will depend on the aqueous chloride concentration. It is not known whether a particular metal complex is extracted by TOAHCl, or whether all the aqueous metal species can be extracted by either adding or losing ligands during

extraction, so that in effect neutral CoCl_2 enters the organic phase. In the latter case, the dependency of the distribution coefficient on the ligand concentration will be expected to vary. The basis of this statement is developed in the following argument.

From Equation (7E3) the extraction equilibrium constant K_{ex} is given by:

$$K_{\text{ex}} = \frac{[(\text{TOAH})_2\text{CoCl}_4 \cdot 0.3(\text{TOAHCl})] \bar{\gamma}_c \cdot a_{\text{Cl}}^{(n-2)} \cdot a_{\text{H}_2\text{O}}^{2.3x}}{[\text{CoCl}_n^{(2-n)}] \gamma_n [(\text{TOAHCl} \cdot x\text{H}_2\text{O})_b]^a \bar{\gamma}_b^a} \quad (7E4)$$

where $\bar{\gamma}_c$ = activity coefficient of the organic metal complex.

$\bar{\gamma}_b$ = activity coefficient of the amine salt species.

γ_n = activity coefficient of the extractable aqueous metal complex.

$$\text{Assuming - } D_{\text{Co}} = \frac{[(\text{TOAH})_2\text{CoCl}_4 \cdot 0.3(\text{TOAHCl})]}{X_{\text{Co}}} \quad (7E5)$$

where : X_{Co} = equilibrium aqueous cobalt concentration.

From Equations (7E4) and (7E5) :

$$D_{\text{Co}} = \frac{K_{\text{ex}} [\text{CoCl}_n^{(2-n)}] \gamma_n [(\text{TOAHCl} \cdot x\text{H}_2\text{O})_b]^a \bar{\gamma}_b^a}{X_{\text{Co}} \cdot \bar{\gamma}_c \cdot a_{\text{Cl}}^{(n-2)} \cdot a_{\text{H}_2\text{O}}^{2.3x}} \quad (7E6)$$

$$\begin{aligned} \therefore \log D_{\text{Co}} &= \log K_{\text{ex}} + \log [\text{CoCl}_n^{(2-n)}] X_{\text{Co}}^{-1} + \log \gamma_n + a \log [(\text{TOAHCl} \cdot x\text{H}_2\text{O})_b] \\ &\quad + \log \bar{\gamma}_b^a \cdot \bar{\gamma}_c^{-1} - (n-2) \log a_{\text{Cl}} - 2.3x \log a_{\text{H}_2\text{O}} \end{aligned} \quad (7E7)$$

For conditions where the amine salt concentration in the organic phase is kept constant, and the organic metal concentration is very low, $\bar{\gamma}_b$ and $\bar{\gamma}_c$ may be assumed constant. Thus differentiating Equation (7E7) with respect to $\log a_{Cl}$ gives:

$$\frac{d \log D_{Co}}{d \log a_{Cl}} = \frac{d \log [CoCl_n^{(2-n)}] X_{Co}^{-1}}{d \log a_{Cl}} + \frac{d \log \gamma_n}{d \log a_{Cl}} + 2.3x \frac{d \log a_{H_2O}}{d \log a_{Cl}} - (n-2) \quad (7E8)$$

The first term on the right-hand side of Equation (7E8) may be simplified:

$$i) \quad [CoCl_n^{(2-n)}] = [Co^{2+}] \beta_n^* a_{Cl}^n$$

where β_n^* is the overall apparent equilibrium constant.

$$ii) \quad X_{Co} = [Co^{2+}] \sum_0^n \beta_n^* a_{Cl}^n$$

From (i) and (ii):

$$\log [CoCl_n^{(2-n)}] X_{Co}^{-1} = \log \beta_n^* + n \log a_{Cl} - \log \sum_0^n \beta_n^* a_{Cl}^n$$

$$\therefore \quad \frac{d \log [CoCl_n^{(2-n)}] X_{Co}^{-1}}{d \log a_{Cl}} = n - \bar{n} \quad (7E9)$$

where $\bar{n}$ = average ligand number which is given by :

$$\bar{n} = \frac{\sum_1^n \beta_n^* a_{Cl}^n}{\sum_0^n \beta_n^* a_{Cl}^n}$$

Substituting Equation (7E9) into (7E8) gives:

$$\frac{d \log D_{Co}}{d \log a_{Cl}} = \frac{d \log \gamma_n}{d \log a_{Cl}} + 2.3x \frac{d \log a_{H_2O}}{d \log a_{Cl}} + 2 - \bar{n} \quad (7E10)$$

Equation (7E10) gives the change in $\log D_{Co}$ with the log of the chloride activity for the situation where all of the aqueous metal species are extractable. The terms $\log \gamma_n$ and $\log a_{H_2O}$ will both change with $\log a_{Cl}$ but the differential functions in Equation (7E10) are likely to vary only slowly with $\log a_{Cl}$. Thus the major influence on $\log D_{Co}$ will be the change in $\bar{n}$ with $\log a_{Cl}$, and variations in $\bar{n}$ should be reflected by variations in the slope of $\log D_{Co}$ against $\log a_{Cl}$. This type of behaviour has been observed for the extraction of certain metals such as In^{77} , $Zn^{76,78}$, Ag^{79} and Cd^{76} from halide solutions by both tertiary amines and quaternary ammonium salts and also by anion-exchange resins.

In the cobalt-chloride system, $\bar{n}$ can vary from zero to four. Calculated values of $\bar{n}$ for cobalt in lithium chloride solutions are shown in Figure 4.11. These rise from zero to a value of 2.2 at 6M LiCl. This change in $\bar{n}$ should result in a change in the slope of $\log D_{Co}$ against $\log a_{Cl}$. However this is not the observed behaviour. In Figure 7.3, experimental values of $\log D_{Co}$, obtained for the extraction of trace quantities of cobalt ($2 \times 10^{-5}M$) from lithium chloride solutions, are plotted against $\log a_{Cl}$, where a_{Cl} is the effective chloride activity, given by $m_{LiCl} \cdot \gamma_{\pm LiCl}$. For the chloride concentration range investigated - 3.0 to 7.5M - $\log D_{Co}$ increases linearly with $\log a_{Cl}$, the slope of the line being 3.16. This slope is close to the value 3 previously reported by Venkateswarlu and Lal⁴⁷ for the extraction of cobalt from HCl solutions by both trihexylamine and trinonylamine.

From these results it is concluded that either the terms on the right-hand side of Equation (7E10) change fortuitously in relation to each other to maintain the observed constant dependency, or more probably, the basis of the analysis is wrong, for the system under consideration.

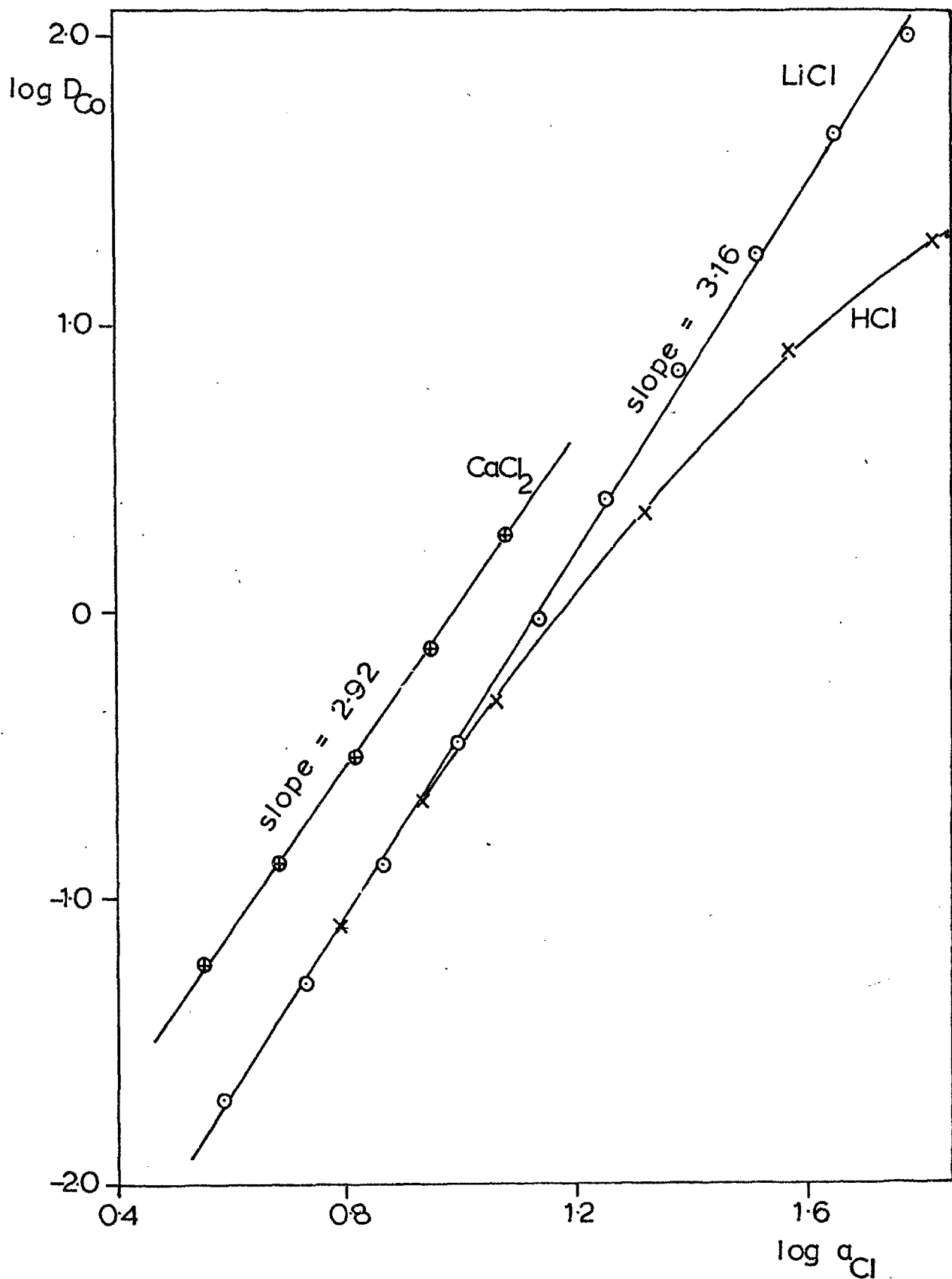


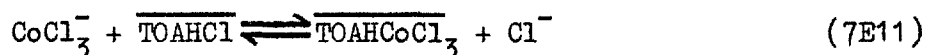
FIGURE 7.3 $\log D_{Co}$ AGAINST $\log a_{Cl}$ FOR VARIOUS CHLORIDE SOLUTIONS.

$$[TOAHCl] = 9.83 \times 10^{-2} M \quad [Co]_{total} = 2 \times 10^{-5} M$$

Data from Table 3.1.X.

Further information about the extraction mechanism in this system can be obtained by comparing the distribution data with the stability constant data given in Chapter 4. It was shown that only three cobalt species can be detected in LiCl solutions up to 6M, i.e. Co^{2+} , CoCl^+ and CoCl_3^- . The fractions of total cobalt contained in these three species, α_n , were calculated as a function of the total chloride concentration in Section 4.E(vi).

In order to compare the extraction data with the α_n values, the distribution coefficients obtained for the extraction of trace cobalt from LiCl solutions are plotted against aqueous chloride concentration in Figure 7.4, together with the α_n values calculated in Section 4.E(vi). It is evident that the beginning of extraction of cobalt into the organic phase coincides almost exactly with the beginning of the stability region of the trichlorocobalt complex, CoCl_3^- , in the aqueous phase. This strongly suggests that CoCl_3^- is the extractable metal species, at least for concentrations up to 6M chloride. At higher chloride concentrations other anionic metal complexes start to form and these may also be extractable. If CoCl_3^- is the extractable species, then the transfer of metal at the aqueous • organic interface can be envisaged as a simple bimolecular anion exchange of the anionic metal complex with an organic chloride ion:



This reaction is analogous to that which has been shown to describe the extraction of nitrate ions by TOAHCl - Equation (7A1). Following the transfer of CoCl_3^- , further reaction within the organic phase will lead to the formation of $(\text{TOAH})_2\text{CoCl}_4$.

In the following discussion, it is assumed that for aqueous chloride concentrations of 6M and below, the extraction of cobalt by TOAHCl is due to the transfer of CoCl_3^- ions from the aqueous to the organic phase.

Examination of Figure 7.4 shows that although values of D_{Co} and α_3 initially coincide, they rapidly diverge as the aqueous chloride is increased, with D_{Co} becoming larger than α_3 . The fraction of CoCl_3^- in the aqueous phase, α_3 , will be independent of the total aqueous cobalt concentration, providing this is small compared with the aqueous

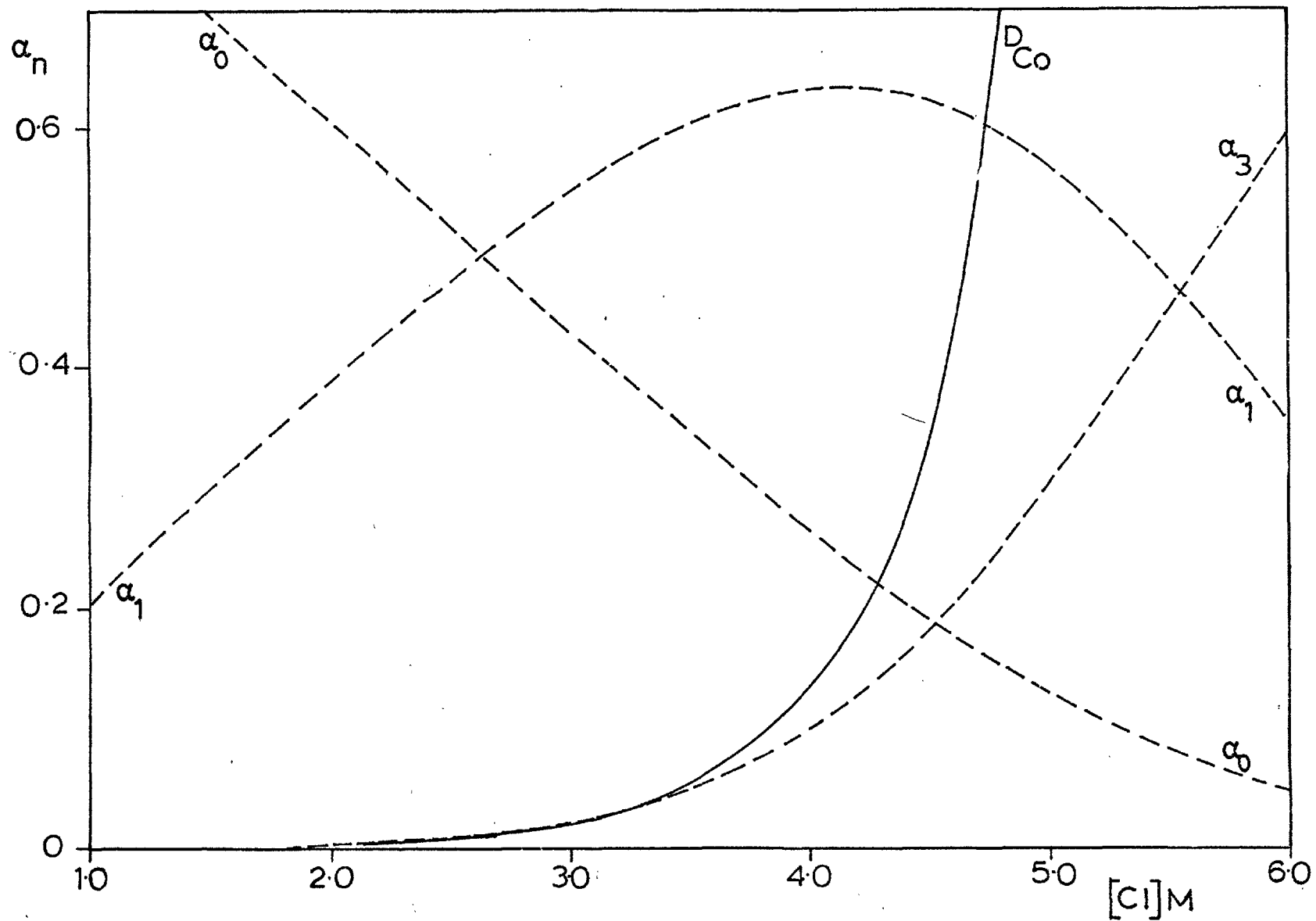


FIGURE 7.4 D_{Co} AND α_n AGAINST AQUEOUS CHLORIDE CONCENTRATION.

Data from Tables 3.1.X and 4.6.X.

chloride concentration. The data under consideration were obtained for the extraction of trace cobalt ($2 \times 10^{-5} \text{M}$) so this condition is met. If the metal complex behaved ideally in both phases then D_{Co} and α_3 should remain in a constant ratio, since:

$$D_{\text{Co}} = \frac{Y_{\text{Co}}}{X_{\text{Co}}} \quad \text{and} \quad \alpha_3 = \frac{[\text{CoCl}_3^-]}{X_{\text{Co}}}$$

At equilibrium the activities of the extractable species in each phase will be in a constant ratio, this ratio being the partition coefficient, P , of the extractable species. For ideal behaviour in both phases, the partition coefficient is equal to the ratio of the concentrations of the extractable species in each phase:

$$P = \frac{Y_{\text{Co}}}{[\text{CoCl}_3^-]}$$

Combination of the above expressions for D_{Co} , α_3 and P gives:

$$D_{\text{Co}} = P \cdot \alpha_3 \quad (7E12)$$

Apparent values of P were calculated from the data for D_{Co} (Table 3.1.X) and α_3 (Table 4.6.X), and the results are given in Table 7.2. It is evident that P is not constant. This indicates non-ideal behaviour of the extractable species in either one or both of the phases.

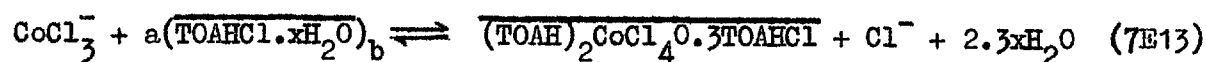
In the organic phase, since the concentration of the organic metal complex is very low for trace metal extraction, and the total amine concentration is held constant, the activity coefficient of the complex may be assumed constant. In the aqueous phase, the activity coefficients of the metal species will be controlled largely by the concentration of the bulk electrolyte, LiCl . Since the chloride concentration is the variable under investigation, the activity coefficient of CoCl_3^- in the aqueous phase is likely to vary. The criterion of equilibrium in a

Table 7.2. Apparent values of the partition coefficient P calculated from Equation (7E12). Data for the extraction of trace cobalt from LiCl solutions.

$[\text{LiCl}]_M$	D_{Co}	α_3	P
3.0	0.020	0.024	0.834
3.5	0.052	0.050	0.962
4.0	0.136	0.097	1.402
4.5	0.348	0.179	1.943
5.0	0.936	0.312	3.000
5.5	2.492	0.446	5.680
6.0	6.685	0.601	11.120

two-phase distribution system is that the ratio of the activities in each phase of the distributing species is constant. Hence, under conditions where the activity coefficient of the metal species in the organic phase remains constant, the equilibrium concentration of metal in the organic phase is a measure of the activity of the extractable metal species in the aqueous phase. The non-constancy of the apparent partition coefficient, P, can be attributed to non-ideal behaviour in the aqueous phase. Specifically, it can be attributed to variations in γ_3 with chloride concentration, where γ_3 is the activity coefficient of CoCl_3^- in the aqueous phase, since α_3 in Equation (7E12) is a measure of the concentration rather than the activity of this species. This argument can be quantified for extraction from LiCl solutions up to 6M, where values of α_3 are available.

The relevant extraction equation can be obtained by putting n equal to 3 in Equation (7E3):



The equilibrium constant for this reaction K_{ex} is given by an expression similar to Equation (7E4):

$$K_{\text{ex}} = \frac{[(\text{TOAH})_2\text{CoCl}_4 \cdot 0.3\text{TOAHCl}] a_{\text{Cl}}^{2.3x} a_{\text{H}_2\text{O}}^{2.3x} \bar{\gamma}_c}{[\text{CoCl}_3^-] \gamma_3 [(\text{TOAHCl} \cdot x\text{H}_2\text{O})_b]^a \bar{\gamma}_b^a} \quad (7E14)$$

This expression for K_{ex} may be simplified by introducing the terms D_{Co} and α_3 , since:

$$D_{\text{Co}} = \frac{[(\text{TOAH})_2\text{CoCl}_4 \cdot 0.3\text{TOAHCl}]}{X_{\text{Co}}} \quad \text{and} \quad \alpha_3 = \frac{[\text{CoCl}_3^-]}{X_{\text{Co}}}$$

$$\therefore K_{\text{ex}} = \frac{D_{\text{Co}} a_{\text{Cl}}^{2.3x} a_{\text{H}_2\text{O}}^{2.3x} \bar{\gamma}_c}{\alpha_3 [(\text{TOAHCl} \cdot x\text{H}_2\text{O})_b]^a \gamma_3 \bar{\gamma}_b^a} \quad (7E15)$$

Taking logs and rearranging the above expression gives:

$$\begin{aligned} \log \gamma_3 &= \log D_{\text{Co}} + \log a_{\text{Cl}} + 2.3x \log a_{\text{H}_2\text{O}} - \log \alpha_3 - \log K_{\text{ex}} \\ &\quad - a \cdot \log [(\text{TOAHCl} \cdot x\text{H}_2\text{O})_b] \bar{\gamma}_b + \log \bar{\gamma}_c \end{aligned} \quad (7E16)$$

For conditions where the amine salt concentration in the organic phase is kept constant, and where the organic metal concentration is very low, the last two terms on the right-hand side of Equation (7E16) can be assumed constant. Differentiating this equation with respect to the aqueous molal chloride concentration eliminates the constant terms

and gives an expression which relates the change in $\log \gamma_3$, the aqueous activity coefficient of CoCl_3^- to the change in the bulk chloride concentration:

$$\frac{d \log \gamma_3}{d m_{\text{Cl}}} = \frac{d (\log D_{\text{Co}} + \log a_{\text{Cl}} + 2.3x \log a_{\text{H}_2\text{O}} - \log \alpha_3)}{d m_{\text{Cl}}} \quad (7E17)$$

All terms of the function within parentheses on the right hand side of Equation (7E17) are known and thus the change of $\log \gamma_3$ with chloride concentration can be calculated. The results of these calculations for chloride concentrations up to 6M are given in Table 7.4.X. and plotted in Figure 7.5. Values of a_{Cl} and $a_{\text{H}_2\text{O}}$ used in these calculations were assumed equal to those for pure LiCl^2 solutions, since only trace quantities of cobalt were present, and values of x , the degree of hydration of amine hydrochloride, were obtained from Figure 5.3. Examination of Figure 7.5 shows that the change in the bracketed function in Equation (7E17) with aqueous chloride concentration is approximately represented by a straight line with a slope of 0.47. From the above equation, it is evident that this is also the behaviour of $\log \gamma_3$ with chloride concentration, i.e.

$$\frac{d \log \gamma_3}{d m_{\text{Cl}}} = 0.47$$

Integration of this expression gives:

$$\log \gamma_3 = C + 0.47 m_{\text{Cl}} \quad (7E18)$$

This equation shows that the log of the activity coefficient of trace quantities of CoCl_3^- is a linear function of the concentration of the bulk electrolyte, lithium chloride. The equation also shows that γ_3 increases very rapidly with lithium chloride concentration, since an increase of m_{Cl} by 2 molal units leads to approximately an order of

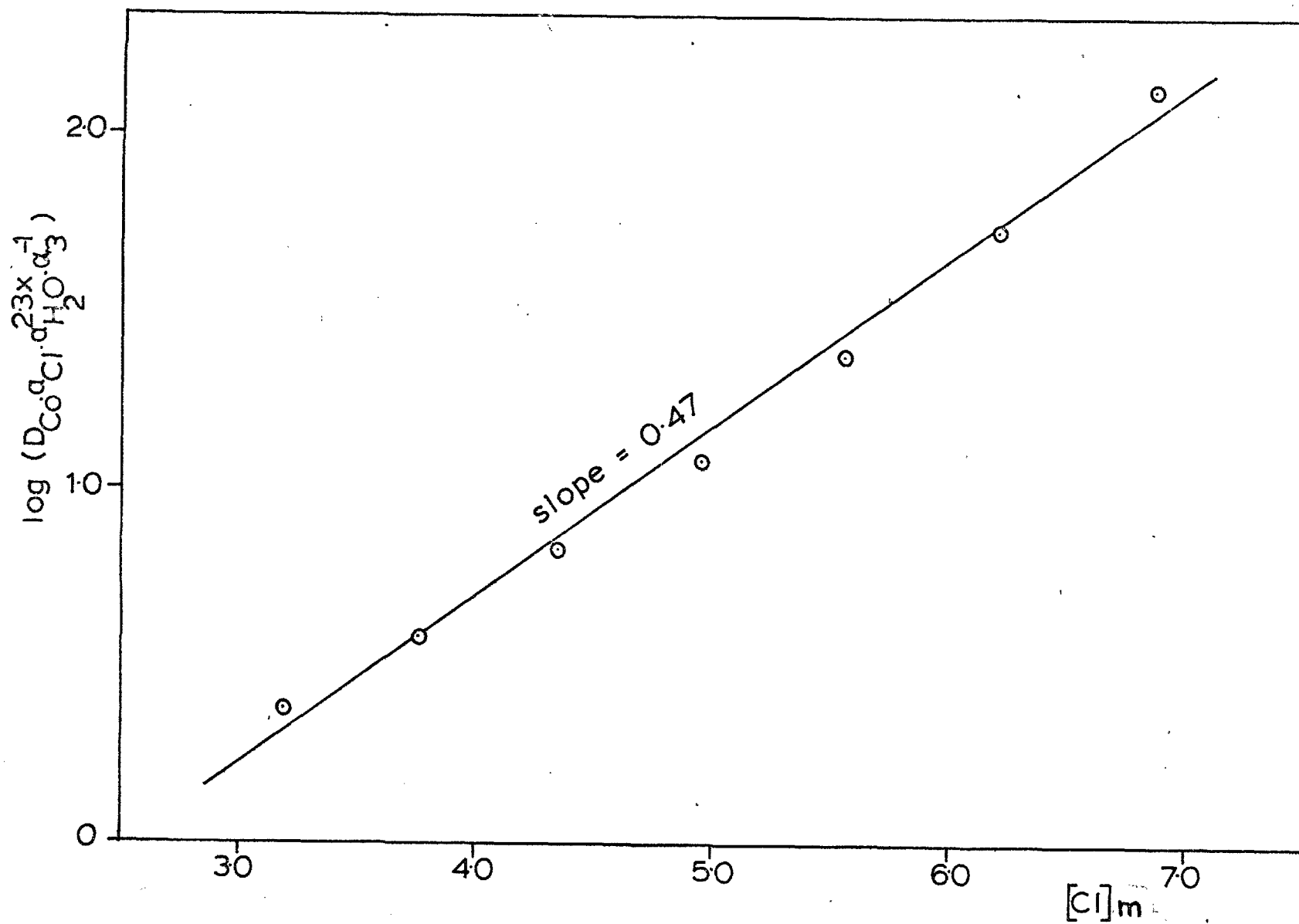


FIGURE 7.5 PLOT OF EQUATION (7E17)

Data from Table 7.4.X.

magnitude increase in γ_3 . In a study of the activities of NiCl_2 and CoCl_2 in hydrochloric acid solutions by vapour pressure techniques, Moore and co-workers⁸⁰ noted an "enormous increase in the salt activity in the acid solutions relative to that in aqueous solutions." An example quoted was for 1m NiCl_2 in 6.86m HCl , where the salt activity was ca. 10^5 as great as it was in water. Because of complex formation, Moore was unable to quantify his results for CoCl_2 in HCl , so a direct comparison with the present work is not possible. It is interesting to note, however, that an equation derived by Moore to describe the behaviour of the mean activity coefficient of HCl in mixed nickel chloride - hydrochloric acid solutions, bears a close resemblance to Equation (7E18):

$$\log \gamma_{\pm\text{HCl}} = B + 0.45m_{\text{NiCl}_2}$$

where $B = \log \gamma_{\pm}$ for HCl at zero concentration in NiCl_2 at the same ionic strength as the mixture.

Although the lack of information on activity coefficients in transition metal chloride - alkali metal chloride systems precludes direct justification of Equation (7E18), by using certain well proved empirical relationships, it may be shown that an equation of this form may be expected to apply. To do this, it is assumed that the system can be considered as a mixture of lithium chloride and trace quantities of the hypothetical 1:1 electrolyte $\text{Li}^+\text{CoCl}_3^-$. The empirical relationship, known as Harned's Rule⁷¹, describes the behaviour of the mean activity coefficients of many binary mixtures of electrolytes. For a mixture of electrolytes A and B, Harned's Rule states that:

$$\log \gamma_{A(B)} = \log \gamma_{A(0)} - \alpha_{A^mB} \quad (7E19)$$

where: $\gamma_{A(B)}$ = mean activity coefficient of salt A in a mixture of A and B of total molality m .

$\gamma_{A(0)}$ = mean activity coefficient of A in its own solution of molality m .

$$\begin{aligned}\alpha_A &= \text{empirical coefficient,} \\ m_B &= \text{molality of salt B in the mixture.}\end{aligned}$$

For trace quantities of A in B, Equation (7E19) reduces to :

$$\log \gamma_{A(B)} = \log \gamma_{A(0)} - \alpha_A m \quad (7E20)$$

where m , the total molality of the solution, is equal to m_B , the molality of B.

In the system under consideration, salt A will be the hypothetical electrolyte LiCoCl_3 . Thus $\log \gamma_{A(0)}$ is the mean activity coefficient of LiCoCl_3 in its own solution at molality m . This of course is unknown. However if it is assumed that this hypothetical electrolyte would behave similarly to many other electrolytes at high concentrations, then its mean activity coefficient should obey the empirical relationship:

$$\log \gamma_{\pm} = P + Qm \quad (7E21)$$

This equation was discussed in Section 4.B - Equation (4B7). It states that in concentrated solutions, the log of the mean activity coefficient of an electrolyte is a linear function of its molal concentration.

Substituting $\log \gamma_{\pm}$ for $\log \gamma_{A(0)}$ in Equation (7E20) gives:

$$\log \gamma_{A(B)} = P + (Q - \alpha_A)m \quad (7E22)$$

Equation (7E22) thus describes the behaviour of the mean activity coefficient of trace quantities of LiCoCl_3 in the bulk electrolyte LiCl . Comparison of this equation with Equation (7E18) shows that they are of the same form, as required. It should be noted that γ_z in Equation (7E18) is a single ion activity coefficient, whereas $\gamma_{A(B)}$ is a mean ion activity

coefficient. However this discrepancy is overcome by the fact that for 1:1 electrolytes it is conventional to equate the single ion and the mean ion activity coefficients. By equating coefficients of m in the two equations:

$$Q - \alpha_A = 0.47$$

If Q is assumed to be approximately 0.2, a typical value for several chloride electrolytes, then α_A , the Harned's coefficient for LiCoCl_3 in LiCl becomes approximately -0.27. The reasonableness of this value is difficult to judge, since it is based on a hypothetical situation. The only reported Harned's coefficients for systems containing transition metal chlorides are for mixtures with HCl ⁷². For the system $\text{CdCl}_2 - \text{HCl}$, $\alpha_{\text{HCl}} = 0.18$, for $\text{NiCl}_2 - \text{HCl}$, $\alpha_{\text{HCl}} = 0.13$, and for $\text{ZnCl}_2 - \text{HCl}$, $\alpha_{\text{HCl}} = 0.069$. Since in a mixture of salts A and B, α_A and α_B are empirically found to be generally of the same magnitude but of opposite sign, the value of approximately -0.27 found above is possibly reasonable, both in magnitude and sign.

It may be concluded that the preceding argument shows that the extraction of trace quantities of cobalt from lithium chloride solutions up to 6M by trioctylamine hydrochloride can be considered as an equilibrium reaction involving the extraction of the aqueous species CoCl_3^- , providing that the effects of changes in the concentration of the bulk electrolyte on the activity coefficient of this species, γ_3 , are taken into account. Because of the unknown constant of integration, C , in the equation for $\log \gamma_3$ (Equation (7E18)), it is not possible to calculate numerical values of γ_3 . This unknown factor also prevents calculation of the extraction equilibrium constant K_{ex} .

The preceding analysis is valid only for LiCl concentrations of up to 6M, since values of α_3 are not available for concentrations greater than this. However examination of Figure 7.3 shows that the slope of $\log D_{\text{Co}}$ against $\log a_{\text{Cl}}$ remains constant at least up to 7.5M LiCl , the highest concentration examined in this investigation. This may be an indication that the extraction reaction remains unchanged up to 7.5M LiCl . Aqueous solutions with this chloride concentration probably contain appreciable quantities of CoCl_4^{2-} , which may also be extractable by TOAHCl . Extraction of this species as well as CoCl_3^- would be expected

to cause a change in the slope of $\log D_{Co}$ against $\log a_{Cl}$. However in view of the apparent extreme sensitivity of the activity coefficients of the metal complexes to the bulk chloride concentration, small changes in the slope of the line, due to a gradual change in the extraction reaction, may be masked by gross changes in the aqueous activity coefficients.

7.E(ii) Extraction from calcium chloride solutions

The results for the extraction of trace cobalt from calcium chloride solutions are plotted as $\log D_{Co}$ against $\log a_{Cl}$ in Figure 7.3, where a_{Cl} , the effective chloride activity of calcium chloride is given by:

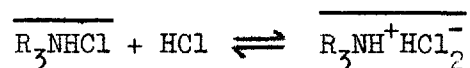
$$2m_{CaCl_2} \cdot \gamma_{\pm CaCl_2}$$

The results lie on a straight line with a slope of 2.92. The similarity of this slope with that obtained for extraction from lithium chloride solutions indicates that the extraction reaction is probably the same in both systems. This similarity of slopes is further evidence against the co-extraction of the bulk cation with cobalt. If Li^+ in the one case, and Ca^{2+} in the other, were co-extracted with cobalt, then the slopes of the lines in Figure 7.3 would be expected to differ, due to the difference in valency between these two cations.

The distribution coefficients for extraction from calcium chloride solutions are larger than those from lithium chloride solutions of equal effective chloride activity. This may be due to a specific ion effect in which the presence of calcium ions may increase the stability constants of the cobalt chlorocomplexes relative to those in the presence of lithium ions. This type of effect has been reported for the chlorocomplexes of cadmium⁷³ and of lead⁷⁴ as the cation of the bulk chloride salt is changed. In addition to causing an increase in the stability constants, changing the bulk cation may also increase the activity coefficients of the metal complexes. Both these effects would lead to an enhanced extraction of cobalt.

7.E(iii) Extraction from hydrochloric acid solutions

Up to a concentration of about 4M, values of $\log D_{\text{Co}}$ for the extraction of trace cobalt from hydrochloric acid solutions coincide with those obtained from lithium chloride solutions, when plotted against the log of the effective chloride activity. This again indicates a similar extraction reaction for both systems. As shown in Figure 7.3, at concentrations greater than 4M, extraction of cobalt from HCl is less than from LiCl. This phenomenon, known as the "hydrochloric acid effect" occurs in many metal chloride - amine extraction systems. It is generally attributed to preferential extraction of excess hydrochloric acid instead of the metal complex by the amine salt, resulting in the formation of amine hydrogen dichloride.



The effect has been studied in detail for the extraction of cobalt from HCl by trihexylamine by Good and co-workers⁴². They showed that the characteristic infra-red absorption of the HCl_2^- ion was exhibited by amine hydrochloride solutions containing excess hydrochloric acid. They concluded that the decreased extraction of cobalt from HCl solutions compared with LiCl solutions was largely due to the preferential formation of the amine hydrogen dichloride. They did not rule out the formation of non-extractable halo-acid complexes such as HCoCl_4^- and H_2CoCl_4 in concentrated acid solutions. However they pointed out that if these were the cause of the decreased extraction, then the same decrease in extraction should be observed for extraction by quaternary ammonium chlorides. In practice, these salts, which extract more excess HCl than the tertiary salts, show a greater decrease in extraction of cobalt.

Bertocci and Rolandi⁶² have shown that solutions of trioctylamine in xylene begin to dissolve HCl in excess of that required for formation of the stoichiometric amine hydrochloride when the aqueous acid concentration is greater than 3.5M. This corresponds well to the acid concentration at which the curves for extraction from HCl and LiCl shown in

Figure 7.3 begin to diverge.

The data of Bertocci and Rolandi can be used to show quantitatively that the decrease in extraction observed from HCl solutions in this study can be accounted for entirely by the formation of amine dichloride, on the assumption that this species does not take part in the extraction. This is done by adjusting the observed $\log D_{Co}$ values in HCl by a correction factor, which allows for the amount of amine in the non-reactive dichloride form, and showing that the adjusted $\log D_{Co}$ values are very close to those obtained from LiCl solutions of equal chloride activity.

It has been shown in Section 7.D that, for conditions where the aggregation in the organic phase remains constant, D_{Co} varies with the concentration of free amine hydrochloride to the power 2.3, i.e.

$$\log D_{Co} = \log k + 2.3 \log [\overline{TOAHCl}]_{free}$$

where k is a proportionality constant.

Thus for two different free amine hydrochloride concentrations, (1) and (2), the $\log D_{Co}$ values are related by:

$$\log D_{Co(2)} = \log D_{Co(1)} + 2.3(\log [\overline{TOAHCl}]_{free(2)} - \log [\overline{TOAHCl}]_{free(1)}) \quad (7E23)$$

If the aggregation in the organic phase is assumed constant in the presence of amine dichloride, then Equation (7E23) will apply, and can be used to adjust the observed $\log D_{Co}$ values to allow for the effect of dichloride formation. Dichloride formation is assumed to reduce the concentration of free amine hydrochloride available for extraction.

Thus :

$$[\text{TOAHCl}]_{\text{free}} = [\text{TOAHCl}]_{\text{total}} - [\text{TOAH}_2\text{Cl}_2] \quad (7E24)$$

The concentration of amine dichloride in the organic phase, $[\text{TOAH}_2\text{Cl}_2]$, was obtained by interpolation from Bertocci and Rolandi's data for the proportion of excess HCl in the organic phase as a function of aqueous acid concentration for 0.1M TOA in xylene. It was assumed that excess acid in the organic phase, $[\text{HCl}]_{\text{xs}}$, was present as the amine dichloride, i.e.

$$[\text{HCl}]_{\text{xs}} = [\text{TOAH}_2\text{Cl}_2] \quad (7E25)$$

Using Equations (7E24) and (7E25), the concentration of free amine hydrochloride can be obtained as a function of the equilibrium aqueous phase acid concentration. The observed $\log D_{\text{Co}}$ values can then be corrected to give values which would be obtained in the absence of amine dichloride formation. The equation used for this correction is analogous to Equation (7E23):

$$\log D_{\text{Co}(\text{corr})} = \log D_{\text{Co}(\text{obs})} + 2.3(\log[\text{TOAHCl}]_{\text{total}} - \log[\text{TOAHCl}]_{\text{free}}) \quad (7E26)$$

where $[\text{TOAHCl}]_{\text{free}}$ is given by Equation (7E24).

Values of $\log D_{\text{Co}(\text{corr.})}$ are given in Table 7.3 together with $\log D_{\text{Co}(\text{LiCl})}$ values, which are those observed for extraction from LiCl solutions with effective chloride activities equal to the corresponding HCl solutions. Good agreement between the two sets of results is observed, indicating that the decreased extraction of cobalt from HCl solutions can be accounted for entirely by formation of amine dichloride in the organic phase, which does not extract the metal.

Table 7.3 Adjusted values of $\log D_{Co}$ for extraction from HCl solutions, using Equation (7E26).

$[HCl]$ (M)	$[HCl]_{xs}^*$ (M)	$[TOAHCl]_{free}^{**}$ (M)	$\log D_{Co(obs)}$	$\log D_{Co(calc)}$	$\log D_{Co(LiCl)}$
3.5	0	0.098	-1.111	-1.111	-1.10
4.5	0.012	0.086	-0.320	-0.189	-0.20
5.5	0.027	0.071	0.352	0.672	0.62
6.5	0.042	0.056	0.910	1.471	1.42
7.5	0.058	0.040	1.270	2.167	2.20

*From Reference 62, Table 3.

**From Equations (7E24) and (7E25).

7.F. Extraction from mixed lithium chloride - lithium nitrate solutions

The distribution coefficients obtained for the extraction of cobalt from two series of solutions containing mixtures of lithium chloride and lithium nitrate at constant total molarities of 6.5M and 7.5M respectively are shown as a function of aqueous chloride concentration in Figure 3.2. These results are replotted against the log of the effective chloride activity in the mixed solutions* in Figure 7.6. Also plotted in this figure are the results obtained for the extraction of trace cobalt from solutions containing only lithium chloride. It is evident that for

*Calculations of effective chloride activities in $LiCl-LiNO_3$ solutions are given in Appendix 1.

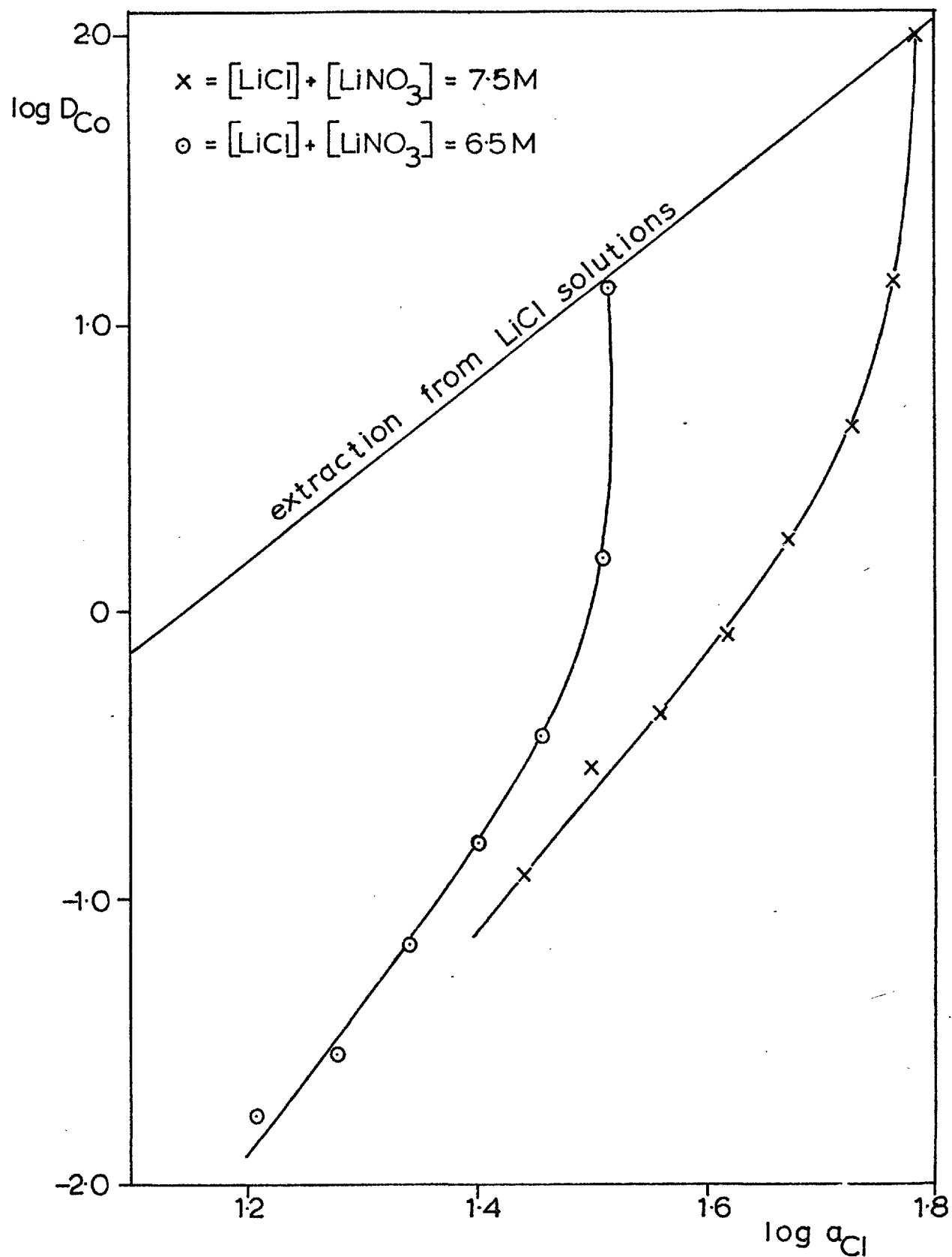


FIGURE 7.6 $\log D_{\text{Co}}$ AGAINST $\log a_{\text{Cl}}$ FOR $\text{LiCl} - \text{LiNO}_3$ SOLUTIONS.

$$[\text{TOAHX}] = 9.83 \times 10^{-2} \text{M} \quad [\text{Co}]_{\text{total}} = 9.60 \times 10^{-4} \text{M}$$

Data from Table 3.2.X

a given chloride activity, extraction from the mixed solutions is less than from lithium chloride solutions.

It has been shown that trioctylamine extracts nitrate ions in preference to chloride ions. It can be postulated that the decrease in the extraction of cobalt from the mixed solutions is due to the partial conversion of the amine hydrochloride to the nitrate form, the amine nitrate being unlikely to extract the cobalt chlorocomplex. In Figure 7.7 the $\log D_{Co}$ values obtained in the mixed solutions, are plotted against the log of the concentration of amine hydrochloride that is in equilibrium with each chloride - nitrate aqueous solution, given in Table 7.2.X. The results lie on two almost parallel straight lines of slopes 2.53 and 2.50. Each line represents extraction from a series of mixed solutions of constant total molarity. Thus, by experiment, D_{Co} varies with the concentration of the amine hydrochloride to the power 2.5. This value is close to the value 2.3 obtained in Section 7.D for variation of D_{Co} with free amine hydrochloride and also shown to apply in Section 7.C for variations in total amine concentration when aggregation is taken into account. At first sight it would appear that the value 2.5 obtained here is a further manifestation of the solvation of the organic metal complex. However there is a significant difference between the present results and those previously discussed. This is that the chloride concentration, and thus the chloride activity, of the mixed solutions in each series is varied, although the total electrolyte concentrations of the solutions in each series are kept constant by replacement of the chloride with nitrate. Under these circumstances it would be expected that the decrease in the extraction of cobalt from the mixed solutions would be caused by two effects: firstly, a decrease in the equilibrium concentration of amine hydrochloride in the organic phase due to preferential extraction of nitrate; and secondly, a decrease in the concentration of the extractable aqueous cobalt chlorocomplex as the chloride concentration of the aqueous phase is reduced.

In Figure 7.7, the vertical dotted line is drawn at the Y_{Cl} value which corresponds to all the amine being in the hydrochloride form. This situation occurs when extraction is carried out from solutions containing lithium chloride only. Also plotted on this diagram are the $\log D_{Co}$ values obtained for extraction from lithium chloride solutions of concentrations 6.5 and 7.5M. These points lie on the dotted line. They also happen to lie on the extrapolations of the lines passing

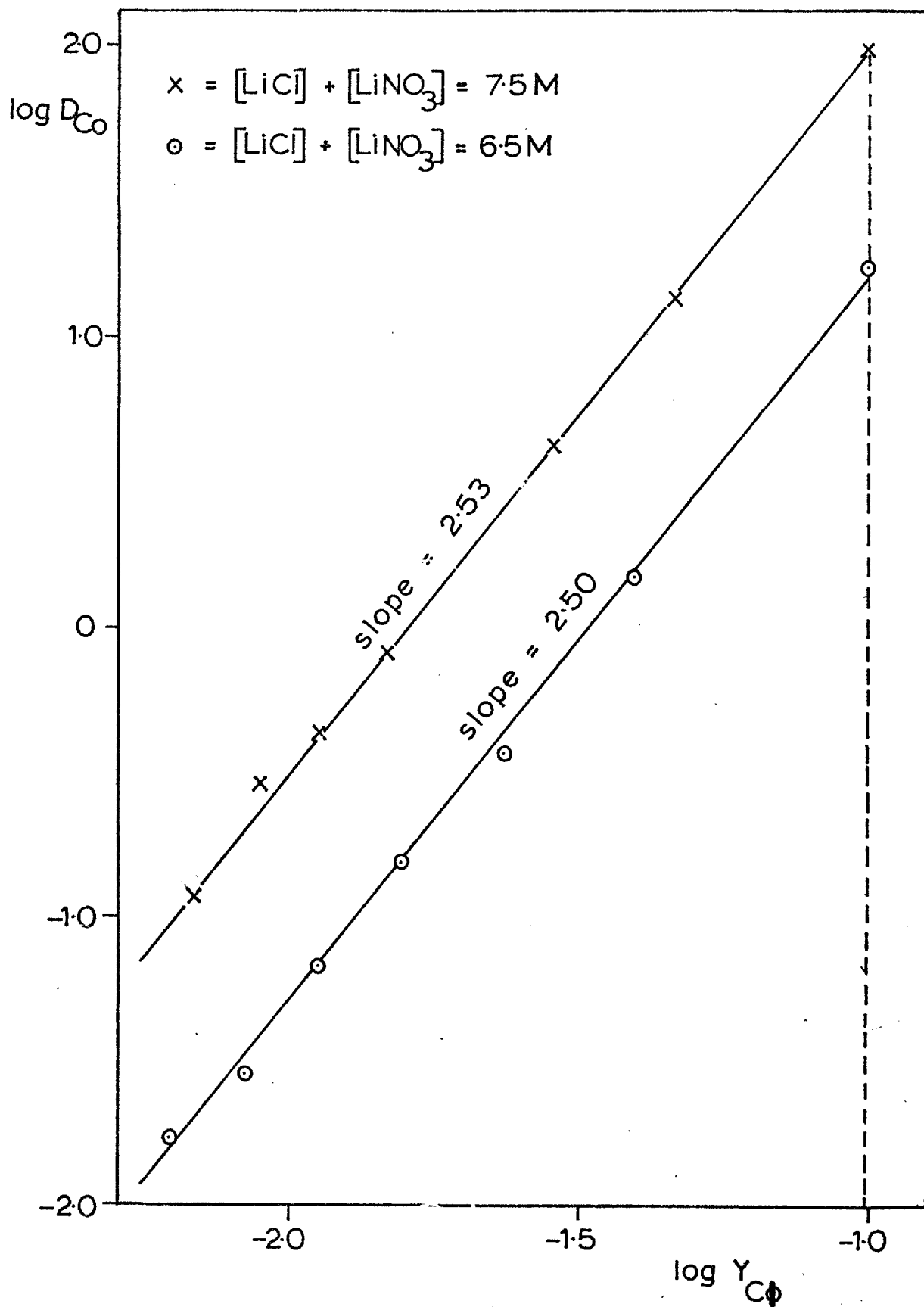


FIGURE 7.7 $\log D_{\text{Co}}$ AGAINST $\log Y_{\text{Cl}}$ FOR EXTRACTION FROM $\text{LiCl} - \text{LiNO}_3$ SOLUTIONS.

$$[\text{TOAHX}] = 9.83 \times 10^{-2} \text{ M} \quad [\text{Co}]_{\text{total}} = 9.60 \times 10^{-4} \text{ M}$$

Data from Tables 3.2.X and 7.2.X.

through the $\log D_{Co}$ values obtained from the mixed solutions. This is interpreted to mean that in the hypothetical situation where nitrate was not extracted by the amine, then the distribution coefficients of cobalt from lithium chloride - lithium nitrate solutions of constant total molarity would be equal to those obtained from solutions containing only lithium chloride, at concentrations equal to the total molarities of the mixed solutions. This conclusion is surprising and requires examination. Assuming the extractable species is $CoCl_3^-$, then the concentration of this species in a solution containing, say, 5.5M lithium chloride and 2.0M lithium nitrate, would be expected to be different from a solution containing an equal total molarity, 7.5M, of lithium chloride. The chloride activity of the latter would be larger and thus this solution would be expected to contain a greater proportion of the higher chlorocomplexes than the former solution, providing the stability constants of the complexes in the two types of solution were not significantly different. However the argument given above leads to the conclusion that the activity of the extractable cobalt chlorocomplex in two such solutions must be equal, since the D_{Co} value for the hypothetical situation where nitrate is not extracted by the amine from the mixed aqueous solution, is equal to the D_{Co} value obtained from the chloride only solution. Thus the activity of the extractable metal complex appears to be controlled by the total molar concentration of the solution rather than the chloride concentration or activity. This can be explained by an increase in the activity coefficient of the $CoCl_3^-$ ion in the aqueous phase, as $LiCl$ is replaced by $LiNO_3$, which compensates for the decrease in the concentration of this complex which occurs as the chloride concentration is decreased. The rise in the activity coefficient apparently maintains the activity of this complex at a constant value. This effect may be regarded as a "salting out" of the metal from the aqueous phase due to the addition of the second electrolyte. If it were not for the fact that nitrate is preferentially extracted by the amine, to form the apparently non-reactive amine nitrate salt, the distribution coefficients of cobalt would be expected to be greater from solutions containing $LiCl$ plus additional $LiNO_3$, compared with those containing $LiCl$ only.

7.G. Extraction from mixed chloride - sulphate solutions

The activity effects discussed in the preceding section indicated that enhanced extraction of cobalt should be observed from solutions containing a second electrolyte having an anion which was not preferentially extracted by the amine. It has been shown that the sulphate ion is less extractable than the chloride ion by tertiary amines^{1,75}. Since sulphate solutions are of great importance in hydro-metallurgical processes, some experiments were carried out to determine whether the addition of sulphate salts would increase the extraction of cobalt from chloride solutions by TOA.

In one series of experiments, lithium sulphate was added to solutions containing 4.0M HCl and 2×10^{-5} M cobalt chloride. It was found that $\log D_{Co}$ increased linearly with the molar concentration of added lithium sulphate. The results are shown in Figure 7.8. (Table 3.6.X). The observed rise in the distribution coefficients is attributed to two effects, both caused by the presence of the second electrolyte in the chloride solutions: firstly, an increase in the chloride ion activity, which leads to an increase in the concentration of the extractable complex, assuming extraction of $CoCl_3^-$; secondly, an increase in the activity coefficient of this species.

Having demonstrated the beneficial effects of the addition of sulphate, a second series of experiments was carried out on solutions prepared to simulate purified leach liquors. The solutions contained 0.0678M $CoSO_4$, 0.933M $NiSO_4$ and various concentrations of HCl, ranging from 1 to 6M. The $\log D_{Co}$ values for these solutions are plotted in Figure 7.9 against the molar concentration of hydrochloric acid. Also plotted on this diagram are results for solutions containing only 0.0678M $CoSO_4$ and similar amounts of hydrochloric acid. The distribution coefficients are higher in the presence of nickel sulphate, which acts as a salting-out agent for the cobalt extraction. The decrease in slope of the lines in Figure 7.8, at high acid concentrations, is due mainly to the fact that the amine is approaching full loading. Similar effects have been reported by Brooks and Rosenbaum³⁸ who noted that the addition of sodium sulphate to solutions containing nickel and cobalt chlorides improved the extraction of cobalt by tri-iso-octylamine.

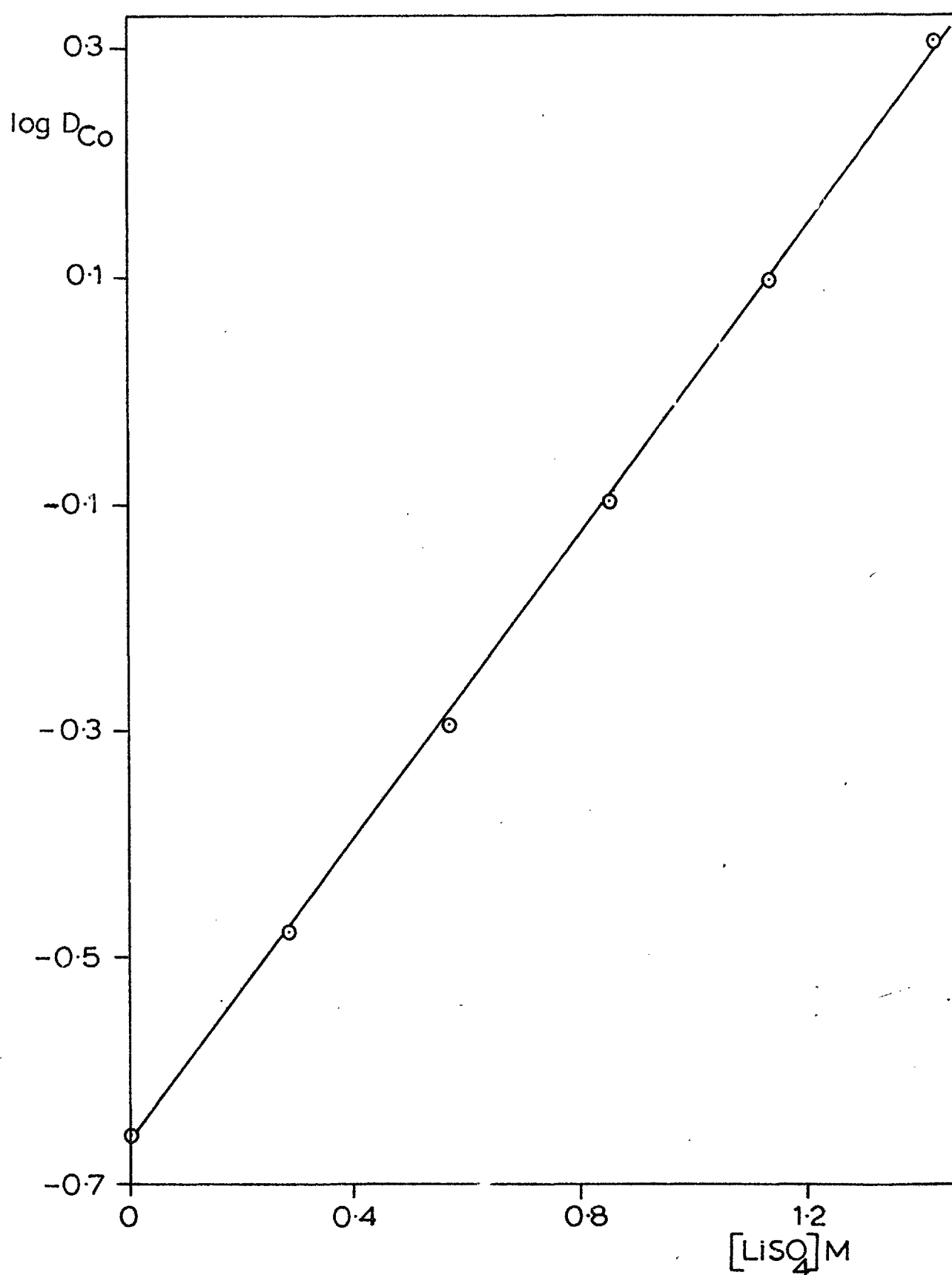


FIGURE 7.8 EFFECT OF LiSO₄ ON THE EXTRACTION OF COBALT FROM HYDROCHLORIC ACID.

$[\text{TOAHCl}] = 9.83 \times 10^{-2} \text{ M}$ $[\text{Co}] = 2 \times 10^{-5} \text{ M}$ $[\text{HCl}] = 4.0 \text{ M}$

Data from Table 3.6.X.

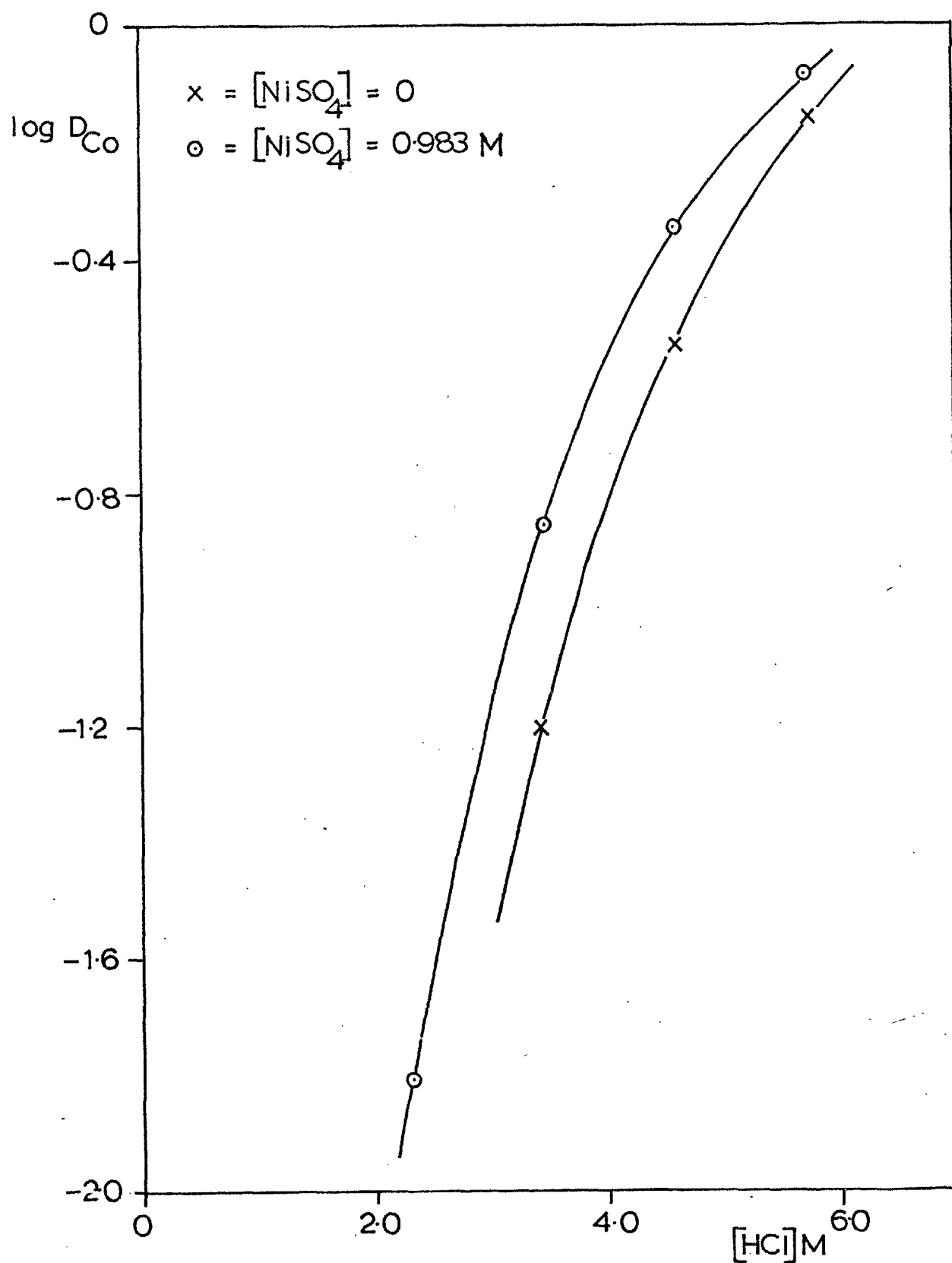


FIGURE 7.9 EFFECT OF NiSO_4 ON THE EXTRACTION OF COBALT FROM HYDROCHLORIC ACID.

$$[\text{TOAHCl}] = 9.83 \times 10^{-2} \text{ M} \quad [\text{CoSO}_4] = 6.78 \times 10^{-2} \text{ M}$$

Data from Table 3.7.X.

These demonstrations of enhanced extraction in the presence of sulphate are considered to be of practical importance when considering the application of amine extraction to cobalt - nickel separations. Sulphate is present in many leach liquors and electrolysis solutions and can have a beneficial effect on the extraction of cobalt.

7.H. General Observations

The use of slope analysis to establish reaction mechanisms in metal extraction systems has come under increasing criticism recently^{28,86,87}. In the case of extraction by amines and quaternary ammonium salts, much of the criticism has been engendered by interpretations which have utilised slope analysis indiscriminately, without taking into account the non-ideal behaviour exhibited by these salts in many solvents.

It is considered that slope analysis has been used with some success in this investigation, and the following are some observations about its application to amine systems.

The validity of slope analysis depends on the applicability of the law of mass action to the system under consideration. Since most metal extraction reactions are reversible equilibria, the law of mass action will apply, providing the activities of the reactants and products are known or can be obtained. In many extraction systems it is possible to avoid the difficulties of activity measurements by firstly, maintaining a constant ionic strength in the aqueous phase and then assuming constant aqueous activity coefficients, and secondly, assuming ideal behaviour of solutes in the organic phase.

In amine extraction systems, only exceptionally can either of the above assumptions be used. Generally high anion concentrations in the aqueous phase are required to bring about metal extraction. This makes impracticable the application of the constant ionic strength method. In the organic phase it is known that, in many diluents, amine salts behave non-ideally in that they aggregate to form polymeric species. Thus slope analysis in this type of system has to be applied with some care.

Many investigations of amine extraction have utilised the slope of $\log D_M$ against $\log [\overline{R_3NHX}]_{total}$ to establish the charge on the metal complex in the organic phase. Very often the result obtained is not in agreement with spectral and other data for the organic metal complex. In this investigation it has been possible to rationalise the observed slopes of $\log D_{Co}$ against $\log [\overline{TOAHCl}]_{total}$ in terms of extraction by either (or both) the monomer or the dimer of the amine salt. However this rationalisation required a knowledge of:

- i) the change in concentration of the various amine salt species in the organic phase as the total amine salt concentration was varied;
- ii) the charge on the metal complex in the organic phase;
- iii) the number of excess amine salt molecules associated with the metal complex.

Without this type of information, because of the variations in aggregation and, possibly, in solvation, the interpretation of results obtained under conditions of varying amine salt concentration seems fraught with difficulties.

On the other hand, for conditions where the amine salt concentration is held constant, the behaviour of solutes in the organic phase appears to be surprisingly simple. There are several examples in this work where the organic phase exhibited pseudo-ideal behaviour, in spite of gross changes in the composition of the phase. For example, the chloride - nitrate exchange reaction was successfully interpreted by the mass action law by assuming equality of the activity coefficients of the chloride and nitrate salts of amine, and taking into account only changes in the activity coefficients of the aqueous ions. Under the conditions of the experiments up to 90% of the chloride in the organic phase was replaced by nitrate. In spite of the considerable difference in aggregation behaviour exhibited by these two salts individually, they appear to behave similarly when mixed. A similar effect was observed by Lindenbaum and Boyd⁸⁴ for the extraction of trace quantities of bromide from alkali metal chloride solutions by TOAHCl in benzene. By using the assumption of equal activity coefficients in the organic phase, they also were able to quantify their results for the extraction of bromide in terms of non-ideal behaviour of the aqueous phase only.

A second example in this work of pseudo-ideal behaviour in the organic phase is that of solutions containing the amine hydrochloride and the organic metal complex. The results discussed in Section 7.D suggest that the aggregation of the free amine hydrochloride is unaffected when up to 50% of the total salt is bound in the organic metal complex.

The implication of all these results is that at a constant amine salt concentration, the aggregation in the organic phase is determined by the total salt concentration, rather than the chemical nature of the species present. This type of behaviour has been observed experimentally in mixtures of trilaurylamine salts. Orlandini and co-workers⁸⁵ have shown that the average aggregation numbers for solutions of trilaurylamine perchlorate in benzene, obtained by vapour pressure osmometry, are also obtained in solutions where up to 50% of the perchlorate salt is replaced by the chloride salt. Thus it appears that, over certain composition ranges, the structure of the organic phase is determined by one component of the mixed amine salt solute, and that the other component arranges itself to keep the overall aggregation constant.

An equilibrium study such as the present one cannot be expected to provide conclusive evidence about the path of a reaction. Nevertheless, there is strong circumstantial evidence which suggests that the extraction of cobalt occurs by transfer of the uninegative trichlorocobaltous ion, CoCl_3^- , from the aqueous to the organic phase. Preferential extraction of the monovalent complex anion by TOA is quite feasible, since, in the case of extraction of simple anions, all tertiary amines extract monovalent anions more strongly than polyvalent anions such as sulphate and phosphate. By analogy with the Cl-NO_3 system, the anomalous slope obtained for $\log D_{\text{Co}}$ against $\log a_{\text{Cl}}$ was interpreted in terms of non-ideal behaviour in the aqueous phase. Pseudo-ideality of the organic phase was assumed, since constant amine salt concentrations were used. This interpretation enabled the change in γ_3 , the aqueous activity coefficient of CoCl_3^- , to be calculated as a function of the bulk chloride concentration of the aqueous phase. It was shown that γ_3 increases very rapidly with chloride concentration. There is a small amount of evidence in the literature which supports the concept of a rapid rise in the activity coefficients of the aqueous cobalt species. The work of Moore and co-workers⁸⁰ has already been quoted in Section 7.E(i). Additional evidence is provided by an early polarographic investigation of cobalt

in calcium chloride solutions⁹¹. The large rise observed in the cathodic deposition potential of cobalt from concentrated calcium chloride solutions was explained in terms of a large increase in the activity of cobalt ions in these solutions.

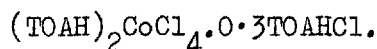
If the above interpretation of the extraction mechanism is indeed correct, it indicates that, for metal-ligand systems where the distribution of the metal amongst its various complexes in the aqueous phase is known, amine extraction, using trace quantities of the metal, may be a method of gaining information about the activity coefficients of at least the anionic metal complexes.

C H A P T E R 8

CONCLUSIONS

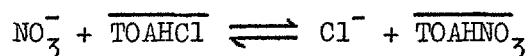
1. Analysis of extinction coefficient data, obtained from solutions containing cobaltous ions and lithium chloride, indicates that three cobalt species, i.e. Co^{2+} , CoCl^+ and CoCl_2^- , exist in the lithium chloride concentration range 0 to 6 molar. The apparent equilibrium constants of these complexes, which relate their concentrations to the effective chloride activity of the solutions, are: $K_1^* = 0.33 \text{ mole}^{-1}$ and $\beta_2^* = 0.97 \times 10^{-3} \text{ mole}^{-2}$. No evidence was found to support the existence of CoCl_2 in these solutions.
2. Trioctylamine in benzene, and the organic cobalt complex in benzene, after equilibration with aqueous solutions, are essentially unhydrated.
3. Solutions of trioctylamine hydrochloride in benzene, formed by equilibration with aqueous solutions, contain water. When the water activity of the aqueous phase is close to unity, the molar ratio of $\overline{\text{H}_2\text{O}} : \overline{\text{TOAHCl}}$ is 1:1. The water concentration of the organic phase decreases linearly with the equilibrium aqueous phase water activity.
4. Trioctylamine hydrochloride forms aggregates when dissolved in benzene. The aggregation follows a monomer-dimer equilibrium up to solute concentrations of approximately 0.1m, with a dimerisation constant, $K_2 = 24.4 \text{ mole}^{-1}$ at 32.5°C .
5. Trioctylamine nitrate in benzene is in general more highly aggregated than the chloride salt. The monomer-dimer equilibrium is obeyed only up to 0.03m, higher polymers being formed at higher solute concentrations. $K_2 = 25 \text{ mole}^{-1}$ at 32.5°C .

6. The cobalt salt of trioctylamine hydrochloride exists in the organic phase as a solvated complex. The composition of this complex may be represented as:



This complex forms aggregates in benzene, but as its concentration approaches zero, the apparent molecular weight of the complex approaches the theoretical molecular weight calculated assuming a monomeric solute of the above composition.

7. The extraction of nitrate ions by trioctylamine hydrochloride in benzene obeys the following equilibrium:

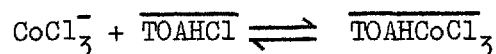


The equilibrium constant for this reaction, K_x , is given by:

$$K_x = \frac{a_{\text{Cl}^-} [\overline{\text{TOAHNO}_3}]}{a_{\text{NO}_3^-} [\overline{\text{TOAHCl}}]} = 24.4$$

8. The anomalous slopes observed for plots of $\log D_{\text{Co}}$ against $\log [\overline{\text{TOAHCl}}]$ have been rationalised in terms of the law of mass action by taking into account the effects of the aggregation of the amine salt in the organic phase.

9. Circumstantial evidence has been obtained which indicates that the extraction of cobalt from solutions containing up to 6M lithium chloride takes place by extraction of CoCl_3^- into the organic phase:



Reaction within the organic phase with further TOAHCl would lead to the formation of the solvated complex given in '6' above.

10. On the assumption that the mechanism given in '9' is correct, an expression has been derived which enables the change in γ_3 , the aqueous activity coefficient of CoCl_3^- , to be calculated as a function of the chloride concentration of the aqueous phase. It has been shown that γ_3 increases very rapidly with chloride concentration.

11. The extraction of cobalt from calcium chloride solutions gave results similar to those obtained for lithium chloride solutions, and it is concluded that a similar mechanism is involved.

12. The extraction of cobalt from hydrochloric acid solutions has been shown to be hindered by the preferential formation of amine dichloride, TOAH_2Cl_2 , when the aqueous acid concentration is greater than 3.5M.

13. Analysis of the results obtained for the extraction of cobalt from mixed lithium chloride - lithium nitrate solutions indicated that the extraction of the metal could be enhanced by the presence in the aqueous phase of a suitable second electrolyte. This effect has been demonstrated for the case of extraction from chloride - sulphate solutions.

APPENDIX 1CALCULATIONS OF EFFECTIVE LIGAND ACTIVITIES

In aqueous systems where it is not possible to maintain constant the activity coefficients of species in solution by the use of a constant ionic medium, it is conventional to use the concept of the effective ligand activity, a_A , where:

$$a_A = m_A \gamma_{\pm CA}$$

m_A = molal concentration of the anion of the bulk electrolyte CA.

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

a_A is assumed to be a measure of the anion activity of the electrolyte CA providing the concentrations of any other species in solution, e.g. metal ions, are very small compared with the concentration of CA.

Activities on the molal and molar concentration scales are related by:

$$m \gamma_{\pm} = c \gamma_{\pm} / d_o$$

where: m = molal concentration

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

c = molar concentration

$\gamma_{\pm}$ = mean molar activity coefficient

d_o = density of water

Since at 25°C, d_o is very close to unity:

$$a_A = m_A \gamma_{\pm CA} = c_A \gamma_{\pm CA}.$$

Thus the effective ligand activity is the same (at 25°C) when expressed in either molar or molal units.

A(i) Effective chloride activities in LiCl, HCl, and CaCl₂ solutions

As most compilations of activity coefficient data in the literature are expressed in molal concentration units, whereas for convenience most practical work is carried out using molar units, it is necessary to convert molar to molal units, in order to calculate effective ligand activities.

In the case of solutions containing one bulk electrolyte only the following equation can be used to convert from one concentration scale to the other:

$$\frac{c}{m} = d_o \left(1 - \frac{c \phi_v}{1000} \right) \quad (A1)$$

$$\phi_v = \phi_v^o + S_v c^{\frac{1}{2}} \quad (A2)$$

where: ϕ_v = Apparent molal volume

ϕ_v^o = Partial molal volume in the standard state

S_v = Experimental slope for the apparent molal volume.

Values of ϕ_v^0 and S_v are available in the literature ⁸⁸.

Electrolyte	ϕ_v^0	S_v
LiCl	17.00	1.488
HCl	18.20	0.83
CaCl ₂	18.25	5.99

The calculated molalities, together with molal activity coefficients^{88,89} and effective chloride activities for LiCl, HCl, and CaCl₂ are given in Tables A1, A2, A3 respectively. For calcium chloride, the effective chloride activities were calculated from:

$$a_{Cl} = 2m_{CaCl_2} \gamma_{\pm CaCl_2}$$

A(ii) Effective ligand activities in lithium chloride - lithium nitrate solutions.

As far as is known, the concept of effective ligand activities has not previously been used for solutions containing a mixture of two electrolytes. However it appears logical that the concept can be extended to include such solutions, provided the mean activity coefficients of each electrolyte in the mixture are known. Thus for a solution containing two 1:1 electrolytes CA and CB, the effective

ligand activities a_A and a_B will be given by:

$$a_A = m_A \gamma_{\pm A(B)} \quad (A3)$$

$$a_B = m_B \gamma_{\pm B(A)} \quad (A4)$$

where: m_A is the molal concentration of anion A,
 m_B is the molal concentration of anion B.
 $\gamma_{\pm A(B)}$ is the mean activity coefficient of
 CA in the presence of CB.
 $\gamma_{\pm B(A)}$ is the mean activity coefficient of
 CB in the presence of CA.

The behaviour of the mean activity coefficients in many electrolyte mixtures of constant molality and varying mole fraction can be expressed by the equations known as Harned's Rule⁷¹:

$$\log \gamma_{A(B)} = \log \gamma_{A(o)} - \alpha_{AB} m - \beta_{AB} m^2 \quad (A5)$$

$$\log \gamma_{B(A)} = \log \gamma_{B(o)} - \alpha_{BA} m - \beta_{BA} m^2 \quad (A6)$$

where: $\gamma_{A(B)}$ = mean activity coefficient of salt A
 in a mixture of salts A and B of
 total molality m.

$\gamma_{A(o)}$ = mean activity coefficient of salt A
in its own solution at molality m .

α_A, β_A = experimentally determined coefficients.

m_B = molality of salt B in the mixture.

and similarly for $\gamma_{B(A)}$.

Data for the α and β coefficients for mixed lithium chloride - lithium nitrate solutions were taken from the work of Robinson and Lim⁵⁵.

Since all the solutions used in the solvent extraction work were made up on a molar concentration basis, it was necessary to experimentally determine the molal concentrations of the two electrolytes in the mixtures. This was done by first calculating the molal concentrations of the LiCl and LiNO₃ stock solutions. A series of mixed solutions, representative of those used in the solvent extraction experiments, were then made up by titrating the required volumes of the stock solutions into standard flasks and making up with water. The flask was weighed before and after the addition of each solution, so that the weights of each solution and the weight of water required to make up the volume were known. From this information the number of moles of each salt plus the total weight of water in the solution was calculated, thus giving the molality of each salt in the mixed solution. The calculated molalities are given in Tables A4 and A5, together with the mean activity coefficients of the salts in the mixed solutions calculated using Equations (A5) and (A6), and the effective chloride and nitrate activities.

Table A1 Effective chloride activities in LiCl solutions.

$[\text{LiCl}]_M$	$[\text{LiCl}]_m$	$\gamma_{\pm\text{LiCl}}$	a_{Cl}	$\log a_{\text{Cl}}$	$a_{\text{H}_2\text{O}}^*$
0.5	0.504	0.740	0.373	-0.428	0.9813
1.0	1.019	0.777	0.791	-0.102	0.9625
1.5	1.543	0.845	1.302	0.115	0.9412
2.0	2.080	0.938	1.951	0.290	0.9174
2.5	2.630	1.060	2.790	0.446	0.8900
3.0	3.185	1.204	3.835	0.583	0.8597
3.5	3.760	1.41	5.30	0.724	0.827
4.0	4.340	1.67	7.25	0.860	0.790
4.5	4.950	1.99	9.85	0.993	0.749
5.0	5.565	2.45	13.63	1.135	0.708
5.5	6.20	2.89	17.91	1.253	0.664
6.0	6.84	3.51	24.00	1.380	0.620
6.5	7.52	4.38	32.90	1.517	0.572
7.0	8.22	5.45	44.80	1.651	0.523
7.5	8.91	6.80	60.50	1.782	0.477
8.0	9.62	8.45	81.25	1.910	0.432
9.0	11.11	12.93	143.7	2.157	0.350
10.0	12.69	19.4	246.0	2.391	0.277

* Data from Reference 90

Table A2 Effective chloride activities in HCl solutions.

$[\text{HCl}]_{\text{M}}$	$[\text{HCl}]_{\text{m}}$	$\gamma_{\pm\text{HCl}}$	a_{Cl}	$\log a_{\text{Cl}}$
0.5	0.505	0.76	0.384	-0.416
1.5	1.543	0.89	1.372	0.138
2.5	2.630	1.18	3.11	0.492
3.5	3.760	1.64	6.16	0.790
4.0	4.358	1.95	8.50	0.930
4.5	4.950	2.34	11.59	1.064
5.5	6.190	3.40	21.05	1.323
6.5	7.49	5.04	37.80	1.577
7.5	8.86	7.55	66.90	1.826

Table A3 Effective chloride activities in CaCl_2 solutions.

$[\text{CaCl}_2]_{\text{M}}$	$[\text{CaCl}_2]_{\text{m}}$	$\gamma_{\pm\text{CaCl}_2}$	a_{Cl}	$\log a_{\text{Cl}}$
2.00	2.113	0.845	3.565	0.552
2.25	2.400	1.000	4.800	0.681
2.50	2.690	1.210	6.51	0.814
2.75	2.981	1.470	8.76	0.942
3.00	3.284	1.815	11.93	1.076

Table A4 Effective chloride activities in LiCl - LiNO₃ solutions.(i) Total molarity = 7.5M

$[\text{LiCl}]_M$	$[\text{LiNO}_3]_M$	$[\text{LiCl}]_m^*$	$\log \gamma^{**}$	$\log a_{\text{Cl}}^{***}$	a_{Cl}^{***}
7.5	0	8.91	0.829	1.782	60.5
7.0	0.5	8.51	0.833	1.763	57.9
6.5	1.0	8.02	0.824	1.728	53.4
6.0	1.5	7.44	0.801	1.673	47.1
5.5	2.0	6.86	0.784	1.620	41.7
5.0	2.5	6.26	0.763	1.559	36.2
4.5	3.0	5.67	0.745	1.499	31.6
4.0	3.5	5.11	0.734	1.442	27.7
3.5	4.0	4.48	0.713	1.365	23.2

(ii) Total molarity = 6.5M

$[\text{LiCl}]_M$	$[\text{LiNO}_3]_M$	$[\text{LiCl}]_m^*$	$\log \gamma^{**}$	$\log a_{\text{Cl}}^{***}$	a_{Cl}^{***}
6.5	0	7.52	0.640	1.517	32.9
6.0	0.5	7.18	0.653	1.509	32.3
5.5	1.0	6.62	0.634	1.455	28.5
5.0	1.5	6.05	0.618	1.400	25.1
4.5	2.0	5.46	0.603	1.340	21.8
4.0	2.5	4.90	0.589	1.279	19.0
3.5	3.0	4.29	0.572	1.204	16.0

* - Experimentally determined molal concentrations.

** - $\gamma_{\pm}$ of LiCl in the mixed solutions calculated from Eqn.(A5).

*** - Effective chloride activity calculated from Eqn.(A3).

Table A5 Effective nitrate activities in LiCl - LiNO₃ solutions.(i) Total molarity = 7.5M

$[\text{LiNO}_3]_{\text{M}}$	$[\text{LiCl}]_{\text{M}}$	$[\text{LiNO}_3]_{\text{m}}^*$	$\log^{**} \gamma$	$\log a_{\text{NO}_3}^{***}$	$a_{\text{NO}_3}^{***}$
0.5	7.0	0.613	0.645	0.433	2.71
1.0	6.5	1.245	0.630	0.726	5.32
1.5	6.0	1.855	0.605	0.873	7.46
2.0	5.5	2.515	0.583	0.984	9.61
2.5	5.0	3.15	0.560	1.058	11.40
3.0	4.5	3.81	0.539	1.120	13.20
3.5	4.0	4.49	0.524	1.176	15.00
4.0	3.5	5.15	0.502	1.214	16.37

(ii) Total molarity = 6.5M

$[\text{LiNO}_3]_{\text{M}}$	$[\text{LiCl}]_{\text{M}}$	$[\text{LiNO}_3]_{\text{m}}^*$	$\log^{**} \gamma$	$\log a_{\text{NO}_3}^{***}$	$a_{\text{NO}_3}^{***}$
0.5	6.0	0.609	0.526	0.310	2.05
1.0	5.5	1.195	0.502	0.580	3.80
1.5	5.0	1.808	0.480	0.737	5.46
2.0	4.5	2.45	0.460	0.849	7.03
2.5	4.0	3.07	0.441	0.928	8.47
3.0	3.5	3.71	0.421	0.989	9.75

* - Experimentally determined molal concentrations.

** - $\gamma_{\pm}$ of LiNO₃ in the mixed solutions calculated from Eqn. (A6).

*** - Effective nitrate activity calculated from Eqn. (A4).

APPENDIX 2

TABLES OF RESULTS AND DERIVED DATA.

Table 3.1.X. Extraction of trace cobalt from chloride solutions

$$[\text{TOAHCl}] = 0.0983\text{M}, \quad [\text{Co}^{2+}]_{\text{total}} = 2 \times 10^{-5}\text{M}$$

a) From LiCl solutions

$[\text{LiCl}]\text{M}$	$\log a_{\text{Cl}}$	$\text{pH}^*_{(\text{b})}$	$\text{pH}^*_{(\text{a})}$	D_{Co}	$\log D_{\text{Co}}$	% Mass Balance	α_{E}
3.0	0.583	1.44	1.63	0.020	-1.701	98.9	0.019
3.5	0.724	1.21	1.38	0.052	-1.282	98.9	0.049
4.0	0.860	1.10	1.29	0.136	-0.867	98.5	0.120
4.5	0.993	0.98	1.18	0.348	-0.458	99.9	0.258
5.0	1.135	0.90	1.04	0.936	-0.029	98.1	0.484
5.5	1.253	0.75	0.92	2.492	0.396	99.0	0.714
6.0	1.380	0.59	0.78	6.685	0.825	99.0	0.870
6.5	1.517	0.45	0.64	17.35	1.239	99.3	0.946
7.0	1.651	0.28	0.50	44.90	1.652	98.6	0.978
7.5	1.782	0.18	0.37	99.50	1.998	100.5	0.990

* $\text{pH}_{(\text{b})}$ = pH before extraction, $\text{pH}_{(\text{a})}$ = pH after extraction.

b) From HCl solutions

$[\text{HCl}]\text{M}$	$\log a_{\text{Cl}}$	D_{Co}	$\log D_{\text{Co}}$	% Mass Balance
3.5	0.790	0.078	-1.111	99.4
4.0	0.930	0.220	-0.658	98.5
4.5	1.064	0.479	-0.320	98.1
5.5	1.323	2.250	0.352	99.9
6.5	1.577	8.142	0.910	99.1
7.5	1.826	18.64	1.270	104.9

(continued)

Table 3.1.X. (continued)c) From CaCl_2 solutions

$[\text{CaCl}_2]\text{M}$	$\log a_{\text{Cl}}$	D_{Co}	$\log D_{\text{Co}}$	% Mass Balance
2.00	0.552	0.060	-1.222	105.9
2.25	0.681	0.135	-0.870	102.8
2.50	0.814	0.309	-0.510	99.1
2.75	0.942	0.744	-0.128	99.8
3.00	1.076	1.817	0.260	96.6

Table 3.2.X. Extraction of cobalt from lithium chloride - lithium nitrate solutions.

$$[\text{TOA}/\text{HCl}] = 0.0983\text{M}$$

a) Total Molarity = 6.5M

Aqueous phase composition	$[\text{Co}]_{\text{total}}$ ($\text{M} \times 10^3$)	X_{Co} ($\text{M} \times 10^3$)	Y_{Co} ($\text{M} \times 10^3$)	% Mass Balance	D_{Co}	$\log D_{\text{Co}}$
$[\text{LiCl}] = 3.5\text{M}$	0.960	0.926	0.016	98.2	0.0173	-1.762
$[\text{LiNO}_3] = 3.0\text{M}$	4.800	4.685	0.077	99.3	0.0164	-1.785
$\log a_{\text{Cl}} = 1.204$	9.600	9.415	0.167	99.8	0.0178	-1.750
$\log a_{\text{NO}_3} = 0.989$						
$[\text{LiCl}] = 4.0\text{M}$	0.0960	0.915	0.026	98.0	0.0285	-1.545
$[\text{LiNO}_3] = 2.5\text{M}$	1.920	1.840	0.052	98.8	0.0285	-1.545
$\log a_{\text{Cl}} = 1.279$	4.800	4.630	0.149	99.6	0.0321	-1.494
$\log a_{\text{NO}_3} = 0.928$	9.600	9.252	0.282	99.4	0.0305	-1.516
	14.400	13.690	0.428	98.1	0.0313	-1.504

(continued)

Table 3.2.X. (continued)

[LiCl]=4.5M	0.960	0.894	0.064	99.8	0.0677	-1.170
[LiNO ₃]=2.0M	1.920	1.768	0.138	99.3	0.0780	-1.108
log a _{Cl} =1.340	4.800	4.450	0.263	98.2	0.0591	-1.299
log a _{NO₃} =0.849	9.600	8.820	0.556	97.8	0.0631	-1.200
	14.400	13.615	0.861	100.4	0.0632	-1.199
[LiCl]=5.0M	0.960	0.813	0.013	98.2	0.158	-0.802
[LiNO ₃]=1.5M	1.920	1.702	0.304	104.5	0.179	-0.748
log a _{Cl} =1.400	4.800	4.086	0.731	100.3	0.179	-0.748
log a _{NO₃} =0.737	9.600	8.118	1.443	99.9	0.178	-0.750
	14.400	12.573	1.672	99.0	0.134	-0.872
[LiCl]=5.5M	0.960	0.695	0.257	99.1	0.369	-0.433
[LiNO ₃]=1.0M	1.920	1.387	0.522	99.5	0.376	-0.425
log a _{Cl} =1.455	4.800	3.476	1.276	99.1	0.67	-0.435
log a _{NO₃} =0.580	9.600	6.980	2.482	98.7	0.356	-0.449
	14.400	10.820	3.630	100.4	0.336	-0.474
[LiCl]=6.0M	0.960	0.379	0.590	100.7	1.561	0.194
[LiNO ₃]=0.5M	1.920	0.730	1.198	100.4	1.642	0.216
log a _{Cl} =1.509	4.800	1.946	2.850	99.9	1.465	0.166
log a _{NO₃} =0.310	9.600	4.260	5.190	98.5	1.216	0.085
	14.400	6.830	7.730	101.1	1.132	0.054

b) Total Molarity = 7.5M

Aqueous phase composition	[Co] _{total} (Mx10 ³)	X _{Co} (Mx10 ³)	Y _{Co} (Mx10 ³)	% Mass Balance	D _{Co}	log D _{Co}
[LiCl]=4.0M	0.960	0.851	0.101	99.2	0.118	-0.927
[LiNO ₃]=3.5M						
log a _{Cl} =1.442						
log a _{NO₃} =1.176						

(continued)

Table 3.2.X. (continued)

[LiCl]=4.5M	0.960	0.747	0.217	100.4	0.291	-0.536
[LiNO ₃]=3.0M						
log a _{Cl} =1.499						
log a _{NO₃} =1.120						
[LiCl]=5.0M	0.960	0.646	0.275	96.0	0.427	-0.370
[LiNO ₃]=2.5M						
log a _{Cl} =1.559						
log a _{NO₃} =1.058						
[LiCl]=5.5M	0.960	0.520	0.426	98.7	0.820	-0.086
[LiNO ₃]=2.0M	1.920	1.030	0.870	98.9	0.868	-0.062
log a _{Cl} =1.620	4.800	2.734	2.115	100.9	0.774	-0.112
log a _{NO₃} =0.984	9.600	5.460	4.000	98.6	0.732	-0.136
[LiCl]=6.0M	0.960	0.343	0.609	99.1	1.778	0.250
[LiNO ₃]=1.5M	1.920	0.712	1.212	100.2	1.703	0.231
log a _{Cl} =1.673	4.800	1.851	2.933	99.7	1.585	0.200
log a _{NO₃} =0.873	9.600	3.927	5.390	97.1	1.373	0.138
[LiCl]=6.5M	0.960	0.175	0.760	97.4	4.335	0.637
[LiNO ₃]=1.0M	1.920	0.384	1.559	101.2	4.071	0.610
log a _{Cl} =1.728	4.800	1.014	3.786	100.0	3.742	0.573
log a _{NO₃} =0.726	9.600	2.350	7.200	99.5	3.095	0.491
	14.400	3.950	10.270	98.7	2.598	0.415
[LiCl]=7.0M	0.960	0.063	0.886	98.9	14.08	1.148
[LiNO ₃]=0.5M	1.920	0.128	1.788	99.8	13.91	1.143
log a _{Cl} =1.763	4.800	0.363	4.400	99.3	12.11	1.083
log a _{NO₃} =0.433	9.600	0.926	8.365	96.9	9.03	0.954
	14.400	1.830	12.440	99.1	6.80	0.832

Table 3.3.X. Variation of the amine concentration of the organic phase

(a) Aqueous phase composition : $[\text{LiCl}] = 6.5\text{M}$, $[\text{Co}]_{\text{total}} = 1.92 \times 10^{-3}\text{M}$

$[\text{TOA}]$ ($\text{M} \times 10^2$)	$\log[\text{TOA}]$	X_{Co} ($\text{M} \times 10^3$)	Y_{Co} ($\text{M} \times 10^3$)	% Mass Balance	D_{Co}	$\log D_{\text{Co}}$
0.983	-2.007	1.479	0.444	100.1	0.300	-0.523
1.966	-1.706	0.973	0.946	100.0	0.972	-0.012
4.915	-1.308	0.340	1.569	99.4	4.621	0.665
9.830	-1.007	0.132	1.766	99.0	13.11	1.118
19.660	-0.706	0.040	1.874	99.7	47.30	1.675

(b) Aqueous phase composition : $[\text{LiCl}] = 4.0\text{M}$, $[\text{Co}]_{\text{total}} = 1.92 \times 10^{-3}\text{M}$

$[\text{TOA}]$ ($\text{M} \times 10^2$)	$\log[\text{TOA}]$	X_{Co} ($\text{M} \times 10^3$)	Y_{Co} ($\text{M} \times 10^3$)	% Mass Balance	D_{Co}	$\log D_{\text{Co}}$
4.915	-1.308	1.818	0.084	99.1	0.046	-1.337
9.830	-1.007	1.708	0.226	100.8	0.133	-0.878
19.660	-0.706	1.380	0.534	99.7	0.387	-0.413
49.150	-0.308	0.488	1.409	98.8	2.888	0.416
98.300	-0.007	0.113	1.755	97.3	15.82	1.200

(c) Aqueous phase composition : $[\text{LiCl}] = 5.5\text{M}$, $[\text{LiNO}_3] = 1.0\text{M}$,
 $[\text{Co}]_{\text{total}} = 1.92 \times 10^{-3}\text{M}$

$[\text{TOA}]$ ($\text{M} \times 10^2$)	$\log[\text{TOA}]$	X_{Co} ($\text{M} \times 10^3$)	Y_{Co} ($\text{M} \times 10^3$)	% Mass Balance	D_{Co}	$\log D_{\text{Co}}$
0.490	-2.310	1.906	0.006	99.6	0.003	-2.523
0.980	-2.008	1.889	0.022	99.6	0.012	-1.921
1.960	-1.708	1.824	0.064	98.6	0.036	-1.444
4.900	-1.310	1.656	0.255	99.5	0.154	-0.813

(continued)

Table 3.3.X. (continued)

9.800	-1.008	1.337	0.558	99.0	0.419	-0.378
19.500	-0.710	0.886	1.023	99.4	1.156	0.063
48.800	-0.311	0.290	1.603	98.7	5.538	0.744
97.500	-0.011	0.055	1.820	99.8	33.50	1.525

Table 3.4.X. Variation of the aqueous metal concentration - extraction from LiCl solutions.

$$[\text{TOAHCl}] = 0.0983\text{M}$$

[LiCl] (M)	[Co] _{total} (Mx10 ³)	X _{Co} (Mx10 ³)	Y _{Co} (Mx10 ³)	% Mass Balance	D _{Co}	log D _{Co}
4.0	0.0200	0.0173	0.0024	98.5	0.1357	-0.868
4.0	1.920	1.708	0.226	100.8	0.1326	-0.878
4.0	9.870	8.510	1.390	100.4	0.1635	-0.786
5.0	0.0200	0.0102	0.0094	98.1	0.936	-0.029
5.0	9.870	4.750	5.080	99.6	1.068	0.028
6.0	0.0200	0.0026	0.0172	99.0	6.685	0.825
6.0	9.870	1.340	8.610	100.8	6.430	0.808
7.0	0.0200	0.0004	0.0193	98.6	44.90	1.652
7.0	0.960	0.023	0.939	100.2	41.80	1.622
7.0	1.920	0.047	1.847	98.7	38.00	1.570
7.0	4.800	0.139	4.566	98.0	32.90	1.517
7.0	9.600	0.387	8.993	97.7	23.20	1.366
7.0	14.400	0.737	13.515	99.0	18.34	1.263
7.5	0.0200	0.0002	0.0199	100.5	99.50	1.998
7.5	0.960	0.0097	0.928	97.7	95.70	1.981
7.5	1.920	0.021	1.907	100.4	92.60	1.967
7.5	4.800	0.058	4.700	99.1	81.00	1.908
7.5	9.600	0.170	9.240	98.2	54.30	1.736
7.5	14.400	0.358	14.220	101.2	39.60	1.598

Table 3.5.X. Extraction Isotherm

$$[\text{TOAHCl}] = 0.0983\text{M}, [\text{LiCl}] = 6.5\text{M}$$

$[\text{Co}]_{\text{total}}$ ($\text{M} \times 10^2$)	X_{Co} ($\text{M} \times 10^2$)	Y_{Co} ($\text{M} \times 10^2$)	% Mass Balance	D_{Co}
0.0987	0.0045	0.0949	101.2	21.31
0.4935	0.0270	0.4610	98.9	17.05
0.987	0.069	0.917	99.9	13.21
1.974	0.227	1.698	97.8	7.480
3.954	1.113	2.805	99.2	2.520
5.932	2.544	3.278	98.2	1.289
7.909	4.301	3.561	99.5	0.829
9.886	6.010	3.764	98.9	0.627
19.772	15.488	4.014	98.7	0.259
29.658	25.391	4.270	100.0	0.169
39.544	34.628	4.282	98.4	0.124

Table 3.6.X. Extraction of trace cobalt from hydrochloric acid - lithium sulphate solutions.

$$[\text{TOAHCl}] = 0.0983\text{M}, [\text{Co}]_{\text{total}} = 2 \times 10^{-5}\text{M}$$

$[\text{HCl}]$ (M)	$[\text{Li}_2\text{SO}_4]$ (M)	D_{Co}	$\log D_{\text{Co}}$	% Mass Balance	% Extn.
4.0	0	0.220	-0.658	98.5	17.8
4.0	0.283	0.332	-0.478	101.0	25.6
4.0	0.566	0.507	-0.294	101.1	33.1
4.0	0.849	0.801	-0.097	99.6	44.3
4.0	1.132	1.251	0.097	102.0	56.8
4.0	1.415	2.020	0.305	99.7	66.7

Table 3.7.X. Extraction of cobalt from hydrochloric acid - nickel sulphate solutions.

$$[\text{TOAHCl}] = 0.0983\text{M}, \quad [\text{CoSO}_4] = 0.0678\text{M}$$

$[\text{HCl}]$ (M)	$[\text{NiSO}_4]$ (M)	D_{Co}	$\log D_{\text{Co}}$	% Mass Balance	% Extn.
3.45	0	0.0625	-1.204	97.6	5.7
4.60	0	0.2825	-0.550	99.2	21.8
5.75	0	0.688	-0.162	99.5	40.6
1.15	0.933	0.0017	-2.770	99.5	0
2.30	0.933	0.0155	-1.808	98.3	1.5
3.45	0.933	0.1384	-0.859	100.9	12.8
4.60	0.933	0.451	-0.346	98.1	30.4
5.75	0.933	0.821	-0.085	100.7	45.5

Table 4.1.X. Calculation of K_1^* and ϵ_1^λ from Equation (4E7).

<u>$\lambda = 500 \text{ nm.}$</u>		$\epsilon_0^{500} = 4.595$			
$[\text{LiCl}]_M$	$(a_{\text{Cl}})^{-1}$	ϵ^{500}	$\epsilon^{500} - \epsilon_0^{500}$	$(\epsilon^{500} - \epsilon_0^{500})^{-1}$	
1.0	1.265	4.963	0.368	2.720	Slope = 1.773
1.5	0.723	5.098	0.503	1.990	Intercept = 0.538
2.0	0.514	5.269	0.674	1.485	Corr. coeff. = 0.996
2.5	0.358	5.464	0.869	1.150	$K_1^* = 0.304 \text{ mole}^{-1}$
3.0	0.261	5.646	1.051	0.951	$\epsilon_1^{500} = 6.455$
<u>$\lambda = 505 \text{ nm.}$</u>		$\epsilon_0^{505} = 4.766$			
$[\text{LiCl}]_M$	$(a_{\text{Cl}})^{-1}$	ϵ^{505}	$\epsilon^{505} - \epsilon_0^{505}$	$(\epsilon^{505} - \epsilon_0^{505})^{-1}$	
1.0	1.265	5.152	0.386	2.590	Slope = 1.637
1.5	0.723	5.333	0.567	1.765	Intercept = 0.521
2.0	0.514	5.514	0.748	1.335	Corr. coeff. = 0.998
2.5	0.358	5.622	0.856	1.170	$K_1^* = 0.318 \text{ mole}^{-1}$
3.0	0.261	5.857	1.091	0.917	$\epsilon_1^{505} = 6.686$
<u>$\lambda = 510 \text{ nm.}$</u>		$\epsilon_0^{510} = 4.816$			
$[\text{LiCl}]_M$	$(a_{\text{Cl}})^{-1}$	ϵ^{510}	$\epsilon^{510} - \epsilon_0^{510}$	$(\epsilon^{510} - \epsilon_0^{510})^{-1}$	
1.0	1.265	5.224	0.408	2.450	Slope = 1.543
1.5	0.768	5.414	0.598	1.671	Intercept = 0.505
2.0	0.514	5.567	0.751	1.333	Corr. coeff. = 0.999
2.5	0.358	5.762	0.946	1.058	$K_1^* = 0.327 \text{ mole}^{-1}$
3.0	0.261	5.942	1.126	0.890	$\epsilon_1^{510} = 6.799$

(continued)

Table 4.1.X. (continued)

<u>$\lambda = 515 \text{ nm.}$</u> $\epsilon_0^{515} = 4.725$					
$[\text{LiCl}]_M$	$(a_{Cl})^{-1}$	ϵ^{515}	$\epsilon^{515} - \epsilon_0^{515}$	$(\epsilon^{515} - \epsilon_0^{515})^{-1}$	
1.0	1.265	5.127	0.402	2.490 ⁺	Slope = 1.438
1.5	0.768	5.361	0.636	1.573	Intercept = 0.472
2.0	0.514	5.549	0.824	1.214	Corr. coeff. = 1.000
2.5	0.358	5.731	1.006	0.995	$K_1^* = 0.328 \text{ mole}^{-1}$
3.0	0.261	5.917	1.192	0.839	$\epsilon_1^{515} = 6.845$
<u>$\lambda = 520 \text{ nm.}$</u> $\epsilon_0^{520} = 4.547$					
$[\text{LiCl}]_M$	$(a_{Cl})^{-1}$	ϵ^{520}	$\epsilon^{520} - \epsilon_0^{520}$	$(\epsilon^{520} - \epsilon_0^{520})^{-1}$	
1.0	1.265	4.980	0.433	2.310	Slope = 1.502
1.5	0.768	5.175	0.628	1.591	Intercept = 0.422
2.0	0.514	5.393	0.846	1.182	Corr. coeff. = 1.000
2.5	0.358	5.587	1.040	0.962	$K_1^* = 0.281 \text{ mole}^{-1}$
3.0	0.261	5.817	1.270	0.788 ⁺	$\epsilon_1^{520} = 6.914$
<u>$\lambda = 525 \text{ nm.}$</u> $\epsilon_0^{525} = 4.239$					
$[\text{LiCl}]_M$	$(a_{Cl})^{-1}$	ϵ^{525}	$\epsilon^{525} - \epsilon_0^{525}$	$(\epsilon^{525} - \epsilon_0^{525})^{-1}$	
1.0	1.265	4.702	0.463	2.180	Slope = 1.348
1.5	0.768	4.920	0.681	1.470	Intercept = 0.476
2.0	0.514	5.065	0.826	1.211	Corr. coeff. = 0.997
2.5	0.358	5.241	1.002	0.998	$K_1^* = 0.353 \text{ mole}^{-1}$
3.0	0.261	5.521	1.282	0.780	$\epsilon_1^{525} = 6.344$

(continued)

Table 4.1.X. (continued)

<u>$\lambda = 530 \text{ nm.}$</u>		$\epsilon_0^{530} = 3.825$			
$[\text{LiCl}]_M$	$(a_{\text{Cl}})^{-1}$	ϵ^{530}	$\epsilon^{530}_0 - \epsilon^{530}_0$	$(\epsilon^{530}_0 - \epsilon^{530}_0)^{-1}$	
1.0	1.265	4.319	0.494	2.025 ⁺	Slope = 1.404
1.5	0.768	4.476	0.651	1.538	Intercept = 0.479
2.0	0.514	4.642	0.817	1.225	Corr. coeff. = 0.993
2.5	0.358	4.807	0.982	1.019	$K_1^* = 0.341 \text{ mole}^{-1}$
3.0	0.261	5.071	1.246	0.803	$\epsilon_1^{530} = 5.915$
<u>$\lambda = 535 \text{ nm.}$</u>		$\epsilon_0^{535} = 3.368$			
$[\text{LiCl}]_M$	$(a_{\text{Cl}})^{-1}$	ϵ^{535}	$\epsilon^{535}_0 - \epsilon^{535}_0$	$(\epsilon^{535}_0 - \epsilon^{535}_0)^{-1}$	
1.0	1.265	3.852	0.484	2.065 ⁺	Slope = 1.532
1.5	0.768	3.982	0.615	1.627	Intercept = 0.457
2.0	0.514	4.161	0.793	1.261	Corr. coeff. = 0.999
2.5	0.358	4.373	1.005	0.995	$K_1^* = 0.298 \text{ mole}^{-1}$
3.0	0.261	4.625	1.257	0.796 ⁺	$\epsilon_1^{535} = 5.556$

Table 4.2.X. Data for the combined method for calculating K_1^* from Equation (4E6).

$[LiCl] (a_{Cl})^{-1}$ (M)		Values of $(\epsilon_1^\lambda - \epsilon_0^\lambda)/(\epsilon^\lambda - \epsilon_0^\lambda)$								Average
		500	505	510	515	520	525	530	535	
1.0	1.265	5.052	4.972	4.853	5.271	5.473	4.538	4.227	4.521	4.864
1.5	0.768	3.696	3.384	3.311	3.332	3.774	3.085	3.207	3.558	3.418
2.0	0.514	2.758	2.566	2.636	2.572	2.801	2.544	2.556	2.759	2.648
2.5	0.358	2.139	2.242	2.093	2.106	2.279	2.097	2.126	2.177	2.157
3.0	0.261	1.769	1.759	1.758	1.778	1.866	1.639	1.676	1.741	1.748

Corr. coeff. = 0.999

Slope = 3.057

Intercept = 1.032

 $K_1^* = 0.327 \text{ mole}^{-1}$

Table 4.3.X. Calculation of ϵ_1^λ and β_1^* from Equation (4E19).

$$\text{Note : } A = (a_{Cl})^{-3}(\epsilon^\lambda - \epsilon_0^\lambda)$$

$$B = (a_{Cl})^{-2}K_1^*(\epsilon^\lambda - \epsilon_1^\lambda)$$

$$\lambda = 500 \text{ nm.} \quad \epsilon_0^{500} = 4.595 \quad \epsilon_1^{500} = 6.455$$

$[LiCl]M$	ϵ^{500}	$\epsilon^{500} - \epsilon_0^{500}$	$\epsilon^{500} - \epsilon_1^{500}$	$A \times 10^3$	$B \times 10^3$	$(A+B) \times 10^3$
3.5	5.886	1.291	-0.569	8.960	-6.690	2.000
4.0	6.210	1.615	-0.245	4.290	-1.550	2.740
4.5	6.584	1.989	0.129	2.080	0.439	2.520
5.0	6.961	2.366	0.506	0.894	0.870	1.764
6.0	7.730	3.135	1.275	0.227	0.732	0.959
7.0	8.350	3.755	1.895	0.042	0.314	0.356
8.0	8.563	3.968	2.108	0.008	0.107	0.115

(continued)

Table 4.3.X. (continued)

 $\lambda = 500 \text{ nm.}$

Corr. coeff. = 0.99490

Intercept = 0.00986

Slope = -0.00114

 $\beta_3^* = 1.14 \times 10^{-3} \text{ mole}^{-3}$ $\epsilon_3^{500} = 8.633$ $\lambda = 505 \text{ nm.}$ $\epsilon_0^{505} = 4.766$ $\epsilon_1^{505} = 6.686$

$[\text{LiCl}]_M$	ϵ^{505}	$\epsilon^{505} - \epsilon_0^{505}$	$\epsilon^{505} - \epsilon_1^{505}$	$A \times 10^3$	$B \times 10^3$	$(A+B) \times 10^3$
3.5	6.108	1.342	-0.578	9.050	-6.800	2.250
4.0	6.450	1.684	-0.236	4.480	-1.430	3.050
4.5	6.839	2.073	0.153	2.170	0.520	2.690
5.0	7.287	2.521	0.601	0.952	1.032	1.984
6.0	8.149	3.383	1.463	0.245	0.840	1.085
7.0	8.838	4.072	2.152	0.046	0.357	0.403
8.0	9.175	4.409	2.489	0.009	0.131	0.140

Corr. coeff. = 0.99723

Intercept = 0.01003

Slope = -0.00109

 $\beta_3^* = 1.09 \times 10^{-3} \text{ mole}^{-3}$ $\epsilon_3^{505} = 9.222$ $\lambda = 510 \text{ nm.}$ $\epsilon_0^{510} = 4.816$ $\epsilon_1^{510} = 6.799$

$[\text{LiCl}]_M$	ϵ^{510}	$\epsilon^{510} - \epsilon_0^{510}$	$\epsilon^{510} - \epsilon_1^{510}$	$A \times 10^3$	$B \times 10^3$	$(A+B) \times 10^3$
3.5	6.258	1.442	-0.541	9.710	-6.360	3.350
4.0	6.631	1.815	-0.168	4.830	-1.065	3.765
4.5	7.053	2.237	0.254	2.340	0.864	3.204
5.0	7.500	2.684	0.701	1.014	1.207	2.221
6.0	8.428	3.612	1.629	0.262	0.934	1.196
7.0	9.263	4.447	2.464	0.051	0.409	0.460
8.0	9.700	4.884	2.901	0.010	0.152	0.162

(continued)

Table 4.3.X. (continued)

 $\lambda = 510\text{nm.}$

Corr. coeff. = 0.98821

Intercept = 0.01203

Slope = -0.00127

$$\beta_3^* = 1.27 \times 10^{-3} \text{ mole}^{-3}$$

$$\epsilon_3^{510} = 9.485$$

 $\lambda = 515\text{nm.}$

$$\epsilon_0^{515} = 4.725$$

$$\epsilon_1^{515} = 6.845$$

$[\text{LiCl}]_M$	ϵ^{515}	$\epsilon^{515} - \epsilon_0^{515}$	$\epsilon^{515} - \epsilon_1^{515}$	$A \times 10^3$	$B \times 10^3$	$(A+B) \times 10^3$
3.5	6.257	1.532	-0.588	10.310	-6.910	3.400
4.0	6.639	1.914	-0.206	5.100	-1.306	3.794
4.5	7.070	2.345	0.225	2.450	0.765	3.215
5.0	7.588	2.863	0.743	1.083	1.278	2.361
6.0	8.742	4.017	1.897	0.291	1.088	1.379
7.0	9.725	5.000	2.880	0.057	0.478	0.535
8.0	10.275	5.500	3.430	0.011	0.180	0.191

Corr. coeff. = 0.99108

Intercept = 0.01052

Slope = -0.00104

$$\beta_3^* = 1.04 \times 10^{-3} \text{ mole}^{-3}$$

$$\epsilon_3^{515} = 10.126$$

 $\lambda = 520\text{nm.}$

$$\epsilon_0^{520} = 4.547$$

$$\epsilon_1^{520} = 6.914$$

$[\text{LiCl}]_M$	ϵ^{520}	$\epsilon^{520} - \epsilon_0^{520}$	$\epsilon^{520} - \epsilon_1^{520}$	$A \times 10^3$	$B \times 10^3$	$(A+B) \times 10^3$
3.5	6.119	1.572	-0.795	10.600	-9.340	1.260
4.0	6.511	1.964	-0.403	5.220	-2.560	2.660
4.5	6.994	2.447	0.080	2.560	0.272	2.832
5.0	7.547	3.000	0.633	1.133	1.088	2.221
6.0	8.721	4.174	1.807	0.302	1.036	1.338
7.0	9.963	5.416	3.049	0.061	0.506	0.567
8.0	10.825	6.278	3.911	0.013	0.205	0.218

(continued)

Table 4.3.X. (continued)

 $\lambda = 520 \text{ nm.}$

Corr. coeff. = 0.99452

 $\beta_3^* = 0.75 \times 10^{-3} \text{ mole}^{-3}$

Intercept = 0.00796

 $\epsilon_3^{520} = 10.628$

Slope = -0.00075

 $\lambda = 525 \text{ nm.}$ $\epsilon_0^{525} = 4.239$ $\epsilon_1^{525} = 6.344$

$[\text{LiCl}]_M$	ϵ^{525}	$\epsilon^{525} - \epsilon_0^{525}$	$\epsilon^{525} - \epsilon_1^{525}$	$A \times 10^3$	$B \times 10^3$	$(A+B) \times 10^3$
3.5	5.891	1.652	-0.453	11.120	-5.330	5.790
4.0	6.318	2.077	-0.026	5.520	-0.165	5.355
4.5	6.784	2.545	0.440	2.660	1.498	4.160
5.0	7.355	3.116	1.011	1.178	1.739	2.917
6.0	8.700	4.461	2.356	0.323	1.350	1.673
7.0	10.075	5.836	3.731	0.066	0.619	0.685
8.0	11.475	7.236	5.131	0.014	0.269	0.283

Corr. coeff. = 0.97258

 $\beta_3^* = 1.25 \times 10^{-3} \text{ mole}^{-3}$

Intercept = 0.01281

 $\epsilon_3^{525} = 10.271$

Slope = -0.00125

 $\lambda = 530 \text{ nm.}$ $\epsilon_0^{530} = 3.825$ $\epsilon_1^{530} = 5.915$

$[\text{LiCl}]_M$	ϵ^{530}	$\epsilon^{530} - \epsilon_0^{530}$	$\epsilon^{530} - \epsilon_1^{530}$	$A \times 10^3$	$B \times 10^3$	$(A+B) \times 10^3$
3.5	5.450	1.625	-0.465	10.930	-5.460	5.470
4.0	5.890	2.065	-0.025	5.490	-0.016	5.474
4.5	6.427	2.602	0.512	2.700	1.740	4.460
5.0	6.941	3.116	1.206	1.178	1.763	2.941
6.0	8.371	4.545	2.455	0.329	1.407	1.736
7.0	9.938	6.113	4.023	0.069	0.669	0.738
8.0	11.588	7.763	5.673	0.016	0.297	0.313

(continued)

Table 4.3.X. (continued) $\lambda = 530 \text{ nm.}$

Corr. coeff. = 0.96772

Intercept = 0.01162

Slope = -0.00114

$$\beta_3^* = 1.14 \times 10^{-3} \text{ mole}^{-3}$$

$$\epsilon_3^{530} = 10.221$$

 $\lambda = 535 \text{ nm.}$

$$\epsilon_0^{535} = 3.368$$

$$\epsilon_1^{535} = 5.556$$

$[\text{LiCl}]_M$	ϵ^{535}	$\epsilon^{535}_{\epsilon_0^{535}}$	$\epsilon^{535}_{\epsilon_1^{535}}$	$A \times 10^3$	$B \times 10^3$	$(A+B) \times 10^3$
3.5	4.995	1.627	-0.561	10.950	-6.600	4.350
4.0	5.378	2.010	-0.178	5.350	-1.130	4.220
4.5	5.876	2.508	0.320	2.615	1.087	3.702
5.0	6.445	3.077	0.889	1.162	1.530	2.692
6.0	7.898	4.530	2.342	0.328	1.343	1.671
7.0	9.375	6.007	3.819	0.068	0.635	0.703
8.0	11.163	7.795	5.607	0.016	0.294	0.310

Corr. coeff. = 0.98790

Intercept = 0.00869

Slope = -0.00087

$$\beta_3^* = 0.87 \times 10^{-3} \text{ mole}^{-3}$$

$$\epsilon_3^{535} = 9.979$$

Table 4.4.X. Calculation of the average value of the function F' in Equation (4E20).

[LiCl] (M)	Value of the function F' at the given wavelength								F'_{av}
	500	505	510	515	520	525	530	535	
3.5	0.108	0.108	0.154	0.130	0.040	0.196	0.170	0.130	0.129
4.0	0.427	0.397	0.496	0.408	0.244	0.510	0.463	0.345	0.411
4.5	1.180	1.070	1.271	1.015	0.747	1.152	1.138	0.872	1.056
5.0	2.790	2.725	2.965	2.465	1.912	2.650	2.630	2.020	2.520
6.0	14.58	13.93	15.63	13.75	9.69	14.70	12.96	11.10	13.29
7.0	112.0	93.5	183.1	118.0	75.6	309.5	230.0	102.9	153.1

Table 4.5.X. Data for Equations (4E20) and (4E21).

[LiCl]M	a_{Cl}	$(a_{Cl})^3$	F'_{av}	$\log a_{Cl}$	$\log F'_{av}$
3.5	5.30	148.9	0.129	0.724	-0.888
4.0	7.21	374.8	0.411	0.858	-0.386
4.5	9.85	955.7	1.056	0.994	0.023
5.0	13.83	2645.3	2.520	1.141	0.399
6.0	24.00	13824.0	13.29	1.380	1.123
7.0	44.60	88716.5	153.1	1.650	2.185

Table 4.6.X. Calculated values of α_n and $\bar{n}$.

Using $K_1^* = 0.33 \text{ mole}^{-1}$ and $\beta_3^* = 0.97 \times 10^{-3} \text{ mole}^{-3}$

$[\text{LiCl}]_M$	a_{Cl}	α_0	α_1	α_3	$\bar{n}$
0	0	1.000	0	0	0
0.5	0.373	0.890	0.110	0	0.110
1.0	0.791	0.794	0.207	0	0.208
1.5	1.302	0.698	0.301	0.001	0.305
2.0	1.951	0.607	0.390	0.005	0.403
2.5	2.790	0.515	0.474	0.011	0.507
3.0	3.835	0.432	0.546	0.024	0.617
3.5	5.30	0.345	0.605	0.050	0.753
4.0	7.25	0.267	0.636	0.097	0.926
4.5	9.85	0.193	0.628	0.179	1.165
5.0	13.63	0.123	0.562	0.312	1.509
5.5	17.91	0.080	0.474	0.446	1.810
6.0	24.00	0.045	0.355	0.601	2.160

Table 4.7.X. Comparison of the measured overall extinction coefficients with the theoretical values calculated from Equation (4B2).

$\lambda = 500 \text{ nm.}$ $\epsilon_0^{500} = 4.595$ $\epsilon_1^{500} = 6.455$ $\epsilon_3^{500} = 8.633$

$[\text{LiCl}]_M$	$\epsilon_0^{500} \alpha_0$	$\epsilon_1^{500} \alpha_1$	$\epsilon_3^{500} \alpha_3$	$\epsilon_{\text{calc.}}^{500}$	$\epsilon_{\text{exp.}}^{500}$
0	4.595	0	0	4.595	4.595
1.0	3.645	1.337	0	4.982	4.963
2.0	2.785	2.515	0.013	5.313	5.269
3.0	1.983	3.525	0.205	5.713	5.646
4.0	1.227	4.110	0.839	6.176	6.210
5.0	0.566	3.625	2.725	6.916	6.961
6.0	0.206	2.290	5.190	7.686	7.730

(continued)

Table 4.7.X. (continued)

$$\lambda = 530 \text{ nm.} \quad \epsilon_0^{530} = 3.825 \quad \epsilon_1^{530} = 5.915 \quad \epsilon_3^{530} = 10.221$$

$[\text{LiCl}]_M$	$\epsilon_0^{530} \alpha_0$	$\epsilon_1^{530} \alpha_1$	$\epsilon_3^{530} \alpha_3$	$\epsilon_{\text{calc.}}^{530}$	$\epsilon_{\text{exp.}}^{530}$
0	3.825	0	0	3.825	3.825
1.0	3.035	1.224	0	4.259	4.319
2.0	2.320	2.305	0.046	4.671	4.642
3.0	1.652	3.230	0.243	5.125	5.071
4.0	1.021	3.762	0.994	5.777	5.890
5.0	0.472	3.325	3.225	6.922	6.941
6.0	0.172	2.100	6.140	8.412	8.371

Table 6.1.X. V.P.O. results for Benzil.

C (gm/kg)	V (mV)	(V/C)	Linear regression analysis of V/C vs. C : Slope = 0.0000 Intercept = 0.0635 Corr. coeff. = -0.1902 K = 13.352 mV/molal
18.471	1.185	0.0642	
24.581	1.540	0.0627	
31.667	2.000	0.0632	
48.308	3.070	0.0636	
60.863	3.850	0.0632	
72.327	4.570	0.0633	

Table 6.2.X. V.P.O. results for Trioctylamine

C (gm/kg)	V (mV)	(V/C)	Linear regression analysis of V/C vs. C : Slope = 0.00005 Intercept = 0.0383 Corr. coeff. = 0.9642 Mol. wt. of TOA = $K.(V/C)^{-1}_{C=0} = 349$
14.525	0.565	0.0389	
17.290*	0.675	0.0390	
22.626	0.910	0.0402	
30.818	1.225	0.0398	
34.998	1.403	0.0401	
35.310*	1.410	0.0400	
41.869	1.690	0.0404	
44.915*	1.833	0.0408	
51.049	2.100	0.0412	
60.891	2.530	0.0416	
69.589	2.925	0.0420	

Results for water-saturated solutions,
except those marked * which are water
free

Table 6.3.X. V.P.O. results for Pure TOAHCl

C (gm/kg)	C (molal)	V (mV)	(V/C)	App. M.W.	$\bar{n}$	$\frac{\bar{n}(\bar{n}-1)}{(2-\bar{n})^2}$
1.553	0.0040	0.050	0.0322	415	1.065	0.079
3.234	0.0083	0.100	0.0309	432	1.109	0.153
6.561	0.0169	0.190	0.0290	461	1.184	0.327
12.251	0.0315	0.325	0.0265	503	1.292	0.753
13.223	0.0330	0.350	0.0265	505	1.295	0.768
17.490	0.0449	0.445	0.0254	525	1.347	1.100
22.930	0.0588	0.570	0.0249	537	1.379	1.353
34.628	0.0889	0.817	0.0236	566	1.453	2.205
40.312	0.1035	0.940	0.0233	573	1.470	2.460
48.032	0.1235	1.090	0.0227	588	1.511	3.240
62.099	0.1595	1.360	0.0219	610	1.565	4.660
74.008	0.1900	1.570	0.0212	629	1.616	6.760

Table 6.4.X. Monomer and dimer concentrations in TOAHCl, calculated from Equation (6D10).

S (m)	S (M)	log S	T_1 (M)	log T_1	T_2 (M)	log T_2
0.0040	0.0031	-2.509	0.0027	-2.566	0.0002	-3.698
0.0083	0.0064	-2.194	0.0051	-2.288	0.0006	-3.222
0.0169	0.0131	-1.883	0.0090	-2.045	0.0020	-2.698
0.0315	0.0244	-1.612	0.0134	-1.873	0.0055	-2.360
0.0330	0.0256	-1.592	0.0140	-1.854	0.0058	-2.336
0.0449	0.0348	-1.458	0.0169	-1.772	0.0090	-2.045
0.0588	0.0456	-1.341	0.0206	-1.686	0.0125	-1.903
0.0899	0.0696	-1.157	0.0262	-1.582	0.0217	-1.663
0.1035	0.0802	-1.096	0.0290	-1.538	0.0256	-1.592

Table 6.5.X. V.P.O. results for Practical TOAHCl.

C (gm/kg)	C (molal)	V (mV)	(V/C)	App. M.W.
10.999	0.0233	0.280	0.0255	525
20.969	0.0442	0.530	0.0253	528
29.967	0.0632	0.723	0.0241	553
40.721	0.0860	0.980	0.0240	555
52.275	0.1102	1.195	0.0229	584
60.304	0.1272	1.378	0.0229	584
72.262	0.1524	1.615	0.0224	597
83.477	0.1760	1.855	0.0222	601

Table 6.6.X. V.P.O. results for TOAHNO₃.

C (molal)	V (mV)	(V/C)	$\bar{n}$	$\frac{\bar{n}(\bar{n}-1)}{(2-\bar{n})^2}$
0.0085	0.100	11.765	1.135	0.205
0.0175	0.195	11.143	1.198	0.368
0.0297	0.307	10.337	1.292	0.754
0.0430	0.413	9.605	1.390	1.457
0.0622	0.553	8.891	1.502	3.045
0.0877	0.690	7.867	1.697	12.87
0.1182	0.800	6.768	1.973	2630

Table 6.7.X. V.P.O. results for the Cobalt salt of TOAHCl.

C (gm/kg)	[Co] (M)	V (mV)	(V/C)	App. M.W.	$\bar{n}^*$
7.29	0.0055	0.115	0.0158	846.5	1.086
16.12	0.0122	0.252	0.0156	854.2	1.097
27.69	0.0209	0.390	0.0141	948.1	1.218
41.07	0.0311	0.555	0.0135	988.1	1.270
46.16	0.0349	0.605	0.0131	1018.8	1.309
53.22	0.0402	0.705	0.0133	1008.0	1.295
68.74	0.0520	0.885	0.0129	1037.2	1.333
83.91	0.0635	1.035	0.0123	1082.6	1.392

* See Section 6.D(vii)

Table 7.1.X. Calculation of K for Cl-NO_3 exchange from Equation (7A4).

$$[\text{TOAHCl}]_i = 0.0983\text{M}$$

$[\text{Cl}]$ (M)	$[\text{NO}_3]$ (M)	a_{Cl}^*	$a_{\text{NO}_3}^*$	$[\text{TOAHCl}]^{**}$ (M)	$Y_{\text{NO}_3}^{***}$ (M)	$\frac{a_{\text{Cl}}}{a_{\text{NO}_3}}$	$\frac{[\text{TOAHCl}]}{Y_{\text{NO}_3}}$
4.0	3.5	27.7	15.00	0.0059	0.0924	1.85	0.0639
5.0	2.5	36.2	11.40	0.0115	0.0868	3.17	0.1325
6.0	1.5	47.1	7.46	0.0185	0.0798	6.31	0.2318
6.5	1.0	53.4	5.32	0.0285	0.0698	10.03	0.4083
7.0	0.5	57.9	2.71	0.0462	0.0521	21.30	0.8868
4.0	2.5	19.0	8.47	0.0079	0.0904	2.24	0.0874
5.0	1.5	25.1	5.46	0.0147	0.0836	4.60	0.1758
6.0	0.5	32.3	2.05	0.0371	0.0612	15.75	0.6062

* - Data from Appendix 1

** - Data from Table 3.3

*** - $Y_{\text{NO}_3} = \frac{[\text{TOAHNO}_3]}{[\text{TOAHCl}]_i - [\text{TOAHCl}]}$

Table 7.2.X. Calculation of organic chloride concentrations of TOA solutions in equilibrium with LiCl-LiNO_3 solutions.

For $[\text{TOA}] = 0.0983\text{M}$, using Equation (7A4) with $K_x = 24.4$.

$[\text{Cl}]$ (M)	$[\text{NO}_3]$ (M)	a_{Cl}	a_{NO_3}	$[\text{TOAHCl}]_{\text{calc.}}$ (M)	$[\text{TOAHCl}]_{\text{exptl.}}$ (M)
7.0	0.5	57.9	2.71	0.0458	0.0462
6.5	1.0	53.4	5.32	0.0286	0.0285
6.0	1.5	47.1	7.46	0.0202	0.0185
5.5	2.0	41.7	9.61	0.0148	-
5.0	2.5	36.2	11.40	0.0113	0.0115

(continued)

Table 7.2.X. (continued)

4.5	3.0	31.6	13.20	0.0088	-
4.0	3.5	27.7	15.00	0.0069	0.0059
6.0	0.5	32.3	2.05	0.0385	0.0371
5.5	1.0	28.5	3.80	0.0232	-
5.0	1.5	25.1	5.46	0.0156	0.0147
4.5	2.0	21.8	7.03	0.0111	-
4.0	2.5	19.0	8.47	0.0083	0.0079
3.5	3.0	16.0	9.75	0.0062	-

Table 7.3.X. Variation of D_{Co} with free amine salt concentration.a) Amine hydrochloride systems.

$$[TOAHCl]_{free} = [TOAHCl]_{total} - 2.3Y_{Co}$$

$$[Cl] = 7.5M, [TOAHCl]_{total} = 0.0985M$$

Y_{Co} ($M \times 10^3$)	$[TOAHCl]_{free}$ ($M \times 10^2$)	$\log [TOAHCl]_{free}$	D_{Co}	$\log D_{Co}$
0.93	9.63	-1.016	96.2	1.984
1.91	9.40	-1.028	92.9	1.964
4.70	8.76	-1.058	81.0	1.909
9.24	7.70	-1.114	54.5	1.736
14.22	6.57	-1.182	39.6	1.598

(continued)

Table 7.3.X. (continued)

$$[Cl] = 7.0M, [TOAHCl]_{total} = 0.0983M$$

Y_{Co} ($M \times 10^3$)	$[TOAHCl]_{free}$ ($M \times 10^2$)	$\log [TOAHCl]_{free}$	D_{Co}	$\log D_{Co}$
0.94	9.61	-1.017	41.8	1.622
1.85	9.41	-1.026	38.0	1.580
4.57	8.78	-1.056	32.9	1.518
8.99	7.76	-1.110	23.2	1.366
13.52	6.72	-1.172	18.3	1.264

$$[Cl] = 6.5M, [TOAHCl]_{total} = 0.0983M$$

Y_{Co} ($M \times 10^3$)	$[TOAHCl]_{free}$ ($M \times 10^2$)	$\log [TOAHCl]_{free}$	D_{Co}	$\log D_{Co}$
0.95	9.61	-1.017	21.31	1.328
4.61	8.77	-1.057	17.05	1.232
9.17	7.72	-1.112	13.21	1.121
16.98	5.92	-1.228	7.48	0.874

b) Amine hydrochloride - amine nitrate systems.

$$[TOAHX]_{free} = [TOAHX]_{total} - 2.3Y_{Co}$$

$$\text{where : } X = Cl + NO_3$$

$$[Cl] = 7.0M, [NO_3] = 0.5M, [TOAHX]_{total} = 0.0985M$$

(continued)

Table 7.3.X. (continued)

Y_{Co} ($M \times 10^3$)	$[TOAHX]_{free}$ ($M \times 10^2$)	$\log [TOAHX]_{free}$	D_{Co}	$\log D_{Co}$
0.89	9.75	-1.011	14.08	1.149
1.79	9.44	-1.025	13.91	1.144
4.40	8.85	-1.053	12.11	1.084
8.37	7.83	-1.106	9.03	0.955
12.44	7.02	-1.154	6.80	0.833

$$[Cl] = 6.5M, [NO_3] = 1.0M, [TOAHX]_{total} = 0.0976M$$

Y_{Co} ($M \times 10^3$)	$[TOAHX]_{free}$ ($M \times 10^2$)	$\log [TOAHX]_{free}$	D_{Co}	$\log D_{Co}$
0.76	9.58	-1.018	4.34	0.638
1.56	9.40	-1.027	4.07	0.610
3.79	8.89	-1.051	3.74	0.573
7.20	8.10	-1.091	3.10	0.491
10.27	7.40	-1.130	2.60	0.415

$$[Cl] = 6.0M, [NO_3] = 0.5M, [TOAHX]_{total} = 0.0980M$$

Y_{Co} ($M \times 10^3$)	$[TOAHX]_{free}$ ($M \times 10^2$)	$\log [TOAHX]_{free}$	D_{Co}	$\log D_{Co}$
0.59	9.66	-1.015	1.561	0.192
1.20	9.52	-1.020	1.642	0.216
2.85	9.14	-1.039	1.465	0.166
5.19	8.61	-1.065	1.216	0.085
7.73	8.02	-1.096	1.132	0.054

Table 7.4.X. Calculations for Equation (7E17).

[Cl]M	[Cl]m	a_{H_2O}	$\log a_{H_2O}$	x	$2.3 \times \log a_{H_2O}$	$\log a_{Cl}$	$\log D_{Co}$	$-\log \alpha_3$	Total*
3.0	3.185	0.860	-0.065	0.81	-0.121	0.583	-1.701	1.620	0.381
3.5	3.760	0.827	-0.083	0.78	-0.149	0.724	-1.282	1.301	0.594
4.0	4.340	0.790	-0.102	0.74	-0.173	0.860	-0.867	1.013	0.833
4.5	4.950	0.749	-0.125	0.71	-0.204	0.993	-0.458	0.747	1.078
5.0	5.565	0.708	-0.150	0.68	-0.234	1.135	-0.029	0.506	1.378
5.5	6.20	0.664	-0.178	0.65	-0.266	1.253	0.396	0.351	1.734
6.0	6.84	0.620	-0.208	0.62	-0.296	1.380	0.825	0.221	2.130

* Total = $\log \gamma_3$

APPENDIX 3LIST OF SYMBOLS

The equation where first used is given in parentheses after some of the symbols. Overlined symbols indicate that the species or quantities pertain to the organic phase.

a_A	Effective ligand activity.
a_{Cl}	Effective chloride activity.
a_x	Activity of species x.
a_1	Number of amine salt monomers involved in the extraction (7C6).
a_2	Number of amine salt dimers involved in the extraction (7C8).
C	Solute concentration in gm./kg. solvent (6D1).
C_H	Molar concentration of water associated with the amine salt (5D2).
C_s	Molar concentration of amine salt (5D1).
C_w	Total molar concentration of water in the organic phase (5D1).
C_{wo}	Water solubility in the pure solvent at $a_{H_2O} = 1$ (5D1).
D_{Co}	Distribution coefficient of cobalt.
F	Activity coefficient function (4B4).
$[HCl]_{xs}$	Excess HCl in the organic phase (7E25).
h	Degree of hydration of the amine salt at $a_{H_2O} = 1$ (5D1).
I	Ionic strength.

K	Empirical calibration constant for the vapour pressure osmometer (6D1).
K_{ex}	Extraction equilibrium constant.
K_n	Thermodynamic stepwise equilibrium constant.
K_n^*	Apparent stepwise equilibrium constant (4B9).
K_n^{**}	Apparent stepwise equilibrium constant involving water activities (Section 4.F).
K_x	Cl-NO ₃ exchange constant (7A2).
K_{11}	Amine-acid association constant (7A5).
K_2	Dimerisation constant.
M	Molar concentration, or molecular weight of solute (6D1).
M_o	Monomer molecular weight of the solute.
M_p	Apparent molecular weight by potentiometric titration.
M_s	Molecular weight of standard solute (6D3).
M_t	Theoretical molecular weight.
M_v	Apparent molecular weight by vapour pressure osmometry.
m	Molal concentration.
$\bar{n}$	Average aggregation number (Chapter 6), or average ligand number.
$\bar{n}^*$	Overall apparent aggregation number (Section 6.D(vii)).
O.D.	Optical density.
P.L.	Path length in cm.
S	Total stoichiometric molal concentration of TOAHCl (6D7).
S_v	Experimental slope for the apparent molal volume (A2).
s	Number of amine salt molecules solvating the organic metal complex (7E1).
TBP	Tributyl phosphate.
THA	Tri-n-hexylamine.
TIOA	Tri-iso-octylamine.

TLA	Trilaurylamine (tridodecylamine).
TOA	Tri-n-octylamine.
T_1	Molal concentration of monomer.
T_2	Molal concentration of dimer.
X_{Co}	Aqueous phase cobalt concentration.
X_{Cl}	Aqueous phase chloride concentration.
X_n	Mole fraction of substance n (6D4).
x	Degree of hydration (5D3).
Y_{Co}	Organic phase cobalt concentration.
Y_{Cl}	Organic phase chloride concentration.
$\gamma_{\pm}$	Mean molar activity coefficient.
$z_+(z_-)$	Valency of cation (anion).
α_A	Empirical coefficient in the Harned Equation (7E19).
α_n	Fraction of metal present as nth complex.
β_n	Thermodynamic overall equilibrium constant.
β_n^*	Apparent overall equilibrium constant (4E18).
β_n^{**}	Apparent overall equilibrium constant involving water activities (Section 4.F).
$\gamma_{\pm}$	Mean molal activity coefficient.
$\gamma_{A(B)}$	Mean activity coefficient of salt A in a mixture of salts A and B of total molality m (7E19).
$\gamma_{A(0)}$	Mean activity coefficient of salt A in its own solution of molality m (7E19).
$\bar{\gamma}_b$	Activity coefficient of the amine salt species (7E4).
$\bar{\gamma}_c$	Activity coefficient of the organic metal complex (7E4).
γ_{Cl}	Activity coefficient of chloride ions.
γ_n	Activity coefficient of the nth metal complex.
ϵ^λ	Overall extinction coefficient at wavelength λ

ϵ_n^λ	Extinction coefficient of nth complex at wavelength λ
λ	Wavelength.
ϕ_v	Apparent molal volume.
ϕ_v^o	Partial molal volume in the standard state.
[]	Concentration.
{ }	Activity.
$\bar{X}$	Species existing in the organic phase.

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ACKNOWLEDGEMENTS

The author sincerely thanks Dr. A.R. Burkin, Reader in Hydrometallurgy, for his advice and guidance during the course of this work, and also for his consideration and many personal kindnesses.

The author is indebted to Professor F.D. Richardson, Professor of Extractive Metallurgy, for providing him with the opportunity to undertake this research.

Thanks are also due to Mrs. M.J. Rogers for carrying out many of the spectrophotometric measurements, and to Mr. J.E.A. Burgess for his general assistance and efficiency.

In particular, the author is grateful to his wife, Johanna, for her patience and encouragement, and for the many hours spent typing and painstakingly checking the typescript of this thesis.

Royal School of Mines,
London.
March 1972.