

Removal of EDTA-Cu complex from wastewater of electroless copper plating by solvent extraction with quaternary ammonium salt

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1. Introduction

Electroless copper plating is a technique for coating copper on the surface of a material. It can be applied to surfaces such as plastics and resins. It is used for plating printed circuit boards.

Table 1 shows an example of a electroless copper plating solution[1]. Since copper and ethylenediaminetetraacetic acid (EDTA) are contained in the plating solution. They are one of environmental pollutant and harmful for living things. it is necessary to remove copper and EDTA before discharging it. Conventionally, copper in water is removed by adjusting the pH and adding a precipitation agent to form a precipitate of hydroxide ($\text{Cu}(\text{OH})_2$).

EDTA work as a stabilizer to prevent precipitation. EDTA is a kind of chelating agent and forms stable water-soluble complexes with Cu even under acidic conditions. Therefore, it is difficult to remove copper from electroless copper plating wastewater containing EDTA by conventional wastewater treatment. Currently, representative treatment methods are electrolysis method and Fenton method. Electrolytic method is used to reduce and deposit copper by electrolysis. the Fenton method was used to oxidize and decompose EDTA [2]. Since these methods are complicated and consume a lot of energy, there is a need for a new wastewater treatment method.

In general, solvent extraction was used for treatment of wastewater contained metals. Tri-n-octylmethylammonium chloride (TOMACl) is one of the quaternary ammonium salts and is being studied as an extractant for metals such as chromium and mercury, as well as organic acids. It has also been applied for in solvent extraction for highly concentrated metal effluents.

In this study, the removal of Cu-EDTA complex in wastewater from Electroless copper plating was studied by the solvent extraction with quaternary ammonium as extractant. So, liquid-liquid equilibrium using organic solvent with extractant was measured and calculated with extraction equilibrium constants.

2. Experimental

The experimental conditions of extraction equilibrium are shown in Table 2. Here organic solvent was used as the diluent of the extractant. Aqueous phase is solution of $\text{EDTA} \cdot 2\text{Na}$ and CuSO_4 . The aqueous solution of the copper were prepared by dissolution of Copper(II) Sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in deionized water. The aqueous solutions of the EDTA were prepared by the dissolution of ethylenediaminetetraacetic acid disodium dihydride salt ($\text{EDTA} \cdot 2\text{Na} \cdot 2\text{H}_2\text{O}$) in deionized water. pH

in the aqueous phase was adjusted by NaOH.

The experiments were carried out in a 50mL conical flask with a screw top. Equal volumes (20mL) of aqueous and organic solutions were stirred with thermostatic bath for 3 days at 300 K to attain the equilibrium. After the equilibrium, these two phases were separated by separating funnel.

The pH value in the aqueous phase was measured by digital pH meter (F-74, HORIBA). The pH did not change before and after equilibrium. The concentration of Cu in aqueous phase was determined using ICP-OES (5100 VDV, Agilent Technologies), and the concentration of EDTA in aqueous phase was determined using chelatometric titration and spectrophotometer (UV2000, Simadzu). In organic phase was calculated by material balance.

Table 1 An example of solution of electroless copper plating

Component		
CuSO_4	[kmol m^{-3}]	0.04-0.063
EDTA	[kmol m^{-3}]	0.086-0.103
Methanal	[kmol m^{-3}]	0.043
NaOH	[kmol m^{-3}]	0.25
pH	[-]	12.5

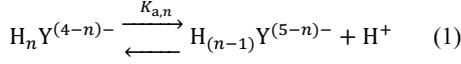
Table 2 Experimental conditions of liquid-liquid extraction

Feed		
Aqueous solution of $\text{EDTA} \cdot 2\text{Na}$, CuSO_4		
Initial conc. of EDTA in aqueous phase, $C_{\text{EDTA, aq}, 0}$	[kmol m^{-3}]	0.1
Initial conc. of CuSO_4 in aqueous phase, $C_{\text{Cu, aq}, 0}$	[kmol m^{-3}]	0.04
Volume of Feed, $V_{\text{aq}, 0}$	[m^3]	2.0×10^{-5}
pH ₀		4.0-14.0
Solvent		
Heptanol, Octanol, Decanol, Heptane, Toluene, Kerosine, Methyl benzoate, Benzaldehyde, Benzyl alcohol		
Extractant		TOMACl
Initial conc. of TOMACl in solvent, $C_{\text{TOMACl, org}, 0}$	[kmol m^{-3}]	0.4
Volume of solvent, $V_{\text{org}, 0}$	[m^3]	2.0×10^{-5}
Time, t	[h]	300
Temperature, T	[T]	72

3. Result and Discussion

3.1. Basic equations by EDTA-Cu removal models

Dissociation equilibrium of EDTA can be represented by Eq. (1) and (2).



$$K_{a,n} = \frac{c_{H_{(n-1)} Y^{(5-n)-},aq,1} c_{H^+,aq,1}}{c_{H_n Y^{(4-n)-},aq,1}} \quad (0 \leq n \leq 4) \quad (2)$$

Where H_4Y is represented by EDTA. $K_{a,n}$ is dissociation constant of EDTA, listed table3 [3]. Fig. 1 shows the fractional composition of EDTA species.

Table 3 Acid dissociation constant of EDTA

$K_{a,1}$	[kmol m ⁻³]	0.01
$K_{a,2}$	[kmol m ⁻³]	0.0022
$K_{a,3}$	[kmol m ⁻³]	6.9×10^{-7}
$K_{a,4}$	[kmol m ⁻³]	5.5×10^{-11}

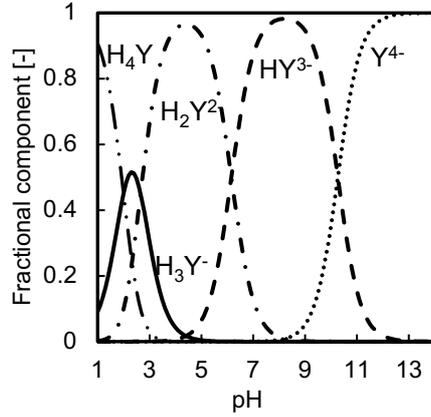
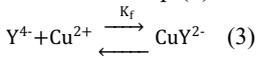


Fig. 1 Fractional composition of EDTA species on pH

Eq. (3) and (4) shows complex formation reaction of Cu and EDTA. Eq. (5) shows fractional ratio of Cu^{2+} .

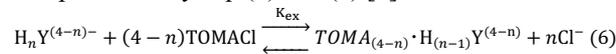


$$K_f = \frac{c_{CuY^{2-},aq,1}}{c_{Y^{4-},aq,1} c_{Cu^{2+},aq,1}} = 6.3 \times 10^{18} \quad (4)$$

$$F = \frac{c_{Cu^{2+},aq,1}}{c_{CuY^{2-},aq,1} + c_{Cu^{2+},aq,1}} \quad (5)$$

Where K_f is complex formation constant. Fig. 2 shows fraction of Cu^{2+} on $C_{Cu,aq,0}=0.04$ kmol m⁻³, $C_{EDTA,aq,0}=0.1$ kmol m⁻³. Cu-EDTA forms strongly stable complex. therefore, in this experiment, calculated with an assumption Cu^{2+} in aqueous phase was formed completely with EDTA.

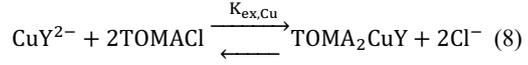
Liquid-liquid extraction equilibrium with TOMACl can be represented by Eq. (6) and (7) [4].



$$K_{ex,H_n Y^{(4-n)-}} = \frac{c_{TOMA_{(4-n)} \cdot H_{(n-1)} Y^{(4-n)},org,1} c_{Cl^-,aq,1}^{(4-n)}}{c_{H_n Y^{(4-n)-},aq,1} c_{TOMACl,org,1}^{(4-n)}} \quad (0 \leq n \leq 3) \quad (7)$$

Where K_{ex} is extraction equilibrium constant.

Eq. (8) and (9) show extraction equilibrium Cu with TOMACl.



$$K_{ex,Cu} = \frac{c_{TOMA_2 \cdot CuY,org,1} c_{Cl^-,aq,1}^2}{c_{CuY^{2-},aq,1} c_{TOMACl,org,1}^2} \quad (9)$$

Where $K_{ex,Cu}$ is extraction constant of EDTA and Cu.

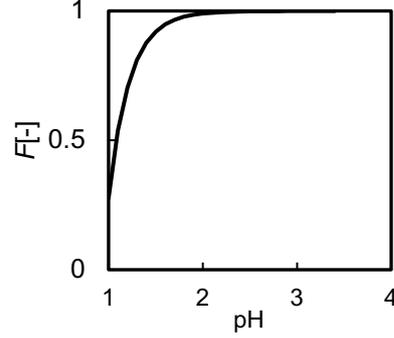


Fig. 2 Fraction of Cu^{2+} on aqueous phase

Eq. (10) shows material balance equations for liquid-liquid equilibrium.

$$C_{i,aq,0} V_{aq} + C_{i,org,0} V_{org} = C_{i,aq,1} V_{aq} + C_{i,org,1} V_{org} \quad (10)$$

Eq. (11) shows the fractional removal of component i .

$$R_i = \frac{(C_{i,aq,0} - C_{i,aq,1}) \times V_{aq}}{C_{i,aq,0} \times V_{aq}} \quad (11)$$

Eq. (12) and (13) show distribution ratio of EDTA and Cu.

$$D_{EDTA} = \frac{c_{TOMA_2 \cdot H_2Y,org,1} + c_{TOMA_3 \cdot HY,org,1} + c_{TOMA_4 \cdot Y,org,1} + c_{TOMA_2 \cdot CuY,org,1}}{c_{H_2Y^{2-},aq,1} + c_{HY^{3-},aq,1} + c_{Y^{4-},aq,1} + c_{CuY^{2-},aq,1}} \quad (12)$$

$$D_{Cu} = \frac{c_{TOMA_2 \cdot CuY,org,1}}{c_{CuY^{2-},aq,1}} = K_{ex,Cu} \frac{c_{TOMACl,org,1}^2}{c_{Cl^-,aq,1}^2} \quad (13)$$

Where V_{aq} and V_{org} is volume of liquid of aqueous phase and organic phase. $C_{i,org,0}$ and $C_{i,org,1}$ were calculated with an assumption that the volumes of aqueous and organic phases were constant before and after the experiment.

3.2. Removal of EDTA and Cu with various solvent

Liquid-liquid extraction was performed using Heptanol, octanol, decanol, benzyl alcohol, Heptane, heptanol, toluene, benzaldehyde, and methyl benzoate at $T=300$ K, $C_{EDTA,0,aq}=0.1$ kmol m⁻³, $C_{Cu,0,aq}=0$ kmol m⁻³ and $C_{TOMACl,0,aq}=0.0$ kmol m⁻³ pH4.4-12.0. EDTA was not removed by either solvent.

Liquid-liquid extraction was performed using heptane, at $T=300$ K, $C_{EDTA,0,aq}=0$ kmol m⁻³, $C_{Cu,0,aq}=0.04$ kmol m⁻³, $C_{TOMACl,0,aq}=0.0$ kmol m⁻³, pH3.3. Cu was not removed. As a results, EDTA and Cu present as ion in aqueous

phase. Thus, EDTA and Cu were not removed by either solvent.

3.3. Solvent extraction of EDTA Cu with quaternary ammonium salt

Fig.3 shows experimental results of the fractional removal of EDTA using kerosene at $T=300\text{ K}$, $C_{\text{EDTA,aq},0}=0.1\text{ kmol m}^{-3}$, $C_{\text{Cu,aq},0}=0\text{ kmol m}^{-3}$ and $C_{\text{TOMACl,org},0}=0.4\text{ kmol m}^{-3}$ as shown by plot.

Fractional removal decreased as pH increased.

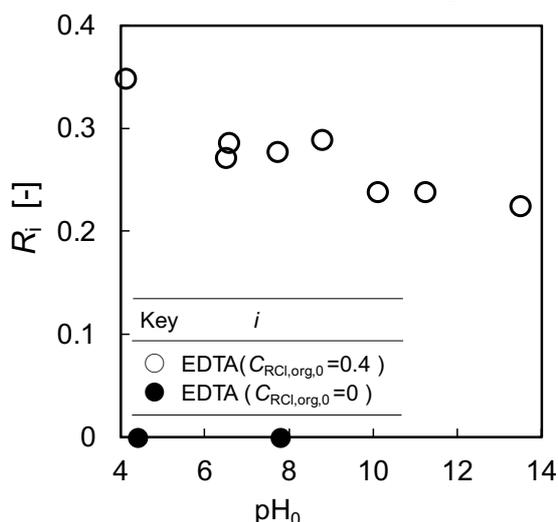


Fig. 3 Effect of pH_0 on fractional removal of EDTA

Fig. 4 shows distribution ratio of EDTA. pH increased, and the distribution ratio of EDTA decreased. From experimental results, the extraction equilibrium constants of EDTA were calculated and assuming that there is only one species of EDTA ion, H_2Y^{2-} , HY^{3-} , Y^{4-} at pH 4.1, pH 7.7, and pH 13.5. Key shows experimental result and line was fitted along by result using $K_{\text{ex,H}_n\text{Y}^{(4-n)-}}$.

Table 4 Extraction equilibrium constants

$K_{\text{ex,H}_2\text{Y}^{2-}}$	[-]	0.0236
$K_{\text{ex,HY}^{3-}}$	[-]	0.00684
$K_{\text{ex,Y}^{4-}}$	[-]	0.00203
$K_{\text{ex,Cu}}$	[-]	0.0234

Fig. 5 shows the results of EDTA ions concentration in the aqueous phase and TOMACl concentration in the organic phase at equilibrium. With this reaction, the concentration of Cl^- is increased.

H_2Y^{2-} is major in acidic condition, HY^{3-} is major in neutral pH and Y^{4-} is major in basic condition of EDTA ions. For each EDTA ion, the same number of TOMACl reacts as the valence of the EDTA ion. The more EDTA ion valences, the greater the number of TOMACl react ion exchange to EDTA ions. In case of extraction equilibrium, extraction reaction of TOMACl with Y^{4-} is difficult to progress at compared to HY^{2-} , also due to increasing steric hindrance between TOMACl and EDTA ions. H_2Y^{2-} ,

HY^{3-} , Y^{4-} are also ranked in the order of the quantity of K_{ex} value.

In this experiment, the tendency that the distribution of EDTA in acidity solution was larger than in basic solution.

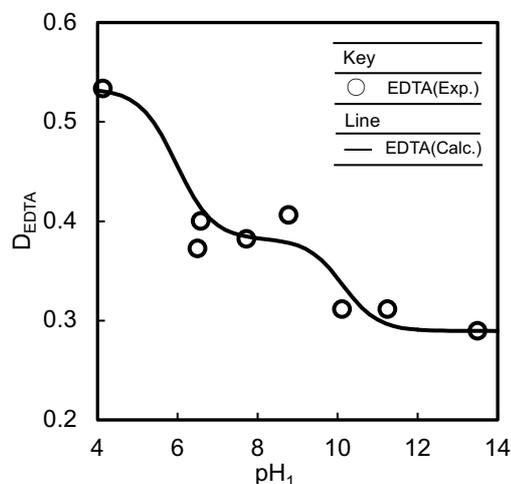


Fig. 4 Effect of pH_1 on distribution of EDTA

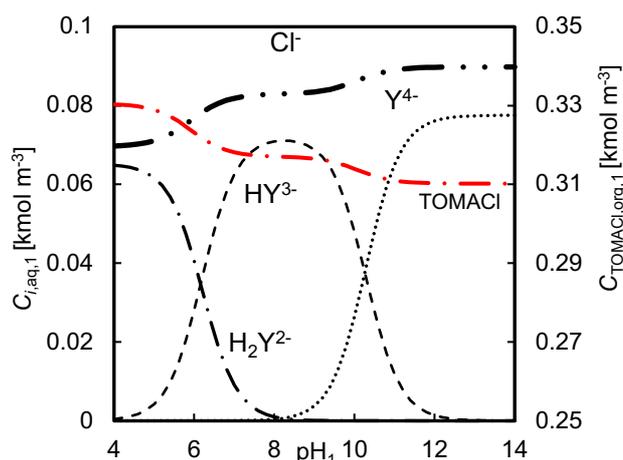


Fig. 5 Concentration of EDTA ions and TOMACl at equilibrium

Fig. 6 shows fractional removal of Cu and EDTA at $C_{\text{EDTA,aq},0}=0.1\text{ kmol m}^{-3}$, $C_{\text{Cu,aq},0}=0.04\text{ kmol m}^{-3}$, $C_{\text{TOMACl,aq},0}=0.4\text{ kmol m}^{-3}$ as a plot. Both EDTA and Cu were removed from the aqueous phase. Fig. 7 shows the distribution ratio of EDTA and Cu. the extraction equilibrium constant of Cu was calculated and are listed in Table 4. Extraction equilibrium constant was calculated using this result. Key shows experimental result and lines were fitted along by result using extraction equilibrium constants of EDTA and Cu.

According to Fig. 7 in the high pH region above pH 13, there is a difference between the experimental and calculated results. the effect of hydroxide ions must be considered. OH^- reacts with Cu^{2+} in a competitive response with EDTA.

Fig. 8 shows the concentration of EDTA ions and Cu in aqueous phase and TOMACl in organic phase. The concentration of CuY^{2-} in the aqueous phase was

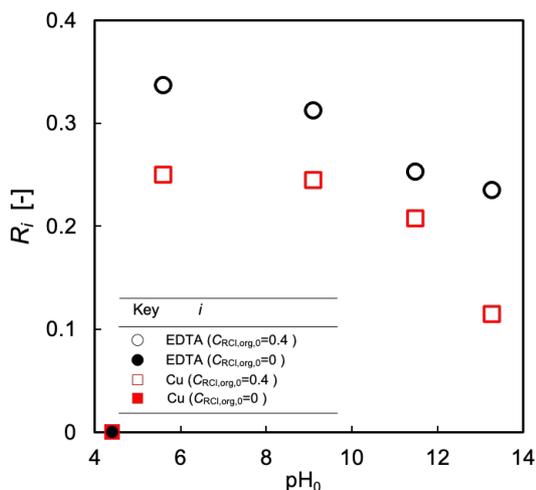


Fig.6 Effect of pH_0 on fractional removal of EDTA and Cu

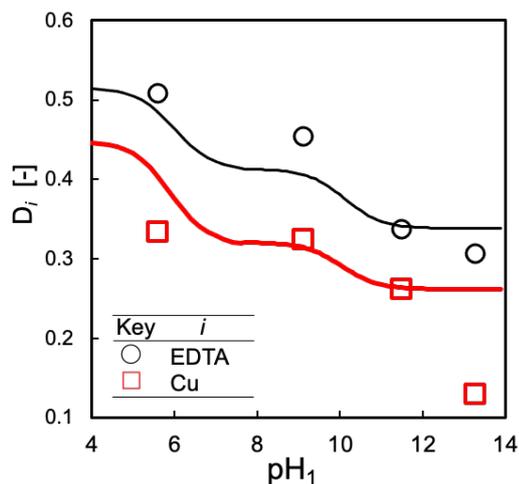


Fig.7 Effect of pH_1 on distribution of EDTA and Cu

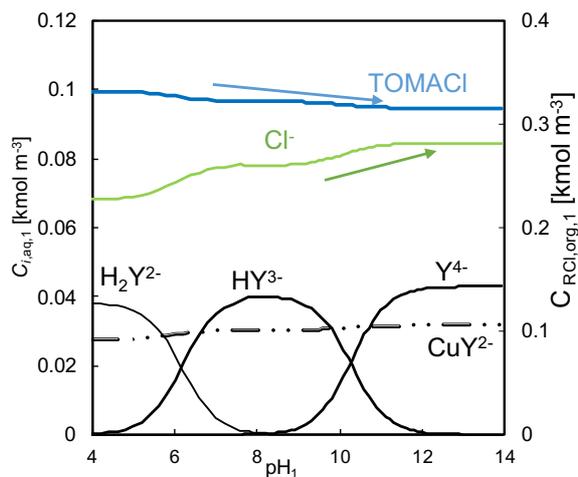


Fig.8 Concentration of EDTA ions, CuY and TOMACl at equilibrium

independent against pH. As pH was increased, extraction ratio of Cu is decreased. Distribution ratio was affected by concentration of Cl^- and TOMACl. Figure 8 shows that as pH increased, concentration of Cl^- was increased and TOMACl decreased. Therefore, increasing with pH, it had been indicated that the distribution ratio of Cu decreases.

However, the actual plating wastewater is below pH 12, copper is able to be removed by solvent extraction.

4. Conclusion

In the liquid-liquid equilibrium extraction of EDTA using TOMACl as an extractant, EDTA-Cu complex was extracted.

The extraction behavior was shown by equations. the solvent extraction method using TOMACl was proposed as one of the treatment methods for wastewater from electroless copper plating.

Acknowledgement

Analysis of Cu concentration was performed using ICP-OES at Open Facility Center, Materials Analysis Division, Tokyo Institute of Technology.

Nomenclature

C	Concentration in liquid phase	$[\text{kmol m}^{-3}]$
V	Volume of liquid phase	$[\text{m}^3]$
D	Distribution ratio	$[-]$
E	Extraction yield	$[-]$
K_{ex}	Extraction equilibrium constant	$[-]$
K_a	Acid dissociation constant	$[\text{m}^3 \text{ kmol}^{-1}]$
n	Valency of ion	$[-]$
H_4Y	EDTA free acid	
TOMACl	Tri-n-octylmethyl ammonium chloride	

Subscript

0	At initial state
1	At equilibrium state
i	Component i
aq	In aqueous phase
org	In organic phase

4. References

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