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Copper–LIX 84 Extraction Equilibrium

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ABSTRACT

Extraction of copper from water using LIX 84 extractant was investigated. Binary equilibrium data are reported and predictive models have been developed. With a simple, concentration-based equilibrium model, an equilibrium constant of 3.9 was obtained. This model is adequate when no acid is present in the aqueous phase. As the acidity of the aqueous phase increases, nonideality becomes significant and needs to be considered to predict extraction equilibrium properly. Our second model incorporates activities and major ionic reactions for the aqueous phase species; nonideality of the aqueous phase is successfully modeled. Nonideality of the organic phase is lumped into a concentration-dependent equilibrium constant. Equilibrium constants of 27.2, 13.1, and 6.2 were obtained for 5, 10, and 20 v/v% LIX 84 in tetradecane, respectively. This model can effectively predict the extraction equilibrium over a wide range of pH.

INTRODUCTION

The extraction of copper by β-hydroxy aromatic oxime molecules has received considerable attention. These extractants can selectively extract copper from ferric iron-containing solutions. The low solubility of the compounds, achieved by inserting a long-chain alkyl substituent in the ring, provides further incentive for commercial development (1). Published data on copper extraction equilibrium are available primarily for older extracting agents (such as LIX 64N, LIX 63, and LIX 65) that are no longer marketed commercially. Current extractants such as LIX 84 (2-hydroxy-5-nonylace-

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tophenone oxime), LIX 860 (2-hydroxy-5-dodecylsalicylaldoxime), and LIX 980 (equivolume mixture of the two) allow faster extraction kinetics, easier phase disengagement, higher selectivity, and strong extraction of copper even at a pH value as low as 1 (2). Data on these newer, more efficient reagents are lacking.

Studies on copper–hydroxy oxime extraction equilibrium are abundant. For example, Yun et al. studied the copper–LIX 84–heptane system and obtained a concentration-based equilibrium constant of 1.7; Tutkun and Kumbasar studied the copper–LIX 860 system using kerosene as diluent (3, 4). Most of these studies used concentration-based equilibrium models that frequently fell short at lower pH. To amend such limitations, semiempirical approaches have been explored on Cu–Kelex 100 and Cu–Acorga P5000 extraction (5, 6). For an equilibrium model to be truly effective over broad conditions, however, one needs to account for nonideality and all major ionic equilibria in the aqueous phase. More recently, Raghuraman et al. reported the binary equilibrium data for copper–LIX 860 and copper–LIX 980 and developed a predictive model that incorporates aqueous-phase nonideality and all aqueous-phase ionic reactions.

This article presents binary equilibrium data as well as equilibrium models of copper extraction by LIX 84, one of the newer commercially available extractants for which there is very little information reported in the literature. The concentration-based equilibrium model is compared with a model that incorporates activities and ionic equilibria of aqueous species under various conditions. Tetradecane was selected as the diluent for the study because: 1) it is more environmentally friendly than solvents such as MIBK because of its low toxicity; 2) it is less volatile than solvents such as toluene and heptane so it is easier to handle; and 3) it is compatible with most polymer material so it is more suitable for membrane extraction devices.

THEORY

It is generally accepted that the reaction between copper ions and oxime molecules proceeds at the oil–water interface (7). The chelating extraction is an acid–base reaction in which the oxime molecules donate protons in exchange for copper ions. The reaction is described by

$$\mathrm{Cu}^{2+}_{(\mathrm{aq})} + 2\mathrm{RH}_{(\mathrm{org})} \leftrightarrow \mathrm{CuR}_{2(\mathrm{org})} + 2\mathrm{H}^{+}_{(\mathrm{aq})} \tag{1}$$

where RH represents oxime molecules. From Eq. (1), a concentration-based equilibrium constant K^{*}_{eq}, is defined as

$$K^{*}_{\mathrm{eq}} = \frac{[\mathrm{CuR}_2][\mathrm{H}^{+}]^2}{[\mathrm{Cu}^{2+}][\mathrm{RH}]^2} \tag{2}$$

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Terms in brackets, [ ], represent the concentration of a given component. A concentration-based equilibrium model is usually adequate only when the concentrations of the species involved are low and the solutions are relatively ideal.

To predict copper–LIX 84 extraction equilibria accurately at more extreme conditions, a thermodynamic equilibrium constant (K_{eq}) must be used:

$$K_{eq} = \frac{\{CuR_2\}\{H^+\}^2}{\{Cu^{2+}\}\{RH\}^2} \tag{3}$$

where terms in braces, { }, represent activities that are products of concentrations and activity coefficients. In addition, all the major ionic reactions must be accounted for. These include association and dissociation of cupric sulfate, sulfuric acid, and water:

$$Cu^{2+} + SO_4^{2-} \leftrightarrow CuSO_4 \qquad K_1 = 229 \tag{4}$$

$$H_2SO_4 \leftrightarrow HSO_4^- + H^+ \qquad K_2 = 95.49 \tag{5}$$

$$HSO_4^- \leftrightarrow SO_4^{2-} + H^+ \qquad K_3 = 0.0105 \tag{6}$$

$$H_2O \leftrightarrow H^+ + OH^- \qquad K_4 = 1 \times 10^{-14} \tag{7}$$

The equilibrium constants for the ionic equilibria were taken from Lindsay (8). Hydrolysis of copper is usually negligible in acidic environment (all experiments in the current study were conducted at pH 4.9 or lower).

To calculate activity coefficients for the ionic species, the modified Guggenhein equation is used (8):

$$\log \gamma_i = -Az_i^2 \frac{I^{0.5}}{1 + I^{0.5}} + BI \tag{8}$$

where I is the ionic strength of solution

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2 \tag{9}$$

z_i is the ionic charge, c_i is the concentration of ionic species, A is a constant (0.509), and B is equal to 0.15 for the unmodified equation valid for $I < 0.1$ M and is an adjustable parameter in the modified equation for higher ionic strengths. For neutral species (8):

$$\log \gamma_i = 0.1I \tag{10}$$

and the activity for water is given by (8)

$$\alpha_{H_2O} = 1 - 0.017\sum_{i=1}^{n} c_i \tag{11}$$

The organic phase is assumed to be ideal initially. Experimental result will be used to assess the validity of such an assumption. Within this context, a modified equilibrium constant K'_{eq} (not to be confused with K^{*}_{eq}) is defined as

$$K'_{\mathrm{eq}} = \frac{[\mathrm{CuR_2}]\{\mathrm{H^+}\}^2}{\{\mathrm{Cu^{2+}}\}[\mathrm{RH}]^2} \tag{12}$$

The ionic equilibria reactions in the aqueous phase (Eqs. 4–7) can be written in terms of activities:

$$K_1 = \frac{\{\mathrm{CuSO_4}\}}{\{\mathrm{Cu^{2+}}\}\{\mathrm{SO_4^{2-}}\}} \tag{13}$$

$$K_2 = \frac{\{\mathrm{HSO_4^-}\}\{\mathrm{H^+}\}}{\{\mathrm{H_2SO_4}\}} \tag{14}$$

$$K_3 = \frac{\{\mathrm{SO_4^{2-}}\}\{\mathrm{H^+}\}}{\{\mathrm{HSO_4^-}\}} \tag{15}$$

$$K_4 = \frac{\{\mathrm{H^+}\}\{\mathrm{OH^-}\}}{\{\mathrm{H_2O}\}} \tag{16}$$

In addition to the reaction equilibria, the system can be further characterized by mass and charge balances. The mass balance equation for copper is written as

$$[\mathrm{CuSO_4}]_0 V_\mathrm{a} = ([\mathrm{Cu^{2+}}] + [\mathrm{CuSO_4}])V_\mathrm{a} + [\mathrm{CuR_2}]V_\mathrm{o} \tag{17}$$

The mass balance equation for sulfur is

$$[\mathrm{CuSO_4}]_0 + [\mathrm{H_2SO_4}]_0 = [\mathrm{CuSO_4}] + [\mathrm{SO_4^{2-}}] + [\mathrm{HSO_4^-}] + [\mathrm{H_2SO_4}] \tag{18}$$

while that for LIX 84 is

$$[\mathrm{RH}]_0 = [\mathrm{RH}] + 2[\mathrm{CuR_2}] \tag{19}$$

Aqueous phase species must satisfy a charge balance equation:

$$2[\mathrm{Cu^{2+}}] + [\mathrm{H^+}] = [\mathrm{OH^-}] + [\mathrm{HSO_4^-}] + 2[\mathrm{SO_4^{2-}}] \tag{20}$$

Overall, nine equations (Eqs. 12–20) are available to characterize the equilibrium of nine species (aqueous phase: $\mathrm{Cu^{2+}}$, $\mathrm{H^+}$, $\mathrm{CuSO_4}$, $\mathrm{H_2SO_4}$, $\mathrm{HSO_4^-}$, $\mathrm{SO_4^{2-}}$, $\mathrm{OH^-}$; organic phase: RH, $\mathrm{CuR_2}$). If the modified equilibrium constant K'_{eq} is known, one can calculate the equilibrium concentrations of the species involved from the initial concentrations of cupric sulfate, sulfuric acid, LIX 84, and the volumes of the aqueous and organic phases.

EXPERIMENTAL SECTION

The source for copper was copper(II) sulfate pentahydrate (Certified ACS grade, Fisher Scientific). LIX 84 was supplied as approximately 48 wt% in kerosene by Henkel (Lot Number 0084030) and was used without further purification. Diluent tetradecane (99%, technical grade) was purchased from Humphrey Chemicals. Sulfuric acid (trace metal grade) was purchased from Fisher.

Aqueous solutions of copper were prepared by dissolving the salt in deionized water. The organic phases containing the extracting agent in the tetradecane diluent were prepared on a volume/volume basis. A 10 v/v% LIX 84 solution refers to 10 v/v% of the LIX 84 (as received from Henkel) in tetradecane or heptane. LIX 84, as shipped from Henkel, contains 48 wt% of the active ingredient with an overall density of 0.9 g/mL. The molecular weight of LIX 84 is 277.40 g/mol, which makes the molar concentration of 100% LIX 84 1.557 mol/L (9). This value was used in subsequent calculations. Volume change due to mixing was ignored.

Equilibrium distribution experiments were carried out by mixing copper solutions of various concentrations with LIX 84 solutions of various concentrations at various volume ratios overnight. The mixtures were then centrifuged and the two phases were separated. The aqueous phase, after proper dilution, was directly analyzed on a Perkin-Elmer Plasma 400 ICP spectrophotometer. The wavelength used was 324.8 nm. The organic phase was backextracted with 6 N sulfuric acid and then analyzed on the same instrument. A mass balance between the two phases was used to verify the analysis; the differences between measurements from the aqueous phase and those from the organic phase were less than 6% in all cases, and the averages were used.

RESULTS AND DISCUSSION

Concentration-Based Equilibrium Constant K^*_{eq}

Table 1 shows the initial conditions and results of each extraction. At equilibrium, a partition coefficient K_p, can be defined from Eq. (2):

$$\log K_p = \log\left(\frac{[\mathrm{CuR_2}]}{[\mathrm{Cu^{2+}}]}\right) = \log K^*_{eq} + 2\log\left(\frac{[\mathrm{RH}]}{[\mathrm{H^+}]}\right) \qquad (21)$$

Thus, the concentration-based equilibrium constant K^*_{eq} can be determined from the intercept of the plot $\log K_p$ vs $\log([\mathrm{RH}]/[\mathrm{H^+}])$ with a slope 2, as shown in Fig. 1. When $K_p \geq 5$, the data generally follow a slope of 2. A linear regression with a preset slope of 2 leads to a K^*_{eq} of 3.9 ± 0.1. The data of $K_p < 5$ were excluded from the regression (to be discussed in the next section).

TABLE 1
Distribution Coefficient of Copper with LIX 84 in Tetradecane

Starting aqueous phase		Aqueous phase after equilibrium								
		5% v/v LIX 84			10% v/v LIX 84			20% v/v LIX 84		
mg/L	pH	mg/L	pH	K_p	mg/L	pH	K_p	mg/L	pH	K_p
250	4.90	0.21	2.19	1171.61	0.0871	2.16	2,869.26	0.03	2.17	8,089.61
500	4.75				0.752	1.81	663.89	0.36	1.91	1,406.66
800	4.65	7.73	1.66	102.49	2.630	1.64	303.18	1.28	1.68	622.54
1,000	4.60	17.45	1.60	56.31	5.920	1.58	167.92	2.45	1.59	407.50
1,500	4.51	77.00	1.50	18.48	22.32	1.47	66.20	9.23	1.45	161.51
2,000	4.43	245.30	1.40	7.15	57.70	1.38	33.66	22.36	1.36	88.45
2,500	4.38	524.30	1.40	3.77	134.10	1.32	17.64	44.62	1.33	55.03
3,500	4.26	1,277.00	1.36	1.74	411.80	1.23	7.50	140.00	1.23	24.00
4,000	4.22	1,713.00	1.28	1.34	498.00	1.18	7.03	189.00	1.23	20.16
5,000	4.10	2,633.00	1.32	0.90	1,116.00	1.15	3.48	392.00	1.19	11.76
10,000	3.89	7,357.00	1.28	0.36	5,562.00	1.11	0.80	2,792.00	0.96	2.58
20,000	3.49	16,888.00	1.38	0.18	15,166.00	1.16	0.32	11,068.00	0.94	0.81

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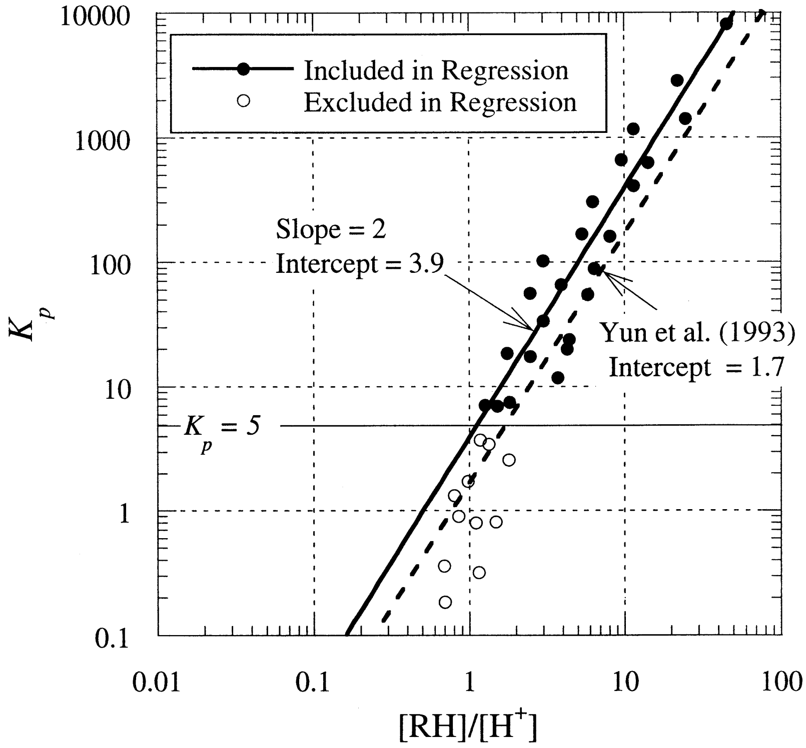

FIG. 1 Equilibrium constants of copper–LIX 84 systems. The results from the equilibrium partitioning experiments were plotted according to Eq. (21). The data of $K_p < 5$ are excluded from regression. The intercept of the regressed line is the estimated equilibrium constant K^*_{eq} which was found to be 3.9 in this study. The constant 1.7 obtained by Yun et al. (3), who used heptane as the diluent, is also plotted for comparison (dashed line).

This value is slightly higher than but close to the value of 1.7 reported by Yun et al. who used heptane as diluent (3). The values predicted by the equation of Yun et al. are shown in Fig. 1 as a dashed line.

Determination of K'_{eq}

The modified equilibrium constants K'_{eq} were calculated from the same data in Table 1. As discussed earlier, if K'_{eq} is known, nine equations (Eqs. 12–20) are available to characterize the equilibrium of copper–LIX 84. Conversely, K'_{eq} may be regressed from the equilibrium data through the minimization of an objective function:

$$\frac{1}{n}\sum^{n}(C_{exp} - C_{pred})^2/C_{exp} \tag{22}$$

C_{exp} is the equilibrium concentration obtained from experiments and C_{pred} is the concentration predicted by the model. n is the number of samples. This function represents a weighted error from the equilibrium model; the best estimate of K'_{eq} must result in a minimum error. Regression of K'_{eq}, or minimization of Eq. (22), is carried out through numerical optimization using Powell's method (10). During each iteration of Powell's method a new K'_{eq} is generated and is used to solve the equation set (12) to (20). The equations are nonlinear and must be solved numerically; Broydn's method was used for this purpose (10). Once a new copper concentration C_{pred} is solved, Eq. (22) is evaluated again and is used by Powell's method to determine the next K'_{eq} to try until the minimum of Eq. (22) is reached. The algorithm was implemented in a FORTRAN program.

Using all the data in Table 1, this regression leads to a K'_{eq} of 13.2. Model prediction (solid lines) and experimental data (circles for 5 v/v% LIX 84, squares for 10 v/v % LIX 84, diamonds for 20 v/v% LIX 84) are compared in Fig. 2. It can be observed that the model generally overpredicts when 5 v/v% LIX 84 is used and underpredicts when 20 v/v% LIX 84 is used. Such deviations may be explained by three effects: dimerization of LIX 84 in the organic phase, modification of the diluent, and nonideal behavior of the organic phase. Dimerization of oxime molecules makes the reaction stoichiometry deviate from the one-to-two ratio exhibited by Eq. (1). LIX 84 is made up of less than

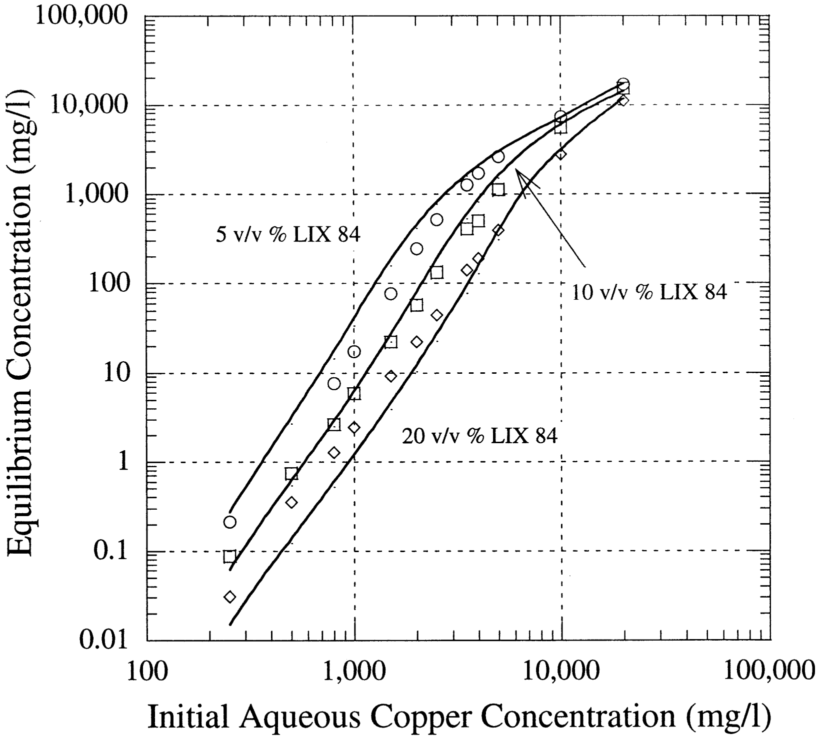

FIG. 2 Extraction equilibrium prediction—$K'_{eq} = 13.2$. Based on data from equilibrium partitioning experiments, the apparent equilibrium constant K'_{eq} was regressed to be 13.2. The experimental data (symbols) were then compared with model predictions (lines) using $K'_{eq} = 13.2$ at various LIX 84 concentrations. The model slightly overpredicts the equilibria when 5 v/v% LIX 84 is used and underpredicts when 20 v/v% LIX 84 is used, suggesting that the organic phase is not an ideal mixture.

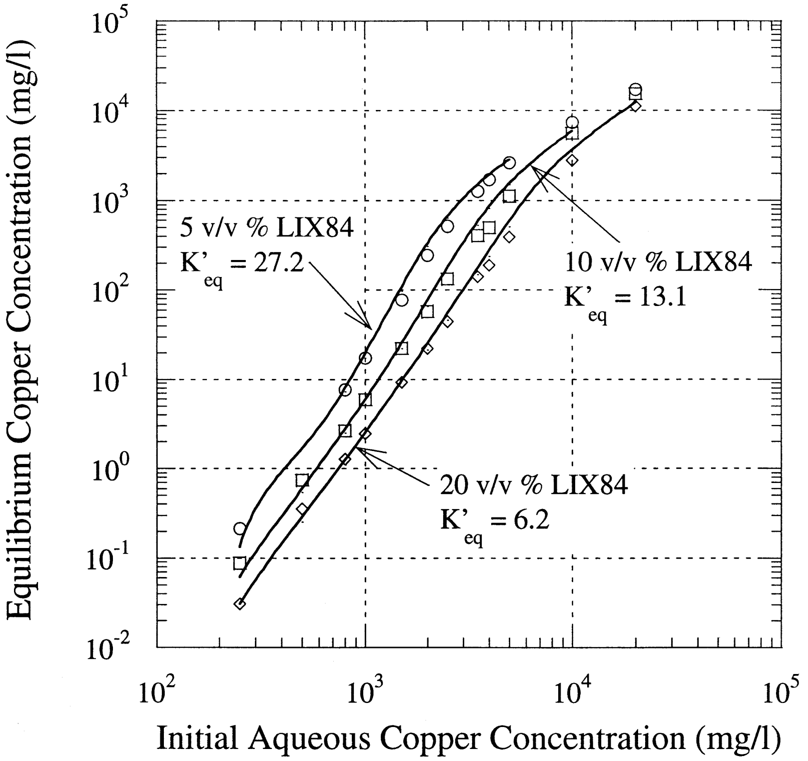

FIG. 3 Extraction equilibrium prediction—Individual values of K'_{eq}. The experimental data are the same as in Fig. 2 but K'_{eq} was regressed at each LIX concentration. In this regression the organic phase nonidealities are lumped into K'_{eq} and the prediction from the model is much improved. The predictive model failed to converge on three extreme conditions (10,000 mg/mL initial copper concentration at 5% LIX 84 and 10,000 and 20,000 mg/mL initial copper concentrations at 10% LIX 84). Such divergences are not uncommon in solving more than one nonlinear simultaneous equations (10). These three points were excluded in evaluating Eq. (22).

50% of oxime compounds in kerosene. Since the highest LIX 84 concentration used in the current study is less than 20%, the concentrations of pure oxime are less than 10% in all experiments and dimerization should not be significant (11, 12). The presence of an aromatic hydrocarbon in the diluent is reported to modify the partitioning behavior of copper dramatically as the concentration of 2-hydroxy-5-nonylacetophenone oxime increases (13). According to the manufacturer, the kerosene used in LIX 84 is strictly aliphatic. Such a modification effect should not be a factor. Thus, the deviation observed in Fig. 2 is most likely due to the nonideality of the organic phase.

To account for the nonideality of the organic phase, we regressed the equilibrium constant at individual LIX 84 concentrations. This implicitly lumped the activity coefficient of the organic phase into the modified equilibrium constant K'_{eq}. K'_{eq} values of 27.2, 13.1 and 6.2 were obtained for 5, 10, and 20% LIX 84, respectively. The model predictions are much more accurate in this case, as shown in Fig. 3. Extraction equilibria were accurately predicted over a wide range of initial copper concentration at all three LIX 84 concentrations. These results suggest that the equilibrium model successfully accounts for aqueous phase nonideality. In addition, the activity coefficient of the organic phase depends mainly on its LIX 84 content and very little on its copper loading. Raghuraman et al. used a similar model on Cu–LIX 860 extraction and Cu–LIX 980 extraction and found a single value for the equilibrium constant for each of the two systems is accurate over a large range of pH (14). However, only one LIX concentration, 10 wt%, was used in these studies.

The model performs well at high loading, which suggests that the deviation of the data from a slope of 2 in Fig. 1 (at low K_p values) may not result from a change of reaction stoichiometry at high loading as suggested by Yun et al. (3). Rather, it is a reflection of the nonideality exhibited by the aqueous phase at high copper concentration. This aqueous nonideality leads to the exclusion of the points below K_p from our concentration-based equilibrium model. The fact that the concentration-based equilibrium constant K^*_{eq} inherits certain activity-based error also explains the negative deviation from a slope of 2 seen by Yun et al. at high loading while a positive deviation was shown by this study (3). In these two studies, different initial aqueous phase pH values [pH = 4.6 here vs 3.92 in Yun et al. (3)] were measured even though the same initial copper concentrations were used. This suggests that some trace impurities in cupric sulfate solutions prepared from different sources may affect the ionic activities.

The merits of the activity-based model are most obvious when the aqueous phase is highly nonideal, especially when it is highly acidic, as is often encountered in these extraction systems. For example, 0, 0.83, 1.94, and 2.88 N sulfuric acid solutions containing 1000 mg/L copper(II) were mixed with 10 v/v% LIX 84 solution at various volume ratios. The equilibrium concentrations are shown in Fig. 4. The same K'_{eq} obtained above (13.1 for 10 v/v% LIX 84) was used to predict the equilibria, and the results were very accurate as indicated by the solid lines in the plot. The same data were also compared to the model of concentration-based equilibrium constant ($K^*_{eq} = 3.9$), and the results are indicated by the dash lines in Fig. 4. Both estimations are adequate at zero sulfuric acid concentration. When the concentration of sulfuric acid is increased to 0.83 N, the predictions become erroneously low when using the concentration-based model. At even higher sulfuric acid concentrations (1.94 and 2.88 N), the concentration-based model predicts near-zero copper concentrations in the organic phase in all cases (since a log scale was used for the Y axis, the lines were not plotted in the figure). Thus, models based on K'_{eq} are superior to the typical concentration-based equilibrium models (K^*_{eq}) when extrapolating to extremes in pH.

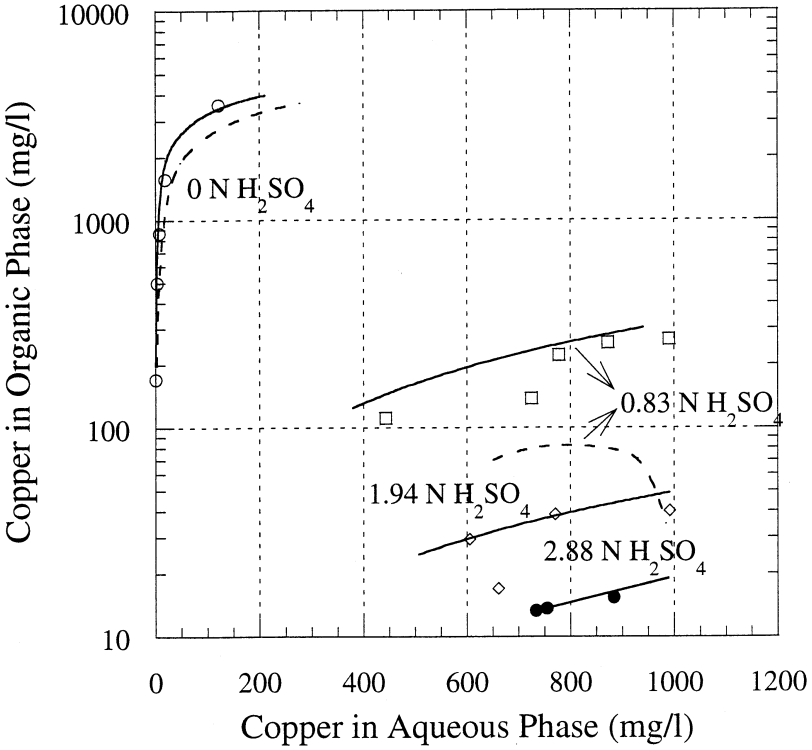

FIG. 4 Equilibrium prediction at various sulfuric acid concentrations. Experimental data (symbols) were compared with prediction by K'_{eq} (solid lines) and K^*_{eq} (dashed lines). Both models are adequate at low acid concentrations. At higher concentrations, K^*_{eq} vastly underpredicts the equilibria while K'_{eq}, which incorporates aqueous nonidealities and ionic equilibrium, remains accurate.

SUMMARY

Equilibria of copper–LIX 84 extraction were studied and equilibrium models based on concentration and activity was developed. Tetradecane was used as the diluent. An equilibrium constant K^*_{eq} of 3.9 was obtained in the concentration-based model. In the activity-based model, aqueous phase nonideality as well as major aqueous phase ionic equilibria were incorporated explicitly. A modified equilibrium constant K'_{eq} was regressed from the experimental data. When K'_{eq} is regressed from all the data, the equilibrium model shows bias at lower and higher LIX 84 concentrations. Such bias is most likely due to the nonideality of the organic phase. Such nonideality is lumped into a concentration-dependent equilibrium constant. These equilibrium constants (K'_{eq}) are 27.2 for 5 v/v% LIX 84 in tetradecane, 13.1 for 10 v/v%, and 6.2 for 20 v/v%. Once the appropriate value for K'_{eq} is chosen, the model can successfully predict copper–LIX 84 extraction equilibrium over a wide range of pH. The models were tested on extractions from normal to highly acidic environments. The concentration-based model can adequately predict the equilibria of copper–LIX 84 extraction when no acid is present in the aqueous solution. At lower pH, the activity-based model is effective over a wide range of pH; the nonideality of the aqueous phase was successfully predicted.

NOMENCLATURE

γ	activity coefficient of a component
α	activity of water
$[\,]$	concentration of a component (mol/cm^3)
$\{\,\}$	activity of a component
A	Constant A in the modified Guggenhein equation, 0.509
B	Constant B in the modified Guggenhein equation, 0.15
c	concentration of a species
I	ionic strength
K^*_{eq}	concentration-based equilibrium constant
K'_{eq}	apparent equilibrium constant
$K_1, \ldots, K_5$	equilibrium constants of aqueous phase ionic reaction
K_{eq}	thermodynamic equilibrium constant
K_p	partition coefficient
n	number of successfully converged data sets in the predictive model
V	volume (cm^3)
z	charge of a component

Subscripts

0	initial conditions
a	aqueous phase properties
exp	values from experiment
o	organic phase properties
prd	values from model prediction

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