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Modelling copper (II) liquid–liquid extraction: the system Acorga M5640-Exxsol D100–$CuSO_4$–H_2SO_4

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A predictive model, which consists in a set of non-linear mass action and mass balance equations solved by using a taylor-made equation-solving program, is used as a basis to predict experimentally measured distribution coefficients for the Acorga M5640-Exxsol D100–$CuSO_4$–H_2SO_4 liquid–liquid extraction system at 20°C and aqueous copper concentrations in the range 0.0016–0.0032 mol l^{-1}. The model is also used to obtain the copper loading isotherm at various equilibrium aqueous pH values.

Keywords: liquid–liquid extraction, Acorga M5640-Exxsol D100–$CuSO_4$–H_2SO_4

Stringent environmental considerations had led to industries to reduce the amount and to increase environmental safety of the liquid waste they produce. In most cases, a closed-cycle process is the ultimate objective, where the only end-product from the process is a saleable one and all waste streams are recycled or self-treated by the industry. Liquid effluents have traditionally been treated by one or a combination of physico-chemical or biological processes.[1] However, they often fail to reduce the concentration of heavy metals below permissible limits, furthermore, they are not sufficiently selective to create valuable product streams suitable for recycle or re-use. Separation processes provide the means for approaching these latter objectives. The most established separations technology for liquid effluent recycling is liquid–liquid extraction.[2]

In the particular case of copper (II), metal liquid–liquid extraction is performed using oxime-based extractants.[3] Before scaling up the technology, either in the form of mixer–settler or column extraction, a theoretical model of the extraction system is needed in order to design an efficient recovery process in terms of better stability, thus, the equilibrium reaction of copper (II) ions using these extractants has attracted interest and relatively recently several models have been proposed.[4-8]

In the present investigation, the extraction equilibrium of copper from sulfate-sulfuric aqueous solutions by Acorga M5640 in Exxsol D100 was studied, and a model was build-up and solved to predict the distribution coefficients and the copper loading isotherms. The predicted values were compared with the experimental data.

The extractant used in the present work was Acorga M5640, whose active substance is 2-hydroxy-5-nonylsalicylaldoxime.[3] This extractant was obtained from Avecia and used as received without further purification. Exxsol D100 obtained from ExxonMobil Chem. Iberia (Spain), containing 0.9 % aromatics, boiling range 234–264°C, flash point 99°C was used as the diluent also without further purification. The practical organic phase was prepared by dissolution of Acorga M5640 in the diluent. The concentration of Acorga M5640 in the organic solutions (Table 1) was determined by the ultimate loading.[9] The aqueous copper solutions were prepared by dissolving copper (II) sulphate of AR grade (Fluka) in distilled water. Extraction experiments were carried out in separatory funnels thermostatted (water jacket) at 20°C and mechanically shaken (750 min^{-1}), data were obtained in a 1:1 ratio aqueous/organic phase. Contact time was in all cases 15 min, as previous experiments showed that this time was adequate to achieve equilibrium. Copper was analysed by AAS (Perkin Elmer 1100B spectrophotometer); an average 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.

Table 1 Loading capacity of Acorga M5640 in Exxsol D100

Acorga M5640/mol l^{-1}	$[Cu]_{org.phase}$/mol l^{-1}
0.176	0.088
0.045	0.021

Aqueous phase: 0.016 mol l^{-1} copper. pH_{eq}: 3.0.

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

$$Cu^{2+}_{aq} + 2HR_{org} \Leftrightarrow CuR_{2_{org}} + 2H^{+}_{aq} \qquad (1)$$

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:

$$D_{Cu} = \frac{\left[Cu^{2+}\right]_{org}}{\left[Cu^{2+}\right]_{aq}} \qquad (2)$$

where $[Cu^{2+}]_{org}$ and $[Cu^{2+}]_{aq}$ represent the equilibrium 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:

$$\left[CuR_2\right]_{org} = K_{ext}\frac{\left[Cu^{2+}\right]_{aq}\left[HR\right]^2_{org}}{\left[H^{+}\right]^2_{aq}}\frac{\gamma_{Cu^{2+}}\gamma^2_{HR}}{\gamma_{CuR_2}\gamma^2_{H^{+}}} \qquad (3)$$

The model also includes the following mass-balance equations:

$$\left[Cu\right]_{INITIAL} = \left[Cu^{2+}\right]_{aq} + V_{O/A}\left[CuR_2\right]_{org} \qquad (4)$$

$$\left[HR\right]_{INITIAL} = \left[HR\right]_{org} + 2\left[CuR_2\right]_{org} \qquad (5)$$

where $[Cu]_{INITIAL}$ and $[HR]_{INITIAL}$ are the initial copper and extractant concentrations in the system, respectively, and $V_{O/A}$ is the organic to aqueous volume phase ratio. Thus, all equilibrium concentrations can be calculated from these parameters and knowing the $[H^+]_{aq}$ (pH_{eq}) of the aqueous solution after equilibration with the corresponding organic solution. The equations describing the model are a set of non-linear equations that can not be simultaneously solved analytically, thus a BASIC.2 programm has been used to do the calculations.[8] The equilibrium constant of the overall copper extraction [eqn(1)] was calculated numerically using the program LETAGROP-DISTR.[10] The program searches, for a given reaction, the best set of equilibrium constants that minimises the expression:

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$$U = \sum \left(\log D_{\mathrm{cal}} - \log D_{\mathrm{exp}}\right)^2 \qquad (6)$$

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 0.66 (σ(log K_{ext})= 0.04) with U= 0.033 (σ = 0.08).

The equilibrium data obtained in the present work, using organic solutions 0.018 to 0.09 M Acorga M5640 in Exxsol D100, and calculated using the predictive model and equilibrium values [eqns (3), (4) and (5)] are given in Table 2. 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 0.97 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, in the present work, equilibrium isotherms were obtained using the model at equilibrium pH values of 1.0, 2.0, 3.0. Figure 2 shows the extraction isotherms for copper extraction with 0.045 M Acorga M5640 in Exxsol D100. The equilibrium isotherm curves can be mathematically represented by the following equation:

$$[\mathrm{Cu}]_{\mathrm{org}} = \frac{A[\mathrm{Cu}]_{\mathrm{aq}}}{B + [\mathrm{Cu}]_{\mathrm{aq}}} \qquad (7)$$

where $[\mathrm{Cu}]_{\mathrm{org}}$ and $[\mathrm{Cu}]_{\mathrm{aq}}$ represent the metal concentrations in the respective phases, at equilibrium. The values of the coefficients A and B are given in Table 3. The IR spectrum of a copper-loaded Acorga M5640 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.[3] The results of the present study indicate that the predictive model used can adequately describe the extraction equilibrium in the Acorga M5640-Exxsol D100–$CuSO_4$–H_2SO_4 system, and that Acorga M5640 is a moderate copper extractant based on the fact that the organic phase becomes saturated at relatively low copper concentrations, as shown in Fig.2, and on the relatively low value of K_{ext} found for the system.

Table 2 Experimental and calculated equilibrium data for the extraction of copper in the Acorga M5640-Exxsol D100–$CuSO_4$–H_2SO_4 system

$[\mathrm{HR}]_{\mathrm{INITIAL}}$/ % v/v	$[\mathrm{Cu}]_{\mathrm{INITIAL}}$/ g l^{-1}	pH_{eq}	log D_{Cu} (exp.)	log D_{Cu} (cal.)
0.09	0.0016	0.50	–0.50	–0.44
		0.75	0.02	–0.08
		0.93	0.39	0.41
		1.02	0.60	0.60
	0.0032	0.54	–0.35	–0.36
		0.87	0.22	0.28
0.045	0.0016	0.95	–0.27	–0.15
		1.03	0	0
		1.20	0.27	0.33
	0.0032	0.80	–0.60	–0.46
		1.04	0	–0.01
		1.34	0.60	0.54
0.018	0.0016	1.25	–0.37	–0.37
		1.38	–0.16	–0.12
		1.60	0.33	0.27
		1.64	0.37	0.34
	0.0032	1.18	–0.50	–0.54
		1.45	0.02	–0.07
		1.69	0.41	0.33

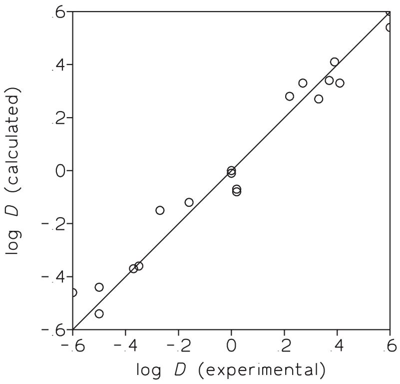

Fig.1 Comparison between calculated and experimental distribution coefficient for copper (II) extraction by Acorga M5640.

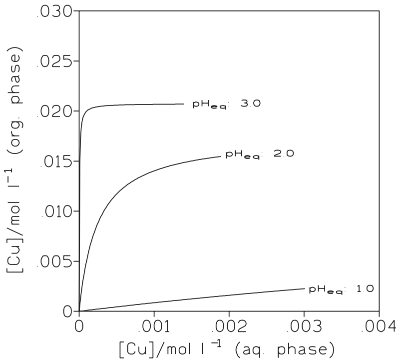

Fig.2 Predicted equilibrium loading isotherms for copper (II) extraction by Acorga M5640 in Exxsol D100.

Table 3 Values of the coefficients A and B for eqn(7)

pH_{eq}	A	B
3.0	0.020	3.8×10^{-6}
2.0	0.017	2.5×10^{-4}
1.0	0.013	0.014

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