A THERMODYNAMIC MODEL FOR THE LIQUID-LIQUID EXTRACTION
OF COBALTOUS CHLORIDE COMPLEXES FROM AQUEOUS
HYDROCHLORIC ACID SOLUTIONS BY TRIBUTYL PHOSPHATE

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M. S. Thesis Submitted to Iowa State University

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A thermodynamic model for the liquid-liquid extraction of
cobaltous chloride complexes from aqueous hydrochloric
acid solutions by tributyl phosphate

by

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NOMENCLATURE

a	activity of a particular species
A	absorbance
c	moles of solute per liter of solution
I	ionic strength
k	liquid-liquid extraction equilibrium constant
k'	effective liquid-liquid extraction equilibrium constant
K_D	distribution coefficient
K_n	stoichiometric step stability constant
TK_n	thermodynamic step stability constant
m_i	molarity of a particular species in solution
M	molarity concentration units
V	volume of phase
z_i	charge of a particular ion
α_n	fraction of A in form of AB_n
β_n	stoichiometric overall stability constant
$T\beta_n$	thermodynamic overall stability constant
γ	activity coefficient in the aqueous phase
γ^*	activity coefficient in the organic phase

Subscripts

A	refers to the equilibrated aqueous phase
i	refers to the i th species
I	refers to initial conditions
n	number of ligand ions in a complex
o	refers to the equilibrated organic phase

± refers to mean

Superscript

T refers to the thermodynamic nature of the stability constant

Other

() molarity of enclosed species

[] activity of enclosed species

DEDICATION

To my loving parents, whose understanding is an inspiration in my life.

A thermodynamic model for the liquid-liquid extraction of
cobaltous chloride complexes from aqueous
hydrochloric acid solutions by tributyl phosphate

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Iowa State University

A thermodynamic model has been developed for the liquid-liquid extraction of cobalt (II) in the $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ system. Evidence was found to support the mechanism

as predominant in the system. The liquid-liquid extraction of cobalt in this system can be represented by the equation

$$K_D = \frac{k_1' \beta_2 (\text{Cl}^-)_A^2 (\text{HCl} \cdot \text{TBP})_A^2}{1 + \beta_1 (\text{Cl}^-)_A + \beta_2 (\text{Cl}^-)_A^2 + \beta_3 (\text{Cl}^-)_A^3 + \beta_4 (\text{Cl}^-)_A^4}$$

The model makes use of the stoichiometric overall stability constants for the complexes CoCl_n^{2-n} where n varies from 1 to 4, the equilibrium chloride ion concentration, and the equilibrium $\text{HCl} \cdot \text{TBP}$ monosolvate concentration. Using a linear regression technique, the value of the effective liquid-liquid equilibrium constant (k_1') was found to be 2.0648×10^6 .

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Simplification of the model equation was achieved by substitution of the degree of formation for the neutral CoCl_2 complex (α_2) to yield the model equation

$$K_D = k_1' \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2$$

The model was used to predict the value of the distribution coefficients for the extraction data published by several investigators in addition to those obtained in this investigation. A reasonable estimate was achieved in each case.

INTRODUCTION

Liquid-liquid extraction is one of the few methods by which it is possible to quantitatively separate elements which are similar in properties. The use of liquid-liquid extraction to separate cobalt and nickel, which very frequently occur together, is an important separation problem in nonferrous metallurgy.

In order to have a fuller understanding of the feasibility of the separation of cobalt and nickel by liquid-liquid extraction, the investigation of the extractability of each element in a given system is desirable. Cobalt is more readily extracted than nickel from aqueous solutions by tributyl phosphate and this investigation deals in particular with the readily extractable cobalt chloride complex.

Lack of precise information have hindered to some extent the thermodynamic description of the nature of equilibrium of the liquid-liquid extraction of cobalt. First, cobalt has been shown to form four complexes in an aqueous chloride solution and the species CoCl^+ , CoCl_2 , CoCl_3^- , and $\text{CoCl}_4^{=}$ have been identified. Second, until very recently the mechanism of their extraction was not well defined. Third, the coextraction of hydrochloric acid (HCl) and water (H_2O) to the organic phase was found to have considerable influence in the distribution of cobalt between the phases. Fourth, the search for a suitable organic extractant required consideration of both its solubility in the aqueous phase and the solubility of cobalt in the organic phase.

The goals of this investigation, which are related to the previously described problems, are the following:

1. To review the progress that has been achieved in the mastery and interpretation of the liquid-liquid extraction of cobalt from aqueous solutions of cobaltous chloride by organic extractants, in particular tributyl phosphate (TBP).
2. To experimentally study the liquid-liquid extraction of cobalt from cobaltous chloride aqueous HCl solutions by TBP.
3. To make optimum use of available data in the literature to relate the cobaltous chloride complex formation in the aqueous phase to the liquid-liquid extraction equilibria.
4. To develop a suitable thermodynamic model for describing and predicting quantitatively the liquid-liquid extraction of cobaltous chloride from aqueous HCl solutions by TBP.

LITERATURE REVIEW

Cobaltous Chloride Complexes in Aqueous Solution

A considerable number of investigations have been made on the composition and stability of cobalt (II) chlorides in aqueous solution. The reported values have been compiled by Sillén (37) in a publication on stability constants of metal-ion complexes.

Some important investigations include the work of Morris and Short (31) in 1962, which reported stoichiometric stability constants for the CoCl_n^{2-n} ($n = 1, 2, 3, 4$) complexes at 20 °C and ionic strength of 0.691 M maintained with perchloric acid (HClO_4). By 1968, Zeltmann, et al. (43) measured the thermodynamic step stability constants of cobaltous chloride complexes making use of a nuclear magnetic resonance technique. They also reported the relative abundances of solution species. Quantitative treatment of the data was based on equilibria among the several proposed complexes. The minimum number of steps among the appropriate species were represented by the equations:

The successive equilibrium constants measured are given by the expressions:

$$T_{K_1} = \left(\frac{\alpha_1}{\alpha_0}\right) \left(\frac{a_1}{a_{+}}\right) \quad (5)$$

$$T_{K_2} = \left(\frac{\alpha_2}{\alpha_1}\right) \left(\frac{a_1^3}{a_{+}}\right) \quad (6)$$

$$T_{K_3} = \left(\frac{\alpha_3}{\alpha_2}\right) \left(\frac{a_1}{a_{+}}\right) \quad (7)$$

$$T_{K_4} = \left(\frac{\alpha_4}{\alpha_3}\right) \left(\frac{a_1}{a_{+}}\right) \quad (8)$$

where the cobalt (II) species are designated by the fractional abundances, α_n with n specifying the number of coordinated Cl^- , the water activity by a_1 and the mean HCl activity by a_{+} . These investigators assumed that the ratio of the activity coefficients for the cobaltous chloride complexes is constant.

In 1972, Belousov, et al. (8) investigated cobalt chloride complexes spectrophotometrically in aqueous solutions of a mixture of perchloric and hydrochloric acids at ionic strengths $I = 5, 7, 8, 9$, and 10 M . They also observed the formation of four mononuclear complexes CoCl_n^{2-n} with $n = 1$ to 4 and reported values for the overall stoichiometric stability constants and its variation with ionic strength. In 1974, Belousov, et al. (9) found that their new spectrophotometric measurements of the thermodynamic overall stability constants at varying ionic strength were different from those reported by Zeltmann, et al. (43). However, they are in agreement with those obtained by extrapolation of their own data on the variation of the stability constants with ionic strength. The reported values are given in Table 1. The method

Table 1. Overall thermodynamic stability constants ($\log K_n$) of cobaltous chloride complexes (CoCl_n^{2-n}) in aqueous solutions at 25 °C obtained by different methods

Complex	Method 1	Method 2	Method 3
CoCl^+	2.2×10^{-2}	1.8×10^{-2}	1.78×10^{-1}
CoCl_2	4.5×10^{-5}	2.8×10^{-5}	3.5×10^{-4}
CoCl_3^-	1.1×10^{-7}	3.2×10^{-7}	1.3×10^{-6}
CoCl_4^{2-}	5.0×10^{-10}	7.9×10^{-10}	6.9×10^{-9}

Method No.	Measuring technique	References
1	Spectrophotometry, $I = \text{const}$	6, 7
2	Spectrophotometry, $I \neq \text{const}$	6
3	Nuclear magnetic resonance	43

to obtain the thermodynamic stability constant from measurements of the stoichiometric constants used by Belousov, et al. (9) was proposed in 1962 by Vasil'ev (38). This method followed the Debye-Hückel approach and Vasil'ev suggested that the relationship between stoichiometric and thermodynamic stability constants can be conveniently expressed by

$$\text{p}K_c = \text{p}K_o - \frac{\Delta Z^2 A I^{1/2}}{1 + 1.6 I^{1/2}} + bI \quad (9)$$

for aqueous solutions at 25 °C. In this equation

K_o = thermodynamic instability constant

K_c = stoichiometric instability constant

$\text{p}K_o = -\log K_o$

ΔZ^2 = algebraic sum of the squares of the ionic charges

A = Debye-Hückel normal constant

I = ionic strength

b = an empirical constant characterizing the change in dielectric constant of the medium near an ion.

They reported the values of the thermodynamic stability constants for all the complexes of divalent cobalt chlorides in aqueous solutions. This information proved to be useful in extending the understanding of the extraction of cobaltous chlorides from HCl aqueous solutions into TBP.

Liquid-Liquid Extraction of Cobaltous Chlorides

The separation of cobalt and nickel is an important problem and is of current interest as far as mineral resources development is concerned. Rhodes and Hosking (34) reported that a commonly used commercial method of separation consists of the treatment of an acid solution of the divalent metal salts with an alkaline solution of an oxidizing agent, the cobalt is oxidized and precipitated as the hydrated cobaltic oxide. This method has been used by Deloro Smelting, and Refining Company, of Toronto, Ontario. Bautista (6) summarized the commercial method used by Sheritt Gordon Mines Limited of Canada, the largest producer of cobalt in the North American continent. This method was first used in 1954 and involves reacting the ore with a liquid solvent that selectively dissolves the metals in it. The separation of metals from each other is achieved by chemical means. These metals are then concentrated, purified, and are usually powdered into finished

products. Lately, attention has been directed toward the possibility of effecting the separation of metals by a liquid-liquid extraction process.

Garwin and Hixson (16) in 1949, investigated the use of liquid-liquid extraction as a means of separating cobalt and nickel chlorides. They made extensive studies on the suitability of solvents for the process. They recommended capryl alcohol as a solvent after taking into consideration the solubilities of the anhydrous salts in a variety of organic compounds and other relevant properties. Nevertheless, little extraction took place from a simple aqueous solution of the salt. In other words, the distribution coefficient of cobalt chloride was found to be so small that enormous quantities of solvent would be required for its extraction. However, extraction was observed to take place to some extent in the presence of high concentrations of certain added electrolytes but the magnitude of the distribution coefficients for extractions performed using hydrochloric acid and calcium chloride was small. These investigations were later extended by Yates, et al. (42) in 1953. The scope of their investigations included studies on promoting the effectiveness of several electrolytes in the extraction and the variations in the aqueous and organic phase activity coefficients with salt concentration.

Gindin, et al. (17) in 1960, worked a detailed study of the extraction of cobalt using various oxygen containing organic solvents similar to that of Garwin and Hixson and reported distribution data of cobalt and nickel chlorides between water and isoamyl alcohol, 2-ethylhexanol, and the higher alcohol fraction $C_7 - C_9$ in the presence

of HCl and CaCl_2 . They also studied the equilibria involved in the extraction of HCl and CaCl_2 into isoamyl alcohol.

In 1958, Irving and Edgington (23) investigated the extraction of some metal chlorides, including cobaltous chloride, into tributyl phosphate. They also considered the extraction of HCl and H_2O into TBP, and the dilution of TBP with inert diluents to improve the phase separation. A considerable amount of data was reported concerning these areas. The cobalt distribution coefficients were measured using radioactive tracers. This work motivated many other researchers to conduct studies that have contributed significantly to the understanding of the particular phenomena concerning the extraction of cobalt chlorides from aqueous solutions using TBP as solvent.

In 1959, Morris and Bell (30) reported useful data on the distribution coefficients of cobalt and HCl in the Cobalt-HCl- H_2O -TBP and Cobalt-HCl- H_2O -TBP-Benzene systems using techniques similar to those used by Irving and Edgington (23). The Soviet researchers developed interest in this particular problem and in 1960, Levin, et al. (27) reported results on the effect of cobalt concentration on its extractability, data on cobalt extraction from HCl solution of varying concentration and attempted a method to separate cobalt and nickel by liquid-liquid extraction. Morris and Short (31) in 1962 reported values for the distribution coefficients of cobalt in the Cobalt-HCl- H_2O -TBP system valid for 20 °C and ionic strength of 0.691 M maintained with perchloric acid.

Ezhovska-Tshebyatovska and Kopach (12), in 1966, examined the progress so far made in the interpretation of the extraction of cobaltous chlorides from aqueous solutions by organic extractants. They noted

that most required multistage extraction processes due mainly to low separation coefficients of cobalt and nickel chlorides or to high solubility of the extractants in water and HCl solutions. Although some degree of success had been achieved by the use of TBP, solving problems associated with the process, such as phase separation, led to a decrease in the distribution coefficients thus reducing the value of TBP as extractant. Ways to minimize disadvantageous phenomena such as the one described above were examined by these investigators and considerable amount of data were published on the systems $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$, $\text{CoCl}_2\text{-CaCl}_2\text{-H}_2\text{O-TBP}$, and $\text{CoCl}_2\text{-CaCl}_2\text{-HCl-H}_2\text{O-TBP}$ (12). The distribution coefficients presented were obtained using the radioactive tracer method.

In 1968, Jezowska-Trzebiatowska, et al. (24) examined the structure of the cobalt (II) complexes in HCl and CaCl_2 solutions and the mechanism by which cobalt is extracted in an effort to clarify some apparent contradiction in the literature. The study was conducted using spectrophotometric techniques. The results suggested that cobalt is extracted from weakly acidic HCl solutions in the form of tetrahedral complexes having a mixed coordination sphere, and from concentrated HCl solutions, in which cobalt exists in the form of the tetrahedral $\text{CoCl}_4^{=}$ anion, as the complex $[\text{TBP} \cdot \text{H}(\text{H}_2\text{O})_4]_2^+ \cdot \text{CoCl}_4^{=}$. Some aspects concerning the extraction of bivalent cobalt from chloride solutions by TBP that had not been studied in detail were examined spectrophotometrically by Belousov and Trofimov (7), in 1969. These included:

- a. the part played by water in the extraction

- b. the composition and structure of the solvate and the cobalt compounds extracted
- c. the influence of the composition of the aqueous phase on the distribution constant of cobalt
- d. the influence of the equilibrium concentration of HCl, LiCl, and CaCl_2 in the aqueous phase
- e. the equilibrium concentration of hydrogen ions at constant ionic strength and constant concentration of cobalt ions
- f. the influence of the original concentration of cobalt ions at constant ionic strength of the aqueous solution
- g. the hydration of the compounds extracted into the organic phase.

In 1974, Belousov, et al. (9) related the chloride complexing of cobalt (II) to its extraction by TBP. This work included a determination of the composition and stability of chloride complexes of cobalt (II) in aqueous solutions of HCl, LiCl, NaCl, and CaCl_2 with variable ionic strength by spectrophotometric measurements at 25 °C. They found that the complexes formed can be represented by the formula CoCl_n^{2-n} with the maximum values of $n = 4, 3, 1,$ and 2 corresponding to HCl, LiCl, NaCl, and CaCl_2 . On the basis of these results, they proposed that the extraction of cobalt into TBP from aqueous solutions containing HCl can be attributed to the neutral (uncharged) complex $\text{CoCl}_2(\text{H}_2\text{O})_2$ and presented the possibility of the following extraction mechanism: The first step is the formation of the neutral complex $\text{CoCl}_2(\text{H}_2\text{O})_2$ in the aqueous phase, with the TBP entering the aqueous phase forming an aqueous solvate $\text{H}(\text{H}_2\text{O})_4^+ \cdot \text{TBP} \cdot \text{Cl}^-$. The second stage is the interaction

of these two molecules with each other to form the extracted aqueous solvate $[\text{TBP} \cdot \text{H}(\text{H}_2\text{O})_4]_2^+ \cdot \text{CoCl}_4^- \cdot (\text{TBP})_2$. This mechanism can be represented by the reaction:

Another possible extraction mechanism was proposed, that of the $\text{CoCl}_2(\text{H}_2\text{O})_2$ molecules reacting with $[\text{H}(\text{H}_2\text{O})_4]^+ \cdot \text{TBP} \cdot \text{Cl}^-$ in the organic phase. The reaction for this case is:

Belousov, et al. (9) also suggested that the first mechanism described is dominant for the $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ extraction system.

Liquid-Liquid Solvent Extraction of Hydrochloric Acid by Tributyl Phosphate

Irving and Edgington (23) observed an appreciable increase in the volume of the organic phase during the extraction of H_2O and HCl itself into TBP. This phenomena had previously been noted and examined to some extent by Baldwin, et al. (5) in 1958. Thereafter it has been the subject of numerous investigations seeking to understand the details of this extraction. This problem is important since it is closely related to that of extracting the cobaltous chloride from HCl aqueous solutions by tributyl phosphate. Some understanding of the mechanism involved is highly desirable in order to study the cobalt extraction

process in depth. Higgins, Baldwin, and Soldano (22) studied the solubility of TBP in water and electrolyte solutions at different concentration.

The work of Baldwin, et al. (5) was extended by Hesford and McKay (21) in 1960. They studied the physical chemistry of the extraction of HCl from aqueous solutions by TBP in some detail. Kertes (26) attempted to identify the species formed in the equilibrium between aqueous HCl and pure TBP. He reported data for the distribution of HCl and the water content of the organic phase, and the physical chemical measurements of density, viscosity, and conductivity of the organic phase. In 1961, Kertes and Halpern (25) observed a great increase in the rate of hydrolysis of the organic TBP as its water content increased and proposed a mechanism for the HCl-TBP mixture degradation based on their newly generated data.

In 1961, Foa, et al. (14) studied the appearance of two liquid organic phases in the quaternary system $\text{HCl-H}_2\text{O-TBP-diluent}$. Naito and Suzuki (32) in 1961 reported the distribution equilibria of several proton acids including HCl between aqueous and TBP phases and also examined their mechanism of extraction.

Apraskin, et al. (3) worked toward establishing the solvation number when HCl is extracted with TBP and the quantitative description of the equilibrium. Using O-xylene as diluent they showed that HCl forms a monosolvate with TBP and experiments confirmed that a hydrated solvate $\text{HCl} \cdot \text{TBP} \cdot n\text{H}_2\text{O}$ (where $n = 2$ or 3) is extracted. Some of their data and results became available in 1962.

Hardy (20), in 1970, critically examined the reproducibility of published data on the distribution of HCl and H₂O between TBP and aqueous solutions of the acid. A complete set of recommended smoothed data for the TBP-HCl-H₂O system at 25 °C was made available as a result. The activity of TBP in equilibrium with HCl-H₂O was obtained by application of the Gibbs-Duhem equation to the smoothed distribution data. Apelblat (2) published results concerning the extraction of HCl by TBP diluted with carbon tetrachloride, benzene, and chloroform. These diluents have been found to be better than kerosene because three phase separation occurred at concentrations below 5 M HCl with kerosene.

EQUILIBRIUM THERMODYNAMICS AND LIQUID-LIQUID EXTRACTION THEORY

The Theory of Mononuclear Complexes Equilibria

A complex may be defined as a chemical species formed by the association of two or more simpler species each capable of independent existence. If two species A and B coexist in solution, they can react to form one or more complexes of the form $A_q B_p$, where $q \geq 1$, $p \geq 0$. A mononuclear complex is one which has only one coordination center and will be represented by the formula $A_q B_p$, with $q = 1$ and $p \geq 0$, that is AB_n . For a system which contains only mononuclear species, the ion or molecule A is considered as the central group and B is called the ligand. Although the numbers of associated solvent molecules is not included in the chemical formula for the representation of the mononuclear complexes in order to simplify the notation, it should be noted that A, B, and AB_n will usually be appreciably solvated.

A large number of metal complexes are mononuclear and consist of one or more neutral or anionic ligands coordinated to a central metal ion. The present investigation studies the complexation of the cobaltous ion with the chloride ion, which is a case of mononuclear metal complexation.

An effective way to describe chemical equilibria on a quantitative basis is by making use of the equilibrium constants that apply to the system being studied. The equilibrium constants provide information on the stability of the complex formed and are called stability constants or complex formation constants. These constants can be related to thermodynamic properties which provide information essential to the

fuller understanding of the factors such as size, shape, electronic structure of the central group and the ligand, temperature, and composition of the solvent which influence the stability of a complex.

The activity of a mononuclear complex species AB_n formed in solution at a given temperature can be related to the activities of the species A and B by the law of mass action. That is, the rate of a reaction is dependent on both the number of molecules involved and on the active masses of the reactants (conveniently replaced by activities). The formation equilibrium constant or stability constant of the single-step reaction

is given by:

$$T_{\beta_n} = \frac{[AB_n]}{[A][B]^n} \quad (13)$$

The stability constant T_{β_n} expressed in terms of the activities of the chemical species in the reaction (12) is called thermodynamic overall stability constant. The word "thermodynamic" in this particular term denotes the fact that activities, not concentrations, are being used in the ratio. In other words, the term is used for those equilibrium constants which are expressed as a ratio or quotient of activities. The term "overall" refers to those expressions which are obtained when reactions of the type presented in (12) are used to describe the equilibrium of the chemical species. In the case where the preceding complex AB_{n-1} also exists, the activity of AB_n can also

be expressed in terms of the activity of AB_{n-1} . If we consider the formation of AB_n as the single-step reaction:

the equilibrium constant expression is given by:

$$T_{K_n} = \frac{[AB_n]}{[AB_{n-1}][B]} \quad (15)$$

This equilibrium constant has been expressed in terms of the activities of the chemical species in the step-reaction (14) and is called thermodynamic step stability constant. In this case the term "step" or sometimes "stepwise" is used to denote that the relation refers to denote that the relation refers to a reaction step of the type presented in (14). The overall and step stability constants are related by the expression:

$$T_{\beta_n} = T_{K_1} T_{K_2} \dots T_{K_n} = \prod_{i=1}^n T_{K_i} \quad (16)$$

The molar (M), molal (m), and mole fraction (x) concentration scales are commonly used in work on complex formation. The molar scale expresses the concentration in moles of solute per liter of solution. The molality is the moles of solute per kilogram of solvent and the mole fraction the moles of solute per mole of solution. Under dilute conditions the mole fraction, molality, and molarity are all proportional to each other. The numerical values of the stability constants depend on the experimental conditions and the units in which the activity terms are expressed. Therefore, the same units should be

consistently used in any investigation. In this work the molar concentration scale was used.

Both, activity and activity coefficient will depend on the standard state specified. For a component in the liquid phase, the independent variables which determine the standard state are the temperature of the system, a fixed composition, and a specified pressure. The choice of a standard state determines the condition at which the value of the activity coefficient reaches one. At constant temperature and pressure the unsymmetric convention of normalization is often used. The convention distinguishes between the solvent (1) and the solute (2) in a solution such that

$$\gamma_1 \rightarrow 1 \text{ as } x_1 \rightarrow 1 \quad (17)$$

$$\gamma_2 \rightarrow 1 \text{ as } x_2 \rightarrow 0 \quad (18)$$

where the activity coefficient of the solute is calculated relative to the mole fraction scale. If the molal activity coefficient is desired

$$\gamma_2 \rightarrow 1 \text{ as } m_2 \rightarrow 0 \quad (19)$$

Another type of activity coefficient refers to the molar concentration scale and its standard state is given by

$$\gamma_2 \rightarrow 1 \text{ as } M_2 \rightarrow 0 \quad (20)$$

The activity coefficients used in this work are consistent with the molar units used to express the concentrations, that is, molar activity coefficients relative to standard state (20).

It is often possible to keep the activity coefficient of each species constant throughout a series of measurements by using a suitable ionic medium. In such cases where experiments are run with a large excess of background salt, it can be assumed that the activity coefficients are independent of the concentration of the reacting species and dependent only on the nature and concentration of the bulk electrolyte. Many investigators attempt to keep activity coefficients constant by using solutions of constant ionic strength after the theoretical relationship between the activity coefficient and ionic strength proposed by Debye and Hückel in 1923.

Debye and Hückel proposed that the departure of electrolytes from the ideal solution behavior can be partially explained by electrostatic attraction between the ions. A solution is considered to be ideal if the chemical potential of every component is a linear function of the logarithm of some suitable measure of its concentration which is usually taken to be the mole fraction. They developed the following formula for the activity coefficient of an electrolyte in solution,

$$\log \gamma_{\pm} = \frac{-A|z_1 z_2| \sqrt{I}}{1 + Ba\sqrt{I}} \quad (21)$$

where

A = Debye-Hückel constant

B = Debye-Hückel constant

z_1 = ionic charge of the cation

z_2 = ionic charge of the anion

a = distance of closest approach to the reference ion

I = ionic strength.

The ionic strength, I , has been defined for a multicomponent electrolyte solution as:

$$I = \frac{1}{2} \sum_{i=1}^c m_i z_i^2 \quad (22)$$

where m_i is the molarity and z_i the charge of a particular ionic species in solution.

The numerator gives the effect of the long-range Coulomb forces (forces that act between ions and those between ions and neutral molecules of solvent). The denominator shows how these forces are modified by the short-range interaction between ions. To get this expression Debye and Hückel assumed the ions to be nondeformable spheres of equal radii. In any actual solution there are short-range interactions and solvent molecules to consider which cannot be adequately represented by the rigid spheres model. Guggenheim (19) proposed the extension of equation (21) to include these interactions assuming they can be approximated by a linear variation term, thus:

$$\log \gamma_{\pm} = \frac{-A|z_1 z_2| \sqrt{I}}{1 + Ba\sqrt{I}} + bI \quad (23)$$

where b is an empirical constant characterizing the change in dielectric constant of the medium near an ion.

No attempt to control the ionic strength was made for the cobaltous chloride extraction system studied in this work. No additional electrolyte was added to the system in the experiments performed in this investigation. Table 2 illustrates the development of the ionic strength expression for this system.

Table 2. Development of the ionic strength expression for the $\text{CoCl}_2\text{-H}_2\text{O-HCl}$ aqueous phase system

Ion or complex	z_i^2	m_i	$\frac{1}{2} z_i^2 m_i$
Co^{++}	4	$\alpha_o^m \text{CoCl}_2$	$2\alpha_o^m \text{CoCl}_2$
CoCl^+	1	$\alpha_1^m \text{CoCl}_2$	$\frac{1}{2} \alpha_1^m \text{CoCl}_2$
CoCl_3^-	1	$\alpha_3^m \text{CoCl}_2$	$\frac{1}{2} \alpha_3^m \text{CoCl}_2$
$\text{CoCl}_4^{=}$	4	$\alpha_4^m \text{CoCl}_2$	$2\alpha_4^m \text{CoCl}_2$
Cl^-	1	$m_{\text{HCl}} + m_{\text{CoCl}_2} (2\alpha_o + \alpha_1 - \alpha_3 - 2\alpha_4)$	$\frac{1}{2} [m_{\text{HCl}} + m_{\text{CoCl}_2} (2\alpha_o + \alpha_1 - \alpha_3 - 2\alpha_4)]$
H^+	1	m_{HCl}	$\frac{1}{2} m_{\text{HCl}}$
			$I = m_{\text{HCl}} + m_{\text{CoCl}_2} (3\alpha_o + \alpha_1 + \alpha_4)$

If the activity coefficients of all species are held effectively constant, an expression for the stoichiometric overall stability constant can be obtained corresponding to reaction (12) as:

$$\beta_n = \frac{(AB_n)}{(A)(B)^n} = T_{\beta_n} \frac{\gamma_A \gamma_B^n}{\gamma_{AB_n}} \quad (24)$$

where β_n is now a quotient of concentrations instead of activities which explains the use of the term "stoichiometric" for this type of equilibrium constant. Similarly, for reaction (14) we have:

$$K_n = \frac{(AB_n)}{(AB_{n-1})(B)} = T_{K_n} \frac{\gamma_{AB_{n-1}} \gamma_B}{\gamma_{AB_n}} \quad (25)$$

which is the stoichiometric step stability constant.

It usually is very difficult to determine accurate values for the formation or stability constants for systems in which several complexes coexist. It has been found that stoichiometric stability constants can usually be determined more conveniently than thermodynamic constants because the values of the activity coefficients need not be known, provided they can be held constant. Any comparison of stoichiometric stability constants must refer to values obtained at the same temperature in substantially the same ionic medium. The computation of the thermodynamic constants from measurements of the total concentration of A, B, and either the activity or concentration of A or AB_n usually requires the knowledge of the activity coefficients of the $M + 2$ species present in the system A, B, AB, AB_2 ... AB_M . Notice that M is the number of ligands B which combine with metal ion. If the ligand is

monodentate, it coordinates using one donor atom. The number of ligands which can combine with an ion of a metal is then equal to the maximum coordination number of the metal. The chloride atom is an example of such monodentate ligands. Stoichiometric stability constants are also thermodynamic quantities, referred to a standard state in which all activity coefficients are unity. They could therefore be obtained by extrapolating to infinite dilution stoichiometric values which have been determined using solutions of known ionic strength.

Stability constants are usually determined by equilibrium methods. There are a number of basic principles and certain nomenclature associated with the description of equilibrium complexes. Some concentration variables that are commonly used are the total concentrations, free concentrations, and secondary concentration variables such as the degree of formation of a complex. Consider the mononuclear complex formation reaction system

The total concentrations of the ligand B and the central group A are as follows:

$$B_T = (B) + (AB) + 2(AB_2) + \dots + n(AB_n) + \dots + M(AB_M) \quad (27)$$

$$A_T = (A) + (AB) + (AB_2) + \dots + (AB_n) + \dots + (AB_M) \quad (28)$$

The free concentrations refer to the equilibrium concentrations of some or all the species present in the system and are represented by parentheses enclosing the particular species. For example, the free concentration of the ligand B is given by (B) and the total ligand concentration by B_T . Equations (27) and (28) can be expressed as

$$B_T = (B) + (A) \sum_{n=1}^M n\beta_n (B)^n \quad (29)$$

$$A_T = (A) \left[1 + \sum_{n=1}^M n\beta_n (B)^n \right] \quad (30)$$

where the definition for the stoichiometric overall stability constant have been used with (A) and (B) corresponding to the free concentrations of A and B. In 1915, Niels Bjerrum (as cited by 36) introduced the use of a new variable by defining the degree of formation of a complex AB_c in the system described in (20) with $n = c$ as follows:

$$\alpha_c = \frac{(AB_c)}{A_T} = \frac{(AB_c)}{(A) + (AB) + (AB_2) + \dots + (AB_c) + \dots + (AB_M)} \quad (31)$$

Equation (31) can also be expressed in terms of the complexes stoichiometric stability constants

$$\alpha_c = \frac{\beta_c (B)^c}{(A) \left[1 + \sum_{n=1}^M n\beta_n (B)^n \right]} \quad (32)$$

These terms are important since they are constantly used and found in the literature concerning stability of complexes in solutions.

DEVELOPMENT OF THE THERMODYNAMIC LIQUID-LIQUID EXTRACTION MODEL

The Case of Cobaltous Chloride Complexes

The development of a suitable thermodynamic model to describe the liquid-liquid extraction of cobaltous chlorides from aqueous acidic solutions by tributyl phosphate was considered in this investigation with the idea of predicting the cobalt distribution coefficient at different experimental conditions. In the search for a suitable model three possibilities were examined. Two of these were based on assumptions that could not be justified theoretically and/or experimentally. In this way we arrived at the model developed below. The two mechanisms proposed for the liquid-liquid extraction by Belousov (9) were considered in relation to this model.

The formation of the cobaltous chloride inorganic complexes in aqueous solution is given by the following complexing reactions:

The representation of the complexes is consistent with the notation introduced in the theoretical part of this work.

The stoichiometric overall stability constants β_1 , β_2 , β_3 , and β_4 are defined by:

$$\beta_1 = \frac{(\text{CoCl}^{+})}{(\text{Co}^{++})(\text{Cl}^{-})} \quad (37)$$

$$\beta_2 = \frac{(\text{CoCl}_2)}{(\text{Co}^{++})(\text{Cl}^-)^2} \quad (38)$$

$$\beta_3 = \frac{(\text{CoCl}_3^-)}{(\text{Co}^{++})(\text{Cl}^-)^3} \quad (39)$$

$$\beta_4 = \frac{(\text{CoCl}_4^{=})}{(\text{Co}^{++})(\text{Cl}^-)^4} \quad (40)$$

where the parentheses stand for the concentration, not the activity of the species in reactions (33) to (36).

Very recently E. A. Belousov, V. V. Bocharov, and V. E. Mironov (9) were able to relate the chloride complexing of cobalt (II) to its extraction by tributyl phosphate. These investigators proposed the following extraction mechanisms:

Mechanism 1

Mechanism 2

where the subscripts A represents the equilibrium aqueous phase and O the organic phase.

Assuming that the first mechanism is predominant, the liquid-liquid extraction equilibrium constant, k_1 , is given by the expression:

$$k_1 = \frac{[\text{H}_2 \cdot \text{CoCl}_4 \cdot 2\text{TBP}]_O}{[\text{CoCl}_2]_A [\text{HCl} \cdot \text{TBP}]_A^2} \quad (43)$$

where the brackets denote activities. Making use of the relation between activity and activity coefficient we can write

$$[\text{CoCl}_2]_A = (\text{CoCl}_2)_A \gamma_{\text{CoCl}_2} \quad (44)$$

$$[\text{HCl} \cdot \text{TBP}]_A = (\text{HCl} \cdot \text{TBP})_A \gamma_{\text{HCl} \cdot \text{TBP}} \quad (45)$$

$$[\text{H}_2 \cdot \text{CoCl}_4 \cdot 2\text{TBP}]_O = (\text{H}_2 \cdot \text{CoCl}_4 \cdot 2\text{TBP})_O \gamma_{\text{H}_2 \cdot \text{CoCl}_4 \cdot 2\text{TBP}}^* \quad (46)$$

The distribution coefficient, K_D , is defined for a single component system by the ratio of the total concentration of metallic species (M) in the organic phase to the total concentration of the metallic species in the aqueous phase:

$$K_D = \frac{\Sigma(M)_O}{\Sigma(M)_A} = \frac{\Sigma(\text{Co})_O}{\Sigma(\text{Co})_A} \quad (47)$$

The total concentration of metallic species in the organic phase is given by

$$\Sigma(M)_O = \Sigma(\text{Co})_O = (\text{H}_2 \cdot \text{CoCl}_4 \cdot 2\text{TBP})_O \quad (48)$$

Substituting equations (45), (46), and (47) into (43) we have

$$k_1 = \frac{(\text{H}_2 \cdot \text{CoCl}_4 \cdot 2\text{TBP})_O \gamma_{\text{H}_2 \cdot \text{CoCl}_4 \cdot 2\text{TBP}}^*}{(\text{CoCl}_2)_A (\text{HCl} \cdot \text{TBP})_A^2 \gamma_{\text{CoCl}_2}^2 \gamma_{\text{HCl} \cdot \text{TBP}}^2} \quad (49)$$

where the star (*) denotes the activity coefficient of a species in the organic phase.

Substituting equation (48) into (47) the latter becomes

$$\Sigma(\text{Co})_O = \frac{k_1 (\text{CoCl}_2)_A (\text{HCl} \cdot \text{TBP})_A^2 \gamma_{\text{CoCl}_2}^2 \gamma_{\text{HCl} \cdot \text{TBP}}^2}{\gamma_{\text{H}_2 \cdot \text{CoCl}_4 \cdot 2\text{TBP}}^*} \quad (50)$$

Equation (32) is now substituted into equation (50) introducing in this way a term which contains the stoichiometric stability constant for the neutral complex, β_2 .

$$\Sigma(\text{Co})_O = \frac{k_1 \beta_2 (\text{Co}^{++})_A (\text{Cl}^-)_A^2 (\text{HCl} \cdot \text{TBP})_A^2 \gamma_{\text{CoCl}_2} \gamma_{\text{HCl} \cdot \text{TBP}}^2}{\gamma_{\text{H}_2 \cdot \text{CoCl}_4 \cdot 2\text{TBP}}^*} \quad (51)$$

The total concentration of metallic species in the aqueous phase can be written:

$$\Sigma(\text{M})_A = \Sigma(\text{Co})_A = (\text{Co}^{++})_A + (\text{CoCl}^+)_A + (\text{CoCl}_2)_A + (\text{CoCl}_3^-)_A + (\text{CoCl}_4^{=})_A \quad (52)$$

Substituting equations (35), (36), (37) and (38) into (52) it becomes

$$\Sigma(\text{Co})_A = (\text{Co}^{++})_A (1 + \beta_1 (\text{Cl}^-)_A + \beta_2 (\text{Cl}^-)_A^2 + \beta_3 (\text{Cl}^-)_A^3 + \beta_4 (\text{Cl}^-)_A^4) \quad (53)$$

Substitution of the expression (51) and (53) in the equation for the distribution ratio gives

$$K_D = \frac{k_1 \beta_2 (\text{Cl}^-)_A^2 (\text{HCl} \cdot \text{TBP})_A^2 \gamma_{\text{CoCl}_2} \gamma_{\text{HCl} \cdot \text{TBP}}^2}{(1 + \beta_1 (\text{Cl}^-)_A + \beta_2 (\text{Cl}^-)_A^2 + \beta_3 (\text{Cl}^-)_A^3 + \beta_4 (\text{Cl}^-)_A^4) \gamma_{\text{H}_2 \cdot \text{CoCl}_4 \cdot 2\text{TBP}}^*} \quad (54)$$

At this point, the assumption is made that the ratio of the activity coefficients of the neutral molecules obtained in equation (49) varies slightly with concentration. Should this assumption hold, then the quotient of activity coefficients for mechanism 1 in equation (49) can be represented as a constant value given by:

$$K_{\gamma_1} = \frac{\gamma_{\text{H}_2 \cdot \text{CoCl}_4 \cdot 2\text{TBP}}^*}{\gamma_{\text{CoCl}_2} \gamma_{\text{HCl} \cdot \text{TBP}}^2} \quad (55)$$

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

$$k'_1 = \frac{k_1}{K_{Y_1}} \quad (56)$$

gives a value for an effective constant k'_1 for the extraction equilibria.

Equation (54) now becomes

$$K_D = \frac{k'_1 \beta_2 (Cl^-)_A^2 (HCl \cdot TBP)_A^2}{(1 + \beta_1 (Cl^-)_A + \beta_2 (Cl^-)_A^2 + \beta_3 (Cl^-)_A^3 + \beta_4 (Cl^-)_A^4)} \quad (57)$$

The expression for the degree of formation of $CoCl_2$ complex is defined by Bjerrum (as cited by 36) as

$$\alpha_2 = \frac{\beta_2 (Cl^-)_A^2}{1 + \beta_1 (Cl^-)_A + \beta_2 (Cl^-)_A^2 + \beta_3 (Cl^-)_A^3 + \beta_4 (Cl^-)_A^4} \quad (58)$$

Equation (57) can be written in the following equivalent form:

$$K_D = k'_1 \alpha_2 (HCl \cdot TBP)_A^2 \quad (59)$$

It should be kept in mind that even though this is undoubtedly a simple and convenient expression, it is dependent on several parameters, such as the chloride and cobaltous free ion concentrations. This dependency is implicit in the α_2 term of equation (59). Pertinent data available in the literature combined with appropriate experiments can be used to test the applicability of this model to the cobaltous chloride extraction into TBP.

If it is assumed that the second mechanism dominates in the extraction the model equation will change only in the $HCl \cdot TBP$ concentration term, the solvate being in the organic phase rather than in the aqueous phase. The expression equivalent to equation (57) for mechanism 2 is, therefore,

$$K_D = \frac{k'_2 (\beta_2 (Cl^-)_A)^2 (HCl \cdot TBP)_O^2}{(1 + \beta_1 (Cl^-)_A + \beta_2 (Cl^-)_A^2 + \beta_3 (Cl^-)_A^3 + \beta_4 (Cl^-)_A^4)} \quad (60)$$

which can be simplified by introducing the degree of formation for $CoCl_2$, α_2 , to give:

$$K_D = k'_2 \alpha_2 (HCl \cdot TBP)_O^2 \quad (61)$$

where

$$k'_2 = \frac{k_2}{K_{\gamma_2}} \quad (62)$$

$$k_2 = \frac{[H_2 \cdot CoCl_4 \cdot 2TBP]_O}{[CoCl_2]_A [HCl \cdot TBP]_O^2} \quad (63)$$

$$K_{\gamma_2} = \frac{\gamma_{H_2 \cdot CoCl_4 \cdot 2TBP}^*}{\gamma_{CoCl_2} \gamma_{HCl \cdot TBP}^{*2}} \quad (64)$$

EXPERIMENTAL SECTION: LIQUID-LIQUID EXTRACTION OF COBALTOUS CHLORIDES
FROM AQUEOUS HYDROCHLORIC ACID SOLUTION BY TRIBUTYL PHOSPHATE

Materials and Apparatus

Cobaltous chloride solutions were prepared from "analytical" grade reagent CoCl_2 . The HCl used was also of "analytical" reagent (A.R.) grade. The concentration of HCl in aqueous solution was determined by titration with A.R. sodium carbonate in the presence of methyl orange indicator. Purified TBP obtained from Fisher Scientific Company was used.

The concentration of cobalt was measured by absorption flame photometry using a Perkin-Elmer Model 303 instrument with a hollow cathode cobalt lamp.

Procedures

HCl solutions ranging from approximately 1.0 M to 11.0 M were prepared by diluting concentrated 12.0 M HCl with distilled water. Four portions of twenty milliliters of each of the HCl solutions were equilibrated with equal amounts of TBP by being agitated in a mechanical shaker for ten minutes. The samples were then centrifuged for fifteen minutes to achieve better separation.

Samples of aqueous cobaltous chlorides were prepared by dissolving 0.01 to 0.13 grams of the salt in 75 ml of the aqueous phase previously equilibrated HCl-TBP mixture to obtain concentrations of approximately 1×10^{-3} to 9×10^{-3} moles per liter. This concentration range had been favored by various investigators (7, 12, 23, 30) since the cobalt

distribution coefficient did not vary significantly over the stated range. Ten milliliters of each of the samples were then contacted at approximately 25 °C (room temperature) with ten milliliters of the organic phase of the previously equilibrated TBP-HCl mixture in separatory funnels and were agitated in a mechanical shaker for five minutes. This time has been shown to be sufficient for attaining equilibrium under the conditions described by various investigators (12, 23, 27, 30). After equilibration both phases were centrifuged for another five minutes and carefully separated.

The distribution of cobalt between the aqueous and organic phase was determined by atomic absorption spectrometry. This technique consists of converting as much of the sample as possible into an atomic vapor and measuring the absorption of this atomic vapor at a selected characteristic wavelength, in this case, cobalt samples. The measured absorbance is proportional to concentration, and analyses are made by comparing this absorbance with that given by reference samples of known composition. The vaporization is achieved by spraying a solution of the sample into a flame. A nitrous oxide-acetylene flame is recommended for cobalt determinations. A light source is required to emit spectra of the element to be determined. In the case of cobalt, a hollow cathode lamp was used, the most sensitive emission wavelength being 345.4 nm. In order to bring the samples to an appropriate reading sensitivity range some had to be diluted ten or a hundred times.

No back extraction was necessary to analyze the cobalt concentration in the organic phase since the atomic absorption spectrometry is applicable to determination of metals in either an aqueous or an organic

solvent. No clogging of the atomizer was observed despite the higher viscosity of the organic phase samples. The equilibrated aqueous phase was titrated with sodium carbonate (Na_2CO_3) using methyl orange indicator and the HCl concentration was calculated from the required Na_2CO_3 volume. Some difficulty was experienced in observing a sharp end point but the method was nevertheless considered satisfactory.

Experimental Results

The recorded absorbance for standard solutions of known cobalt concentration permitted the preparation of calibration curves very similar to the one shown in Figure 1. For each sample, the percentage of absorbance read from the instrument was converted to the corresponding absorbance value using an extensive table supplied by Perkin-Elmer for such purposes. The concentrations corresponding to each of the absorbance values were then obtained from the calibration curve. These concentrations were multiplied by the dilution factor to obtain the true concentrations for the experimental extraction conditions. These experimental values and the measured distribution coefficients for cobalt are shown in Tables 3 to 8. The corresponding HCl concentrations in the equilibrated aqueous phase are also included. The low HCl concentration data is presented in Figure 2 and the high HCl concentration data is shown in Figure 3. The curve shows a maximum of 1.52 at HCl equilibrium concentration of approximately 9.0 M.

In Figure 4 the experimental data obtained in this investigation is compared to those published under similar conditions by other

Figure 1. Absorbance versus cobalt concentration: calibration curve

Table 3. $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ system experimental data: organic phase - run 1

Sample No.	% A ^a	A	$\mu\text{gCo/ml}$	Dilution factor	$(\text{Co})_o^b$
1	4.28	0.0190	0.62	1	0.62
2	8.40	0.0380	1.19	1	1.19
3	28.27	0.1443	4.55	1	4.55
4	47.78	0.2821	8.93	1	8.93
5	41.44	0.2324	7.55	10	75.5
6	15.50	0.0731	2.30	100	230
7	29.23	0.1502	4.71	100	471
8	43.03	0.2443	7.69	100	769
9	47.64	0.2810	8.91	100	891
10	41.56	0.2333	7.34	100	734
11	37.09	0.2012	6.33	100	633

^aA = Absorbance.

^b $(\text{Co})_o$ = Total cobalt concentration in the equilibrated organic phase in $\mu\text{gCo/ml}$.

Table 4. $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ system experimental data: aqueous phase —
run 1^a

Sample No.	$(\text{HCl})_A$	% A	A	$\mu\text{gCo/ml}$	Dilution factor	$(\text{Co})_A^b$	K_D
1	1.10	39.06	0.2151	6.78	100	678	0.0009
2	2.20	38.67	0.2123	6.66	100	666	0.0018
3	3.25	37.93	0.2071	6.50	100	650	0.0070
4	4.08	35.33	0.1900	5.95	100	595	0.0150
5	5.30	32.57	0.1711	5.36	100	536	0.1408
6	6.02	37.24	0.2023	6.38	100	638	0.3605
7	7.30	33.86	0.1795	5.64	100	564	0.8351
8	8.10	35.73	0.1920	6.04	100	604	1.2732
9	9.15	36.61	0.1980	6.21	100	621	1.4348
10	10.05	37.94	0.2072	6.50	100	650	1.1292
11	11.00	38.46	0.2101	6.59	100	659	0.9605

^aInitial CoCl_2 concentration $\sim 1 - 9 \times 10^{-3}$ moles/liter.

^b $(\text{Co})_A$ = total cobalt concentration in the equilibrated aqueous phase in $\mu\text{gCo/ml}$.

Table 5. $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ system experimental data: organic phase —
run 2

Sample No.	% A ^a	A	$\mu\text{gCo/ml}$	Dilution factor	$(\text{Co})_o^b$
1	2.95	0.0130	0.41	1	0.41
2	6.10	0.0273	0.86	1	0.86
3	26.72	0.1350	4.28	1	4.28
4	53.17	0.3295	10.38	1	10.38
5	8.44	0.0383	1.23	10	12.30
6	12.54	0.0582	1.83	100	183
7	24.85	0.1241	3.93	100	393
8	50.61	0.3064	7.62	100	762
9	40.66	0.2266	7.14	100	714
10	38.67	0.2123	6.66	100	666
11	30.50	0.1580	5.00	100	500

^aA = Absorbance.^b $(\text{Co})_o$ = total cobalt concentration in the equilibrated organic phase
in $\mu\text{gCo/ml}$.

Table 6. $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ system experimental data: aqueous phase - run 2^a

Sample No.	$(\text{HCl})_A$	% A	A	$\mu\text{gCo/ml}$	Dilution factor	$(\text{Co})_A^b$	K_D
1	1.20	33.96	0.1802	5.66	100	566	0.0007
2	2.07	34.33	0.1826	5.76	100	576	0.0015
3	3.30	32.38	0.1700	5.35	100	535	0.0080
4	4.40	31.12	0.1619	5.19	100	519	0.0200
5	5.01	30.23	0.1563	4.93	100	493	0.0250
6	6.30	33.29	0.1758	5.54	100	554	0.3303
7	7.03	30.66	0.1590	5.02	100	502	0.7829
8	8.30	31.97	0.1673	5.28	100	528	1.4432
9	9.50	31.53	0.1645	5.19	100	519	1.3757
10	10.10	34.63	0.1846	5.81	100	581	1.1463
11	11.15	35.03	0.1873	5.88	100	588	0.8503

^aInitial CoCl_2 concentration $\sim 1 - 9 \times 10^{-3}$ moles/liter.

^b $(\text{Co})_A$ = total cobalt concentration in the equilibrated aqueous phase in $\mu\text{gCo/ml}$.

Table 7. $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ system experimental data: organic phase - run 3

Sample No.	% A ^a	A	$\mu\text{gCo/ml}$	Dilution factor	$(\text{Co})_o^b$
1	4.52	0.0210	0.69	1	0.69
2	8.40	0.0381	1.21	1	1.21
3	23.72	0.1176	3.71	1	3.71
4	13.24	0.0617	2.04	10	20.40
5	43.99	0.2517	7.92	10	79.20
6	16.82	0.0800	2.51	100	251
7	41.83	0.2353	7.38	100	738
8	43.36	0.2469	7.77	100	777
9	45.94	0.2671	8.43	100	843
10	34.37	0.1829	5.78	100	578
11	28.35	0.1448	4.56	100	456

^aA = absorbance.

^b $(\text{Co})_o$ = total cobalt concentration in the equilibrated organic phase in $\mu\text{gCo/ml}$.

Table 8. $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ system experimental data: aqueous phase —
run 3^a

Sample No.	$(\text{HCl})_A$	% A	A	$\mu\text{gCo/ml}$	Dilution factor	$(\text{Co})_A^b$	K_D
1	1.50	39.63	0.2192	6.90	100	690	0.0010
2	2.18	38.94	0.2143	6.74	100	674	0.0018
3	3.10	35.97	0.1936	6.19	100	619	0.0060
4	4.35	34.43	0.1833	5.83	100	583	0.0350
5	5.60	33.96	0.1802	5.66	100	566	0.1400
6	6.50	32.55	0.1710	5.40	100	540	0.4648
7	7.60	36.83	0.1995	6.26	100	626	1.1789
8	8.25	34.10	0.1810	5.71	100	571	1.3608
9	9.00	32.87	0.1731	5.47	100	547	1.5411
10	10.15	32.55	0.1711	5.36	100	536	1.0784
11	11.30	31.00	0.1612	5.07	100	507	0.8994

^aInitial CoCl_2 concentration $\sim 1 - 9 \times 10^{-3}$ moles/liter.

^b $(\text{Co})_A$ = total cobalt concentration in the equilibrated aqueous phase in $\mu\text{gCo/ml}$.

Figure 2. Cobaltous chloride distribution coefficient (K_D) in the system $\text{CoCl}_2\text{-H}_2\text{O-HCl-TBP}$ versus the equilibrium hydrochloric acid concentration in the aqueous phase: low concentration range

Figure 3. Cobaltous chloride distribution coefficient (K_D) in the system $\text{CoCl}_2\text{-H}_2\text{O-HCl-TBP}$ versus the equilibrium hydrochloric acid concentration in the aqueous phase: high concentration range.

Figure 4. Cobalt distribution coefficient (K_D) in its extraction by tributyl phosphate versus the equilibrium molar hydrochloric acid concentration in the aqueous layer

investigators. The experimental values obtained are higher than those previously reported but other factors such as purity of reactants, variability of ionic strength of the medium, and the use of atomic absorption technique for determining the cobalt concentration in both phases may explain the differences. A fairly large variation was observed in the data taken by atomic absorption. This may be due to the dilution of samples to attain a desirable sensitivity range. Another possible explanation for the variation is the fact that any contamination of the samples strongly affects the absorption measurements taken in the instrument.

Hardy (20) proposed that there was a systematic error present in the data of Irving and Edgington (23). The possible cause of error in their measurements is the decomposition of TBP in the presence of HCl. This may explain the large deviations observed in Irving and Edgington's (23) and in Morris and Bell's (30) data when these are compared to others and this work in Figure 4.

APPLICATION OF PUBLISHED DATA AND EXPERIMENTAL
RESULTS TO THE LIQUID-LIQUID EXTRACTION MODEL

The stability constants that should be used in testing the model are the stoichiometric formation constants. These constants are often available in the literature and such is the case for cobaltous chloride complexes in aqueous HCl solutions. E. A. Belousov and coworkers (8) reported values for these constants over a wide range of ionic strengths maintained with perchloric acid (HClO_4). These are given in Table 9. Figure 5 shows their reported values for the degree of formation of the complexed species present in solution as a function of the HCl concentration. The degree of formation of the neutral complex can be used in testing the model as expressed in equations (59) and (61).

A regression analysis technique was used to describe the degree of complexation of the neutral complex as a function of the HCl concentration. The results were as follows:

$$\text{For } 0 \leq (\text{HCl})_A \leq 5.5 \text{ M} \quad (65)$$

$$\alpha_2 = 0$$

$$\text{For } 5.5 < (\text{HCl})_A \leq 9.0 \text{ M} \quad (66)$$

$$\alpha_2 = 2.5761 - 1.3305 (\text{HCl})_A + 0.2173 (\text{HCl})_A^2 - 0.0109 (\text{HCl})_A^3$$

$$R^2 = \text{correlation coefficient} = 0.8380$$

$$\text{For } 9.0\text{M} < (\text{HCl})_A \text{ M} \quad (67)$$

$$\alpha_2 = 0.3935 + 0.0227 (\text{HCl})_A - 0.0040 (\text{HCl})_A^2$$

$$R^2 = \text{correlation coefficient} = 0.8212$$

Higgins and coworkers (22) presented a study on the effect of electrolytes and temperature on the solubility of TBP in water. They

Table 9. Stoichiometric overall stability constants of the complexes CoCl_n^{2-n} in aqueous $\text{HClO}_4 + \text{HCl}$ solutions at 25 °C at constant ionic strength as reported by Belousov, et al. (8)

β_n^a for different n	Constants at different ionic strengths				
	10	9	8	7	5
1	6.60	4.40	2.50	1.70	1.10
2	18.0	6.00	2.00	0.70	0.24
3	40.0	5.90	1.05	0.20	0.04
4	27.0	1.60	0.12	0.02	~ 0

^aConstants determined spectrophotometrically at constant ionic strength.

reported that the value for the solubility of TBP in water at 25 °C is 422 mg TBP/liter, or on a molar basis 0.0016 M. It was found that the solubility of TBP in HCl solutions at 25 °C does not differ significantly from that of TBP in pure water.

It has been noted by several investigators that considerable volume increase of the organic phase occurs in the $\text{HCl-H}_2\text{O-TBP}$ system. An explanation to the observed phenomena is the extraction of water and HCl itself into TBP.

The concentrations of the HCl extracted into TBP in moles per liter were obtained from Hardy's (20) data. These values are also useful in testing the model and are presented in Figure 6 together with the concentration of the H_2O extracted into the organic phase. It is assumed that in the concentration range of concern all the HCl present in significant amounts in the TBP phase is in the form of the monosolvate $\text{HCl} \cdot \text{TBP}$.

Figure 5. Degree of complexation (α_n) for cobalt and chloride in the aqueous phase versus the hydrochloric acid equilibrium concentration in the aqueous phase as reported by E. A. Belousov (8).

In the developed thermodynamic model the concentration of the single chloride ion, not of the HCl electrolyte appears in the model expressions. Because the cobalt distribution coefficient in the system under consideration was too small for concentrations less than 1.0 M HCl the liquid-liquid extraction was carried at HCl concentrations greater than 1.0 M. The HCl concentration range used in the experiments was from 1.0 M to 11.5 M.

Figure 6. Equilibrium water and hydrochloric acid concentrations in the organic phase versus the equilibrium hydrochloric acid concentration in the aqueous phase for the system $\text{HCl-H}_2\text{O-TBP}$ at 25°C

A titration technique with Na_2CO_3 provided an estimation of the HCl concentration in the equilibrated aqueous phase. Nevertheless, at the experimental conditions of the extraction these concentrations are very close to those of the free chloride single ion in the equilibrated aqueous phase. This can be better understood if a material balance for chloride is examined.

For the equilibrium aqueous phase

$$(Cl^-)_A = (HCl)_A + (Co)_A (2\alpha_o + \alpha_1 - \alpha_3 - 2\alpha_4) - (HCl \cdot TBP)_A \quad (68)$$

where $(Co)_A$ is the total cobaltous chloride concentration in the equilibrated aqueous phase. This concentration has been measured experimentally for specific concentrations of HCl in the aqueous phase and is given in Tables 3 to 8. For convenience we are concerned with the reference point values of HCl concentration from 1 to 11.5 M with increments of 0.5 to test the thermodynamic model using the average of the experimental values. Therefore, the cobalt concentration in the aqueous phase for these reference points can be calculated from a total cobalt material balance expression:

$$(Co)_I V_I = (Co)_A V_A + (Co)_O V_O \quad (69)$$

where

$(Co)_I$ = total initial cobaltous chloride concentration

$(Co)_A$ = total cobaltous chloride in the equilibrated aqueous phase

$(Co)_O$ = total cobaltous chloride in the equilibrated organic phase

V_I = initial aqueous phase volume

V_A = aqueous phase volume after equilibration

V_O = organic phase volume after equilibration.

This expression takes into account the change in volume during the extraction. Once the total cobaltous chloride concentration in the equilibrated aqueous phase has been obtained the values of the

degree of complexation for the Co^{++} (α_0), CoCl^+ (α_1), CoCl^- (α_3), and $\text{CoCl}_4^{=}$ (α_4) species can be read from Figure 5, corresponding to the HCl aqueous concentrations. The concentration of TBP in the aqueous phase is 0.0016 M. These values make it possible to estimate whether there is a significant difference between the HCl concentration in the aqueous phase and that of the chloride single ion under the same experimental conditions by substituting them into the material balance expression given by equation (68). Tables 10 and 11 summarize all the calculations described above. The values of the volume change for the extraction for the lower range are presented in Figure 7. Those for the higher range were extrapolated by assuming linear behavior. The values for the distribution coefficients obtained experimentally are shown in Figures 2 and 3. Table 10 shows the calculation of the approximate cobaltous chloride concentration in the equilibrated aqueous phase using equation (69). Table 11 shows the solution to equation (68). No significant difference was observed between the HCl concentration and the free chloride ion concentration in the aqueous phase. This can be explained by noting that the cobaltous chloride concentrations are considerably low and the bulk of the chloride concentration is due to the presence of the hydrochloric acid electrolyte.

Once the values of the extracted TBP concentration in the aqueous phase, the degree of complexation of the neutral complex and the cobalt distribution coefficients determined experimentally are known the value of the effective liquid-liquid extraction equilibrium constants for both mechanisms can be calculated. The calculations using a linear regression technique are presented in Tables 12 to 20.

Table 10. Calculation of approximate cobaltous chloride concentration in the aqueous phase for
 $(\text{Co})_I = 1 - 9 \times 10^{-3}$ moles/liter

Reference point No.	$(\text{HCl})_A$	Max ΔV %	V_A (ml)	V_O (ml)	K_D	$(\text{Co})_A = \frac{(\text{Co})_I V_I}{V_A + K_D V_O} \times 10^3$
1	1.0	2.75	9.725	10.275	0.0007	1.027 - 9.248
2	1.5	3.15	9.685	10.315	0.0010	1.031 - 9.283
3	2.0	3.87	9.613	10.387	0.0013	1.039 - 9.349
4	2.5	4.95	9.505	10.495	0.0030	1.049 - 9.437
5	3.0	6.43	9.357	10.643	0.0060	1.061 - 9.553
6	3.5	7.40	9.260	10.740	0.0100	1.067 - 9.608
7	4.0	8.54	9.146	10.854	0.0190	1.069 - 9.623
8	4.5	9.48	9.052	10.948	0.0360	1.059 - 9.527
9	5.0	10.30	8.970	11.030	0.0750	1.021 - 9.186
10	5.5	11.05	8.895	11.105	0.1450	0.9519 - 8.567
11	6.0	11.68	8.832	11.168	0.2700	0.8441 - 7.597
12	6.5	12.28	8.772	11.228	0.4500	0.7233 - 6.510
13	7.0	12.84	8.716	11.284	0.7000	0.6018 - 5.417
14	7.5	13.25	8.675	11.325	1.075	0.4796 - 4.317

Table 10. Continued

Reference point No.	(HCl) _A	Max ΔV %	V _A (ml)	V _O (ml)	K _D	$(Co)_A = \frac{(Co)_I V_I}{V_A + K_D V_O} \times 10^3$
15	8.0	13.96	8.604	11.396	1.314	0.4241 - 3.817
16	8.5	14.52	8.548	11.452	1.450	0.3976 - 3.578
17	9.0	15.08	8.492	11.508	1.520	0.3848 - 3.464
18	9.5	15.64	8.436	11.564	1.450	0.3968 - 3.571
19	10.0	16.20	8.380	11.620	1.160	0.4575 - 4.117
20	10.5	16.76	8.324	11.676	1.018	0.4948 - 4.453
21	11.0	17.32	8.268	11.732	0.9100	0.5279 - 4.751
22	11.5	17.88	8.212	11.788	0.8300	0.5557 - 5.001

Table 11. Calculation of chloride single ion concentration in the equilibrium aqueous phase

$$(\text{Co})_{\text{I}} = 9 \times 10^{-3} \text{ M} \quad (\text{HCl} \cdot \text{TBP})_{\text{A}} \sim 1.6 \times 10^{-3} \text{ M}$$

Reference point No.	$(\text{HCl})_{\text{A}}$	$(\text{Co})_{\text{A}} \times 10^3$	α_0	α_1	α_3	α_4	$(\text{Cl}^-)_{\text{A}}$
1	1.0	9.248	0.975	0.048	~ 0	~ 0	1.017
2	1.5	9.283	0.948	0.073	~ 0	~ 0	1.517
3	2.0	9.349	0.914	0.100	~ 0	~ 0	2.016
4	2.5	9.437	0.865	0.130	~ 0	~ 0	2.516
5	3.0	9.553	0.820	0.160	~ 0	~ 0	3.016
6	3.5	9.608	0.760	0.192	~ 0	~ 0	3.515
7	4.0	9.623	0.697	0.225	~ 0	~ 0	4.010
8	4.5	9.527	0.625	0.260	~ 0	~ 0	4.513
9	5.0	9.186	0.545	0.289	~ 0	~ 0	5.011
10	5.5	8.567	0.446	0.303	0.004	~ 0	5.509
11	6.0	7.597	0.343	0.300	0.038	~ 0	6.006
12	6.5	6.510	0.245	0.279	0.070	~ 0	6.505
13	7.0	5.417	0.160	0.220	0.110	0.020	7.002
14	7.5	4.317	0.080	0.143	0.160	0.068	.501
15	8.0	3.817	0.007	0.080	0.220	0.125	7.995
16	8.5	3.578	~ 0	0.034	0.310	0.185	8.493
17	9.0	3.464	~ 0	~ 0	0.370	0.246	8.991
18	9.5	3.571	~ 0	~ 0	0.400	0.310	9.490
19	10.0	4.117	~ 0	~ 0	0.413	0.378	9.990
20	10.5	4.453	~ 0	~ 0	0.414	0.445	10.490

Table 11. Continued

Reference point No.	$(\text{HCl})_A$	$(\text{Co})_A \times 10^3$	α_o	α_1	α_3	α_4	$(\text{Cl}^-)_A$
21	11.0	4.751	~ 0	~ 0	0.400	0.517	10.990
22	11.5	5.001	~ 0	~ 0	0.375	0.595	11.484

Figure 7. Organic phase volume percent increase versus the equilibrium hydrochloric acid concentration in the aqueous phase for the system HCl-H₂O-TBP at 25 °C (lower range)

Table 12. Calculation of the cobaltous chloride liquid-liquid effective extraction equilibrium constant for the system $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ using α_2 values based on Belousov's data as given in Figure 5

Model: $K_D = k_1' \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2$

$(\text{HCl} \cdot \text{TBP})_A = 1.6 \times 10^{-3} \text{M}$

Reference point No.	$(\text{HCl})_A$	α_2	K_D	$k_1' \times 10^{-6}$
1	5.5	0.040	0.145	1.3942
2	6.0	0.075	0.270	1.3846
3	6.5	0.120	0.450	1.4423
4	7.0	0.170	0.700	1.7446
5	7.5	0.237	1.075	1.6846
6	8.0	0.300	1.314	1.7990
7	8.5	0.310	1.450	2.0879
8	9.0	0.280	1.520	2.2308
9	99.5	0.250	1.450	1.9398
10	10.0	0.230	1.160	1.9398
11	10.5	0.200	1.018	1.9577
12	11.0	0.160	0.910	2.1875
13	11.5	0.135	0.830	2.3647

Table 13. Calculation of the cobaltous chloride liquid-liquid effective extraction equilibrium constant for the system $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ using α_2 values from the regression Equations (65), (66), and (67)

Model: $K_D = k_1' \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2$

$(\text{HCl} \cdot \text{TBP})_A = 1.6 \times 10^{-3} \text{M}$

Reference point No.	$(\text{HCl})_A$	α_2	K_D	$k_1 \times 10^{-6}$
1	5.5	0.0182	0.145	3.1142
2	6.0	0.0615	0.270	1.7149
3	6.5	0.1154	0.450	1.5232
4	7.0	0.1716	0.700	1.5934
5	7.5	0.2220	1.075	1.8915
6	8.0	0.2585	1.314	1.9856
7	8.5	0.2728	1.450	2.0762
8	9.0	0.2568	1.520	2.3166
9	9.5	0.2481	1.450	2.2830
10	10.0	0.2205	1.160	2.0550
11	10.5	0.1908	1.018	2.0836
12	11.0	0.1592	0.910	2.2328
13	11.5	0.1255	0.830	2.5834

The model Equation (59) for mechanism 1 was solved for the effective liquid-liquid extraction equilibrium constant (k'_1) to give

$$k'_1 = \frac{K_D}{\alpha_2 (\text{HCl} \cdot \text{TBP})_A^2} \quad (70)$$

as given in Tables 12 and 13. The values for the degree of complexation for CoCl_2 , α_2 , based on Belousov's data were used in Table 12. No data was reported for HCl concentrations below 5.5M. The values of α_2 obtained using the regression Equations (65), (66), and (67) were used in Table 13. The HCl $\cdot$ TBP concentration as given by Higgins, et al. (22) is $1.6 \times 10^{-3}\text{M}$. The experimental cobalt distribution coefficients obtained in this investigation are shown in Figure 3 and are also given in Tables 12 and 13. Substitution of these values for each reference point yielded a value of k'_1 that corresponded only to the experimental conditions (HCl concentration in the aqueous phase) identified by that number. The fluctuation of the k'_1 values was from 1.3846×10^6 to 2.3647×10^6 in Table 12 and from 1.5232×10^6 to 3.1142×10^6 in Table 13. No particular trend was observed in either case. These are good indications to support the assumption of having a constant activity coefficient ratio.

A linear regression analysis of the data given in Tables 12 and 13 gave the results presented in Tables 14 and 15 respectively. The value of the parameter C_1 in the linear regression model

$$K_D = C_1 + C_2 \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2 + \epsilon \quad (71)$$

was taken to be zero after a statistical student t test was performed as indicated in Tables 16 and 17. From the previous treatment the value of k'_1 was determined for the cases described in Tables 12 and 13. These

Table 14. Results of the linear regression fit of the data presented in Table 12

Linear regression model used

$$K_D = C_1 + C_2 \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2 + \epsilon$$

where

C_1 = constant = intercept

$C_2 = k'_1$ = slope

ϵ = error (independent random variable normally distributed with mean equal to zero)

Linear regression fit

Coefficient	Coefficient estimate value	Coefficient standard deviation
C_1	$- 3.74 \times 10^{-2}$	9.61×10^{-2}
C_2	1.9910×10^6	1.7921×10^5

Analysis of variance table

Source of variance	Degrees of freedom (V)	Sum of squares
Regression	1	2.2591
Error	11	0.2014
Total	12	2.4605

R^2 = regression coefficient = 0.9182

Table 15. Results of the linear regression fit of the data presented in Table 13

Linear regression model used

$$K_D = C_1 + C_2 \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2 + \epsilon$$

where

C_1 = constant = intercept

$C_2 = k'_1$ = slope

ϵ = error (independent random variable normally distributed with mean equal to zero)

Linear regression fit

Coefficient	Coefficient estimate value	Coefficient standard deviation
C_1	$- 3.20 \times 10^{-2}$	8.51×10^{-2}
C_2	2.1387×10^6	1.7109×10^5

Analysis of variance table

Source of variance	Degrees of freedom (V)	Sum of squares
Regression	1	2.2986
Error	11	0.1618
Total	12	2.4604
R^2 = regression coefficient = 0.9342		

Table 16. Statistical procedure for testing the hypothesis of having a true value of the intercept (C_1) in the linear regression model used in Table 14 equal to zero

Test used

Student's T Test

Hypothesis

The true value of C_1 in the linear regression model equation

$K_D = C_1 + C_2 \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2 + \epsilon$ for the data in Table 14 is equal to zero. Hence, $H: C_1 = 0$

Alternate hypothesis

The true value of C_1 is not equal to zero. Hence, $H_A: C_1 \neq 0$ (two sided alternative hypothesis)

Level of significance for the test (ℓ)

$\ell = 0.05$

Test statistic computation

$$T = \frac{c_1 - C_1}{S_{C_1}}$$

where

c_1 = estimated value of intercept C_1

C_1 = true value of the intercept

S_{C_1} = standard deviation for the coefficient C_1

From hypothesis, $C_1 = 0$

From Table 14, $c_1 = -3.74 \times 10^{-2}$

$$S_{C_1} = 9.61 \times 10^{-2}$$

$$T = \frac{-3.74 \times 10^{-2} - 0}{9.61 \times 10^{-2}}$$

$$T = -0.3892$$

Table 16. Continued

Critical region for test statistic

$$|T| > t_{\alpha/2, V}$$

From a table of critical values of the t distribution (39) with

$$\alpha/2 = 0.025$$

$$V = 11$$

we have

$$t_{0.025, 11} = 2.201. \quad \text{The critical region, therefore, is } |T| > 2.201.$$

Since $|T| = 0.3892$, the test statistic does not fall in the critical region.

Conclusion

Accept the hypothesis that the true value of the intercept (C_1) in the linear regression model is equal to zero. Therefore, we can write

$$K_D = k'_1 \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2$$

where

$$k'_1 = 1.9910 \times 10^6$$

Table 17. Statistical procedure for testing the hypothesis of having a true value of the intercept (C_1) in the linear regression model used in Table 15 equal to zero

Test used

Student's T Test

Hypothesis

The true value of C_1 in the linear regression model equation

$K_D = C_1 + C_2 \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2 + \epsilon$ for the data in Table 15 is equal to zero. Hence, $H: C_1 = 0$

Alternative hypothesis

The true value of C_1 is not equal to zero. Hence, $H_A: C_1 \neq 0$ (two sided alternative hypothesis)

Level of significance for the test (ℓ)

$\ell = 0.05$

Test statistic computation

$$T = \frac{c_1 - C_1}{S_{C_1}}$$

where

c_1 = estimated value of intercept C_1

C_1 = true value of the intercept

S_{C_1} = standard deviation for the coefficient C_1

From hypothesis, $C_1 = 0$

From Table 15, $c_1 = - 3.20 \times 10^{-2}$

$$S_{C_1} = 8.51 \times 10^{-2}$$

$$T = \frac{- 3.20 \times 10^{-2} - 0}{8.51 \times 10^{-2}}$$

$$T = - 0.3760$$

Table 17. Continued

Critical region for test statistic

$$|T| > t_{\ell/2, V}$$

From a table of critical values of the t distribution (39) with

$$\ell/2 = 0.025$$

$$V = 11$$

we have

$$t_{0.025, 11} = 2.201. \quad \text{The critical region, therefore, is } |T| > 2.201.$$

Since $|T| = 0.3760$, the test statistic does not fall in the critical region.

Conclusion

Accept the hypothesis that the true value of the intercept (C_1) in the linear regression model is equal to zero. Therefore, we can write

$$K_D = k_1' \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2$$

where

$$k_1' = 2.1387 \times 10^6$$

values were averaged and taken as the value of k'_1 for the $\text{CoCl}_2\text{-HCl-TBP}$ system. This averaging procedure was statistically tested in Tables 18 and 19. A value of k'_1 of 2.0648×10^6 was accepted as the true value for the effective liquid-liquid extraction equilibrium constant.

The model Equation (61) for mechanism 2 can be written as

$$k'_2 = \frac{K_D}{\alpha_2 (\text{HCl} \cdot \text{TBP})_0^2} \quad (72)$$

Table 20 gives the solution to Equation (72) for α_2 values based on Belousov's data given in Figure 5. When the variation of the $\text{HCl} \cdot \text{TBP}$ in the organic phase with the aqueous HCl equilibrium concentration was taken into account the ' range for the k'_2 was from 1.480 to 3.417×10^{-1} for values of HCl ranging from 5.5M to 11.5M respectively. However, a strong trend was observed in these values. The k'_2 values decreased significantly as the HCl concentration in the aqueous phase increased. This led to the rejection of the assumption that the quotient of activity coefficients for mechanism 2 is approximately constant. The order of magnitude of this presumed constant is much lower than that corresponding to mechanism 1. It can, therefore, be expected that mechanism 1 is dominant in the cobaltous chloride liquid-liquid extraction with TBP.

After the model was used to determine the liquid-liquid equilibrium constant, the distribution coefficients at other experimental conditions could now be predicted if all other parameters in the model can be estimated either experimentally or from published data. A practical application of these models would be to approximate the HCl electrolyte

Table 18. Statistical procedure for testing the hypothesis of having equal true value of the slope ($C_2 = k_1'$) in the linear regression models given in Tables 14 and 15

Test used

Student's T Test

Hypothesis

The true value of the liquid-liquid extraction equilibrium constant, that is, the slope (C_2) in the linear regression model equation $K_D =$

$C_2 \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2 + \epsilon$ for Table 14 is equal to that for Table 15. Hence,

$H: C_2 \text{ (Table 14)} = C_2 \text{ (Table 15)}$

Alternative hypothesis

The true value of C_2 is dependent on the set of data used to solve for the linear regression constants. Hence, $H_A: C_2 \text{ (Table 14)} \neq C_2 \text{ (Table 15)}$

(two sided alternative hypothesis)

Level of significance of the test (α)

$\alpha = 0.05$

Test statistic computation

$$T = \frac{c_2 \text{ (Table 14)} - c_2 \text{ (Table 15)}}{\sqrt{S_p^2 \left(\frac{2}{n}\right)}}$$

where

c_2 = estimated value of the slope C_2

S_p^2 = pooled estimate of the variance for the coefficient C_2

From Tables 14 and 15

$$S_p^2 = \frac{(1.7921 \times 10^5)^2 + (1.7109 \times 10^5)^2}{2} = 3.0694 \times 10^{10}$$

Therefore,

Table 18. Continued

$$T = \frac{1.9910 \times 10^6 - 2.1387 \times 10^6}{\sqrt{3.0694 \times 10^{10} \left(\frac{2}{13}\right)}} = \frac{-1.477 \times 10^5}{6.872 \times 10^4} = -2.150$$

$V = \text{degrees of freedom} = 11$

Assumption: σ^2 (Table 14) = σ^2 (Table 15)

Critical region for test statistic

$$|T| > t_{\ell/2, V}$$

From a table of critical values of the t distribution (39) with $\ell/2 = 0.025$ and $V = 11$ we have $t_{0.025, 11} = 2.201$. The critical region, therefore, is $|T| > 2.201$. Since $|T| = 2.150$, the test statistic does not fall in the critical region.

Conclusion

Accept the hypothesis that the true value of the slope (C_2) in the linear regression model given in Table 14 is equal to that given in Table 15. The true value of C_2 can be now taken as the average value of the two coefficients. Therefore, we can write

$$K_D = k_1' \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2$$

where

$$C_2 = k_1' = \frac{1.9910 \times 10^6 + 2.1387 \times 10^6}{2} = 2.0648 \times 10^6$$

Table 19. Statistical procedure for testing the assumption of having equal true value of the variance (σ) in the linear regression models given in Tables 14 and 15

Test used

F Test

Hypothesis

The assumption of having equal variances in the linear regression models given in Tables 14 and 15 is valid. Hence, $H: \sigma^2 \text{ (Table 14)} = \sigma^2 \text{ (Table 15)}$ or $H: \sigma_1^2 = \sigma_2^2$ where the subscripts 1 and 2 refer to Tables 14 and 15 respectively.

Alternative hypothesis

The assumption described above does not apply. Hence, $H_A: \sigma_1^2 \neq \sigma_2^2$ (two sided alternative hypothesis)

Level of significance (α)

$$\alpha = 0.10$$

Test statistic computation

$$F = \frac{S_1^2}{S_2^2} = \frac{(1.7921 \times 10^5)^2}{(1.7109 \times 10^5)^2} = 1.0971$$

where

$$V_1 = 11$$

$$V_2 = 11$$

Critical region for test statistic

$$F < f_{1-\alpha/2, V_1, V_2}$$

$$F > f_{\alpha/2, V_1, V_2}$$

From a table of critical values of the f distribution (39) with $\alpha/2 = 0.05$, $V_1 = 11$, and $V_2 = 11$ we have,

Table 19. Continued

$$f_{0.05,11,11} = 2.82$$

$$f_{0.95,11,11} = \frac{1}{f_{0.05,11,11}} = \frac{1}{2.82} = 0.3546$$

The critical region, therefore, is $F < 0.3546$ and $F > 2.82$. Since $F = 1.0971$, the test statistic does not fall in the critical region.

Conclusion

The assumption of equal variances made in Table 18 is accepted to a 0.10 level of significance.

Table 20. Calculation of the cobaltous chloride liquid-liquid effective extraction equilibrium constant for the system $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ using α_2 values based on Belousov's data as given in Figure 5

Model: $K_D = k'_2 \alpha_2 (\text{HCl} \cdot \text{TBP})_O^2$

Reference point No.	$(\text{HCl})_A$	α_2	$(\text{HCl} \cdot \text{TBP})_O$	K_D	$k'_2 \times 10^1$
1	5.5	0.040	1.565	0.145	14.800
2	6.0	0.075	1.784	0.270	11.311
3	6.5	0.120	2.005	0.450	9.328
4	7.0	0.170	2.227	0.700	8.3025
5	7.5	0.237	2.450	1.075	7.557
6	8.0	0.300	2.670	1.314	6.144
7	8.5	0.310	2.890	1.450	5.600
8	9.0	0.280	3.114	1.520	5.598
9	9.5	0.250	3.342	1.450	5.193
10	10.0	0.230	3.568	1.160	3.962
11	10.5	0.200	3.793	1.018	3.538
12	11.0	0.160	4.018	0.910	3.523
13	11.5	0.135	4.242	0.830	3.417

concentration needed in the initial aqueous solution for obtaining a certain degree of extraction.

From Tables 18 and 19 we concluded that the value for k'_1 is approximately 2.0648×10^6 when mechanism 1 is assumed to be predominant. The model stated in Equation (59) now takes the form

$$K_D = 2.0648 \times 10^6 \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2 \quad (73)$$

where the numerical value for the effective liquid-liquid extraction equilibrium constant has been substituted for k'_1 . Furthermore, the concentration of $\text{HCl} \cdot \text{TBP}$ in the aqueous phase can be assumed to be approximately constant. Based on Higgins, et al. (22) work it was accepted that the concentration of $\text{HCl} \cdot \text{TBP}$ in the aqueous phase is equal to the solubility of TBP in pure water. They reported that the $\text{HCl} \cdot \text{TBP}$ concentrations did not vary significantly with HCl concentrations in the aqueous phase. As previously discussed the reported value for the $\text{HCl} \cdot \text{TBP}$ concentration is $1.6 \times 10^{-3} \text{M}$. This value can be conveniently introduced into Equation (73) to give

$$K_D = 2.0648 \times 10^6 \alpha_2 (1.6 \times 10^{-3})^2 \quad (74)$$

Simplifying Equation (74), it can be shown that a thermodynamic model for the single component extraction system of cobalt from cobaltous chloride in HCl solutions into organic TBP can be represented as

$$K_D = 5.2859 \alpha_2 \quad (75)$$

DISCUSSION OF RESULTS

The Liquid-Liquid Extraction of Cobaltous Chloride
by Tributyl Phosphate

In this investigation, the solvent extraction experiments were conducted with initial cobalt concentrations from 1×10^{-3} M to 9×10^{-3} M. Various investigators (12, 23, 30) have shown that the change in the value of the distribution coefficient is negligible as the concentration of metal increases from 10^{-6} M to 10^{-1} M. It was observed that solutions of cobaltous chloride less than 5.5 M exhibit a pink color while those in HCl concentrations greater than 5.5 M display a blue color. The pink color of the lower HCl molarity cobaltous solutions has been attributed (22) to the presence of the free Co^{++} ion and the blue color to the $\text{CoCl}_4^{=}$ species. This explanation is consistent with the curves presented in Figure 8.

The large amount of information that has been published on the extraction of mineral acids, including HCl, from aqueous solutions by TBP is helpful in explaining the considerable changes in volume for the CoCl_2 -HCl- H_2O -TBP system that were observed during the experimental stage of this investigation. The changes in volume are due to the extraction of HCl and H_2O in significant amounts to the organic phase. Figure 6 graphically describes the amount of H_2O and HCl extracted to the organic phase in the HCl- H_2O -TBP system at 25 °C as measured by Hardy (20). The change in volume of the organic phase as a function of the HCl equilibrium concentration in the aqueous phase as measured by Irving and Edgington (23) is shown in Figure 7. The considerable amount of extraction of HCl and H_2O into

Figure 8. Degree of complexation (α_n) for cobalt and chloride in the aqueous phase and the cobalt distribution coefficient (K_D) versus the equilibrium hydrochloric acid concentration in the aqueous phase

of 1.52 in a 9.0 M HCl solution. This value is slightly higher than those observed by other investigators as shown in Figure 5. However, the experimental conditions were slightly different. The atomic absorption spectrometry technique was introduced in this investigation as a method to obtain the cobalt concentrations in both phases.

The Modeling of the Liquid-Liquid Extraction Phenomena

A functional model has been proposed to describe the behavior of the CoCl_2 -HCl- H_2O -TBP system. This model should predict to a reasonable degree of confidence the distribution coefficient of cobalt for the system under consideration at different experimental conditions. Two mechanisms have been examined to relate the complexation of cobaltous chloride in aqueous HCl solutions to its extraction by TBP.

In order to test the obtained model and its corresponding assumptions, an attempt to predict the experimental distribution coefficients for cobalt under the conditions of this investigation was made. The predictions are given in Table 21 for α_2 based on Belousov's data from Figure 5. Table 22 gives the predictions of the model when the α_2 values from the regression Equations (65), (66), and (67) were used.

If a plot of the distribution coefficient of cobalt is compared to a plot of the degree of formation of the various cobaltous chloride complexes as suggested by Belousov, et al. (9) the graph presented in Figure 9 is obtained. It can be observed from this graph that the cobalt distribution coefficient curve follows a trend in its shape similar to that of the degree of complexation of the neutral species, CoCl_2 , in aqueous HCl solutions. This is a very significant result since it basically supports the findings of this investigation and those of E. A. Belousov and coworkers (7) who also proposed mechanism 1 as the predominant mechanism.

A thermodynamic model for the solvent extraction cobaltous chloride from aqueous HCl solutions by TBP is therefore given by:

Table 21. Model predictions for the cobalt distribution coefficient for the system $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ assuming mechanism 1 is predominant with α_2 values based on Belousov's data given in Figure 5

Reference point No.	$(\text{HCl})_A$	α_2	K_D model	K_D experimental
1	5.5	0.040	0.2038	0.1450
2	6.0	0.075	0.3823	0.2700
3	6.5	0.120	0.6116	0.4500
4	7.0	0.170	0.8665	0.7000
5	7.5	0.232	1.2078	1.0750
6	8.0	0.300	1.3291	1.3140
7	8.5	0.310	1.5800	1.4500
8	9.0	0.280	1.4271	1.5200
9	9.5	0.250	1.2742	1.4500
10	10.0	0.230	1.1723	1.1600
11	10.5	0.200	1.0194	1.0180
12	11.0	0.160	0.8155	0.9100
13	11.5	0.135	0.6881	0.8300

$$K_D = \frac{k'_1 \beta_2 (\text{Cl}^-)_A^2 (\text{HCl} \cdot \text{TBP})_A^2}{1 + \beta_1 (\text{Cl}^-)_A + \beta_2 (\text{Cl}^-)_A^2 + \beta_3 (\text{Cl}^-)_A^3 + \beta_4 (\text{Cl}^-)_A^4} \quad (76)$$

where

k'_1 = effective extraction equilibrium constant

β_n = stoichiometric overall stability constants
for the complexes CoCl_n^{2-n}

Table 22. Model predictions for the cobalt distribution coefficient for the system $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ assuming mechanism 1 is predominant with α_2 values obtained from regression Equations (65), (66), and (67)

Reference point No.	$(\text{HCl})_A$	α_2	K_D model	K_D experimental
1	5.5	0.0182	0.0996	0.1450
2	6.0	0.0615	0.3367	0.2700
3	6.5	0.1154	0.6318	0.4500
4	7.0	0.1716	0.9395	0.7000
5	7.5	0.2220	1.2155	1.0750
6	8.0	0.2585	1.4153	1.3140
7	8.5	0.2728	1.4936	1.4500
8	9.0	0.2568	1.4060	1.5200
9	9.5	0.2481	1.3584	1.4500
10	10.0	0.2205	1.2073	1.1600
11	10.5	0.1908	1.0449	1.0180
12	11.0	0.1592	0.8716	0.9100
13	11.5	0.1255	0.6871	0.8300

$(\text{Cl}^-)_A$ = single chloride equilibrium concentration in the aqueous phase. $(\text{HCl})_A$ = HCl equilibrium concentration in the aqueous phase

$(\text{HCl} \cdot \text{TBP})_A$ = concentration of extracted TBP into the equilibrium aqueous phase.

This expression is useful if the stoichiometric overall formation constants are known as a function of the HCl present in the aqueous equilibrated phase or as a function of ionic strength. However, an equivalent convenient form of expressing Equation (74) is by introducing the degree of complexation of CoCl_2 ,

$$K_D = k'_1 \alpha_2 (\text{HCl} \cdot \text{TBP})_A^2 \quad (77)$$

Equation (77) has been used to model the solvent extraction system and the α_2 values were obtained from Figure 5. Regression analysis fit on the values of Belousov, et al. (9) for α_2 give the relations presented as Equations (65), (66), and (67). Figures 9, 10, and 11 provide a graphical comparison of the model predicted values and those obtained experimentally. Figure 10 represents the results given in Table 14 where α_2 values used in the model were obtained directly from Figure 5. Those results from Table 15 are given in Figure 11 where the α_2 values were estimated from the regression equations. Figure 12 is a comparison between the values of the distribution coefficients obtained by the model using the α_2 estimated directly from the plot in Figure 5 and those obtained using the regression equations. From the low value for the sum of squares of the error it can be seen that no significant difference is observed, therefore, the use of the regression equations for estimating the α_2 values for model predictions was accepted.

The model was then solved following the same linear regression technique previously discussed using the data published by Ezhovska-Tshebyatovska and Kopach (12) and E. V. Belousov, et al. (9). The results are given in Tables 23 and 24 respectively and are presented in graphical form

Figure 9. Comparison between cobalt distribution coefficients predicted by the model and those measured experimentally in this investigation

Figure 10. Comparison between the distribution coefficient predicted by the model using the degree of complexation of CoCl_2 from Figure 5 and those obtained experimentally in this investigation

Figure 11. Comparison between the distribution coefficient predicted by the model using the regression equations to estimate the degree of complexation of CoCl_2 and those obtained experimentally in this investigation

Figure 12. Difference introduced in the predicted distribution coefficient values by making use of the regression equations to estimate the degree of complexation of CoCl_2

Table 23. Model predictions for the cobalt distribution coefficient for the system $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ based on Ezhovska-Tshebyatovska and Kopach (12) experimental data

Reference point No.	$(\text{HCl})_A$	α_2^a	K_D model	K_D experimental
1	5.5	0.0182	0.089	0.110
2	6.0	0.0615	0.301	0.180
3	6.5	0.1154	0.565	0.280
4	7.0	0.1716	0.840	0.400
5	7.5	0.2220	1.087	0.640
6	8.0	0.2585	1.266	0.950
7	8.5	0.2728	1.336	1.370
8	9.0	0.2568	1.258	1.430
9	9.5	0.2481	1.215	1.150
10	10.0	0.2205	1.080	0.970
11	10.5	0.1908	0.935	0.850
12	11.0	0.1592	0.780	0.820

^aUsing the regression Equations (65), (66), and (67).

Table 24. Model predictions for the cobalt distribution coefficient for the system $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ based on Belousov's, et al. (9) experimental data

Reference point No.	$(\text{HCl})_A$	α_2^a	K_D model	K_D experimental
1	5.5	0.0182	0.092	0.140
2	6.0	0.0615	0.313	0.220
3	6.5	0.1154	0.587	0.330
4	7.0	0.1716	0.873	0.450
5	7.5	0.2220	1.129	0.750
6	8.0	0.2585	1.315	1.280
7	8.5	0.2728	1.388	1.450
8	9.0	0.2568	1.307	1.260
9	9.5	0.2481	1.262	1.140
10	10.0	0.2205	1.122	1.050
11	10.5	0.1908	0.971	0.960
12	11.0	0.1592	0.810	0.790

^aUsing the regression Equations (65), (66), and (67).

Figure 13. Comparison between the distribution coefficient predicted by the model and those obtained experimentally by Ezhovska-Tshebyatovska and Kopach (12)

Figure 14. Comparison between the distribution coefficient predicted by the model and those obtained experimentally by Belousov, et al. (9)

in Figures 13 and 14. Large deviations are observable and the thermodynamic model cobalt distribution coefficient predictions are higher than those experimentally measured by these investigators. This can be due to a systematic error in their experimental technique since the predictions of the model are acceptable within the accuracy levels used in this investigation and are very good for the experimental data obtained in this work.

CONCLUSIONS AND RECOMMENDATIONS

A thermodynamic model has been derived for the liquid-liquid extraction of cobalt (II) in the $\text{CoCl}_2\text{-HCl-H}_2\text{O-TBP}$ system. This model should be useful in predicting the distribution coefficient expected for other experimental conditions provided that either the stoichiometric overall stability constants or the degree of complexation for the neutral species CoCl_2 , are known together with the chloride and tributyl phosphate concentrations in the equilibrated aqueous phase. The model makes use of the stoichiometric formation constants which are directly related to the stability of the various complexes of cobalt in aqueous chloride solutions at a given ionic medium. It had been previously reported that four complexes are formed and that they can be represented by the formulas CoCl^+ , CoCl_2 , CoCl_3^- , and $\text{CoCl}_4^{=}$.

Evidence was found to support the hypothesized mechanism

as being predominant in the solvent extraction of cobaltous chloride from aqueous HCl solutions by TBP. The effective liquid-liquid extraction equilibrium constant was estimated to be $k_1' = 2.0648 \times 10^6$. This value was determined by using the experimentally measured distribution coefficients in the system and the estimated concentrations of the pertinent species. These data were analyzed using a linear regression technique.

The model can be derived for any system of mononuclear complexes in aqueous solutions extracted to an organic solvent. The principal limitations of the model are as follows:

- a. The complexes formed must be mononuclear and properly identified
- b. The mechanism of their extraction into a suitable organic solvent must be known
- c. The quotient of activity coefficient of neutral molecules in the expression shall be assumed to be a constant
- d. The concentration of the species in the model expression will have to be known
- e. Either the stoichiometric stability constant for all the complexes formed or the degree of formation for the extractable species must be available.

Verification of the model was achieved by predicting the distribution coefficients for the extraction data published by several investigators in addition to those obtained in this investigation. A reasonable estimate was found and the model was accepted with its corresponding assumptions. The critical assumption, namely that the ratio of activity coefficients of the neutral molecules in the proposed mechanism reaction varies slightly with the hydrochloric acid concentrations has been found to be a very good assumption in this particular system and experimental conditions.

It has been observed that in the solvent extraction of cobaltous chloride by TBP considerable volume increase of the organic phase occurs. This can be explained by the extraction of water and HCl into

the organic TBP layer. Because of these phenomena the concentration of cobalt in the equilibrium aqueous phase after extraction in some cases exceeded the concentration of cobalt in the initial aqueous solution.

The solubility of TBP in the aqueous phase is small and it can be considered very similar to that of TBP in pure water, ca. 1.6×10^{-3} moles/liter. The chloride single ion concentration in the equilibrium aqueous phase can be approximated by the HCl concentration without introducing significant deviations within the cobaltous chloride concentration range studied. This concentration range is important since the cobalt distribution coefficient value reached a maximum value at about 9.0 M. The extraction of cobalt was lower for HCl concentrations below and above 9.0 M. This implies that the optimum conditions for the extraction of cobalt in the system studied required an HCl concentration in the range of 8.5 M to 9.5 M.

This investigation integrated the published data on the CoCl_2 -HCl- H_2O -TBP liquid-liquid extraction system and the theory of cobaltous chloride complex formation. An interesting problem for further research is the extension of the results of this investigation to the CoCl_2 - NiCl_2 -HCl- H_2O -TBP system.

Ezhovska-Tshebyatovska and coworkers have reported the interesting fact that the use of calcium chloride together with HCl might improve the separation of cobalt from aqueous solutions. They suggested that if such is the case a quantitative separation of cobalt from nickel would be highly dependent on the concentrations of both electrolytes in the aqueous phase. It has been previously reported that nickel is not extracted from aqueous HCl solutions in significant amounts by TBP.

On the basis of these findings a challenging problem would be to extend the model to a multicomponent model that considers the presence of the new salting-out agent, CaCl_2 , and that of NiCl_2 in the system. Such a development may not be theoretically simple but if a reasonably simple model can be developed it should be highly functional in finding the optimum conditions for the separation of cobalt and nickel by liquid-liquid extraction.

2

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