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Modeling the phase equilibrium in liquid–liquid extraction of
copper over a wide range of copper and hydroxyoxime
extractant concentrations

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Abstract

The phase equilibrium in the loading and stripping stages of liquid–liquid extraction of copper with hydroxyoxime extractant in kerosene was studied over a wide range of Acorga M5640 extractant (5–25 vol-%) and copper (1–45 g/L) concentrations. A mechanistic mathematical model explaining the phase equilibrium was developed and validated. The model accounts for the non-ideality of both the aqueous and the organic phases. The composition of the aqueous sulphate solution was calculated through speciation of the electrolytes with an ion association model. The concentration of the extractant in the organic phase has a strong effect on the equilibrium constant of the extraction reaction. The organic phase non-ideality in the loading stage was described with an empirical correlation. The model parameters were fitted against the experimental data using nonlinear regression analysis. A Markov chain Monte Carlo algorithm was used to assess the reliability of the modeling results. The model has a significantly wider range of application than previous models and thus facilitates the optimization of extractant concentration.

Keywords

Liquid-liquid extraction; Equilibrium modeling; MCMC; Copper; Acorga M5640

1. Introduction

Liquid–liquid extraction of copper is the most widely used application of liquid–liquid extraction in the metallurgical industry (Schlesinger et al., 2011; Tamminen et al., 2013). Within the hydrometallurgical method of pure copper production, liquid–liquid extraction is responsible for the purification and concentration of copper from a pregnant leach solution (PLS) to generate an electrolyte for the electrowinning of high quality copper cathodes. This process scheme accounts for about 20% of primary copper production in the world (Schlesinger et al., 2011).

The copper liquid–liquid extraction process with hydroxyoxime extractants can be represented as interfacial, reversible, competitive reactions of copper(II) cation, protons, and cationic impurities on the aqueous side with chelating hydroxyoxime extractant molecules on the organic side. Hydroxyoxime extractants exhibit high selectivity for copper over other

metallic cations, especially iron, which is the main impurity in the process. This allows the concentration and purification of copper in the organic phase and the rejection of impurity species in the PLS to the raffinate.

Extraction of copper in the range of low aqueous copper concentrations with hydroxyoxime-type extractants has been extensively studied and reported in the literature (Agarwal et al., 2012; Aminian et al., 2000; Flett et al., 1973; Komasaawa et al., 1980; Piotrowicz et al., 1989; Tanaka, 1990a; Tanaka, 1990b; Tanaka, 1990c). It has been considered sufficient, since according to Kordosky et al. (2006), copper liquid–liquid extraction was applied in order to concentrate and purify copper from solutions generated in heap and dump leaching. In these cases, the PLS typically contained 0.5–8 g/L of copper. However, significant progress in the leaching of high-grade copper sulfide ores and copper concentrates and the application of pressure oxidation leaching has enabled the feeding of liquid–liquid extraction with PLS containing up to 43 g/L of copper. This also requires the use of high extractant concentrations (Kordosky et al., 2006; Schlesinger et al., 2011).

Even though there are many studies on the extraction equilibria of copper with hydroxyoximes (Aminian et al., 2000; Doungdeethaveeratana and Sohn, 1998; Gouvea and Morais, 2010; Molnar and Verbaan, 2003; Ochromowicz and Chmielewski, 2013; Sridhar and Verma, 2011), data on extraction in a wide range of conditions, especially in the range of high aqueous copper concentrations with hydroxyoxime extractants like Acorga M5640, are still insufficient. The equilibrium of liquid–liquid extraction is usually represented in terms of loading extraction isotherms (Agarwal et al., 2010; Deep et al., 2010; Ferreira et al., 2010). However, this representation cannot show the influence of all the variations in the extraction conditions on the phase equilibrium in a compact form. On the other hand, mechanistic mathematical models are reliably able to predict phase equilibrium and create the isotherms under any operating conditions within the calibration range. Information concerning the mechanistic mathematical modeling of the extraction equilibrium of copper(II) with the hydroxyoxime extractants from a sulfate medium is scarce in the literature.

The equilibrium of copper liquid–liquid extraction has usually been described using a simple concentration-based mass action law, when the concentrations of copper and sulfuric acid in the aqueous phase were low or their variation was small. Otherwise, the non-ideality of the aqueous phase was taken into account by introducing the activity formulation of an extraction equilibrium constant (instead of a concentration-based mass action law) using activity

coefficient models for aqueous species (Agarwal et al., 2012; Piotrowicz et al., 1989; Tanaka, 1990a). The non-ideality of the organic phase has been observed when a model with a single parameter for the extraction equilibrium constant was applied to solutions with widely varying total extractant concentrations (Agarwal et al., 2012; Hu and Wiencek, 2000; Lin et al., 2002; Piotrowicz et al., 1989). Non-ideality has also been observed with different values of the apparent extraction equilibrium constant for different total extractant concentrations. Agarwal et al. (2012) and Piotrowicz et al. (1989) tried to explain this phenomenon by the dimerization of the hydroxyoxime molecules in the organic phase; an additional parameter, the dimerization equilibrium constant, was introduced into the models. Agarwal et al. (2012) found that this improved the model fit, whereas Piotrowicz et al. (1989) found that the dimerization of oxime could be neglected for hydroxyoxime concentrations up to 20 vol-%.

Although Agarwal et al. (2012) and Alguacil et al. (2004) reported data and models for the equilibrium of the copper extraction from the aqueous system $\text{CuSO}_4\text{--H}_2\text{SO}_4$ with Acorga M5640 extractant in an aliphatic diluent, the studies cover only low aqueous copper concentrations. Yet for processes with concentrated PLS solution conditions, it is relevant that these models have not covered 5–35 vol-% of extractant in the organic phase and up to 43 g/L of copper in the aqueous phase (Schlesinger et al., 2011). Nor, to our knowledge, has mechanistic mathematical modeling been used to predict the equilibria of the stripping stage of liquid–liquid extraction of copper. To sum up, there is no mechanistic model available in the literature that allows the prediction of the composition of the process phases of copper liquid–liquid extraction equilibrium with a hydroxyoxime extractant in the wide PLS and extractant concentration ranges.

In this work, a mechanistic mathematical model able to explain the equilibrium of copper liquid–liquid extraction in wide concentration ranges of copper and hydroxyoxime extractant was correlated. The developed model was verified with extensive experimentally collected data on the equilibrium of the loading and stripping stages in wide concentration ranges. A new formulation for the copper extraction reaction equilibrium constant was suggested to improve the model prediction. A Markov chain Monte Carlo (MCMC) algorithm (Haario et al., 2006) was used to estimate the reliability of the modeling results.

2. Materials and methods

2.1. Materials

The extractant used was Acorga M5640 (Cytec), whose active substance is 2-hydroxy-5-nonylsalicylaldoxime. The extractant was used after washing twice with 3 M H_2SO_4 . The washed organic and samples taken from the batch equilibrium experiments were centrifuged for 10 min at 4000 rpm prior to analyses to ensure complete phase disengagement. As a diluent, aliphatic diluent kerosene Exxsol D80 (Exxon Mobil) was used. An organic solution of the required hydroxyoxime concentration was prepared by dissolving the washed organic in the solvent. Aqueous stock solutions of copper were prepared by dissolving copper(II) sulfate pentahydrate (Fluka, AR grade), or copper(II) sulfate (VWR Chemicals, AR grade) in purified water (ELGA VEOLIA CENTRA R120), and the pH value was adjusted using H_2SO_4 (Merck, AR grade).

2.2. Experimental procedure

Extraction and stripping experiments were carried out on an orbital shaker in 50 mL separation funnels, with 30 min equilibration time and at 20 °C. Organic to aqueous (O/A) phase ratios were varied. In the loading experiments, aqueous phases with known copper content and acidity were brought into contact with copper-free organic phases of known extractant concentration. In the stripping experiments, copper-free aqueous phases of known acidity were brought into contact with loaded organic phases with known copper and extractant concentrations.

The experimental design of the extraction and stripping experiments is shown in Table 1 and in the supplementary materials. In extraction experiment E1, the initial acidity was varied, and the organic to aqueous phase ratio (O/A) was kept constant. In all the other extraction experiments, E2–E9, only O/A was varied. The equilibrium acidity was not controlled in all the experiments. The loaded organic phases for the stripping experiments (S1–S4) were prepared by bringing fresh organic phases of known extractant concentrations into contact with the aqueous phase containing 45 g/L of copper at pH 4.3. Each experiment was replicated three times. The equilibrium copper concentration in the aqueous phase, the equilibrium acidity of the aqueous phase, and the free oxime-extractant concentration in the organic phase were measured. The copper concentration in the organic phase was calculated from the mass balance. The volume change due to mixing was neglected.

Copper content in the aqueous phase was analyzed by ICP-MS (Agilent technologies, Agilent 7900), and acidity was measured by titration with a standard 0.1 M NaOH (Sigma-Aldrich, AR grade) solution using a Mettler Toledo T50 titrator with a DG 111-SC electrode. The same instrument was used to measure the total free oxime concentration in the organic phases by the ultimate loading method. Measurements of the pH were carried out with a Consort C3010 pH meter using a SenTix Mic glass electrode.

Table 1. Experimental design of the extraction and stripping experiments.

Extraction						
Experiment set ID	Data points	C(Cu) ₀ , g/L	pH ₀	HR, vol-%	Loading ₀ , %	O/A range
E1	28	5	0.11...3.91	10	0	1/1
E2	21	1	1.4	10	0	1/10 ... 10/1
E3	25	5	1.4	10	0	1/10 ... 10/1
E4	29	25	1.4	10	0	1/10 ... 10/1
E5	30	25	1.4	25	0	1/10 ... 10/1
E6	29	32	1.4	25	0	1/10 ... 10/1
E7	26	45	1.4	25	0	1/10 ... 10/1
E8	15	25	1.4	5	0	1/10 ... 10/1
E9	15	25	1.4	17	0	1/10 ... 10/1

Stripping						
Experiment set ID	Data points	C(Cu) ₀ , g/L	C(H ₂ SO ₄) ₀ , g/L	HR, vol-%	Loading ₀ , %	O/A range
S1	15	0	160	10	90	2/1 ... 10/1
S2	15	0	160	25	80	2/1 ... 10/1
S3	15	0	190	10	90	2/1 ... 10/1
S4	15	0	190	25	80	2/1 ... 10/1

3. Extraction and stripping equilibrium model

The distribution equilibrium of copper between the aqueous and organic phases in liquid–liquid extraction with a hydroxyoxime extractant depends on the chemistry and physics of the process.

3.1. Interfacial and organic phase chemistry

The core of liquid–liquid extraction of copper is the ion transfer between the aqueous and organic phases according to a reversible two-step mechanism (Flett et al., 1973):

where the overbar denotes the species in the organic phase, R denotes deprotonated hydroxyoxime, and HR denotes a protonated hydroxyoxime molecule.

The overall extraction reaction, Eq. (3), leads to the expression of the concentration-based extraction equilibrium constant, Eq. (4), which is the same for the two-step mechanism.

$$K_{LLX} = \frac{[\overline{CuR_2}] \cdot [H^+]^2}{[Cu^{2+}] \cdot [\overline{HR}]^2}, \quad (4)$$

When concentrations of species in both phases are small (ideal solutions), the equilibrium of copper extraction is traditionally described and analyzed by slope analyses using a simple linear regression model derived from Eq. (4) (Ritcey and Ashbrook, 1984):

$$\log D = \log(K_{LLX}) + 2 \cdot \log[\overline{HR}] + 2 \cdot pH, \quad (5)$$

where $D = [\overline{CuR_2}] / \sum[Cu^{2+}]$. A linear relationship of $\log D$ vs. equilibrium pH and $\log[\overline{HR}]$ is usually observed with a slope of around 2, which shows the stoichiometry of the extraction reaction, whereas the intersection term gives an estimate for the extraction equilibrium constant, K_{LLX} (Ritcey and Ashbrook, 1984; Szymanowski and Borowiak-Resterna, 1991). However, due to the non-ideality of the aqueous and organic phases, there are considerable deviations from Eq. (5) in systems with high copper and extractant concentrations (Agarwal et al., 2012; Komasa et al., 1980).

When the concentration of hydroxyoximes in the organic phase is high, phenomena such as the association of unreacted hydroxyoximes, the polymerization of the copper-hydroxyoxime complexes, and the solvation of complexes with unreacted hydroxyoxime molecules may occur (Szymanowski and Borowiak-Resterna, 1991). The characteristic feature of hydroxyoxime extractants is to undergo self-association due to the presence of the oximino group (=NOH), which is a weak proton acceptor (Sastre and Szymanowski, 1993). Most likely only two oxime molecules participate in the association, meaning dimerization

(Szymanowski, 1993). In this work, other numbers of molecules involved in self-association were also tested, but this did not show an improvement in model fit. The dimerization of extractant molecules can be described using the equilibrium constant determined for a given system:

$$K_D = \frac{[\overline{(HR)_2}]}{[\overline{HR}]^2}. \quad (7)$$

The dimerization depends mainly on the diluent. Dimerization constants are in the order of a few units (L/mol) in aromatic hydrocarbon diluents and in the range of 20 to 200 L/mol in aliphatic hydrocarbon diluents (Sastre and Szymanowski, 2004; Szymanowski and Borowiak-Resterna, 1991; Szymanowski, 1993). Therefore, the higher the extractant concentration in the organic phase, the more deviation from the straight line, according to Eq. (5), will be observed (Agarwal et al., 2012; Komasa et al., 1980; Piotrowicz et al., 1989).

According to Szymanowski and Borowiak-Resterna (1991), polymerization of the copper-oxime complex is not usually observed in systems with commercial copper extractants, and there is little probability of solvation of the copper complex by hydroxyoxime molecules. However, the reaction of the copper(II) cation with the dimeric extractant has been considered by Russell and Rickel (1990), while Amores et al. (1997) have also considered the formation of another copper complex present in the organic phase (1997) according to reaction Eq. (8). Amores et al. (1997) reported that the introduction of reaction Eq. (8) to the extraction mechanism enabled a better explanation of their experimental data on copper extraction equilibrium.

However, it is deemed unlikely here that copper-extractant complexes are formed to a significant extent according to Eq. (8). This is because the structure of the dimer significantly reduces its adsorption on the phase interface and thus limits the probability of its reaction with the copper cations in the aqueous phase. It is more likely that the complex is formed in the bulk organic phase in a solvation reaction with the unreacted hydroxyoxime, as in Eq. (9), or with the dimer, as in Eq. (11).

$$K_{S1} = \frac{[\overline{Cu(HR_2)_2}]}{[\overline{CuR_2}][\overline{HR}]^2}, \quad (10)$$

$$K_{S2} = \frac{[\overline{Cu(HR_2)_2}]}{[\overline{CuR_2}][\overline{(HR)_2}]}, \quad (12)$$

To conclude, equilibrium liquid–liquid extraction of copper is governed by the interfacial chelating reaction, Eq. (3). However, when the extractant concentration is high, the reaction equilibrium may be influenced by organic phase non-ideality, which can be caused by extractant dimerization Eq. (6) and/or by the solvation of the extracted complex Eq. (9) or Eq. (11). All these phenomena, Eq. (3), Eq. (6), Eq. (9), and Eq. (11), are considered in this work in order to find the best way to explain the measured experimental data using mechanistic mathematical modeling.

3.2. Aqueous-side chemistry

In liquid–liquid extraction of copper from concentrated sulfate solutions, the aqueous phase contains the dissolution products of electrolytes $CuSO_4$ and H_2SO_4 , so that the principal species present in the solution are cupric ion (Cu^{2+}), bisulfate (HSO_4^-), cupric sulfate ($CuSO_{4aq}$), proton (H^+), and sulfate ion (SO_4^{2-}). The concentration of undissociated H_2SO_4 is negligibly small (Casas et al., 2000). Therefore, not all the copper in the aqueous solution is available for the reaction with the hydroxyoxime extractant in the form of Cu^{2+} . In the same way, the degree of sulfuric acid dissociation affects the liquid–liquid phase equilibrium. The higher the concentrations of copper sulfate and sulfuric acid, the more non-ideal is the aqueous phase, and the more there is deviation from the straight-line relationship of Eq. (5) (Agarwal et al., 2012; Komasa et al., 1980; Piotrowicz et al., 1989; Tanaka, 1990a). Thus, speciation in the aqueous phase has to be taken into account when modelling liquid–liquid extraction of copper from concentrated aqueous solutions. The aqueous phase model used in this study contains the reactions presented in Table 2.

Table 2. Aqueous phase dissociation reactions in the system $H_2SO_4 - CuSO_4$.

Chemical reaction	Equation for equilibrium constant
$H^+ + HSO_4^- = H_2SO_4$	$K_1 = \frac{[H_2SO_4]}{[H^+][HSO_4^-]} \quad (13)$
$H^+ + SO_4^{2-} = HSO_4^-$	$K_2 = \frac{[HSO_4^-]}{[H^+][SO_4^{2-}]} \quad (14)$
$Cu^{2+} + SO_4^{2-} = CuSO_4$	$K_3 = \frac{[CuSO_4]}{[Cu^{2+}][SO_4^{2-}]} \quad (15)$

The values of the concentration-based dissociation constants of the electrolytes in concentrated aqueous solutions are known to depend on the composition of the solutions and on their amounts. Here, the first step of sulfuric acid dissociation was assumed to be complete ($\log K_1 = -3$). The sulfate–bisulfate equilibrium and sulfate–copper sulfate equilibrium were calculated by using correlations $\log K_2 = 1.99 - \Delta \log K_2$ and $\log K_3 = 2.35 - \Delta \log K_3$ (Tamminen et al., 2013), where $\Delta \log K$ describes the effect of the ionic strength and is defined as follows:

$$\Delta \log K = 0.51 \left(\frac{\sqrt{I}}{1 + 1.50\sqrt{I}} - CI \right) \chi + CI \quad (19)$$

The value of $\chi = 4$ for bisulfate (K_2) and of $\chi = 8$ for copper sulfate (K_3). At a relatively low ionic strength range ($I < 0.5$), the value of $C = 0.09$ is used for both electrolytes, whereas the value of $C = 0.01$ is used up to $I = 3$ (Tamminen et al., 2013).

3.3. Numerical methods in solution

The model of the copper liquid–liquid extraction phase equilibrium consists of non-linear algebraic equations for the equilibrium constants of all the reactions of the assumed mechanism and of mass balance equations for the species in the system. In addition, a semi-empirical equation is used to account for aqueous phase non-ideality by correcting the equilibrium constants of the aqueous phase reactions.

The model equations can be solved for the equilibrium composition of the process phases using, for example, the Newton-Raphson algorithm. However, a good initial guess is needed, since otherwise, erroneous or inaccurate results can be obtained. An alternative is a rate-based approach (Kuitunen, 2014; Salmi et al., 2011), where both the forward and reverse

parts of the reactions are represented as irreversible, and a reaction rate equation is formed for each of them according to the mass action law Eq. (16). The forward reaction rate constant was chosen to be $k_f = 1000$, the same for all the reactions, since it does not influence equilibrium but influences the time required to reach it. The expression of the reaction equilibrium constant Eq. (17) sets the relationship between the forward and backward parts of the reversible reactions. With this mathematical manipulation, all the nonlinear algebraic equations are converted into differential equations that can be solved simultaneously as an initial value problem by integration, and the solution of the model can be significantly eased.

$$r_i = -k_i[A]^\alpha[B]^\beta, \quad (16)$$

$$k_{f,i} = k_{r,i}K_i, \quad (17)$$

where k_f and k_r are the reaction rate constants of the forward and reverse reactions, respectively, K is the equilibrium constant, r is the reaction rate, i is the index of equilibrium reactions, $[A]$ and $[B]$ are molar concentrations of components, and α and β are stoichiometric coefficients of the forward or reverse reactions.

In theory, the same model described above can be used to predict the equilibrium of both the extraction and stripping stages of the copper solvent extraction process. However, in practice, different equilibrium constants may be needed, due to the large difference in the acidity of the extraction and stripping stages of the copper liquid–liquid extraction.

3.4. Parameter estimation and model selection

The unknown model parameters were estimated by nonlinear regression fitting of the experimentally measured total copper concentration in the aqueous phase, the total acidity in the aqueous phase, and the total free oxime concentration in the organic phase; in other words, the expression in Eq. (18) was minimized. A similar approach was used when Russell and Rickel (1990) fitted the model parameters by minimizing the sum of squares of the difference between the calculated and experimentally measured copper concentration in the organic phase. The estimation of model parameters has traditionally been done by fitting $\log D$ only (Agarwal et al., 2012; Alguacil et al., 2004; Doungdeethaveeratana and Sohn, 1998; Tanaka, 1990b), but the approach used in this work is more accurate, since it directly utilizes experimentally measured data. The logarithmic function has a different behavior of errors in comparison with the function responses

(concentration of copper in both phases), while in this study, the goal is the accurate prediction of concentrations of the species in the process phases instead of their distribution.

$$Res = \sum_{g=1}^G \sum_{m=1}^M \sum_{j=1}^N \left(\frac{Y_{j,i}^{exp} - Y_{j,i}^{mod}}{\max(Y_{g,j,i}^{exp})} \right)^2 \quad (18)$$

where Res is the weighted sum of squares residual, Y is the total equilibrium molar concentration of copper or protons in the aqueous phase or is the total extractant concentration in the organic phase, m is the number of responses, j is the number of experiments, N is the total number of experiments in the experimental group, M is the total number of responses, g is number of the group, and G is the total number of experimental groups.

The range of the measured values of total concentrations was very wide, giving extremely high weightings to some experimental results and disregarding others. Therefore, the experimental data were weighted inside data groups (E1–E9 or S1–S4), so that the data from different groups had equal importance in the estimation of the model parameters.

The selection of the most appropriate model for the copper liquid–liquid extraction equilibrium in our study was done by the following principle: the preferable model was the one with the minimum mean squared error (MSE), Eq. (19), explaining the experimental data well enough according to visual observations of the loading isotherms and with the minimum number of parameters (Beck and Arnold, 1977).

$$MSE = \frac{Res}{N * m - p} \quad (19)$$

where p is the number of fitted parameters in the model.

All the modeling in the current study was done in Matlab. An open source MCMC code package developed by Laine (2015) was used to estimate the reliability of the modeling results.

4. Results

4.1. Modeling of loading stage

In the present study, liquid–liquid extraction of copper from sulfuric acid solutions with hydroxyoxime extractant Acorga M5640 in the aliphatic diluent Exxsol D80 was studied with 218 phase equilibrium experiments according to the design of experiments in Table 1. The measured experimental data are presented as supplementary material. Figure 1 shows that a simple linear regression model, Eq. (5), which is usually used to analyze the equilibrium in ideal solutions, is unable to explain well all the variation in the collected experimental data. An underlying reason may be the non-ideality of both the aqueous and organic phases, since the concentrations are rather high in many of the data points.

Figure 1. Overview of the experimental data using the classical log–log representation.

4.1.1. Mechanistic models

Several mechanistic models for liquid–liquid extraction of copper were considered in order to find the one that would best explain the collected experimental data in this work. The same aqueous speciation model, Eq. (13), Eq. (14), and Eq. (15), was used in all the cases, whereas the organic phase phenomena were modeled with the models listed in Table 3.

Table 3. Mechanistic models used for the organic-side phenomena and interfacial reactions of liquid–liquid extraction of copper.

Model ID	Model	Equations
1	Overall equilibrium complexation reaction	Eq. (3)
2	Overall equilibrium complexation reaction + dimerization of unreacted hydroxyoxime molecules	Eq. (3) and Eq. (6)
3	Overall equilibrium complexation reaction + dimerization of unreacted hydroxyoxime molecules + solvation of the extracted metal complex by dimer	Eq. (3), Eq. (6), and Eq. (11)
4	Overall equilibrium complexation reaction + dimerization of unreacted hydroxyoxime molecules + solvation of the copper-extractant complex by monomers in bulk organic phase	Eq. (3) and Eq. (9)

The parameters of the models in Table 3 were estimated from the experimental data and are shown in Table 4 together with indicators of their significance and their goodness of fit. According to the MSE values, the best fit is obtained with Models 2 and 3; however, the superiority of these models over Model 1 is small and is owed to a higher number of parameters. Although Model 4 provides a fit that is better than Model 1 according to MSE value, the difference is small, and parameter K_{S1} is not significant ($t\text{-stat} = 1.2 < 3$) according to the t-test. There is 23% probability that $K_{S1} = 0$ according to the p-value. Therefore, the differences in predictive power between Models 1–3 are rather small, and in these circumstances, the preference should be given to the simplest model with the minimum number of parameters, i.e., Model 1. Moreover, the parameters K_{LLX} and K_D are heavily correlated (correlation coefficient 0.96) according to the posterior distribution of parameters obtained with the MCMC method (Figure 2), which reveals that the parameters are linearly dependent on each other. Therefore, the parameters cannot be determined simultaneously. The same applies to the parameters K_{LLX} and K_D in Model 3 (Figure 3). It is worth noting that the estimated values of the dimerization constant are lower than expected for the system with aliphatic diluents. This indicates the relatively low importance of the dimerization phenomenon in the extraction mechanism.

Table 4. Comparison of models for prediction of copper solvent extraction phase equilibrium in the loading stage.

Model ID	Parameter	SE	t-stat	p-value	MSE	
1	K_{LLX}	19.78	2.18	9.09	~0	7.65e-4
2	K_{LLX}	39.20	5.10	7.70	5.26e-14	4.55e-4
	K_D	4.37	1.12	3.91	1.03e-4	
3	K_{LLX}	44.71	7.16	6.25	7.57e-10	3.94e-4
	K_D	6.15	1.81	3.40	7.09e-4	
	K_{S2}	1.33	0.35	3.77	1.78e-4	
4	K_{LLX}	17.52	0.78	22.36	~0	6.64e-4
	K_{S1}	0.57	0.35	1.2	0.23

Figure 2. Posterior distribution of parameters with the two-parameter model that includes aqueous phase speciation, interfacial extraction reaction, and dimerization of the extractant molecules in the organic phase.

Although Model 1 seems to provide a compromise between the simplicity of the model and the goodness of fit, the explanation of the experimental data by the model cannot be admitted to be sufficiently good, as can be seen from Figure 4 and Figure 5. An overprediction of

organic copper concentration and a corresponding underprediction of aqueous copper concentration is observed for experiments with 10 vol-% reagent concentration, whereas an underprediction is observed for experiments with 17 vol-% and 25 vol-% concentrations (Figure 4). The same is observed with the predictions of Models 2–4. This fact suggests that there is a dependency in the phase equilibrium that is not accounted for by Models 1–4. The same was observed by Hu et al. (2000), and the suggested explanation was the non-ideality of the organic phase.

Figure 3. Posterior distribution of parameters with the three-parameter Model 3 that includes aqueous phase speciation, interfacial extraction reaction, dimerization of the extractant molecules, and solvation of the extracted complex by dimer in the organic phase. Based on the density estimation, 50% and 95% confidence regions and the one-dimensional marginal densities are calculated.

Figure 4. Measured equilibrium concentrations of copper in aqueous and organic phases at uncontrolled equilibrium acidity. a) Cu_0 1 g/L, HR 10%; b) Cu_0 5 g/L, HR 10%; c) Cu_0 25 g/L, HR 10%; d) Cu_0 25 g/L, HR 25%; e) Cu_0 32 g/L, HR 25%; f) Cu_0 45 g/L, HR 25%; g) Cu_0 25 g/L, HR 5%; h) Cu_0 25 g/L, HR 17%. Modeled values are calculated with the one-parameter Model 1 that includes aqueous speciation and interfacial extraction reaction. Simultaneous fitting for experimental sets E1–E9.

Figure 5. Goodness of fit of the one-parameter Model 1 in the experiments with uncontrolled equilibrium acidity. Simultaneous fitting for experimental sets E1–E9.

4.1.2. Empirical correction for organic phase non-ideality

It was observed that the value of the equilibrium constant of the extraction reaction, Eq. (3), changes systematically when fitted individually against data for each extractant concentration (Table 5). There were 15 experimental points in each data set for a fixed extractant concentration, which makes identification of the equilibrium constant comparable and

reliable. The correlation of the equilibrium constant and the total extractant concentration is characterized by the correlation coefficient -0.95 with a 4.5% probability that there is no correlation (p -value = 0.045). The same trend of a decreasing equilibrium constant with an increase of extractant concentration (Table 5) was reported by Hu et al. (2000) and Lin et al. (2002) in the extraction systems with hydroxyoxime extractants LIX64N and LIX84 in aliphatic diluents. This behavior was explained through the non-ideality of the organic phase. In this work, no other correlations with other varying experimental conditions were found to be significant using correlation analysis.

An excellent fit is observed when Model 1 is individually fitted for each extractant concentration data set (Figure 6). The calculated copper loading (filled symbols) is very close to the experimental values (open symbols) in all cases. The lines are added to demonstrate the shape of the loading isotherm at a hypothetical constant equilibrium pH. These results suggest that equilibrium Model 1 successfully accounts for aqueous phase non-ideality. However, it is unable to explain the non-ideality of the organic phase, because a different value of K_{LLX} is needed for each $[HR]_{tot}$.

Table 5. Dependency of the copper liquid–liquid extraction equilibrium constant in the loading stage on the total extractant concentration. O/A ratio was varied while keeping all other initial conditions the same.

HR_{tot} , vol-%	$[HR]_{tot}$, M	K_{LLX}	SE	t-stat	p-value	MSE
5	0.055	36.02	24.3	1.48	0.15	3.699e-3
10	0.170	22.75	3.09	7.38	3.2e-9	3.729e-4
17	0.306	9.33	1.70	5.46	2.1e-6	6.916e-4
25	0.462	6.48	1.07	6.06	2.7e-7	7.258e-4

Figure 6. Equilibrium concentrations of copper in aqueous and organic phases with uncontrolled equilibrium acidity with the one-parameter Model 1, including aqueous speciation and interfacial extraction reaction. Fitting for individual datasets with constant extractant concentration. $\star$ = HR 25 vol-%; $\triangleleft$ = HR 17 vol-%; $\triangleright$ = HR 10 vol-%; $\circ$ = HR 25 vol-%; empty symbols = experimental results; filled symbols = predicted results. The lines show predicted extraction isotherms with an arbitrarily chosen equilibrium acidity of 0.76 M.

Two functions were considered in order to account for the dependence between the total extractant concentration and the extraction equilibrium constant (Table 6): a linear function ($K_{LLX} = K_{LLX,0} + A \cdot [HR]_{tot}$) and a hyperbolic tangent function ($K_{LLX} = K_{LLX,0} \cdot (1 - \tanh(A \cdot [HR]_{tot}))$). Both functions were used to calculate the apparent extraction equilibrium constant for Model 1 described earlier in Table 4. The nonlinear hyperbolic tangent function is clearly able to predict the nonlinear variations in the experimental data better in comparison to the linear function, according to the MSE value. The hyperbolic tangent function is also characterized by a gradual approaching of the x -coordinate with increasing extractant concentrations that is more natural in comparison with the linear function. MSE values with both functions are also lower than those of all the considered mechanistic Models 1–4 (Table 4), which confirms the significance of the correlation of the extraction equilibrium constant and the total extractant concentration.

Table 6. Comparison of the correction functions for the model predicting equilibrium in liquid–liquid extraction of copper.

Extraction	Parameter	Value	SE	MSE
$K_{LLX} = K_{LLX,0} + A \cdot [HR]_{tot}$	$K_{LLX,0}$	39.47	1.32	1.401e-4
	A	-74.71	2.92	
$K_{LLX} = K_{LLX,0} \cdot (1 - \tanh(A \cdot [HR]_{tot}))$	$K_{LLX,0}$	50.23	3.24	1.292e-4
	A	3.16	0.08	
Stripping	Parameter	Value	SE	MSE
$K_{LLX} = K_{LLX,0} + A \cdot [HR]_{tot}$	$K_{LLX,0}$	13.77	0.01	2.68e-4
	A	-23.16	0.00	

Figure 7 demonstrates a very good fit of the experimental data by Model 1, supplemented with a correction of the apparent extraction equilibrium constant by the two-parameter hyperbolic tangent function. Figure 8 shows how well the corrected model is able to predict the loading isotherms with uncontrolled equilibrium acidity. Comparing Figure 7 and Figure 8 with Figure 4 and Figure 5, it can be seen that the correction of the equilibrium constant using the hyperbolic tangent function enables a more accurate explanation of the equilibrium phase composition. Hence, organic phase non-ideality is obviously present in the liquid–liquid extraction with hydroxyoxime extractants in aliphatic diluents.

Figure 7. Goodness of fit for the model that includes correction of extraction equilibrium constant for organic phase non-ideality by hyperbolic tangent function.

Figure 8. Equilibrium concentrations of copper in aqueous and organic phases in experiments with uncontrolled equilibrium acidity. a) Cu_0 1 g/L, HR 10%; b) Cu_0 5 g/L, HR 10%; c) Cu_0 25 g/L, HR 10%; d) Cu_0 25 g/L, HR 25%; e) Cu_0 32 g/L, HR 25%; f) Cu_0 45 g/L, HR 25%; g) Cu_0 25 g/L, HR 5%; h) Cu_0 25 g/L, HR 17%. The two-parameter model includes aqueous speciation and interfacial extraction reaction corrected for the organic phase non-ideality extraction equilibrium constant.

The utilization of the hyperbolic tangent function allows not only a correction for the organic phase non-ideality and thus for the improvement of the model fit, but it also enhances the identifiability of the model parameters (Figure 9). Parameters K_{LLX} and A of the hyperbolic tangent function in Figure 9 are less correlated (correlation coefficient 0.81) than the parameters K_{LLX} and K_{dim} (dimerization constant) in Figure 2, which once again proves the superiority of Model 1 with the corrected apparent equilibrium constant over Models 2–4.

Figure 9. Posterior distribution of parameters with the two-parameter model that includes aqueous phase speciation and interfacial extraction reaction. The equilibrium constant of the extraction reaction is corrected for the organic phase non-ideality by the hyperbolic tangent function.

Since the apparent extraction equilibrium constant depends on the extractant concentration, it affects the copper liquid–liquid extraction process design. Calculated using the developed model, Figure 10 demonstrates how the extraction of copper from the aqueous phase increases nonlinearly with the increase in the extractant concentration in the organic phase. The effect is insignificant until the extractant concentration reaches 0.25 M (~14 vol-%). A further increase in the extractant concentration leads to a less pronounced increase in copper extraction. If there was no effect of organic phase non-ideality on the copper extraction, loading of the extractant in the organic phase could be expected to increase slowly starting from the extractant concentration of about 0.14 M (~8 vol-%). However, according to the developed model, loading gradually decreases due to organic phase non-ideality. Thus, in addition to the physical limitations (high viscosity of concentrated extractant leading to high operational costs), there are also chemical limitations to the application of high extractant concentrations in copper liquid–liquid extraction with hydroxyoxime extractants.

Figure 10. Extent of extraction of copper and utilization of extractant in copper liquid–liquid extraction depending on extractant concentration. The curves are calculated using the developed model with corrected apparent extraction equilibrium constant and Model 1. Initial aqueous and organic copper concentrations are correspondingly 45 g/L and 0 g/L, O/A = 1, and equilibrium acidity is 0.77 M.

4.2. Stripping stage modeling

Since modeling the loading stage of the copper liquid–liquid extraction with aqueous speciation and a corrected extraction reaction equilibrium constant gives an excellent result, the same approach was applied to modeling the equilibrium of the stripping stage of the process. The extraction equilibrium constant for Model 1 (Table 3) was fitted against the collected experimental data individually for each set of data points with a given total extractant concentration and acidity of the aqueous phase. There were 15 experimental points in each data set. Table 7 shows that the equilibrium constant of the extraction reaction in the stripping stage depends on the concentration of the extractant in the organic phase, just as in the loading stage. The variation in the extractant equilibrium constant due to the variation in the aqueous phase acidity is negligible. This is seen in Table 7, where the 95% confidence intervals ($K_{LLX} \pm 2 \cdot SE$) of the equilibrium constants, with the same extractant concentrations but different acidities, overlap.

Table 7. Variation in the copper liquid–liquid equilibrium constant in the stripping stage due to varying extractant and acid concentrations. Equilibrium data were collected experimentally by varying the O/A ratio individually for each extractant concentration while keeping all other initial conditions the same.

Experiment ID	HR _{tot} , vol-%	[HR] _{tot} , M	[H ₂ SO ₄] _{tot}	K _{LLX}	SE	MSE
S1	10	0.17	3.42	10.26	0.27	1.399e-4
S2	28	0.51	3.91	2.25	0.003	3.890e-4
S3	10	0.17	3.91	10.82	0.008	4.278e-4
S4	28	0.51	3.42	2.22	0.018	3.993e-4

A linear correction function for the apparent equilibrium constant of the extraction reaction in the stripping stage was fitted against the experimental data. The estimated model parameters in Table 6 are significantly different from the parameters estimated for the loading stage. The difference may be explained by the large differences in the acidity in the stripping and loading stages. In other words, the speciation model for the aqueous phase is not accurate at very high acid concentrations, and this inaccuracy is included in the values of the parameters of the linear correction function. However, the determined stripping stage parameters are significant, since the estimated standard error (SE) is small compared to the values of the parameters. Figure 11 and Figure 12 demonstrate a satisfactory fit of the experimental data. This verifies the good applicability of the fitted model to explain the phase equilibrium in the stripping stage of the liquid–liquid extraction of copper from the extractant diluted in the organic phase.

Figure 11. Goodness of fit for the one-parameter model for the stripping stage (experiments S1–S4) with uncontrolled equilibrium acidity. The model contains the two-parameter linear function for the correction of organic phase non-ideality.

Figure 12. Experimental and calculated loading isotherms in stripping, experiments S1–S4. Initial acidity of the stripping solution: a) 160 g/L H_2SO_4 ; b) 190 g/L H_2SO_4 . The modeled values have been calculated with the two-parameter linear function for correction of organic phase non-ideality.

5. Conclusions

A mechanistic mathematical model was developed to explain the equilibrium of the loading and stripping stages of liquid–liquid extraction of copper from concentrated aqueous sulfate solutions with a hydroxyoxime extractant in an aliphatic diluent in a wide range of copper and extractant concentrations. The model was validated against an extensive amount of new experimental data.

Several mechanistic mathematical models that included the speciation of aqueous phase species, reversible interfacial extraction reactions, the dimerization of extractant molecules in the organic phase, and the solvation of the extracted complex in the organic phase were considered. Nonlinear regression analysis was used to fit the model parameters against the collected experimental data. In addition, a Markov chain Monte Carlo (MCMC) algorithm was used to identify correlations in the estimated parameters of the considered models and to prove the reliability of the models.

It was found that the extraction is best modeled by an ion association model to describe the speciation of aqueous phase species and the overall reversible interfacial extraction reaction. However, it was observed that the value of the equilibrium constant of the extraction reaction was heavily correlated with the total concentration of the extractant in the organic phase. This is evidence of organic phase non-ideality. Neither the dimerization of the unreacted extractant molecules nor the solvation of the copper-extractant complexes was sufficient to explain the organic phase non-ideality, and too many parameters led to poor identifiability. The organic phase non-ideality was taken into account by an empirical correction of the extraction equilibrium constant. The suggested correction function is the hyperbolic tangent function $K_{LLX} = 50.23 \cdot (1 - \tanh(3.16 \cdot [HR]_{tot}))$ for the loading stage and the linear function $K_{LLX} = 13.77 - 3.16 \cdot [HR]_{tot}$ for the stripping stage. The developed models were shown to serve as excellent explanations of the measured experimental data.

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Nomenclature

Abbreviations

MCMC	Markov chain Monte Carlo
MSE	Mean squared error

PLS Pregnant leach solution

SE Standard error

Letters

A parameter in regression model

I ionic strength

G number of experimental groups

HR protonated hydroxyoxime

K equilibrium constant

k reaction rate constant

M number of measured responses

N number of experimental points in an experimental group

R deprotonated hydroxyoxime

r reaction rate

Subscripts and superscripts

D dimerization

eq equilibrium

Exp measured experimental data

f forward

i index of chemical reactions

Mod data calculated with model

LLX liquid–liquid extraction

r reverse

S solvation
tot total

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Highlights

- A mechanistic model for copper liquid-liquid extraction equilibrium
- A useful empirical correlation for organic phase non-ideality is introduced
- MCMC is used for identification of the best models with significant parameters
- The model is shown to be applicable over a wide range of operating conditions

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