

Effect of formaldehyde on Cu(II) removal from synthetic complexed solutions by solvent extraction

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Abstract

The effect of formaldehyde (HCHO) on the extraction of Cu(II) from an equimolar EDTA (ethylenediaminetetraacetic acid, H₄L) solution with Aliquat 336 in kerosene (a quaternary amine) was examined. Experiments were carried out at different initial concentrations of Cu(II) (1.57–5 mol/m³), solution pH (3.0–8.0), HCHO concentrations (0–3 vol.%), Aliquat 336 concentrations (80–400 mol/m³), and temperatures (15–35 °C). It was shown that the distribution ratios (*D*) of Cu(II), which exists in the form of complexed anions CuL²⁻, increased with increasing equilibrium pH (pH_{eq}), but reached a plateau at pH_{eq} > 4 for the system without HCHO and at pH_{eq} > 4.5 for the system with 1 vol.% HCHO. The *D* values increased with increasing HCHO concentration, likely due to the reduction of Cu(II) to Cu(I) by HCHO in solution. A semi-empirical two-parameter model was proposed to describe the extraction equilibrium, in which the non-ideality in organic phases was considered. The thermodynamic parameters were also evaluated and discussed.

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1. Introduction

Discharges from the manufacturing of printed circuit boards for electroless copper plating [1], chemical cleaning solutions for (power) plant boilers [2,3], and washing effluents for remediation of metal-contaminated soils [4,5] always contain various complexing agents. It is recognized that the presence of strong complexing agents such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and citrate makes removal of heavy metals from water unsatisfactory using conventional chemical precipitation methods (such as hydroxides and sulfides) as well as chemical coagulation and flocculation processes [6]. Furthermore, the high buffer capacity provided by the complexing agents requires excessive amounts of chemicals to neutralize the alkalinity. These problems and restrictions warrant investigations on other recovery alternatives.

In general, the methods for treating such complexed solutions depend greatly on the particular complexing agents and metals involved and on their concentrations. Adsorption using activated carbons has been found to be insufficient although it is widely applied for the removal of organic pollutants [7]. Reverse osmosis has high operation and maintenance costs for dilute solutions and is subject to fouling. Ion exchange and solvent extraction are hence the two promising candidates for the removal of metals from wastewater. They are operated in different devices although they have similar chemical principles [8]. Previous studies have shown that Cu(II) can be effectively co-extracted with EDTA or NTA in the form of the complexed anions from aqueous streams with quaternary amines such as Aliquat 336 (tri-*n*-octylmethylammonium chloride) [9–11]. Thus, the acceptable distribution ratio offers the possibility of using solvent extraction for removal of Cu(II) from such complexed solutions.

Besides Cu(II) and strong complexing agents such as EDTA, however, the solution typically contains 1–3 vol.%

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Nomenclature

a_i	activity of species i
CuL^{2-}	Cu(II)–EDTA complexed anion
CuL^{3-}	Cu(I)–EDTA complexed anion
D	distribution ratio of CuL^{2-} or CuL^{3-}
H_4L	EDTA molecule
NR_4Cl	Aliquat 336
K_{ex}	concentration-based equilibrium constant defined in Eq. (8) (–)
K_γ	equilibrium constant based on activity coefficient defined in Eq. (9)
T	absolute temperature (K)
[]	molar concentration of species in the bracket (mol/m^3)

Greek letter

γ_i	activity coefficient of species i
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Superscript

0	thermodynamic basis
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Subscripts

eq	equilibrium value
0	initial (total) value

of formaldehyde (HCHO) as the reducing agent in electroless copper plating for printed circuit board manufacturing [1]. In this work, effect of the presence of HCHO on the extraction of Cu(II) from synthetic, equimolar complexed solution using Aliquat 336 was studied. This knowledge is quite essential whether solvent extraction is operated in the devices of packed towers, mixer-settlers or membrane contactors. The rinse solution, instead of the *original* waste effluent, was focused here. Experiments were performed as a function of initial concentration of Cu(II) ($1.57\text{--}5\text{ mol}/\text{m}^3$), solution pH (3.0–8.0), HCHO concentration (0–3 vol.%), Aliquat 336 concentration (80–400 mol/m^3), and temperature (15–35 °C). The extraction equilibrium constants and related thermodynamic parameters including ΔG^0 , ΔH^0 , and ΔS^0 in the present extraction process were also evaluated.

2. Experimental

2.1. Reagents and solutions

Aliquat 336 (FW 404.16) was supplied from Aldrich Co. Prior to use it was washed with dilute HCl ($0.1\text{ mol}/\text{dm}^3$) solution to remove water-soluble impurities. Kerosene, offered from the Union Chemical Ltd., Taiwan, was washed twice with 20 vol.% H_2SO_4 to remove aromatics before use. It was finally washed three times with deionized water (Millipore Milli-Q). In this work, 5 vol.% of *n*-decanol (Merck Co.) was

added in the organic solution to avoid the formation of third phase or emulsions. Formaldehyde, disodium salt of EDTA, CuCl_2 , CuCl , and other inorganic chemicals (NaOH, HCl) were all supplied by Merck Co., as analytical reagent grade.

The organic solution was prepared by diluting Aliquat 336 in kerosene and *n*-decanol, and the initial concentration of Aliquat 336 ranged from 80 to 400 mol/m^3 . The aqueous solution was prepared by dissolving equimolar amounts of CuCl_2 (or CuCl) and EDTA in deionized water, to which 1–3 vol.% of HCHO was added in some cases. The initial concentration of Cu(II) ranged from 1.57 to 5 mol/m^3 .

2.2. Experimental procedures

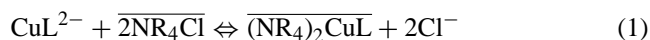
In extraction experiments, equal volumes (50 cm^3 , each) of the organic and aqueous phases were placed in a 250- cm^3 glass-stoppered flask, and were agitated with a magnetic stirrer at 400 rpm for 24 h. Preliminary experiments had shown that the extraction reactions were complete within 12 h [10,11]. The temperature was controlled in the range 15–35 °C in water bath. After phase separation, the concentration of Cl^- in aqueous phase was analyzed with an ICP-AES (Jovin Yvon, JY-38S, France) equipped with a flame ionization detector, and that of metal was analysed with an atomic absorption spectrophotometer (Varian 220FS, USA). The concentration of HCHO in aqueous phase was determined by gas chromatography (Varian CP-3800, USA). Moreover, the concentration of copper in organic phase was obtained from a mass balance. Each experiment was duplicated at least under identical conditions. The reproducibility of concentration measurements was mostly within 3%.

3. Results and discussion

3.1. Effect of pH on extraction

It is known that EDTA (H_4L) exists in a number of protonated forms in aqueous phase, which readily forms stable complexes with most heavy metals in a 1:1 molar ratio. For a dilute equimolar solution of Cu(II) and EDTA, e.g., 10 mol/m^3 , the divalent anions CuL^{2-} absolutely predominate at $3 < \text{pH} < 12$ and the univalent anions CuHL^- at $\text{pH} < 3$ [10].

Under the initial pH ranges studied here (3.0–8.0), the extraction reaction of CuL^{2-} with Aliquat 336 (NR_4Cl) can be expressed by



where the overbar refers to the organic phase. Fig. 1 shows the distribution ratios D of CuL^{2-} at different equilibrium pH (pH_{eq}), in which D is defined by

$$D_{\text{CuL}^{2-}} = \frac{[\overline{(\text{NR}_4)_2\text{CuL}}]}{[\text{CuL}^{2-}]} = \frac{[\text{CuL}^{2-}]_0 - [\text{CuL}^{2-}]}{[\text{CuL}^{2-}]} \quad (2)$$

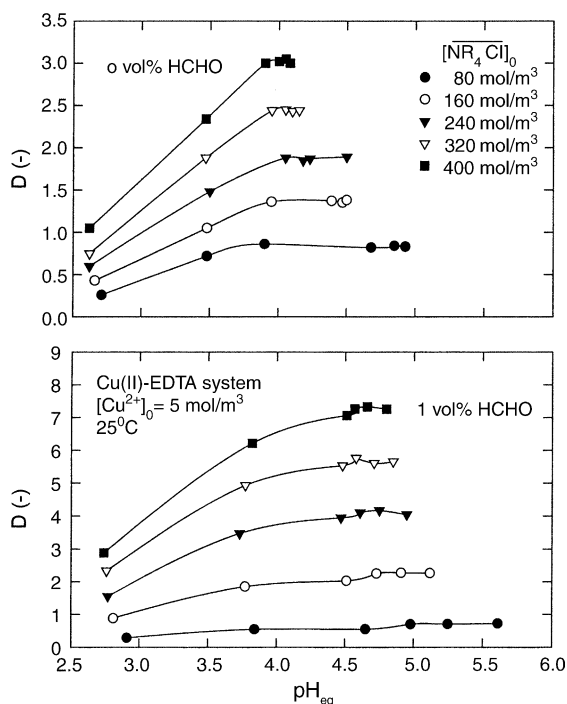


Fig. 1. Effect of equilibrium pH (pH_{eq}) on the distribution ratio D ($[Cu^{2+}]_0 = 5 \text{ mol/m}^3$, $[NR_4Cl]_0 = 80\text{--}400 \text{ mol/m}^3$).

It is found that the D value increases with increasing pH_{eq} and reaches a plateau at $pH_{eq} > 4$; but the plateau D value is present at $pH_{eq} = 4.5$ when aqueous solution contains 1 vol.% HCHO (Fig. 1b).

3.2. Effect of extractant concentration on extraction

The D values of CuL^{2-} at different Aliquat 336 concentrations are shown in Fig. 2. A linear increase of D is found with increasing extractant concentration. The slope is larger at higher pH_0 and this effect is less pronounced at $pH_0 > 5$ (Fig. 2a). However, such behavior occurs at $pH_0 > 7$ with 1 vol.% HCHO (Fig. 2b). This indicates that the extraction efficiency would increase by the addition of HCHO.

3.3. Effect of formaldehyde on extraction

The effect of HCHO concentration on extraction of CuL^{2-} with Aliquat 336 at $pH_0 = 5$ and 7 is shown in Fig. 3. It is found that the D value increases with increasing HCHO concentration, and the larger extraction is obtained at a higher pH_0 . HCHO is chemically the most reactive among the aldehydes. Ordinary oxidizing agents readily oxidize HCHO to HCOOH [12,13]. The increased D value is likely because an amount of Cu(II) is, at least partially, reduced to Cu(I), which exists in the form of trivalent anions CuL^{3-} , by HCHO. As expected, Fig. 4 justifies the higher D values of CuL^{3-} anions for extraction with Aliquat 336 compared to CuL^{2-} anions. It should be noted that these experiments were separately con-

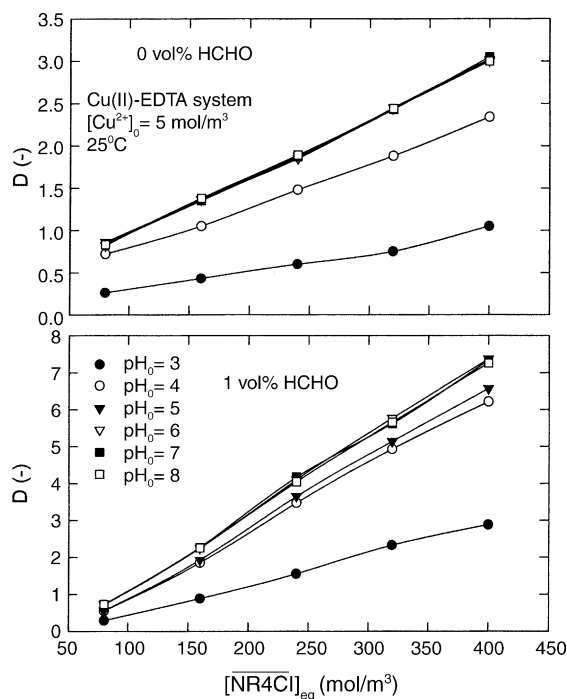


Fig. 2. Effect of equilibrium Aliquat 336 concentration on the distribution ratio D ($[Cu^{2+}]_0 = 5 \text{ mol/m}^3$, $pH_0 = 3\text{--}8$).

ducted in single Cu(I)– and Cu(II)–EDTA solutions, rather than the mixed solutions.

Besides EDTA, Cu(II), and HCHO, the typical electroless copper plating solution for printed circuit board manufacturing consists of 6–10 g/L NaOH [1]. The rinse solution pH is near 10 and 11. Under this circumstance, the following oxidation–reduction reaction takes place

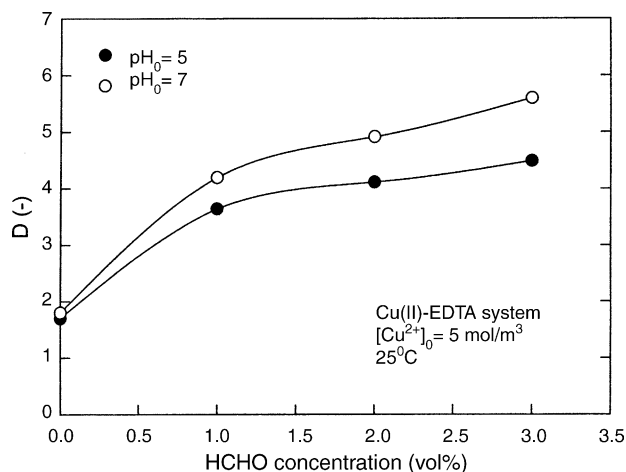
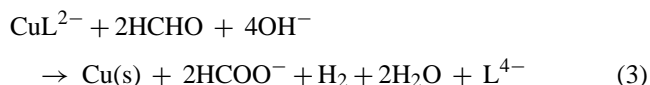


Fig. 3. Effect of HCHO concentration on the distribution ratio D ($[Cu^{2+}]_0 = 5 \text{ mol/m}^3$, $[NR_4Cl]_0 = 240 \text{ mol/m}^3$).

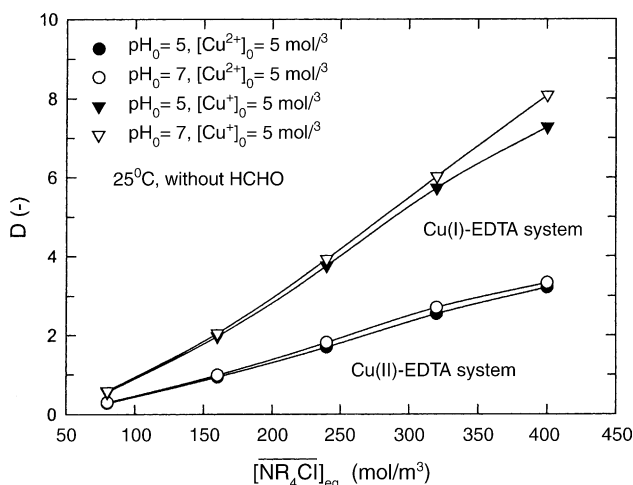
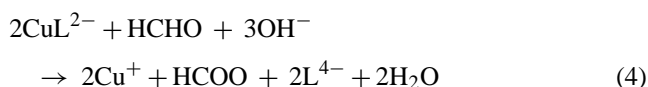


Fig. 4. Effect of equilibrium Aliquat 336 concentration on the distribution ratio of CuL^{2-} and CuL^{3-} at $\text{pH}_0 = 5$.

In this work, the solution pH should be adjusted below 8 because OH^- will strongly compete with CuL^{2-} for extraction at alkaline solutions [10].

Table 1 shows that the consumption of HCHO in the solution occurs after extraction process. Although Moussavi et al. [13] have reported that HCHO in effluents can be oxidized by air oxygen, this experimental factor was carefully checked and was excluded here. In blank experiments (i.e., without extraction), however, no colloidal $\text{Cu}(\text{s})$ particles were detected in complexed solutions at $\text{pH}_0 = 6$ even with 6 vol.% HCHO by comparing metal concentration of the samples taken before and after high-speed centrifugation (6000 rpm). It is reasonable to deduce that the product of partial reduction, $\text{Cu}(\text{I})$, is present in the solution according to



The relationship between the D value and HCHO concentration is shown in Fig. 5. In the present systems, the following equations are obtained at 25 °C.

$$\log D = 0.77 + \log [\text{HCHO}]^{0.13} \quad (\text{pH}_{\text{eq}} = 4) \quad (5)$$

$$\log D = 0.83 + \log [\text{HCHO}]^{0.15} \quad (\text{pH}_{\text{eq}} = 6) \quad (6)$$

Table 1

Relationship between the distribution ratio of CuL^{2-} or CuL^{3-} at 25 °C and the amount of HCHO consumed after solvent extraction

Aqueous solution	Total consumption of HCHO (mL/L)	HCHO Aliquat extracted by 336 (mL/L)	HCHO reacted with CuL^{2-} (mL/L)	D (-)
CuL^{2-} , 0 vol.% HCHO	–	–	–	4.6
CuL^{2-} , 1 vol.% HCHO	1.6	1.0	0.6	5.1
CuL^{2-} , 2 vol.% HCHO	2.9	1.8	1.1	5.5
CuL^{2-} , 3 vol.% HCHO	5.2	3.8	1.4	5.9
CuL^{3-} , 0 vol.% HCHO	–	–	–	9.0

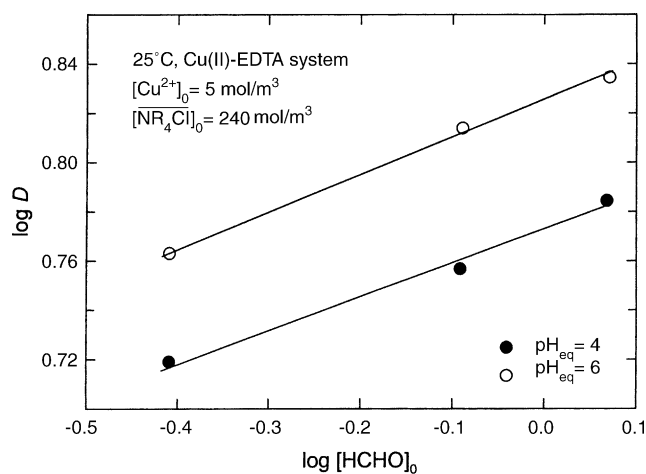


Fig. 5. Relationship between $\log D$ and $\log [\text{HCHO}]$ at $\text{pH}_{\text{eq}} = 4$ and 6 ($[\text{NR}_4\text{Cl}]_0 = 240 \text{ mol/m}^3$, $[\text{Cu}^{2+}]_0 = 5 \text{ mol/m}^3$).

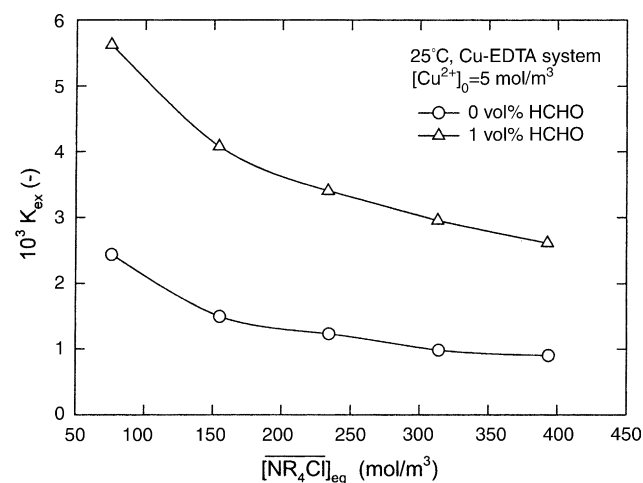


Fig. 6. Effect of equilibrium Aliquat 336 concentration on the concentration-based equilibrium constant ($[\text{Cu}^{2+}]_0 = 5 \text{ mol/m}^3$).

3.4. Extraction reaction equilibrium

It is evident from Fig. 6 that the K_{ex} value does not remain constant; it changes with extractant concentration. We carefully repeat the experiments and do obtain reproducible results. This likely means the non-ideal behavior in organic phases no matter with HCHO or not [10,14–16].

The thermodynamic equilibrium constant of Eq. (1), K_{ex}^0 , for the $\text{Cu}(\text{II})$ –EDTA system, for example, can be

written as

$$K_{\text{ex}}^0 = \frac{a_{(\text{NR}_4)_2\text{CuL}^2\text{Cl}^-}}{a_{(\text{NR}_4\text{Cl})^2}^2 a_{\text{CuL}^{2-}}} = K_{\text{ex}} K_{\gamma} \quad (7)$$

where K_{ex} is the concentration-based equilibrium constant defined as

$$K_{\text{ex}} = \frac{[(\text{NR}_4)_2\text{CuL}][\text{Cl}^-]^2}{[\text{NR}_4\text{Cl}]^2 [\text{CuL}^{2-}]} \quad (8)$$

In addition, K_{γ} is given as function of the activity coefficients by

$$K_{\gamma} = \frac{\gamma_{(\text{NR}_4)_2\text{CuL}} \gamma_{\text{Cl}^-}^2}{\gamma_{\text{NR}_4\text{Cl}}^2 \gamma_{\text{CuL}^{2-}}} \quad (9)$$

where γ_i represents the activity coefficient of species i . K_{γ} will equal 1 if ideal solutions (extremely diluted solutions) are assumed.

The non-ideality of organic phase in reactive extraction systems is usually expressed in terms of ideal associated solution concept, i.e., aggregation of complexes [10,11,14–17]. In extraction of HNO_3 with the nitrate salt of Aliquat 336, the non-ideal behavior of organic phase was considered assuming that the logarithm of activity coefficient ratio of the complex to extractant is proportional to extractant concentration [15]. To simplify the description of the non-ideality of organic phase, the following expression is adopted here [18,19].

$$\left(\frac{\gamma_{(\text{NR}_4)_2\text{CuL}}}{\gamma_{\text{NR}_4\text{Cl}}^2} \right) \propto [\text{NR}_4\text{Cl}]^n \quad (10)$$

Under the conditions studied, the concentrations of Cl^- and CuL^{2-} are low enough compared to extractant concentration so their activity coefficients are assumed to be kept constant [10,11]. Thus, the thermodynamic equilibrium constant can be expressed as follows by substituting Eqs. (8)–(10) into Eq. (7).

$$\log K_{\text{ex}}^0 = \log K_{\text{ex}} + \log [\text{NR}_4\text{Cl}]^n \quad (11)$$

Fig. 7 shows the good linear plot of $\log K_{\text{ex}}$ versus $\log[\text{NR}_4\text{Cl}]$ (correlation coefficient, $R^2 = 0.994$). The values of K_{ex}^0 at 25 °C are obtained to be 3.3×10^{-2} and 4.1×10^{-2} for Cu(II)– and Cu(I)–EDTA systems, respectively. Finally, the extraction equilibrium relationships with and without HCHO are given by

$$\log K_{\text{ex}} = -1.48 - \log [\text{NR}_4\text{Cl}]^{0.61} \quad (\text{without HCHO}) \quad (12)$$

$$\log K_{\text{ex}} = -1.39 - \log [\text{NR}_4\text{Cl}]^{0.46} \quad (\text{without 1 vol.\% HCHO}) \quad (13)$$

It is noticed that all concentration units in Eqs. (12) and (13) are in mol/m^3 . The non-ideality of organic phase is likely

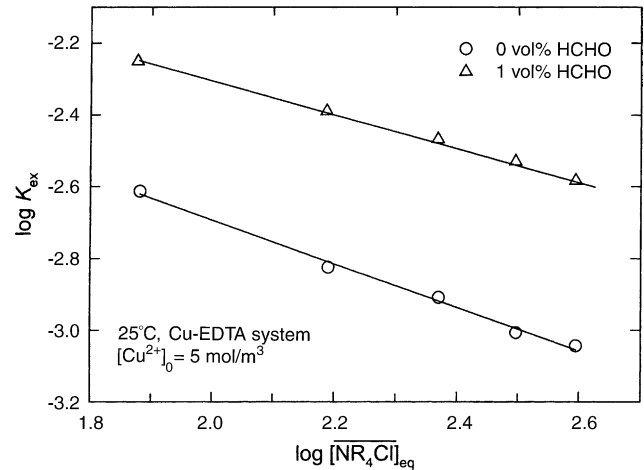


Fig. 7. Relationship between $\log K_{\text{ex}}$ and $\log[\text{NR}_4\text{Cl}]_{\text{eq}}$ ($[\text{CuL}^{2-}]_0 = 5 \text{ mol/m}^3$).

due to the interaction or aggregation of the organic-phase species involving quaternary amines [20–22]. For example, it was found that most of tri-*n*-octylmethylammomium nitrate in benzene forms tetramers in the range of amine concentration of 10–1000 mol/m^3 [21], because of the possible formation of O–H bonds within a given compound.

3.5. Thermodynamic parameters

The amounts of CuL^{2-} extracted by Aliquat 336 were also measured at other temperatures (Fig. 8). The following van't Hoff relationships are used to evaluate the thermodynamic parameters ΔG^0 , ΔH^0 , and ΔS^0 [23]

$$\Delta G^0 = -2.303RT \log K_{\text{ex}}^0 \quad (14)$$

$$\log K_{\text{ex}}^0 = \left(\frac{\Delta H^0}{2.303R} \right) \frac{1}{T} + \frac{\Delta S^0}{2.303R} \quad (15)$$

The change in free energy (ΔG^0) is calculated to be 8.9 (without HCHO) and 7.6 kJ/mol (with 1 vol.% HCHO) at 25 °C from Eq. (14). On the other hand, a linear plot of $\log K_{\text{ex}}^0$ versus $1/T$ yields ΔH^0 and ΔS^0 (Fig. 9), which are 43.6 kJ/mol and 45.8 J/(mol K) without HCHO as well as 31.3 kJ/mol and 79.6 J/(mol K) with 1 vol.% HCHO, respectively, at 25 °C. The endothermic nature of this process is consistent with common solid ion exchange processes, and the magnitude of ΔH^0 lies within the range of ion exchange mechanism [23]. Compared to the absence of HCHO, the smaller ΔH^0 value obtained with 1 vol.% HCHO reflects the fact that trivalent anions CuL^{3-} have stronger affinity than divalent anions CuL^{2-} toward the extractant. The positive ΔS^0 indicates that not only the bonding between Cu–EDTA complexed anions and Aliquat 336 (e.g., Eq. (1)) but also the release of water molecules surrounded the complexed anions play important roles during the present extraction processes.

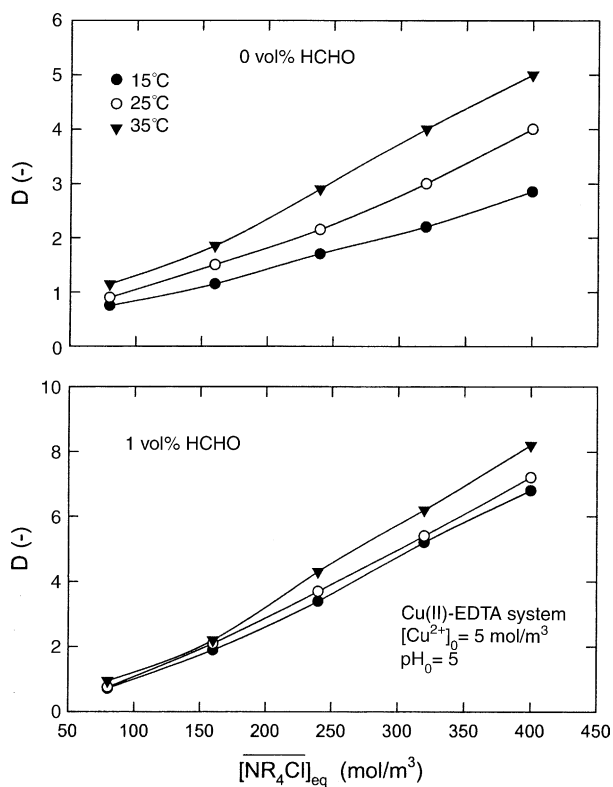


Fig. 8. Effect of equilibrium Aliquat 336 concentration on the distribution ratio D at different temperatures ($[Cu^{2+}]_0 = 5 \text{ mol/m}^3$, $pH_0 = 5$).

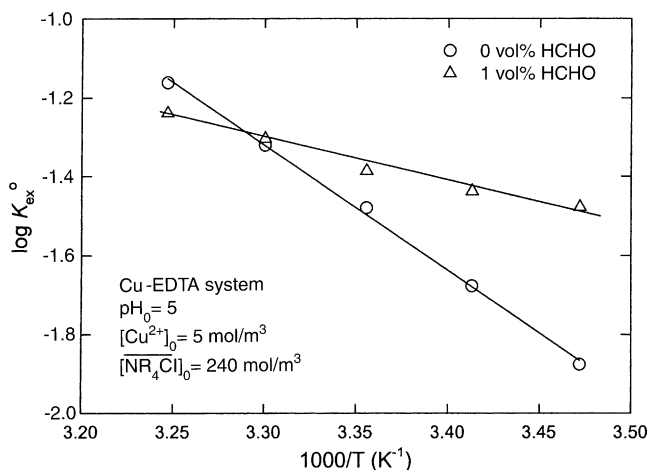


Fig. 9. Determination of thermodynamic parameters for the extraction of copper with and without HCHO by Aliquat 336.

4. Conclusions

Solvent extraction of Cu(II)–EDTA complexed anions from the solutions with and without formaldehyde (HCHO) to a kerosene solution of Aliquat 336 was studied. It was shown that the distribution ratio D increased with increasing HCHO concentration up to 3 vol.%. This effect was more pronounced at higher equilibrium pH (pH_{eq}), which was proba-

bly caused by the reduction of CuL^{2-} to CuL^{3-} by HCHO. The value of D increased with increasing pH_{eq} and reached a plateau at $pH_{eq} > 4.5$ for system with 1 vol.% HCHO.

Under the conditions tested, the ΔH^0 and ΔS^0 values for the present extraction system without HCHO were 43.6 kJ/mol and 45.8 J/(mol K), respectively, at 25 °C. They became 31.3 kJ/mol and 79.6 J/(mol K), respectively, for the system with 1 vol.% HCHO. The smaller ΔH^0 obtained with 1 vol.% HCHO reflected the fact that the Cu(I)–EDTA complexed anions had higher affinity than the Cu(II)–EDTA complexed anions toward the extractant. The positive ΔS^0 deduced the crucial role of the de-attachment of water molecules from the complexed anions in the extraction process.

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