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Amine-Based Extraction Recovery of Cu(II) from Aqueous Solutions in the Presence of EDTA. Equilibrium Studies

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ABSTRACT

The distribution ratios of Cu(II) between kerosene solutions of Aliquat 336 and water containing EDTA (ethylenediaminetetraacetic acid) are measured. Experiments were performed as a function of the pH, the concentration of Cu(II), the concentration ratio of EDTA to Cu(II), and the concentration of amine. It is shown that the distribution ratios first increase with pH and then decrease with a further increase in pH up to 7.0. The effect of temperature on the extraction was studied, and the enthalpy of the extraction reaction was determined. Finally, the nonideal behavior of the organic phase is discussed.

Key Words. Extraction equilibrium; Distribution ratio; Cu(II); Tri-*n*-octylamine; Aliquat 336, EDTA

INTRODUCTION

Solutions containing metals and complexing agents are mainly discharged from manufacturing processes of electrodeless copper plating for printed circuit boards and metal finishing industries (1, 2), as well as from washing effluents of metal-contaminated soils (3, 4). Chemical precipitation methods (e.g., hydroxide, sulfide) are the most economical for the treatment of metal-bearing solutions. However, the presence of strong complexing agents such as EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), citrate,

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and tartarate may make the precipitation processes ineffective for this purpose, even coupled with high levels of metals (5). Also, the high buffer capacity provided by complexing agents requires excessive amounts of chemicals to neutralize alkalinity. These problems and restrictions warrant studies on other recovery alternatives.

In general, the treatment methods depend greatly on the particular complexing agents and metals involved as well as their concentrations. In the case of dilute solutions, ion exchange and reverse osmosis have high operation and maintenance costs and are subject to fouling. The performance of activated carbon adsorption is unsatisfactory for this subject, although it is widely used for the treatment of organic and inorganic contaminants (2).

Solvent extraction processes are promising for the recovery and separation of negatively charged species from aqueous solutions (6). Work conducted in our laboratory has evaluated the possibility of extraction recovery of Cu(II) from dilute solutions containing strong complexing agents such as EDTA. Equilibrium results with Aliquat 336 in kerosene are presented in this paper. Experiments were performed as a function of pH, the aqueous-phase concentration of Cu(II), the concentration ratio of EDTA to Cu(II), and the organic-phase concentration of Aliquat 336. The influence of temperature on extraction was also studied, and the enthalpy change due to the extraction reaction was evaluated.

EXPERIMENTAL

Reagents and Solutions

Aliquat 336 (tri-*n*-octylmethylammonium chloride, FW 404.16) was supplied from Aldrich Co. Prior to use it was washed with dilute HCl solutions to remove water-soluble impurities. In some cases a tertiary amine tri-*n*-octylamine (TOA, Merck) was used for comparison. Kerosene from Union Chemical Works Ltd., Taiwan, was washed twice with 20 vol % H_2SO_4 to remove aromatics completely before use. It was finally washed thrice with deionized water (Millipore Milli-Q). EDTA, $CuSO_4$, and other inorganic chemicals were supplied by Merck Co. as analytical reagent grade.

The organic phase was prepared by diluting Aliquat 336 or TOA in kerosene. The initial amine concentration ranged from 0.05 to 0.5 M. The aqueous phase was prepared by dissolving $CuSO_4$ and EDTA in deionized water for which the pH was adjusted by adding a small amount of H_2SO_4 or NaOH. The initial concentration of Cu(II) ranged from 0.79 to 3.14 mM, and the initial pH varied from 3.0 to 9.0. The concentration ratio of EDTA to Cu(II) changed from $\frac{1}{2}$ to 2.

Experimental Procedures

For measuring the distribution ratio of Cu(II), equal volumes (40 cm^3) of the organic and aqueous phases were mixed in glass flasks by a magnetic stir-

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rer for at least 12 hours. Because of the formation of emulsions, the two phases were separated by pressurized membrane filtration (Amicon YM3 regenerated cellulose filter, 0.5 atm) after they had been allowed to settle for 1 hour. The pH was measured using a Horiba pH meter (Model F-23). The concentration of Cu(II) in the aqueous phase was measured with a GBC atomic absorption spectrophotometer (Model 932). The organic-phase concentration of Cu(II) was obtained from a mass balance. The concentration of Cl^- in the aqueous phase was analyzed using an ion chromatograph (Dionex Model 2000) equipped with a conductivity detector. In this work a Dionex IonPac AS4A column (4 × 250 mm) was used, which operated at a flow rate of 2 cm^3/min with an eluant containing 0.75 mM $NaHCO_3$ and 2.2 mM Na_2CO_3. The regenerant was 12.5 mM H_2SO_4 and flowed at 3 cm^3/min. Experiments were performed in the 288–308 K temperature range, and each experiment was duplicated under identical conditions. The distribution ratio of Cu(II), D, was calculated by

$$D = [\overline{\mathrm{Cu}}]_t/[\mathrm{Cu}]_t \qquad (1)$$

where the overbar refers to the organic phase and the subscript "t" represents the total molarity of Cu(II) in all forms.

RESULTS AND DISCUSSION

Complexation Equilibria in Cu–EDTA Solutions

EDTA, a polyprotic acid (H_4L), exists in a number of protonated forms in aqueous solutions. It readily forms stable complexes with most heavy metals in a 1:1 molar ratio. Table 1 lists the related overall formation constants at 298

TABLE 1
The Overall Formation Constant (log K_f) of the Complex between Cations and Ligand (L) at 298 K and Zero Ionic Strength (7)[a]

Cation	L = OH^-		L = SO_4^{2-}		L = $EDTA^{4-}$	
H^+	HL	14.00	HL	1.99	HL	11.12
					H_2L	17.80
					H_3L	21.04
					H_4L	23.76
					H_5L	24.76
Cu^{2+}	CuL	6.3	CuL	2.4	CuL	20.5
	CuL_2	11.8			CuHL	23.9
	CuL_4	16.4			CuOHL	22.6
	Cu_2L_2	17.7				

[a] $K_f = [M_xH_yL_z]/[M]^x[H^+]^y[L]^z$ (in molar unit) for the reaction $xM + yH^+ + zL \Leftrightarrow M_xH_yL_z$

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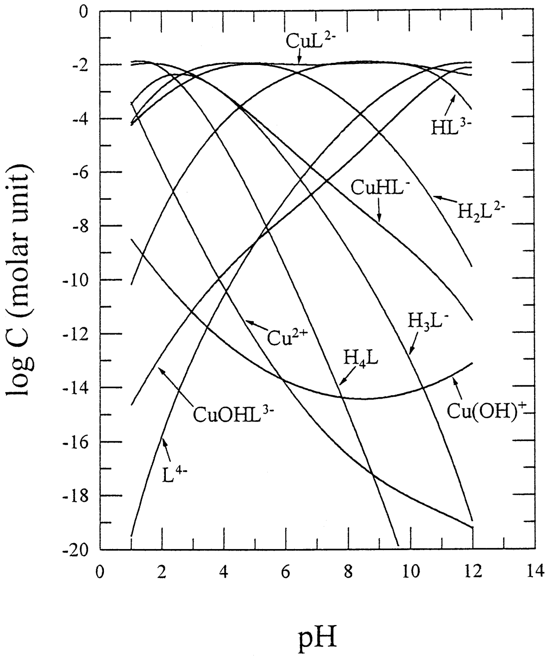

FIG. 1 Distribution of species in an aqueous solution containing Cu(II) and EDTA at 298 K. $[Cu^{2+}]_0 = 10$ mM, $\alpha = 2$.

K and zero ionic strength (7). In principle, the distribution of each species at different pH values can be obtained from mass-balance equations of metals and EDTA. For a diluted equimolar (10 mM) solution of Cu(II) and EDTA, it was shown that the divalent anions CuL^{2-} dominate at pH 3–12 and the univalent anions $CuHL^{-}$ at pH < 3 (8).

Figure 1 illustrates the results for solutions containing an excess of EDTA over Cu(II). The aqueous complexations of Cu(II) with SO_4^{2-} are neglected due to their much small overall formation constants compared to EDTA (Table 1). The pH trends of distribution of CuL^{2-} and $CuHL^{-}$ are similar to those of equimolar solutions. Due to the excess of EDTA, moreover, the anions of HL^{3-} dominate at pH 6.3–10 and of H_2L^{2-} at pH 3.0–6.3. Such results are useful to explain the change of extractability of Cu(II) with pH in the presence of EDTA with amines.

Extraction of Cu(II) with Amines

Effect of Initial Aqueous pH and Amine Concentration

Figures 2 and 3 show the distribution ratios of Cu(II) between Aliquat 336/kerosene and water in the presence of EDTA at different initial pH and

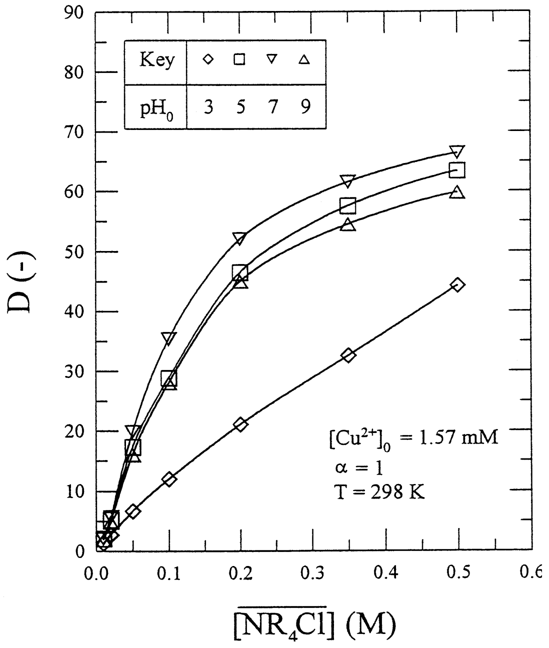

FIG. 2 Extraction of the Cu–EDTA chelated anions with Aliquat 336 at different pH values. $\alpha = 1$.

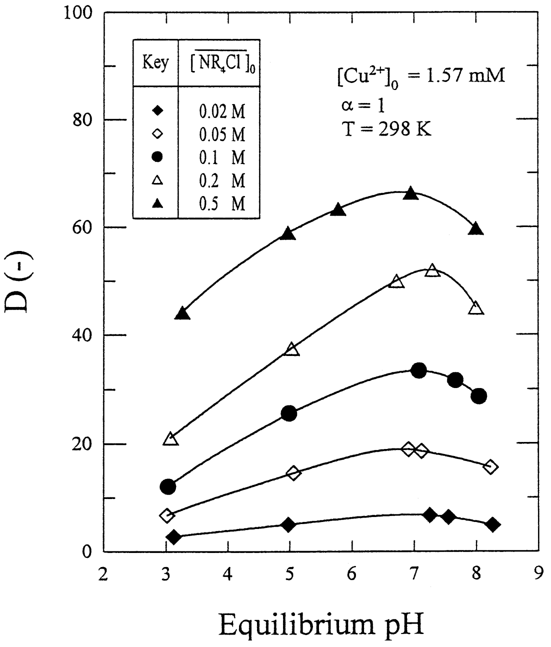

FIG. 3 Extraction of the chelated anions at different Aliquat 336 concentrations. $\alpha = 1$.

amine concentrations. Here, the initial concentration ratio of EDTA to Cu(II), α, equals 1. It is seen that the amount of extraction increases with increasing amine concentration. In addition, for a given amine concentration, D first increases with increasing equilibrium pH but then decreases at pH beyond 7. That is, there is a maximum near an equilibrium pH of 7 (Fig. 3). It should be noted that the initial pH of the data in Fig. 3 ranges from 3 to 9. The changes in aqueous pH after extraction will be discussed in the followin section.

As is widely done for the extraction of anionic species with quaternary amines (9–11), the reaction of the Cu-EDTA chelated anions and Aliquat 336 (NR_4Cl) in kerosene under the pH range studied can be expressed as follows:

$$\text{CuL}^{2-} + \overline{2\text{NR}_4\text{Cl}} \Leftrightarrow \overline{(\text{NR}_4)_2\,\text{CuL}} + 2\text{Cl}^- \tag{2}$$

When the initial pH is greater than 7, it is believed that competitive reactions of OH^- and amine with the chelated anions occur to some extent (12):

$$\text{OH}^- + \overline{\text{NR}_4\text{Cl}} \Leftrightarrow \overline{\text{NR}_4\text{OH}} + \text{Cl}^- \tag{3}$$

In fact, it is experimentally found (Table 2) that when the initial pH is not more than 7, the pH increases after extraction. However, if the initial pH is far beyond 7 (e.g., pH 9) it drops, indicating that the reaction of Eq. (3) becomes

TABLE 2

The Change of Aqueous pH after Equal-Volume Extraction with Aliquat 336 at $[Cu^{2+}]_0 = 1.52$ mM and 298 K

α	pH_0	$[\overline{NR_4Cl}]_0$ (M)	pH_{eq}
1	2.99	0.05	3.33
		0.1	3.32
		0.2	3.31
		0.5	3.27
	4.98	0.05	6.56
		0.1	6.44
		0.2	6.35
		0.5	6.26
	6.97	0.05	8.63
		0.1	8.43
		0.2	7.66
		0.5	7.16
	9.01	0.05	8.64
		0.1	8.24
		0.2	8.18
		0.5	7.28
2	5.03	0.05	6.38
		0.1	6.22
		0.5	6.19
	7.03	0.05	8.07
		0.1	7.42
		0.5	6.50
	9.02	0.1	7.96
		0.5	6.55
1/2	5.02	0.05	4.51
		0.1	3.87
		0.5	3.63
	6.98	0.05	6.80
		0.1	5.13
		0.5	3.87
	8.97	0.1	6.07
		0.5	4.07

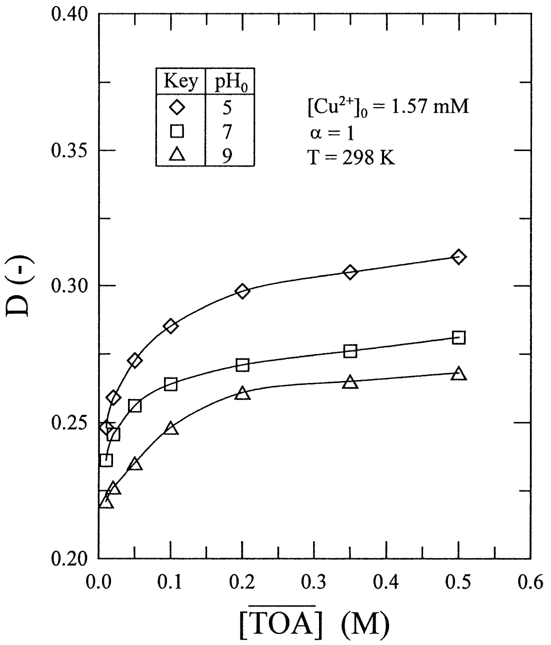

FIG. 4 Extraction of the chelated anions with TOA at different pH values.

significant. This leads to a drop in effective amine concentration for extraction, thus reducing *D*. This finding may show that compared to the hydroxide salts, the chloride salts of quaternary amines are more effective for this purpose, probably due to the more hydrophobic nature of the chloride salts (6). Another possible reason is that increasing extraction of $Cu(OH)L^{3-}$ will tend to suppress Cu(II) extraction because this trivalent ion has a lower phase transferability than does the divalent CuL^{2-}. As shown in Table 2, on the other hand, the equilibrium pH decreases as the amine concentration increases at constant α and initial pH. This also results from the greater extent of Eq. (3) at higher amine concentration.

In the case of TOA (NR'_3), it is seen that at pH > 3 the amount of extraction drops with increasing pH (Fig. 4). This is understood by the mechanism involving protonation and exchange reactions (13–16):

$$2H^+ + SO_4^{2-} + \overline{2NR'_3} \Leftrightarrow \overline{(NR'_3H)_2SO_4} \tag{4}$$

$$CuL^{2-} + \overline{(NR'_3H)_2SO_4} \Leftrightarrow \overline{(NR'_3H)_2\,CuL} + SO_4^{2-} \tag{5}$$

Compared to Aliquat 336 (Fig. 2), the much low extractability with TOA is likely due to relatively small fraction of the protonated TOA and/or partly to the difficulty of exchange between the divalent anions CuL^{2-} and SO_4^{2-} (Eq. 5). Hence, Aliquat 336 was selected for further studies.

Effect of Aqueous-Phase Concentration of Cu(II)

The values of *D* at different Cu(II) concentrations are shown in Fig. 5. Although *D* drops with an increasing concentration of the chelated anions, the amount of extraction still increases smoothly. Figure 6 shows that the distribution ratio decreases with increasing α. Here, increasing α means an increase in EDTA concentration. When $\alpha > 1$, an excess of EDTA exist as H_2L^{2-} or HL^{3-}, depending on the pH (Fig. 1). These negatively charged species partly react with the amine according to Eq. (6), thus reducing the effective amine concentration for extraction.

$$H_xL^{x-4} + (4-x)\overline{NR_4Cl} \Leftrightarrow \overline{(NR_4)_{4-x}(N_xL)} + (4-x)Cl^- \qquad (6)$$

The resulting amine species have a great difficulty in exchanging the divalent CuL^{2-} with the nonunivalent anions H_xL^{x-4} ($x = 1$ or 2).

When $\alpha < 1$, on the other hand, not enough EDTA is present to form extractable 1:1 chelated anions with all Cu(II). This corresponds to the case of low Cu(II) concentration, which gives a higher *D* (Fig. 5). As clearly shown in Table 2, the pH always drops after extraction whether the solution is initially acidic or basic if Cu(II) is in excess of EDTA ($\alpha = 1/2$). This is partly because the extent of Eq. (3) is more apparent compared to those of $\alpha = 2$ and 1. One possible reason leading to the pH drop at pH 5–7 is the formation of the water-soluble hydroxyl complexes $Cu(OH)^+$ and $Cu(OH)_2$ (12).

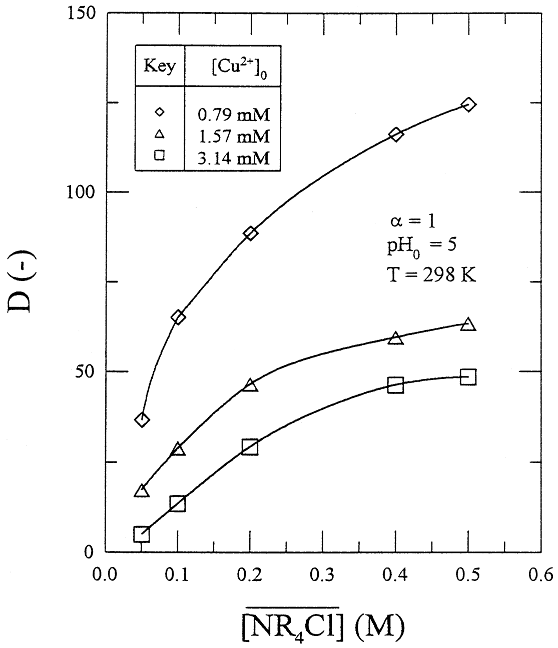

FIG. 5 Extraction of the chelated anions with Aliquat 336 at different Cu(II) concentrations.

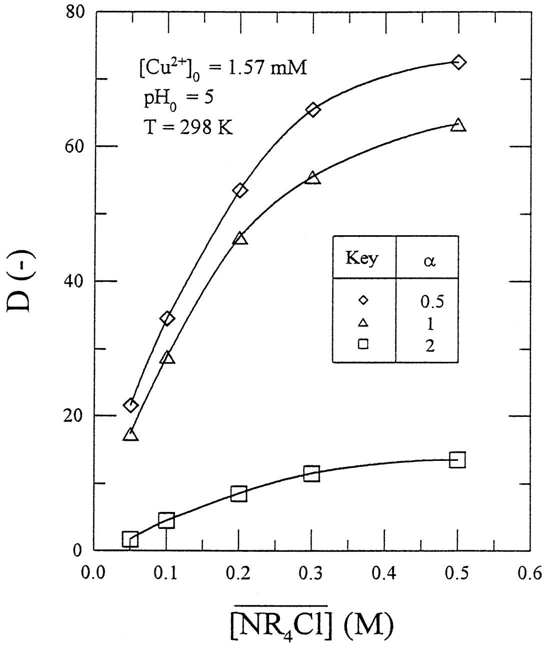

FIG. 6 Extraction of the chelated anions with Aliquat 336 at different concentration ratios of EDTA to Cu(II), α.

Effect of Temperature on the Extraction

It was found that the amount of extraction increases as the temperature is raised (Fig. 7). The apparent enthalpy change for the extraction reaction can be obtained from an Arrhenius plot of the distribution ratio *D* (not shown) according to

$$\frac{d(\ln D)}{d(1/T)} = -\frac{\Delta H}{R} \tag{7}$$

The values of ΔH obtained (Table 3) are in the 5.78–12.2 kJ/mol range, depending on the amine concentration and pH. These are different from those obtained previously. For example, the reaction between the protonated tertiary amine Alamine 304 in xylene and $PtCl_6^{2-}$ has an enthalpy of −1.9 kJ/mol (14).

The positive ΔH obtained can be understood because the present ion-exchange process corresponds to the results of two simple steps: 1) exchange of the molecules of the solvent (water) previously extracted with the amine, and 2) exchange of the chelated anions. Each molecule of the chelated anions has to displace more than one molecule of water. The net result corresponds to an endothermic process (17). As shown in Table 3, the value of ΔH increases with increasing amine concentration at pH 3; however, there is a reverse trend at pH 5 and 7. These discrepancies possibly result from the relative effects of the above two steps.

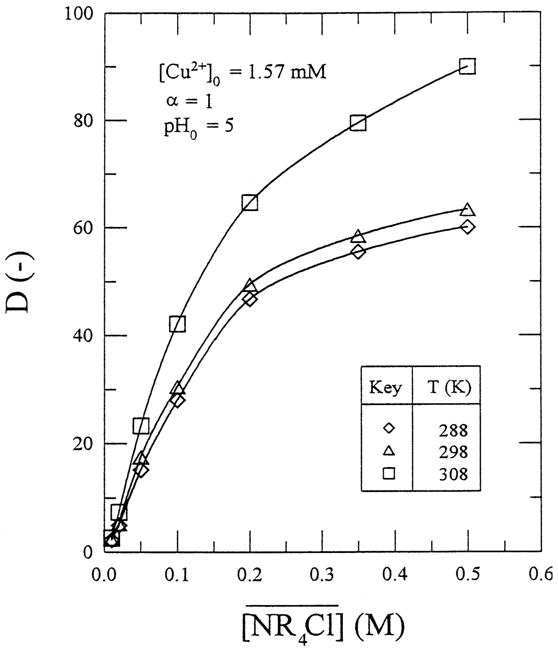

FIG. 7 Effect of temperature on the extraction of the chelated anions with Aliquat 336.

Determination of Extraction Equilibrium Constant

As stated above, univalent $CuHL^-$ is dominant in the aqueous solution at pH $<$ 3 and the side reaction of Eq. (3) is considerable at pH $>$ 7; both make determination of the free amine concentration $[\overline{NR_4Cl}]$ complicated and difficult. Hence, only the data obtained at pH 3–5 and $\alpha = 1$ are considered here. The thermodynamic equilibrium constant of Eq. (2) can be written as

$$K_{ex}^0 = \frac{a_{\overline{(NR_4)_2CuL}}a_{Cl^-}^2}{a_{CuL^{2-}}a_{\overline{NR_4Cl}}^2} = \frac{[\overline{(NR_4)_2CuL}][Cl^-]^2\,\gamma_{\overline{(NR_4)_2CuL}}\gamma_{Cl^-}^2}{[CuL^{2-}][\overline{NR_4Cl}]^2\,\gamma_{CuL^{2-}}\gamma_{\overline{NR_4Cl}}^2} \qquad (8)$$

TABLE 3
Apparent Enthalpy Change ΔH (kJ/mol) for the Extraction of Cu-EDTA Chelated Anions with Aliquat 336 in the Temperature Range 288–308 K ($\alpha = 1$)

$[\overline{NR_4Cl}]_0$ (M)	$pH_{eq} = 3$	$pH_{eq} = 5$	$pH_{eq} = 7$
0.02	5.78	11.8	12.2
0.05	6.41	10.6	11.4
0.1	7.53	10.2	10.1
0.2	8.10	9.25	9.45
0.5	8.91	7.89	7.31

where a_i and γ_i represent the activity and activity coefficient of species i, respectively.

By rearranging Eq. (8), the following equation can be obtained:

$$K_{\mathrm{ex}}^{0} = K_{\mathrm{ex}}\Gamma_1 \tag{9}$$

where K_{ex} is the stoichiometric equilibrium constant based on a concentration scale:

$$K_{\mathrm{ex}} = \frac{[\overline{(\mathrm{NR_4})_2\,\mathrm{CuL}}][\mathrm{Cl^-}]^2}{[\mathrm{CuL^{2-}}][\overline{\mathrm{NR_4Cl}}]^2} = \frac{D[\mathrm{Cl^-}]^2}{[\overline{\mathrm{NR_4Cl}}]^2} \tag{10}$$

and Γ_1 is a term containing all the activity coefficients.

Although the thermodynamic K_{ex}^{0} is a true “constant” that can be definitely compared with other literature results, simplification of the expression make it more suitable to practical use. As a reasonable assumption, Γ_1 is expected to remain constant as long as the variations in aqueous-phase environments and in organic-phase compositions are small (18). This may be the case here because the initial Cu(II) concentration is fixed and low enough (<3.14 mM). Furthermore, the amount of extraction is less than the total amine concentration (<15 mol%).

The term $[\overline{\mathrm{NR_4Cl}}]$ in Eq. (10) is calculated by the following mass balance because the aqueous solubility of Aliquat 336 is negligibly small (19, 20):

$$[\overline{\mathrm{NR_4Cl}}] = [\overline{\mathrm{NR_4Cl}}]_0 - 2[\overline{(\mathrm{NR_4})_2\,\mathrm{CuL}}] \tag{11}$$

It is found that K_{ex} calculated from Eq. (10) mainly depends on amine concentration and decreases with increasing amine concentration. It is located between 0.056 and 1.98 at 298 K at $[\overline{\mathrm{NR_4Cl}}]_0 = 0.05$–$0.5$ M. These values roughly agree with that obtained for extraction of $\mathrm{CrO_4^{2-}}$ from aqueous solutions with Aliquat 336 in kerosene (11).

The fact that K_{ex} depends on amine concentration demonstrates that ideal behavior occurs only in the aqueous phase. The nonideal behavior in the organic phase containing Aliquat 336 has been examined for the extraction of anions using several models (11, 21). The following empirical expression is adopted here because of its simplicity:

$$\left(\frac{\gamma_{\overline{(\mathrm{NR_4})_2\mathrm{CuL}}}}{\gamma^{2}_{\overline{\mathrm{NR_4Cl}}}}\right) = [\overline{\mathrm{NR_4Cl}}]^n \tag{12}$$

Substituting Eq. (12) into Eq. (8), we optimize n to be 1.25 as shown in Fig. 8. This result is acceptable although the number of data points are insufficient and thus lack appropriate statistical parameters. The extraction equilibrium at 298 K can be described as Eq. (13) under the ranges studied ($\alpha = 1$, pH 3–5,

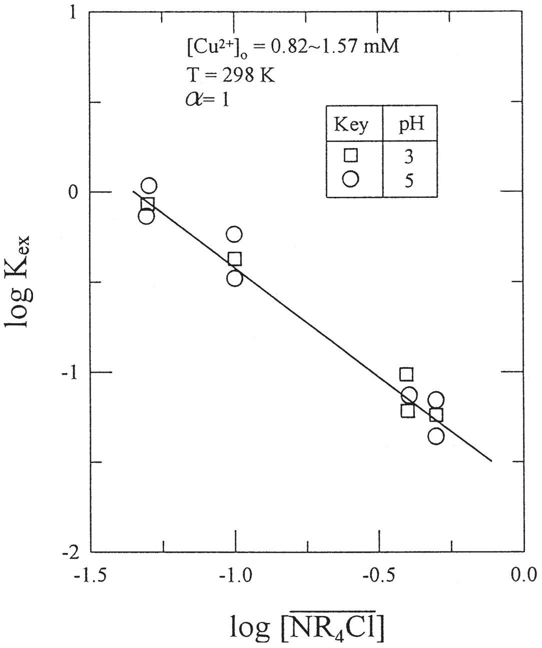

FIG. 8 Correlation between concentration-based constant and extractant concentration.

amine concentration 0.02–0.5 M):

$$0.036 = \left(\frac{[\overline{(NR_4)_2CuL}][Cl^-]^2}{[CuL^{2-}][\overline{NR_4Cl}]^2} \right) [\overline{NR_4Cl}]^{\frac{5}{4}} \qquad (13)$$

The quarter-order nature probably implies that some association reactions of amine or the complex occur in the organic phase. It was actually found that most of the tri-*n*-octyl-methylammomium nitrate in benzene forms a tetramer in the amine concentration range of 0.01 to 1 M (19), possibly due to the formation of O—H bonds within a given compound. Although association of the chloride salts was reported (20), further studies on the subject should be made.

CONCLUSIONS

The extraction equilibrium of Cu(II) from aqueous solutions containing EDTA with amines in kerosene has been studied. Tertiary amines such as TOA are significantly inefficient for this purpose compared to quaternary amines such as Aliquat 336. When the initial pH is far beyond 7.0, it decreases after extraction with Aliquat 336, indicating the occurrence of a reaction between OH^- and the amine (Eq. 3). The apparent enthalpy change of the extraction reaction is found to be 5.78–12.2 kJ/mol from the temperature depen-

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dence of the distribution ratio. The positive ΔH value means that the extraction process corresponds to the net result of two steps: exchange of the molecules of water previously extracted and exchange of the chelated anions. Under the experimental ranges of $\alpha = 1$, pH 3–5, and amine concentration 0.02–0.5 M, the reaction equilibrium can be described by Eq. (13) by considering the nonideal behavior of the organic phase. The relatively high distribution obtained in this work provides the possibility of solvent extraction for the removal or recovery of Cu(II) from such complexed solutions.

NOTATION

a_i	activity of species i
D	distribution ratio of Cu(II) defined in Eq. (1)
EDTA	ethylenediaminetetraacetic acid (H_4L)
ΔH	apparent enthalpy change, kJ/mol
K_{ex}	extraction equilibrium constant defined in Eq. (10)
NR_4Cl	Aliquat 336
R	universal gas constant (J/mol·K)
T	absolute temperature (K)
[ ]	molar concentration of species in the brackets (M)

Greek Letters

α	initial concentration ratio of EDTA to Cu(II) in the aqueous phase
γ_i	activity coefficient of species i

Superscripts

0	thermodynamic scale
$\overline{}$ (overbar)	species in the organic phase

Subscripts

eq	equilibrium
t	total
0	initial

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REFERENCES

1. R. M. Spearot and J. V. Peck, *Environ. Prog.*, *3*, 124 (1984).
2. B. E. Reed, S. Arunachalam, and B. Thomas, *Ibid.*, *13*, 60 (1994).
3. R. Abumaizar and L. I. Khan, *J. Air Waste Manage. Assoc.*, *46*, 765 (1996).
4. S. B. Martin and H. E. Allen, *Chemtech*, *26*(4), 23 (1996).
5. O. Tunay, I. Kabdasli, and R. Tasli, *Water Sci. Technol.*, *29*(9), 265 (1994).
6. T. Sekine and Y. Hasegawa, *Solvent Extraction Chemistry. Fundamentals and Applications* (p. 217), Dekker, New York, NY, 1977.
7. F. M. M. Morel and J. G. Hering, *Principles and Applications of Aquatic Chemistry* (p. 332), Wiley, New York, NY, 1993.
8. R. S. Juang and L. D. Shiau, *Ind. Eng. Chem. Res.*, *37*, 555 (1998).
9. A. I. Alonso, A. M. Urtiaga, A. Irabien, and M. I. Oritz, *Chem. Eng. Sci.*, *49*, 901 (1994).
10. A. I. Alonso and C. C. Pantelides, *J. Membr. Sci.*, *110*, 151 (1996).
11. A. I. Alonso, B. Galan, A. Irabien, and M. I. Oritz, *Sep. Sci. Technol.*, *32*, 1543 (1997).
12. R. S. Juang and M. N. Chen, *Ind. Eng. Chem. Res.*, *35*, 1935 (1996).
13. F. J. Alguacil and C. Caravaca, *Hydrometallurgy*, *34*, 91 (1993).
14. F. J. Alguacil, A. Cobo, A. G. Coedo, M. T. Dorado, and A. M. Sastre, *Ibid.*, *44*, 203 (1997).
15. M. W. Horn, B. G. Fraser, M. D. Pritzker, and R. L. Legge, *Sep. Sci. Technol.*, *29*, 535 (1994).
16. N. A. Yakubu and A. W. L. Dudeney, *Hydrometallurgy*, *18*, 93 (1987).
17. B. K. Singh and N. S. Rawat, *J. Chem. Technol. Biotechnol.*, *61*, 307 (1994).
18. J. L. Cortina, N. Miralles, M. Aguilar, and A. M. Sastre, *Solv. Extr. Ion Exch.*, *12*, 371 (1994).
19. I. Komasawa, K. Hisada, and M. Miyamura, *J. Chem. Eng. Jpn.*, *23*, 308 (1990).
20. Y. Belaustegi, N. Etxebarria, M. A. Olazabal, L. A. Fernandez, and J. M. Madariaga, *J. Solution Chem.*, *25*, 1113 (1996).
21. B. Galan, A. M. Urtiaga, A. I. Alonso, J. A. Irabien, and M. I. Oritz, *Ind. Eng. Chem. Res.*, *33*, 1765 (1994).

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