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NONIDEALITY IN TWO-PHASE SYSTEMS OF COPPER(II) EXTRACTION FROM SULFATE SOLUTIONS WITH LIX64N IN KEROSENE

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ABSTRACT

Distribution equilibrium of Cu^{2+} between sulfate solutions and kerosene containing LIX64N was studied. Distribution ratio of Cu^{2+} increased with increase in the concentration of extractant (10–50 mol/dm^3) and the initial aqueous pH (1∽5). A simplified model with three parameters was proposed to describe the equilibrium behavior, in which the non-idealities in both aqueous and organic phases were considered. Under the conditions studied (initial pH 2–5; Cu^{2+} concentration <10 mol/m^3; LIX64N concentration 10–50 mol/m^3), it was shown that the results calculated by the present model were in reasonable agreement with the measured ones (standard deviation <12.3%). This model gave a prediction comparable to the one estimated based on Davis equation for correlation of aqueous-phase activity alone, but superior to the one calculated based on the regular solution theory of Hildebrand/Scott for correlation of organic-phase activity alone.

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Key Words: Extraction equilibrium; Distribution ratio; Nonideality; Copper(II); LIX64N

INTRODUCTION

Due to the growing demand for high purity metals, concerns over environmental issues, the need for lower production costs, and continuous depletion of high-grade ores, solvent extraction has become one of the most promising techniques for this subject (1,2). For example, the demand for copper is increasing, especially with the rapid development in the process of printed circuit boards for electrodeless copper plating (3). It is also important to recover Cu^{2+} from waste streams produced in metal plating industries or in remediation of contaminated soils. Solvent extraction has been used in devices such as packed towers, mixer–settlers, and hollow fibers. Whatever equipment was applied to extract Cu^{2+} from aqueous streams, the equilibrium concentrations are essential to design a good contactor. Thus, it is desired to have a good knowledge on the extraction behavior in two immiscible phases containing extractants.

The equilibrium relationship of an extraction reaction was described in general by the law of mass action, mostly for dilute solutions. This is not necessarily true in certain cases, e.g., when the aggregates form in the organic phase or the metals of interest react with the ligands in the aqueous phase (4–12). Raghuraman et al. (4) found a single value for the equilibrium constant to be accurate over a large range of pH and ionic strength for both Cu–LIX860 and Cu–LIX980 extraction systems when the aqueous non-ideality is considered. In the extraction of Cr(VI) species with Aliquat 336 in kerosene, it was observed that the distribution ratio decreases linearly with increase in aqueous CrO_4^{2-} concentration, even in the initial concentration range of Cr(VI) (10–200 mg/L) (6). Cerna et al. (7) studied the distribution of HNO_3 between water or aqueous NH_4NO_3 solution and xylene solution of nitrate salt of Aliquat 336. The extraction of HNO_3 increased with increase in NH_4NO_3 concentration in the aqueous phase. A four-parameter mathematical model was proposed to describe such non-ideal behavior. Nakashio et al. (8) examined the extraction of Cu^{2+} and Zn^{2+} with alkylphosphonic acid monoester. They explained the non-ideality in terms of dimerization of the extractants. Juang et al. (9) also discussed the non-ideal behavior of a xylene solution of Aliquat 336 when it equilibrates with the aqueous phase containing chelated copper anions, but they did not examine the effect of aqueous-phase non-ideality on extraction equilibrium.

Although a smaller standard deviation (<10%) has been obtained according to the model proposed previously to account for the aggregation of species in the organic phase (12), it contains six fitting parameters. From a technical point of view, a model with fewer parameters would facilitate its use for process design of such mass transfer process. It is known that LIX-series extractants are the most effective and selective for Cu^{2+} and have been used at present (1,2,13–17). In this work, extraction equilibrium of Cu^{2+} from sulfate solutions with LIX64N/kerosene was investigated. A new, simplified model with three parameters was proposed, in which the non-idealities in both aqueous and organic phases were considered.

EXPERIMENTAL

Reagents and Solutions

The extractant LIX64N (Henkel Co., now Cognis Co., Tucson, AZ) was used as received, i.e., a mixture of 99 vol% LIX65N (2-hydroxy-5-nonylbenzophenone oxime) and 1 vol% LIX63 (5,8-diethyl-7-hydroxy-6-dodecanone oxime). The former is known to be effective for Cu^{2+} extraction and the latter is a kinetic accelerator. Kerosene (Union Chemical Works Ltd., Taiwan) was washed twice with 20 vol% H_2SO_4 to remove aromatics and then washed with deionized water before use. Copper(II) sulfate and other inorganic chemicals were supplied by Merck Co. (Darmstadt, Germany) as analytical grade reagents.

The organic solution was prepared by diluting LIX64N in kerosene to the required concentrations (10–50 mol/m^3) based on the average molar mass of LIX64N (338.3), if the identical densities of LIX65N and LIX63 are assumed. The aqueous solutions were prepared by dissolving $CuSO_4$ in deionized water (Millipore, Milli-Q), in which the initial pH was adjusted to be 1–5 by adding a small amount of H_2SO_4 or NaOH. The initial concentration of Cu^{2+} ranged from 5 to 10 mol/m^3.

Experimental Procedures

Extraction equilibrium experiments were made as follows. Equal volumes (50 cm^3) of the organic and aqueous phases were placed in 250 cm^3 glass-stoppered flasks, and were agitated with magnetic stirrers at 400 rpm for 24 hr. The temperature of the water bath was fixed at 298K. Preliminary test showed that the extraction reached equilibrium after stirring for 6 hr. After phase separation, the aqueous pH was measured using a Horiba pH meter (Horiba, Kyoto, Japan, Model F-23) and the concentration of Cu^{2+} was analyzed with a Varian atomic absorption spectrophotometer (Varian Optical Spectroscopy Instruments, Victoria, Australia, Model 220FS). The concentration of Cu(II) in the organic phase was obtained from a mass balance. Each experiment was at least duplicated under identical conditions and reproducibility of concentration measurements was usually within 3%.

RESULTS AND DISCUSSION

Effect of Extractant Concentration and Equilibrium pH

The present extraction system is known to be the reversible reaction of Cu^{2+} with the acidic chelating extractant LIX65N (13–15,17):

$$Cu^{2+} + 2\overline{HR} \Leftrightarrow \overline{CuR_2} + 2H^+ \tag{1}$$

where, the overbar refers to the organic phase and HR is LIX65N. The concentration-based (conditional) equilibrium constant K_{ex} is commonly given by

$$K_{ex} = \frac{[\overline{CuR_2}][H^+]^2}{[Cu^{2+}][\overline{HR}]^2} \tag{2}$$

The effects of LIX64N concentration and the initial pH on K_{ex} are shown in Figs. 1 and 2. It is observed that K_{ex} does not remain constant; it changes with solution pH and extractant concentration. We carefully repeat the experiments and do obtain reproducible results. This probably means that the aqueous and organic phases are both non-ideal (6,7,9).

The thermodynamic equilibrium constant of Eq. (1), K^0_{ex}, can be written as

$$K^0_{ex} = \frac{a_{\overline{CuR_2}} a^2_{H^+}}{a_{Cu^{2+}} a^2_{\overline{HR}}} = K_{ex}K_\gamma \tag{3}$$

where K_γ is a function of activity coefficient defined by Eq. (4)

$$K_\gamma = \frac{\gamma_{\overline{CuR_2}} \gamma^2_{H^+}}{\gamma_{Cu^{2+}} \gamma^2_{\overline{HR}}} \tag{4}$$

where γ_i represents the activity coefficient of species i in each phase. K_γ will equal 1 if ideal solutions (extremely diluted solutions) are assumed.

The non-ideality of the organic phase in the reactive extraction systems was usually expressed in terms of the ideal associated solution concept, i.e., aggregation of complexes (7,9–11,18). In the extraction of HNO_3 with the nitrate salt of Aliquat 336, the non-ideal behavior of the organic phase was considered by assuming that the logarithm of activity coefficient ratio of the complex to extractant is proportional to extractant concentration (7). However, Juang et al. (9) proposed that the non-ideal behavior of the organic phase follows the form

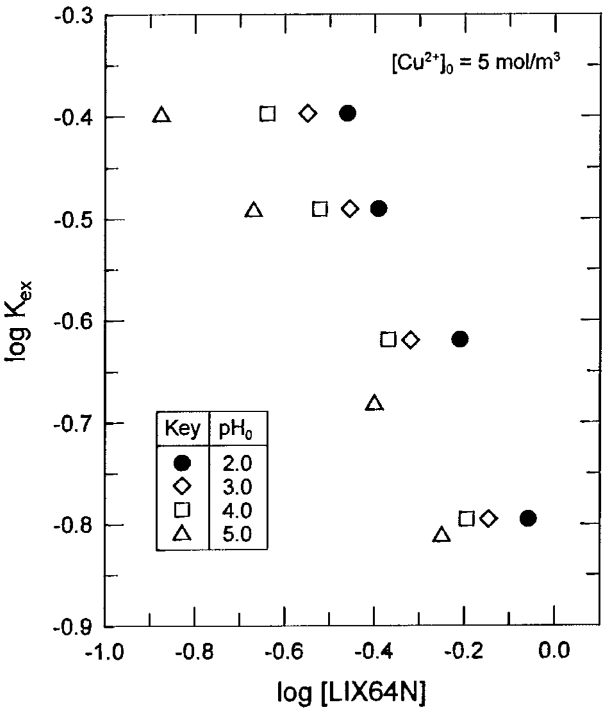

Figure 1. Effect of LIX64N concentration on the concentration-based equilibrium constant. $[\mathrm{Cu}^{2+}]_0 = 5\,\mathrm{mol/m^3}$, $[\mathrm{LIX64N}]_0 = 16 \backsim 32\,\mathrm{mol/m^3}$.

$(\gamma_{\mathrm{complex}}/\gamma^2_{\mathrm{amine}}) \propto [\mathrm{amine}]^n$ for extraction of Cu-EDTA chelated anions with Aliquat 336. Here, to simplify the description of the non-ideality of organic phase the following expression is adopted (9–11):

$$\left(\frac{\gamma_{\overline{\mathrm{CuR_2}}}}{\gamma^2_{\overline{\mathrm{HR}}}}\right) \propto [\overline{\mathrm{HR}}]^n \tag{5}$$

The Debye–Huckel equation is often used to calculate the activity coefficients of strong electrolytes in very dilute solutions. However, the Davis equation is recommended in the molality range up to 0.1 mol/kg (19). The present experiments were carried out at an ionic strength ranging from 0.001 to 0.1 mol/kg. Due to the strong dependence of $[\mathrm{H}^+]$ on K_{ex} as shown in Fig. 2, we simply replace a square root of ionic strength by $[\mathrm{H}^+]$ in the Davis equation, Eq. (10). Moreover, the activity coefficient of Cu^{2+} is assumed as 1 at such dilute concentrations. Thus, we have

$$\log(\gamma_{H^+}^2) \propto \frac{[H^+]}{1 + (\text{const})[H^+]} \tag{6}$$

The form of Eq. (6) is selected mainly because of the shape of pH dependence on K_{ex} (Fig. 2). This form is different from the one proposed in the extraction of HNO_3 with nitrate salt of Aliquat 336 (7), which has an extra term of $[NO_3^-]^2$. Substituting Eqs. (4)–(6) into Eq. (3), the thermodynamic equilibrium constant can be thus expressed as

$$\log K_{ex}^0 = \log K_{ex} + A_1[\overline{HR}]^n + \frac{B_1[H^+]}{1 + B_2[H^+]} \tag{7}$$

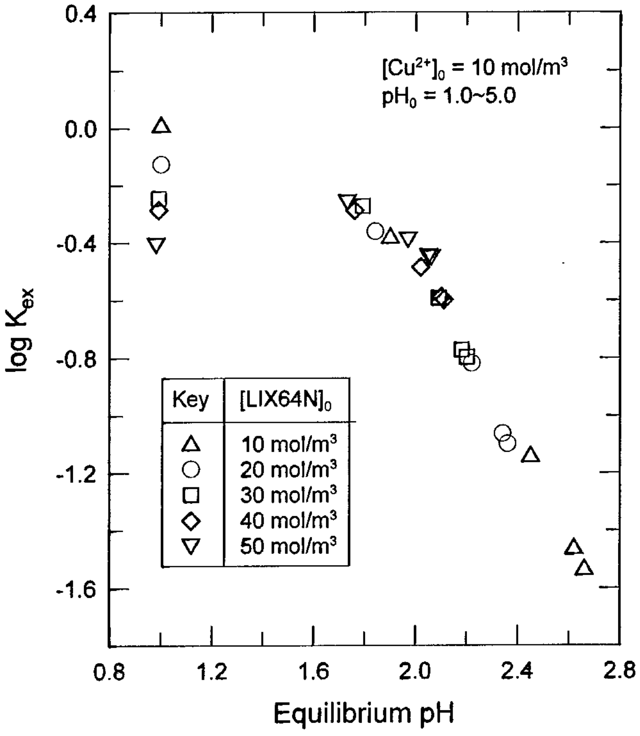

Figure 2. Effect of equilibrium pH on the concentration-based equilibrium constant.

Comparison of the Measured and Calculated Results

The mathematical model was compared with experimental data using the BSOLVE optimization procedure (based on Marquardt's least-squares algorithm) to calculate the model parameters (7). Finally, the equilibrium model is given by

$$\log K_{\mathrm{ex}}^{0} = \log K_{\mathrm{ex}} + 3.98 \times 10^{-3}[\overline{\mathrm{HR}}]^{0.8} - \frac{14.8[\mathrm{H}^{+}]}{1 + 1.91[\mathrm{H}^{+}]} \tag{8}$$

It should be noted that the concentrations of species in Eq. (8) are all in mol/m^3. The value of K_{ex}^{0} at 298K is found to be 1.47×10^{-8} (dimensionless).

Figures 3 and 4 compare the measured and calculated results. The parameter n is nearly identical to the absolute value of the slope shown in the Fig. 3. The solid curves are obtained from Eq. (8). The validity of this model is checked quantitatively by the standard deviation (SD) defined by Eq. (9),

$$\mathrm{SD}\,(\%) = 100 \times \sqrt{\frac{\sum\left[\left(\frac{[\mathrm{Cu}^{2+}]^{\mathrm{cal}}}{[\mathrm{Cu}^{2+}]^{\mathrm{exp}}}\right) - 1\right]^{2}}{(N-1)}} \tag{9}$$

where N is the number of data points. The superscripts "cal" and "exp" are the calculated and experimental results, respectively. The SD value in the present model is found to be 12.3% under the ranges studied. It is found from Fig. 4 that the model prediction is not so good at low extractant concentrations ($<20\,\mathrm{mol/m^3}$). This is probably due to the higher organic loading (the ratio of complex concentration to the initial extractant concentration in the organic phase), in contrast to the case of higher extractant concentrations.

On the other hand, the larger deviation at relatively higher LIX64N concentrations (Fig. 3) is due to the possible interaction of the organic solutions. In fact, hydroxyoximes tend to be dimers in the bulk organic phase and the degree of dimerization varies with the diluent; and a dimer would adsorb at the organic/aqueous interface at high extractant concentrations (20). The deviation probably results from the simplification of the parameters, particularly at high LIX64N concentrations. Although the chemical model with six fitting parameters given by Calvarin et al. (12) could account for the aggregation of species in organic phase and obtain a deviation below 10%, the mathematical complexity makes it inconvenient for further application.

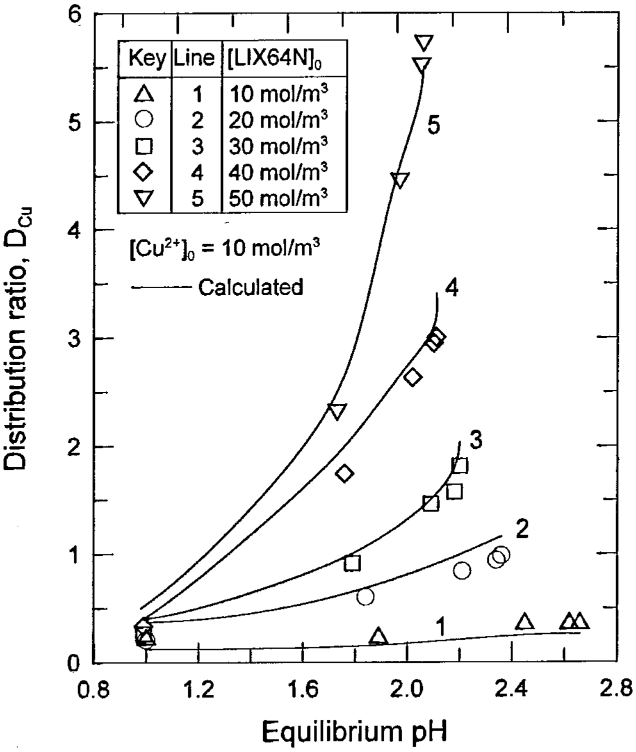

Figure 3. Comparison of the calculated and measured distribution ratios at different LIX64N concentrations.

Comparison of the Present Model and Other Models

Here, an attempt was made to compare the results calculated by the present model with those obtained from the other two models. One is based on Davis equation for correlation of aqueous-phase activity coefficients alone (19):

$$\log \gamma_i = -\frac{0.511\, z_i^2 \sqrt{I}}{1+\sqrt{I}} + 0.102\, z_i^2 I \quad \text{at}\, 298\text{K} \tag{10}$$

where z_i is the valence of the ions and I denotes the ionic strength. It is noted that Eq. (10) gives a reasonable estimate at a molality up to 0.1 mol/kg.

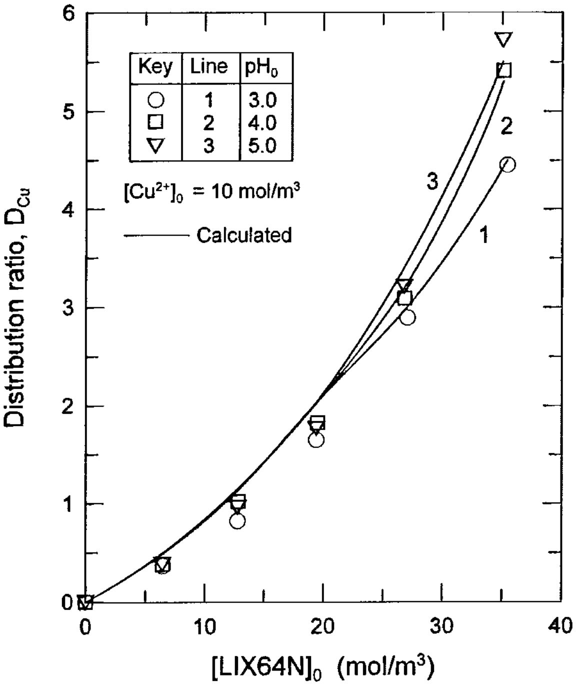

Figure 4. Comparison of the calculated and measured distribution ratios at different aqueous pH values.

The other is based on the regular solution theory of Hildebrand/Scott for correlation of organic-phase activity coefficients alone (21,22):

$$\ln \gamma_i = \frac{V_i}{RT}\left(\frac{V_j x_j}{V_i x_i + V_j x_j}\right)^2 (\delta_j - \delta_i)^2 \tag{11}$$

where V is the molar volume at its normal boiling point (cm^3/mol), x is the mole fraction, and δ is the Hildebrand parameter (MPa). The subscripts i and j refer to kerosene and the extractant, respectively, and vice versa. At 298K, the values of V and δ are found to be 228.6 cm^3/mol and 16.0 MPa$^{1/2}$, respectively for kerosene, and are 93.3 cm^3/mol and 38.4 MPa$^{1/2}$ for the extractant (21,23).

Figure 5 compares the results. The deviations are 16.3 and 23.0% based on Davis equation and the regular solution theory, respectively. It is found that there is no further improvement, even by combining both correlation equations (not shown), compared to the present model. It is evident that the present model does not give a better fit at either high or low Cu^{2+}

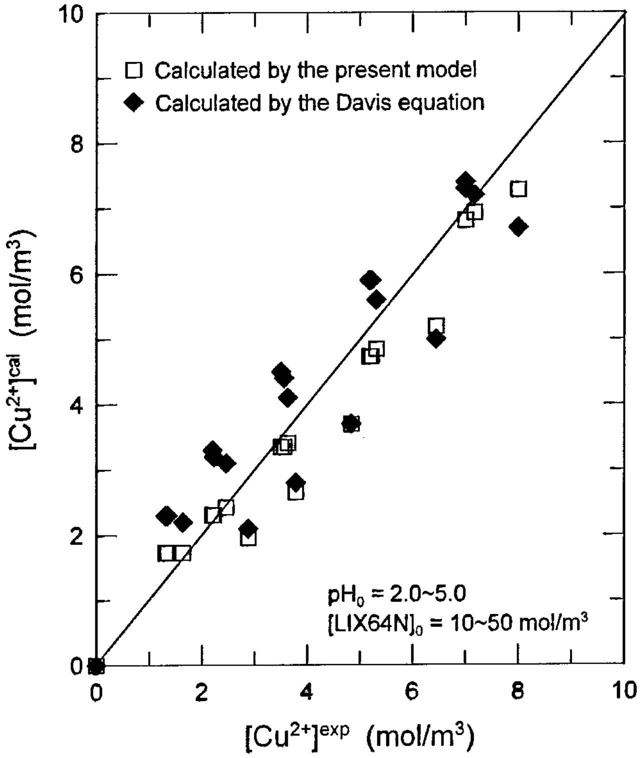

Figure 5. Comparison of the calculated and measured Cu^{2+} concentrations in the aqueous phase by two different models.

concentration ranges. This probably proves the possibility of neglecting the term [Cu^{2+}] in Eq. (7). The improvement by the present model compared to the one based on the Davis equation, although not much, proves the need for correlation of organic-phase non-ideality. To our best knowledge, few literature results are available to compare while using similar model or the same extraction systems.

CONCLUSIONS

Thermodynamic equilibrium of Cu^{2+} extraction from sulfate solutions with LIX64N in kerosene was studied at 298K. A simplified model for description of the equilibrium constant was deduced by activity concept. The nonidealities in both aqueous and organic phases were taken into account. The following results were obtained.

(1) The commonly conditional equilibrium constant decreased with increase in extractant concentration and aqueous pH. This implied that the non-idealities in both aqueous and organic phases were affected.

(2) A thermodynamic equilibrium model was proposed to be Eq. (8) at 298K. Under the conditions studied ($pH_0 = 2\text{–}5$; $[Cu^{2+}]_0 < 10\,\text{mol/m}^3$; $[\text{LIX64N}]_0 = 10\text{–}50\,\text{mol/m}^3$), the results calculated by the present model were in reasonable agreement with the experimental ones (with a standard deviation 12.3%).

(3) This simplified model was comparable to the one predicted based on the Davis equation (with a standard deviation 16.3%) for correlation of aqueous-phase activity coefficient alone, but was superior to the one predicted based on the regular solution theory of Hildebrand/Scott (with a standard deviation 23.0%) for correlation of organic-phase activity coefficient alone.

NOMENCLATURE

a_i	activity of species *i*
D_{Cu}	distribution ratio of Cu^{2+}
HR	LIX65N
I	ionic strength (mol/kg)
K_{ex}	concentration-based equilibrium constant defined in Eq. (2)
K_γ	equilibrium constant based on activity coefficient defined in Eq. (4)
[ ]	molar concentration of species in the brackets (mol/m^3)

Greek letter

γ_i	activity coefficient of species *i*

Superscripts

0	thermodynamic basis
$\overline{(\text{overbar})}$	species in the organic phase

Subscript

0	initial (total)

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