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Chemically based models to predict distribution coefficients in the copper (II) and zinc (II) chloride-Tri-n-octylamine extraction systems

by

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NOMENCLATURE

α_i	degree of formation of a particular ion
B	ligand
E	overall electrode voltage (millivolts)
E_a	reference electrode voltage (millivolts)
F	Faraday's electrochemical constant
I	ionic strength of solution
D	distribution coefficient
K_e	liquid-liquid extraction equilibrium constant
K_1	effective liquid-liquid extraction equilibrium constant
K_1'	K_1/K_e
K_{M-N}	K_{1M}/K_{1N}
K'_{M-N}	K'_{1M}/K'_{1N}
K_γ	activity coefficient quotient
K_x	selectivity constant
M	metallic ion
ϕ	the ratio of the organic concentration to the ligand concentration in the aqueous phase
γ_i	activity coefficient of a particular specie
S_{M-N}	separation factor for species M and N
T	absolute temperature, °K
Z_i	charge of particular ion

<u>Subscripts</u>

A	refers to the aqueous phase
i	refers to the ith species

n	number of ligand ions in a complex
O	refers to organic phase

Superscripts

E	refers to equilibrium conditions
I	refers to initial conditions
T	refers to total conditions
[ ]	refers to activity conditions
( )	refers to concentration conditions

ABSTRACT[1]

The fundamental chemistry of copper (II) and zinc (II) chloride extraction by the extractant tri-n-octylamine is reviewed. The chemically based model (1, 2, 3) is derived for both the single systems and the binary system. The predictive model makes use of the aqueous phase metal chloride complexes' stability constants, their extraction mechanism, and the equilibrium constant for the extraction reaction. The distribution coefficient of copper and zinc can be predicted by the equation $D = K_1 \alpha_o \phi^2$, where ϕ is the product of the equilibrated organic concentration and the chloride ion concentration in the aqueous phase, K_1 is the effective equilibrium constant containing the quotient of the activity coefficients of the reacting species and α_o is the degree of formation of the free metal ion in the equilibrated aqueous phase. Excellent agreement between the experimental data and the predicted values was obtained.

The multicomponent, binary metal extraction is examined in a quantitative manner. The separation factor can be predicted by the equation $S_{M,N} = K_1' \frac{(\alpha_o)_M}{(\alpha_o)_N}$. This model was based on the assumption that the activity coefficient varies slightly with its concentration. The experimental results show that the data fit the binary model very well. The suppression of copper extraction in the presence of zinc was noticed.

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I. INTRODUCTION

Solvent extraction is undoubtedly one of the older known separation techniques used in processing of materials. In 1872, Berthelot and Jungfleisch (4) reported that "A body that can dissolve in each of them separately, simultaneously put in the presence of two liquids, never dissolves completely in one of them to the exclusion of the other... the solute body always partitions itself between the two solvents, following a simple relation... the amounts dissolved by equal volumes of the two liquids are in constant ratio."

A solvent extraction system consists of an extractant, an organic diluent, water, an acid or base, the species being separated and concentrated, and the impurities being discarded. Such a system is very complicated from a thermodynamic viewpoint, the modeling of this system using the chemical solution properties as the basis rather than using purely mathematical and/or statistical correlation is simpler and more general. The development of a chemically based thermodynamic equilibrium model for describing and predicting the distribution coefficient has been reported (1, 2, 3).

The first transition elements constitute a family of metals which often exhibit very similar chemical behavior. The similarity is most easily observed with the cation in the plus 2 oxidation state. The two important metals in the first transition series that is the subject of this research are copper and zinc.

Solvent extraction studies previously reported on this system were usually carried out at low concentrations of copper and zinc. Studies at higher concentrations were not carried out because the mechanism for the reactions involved are extremely complicated and have not been completely defined. This study considered both the low and the high concentration ranges of copper and zinc.

The presence of both copper and zinc in many effluent wastes (i.e., municipal and others) and their high unit prices make their recovery of interest if it can be done economically (5, 6). For this reason, a hydrometallurgical solvent extraction process for the recovery of both copper and zinc from the primary ore, the low grade ore, or from recycled materials is perhaps feasible (7). The hydrometallurgical process usually consists of three steps: 1) a leaching step where the metals are dissolved and introduced to the aqueous phase, 2) the separation and concentration by a solvent extraction step, and 3) the metal reduction step from solution. The choice of a leaching reagent, often a mineral acid, is important to all three steps. For example, tri-n-octylamine (TOA) extracts both copper and zinc from a chloride media much more efficiently than from a sulfate media. The leaching reagent chosen for this system is hydrochloric acid which is a better reagent than sulfuric acid. The chloride media is very corrosive, but the availability of chloride resistant construction materials helps alleviate this problem (5).

The extractant used for this study is tri-n-octylamine (TOA), which was used as a hydrochloride. An advantage of using this extractant is that amines are amenable to chloride chemistry. Tri-n-octylamine (TOA = R_3N, R = C_7H_{18}) has been reported to be a very good extractant for this system as reported in the literature (8). The diluent used for this extractant is benzene, which is insoluble in water and is a good diluent for TOA.

The extraction of mineral acids by long chain aliphatic amines in organic solvents has received increasing attention since the work of Smith and Page (8) who suggested the possibility of using the process for the extraction of many different inorganic and organic acids. Furthermore, amines of high molecular weight in organic solvents have recently been used to extract various metal ions from acid solutions. Data on the extraction of nitric, hydrochloric, hydrofluoric and sulfuric acids by various amines have been reported in the literature (9-14). To minimize the co-extraction of hydrochloric acid by TOA in this work, the TOA was pre-equilibrated with hydrochloric acid before being used.

Few quantitative studies have been done on the simultaneous extraction of copper and zinc. The purpose of this study is to develop quantitative information on the separation of copper and zinc in TOA in single metal and binary metal systems.

The objectives of this study are: 1) to review the state of the art of liquid-liquid extraction of copper, zinc and copper-zinc from aqueous salt solutions by TOA; 2) to develop a model analogous to that of Hoh and Bautista (1), Hoh (2), and O'Brien (3) for single metal and binary metal systems; 3) to experimentally study the liquid-liquid extraction of copper, zinc and copper-zinc from its chloride solutions by TOA; 4) to test the consistency between the predicted values and the experimental results for a) the reported literature data and b) the experimental results obtained; and 5) to be able to predict the extraction trends of copper, zinc and copper-zinc systems from minimum numbers of experimental data.

II. LITERATURE REVIEW

A. The Chemistry of Extraction of the First Transition Metals

Kolarik and Grimm (15) worked with the extraction of copper (II), nickel (II), zinc (II) and cadmium (II) by di-(2-ethylhexyl)phosphoric acid (HDEHP). The extractability of HDEHP in n-dodecane for $1 \times 10^3 \frac{\text{moles}}{\text{m}^3}$ (Na, H)NO_3 and $1 \times 10^3 \frac{\text{moles}}{\text{m}^3}$ (Na, H)Cl was found to decrease in the orders of Zn(II) $>$ Cd(II) $>$ Cu(II) $>$ CO(II) $>$ Ni(II) and Zn(II) $>$ Cu(II) $>$ Cd(II) $\approx$ CO(II) $>$ Ni(II), respectively. From this order, it is seen that zinc and copper can be effectively separated from the other metals. Grimm and Kolarik (16) also studied the polymerization behavior of Cu(II), Cd(II), Zn(II) and CO(II) complexes of di-(2-ethylhexyl)phosphoric acid in fully loaded organic phases. Grimm and Kolarik concluded from the polymerization behavior that the complexes can be divided into two groups. The Cu(II) and Cd(II) complexes do not tend to form indefinitely large polymeric species and are not polymerized by ethylene glycol. The Zn(II) and CO(II) complexes tend to form very large polymeric species in dodecane and benzene, which are strongly polymerized by ethylene glycol and free HDEHP. This shows that zinc is more capable of forming extractable species with HDEHP than copper. Furthermore, Kolarik and Grimm (17) examined the properties of the complexes formed by Cu(II), CO(II), Ni(II), Zn(II) and Cd(II) with di-(2-ethylhexyl)phosphoric acid. It was concluded that the metal to HDEHP ratio is 1:2 and the anions of HDEHP occupy four coordination sites. The ratio coincides with the oxidation state of the metals (i.e., + 2) and the same ratio is observed in our system.

Sato and co-workers (18) studied the extraction of transition metals from hydrochloric acid solutions by HDEHP acid. The aqueous and organic phases were examined spectrophotometrically. The extraction efficiency of HDEHP for divalent metals was found to be Fe > Zn > Mn > Cu > CO > Ni. Zinc and copper are extracted more efficiently by HDEHP than cobalt and nickel.

Vander Zeeuw (19) studied the extraction of Cu(II), Ni(II), CO(II), Zn(II), Fe(III) and CO(III) with carboxylic acids as an extractant. The distribution coefficients of Cu(II), Zn(II), Ni(II) and CO(III) were found to change only marginally, if at all, when the extraction temperature was increased from 20^{o} to $80^{o}C$. In the present work, the temperature is at $22^{o}C$ (i.e., room temperature).

B. The Chemistry of Extraction of Tri-n-Octylamine

Tri-n-octylamine is characterized as a neutral extractant. The extraction of metal ions from hydrochloric acid solutions by high molecular weight amines has been studied by several investigators (20, 21, 22).

The distribution of uranium (VI) between sulfuric acid solutions and solutions of tri-n-octylamine in benzene was investigated by Sato (9) at varying concentrations of sulfuric acid, solvent and uranium and also at different temperatures. The solvent was found to extract the acid according to the equation

$$[H_2SO_4]_A + [2R_3N]_O \rightleftharpoons [(R_3NH)_2SO_4]_O \qquad (1)$$

at low acidities and according to the equation

$$[(R_3NH)_2SO_4]_O + [H_2SO_4]_A \rightleftharpoons [2(R_3NH)HSO_4]_O \qquad (2)$$

at high acidities. The temperature effect on the distribution coefficient of uranium (VI) was found to decrease with temperature.

The distribution of uranium (VI) between nitric acid solutions and solutions of tri-n-octylamine in benzene was investigated by Sato (10). The distribution coefficient in the presence of nitric acid passes through a maximum at ~ $7 \frac{\text{moles}}{m^3} \times 10^3$ initial aqueous HNO_3 concentration. When the nitric acid in the aqueous phase is partially replaced by sodium nitrate, the distribution coefficient increases with the total nitrate ion concentration and the maximum disappears. Before Sato's study, Baroncelli and co-workers (11) explained that this maximum is due to the presence of different types of uranium complexes in the aqueous phase. Sato proved that this conclusion was wrong. Sato explained that the extraction of nitric acid by TOA may be represented by the reaction

$$[HNO_3]_A + [R_3N]_O \rightleftharpoons [R_3NHNO_3]_O \qquad (3)$$

This shows that nitric acid is coextracted by the available TOA resulting in a maximum in the distribution coefficient. Sato found that the extractable species, the amine nitrate complex, has the stoichiometry $(R_3NH)_2UO_2(NO_3)_4$.

The distribution of uranium (VI) between hydrochloric acid solutions and solutions of tri-n-octylamine in benzene was investigated by Sato (12). It was concluded that although the extraction efficiency of TOA for uranium depends on the diluent, the distribution coefficient in various TOA-organic solvent systems (except for chloroform and octyl-alcohol, which are very poor extraction solvents) rises with the acidity in the aqueous phase at low acidities, passes through a maximum at 6-8 $\frac{\text{moles}}{\text{m}^3} \times 10^3$ initial acidity, and then decreases at higher acidities. In the extraction with solutions of TOA in benzene, the maximum distribution coefficient appears at 8 $\frac{\text{moles}}{\text{m}^3} \times 10^3$ initial aqueous acidity. When the acid in the aqueous phase is partly replaced by lithium chloride, the decrease in the distribution coefficient beyond the maximum is checked. It may be that lithium chloride is not extracted by the amine, but is effective as a salting-out agent for the extraction of uranium. Sato and co-workers assumed that at low aqueous acidities the increase in the distribution coefficient D arises either from the salting-out of chloride ion in the aqueous solution or from the formation of a uranyl chloride hydrochloric acid complex. At higher aqueous acidities, the decrease in D is attributed either to competition between uranium and hydrochloric acid for association with amine or to the formation of less-readily extractable species. The extraction of the acid by the solvent may be represented by

$$[\mathrm{HCl}]_A + [\mathrm{R_3N}]_O \rightleftharpoons [\mathrm{R_3NHCl}]_O \tag{4}$$

Sato (13) studied the extraction of cobalt (transition metal) from hydrochloric acid solution by TOA. Sato proposed the following extraction mechanism

$$[\mathrm{COCl_2}]_A + [\mathrm{2R_3NHCl}]_O \rightleftharpoons [\mathrm{(R_3NH)_2COCl_4}]_O \tag{5}$$

This is similar to the extraction mechanism for copper and zinc.

The distribution equilibrium of nitric, hydrochloric, perchloric, sulfuric and phosphoric acids between aqueous solutions and benzene solutions of TOA was investigated by Sato (14). The distribution and infrared results indicate that the extraction of these acids is governed by the formation of the mono-amine salts of mono-basic acids, and of the mono-, di- (and tri-) amino salts of di- (and tri-) basic acids. It is thought that at low aqueous acidities, these strong mono-basic acids are extracted into TOA by the following reaction:

$$[H^+]_A + [X^-]_A + [R_3N]_O \rightleftharpoons [R_3NHX]_O \qquad (6a)$$

It is postulated that the nature of the bonding in the organic phase is analogous to that of hydrogen bonds. This was also supported by the infrared result obtained in this experiment. In consequence, the distribution equilibrium of acids between aqueous solutions and TOA can be expressed, in general, by the following equation:

$$[nH^+]_A + [X^{n-}]_A + [nR_3N]_O \rightleftharpoons [(R_3NH)_nX]_O \qquad (6b)$$

C. Complexes of Copper and Zinc and Their Stability Constants

In a spectrophotometric study by Nasanen (23) on the complex formation between cupric and sulfate ions, the first stability constant of cupric sulfate was determined in lithium sulfate solutions. The stability constant was found to be a function of ionic strength. The possibility of the existence of other complexes in this system was discussed. It was concluded that the other complexes' effect can appear only at high ionic strength and is not expected to be very significant.

Sandell (24) studied the stability constants of the mononuclear complexes formed by copper (II) ion in aqueous solutions with methoxyacetate, ethoxyacetate, (ethylthio)acetate, and thiodiacetate ions. The stability constants were determined by potentiometric methods at 293°K. The investigations were carried out in a perchlorate medium at ionic strength I = 1.0 x $10^3 \frac{\text{moles}}{\text{m}^3}$. Sandell (25) also studied the formation in aqueous solution of ethyoxyacetate and (ethylthio)-acetate complexes of Zn^{2+} by determination of the concentration of free ligand in the complex solutions. The measurements were performed at 298°K in a perchlorate medium at an ionic strength of 1 x $10^3 \frac{\text{moles}}{\text{m}^3}$. Sandell concluded that in all of these systems at least two mononuclear complexes are formed. Sandell also concluded that those metals showed parallel behavior in forming their complexes with those ligands where the zinc forms stronger complexes at a very high rate. This behavior is ascribed to a certain degree of chelate formation in the zinc system.

Morris and Short (26) have determined the stability constants of copper (II) chloride complexes using a cation-exchange resin in the H^+-form. Values have been obtained for the stability constants, β_i, which are valid for 293°K and an ionic strength of 0.691 $\frac{\text{moles}}{\text{m}^3}$ x 10^3. The ionic strength was maintained with perchloric acid. The distribution of the metal between the resin and the solution was determined spectrophotometrically. Short and Morris (27) conducted a similar study with zinc by using a radiochemical method. The stability constants for zinc were also determined.

Mihailov (28) in Bulgaria has calculated the overall stability constants for cupric chloride and zinc chloride using a mathematical correlation. The model is concerned with the formation of a stepwise series of mononuclear complexes of the metal M^{m+} and the ligand L. The model equation is represented by the equation

$$\beta_n = A \cdot \frac{a^n}{n!} \tag{7}$$

where: β_n is the overall stability constant of the ML_n complex; n is the number of ligands in a particular complex ($1 \leq n \leq N$); N is the coordination number of the complex forming metal M; and A and a are constants. The applicability of this model equation has been demonstrated for nine metal-ligand systems. The systems are cupric-chloride, zinc-chloride, cadmium-chloride, indium-chloride, indium-chloride (different ligand concentration than the first), gallium-chloride, lead-chloride, zinc-bromide and cadmium-bromide.

Sato and Murakami (29) calculated the stability constants of the complexes formed in aqueous phase in the extraction of zinc (II) from hydrochloric acid solutions by Aliquat-336. In their work, the activity of the solvent (benzene), a_o, is first obtained by means of an activity coefficient equation based on the vapor-pressure method. Then by using the Gibbs-Duhem equation, the activity coefficient of Aliquat-336 in benzene was determined by graphical integration methods. The extraction mechanism may be represented by

$$[ZnCl_4^{2-}]_A + [2R_3R'NCl]_O \rightleftharpoons [R_3R'N)_2ZnCl_4]_O + [2Cl^-]_A \tag{8}$$

where $R_3R'NCl$ stands for tricaprylmethylammoniumchloride. The model equation for the distribution coefficient is represented by

$$D = \frac{K_1[Cl^-]_A^2[R_3R'NCl]_O^2}{1 + \sum_{i=1}^{N} \beta_i[Cl^-]_A^i} \qquad (9)$$

This equation can be considered as a function containing five parameters and two variables. The parameters were determined using a computer iterative technique.

Sato and Kato (30) calculated the stability constants of the chloro-complexes of copper (II) and zinc in the aqueous phase from equilibrium data using the solvent TOA. In order to use the activity rather than the concentration of the extractant (TOA), the activity coefficient of TOA hydrochloride in benzene was first determined by a vapor-pressure method. The calculated stability constants are as follows: for copper (II), $\beta_1 = 11.6$, $\beta_2 = 3.15$, $\beta_3 = 1.02$ and $\beta_4 = 0.51$; for zinc (II), $\beta_1 = 5.35$, $\beta_2 = 2.76$, $\beta_3 = 1.07$ and $\beta_4 = 0.27$.

Thiel (31) and McConnell and Davidson (32) studied the extraction of copper and zinc chlorides by tri-iso-octylamine (TIOA). The model equation used was represented by

$$K'_{eq} = \frac{[(R_3NHCl)_2MCl_2]_O[Cl^-]_A^n}{[MCl_{n+2}^{-n}]_A[R_3NHCl]_O^2} \qquad (10)$$

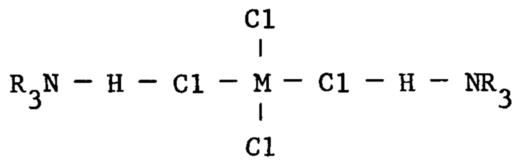
The average value for K'_{eq} was obtained from data reported in the literature. The concentrations of the aqueous chloride ion and the free extractant in the organic phase were measured experimentally. By using the model equation, the extractable specie concentration, $(R_3NHCl)_2MCl_2$, was then calculated. The concentration of the extractable specie in the organic phase is assumed to be equal to the metal concentration in the organic phase. The concentration of the metal in the aqueous phase was determined experimentally. Finally, the distribution coefficient D was calculated as the ratio of the metal concentration in the organic phase to the metal concentration in the aqueous phase. Thiel concluded that the aqueous phase copper chloride stability constants used are either wrong or inaccurate over the range of experimental conditions. Thiel also concluded that in the binary system, zinc is favorably extracted over copper.

D. The Mechanism of the Extraction of Copper and Zinc by Tri-n-octylamine

Sato and Adachi (33) reported that the extraction of copper (II) from solutions containing $6 \times 10^3 \frac{\text{moles}}{\text{m}^3}$ (6M) hydrochloric acid or $0.1 \times 10^3 \frac{\text{moles}}{\text{m}^3}$ (0.1 M) hydrochloric acid in the presence of $6 \times 10^3 \frac{\text{moles}}{\text{m}^3}$ (6M) lithium chloride approached a limiting value of $\sim 50 \frac{\text{moles}}{\text{m}^3}$ (0.05 M) as the initial aqueous copper concentration was increased. This implies that two amine molecules are associated with each copper ion. This conclusion was supported by the extractant dependence of the D, which shows a second-power dependency on the TOA concentration. Thus, the equilibrium expression for the reaction of the organic species with a metal cupric chloride molecule is given by the reaction

$$[\mathrm{CuCl_2}]_A + [2\mathrm{R_3NHCl}]_O \rightleftharpoons [(\mathrm{R_3NH})_2\mathrm{CuCl_4}]_O \qquad (11)$$

The complex was found to contain copper:chloride:TOA in the mole ratio 1:4:2, i.e., $(R_3NH)_2CuCl_4$ or $(R_3NHCl)_2CuCl_2$. A Karl Fischer titration test was used to check whether the complex contained water. The test was negative. The structure of the amine complex of the tetra chloro cuprate ion exists in a square-planar arrangement for a primary amine, and in a tetrahedral arrangement for secondary, tertiary and quarternary amines (34). The most probable structure of the metal-TOA salt complex is:



$$R_3N - H - Cl - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{M}} - Cl - H - NR_3$$

The same mechanism is assumed for zinc by Sato and Kato (30). The D in the presence of hydrochloric acid alone passes through a maximum at about $6 \times 10^3 \ \frac{\text{moles}}{m^3}$ (6M) and (3-4) $\times 10^3 \ \frac{\text{moles}}{m^3}$ (3-4M) initial aqueous hydrochloric acid concentration for copper and zinc, respectively. But, in the presence of lithium chloride, each maximum is checked because the chloride ion no longer competes for the amine salt.

It has been reported by Lindenbaum and Boyd (35) that the spectra of copper (II) in organic amine phases are characteristic of the four coordinated $CuCl_4^{2-}$ ion. In the spectra of the aqueous solutions, the absorption due to the aquo-ion $Cu(H_2O)_6^{2+}$ at low acidity and the tetrahedral species $CuCl_4^{2-}$ at high acidity are observed.

The three chemical reactions (30) required for the metal extraction are: 1) the metal chloride complex formation, 2) the amine salt formation, and 3) the extraction reaction occurring at or near the two phase interface. The first two of these steps may be written as

$$1) \quad [M^{2+}]_A + [nCl^-]_A \rightleftharpoons [MCl_n^{-(n-2)}]_A \qquad (12)$$

$$[M^{2+}]_A + [Cl^-]_A \rightleftharpoons [MCl^+]_A \qquad (13)$$

$$[M^{2+}]_A + [2Cl^-]_A \rightleftharpoons [MCl_2]_A \qquad (14)$$

$$[M^{2+}]_A + [3Cl^-]_A \rightleftharpoons [MCl_3^-]_A \qquad (15)$$

$$[M^{2+}]_A + [4Cl^-]_A \rightleftharpoons [MCl_4^=]_A \qquad (16)$$

and 2) $$[R_3N]_O + [HCl]_A \rightleftharpoons [R_3NHCl]_O \qquad (17)$$

The metal extraction reaction itself can occur by one of two mechanisms, both resulting in the double salt complex. The two mechanisms are addition,

$$[MCl_2]_A + [2R_3NHCl]_O \rightleftharpoons [(R_3NHCl)_2MCl_2]_O \qquad (18)$$

or anion exchange,

$$[MCl_{n+2}^{-n}]_A + [2R_3NHCl]_O \rightleftharpoons [(R_3NHCl)_2MCl_2]_O + [nCl^-]_A \qquad (19)$$

the difference being in whether or not a chloride ion is released (36). Also, the difference in the two mechanisms depends upon whether the metal chloride being extracted is negatively charged or neutral. The copper and zinc are in the plus 2 oxidation state. The two alternative reaction mechanisms are similar since the extractable species is the same.

E. The Cu-Zn-TOA Binary Metal System

The assumption here is that the binary system is considered to behave ideally with each chemical reaction equilibrating simultaneously but independently of the others. This assumption was proposed by Thiel (31). Hence, the metal complex formation in the aqueous phase involves a competition between both metals for available chloride ions. This is a function of the metal's ability to form complexes in the aqueous phase and depends on the stabilities of these complexes. Each extraction reaction is envisioned to take place independently. Then the available amine salt starts reacting with the available complexes in the aqueous phase forming the extractable species. This process is a function of the rate of formation of the extractable species and of the rate of mass transfer of that species from one phase into the second phase. The distribution coefficients for the single systems should provide good estimates of the true separation factor for the binary system if there is no interaction between the two metals and the above simplifying assumptions about the aqueous and organic phases are valid (2).

The model was based on the assumption that the activity coefficient varies only slightly with its concentration. This assumption is true (30) if the extractant concentrations are below 1 $\frac{\text{moles}}{\text{m}^3}$ (0.001 M) (when $\gamma_1 \approx 1$) or above 50 $\frac{\text{moles}}{\text{m}^3}$ (0.05 M) (when γ_1 is nearly constant).

III. THEORY

A. Rate of Equilibrium in Extraction Systems

Examination of the phenomena occurring in a liquid-liquid extraction system reveals that two kinds of processes are taking place — chemical reactions and physical transport. Either or both of these processes can be very slow and hence determine the rate at which the entire system reaches equilibrium. In other words, the rate of attainment of equilibrium in a liquid-liquid extraction system depends upon the rate of formation of the extractable species and upon the rate of mass transfer of that species from one phase into the second phase.

The process of mass transfer can occur by two mechanisms — diffusion (due to concentration gradients) and convection (stirring, shaking). Both of these mechanisms take place in the extraction of a solute from one liquid into another. The mass transfer process could be represented by the two film theory in the following manner. The first is the movement of the solute species from the bulk of the solution to the surface layer next to an interface. This is followed by the transfer of the solute from the surface layer of one liquid across the interface to the surface layer of the second liquid. Once in the second liquid, the solute moves away from the surface layer into the bulk of the solution.

The thinness of the surface layer of the liquids is important and is determined by the relative velocity of the two phases past each other, for example, the rate of shaking. The rate of transfer of the solute from one surface layer to the second depends upon the size and shape of the solute, the viscosity of the two solvents and the interfacial tension between them. In most liquid-liquid extraction systems, the rate of mass transfer is quite rapid and hence not the rate-determining step in the extraction process.

The slowest step in most extractions is believed to be the chemical reaction forming the extractable species. This is the rational for basing the model development in this work on the extraction mechanism reaction.

B. Choice of the Extractant

The choice of solvent to be used as the extractant is obviously critical. The factors that are taken into account in choosing an extractant are: 1) The solute should be relatively soluble in the solvent in order to have a high value of D and thus require only one or two extraction stages. 2) The solvent should be as immiscible in water as possible. 3) The solvent should have as great a density difference from water as possible to permit easy separation of the two liquid phases after extraction. 4) The viscosity of the solvent should be low to permit good contact and rapid settling between the two phases during and after mixing. 5) The solvent should have a sufficiently high boiling point so that evaporation of the solvent is not a problem. 6) The extractable species should be readily recovered by back extraction from the solvent for subsequent reuse. 7) The solvent should not form stable emulsions with water. 8) The solvent should be easy to purify. 9) The solvent should be inexpensive and not hazardous to health.

IV. DEVELOPMENT OF THE MODEL

O'Brien (1974, 3) and O'Brien and Bautista (1974, 37) developed a thermodynamic model to predict the distribution coefficient for the single component system $Nd(NO_3)_3$-HNO_3-H_2O-HDEHP-AmSCO.

Nevarez (1975, 38) and Nevarez and Bautista (1978, 39) derived a predictive thermodynamic equilibrium model for the liquid-liquid extraction of cobalt (II) in the $COCl_2$-HCl-H_2O-TBP system.

Relying on Nevarez (1975, 38) and Nevarez and Bautista's (1978, 39) assumption, Hoh (1977, 2) and Hoh and Bautista (1978, 1) developed thermodynamic equilibrium models to describe and predict the distribution coefficients in the liquid-liquid extraction systems for several of the lanthanides, actinides and copper. Very good agreement between experimental data and models was obtained.

A. Copper and Zinc Chloro Complexes for Single and Binary Systems

The extraction mechanism for the metal chloride by TOA was proposed by Sato and Kato (30) as:

$$[M^{2+}]_A + [2Cl^-]_A + [2R_3NHCl]_O \rightleftharpoons [(R_3NH)_2MCl_4]_O \qquad (20)$$

Here, R_3NHCl represents the extractant TOA after it was pre-equilibrated with hydrochloric acid. The equilibrium constant K_e can be represented by:

$$K_e = \frac{[(R_3NH)_2MCl_4]_O}{[M^{2+}]_A[Cl^-]_A^2[R_3NHCl]_O^2} \qquad (21)$$

where the [ ] represent the activities and the subscripts A and O denote the aqueous and organic phases, respectively. By using the relation between the activity and activity coefficient, Equation 2 can be written as:

$$K_e = \frac{((R_3NH)_2MCl_4)_O}{(M^{2+})_A(Cl^-)_A^2(R_3NHCl)_O^2} \frac{\gamma_{(R_3NH)_2MCl_4}}{\gamma_{M^{2+}}\gamma_{Cl^-}^2\gamma_{R_3NHCl}^2} \qquad (22)$$

The total metal ion concentration in the organic phase can be written as

$$(M)_O^T = K_e(M^{2+})_A(Cl^-)_A^2(R_3NHCl)_O^2 \frac{\gamma_{M^{2+}}\gamma_{Cl^-}^2\gamma_{R_3NHCl}^2}{\gamma_{(R_3NH)_2MCl_4}} \qquad (23)$$

For weak complexing anions such as in the present work, it is generally assumed that the metal species present in the aqueous phase are M^{2+}, MCl^+, MCl_2, MCl_3^-, $MCl_4^=$ (26-30). The formation of the metal chloride complexes in the aqueous solutions are given by the following reactions:

$$[M^{2+}]_A + [Cl^-]_A = [MCl^+]_A \qquad (24)$$

$$[M^{2+}]_A + [2Cl^-]_A = [MCl_2]_A \qquad (25)$$

$$[M^{2+}]_A + [3Cl^-]_A = [MCl_3^-]_A \qquad (26)$$

$$[M^{2+}]_A + [4Cl^-]_A = [MCl_4^=]_A \qquad (27)$$

The stoichiometric overall stability constants β_1, β_2, β_3, and β_4 are represented by the following equations (40):

$$\beta_1 = \frac{(MCl^-)}{(M^{2+})(Cl^-)} \tag{28}$$

$$\beta_2 = \frac{(MCl_2)}{(M^{2+})(Cl^-)^2} \tag{29}$$

$$\beta_3 = \frac{(MCl_3^-)}{(M^{2+})(Cl^-)^3} \tag{30}$$

$$\beta_4 = \frac{(MCl_4^{=})}{(M^{2+})(Cl^-)^4} \tag{31}$$

where the parentheses refer to the concentrations of the species. The total metal ion concentration in the aqueous phase is given by:

$$(M)_A^T = (M^{2+}) + (MCl^+) + (MCl_2) + (MCl_3^-) + (MCl_4^{=}) \tag{32}$$

Substitution of Equations 28-31 into Equation 32 gives:

$$\begin{aligned} (M)_A^T &= (M^{2+})(1 + \beta_1(Cl^-) + \beta_2(Cl^-)^2 + \beta_3(Cl^-)^3 + \beta_4(Cl^-)^4) \\ &= (M^{2+})(1 + \sum_{i=1}^{n} \beta_i(Cl^-)^i). \end{aligned} \tag{33}$$

The distribution coefficient D is defined for a single component system by the ratio of the total concentration of the metal species in the organic phase to the total concentration of the metal species in the aqueous phase:

$$D = \frac{(M)_O^T}{(M)_A^T} \tag{34}$$

Substitution of Equations 23 and 33 yields:

$$D = (Cl^-)_A^2(R_3NHCl)_O^2 \cdot \frac{1}{1 + \sum_{i=1}^{n} \beta_i (Cl^-)^i} \cdot K_e \frac{\gamma_{M^{2+}} \gamma_{Cl^-}^2 \gamma_{R_3NHCl}^2}{\gamma_{(R_3NH)_2MCl_4}} \tag{35}$$

At this point, the assumption is made that the ratio of the activity coefficients of the molecules obtained in Equation 35 varies slightly with concentration. Should this assumption hold, then the quotient of activity coefficients in Equation 35 can be represented as a constant value given by:

$$K_\gamma = \frac{\gamma_{(R_3NH)_2MCl_4}}{\gamma_{M^{2+}} \gamma_{Cl^-}^2 \gamma_{R_3NHCl}^2} \tag{36}$$

Combining this activity coefficient ratio constant with the liquid-liquid extraction equilibrium constant, that is

$$K_1 = \frac{K_e}{K_\gamma} \tag{37}$$

gives a value for an effective equilibrium constant K_1 for the extraction equilibria.

The degree of formation (α_i) of an inorganic metal complex MA_i can be defined (40) as:

$$\alpha_i = \frac{(MA_i)}{(M)_A^T} = \frac{(MA)_i}{(M) + (MA) + (MA_2) + \cdots + (MA_n)}$$

$$= \frac{\beta_i (A^-)^i}{1 + \sum_{i=1}^{n} \beta_i (A^-)^i} \tag{38}$$

The terms (A) and (M) are the corresponding free concentration. From

Equation 38, the degree of formation can be written as:

$$\alpha_0 = \frac{1}{1 + \sum_{i=1}^{n} \beta_i (Cl^-)^i} \tag{39}$$

Substitution of Equations 36, 37, 38 and 39 into Equation 35 gives:

$$D = K_1 \alpha_0 (Cl^-)_A^2 (R_3NHCl)_0^2 \tag{40}$$

Defining

$$\phi = (Cl^-)_A (R_3NHCl)_0 \tag{41}$$

then, Equation 21 becomes

$$D = K_1 \alpha_0 \phi^2 \tag{42}$$

By definition, the separation factor for a binary component system of two different metals, M and N, can be written as:

$$S_{M-N} = \frac{(D)_M}{(D)_N} = \frac{K_{1M} \alpha_{OM} \phi_M^2}{K_{1N} \alpha_{ON} \phi_N^2} \, . \tag{43}$$

Since a binary system has the same organic and aqueous phases, it can be written:

$$\phi_M = \phi_N \tag{44}$$

By defining

$$\frac{K_{1M}}{K_{1N}} = K_{M-N} \tag{45}$$

then, Equation 43 can be written as

$$S_{M-N} = K_{M-N} \frac{\alpha_{OM}}{\alpha_{ON}} \tag{46}$$

From this equation, it can be seen that the separation factor for two metallic species in a binary component system is dependent only on the degrees of formation of the two components in the aqueous phase. The usefulness of this approach is that it simplifies the analysis of a liquid-liquid extraction system containing two or more metals.

V. EXPERIMENTAL PROCEDURES

A. Materials

The metal chlorides used in this work have a high purity and were supplied by the Ames Laboratory. Cupric chloride ($CuCl_2 \cdot 2H_2O$) is made by the Mallinckrodt Company. Zinc chloride ($ZnCl_2$) is made by the Fisher Scientific Company.

The TOA, obtained from Eastman Kodak Corporation, was of high purity and was used without further purification. The characteristics of TOA used were molecular weight = 353, density = 0.8120 gcm^{-3}, refractive index = 1.4509, boiling point = 202/10^{o}C/mm Hg, solubility in water = 0.001% and purity = 97.7%. Benzene was obtained from the Fisher Scientific Company. It was used as the diluent for the TOA. TOA (R_3N, $R = C_8H_{17}$), was used as a hydrochloride. 200 $\frac{\text{moles}}{m^3}$ (0.2 M) TOA in benzene was pre-equilibrated with 1000 $\frac{\text{moles}}{m^3}$ (1 M) HCl (aqueous) and then was diluted with benzene to the required concentration. Copper and zinc metals were obtained from Fisher Scientific Company. The metals were used to make the standard solutions for the atomic absorption analysis. The other chemicals were analytical reagent grade and were used without further purification.

Aqueous solutions of divalent copper and zinc were prepared by dissolving their chlorides in hydrochloric acid.

B. Equilibrium Studies

The procedure for obtaining the distribution coefficient was as follows. Equal volumes of initial aqueous solutions and organic solutions were introduced in a separatory funnel and then shaken vigorously twice for half an hour in a shaking machine. A settling time of 30 minutes was allowed between shakings and after the shakings the solution was allowed to stand for at least 12 hours before the two phases were separated. The total chloride concentration in the aqueous phase was measured with a chloride ion electrode.

The total chloride concentration in the organic phase was also measured with the chloride ion electrode. A volumetric sample of an organic phase is contacted several times with a strong acid. The acid must have a very small selectivity constant relative to the chloride ion electrode in order to minimize the interface effect of the electrode. Selectivity constant is an approximate number and can be used only to estimate orders of magnitude of interference to be expected in a given application. It cannot be used to make corrections to electrode readings obtained in solutions in which the level of interference is appreciable. Sulfuric acid with a selectivity constant $K_x = 1.4 \times 10^{-1}$ was chosen for this purpose. Equal volumes of $1 \times 10^3 \frac{\text{moles}}{\text{m}^3}$ (1M) sulfuric acid were contacted three times with the organic equilibrated phase. This back-extraction of copper was tested for completeness by noting discoloration of the solution. No such advantage was noted for zinc. Then the total chloride ion concentration was analyzed by the chloride ion electrode.

The hydrogen ion concentration of the equilibrated aqueous phase was determined with an Orion 801 digital pH/mv meter. The pH electrode was calibrated before and during use with buffer solutions of suitable concentrations.

The metal concentration in the aqueous phase was determined by the technique of atomic absorption. Then the metal concentration in the organic phase is equal to the initial metal aqueous phase concentration minus the final metal aqueous phase concentration after extraction. The back-extracted organic phase was also analyzed for the metal concentration in the organic phase as a check on the material balance.

C. Ion Selective Electrode Measurements

The Orion chloride ion-selective electrode (model 93-17) and the Orion double junction reference electrode (model 90-02) were used in the determination of chloride ion concentration both in the aqueous phase and in the organic phase. The chloride electrode provides accurate rapid analysis of the free chloride ion over a concentration range of 100 $\frac{\text{moles}}{\text{m}^3}$ (10^{-1}M) to 0.01 $\frac{\text{moles}}{\text{m}^3}$ (10^{-5}M). The electrode is calibrated in standard solutions of known concentrations of chloride ion. The double junction reference electrode gave a stable reference of the voltage regardless of the sample concentration. The Orion 801 digital pH/mv meter, which covers an average of + 1000 mv to - 1000 mv with a precision of 0.1 mv, was used to measure the electromotive potential between both electrodes. Figures 1 and 2 show the details of the chloride ion selective electrode, the reference electrode, and the electrode system.

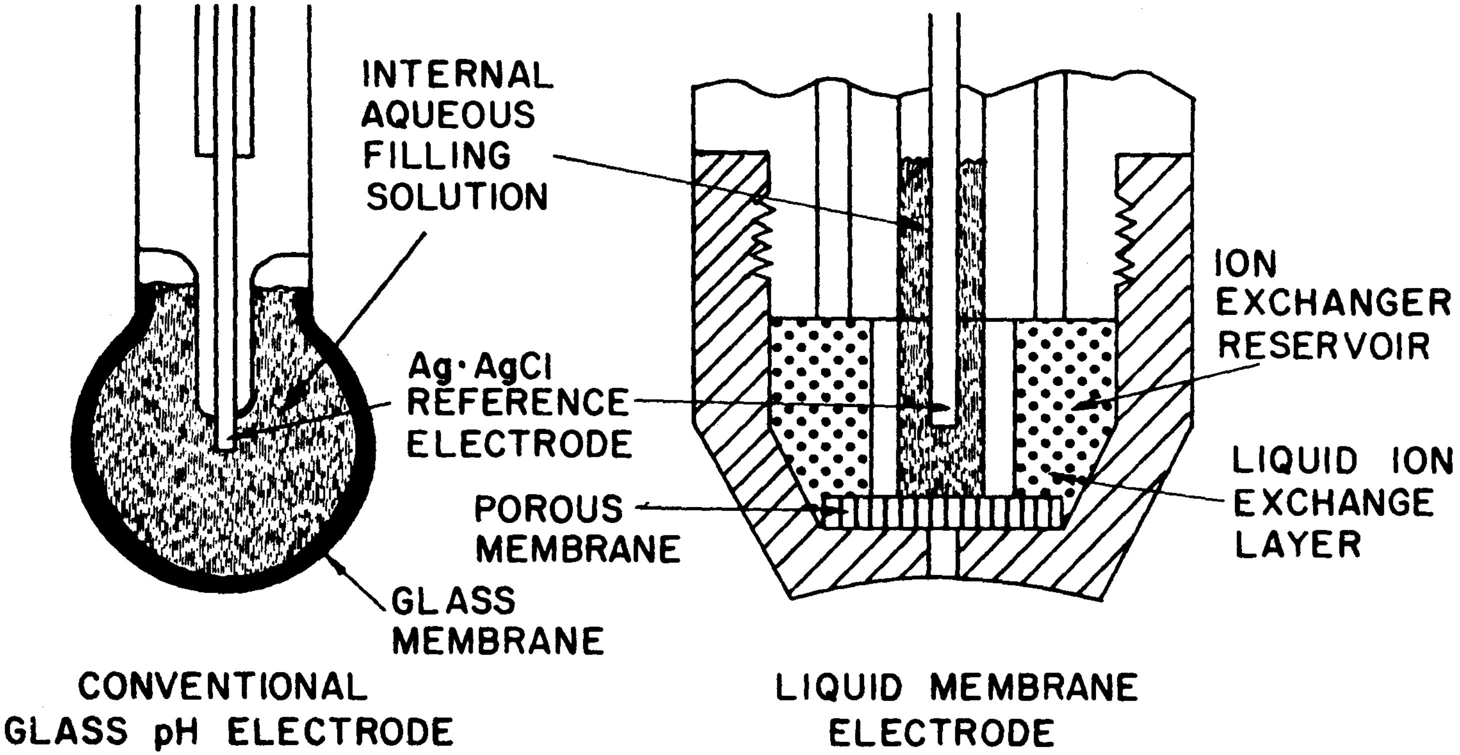


Figure 1. Comparison between the conventional glass pH electrode and the liquid membrane electrode

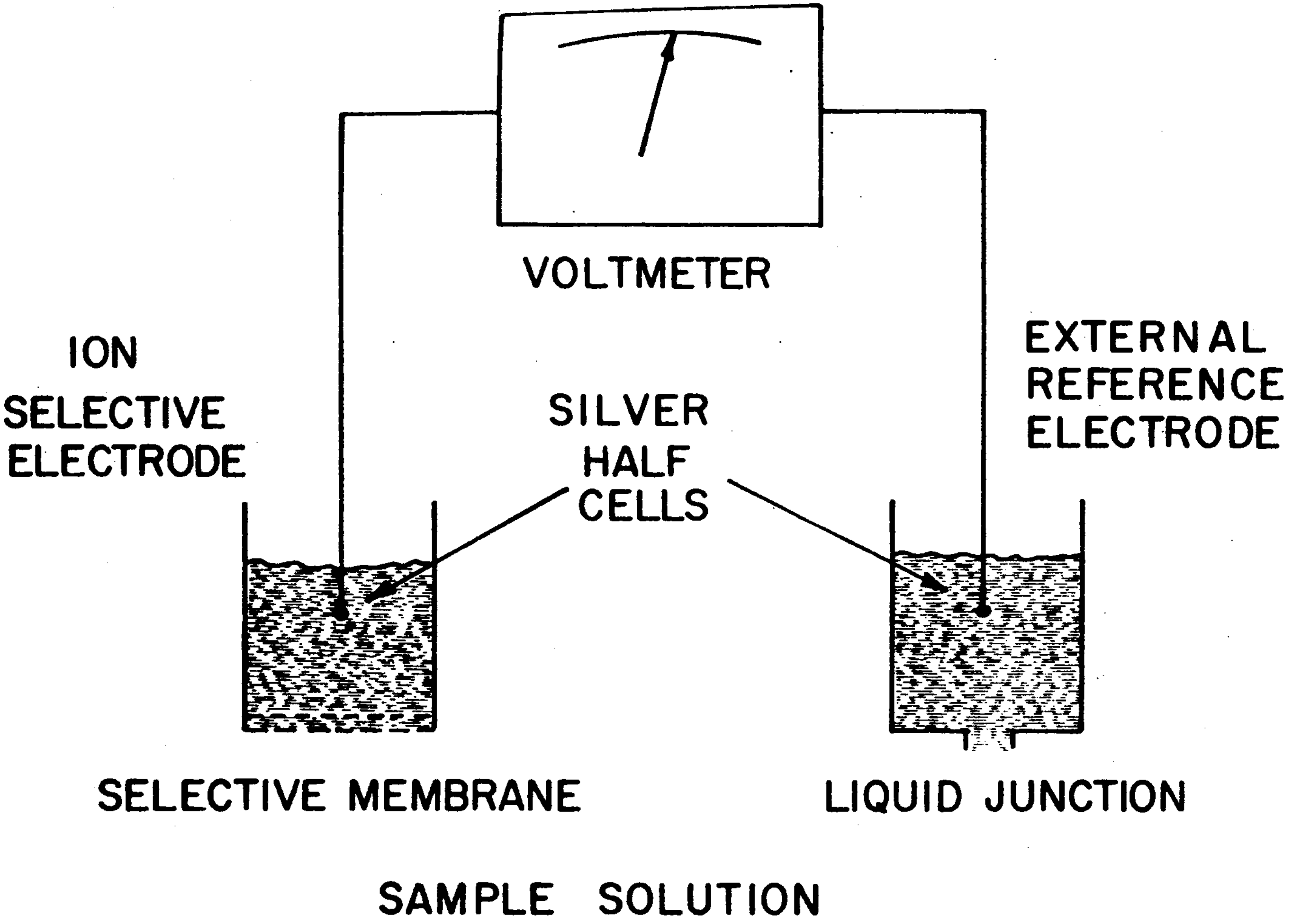


Figure 2. General ion selective electrode system

The standardization of the electrode system with a suitable electrolyte should be done before the electrode is used. As suggested by Bates and Alfenaar (41), the sodium chloride solution was used as the standard solution and the chloride convention which was proposed by Bates and Guggenheim (42) was used to determine the chloride ion activities in the sodium chloride solution. A set of standards of sodium chloride was prepared to bracket the expected unknown chloride concentration range. The standards should be one decade apart in chloride concentration. Beginning with the most dilute standard, the meter millivolt reading of the standards was recorded and plotted against the chloride ion concentration on a semi-logarithmic graph paper. The electrode was found to exhibit a good Nernstion response to chloride ion standard solutions within the experimental range studied. Table 1 and Figure 3 show the results of the standard curves of the chloride electrode calibration. The Nernst equation is written as:

$$E = \text{constant} + 2.3(RT/2F)\log \bar{a} \qquad (47)$$

Here E is the potential, in millivolts, RT/F is the Nernst factor, which depends on the temperature, $\bar{a}$ is the activity of the ion to which the membrane is permeable, and Z is its charge. The constant term in this equation is dependent on what reference electrode is used, on the choice of ion activity in the inner solution and also on the liquid-liquid junction potential at the salt bridge connection. Because the constant term is very sensitive to change in the reference electrode, it was calibrated before and after the measurements.

The chloride convention was to formulate standards for use in

Table 1. Chloride electrode data for chloride standards ion-selective electrode measurements

Standard No.	$(\mathrm{Cl}^-)_A$, ppm	$[\mathrm{Cl}^-]_A$, ppm	mv
1	1.0	1.0	218.3
2	2.0	2.0	207.8
3	10.0	9.9	181
4	20.0	19.6	160.1
5	100.0	97.0	124.4

Standard No.	$(\mathrm{Cl}^-)_A$, $\frac{\mathrm{moles}}{\mathrm{m}^3} \cdot 10^3$	$[\mathrm{Cl}^-]_A$, $\frac{\mathrm{moles}}{\mathrm{m}^3} \cdot 10^3$	mv
1	0.001	0.0009	147.3
2	0.002	0.0019	132.1
3	0.01	0.009	94.9
4	0.02	0.0174	79.2
5	0.1	0.075	40.9

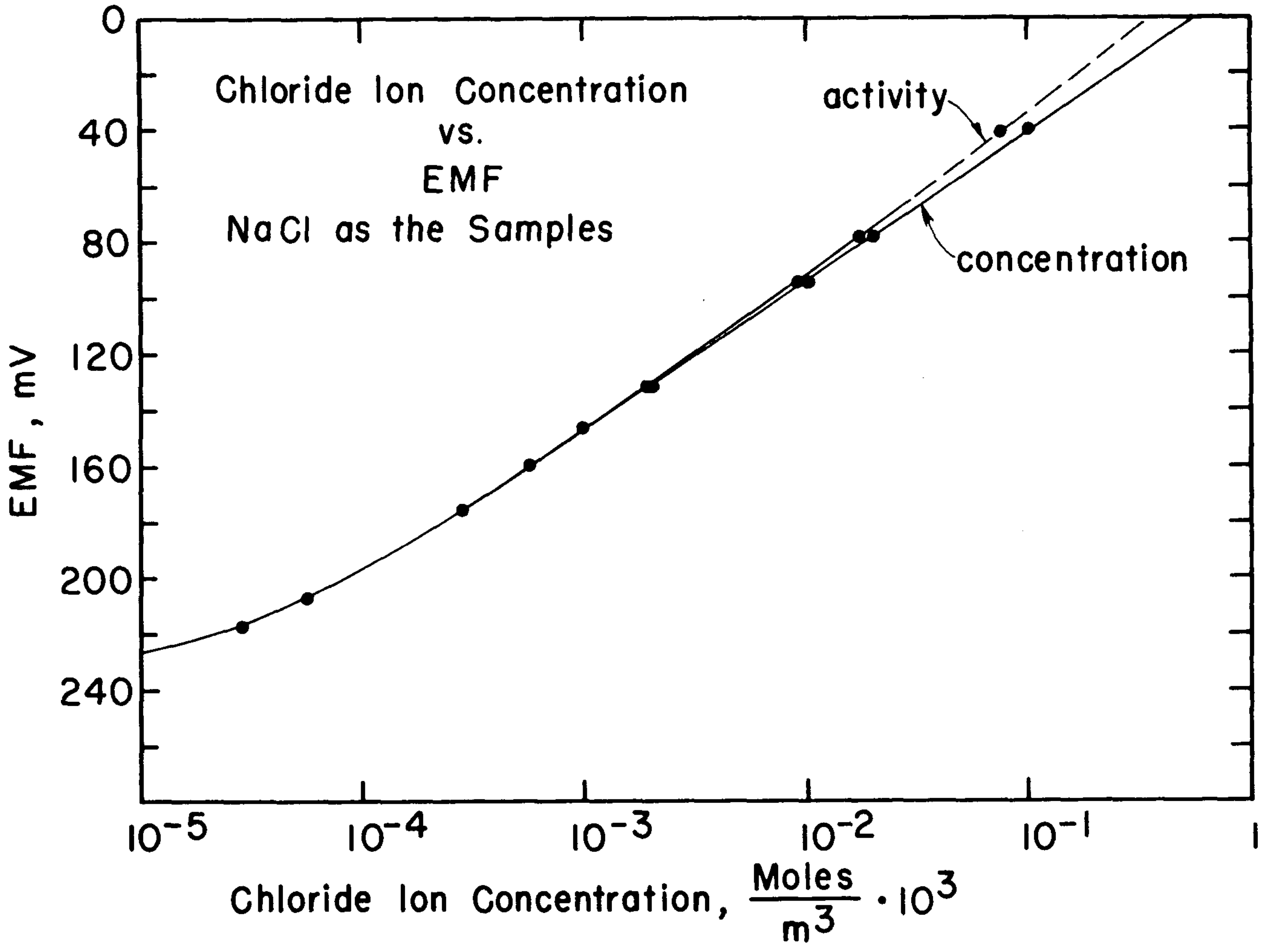


Figure 3. Calibration curve for the chloride ion-selective electrode

calibrating the chloride ion electrode. The chloride convection is written as:

$$- \log \gamma_{Cl^-} = \frac{0.509I^{1/2}}{1 + 1.5I^{1/2}} \qquad (48)$$

It was originally intended that this formula be used at ionic strengths of 0.1 or less but Bates and Guggenheim (42) has recently suggested that it be applied without restriction to any ionic strength and thus form a basis for all ionic activity standards. Using the definition of mean ionic activity which is written as:

$$\log \gamma_{A^-} = \log \gamma_{Cl^-} + 2 \log(\gamma_{MA}/\gamma_{MCl}) \qquad (49)$$

and since $A^- = Cl^-$ in our case, then the equation simplifies

$$\log \gamma_A = \log \gamma_{Cl^-} \qquad (50)$$

Thus, the suggested standard for the chloride ion electrode is sodium chloride.

Certain general procedures were followed for electrode measurements which tend to increase the experimental accuracy: 1) The initial electrode preparation should be the same for both experimental and standardization measurements. In this work, both electrodes were rinsed with distilled water and patted dry with absorbent tissue for each measurement. 2) The electrode equilibrium time should be the same for both the unknown and the standard. An equilibrium time of 200 seconds was found to give good reproducible results over the concentration range studied. 3) It was also found that the electrode exhibits quicker response times when going from lower to higher concentration solution than it does when going from higher to lower solution concentrations. 4) Standardization with several standard solutions bracketing the unknown solution concentrations is beneficial.

D. Atomic Absorption Analysis

Atomic absorption is an analytical method based on the absorption of ultraviolet or visible light by atoms in the vapor state. Conversion (at least partial) of the sample into an atomic vapor is accomplished by spraying a solution into a flame. A hollow-cathode lamp containing the element to be determined is used as the light source. The atoms of this element in the flame absorb at precisely the same wavelength as that emitted by the light source. The wavelength spread is extremely narrow both for the emission line of the light source and for the absorption line of the same element in the flame. For this reason, the chance of interference by absorption of spectral lines of other elements is almost nil.

Atomic absorption is essentially the opposite of flame emission spectrometry. Although the sample is sprayed into a flame in both methods, flame emission methods depend on emission of light by excited atoms in the flame, while atomic absorption is based on absorption of light by neutral, unexcited atoms in the flame. Several advantages of atomic absorption over flame emission photometry may be cited. 1) There is less interference from salts of foreign metals than is encountered in ordinary flame atomic emission. 2) Atomic absorption is less dependent on experimental conditions, and there is no need (as in flame emission) to use an internal standard to correct minor differences in the flame or other conditions. 3) For some elements, the sensitivity and precision of atomic absorption is better. A disadvantage of atomic absorption is the necessity of acquiring and maintaining a separate, expensive light source for each element to be determined.

Like solution spectrophotometry and flame emission spectrometry, atomic absorption is used primarily for measurement of small to trace amounts of elements. The sensitivity for most elements is of the order of 1 ppm (1 μg per ml of solution). This sensitivity order is true for zinc. For copper, the sensitivity order is extended to 5 ppm. The accuracy of this technique is within approximately ± 2%, which is quite satisfactory for small amounts but is often inadequate for analysis of samples for major constituents.

1. Preparation of standard zinc and copper solutions

Using an analytical balance, 0.5000 g of high purity zinc metal was weighed in a 150 ml beaker. The actual weight is not critical, but it should be reasonably close to the value specified and known to four significant figures. Slowly, 10 ml of $6 \times 10^3 \frac{\text{moles}}{\text{m}^3}$ (6M) HCl were added to the beaker. It was covered rapidly with a small watch glass, and the zinc metal was allowed to dissolve completely. Initially, the reaction is quite vigorous and much of the zinc solution will be lost by splattering if the beaker is not covered quickly. When it appeared that the dissolution was completed, checks were made to insure that all of the small particles of metallic zinc had been dissolved.

This dissolution often took as long as an hour, for the process slows down after its initial vigor. When the reaction slowed down, the solution was heated on a steam bath to speed the dissolution. After all the zinc metal dissolved, the solution was transferred quantitatively into a 1000-ml volumetric flask. It was diluted to the mark with 1% V/V HCl and mixed thoroughly by upending the flask slowly at least ten times.

The same thing was done with copper except that 1.0 g of high-purity copper metal was dissolved in 10 ml of (1 + 1) HNO_3. It was diluted to 1 liter with 1% V/V HNO_3.

E. Separation Factor Studies

The binary system cupric chloride-zinc chloride-water-hydrochloric acid-TOA-benzene was also studied. The same technique as in the single component system was utilized in order to obtain the total metal concentrations in the equilibrated aqueous and organic phases. The distribution coefficient was calculated from the ratio of the metal concentration in the organic phase to the metal concentration in the aqueous phase. Then the separation factor was determined as the ratio of the distribution coefficients.

F. Calculation Methods

The equilibrated concentration of the R_3NHCl was estimated from the balance equation:

$$(R_3NHCl)_0^E = (R_3NHCl)_0^I - 2(M)_0^T + (Cl^-)_0^T \tag{51}$$

G. Simple Linear Regression Analysis

Statistical methods applicable to scientific research have been discussed in detail by many authors (43, 44). The statistical method used in this investigation was the simple linear regression analysis technique. The least square criterion was used to minimize the sum of the squares of the vertical distances between the data points and the appropriate line. The line which minimizes this sum is called the least square regression line, which represents the best fit. In order to seek a correlation that reflects the accuracy of the fit, the correlation coefficient is defined as

$$R^2 = \frac{\text{Sum of squares due to regression}}{\text{Total (corrected) sum of squares}} , \tag{52}$$

with the limit $0 \leq R^2 \leq 1$. If the data fit the regression line very well, R^2 will approach 1. Similarly, if the regression line is a poor fit, the data points will be widely scattered about the regression line and R^2 will approach 0, reflecting very poor correlation. Since the model equation used in the experiment is complex, R^2 was not expected to be close to 1. The model equation is nonlinear.

VI. RESULTS AND DISCUSSION

A. Application of Published Data to the Model

1. The system zinc chloride-hydrochloric acid-water-TOA-benzene

a. Using Sato's stability constants Sato and Kato (30) studied the complex formation of zinc chloride by the liquid-liquid extraction method at different ionic strengths. The stoichiometric stability constants of the chloro-complexes of zinc (II) obtained by Sato and other investigators (25-29) are shown in Table 2. The equilibrium data of Sato are shown in Table 3. The degrees of formation can be calculated from the equilibrium data according to Equation 38.

$$\alpha_i = \frac{\beta_i (Cl^-)^i}{1 + \sum_{i=1}^{n} \beta_i (Cl^-)^i} \tag{38}$$

When the degrees of formation and the equilibrium data are available, the effective equilibrium constant K_1 for each data point can be calculated by the model Equation 40

$$D = K_1 \alpha_0 (Cl^-)_A^2 (R_3NHCl)_O^2 \tag{40}$$

or

$$K_1 = \frac{D}{\alpha_0 (Cl^-)_A^2 (R_3NHCl)_O^2} \tag{53}$$

Figure 4 is the plot of the degrees of formation α_i versus the chloride ion concentrations. The plot shows the degree of formation (α_0) decreases slowly as the chloride ion concentration increases from 0 to 1 x $10^3 \frac{\text{moles}}{\text{m}^3}$ (1M). The other α_i's behave in an opposite

Table 2. Stability constants of the chloro complexes of zinc (II) in aqueous solutions

Ionic strength	Stability constants				K_e[a]	Remark	Researcher
	β_1	β_2	β_3	β_4			
Variable	5.35	2.76	1.07	0.27	5×10^6	TOA EXT	(30)
0.691	5.25	3.09	0.65	1.5	–	–	(27)
4.0	5.20	3.38	1.46	0.48	–	–	(28)
0.54	3.07	1.01	8.25	1.04	4.9×10^8	Aliquat-336	(29)

[a] K_e = equilibrium constant for the extraction reaction.

Table 3. Equilibrium data of Sato and Kato (30) for the system zinc chloride-hydrochloric acid-water-TOA-benzene. Initial metal concentration = 7.3 $\frac{\text{moles}}{\text{m}^3}$

Initial (R_3NHCl) $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$	Initial aq. (HCl) $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$	Distribution coefficient D	$(Cl^-)_A$ $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$	$(R_3NHCl)_O$ $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$
0.02	0.01	0.0259	0.0172	0.00611
	0.03	0.0644	0.0347	0.00598
	0.05	0.105	0.603	0.00588
	0.07	0.151	0.0832	0.00581
	0.1	0.231	0.135	0.00563
	0.2	0.544	0.316	0.00513
	0.3	0.821	0.525	0.00481
0.03	0.01	0.053	0.0209	0.00725
	0.03	0.112	0.0355	0.00719
	0.05	0.200	0.0589	0.00707
	0.07	0.325	0.0812	0.00690
	0.1	0.450	0.138	0.00681
	0.2	0.945	0.302	0.00647
	0.3	1.56	0.437	0.00614
	0.5	2.36	0.631	0.00587
0.05	0.01	0.105	0.0174	0.00839
	0.03	0.227	0.343	0.00845
	0.05	0.418	0.0575	0.00825
	0.07	0.605	0.0813	0.00810
	0.1	0.913	0.120	0.00801
	0.2	2.512	0.302	0.00788
	0.3	4.30	0.506	0.00777
	0.5	6.07	0.728	0.00770
0.1	0.01	0.291	0.0207	0.0100
	0.03	0.600	0.0417	0.00983
	0.05	1.092	0.0617	0.000995
	0.07	1.57	0.0912	0.00987
	0.1	2.60	0.135	0.00972
	0.2	7.68	0.338	0.000984
	0.3	14.7	0.575	0.000976

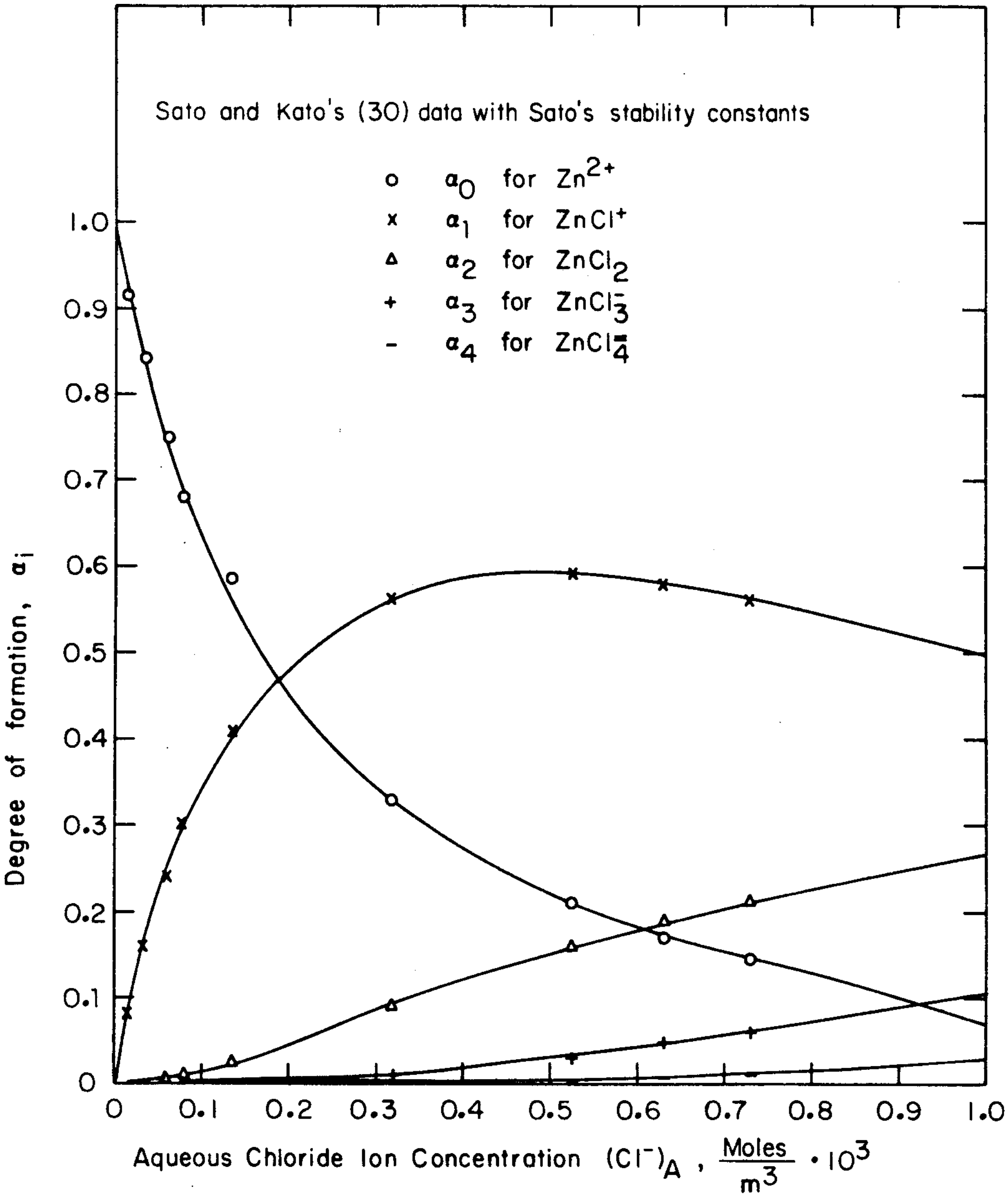


Figure 4. The degree of formation α_i for $ZnCl_2$ as a function of the aqueous chloride ion concentration

manner. The value of effective equilibrium constant K_1 found by linear regression analysis of the available data was equal to 1865188. Table 4 shows the results of the calculated degrees of formation and the effective equilibrium constants. Using the value of the effective equilibrium constant, the model Equation 21 can now be written as

$$D = (1865188)\alpha_0(Cl^-)_A^2(R_3NHCl)_0^2 \qquad (54)$$

The distribution coefficients were calculated at different chloride ion and R_3NHCl concentrations using this model equation. Table 3 also shows the comparison between the calculated D values obtained by Equation 54 and the experimental D data reported by Sato and Kato (30). The plot of D(model) versus D(data) is shown in Figure 5. The correlation coefficient is $R^2 = 0.8572$. It shows that the model equation 54 gives good predictive distribution coefficients within the experimental conditions.

b. <u>Using Mihailov's stability constants</u> Mihailov (28) determined the stability constants for chloro-complexes of zinc. Figure 6 is the plot of the degrees of formation α_i versus the chloride ion concentrations. The plot shows that the degrees of formation α_i increase as the chloride ion concentration increases from 0 to $1.0 \times 10^3 \frac{\text{moles}}{m^3}$ (1.0M) except α_0, which decreases sharply. The value of effective equilibrium constant K_1 was found by linear regression analysis of the available data and was equal to 1946984. Table 5 shows the results of the calculated degrees of formation and the effective equilibrium constants. Using the value of the effective equilibrium constant, model Equation 40 can now be written as:

Table 4. The degree of formation calculated from the equilibrium data and the stability constants of Sato and Kato (30), the effective equilibrium constant (K_1) and the D(model) for the system $ZnCl_2$-HCl-H_2O-TOA-C_6H_6

Run	Distribution coefficient D(data)	$(Cl^-)_A$, $\frac{moles}{m^3} \cdot 10^3$	$(R_3NHCl)_O$, $\frac{moles}{m^3} \cdot 10^3$	$\alpha_{Zn^{2+}}$ α_0	α_{ZnCl^+} α_1
1	0.0259	0.0172	0.00611	0.915045	0.084202
2	0.0644	0.0347	0.00598	0.841033	0.156134
3	0.1050	0.0603	0.00588	0.750256	0.242036
4	0.1510	0.0832	0.00581	0.682662	0.303866
5	0.2310	0.1350	0.00563	0.563294	0.406839
6	0.5440	0.3160	0.00513	0.333038	0.563034
7	0.8210	0.5250	0.00481	0.210756	0.591961
8	0.0530	0.0209	0.00725	0.898448	0.100460
9	0.1120	0.0355	0.00719	0.837906	0.159139
10	0.2000	0.0589	0.00707	0.754767	0.237838
11	0.3250	0.0812	0.00690	0.688135	0.298940
12	0.4500	0.1380	0.00681	0.557485	0.411591
13	0.9450	0.3020	0.00647	0.344930	0.557303
14	1.5600	0.4370	0.00614	0.252260	0.589771
15	2.3600	0.6310	0.00587	0.172819	0.583411
16	0.1050	0.0174	0.00839	0.914134	0.085097
17	0.2270	0.0343	0.00845	0.842605	0.154622
18	0.4180	0.0575	0.00825	0.759326	0.233588
19	0.6050	0.0813	0.00810	0.687860	0.299188
20	0.9130	0.1200	0.00801	0.593948	0.381315
21	2.5120	0.3020	0.00788	0.344930	0.557303
22	4.3000	0.5060	0.00777	0.218814	0.592353
23	6.0700	0.7280	0.00770	0.146066	0.568897
24	0.2910	0.0207	0.01000	0.899331	0.099596
25	0.6000	0.0417	0.00983	0.814350	0.181677
26	1.0920	0.0617	0.00995	0.745792	0.246182
27	1.5700	0.0912	0.00987	0.661504	0.322761
28	2.6000	0.1350	0.00972	0.563294	0.406839
29	7.6800	0.3380	0.00984	0.315611	0.570720
30	14.7000	0.5750	0.00976	0.191508	0.589127

α_{ZnCl_2} α_2	$\alpha_{ZnCl_3^-}$ α_3	$\alpha_{ZnCl_4^=}$ α_4	Effective equilibrium constant K_1[a]	Equation (54) D(model)
0.000747	0.0000050	0.0000000	2562818	0.0188
0.002795	0.0000376	0.0000003	1778326	0.0675
0.007529	0.0001760	0.0000027	1113245	0.1759
0.013043	0.0004207	0.0000088	946613	0.2975
0.028334	0.0014829	0.0000505	709893	0.6069
0.091786	0.0112445	0.0008966	621578	1.6324
0.160328	0.0326319	0.0043230	610877	2.5068
0.001083	0.0000088	0.0000000	2569297	0.0385
0.002914	0.0000401	0.0000004	2051674	0.1018
0.007227	0.0001650	0.0000025	1528085	0.2441
0.012523	0.0003942	0.0000081	1504524	0.4029
0.029302	0.0015677	0.0000546	913960	0.9183
0.086827	0.0101657	0.0007747	717594	2.4563
0.132960	0.0225256	0.0024839	858968	3.3874
0.189915	0.0464583	0.0073973	995373	4.4223
0.000764	0.0000052	0.0000000	5389605	0.0363
0.002736	0.0000364	0.0000003	3207009	0.1320
0.006929	0.0001545	0.0000022	2446269	0.3187
0.012548	0.0003955	0.0000081	2028170	0.5564
0.023606	0.0010982	0.0000333	1663776	1.0235
0.086827	0.0101657	0.0007747	1285946	3.6435
0.154627	0.0303327	0.0038729	1271304	6.3087
0.213659	0.0603013	0.0110774	1322501	8.5608
0.001064	0.0000085	0.0000000	7551488	0.0719
0.003908	0.0000632	0.0000007	4384911	0.2552
0.007836	0.0001874	0.0000029	3884979	0.5243
0.015186	0.0005369	0.0000124	2929160	0.9997
0.028334	0.0014829	0.0000505	2680640	1.8091
0.099516	0.0130403	0.0011122	2199810	6.5118
0.174756	0.0389560	0.0056523	2437219	11.2498

[a] K_1(regressed) = 1865188 ± 143846.

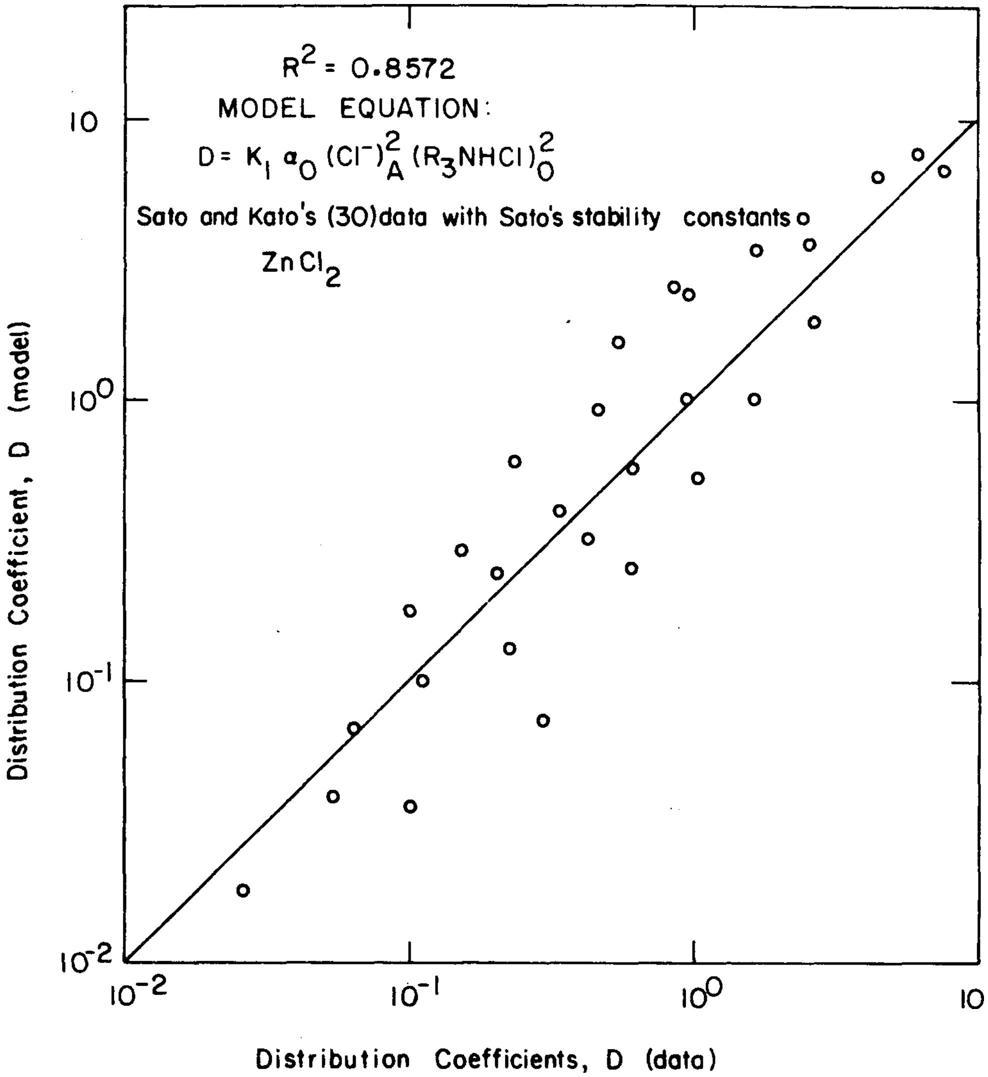


Figure 5. The comparison between the predicted D(model) and the D(data) obtained experimentally by Sato and Kato (30) for the system $ZnCl_2$-HCl-H_2O-TOA-C_6H_6

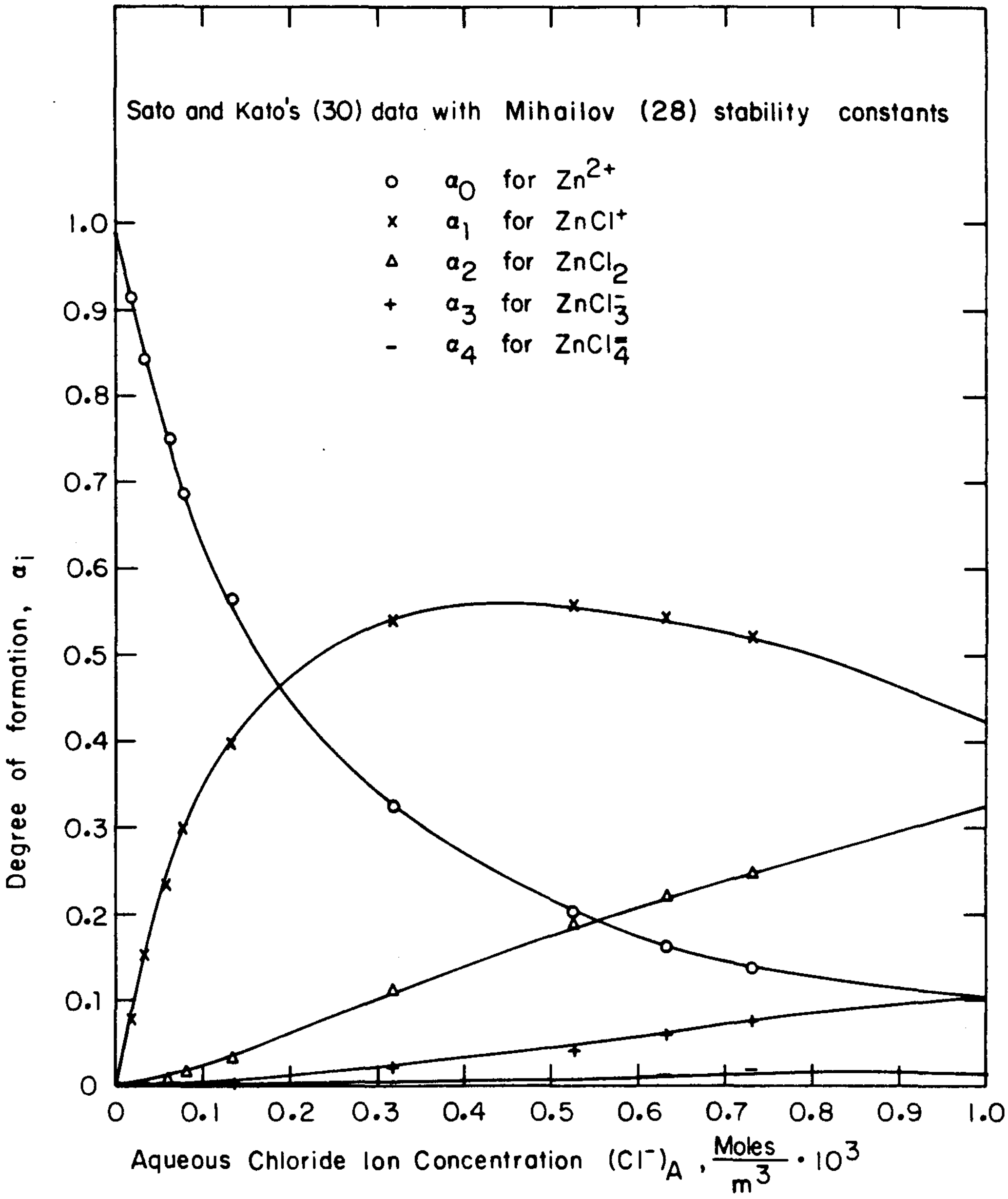


Figure 6. The degree of formation α_i for $ZnCl_2$ as a function of the aqueous chloride ion concentration

Table 5. The calculated degree of formation from Sato and Kato's (30) data with Mihailov (28) stability constants, the effective equilibrium constant (K_1) and the D(model) for the system zinc chloride-hydrochloric acid-water-TOA-benzene

Run	Distribution coefficient D(data)	$(Cl^-)_A$, $\frac{moles}{m^3} \cdot 10^3$	$(R_3NHCl)_O$, $\frac{moles}{m^3} \cdot 10^3$	$\alpha_{Zn^{2+}}$ α_0	α_{ZnCl^+} α_1
1	0.0259	0.0172	0.00611	0.917055	0.082021
2	0.0644	0.0347	0.00598	0.844187	0.152325
3	0.1050	0.0603	0.00588	0.754047	0.236439
4	0.1510	0.0832	0.00581	0.686388	0.296959
5	0.2310	0.1350	0.00563	0.565818	0.397204
6	0.5440	0.3160	0.00513	0.329862	0.542030
7	0.8210	0.5250	0.00481	0.203693	0.556082
8	0.0530	0.0209	0.00725	0.900763	0.097895
9	0.1120	0.0355	0.00719	0.841095	0.155266
10	0.2000	0.0589	0.00707	0.758547	0.232328
11	0.3250	0.0812	0.00690	0.691884	0.292141
12	0.4500	0.1380	0.00681	0.559917	0.401796
13	0.9450	0.3020	0.00647	0.342129	0.537279
14	1.5600	0.4370	0.00614	0.246474	0.560088
15	2.3600	0.6310	0.00587	0.164748	0.540570
16	0.1050	0.0174	0.00839	0.916161	0.082894
17	0.2270	0.0343	0.00845	0.845740	0.150846
18	0.4180	0.0575	0.00825	0.763092	0.228165
19	0.6050	0.0813	0.00810	0.691608	0.292384
20	0.9130	0.1200	0.00801	0.596910	0.372472
21	2.5120	0.3020	0.00788	0.342129	0.537279
22	4.3000	0.5060	0.00777	0.211989	0.557787
23	6.0700	0.7280	0.00770	0.137456	0.520352
24	0.2910	0.0207	0.01000	0.901631	0.097052
25	0.6000	0.0417	0.00983	0.817779	0.177327
26	1.0920	0.0617	0.00995	0.749593	0.240499
27	1.5700	0.0912	0.00987	0.665118	0.315425
28	2.6000	0.1350	0.00972	0.565818	0.397204
29	7.6800	0.3380	0.00984	0.311878	0.548156
30	14.7000	0.5750	0.00976	0.183907	0.549881

α_{ZnCl_2} α_2	$\alpha_{ZnCl_3^-}$ α_3	$\alpha_{ZnCl_4^=}$ α_4	Effective equilibrium constant K_1[a]	Equation (55) D(model)
0.000917	0.0000068	0.0000000	2557203	0.0197
0.003436	0.0000515	0.0000006	1771682	0.0708
0.009267	0.0002414	0.0000048	1107647	0.1846
0.016060	0.0005772	0.0000158	941473	0.3123
0.034855	0.0020325	0.0000902	706725	0.6364
0.111333	0.0151966	0.0015788	627563	1.6877
0.189763	0.0430336	0.0074277	632059	2.5290
0.001330	0.0000120	0.0000001	2562694	0.0403
0.003583	0.0000549	0.0000006	2043893	0.1067
0.008895	0.0002263	0.0000044	1520471	0.2561
0.015419	0.0005408	0.0000144	1496372	0.4229
0.036041	0.0021484	0.0000975	909990	0.9628
0.105468	0.0137583	0.0013660	723469	2.5432
0.159093	0.0300309	0.0043146	879131	3.4549
0.221715	0.0604311	0.0125365	1044138	4.4006
0.000938	0.0000070	0.0000000	5377681	0.0380
0.003363	0.0000498	0.0000006	3195120	0.1383
0.008528	0.0002118	0.0000040	2434197	0.3343
0.015451	0.0005426	0.0000145	2017179	0.5839
0.029053	0.0015059	0.0000594	1655520	1.0737
0.105468	0.0137583	0.0013660	1296474	3.7724
0.183456	0.0400976	0.0066705	1312234	6.3800
0.246230	0.0774300	0.0185323	1405343	8.4095
0.001306	0.0000117	0.0000001	7532229	0.0752
0.004806	0.0000866	0.0000012	4366529	0.2675
0.009645	0.0002571	0.0000052	3865277	0.5501
0.018698	0.0007366	0.0000221	2913247	1.0493
0.034855	0.0020325	0.0000902	2668679	1.8969
0.120430	0.0175828	0.0019539	2226145	6.7169
0.205518	0.0510451	0.0096496	2537959	11.2770

[a] K_1(regressed) = 1946984 ± 148435.

$$D = (1946984)\alpha_0(Cl^-)_A^2(R_3NHCl)_0^2 \qquad (55)$$

The distribution coefficients can be calculated at different chloride ion and R_3NHCl concentrations using this model equation. Table 5 also shows the comparison between the calculated D values obtained by Equation 55 and the experimental D data reported by Sato and Kato (30). Figure 7 is the plot for D(model) versus D(data) with a correlation coefficient $R^2 = 0.860$. It shows that the model Equation 55 gives good predictive distribution coefficients within the experimental conditions. It shows also that Mihailov (28) stability constants are as good as those of Sato and Kato (30).

c. Using Short's stability constants Short and Morris (27) determined the stability constants for chloro-complexes of zinc by using a cation exchange resin method. Figure 8 is the plot of the degrees of formation α_i versus the chloride ion concentrations. The same trend for the α_i is noted. The value of effective equilibrium constant K_1, found by linear regression analysis of Sato and Kato's data (30), is equal to 1920772. Table 6 shows the results of the calculated degrees of formation and the effective equilibrium constants. Using the value of the effective equilibrium constant, model Equation 21 can now be written as:

$$D = (1920772)\alpha_0(Cl^-)_A^2(R_3NHCl)_0^2 \qquad (56)$$

The distribution coefficients can be calculated at different chloride ion and R_3NHCl concentrations using this model equation. Table 6 also shows the comparison between the calculated D values obtained by Equation 56 and the experimental D data reported by Sato and Kato (30). Figure 9

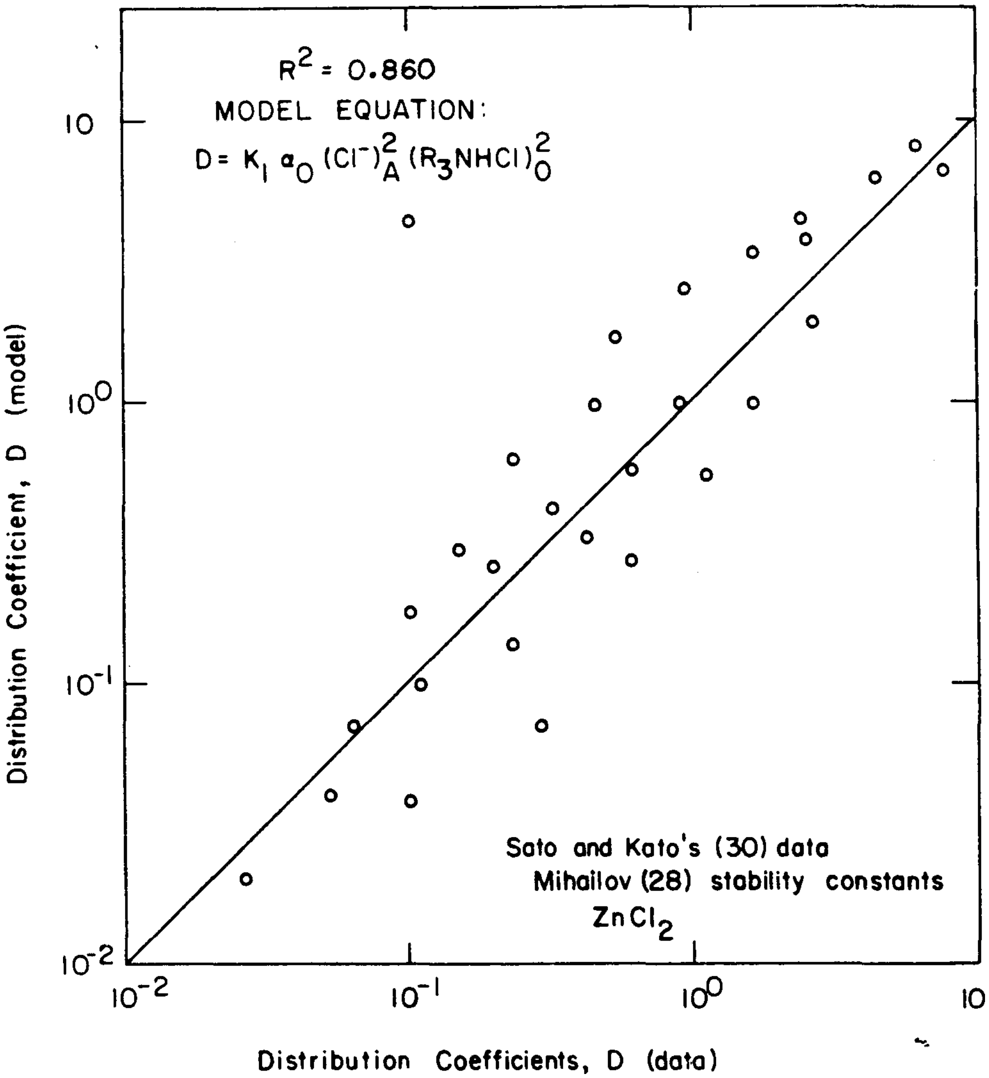


Figure 7. The comparison between the predicted D(model) and the D(data) obtained experimentally by Sato and Kato (30) for the system $ZnCl_2$-HCl-H_2O-TOA-C_6H_6

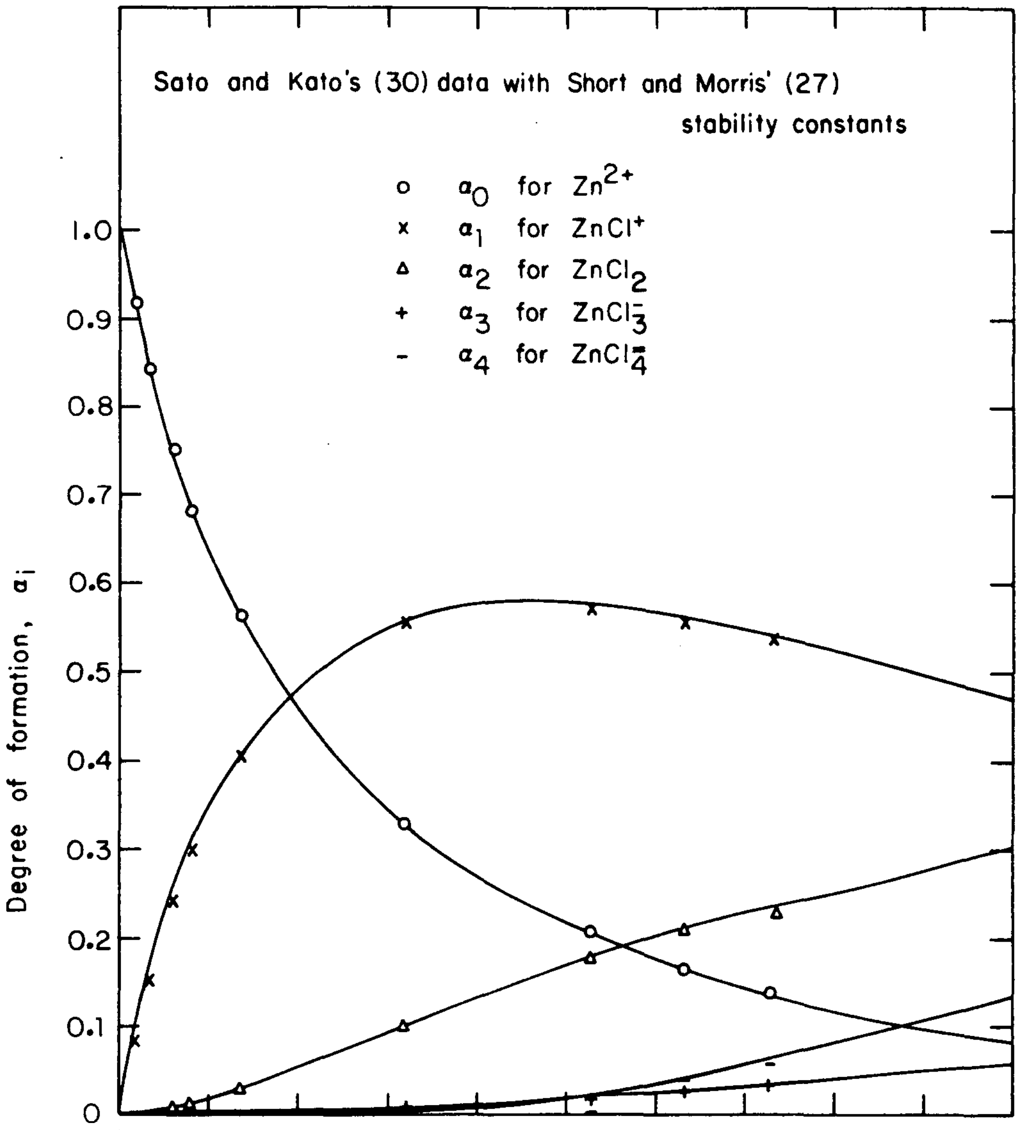


Figure 8. The degree of formation α_i for $ZnCl_2$ as a function of the aqueous chloride ion concentration

Table 6. The calculated degree of formation from Sato and Kato's (30) data with Short and Morris' (27) stability constants, the effective equilibrium constant (K_1) and the D(model) for the system $ZnCl_2$-HCl-H_2O-TOA-C_6H_6

Run	Distribution coefficient D(data)	$(Cl^-)_A$, $\frac{moles}{m^3} \cdot 10^3$	$(R_3NHCl)_O$, $\frac{moles}{m^3} \cdot 10^3$	$\alpha_{Zn^{2+}}$ α_0	α_{ZnCl^+} α_1
1	0.0259	0.0172	0.00611	0.915683	0.083474
2	0.0644	0.0347	0.00598	0.841984	0.154849
3	0.1050	0.0603	0.00588	0.751302	0.240109
4	0.1510	0.0832	0.00581	0.683593	0.301437
5	0.2310	0.1350	0.00563	0.563675	0.403310
6	0.5440	0.3160	0.00513	0.331180	0.554660
7	0.8210	0.5250	0.00481	0.206462	0.574481
8	0.0530	0.0209	0.00725	0.899175	0.099602
9	0.1120	0.0355	0.00719	0.83864	0.157832
10	0.2000	0.0539	0.00707	0.755816	0.235943
11	0.3250	0.0812	0.00690	0.689081	0.296553
12	0.4500	0.1380	0.00681	0.557830	0.407997
13	0.9450	0.3020	0.00647	0.343237	0.549385
14	1.5600	0.4370	0.00614	0.248990	0.576687
15	2.3600	0.6310	0.00587	0.167303	0.559510
16	0.1050	0.0174	0.00839	0.914777	0.084361
17	0.2270	0.0343	0.00845	0.843551	0.153349
18	0.4180	0.0575	0.00825	0.760377	0.231725
19	0.6050	0.0813	0.00810	0.688805	0.296799
20	0.9130	0.1200	0.00801	0.594510	0.378108
21	2.5120	0.3020	0.00788	0.343237	0.549385
22	4.3000	0.5060	0.00777	0.214742	0.575894
23	6.0700	0.7280	0.00770	0.139478	0.538161
24	0.2910	0.0207	0.01000	0.900054	0.098745
25	0.6000	0.0417	0.00983	0.815360	0.180203
26	1.0920	0.0617	0.00995	0.746835	0.244223
27	1.5700	0.0912	0.00987	0.662369	0.320163
28	2.6000	0.1350	0.00972	0.563675	0.403310
29	7.6800	0.3380	0.00984	0.313495	0.561594
30	14.7000	0.5750	0.00976	0.186634	0.568768

α_{ZnCl_2} α_2	$\alpha_{ZnCl_3^-}$ α_3	$\alpha_{ZnCl_4^=}$ α_4	Effective equilibrium constant K_1[a]	Equation (56) D(model)
0.000840	0.0000030	0.0000001	2561033	0.0194
0.003143	0.0000225	0.0000018	1776319	0.0696
0.008469	0.0001054	0.0000149	1111694	0.1814
0.014669	0.0002520	0.0000491	945324	0.3068
0.031846	0.0008876	0.0002808	709412	0.6254
0.102518	0.0066881	0.0049534	625066	1.6717
0.176409	0.0191205	0.0235271	623582	2.5289
0.001218	0.0000053	0.0000003	2567219	0.0397
0.003277	0.0000240	0.0000020	2049329	0.1050
0.008128	0.0000988	0.0000136	1525965	0.2517
0.014085	0.0002361	0.0000449	1502459	0.4155
0.032932	0.0009383	0.0003035	913395	0.9463
0.097044	0.0060506	0.0042827	721133	2.5171
0.147403	0.0132986	0.0136207	870246	3.4432
0.206502	0.0269012	0.0397843	1028192	4.4087
0.000859	0.0000031	0.0000001	5385815	0.0374
0.003077	0.0000218	0.0000018	3203413	0.1361
0.007793	0.0000925	0.0000125	2442890	0.3287
0.014114	0.0002369	0.0000451	2025386	0.5738
0.026539	0.0006575	0.0001849	1662203	1.0550
0.097044	0.0060506	0.0042827	1292287	3.7337
0.170443	0.0178052	0.0211159	1295415	6.3758
0.229155	0.0344412	0.0587654	1384968	8.4183
0.001196	0.0000051	0.0000002	7545424	0.0741
0.004395	0.0000378	0.0000037	4379479	0.2832
0.008814	0.0001123	0.0000162	3879550	0.5407
0.017079	0.0003216	0.0000687	2925337	1.0309
0.031846	0.0008876	0.0002808	2678824	1.8643
0.111026	0.0077475	0.0061375	2214662	6.6608
0.191288	0.0227078	0.0306023	2500869	11.2902

[a] K_1(regressed) = 1920772 ± 146484.

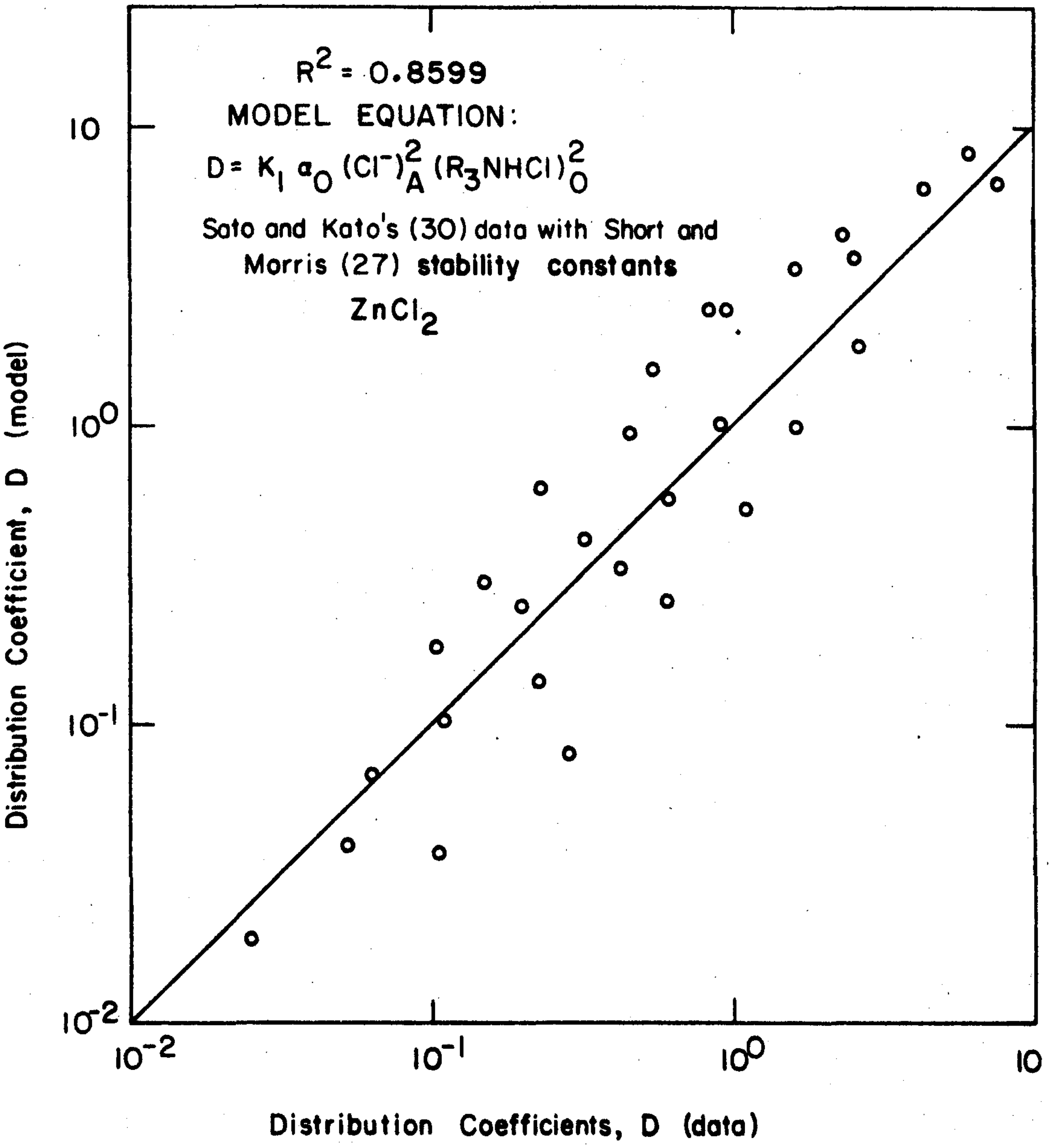


Figure 9. The comparison between the predicted D(model) and the D(data) obtained experimentally by Sato and Kato (30) for the system $ZnCl_2$-HCl-H_2O-TOA-C_6H_6

is the plot for D(model) versus D(data) with a correlation coefficient $R^2 = 0.8599$. It shows that the model Equation 56 gives good predictive distribution coefficients within the experimental conditions. It shows also that Short and Morris' (27) stability constants are as good as those of Sato and Kato (30) and Mihailov (28).

d. Using Murakami's stability constants Sato and Murakami (29) determined the stability constants for the chloro-complexes of zinc by the solvent extraction method using Aliquat-336 as the extractant and benzene as the diluent. Figure 10 is the plot of the degrees of formation versus the chloride ion concentrations. The same trend of the α_i was noted. The value of effective equilibrium constant K_1 was found by linear regression analysis of Sato and Kato's (30) data and is equal to 1700373. Table 7 shows the results of the calculated degrees of formation and the effective equilibrium constants. Using the value of the effective equilibrium constant, model Equation 40 can now be written as:

$$D = (1700373)\alpha_0(Cl^-)_A^2(R_3NHCl)_0^2 \tag{57}$$

The distribution coefficients can be calculated at different chloride ion and R_3NHCl concentrations using this model equation. Table 7 also shows the comparison between the calculated D values obtained by Equation 57 and the experimental D data reported by Sato and Kato (30). Figure 11 is the plot for D(model) versus D(data) with a correlation coefficient $R^2 = 0.8598$. It shows that the model Equation 57 gives good predictive distribution coefficients within the experimental conditions. It shows

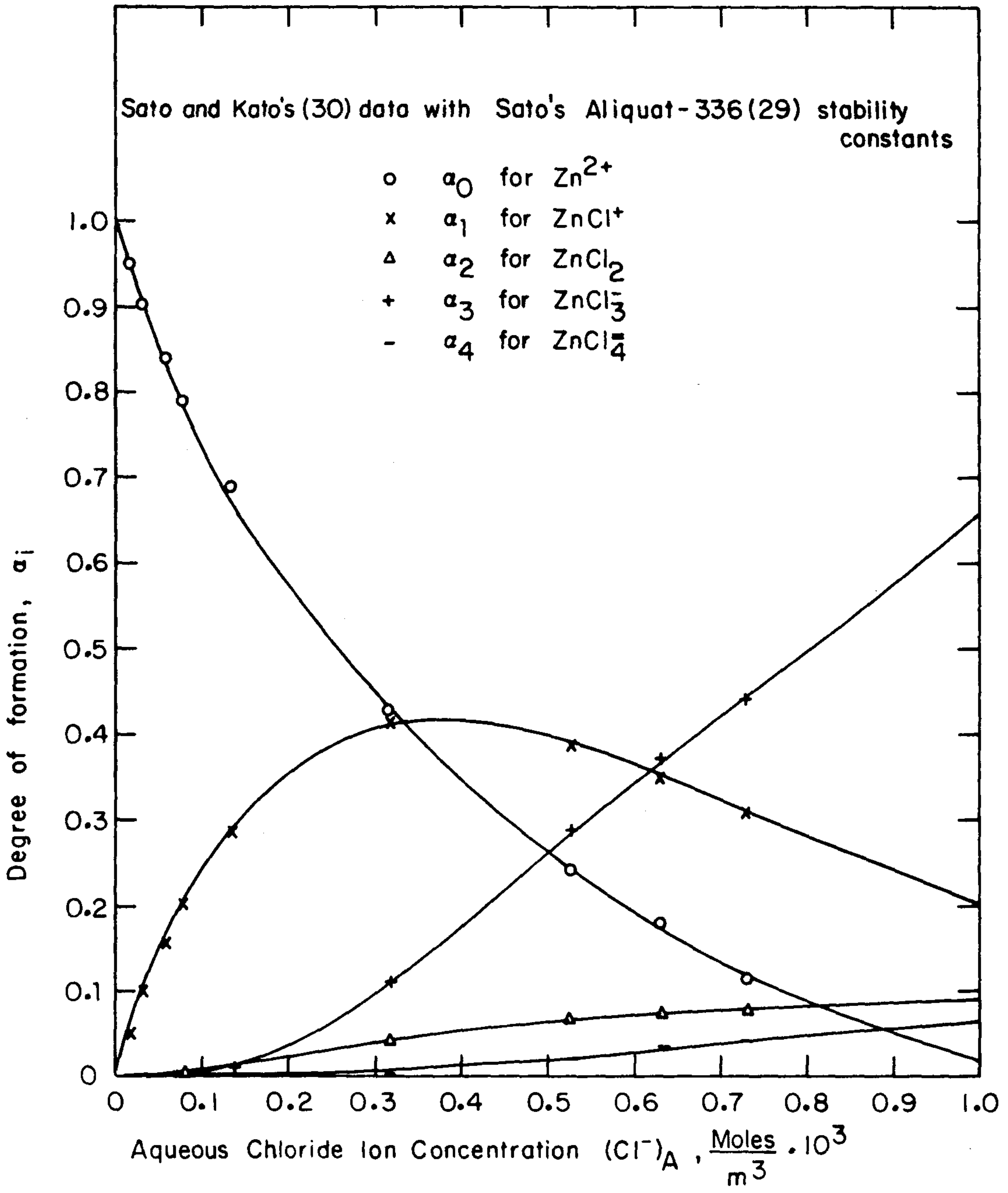


Figure 10. The degree of formation α_i for $ZnCl_2$ as a function of the aqueous chloride ion concentration

Table 7. The calculated degree of formation from Sato and Kato's (30) data with Sato and Murakami's (29) Aliquat-336 stability constants, the effective equilibrium constant (K_1) and the D(model) for the system $ZnCl_2$-HCl-H_2O-TOA-C_6H_6

Run	Distribution coefficient D(data)	$(Cl^-)_A$, $\frac{\text{moles}}{m^3} \cdot 10^3$	$(R_3NHCl)_O$, $\frac{\text{moles}}{m^3} \cdot 10^3$	$\alpha_{Zn^{2+}}$ α_0	α_{ZnCl^+} α_1
1	0.0259	0.0172	0.00611	0.949537	0.050139
2	0.0644	0.0347	0.00598	0.902453	0.096137
3	0.1050	0.0603	0.00588	0.839901	0.155483
4	0.1510	0.0832	0.00581	0.789131	0.201563
5	0.2310	0.1350	0.00563	0.687994	0.285139
6	0.5440	0.3160	0.00513	0.427046	0.414286
7	0.8210	0.5250	0.00481	0.240215	0.387166
8	0.0530	0.0209	0.00725	0.939250	0.060265
9	0.1120	0.0355	0.00719	0.900391	0.098129
10	0.2000	0.0589	0.00707	0.843152	0.152461
11	0.3250	0.0812	0.00690	0.793395	0.197781
12	0.4500	0.1380	0.00681	0.682616	0.289197
13	0.9450	0.3020	0.00647	0.443431	0.411123
14	1.5600	0.4370	0.00614	0.306665	0.411419
15	2.3600	0.6310	0.00587	0.179311	0.347355
16	0.1050	0.0174	0.00839	0.948976	0.050692
17	0.2270	0.0343	0.00845	0.903486	0.095138
18	0.4180	0.0575	0.00825	0.846422	0.149415
19	0.6050	0.0813	0.00810	0.793181	0.197971
20	0.9130	0.1200	0.00801	0.715607	0.263630
21	2.5120	0.3020	0.00788	0.443431	0.411123
22	4.3000	0.5060	0.00777	0.253228	0.393369
23	6.0700	0.7280	0.00770	0.138018	0.308464
24	0.2910	0.0207	0.01000	0.939801	0.059723
25	0.6000	0.0417	0.00983	0.884661	0.113253
26	1.0920	0.0617	0.00995	0.836668	0.158481
27	1.5700	0.0912	0.00987	0.772371	0.216252
28	2.6000	0.1350	0.00972	0.687994	0.285139
29	7.6800	0.3380	0.00984	0.402384	0.417538
30	14.7000	0.5750	0.00976	0.209149	0.369201

α_{ZnCl_2} α_2	$\alpha_{ZnCl_3^-}$ α_3	$\alpha_{ZnCl_4^=}$ α_4	Effective equilibrium constant K_1[a]	Equation (57) D(model)
0.0002837	0.000040	0.0000001	2469725	0.0178
0.0010975	0.000311	0.0000014	1657296	0.0661
0.0030845	0.001519	0.0000115	994424	0.1795
0.0055172	0.003749	0.0000393	818896	0.3135
0.0126641	0.013965	0.0002377	581223	0.6758
0.0430695	0.111171	0.0044285	484747	1.9082
0.0668713	0.286769	0.0189789	535963	2.6047
0.0004144	0.000071	0.0000002	2457685	0.0367
0.0011461	0.000332	0.0000015	1909292	0.0997
0.0029543	0.001421	0.0000106	1367900	0.2486
0.0052835	0.003504	0.0000359	1304919	0.4235
0.0131297	0.014800	0.0002575	746421	1.0251
0.0408471	0.100763	0.0038361	558191	2.8787
0.0591491	0.211136	0.0116312	706579	3.7541
0.0721085	0.371662	0.0295636	959336	4.1830
0.0002902	0.000041	0.0000001	5191724	0.0344
0.0010736	0.000301	0.0000013	2990905	0.1291
0.0028265	0.001328	0.0000096	2194552	0.3239
0.0052951	0.003516	0.0000360	1758362	0.5849
0.0104078	0.010202	0.0001543	1380921	1.1242
0.0408471	0.100763	0.0038361	1000293	4.2701
0.0654838	0.270655	0.0172642	1098536	6.6558
0.0738787	0.439322	0.0403175	1399618	7.3743
0.0004067	0.000069	0.0000002	7226307	0.0685
0.0015537	0.000529	0.0000028	4036410	0.2528
0.0032170	0.001621	0.0000126	3463003	0.5362
0.0064884	0.004834	0.0000556	2508706	1.0641
0.0126641	0.013965	0.0002377	2194768	2.0143
0.0464296	0.128187	0.0054619	1725429	7.5685
0.0698416	0.328031	0.0237772	2231645	11.2005

[a] K_1 (regressed) = 1700373 ± 129747.

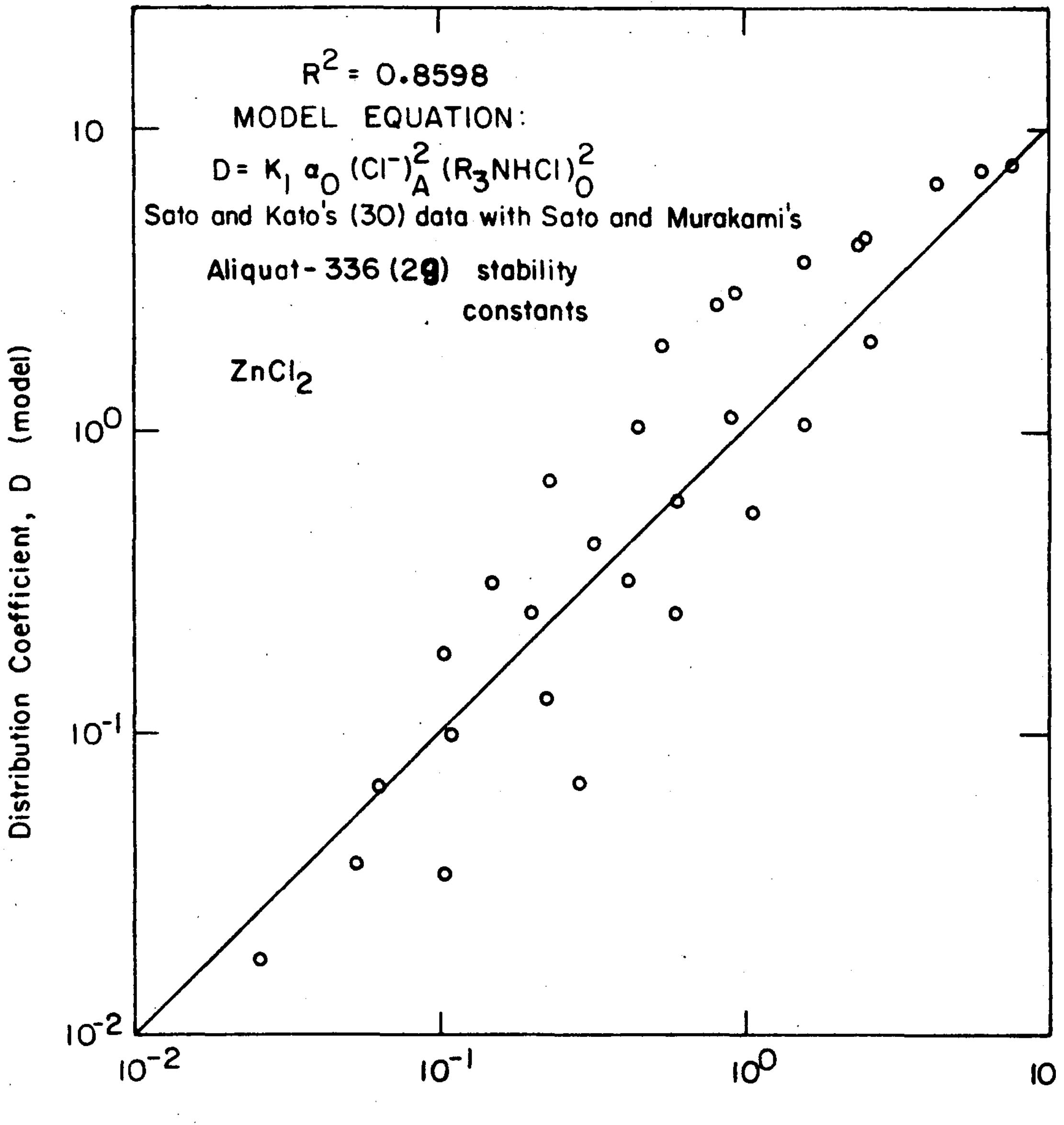


Figure 11. The comparison between the predicted D(model) and the D(data) obtained experimentally by Sato and Kato (30) for the system $ZnCl_2$-HCl-H_2O-TOA-C_6H_6

also that Sato and Murakami's (29) Aliquat stability constants are as good as the other stability constants.

2. The system copper chloride-hydrochloric acid-water-TOA-benzene

a. Using Sato's stability constants Sato and Kato (30) studied the complex formation of copper chloride by using a liquid-liquid extraction method at different ionic strengths. The stoichiometric stability constants of the chloro-complexes of copper (II) of Sato and several other investigators (26-29) are shown in Table 8. Sato's experimental data are tested using his own and the other reported stability constants. Sato's equilibrium data are shown in Table 9. Figure 12 is the plot of the degrees of formation α_i versus the chloride ion concentrations. The plot shows that the degrees of formation (α_i) increase as the chloride ion concentration increases from 0 to $1.0 \times 10^3 \frac{\text{moles}}{\text{m}^3}$ (1.0M) except α_0 which decreases sharply. The value of effective equilibrium constant K_1 was found by linear regression analysis of Sato and Kato's data (30) and is equal to 6973. Table 10 shows the results of the calculated degrees of formation and the effective equilibrium constants. Using the value of the effective equilibrium constant, model Equation 40 can now be written as:

$$D = (6973)\alpha_0(\text{Cl}^-)_A^2(\text{R}_3\text{NHCl})_0^2 \qquad (58)$$

The distribution coefficients can be calculated at different chloride ion and R_3NHCl concentrations using this model equation. Table 10 also shows the comparison between the calculated D values obtained by Equation 58 and the experimental D data represented by Sato and Kato (30). Figure 13

Table 8. Stability constants of the chloro complexes of copper (II) in aqueous solutions

Ionic strength	Stability constants						
	β_1	β_2	β_3	β_4	K_e[a]	Remark	Researcher
~	11.5	3.15	1.02	0.51	5×10^3	TOA EX	(30)
0.691	9.55	4.90	3.55	1.00	–	–	(26)
0.69	8.6	6.10	2.89	1.03	–	–	(28)
1.0	1.44	0.53	~	~	–	–	(32)

[a] K_e = equilibrium constant for the extraction reaction.

Table 9. Equilibrium data of Sato and Kato (30) for the system copper chloride hydrochloric acid-water-TOA-benzene. Initial metal concentration = 7.4 $\frac{\text{moles}}{\text{m}^3}$

Initial (R_3NHCl) $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$	Initial aq. (HCl) $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$	Distribution coefficient D	$(Cl^-)_A$ $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$	$(R_3NHCl)_O$ $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$
0.05	0.1	0.00447	0.120	0.00868
	0.15	0.00319	0.145	0.00868
	0.2	0.0107	0.282	0.00865
	0.25	0.00842	0.195	0.00867
	0.3	0.00934	0.282	0.00866
	0.35	0.00873	0.331	0.00866
0.06	0.1	0.00349	0.115	0.00926
	0.15	0.00439	0.170	0.00926
	0.2	0.00555	0.295	0.00925
	0.25	0.00605	0.218	0.00925
	0.3	0.00826	0.282	0.00925
	0.35	0.00877	0.339	0.00924
	0.4	0.0183	0.398	0.00922
	0.5	0.0186	0.501	0.00922
0.08	0.15	0.00357	0.162	0.00983
	0.2	0.00348	0.269	0.00983
	0.25	0.00276	0.208	0.00983
	0.3	0.00917	0.338	0.00983
	0.35	0.00705	0.330	0.00981
	0.4	0.01598	0.436	0.00980
0.1	0.1	0.00440	0.130	0.01006
	0.15	0.00705	0.209	0.01008
	0.2	0.00805	0.302	0.01006
	0.25	0.0122	0.400	0.01006
	0.3	0.0130	0.480	0.01005
	0.35	0.0195	0.560	0.01004
	0.4	0.0380	0.700	0.01004
	0.5	0.04	0.950	0.01004

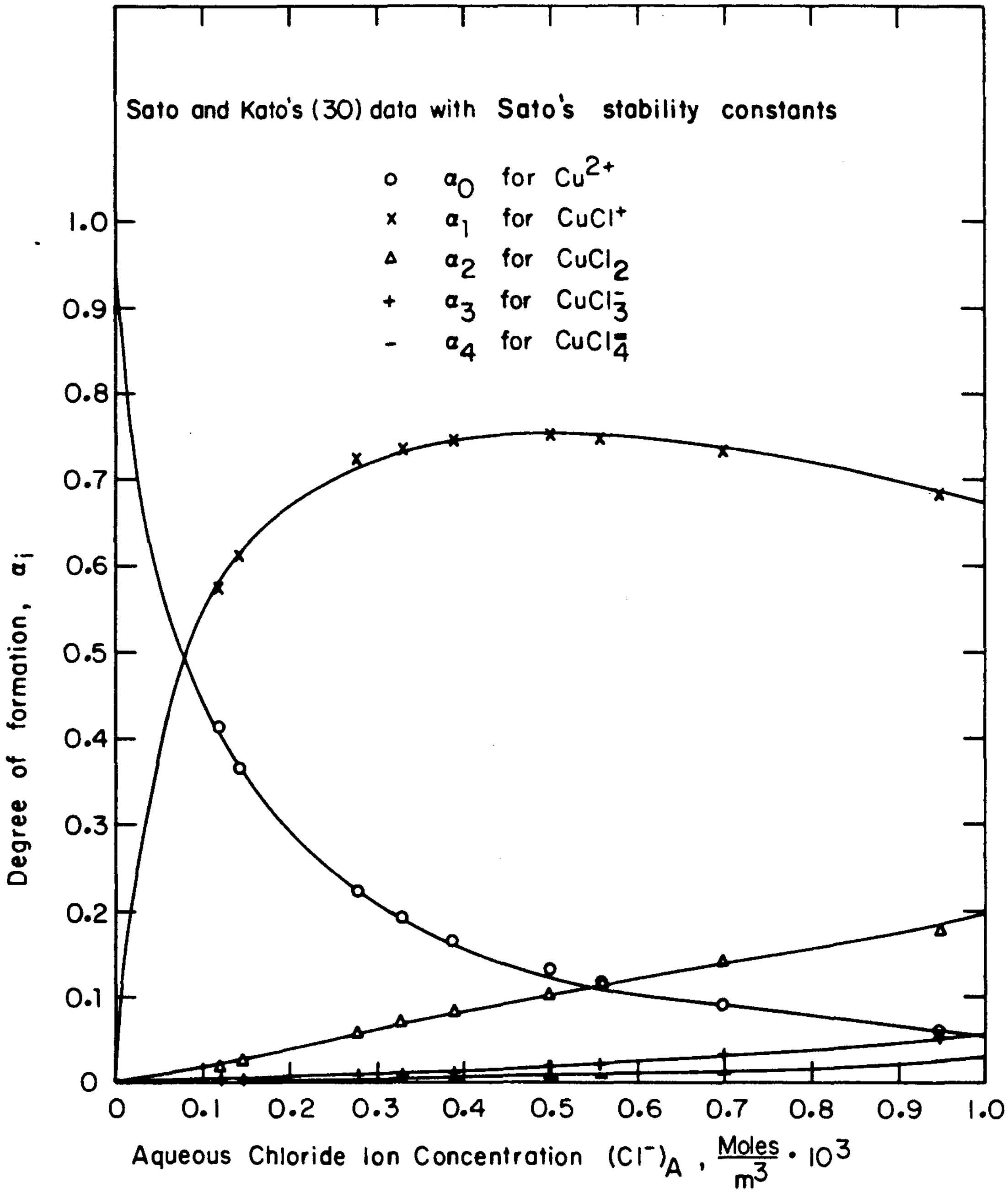


Figure 12. The degree of formation α_i for $CuCl_2$ as a function of the aqueous chloride ion concentration

Table 10. The calculated degree of formation from Sato and Kato's (30) data with Sato and Murakami's (29) stability constants, the effective equilibrium constant (K_1) and the D(model) for the system $CuCl_2$-HCl-H_2O-TOA-C_6H_6

Run	Distribution coefficient D(data)	$(Cl^-)_A$, $\frac{moles}{m^3} \cdot 10^3$	$(R_3NHCl)_O$, $\frac{moles}{m^3} \cdot 10^3$	$\alpha_{Cu^{2+}}$ α_0	α_{CuCl^+} α_1
1	0.00447	0.120	0.008	0.409966	0.570672
2	0.00319	0.145	0.008	0.363430	0.611289
3	0.01070	0.282	0.008	0.219887	0.719293
4	0.00842	0.195	0.008	0.294978	0.667241
5	0.00934	0.282	0.008	0.219887	0.719293
6	0.00873	0.331	0.008	0.191284	0.734454
7	0.00349	0.115	0.009	0.420645	0.561141
8	0.00439	0.170	0.009	0.325895	0.642665
9	0.00555	0.295	0.009	0.211588	0.724052
10	0.00605	0.218	0.009	0.270987	0.685271
11	0.00826	0.282	0.009	0.219887	0.719293
12	0.00877	0.339	0.009	0.187235	0.736284
13	0.01830	0.390	0.009	0.164598	0.744640
14	0.01860	0.501	0.009	0.128822	0.748662
15	0.00357	0.162	0.009	0.337091	0.633462
16	0.00348	0.269	0.009	0.228788	0.713910
17	0.00276	0.208	0.009	0.280961	0.677902
18	0.00917	0.338	0.009	0.187733	0.736064
19	0.00705	0.330	0.009	0.191801	0.734214
20	0.01598	0.436	0.009	0.147943	0.748235
21	0.00440	0.130	0.010	0.390073	0.588230
22	0.00705	0.209	0.010	0.279933	0.678670
23	0.00805	0.302	0.010	0.207347	0.726379
24	0.01220	0.400	0.010	0.160711	0.745701
25	0.01300	0.480	0.010	0.134524	0.749028
26	0.1950	0.560	0.010	0.114769	0.745542
27	0.03800	0.700	0.010	0.089800	0.729179
28	0.04000	0.950	0.010	0.061909	0.682235

α_{CuCl_2} α_2	$\alpha_{CuCl_3^-}$ α_3	$\alpha_{CuCl_4^=}$ α_4	Effective equilibrium constant K_1[a]	Equation (58) D(model)
0.018596	0.0007226	0.0000434	11830.9	0.0026346
0.024069	0.0011301	0.0000819	6523.1	0.0034101
0.055082	0.0050297	0.0007092	9561.1	0.0078038
0.035332	0.0022310	0.0002175	11729.3	0.0050057
0.055082	0.0050297	0.0007092	8345.8	0.0078038
0.066015	0.0070756	0.0011710	6508.8	0.0093528
0.017524	0.0006525	0.0000375	7745.1	0.0031421
0.029668	0.0016331	0.0001388	5754.5	0.0053197
0.058002	0.0055406	0.0008172	3721.1	0.0104003
0.040567	0.0028636	0.0003121	5799.8	0.0072740
0.055082	0.0050297	0.0007092	5831.7	0.0098766
0.067779	0.0074402	0.0012611	5031.8	0.0121534
0.078861	0.0099590	0.0019420	9024.3	0.0141405
0.101854	0.0165235	0.0041391	7101.7	0.0182632
0.027867	0.0014618	0.0001184	4982.0	0.0049968
0.052149	0.0045424	0.0008110	2595.1	0.0093508
0.038290	0.0025789	0.0002682	2803.2	0.0068657
0.067559	0.0073942	0.0012496	5278.5	0.0121140
0.065794	0.0070306	0.0011600	4167.0	0.0117975
0.088588	0.0125070	0.0027265	7015.0	0.0158847
0.020766	0.0008741	0.0000568	6674.5	0.0045968
0.038517	0.0026067	0.0002724	5765.6	0.0085266
0.059569	0.0058253	0.0008796	4256.8	0.0131868
0.080999	0.0104912	0.0020982	4744.5	0.0179305
0.097632	0.0151748	0.0036419	4194.3	0.0216127
0.113374	0.0205584	0.0057564	5417.9	0.0250974
0.138607	0.0314176	0.0109961	8635.9	0.0306832
0.175999	0.0541406	0.0257168	7159.1	0.0389607

[a] K_1(regressed) = 6973 ± 568.

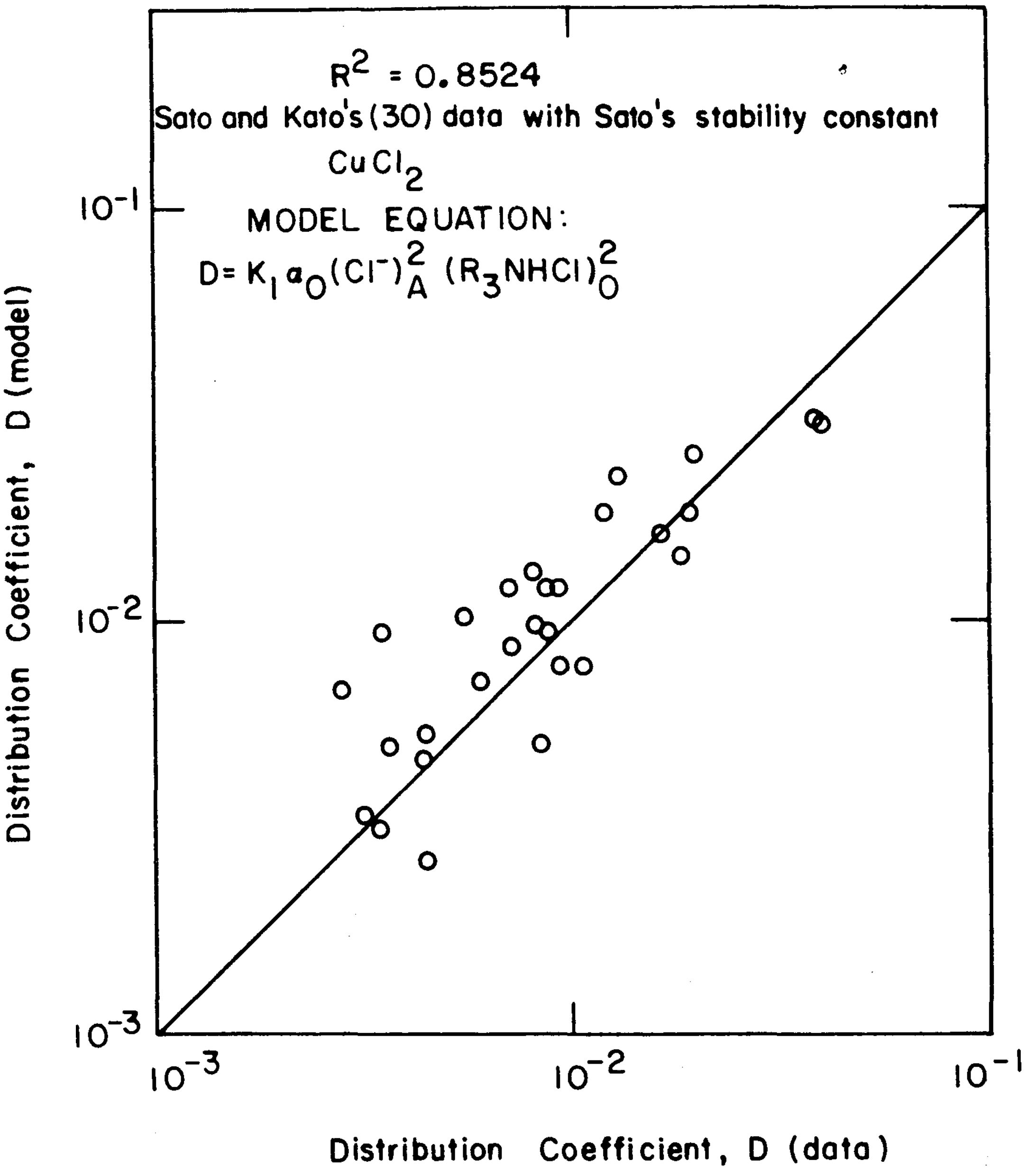


Figure 13. The comparison between the predicted D(model) and the D(data) obtained experimentally by Sato and Kato (30) for the system $CuCl_2$-HCl-H_2O-TOA-C_6H_6

is the plot for D(model) versus D(data) with a correlation coefficient $R^2 = 0.852$. It shows that the model Equation 58 gives good predictive distribution coefficients within the experimental conditions.

b. Using Mihailov's stability constants Mihailov (28) determined the stability constants for the chloro-complexes of copper. Figure 14 is the plot of the degrees of formation α_i versus the chloride ion concentrations. The same behavior for α_i was noted. The value of effective equilibrium constant K_1 was found by linear regression analysis of Sato and Kato's (30) data and is equal to 7173. Table 11 shows the results of the calculated degrees of formation and the effective equilibrium constants. Using the value of the effective equilibrium constant, the model Equation 21 can now be written as:

$$D = (7173)\alpha_0(Cl^-)_A^2(R_3NHCl)_0^2 \tag{59}$$

The distribution coefficients can be calculated at different chloride ion and R_3NHCl concentrations using this model equation. Table 11 also shows the comparison between the calculated D values obtained by Equation 59 and the experimental D data reported by Sato and Kato (30). Figure 15 is the plot for D(model) versus D(data) with a correlation coefficient $R^2 = 0.803$. It shows that the model Equation 59 gives good predictive distribution coefficients within the experimental conditions. It shows also that Mihailov's (28) stability constants are as good as those of Sato and Kato (30).

c. Using Morris' stability constants Morris and Short (26) determined the stability constants for chloro-complexes of copper by using a cation exchange resin method. Figure 16 is the plot of the degrees of

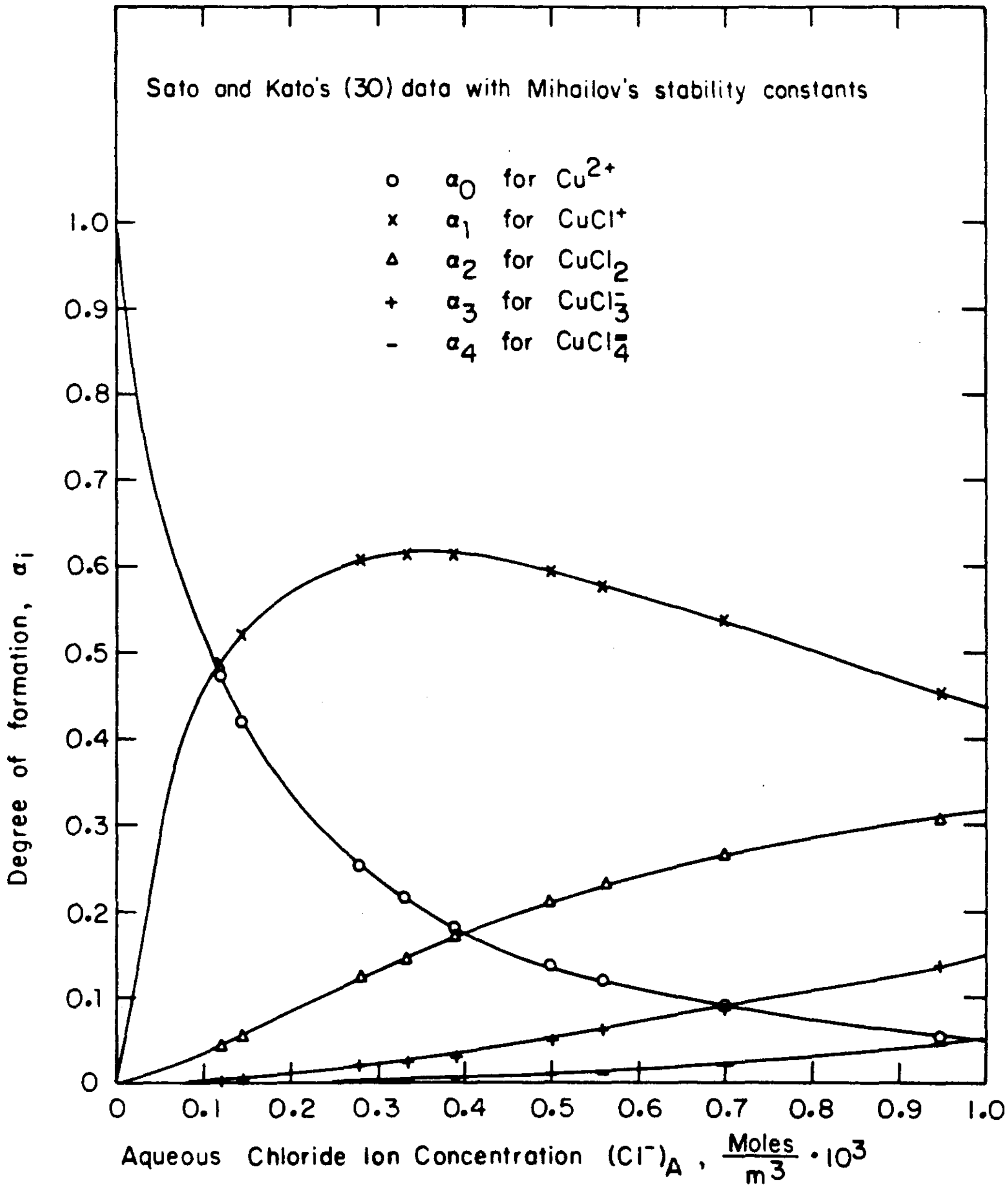


Figure 14. The degree of formation α_i for $CuCl_2$ as a function of the aqueous chloride ion concentration

Table 11. The calculated degree of formation from Sato and Kato's (30) data with Mihailov's (28) stability constants, the effective equilibrium constant (K_1) and the D(model) for the system $CuCl_2$-HCl-H_2O-TOA-C_6H_6

Run	Distribution coefficient D(data)	$(Cl^-)_A$, $\frac{moles}{m^3} \cdot 10^3$	$(R_3NHCl)_O$, $\frac{moles}{m^3} \cdot 10^3$	$\alpha_{Cu^{2+}}$ α_0	α_{CuCl^+} α_1
1	0.00447	0.120	0.008	0.470578	0.485636
2	0.00319	0.145	0.008	0.419372	0.522957
3	0.01070	0.282	0.008	0.251154	0.609099
4	0.00842	0.195	0.008	0.341079	0.571990
5	0.00934	0.282	0.008	0.251154	0.609099
6	0.00873	0.331	0.008	0.215885	0.614539
7	0.00349	0.115	0.009	0.482102	0.476799
8	0.00439	0.170	0.009	0.376882	0.551002
9	0.00555	0.295	0.009	0.240973	0.611348
10	0.00605	0.218	0.009	0.312797	0.586431
11	0.00826	0.282	0.009	0.251154	0.609099
12	0.00877	0.339	0.009	0.210854	0.614725
13	0.01830	0.390	0.009	0.182579	0.612371
14	0.01860	0.501	0.009	0.137589	0.592816
15	0.00357	0.162	0.009	0.389668	0.542886
16	0.00348	0.269	0.009	0.262024	0.606166
17	0.00276	0.208	0.009	0.324607	0.580658
18	0.00917	0.338	0.009	0.211473	0.614711
19	0.00705	0.330	0.009	0.216527	0.614503
20	0.01598	0.436	0.009	0.161657	0.606149
21	0.00440	0.130	0.010	0.448887	0.501855
22	0.00705	0.209	0.010	0.323394	0.581268
23	0.00805	0.302	0.010	0.235754	0.612300
24	0.01220	0.400	0.010	0.177704	0.611303
25	0.01300	0.480	0.010	0.144765	0.597592
26	0.01950	0.560	0.010	0.119936	0.577611
27	0.03800	0.700	0.010	0.088908	0.535227
28	0.04000	0.950	0.010	0.055580	0.454091

α_{CuCl_2} α_2	$\alpha_{CuCl_3^-}$ α_3	$\alpha_{CuCl_4^=}$ α_4	Effective equilibrium constant K_1 [a]	Equation (59) D(model)
0.041336	0.002350	0.0001005	10307.0	0.0031111
0.053785	0.003695	0.0001909	5653.0	0.0040481
0.121834	0.016277	0.0016360	8370.8	0.0091698
0.079114	0.007309	0.0005080	10144.0	0.0059545
0.121834	0.016277	0.0016360	7306.8	0.0091698
0.144281	0.022626	0.0026696	5767.1	0.0108592
0.038892	0.002119	0.0000868	6757.8	0.0037048
0.066441	0.005351	0.0003242	4976.0	0.0063289
0.127921	0.017879	0.0018797	3267.4	0.0121853
0.090679	0.009365	0.0007277	5024.5	0.0086377
0.121834	0.016277	0.0016360	5105.7	0.0116055
0.147813	0.023740	0.0028683	4468.2	0.0140801
0.169399	0.031300	0.0043513	8135.5	0.0161364
0.210663	0.050003	0.0089284	6649.2	0.0200671
0.062381	0.004788	0.0002764	4309.8	0.0059422
0.115658	0.014740	0.0014131	2265.9	0.0110172
0.085667	0.008442	0.0006258	2426.3	0.0081604
0.147373	0.023600	0.0028429	4685.9	0.0140383
0.143837	0.022488	0.0026449	3691.2	0.0137014
0.187455	0.038721	0.0060170	6419.8	0.0178563
0.046276	0.002850	0.0001321	5800.0	0.0054421
0.086170	0.008532	0.0006356	4990.7	0.0101336
0.131160	0.018766	0.0020199	743.9	0.0154245
0.173439	0.032868	0.0046857	4290.8	0.0203966
0.203459	0.046269	0.0079153	3897.6	0.0239269
0.229433	0.060871	0.0121489	5184.5	0.0269814
0.265746	0.088132	0.0219872	8722.6	0.0312519
0.305983	0.137717	0.0466286	7974.3	0.0359838

[a] K_1 (regressed) = 7173 ± 696.

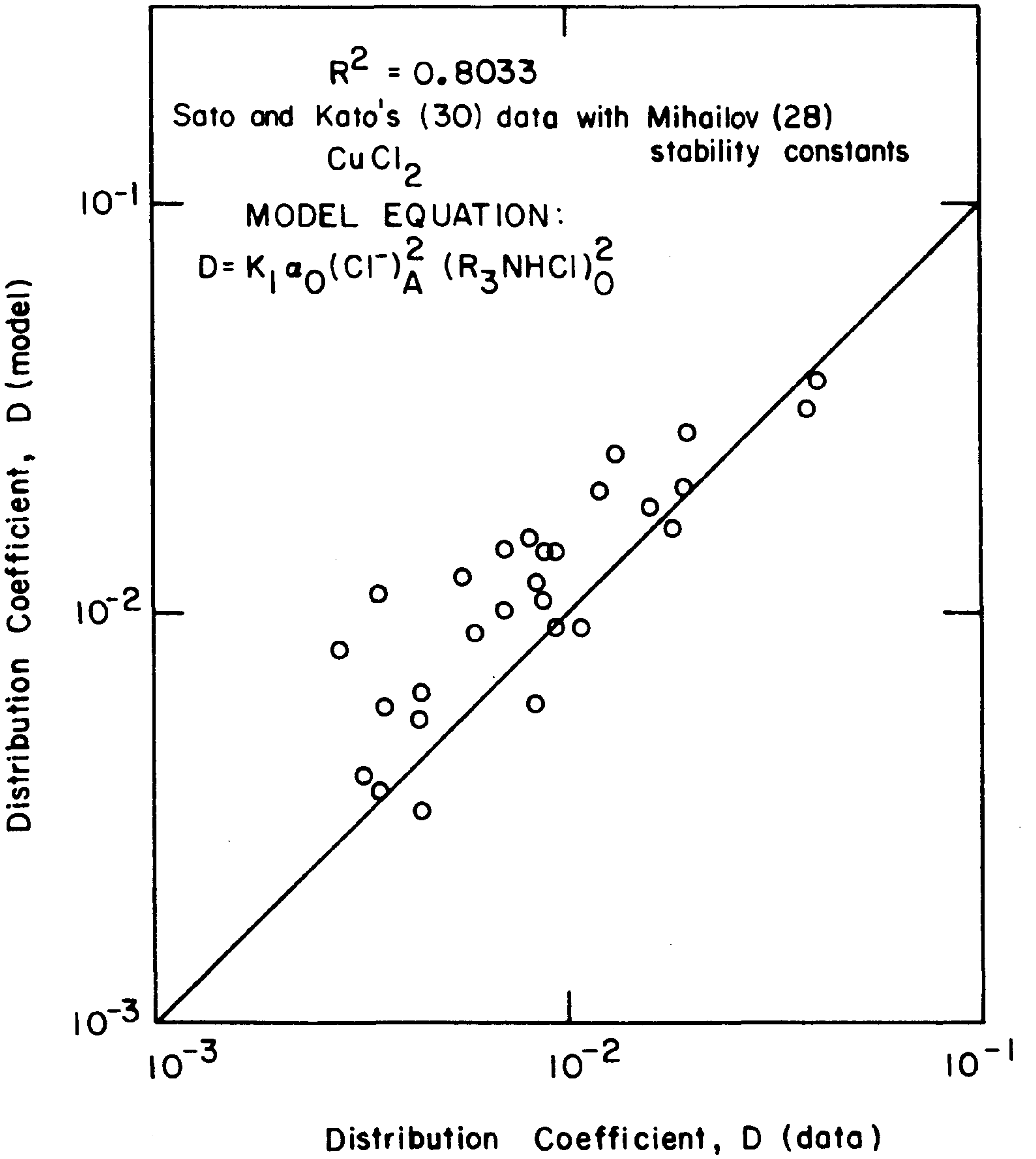


Figure 15. The comparison between the predicted D(model) and the D(data) obtained experimentally by Sato and Kato (30) for the system $CuCl_2$-HCl-H_2O-TOA-C_6H_6

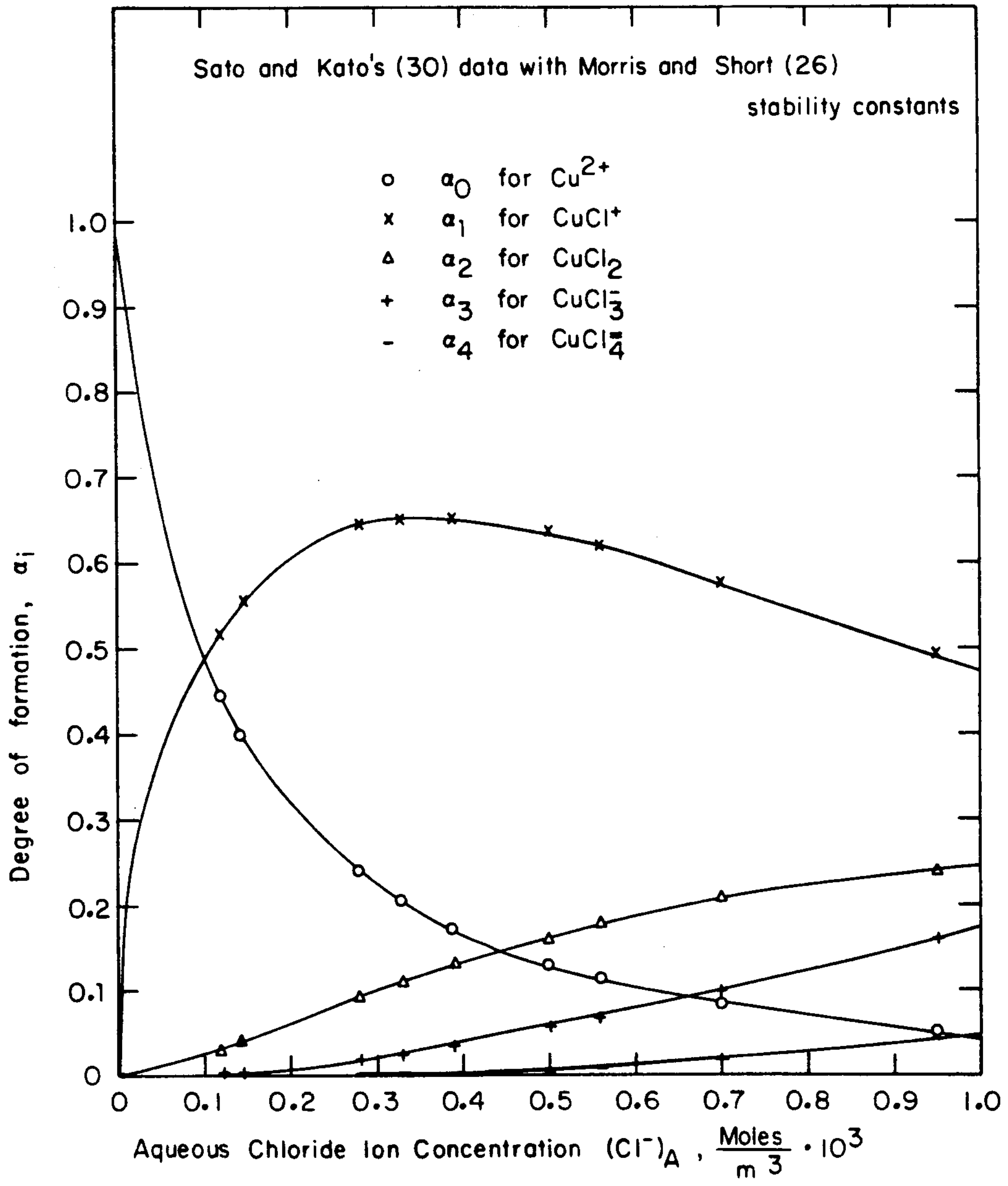


Figure 16. The degree of formation α_i for $CuCl_2$ as a function of the aqueous chloride ion concentration

formation α_i versus the chloride ion concentrations. The same trend of the α_i with the chloride ion concentration was noted. The value of effective equilibrium constant K_1 was found by linear regression analysis of Sato and Kato's (30) data and is equal to (7389). Table 12 shows the results of the calculated degrees of formation and the effective equilibrium constants. Using the value of the effective equilibrium constant, model Equation 40 can now be written as:

$$D = (7389)\alpha_0(Cl^-)_A^2(R_3NHCl)_0^2 \qquad (60)$$

The distribution coefficients can be calculated at different chloride ion and R_3NHCl concentrations using this model equation. Table 12 also shows the comparison between the calculated D values obtained by Equation 60 and the experimental D data reported by Sato and Kato (30). Figure 17 is the plot for D(model) versus D(data) with a correlation coefficient $R^2 = 0.8103$. It shows that the model Equation 60 gives good predictive distribution coefficients within the experimental conditions. It shows also that the stability constants of Morris and Short (26) are as good as those of the other two sets.

d. Using McConnell's stability constants McConnell and Davidson (32) determined the stability constants for the chloro-complexes of copper by using spectrophotometric methods. These stability constants are wrong or inaccurate over the range of experimental conditions. The stability constant values are very small when compared to the other stability constants. McConnell's stability constants were tested with Sato's equilibrium data and no fit was obtained. For this reason, McConnell's stability constants were disregarded. Thiel (31) verified the same conclusion.

Table 12. The calculated degree of formation from Sato and Kato's (30) data with Morris and Short's (26) stability constants, the effective equilibrium constant (K_1) and the D(model) for the system $CuCl_2$-HCl-H_2O-TOA-C_6H_6

Run	Distribution coefficient D(data)	$(Cl^-)_A$, $\frac{\text{moles}}{m^3} \cdot 10^3$	$(R_3NHCl)_O$, $\frac{\text{moles}}{m^3} \cdot 10^3$	$\alpha_{Cu^{2+}}$ α_0	α_{CuCl^+} α_1
1	0.00447	0.120	0.008	0.448604	0.516792
2	0.00319	0.145	0.008	0.398944	0.555330
3	0.01070	0.282	0.008	0.239022	0.647080
4	0.00842	0.195	0.008	0.323978	0.606487
5	0.00934	0.282	0.008	0.239022	0.647080
6	0.00873	0.331	0.008	0.205918	0.654326
7	0.00349	0.115	0.009	0.459856	0.507681
8	0.00439	0.170	0.009	0.358126	0.584461
9	0.00555	0.295	0.009	0.229458	0.649824
10	0.00605	0.218	0.009	0.297146	0.621868
11	0.00826	0.282	0.009	0.239022	0.647080
12	0.00877	0.339	0.009	0.201201	0.654789
13	0.01830	0.390	0.009	0.174695	0.654057
14	0.01860	0.501	0.009	0.132447	0.637019
15	0.00357	0.162	0.009	0.370374	0.576005
16	0.00348	0.269	0.009	0.249242	0.643642
17	0.00276	0.208	0.009	0.308337	0.615687
18	0.00917	0.338	0.009	0.201782	0.654741
19	0.00705	0.330	0.009	0.206520	0.654255
20	0.01598	0.436	0.009	0.155069	0.649056
21	0.00440	0.130	0.010	0.427503	0.533523
22	0.00705	0.209	0.010	0.307186	0.616339
23	0.00805	0.302	0.010	0.224558	0.651038
24	0.01220	0.400	0.010	0.170124	0.653275
25	0.01300	0.480	0.010	0.139199	0.641431
26	0.01950	0.560	0.010	0.115802	0.622552
27	0.03800	0.700	0.010	0.086369	0.580398
28	0.04000	0.950	0.010	0.054369	0.495847

α_{CuCl_2} α_2	$\alpha_{CuCl_3^-}$ α_3	$\alpha_{CuCl_4^=}$ α_4	Effective equilibrium constant K_1 [a]	Equation (60) D(model)
0.031783	0.002729	0.0000930	10811.9	0.0030552
0.041268	0.004281	0.0001764	5942.4	0.0039670
0.093519	0.018868	0.0015116	8795.7	0.0089897
0.060611	0.008456	0.0004684	10679.4	0.0058263
0.093519	0.018868	0.0015116	7677.7	0.0089897
0.110998	0.026286	0.0024716	6046.2	0.0106699
0.029921	0.002462	0.0000804	7084.7	0.0036403
0.050921	0.006193	0.0002991	5236.6	0.0061951
0.098245	0.020735	0.0017378	3431.3	0.0119526
0.069478	0.010836	0.0006711	5289.2	0.0084527
0.093519	0.018868	0.0015116	5364.9	0.0113776
0.113761	0.027591	0.0026572	4682.6	0.0138403
0.130730	0.036477	0.0040413	8502.7	0.0159046
0.163562	0.058627	0.0083444	6907.3	0.0198991
0.047823	0.005543	0.0002551	4534.3	0.0058181
0.088734	0.017077	0.0013051	2382.1	0.0107954
0.065632	0.009767	0.0005771	2554.3	0.0079848
0.113417	0.027427	0.0026336	4911.0	0.0137984
0.110651	0.026124	0.0024492	3870.0	0.0134618
0.145032	0.045240	0.0056036	6692.6	0.0176446
0.035546	0.003306	0.0001221	6090.1	0.0053389
0.066018	0.009872	0.0005861	5254.1	0.0099157
0.100764	0.021772	0.0018679	3930.6	0.0151346
0.133921	0.038325	0.0043552	4482.0	0.0201147
0.157792	0.054188	0.0073893	4053.4	0.0237000
0.178672	0.071585	0.0113885	5369.6	0.0268362
0.208218	0.104278	0.0207371	8979.1	0.0312739
0.241416	0.164084	0.0442841	8151.9	0.0362601

[a] K_1(regressed) = 7389 ± 701.

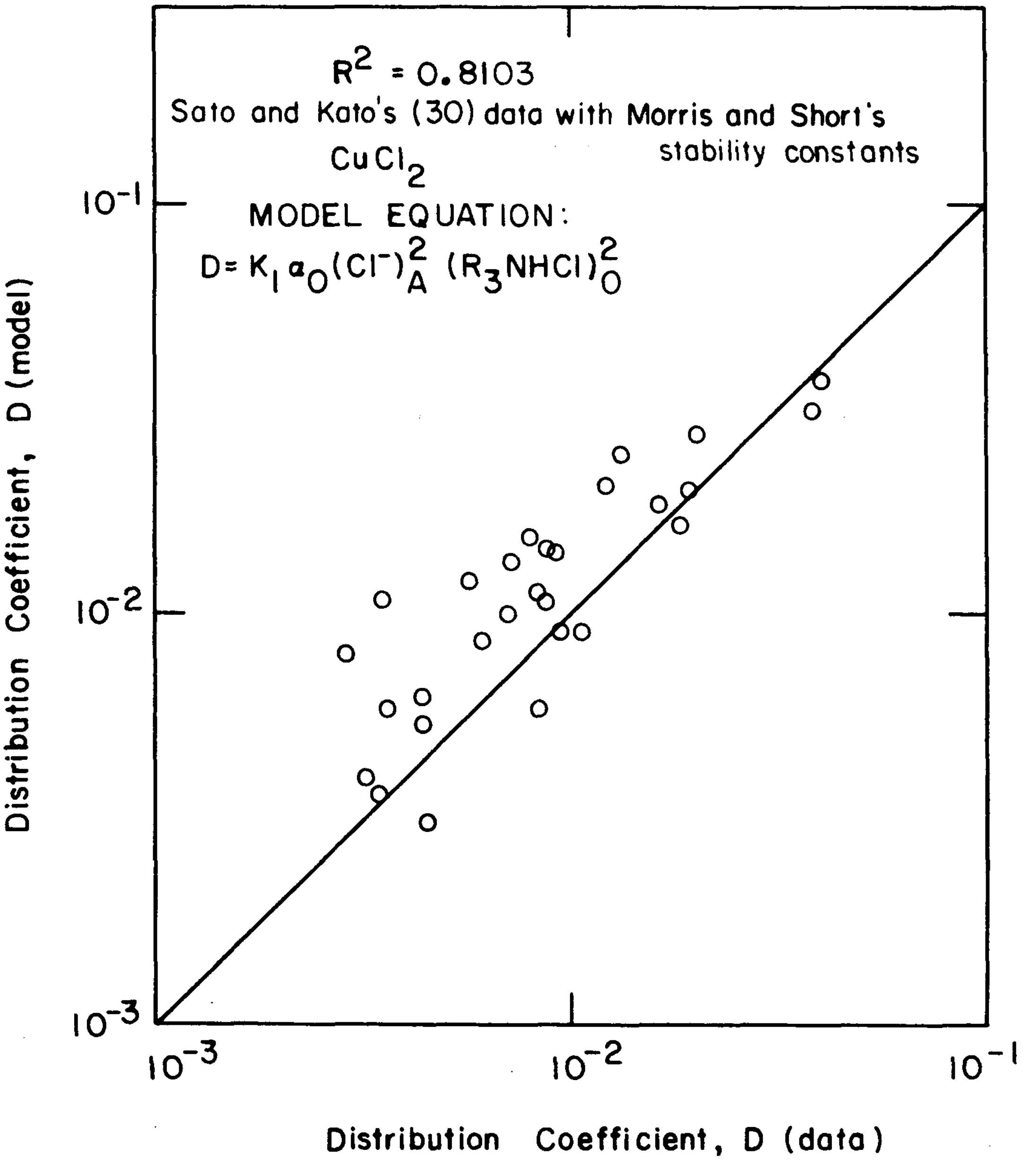


Figure 17. The comparison between the predicted D(model) and the D(data) obtained experimentally by Sato and Kato (30) for the system $CuCl_2$-HCl-H_2O-TOA-C_6H_6

Based on the above model application, the modeling procedures can be summarized as follows:

1. From Equation 38, the degrees of formation are calculated using the equilibrium data and the reported stability constants.

2. Linear regression analysis technique is used to calculate the effective equilibrium constant using the equilibrium data and the calculated degrees of formation.

3. The predictive distribution coefficients (or separation factors) are calculated using the equilibrium data, the regression value of effective equilibrium constant as well as the suitable model equation.

B. TOA Solvent Extraction Analysis

1. The system zinc chloride-hydrochloric acid-water-TOA-benzene

a. Low concentrations An equilibrium study on this system was performed as described in the Procedure section. Table 13 shows the equilibrium data for this system at 7.5 $\frac{\text{moles}}{\text{m}^3}$ (0.0075M) initial metal concentrations.

The chloride ion concentration in the equilibrium aqueous phase was measured by a chloride ion selective electrode as described in the Procedure section. Table 14 and Figure 18 show the chloride standards and calibration curve for the chloride ion-selective electrode, respectively. Table 15 shows the chloride ion concentration in the equilibrated aqueous phase at 20 $\frac{\text{moles}}{\text{m}^3}$ (0.02M) TOA.

The chloride ion concentration in the equilibrated organic phase

Table 13. Equilibrium data obtained in this work for the system $ZnCl_2$-HCl-TOA-C_6H_6. Initial metal concentration = 7.5 $\frac{moles}{m^3}$

Initial (R_3NHCl) $\frac{moles}{m^3} \cdot 10^3$	Initial aq. (HCl) $\frac{moles}{m^3} \cdot 10^3$	D	$(Cl^-)_A$ $\frac{moles}{m^3}$	$(R_3NHCl)_O$ $\frac{moles}{m^3}$	$(Zn)_A^T$ Kg/m^3	$(Zn)_O^T$ Kg/m^3
0.02	0.01	0.0250	16.75	9.53	0.4620	0.012
	0.05	0.0982	52.50	9.22	0.4800	0.0471
	0.1	0.2431	100.00	8.73	0.4420	0.1074
	0.2	0.4913	230.00	7.71	0.4600	0.2260
	0.3	0.7530	282.5	1.02	0.3660	0.2756
	0.5	1.6321	600.00	6.43	0.2860	0.4668
0.03	0.01	0.5919	140.00	1.28	0.4320	0.0224
	0.05	0.2134	350.00	8.97	0.5100	0.1088
	0.1	0.4200	85.00	7.83	0.4760	0.1999
	0.2	1.1370	210	7.43	0.3260	0.4214
	0.3	1.6893	325	5.33	0.1820	0.3674
	0.5	2.9735	612.5	5.27	0.2560	0.7612
0.05	0.01	0.1131	14.75	16.8	0.5320	0.0602
	0.05	0.3900	242.5	16.4	0.5000	0.1950
	0.1	0.9781	67.5	6.3	0.4600	0.4499
	0.2	2.8321	190	16.1	0.2820	0.7986
	0.3	3.9346	310	15.9	0.2520	0.9915
	0.5	7.000	595	15.8	0.1380	0.9660
0.1	0.01	0.3170	13.95	23.4	0.5100	0.1616
	0.05	0.9813	16.75	20.6	0.4880	0.4788
	0.1	2.015	275	20.4	0.5000	1.0075
	0.2	4.5374	13.75	20.3	0.2320	1.0526
	0.3	8.3140	24.98	20.2	0.1040	0.8646
	0.5	15.5300	500	20.3	0.1060	1.6462

Table 14. Chloride ion electrode data for the chloride standards

Standard No.	$(Cl^-)_A$ $\frac{moles}{m^3} \cdot 10^3$	$[Cl^-]_A$ $\frac{moles}{m^3} \cdot 10^3$	mv
1	0.1	0.075	57.2
2	0.02	0.0174	93.2
3	0.01	0.009	109.1
4	0.002	0.0019	145.9
5	0.001	0.00097	160.9

Table 15. Chloride ion concentration in the equilibrated aqueous phase for the system $ZnCl_2$-HCl-H_2O-TOA-C_6H_6 at 20 $\frac{moles}{m^3}$ initial TOA

Sample No.	EMF mv	DF[b]	Chloride ion conc.[a] $\frac{moles}{m^3} \cdot 10^3$	Chloride ion conc. in aq. $\frac{moles}{m^3}$
1	151.1	10	0.0016	16.75
2	124.0	10	0.0052	52.5
3	109.1	10	0.01	100
4	142.5	10	0.023	230
5	137.4	10	0.0282	282.5
6	120.0	10	0.06	600

[a] Read from Figure 18.

[b] DF = dilution factor.

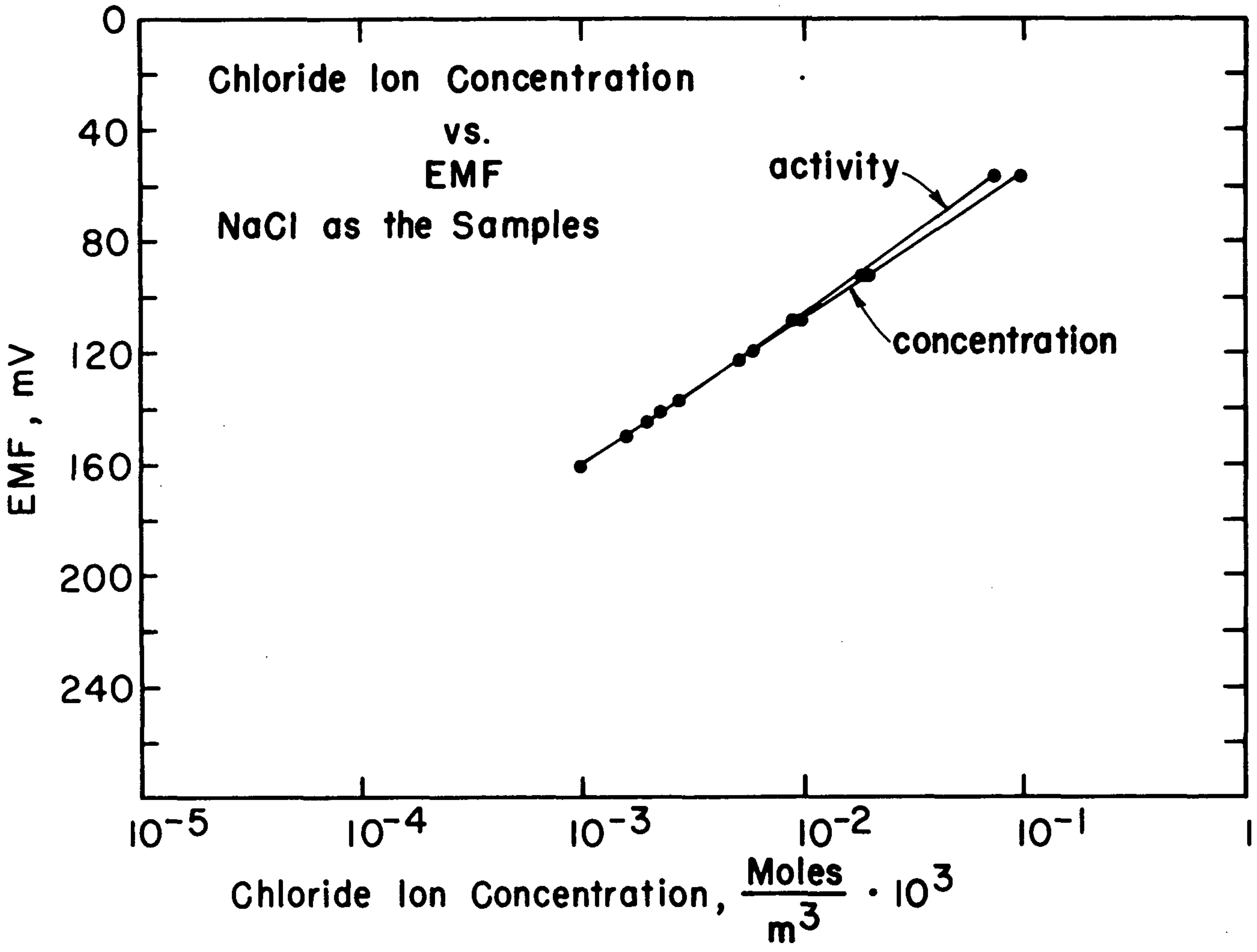


Figure 18. Calibration curve for the chloride ion-selective electrode

can also be determined as outlined in the Procedure section. Volumetric samples of the equilibrated organic phase were first back-extracted three times with $1 \times 10^3 \frac{\text{moles}}{\text{m}^3}$ (1M) sulfuric acid, diluted and then the chloride ion concentration was measured by using the chloride ion-selective electrode. The details of this technique will be elaborated on the $0.2 \times 10^3 \frac{\text{moles}}{\text{m}^3}$ (0.2M) TOA experiments. The interference of the sulphate ion for the chloride electrode was found to be negligible (1). Table 16 and Figure 19 show the chloride standards and calibration curve for the chloride ion-selective electrode in the organic phase, respectively. Table 17 shows the chloride ion concentration in the equilibrated organic phase at $20 \frac{\text{moles}}{\text{m}^3}$ (0.02M) TOA.

The stability constants used for this system were an average value of the first three data sets reported in Table 1. The fourth set was not averaged since $\beta_3 = 8.25$ was too extensively different from the others. The new values are: $\beta_1 = 5.26$, $\beta_2 = 3.08$, $\beta_3 = 1.06$, $\beta_4 = 0.75$.

The degrees of formation and the effective equilibrium constant were calculated from the average stability constants and the equilibrium data using Equations 38 and 40, respectively. Table 18 shows these results. The degrees of formation are plotted in Figure 20. By using linear regression analysis, the value of effective equilibrium constant K_1 was found to be equal to 592696. The predicted distribution coefficients were then calculated using the model Equation 21. Table 22 also shows the predicted distribution coefficients as compared to the experimental values. Figure 21 is the plot of D(model) versus D(data) with a regressed value of $R^2 = 0.8626$. It can be seen that

Table 16. Chloride ion electrode data for the chloride-sulfate standards

Standard No.	$(Cl^-)_A$ $\frac{\text{moles}}{m^3} \cdot 10^3$	EMF, mv
1	0.1	56.4
2	0.02	91.2
3	0.01	106.8
4	0.002	141.1
5	0.001	155.0

Table 17. Chloride ion electrode data for organic samples back-extracted with sulfuric acid. Initial TOA concentration = 20 $\frac{\text{moles}}{m^3}$

Sample No.	EMF, mv	DF[b]	Chloride ion conc.[a] $\frac{\text{moles}}{m^3}$	Chloride ion conc. in org. $\frac{\text{moles}}{m^3}$
1	149.2	10	1.353	13.53
2	109.8	10	8.342	83.42
3	88.6	10	20.4	203.5
4	74.1	10	44	439.7
5	71.3	10	53.2	532.2
6	58.9	10	92	920.0

[a] Read from Figure 19.

[b] DF = dilution factor.

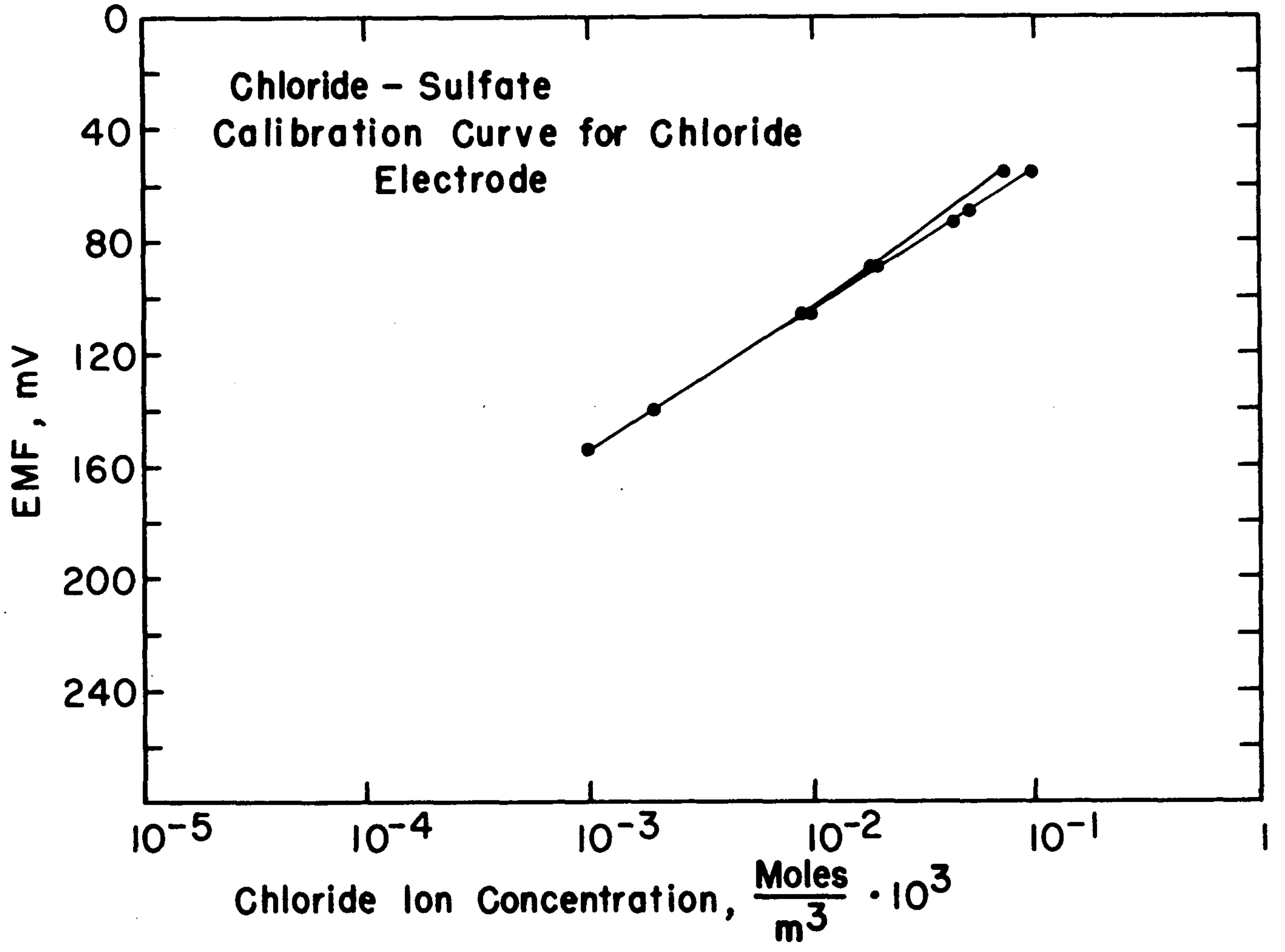


Figure 19. Chloride-sulfate calibration curve for chloride ion-selective electrode

Table 18. The degree of formation calculated from this work data with the average stability constants of Sato and Kato (30), Short and Morris (27) and Mahailov (28) and the effective equilibrium constant for the system $ZnCl_2$-HCl-H_2O-TOA-C_6H_6

Run	Distribution coefficient D(data)	$(Cl^-)_A$, $\frac{\text{moles}}{m^3} \cdot 10^3$	$(R_3NHCl)_O$, $\frac{\text{moles}}{m^3} \cdot 10^3$	$\alpha_{Zn^{2+}}$ α_0	α_{ZnCl^+} α_1
1	0.0250	0.01673	0.00950	0.950801	0.048893
2	0.0982	0.05250	0.00922	0.858251	0.138329
3	0.2431	0.10000	0.00873	0.754458	0.231619
4	0.4913	0.23000	0.00771	0.536821	0.379050
5	0.7530	0.28250	0.00102	0.467180	0.405174
6	1.6321	0.60000	0.00643	0.195222	0.359598
7	0.0519	0.14000	0.00128	0.679056	0.291858
8	0.2134	0.03500	0.00897	0.901679	0.096885
9	0.4200	0.08500	0.00783	0.785319	0.204929
10	1.1370	0.21000	0.00743	0.565717	0.364718
11	1.6893	0.32500	0.00533	0.416798	0.415861
12	2.9735	0.61250	0.00527	0.188631	0.354696
13	0.1131	0.01475	0.01680	0.956454	0.043311
14	0.3900	0.24250	0.01640	0.519449	0.386717
15	0.9781	0.06750	0.01630	0.823462	0.170642
16	2.8210	0.19000	0.01610	0.596053	0.347678
17	3.9346	0.31000	0.01590	0.434001	0.413039
18	7.0000	0.59500	0.01580	0.197926	0.361542
19	0.3170	0.01395	0.02340	0.958731	0.041059
20	0.9813	0.01675	0.02060	0.950801	0.048893
21	2.0150	0.02750	0.02040	0.921352	0.077785
22	4.5374	0.13750	0.02030	0.683509	0.288526
23	8.3140	0.24980	0.02020	0.509539	0.390759
24	15.5300	0.50000	0.02030	0.257483	0.395237

α_{ZnCl_2} α_2	$\alpha_{ZnCl_3^-}$ α_3	$\alpha_{ZnCl_4^=}$ α_4	Effective equilibrium constant K_1 [a]	D(model)
0.0002694	0.000037	0.0000001	1038421	0.0119
0.0023892	0.001025	0.0000068	488334	0.0997
0.0076200	0.006224	0.0000785	422787	0.2851
0.0286818	0.053885	0.0015623	291040	0.8371
0.0376567	0.086895	0.0030945	19412134	0.0192
0.0709826	0.347885	0.0263127	561687	1.4410
0.0134426	0.015372	0.0002713	2380050	0.0108
0.0011156	0.000319	0.0000014	2401163	0.0441
0.0057307	0.003979	0.0000426	1207374	0.1725
0.0251976	0.043223	0.0011442	825552	0.6830
0.0444646	0.118040	0.0048361	1350702	0.6202
0.0714736	0.357589	0.0276112	1512942	0.9747
0.0002102	0.000025	0.0000000	1925733	0.0291
0.0308523	0.061113	0.0018682	47469	4.0744
0.0037894	0.002089	0.0000178	981199	0.4943
0.0217327	0.033729	0.0008079	505777	2.7660
0.0421246	0.106667	0.0041684	373157	5.2290
0.0707716	0.343961	0.0257991	400172	8.6748
0.0001884	0.000021	0.0000000	3103004	0.0507
0.0002694	0.000037	0.0000001	8668582	0.0561
0.0007037	0.000158	0.0000005	6949020	0.1438
0.0130518	0.014659	0.0002541	852051	2.6409
0.0321132	0.065525	0.0020634	640833	6.4339
0.0650145	0.265529	0.0167364	585451	13.1549

[a] K_1 (regressed) = 574613 ± 49170.

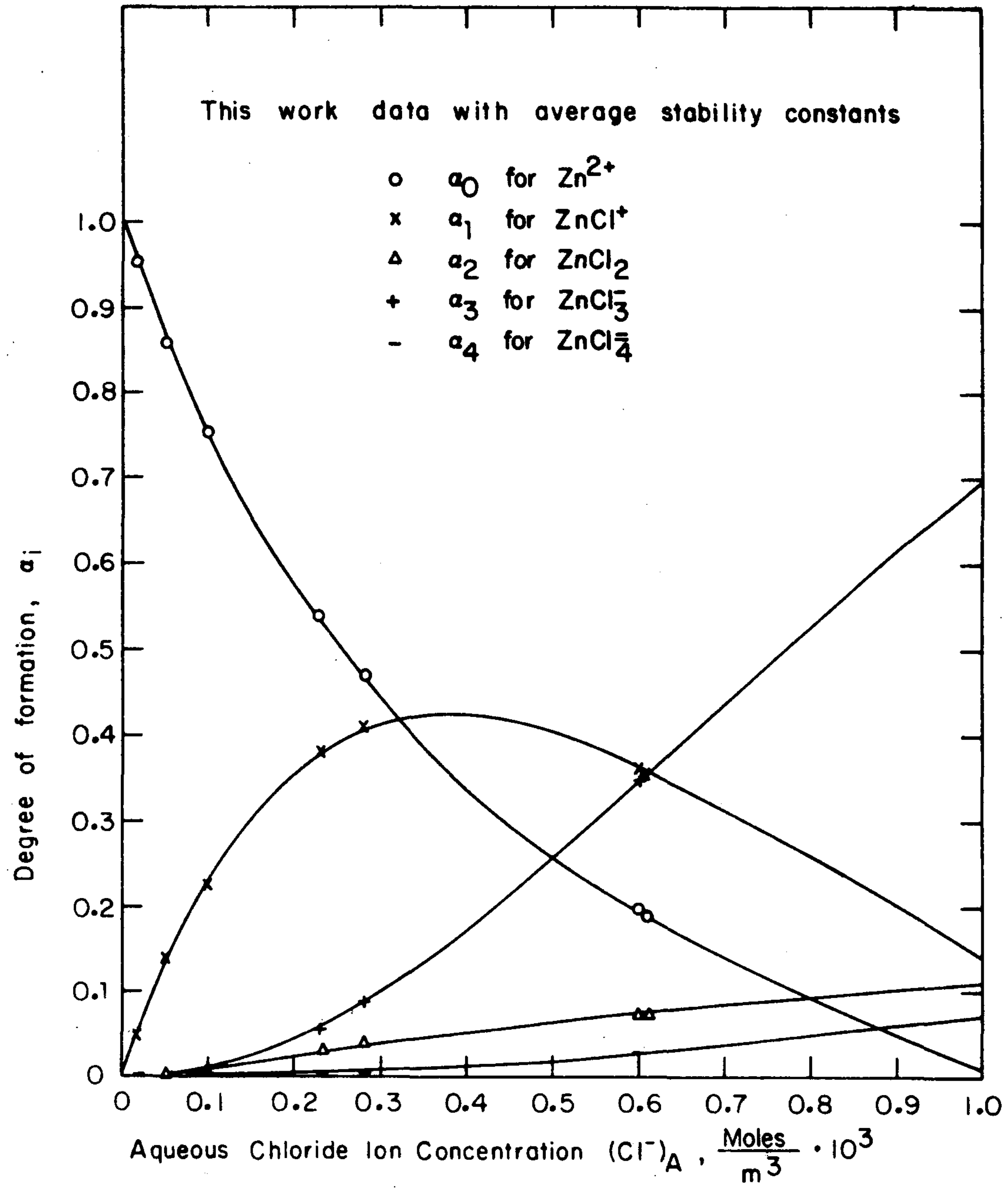


Figure 20. The degree of formation α_i for $ZnCl_2$ as a function of the aqueous chloride ion concentration

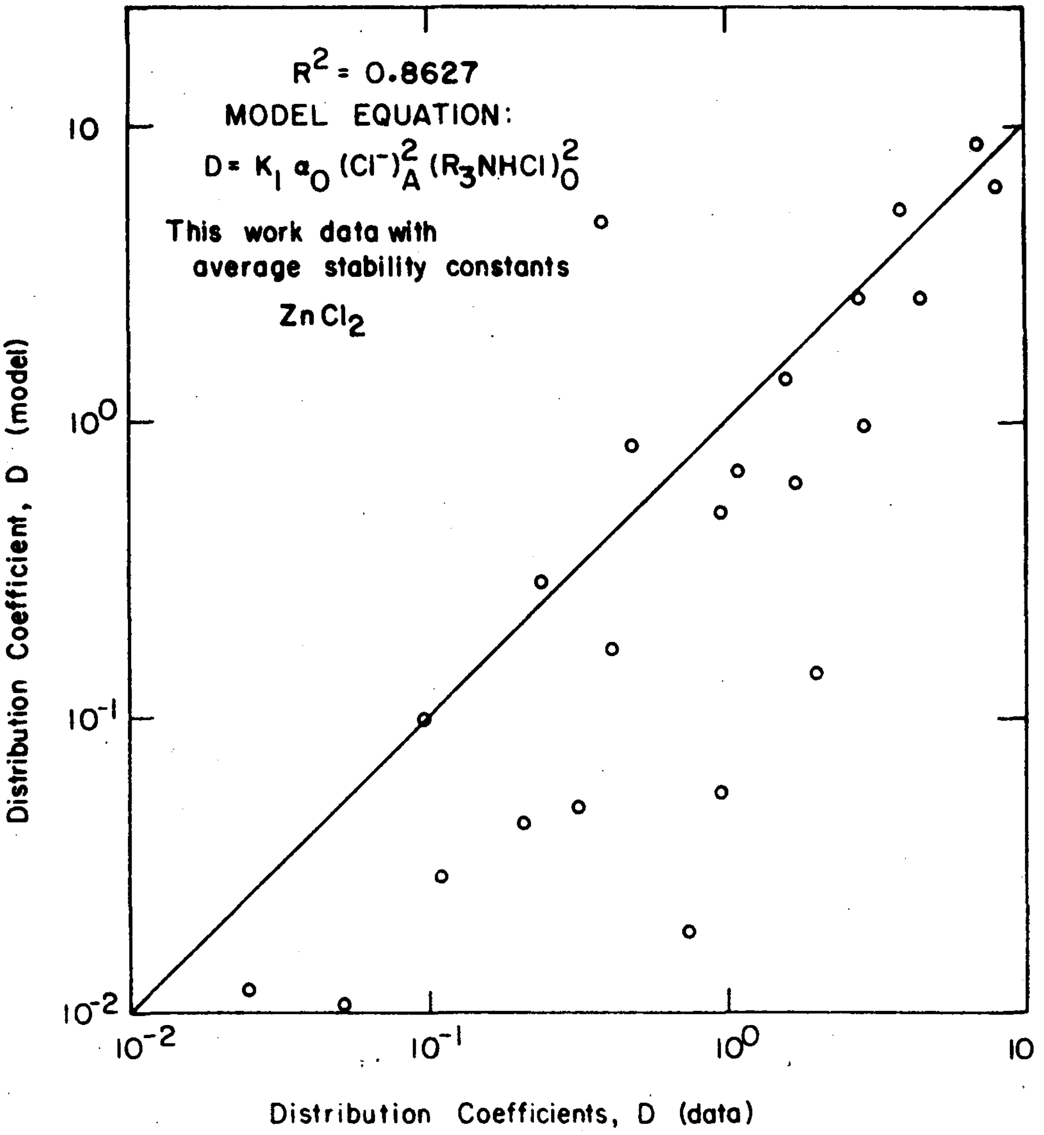


Figure 21. The comparison between the predicted D(model) and the D(data) for the system $ZnCl_2$-HCl-H_2O-TOA-C_6H_6

better agreement between the experimental and predicted data were obtained here than was accomplished in previous work.

b. High concentrations The initial metal concentration was $10 \frac{\text{moles}}{\text{m}^3}$ (0.01M). The equilibrium amine salt concentration, chloride ion concentration of the aqueous phase, and the calculated distribution coefficients are presented in Table 19. The analysis of the organic phase for the estimation of the equilibrium TOA concentration was performed as described in the Procedure section. It is noted that the values for the equilibrium concentration of the extractant $(R_3NHCl)_0$ are out of range by a factor of 10^3. This means that the balance equation

$$(R_3NHCl)_0^E = (R_3NHCl)_0^E - 2(M)_0^T + (Cl^-)_0^T \qquad (51)$$

does not apply at this concentration range. It also means that the reaction mechanism is not applicable at this concentration range. It appears that other extractable species are present in significant amounts besides $MCl_2 \cdot 2(R_3NHCl)$. When these data were regressed, the correlation coefficient R^2 was equal to 0.011, which is a very poor fit of the data.

2. The system cupric chloride-hydrochloric acid-water-TOA-benzene

a. Low concentrations Analysis of equilibrium TOA extraction data on this system was performed as described in the Procedure section. The equilibrium metal concentrations in the aqueous and organic phase, the equilibrium amine salt concentration, chloride ion concentration of the aqueous phase, and the calculated distribution

Table 19. Equilibrium data obtained in this work for the system $ZnCl_2$-HCl-H_2O-TOA-C_6H_6. Initial metal concentration = 10 $\frac{moles}{m^3}$

Initial (R_3NHCl) $\frac{moles}{m^3} \cdot 10^3$	Initial aq. (HCl) $\frac{moles}{m^3} \cdot 10^3$	Distribution coefficient D	$(Cl^-)_A$ $\frac{moles}{m^3} \cdot 10^3$	$(R_3NHCl)_O$ $\frac{moles}{m^3} \cdot 10^3$	$(Zn)^T_A$ Kg/m^3	$(Zn)^T_O$ Kg/m^3
0.05	0.5	8.2	0.2450	0.4717	0.0564	0.4649
	1.0	23.5	0.2200	0.4913	0.0216	0.509
	1.5	48.9	0.1900	0.4651	0.0139	0.6805
	2.0	104.7	0.1625	0.4675	0.0059	0.6181
	3.0	171.9	0.1213	0.4666	0.0035	0.6018
	4.0	113.6	0.1025	0.4903	0.0048	0.5453
0.08	0.5	204.0	0.2450	0.5102	0.0032	0.6504
	1.0	791.0	0.2150	0.5143	0.00096	0.7626
	1.5	2257.3	0.1920	0.5167	0.00030	0.6844
	2.0	2428.2	0.1725	0.5159	0.00029	0.7117
	3.0	249.7	0.1250	0.5429	0.0028	0.6900
	4.0	2727.7	0.1075	0.5830	0.00027	0.7253
0.1	0.5	149.2	0.2500	0.4627	0.0043	0.6492
	1.0	1368.4	0.2225	0.4593	0.00056	0.7630
	1.5	23941	0.2050	0.4527	0.00003	0.6847
	2.0	23970	0.2975	0.4504	0.0000297	0.7119
	3.0	9701.7	0.1120	0.4504	0.0714×10^{-3}	0.6927
	4.0	2863.4	0.0893	0.4500	0.2533×10^{-3}	0.7253
0.15	0.5	365.6	0.2500	0.5127	1.7825×10^{-3}	0.6518
	1.0	4593.3	0.2225	0.5018	0.1662×10^{-3}	0.7634
	1.5	9215.3	0.1975	0.5306	0.0743×10^{-3}	0.6847
	2.0	14499	0.2050	0.5004	0.0491×10^{-3}	0.7119
	3.0	6810.2	0.1125	0.4995	0.1017×10^{-3}	0.6926
	4.0	5211.2	0.0948	0.5030	0.1392×10^{-3}	0.7254

coefficients are presented in Table 20. The analysis of organic phase for the estimation of the equilibrium TOA concentration was performed as described in the Procedure section.

The stability constants used for this system were an average value of the first three data sets reported in Table 8. The fourth set was not used because it was inaccurate. The new values are: $\beta_1 = 9.92$, $\beta_2 = 4.72$, $\beta_3 = 2.49$, and $\beta_4 = 0.85$.

The degree of formation and the effective equilibrium constants were calculated using Equations 38 and 40, respectively and using the new averaged stability constants. Table 21 shows these results as well as the calculated D(model) values. Figure 22 is the plot of the degrees of formation α_i versus the chloride ion concentration. Figure 23 shows the good agreement between the experimental and predicted distribution coefficients with a correlation coefficient $R^2 = 0.7602$. Better agreements between the predicted and the experimental distribution coefficients were obtained at lower concentrations. For dilute solutions, the quotient of activity coefficients is nearly constant for the ionic species present in the solution.

b. <u>High concentrations</u> Table 22 shows the equilibrium data for the system $CuCl_2$-HCl-H_2O-TOA-C_6H_6 at 10 $\frac{\text{moles}}{m^3}$ (0.01M) initial metal concentrations. It is noted here that the values for the equilibrium concentration of the free extractant are out of range by a factor of 10^3. When these data were analyzed, the correlation coefficient value R^2 was equal to 0.17. This low value of R^2 means that the model equation is not predicting as well as expected. The variables in the model equation are all measured experimentally

Table 20. Equilibrium data obtained in this work for the system $CuCl_2$-HCl-H_2O-TOA-C_6H_6. Initial metal concentration = 7.05 $\frac{\text{moles}}{m^3}$

Initial (R_3NHCl) $\frac{\text{moles}}{m^3} \cdot 10^3$	Initial (HCl) $\frac{\text{moles}}{m^3} \cdot 10^3$	D	$(Cl^-)_A$ $\frac{\text{moles}}{m^3} \cdot 10^3$	$(R_3NHCl)_O$ $\frac{\text{moles}}{m^3} \cdot 10^3$	$(Cu)_A^T$ Kg/m^3	$(Cu)_O^T$ Kg/m^3
0.05	0.5	0.031	0.0090	0.0034	0.43	0.0131
	0.6	0.032	0.0093	0.0034	0.625	0.0200
	0.7	0.035	0.0097	0.0034	0.72	0.0253
	0.8	0.047	0.0125	0.0032	0.60	0.0283
	0.9	0.066	0.016	0.0030	0.595	0.0396
	1.0	0.198	0.0460	0.0015	0.598	0.1184
	1.5	0.250	0.0935	0.001	0.632	0.158
0.06	0.5	0.007	0.0096	0.0045	0.590	0.0043
	0.6	0.115	0.0147	0.0040	0.72	0.0828
	0.7	0.134	0.0185	0.0038	0.499	0.0669
	0.8	0.333	0.0498	0.0019	0.50	0.1998
	1.0	0.440	0.080	0.0010	0.74	0.3256
0.08	0.5	0.076	0.012	0.0066	0.632	0.0480
	0.6	0.128	0.0170	0.0061	0.542	0.0694
	0.7	0.174	0.0214	0.0056	0.476	0.0828
	0.8	0.475	0.057	0.0031	0.605	0.2874
	1.0	0.690	0.1028	0.0019	0.650	0.4485
0.1	0.5	0.131	0.0099	0.0093	0.74	0.0969
	0.6	0.170	0.0144	0.0089	0.595	0.1012
	0.7	0.258	0.0181	0.0080	0.295	0.0761
	0.8	0.771	0.0498	0.0047	0.632	0.4873
	0.9	1.27	0.0950	0.0028	0.3394	0.431
	1.0	2.20	0.534	0.0010	0.2818	0.62
0.2	0.5	0.224	0.0082	0.0207	0.71	0.1590
	0.6	0.320	0.0150	0.0185	0.6	0.192
	0.7	0.430	0.0191	0.018	0.59	0.2537
	0.8	1.47	0.0504	0.0128	0.4068	0.72
	1.0	4.16	0.093	0.0103	0.1707	0.71

Table 21. The degree of formation calculated from this work with the average stability constants of Sato and Kato (30), Morris and Short (26) and Mahailov (28), the effective equilibrium constant and the D(model) for the system $CuCl_2$-HCl-H_2O-TOA-C_6H_6

Run	Distribution coefficient D(data)	$(Cl^-)_A$, $\frac{moles}{m^3} \cdot 10^3$	$(R_3NHCl)_O$, $\frac{moles}{m^3} \cdot 10^3$	$\alpha_{Cu^{2+}}$ α_0	α_{CuCl^+} α_1
1	0.2240	0.00826	0.02070	0.923990	0.075711
2	0.3200	0.01500	0.01850	0.869663	0.129406
3	0.4300	0.01910	0.01770	0.839482	0.159058
4	1.7700	0.05040	0.01280	0.661252	0.330605
5	4.1600	0.09270	0.01030	0.509634	0.468652
6	0.1310	0.00993	0.00930	0.909940	0.089634
7	0.1700	0.01440	0.00886	0.874253	0.124885
8	0.2580	0.01810	0.00802	0.846659	0.152019
9	0.7710	0.04980	0.00466	0.663995	0.328024
10	1.2700	0.09490	0.00278	0.503496	0.473995
11	2.2000	0.53400	0.00101	0.123587	0.654673
12	0.0760	0.01200	0.00668	0.893077	0.106312
13	0.1280	0.01700	0.00608	0.854689	0.144135
14	0.1740	0.02140	0.00558	0.823402	0.174798
15	0.4750	0.05700	0.00312	0.632413	0.357592
16	0.6900	0.10280	0.00188	0.482519	0.492062
17	0.0730	0.00960	0.00451	0.912684	0.086917
18	0.1150	0.01470	0.00399	0.871952	0.127152
19	0.1340	0.01850	0.00379	0.843774	0.154849
20	0.3330	0.04980	0.00189	0.663995	0.328024
21	0.4400	0.07980	0.00105	0.548554	0.434245
22	0.0305	0.00897	0.00342	0.917967	0.081683
23	0.0320	0.00931	0.00346	0.915109	0.084515
24	0.0352	0.00973	0.00336	0.911601	0.087989
25	0.0471	0.01250	0.00320	0.889092	0.110247
26	0.0664	0.01600	0.00296	0.862115	0.136835
27	0.1980	0.04600	0.00150	0.681871	0.311151
28	0.2500	0.09350	0.00100	0.507387	0.470611

α_{CuCl_2} α_2	$\alpha_{CuCl_3^-}$ α_3	$\alpha_{CuCl_4^=}$ α_4	Effective equilibrium constant K_1 [a]	D(model)
0.000298	0.0000013	0.00000000	8292393	0.21125
0.000924	0.0000073	0.00000004	4778295	0.52373
0.001446	0.0000146	0.00000009	4481713	0.75033
0.007928	0.0002108	0.00000363	6431688	2.15218
0.020671	0.0010109	0.00003199	8953660	3.63348
0.000423	0.0000022	0.00000001	16880842	0.06069
0.000856	0.0000065	0.00000003	11945919	0.11129
0.001309	0.0000125	0.00000008	14461233	0.13952
0.007773	0.0002042	0.00000347	21560498	0.27966
0.021403	0.0010715	0.00003471	36239797	0.27406
0.166340	0.0468592	0.00854192	61196435	0.28114
0.000607	0.0000038	0.00000002	13243695	0.04488
0.001166	0.0000105	0.00000006	14018350	0.07141
0.001780	0.0000201	0.00000015	14819774	0.09182
0.009698	0.0002916	0.00000567	23748380	0.16642
0.024068	0.0013052	0.00004580	38285341	0.14094
0.000397	0.0000020	0.00000001	42668440	0.01338
0.000889	0.0000069	0.00000003	38337582	0.02346
0.001363	0.0000133	0.00000008	32304031	0.03244
0.007773	0.0002042	0.00000347	56610485	0.04600
0.016488	0.0006941	0.00001891	114247978	0.03012
0.000349	0.0000016	0.00000001	35304962	0.00676
0.000374	0.0000018	0.00000001	33699676	0.00743
0.000407	0.0000021	0.00000001	36127131	0.00762
0.000656	0.0000043	0.00000002	33109604	0.01112
0.001042	0.0000088	0.00000005	34338371	0.01512
0.006810	0.0001653	0.00000280	60990891	0.02539
0.020937	0.0010327	0.00003296	56360883	0.03469

[a] K_1(regressed) = 5503556 ± 536112.

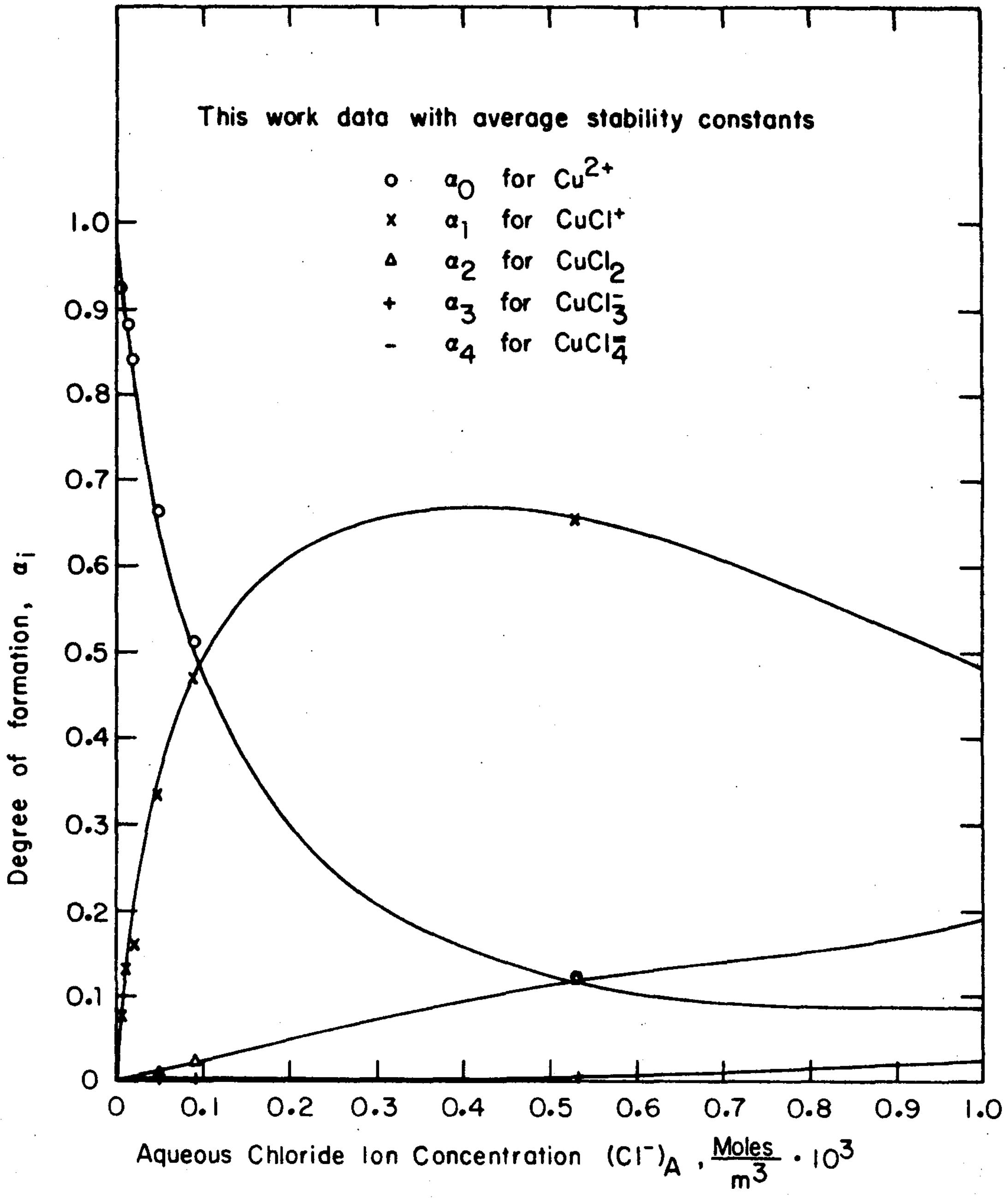


Figure 22. The degree of formation α_i for $CuCl_2$ as a function of the aqueous chloride ion concentration

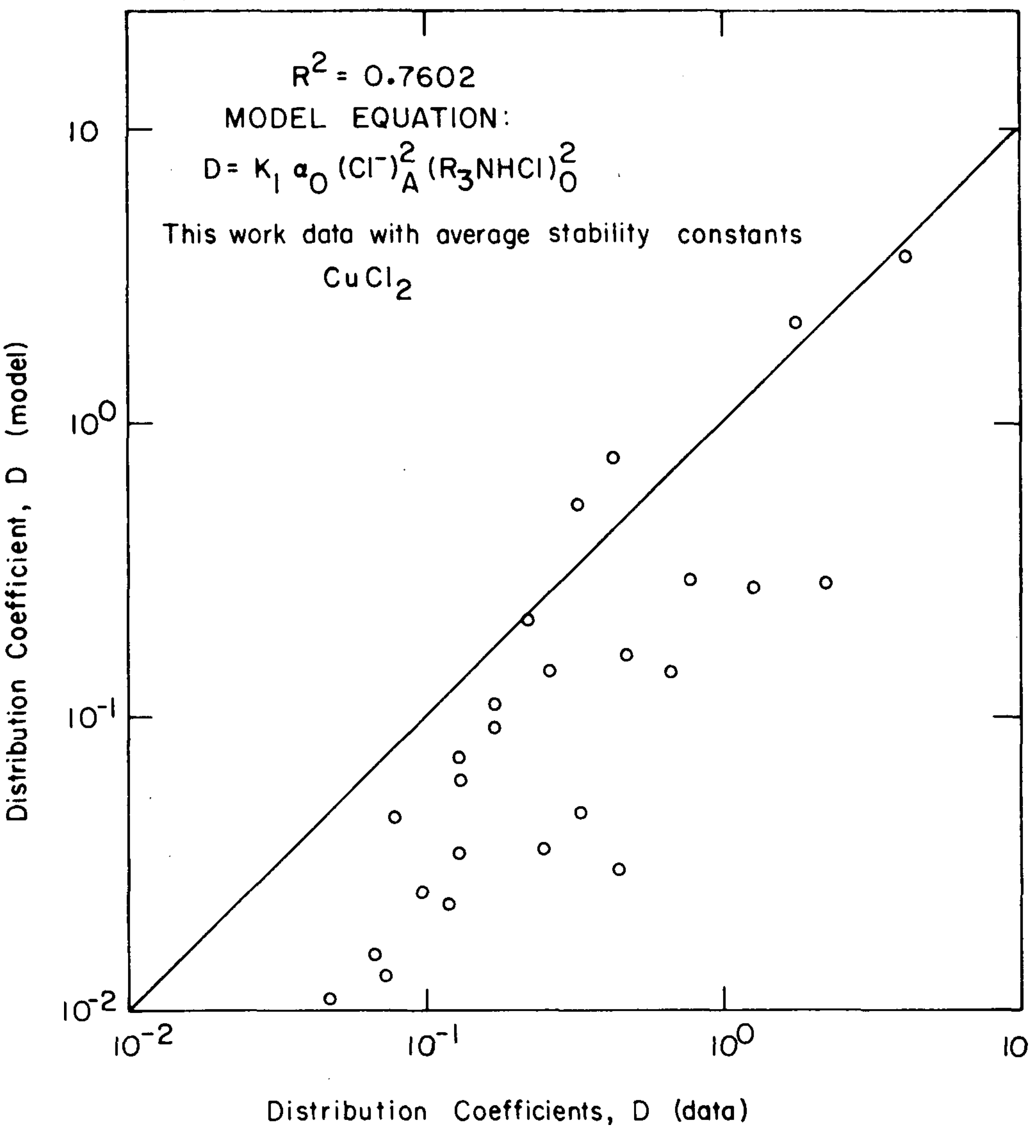


Figure 23. The comparison between the predicted D(model) and the D(data) for the system $CuCl_2$-HCl-H_2O-TOA-C_6H_6

Table 22. Equilibrium data obtained in this work for the system $CuCl_2$-HCl-H_2O-TOA-C_6H_6. Initial metal concentration = 10 $\frac{\text{moles}}{\text{m}^3}$

Initial (R_3NHCl) $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$	Initial (HCl) $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$	Distribution coefficient D	$(Cl^-)_A$ $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$	$(R_3NHCl)_O$ $\frac{\text{moles}}{\text{m}^3} \cdot 10^3$	$(Cu)_A^T$ Kg/m^3	$(Cu)_O^T$ Kg/m^3
0.05	1	0.0215	0.2700	0.9796	0.6706	0.0144
	2	0.1289	0.2250	0.9855	0.4816	0.0621
	3	0.6036	0.1950	1.0328	0.3840	0.2318
	4	1.3395	0.1550	1.0655	0.2842	0.3807
	5	2.8827	0.1350	1.1282	0.1842	0.5310
	6	4.5130	0.1634	1.5687	0.1310	0.5912
0.1	1	0.0616	0.0278	1.0065	0.5312	0.0327
	2	0.4117	0.2275	1.0167	0.4430	0.1824
	3	1.5455	0.5000	1.0624	0.2594	0.4009
	4	3.5241	0.1575	1.0813	0.1454	0.5124
	5	8.0336	0.1375	1.1306	0.0768	0.6169
	6	12.2297	0.1300	1.2932	0.0566	0.6922
0.15	1	0.0970	0.3050	0.9509	0.5446	0.0528
	2	0.5346	0.2375	0.9536	0.3818	0.2041
	3	2.9609	0.1663	0.9594	0.1688	0.4998
	4	5.8713	0.1425	0.9714	0.1010	0.5930
	5	14.7227	0.1125	1.0055	0.0476	0.7008
	6	18.6005	0.1025	1.2534	0.0368	0.6845
0.2	1	0.1439	0.3500	1.0147	0.6204	0.0893
	2	0.6546	0.2375	0.9868	0.4007	0.2623
	3	3.1875	0.1825	1.0019	0.1563	0.4982
	4	10.0748	0.1475	1.0281	0.0615	0.6196
	5	19.4928	0.1250	1.0411	0.0349	0.6803
	6	37.427	0.1025	1.0774	0.0192	0.7186

except the free extractant concentration, which is calculated by material balance. This balance is based on the reaction mechanism and on the extractable species formed. It is concluded that both the reaction mechanism and the extractable species formed do not apply at high concentrations.

The unexpected behavior in the metal equilibrium data is explained by the following: 1) The extracted metal chloride-TOA complex or complexes formed may be different when excess chloride ion is present. 2) The aqueous phase metal chloride stability constants used are not applicable over the range of experimental conditions. 3) The model equation was nonlinear and its behavior was unknown. An unsuccessful attempt was made to fit stability constant values to the data using a nonlinear least square fitting routine. 4) Much more work on the aqueous solution properties will be required to establish reliable stability constant values and activity coefficients.

The nonlinear model fitting routine, NLIN & ZXSSQ, appears to converge to parameters giving ridiculously large residuals and too unreasonable (negative) parameter values. Several possible reasons can be cited for the failure of the statistical method: 1) The assumption of linearity in the proposed equilibrium model is not valid. 2) The assumption of constant activity coefficient may be incorrect or inadequate. 3) The model equation is very complex. It contains two variables and five unknown parameters to be determined. 4) The assumption of ideality of the binary system does not hold. 5) The model equation cannot be expressed in a single explicit equation like the one that Hoh and Bautista (1) developed. So all three methods (Fomin and Maiorova;

Fronaeus; Day and Stoughton) (2) failed to determine the stability constants.

Some of these problems are cited by another group of investigators who experienced convergence difficulties when trying to apply nonlinear least squares fitting to data for the tributylphosphate and tri-iso-octylamine systems (31, 41).

3. The binary system $CuCl_2$-$ZnCl_2$-HCl-H_2O-TOA-C_6H_6

a. Low concentrations Equilibrium study of the above binary metal system was performed as described in the Procedure section. Equal molar concentrations of both cupric chloride and zinc chloride were mixed together to form the aqueous phase. 10 $\frac{\text{moles}}{\text{m}^3}$ (0.01M) of each was used. Then equal molar volumes of the aqueous and organic phase were contacted with each other. The concentrations of the organic extractant were varied from 50 $\frac{\text{moles}}{\text{m}^3}$ (0.05M) to 200 $\frac{\text{moles}}{\text{m}^3}$ (0.2M). The hydrochloric acid concentrations were (1, 2, 3, 4, 5, 6) x 10^3 $\frac{\text{moles}}{\text{m}^3}$ (1, 2, 3, 4, 5, and 6M). The chloride ion concentration in the equilibrated aqueous phase was measured by chloride ion-selective electrodes. Table 23 presents the equilibrium data for this binary system. It can be seen in Table 23 that the separation factor is not a constant due to the difference in behavior between copper and zinc. The separation factor first increases and then decreases. This behavior was expected from the single system behavior where each metal has a maximum at different concentrations.

Table 24 shows the degree of formation for these two metals, which was calculated as described in the Theoretical section. The

Table 23. Equilibrium data obtained in this work for the system $ZnCl_2$-$CuCl_2$-HCl-H_2O-TOA-C_6H_6 at low concentrations. Ratio (organic/aqueous) = 1 (10 $\frac{\text{moles}}{m^3}$ $ZnCl_2$ + 10 $\frac{\text{moles}}{m^3}$ $CuCl_2$)

Initial (R_3NHCl) $\frac{\text{moles}}{m^3} \cdot 10^3$	Initial aq. (HCl) $\frac{\text{moles}}{m^3} \cdot 10^3$	$(Zn)_A$ Kg/m^3	$(Zn)_O$ Kg/m^3	$(D)_{Zn}$	$(Cu)_A$ Kg/m^3	$(Cu)_O$ Kg/m^3	$(D)_{Cu}$	$(Cl^-)_A$ $\frac{\text{moles}}{m^3} \cdot 10^3$	Separation factor $S_{Zn\text{-}Cu}$
0.05	1	0.0295	0.6517	22.09	0.6778	0.2707	0.0399	1.13	553.6
	2	0.0146	0.6422	43.98	0.6584	0.0524	0.0795	2.50	553.2
	3	0.0161	0.6647	41.28	0.6239	0.0157	0.0252	4.40	1638.3
	4	0.0213	0.6995	32.84	0.5639	0.0733	0.1300	5.6	252.6
	5	0.0253	0.6403	25.30	0.4324	0.2056	0.4755	7.60	53.2
	6	0.0572	0.7412	12.95	0.4278	0.2210	0.5166	9.30	25.0
0.1	1	0.0085	0.6727	79.14	0.6705	0.0448	0.0668	1.12	1184.7
	2	0.0045	0.6523	144.95	0.5829	0.0531	0.0911	2.50	1591.1
	3	0.0038	0.6770	178.15	0.3945	0.2451	0.6213	4.70	286.7
	4	0.0064	0.7144	111.62	0.2645	0.3727	1.409	5.60	79.2
	5	0.0072	0.6584	91.44	0.1467	0.4913	3.3490	7.49	27.3
	6	0.0117	0.7867	67.23	0.1261	0.5227	4.1451	9.10	16.2
0.15	1	0.0066	0.6746	102.21	0.6595	0.0779	0.1182	1.10	864.7
	2	0.0051	0.6517	127.78	0.6092	0.0268	0.0440	2.50	2904.1
	3	0.0052	0.6756	129.92	0.3279	0.3117	0.9506	4.70	136.6
	4	0.0053	0.7155	135.00	0.1968	0.4404	2.2378	5.60	60.3
	5	0.0044	0.6612	150.27	0.0959	0.5421	5.6528	7.30	26.5
	6	0.0079	0.7905	100.06	0.0868	0.5620	6.4747	7.40	15.4
0.2	1	0.0070	0.6742	96.31	0.6380	0.1144	0.1794	1.15	536.8
	2	0.0046	0.6522	141.78	0.5573	0.0787	0.1412	2.50	1004.1
	3	0.0045	0.6763	150.28	0.2427	0.3969	1.6354	4.27	91.8
	4	0.0043	0.7163	166.62	0.1337	0.5035	3.7659	5.40	44.2
	5	0.0059	0.6597	111.81	0.0786	0.5594	7.1170	7.30	15.7
	6	0.0065	0.7919	121.83	0.0718	0.5770	8.0362	8.79	15.1

Table 24. The calculated degree of formation obtained in this work for zinc and copper in the system $ZnCl_2$-$CuCl_2$-HCl-H_2O-TOA-C_6H_6

Run	Separation factor S_{Zn-Cu}	$(Cl^-)_A$ $\frac{moles}{m^3} \cdot 10^3$	$\alpha_{Zn^{2+}}$ $(\alpha_0)_{Zn}$	$\alpha_{Cu^{2+}}$ $(\alpha_0)_{Cu}$	$\frac{(\alpha_0)_{Zn}}{(\alpha_0)_{Cu}}$	Effective equilibrium constant ratio K_{Zn-Cu}
1	553.6	1.13	0.0003503	0.004375	0.0800	6915.7
2	553.2	2.50	0.0000203	0.000265	0.0763	7243.8
3	1638.3	4.40	0.0000023	0.000030	0.0796	20557.7
4	252.6	5.60	0.0000009	0.000011	0.0812	3110.4
5	53.2	7.60	0.0000002	0.000003	0.0829	641.5
6	25.0	9.30	0.0000001	0.000001	0.0839	298.7
7	1184.7	1.12	0.0003611	0.004501	0.0802	14765.4
8	1591.1	2.50	0.0000203	0.000265	0.0763	20832.0
9	286.7	4.70	0.0000018	0.000023	0.0801	3579.1
10	79.2	5.60	0.0000009	0.000011	0.0812	975.4
11	27.3	7.49	0.0000003	0.000003	0.0828	329.4
12	16.2	9.10	0.0000001	0.000001	0.0838	193.4
13	864.7	1.10	0.0003841	0.004764	0.0806	10727.0
14	2904.1	2.50	0.0000203	0.000265	0.0763	38022.5
15	136.6	4.70	0.0000018	0.000023	0.0801	1705.9
16	60.3	5.60	0.0000009	0.000011	0.0812	742.8
17	26.5	7.30	0.0000003	0.000004	0.0827	321.3
18	15.4	9.40	0.0000001	0.000001	0.0840	183.9
19	536.8	1.15	0.0003298	0.004137	0.0797	6734.2
20	1004.1	2.50	0.0000203	0.000265	0.0763	13146.3
21	91.9	4.27	0.0000026	0.000033	0.0795	1155.9
22	44.2	5.40	0.0000010	0.000013	0.0809	546.3
23	15.7	7.30	0.0000003	0.000004	0.0827	189.9
24	15.1	8.79	0.0000001	0.000001	0.0837	181.1

K_{Zn-Cu} (regressed) = 209011 ± 43666 ratio of the degree of formation of zinc to copper is also presented in Table 24. The ratio of effective equilibrium constant for zinc and copper, K_{Zn-Cu}, was calculated by the model Equation 27 using the degrees of formation as well as the equilibrium data for this binary component system. Linear regression analysis was applied to estimate the regressed value of K_{Zn-Cu}. The correlation coefficient for R^2 was equal to 0.5101 for the whole data. Note that this is for all the data. When R^2 was calculated for the second set at 100 $\frac{\text{moles}}{\text{m}^3}$ (0.1M) (R_3NHCl), a better value, 0.74, was obtained. The calculated K_{Zn-Cu} data are also presented in Table 24.

b. <u>High concentrations</u> Different concentrations of cupric chloride and zinc chloride were mixed together to form the aqueous phase. Then the organic phase was contacted with the aqueous phase with a ratio of 2:1. The organic phase concentration was kept constant at 200 $\frac{\text{moles}}{\text{m}^3}$ (0.2M). Table 25 presents the equilibrium data for this binary system. It can be seen in Table 25 that the separation factor goes through a maximum resembling the distribution coefficient for the single system.

Table 26 shows the degree of formation for these two metals, the ratio of the degree of formation of zinc to copper, and the ratio of the effective equilibrium constant for zinc and copper, K_{Zn-Cu}, which was calculated by the model equation for the binary system. Linear regression analysis was applied to estimate the regressed value of K_{Zn-Cu}. The correlation coefficient value was equal to 0.33. This value was for all the data at different concentrations.

Table 25. Equilibrium data obtained in this work for the system $ZnCl_2$-$CuCl_2$-HCl-H_2O-TOA-C_6H_6 at high concentrations. Ratio (organic/aqueous) = 2

Initial (R_3NHCl) $\frac{\text{moles}}{m^3} \cdot 10^3$	Initial aq. (HCl) $\frac{\text{moles}}{m^3} \cdot 10^3$	Initial $CuCl_2$ $\frac{\text{moles}}{m^3} \cdot 10^3$	Initial $ZnCl_2$ $\frac{\text{moles}}{m^3} \cdot 10^3$	$(Zn)_A$ Kg/m^3	$(Zn)_0$ Kg/m^3
0.2	1	0.2500	0.25	0.23	7.23
0.2	1	0.500	0.25	0.2165	12.63
0.2	1	0.600	0.15	0.1975	10.23
0.2	1	0.6675	0.0825	0.1675	6.99
0.2	2	0.2500	0.25	0.3095	9.25
0.2	2	0.500	0.25	0.6180	6.77
0.2	2	0.600	0.15	0.2020	6.20
0.2	2	0.6675	0.0825	8.04	8.88
0.2	3	0.25	0.25	0.09	1.35
0.2	3	0.50	0.25	0.3665	10.69
0.2	3	0.600	0.15	0.2495	4.46
0.2	3	0.6675	0.0825	0.4075	2.63
0.2	4	0.25	0.25	0.30	9.35
0.2	4	0.50	0.25	0.3515	7.83
0.2	4	0.600	0.15	0.265	5.68
0.2	4	0.6675	0.0825	0.279	3.02

$(Cu)_A$ Kg/m^3	$(Cu)_O$ Kg/m^3	Distribution coefficients		$(Cl^-)_a$ $\frac{moles}{m^3} \cdot 10^3$	Separation factors S_{Zn-Cu}
		$(D)_{Zn}$	$(D)_{Cu}$		
5.95	1	31.44	0.2024	2.30	155.35
13.42	1.88	58.45	0.4401	3.10	417.27
14.27	4.55	51.83	0.3189	2.760	162.52
14.17	7.85	41.75	0.5541	3.13	75.36
4.27	4.42	29.90	1.0351	4.75	28.89
7.25	8.30	10.96	1.1448	4.85	9.58
9.97	12.67	10.04	1.2708	5.4	7.90
11.09	11.60	1.10	1.0460	5.6	1.05
1.26	6.18	15.00	4.9048	7.0	3.05
8.86	7.19	29.18	0.8115	7.35	35.96
8.26	1.14	17.88	0.1283	7.80	139.40
7.20	15.46	6.47	2.1472	8.90	3.01
1.55	7.68	31.18	4.9421	10.5	6.30
12.29	4.13	22.30	0.3360	11.0	66.36
12.56	11.15	4.44	0.8877	10.0	24.15
16.10	7.40	10.84	0.4598	11.0	23.5

Table 26. The calculated degree of formation in this work for zinc and copper in the system $ZnCl_2$-$CuCl_2$-H_2O-HCl-TOA-C_6H_6

Run	Separation factor S_{Zn-Cu}	$(Cl^-)_A$ $\frac{moles}{m^3} \cdot 10^3$	$\alpha_{Zn^{2+}}$ $(\alpha_0)_{Zn}$	$\alpha_{Cu^{2+}}$ $(\alpha_0)_{Cu}$	$\frac{(\alpha_0)_{Zn}}{(\alpha_0)_{Cu}}$	Effective equilibrium constant ratio K_{Zn-Cu}
1	155.35	2.30	0.01585	0.009721	1.63077	95.264
2	417.27	3.10	0.00679	0.004351	1.56093	267.322
3	169.52	2.76	0.00957	0.006023	1.58980	102.232
4	75.36	3.13	0.00659	0.004233	1.55847	48.356
5	28.89	4.75	0.00169	0.001170	1.45064	19.916
6	9.58	4.85	0.00158	0.001093	1.44546	6.629
7	7.90	5.40	0.00108	0.000765	1.41944	5.566
8	1.05	5.60	0.00095	0.000676	1.41093	0.745
9	3.05	7.00	0.00042	0.000312	1.36239	2.245
10	35.96	7.35	0.00035	0.000263	1.35267	26.588
11	139.01	7.80	0.00028	0.000213	1.34128	103.643
12	3.01	8.90	0.00017	0.000132	1.31773	2.287
13	6.30	10.50	0.00009	0.000072	1.29148	4.885
14	66.36	11.00	0.00007	0.000060	1.28472	51.660
15	24.15	10.00	0.00011	0.000086	1.29886	18.596
16	23.59	11.00	0.00007	0.000060	1.28472	18.367

$K_{Zn-Cu} = 533.76 \pm 200$

Better values of about 0.75 were calculated for constant concentration sets.

VII. EVIDENCE FOR OTHER EXTRACTION MECHANISMS AND OTHER EXTRACTION MODELS IN THE LITERATURE

The extraction of zinc by tributyl phosphate from chloride solutions has been studied by Lietzke and Stoughton (45). According to the data of this study, at low concentrations of acid, the complex $ZnCl_2 \cdot 2TBP$ is extracted from aqueous solutions of HCl and NaCl. When the acidity is increased, the complex $HZnCl_3 \cdot 3TBP$ and $H_2ZnCl_4 \cdot 2TBP$ participate in extraction, and the latter predominates at HCl concentrations $> 2.7 \times 10^3 \frac{\text{moles}}{\text{m}^3}$ (2.7M). The authors concluded that in the extraction of zinc from solutions of $CuCl_2$ + HCl and NaCl + HCl, primarily trisolvates pass into the organic phase, although there are also indications of the extraction of a disolvate.

The extraction of microquantities of zinc from solutions of HCl and NaCl by tributyl phosphate was studied by Abdukayumov (46). It was shown that for a HCl activity in the aqueous phase from 1 to 58 (HCl concentration $\simeq (1\text{-}7) \cdot 10^3 \frac{\text{moles}}{\text{m}^3}$ (1-7M), zinc is extracted in the form of the complex $HZnCl_3 \cdot 3TBP$ with extraction constant $K_{e,1}$ = 3.4 ± 0.2. In the higher case of HCl activities, extraction of the complex $H_2ZnCl_4 \cdot 3TBP$ with extraction constant $K_{e,2} = (2.8 \pm 0.7) \cdot 10^{-3}$ predominates. Also, the possibility of extraction of zinc from solutions of NaCl + HCl in the form of $NaZnCl_3 \cdot nTBP$ (in addition to the extraction of $HZnCl_3 \cdot 3TBP$) was also noted. The distribution coefficient was determined in terms of $K_{e,1}$ and $K_{e,2}$ together.

A study by Levin (47) of the extraction of microamounts of copper from HCl and HCl + NaCl solutions by tributyl phosphate showed that with HCl activity in the aqueous phase from 1 to 8.47 (HCl concentrations) ~ (1-4) · $10^3 \frac{\text{moles}}{\text{m}^3}$ (1-4M), the copper is extracted predominately in the form of the solvate $CuCl_2 \cdot 3TBP$ to which the thermodynamic extraction constant $K_{e,1} = (3.65 \pm 0.19) \cdot 10^{-4}$ corresponds. At higher activities of HCl, the extraction of the complex $HCuCl_3 \cdot 3TBP$ predominates and the extraction constant of this equals $K_{e,2} = (1.27 \pm 0.24) \cdot 10^{-6}$. From the results of the study of the extraction of copper (2+), an estimate was also made of the thermodynamic stability constant of the first chloride complex $CuCl^+$: $\beta_1 = (4.55 \pm 0.85) \cdot 10^{-2} M^{-1}$.

The extraction of microquantities of cobalt from solutions of HCl + NaCl by tributyl phosphate was studied by Kozolova (48). It was shown that at a HCl activity in the aqueous phase less than 10, the extraction of cobalt occurs primarily in the form of $COCl_2 \cdot 3TBP$. The extraction constant of this complex is equal to $K_{e,1} = (9.7 \pm 0.9) \cdot 10^{-6}$. At higher HCl activities, the extraction of $HCOCl_3 \cdot 3TBP$ predominates with extraction constant $K_{e,2} = (5.4 \pm 0.7) \cdot 10^{-8}$.

The extraction of microquantities of chromium (III) from aqueous solutions of HCl and HCl + NaCl by tributyl phosphate was studied by Sevast'Yanova (49). It was observed that the equilibrium between the phases is rapidly established during extraction, but more slowly during the reextraction, the cause of which is the slowness of the establishment of equilibrium between aquo-chloro complexes of chromium in the aqueous phase. However, in view of the smallness of the fraction of the extractable complex in the aqueous phase and the smallness of its distribution coefficient, the measured distribution coefficients do not differ significantly from the equilibrium values. It was shown that at an activity of HCl in the aqueous phase < 8.5 (HCl concentration) (1-4) x $10^3 \frac{\text{moles}}{\text{m}^3}$ (~ 1-4M), chromium is extracted in the form of the complex $[Cr(H_2O)_3Cl_3] \cdot 3TBP$ or $[Cr(H_2O)_2(OHCl_3]^- H^+(H_2O) \cdot 3TBP]^+$. The extraction constant of this complex is $(3.026 \pm 0.16) \cdot 10^{-5}$. At higher activities of HCl, extraction of the complex $[Cr(H_2O)_2Cl_4]^-[H^+(H_2O) \cdot 3TBP]^+$ with extraction constant $(1.10 \pm 0.076) \cdot 10^{-7}$ predominates.

On the basis of this evidence, we can draw the following conclusions: 1) The mechanism for the reaction is more complex than it was originally thought to be. 2) In the work of Kozolova (48), only one stability constant was cited which was $CuCl^+$ with a value of $(4.55 \pm 0.85) \cdot 10^{-2}$. This contradicts the assumption of four stability constants made in this work. Also, the value for β_1 is very small compared to 11.6 reported by Sato and Kato (30). 3) In this work, the distribution coefficient was a function of one effective equilibrium constant and one extractable species. It should be a function of two effective equilibrium constants ($K_{e,1}$, $K_{e,2}$) and two extractable species. 4) The model equation should be derived in terms of these new parameters. 5) According to this, the distribution coefficient could be a function of those new parameters discussed by Hoh (1) in his appendix. 6) It is concluded that this was the main source of reason for the failure to fit the second equilibrium sets of data at higher chloride ion concentrations.

VIII. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are drawn from the work described in this thesis.

1. Chemically based thermodynamic models to predict the distribution coefficients and the separation factors for the liquid-liquid extraction of copper and zinc chlorides in TOA have been derived and tested according to the reaction mechanisms reported in the literature. The models are based on the assumptions that the quotient of the activity coefficients of each species varies slightly with its concentrations.

2. For a single component system, the thermodynamic model equation which predicts the distribution coefficients is dependent on the free organic concentration, the equilibrated ligand, the degree of formation, and on the extraction mechanism.

3. For a binary component system, the thermodynamic model equation which predicts the separation factors is very simple. This model equation is dependent on the degrees of formation of each species in their binary system.

4. When using the developed model by Hoh (2), the following information should be available: a) the stability constants, b) the equilibrated ligand concentration in the aqueous phase, c) the equilibrated organic concentration, and d) the distribution coefficients and the separation factors for single and binary systems.

5. The single component system gives the best predicted data. The slight decrease in agreement between the single component system and the binary system is due to the interaction effects between the molecules

which are not taken into account in developing the binary model.

6. The developed model equation can be used with a few data points to predict extraction trends which would otherwise be difficult to determine experimentally.

7. Zinc can be easily separated from a copper-zinc solution.

8. Increased chloride ion level in the aqueous phase for both copper (II) and zinc (II) chloride increases the extraction of the metal by the TOA salt.

9. The presence of zinc (II) chloride suppresses copper (II) chloride extraction by the TOA salt.

Recommendations for future work:

1. Better values of stability constants are needed at higher ionic strengths. Reliable stability constants are needed for metal chlorides and metal sulphates like the transition metals.

2. A better extraction mechanism is required to define accurately the extraction process taking place.

3. The nonidealities of the binary system should be explained in terms of suppression of one metal to the other.

4. A better, more reliable method for solving nonlinear systems using least square analysis should be developed so that the calculations of the stability constants can be carried out from equilibrium data.

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