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Liquid–liquid extraction equilibrium in the $CuSO_4$–H_2SO_4–MOC 80TD–Iberfluid system

Francisco José Alguacil, Manuel Alonso and Antonio Cobo

Centro Nacional de Investigaciones Metalúrgicas (CSIC), Avda. Gregorio del Amo 8, Ciudad Universitaria, 28040 Madrid, Spain

A predictive model, which consists of a set of non-linear mass action and mass balance equations solved by using a tailor-made equation-solving program, is used as a basis to predict experimentally measured distribution coefficients for the $CuSO_4$–H_2SO_4–MOC 80TD-Iberfluid liquid–liquid extraction system at 20°C and aqueous copper concentrations in the range 0.1-1.0 g l^{-1}. The model is also used to obtain the copper loading isotherm at various initial aqueous pH values.

Keywords: liquid–liquid extraction equilibrium, $CuSO_4$–H_2SO_4–MOC 80TD-Iberfluid system

Copper solvent extraction is actually performed using oxime-based extractants: ketoximes, aldoximes and ketoximes/aldoximes mixtures. The main properties of these reagents are obtained elsewhere, in addition the three types show an excellent copper (II)–iron (III) selectivity.[1] The equilibrium reaction for the extraction of copper (II) ions using these extractants has attracted interest and several models have been proposed.[2–10] In the present work, the extraction equilibrium of copper from sulfate–sulfuric aqueous solutions by MOC 80TD in Iberfluid was studied, and a model was build-up and solved to predict the distribution coefficients and the copper loading isotherms. The experimental data were compared with the predicted values.

The extractant used in the present work was MOC 80TD, which is a mixture of MOC 45 (5-nonyl-2-hydroxyacetophenone oxime) and MOC 35TD (tridecanol modified 5-nonylsalicylaldoxime) in a high flash point hydrocarbon diluent.[11] This extractant was obtained from Allco Chem. Corp. (actually Cognis Corp., through its Chilean branch) and used as received without further purification. Iberfluid supplied by CS (Spain), containing 2% aromatics, boiling range 210–284°C, flash point 96°C was used as the diluent also without further purification. The practical organic phase was prepared by dissolution of MOC 80TD in the diluent. The concentration of MOC 80TD in the organic solutions was determined by the ultimate loading.[12] The aqueous copper solutions were prepared by dissolving copper (II) sulfate of AR grade (Fluka) in distilled water. Extraction experiments were carried out in separatory funnels thermostatted (water jacket) at 20°C and mechanically shaken (700 min^{-1}), data were obtained in a 1:1 ratio aqueous/organic phase. 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 analysing the copper concentration in both aqueous and organic phases, before and after the reaction. Copper was analysed by AAS (Perkin Elmer 1100B spectrophotometer); 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:

$$Cu^{2+}_{aq} + 2HR_{org} \rightleftharpoons CuR_{2\,org} + 2H^{+}_{aq} \tag{1}$$

where HR represents the active substance of the extractant and org and aq the organic and aqueous phases, respectively. The distribution coefficient of copper is defined as:

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

where $[Cu^{2+}]_{org}$ and $[Cu^{2+}]_{aq}$ represent the total concentration of copper in the respective phases.

The assumed reaction in building the model is represented by eqn (1), whereas the mass-action equilibrium expression for the reaction is:

$$[CuR_2]_{org} = K_{ext} \frac{[Cu^{2+}]_{aq}\,[HR]^2_{org}}{[H^+]^2_{aq}} \quad \frac{\gamma_{Cu2+}\,\gamma^2_{HR}}{\gamma_{Cu2+}\,\gamma^2_{H^+}} \tag{3}$$

The model also includes the following mass-balance equations:

$$[Cu]_{TOTAL} = [Cu^{2+}]_{aq} + V_{O/A}\,[CuR_2]_{org} \tag{4}$$

$$[HR]_{TOTAL} = [HR]_{org} + 2\,[CuR_2]_{org} \tag{5}$$

where $[Cu]_{TOTAL}$ and $[HR]_{TOTAL}$ are the total copper and extractant concentrations in the system, respectively, and $V_{O/A}$ is the organic to aqueous volume phase ratio. If only the pH of the aqueous feed is known, the hydrogen balance equation:

$$[H^+]_{aq} = [H^+]_{INITIAL} + 2\,V_{O/A}\,[CuR_2]_{org} \tag{6}$$

must be added to the model. Thus, all equilibrium concentrations can be calculated from the total extractant ($[HR]_{TOTAL}$), total copper ($[Cu]_{TOTAL}$), initial pH ($[H^+]_{INITIAL}$) and the O/A phase ratio ($V_{O/A}$). The equations describing the model are a set of non-linear equations that cannot be analytically simultaneously solved, thus a BASIC.2 programm (Tables 1a and 1b of the full text version of the paper or available on request to the authors) has been developed to do the calculations. The equilibrium constant of the overall copper extraction [eqn (1)] was calculated numerically using the program LETAGROP-DISTR.[13] The program searches for a given reaction, the best set of equilibrium constants that minimizes the expression:

$$U = \sum (\log D_{cal} - \log D_{exp})^2 \tag{7}$$

where D_{exp} is the distribution coefficient of Cu (II) determined experimentally and D_{cal} is the value calculated by the program. 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 1.01±0.25 [$\sigma(\log K_{ext}) = 0.08$] with $U = 1.4$ ($\sigma = 0.31$).

The equilibrium data obtained in the present work, using organic solutions of 2.5% and 10% v/v MOC 80TD in Iberfluid, and calculated using the predictive model and equilibrium values (eqns (3), (4) and (5)) are given in Table 1. The experimental and calculated values of the copper distribution

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* To receive any correspondence. E-mail: fjalgua@cenim.csic.es

Table 1 Experimental and calculated equilibrium data for the extraction of copper in the $CuSO_4$–H_2SO_4–MOC 80TD-Iberfluid system

$[HR]_{INITIAL}$/ % v/v	$[Cu]_{INITIAL}$/ g l^{-1}	pH_e	log D_{Cu} (exp.)	log D_{Cu} (cal.)
10	0.1	0.54	0.60	0.57
		0.46	0.44	0.40
		0.40	0.34	0.36
		0.21	0	0.10
		0.13	–0.14	–0.20
		0.05	–0.26	–0.30
	1.0	0.52	0.54	0.50
		0.24	0.07	0.12
		0.04	–0.32	–0.30
2.5	0.1	1.12	0.60	0.55
		0.84	0	0.10
		0.53	–0.60	–0.50
	1.0	1.06	0.51	0.47
		0.95	0.25	0.30
		0.89	0.096	0
		0.77	–0.08	–0.10
		0.70	–0.23	–0.30
		0.60	–0.47	–0.50

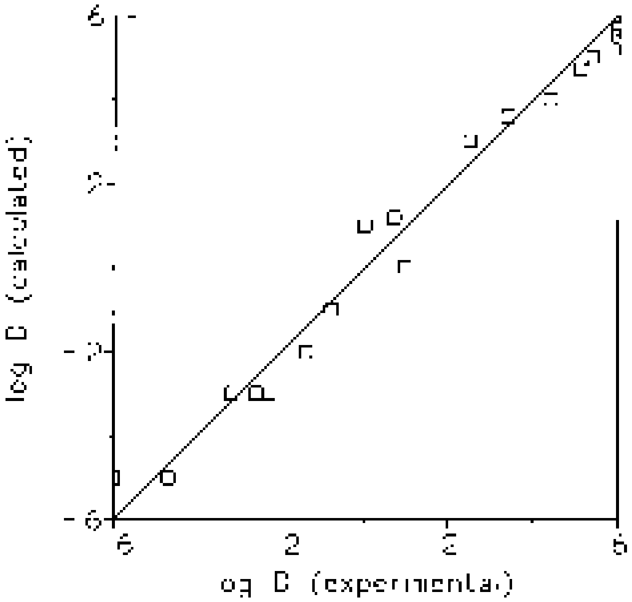

Fig.1 Comparison between calculated and experimental distribution coefficient for copper (II) extraction by MOC 80TD.

coefficients are plotted in Fig.1. Good agreement between both sets of values is indicated by the r^2 value of 0.97 between these two data sets of values and the standard deviation, 0.06, of residuals from the line. As the extraction of copper is normally carried out in the pH range of 1–3,[14] in the present work, equilibrium isotherms were obtained using the model [eqns (3), (4), (5) and (6)] at initial pH values of 1.0, 2.0, 3.0. Figure 2 shows the extraction isotherms for copper extraction with MOC 80TD 10% v/v in Iberfluid. The equilibrium isotherm curves can be mathematically represented by the following equation:

$$[Cu]_{org} = \frac{A\,[Cu]_{aq}}{B + [Cu]_{aq}} \qquad (8)$$

where $[Cu]_{org}$ and $[Cu]_{aq}$ represent the metal concentrations in the respective phases, at equilibrium. The values of the coefficients A and B are given in Table 2. The IR spectrum of a copper-loaded MOC 80TD 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 copper-extracted complex.[15] The results of the present study indicate that the predictive model used can adequately describe the extraction equilibrium in the $CuSO_4$–H_2SO_4–MOC 80TD-Iberfluid system, and that MOC 80TD 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.

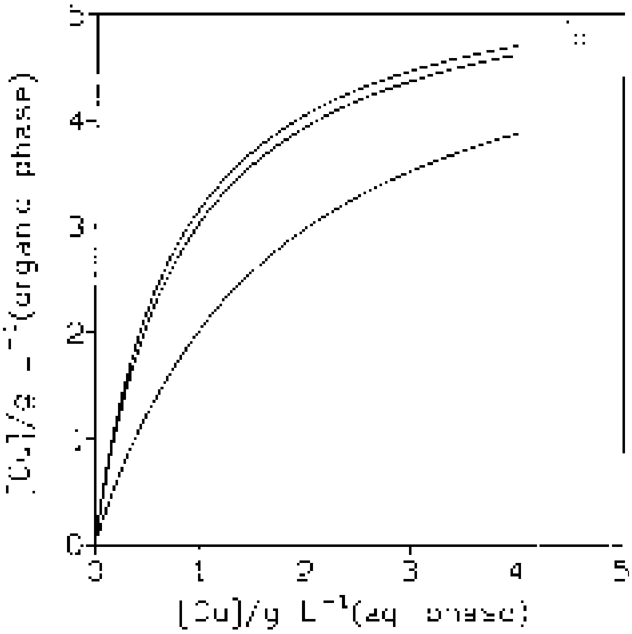

Fig.2 Predicted equilibrium loading isotherms for copper (II) extraction by MOC 80TD in Iberfluid.

Table 2 Values of the coefficients A and B for eqn (8)

pH	*A*	*B*
3.0	5.58	0.75
2.0	5.56	0.82
1.0	5.54	1.71

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