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# EFFECT OF ADDED COMPLEXING AGENTS ON EXTRACTION OF Cu(II) FROM SULFATE SOLUTIONS BY DI(2-ETHYLHEXYL)PHOSPHORIC ACID

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## ABSTRACT

The efficiencies of Cu(II) extraction from 0.5 mol/dm$^3$ (Na,H)SO$_4$ solutions by di(2-ethylhexyl)phosphoric acid (D2EHPA) in kerosene were measured in the presence of complexing agents EDTA, nitrilotriacetic acid (NTA), and citric acid. All experiments were performed in solution at pH 1.8–4.1; Cu(II) concentration of 0.005, 0.01, and 0.02 mol/dm$^3$; the concentration of complexing agent to Cu(II) as 0, 0.1, 0.2, 0.5; and a D2EHPA concentration of 0.01–0.5 mol/dm$^3$. The extraction efficiency of Cu(II) decreased with the addition of EDTA and NTA, but not with citric acid. The presence of complexing agents resulted in a change of reaction stoichiometry of Cu(II) and D2EHPA, likely due to the mutual interaction of Cu(II)-D2EHPA complexes and the complexing agents. The coextraction of citric acid into the organic phase could explain the increase in extraction efficiency with increasing citric acid concentration.

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## INTRODUCTION

Complexing agents, such as citrate, NTA (nitrilotriacetic acid), and EDTA, are critical allies in the war against metal ion–induced equipment and process problems. Used in applications for paper and pulp processing, textile processing, metal plating/finishing, water treatment, and gas scrubbing, the complexing agents bind with metal ions, preventing them from forming insoluble salts or causing other process troubles (1). However, the presence of complexing agents, even at trace levels, makes chemical precipitation processes (e.g., $OH^-$, $S^{2-}$) ineffective and reduces the effectiveness of biological treatment (2).

Complexing agents may affect the adsorption performance of charged or uncharged species from process or waste streams on activated carbon or other adsorbents (3,4) and the effectiveness of cation-exchange resins for metal ions (5–7). Although solvent extraction has been shown to be practical and promising for the recovery and separation of metal ions from aqueous solutions (8), little attention has been paid to examining how the extraction phenomena of metal ions, including the extractability and reaction stoichiometry, are affected by the addition of complexing agents (9). The aim of this work was to give an insight into the extraction of metal ions through a study of the complex reactions involved. The extraction efficiencies of Cu(II) from acidic sulfate solutions with kerosene solutions of di(2-ethylhexyl)phosphoric acid (D2EHPA), a commercially available extractant, were measured as a function of pH, aqueous-phase concentration of Cu(II), molar concentration ratio of complexing agent to Cu(II), and the organic-phase concentration of D2EHPA. Three common complexing agents, EDTA, NTA, and citric acid were selected for study in the experiments. Finally, the reaction stoichiometry of Cu(II) and D2EHPA in the presence of complexing agents was analyzed through a study of possible equilibrium relationships of the chemical reactions occurring in 2 immiscible phases.

## EXPERIMENTAL

### Reagents and Solutions

The extractant D2EHPA (Merck Co., Darmstadt, Germany) had a purity of 98.5% and was used without further purification. Kerosene, purchased from Union Chemical Ltd (Taiwan), was washed 2 times at 298 K with 20 vol % $H_2SO_4$ to remove some aromatics and was then washed with deionized water (Millipore Milli-Q) 3 times. EDTA, NTA, citric acid, and other analytical-reagent grade inorganic chemicals were also supplied by Merck Co.

The aqueous phase contained 0.5 mol/dm$^3$ (Na,H,Cu)$SO_4$, which means that the total sulfate concentration was kept constant. This constant ion-medium method can provide a fixed activity coefficient of $H^+$ and $Cu^{2+}$ in a wide $H_2SO_4$ concentration range (0.001–0.1 mol/dm$^3$) (10). In addition, such composition can serve as a type of buffer medium. The initial aqueous pH was adjusted to 1.8 and 4.1 by changing different combinations of $Na_2SO_4$ and $H_2SO_4$. To simulate most practical situations, such adjustments were made before the addition of complexing agents. The initial concentrations of Cu(II) were 0.005, 0.01, and 0.02 mol/dm$^3$, and the molar concentration of complexing agent to Cu(II), $\beta$, were 0, 0.1, 0.2, and 0.5. The organic solutions were prepared by diluting D2EHPA in kerosene, and the initial D2EHPA concentrations ranged from 0.01 to 0.5 mol/dm$^3$.

### Experimental Procedures

For measuring the distribution ratios of Cu(II), equal volumes (40 cm$^3$) of the organic and aqueous phases were mixed in glass flasks by a magnetic stirrer for 12 h. Then, they were allowed to settle for 1 h. After phase separation, the pH was measured using a Horiba pH meter (Model F-23) and the concentration of Cu(II) in the aqueous phase was analyzed with a GBC atomic absorption spectrophotometer (Model 932). The organic-phase concentration of Cu(II) was obtained from a mass balance. The temperature was fixed at 298 K. Each experiment was duplicated at least under identical conditions. The extraction efficiency $E$ at an equal phase volume could be calculated by (8)

$$E(\%) = 100 \times \frac{[\overline{\mathrm{Cu}}]_t}{[\mathrm{Cu}]_0} = 100 \times \frac{[\overline{\mathrm{Cu}}]_t}{[\mathrm{Cu}]_t + [\overline{\mathrm{Cu}}]_t} = \frac{100D}{D+1} \qquad (1)$$

where the over bar refers to the organic phase and $D$ is the distribution ratio of Cu(II). The subscripts 0 and $t$ refer to the initial and equilibrium values, respectively.

## RESULTS AND DISCUSSION

### Complexation Equilibria in Aqueous Solutions

EDTA, NTA, and citric acid are polyprotic acids ($H_xL$) that may exist in a number of protonated forms in aqueous solutions. They readily form stable complexes with most heavy metals in a 1:1 molar ratio (11). Table 1 lists the overall formation constants of the complexes at 298 K and ionic strength ($I$) = 0. The distribution of species at different pH can be calculated from a set of mass-balance equations of metals and complexing agent. For a dilute equimolar solution of Cu(II) and EDTA (0.01 mol/dm$^3$), the divalent anions $CuL^{2-}$ (where L is the an-

***Table 1.*** The Overall Formation Constants (log $K_f$) for the Aqueous Complexes of Cations and Anionic Ligands (L) at 298 K and Zero Ionic Strength

| Cation | $L^-(OH^-)$ | | $L^{2-}(SO_4{}^{2-})$ | | $L^{3-}$(citrate) | | $L^{3-}$(NTA) | | $L^{4-}$(EDTA) | |
|---|---|---|---|---|---|---|---|---|---|---|
| $H^+$ | HL | 14.0 | HL | 1.99 | HL | 6.40 | HL | 10.33 | HL | 11.12 |
| | | | | | $H_2L$ | 11.16 | $H_2L$ | 13.27 | $H_2L$ | 17.80 |
| | | | | | $H_3L$ | 14.29 | $H_3L$ | 14.92 | $H_3L$ | 21.04 |
| | | | | | | | $H_4L$ | 16.02 | $H_4L$ | 23.76 |
| | | | | | | | | | $H_5L$ | 24.76 |
| $Na^+$ | | | NaL | 1.06 | NaL | 1.40 | NaL | 1.90 | NaL | 2.50 |
| $Cu^{2+}$ | CuL | 6.3 | CuL | 2.4 | CuL | 7.2 | CuL | 14.2 | CuL | 20.5 |
| | $CuL_2$ | 11.8 | | | CuHL | 10.7 | $CuL_2$ | 18.1 | CuHL | 23.9 |
| | $CuL_4$ | 16.4 | | | $CuH_2L$ | 13.8 | CuOHL | 18.6 | CuOHL | 22.6 |
| | | | | | CuOHL | 16.4 | | | | |

$K_f$ is defined as formation constant in the unit of mol/dm$^3$, for example, $K_f = [MH_yL_z]/[M]^x[H]^y[L]^z$ for the reaction $xM + yH + zL \Leftrightarrow M_xH_yL_z$

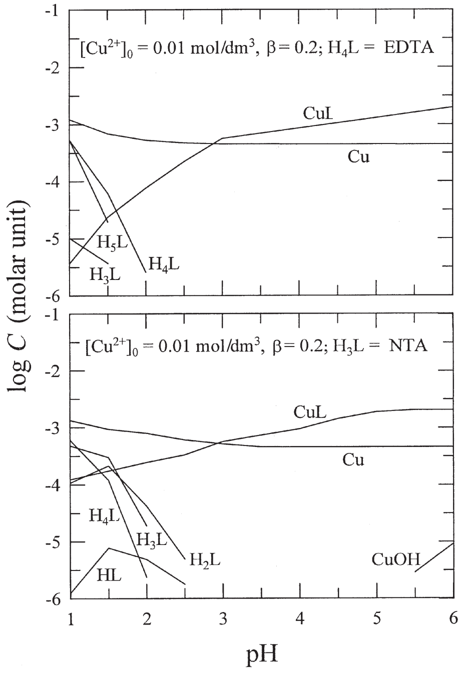

***Figure 1.*** Distribution of species in the aqueous sulfate solution containing EDTA and NTA at 298 K (β = 0.2).

ionic portion of complexing agent) absolutely dominate at pH 3–12 and the univalent anions $CuHL^-$ dominate at pH $< 3$ (12).

Figures 1 and 2 show the calculated results for solutions containing an excess of Cu(II) over the complexing agents ($\beta = 0.2$). They are numerically obtained using Mathematica 3.0 (Wolfram Research, Inc). The aqueous complexation of $SO_4^{2-}$ with Cu(II) is negligible due to its much smaller overall formation constant ($K_f$) than the reaction between Cu(II) and EDTA, NTA, or citrate. The values of $K_f$ in Table 1 are given at $I = 0$; the effect of ionic strength should be correlated with $K_f$ in this work. Although it is not identical before and after extraction, the ionic strength was determined as 1.26 mol/kg for simplicity. For example, from the formation reaction,

$$Cu^{2+} + L^{x-} \Leftrightarrow CuL^{2-x}, \qquad K_f \tag{2}$$

the following can be obtained:

$$\log\left(\frac{K_f}{K_f^0}\right) = \log\left(\frac{\gamma_{CuL^{2-x}}}{\gamma_{Cu^{2+}}\,\gamma_{L^{x-}}}\right) \tag{3}$$

where the superscript 0 represents the state of zero ionic strength. The term $\gamma_i$ denotes the activity coefficient of species $i$ and is calculated by the Davis equation (13).

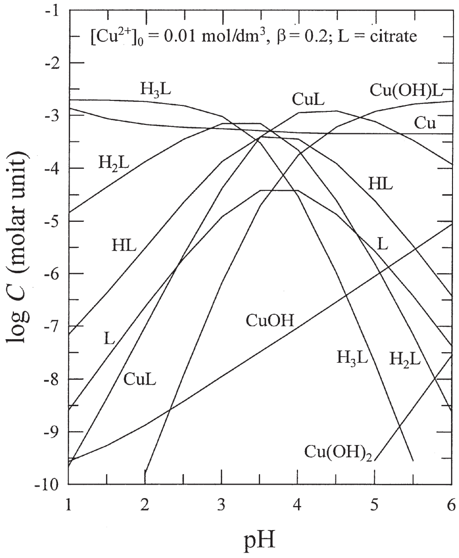

***Figure 2.*** Distribution of species in the aqueous sulfate solution containing citric acid at 298 K ($\beta = 0.2$).

$$\log \gamma_i = -\left[\frac{0.511 z_i^2 I^{1/2}}{(1 + I^{1/2})}\right] + 0.102 z_i^2 I \qquad (4)$$

Although Eq. (4) gives a reasonable estimate only at a molality up to 0.1 mol/kg (13), its simplicity and universal applicability for more complicated ions make it practically useful as the first approximation for ionic strength.

In the presence of EDTA and NTA, complexed $CuL^-$ dominate at $pH > 3$ and the free metal ions $Cu^{2+}$ at $pH < 3$ (Fig. 1). However, in the case of citric acid (Fig. 2), the dominant complex species are $CuL^-$ at pH 3.7–4.7, $H_2L^-$ at pH 3.2–3.7, and the neutral acid $H_3L$ at $pH < 3.0$. The D2EHPA-extractable Cu ions are the second most abundant species in the citrate system. Such different pH trends of species distribution are probably due to the different acidities of the complexing agents ($pK_a$ values) and the complexing abilities of the agents with metals ($K_f$ values). This information would be useful to explain the pH effect of added complexing agents on the extractability of Cu(II) with D2EHPA.

## Extraction Efficiency of Cu(II) with D2EHPA

In the absence of complexing agents, the extraction, $K_{ex,n}$, of divalent metal cations ($M^{2+}$) such as Cu(II) and Zn(II) from aqueous solutions with D2EHPA (HR) in kerosene can be expressed as follows (14,15):

$$M^{2+} + \left[\frac{(2+n)}{2}\right] \overline{(HR)_2} \Leftrightarrow \overline{MR_2\,(HR)_n} + 2H^+, \qquad K_{ex,n} \qquad (5)$$

where $n$ represents the number of free D2EHPA involved in the complexes, which depends on the types of metal ions (14,15). The symbol $(HR)_2$ indicates that the D2EHPA in low-polarity kerosene mainly exists as dimers due to its strong intermolecular hydrogen-bonding capabilities (16–18). The dimerization constant, $K_d$, at 298 K was reported to be $3.02 \times 10^4$ dm$^3$/mol (17) and can be expressed as follows:

$$2\overline{HR} \Leftrightarrow \overline{(HR)_2}, \qquad K_d \qquad (6)$$

That is, more than 98% of D2EHPA exist as dimers under the ranges studied. Regardless of complexing agents added, Eq. (5) suggests that the extraction of Cu(II) with D2EHPA is dependent on pH.

Figures 3–5 show the extraction efficiencies of Cu(II) in the presence of complexing agents at different β and D2EHPA concentrations. The initial pH was set at 4.1 before the addition of complexing agents.

Figures 6–8 compare the extraction efficiencies at different β and D2EHPA concentrations at an initial pH of 1.8. The extraction efficiency $E$ increased with increased D2EHPA concentration. For a given D2EHPA concentration, $E$ decreased with increasing β, except when citric acid was added at $pH_0 = 4.1$ (Fig.

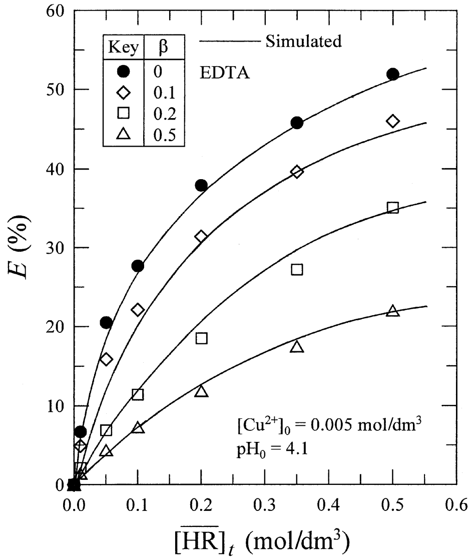

*Figure 3.* Effect of D2EHPA concentration on extraction efficiency of Cu(II) at different EDTA concentrations ($pH_0 = 4.1$).

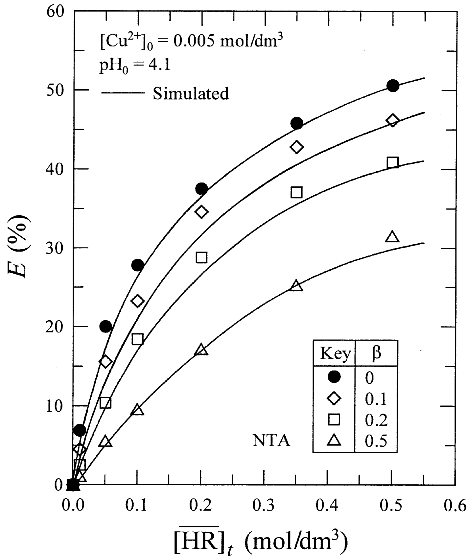

*Figure 4.* Effect of D2EHPA concentration on extraction efficiency of Cu(II) at different NTA concentrations ($pH_0 = 4.1$).

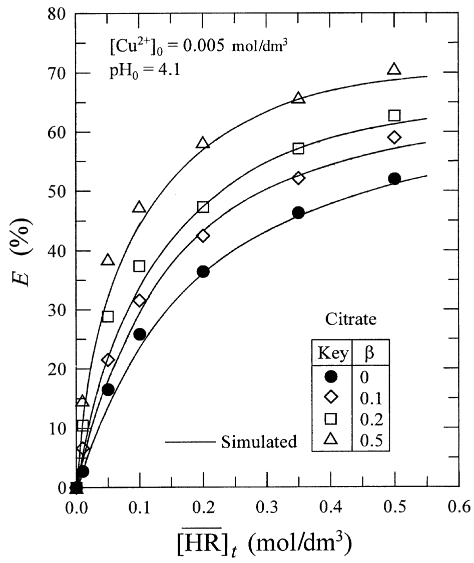

***Figure 5.*** Effect of D2EHPA concentration on extraction efficiency of Cu(II) at different citrate concentrations ($pH_0 = 4.1$).

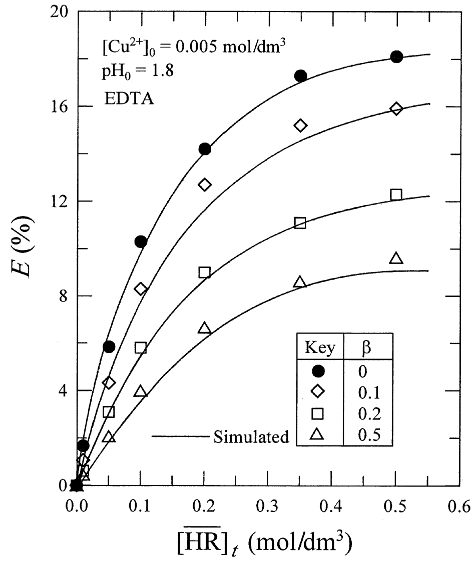

***Figure 6.*** Effect of D2EHPA concentration on extraction efficiency of Cu(II) at different EDTA concentrations ($pH_0 = 1.8$).

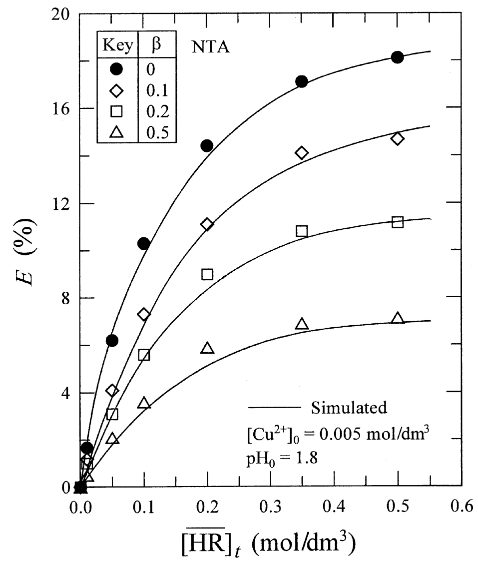

***Figure 7.*** Effect of D2EHPA concentration on extraction efficiency of Cu(II) at different NTA concentrations ($pH_0 = 1.8$).

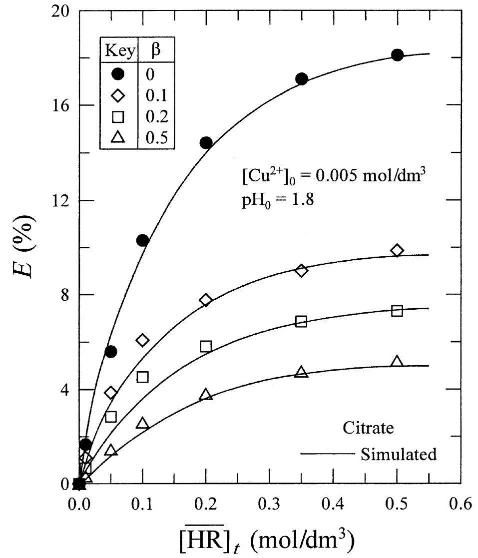

***Figure 8.*** Effect of D2EHPA concentration on extraction efficiency of Cu(II) at different citrate concentrations ($pH_0 = 1.8$).

5). The different effect of citrate at $pH_0$ 4.1 from that of EDTA and NTA may be related to the different pH trends of species distribution (Figs. 1 and 2). In the aqueous Cu(II)-citrate solutions, the dominant species was $H_2L^-$ or the neutral $H_3L$, rather than $Cu^{2+}$, because the equilibrium pH of the Cu(II)-citrate solution was between 2.73 and 3.34 when the initial pH was 4.1 (Table 2). Detailed explanation cannot be given at this stage because the environments of aqueous and organic solutions are very complicated; e.g., mutual repulsion between D2EHPA and the complexing agents occur as do competitive interactions of D2EHPA and the complexing agents with metals. However, quantitative discussion on the reaction stoichiometry of Cu(II) and D2EHPA in the following section provides insight into this subject.

## Reaction Stoichiometry of Cu(II) Extraction

In the absence of strong complexing agents ($\beta = 0$), no additional aqueous- or organic-phase complexation reactions occur; therefore, slope analysis technique can be easily used to determine the extraction stoichiometry (9). When the aqueous complexes between Cu(II), sulfate, and hydroxide are ignored, Eq. (7) can be obtained from Eq. (5):

$$\log(D[H^+]^2) = \log K_{ex,n} + \frac{(2+n)}{2}\log[\overline{(HR)_2}] \tag{7}$$

The value of $n$ is derived from the slope of log-log plot (Fig. 9) and equals approximately 2. The extraction equilibrium constant, $K_{ex,2}$, was calculated to be

*Table 2.* The Equilibrium Aqueous pH of Cu(II) Extraction by D2EHPA With and Without Complexing Agents ($[Cu^{2+}]_0 = 0.005$ mol/dm$^3$)

| $pH_0$ | $[HR]_0$ (mol/dm$^3$) | $\beta = 0$ | EDTA | | NTA | | Citrate | |
|---|---|---|---|---|---|---|---|---|
| | | | $\beta = 0.1$ | $\beta = 0.5$ | $\beta = 0.1$ | $\beta = 0.5$ | $\beta = 0.1$ | $\beta = 0.5$ |
| 4.1 | 0.01 | 3.93 | 3.24 | 2.96 | 3.59 | 2.99 | 3.71 | 3.34 |
| | 0.05 | 3.74 | 3.22 | 2.93 | 3.30 | 2.95 | 3.38 | 3.27 |
| | 0.1 | 3.07 | 3.18 | 2.91 | 3.25 | 2.91 | 3.30 | 3.13 |
| | 0.2 | 2.82 | 2.96 | 2.85 | 2.99 | 2.86 | 3.01 | 2.96 |
| | 0.35 | 2.79 | 2.84 | 2.79 | 2.87 | 2.81 | 2.90 | 2.87 |
| | 0.5 | 2.76 | 2.73 | 2.70 | 2.75 | 2.71 | 2.76 | 2.73 |
| 1.8 | 0.01 | 1.73 | 1.75 | 1.78 | 1.75 | 1.78 | 1.77 | 1.78 |
| | 0.05 | 1.72 | 1.73 | 1.77 | 1.74 | 1.78 | 1.76 | 1.78 |
| | 0.1 | 1.71 | 1.73 | 1.76 | 1.74 | 1.77 | 1.76 | 1.78 |
| | 0.2 | 1.70 | 1.73 | 1.76 | 1.74 | 1.77 | 1.76 | 1.78 |
| | 0.35 | 1.69 | 1.73 | 1.76 | 1.74 | 1.77 | 1.76 | 1.78 |
| | 0.5 | 1.68 | 1.73 | 1.75 | 1.74 | 1.77 | 1.76 | 1.78 |

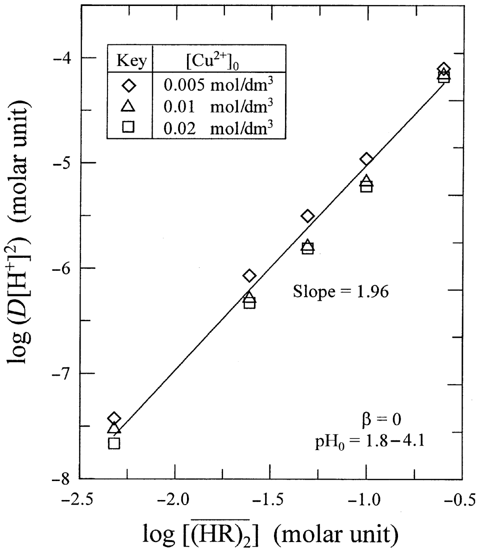

***Figure 9.*** Determination of extraction stoichiometry of Cu(II) with D2EHPA and no complexing agents.

$7.5 \times 10^{-4}$ at 298 K, which reasonably agrees with the previous results observed in different aqueous media (15).

However, the presence of acidic complexing agents may change the reaction stoichiometry of Cu(II) and D2EHPA due to the mutual interactions among metals, D2EHPA, the metal-D2EHPA complex, and the complexing agents, as well as due to the coextraction of complexing agents into the organic phase. In the coextraction of complexing agents in the organic phase, the common slope analysis technique cannot be applied (9), and a numerical method must be used. Because of the abnormal extraction behavior of Cu(II) in the presence of citrate at pH 4.1 (Fig. 5), we expected the equilibrium model to be complicated. Hence, we first analyzed the extraction data in the cases of NTA and EDTA.

Taking the presence of EDTA as an example, the reactions considered with regard to these 2-phase extraction systems of Cu(II) are listed in Table 3. The acid dissociation constant of D2EHPA monomer, $K_a$, was calculated from data taken in a system of kerosene and 0.5 mol/dm$^3$ (Na,H)SO$_4$ (14). Furthermore, the following mass-balance equations are involved:

$$[\mathrm{Cu}^{2+}]_t = \left[\frac{(\mathrm{Cu}^{2+})_0}{(1+D)}\right] = [\mathrm{Cu}^{2+}] + [\mathrm{CuSO_4}] + [\mathrm{CuOH}] + [\mathrm{Cu(OH)_2}] + [\mathrm{CuL}^{2-}] + [\mathrm{CuHL}^{-}] + [\mathrm{Cu(OH)L}^{3-}] \quad (8)$$

***Table 3.*** Reactions Involved in the Extraction of Cu(II) from Sulfate Solutions Containing EDTA with D2EHPA

| Reaction | Equilibrium Constant | Source |
|---|---|---|
| $H^+ + SO_4^{2-} \Leftrightarrow HSO_4^-$ | $K^0 = 9.78 \times 10^1$ dm$^3$/mol | (11) |
| $Na^+ + SO_4^{2-} \Leftrightarrow NaSO_4^-$ | $K^0 = 1.15 \times 10^1$ dm$^3$/mol | (11) |
| $Cu^{2+} + SO_4^{2-} \Leftrightarrow CuSO_4$ | $K^0 = 2.51 \times 10^2$ dm$^3$/mol | (11) |
| $Cu^{2+} + OH^- \Leftrightarrow CuOH$ | $K^0 = 2.00 \times 10^6$ dm$^3$/mol | (11) |
| $Cu^{2+} + 2OH^- \Leftrightarrow Cu(OH)_2$ | $K^0 = 6.31 \times 10^{11}$ dm$^6$/mol$^2$ | (11) |
| $H^+ + L^{4-} \Leftrightarrow HL^{3-}$ | $K^0 = 1.32 \times 10^{11}$ dm$^3$/mol | (11) |
| $2H^+ + L^{4-} \Leftrightarrow H_2L^{2-}$ | $K^0 = 6.31 \times 10^{17}$ dm$^6$/mol$^2$ | (11) |
| $3H^+ + L^{4-} \Leftrightarrow H_3L^-$ | $K^0 = 1.10 \times 10^{21}$ dm$^9$/mol$^3$ | (11) |
| $4H^+ + L^{4-} \Leftrightarrow H_4L$ | $K^0 = 5.75 \times 10^{23}$ dm$^{12}$/mol$^4$ | (11) |
| $5H^+ + L^{4-} \Leftrightarrow H_5L^+$ | $K^0 = 5.75 \times 10^{24}$ dm$^{15}$/mol$^5$ | (11) |
| $Na^+ + L^{4-} \Leftrightarrow NaL^{3-}$ | $K^0 = 3.16 \times 10^2$ dm$^3$/mol | (11) |
| $Cu^{2+} + L^{4-} \Leftrightarrow CuL^{2-}$ | $K^0 = 3.16 \times 10^{20}$ dm$^3$/mol | (11) |
| $Cu^{2+} + H^+ + L^{4-} \Leftrightarrow CuHL^-$ | $K^0 = 7.94 \times 10^{23}$ dm$^6$/mol$^2$ | (11) |
| $Cu^{2+} + OH^- + L^{4-} \Leftrightarrow Cu(OH)L^{3-}$ | $K^0 = 3.98 \times 10^{22}$ dm$^6$/mol$^2$ | (11) |
| $\overline{HR} \Leftrightarrow H^+ + R^-$ | $K_a = 5.37 \times 10^{-2}$ mol/dm$^3$ | (14) |
| $2\overline{HR} \Leftrightarrow \overline{(HR)_2}$ | $K_d = 3.02 \times 10^4$ dm$^3$/mol | (17) |
| $Cu^{2+} + \left[\frac{(2+n)}{2}\right]\overline{(HR)_2} \Leftrightarrow \overline{CuR_2\,(HR)_n} + 2H^+$ | $K_{ex,n}$ | This work |

$$[Na^+]_t = [Na^+] + [NaSO_4^-] + [NaL^{3-}] \tag{9}$$

$$[SO_4^{2-}]_t = [SO_4^{2-}] + [HSO_4^-] + [NaSO_4^-] + [CuSO_4] \tag{10}$$

$$\begin{aligned}[L^{4-}]_t = [L^{4-}] + \sum_{y=1}^{5} [H_yL^{y-4}] + [NaL^{3-}] \\ + [CuL^{2-}] + [CuHL^-] + [Cu(OH)L^{3-}]\end{aligned} \tag{11}$$

$$\begin{aligned}[\overline{HR}]_t &= [\overline{HR}] + 2[\overline{(HR)_2}] = [\overline{HR}] + 2K_d\,[\overline{HR}]^2 \\ &= [\overline{HR}]_0 - (2+n)[\overline{CuR_2\,(HR)_n}] - [R^-] \\ &= [\overline{HR}]_0 - (2+n)\,K_dK_{ex,n}\,[Cu^{2+}][\overline{HR}]^{2+n}\,[H^+]^{-2} - K_a[\overline{HR}][H^+]^{-1}\end{aligned} \tag{12}$$

Equations 8–12 can be numerically solved for the 5 unknowns ($[Cu^{2+}]$, $[Na^+]$, $[SO_4^{2-}]$, $[L^{4-}]$, and [HR] through Mathematica 3.0. The initial Cu(II) and D2EHPA concentrations, the measured equilibrium pH (Table 2), and the distribution ratio $D$, if the values of $n$ ranging from 0 to 4, must be known for effective mass-balance calculations. The Mathematica program also provides the standard deviation of each calculation.

Irrespective of EDTA or NTA addition, or initial concentrations of D2EHPA (0.01–0.5 mol/dm$^3$) and Cu(II) (0.005–0.02 mol/dm$^3$), the optimal $n$ value is 1 at $pH_0 = 4.1$ but becomes 0 at $pH_0 = 1.8$ due to the magnitude of standard deviation. The corresponding $K_{ex,1}$ was $5.27 \times 10^{-4} \pm 5.26 \times 10^{-5}$ (mol/dm$^3$)$^{1/2}$ and $K_{ex,0}$ was $3.44 \times 10^{-4} \pm 4.13 \times 10^{-5}$ mol/dm$^3$ at 298 K. A correlation between $K_{ex,n}$ and ionic strength effect was also done. The activity coefficient of species in the organic phase was assumed to be kept constant because the variation in organic-phase composition was small; i.e., the amount of extraction was far less than the total D2EHPA concentration ($<$ 5 mol %). The stoichiometry of $n = 2$ is also justified at $\beta = 0$, but the value of $K_{ex,2}$ was $1.4 \times 10^{-3}$. Based on the best-fit $K_{ex,n}$ and Eqs. (8–12), the simulated and measured results of $E$ for EDTA and NTA are compared in Figs. 3, 4, 6, and 7.

The stoichiometry changed with the existence of strong complexing agents. The lower the pH, the fewer numbers of free D2EHPA molecules were involved in the complexes. This may be due to the mutual interaction of Cu-D2EHPA complexes and acidic complexing agents. To our best knowledge, no similar results have been reported. However, previous work (19) showed that the complex formulation is $CuR_2(HR)$ in the extraction of Cu(II) from sulfate solutions using D2EHPA-impregnated macroporous resins, such as Amberlite XAD-2. This result differs from the composition of $CuR_2(HR)_2$ reported to be found in common liquid-liquid extraction systems (15).

Another possibility is that the Cu(II)-unreacted citrate anions are coextracted into the organic phase because citric acid is a weaker acidic complexing agent than EDTA or NTA (20). Juang and Lo (20) studied the effect of acetate ($OAc^-$) on Co(II) extraction from sulfate media with D2EHPA. The composition of the complex was $CoR_2(HR)_2$ at low loads of D2EHPA (i.e., $[Co]/[HR] < 0.06$) in the absence of acetate ions. However, the primary composition became $Co_2(OAc)_pR_{4-p}(HR)_q$ in the presence of acetate (0.1–1.0 mol/dm$^3$) at a relatively high loading of D2EHPA (0.1–0.34 mol/dm$^3$), where $p = 0$–4 and $q = 2$–4.

In this work, the equilibrium pH for complexing agents was between 2.70 and 3.71 at $pH_0 = 4.1$ (Table 2), in which the dominant citrate species were $H_3L$ and $H_2L^-$ (Fig. 2). An increase in extraction efficiency through the addition of citric acid at $pH_0 = 4.1$ (Fig. 5) can result from the extra formation of the complexes with general stoichiometry $Cu_x(H_2L)_yR_{2x-y}(HR)_z$ and a formation constant $K_{xyz}$. Because low amounts of D2EHPA (in most cases $<$ 0.1 mol/dm$^3$) was usually used, a composition of $Cu(H_2L)R(HR)_2$ was described for simplicity. That is, the following equation describes the reaction for constant $K_{111}$, which reflects Cu(II) extraction with a complexing agent:

$$Cu^{2+} + H_2L^- + \left(\tfrac{3}{2}\right)\overline{(HR)_2} \Leftrightarrow \overline{Cu(H_2L)R(HR)_2} + H^+ \tag{13}$$

The existence of $K_{111}$ means that the mass-balance equation Eq. (12) must be modified as

$$\begin{aligned}[\overline{\mathrm{HR}}]_t &= [\overline{\mathrm{HR}}]_0 - (2+n)[\overline{\mathrm{CuR_2\,(HR)}_n}] - 3[\overline{\mathrm{Cu(H_2L)R(HR)_2}}] - [\mathrm{R^-}]\\ &= [\overline{\mathrm{HR}}]_0 - (2+n)K_dK_{ex,n}\,[\mathrm{Cu^{2+}}][\overline{\mathrm{HR}}]^{2+n}\,[\mathrm{H^+}]^{-2}\\ &\qquad - 3K_dK_{111}\,[\mathrm{Cu^{2+}}][\mathrm{H_2L^-}][\overline{\mathrm{HR}}]^3[\mathrm{H^+}]^{-1} - K_a[\overline{\mathrm{HR}}][\mathrm{H^+}]^{-1}\end{aligned} \tag{14}$$

The calculation results show that the optimal $n = 1$ in the composition $CuR_2(HR)_n$. However, the standard deviation was reduced to 4% when the complex formation was described as $Cu(H_2L)R(HR)_2$. This justifies the coextraction of citrate to the organic phase. The value of $K_{111}$ at 298 K = $6.38 \times 10^3$ $(dm^3/mol)^{3/2}$.

The extraction efficiency decreased when citric acid was added at $pH_0 = 1.8$ (Fig. 8) because the only dominant citrate species was $H_3L$ (the equilibrium pH, 1.78). In this case, the analysis results were the same as those of EDTA and NTA. That is, the optimal $n$ value was 0 and the corresponding $K_{ex,0}$ was $3.32 \times 10^{-4}$ mol/dm$^3$ at 298 K.

## CONCLUSIONS

The extractability of Cu(II) from sulfate solutions containing complexing agents ($H_xL$) such as EDTA, NTA, and citric acid with D2EHPA in kerosene was studied at 298 K. In the presence of EDTA and NTA, $CuL^{2-x}$ dominated at pH > 3, and $Cu^{2+}$ was most prevalent at pH < 3. In the case of citric acid, the dominant species was $CuL^-$ at pH 3.7–4.7, $H_2L^-$ at pH 3.2–3.7, and the neutral acid $H_3L$ at pH < 3. At any D2EHPA concentration, the extraction efficiency decreased when $\beta$ was increased except when citrate was added at pH 4.1. Considering all possible reactions involved in these 2-phase systems, the complex composition was determined as $CuR_2(HR)$ at an initial pH of 4.1 and $CuR_2$ at pH 1.8 regardless of EDTA and NTA presence, or initial concentrations of D2EHPA (0.01–0.5 mol/dm$^3$) and Cu(II) (0.005–0.02 mol/dm$^3$). The corresponding equilibrium constant $K_{ex,1}$ was $5.27 \times 10^{-4}$ $(mol/dm^3)^{1/2}$, and $K_{ex,0}$ was $3.44 \times 10^{-4}$ mol/dm$^3$. The change of reaction stoichiometry after the addition of complexing agent is likely due to mutual interactions of the Cu-D2EHPA complex and the acidic complexing agents. The abnormal, opposite effect of citrate at pH 4.1, when compared to the cases of EDTA and NTA, may be explained by the coextraction of citrate to the organic phase. The formation of the complexes with general stoichiometry $Cu_x(H_2L)_yR_{2x\text{-}y}(HR)_z$, such as $Cu(H_2L)R(HR)_2$ is confirmed in the present system, which has a relatively low loading of D2EHPA (< 0.1 mol/dm$^3$).

## NOMENCLATURE

| | |
|---|---|
| $D$ | distribution ratio of Cu(II) |
| $E$ | extraction efficiency of Cu(II) (%) |
| $H_xL$ | complexing agent (EDTA, $x = 4$; NTA, $x = 3$; citric acid, $x = 3$) |
| HR | D2EHPA monomer |
| $I$ | ionic strength (mol/kg) |
| $K_a$ | acid dissociation constant of D2EHPA monomer (mol/dm$^3$) |
| $K_d$ | dimerization constant of D2EHPA (dm$^3$/mol) |
| $K_f$ | overall formation constant of aqueous complexes (mol/dm$^3$) |
| $K_{ex,n}$ | extraction equilibrium constant |
| $z_i$ | valence of ion $I$ |

### Greek Letters

| | |
|---|---|
| $\beta$ | initial concentration ratio of complexing agent to Cu(II) in the aqueous phase |
| $\gamma_i$ | activity coefficient of ion $I$ |

### Superscript

| | |
|---|---|
| 0 | zero ionic strength |

### Subscripts

| | |
|---|---|
| $t$ | total amount at equilibrium |
| 0 | initial amount |

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