

## Recovery of copper from simulated ammoniacal spent etchant using sterically hindered beta-diketone

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**Abstract:** The solvent extraction of copper from simulated ammoniacal spent etchant with 1-(4'-dodecyl)-phenyl-3-tertiary butyl-1, 3-octadione (HR) was studied, and a model of extraction isotherm was proposed and verified with equilibrium extraction constant. The influence of equilibration time, extractant concentration and phase ratio on the extraction of copper was studied at (298±0.5) K. For the spent etching solutions containing 112.98 g/L Cu, 6 mol/L NH<sub>3</sub> and 1 mol/L NH<sub>4</sub><sup>+</sup>, the optimal solvent extraction condition of copper was obtained in one-stage solvent extraction at phase ratio of 5:4 with 40% HR in sulphonated kerosene for 5 min. The copper concentration in the raffinate decreased to 63.24 g/L and raffinate can be favorably recycled to the etching solution. The stripping studies were carried out with the simulated copper spent electrolyte containing 30 g/L Cu and 180 g/L H<sub>2</sub>SO<sub>4</sub>. The stripping ratio is 98.27% from the loaded organic phase after one-stage stripping at phase ratio of 1:2 at (298±0.5) K.

**Key words:** spent ammoniacal etchant; copper recovery; solvent extraction; beta-diketone

### 1 Introduction

Printed circuit boards (PCBs) are important components of modern electronic products, which have generated more than 40 billion US dollars globally in 2009 [1–3]. The manufacture of PCBs involves several technical processes, and etching is one of the most important steps. According to the design of PCB [4], the unmasked copper is chemically dissolved into the etchant and the desired circuit pattern is produced. Numerous etching solutions have been used including ferric chloride solution, chromic acid/sulfuric acid solution, sulfuric acid/hydrogen peroxide solution, hydrochloride/hydrogen peroxide solution, acidic copper chloride solution and ammoniacal spent etchant (ammoniacal copper chloride). The ammoniacal etchant presents advantages of fast etching, stability and high efficiency, so it is widely used in the PCB process. With the rapid growth of PCB industry, the total volume of generated spent ammoniacal etchant keeps increasing. Based on a market analysis in China conducted in 2009 [5], it is estimated that 600 t ammoniacal spent etchant is produced every day by local PCB plants. Copper presented in ammoniacal spent etchant must be

recovered due to economical and environmental reasons.

Numerous methods such as chemical precipitation [6], flotation [7], adsorption [8], evaporation [9], ion exchange [10], electrolysis [11], solvent extraction [12–15], membrane filtration [16] and membrane bioreactors [17] for copper removal from various process streams have been proposed in the journal papers and patents, the application of the solvent extraction process is considered an attractive option for the recovery of copper from spent etching solutions. Compared with other technologies, solvent extraction has the advantage that large volume of wastewater can be treated and recycled copper can be directly used in the plating bath process.

A number of extractants which extract copper from ammoniacal spent etchant was studied, including hydroxyoximes (LIX 84) and beta-diketons (LIX 54) [14, 18–19]. The advantages of hydroxyoximes were high efficiency and excellent selectivity, but the hydroxyoximes were easy to deteriorate under strong acid stripping conditions [20–21]. It was noted that LIX 54 provides easy stripping and fast kinetics, unexpectedly, it has recently been found that at the Escondida plant LIX 54 reacted with ammonia to give surface active molecules leading to the increase of

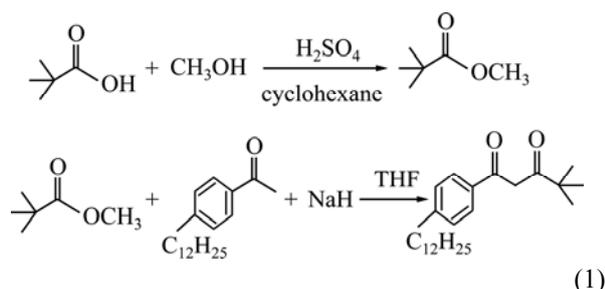
entrainment of aqueous phase in the loaded organic phases and the decrease of copper stripping kinetics [22]. Compared with LIX 54, the sterically hindered beta-diketone which displayed more excellent properties than LIX 54 [23] can overcome the problem of deterioration of the extractant in the ammoniacal solutions.

In the present work, the solvent extraction of copper from simulated ammoniacal spent etchant with a sterically hindered beta-diketone (HR) 1-(4'-dodecyl)-phenyl-3-tertiary butyl-1,3-octadione was studied. The extraction of copper was carried out at different extraction time, extractant concentrations and phase ratios, and a model of extraction isotherm was proposed. The loaded organic phases were stripped using simulated copper spent electrolyte, and the effects of stripping solutions with different concentrations of H<sub>2</sub>SO<sub>4</sub> on the stripping ratio were also examined.

## 2 Experimental

### 2.1 Materials

The extractant 1-(4'-dodecyl)-phenyl-3-tertiary butyl-1,3-octadione (HR) was made by Claisen condensation of 4'-dodecylacetophenone and 2, 2-dimethyl-methyl propionate in the presence of sodium hydride according to reaction (1) [24]. The crude product was acidified with sulfuric acid and washed with water and brine. After being dried by passing through anhydrous sodium sulfate, vacuum distillation (1.45 kPa) yielded the product in the heart cut (95% purity; 38% yield; bp: 210–228 °C).



The diluent for the extractant was a type of sulphonated kerosene purchased from Shanghai Rare-earth Chemical Co., Ltd. Analytical grade reagents H<sub>2</sub>SO<sub>4</sub>, CuCl<sub>2</sub>, NH<sub>4</sub>Cl and NH<sub>3</sub> were used to prepare aqueous solutions.

### 2.2 Experimental procedures

#### 2.2.1 Preparation of organic phase

An example was given for the preparation of the organic phase with 40% HR (volume fraction) as follows: 100 mL HR and some sulphonated kerosene were added into a 250 mL beaker and dissolved completely in this beaker, the solution was converted into a 250 mL

volumetric flask and calibrated in this volumetric flask by sulphonated kerosene, the volumetric flask was completely shaken, then organic phase with HR concentration of 40% was obtained.

#### 2.2.2 Solvent extraction

The solvent extraction was performed by a batch technique in thermostatted vessels at (298±0.5) K. The simulated ammoniacal spent etchant and organic phase with a certain phase ratio (abbreviated as O/A) were shaken for a certain period. Then the solutions were settled and separated by gravity. The copper concentration ( $\rho_{\text{Cu}}$ ) in raffinate was determined by iodimetry (calculated by Eq. (2)), and the copper concentration ( $\rho_{\text{Cu, org}}$ ) in the organic phase is calculated by mass balance Eq. (3).

$$\rho_{\text{Cu}} = \frac{\rho_1(V_1 - V_2)M_{\text{Cu}}}{V_3} \quad (2)$$

where  $\rho_1$  is the concentration of sodium thiosulfate standard solution;  $V_1$  is the volume of sodium thiosulfate standard solution used up in the end point;  $V_2$  is the volume of sodium thiosulfate standard solution used up in the blank;  $M_{\text{Cu}}$  represents the relative atomic mass of copper;  $V_3$  represents the volume of raffinate.

$$\rho_{\text{Cu, org}} = \frac{\rho_4V_4 - \rho_5V_5}{V_6} \quad (3)$$

where  $V_4$  represents the volume of simulated ammoniacal spent etchant;  $\rho_4$  represents the copper concentration in simulated ammoniacal spent etchant;  $V_5$  represents the volume of the raffinate;  $\rho_5$  represents the copper concentration in the raffinate; and  $V_6$  represents the volume of the loaded organic phase.

#### 2.2.3 Extraction isotherm

When the total volume of the aqueous and the organic phases was constant, the solutions with different phase ratios (O/A) were shaken for 30 min at (298±0.5) K. Then the solutions were settled and separated by gravity. The copper concentration  $\rho_{\text{Cu}}$  in raffinate was determined by iodimetry, and the copper concentration  $\rho_{\text{Cu, org}}$  in the organic phase was calculated by mass balance. The extraction isotherm was obtained.

#### 2.2.4 Stripping

The stripping was also performed using a batch technique in thermostatted vessels at (298±0.5) K. The simulated copper spent electrolyte and loaded organic phase with a certain phase ratio (O/A) were shaken for 30 min. Previous experiments show that this equilibration time was sufficient to achieve equilibrium. Then the solutions were settled and separated by gravity. The copper concentration in pregnant copper electrolyte was determined by iodimetry, whereas the copper

stripping ratio  $\eta_1$  can be calculated as:

$$\eta_1 = \frac{V_7(\rho_7 - \rho_8)}{V_9\rho_9 - V_{10}\rho_{10}} \times 100\% \quad (4)$$

where  $V_7$  represents the volume of simulated spent electrolyte;  $\rho_7$  represents the copper concentration in pregnant copper electrolyte;  $\rho_8$  represents the copper concentration in simulated spent electrolyte;  $V_9$  represents the volume of simulated ammoniacal spent etchant;  $\rho_9$  represents the copper concentration in simulated ammoniacal spent etchant;  $V_{10}$  represents the volume of raffinate;  $\rho_{10}$  represents the copper concentration in raffinate.

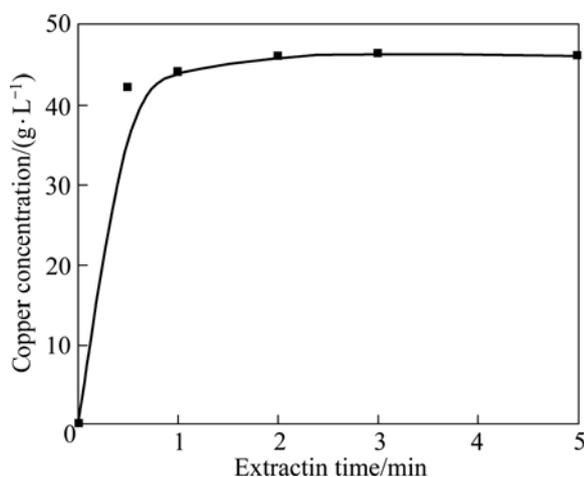
### 2.2.5 Stripping isotherms

When the total volume of the aqueous and the loaded organic phases was constant, the simulated spent electrolyte and the loaded organic phase with different phase ratios were shaken for 30 min at  $(298 \pm 0.5)$  K. Then the solutions were settled and separated by gravity. The copper concentration ( $\rho'_{\text{Cu}}$ ) in pregnant copper electrolyte was determined by iodimetry, and the copper concentration ( $\rho'_{\text{Cu, org}}$ ) in the unloaded organic phase was calculated by mass balance. The stripping isotherm was obtained.

## 3 Results and discussion

### 3.1 Extraction rate

The solvent extraction of copper from simulated ammoniacal spent etchant by HR was studied. Figure 1 shows the extraction rate of copper using the organic phase 40% of HR. The aqueous phase was simulated ammoniacal spent etchant containing 112.98 g/L Cu and 7 mol/L total ammonia ( $[\text{NH}_3] + [\text{NH}_4^+]$ ).

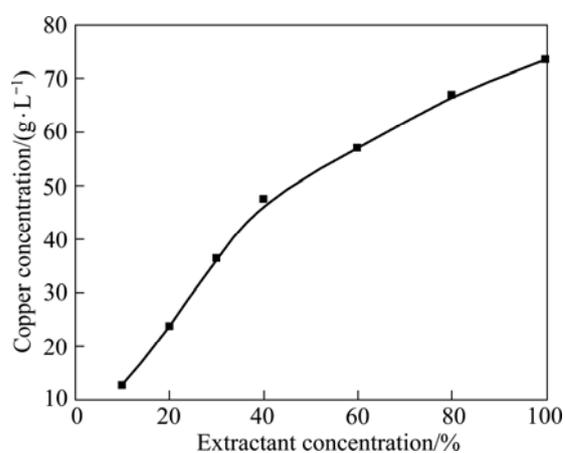


**Fig. 1** Effect of extraction time on copper recovery (Aqueous phase: 112.98 g/L Cu, 6 mol/L  $\text{NH}_3$ , 1 mol/L  $\text{NH}_4^+$  and 3.50 mol/L  $\text{Cl}^-$ . Organic phase: 40 HR in sulphonated kerosene)

It can be seen that the equilibrium was reached within 2 min of contact. Beyond this, no further improvement was achieved.

### 3.2 Effect of extractant concentration

In order to study the effect of extractant concentration on the extraction of copper, a series solvent extraction experiments were carried out from the simulated ammoniacal spent etchant with HR at a phase ratio of 1:1 and equilibrium pH of 10.82–10.87. The raffinates were analyzed and the influence of the concentrations of extractant on copper extraction was plotted in Fig. 2.



**Fig. 2** Effect of extractant concentration on copper recovery (Initial aqueous phase: 112.98 g/L Cu, 6 mol/L  $\text{NH}_3$ , 1 mol/L  $\text{NH}_4^+$  and 3.50 mol/L  $\text{Cl}^-$ )

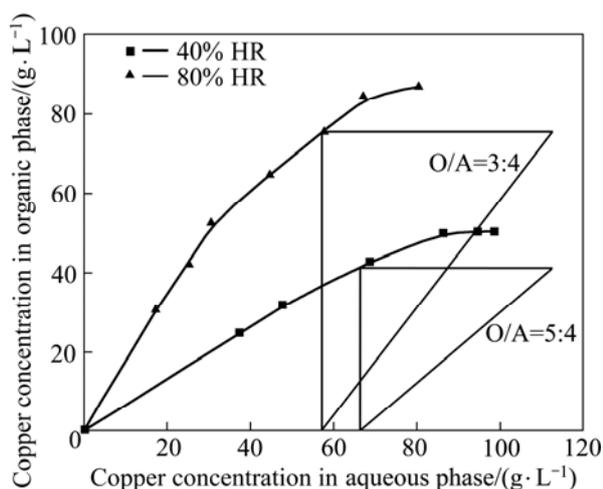
It was observed that the concentration of copper in the loaded organic phase increased from 12.79 to 73.56 g/L. When the extractant concentration was more than 40%, the increasing degree of copper concentration in organic phase decreased continuously.

### 3.3 Extraction isotherm

The maximum etching efficiency was obtained when ammoniacal solution contained 50–70 g/L copper and then gradually decreased when the copper concentration was 150–170 g/L [26]. Thus, in order to keep the etching efficiency constant and optimal, the etching solution must be continuously removed and regenerated. In the MECER process [14], the initial copper concentration of 120–130 g/L in the etching solution was reduced to 50–70 g/L with solvent extraction. To extract copper from the ammoniacal spent etchant, it was required to determine the number of extraction stages and the phase ratio, from which the extraction isotherm was constructed. The ammoniacal spent etchant containing 112.98 g/L copper for 40% or 80% HR was equilibrated at different phase ratios from 1:4 to 4:1. The aqueous and organic phases were analyzed and the McCabe–Thiele

plot was obtained, as shown in Fig. 3.

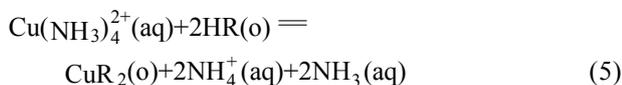
It was observed that single stage counter-current simulation studies at phase ratio of 5:4 for 40% HR and at phase ratio of 3:4 for 80% HR were carried out for the extraction of copper to confirm the above predictions. The copper concentration in raffinates is 63.24 g/L for 40% HR or 57.10 g/L copper for 80% HR, respectively.



**Fig. 3** Extraction isotherm for copper with 40% and 80% HR (Aqueous phase: 112.98 g/L Cu, 6 mol/L NH<sub>3</sub>, 1 mol/L NH<sub>4</sub><sup>+</sup> and 3.50 mol/L Cl<sup>-</sup>. Organic phase: 40% or 80% HR in sulphonated kerosene)

### 3.4 Simulated extraction isotherm

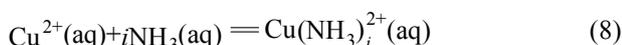
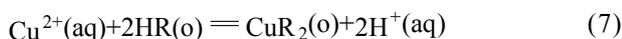
The equilibrium conditions can be checked as a basic study for mass transfer calculations. In previous study, ISMAEL and GAMEIRO [26] demonstrated that in ammoniacal copper chloride solution with an excess of NH<sub>3</sub>, complex Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> was the predominant metallic species. Thus, the extraction of copper with HR can be described as:



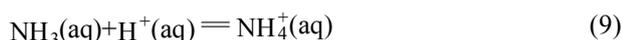
The extraction constant  $K_{\text{ex}}$  can be expressed as:

$$K_{\text{ex}} = \frac{[\text{CuR}_2]_{\text{o}}[\text{NH}_4^+]_{\text{aq}}^2[\text{NH}_3]_{\text{aq}}^2}{[\text{Cu}(\text{NH}_3)_4^{2+}]_{\text{aq}}[\text{HR}]_{\text{o}}^2} \quad (6)$$

On the other hand, reaction (5) can be expressed as:



where  $i=1, 2, 3$  and  $4$ , and



with the following equilibrium constants

$$K_6 = \frac{[\text{CuR}_2]_{\text{o}}[\text{H}^+]_{\text{aq}}^2}{[\text{Cu}^{2+}]_{\text{aq}}[\text{HR}]_{\text{o}}^2} \quad (10)$$

$$\beta_i = \frac{[\text{Cu}(\text{NH}_3)_i^{2+}]_{\text{aq}}}{[\text{Cu}^{2+}]_{\text{aq}}[\text{NH}_3]_{\text{aq}}^i} \quad (11)$$

$$K_8 = \frac{[\text{NH}_4^+]_{\text{aq}}}{[\text{NH}_3]_{\text{aq}}[\text{H}^+]_{\text{aq}}} \quad (12)$$

The mass balance equation of copper in the aqueous phase is expressed as:

$$[\text{Cu}]_{\text{aq}} = [\text{Cu}^{2+}]_{\text{aq}} + \sum_{i=1}^4 \beta_i [\text{NH}_3]_{\text{aq}}^i \quad (13)$$

Thus, the equilibrium constant  $K_6$  can be expressed as:

$$K_6 = \frac{1}{K_5} \frac{[\text{CuR}_2]_{\text{o}}[\text{NH}_4^+]_{\text{aq}}^2}{[\text{Cu}]_{\text{aq}}[\text{HR}]_{\text{o}}^2[\text{NH}_3]_{\text{aq}}^2} \left(1 + \sum_{i=1}^4 \beta_i [\text{NH}_3]_{\text{aq}}^i\right) \quad (14)$$

At appropriate high ammonia concentrations, when

$$\sum_{i=1}^4 \beta_i [\text{NH}_3]_{\text{aq}}^i \gg 1 \quad (15)$$

and

$$\beta_4 [\text{NH}_3]_{\text{aq}}^4 \gg \sum_{i=1}^3 \beta_i [\text{NH}_3]_{\text{aq}}^i \quad (16)$$

Therefore, Eq. (13) can be written as:

$$K_3 = \frac{\beta_4 [\text{CuR}_2]_{\text{o}}[\text{NH}_4^+]_{\text{aq}}^2[\text{NH}_3]_{\text{aq}}^2}{K_5 [\text{Cu}]_{\text{aq}}[\text{HR}]_{\text{o}}^2} \quad (17)$$

As a result,

$$\lg [\text{CuR}_2]_{\text{o}} = \lg K_{\text{ex}} + \lg [\text{Cu}]_{\text{aq}} + 2\lg [\text{HR}]_{\text{o}} - 2\lg [\text{NH}_4^+]_{\text{aq}} - 2\lg [\text{NH}_3]_{\text{aq}} \quad (18)$$

where

$$K_{\text{ex}} = K_6 K_8^2 \beta_4^{-1} \quad (19)$$

The description of Eqs. (6)–(19) implies that the extraction equilibrium constant depends on the concentrations of different species in solution. Such an effect was reported previously on copper extraction by BOUVIER et al [27]. The strong effect of the ionic strength was demonstrated and it was found that the extraction equilibrium constant increases as the ionic strength rises. As a result, the following additional equation is here considered

$$\ln K_{\text{ex}} = a + bI \quad (20)$$

where  $a$  and  $b$  are the regression coefficients. In Eq. (20),

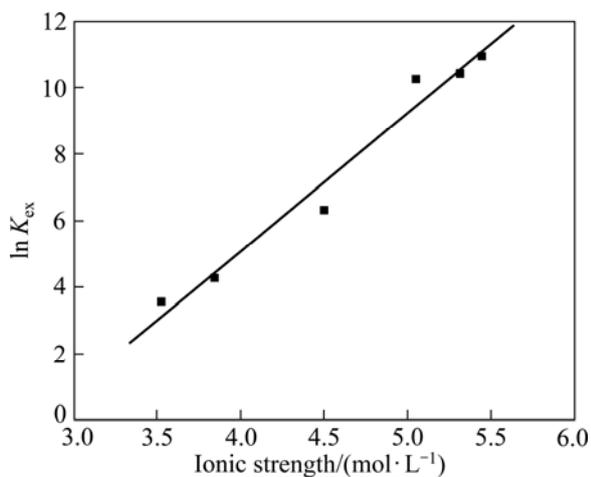
$I$  denotes the ionic strength and it is calculated as:

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (21)$$

where  $m_i$  and  $z_i$  represent the ionic molalities and the ion charge of ionic component  $i$ , respectively. The ionic molalities changes from 4 to 7 mol/kg.

Extraction of copper from simulated ammoniacal spent etchant containing 112.98 g/L Cu, 3.50 mol/L  $\text{Cl}^-$ , 1 mol/L  $\text{NH}_3$  and 6 mol/L  $\text{NH}_4^+$  was carried out using 40% HR at phase ratio of 1:1 or 1:2 for 5 min, respectively. One raffinate obtained at O/A ratio of 1:1 contains 68.16 g/L Cu, 3.50 mol/L  $\text{Cl}^-$  and 6.96 mol/L total ammonia, the other raffinate obtained at O/A ratio of 1:2 contains 86.25 g/L Cu, 3.50 mol/L  $\text{Cl}^-$  and 6.97 mol/L total ammonia.

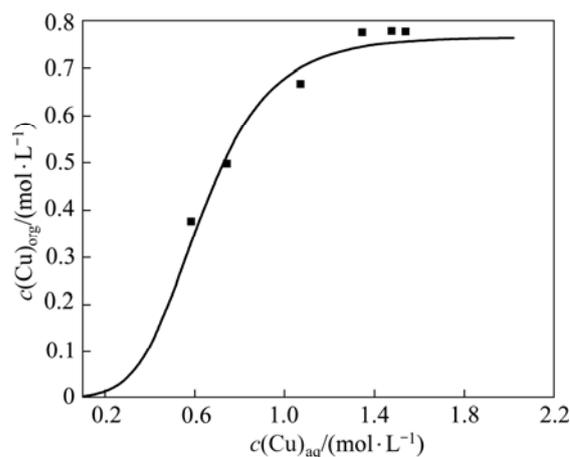
The extraction constant  $K_{\text{ex}}$  is calculated by Eq. (6) with the experimental data. Then the simulated values of  $a$  and  $b$  obtained by using the speciation model stated previously are equal to  $-11.41$  and  $4.125$ , respectively. The effect of the ionic strength on the extraction constant is shown in Fig. 4. The experimental data (marks) are compared with the simulated values (solid line).



**Fig. 4** Effect of ionic strength on extraction equilibrium constant ( $K_{\text{ex}}$ )

Figure 5 shows the equilibrium results for the extraction of copper from simulated ammoniacal spent etchant using 40% HR. In Fig. 5, the experimental data (marks) were compared with the simulated values (solid line). The simulated values were obtained by using the speciation model stated previously, and the stoichiometry was proposed with Eqs. (6)–(21).

As observed, the simulated extraction isotherms presented in Fig. 5 was basically identical with the experimental data. The simulated isotherm became steep in the low region of copper concentration from the aqueous phase and the maximum loading of the organic phase was 48.64 g/L.



**Fig. 5** Comparison of model (Eqs. (5)–(20), solid line) with experimental data (Aqueous phase: 112.98 g/L Cu, 6 mol/L  $\text{NH}_3$ , 1 mol/L  $\text{NH}_4^+$  and 3.50 mol/L  $\text{Cl}^-$ ; Organic phase: 40% HR in sulphonated kerosene)

### 3.5 Effect of sulphuric acid concentration on copper stripping

The copper in the loaded organic phases with 40% HR was stripped with different concentrations of  $\text{H}_2\text{SO}_4$  solution (10–200 g/L) at 1:1 phase ratio for 30 min and the solutions were settled and separated by gravity. The experimental result is given in Table 1.

**Table 1** Stripping of copper from loaded organic phase (40% HR) using  $\text{H}_2\text{SO}_4$  with various concentrations

Concentration of $\text{H}_2\text{SO}_4/(\text{g}\cdot\text{L}^{-1})$	Cu stripping ratio/%
10	9.52
20	27.11
30	40.29
60	67.40
100	96.70
140	97.44
160	97.80
180	98.17
200	98.32

As listed in Table 1, the stripping ratio of copper increases from 9.52% to 98.32% from the loaded organic phase with stripping solutions of different  $\text{H}_2\text{SO}_4$  concentrations. The stripping efficiency increases with increasing the acid concentration, although higher copper recoveries can be obtained even using stripping solution with low acidic concentration. During the stripping process, the hydrogen ion displaces the metal ion from the organic phase. When the stripping is completed, almost all metal ions are converted from the organic phase into aqueous phase, and hence, further acid addition is ineffective.

### 3.6 Stripping isotherm and counter-current simulation for Cu stripping

To strip copper from the loaded organic phases (40% or 80% HR), it was required to determine the number of stages and the phase ratio, and then the stripping isotherm was constructed. The loaded organic phase and stripping solution of 180 g/L  $H_2SO_4$  were equilibrated at different phase ratios from 1:4 to 3:1. The aqueous and organic phases were analyzed and the stripping isotherms are plotted in Fig. 6.

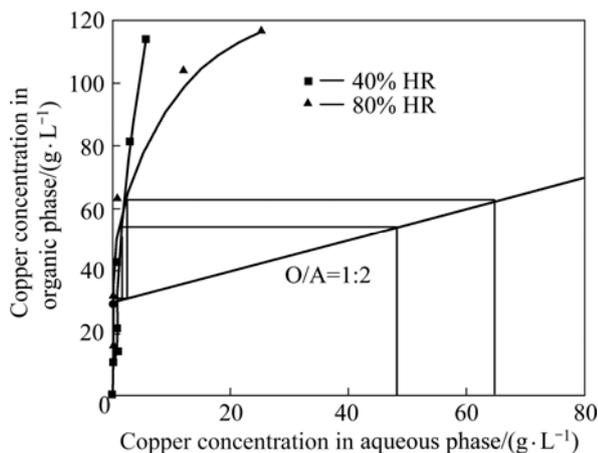


Fig. 6 Stripping isotherm of loaded organic phase

Consider the electrowinning process [28], simulated spent electrolyte of 30 g/L Cu (II) and 180 g/L  $H_2SO_4$  was used to strip copper from the loaded organic phase. The McCabe-Thiele plot (shown in Fig. 6) illustrates the quantitative stripping of copper in one-stage at phase ratio of 1:2 with 40% HR and in two-stage at phase ratio of 1:2 with 80% HR. To confirm this process, a single stage counter-current simulation study at phase ratio of 1:2 for 40% HR and a two-stage counter-current simulation study at phase ratio of 1:2 for 80% HR were carried out. The stripping ratio of the loaded organic phases with 40% or 80% HR reached 98.27% or 98.77%, respectively. The loaded organic phases with 40% HR were easier to strip than those with 80% HR.

## 4 Conclusions

1) 1-(4'-dodecyl)-phenyl-3-tertiary butyl-1,3-octadione (HR) is proved to be an effect solvent extractant for copper extraction from ammoniacal spent etchant. The extraction isotherm can be well modeled by the chemical model that takes into account the positive effect of the ionic strength.

2) The loaded organic phase with 40% HR contains 46.82 g/L copper and that with 80% HR contains 64.12 g/L copper. Both the raffinates can reuse in etching processes.

3) The stripping ratio of loaded organic phase with

40% HR reaches 98.27% in one-stage at phase ratio of 1:2 in the presence of copper spent electrolyte, whereas 98.77% copper is striped from loaded organic phase with 80% HR in two-stage at phase ratio of 1:2.

4) The results of solvent extraction in counter-current simulation in the case of 40% HR show excellent capability of copper recovery from a ammoniacal spent etchant. These results support the established commercial use of this system for the copper recovery from ammoniacal printed circuit board etch solutions.

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## 高位阻 $\beta$ -二酮从氨性蚀刻废液中萃取铜

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**摘要:** 采用高位阻  $\beta$ -二酮(1-(4'-十二烷基)苯基-3-叔丁基-1,3-丙二酮)作为萃取剂从模拟印刷电路板(PCBs)蚀刻废液中萃取铜。利用离子强度与萃取反应平衡常数的关系校正模拟的萃取等温线, 该模拟萃取等温线与实验测得萃取等温线基本相符。通过实验确定萃取剂浓度、相比、萃取级数和反萃级数等萃取工艺参数。结果表明, 在室温下对于铜离子浓度为 112 g/L、总氨浓度为 7 mol/L 的模拟氨性蚀刻废液的最佳萃取条件为: 萃取剂浓度为 40%, 相比为 5:4, 萃取时间为 5 min。在此条件下, 经过一级萃取, 蚀刻废液中铜离子浓度可降低至 63.24 g/L, 能返回到电路板的生产中循环使用。用含铜 30 g/L, 硫酸浓度 180 g/L 的模拟废电解液对负载有机相进行反萃, 相比(O/A)为 1:2, 经一级反萃, 铜的反萃率可达 98.27%。

**关键词:** 氨性蚀刻废液; 铜回收; 溶液萃取;  $\beta$ -二酮

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