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Extraction of Copper(II)–NTA Chelated Anions from Water with Aliquat 336

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ABSTRACT

Streams containing metals and complexing agents, which are often encountered in industrial and environmental applications, are not easily treated using conventional chemical precipitation processes. A solvent extraction method is thus proposed in this work. The distribution ratios of Cu(II) between kerosene solutions of Aliquat 336 (tri-*n*-octylmethylammonium chloride) and the water-containing complexing agent NTA (nitrilotriacetic acid) were measured. Experiments were carried out as a function of aqueous pH, the concentration of amine, and temperature. It is shown that the distribution ratios first increased with increasing pH and then decreased with a further increase in pH. The enthalpy of the extraction was determined. Finally, the nonideal behavior of the organic phase is discussed.

Key Words. Extraction; Distribution ratio; Copper(II); Aliquat 336; NTA

INTRODUCTION

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

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

The existing treatment methods depend greatly on the particular complexing agent and metals used as well as their concentrations (1). For dilute solutions, reverse osmosis and ion exchange have high operational and maintenance costs and are subject to fouling. It was also shown that liquid-phase adsorption using activated carbon is not efficient for this subject, although it is widely used for the treatment of organic pollutants (2). Liquid–liquid extraction has been proposed for the recovery and separation of negatively charged species from aqueous solutions (6). In this work the extraction of Cu–NTA chelated anions from water with Aliquat 336 (a quaternary amine) in kerosene was studied. Experiments were performed as a function of two system variables, i.e., aqueous pH and the organic-phase concentration of the amine. The effect of temperature on the extraction was studied and the enthalpy change was evaluated.

EXPERIMENTAL

Reagents and Solutions

Aliquat 336 (tri-*n*-octylmethylammonium chloride, FW 404.16) was purchased from Aldrich Chemical Co. Prior to use it was washed with an equal volume of diluted HCl solutions (0.1 M) to remove water-soluble impurities. In minor cases a tertiary amine tri-*n*-octylamine (TOA, Merck Co.) was used for comparison. Kerosene from Union Chemical Co., Taiwan, was washed twice with 20 vol% H_2SO_4 to remove aromatics and then thrice with deionized water (Millipore Milli-Q). NTA, $CuSO_4$, and other inorganic chemicals were supplied by Merck Co. as analytical reagent grade.

The organic solutions were prepared by diluting Aliquat 336 or TOA in kerosene. The initial concentration of amine varied from 0.1 to 0.5 M. The aqueous phase was prepared by dissolving equimolar amounts of $CuSO_4$ and NTA 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) was fixed at 1.57 mM and the initial pH was varied from 2 to 9.

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 stirrer for 12 hours. Experiments were performed at each fixed temperature (288, 298, and 308 K). Due to the formation of stable emulsions during mixing, the two phases were separated by pressurized membrane filtration (Amicon YM3 regenerated cellulose filters, 0.5 atm) after it had been allowed to settle for 2 hours. The aqueous pH was measured using a Horiba pH meter (Model F-23), and the concentration of Cu(II) was measured with an atomic absorption spectrophotometer (GBC Model 932). The organic-phase concentration of Cu(II) was obtained from a mass balance.

The concentrations of Cl^- in the aqueous phase were analyzed by 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. It 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. The distribution ratio of Cu–NTA chelated anions, D, was calculated by

$$D = [\overline{\mathrm{Cu}}]_t/[\mathrm{Cu}]_t \tag{1}$$

where the overbar refers to the organic phase and the subscript "t" denotes the total molarity of all forms of Cu(II). Each distribution experiment was duplicated under identical conditions.

RESULTS AND DISCUSSION

Complexation Equilibria in the Aqueous Phase

NTA, which is a polyprotic acid, exists in many protonated forms in the aqueous phase. It can readily form stable complexes with most heavy metals in a 1:1 molar ratio (7). The concentration profiles of the species at different pH values can be basically obtained from a set of mass-balance equations of metals and complexing agents considering the related overall formation constants (Table 1).

Figure 1 illustrates the results for a solution containing equimolar amounts (10 mM) of Cu(II) and NTA (H_3L). Here, the possible complexations of

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

Cation	$L = OH^-$		$L = SO_4^{2-}$		$L = NTA^{3-}$	
H1	HL	14.00	HL	1.99	HL	10.33
					H_2L	13.27
					H_3L	14.92
					H_4L	16.02
Cu^{2+}	CuL	6.3	CuL	2.4	CuL	14.2
	CuL_2	11.8			CuL_2	18.1
	CuL_4	16.4			CuOHL	18.6
	Cu_2L_2	17.7				

[a] $K_f = [M_xL_y]/[M]^x\,[L]^y$ (in molar unit) for the complexation reaction $xM + yL \Leftrightarrow M_xL_y$

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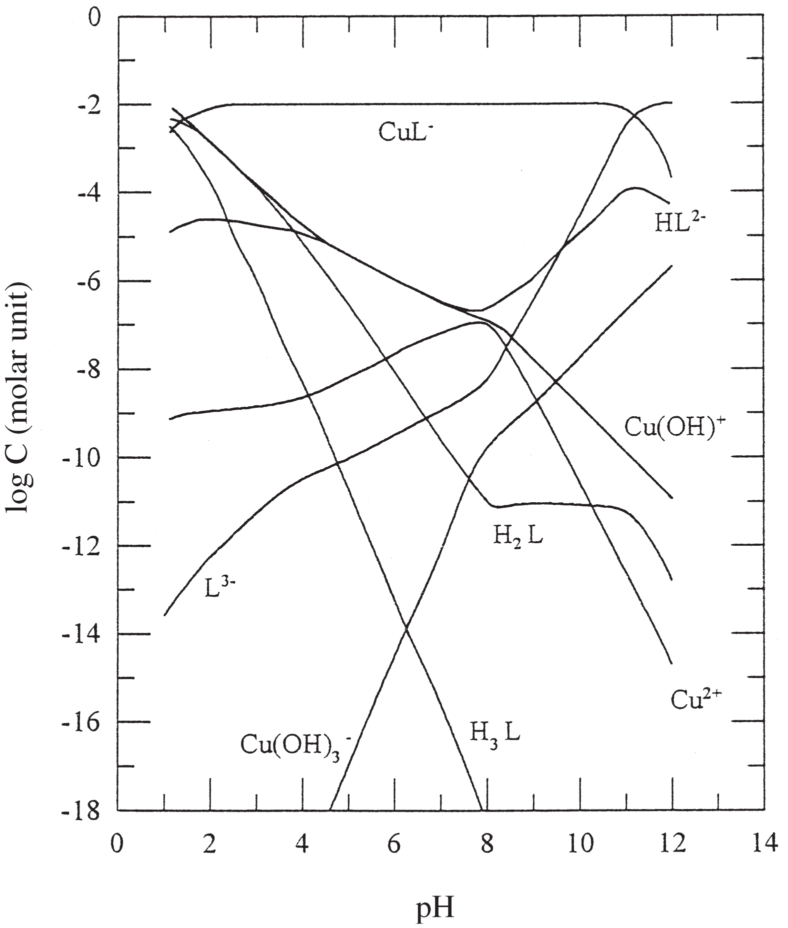

FIG. 1 Concentration profiles of species in aqueous solutions containing equimolar amounts of Cu(II) and NTA (10 mM) at 298 K.

Cu(II) with sulfate anions are neglected due to their small overall formation constants compared to NTA (Table 1). It is clearly shown that the univalent chelated anions CuL^- absolutely predominate at pH 2–11. This information is very useful to explain the pH trends of the distribution of Cu(II) in the presence of NTA with amine.

Extraction of Cu–NTA Chelated Anions with Amines

Effect of Aqueous pH and Amine Concentration

Figures 2–4 show the distribution ratio of Cu(II) between Aliquat 336/kerosene and water containing NTA at different pH values, temperatures, and amine concentrations. It is evident that *D* increases with increasing amine concentration. Also, for a given amine concentration *D* first increases with increasing equilibrium pH, but then starts to decrease at pH $>$ 6. Such phenomena are more apparent at higher amine concentrations and higher temperatures (Figs. 2 and 3). That is, there is a maximum near pH 5. As often done previously for extraction of other anionic species (8–10), reaction between the Cu–NTA chelated anions and Aliquat 336 (NR_4Cl) in kerosene can be represented as

$$CuL^- + \overline{NR_4Cl} \Leftrightarrow \overline{NR_4CuL} + Cl^- \qquad (2)$$

In fact, it was experimentally found that when the initial pH is not more than 7, the pH increases after extraction. However, if the initial pH is greater than 7 (e.g., pH 9) the pH decreases. In the case of equilibrium pH larger than 6, it is believed that the competitive reactions between OH^- and amine with the chelated anions occur to some extent (11):

$$OH^- + \overline{NR_4Cl} \Leftrightarrow \overline{NR_4OH} + Cl^- \qquad (3)$$

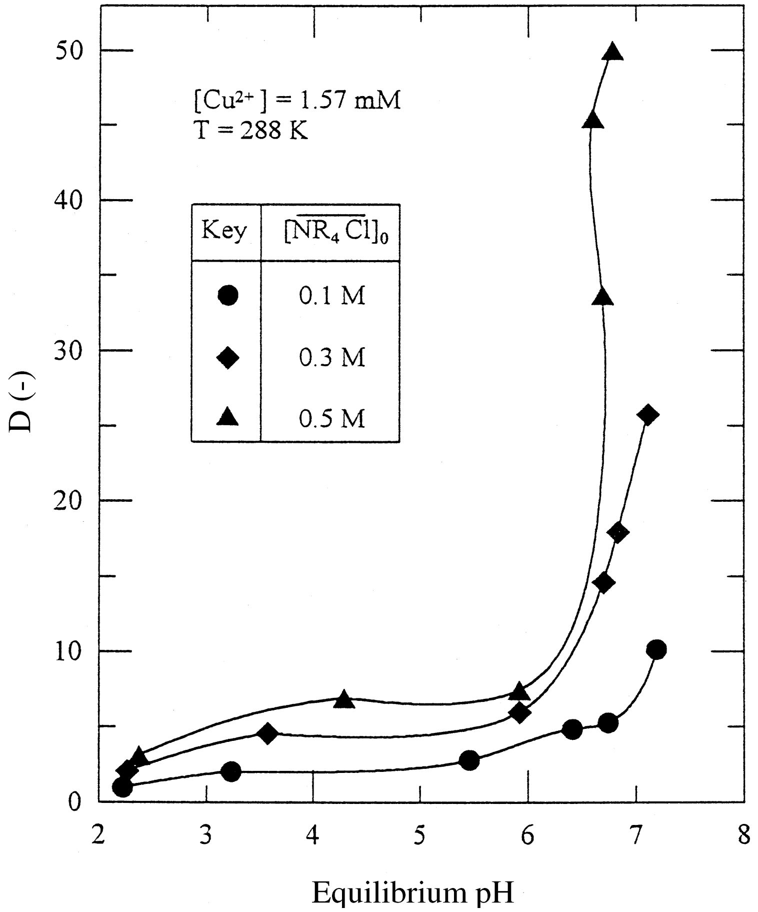

FIG. 2 Effect of Aliquat 336 concentration and pH on the extraction of Cu(II) at 288 K.

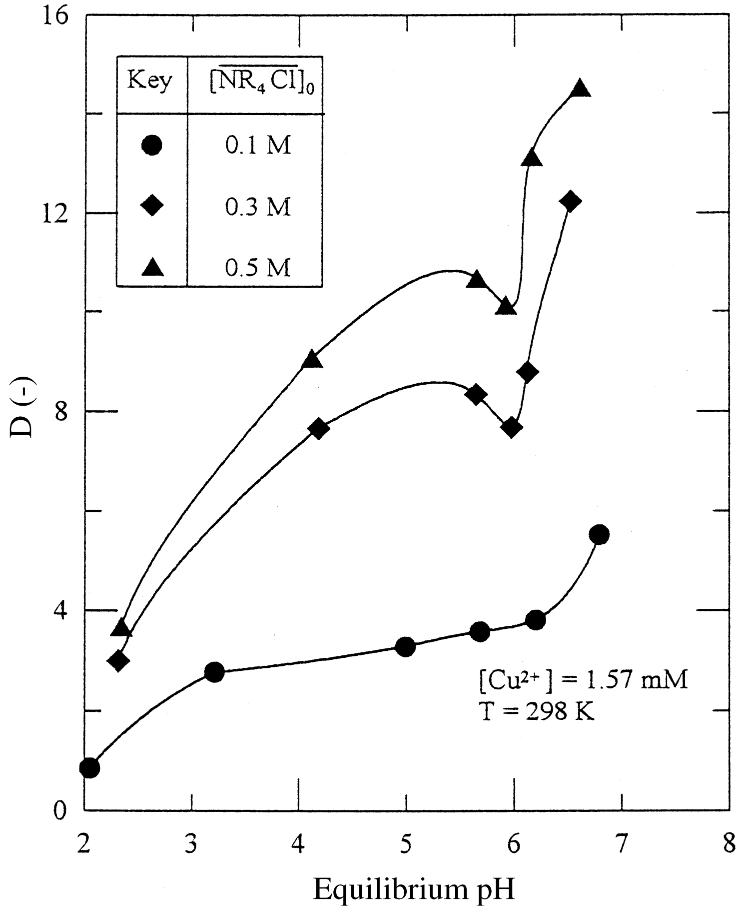

FIG. 3 Effect of Aliquat 336 concentration and pH on the extraction of Cu(II) at 298 K.

This leads to a decrease of Aliquat 336 concentration, thus decreasing the distribution ratio. The data also show that, compared to the hydroxide salts, the chloride salts of quaternary amines is more effective for this purpose, probably due to the more hydrophobic nature of the chloride salts (6).

In contrast to the case of tertiary amine TOA (NX_3), it was found that the distribution decreases with increased pH at pH $>$ 3 (Fig. 5). This can be understood by the mechanism involving protonation and exchange reactions (12–15):

$$2H^+ + SO_4^{2-} + 2\overline{NX_3} \Leftrightarrow \overline{(NX_3H)_2SO_4} \tag{4}$$

$$2CuL^- + \overline{(NX_3H)_2SO_4} \Leftrightarrow 2\overline{(NX_3H)CuL} + SO_4^{2-} \tag{5}$$

Because of the comparatively low extractability of the chelated anions by tertiary amines (probably due to the small fraction of the protonated amines and/or partly to the difficulty of exchange with the divalent anions SO_4^{2-}), Aliquat 336 was selected for further studies.

Effect of Temperature

Figure 6 shows the typical temperature dependence of distribution ratios. It was found that *D* increases at pH < 6.5 when the temperature is raised from 288 to 308 K. However, beyond that pH it has a highest *D* at 288 K, which again indicates that other mechanisms dominate such as the reaction between OH^- and amine (Eq. 3).

Figure 7 gives typical Arrhenius plots of the distribution ratio obtained at pH 3–5. The apparent enthalpy change can be obtained as follows:

$$\frac{d(\ln D)}{d(1/T)} = -\frac{\Delta H}{R} \tag{6}$$

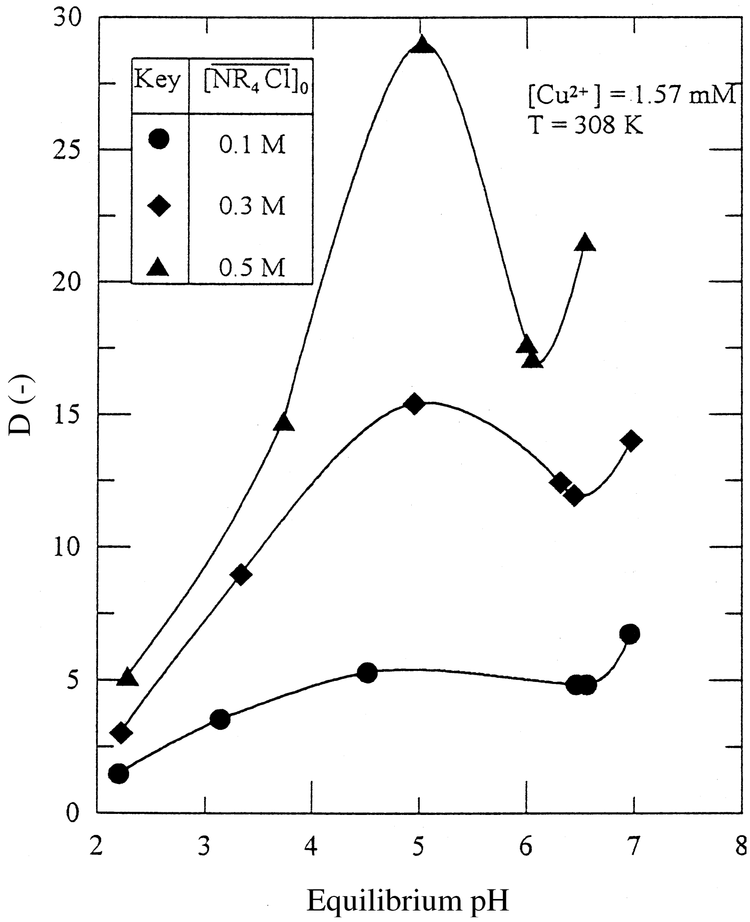

FIG. 4 Effect of Aliquat 336 concentration and pH on the extraction of Cu(II) at 308 K.

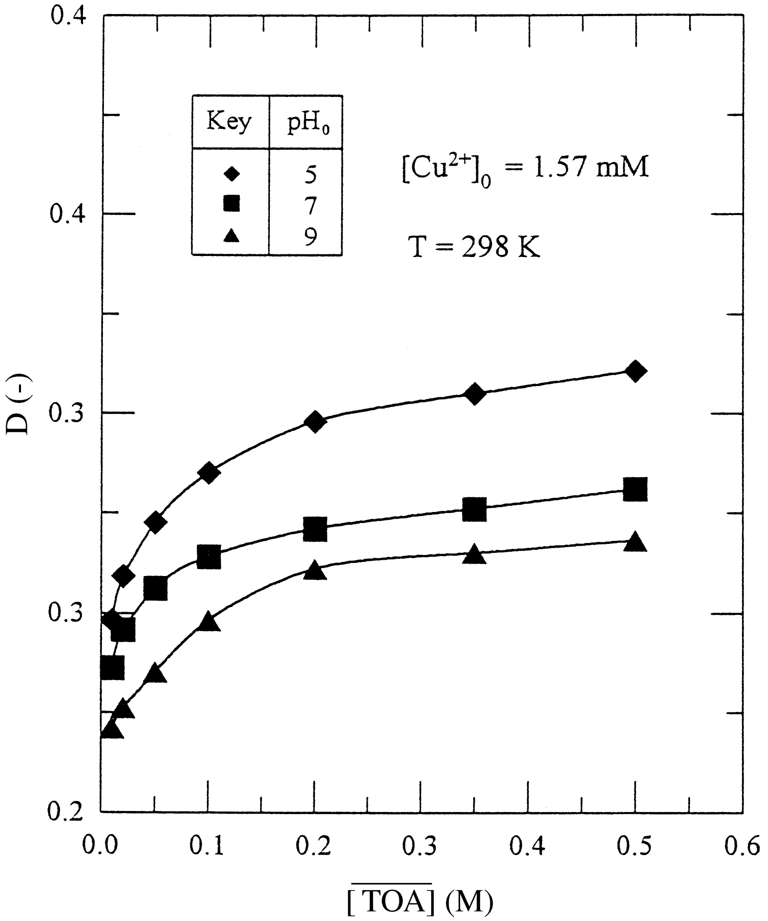

FIG. 5 Effect of TOA concentration and initial pH on the extraction of Cu(II) at 298 K.

The results are listed in Table 2. The values of ΔH obtained are in the 21.7–45.4 kJ/mol range, depending on amine concentration and pH. These are different from those obtained previously. For example, the distribution of $PtCl_6^{2-}$ between the protonated tertiary amine Alamine 304 in xylene and water has an enthalpy of -1.9 kJ/mol (13).

The positive ΔH is understood because the present extraction process corresponds to the results of two simple processes: 1) exchange of the molecules of 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. Thus, the net result corresponds to an endothermic process (16).

Determination of Extraction Equilibrium Constant

As indicated above, the univalent species CuL^- dominates in the aqueous solution at pH 2–11; also, the side reaction between OH^- and the amine be-

TABLE 2
Apparent Enthalpy Change ΔH (kJ/mol) for the Extraction of the Cu–NTA Chelated Anions with Aliquat 336 in Kerosene in the Temperature Range 288–308 K

$[\overline{NR_4Cl}]_0$ (M)	pH 3	pH 4	pH 5
0.1	21.7	23.2	24.9
0.3	26.5	32.6	38.8
0.5	30.2	37.8	45.4

comes relatively important at pH > 6. In order to prevent the difficulty in determination of the free amine concentration $[\overline{\mathrm{NR_4Cl}}]$, only the data obtained at pH 3–5 are considered. The extraction equilibrium constant of Eq. (2) can be written as

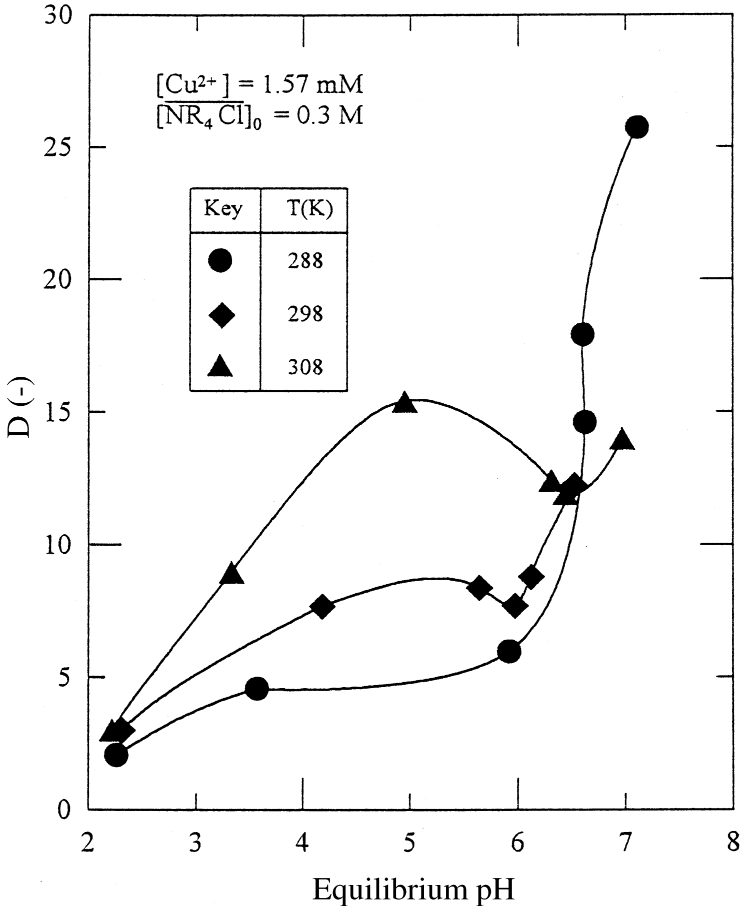

FIG. 6 Effect of temperature and pH on the extraction of Cu(II) at 0.3 M Aliquat 336.

$$K_{\mathrm{ex}}^{0} = \frac{a_{\overline{\mathrm{NR_4CuL}}}\,a_{\mathrm{Cl^-}}}{a_{\mathrm{CuL^-}}\,a_{\overline{\mathrm{NR_4Cl}}}} = \frac{[\overline{\mathrm{NR_4CuL}}]\,[\mathrm{Cl^-}]\,\gamma_{\overline{\mathrm{NR_4CuL}}}\,\gamma_{\mathrm{Cl^-}}}{[\mathrm{CuL^-}][\overline{\mathrm{NR_4Cl}}]\,\gamma_{\mathrm{CuL^{2-}}}\,\gamma_{\overline{\mathrm{NR_4Cl}}}} \qquad (7)$$

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

Rearranging Eq. (7), the following equation can be obtained:

$$K_{\mathrm{ex}}^{0} = K_{\mathrm{ex}}\Gamma_1 \qquad (8)$$

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

$$K_{\mathrm{ex}} = \frac{[\overline{\mathrm{NR_4CuL}}][\mathrm{Cl^-}]}{([\mathrm{CuL^-}][\overline{\mathrm{NR_4Cl}}])} = \frac{D[\mathrm{Cl^-}]}{[\overline{\mathrm{NR_4Cl}}]} \qquad (9)$$

and Γ_1 is the term containing all the activity coefficients.

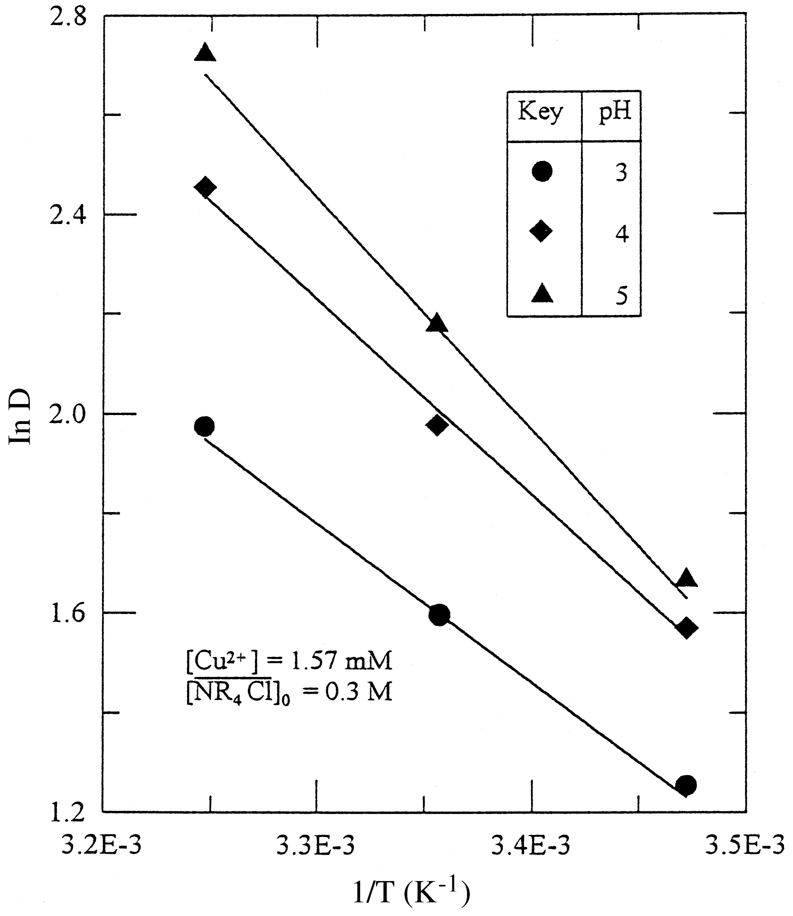

FIG. 7 The Arrhenius plot of the distribution ratios of Cu(II).

The thermodynamics-based value K_{ex}^{0} is a true "constant" that can definitely be compared with other literature results. However, simplification of the expression make it more suitable to practical use. As a reasonable assumption, the term Γ_1 is expected to remain constant as long as the variations in the aqueous environment (ionic strength, etc.) and in the organic-phase concentrations are small (17). This may be the case here because the initial Cu(II) concentration is fixed and low enough (1.57 mM). Also, the fraction of amine reacted with the Cu–NTA chelated anions is considered to be low (<12 mol%).

The term $[\overline{NR_4Cl}]$ in Eq. (9) can be obtained by the following mass balance because the solubility of Aliquat 336 in water is negligibly small (~2.03 cm^3/dm^3) (18, 19):

$$[\overline{NR_4Cl}] = [\overline{NR_4Cl}]_0 - [\overline{NR_4CuL}] \tag{10}$$

It is seen from Fig. 8 that the value of K_{ex} calculated from Eq. (9) depends on

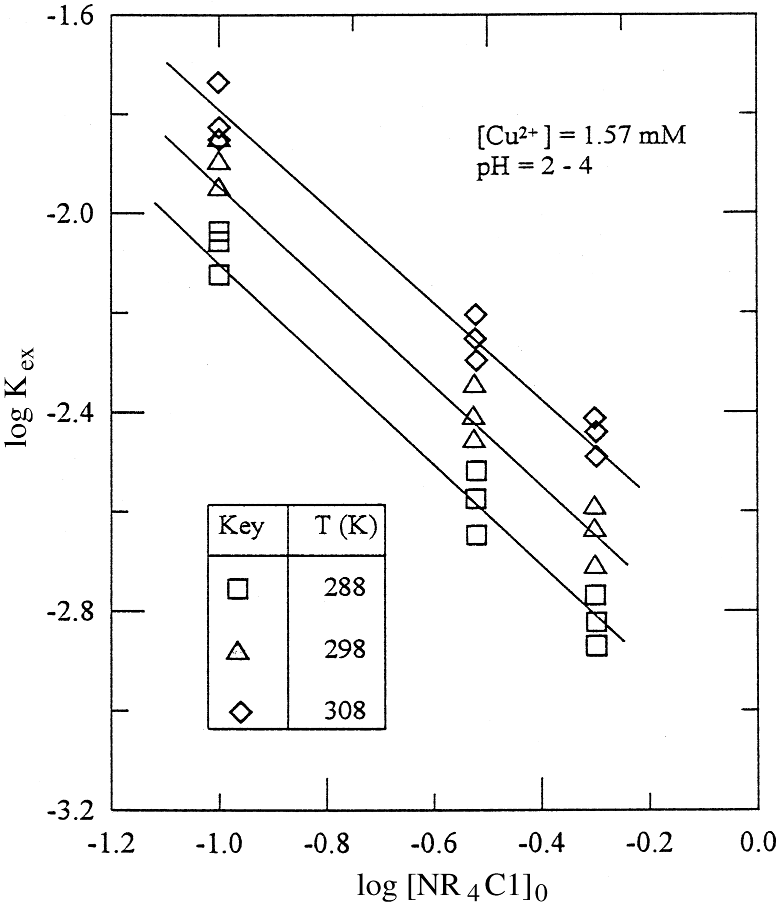

FIG. 8 Correlation between concentration-based constant and extractant concentration.

Aliquat 336 concentration. For example, it decreases from 1.26×10^{-2} and 2.50×10^{-3} at 298 K by changing the amine concentration from 0.1 to 0.5 M. They are less than those obtained in the extraction of CrO_4^{2-} from aqueous solutions with Aliquat 336/kerosene under comparable conditions (13).

The fact that K_{ex} depends on extractant concentration indicates ideal behavior occurs only in the aqueous phase. The nonideal behavior of the organic phase containing Aliquat 336 has been examined in metallic anion extraction (10, 13, 20). The simplicity of the following empirical expression makes it more easily applicable (10):

$$(\gamma_{\overline{NR_4CuL}}/\gamma_{\overline{NR_4Cl}}) = [\overline{NR_4Cl}]_0^n \tag{11}$$

By substituting Eq. (11) into Eq. (7), n is optimized to be 1 as shown in Fig. 8. Hence, the extraction equilibrium at 298 K can be expressed as Eq. (12) under the amine concentration range of 0.1–0.5 M.

$$1.25 \times 10^{-3} = \left(\frac{[\overline{NR_4CuL}][Cl^-]}{[CuL^-][\overline{NR_4Cl}]}\right)[\overline{NR_4Cl}]_0 \tag{12}$$

The characteristics of Eq. (12) likely indicate that some association reactions between amines or the complexes occur in the organic phase. It was actually reported that most of the tri-*n*-octylmethylammomium nitrate in benzene forms tetramer in the amine concentration range of 0.01 to 1 M (18), possibly due to the formation of O—H bonds within a given quaternary amine. Although the chloride salts tend to be less associated compared to the hydroxide or nitrate salts (19), further studies on the subject should be made.

CONCLUSIONS

The extraction equilibria of Cu–NTA chelated anions from water with Aliquat 336 in kerosene have been examined. Quaternary amines such as Aliquat 336 facilitate more distribution than tertiary amines such as TOA. The distribution ratio first increases with increasing equilibrium pH and then decreases with a further increase in pH. There is a maximum at about pH 5. As the initial pH is beyond 7, it drops after extraction, indicating reaction between OH^- and the amine (Eq. 4). The enthalpy change of the extraction reaction occurring at pH < 6.5 is within 21.7–45.4 kJ/mol under the ranges studied. The positive ΔH is understandable because 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. The extraction equilibrium can be described as in Eq. (12) by considering the effect of the nonideal behavior of the organic phase. The high distribution ratio obtained in this study provides the possibility of using solvent extraction for removal of Cu(II) from complexed metal solutions.

NOMENCLATURE

a_i	activity of species *i*
D	distribution ratio of Cu(II)
ΔH	apparent enthalpy change (kJ/mol)
K_{ex}	equilibrium constant defined in Eq. (9)
NR_4Cl	Aliquat 336
NTA	nitrilotriacetic acid (H_3L)
R	universal gas constant (J/mol·K)
T	absolute temperature (K)
TOA	tri-*n*-octylamine
[ ]	molar concentration of species in the bracket (M)

Greek Letter

γ_i	activity coefficient of species *i*

Superscripts

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

Subscripts

t	total
0	initial

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