Solvent Extraction Equilibrium in the CuSO$_4$–H$_2$SO$_4$–LIX 984–ESCAID 103 System†

Francisco José Alguacil,[*a] **Jaime Simpson**[b] **and Patricio Navarro**[b]

[a]*Centro Nacional de Investigaciones Metalurgicas (CSIC), Avda. Gregorio del Amo 8, Ciudad Universitaria, 28040 Madrid, Spain*

[b]*Departamento de Ingeniería Metalurgica, Facultad de Ingeniería, Universidad de Santiago, Avda. L.B.O'Higgins 3363, Casilla 10233, Santiago, Chile*

A previously determined thermodynamic model for extraction equilibrium is used as a basis to predict experimentally measured distribution coefficients for the CuSO$_4$ – H$_2$SO$_4$ – LIX 984–Escaid 103 solvent extraction system at 25 °C and aqueous copper concentrations in the range 0.01–2.0 g L^{-1}, the copper loading isotherm is also obtained.

Nearly thirty years ago a new period began in copper hydrometallurgy when extraction techniques were introduced to electrolytic copper production. Chelating extractants, mainly hydroxyoximes, have been applied as selective extractants.[1] The equilibrium reaction for the extraction of Cu^{II} ions using these extractants has attracted interest and several models have been proposed.[2–9] In the present work, the extraction equilibrium of copper from sulfate–sulfuric aqueous solutions by LIX 984 in Escaid 103 was studied, and a previously developed model[8] was taken as a basis to predict the distribution coefficients. The experimental data were compared with the predicted values.

The extractant used in the present work was LIX 984, which is an equivolume mixture of LIX 84 (2-hydroxy-5-nonylacetophenone oxime) and LIX 860 (5-dodecylsalicylaldoxime) in a high flash point hydrocarbon diluent.[10] This extractant was obtained from Henkel Corp. (through its Chilean branch) and used as received without further purification. Escaid 103 supplied by Esso Chile Petrolera (Chile), containing 10% aromatics, boiling range 205–240 °C, flash point 81 °C was used as the diluent also without further purification. The practical organic phase was prepared by dissolution of LIX 984 in the diluent. The concentration of LIX 984 in the organic solutions was determined by the ultimate loading.[11] The aqueous copper solutions were prepared by dissolving copper(II) sulfate of AR grade (Fluka) in water. The pH of the aqueous phases was controlled by adding sulfuric acid (Merck AR grade). The equilibrium extraction isotherm was obtained by contacting the aqueous and organic solutions to equilibrium at various A/O phase ratios. Other data were obtained in a 1:1 ratio A/O phase. Extraction experiments were carried out in separatory funnels thermostatted (water jacket) at 25 °C and mechanically shaken (700 min^{-1}). Contact time was in all cases 10 min, as previous experiments showed that this time was adequate to achieve equilibrium. In each experiment, the metal mass balance was calculated by analyzing the copper concentration in both aqueous and organic phases, before and after the reaction. Copper was analysed by AAS; an average of 98% accuracy was regularly obtained. The pH of the aqueous phase was measured by a Crison 506 pH-meter. IR measurements were obtained using a Nicolett-Magna 550 spectrophotometer and CsI windows.

The extraction reaction in the present extraction system can be expressed as:

$$2HR_{org} + Cu^{2+}_{aq} \rightleftharpoons CuR_{2\,org} + 2H^+_{aq} \tag{1}$$
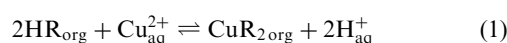
where HR represents the active substance of the extractant and org and aq the organic and aqueous phases, respectively. For the above equation, the equilibrium constant can be expressed by:

$$K_{ext} = \frac{[CuR_2]_{org}[H^+]^2_{aq}}{[HR]^2_{org}[Cu^{2+}]_{aq}} \frac{\gamma CuR_2 \gamma^2_{H^+}}{\gamma^2_{HR}\gamma_{Cu^{2+}}} \tag{2}$$

The distribution coefficient of copper is defined as:

$$D_{Cu} = \frac{[Cu^{2+}]_{org}}{[Cu^{2+}]_{aq}} \tag{3}$$

where $[Cu^{2+}]_{org}$ and $[Cu^{2+}]_{aq}$ represent the total concentration of copper in the respective phases. The equilibrium data obtained in the present work, using an organic solution of 5% v/v LIX 984 in Escaid 103, and calculated following the mathematical model of extraction equilibrium described in the literatures are given in Table 1.

Furthermore, the equilibrium constant of the overall copper extraction [eqn. (1)] was calculated numerically using

Table 1 Experimental and calculated equilibrium data for the extraction of copper in the CuSO$_4$ – H$_2$SO$_4$ – LIX 984–Escaid 103 system

[Cu]$_{initial}$/ g l^{-1}	pH$_e$	[Cu]$_{aq}$ g l^{-1}	log D_{Cu} (exptl.)	log D_{Cu} (calc.)
0.01	0.75	0.002	0.60	0.602
	0.50	0.005	0	0
0.05	0.78	0.011	0.55	0.602
	0.60	0.020	0.18	0.176
	0.43	0.030	−0.18	−0.176
0.1	0.65	0.033	0.31	0.250
	0.50	0.051	−0.02	−0.013
	0.31	0.070	−0.37	−0.381
	0.25	0.074	−0.45	−0.515
0.5	0.79	0.10	0.59	0.597
	0.63	0.19	0.19	0.194
	0.42	0.30	−0.17	−0.176
	0.35	0.32	−0.27	−0.288
	0.28	0.37	−0.44	−0.419
1.0	0.77	0.23	0.53	0.562
	0.65	0.34	0.29	0.250
	0.52	0.50	0	0
	0.39	0.60	−0.18	−0.209
	0.28	0.71	−0.39	−0.421
	0.24	0.79	−0.58	−0.535

the program LETAGROP-DISTR.[12] The program searches for a given model, the best set of equilibrium constants that minimizes the expression:

$$U = \sum (\log D_{calc} - \log D_{exptl})^2 \tag{4}$$

where D_{exptl} is the distribution coefficient of Cu[II] determined experimentally and D_{calc} is the value calculated by the program solving the mass balance equation for copper(II) and the extractant, assuming a particular set of species and constants. The program fits the existence of the CuR$_2$ species in the organic phase and the value of $\log K_{ext}$ was calculated to be 1.21 ± 0.12 [$\sigma(\log K_{ext}) = 0.04$] with $U = 0.106$ ($\sigma = 0.115$).
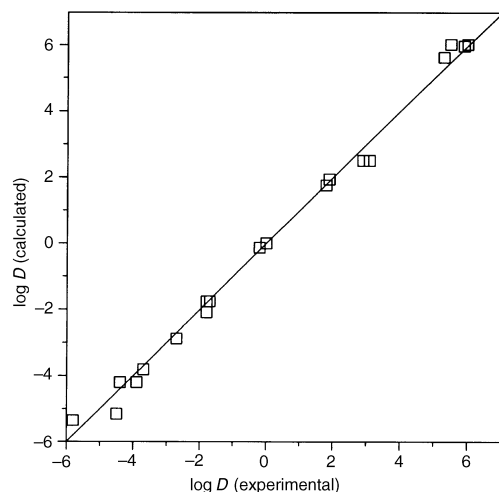

Fig. 1 Comparison between calculated and experimental distribution coefficient for copper(II) extraction by LIX 984

The experimental and calculated values of the copper distribution coefficients are plotted in Fig. 1. Good agreement between both sets of values is indicated by the r^2 value of 0.994 between these two data sets of values and the standard deviation, 0.030, of residuals from the line. Design of continuous counter-current extraction procedure requires information on the respective equilibrium isotherm. As the extraction of copper is normally carried out in the pH range of 1–3,[10] in the present study, an equilibrium isotherm was determined at a starting pH of 2.0. The concentration of copper(II) in the aqueous phase used in this study was in the range of 2.0 g L^{-1}. The extraction isotherm data for the CuSO$_4$–H$_2$SO$_4$–LIX 984–Escaid 103 system obtained from the phase ratio variation method are shown in Table 2. Fig. 2 shows the extraction isotherm for copper extraction with LIX 984 5% v/v (0.08 mol L^{-1}) in Escaid 103. The equilibrium isotherm curve can be mathematically represented by the following equation:

$$[Cu]_{org} = \frac{2.984[Cu]_{aq}}{0.145 + [Cu]_{aq}} \tag{5}$$

where $[Cu]_{org}$ and $[Cu]_{aq}$ represent the metal concentrations, in the respective phases, at equilibrium. At maximum loading, the molar ratio of ligand to metal, in the organic phase, is near 2:1, which supports the complex stoichiometry defined in eqn. (1) and also the numerical calculations performed above. The IR spectrum of a copper-loaded LIX 984 organic phase lacks the peak at *ca.* 3400 cm^{-1} due to the stretching vibration of the phenolic-OH group of the oxime, this is attributable to the formation of the metal-extracted complex.[1,7,13] The
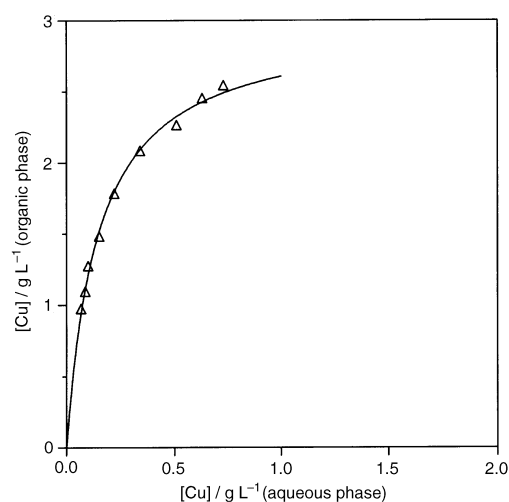

Fig. 2 Equilibrium loading isotherm for copper(II) extraction by LIX 984 in Escaid 103. Initial pH: 2.0.

Table 2 Extraction isotherm data

O/A Ratio	$[Cu]_{aq}$/g l^{-1}	$[Cu]_{org}$/g l^{-1}
2.00	0.066	0.97
1.75	0.086	1.09
1.50	0.099	1.27
1.25	0.15	1.48
1.00	0.22	1.78
0.80	0.34	2.08
0.66	0.51	2.26
0.56	0.63	2.45
0.50	0.73	2.54

results of the present study indicate that the model used can adequately describe the extraction equilibrium in the CuSO$_4$–H$_2$SO$_4$–LIX 984–Escaid 103 system, and that LIX 984 is a moderate copper extractant based on the fact that the organic phase becomes saturated at relatively low copper concentration, as shown in Fig. 2, and on the relatively low value of K_{ext} found for the system.

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