Solvent Extraction of Copper and EDTA in Electroless Copper Plating Wastewater Using a Quaternary Ammonium Salt

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To separate both copper and 2,2',2'',2'''-(ethane-1,2-diyldinitrilo)tetraacetic acid (EDTA) from the waste electroless copper plating solution by solvent extraction, the liquid–liquid equilibria of the copper-EDTA complex and unbound EDTA ion were experimentally measured. An organic solution of tri-*n*-octylmethylammonium chloride (TOMACl) was used as solvent. The kerosene solution of TOMACl could extract both copper-EDTA complexes and EDTA ions from the model wastewater. The fractional removal and distribution ratios of both the copper-EDTA complex and EDTA ions decreased as the pH increased. The valence number of the major copper-EDTA complex or EDTA ion in the aqueous phase increased with pH, and the number of TOMA$^+$ cations required to chelate the complexes and ions increased. These complexes and ions had lower reactivity with TOMACl owing to steric hindrance. These effects caused lower removal of both copper and EDTA in a higher pH range, which is a typical condition of waste electroless copper solution.

1. Introduction

During the production of a printed wiring board, an electroless copper plating method is utilized, in which copper (Cu) metal is deposited directly on the surface of a nonconductive material, for example, resin or glass, by catalytic reduction of Cu(II) ions in the plating solution as an underlying layer for the subsequent electrolytic plating. Table 1 lists the composition of the electroless plating solution commonly used in wiring board production [1]. The solution contains 2,2′,2″,2‴-(ethane-1,2-diyldinitrilo) tetraacetic acid (EDTA), methanal (formaldehyde), and so on, besides Cu. EDTA is one of the most popular chelating agents used to form Cu-EDTA complexes in solution, and it is necessary to enhance the solubility and stability of Cu(II) ions. The solution is adjusted to be strongly basic to stabilize the complex. As Cu and EDTA have a serious influence on the environment, they are removed from the waste plating solution before discharge, mainly using precipitation by pH adjustment [2,3] and electrolysis [4,5], in the present wiring board production process. However, this method of waste solution treatment is extremely energy intensive, and appropriate alternatives must be developed.

Mainly, two kinds of techniques have been considered for removal of Cu and EDTA from the waste plating solution: one is to first decompose EDTA for destabilization of the Cu-EDTA complex and remove Cu by the sequent precipitation [6-8]; the other is direct removal of Cu-EDTA complex and unbound EDTA. In the former, several oxidation methods to decompose EDTA have been employed to destabilize Cu-EDTA

complex, and Cu ion liberated from the complex was removed by sequent precipitation. The latter is accomplished by adsorption [9], ion exchange [10], solvent extraction [11-13], etc. In previous studies on solvent extraction [11-13], quaternary ammonium salts, such as tri-n-octylmethylammonium chloride (TOMACl), have been utilized as extractants for reactive extraction of only Cu, that is, the anion of the Cu-EDTA complex, in the waste solution. Although the removal of EDTA from waste solutions is important for the treatment mentioned above, EDTA removal has been inadequately discussed in these studies. In fields other than wastewater treatment by electroless plating, the separation of EDTA from general wastewater by extraction using TOMACl was studied [14], in which an aqueous solution of EDTA without metal ions was used as the feed solution.

Table 1 An example of conditions of electroless copper plating solution

Concentration of CuSO$_4$	[kmol m^{-3}]	0.04 – 0.063
Concentration of EDTA	[kmol m^{-3}]	0.086 – 0.103
Concentration of Methanal	[kmol m^{-3}]	0.043
Concentration of NaOH	[kmol m^{-3}]	0.25
pH		12.5

In this study, the solvent extraction of not only the Cu-EDTA complex but also the unbound EDTA ions from the waste plating solution was performed using TOMAC. The liquid-liquid equilibria of the Cu-EDTA complex and unbound EDTA ion between the model waste solution and the solvent phase containing TOMAC were experimentally measured under various conditions, and the results were discussed in terms of fractional removal, distribution ratios, and equilibrium constants of both the Cu-EDTA complex and unbound EDTA ion.

2. Experimental

Copper(II) sulfate pentahydrate (CuSO$_4$ 5H$_2$O, purity > 0.995) and 2,2′,2″,2‴-(ethane-1,2-diyldinitrilo) tetraacetic acid disodium dihydride salt (EDTA 2Na 2H$_2$O, purity > 0.99) were used as the Cu ion source and complexing agent, respectively, to prepare a model waste solution from electroless copper plating. Four types of alcohols, (heptan-1-ol (1-heptanol, purity > 0.98), octan-1-ol (1-octanol, purity>0.98), decan-1-ol (1-decanol, purity > 0.95), and phenylmethanol (benzyl alcohol, purity > 0.99)), and three kinds of hydrocarbons (heptane (purity > 0.99), toluene (purity > 0.995), and kerosene (reagent grade)) were used for the preparation of solvent solutions, and tri-n-octylmethylammonium chloride (TOMACl, purity > 0.89) was selected as an extractant, as it is one of the popular quaternary ammonium salts in research for the removal of metal anions from aqueous solutions. All chemicals used in this study were purchased from FUJIFILM Wako Pure Chemical Corporation.

The experimental conditions for extraction equilibrium are shown in Table 2. The feed solution was prepared by dissolving CuSO$_4$·5H$_2$O and EDTA·2Na·2H$_2$O in deionized water. The pH of the aqueous feed phase was adjusted using sodium hydroxide (NaOH). A solvent solution was prepared by dissolving the extractant in each organic compound.

The experiments were carried out in a 50 mL conical flask with a screw top. Equal volumes (20 mL) of the feed and solvent solutions were placed in a flask and shaken in a thermostatic bath for 3 days at 300 K to attain liquid–liquid equilibrium. After equilibrium was reached, the aqueous and organic phases were separated using a separating funnel.
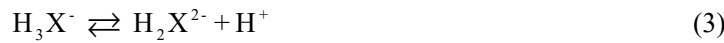
The pH of the aqueous phase was measured using a digital pH meter (F-74, HORIBA). The aqueous solution was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES; 5100 VDV, Agilent Technologies) to determine the overall concentration of Cu in the aqueous phases, $C_{Cu,aq}$. The overall concentration of EDTA in the aqueous phase, $C_{EDTA,aq}$, was determined by the discoloration of Co^{3+}-EDTA complex at 525 nm using a spectrophotometer (UV2000, Shimadzu) [15]. In the cases of solution containing Cu, Cu was precipitated and removed with 5,7-dibrom-8-hydroxyquinoline in advance [16]. The overall concentrations of Cu and EDTA in the organic phase at equilibrium, $C_{Cu,org}$ and $C_{EDTA,org}$, were calculated using material balance.

Table 2. Experimental conditions for extraction equilibrium.

Feed		aqueous solution of CuSO$_4$, EDTA·2Na, NaOH
Initial concentration of CuSO$_4$	[kmol m^{-3}]	0, 0.04
Initial concentration of EDTA	[kmol m^{-3}]	0.10
Initial pH		3.4 – 13.4
Initial volume	[m^3]	20×10^{-6}
Solvent		1-heptanol, 1-octanol, 1-decanol, benzyl alcohol, heptane, toluene, kerosene, and kerosene solution of TOMACl
Initial concentration of TOMACl	[kmol m^{-3}]	0.4
Initial volume	[m^3]	20×10^{-6}
Time	[h]	72
Temperature	[K]	300

3. Results and Discussion

EDTA dissociates in the aqueous solution to form one cation and four kinds of anions, such as [17],

$$H_5X^+ \rightleftarrows H_4X + H^+ \tag{1}$$

$$H_4X \rightleftarrows H_3X^- + H^+ \tag{2}$$

$$H_3X^- \rightleftarrows H_2X^{2-} + H^+ \tag{3}$$

$$H_2X^{2-} \rightleftarrows HX^{3-} + H^+ \tag{4}$$

$$HX^{3-} \rightleftarrows X^{4-} + H^+ \tag{5}$$

where H$_4$X stands for the free form of EDTA which has 4 dissociable protons (the detailed information about used symbols are given in **Nomenclature**). The constant of each dissociation, $K_{X,j}$, was expressed as,

$$K_{X,1} = C_{H_4X,aq} C_{H,aq} / C_{H_5X^+,aq} \tag{6}$$

$$K_{X,2} = C_{H_3X^-,aq} C_{H,aq} / C_{H_4X,aq} \tag{7}$$

$$K_{X,3} = C_{H_2X^{2-},aq} C_{H,aq} / C_{H_3X^-,aq} \tag{8}$$

$$K_{X,4} = C_{HX^{3-},aq} C_{H,aq} / C_{H_2X^{2-},aq} \tag{9}$$

$$K_{X,5} = C_{X^{4-},aq} C_{H,aq} / C_{HX^{3-},aq} \tag{10}$$

The Cu^{2+} was complexed with X^{4-} or OH$^-$ to form five types of complexes in the aqueous phase, expressed as,

$$Cu^{2+} + H^+ + X^{4-} \rightleftarrows CuHX^- \tag{11}$$

$$Cu^{2+} + X^{4-} \rightleftarrows CuX^{2-} \tag{12}$$

$$Cu^{2+} + OH^- + X^{4-} \rightleftarrows CuOHX^{3-} \tag{13}$$

$$Cu^{2+} + 4OH^- \rightleftarrows Cu(OH)_4^{2-} \tag{14}$$

$$2Cu^{2+} + 2OH^- \rightleftharpoons Cu_2(OH)_2^{2+} \tag{15}$$
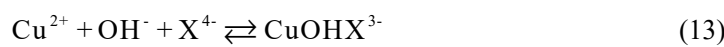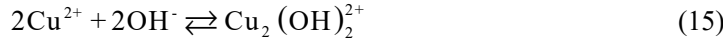
In the case of presence of EDTA, $C_{Cu^{2+}}$ could maintain so low, and the precipitation of Cu(OH)$_2$ was ignored. The complexation constants of eqs. (11)-(15) reactions were expressed as [17],

$$K_{CuX,1} = \frac{C_{CuHX^-,aq}}{C_{Cu^{2+},aq}\, C_{H^+,aq}\, C_{X^{4-},aq}} \tag{16}$$

$$K_{CuX,2} = \frac{C_{CuX^{2-},aq}}{C_{Cu^{2+},aq}\, C_{X^{4-},aq}} \tag{17}$$

$$K_{CuX,3} = \frac{C_{CuOHX^{3-},aq}}{C_{Cu^{2+},aq}\, C_{OH^-,aq}\, C_{X^{4-},aq}} \tag{18}$$

$$K_{CuOH,1} = \frac{C_{Cu(OH)_4^{2-},aq}}{C_{Cu^{2+},aq}\, C_{OH^-,aq}^4} \tag{19}$$

$$K_{CuOH,2} = \frac{C_{Cu_2(OH)_2^{2+},aq}}{C_{Cu^{2+},aq}^2\, C_{OH^-,aq}^2} \tag{20}$$

The complexation constants are listed in Table 3 [17].

At the liquid–liquid equilibrium in the system containing Cu, EDTA, and TOMACl, Cu and EDTA are distributed in both aqueous and organic phases in forms of complexes and ions. The following four assumptions were made.

1. The complexes of Cu-EDTA and Cu-OH, and ions of Cu and EDTA in aqueous phase are not directly extracted into organic phase.
2. TOMACl in organic phase is not directly extracted into aqueous phase.
3. Only anions, including negatively charged complexes, in aqueous phase can react with TOMACl to be extracted into organic phase.
4. Water and solvent do not dissolve into another phase.

Then, the distribution equilibria of EDTA between the aqueous and organic phases with TOMACl were expressed as [14],

$$H_3X^- + \overline{YCl} \rightleftharpoons \overline{YH_3X} + Cl^- \tag{21}$$

$$H_2X^{2-} + 2\overline{YCl} \rightleftharpoons \overline{Y_2H_2X} + 2Cl^- \tag{22}$$

$$HX^{3-} + 3\overline{YCl} \rightleftharpoons \overline{Y_3HX} + 3Cl^- \tag{23}$$

$$X^{4-} + 4\overline{YCl} \rightleftharpoons \overline{Y_4X} + 4Cl^- \tag{24}$$
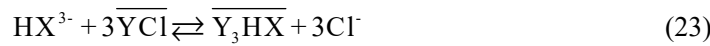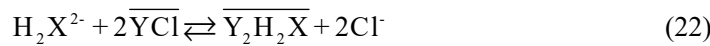
where YCl stands for the TOMACl molecule in the organic phase. Cl$^-$ was released into the aqueous phase by exchange with EDTA anions. The equilibrium constants were expressed as;
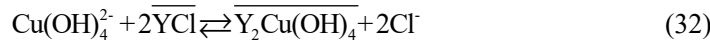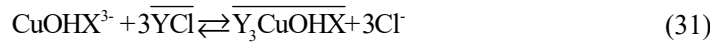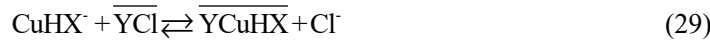
$$K_{XY,1} = \frac{C_{YH_3X,org}\, C_{Cl^-,aq}}{C_{H_3X^-,aq}\, C_{YCl,org}} \tag{25}$$

$$K_{XY,2} = \frac{C_{Y_2H_2X,org}\, C^2_{Cl^-,aq}}{C_{H_2X^{2-},aq}\, C^2_{YCl,org}} \tag{26}$$

$$K_{XY,3} = \frac{C_{Y_3HX,org}\, C^3_{Cl^-,aq}}{C_{HX^{3-},aq}\, C^3_{YCl,org}} \tag{27}$$

$$K_{XY,4} = \frac{C_{XY_4,org}\, C^4_{Cl^-,aq}}{C_{X^{4-},aq}\, C^4_{YCl,org}} \tag{28}$$

The distribution equilibria of Cu between the aqueous and organic phases with TOMACl, in which negatively charged Cu complexes in the aqueous phase, such as $CuHX^-$, CuX^{2-}, $CuOHX^{3-}$, and $Cu(OH)_4^{2-}$ existed, were expressed as;

$$CuHX^- + \overline{YCl} \rightleftarrows \overline{YCuHX} + Cl^- \tag{29}$$

$$CuX^{2-} + 2\overline{YCl} \rightleftarrows \overline{Y_2CuX} + 2Cl^- \tag{30}$$

$$CuOHX^{3-} + 3\overline{YCl} \rightleftarrows \overline{Y_3CuOHX} + 3Cl^- \tag{31}$$

$$Cu(OH)_4^{2-} + 2\overline{YCl} \rightleftarrows \overline{Y_2Cu(OH)_4} + 2Cl^- \tag{32}$$

The equilibrium constants were expressed as;

$$K_{YCuHX} = \frac{C_{YCuHX,org}\, C_{Cl^-,aq}}{C_{CuHX^-,aq}\, C_{YCl,org}} \tag{33}$$

$$K_{Y_2CuX} = \frac{C_{Y_2CuX,org}\, C^2_{Cl^-,aq}}{C_{CuX^{2-},aq}\, C^2_{YCl,org}} \tag{34}$$

$$K_{Y_3CuOHX} = \frac{C_{Y_3CuOHX,org}\, C^3_{Cl^-,aq}}{C_{CuOHX^{3-},aq}\, C^3_{YCl,org}} \tag{35}$$

$$K_{Y_2Cu(OH)_4} = \frac{C_{Y_2Cu(OH)_4,org}\, C^2_{Cl^-,aq}}{C_{Cu(OH)_4^{2-},aq}\, C^2_{YCl,org}} \tag{36}$$

In total, 22 kinds of compounds are related to one another to decide the liquid–liquid equilibrium condition. The detailed expression of material balances of EDTA, Cu, and TOMACl at liquid–liquid equilibrium are shown in the appendix.

The fractional removals of EDTA and Cu, r_{EDTA} and r_{Cu}, were defined as;

$$r_{EDTA} = \frac{EC_{EDTA,org}}{FC_{EDTA,aq,0}} \quad (37)$$

$$r_{Cu} = \frac{EC_{Cu,org}}{FC_{Cu,aq,0}} \quad (38)$$

The distribution ratios of EDTA and Cu, D_{EDTA} and D_{Cu}, were defined as;

$$D_{EDTA} = \frac{C_{EDTA,org}}{C_{EDTA,aq}} \quad (39)$$

$$D_{Cu} = \frac{C_{Cu,org}}{C_{Cu,aq}} \quad (40)$$

Figure 1 shows the concentration profiles of respective complexes and ions along the pH in the aqueous phase, estimated at values of $C_{Cu,aq}$ = 0.04 kmol m^{-3} and $C_{EDTA,aq}$ = 0.1 kmol m^{-3}. As represented by eq. (1), the major form of EDTA ion was changed as H$_5$X$^+$, H$_4$X, H$_3$X$^-$, H$_2$X^{2-}, HX^{3-} and X^{4-} as pH increased. In the wide range of pH, from weak acid to strong basic region, most of Cu existed in the forms of complexes, such as CuHX$^-$, CuX^{2-}, and CuOHX^{3-}. The concentration of Cu^{2+} ion was so low to be negligible, and the effects of Cu(OH)$_2$ precipitation were also ignored. For these ions or complexes of both EDTA and Cu, the valence number of the major ions and complexes increased as pH increased. In the basic region, representing the pH condition of the electroless plating wastewater, two types of EDTA ions, such as HX^{3-} and X^{4-}, and two types of Cu complexes, such as CuX^{2-} and CuOHX^{3-}, were dominant. Here, $C_{Cu(OH)_4^{2-},aq}$ was so small, i.e. $C_{Cu(OH)_4^{2-},aq}$ relative to the total Cu concentration was 1.0×10^{-6} at pH=14, that the effects of the extraction by eq. (32) could be ignored.

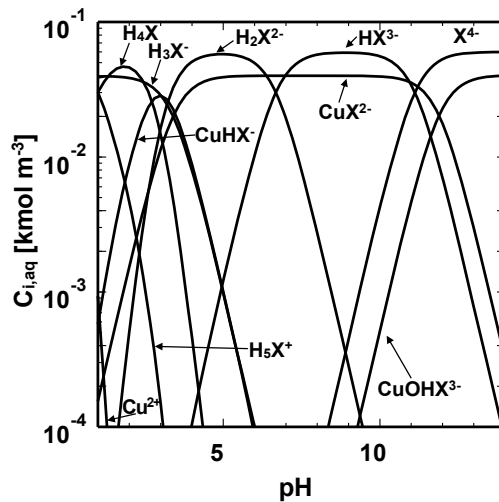Figure 1. Concentration profiles of EDTA ions and Cu-EDTA complexes in aqueous phase along pH. $C_{Cu,aq,0}$ = 0.04 kmol m^{-3} and $C_{EDTA,aq,0}$ = 0.1 kmol m^{-3}.

Figure 2 shows the effects of pH on the fractional removal of EDTA, r_{EDTA}, and distribution ratio of EDTA, D_{EDTA}, when the aqueous solution at $C_{Cu,aq,0}$ = 0 kmol m^{-3} and $C_{EDTA,aq}$ = 0.1 kmol m^{-3}, and kerosene

solution of TOMACl at $C_{\text{YCl,org,0}} = 0.4$ kmol m^{-3} were used as the feed and solvent solutions, respectively. The experimental results are shown by plots in this figure. When any organic solvent, listed in Table 2, was used without TOMACl, EDTA was not extracted at all into the organic phase, i.e., EDTA was insoluble in any organic phase used in this study. Among the organic phases used herein, TOMACl could dissolve only in kerosene with a sufficiently high solubility, and a kerosene solution of TOMACl was used as the organic phase in the subsequent results and discussion. The kerosene solution of TOMACl could extract and remove EDTA from the aqueous phase. Both of r_{EDTA} and D_{EDTA} decreased as pH increased.
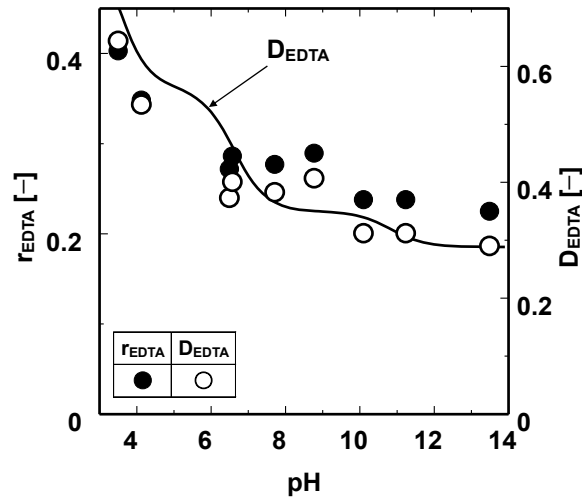

Figure 2. Effects of pH on fractional removal, r_{EDTA}, and distribution ratio of EDTA, D_{EDTA}.
   Feed solution: $C_{\text{Cu,aq,0}} = 0$ kmol m^{-3} and $C_{\text{EDTA,aq,0}} = 0.1$ kmol m^{-3},
   Solvent solution: kesorsene solution of TOMACl at $C_{\text{YCl,org,0}} = 0.4$ kmol m^{-3}.
   Solid line: D_{EDTA} estimated with complexation constants listed in Table 4.

Figure 3 shows the effects of pH on the fractional removals of EDTA and Cu, r_{EDTA} and r_{Cu}, and distribution ratios of EDTA and Cu, D_{EDTA} and D_{Cu}, and the experimental results are shown by plots. In this measurement, the aqueous solution containing EDTA and Cu at $C_{\text{Cu,aq,0}} = 0.04$ kmol m^{-3} and $C_{\text{EDTA,aq,0}} = 0.1$ kmol m^{-3}, and kerosene solution of TOMACl at $C_{\text{YCl,org,0}} = 0.4$ kmol m^{-3} were used as feed and solvent solutions, respectively. The solvent solution containing TOMACl could extract and remove both of Cu and EDTA simultaneously from the feed solution in a wide range of pH. Both of r_i and D_i decreased as the pH increased. In this measurement range, r_{EDTA} was larger than r_{Cu}, and more EDTA was extracted with TOMACl than Cu. Then, experimentally obtained D_{EDTA}s and D_{Cu}s were fitted by equilibrium equations of eqs. (6)–(10), (16)−(20), (25)–(28), (33)−(36) and material balance equations of eqs. (A1)−(A3), to determine values for $K_{\text{XY},j}$, K_{Y2CuX}, K_{YCuHX}, and K_{Y3CuOHX}, as shown in Table 4. Here it was assumed that all equilibrium constants were constant regardless of pH change, and $K_{\text{XY},j}$ was independent of Cu presence. $K_{\text{Y2Cu(OH)4}}$ was not determined since the extraction represented by eq. (32) was ignored as mentioned before.

For obtaining the equilibrium constants, the least square method was utilized to minimize the relative difference of D_{EDTA} or D_{Cu} between experimental and estimated data. Then, the experimental data of 13 for D_{EATA} and 5 for D_{Cu} were used. The program to conduct the least square method was composed by Visual Basic in Microsoft Excel software. The relative root mean square errors of D_{EATA} and D_{Cu} were 0.064 and
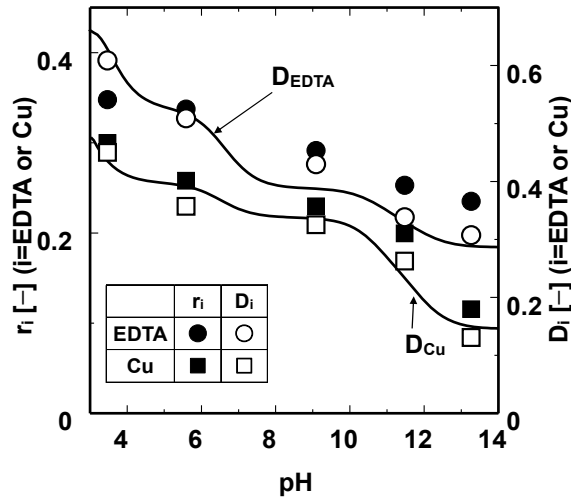
Figure 3. Effects of pH on fractional removals and distribution ratios of EDTA and copper, r_{EDTA} and r_{Cu}, and D_{EDTA} and D_{Cu}.

Feed solution: $C_{Cu,aq,0} = 0.04$ kmol m^{-3} and $C_{EDTA,aq,0} = 0.1$ kmol m^{-3},

Solvent solution: kerosene solution of TOMACl at $C_{YCl,org,0} = 0.4$ kmol m^{-3}

Solid lines: D_{EDTA} and D_{Cu} estimated with complexation constants listed in Table 4.

0.026, respectively. By using the determined equilibrium constants, the D_{EDTA} and D_{Cu} were estimated, as shown in Figures 2 and 3 by solid lines. The extraction model could roughly predict the experimental results. $K_{XY,j}$ decreased as j increased, and the equilibrium constants relating Cu complexes decreased in the order of K_{YCuHX}, K_{Y2CuX}, and $K_{Y3CuOHX}$, i.e. the equilibrium constants decreased as the number of TOMA$^+$ cations of the complex in the organic phase increased. The estimated concentration profiles of the respective compounds against pH are shown in Figures 4 and 5, in which the aqueous solutions containing only EDTA, and both EDTA and Cu were shown, respectively. For both cases, the valence number of major EDTA anion in aqueous phase increased with pH, as follows: H$_2$X^{2-}, HX^{3-} and X^{4-}. Although $C_{H_2X^{2-},aq}$ at around pH=5.0, $C_{HX^{3-},aq}$ at around pH=8.7, and $C_{X^{4-},aq}$ at around pH=14 were attaining the maximum concentrations for respective major ions and were almost same, $C_{Y_2H_2X,org}$ was greater than $C_{Y_3HX,org}$ or $C_{Y_4X,org}$, and they were almost the same. In the case of the aqueous solution containing Cu, the concentrations of major Cu complexes with TOMACl in organic phase decreased in the order of $C_{Y_2CuX,org}$ and $C_{Y_3CuOHX,org}$ even though the maximum $C_{CuX^{2-},aq}$ and $C_{CuOHX^{3-},aq}$ were almost same. In the lower pH range, lower valence anions of EDTA ion and Cu-EDTA complex were dominant, which should require fewer TOMA$^+$ cations to form complex in the organic phase. However, in the higher pH range, higher valence anions of EDTA ion and Cu complex were dominant, and more TOMA$^+$ cations were necessary for these anions to form complexes. Accordingly, this type of complex exhibited steric effects, and the extraction efficiency was lowered. With regard to CuX^{2-}, although $C_{CuX^{2-},aq}$ kept almost constant in the wide range of pH from 5 to 11, $C_{Y_2CuX,org}$ decreased as pH increased. As pH increased, $C_{Cl,aq}$ increased and $C_{YCl,org}$ decreased, and the profiles of $C_{Cl,aq}$ and $C_{YCl,org}$ should make extraction efficiency lower as pH increased, as represented by eqs. (6)–(10) and (25)–(28). Accordingly, while the extraction operation was favorable in the lower pH range to remove both Cu and

EDTA from the wastewater, it is necessary to conduct the operation in a relatively high pH range because of the conditions of the electroless copper plating wastewater.

Table 3. Dissociation constants of EDTA and Cu in aqueous phase, cited from [17].

$K_{X,1}$	[kmol m^{-3}]	1.00×10^{-1}	$K_{CuOH,1}$	[kmol^{-1} m^3]	3.98×10^{-17}
$K_{X,2}$	[kmol m^{-3}]	1.91×10^{-3}	$K_{CuOH,2}$	[kmol^{-1} m^3]	2.51×10^{-18}
$K_{X,3}$	[kmol m^{-3}]	5.75×10^{-4}	$K_{CuX,1}$	[(kmol^{-1} m^3)^2]	3.16×10^{-21}
$K_{X,4}$	[kmol m^{-3}]	2.09×10^{-7}	$K_{CuX,2}$	[(kmol^{-1} m^3)^2]	1.26×10^{-24}
$K_{X,5}$	[kmol m^{-3}]	7.59×10^{-12}	$K_{CuX,3}$	[(kmol^{-1} m^3)^2]	2.51×10^{-23}

Table 4. Equilibrium constants of EDTA-TOMAC and Cu-EDTA-TOMACl complexes.

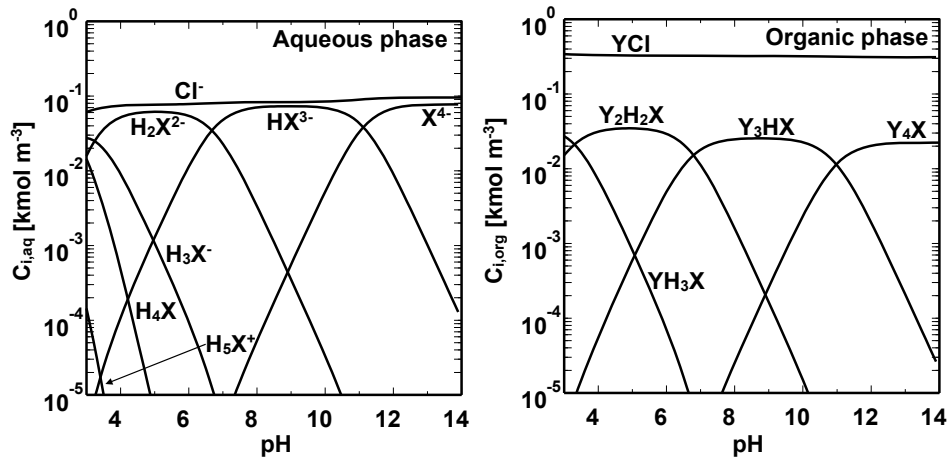|					
$K_{XY,1}$	[–]	1.7×10^{-1}	K_{Y2CuX}	[–]	1.7×10^{-2}
$K_{XY,2}$	[–]	2.7×10^{-2}	K_{YCuHX}	[–]	6.4×10^{-2}
$K_{XY,3}$	[–]	4.9×10^{-3}	$K_{Y3CuOHX}$	[–]	2.7×10^{-3}
$K_{XY,3}$	[–]	2.0×10^{-3}			

Figure 4. Effects of pH on concentration profiles of EDTA ions with TOMACl at liquid–liquid equilibrium (under the same conditions as in Figure 2).
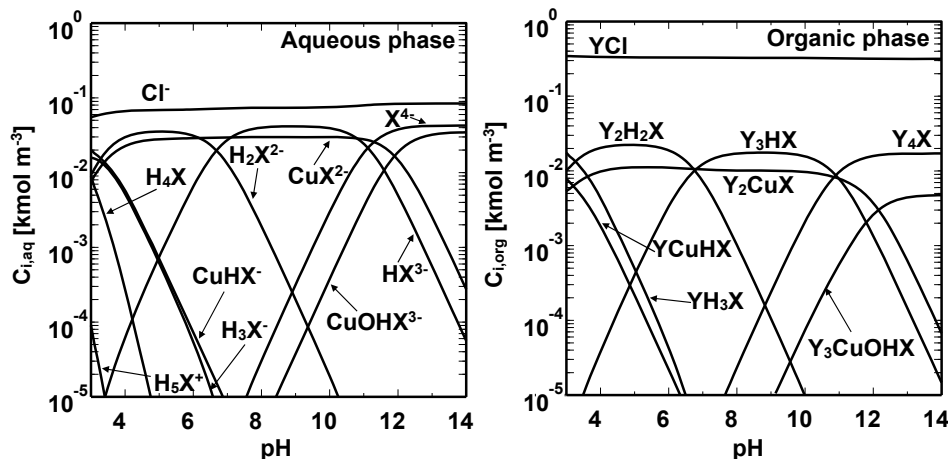

Figure 5. Effects of pH on concentration profiles of EDTA ions and Cu-EDTA complexes with TOMACl at liquid–liquid equilibrium (under the same conditions as in Figure 3).

4. Conclusion

The kerosene solution of TOMACl could extract and remove both EDTA-copper complexes and EDTA ions from model electroless copper plating wastewater. The species of copper-EDTA complexes and EDTA ions in aqueous phase changed according to pH, and the fractional removals and distribution ratios of both copper-EDTA complexes and EDTA ions decreased as pH increased. The equilibrium constants of respective copper-EDTA complexes and EDTA ions in aqueous phase with TOMACl in organic phases were determined, and the contributions of respective complexes and ions to the removal of copper and EDTA were discussed. The valence numbers of the major complexes and ions in aqueous phase increased with pH, and accordingly the number of TOMA$^+$ cations needed to chelate and extract into organic phase became larger in the higher pH range, causing lower removal of both copper and EDTA due to steric hindrance effects.

Appendix

The material balances of EDTA, Cu, and TOMACl at liquid–liquid equilibrium can be expressed as;

$$FC_{Cu,aq,0} + SC_{Cu,org,0} = RC_{Cu,aq} + EC_{Cu,org} \qquad (A1)$$

where $C_{Cu,aq,0}$, $C_{Cu,aq}$, $C_{Cu,org,0}$, and $C_{Cu,org}$ were expressed as;

$$C_{Cu,aq,0} = C_{Cu^{2+},aq,0} + C_{CuHX^-,aq,0} + C_{CuX^{2-},aq,0} + C_{CuOHX^{3-},aq,0} + C_{Cu(OH)_4^{2-},aq,0} + 2C_{Cu_2(OH)_2^{2+},aq,0}$$

$$C_{Cu,aq} = C_{Cu^{2+},aq} + C_{CuHX^-,aq} + C_{CuX^{2-},aq} + C_{CuOHX^{3-},aq} + C_{Cu(OH)_4^{2-},aq} + 2C_{Cu_2(OH)_2^{2+},aq}$$

$$C_{Cu,org,0} = C_{YCuHX,org,0} + C_{Y_2CuX,org,0} + C_{Y_3CuOHX,org,0} + C_{Y_2Cu(OH)_4,org,0}$$

$$C_{Cu,org} = C_{YCuHX,org} + C_{Y_2CuX,org} + C_{Y_3CuOHX,org} + C_{Y_2Cu(OH)_4,org}$$

$$FC_{EDTA,aq,0} + SC_{EDTA,org,0} = RC_{EDTA,aq} + EC_{EDTA,org} \qquad (A2)$$

where $C_{EDTA,aq,0}$, $C_{EDTA,aq}$, $C_{EDTA,org,0}$, and $C_{EDTA,org}$ were expressed as;

$$C_{EDTA,aq,0} = C_{H_5X^+,aq,0} + C_{H_4X,aq,0} + C_{H_3X^-,aq,0} + C_{H_2X^{2-},aq,0} + C_{HX^{3-},aq,0} + C_{X^{4-},aq,0}$$
$$+ C_{CuHX^-,aq,0} + C_{CuX^{2-},aq,0} + C_{CuOHX^{3-},aq,0}$$

$$C_{EDTA,aq} = C_{H_5X^+,aq} + C_{H_4X,aq} + C_{H_3X^-,aq} + C_{H_2X^{2-},aq} + C_{HX^{3-},aq} + C_{X^{4-},aq}$$
$$+ C_{CuHX^-,aq} + C_{CuX^{2-},aq} + C_{CuOHX^{3-},aq}$$

$$C_{EDTA,org,0} = C_{YH_3X^-,org,0} + C_{Y_2H_2X,org,0} + C_{Y_3HX,org,0} + C_{Y_4X,org,0}$$
$$+ C_{YCuHX,org,0} + C_{Y_2CuX,org,0} + C_{Y_3CuOHX,org,0}$$

$$C_{EDTA,org} = C_{YH_3X^-,org} + C_{Y_2H_2X,org} + C_{Y_3HX,org} + C_{Y_4X,org}$$
$$+ C_{YCuHX,org} + C_{Y_2CuX,org} + C_{Y_3CuOHX,org}$$

$$SC_{\text{YCl,S}} = EC_{\text{YCl,E}} \tag{A3}$$

where $C_{\text{YCl,S}}$, and $C_{\text{YCl,E}}$ were expressed as;

$$C_{\text{YCl,S}} = C_{\text{YCuHX,org},0} + 2C_{\text{Y}_2\text{CuX,org},0} + 3C_{\text{Y}_3\text{CuOHX,org},0} + 2C_{\text{Y}_2\text{Cu(OH)}_4,\text{org},0}$$
$$+ C_{\text{YH}_3\text{X,org},0} + 2C_{\text{Y}_2\text{H}_2\text{X,org},0} + 3C_{\text{Y}_3\text{HX,org},0} + 4C_{\text{Y}_4\text{X,org},0} + C_{\text{YCl,org},0}$$

$$C_{\text{YCl,E}} = C_{\text{YCuHX,org}} + 2C_{\text{Y}_2\text{CuX,org}} + 3C_{\text{Y}_3\text{CuOHX,org}} + 2C_{\text{Y}_2\text{Cu(OH)}_4,\text{org}}$$
$$+ C_{\text{YH}_3\text{X,org}} + 2C_{\text{Y}_2\text{H}_2\text{X,org}} + 3C_{\text{Y}_3\text{HX,org}} + 4C_{\text{Y}_4\text{X,org}} + C_{\text{YCl,org}}$$

Here, F, S, R, and E stand for the volumes of feed, solvent, and aqueous and organic phases at equilibrium, respectively, and each aqueous or organic phase was assumed to be constant before and after experiment, as mentioned in assumption 4, i.e., $F = R$ and $S = E$.

Nomenclature

$C_{i,\text{aq}}$:	molar concentration of component i in aqueous phase	[kmol m^{-3}]
$C_{i,\text{org}}$:	molar concentration of component i in aqueous phase	[kmol m^{-3}]
D_{Cu}:	distribution ratio of copper defined in eq. (40)	[–]
D_{EDTA}:	distribution ratio of EDTA defined in eq. (39)	[–]
E:	volume of organic phase at equilibrium	[m^3]
F:	volume of feed phase	[m^3]
$K_{\text{CuX},1}$:	complexation constant of Cu and EDTA in eq. (16)	[kmol^{-2} m^6]
$K_{\text{CuX},2}$:	complexation constant of Cu and EDTA in eq. (17)	[kmol^{-1} m^3]
$K_{\text{CuX},3}$:	complexation constant of Cu and EDTA in eq. (18)	[kmol^{-2} m^6]
$K_{\text{CuOH},1}$:	complexation constant of Cu and OH$^-$ in eq. (19)	[kmol^{-1} m^3]
$K_{\text{CuOH},2}$:	complexation constant of Cu and OH$^-$ in eq. (20)	[kmol^{-3} m^9]
$K_{\text{X},j}$:	dissociation constant of EDTA in eqs. (6)–(10)	[kmol m^{-3}]
$K_{\text{XY},j}$:	extraction equilibrium constant of EDTA and TOMACl complex in eqs. (25)–(28)	[–]
K_{YCuHX}:	extraction equilibrium constant of Cu-EDTA-TOMACl complex in eq. (33)	[–]
$K_{\text{Y}_2\text{CuX}}$:	extraction equilibrium constant of Cu-EDTA-TOMACl complex in eq. (34)	[–]
$K_{\text{Y}_3\text{CuOHX}}$:	extraction equilibrium constant of Cu-OH-EDTA-TOMACl complex in eq. (35)	[–]
$K_{\text{Y}_2\text{Cu(OH)}_4}$:	extraction equilibrium constant of Cu-OH-TOMACl complex in eq. (36)	[–]
R:	volume of aqueous phase at equilibrium	[m^{-3}]
r_{Cu}:	fractional removal of copper ion defined in D_{EDTA} defined in eq. (38)	[–]
r_{EDTA}:	fractional removal of EDTA defined in D_{EDTA} defined in eq. (37)	[–]
S:	volume of solvent phase	[m^3]

Symbols

Cl$^-$: chloride ion

Cu: overall copper

Cu^{2+}: Cu ion

CuHX$^-$: Cu-EDTA complex in aqueous phase in eq. (11)

Cu(OH)$_4{}^{2-}$: Cu-OH complex in aqueous phase in eq. (14)

Cu$_2$(OH)$_2{}^{2+}$: Cu-OH complex in aqueous phase in eq. (15)

CuOHX^{3-}: Cu-OH-EDTA complex in aqueous phase in eq. (13)

CuX^{2-}: Cu-EDTA complex in aqueous phase in eq. (12)

E: extract

EDTA: overall EDTA

H$_4$X: EDTA molecule in aqueous or organic phase

H$_{4-j}$X$^{(j)-}$ (j=1, 2, 3 or 4): EDTA ion in aqueous phase

$\overline{Y_jH_{4-j}X}$ (j=1, 2, 3 or 4): EDTA-TOMACl complex in organic phase in eqs. (21)-(24)

S: solvent

$\overline{YCl}$: TOMACl molecule in organic phase

$\overline{YCuHX}$: Cu-EDTA-TOMACl complex in organic phase in eqs. (29)

$\overline{Y_2Cu(OH)_4}$: Cu-OH-TOMACl complex in organic phase in eq. (32)

$\overline{Y_3CuOHX}$: Cu-OH-EDTA-TOMACl complex in organic phase in eq. (31)

$\overline{Y_2CuX}$: Cu-EDTA-TOMACl complex in organic phase in eq. (30)

Subscripts

0: initial

aq: aqueous phase

i: component i

org: organic phase

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