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Extraction Equilibrium of Copper from Ammoniacal Media with LIX 54

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ABSTRACT

This paper reports a study of the extraction of copper from ammonia/ammonium sulfate medium with LIX 54, a β-diketone. The extraction of copper is very sensitive to the equilibrium pH. The highest extraction efficiency is attained in the range of pH 8–9.5. Above pH 10, the percentage of metal ion extracted decreases sharply. The extraction of copper by LIX 54 can be described by the following equation:

$$Cu(NH_3)^{2+}_{4,aq} + 2HR_{org} \leftrightarrows CuR_{2,org} + 2NH_{3,aq} + 2NH^{+}_{4,aq}$$

The thermodynamic equilibrium constant was evaluated in terms of the aqueous phase and was found to be $10^{(2.89 \pm 0.03)}\,M^2$ at 298 K. The nonideality of the aqueous phase was taken into account by applying

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the Pitzer model and the extended Debye-Hückel equation. The isotherms of extraction for the system copper/ammonia/ammonium sulfate/LIX 54 revealed that the increase in the salt concentration from 0.2 to 1 M makes the extraction process difficult.

Key Words: LIX 54; Copper; Ammonia; Ammonium sulfate; Extraction; Waste treatment.

INTRODUCTION

Liquid-liquid extraction has become an important technique for recovering and separating metallic species in hydrometallurgical processes and is broadening its application field to wastewater treatment. In fact, this technique is very efficient in the treatment of both concentrated and dilute solutions. This is a great advantage of the solvent extraction over other separating processes, since a considerable number of leach liquors are dilute solutions ($1-4\,\mathrm{kg\,m^{-3}}$) arising from the treatment of dump or heap lower-grade materials. It is worth emphasizing that the high efficiency imposed on separating processes is related not only to economic demands but also to concerns over environmental issues that impose a minimum for the concentration of pollutants in treated effluents.

The copper recovery from leach liquors by solvent extraction processes is already a well-implemented process in several industrial plants.[1–3] The reagents used in these processes are mainly β-hydroxyoximes (ketoximes and salicylaldoximes) and β-diketones. The hydroxyoximes are particularly useful in the extraction of copper from acid media.[4–7] These extractants also present a high affinity for copper in ammoniacal solutions.[8–10] However, they are not the most suitable extractants to be used in such conditions due to their tendency to co-extract ammonia. Thus, β-hydroxyoximes have been superseded by β-diketones in the extraction of copper from ammoniacal media because diketones, unlike oximes, do not transfer ammonia.[1,11]

LIX 54 is a β-diketone produced by Cognis Corp. that has been widely applied in the treatment of ammoniacal solutions.[1] Kyuchoukov et al.[12] carried out some studies on copper extraction with LIX 54. The results obtained showed that it is possible to extract copper from an aqueous feed containing $134\,\mathrm{kg\,m^{-3}}$ of Cu^{2+}, $\sim$4.8 M Cl^-, and 8 M NH_3 with a 1.26 M LIX 54 organic solution. The loaded organic solution can be completely stripped with 1.58 M H_2SO_4.

Alguacil and Alonso[13] also carried out studies on the system copper/ammonium sulfate/LIX 54 and they noted that copper is extracted only at pH above 3 and the highest extraction efficiency is obtained in the range of pH 7–9. They also reported that an organic phase containing 0.15 M LIX 54 efficiently extracts copper from an aqueous phase containing 2 kg m^{-3} Cu, 0.15 M $(NH_4)_2SO_4$ at pH 8.5. The loaded LIX 54 (0.15 M) organic phase that contains 4.8 kg m^{-3} Cu is easily stripped with a typical spent electrolyte solution ($H_2SO_4 = 170$ kg m^{-3}; Cu $= 30$ kg m^{-3}).

The results presented by Kyuchoukov et al.[12] and Alguacil and Alonso[13] showed the excellent possibilities on using LIX 54 to recover copper from ammoniacal solutions. In these studies, concentration-based equilibrium models were applied, which restrict the use of the concentration equilibrium constant to a limited range of experimental conditions. The purpose of the present paper is to study the equilibrium of copper extraction in the ammonia/ammonium sulfate/LIX 54 systems in order to establish the stoichiometry of the extraction process and the corresponding thermodynamic equilibrium constant. This involves taking into account the nonideal behavior of the aqueous phase. The calculation of the activity coefficients of aqueous species was carried out by the extended Debye-Hückel equation and by the Pitzer model.[14] This useful model has been used for ionic strengths as high as 7 M and its application to liquid-liquid extraction data is well documented elsewhere.[15–20]

Theory

The extraction equilibrium of copper from ammoniacal solutions by β-diketones and oximes extractants can be described by the following equilibrium:[4,9]

$$\mathrm{Cu(NH_3)_{4,aq}^{2+}} + 2\mathrm{HR_{org}} \leftrightarrows \mathrm{CuR_{2,org}} + 2\mathrm{NH_{3,aq}} + 2\mathrm{NH_{4,aq}^{+}} \tag{1}$$

$$K_{\mathrm{ext}}^{\mathrm{o}} = \frac{c_{\mathrm{CuR_2}}\, a_{\mathrm{NH_3}}^{2}\, a_{\mathrm{NH_4^+}}^{2}}{a_{\mathrm{Cu(NH_3)_4^{2+}}}\, c_{\mathrm{HR}}^{2}} \tag{2}$$

$K_{\mathrm{ext}}^{\mathrm{o}}$ represents the thermodynamic equilibrium constant in terms of the aqueous phase while c is the concentration of species and a is the activity of species. In Eq. (2) HR stands for the extractant molecule. The distribution ratio (D) of copper between aqueous and organic phase is defined as the quotient between the concentration of copper in the organic phase and the concentration of copper in the aqueous phase. If the nonideality of the aqueous phase is taken into account, a modified distribution ratio (D') can be defined as:

$$D' = \frac{c_{\mathrm{CuR_2,org}}}{a_{\mathrm{Cu(NH_3)_{4,\,aq}^{2+}}}} \tag{3}$$

Equation (2) can be therefore written as:

$$\log D' a_{NH_3}^2 a_{NH_4^+}^2 = \log K_{ext}^o + 2 \log c_{HR} \tag{4}$$

Thus, in plotting the first term of Eq. (4) against $\log c_{HR}$, one must obtain a straight line with an intercept equal to $\log K_{ext}^o$ and a slope of 2. The calculation of the ionic aqueous species activities, which appear in Eqs. (2) to (4), requires a complete characterization of the aqueous solution.

Speciation in the $CuSO_4/NH_3/(NH_4)_2SO_4$ Aqueous System

The description of the present system implies the specification of the various species and components in the solution. In the aqueous solution of $CuSO_4/NH_3/(NH_4)_2SO_4$, if a complete dissociation of $(NH_4)_2SO_4$ and $CuSO_4$ is assumed, the following equilibria and equilibria relationships remain:

$$H_2O \leftrightarrows H^+ + OH^- \qquad K_w^o = m_{H^+} m_{OH^-} \gamma_{H^+} \gamma_{OH^-} \tag{5}$$

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^- \qquad K_{NH_3}^o = \frac{m_{NH_4^+} m_{OH^-}}{m_{NH_3}} \times \frac{\gamma_{NH_4^+} \gamma_{OH^-}}{\gamma_{NH_3}} \tag{6}$$

$$Cu^{2+} + iNH_3 \leftrightarrows Cu(NH_3)_i^{2+} \quad K_{Cu(NH_3)_i^{2+}}^o = \frac{m_{Cu(NH_3)_i^{2+}}}{m_{Cu^{2+}} m_{NH_3}^i} \times \frac{\gamma_{Cu(NH_3)_i^{2+}}}{\gamma_{Cu^{2+}} \gamma_{NH_3}^i} \tag{7}$$

where i varies from 1 to 4, K^o denotes the thermodynamic equilibrium constant, m the molality of each species, and γ the activity coefficient. The activity coefficients for the ionic species H^+, OH^-, NH_4^+, SO_4^{2-}, and NH_3 were calculated by applying the Pitzer model. This model was originally formulated to describe the behavior of strong electrolytes.[14,21,22] It was readily combined with explicit treatment of association equilibria[23] and was extended to include neutral solutes.[15,23,24] The Pitzer ion interaction model is based upon an expression for the excess Gibbs energy of the solution in terms of an extended Debye-Hückel function and virial coefficients corresponding to short-range forces among the dissolved species. The Pitzer equation for the activity coefficients of cations (C) and anions (A) is similar.

An example of a cation expression is given below:

$$\ln \gamma_C = z_C^2 f^\gamma + \sum_a m_a \left\{ 2B_{Ca} + \left(2\sum_c m_c z_c \right) C_{Ca} \right\}$$
$$+ \sum_c m_c \left(2\Theta_{Cc} + \sum_a m_a \psi_{Cca} \right) + \sum_c \sum_a m_c m_a (z_C^2 B'_{ca} + |z_C| C_{ca})$$
$$+ \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \psi_{Caa'} + 2\sum_n m_n \lambda_{Cn} + 3\sum_i \sum_j m_i m_j \mu_{Cij} \tag{8}$$

The Pitzer equation for neutral species is the following:

$$\ln \gamma_N = 2\sum_n m_n \lambda_{Nn} + 2\sum_n m_c \lambda_{Nc} + 2\sum_n m_a \lambda_{Na}$$
$$+ 3\sum_i \sum_j m_i m_j \mu_{Nij} \tag{9}$$

In the expressions (8) and (9), c, a, and n signify, respectively, cations, anions and neutral species; whereas i, j, and k cover all species. The f expresses the long-range electrostatic forces. It depends on temperature, solvent properties, and ionic strength and can be obtained by the equation:

$$f^\gamma = -A_\phi \left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right] \tag{10}$$

A_ϕ is 0.3914 $(\text{mol kg}^{-1})^{1/2}$ at 298 K. The parameter b has a constant value of 1.2 (298 K) for 1–1 and 1–2 electrolytes.[14] Theoretically, this is the product of $\beta\,\dot{a}$; β is 0.3288 $(\text{mol kg}^{-1})^{1/2}$ and $\dot{a}$, the hard core ion diameter, is fixed at 3.65 Å. Thus in the Pitzer equation, differences on the effective size of ions in solution are not explicitly accounted for. However, the interaction coefficient terms of Eq. (8) effectively compensate for this. In Eq. (10) I denotes the ionic strength that was calculated by the following expression:

$$I = \frac{1}{2} \sum m_i z_i^2 \tag{11}$$

where z_i represents the ion charge. Short-range interactions of ionic species produce B_{ca} terms for binary interactions and C_{ca} terms for ternary interactions. The parameter Θ is the mixing coefficient for two ions of the same charge while ψ is the mixing coefficient for three ions. The expressions for all the functions are given elsewhere.[14,25,26] The λ_{ij} and μ_{ijk} are the virial coefficients for binary and ternary interactions. The activity coefficients of copper species were calculated from the extended Debye-Hückel equation because there is a lack of literature data concerning Pitzer parameters. The extended Debye-Hückel equation is:

$$\log \gamma_c = -\frac{A_\gamma z_c^2 \sqrt{I}}{1 + \beta \dot{a} \sqrt{I}} \tag{12}$$

where $\dot{a}$ is a parameter that corresponds roughly to the effective size of the hydrated ion[27] and A_γ is 0.5097 $(\mathrm{mol\,kg^{-1}})^{1/2}$ at 298 K. In the strictest sense, the extended Debye-Hückel equation for activity coefficients is valid only at low ionic strengths.[14,28] However, several authors[29−31] found that the extended Debye-Hückel equation can give reasonable predictions for the activity coefficients of species at ionic strengths far higher (up to 3−4 M) than those for which use of such equation is recommended ($<0.1\,m$).[27]

If ones intent to characterize the copper ammoniacal solution, i.e., to define the concentration of Cu^{2+}, $Cu(NH_3)^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$, $Cu(NH_3)_4^{2+}$, NH_3, NH_4^+, OH^-, and H^+ species, nine equations will be necessary. So, besides the equilibria relationships [Eqs. (5), (6), (7) (i = 1−4)], two mass balances and the charge balance are necessary. These are written as follows:

mass balance to copper ion

$$\begin{aligned} m_{(CuSO_4)_{total}} = {} & m_{Cu^{2+}} + m_{Cu(NH_3)^{2+}} + m_{Cu(NH_3)_2^{2+}} \\ & + m_{Cu(NH_3)_3^{2+}} + m_{Cu(NH_3)_4^{2+}} \end{aligned} \tag{13}$$

mass balance to ammonia:

$$\begin{aligned} & m_{NH_3} + m_{NH_4^+} + m_{Cu(NH_3)^{2+}} + 2m_{Cu(NH_3)_2^{2+}} + 3m_{Cu(NH_3)_3^{2+}} \\ & \quad + 4m_{Cu(NH_3)_4^{2+}} = (m_{NH_3} + 2m_{(NH_4)_2SO_4})_{total} \end{aligned} \tag{14}$$

charge balance:

$$\begin{aligned} & m_{H^+} + 2m_{Cu^{2+}} + m_{NH_4^+} + 2m_{Cu(NH_3)^{2+}} + 2m_{Cu(NH_3)_2^{2+}} \\ & \quad + 2m_{Cu(NH_3)_3^{2+}} + 2m_{Cu(NH_3)_4^{2+}} = m_{OH^-} + 2m_{SO_4^{2-}} \end{aligned} \tag{15}$$

The system of equations obtained was solved by an iterative procedure. First, assuming a complete dissociation of $(NH_4)_2SO_4$ and $CuSO_4$, the ionic strength of the solution is calculated [Eq. (11)]. The activity coefficients of overall species are then calculated by using the Pitzer model and the extended

Debye-Hückel equation. The Pitzer and Debye-Hückel parameters are published elsewhere.[14,15,17,24,27,28] Finally, using the "Solver" of Microsoft Excel, the system of equations obtained is solved and the concentrations of the different species in solution are calculated. The calculation is repeated until convergence of result is attained. Some of the results were also tested by using the "DNEQNJ" routine of the commercial software package "Microsoft Fortran PowerStation 4.0." It is worth mentioning that $K^{o}_{NH_3}$, $K^{o}_{Cu(NH_3)}{}^{2+}$, $K^{o}_{Cu(NH_3)_2^{2+}}$, $K^{o}_{Cu(NH_3)_3^{2+}}$, and $K^{o}_{Cu(NH_3)_4^{2+}}$ assume the values 1.778×10^{-5}, 1.10×10^{4}, 2.95×10^{7}, 1.86×10^{10}, and 5.62×10^{11}, respectively.[25,32]

EXPERIMENTAL

Reagents

Analytical grade reagents $(NH_4)_2SO_4$, NH_3, and $CuSO_4$ were used to prepare aqueous solutions. The extractant LIX 54, a β-diketone, was kindly supplied by Cognis (Ireland) as a kerosene solution and used without further purification. The organic phases were prepared by diluting the extractant in ShellSol T (Shell Chemical Ltd.), a commercial diluent (n-paraffins $>99.5\%$) similar to kerosene. The prepared organic solutions were washed with deionised water to remove the soluble impurities.

Procedure

A stock solution of 4–5 M NH_3 was prepared and the concentration of ammonia determined by the phenol-hypochlorite method.[33] The stock solution was used to prepare the $CuSO_4/NH_3/(NH_4)_2SO_4$ aqueous solutions.

In the equilibrium experiments the aqueous and the organic phases were put into contact in an orbital shaker with temperature control (298 K) during at least 4 h. Usually an aqueous/organic volumetric ratio of 2/1 was used, the exception was in the isotherm extraction experiments. In these experiments several volumetric ratios (A/O: 10/1; 5/1; 3/1; 2/1; 1/1; 1/2; 3/1; 5/1; 10/1) were used. After phase separation, the equilibrium pH was measured using a Metrohm pH meter. Copper in both phases was determined by atomic absorption spectrophotometry (Perkin-Elmer 3100: aqueous phase and Perkin-Elmer 373: organic phase). All the extraction tests were carried out in duplicate and the results agree within 5%. The densities of aqueous phases were measured to convert the molarity to the molality scale.

RESULTS AND DISCUSSION

Speciation in the $CuSO_4/NH_3/(NH_4)_2SO_4$ Aqueous System

Table 1 shows the thermodynamic results for several solutions of $CuSO_4$, NH_3, and $(NH_4)_2SO_4$. These results were obtained by applying the Pitzer model and the extended Debye-Hückel equation as stated earlier. The comparison of the experimental data with the calculated pH values is also provided in Table 1.

The results of speciation of copper ammoniacal solutions containing low concentration of Cu (0.00826 *m*, 0.0338 *m*) in relation to NH_3 concentrations (from 0.300 *m* to 1.239 *m*) revealed that the $Cu(NH_3)_4^{2+}$ complexes predominate over all others copper species in solution. The predominance of $Cu(NH_3)_4^{2+}$ species was expected because of its high formation equilibrium constant over other ammine complexes.

Concerning the pH values, the agreement between calculated and experimental pHs is considered satisfactory (relative error $<2\%$). The discrepancies can be attributed in part to experimental errors. It is worth mentioning that the buffers usually available to the calibration of electrodes are dilute solutions while the solutions used in this work contain a considerable amount of salt products. Other authors, namely Gardner et al.,[34] Filippou et al.,[35] Rodil et al.,[36] referred the less accurate pH measurements in solutions with a high ionic strength. Finally, it is worth emphasizing that the calculation of the activity coefficients for copper and copper ammine complexes was carried out by the extended Debye-Hückel equation above its recommendable limit of applicability ($I = 0.1\,m$). Other authors[29–31] had already applied the Debye-Hückel equation at high ionic strength (3–4 M) with reasonable success. Concerning the Pitzer equations, some simplifications have been made. Namely, the terms stemming from copper ammine complexes were neglected due to the lack of literature data. Despite these drawbacks, the acceptable deviation between experimental and calculated pH values allow validation of the model proposed to the speciation of $CuSO_4$, NH_3, and $(NH_4)_2SO_4$ aqueous solutions.

Loading Capacities Experiments

Cognis supplied LIX 54 diluted in kerosene. The concentration of active extractant in this organic solution was determined by loading experiments. Thus, several organic solutions were prepared by diluting the Cognis solution in ShellSol T. The loading capacity of solvent was achieved after two contacts of the organic phase with fresh aqueous solution (2–12 $kg\,m^{-3}$ Cu^{2+}; pH

Table 1. Calculated thermodynamic results for various $CuSO_4$, NH_3, and $(NH_4)_2SO_4$ solutions. Comparison of measured and calculated values of pH.

$CuSO_4/(NH_4)_2SO_4$ m	NH_3 m	I m	m $Cu(NH_3)_4^{2+}$	m (NH_4^+)	m (NH_3)	γ $Cu(NH_3)_4^{2+}$	γ (NH_4^+)	γ (NH_3)	pH_{calc}	pH_{exp} (± 0.02)
0.00834/0.211	1.239	0.66	0.00834	0.440	1.189	0.158	0.607	1.101	9.94	10.04
0.00826/0.418	1.118	1.28	0.00826	0.853	1.068	0.118	0.548	1.158	9.70	9.88
0.00834/0.636	1.133	1.93	0.00834	1.288	1.082	0.100	0.512	1.223	9.55	9.70
0.0322/0.205	0.300	0.71	0.0284	0.414	0.170	0.150	0.600	1.070	9.12	9.11
0.0324/0.207	0.715	0.72	0.0310	0.417	0.587	0.150	0.600	1.086	9.66	9.59
0.0338/1.073	0.483	3.35	0.0318	2.146	0.350	0.080	0.467	1.335	8.92	8.93
0.0329/1.035	1.228	3.24	0.0320	2.070	1.094	0.081	0.468	1.352	9.42	9.45

9.11–9.50) at A/O volumetric phase ratio of 3/1. The results obtained are listed in Table 2.

According to Eq. (1), copper exists in loaded organic phase as the complex CuR_2. So, the Cognis solution LIX 54 has 0.00305 mol of active extractant per g solution.

Influence of pH on the Extraction Efficiency

The effect of pH on the extraction of copper was determined using several solutions containing 7.86×10^{-3} M copper sulfate and 0.2 M ammonium sulfate in the range of pH 2–11. The experimental results are shown in Fig. 1. The results indicate that copper is poorly extracted from $H_2SO_4/(NH_4)_2SO_4$ solutions ($pH_{eq} = 2-3$) with LIX 54. This points to the possibility of using sulfuric acid as a stripping agent for the LIX 54-loaded organic phase. In fact, the stripping test carried out with the LIX 54-loaded organic solution containing, 26.1 kg m^{-3} of copper, showed that copper is easily stripped (~99%) with a 150 kg m^{-3} sulfuric acid solution when an A/O phase ratio = 3/1 is used.

From Fig. 1, it is also noticeable that the extraction of copper increases significantly as the aqueous medium changes from $H_2SO_4/(NH_4)_2SO_4$ ($pH = 2-3$) to $NH_3/(NH_4)_2SO_4$ ($pH > 8$). In the intermediary region of pH 4.5–7.5, copper precipitated from the aqueous phase as copper hydroxide. According to Fig. 1, the best extraction results were attained in the range of pH 8–10. Above this pH, there is a sharp decrease in the percentage of copper extracted with LIX 54. This can be related to the fact that the increase of pH was achieved through the addition of NH_3. According to Eq. (1), the increase in the ammonia concentration will decrease the efficiency of extraction.

Determination of K^{o}_{ext}

Some experiments on copper extraction were carried out with organic phases containing different concentrations of LIX 54 to determine the

Table 2. Loading capacity of LIX 54 solutions.

LIX 54[a] in ShellSol T (kg m^{-3})	18.69	37.3	46.3	57.6	73.0
Cu_{org} (M)	0.0284	0.0565	0.0708	0.0888	0.1112

[a] LIX 54 solution as received from Cognis.

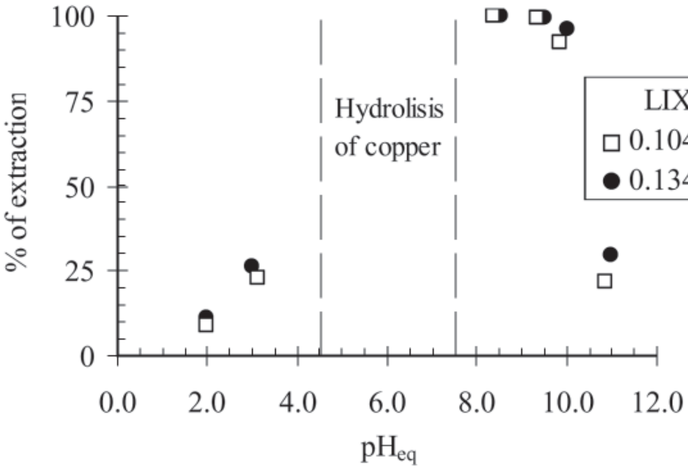

Figure 1. Influence of equilibrium pH on the percentage of copper extracted. Initial aqueous phase: $CuSO_4 = 7.86 \times 10^{-3}$M; $(NH_4)_2SO_4 = 0.2$ M; H_2SO_4 or NH_3. Initial organic phase: LIX 54 in ShellSol T.

equilibrium constant. The experimental results are shown in Fig. 2. The use of a loading ratio of LIX 54, defined as the ratio of copper in the organic phase to the total extractant molecules, was as low as possible. However, in some experiments that ratio attained a value of 0.13. Thus, the concentrations of free LIX 54 (c_{HR} in Fig. 2) were determined from the total concentration of extractant by subtracting the extractant loaded with copper, in agreement with Eq. (1).

Figure 2 shows the influence of the concentration of extractant on $D\, c^2_{NH_4^+}\, c^2_{NH_3}$ and $D'\, a^2_{NH_4^+}\, a^2_{NH_3}$. Straight lines with a slope of ~2.0 are obtained for the representation of $\log D\, c^2_{NH_4^+}\, c^2_{NH_3}$ as well as $\log D'\, a^2_{NH_4^+}\, a^2_{NH_3}$ vs. $\log c_{HR}$. This confirms the stoichiometry of reaction 1 and shows that the assumption of constant ionic strength seems to be applicable. The equilibrium constant for copper extraction with LIX 54 can be obtained from the intercepts of the straight lines shown in Fig. 2. The results obtained show that the concentration-based equilibrium constant is dependent on the ionic strength, as was expected. When the concentration of ammonium sulfate is 0.2 M, the concentration-based equilibrium constant (K_{ext}) is $10^{(2.38 \pm 0.05)}$ M^2. The increase in the concentration of ammonium sulfate to 0.6 M decreases the concentration-based equilibrium constant to $10^{(2.23 \pm 0.07)}$ M^2. The thermodynamic equilibrium constant for copper extraction with LIX 54 was found to be $10^{(2.89 \pm 0.03)}$ M^2.

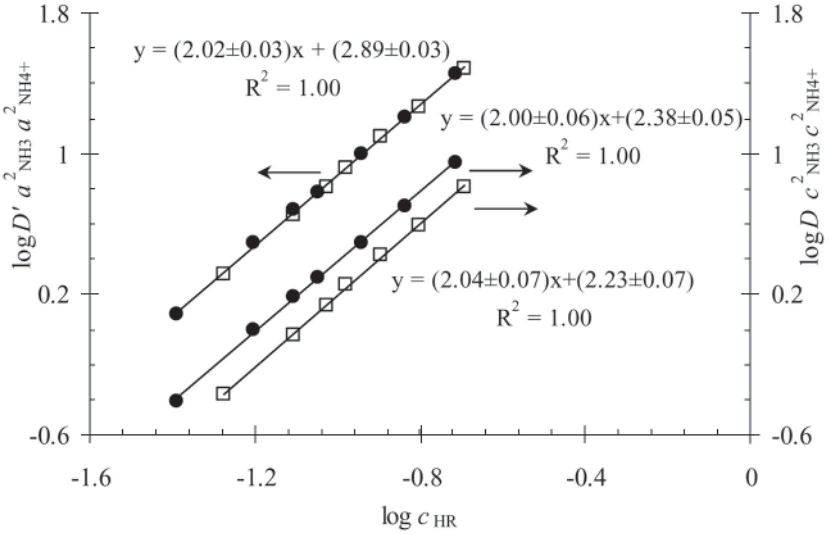

Figure 2. Equilibrium results for the extraction of copper from ammoniacal solution with LIX 54. Initial aqueous phase: $CuSO_4 = 7.86 \times 10^{-3}$ M; $NH_3 = 1.07$ M; $(NH_4)_2SO_4 = 0.2$ M (●), 0.6 M (□).

The literature data concerning the equilibrium constants for the system copper/LIX 54 is scarce. Alguacil et al.[9] assumed the following equilibrium to the extraction of copper by LIX 54:

$$Cu^{2+}_{aq} + 2HR_{org} \leftrightarrows CuR_{2,org} + 2H^{+}_{aq} \tag{16}$$

$$K_{ext} = \frac{c_{CuR_2,org}\, c^2_{H^+_{aq}}}{c_{Cu^{2+}_{aq}}\, c^2_{HR,org}} \tag{17}$$

and K_{ext} was found to be 7×10^{-7}. The authors used 0.15 M of ammonium sulfate aqueous phases with pH varying from 3–9. Equation (17) is useful to predict the extraction of copper with LIX 54 in the range of pH 3–9, where an increase of pH increases the efficiency of the process. However, Eq. (17) does not allow previewing the negative effect of the high pH values on the extraction of copper from ammonia/ammonium sulfate medium with LIX 54, as shown in Fig. 2.

The influence of pH and salt concentration on the extraction of copper from ammonia/ammonium sulfate solutions can be quantified if the thermodynamic equilibrium constant [Eq. (2)] corresponding to equilibrium stoichiometry [Eq. (1)] is known. It is worth noting that, in the system $NH_3/(NH_4)_2SO_4$, the increase in pH is associated with the increase in NH_3 concentrations.

Figure 3 shows the equilibrium results for the extraction of copper from $(NH_4)_2SO_4/NH_3$ aqueous solutions with LIX 54. In Fig. 3, the experimental data (marks) are compared with the simulated values (solid lines). The simulated values were obtained by using the speciation model stated previously, the stoichiometry proposed by Eq. (1), and the respective equilibrium constant $10^{(2.89 \pm 0.03)}\,M^2$. As one may observe, the isotherms of extraction presented in Fig. 3 are well predicted.

The results presented in Fig. 3 also allow analyzing the influence of ammonium sulfate concentration on the extraction of copper. In Fig. 3, a decreasing trend in metal extraction along with an increase in the salt concentration from 0.2 to 1 M is perceptible. The isotherms obtained for 0.2M $(NH_4)_2SO_4$ are very steep, consequently the concentration of copper in the organic phase is high whereas the concentration of metal ion in the raffinate is low, as is desirable. So, it is possible to conclude that under these conditions the extraction of copper is an efficient process. Concerning the isotherm obtained for 1 M $(NH_4)_2SO_4$, it denotes a less favourable shape. In fact, this isotherm shows that the concentration in the extract increases slowly for

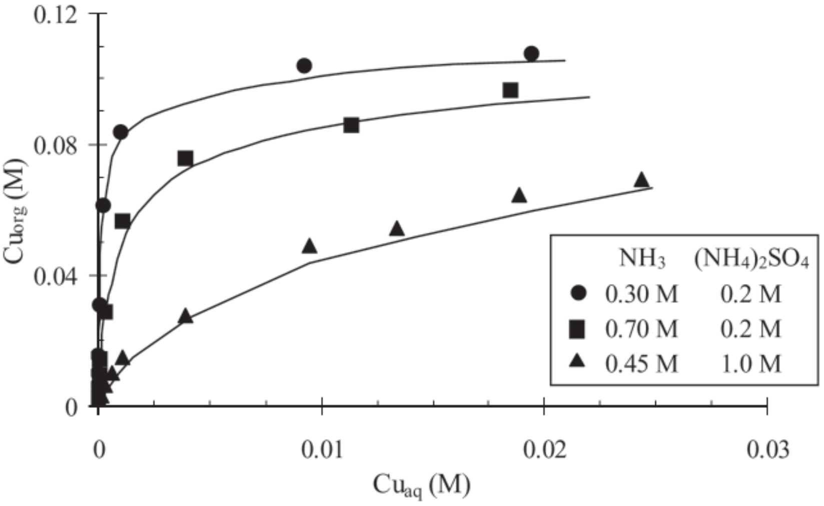

Figure 3. Isotherms of equilibrium for copper extraction with LIX 54. Initial aqueous phase: $CuSO_4 = 3.15 \times 10^{-2}\,M$; $(NH_4)_2SO_4$; NH_3. Initial organic phase: LIX 54 = 0.222 M in ShellSol T.

lower copper concentration in the raffinate. The use of low concentrations of ammonium salt in aqueous solutions is, therefore, recommended. Several authors[37–39] have already reported the depressing effect of ammonium sulfate, nitrate, chloride, and carbonate on the extraction of metals with hydroxyoximes and β-diketones.

CONCLUSIONS

The extraction of copper from ammoniacal solutions with LIX 54 is very dependent on the equilibrium pH. The highest extraction efficiency was obtained in the range of pH 8–9.5. The increase of pH to values higher than 10 decreases sharply the extraction of copper. The reaction for copper extraction with LIX 54 can be described by the overall stoichiometry:

$$\mathrm{Cu(NH_3)_{4,aq}^{2+} + 2HR_{org} \leftrightarrows CuR_{2,org} + 2NH_{3,aq} + 2NH_{4,aq}^{+}}$$

The thermodynamic equilibrium constant was found to be $10^{(2.89 \pm 0.03)}\,\mathrm{M}^2$, at 298 K, by applying the Pitzer model and the extended Debye-Hückel equation to take into account the nonideality of the aqueous phase. The use of this value allowed the satisfactory prediction of isotherms for copper extraction from $\mathrm{NH_3/(NH_4)_2SO_4}$ aqueous solutions with LIX 54.

APPENDIX A

The parameter B_{Ca} and B'_{Ca} in the Pitzer equation (8) can be obtained by the following expressions:

$$B_{Ca} = \beta^0_{Ca} + \beta^1_{Ca} f(\alpha_1 \sqrt{I}) \tag{A.1}$$

$$B'_{Ca} = \frac{\beta^1_{Ca} f'(\alpha_1 \sqrt{I})}{I} \tag{A.2}$$

α_1 is 2 $(\mathrm{kg\,mol^{-1}})^{1/2}$ for 1 : 1 and 1-2 electrolytes, $f(\mathrm{x})$ and $f'(\mathrm{x})$ are expressed by the equations:

$$f(x) = \frac{2(1 - (1 + x)e^{-x})}{x^2} \tag{A.3}$$

$$f'(x) = \frac{-2(1 - (1 + x + 0.5x^2)e^{-x})}{x^2} \tag{A.4}$$

Table A.1. Interaction Pitzer's parameters (298 K).

	β^0	β^0	Ref.		λ	Ref.
$H-OH^-$	0.208	0.6545	[28]	NH_3-NH_3	0.01472	[25]
$H^+-SO_4^{2-}$	0.0642	0.2259	[14]	NH_3-OH^-	0.107	[25]
H^+-NH_3	0.015	—	[28]	$NH_3-NH_4^+$	-0.002	[25]
$NH_4^+-SO_4^{2-}$	0.039	0.6638	[14]	$NH_3-SO_4^{2-}$	0.137	[25]
$NH_4^+-OH^-$	0.06	0.2016	[28]			
	C^ϕ		Ref.		μ	Ref.
$(NH_4)_2SO_4$	-1.872×10^{-3}		[14]	$NH_3-NH_3-NH_4^+$	-7.5×10^{-4}	[25]
				$NH_3-NH_4^+-SO_4^{2-}$	-1.53×10^{-4}	[25]

The parameters C_{Ca} and C_{Ca}^{ϕ} are related by:

$$C_{Ca} = \frac{C_{Ca}^{\phi}}{2\sqrt{|z_C z_A|}} \tag{A.5}$$

being z_i the ion charge. Table A.1 the interaction Pitzer's parameters at 298 K used to determine the activity coefficients for the ionic species H^+, OH^-, NH_4^+, SO_4^{2-}, and NH_3.

NOTATION

a	activity
A_γ	constant at extended Debye-Hückel equation
$\dot{a}$	constant at extended Debye-Hückel equation
B	second virial coefficient of Pitzer model, kg mol^{-1}
c	concentration in the molarity scale, mol L^{-1} (M)
C	third virial coefficient of Pitzer model, kg^2 mol^{-2}
D	distribution ratio
D'	modified distribution ratio (Eq. 3)
HR	general designation of extractant
I	ionic strength, mol kg^{-1}
K^o	thermodynamic equilibrium constant
K^o_{ext}	thermodynamic extraction constant in terms of aqueous phase (Eq. (2), M^2
K_{ext}	concentration-based extraction constant, M^2
m	molality, mol kg^{-1} of solvent

Greek Letters

β	constant at extended Debye-Hückel equation
γ_i	activity coefficient of species i (molality scale)
Θ	second virial coefficient of mixing for the Pitzer model
ψ	third virial coefficient of mixing for the Pitzer model
λ_{ij}	virial coefficients for binary interaction
μ_{ijk}	virial coefficients for ternary interaction

Subscripts

a, a′	denotes anions in the mixture
C, c, c′	denotes cations in the mixture
aq	denotes aqueous phase
calc	denotes a calculated value
exp	denotes a measured value
org	denotes organic phase

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