Equilibrium Modeling of the Extraction of Copper and Ammonia from Alkaline Media with the Extractant LIX84I

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Here we examined the equilibrium distribution ratios of copper(II) and ammonia between an ammonium salt solution (nitrate, sulfate, or chloride) and the extractant LIX84I (active component, 2-hydroxy-5-nonylacetophenone oxime) dissolved in a non-polar diluent Shell sol D70 at pH 2–10 and 298 K. The effects of pH, ammonium salt concentration in the aqueous phase, counter anion type, and phase ratio on the co-extraction of copper and ammonia were investigated. The values of the extraction constant of ammonia and the distribution constant of copper-oxime complex were independent of the type and concentration of ammonium salt, and the logarithm of the extraction constant of copper linearly increased with the ionic strength of the aqueous phase. Consequently, we constructed an equilibrium model that enabled quantitative calculation of the distribution ratios of copper and ammonia at a given equilibrium pH. Full loading of copper was found to minimize the accumulation of ammonia in the organic phase, which may reduce the need for ammonia scrubbing in practical operations.

1. Introduction

Solvent extraction is a common means of extracting copper(II) from ammoniacal alkaline solutions. Chelating agents such as β-hydroxyoxime and β-diketone have been used as the extractant to separate copper(II) from ores, deep-sea mineral resources such as ferromanganese nodules, spent etching solutions, and waste printed circuit boards. However, when copper(II) is extracted from weakly alkaline solutions, small amounts of ammonia are also extracted, which must be removed by scrubbing with a dilute acid prior to stripping of the extract to avoid precipitation of ammonium salt into the stripping solution.

Quantitative modeling is an important part of the design and control of solvent extraction processes; however, no previous studies have modeled copper(II) extraction from ammoniacal alkaline solutions by using a chelating reagent while also taking into account the co-extraction of ammonia.

In our previous paper, we examined the equilibria established during the extraction of ammonia with LIX84I (active component, 2-hydroxy-5-nonylacetophenone oxime, HR) from a 3 kmol m$^{-3}$ solution of ammonium nitrate in the absence of metal ions, and found that the distribution ratios obtained experimentally were in good agreement with those calculated by an equilibrium model which assumed the formation of adducts between ammonia and the extractant.

In the present study, we first extended the applicability of our previously reported model of ammonia extraction to include a wider range of ammonium nitrate concentrations in the aqueous phase. Then, we examined the equilibria established during the co-extraction of copper(II) and ammonia from different ammoniacal solutions with the extractant LIX84I at 298 K. Next, we studied the effects of pH, total ammonium salt concentration, counter anion type, and phase ratio on the co-extraction of copper(II) and ammonia. Finally, we constructed a quantitative model based on the relevant equilibrium relationships.

2. Experimental

2.1 Reagents and solution preparation

All of the chemicals used were of reagent grade except for the extractant and diluent. LIX84I (Cognis Ireland Ltd., lot no. 0684I001) was used as the extractant without further purification. Total HR concentration, $C_{HR}$, in 20 vol% LIX84I was determined to be 0.323 kmol m$^{-3}$ by the full loading of copper(II). The aliphatic solvent Shell sol D70 (Shell Japan Ltd., lot no. 50713) was used as the diluent without further purification.

Solutions of $\text{NH}_4\text{NO}_3$ (1.25–6.25 kmol m$^{-3}$) in the presence or absence of $\text{Cu(NO}_3\text{)}_2$ (0.0625 kmol m$^{-3}$), $\text{(NH}_4\text{)}_2\text{SO}_4$ (0.625–3.125 kmol m$^{-3}$)–$\text{Cu(NO}_3\text{)}_2$ (0.0625 kmol m$^{-3}$), or $\text{NH}_4\text{Cl}$ (3.75 kmol m$^{-3}$)–$\text{Cu(NO}_3\text{)}_2$ (0.0625 kmol m$^{-3}$) were prepared and used as the aqueous phase in the solvent extraction. Sodium hydroxide and nitric acid at various concentrations were used as pH adjusting reagents.

2.2 Extraction of copper and ammonia

In all of the experiments, the initial organic phase, the initial aqueous phase, and a pH adjusting reagent were poured into a 50 cm$^3$ centrifugal bottle at a volume ratio of 5:4:1 except those examining the effects of phase ratio on extraction. The bottle was first shaken vertically at room temperature (approximately 298 K) and then horizontally shaken in a water bath kept at 298 ± 0.1 K until equilibrium was reached. This operation was equivalent to placing aqueous phases with total ammonia concentrations of 1–5 kmol m$^{-3}$, in the presence or absence of 0.05 kmol m$^{-3}$ copper(II), in

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contact with an equal volume of organic phase at various pH. After equilibrium was reached, the mixture was centrifuged at 2000 rpm for 10 min, and the organic phase was removed by pipette. The pH of the aqueous phase was measured with a pH meter (DKK–TOA Corp. Ltd., Japan; HM–30R) at 298 K.

The concentration of copper remaining in the aqueous raffinate was determined by means of inductively coupled plasma atomic emission spectroscopy (Horiba Ltd., Japan; ULTIMA2) after appropriate dilution. The concentration of copper in the loaded organic phase was determined from the mass balance before and after the extraction, except for the single case when the concentration was less than 0.0015 kmol m$^{-3}$. In this exceptional case, the concentration of copper was determined by means of inductively coupled plasma atomic emission spectroscopy after the organic phase had been completely stripped with 2 kmol m$^{-3}$ HCl.

The initial concentration of ammonia in the aqueous phase was determined by means of capillary electrophoresis (Agilent Technologies, U.S.; G1600A) after appropriate dilution. In the capillary electrophoresis, a silica capillary (50 μm i.d. × 72 cm effective length) and 20 mol m$^{-3}$ imidazole buffer (pH = 4.5) were used and the voltage was set at +20 kV$^{-20}$). The concentration of ammonia in the loaded organic phase was determined in the same manner after complete stripping with 0.1 kmol m$^{-3}$ HCl.

The distribution ratios of Cu and NH$_3$, $D$(Cu) and $D$(NH$_3$), respectively, were calculated as

$$D$(Cu) = $[Cu]_{org}/[Cu]_T$, aq (1)

$$D$(NH$_3$) = $[NH_3]_{org}/([NH_3]_{init}, aq - [NH_3]_{org}) (2)

where the subscripts org, aq, init and T denote the organic phase, aqueous phase, and initial and total concentrations, respectively. The quintuplicate runs under the same conditions (organic phase: C$_{org}$ = 0.16 kmol m$^{-3}$; aqueous phase: 3 kmol m$^{-3}$ NH$_4$NO$_3$–0.05 kmol m$^{-3}$ Cu(NO$_3$)$_2$–1.6 kmol m$^{-3}$ NaOH) revealed that log $D$(Cu), log $D$(NH$_3$), and pH at equilibrium were ca. 3.2, 2.3 and 9.5 with standard deviations of 0.010, and 0.008, and 0.006, respectively.

3. Equilibria and Material Balances

The following equilibria and material balances were taken into consideration in our analysis of the experimental data.

3.1 Equilibria in the aqueous phase

Ammonium ion dissociates into ammonia as

$$NH_4^{+}_{aq} \leftrightarrow NH_3_{aq} + H^+_{aq} \quad (3)$$

$$K_a(NH_3) = [NH_3]_{aq}[H^+_{aq}]/[NH_4^{+}_{aq}] \quad (4)$$

where $K_a$($NH_3$) is the acid dissociation constant of ammonium ion.

Copper(II) forms ammonia complexes as

$$Cu^{2+}_{aq} + m NH_3_{aq} \leftrightarrow Cu(NH_3)_{m+2}^{2+}_{aq}; \ m = 1–4 \quad (5)$$

$$\beta_m = [Cu(NH_3)_{m+2}]_{aq}/[[Cu^{2+}]_{aq}[NH_3]_{aq}^m] \quad (6)$$

where $\beta_m$ is the overall stability constant of the $m$th copper-ammine complex.

In the sulfate system, hydrogen sulfate ion undergoes acid dissociation as

$$HSO_4^{-}_{aq} \leftrightarrow H^+_{aq} + SO_4^{2-}_{aq} \quad (7)$$

$$K_a(HSO_4) = [H^+_{aq}][SO_4^{2-}_{aq}]_{aq}/[HSO_4^{-}_{aq}] \quad (8)$$

where $K_a$($HSO_4$) is the acid dissociation constant of hydrogen sulfate ion.

Copper(II) associates with sulfate ion as

$$Cu^{2+}_{aq} + SO_4^{2-}_{aq} \leftrightarrow CuSO_4_{aq} \quad (9)$$

$$\beta(CuSO_4) = [CuSO_4]_{aq}/[[Cu^{2+}]_{aq}[SO_4^{2-}]_{aq}] \quad (10)$$

where $\beta$($CuSO_4$) is the stability constant of copper-sulfate complex.

In the chloride system, copper(II) associates with chloride ion as

$$Cu^{2+}_{aq} + nCl^-_{aq} \leftrightarrow CuCl_n^{2-n}_{aq}; \ n = 1–4 \quad (11)$$

$$\beta(CuCl_n^{2-n}) = [CuCl_n^{2-n}]_{aq}/[[Cu^{2+}]_{aq}[Cl^-]_{aq}^n] \quad (12)$$

where $\beta$(CuCl$_n^{2-n}$) is the overall stability constant of the $n$th copper-chloride complex.

These equilibrium constants of the aqueous phase are listed in Table 1, where $I$ denotes ionic strength.

3.2 Aggregation of HR in the organic phase

HR aggregates in nonpolar solvents through intermolecular hydrogen bonding, which is expressed by the following successive aggregation model$^{26}$:

$$(HR)_i_{org} + HR_{org} \leftrightarrow (HR)_{i+1}^{1}_{org} \quad (13)$$

$$K_m = [(HR)_{i+1}^{1}_{org}/[[HR]_{log}[HR]_{org}]] \quad (14)$$

where $i$ is a positive integer and the order of aggregation,

<table>
<thead>
<tr>
<th>Eq. const.</th>
<th>Unit</th>
<th>Equation or logarithmic value</th>
<th>Aqueous medium</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_a(NH_3)$</td>
<td>kmol m$^{-3}$</td>
<td>p$K_a$ = 0.0562$^{9} + 9.33$</td>
<td>NH$_3$NO$_3$</td>
<td>(21)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>kmol m$^{-3}$$^{-m}$</td>
<td>log $\beta_m$ = $\Sigma$ $n$ (log $K_m^n$ + 0.08[HN$_3$]$_T$ + 0.065)</td>
<td>NH$_3$NO$_3$</td>
<td>(22)</td>
</tr>
<tr>
<td>$K_a(HSO_4)$</td>
<td>kmol m$^{-3}$</td>
<td>-0.67</td>
<td>3 kmol m$^{-3}$ NaClO$_4$</td>
<td>(23)</td>
</tr>
<tr>
<td>$\beta$($CuSO_4$)</td>
<td>kmol m$^{-3}$$^{-1}$</td>
<td>1.084</td>
<td>3 kmol m$^{-3}$ NaClO$_4$</td>
<td>(24)</td>
</tr>
<tr>
<td>$\beta$(CuCl$_n^{2-n}$)</td>
<td>kmol m$^{-3}$$^{-n}$</td>
<td>-0.28 ($n = 1$), -0.24 ($n = 2$), -1.96 ($n = 3$), -2.44 ($n = 4$)</td>
<td>3 kmol m$^{-3}$ NaClO$_4$</td>
<td>(25)</td>
</tr>
</tbody>
</table>

$^{*}$: Values of log $K_m^n$ ($m = 1, 2, 3, 4$) are 3.99, 3.34, 2.73, 1.97, respectively.
and $K_m$ is the successive aggregation constant. Here $K_m$ is assumed to be independent of $i$. The $K_m$ of LIX84I dissolved in Shellol D70 at 298 K is 9.9 m$^3$ kmol$^{-1}$.\(^{21}\)

### 3.3 Equilibria established during the extraction of copper and ammonia

The extraction of copper(II) with LIX84I proceeds as:\(^{27}\)

$$\text{Cu}^{2+} + 2 \text{HR}_{\text{org}} \leftrightarrow \text{CuR}_2 \text{org} + 2 \text{H}^+$$

$$K_e = [\text{CuR}_2 \text{org}] / ([\text{HR}]_{\text{aq}}^2)$$

where $K_e$ is the extraction constant of copper(II). Though included in eq. (15), the distribution of CuR$_2$ is explicitly considered as

$$\text{CuR}_2 \text{aq} \leftrightarrow \text{CuR}_2 \text{org}$$

$$K_d = [\text{CuR}_2 \text{org}] / ([\text{CuR}_2]_{\text{aq}})$$

where $K_d$ is the distribution constant of CuR$_2$.

In our previous paper\(^{19}\), we expressed the extraction of ammonia with LIX84I as

$$\text{NH}_3_{\text{aq}} + \text{HR}_{\text{org}} \leftrightarrow \text{HR} \cdot \text{NH}_3_{\text{org}}$$

$$K_1 = [\langle \text{HR} \cdot \text{NH}_3 \rangle_{\text{org}}] / ([\text{HR}]_{\text{aq}} \cdot [\text{NH}_3]_{\text{aq}})$$

$$K_2 = [\langle \text{HR} \cdot \text{NH}_3 \rangle_{\text{org}}] / ([\langle \text{HR} \cdot \text{NH}_3 \rangle_{\text{org}}]_{\text{org}})$$

$$K_3 = [\langle \text{HR} \cdot \text{NH}_3 \rangle_{\text{org}}] / ([\langle \text{HR} \cdot \text{NH}_3 \rangle_{\text{org}}]_{\text{org}})$$

where $j$ and $k$ are positive integers, and $K_1$ is the extraction constant of ammonia, and $K_2$ and $K_3$ are the adduct formation constants. Here we assume that $K_2$ and $K_3$ are independent, respectively, of $j$ and $k$.

### 3.4 Material balances

The material balances of hydroxyoxime, ammonia, copper, sulfate and chloride are expressed by the following equations, respectively:

$$V_{\text{org}} C_{\text{BO}} = 2V_{\text{org}}[\text{CuR}_2]_{\text{aq}} + V_{\text{aq}}[\text{CuR}_2]_{\text{aq}}$$

$$+ V_{\text{org}} \left( \sum_{i=1}^{\infty} i[\langle \text{HR} \rangle_{\text{org}}] + \sum_{i=1}^{\infty} i[\langle \text{HR} \rangle \cdot \text{NH}_3_{\text{org}}] \right)$$

$$+ \sum_{i=2}^{\infty} i[\langle \text{HR} \cdot \text{NH}_3 \rangle_{\text{org}}]$$

$$V_{\text{aq}} C(\text{NH}_3)_{\text{aq}} = V_{\text{aq}}[\text{NH}_3]_{\text{aq}} + [\text{NH}_4^+]_{\text{aq}}$$

$$+ V_{\text{org}} \left( \sum_{i=1}^{\infty} i[\langle \text{HR} \rangle \cdot \text{NH}_3_{\text{org}}] \right)$$

$$+ \sum_{i=2}^{\infty} i[\langle \text{HR} \cdot \text{NH}_3 \rangle_{\text{org}}]$$

$$V_{\text{aq}} C(\text{Cu})_{\text{aq}} = V_{\text{aq}}[\text{CuR}_2]_{\text{aq}} + V_{\text{aq}}[\text{CuR}_2]_{\text{aq}}$$

$$+ \sum_{i=1}^{\infty} i[\langle \text{CuNH}_3 \rangle_{\text{aq}}]$$

$$+ \sum_{i=1}^{\infty} i[\langle \text{CuCl}^2- \rangle_{\text{aq}}] + [\text{CuSO}_4_{\text{aq}}]$$

$$C(\text{SO}_4)_{\text{aq}} = [\text{CuSO}_4_{\text{aq}}] + [\text{SO}_4^{2-}]_{\text{aq}} + [\text{HSO}_4^-]_{\text{aq}}$$

$$C(\text{Cl})_{\text{aq}} = \sum_{i=1}^{\infty} i[\langle \text{CuCl}^2- \rangle_{\text{aq}}] + [\text{Cl}^-]_{\text{aq}}$$

Here the infinite series in eqs. (25) and (26) are convergent and thus can be rearranged, respectively, as

$$\sum_{i=1}^{\infty} i[\langle \text{HR} \rangle \cdot \text{NH}_3_{\text{org}}] + \sum_{i=1}^{\infty} i[\langle \text{HR} \rangle \cdot \text{NH}_3_{\text{org}}]$$

$$+ \sum_{i=2}^{\infty} i[\langle \text{HR} \cdot \text{NH}_3 \rangle_{\text{org}}]$$

$$= [\text{HR}]_{\text{org}} / (1 - K_m \text{[HR]})$$

$$+ [\text{HR} \cdot \text{NH}_3_{\text{org}}] / (1 - K_2 \text{[HR]})$$

$$+ [\text{HR} \cdot \text{NH}_3_{\text{org}}] / (1 - K_3 \text{[HR] \cdot NH}_3_{\text{org}})$$

$$- \text{[HR] \cdot NH}_3_{\text{org}}$$

### 4. Results and Discussions

#### 4.1 Effect of ammonium nitrate concentration on the extraction of ammonia in the absence of copper

Previously, we examined the equilibria established during the extraction of ammonia from 3 kmol m$^{-3}$ solutions of ammonium nitrate at equilibrium pH (pH$_\text{eq}$) = 8–11 and C$_\text{BO}$ = 0.02–0.65 kmol m$^{-3}$.\(^{19}\) We then constructed a model describing the observed results that included the equilibria expressed by eqs. (19), (20), and (21). To broaden the applicability of this previous model, in the present study we examined the effect of the concentration of ammonium nitrate (1.07–5.33 kmol m$^{-3}$, five concentrations) on the distribution ratio when C$_\text{BO}$ = 0.16 kmol m$^{-3}$.

The experimental results in Fig. 1 show that the log $D(\text{NH}_3)$ value at a constant ammonium nitrate concentration monotonically increased with pH$_\text{eq}$ from 8 to 10 and then tended to be constant, which was the same trend as our previous results.\(^{19}\) On the other hand, the log $D(\text{NH}_3)$ slightly decreased with increasing ammonium nitrate concentration at pH$_\text{eq}$ 8–10.

In our model, the effect of ammonium nitrate concentration on the acid dissociation equilibrium of ammonium ion is described by eq. (3) and that in eq. (22) is unknown. Therefore, to examine the effect of ammonium nitrate concentration on the $K_1$ value, we preliminarily analyzed the experimental data at each ammonium nitrate concentration by using our model consisting of eqs. (2), (4), (22)–(26); that is, we fitted the model to the distribution ratios at each ammonium nitrate concentration shown in Fig. 1 by using nonlinear least squares method regarding $K_1$ as an adjustable parameter at fixed $K_2$ and $K_3$, respectively, of 14, and 35 m$^3$ kmol$^{-1}$ which were obtained in our previous paper.\(^{19}\) During this procedure, we found that the fitting by the model became worse, when the concentration of ammonia in the organic phase exceeded 0.045 kmol m$^{-3}$. The reason for the worse fitting was likely that at a concentration 0.045 kmol m$^{-3}$ the organic phase was almost saturated with ammonia.
and therefore the activity coefficient of ammonia-HR adducts would have been maximal at this concentration. Thus, we fitted the model excluding the data when ammonia concentration in the organic phase was greater than 0.045 kmol m\(^{-3}\). As a result, \(K_1\) obtained at each ammonium nitrate concentration were almost the same, which meant that \(K_1\) was independent of ammonium nitrate concentration. On the basis of these preliminary results, we fitted the model using nonlinear least squares method to all of the experimental data in our previous study\(^{19}\) collected by using a 3 kmol m\(^{-3}\) solution of ammonium nitrate at various pH values and total hydroxyoxime concentrations together with those in Fig. 1 in the present study. In this fitting, the data when the concentration of ammonia in the organic phase was greater than 0.045 kmol m\(^{-3}\), were excluded, and \(K_1\), \(K_2\), and \(K_3\) were regarded as adjustable parameters. Values of \(K_1/\text{uni}\), \(K_2/\text{uni}\), and \(K_3/\text{uni}\) were obtained with a coefficient of determination, \(r^2\) (log\(D\)), of 0.972 and root mean square error (RMSE) of 0.086, as defined by the following equation:

\[
\text{RMSE} = \sqrt{\frac{1}{N} \sum (\log D_{\text{calc}} - \log D_{\text{expt}})^2}
\]

The curves in Fig. 1 represent the fitted values. Figure 2 shows the correlation between log \(D_{\text{calc}}\) and log \(D_{\text{expt}}\) for our previous data\(^{19}\). These results indicate that the fitting was satisfactory.

As discussed above, \(K_1\) remained invariant regardless of the concentration of ammonium nitrate, suggesting that the effect of the ionic strength of the aqueous phase on the activity coefficient of neutral species of NH\(_3\) was negligible under the present experimental conditions. Thus, the slight decrease in \(D(\text{NH}_3)\) with increasing ammonium nitrate concentration when \(\text{pH}_{\text{eq}}\) was fixed must have been due to a decrease in \(K_a(\text{NH}_4^+)\) as expressed in Table 1.

Flett and Melling\(^{28}\) examined ammonia extraction with LIX65N in an aliphatic diluent and determined the \(K_1\) value by assuming eq. (19). Although their work was pioneering, they did not consider the nonideality of the extractant (e.g., dimerization or aggregation of hydroxyoxime), and therefore the reported \(K_1\) value was applicable only at a fixed concentration of extractant (10 vol%). In our previous\(^{19}\) and present studies, we have extended the applicability of the finding by Flett and Melling\(^{28}\) to allow for various concentrations of extractant and ammonium salt.

4.2 Effect of ammonium nitrate concentration on copper and ammonia extraction

We first used an acidic nitrate system to examine the extraction of copper because nitrate ion does not form a complex with copper(II). These results were then compared with those obtained by using alkaline sulfate and nitrate, and acidic – alkaline chloride solutions. Because nitric acid at high concentrations was known to degrade hydroxyoxime, the extractions were performed at \(\text{pH}_{\text{eq}}>1.4\).

Figure 3 shows a plot of log \(D(\text{Cu})\) versus \(\text{pH}_{\text{eq}}\) at various values of \(I = [\text{NH}_4\text{NO}_3]\) in acidic nitrate solution. At \(\text{pH}_{\text{eq}} < 3\), log \(D(\text{Cu})\) increased with increasing \(\text{pH}_{\text{eq}}\) with a slope of 2 (see eq. (15)) at a constant \(I\) and slightly increased with increasing \(I\) at a fixed \(\text{pH}_{\text{eq}}\).

Figure 4 shows the average log \(K_e\) values obtained by using eq. (16) and the data of log \(D(\text{Cu}) < 3.2\) at each ammonium nitrate concentration as a function of \(I\), in which the

![Fig. 1](image1.png)

Fig. 1 Log \(D(\text{NH}_3)\) as a function of \(\text{pH}_{\text{eq}}\) at various ammonium nitrate concentrations and \(C_{\text{NO}} = 0.162\) kmol m\(^{-3}\).

![Fig. 2](image2.png)

Fig. 2 Results of the fitting of our equilibrium model to the log \(D(\text{NH}_3)\) values obtained in our previous study (ammonium nitrate concentration = 2.87 kmol m\(^{-3}\)).

![Fig. 3](image3.png)

Fig. 3 Log \(D(\text{Cu})\) as a function of \(\text{pH}_{\text{eq}}\) at various ammonium nitrate concentrations and \(C_{\text{NO}} = 0.162\) kmol m\(^{-3}\).
straight line expressed by eq. (33) was drawn by using the least squares method:

$$\log K_e = 0.112I + 1.07$$  \hspace{1cm} (33)$$

Kyuchoukov et al.\(^2\) determined the extraction constant of copper from ammonia solution containing chloride ion with the extractant LIX84. Although their study was done in alkaline media, they obtained a similar linear relationship between \(\log K_e\) and \(I\).

At \(pH_{eq} = 4-7\), \(\log D(Cu)\) remained constant regardless of \(pH_{eq}\) and \(I\). The copper species in the aqueous phase in this pH range is CuR\(_2\), which is in equilibrium with that in the organic phase; therefore, the equilibrium expressed by eq. (17) is dominant in this pH region. This means that \(K_d\) is independent of \(I\) as in the case of \(K_1\). As a representative calculation, by taking the average of the \(\log D(Cu)\) values obtained at \(I = 3.02\) kmol m\(^{-3}\) and \(pH_{eq} = 4-7\), we determined \(\log K_d\) to be 4.2 (\(K_d = 1.6 \times 10^4\)).

The curves shown in Fig. 3 were calculated by using eqs. (1), (2), (4), (6), (16), (18), (22)–(27) and (33), and the results were in good agreement with the experimental data.

### 4.3 Effect of ammonium sulfate concentration on the extraction of copper and ammonia at alkaline region

From a practical standpoint, ammonium sulfate solution is the most commonly used ammoniacal media. Therefore, we studied the effect of the concentration of ammonium sulfate on the extraction of copper and ammonia at alkaline region. Figure 5 shows plots of \(\log D(Cu)\) and \(\log D(NH_3)\) versus \(pH_{eq}\) at various values of \(I\) (total ammonium sulfate concentration = 0.46–2.29 kmol m\(^{-3}\)), and \(C_{BO} = 0.162\) kmol m\(^{-3}\). At \(pH_{eq} = 8-10\), the value of \(\log D(Cu)\) at each \(I\) decreased with increasing \(pH_{eq}\) due to the formation of copper-ammine complexes. \(\log D(Cu)\) at a fixed \(pH_{eq}\) also decreased with \(I\) because the increase in the concentration of ammonia was a major governing factor even though \(K_e\) increased based on eq. (33). The variation in \(\log D(NH_3)\) was similar to that shown in Fig. 1.

The curves in Fig. 5 were calculated by using eqs. (1), (2), (4), (6), (8), (10), (12), (16), (18), (22)–(28) and (33); considering we did not conduct any parameter fitting here, the agreement with the experimental data was acceptable. These results suggest that the equilibrium constants of \(K_a(NH_4^+), K_1, K_2, K_3, K_e\) and \(K_d\) determined from nitrate media are also applicable to sulfate solutions.

### 4.4 Comparison of the extraction of copper and ammonia from nitrate, sulfate, and chloride solutions

Figure 6 shows a comparison of the extraction of copper and ammonia from ammonium nitrate, sulfate, and chloride solutions containing 3 kmol m\(^{-3}\) total ammonia at \(C_{BO} = 0.162\) kmol m\(^{-3}\) and \(pH 2–10\). The curves were calculated by using eqs. (1), (2), (4), (6), (8), (10), (12), (16), (18), (22)–(29) and (33). The calculated values were in good agreement with the experimental data, suggesting that our model is applicable also to chloride solutions. Table 2 shows the agreement between calculated and experimental values in these ammonium salt systems examined.

At \(pH_{eq} < 4\), the \(\log D(Cu)\) of each anion system increased with increasing \(pH_{eq}\) with a slope of 2; however, the \(\log D(Cu)\) for the sulfate or chloride systems were less than that for the nitrate system at a given \(pH_{eq}\). This was likely due to the formation of copper-sulfate or copper-chloride complexes.

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**Fig. 4** Average \(\log K_e\) at each \(I\) and its dependency on \(I\) in nitrate system.

**Fig. 5** \(\log D\) as a function of \(pH_{eq}\) at various ammonium sulfate concentrations and \(C_{BO} = 0.162\) kmol m\(^{-3}\).

**Fig. 6** \(\log D\) as a function of \(pH_{eq}\) for various ammonium salt solutions at \(C_{BO} = 0.162\) kmol m\(^{-3}\) and total ammonia concentration = 3 kmol m\(^{-3}\).
complexes. At pH_{eq} 4–8, D(Cu) remained constant at approximately 4.2 regardless of pH_{eq} or anion type. At pH_{eq} > 8, log D(Cu) decreased with pH_{eq} up to pH_{eq} 9.7, 10, and 9.4 for nitrate, sulfate, and chloride solutions, respectively, because of the formation of copper-ammine complexes. Thereafter, log D(Cu) increased as it did at acidic pH because of the formation of copper-ammine complexes. At pH_{eq} 4–8, log D(Cu) remained constant at approximately 4.2 regardless of pH_{eq} or anion type. At pH_{eq} > 8, log D(Cu) decreased with pH_{eq} up to pH_{eq} 9.7, 10, and 9.4 for nitrate, sulfate, and chloride solutions, respectively, because of the formation of copper-ammine complexes. Thereafter, log D(Cu) increased as it did at acidic pH because of the formation of copper-ammine complexes.

Table 2  Agreement between calculated and experimental values in the ammonium salt systems examined.

<table>
<thead>
<tr>
<th>System</th>
<th>r(log D)²</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>Cu(II)</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>0.993</td>
</tr>
<tr>
<td>Chloride</td>
<td>Cu(II)</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>0.980</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Cu(II)</td>
<td>0.958</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>0.986</td>
</tr>
</tbody>
</table>

* Here r(log D)², and RMSE denote coefficient of determination, and root mean square error (shown in eq. 32), respectively.

4.5 Effect of phase ratio on copper and ammonia extraction

In the experiments described above, the amounts of hydroxyoxime were in excess of those of copper. To examine the effect of the presence of an excess amount of copper, we carried out the extraction at different phase ratios (V_a/V_o = 1–10) with C_{BO} = 0.323 kmol m⁻³ using the initial aqueous solution of 1.64 kmol m⁻³ (NH₄)₂SO₄−0.0625 kmol m⁻³ Cu(NO₃)₂ and the pH adjustment reagent of 5 kmol m⁻³ NaOH, in which these two solutions were mixed at volume ratio 4:1 (Fig. 7: pH_{eq} = 9.50–9.55). The amount of ammonia extracted decreased via a process of copper loading because of the preferential extraction of copper and simultaneous decrease in the amount of hydroxyoxime available for ammonia extraction. When V_a/V_o was greater than 4, the organic phase was saturated with copper, and ammonia co-extraction was minimized (< 5 mol m⁻³). In practical operation, this phenomenon may reduce the need for ammonia scrubbing of the extract. In addition, our calculated values were in good agreement with the experimental values.

5. Conclusions

Here we examined the equilibria established during extraction of copper and ammonia from ammoniacal solutions with LIX84I in Shellsol D70 as the extractant at 298 K, and determined the equilibrium constants for ammonia extraction applicable at various concentrations of ammonium salts. A linear relationship between the logarithm of extraction constant of copper and the ionic strength of the aqueous phase (1–5 kmol m⁻³) was found. By using these equilibrium relations and the appropriate material balances, we were able to quantitatively predict the distribution ratios of copper and ammonia in a nitrate, sulfate, or chloride system at a given pH_{eq}. Preferential extraction of copper decreased the concentration of ammonia in the organic phase, which may reduce the need for ammonia scrubbing in practical operations.

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REFERENCES