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SELECTIVE METAL-ION EXTRACTION FOR MULTIPLE-ION LIQUID-LIQUID EXCHANGE REACTIONS

Final Report
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L. L. Tavlarides

NOTICE

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ABSTRACT

This research in hydrometallurgical solvent extraction is to develop a fundamental means to predict selectivity during simultaneous solvent extraction of multiple metal ions when the kinetic rates and thermodynamic equilibria both do not favor the desired metal. To this end the chemical kinetics and thermodynamic chemical equilibria models for the system copper-iron-acid sulfate solutions extracted by β-alkenyl-8-hydroxy quinoline in xylene are studied. These models can be employed with appropriate design equations to predict selectivity factors for two phase contactors.

In the first two years, a thermodynamic equilibrium model was developed to describe the distribution of copper metal ions between the aqueous and organic phases. The model includes the aqueous phase ionic equilibria, is temperature dependent, and accounts for impurities in the extractant. The enthalpy of the reaction and the entropy change are -1275 cal/g-mol and 3.46 cal/g-mol, °K respectively.

A kinetic model was also obtained for the copper-sulfate-β-alkenyl-8-hydroxy quinoline-xylene system by analysis of rate data obtained from the liquid jet recycle reactor. The flux of copper is not mass transfer limited but either reaction controlled or mass transfer and reaction controlled. A four parameter kinetic model is determined for the forward rate. The mechanism which supports the model is based on an interfacial reaction where the adsorbed organic chelation acid is undissociated and the rate limiting step is the formation of CuR^+.

The work completed and in progress during the first half of the third funding period is on chemical equilibria studies for the iron-acid-sulfate-β-alkenyl-8-hydroxy quinoline-xylene system. An aqueous phase ionic equilibrium

model is available which can be used to calculate concentration of various Fe(III) ionic species present. Iron extraction data were obtained using both the AKUFVE, a high intensity stirrer with an in line centrifugal separator, and a shaker bath apparatus. Analysis of the data to determine a thermodynamic quilibrium model is in progress.

INTRODUCTION

The purpose of the research in hydrometallurgical solvent extraction is to develop a fundamental means to predict selectivity during simultaneous solvent extraction of multiple metal ions. The approach is to understand the interplay between mass transfer with interfacial chemical reaction and chemical equilibria for multiple metal systems. The results will provide a rational appraoch for the design of multiple solvent extraction processes [1].

A four point program is in progress with the following objectives:

- Select a model system
- Obtain distribution data for proposed thermodynamic models
- Conduct chemical reaction experiments and analyze to obtain kinetic models
- Compare predictions of selectivity with experimental results for single stage contactors and conduct an analysis for multiple stage operation

The program is in the middle of the third year. This final report is given now as the principal investigation has accepted a position with Syracuse University during this funding period and it is necessary to establish a contract with Syracuse University. The original objectives of the program are not fulfilled but substantial progress has been made. The report is divided into two sections to emphasize the results completed in the first two years and that during the first half of the third period. Nevertheless, overlap exists both ways. It is noted that some loss time occurred this summer and fall as equipment had to be transferred and setup from Illinois Institute of Technology to Syracuse University.

PROGRESS DURING JUNE, 1979 to MAY, 1981

A. Selection of Model System

The model system selected should exhibit the interplay between kinetics and chemical equilibria in determining the selectivity of a metal ion in a competitive extraction or stripping reactions. The system of copper, iron acid sulfate solutions extracted by β-alkenyl-8-hydroxy quinoline (Kelex 100) in xylene is interesting as the kinetics favor the extraction of copper but the chemical equilibria favor the iron complex. A reversal of flux occurs when the organic acid is limiting the total extraction for the multiple metal system. At 30° - 50° C, the maximum extraction of copper occurs in less than five minutes [2]. Xylene is selected as the solvent because it prevents sulfuric acid extraction by Kelex and aggregation of extractant molecules is suppressed.

B. Chemical Equilibrium Studies for Cu(II)-Sulfuric Acid-Kelex 100 Xylene System

Thermodynamic models have been proposed [1] to predict the distribution of copper and iron at equilibrium between the two phases. Also, the separation factor of these two metals can also be determined by appropriate analysis of equilibrium data. Work is completed on the copper system and the results are discussed below. Work is in progress for the iron system.

A thermodynamic equilibrium model for the Cu(II)-Sulfuric Acid-Kelex 100 Xylene system wad developed as previous work did not appropriately account for the aqueous phase equilibria and impurities contained in the Kelex 100, [3,4,5, 6].

Copper extraction by Kelex 100 may be expressed as

$$Cu^{++} + \overline{HR} \rightleftharpoons \overline{CuR}_n + NH^+ \qquad (1)$$

where $\overline{HR}$ and $\overline{CuR}_n$ represent the chelation acid and metal complex in the organic phase. The thermodynamic equilibrium constant can be expressed as

$$K_{eq} = \frac{a_{\overline{CuR}_n}\, a^n_{H^+}}{a_{Cu^{++}}\, a^n_{\overline{HR}}} = \frac{[\overline{CuR}_n][H^+]^n}{[Cu^{++}][\overline{HR}]^n} \cdot \frac{\gamma_{\overline{CuR}_n}\, \gamma^n_{H^+}}{\gamma_{Cu^{++}}\, \gamma^n_{\overline{HR}}} \qquad (2)$$

where a, the brackets, and γ represent the activity, concentration and activity coefficients, respectfully. By assuming the organic phase species have unity activity, the above can be written the form

$$\ln\left\{\frac{D\alpha_o}{\gamma_{Cu^{++}}}\right\} = \beta_o + \beta_1\left(\frac{1}{T} - \frac{1}{\overline{T}}\right) + \beta_2 \ln\left\{\frac{[\overline{HR}]}{[H^+]\ \gamma_{H^+}}\right\} \qquad (3)$$

where the parameters are $\beta_o = \frac{\Delta S°}{R} - \frac{\Delta H°}{T}$, $\beta_1 = -\frac{\Delta H°}{R}$, $\beta_2 = n$, and $\overline{T}$ is the reference temperature. Here D is the metal distribution ratio between the organic and aqueous phases and α_o is the inverse of the degree of formation. Values of D, $[H^+]$, α_o, $[\overline{HR}]$, $\gamma_{Cu^{++}}$ and γ_{H^+} can be calculated from experimental data and known correlations. Nonlinear regression of equilibrium data permits best estimates of the parameters β_o, β_1, and β_2 from which $\Delta S°$, $\Delta H°$ and n are evaluated.

The compositions of the ionic species are obtained by modelling bisulfate dissociation and copper sulfate dissociation by the method proposed by Freeman and Tavlarides [7].

Extraction experiments were conducted in an Eberback 6250 Shakerbath and analysis of copper is by atomic absorption spectroscopy. Composition and temperature changes studied are Cu [0.005-0.02M], Kelex 100 [0.02-0.06M], $SO_4^=$ [0.05-0.2M], and T [20°,25° and 30°C].

A modified nonlinear regression method of data analysis yields the best correlation to be

$$\ln \left(\frac{D\alpha_o}{Cu^{++}} \right) = 3.83 + 642 \left(\frac{1}{T} - \frac{1}{308} \right) + 2.0 \ln \left(\frac{[\overline{HR}]}{[H^+]\ \gamma_{H^+}} \right) \qquad (4)$$

from which ΔS° and ΔH° are evaluated to be 3.46 cal/g-mol and -1275 cal/g mole respectively.

Further details of the work can be found in the manuscript [8] given in Appendix A.

C. Kinetic Studies for Cu(II)-Sulfuric Acid-Kelex 100 Xylene System

The third phase of the program is to conduct chemical kinetic studies on the copper system, iron system, and the system for both metals reacting simultaneously. Kinetic models are to be developed which are based on realistic mechanistic pathways. A kinetic model has been developed for the copper system and the results follow.

Kinetic studies were conducted on the copper, sulfate-Kelex 100, xylene system using the Liquid Jet Recycle Reactor [1,9]. The LJRR is shown to be an excellent tool to obtain kinetic rate data as the surface area between the phases is precisely known, the effects of mass transfer can be quantified, short contact times exist, and surfactant accumulation at the interface can be controlled.

To analyze the data appropriately it must be determined whether (a) mass transfer controls, (b) reaction controls, or (c) both mass transfer and reaction are both important in controlling the extraction rate.

Analysis of a mass transfer controlled system is accomplished by employing a penetration theory model to analyze copper flux across the jet interface [1,9]. The analysis yields a cubic algebraic equation for the molar rate of transfer of copper, w,

$$a_3w^3 + a_2w^2 + a_1w + a_o = 0 \tag{5}$$

Here the constants $a_j (j = 0,1,2,3)$ are known functions of the jet parameters, bulk concentrations, diffusivities, and the thermodynamic equilibrium coefficient determined in the previous section [10,11]. When the surface reaction is rapid and at equilibrium, the above holds. For a given set of conditions, w can be calculated from eqn. (5), and compared with known experimental values. If the results talley, then mass transfer controls the rate.

For the cases when reaction is slow or of the same order as the mass transfer, then kinetic models based on appropriate mechanistic pathways are postulated and compared with experimental data. A number of models were postulated by considering the pathways of surface adsorption of reactants, surface reaction, and surface desorption of products.

The analysis for slow reactions, again is based on the penetration theory. Here the surface concentrations do not change appreciably down the length of the jet. Thus

$$W = R\,(\overline{C}_j^{\,*})\ \text{Area} \tag{6}$$

where $R(\overline{C}_j^{\,*})$ is the rate of surface reaction, and $\overline{C}_j^{\,*}$ is the vector of average surface concentrations. The surface concentrations can be approximated with an algebraic expression for the case of constant interfacial concentration as discussed earlier [9].

Experiments were conducted on the liquid jet apparatus which consists of an aqueous liquid jet passing downward through a cocurrent, coaxially flowing stream of a less dense organic fluid. The range of experimental conditions were; total copper in the aqueous [0.005-0.02M], total sulfur [0.005-0.06M], Kelex 100 [0.02-0.06M], and temperature levels of [25,35,50°C].

A comparison was made of the calculated copper molar transfer rate with the experimental results assuming mass transfer controls using eqn. (5)[10, 11]. These results indicate that other resistances exist as the ratio of experimental to calculated fluxes range from 1/15 to 1/50.

Kinetic models were postulated based on various mechanistic pathways to compare with the data using linear and nonlinear regression techniques. Screening of twenty-four plausible kinetic rate laws with the use of eqn. (6) was done [10,11].

The results of the study indicates that the extraction rate is not controlled by mass transfer and the regression analysis shows that the rate expression to describe the initial chelation rate is

$$R = \frac{9.42 \times 10^{5}[Cu][HR]}{\{1 + 90[Cu] + 14[\overline{HR}] + 38[H^{+}]\}^{2}} \qquad (7)$$

This kinetic rate law is supported by a mechanism which assumes equilibrium adsorption of all species at the interface. Surface reaction is through an undissociative reaction (the HR does not dissociate at the surface) with formation of CuR^{+} intermediate as the rate determining step.

PROGRESS DURING 6/1/81 - 1/4/82

A. Chemical Equilibrium Model for Iron Sulfuric Acid Kelex 100 Xylene System

The preliminary studies conducted with this system in the first funding period indicate more than one iron species are extracted as organic phase complex. U.V. - visible spectroscopic scans of the iron complex formed in the organic phase at equilibrium support existence of more than one species. Thus a simplified model of the iron extraction equilibrium does not seem possible. To resolve this problem, it is decided to develop a detailed model of the aqueous phase equilibria for iron sulfate solutions. This model can then be used in conjunction with the chemical equilibria models for estimating the distribution of species between the aqueous and organic phases. A similar approach to that given for the copper system is adapted for the iron-sulfate equilibrium studies.

Models for the equilibrium extraction of Fe^{+3} or Fe^{+3} and $FeOH^{+2}$ are presented elsewhere [10] and will not be repeated here.

The work completed during the first half of this last funding period consists of experiments on the two phase equilibria and analysis of the coupled ionic equilibria for the aqueous phase.

<u>Analysis</u>

The pertinent equilibrium reactions for this ferric sulfate system are represented by the following nine equations:

$$Fe_2(SO_4)_3 \overset{K_a}{\rightleftharpoons} 2Fe^{+3} + 3SO_4^{=} \tag{8}$$

$$HSO_4^- \overset{K_b}{\rightleftharpoons} H^+ + SO_4^{=} \tag{9}$$

$$Fe^{+3} + SO_4^{=} \overset{K_c}{\rightleftharpoons} FeSO_4^+ \tag{10}$$

$$Fe^{+3} + HSO_4^- \overset{K_d}{\rightleftharpoons} FeHSO_4^{+2} \tag{11}$$

$$Fe^{+3} + 2SO_4^{=} \overset{K_e}{\rightleftharpoons} Fe(SO_4)_2^- \tag{12}$$

$$Fe^{+3} + H_2O \overset{K_f}{\rightleftharpoons} Fe(OH)^{+2} + H^+ \tag{13}$$

$$2Fe(OH)^{+2} \overset{K_g}{\rightleftharpoons} Fe(OH)_2Fe^{+4} \tag{14}$$

$$Fe^{+3} + 2H_2O \overset{K_h}{\rightleftharpoons} Fe(OH)_2^+ + 2H^+ \tag{15}$$

$$H_2O \overset{K_w}{\rightleftharpoons} H^+ + OH^- \tag{16}$$

These equations can be combined with the total iron balance $[Fe]_T = \sum_{i=1}^{7} [FeX]$, total sulfur balance $[S]_T = \sum_{n=1}^{5} [MS]_i$, the equation of species electroneutrality, and the ionic strength relationship to obtain four nonlinear algebraic equations. The ionic strength dependency of the stability constants is included in this formulation. The independent variables are $[H^+]$, $[SO_4^=]$, $[Fe^{+++}]$ and the ionic strength. These four equations are solved by the secant method [12]. Figures 1 and 2 are plots of the percent dissociation of Fe^{+3} and $FeOH^{+2}$ versus total aqueous phase iron at various total sulfur levels. It is noted that the ratio of total atomic iron to sulfur must be less than 2/3 for meaningful results. Table I lists various aqueous phase species concentrations at extraction conditions performed in the laboratory. The following results are obtained: (a) $FeSO_4^+$ is the predominate species, being one order of magnitude greater than Fe^{+3}; (b) Figure 1 shows that at any total sulfur level, per cent Fe^{+3} formation by dissociation is approximately constant, except near the 2/3 ratio, where the per cent formed decreases. At lower total sulfur (dilute solutions) greater amounts of Fe^{+3} are formed; (c) Figure 2 shows that per cent $FeOH^{+2}$ formed by dissociation varies slightly with total iron, except near the 2/3 ratio, where the formation of this species increases rapidly. At lower total sulfur, greater amounts of $FeOH^{+2}$ are formed.

These results clearly show the highly nonlinear dependency of the per cent dissociation of Fe^{+3} and $FeOH^{+2}$ versus total iron. One cannot assume Fe^{+3} and/or $FeOH^{+2}$ are proportional to $[Fe]_T$ in analysis of equilibrium or kinetic data, particularly in the regions of interest (near the 2/3 ratio).

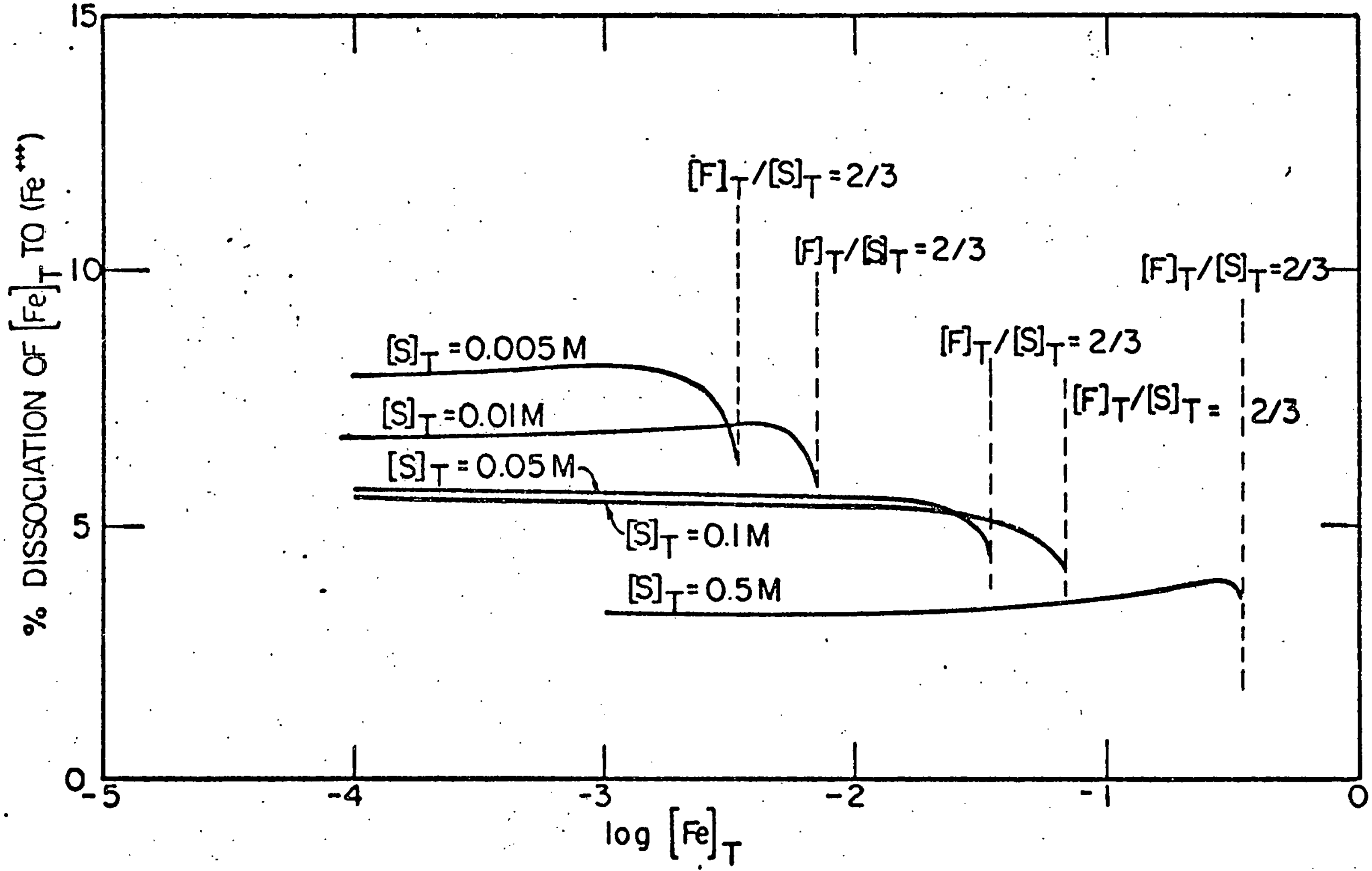
Experiments

Extraction equilibrium data were generated for this ferric sulfate-Kelex

100-xylene system employing either the AKUFVE [13] system or the Eberbach shaker bath. The former instrument is a high intensity stirrer with a high speed centrifuge which separates both phases instantaneously and provides additional mixing. Equal volumes of solutions are used and previously developed experimental methods and treatment of the chemical are employed [12]. Analysis for iron is by A. A. spectroscopy. Experimental conditions under investigation are $[Fe]^T_{aq,i}$ (0.005-0.1M), $[S]^T_{q,i}$ (0.0075-0.15M), $\overline{HR}$ (0.01-0.08M). Part of the experimental results are shown in Table I.

Equilibrium Distribution Studies

The equilibrium experiments are in progress at this writing. A statististical nonlinear regression analysis of the results will be performed with various two phase equilibrium models [10] proposed earlier to obtain an expression for the iron species distribution.



% DISSOCIATION OF [Fe]T TO (Fe+++)
15
10
5
0
-5
-4
-3
-2
-1
0
log [Fe]T
[S]T = 0.005 M
[S]T = 0.01 M
[S]T = 0.05 M
[S]T = 0.1 M
[S]T = 0.5 M
[F]T/[S]T = 2/3
[F]T/[S]T = 2/3
[F]T/[S]T = 2/3
[F]T/[S]T = 2/3
[F]T/[S]T = 2/3

FIGURE 1

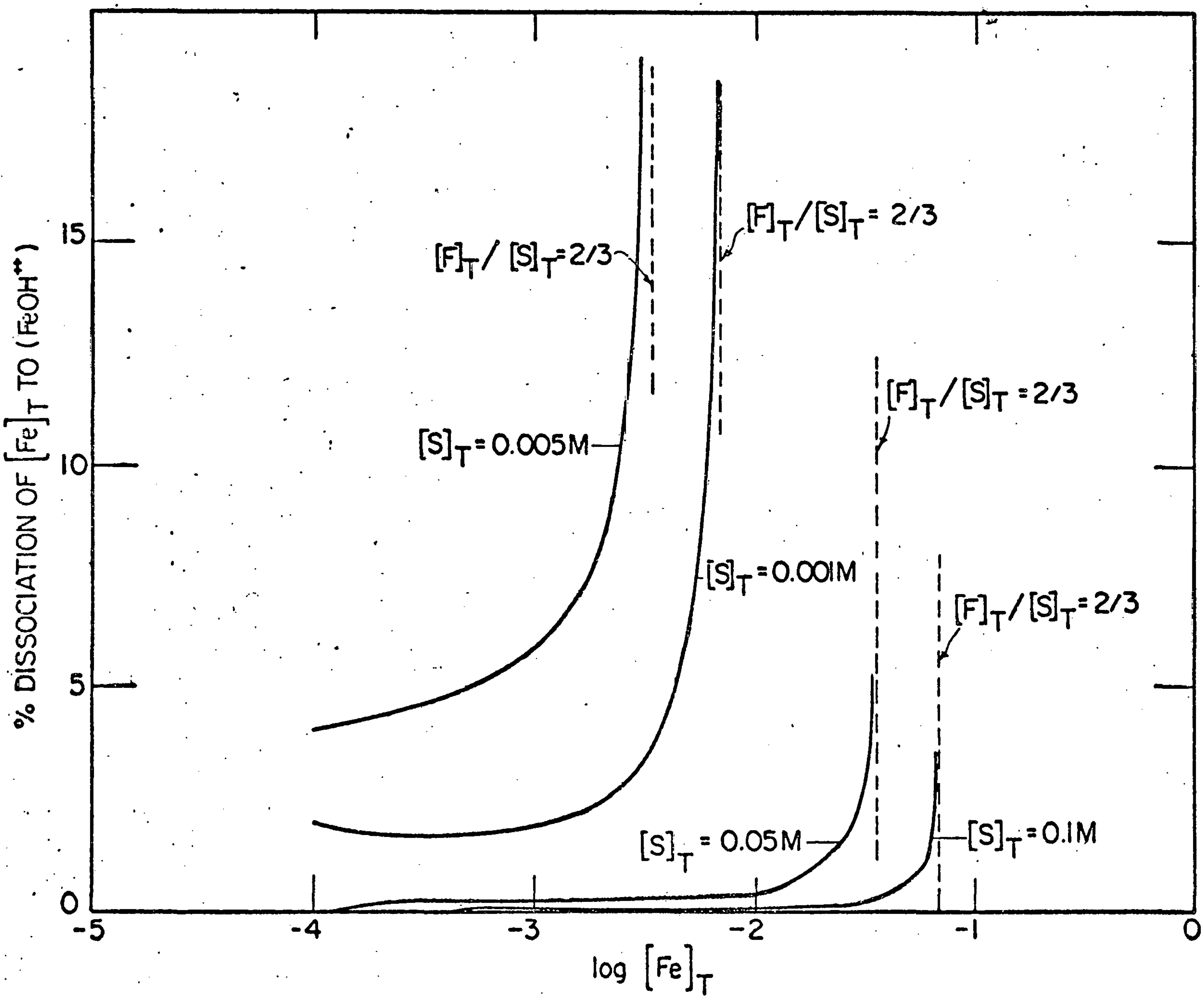

% DISSOCIATION OF $[Fe]_T$ TO $(FeOH^{++})$
0
5
10
15
-5
-4
-3
-2
-1
0
log $[Fe]_T$
$[F]_T/[S]_T = 2/3$
$[F]_T/[S]_T = 2/3$
$[F]_T/[S]_T = 2/3$
$[F]_T/[S]_T = 2/3$
$[S]_T = 0.005M$
$[S]_T = 0.001M$
$[S]_T = 0.05M$
$[S]_T = 0.1M$

FIGURE 2

Table I. Some of Chemical Equilibria data for Iron-Sulfate-Kelex 100-Xylene System

Run(a)	(°C)	Aqueous phase concentration (M)							Organic phase (M)		$D^{(c)}$
No.	Temp.	$[S]_T$	x 10^{-2} $[Fe]_T$	x 10^{-3} $[Fe^{+++}]$	x 10^{-4} $FeOH^{+2}$	x 10^{-2} $FeSO_4^+$	x 10^{-2} $[SO_4^=]$	x 10^{-2} $[H^+]$	x 10^{-2} $[Fe]_T$	$HR^{(b)}$	
A009	25	0.15	8.093	3.738	2.72	6.024	3.54	3.525	1.907	0.04	0.24
A011	25	0.03	0.615	0.354	0.40	0.500	1.118	2.970	1.385	0.06	2.25
A012	25	0.03	1.364	0.764	1.91	1.132	1.060	1.386	0.636	0.02	0.466
A013	25	0.015	0.217	0.137	0.29	0.184	0.726	1.794	0.783	0.04	3.608
A014	25	0.015	0.605	0.386	1.60	0.508	0.639	0.930	0.395	0.01	0.653
A015	25	0.015	0.0454	0.0079	0.04	0.038	0.3367	0.816	0.955	0.08	21.04
B015	25	0.078	3.95	1.950	2.32	3.116	2.163	2.449	1.22	0.02	0.31
B018	25	0.0735	4.00	1.953	3.25	3.163	2.047	1.780	0.90	0.06	0.225
B020	25	0.0102	0.048	0.0323	0.09	0.041	0.571	1.495	0.632	0.06	13.17
B027	25	0.075	0.74	0.4058	0.13	0.572	2.404	8.484	0.360	0.04	0.49
B029	35	0.014	0.36	0.2317	0.67	0.3046	0.654	1.334	0.60	0.04	1.67
B029B	35	0.0048	0.054	0.044	0.29	0.045	0.310	0.68	0.266	0.04	4.93

(a) A, experiments run by Shaker Bath unit; B, experiments run by AKUFVE unit;

(b) Initial Kelex 100 concentration;

(c) Results are based on aqueous phase analysis

PERSONNEL AND PRINCIPAL INVESTIGATOR EFFORT

The personnel employed during this program are:

Research Associates for Masters Degree

1. Mr. K. S. Ho, Illinois Institute of Technology, Chicago, Illinois 60616.
2. Mr. C. K. Lee, Illinois Institute of Technology, Chicago, Illinois 60616.

Special Project Students

1. Dr. E. J. Wang, June, 1979.
2. Mr. S. Agarwal, January - May, 1981.
3. Mr. M. A. Hsia, September - December, 1980.

Research Associates

1. Mr. C. K. Lee, Syracuse University, September, 1981 to present.
2. Mr. S. Agarwal, Syracuse University, January 1, 1982 to present.

Professor L. L. Tavlarides

	AY	SM
6/1/79 - 5/30/80	1.71	1.0
6/1/80 - 5/30/81	1.5	2.25
6/1/81 - 5/30/82	1.0	1.0

PUBLICATIONS AND PRESENTATIONS

1. L. L. Tavlarides, "Modelling and Scaleup of Dispersed Phase Liquid-Liquid Reactors", Chem. Eng. Common, Vol. 8, pp. 133-164 (partial support). Attached in Appendix B.

2. C. K. Lee and L. L. Tavlarides, "Chemical Equilibria Studies on the Copper-Sulfuric Acid Kelex 100-Xylene System", submitted to Metallurgical Trans. B.

3. K. S. Ho, C. K. Lee, and L. L. Tavlarides, "Selective Metal Ion Extraction for Multiple Ion Exchange Reactions in Liquid-Liquid Systems", Paper No. 100, presented at 181st Nat'l ACS Meeting, Atlanta, Georgia, April 2, 1981.

4. K. S. Ho, "Kinetics of Copper Extraction from Sulfate Solutions by Kelex 100 in Xylene", M. S. Thesis, Illinois Institute of Technology, Chicago, Illinois, July, 1981.

5. C. K. Lee, "Chemical Equilibrium in Copper/Kelex 100 and Iron/Kelex 100 Solvent Extraction System", M.S. Thesis, Illinois Institute of Technology, Chicago, Illinois, August, 1981.

DEGREES GRANTED

L. K. S. Ho, M. S. Chemical Engineering, Illinois Institute of Technology, Chicago, Illinois, July, 1981.

2. C. K. Lee, M. S. Chemical Engineering, Illinois Institute of Technology, Chicago, Illinois, August, 1981.

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APPENDIX A

Chemical Equilibrium Studies
on
the Copper-Sulfuric Acid-Kelex 100-Xylene System

by

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manuscript for
Metallurgical Transactions B

ABSTRACT

A thermodynamic equilibrium model is developed for the distribution of copper between the phases for the system copper-sulfuric acid-xylene-β-alkenyl 8-hydroxyquinoline. Chemical equilibrium data were obtained for the range of experimental parameters of $[Cu]^{T}_{aq,i}$ (0.005-0.02 M), $[S]_T$ (0.05-0.2 M), chelation acid (0.02-0.06 M), and temperature (20-50°C). The nonlinear regression analysis best fit model is

$$\ln\left(\frac{D\alpha_o}{\gamma_{Cu^{++}}}\right) = 3.83 + 642\left(\frac{1}{T} - \frac{1}{308}\right) + 2\ln\left(\frac{[\overline{HR}]}{[H^+]\gamma_{H^+}}\right)$$

The analysis of the data considers the aqueous phase ionic equilibria and a technique to estimate the impurities present in the reagent. The results indicate that the enthalpy of the reaction and the entropy change are -1275 cal/g-mol and 3.46 cal/g-mol, °K respectively. Also, the stoichiometric coefficient of two, determined for the extractant with cupric ion is in agreement with other investigators.

Solvent extraction processes are becoming more attractive in hydrometallurgical processing of ores because of potentially low energy costs and minimization of air pollutants. Typically, selective extraction of metal ions from multiple metal aqueous acidic (1,2) or ammoniacal (3,4) leach solutions is required in order to obtain high purity solutions suitable for electrowining techniques. In these selective extraction processes, the interplay of the chemical equilibria between the two phases and the kinetics of interphase determine the selectivity of a given metal ion. It is shown by Fleming (1), that in the extraction of Cu(II) and Fe(III) from acidic solutions by Kelex 100 (a highly branched β-alkenyl-8-hydroxyquinoline) in xylene, the extracttion kinetics of copper is more rapid than those of iron. However, the chemical equilibria favors the iron complex. To propose optional design of such systems it is necessary to have a fundamental understanding of the chemical equilibria and the mass transfer-chemical reaction steps.

In regards to the chemical equilibria of the copper system, fundamental studies are reported (5-8). Spink and Okuhava (5) investigated the extraction of copper into Kelex 100/120 as well as LIX63/65N/64N (an oxime-based acid chelating reagent). They compared the equilibrium data and concluded that the Kelex system effectively extracts copper at a lower pH than LIX; furthermore, the rate of extraction with Kelex is considerably faster than with LIX system. Bauer and Chapman (8) investigated the equilibria of copper by Kelex 100. They used a statistical modelling procedure to correlate experimental data for the extraction of copper from acid sulfate solution by Kelex 100 in xylene. In the model developed they assume that formation of bisulfate and copper sulfate ion pairs should be nearly complete. Accordingly, the ionic strength should probably be calculated on the basis of H^+ and HSO_4^- as the predominant ions. Recently, Hoh and Bautistia (7) developed a chemically based model to predict distribution coefficients in the copper-Kelex 100 system. In their model derivation, they include the aqueous phase cupric sulfate complex stoichiometric stability constant expressed in terms of the degree of formation. It is also assumed that the quotient of the activity coefficients of the chemical species varies slightly with concentration and can be considered a constant. The survey of these articles indicates that although much work has been done on the equilibria studies of copper extraction by Kelex 100 or/and the LIX system, few works consider the aqueous phase equilibria. In addition, the composition of impurities contained in the organic extractant has also been neglected by most of the authors. These two omissions may result in bias conclusions for the data analysis or the models reported. The objective of this paper is to extend previous works and develop a thermodynamic equilibrium model for the copper-sulfate-Kelex-100-xylene system which overcomes these deficiencies. This objective is accomplished by equilibrium experiments with appropriate modelling and analysis.

THEORY

Two Phase Chemical Equilibria

The mechanism of copper extraction by Kelex 100 involving a chelating reaction may be expressed by the stoichiometric equation

$$Cu^{++} + n\overline{HR} \overset{K_{eq}}{\rightleftharpoons} \overline{CuR_n} + nH^{+} \qquad [1]$$

where $\overline{HR}$ represents the pure Kelex 100, $\overline{CuR_n}$ is the metal complex formed in organic phase, Cu^{++} and H^{+} are copper ion and hydrogen ion existing in aqueous phase. The above mechanism is suggested by many authors (7,8,9) by assigning n equal to two in the analysis of experimental equilibrium data. In this work, no assumption will be made concerning the stoichiometry of the reaction.

The stoichiometric coefficient will be determined through statistical fit of the equilibrium data.

The thermodynamic equilibrium constant, K_{eq}, of reaction equation [1] can be represented as the activity quotient or the product of concentration and activity coefficient quotient,

$$K_{eq} = \frac{a_{\overline{CuR}_n}\, a^n_{H^+}}{a_{Cu^{++}}\, a^n_{\overline{HR}}} \qquad [2]$$

or

$$= \frac{[\overline{CuR}_n][H^+]^n}{[\overline{HR}]^n[Cu^{++}]} \cdot \frac{\gamma_{\overline{CuR}_n}\, \gamma^n_{H^+}}{\gamma^n_{\overline{HR}}\, \gamma_{Cu^{++}}} \qquad [3]$$

where a_i represents the activity, the bracket represents the concentration, and γ_i represents the activity coefficient.

In the aqueous phase, since the copper sulfate does not dissociate completely into copper ions (10), the total copper existing will be the summation of copper ion and copper sulfate. Hence,

$$\begin{aligned} [Cu]^T_{aq} &= [Cu^{++}] + [CuSO_4] \\ &= [Cu^{++}]\left(1 + \frac{1}{K_c}[SO_4^=]\right) \qquad [4] \end{aligned}$$

where K_c is the dissociation constant of copper sulfate in the aqueous solution. In the organic phase $\overline{CuR}_n$ is the only metal complex formed, which was also assumed by other authors (5-8), thus

$$[Cu]^T_{org} = [\overline{CuR}_n] \qquad [5]$$

Substituting equations [4] and [5] into equation [3] and assuming the unity activity coefficient of Kelex 100 ($\overline{HR}$) and $\overline{CuR}_n$, equation [3] can be rewritten as

$$\ln\left(\frac{D\alpha_o}{\gamma_{Cu^{++}}}\right) = \beta_o + \beta_1\left(\frac{1}{T} - \frac{1}{\bar{T}}\right) + \beta_2 \ln\left(\frac{[\overline{HR}]}{[H^+]\gamma_{H^+}}\right) \quad [6]$$

where $D = [Cu]^T_{org}/[Cu]^T_{aq}$ [7]

and $\alpha_o = \left(1 + \frac{1}{k_c}[SO_4^=]\right)$ [8]

β_o, β_1 and β_2 are important parameters which can be obtained through statistical regression analysis. The definitions of these parameters are

$$\beta_o = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R\bar{T}} \quad [9]$$

$$\beta_1 = -\frac{\Delta H^0}{R} \quad [10]$$

$$\beta_2 = n \quad [11]$$

where $\bar{T}$ is reference temperature. The thermodynamic parameters of the entropy change ΔS° and the enthalpy of the reaction ΔH° for this extraction system can be estimated from the above relations.

The assumption of unity activity coefficients for $\overline{HR}$ and $\overline{CuR_n}$ can be relaxed by incorporating these activity coefficients in the distribution term on the left hand side of equation [6]. Estimates of the activity coefficients for species in the organic phase can be made using the solubility parameter theory of Scotchard and Hildebrand (11,12).

Equation [6] can be applied to the analysis of two phase extraction equilibria data to obtain values of the parameters β_o, β_1, and β_2. However, first the compositions of the aqueous phase has to be calculated. In the aqueous phase, the concentration of copper and hydrogen ions are complicated by the ionic equilibria. The species considered to be presented in the aqueous phase are Cu^{++}, H^+, HSO_4^- , $SO_4^=$ and $CuSO_4$. Higher associations of copper bisulfate interactions are neglected. Hence, only two equilibrium relations are considered in the aqueous phase:

$$CuSO_4 \underset{}{\overset{K_c}{\rightleftharpoons}} Cu^{++} + SO_4^= \qquad [12]$$

$$HSO_4 \overset{K_A}{\rightleftharpoons} H^+ + SO_4^= \qquad [13]$$

Here K_c and K_A are the dissociation constants. The approach for modelling the aqueous phase equilibria follows that of Freeman and Tavlarides (13). The dissociation constants can be related to the ionic strength, and the thermodynamic equilibrium constants. For K_c, the correlation of Nasenan (10) gives

$$\log \left({}^{1}/K_c \right) = \log K_{eq,c} - \frac{0.05\sqrt{I}}{1 + 1.618\sqrt{I}} + 0.052\ I \qquad [14]$$

where $K_{eq,c}$ is the thermodynamic equilibrium constant for the formation of $CuSO_4$. I is the ionic strength which for this system is given by

$$I = \frac{1}{2} \sum_{i=1}^{n} z_i^2\ C_i$$

$$= \frac{1}{2} (4[Cu^{++}] + [H^+] + [HSO_4^-] + 4\ [SO_4^=]) \qquad [15]$$

Similarly, the correlation of Hsuch and Newman (14) provides the relation for K_A.

$$\ln \left(K_A/K_{eq,A} \right) = \frac{5.29\sqrt{I}}{1 + 0.56\sqrt{I}} \ . \qquad [16]$$

The equilibrium relations of eqns. [12] and [13] can be combined with the total sulfur balance in the aqueous phase

$$[S]_A^T = [SO_4^=] + [CuSO_4] + [HSO_4^-], \qquad [17]$$

the total copper balance in the aqueous phase (eqn [4]), and species electroneutrality

$$2\,[Cu^{++}] + [H^{+}] = 2\,[SO_4^{=}] + [HSO_4^{-}] \qquad [18]$$

to give a cubic equation for copper ion concentration. The cubic equation can be solved for $[Cu^{++}]$ which permits calculation of all species in the aqueous phase. Iterative calculations are performed until the species concentrations satisfies the ionic strength relation of eqn [15].

The activity coefficients of copper and hydrogen ions can be estimated by use of the equations from Debye-Hückel theory as presented by Pytkowicz (15). Here

$$\ln \gamma_i = -\left(\frac{A}{3}\right)|z_1 z_2| \left\{ I^{1/2} / \left(1 + B_D a_D I^{1/2}\right) + 2/B_D a_D \cdot \ln\left(1 + B_D a_D I^{1/2}\right) \right\} ; \qquad \chi = 2 \qquad [19]$$

or

$$\ln \gamma_i = -(4A_D/a)\ |z_1 z_2|\ \left(2I/B_D a_D\right)^{1/3} ; \qquad \chi > 2 \qquad [20]$$

or

$$\ln \gamma_i = -A_D\ |z_1 z_2|\ I^{1/2} \left\{1 + 0.5 B_D a_D I^{1/2}\right\} / \left(1 + B_D a_D I^{1/2}\right) \Big\} \qquad \chi < 2 \qquad [21]$$

where $\chi = B_D a_D I^{1/2}$.

Temperature dependent values of the constants A_D and B_D of the Debye-Hückel theory and the parameter a_D are given by Pytkowicz (15). The estimated values of activity coefficients are valid at low ionic strength ($I < 0.1M$). For this work, the system is not always at these low ionic strength and a small error is expected.

Organic Phase Aggregation

The aggregation of the extractant in the organic solution is reported for the oxime extraction system (16-18). Komasawa (11) reports that for LIX65 oxime system, the degree of aggregation depends on the nature of the diluent and is small for aromatic solvents but large for aliphatic solvents. Ashbrook (19) suggests that aggregation in the oxime system is mainly due to the prevalence of intermolecular hydrogen bonding potential. In the β-alkenyl-8-hydroxyquinoline (Kelex 100) system, Ashbrook indicates that the intermolecular hydrogen bond is not important; however, the intramolecular hydrogen bond is prevalent. Therefore, the degree of aggregation is not important. Based on these considerations, aggregation of the Kelex 100 is not considered important and neglected in this work.

The purity of commercial grades Kelex 100 is reported to be (20) 77.7% wth a molecular weight of 311. In the analysis of the equilibrium data the fraction of the impurity is considered a parameter and is determined by regression analysis of the data.

EXPERIMENTAL

Kelex 100 was supplied by Ashland Chemical Company in commercial grade quality and used as the organic extractant. This extractant is highly viscous and contains impurities which should be removed or quantified. The treatment given here is to wash the desired solution of Kelex 100-xylene three times with 1 normal sulfuric acid and then the solution is washed with distilled water until the pH of the raffinate does not change. The copper sulfate, sulfuric acid and xylene are reagent grade quality and used without further purification.

Experimental Grid

The chemical equilibrium data from the two phase extraction were generated by varying the initial copper concentration, total sulfur concentration, Kelex 100 concentration, and temperature (20, 35 and 50°C). Initial Kelex 100, total copper, and total sulfur concentrations ranged from [0.02M to 0.06M], [0.005M to 0.02M], and [0.05M to 0.2M] respectively. These ranges were selected to correspond to kinetic experiments in progress for multiple metal extraction. It should be noted that the upper limit of Kelex 100 concentration is low, the range of copper concentration falls below most commercial leach solutions (∿ 0.015M the lowest used), and the aqueous phase is comparatively acidic. Figure 1 shows the structure of the experimental plan for the 64 experiments conducted. Thirty-three are replicates used to determine the experimental error.

Experimental Technique

Equal volumes (25 ml) of aqueous phase solution containing copper ion and Kelex 100 in xylene are mixed. The extraction is conducted in a temperature controlled Elerbath model 6250 shakerbath (T ± 1°C) for 12 hours after which equilibrium is reached. The mixture is permitted to disengage completely and the two phases are separated carefully. In the aqueous phase, hydrogen ion concentration is measured roughly via a pH meter. Total copper is measured with a Perkin Elmer model 460 Atomic Absorption spectrophotometer by dilution. Total copper analysis in the organic phase is measured by a stripping technique consisting of the following steps: (a) Several drops of concentrated sulfuric acid (∿ 18M) are mixed with the organic raffinate to precipitate a copper complex; (b) Sufficient volume of (∿ 1.5M) sulfuric acid is added to dissolve the precipitate, whereupon the phases are separated (c) Repeated washing (2 or 3 times) with 1.5M sulfuric acid minimizes residual copper in the funnel; (d) the combined aqueous phase of (b) and (c) is anlyzed via AA spectroscopy. Complete stripping of the organic phase is checked by a UV-visible spectrophotometric scan.

Organic Extractant Composition

The composition of impurity contained in the organic extractant is estimated by using ultimate loading method. This method has been used by previous authors (20,21) to determine the impurity composition for LIX system. Here the aqueous copper sulfate concentration (0.5M) and the pH value are ($\sim$ 3.65) selected such that it is assured that all the active extracant $\overline{HR}$ is complexed to $\overline{CuR_n}$. Total organic copper can be measured as described above and active organic extractant calculated assuming the complex contains 2 moles of extractant per mole of copper. The fraction of active Kelex 100 found to be 0.83 $\pm$ 0.066.

MODEL DISCRIMINATION AND ANALYSIS

The general model derived for analysis of the chemical equilibrium data is given by eqn.[6]. From the chemical equilibrium data and the aqueous phase composition modelling, all the variables can be estimated. A modified nonlinear statistical regression method is employed to determine the best values of the parameters β_0, β_1 and β_2. The nonlinearity is introduced by substitution for $\overline{HR}$ the term $\overline{HR}(1-X)$ where X is the fraction of impurity and is considered as another model parameter. Other models of a simpler nature can be generated from eqn [6] if further assumptions are made (22). These models are also correlated with the known variables and the experimental data to estimate the best values of the parameters. The goodness of fit of the various models is determined by analysis of variance (23). The regression variance due to the model lack of fit is compared to the experimental variance by use of the F statistic test. Results of this analysis indicates that eqn. [6] best describes the data. The F ratio is 1.61 as compared to the tabulated value of 1.66 for 90% confidence level. The final correlation obtained is

$$\ln\left(\frac{D\alpha_o}{\gamma_{Cu^+}}\right) = 3.83 + 642\left(\frac{1}{T} - \frac{1}{308}\right) + 2\ln\left(\frac{\overline{[HR]}}{[H^+]\ \gamma_{H^+}}\right) . \qquad [22]$$

The entropy change and the enthalpy of the reaction can be determined since

$$\frac{\Delta S°}{R} - \frac{\Delta H°}{R\overline{T}} = 3.83$$

and $$\frac{-\Delta H°}{R} = 642$$

Thus, one obtains $\Delta S° = 3.46$ cal/g-mol°K and $\Delta H° = -1275$ cal/g-mol.

DISCUSSION OF RESULTS AND CONCLUSIONS

A thermodynamic equilibrium model is obtained for the copper -H_2SO_4 - Kelex 100-xylene system from a statistical analysis of the equilibrium data. The results of aqueous phase modelling indicates that the percent dissociation of copper sulfate is inversely proportional to the concentrations of both total copper and total sulfate as shown in Figure 2. These results are consistant with those presented elsewhere (13). The activity coefficient for copper and hydrogen ions were calculated using equations [19] - [21] based on the Debye-Hückel theory. Over the range of experimental conditions, the activity coefficient ratio $\gamma^2_{H^+}/\gamma_{Cu^{++}}$ is approximately constant and equal to 1.17. This value is regarded as the activity coefficient constant K_γ for this system as $\gamma_{\overline{HR}}$ and γ_{CuRn} are assumed unity.

Plots of equation [22] at various temperatures are compared with experimental data in Figure 3. There is good agreement over the range studied. Temperature does not affect the value of the distribution coefficient significantly over the range studied. The variations in D calculated are within the experimental error of the data. It is also interesting to note that the active composition of extractant in Kelex 100 determined by the statistical analysis gives a value of 77.5%. This value is within the error range of experimental data of 83% determined by the method of ultimate loading and is considered reasonable. Further, it agrees with the value reported by Ashbrook (20).

The values of the entropy change and heat of reaction are ΔS° = 3.46 cal/g-mol°K and ΔH° = -1275 cal/g-mol. These values indicate a slightly exothermic reaction and a spontaneous reaction.

A thermodynamic equilibrium model useful for the estimation of copper distribution between aqueous and organic phases is obtained for the system copper sulfate-sulfuric acid-Kelex 100-xylene. The model accounts for the aqueous phase species equilibria, the activities of the aqueous phase species, and the impurities present in the Kelex 100. The best fit statistical model is given by equation [22] which applies over the range of experimental variables of $[Cu]^{T}_{aq,i}$ (0.005-0.02M), $[S]_{T}$ (0.05-0.2M), extractant (0.02-0.06M), and temperature (20-50°C). The thermodynamic equilibrium constant, K_{eq}, is given by

$$\ln K_{eq} = 3.827 + 642 \left(\frac{1}{T} - \frac{1}{308}\right)$$

The stoichiometric coefficient is correlated to be 2 for this extraction and is in agreement with earlier investigators. The enthalpy of the reaction and the entropy change are determined to be -1275 cal/g-mol and 3.46 cal/g-mol.°K respectively. These results are themodynamically consistent and indicate a slightly exothermic reaction.

The modelling approach presented have is based on the thermodynamics of both the aqueous phase and interphase chemical equilibrium. Therefore, a sound basis is presented for extrapolation of the model to regions outside the bounds of the data. This can be generalized and applied to other similar systems.

$[S]_T$: 0.05 M

Kelex 100 Concentration	0.005	C.0125	0.02 (M)
0.06 M	35	35	35
0.04 M	35	35,35	35
0.02 M	35	35	35

$[S]_T$: 0.125 M

Kelex 100 Concentration	0.005	0.0125	0.02 (M)
0.06 M	35	35,35 50 20	35
0.04 M	35,35 50 20	35,35,35 35,35,35 35,35,35 50,50 20,20	35,35
0.02 M	35	35,35,35 35,35 50 20	35

$[S]_T$: 0.20 M

Kelex 100 Concentration	0.005	0.0125	0.02 (M)
0.06 M	35	35	35
0.04 M	35	35,35 50 20	35
0.02 M	35	35	35

Initial Copper Concentration

Fig. 1. Structure of Experimental Grid for Equilibrium Measurement.

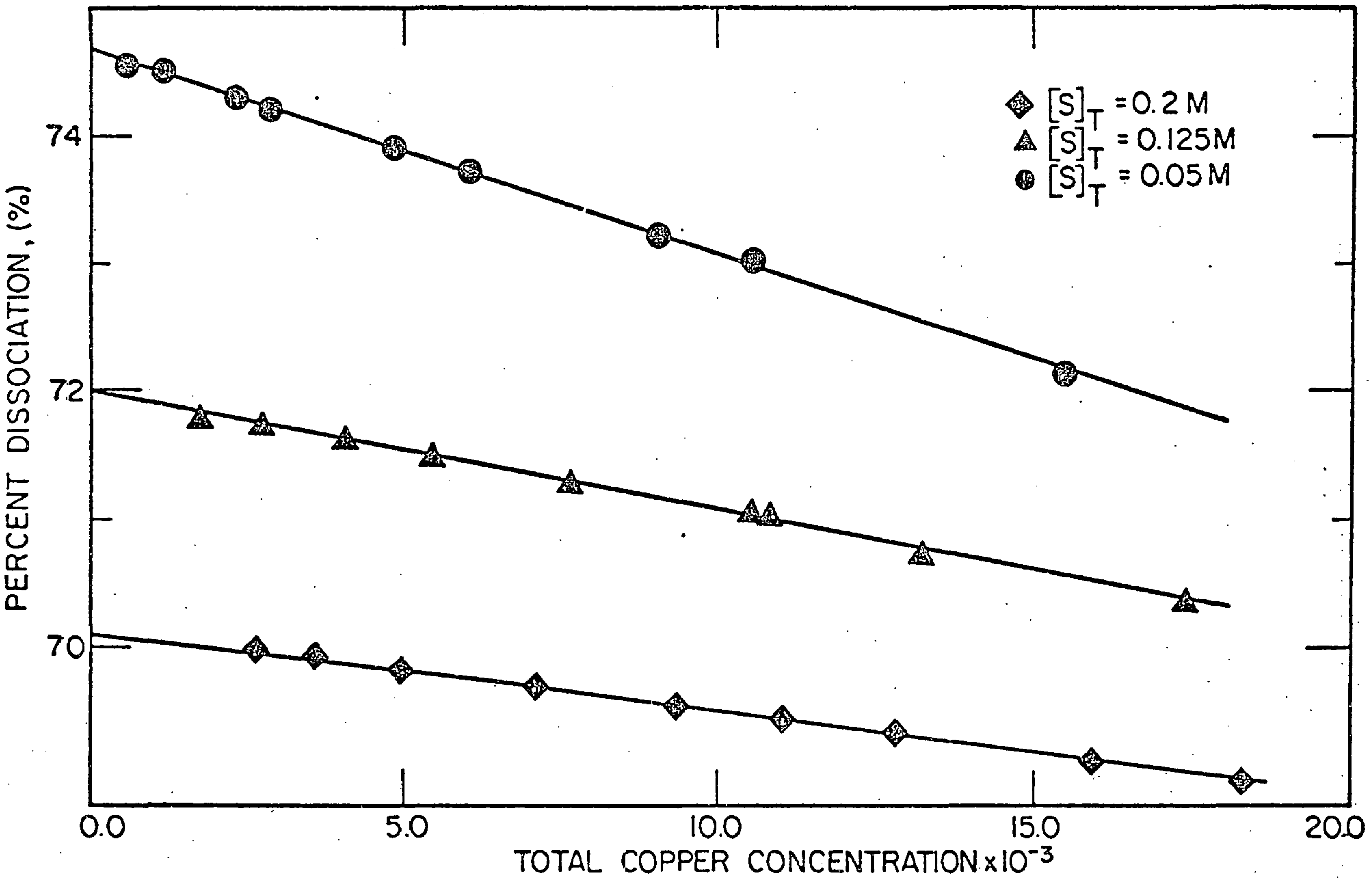

FIGURE 2 PERCENT DISSOCIATION OF COPPER SULFATE ION PAIR AS A FUNCTION OF TOTAL COPPER AT THREE SULFATE LEVELS

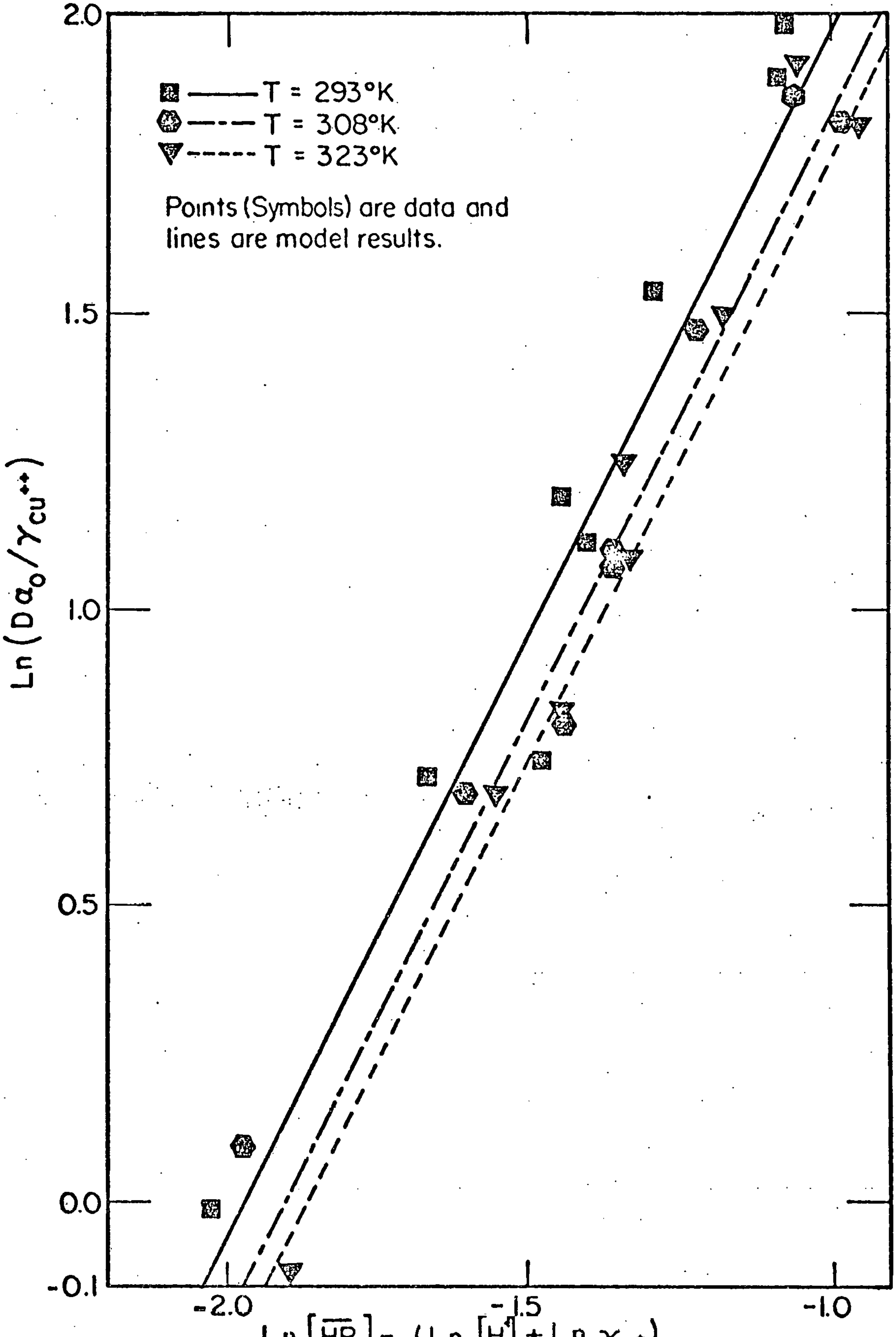

FIGURE 3 Ln$(D\alpha_0/\gamma_{cu^{++}})$ VERSUS Ln$([\overline{HR}]/\gamma_{H^+}[H^+])$

NOTATION

$[Cu]^T_{aq}$, $[Cu]^T_{aq,i}$	total copper in the aqueous phase at phase equilibrium, and initially
$[Cu]^T_{org}$	total copper in the organic phase at phase equilibrium
D	distribution coefficient
$\Delta H°$	enthalpy change at standard state, cal/g-mole
K_{eq}	thermodynamic equilibrium constant
K_C	dissociation constant of copper sulfate
K_A	dissociation constant of bisulfate
$K_{eq,c}$	thermodynamic formation constant for copper sulfate; the value is 125.6 $(mole/l)^2$ at 25°C
$K_{eq,A}$	thermodynamic dissociation constant for bisulfate; the value is 0.0104 mole/l at 25°C
$\Delta S°$	entropy change at standard state, cal/g mole-°K
R	ideal gas constant = 1.987 cal/ g mole-°K
T	temperature, °K

Subscripts

A	aqueous phase
O	organic phase
T	total concentration

Superscripts

$\overline{}$	organic phase species

Greek letters

α_o	defined by equation 8
β_o, β_1, β_2	parameters in the model
γ_i	activity coefficient

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APPENDIX B

Modelling and Scaleup of Dispersed Phase Liquid-Liquid Reactors

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