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Electrochemical behaviour of alkaline copper complexes

C L ARAVINDA [a], S M MAYANNA [a] and V S MURALIDHARAN[b]*
[a]Department of Chemistry, Central College, Bangalore 560 001, India and
[b]Central Electrochemical Research Institute, Karaikudi 630 006, India
e-mail: corr@cscecri.ren.nic.in

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Abstract. A search for non-cyanide plating baths for copper resulted in the development of alkaline copper complex baths containing trisodium citrate [TSC] and triethanolamine [TEA]. Voltammetric studies were carried out on platinum to understand the electrochemical behaviour of these complexes. In TSC solutions, the deposition of copper involves the slow formation of a monovalent species. Adsorption of this species obeys Langmuir isotherm. In TEA solutions the deposition involves the formation of monovalent ions obeying the non-activated Temkin isotherm. Conversion of divalent to monovalent copper is also slow. In TEA and TSC alkaline copper solutions, the predominant species that undergo stepwise reduction contain only TEA ligands.

Keywords. Alkaline copper complexes; non-cyanide plating.

1. Introduction

Earlier polarographic studies revealed that electronation of divalent copper (II) solutions containing complexing agents occurs by a stepwise process [1]. Ammonia and a number of amines and nitrogen-containing heterocyclic compounds, give rise to stepwise electronation of copper complexes [2]. In alkaline solutions, salicyl amide and malonic complexes are reported to exhibit two reversible one-electron waves [3]. In ammonia solutions, ethylene diamine tetraacetic acid exhibits a single two-electron wave at a potential more negative than that of the ammonia complex doublet [4]. A non-cyanide-plating bath for copper has been developed using alkaline trisodium citrate and triethanolamine solutions [5].

The present investigation presents cyclic voltammetric studies on the electrochemical behaviour of alkaline copper complexes, containing either trisodium citrate or triethanolamine or both, used in the copper-plating bath.

2. Experimental

Voltammetric experiments were carried out in a single-compartment three-electrode cell assembly. A platinum miniature electrode and a large platinum foil were used as working and counter electrodes respectively. Working electrode potentials were monitored using a saturated calomel electrode. The desired potentials were swept using a scanning

*For correspondence

potentiostat [EG&G PAR Model 362, USA]. Voltammograms were recorded after obtaining reproducible traces on repeated cycling.

All solutions were prepared using AnalaR grade chemicals $CuSO_4$ solutions (0·01 M) containing trisodium citrate [TSC] [0·01<*x*>0·08 M] or triethanol amine [TEA] [0·01 M<*x*>0·06 M] or both were used along with [0·1<*x*>1 M] NaOH. The *p*H of the solution was 10·5 to 11·5. Experiments were conducted in 298 K. UV/Vis absorption spectra of the solutions were recorded using a Hitachi-150 spectrometer.

3. Results

3.1 *Trisodium citrate solutions*

Figure 1 presents the electrochemical spectrum obtained in 10^{-2} M $CuSO_4$ solutions containing 5×10^{-1} M NaOH + 5×10^{-2} M TSC. When polarised from + 200 mV to –1400 mV, a small hump appears at –375 mV; a cathodic peak (I) appears at –536 mV followed by a sharp peak at –890 mV. Beyond –900 mV, increase in current occurs. In the reverse scan an anodic peak (II) appears at –446 mV followed by a broad peak at –161 mV (IV). On repeated cycling, peaks around –536 mV disappear and a broad peak appears. Disappearance of the two cathodic peaks may be due to (I) Divalent copper citrate complex may undergo reduction to monovalent complex, which further reduces to copper.

Cathodic peak potentials (I) vary with log sweep rate and the value of 122 mV/decade suggests that divalent complex is reduced to monovalent copper, Cu (II) complex + $e \rightarrow$ Cu (I) complex, with the step being slow. Cathodic peak potentials (II) vary with log sweep rate and the value of 62 mV/decade suggests that second electron transfer may take place via adsorbed monovalent copper intermediate.

During the reverse scan, the observed anodic peak potentials (III) and (IV) vary with log sweep rate with values of 27 mV and 60 mV/decade respectively. The deposited copper undergoes stepwise dissolution. Once the monovalent copper species is formed,

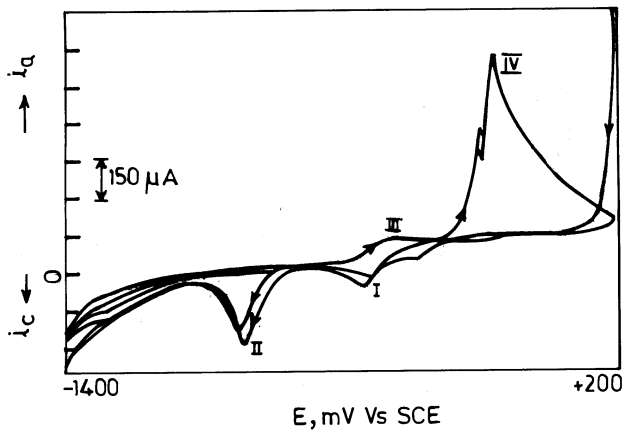

Figure 1. Typical cyclic voltammogram in 0·01 M copper sulphate + 0·05 M TSc + 0·05 M sodium hydroxide. Effect of cycling $E_{\lambda,a} = 0$ mV; $E_{\lambda,c} = -1400$ mV; $v = 25$ mV/s.

its conversion to divalent copper species becomes different. The participation of TSC in the complex formation is shown by the variation of cathodic peak potentials (I) and (II) with log [TSC] concentration. Cathodic peak potentials (I) vary as 210 mV/decade and cathodic potentials (II) vary as 80 mV/decade change of [TSC] concentration. These values suggest the weak participation of (TSC) ligands in copper complex formation.

Anodic peak potentials are invariant with (TSC) concentration. This suggests that dissolution of copper is not dependent on (TSC) concentration. Cathodic peak current (I) and anodic peak current (III) do not vary with [TSC] concentration. This suggests that the electroactive copper species that undergo electron transfers are predominantly hydroxy complexes. The $\Delta E_p = E_{p,c}$ (I) – $E_{p,a}$ (III) vary linearly with log (TSC) concentration. This suggests that the divalent copper complex contains (TSC) ligands.

3.2 *Triethanolamine solutions*

The electrochemical spectrum obtained in 10^{-2} M $CuSO_4$ solutions containing 5×10^{-1} M NaOH + 4×10^{-2} M TEA (figure 2) during the forward sweep shows a cathodic peak (I)

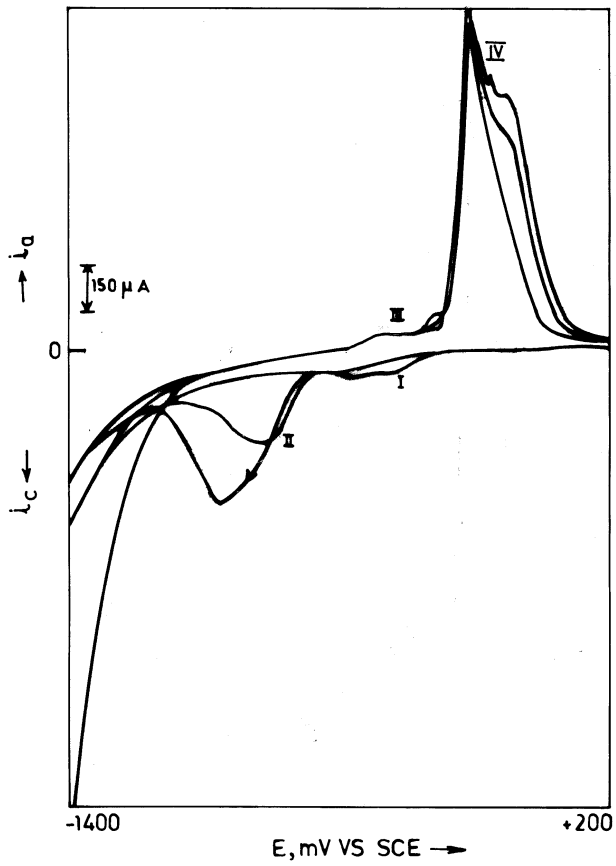

Figure 2. Typical cyclic voltammogram in 0·01 M copper sulphate + 0·04 M TEA + 1·0 M sodium hydroxide. Effect of cycling $E_{\lambda,a}$ = 0 mV; $E_{\lambda,c}$ = –1400 mV; v = 50 mV/s.

at –771 mV followed by a peak at –1074 mV (II). During the reverse scan, an anodic peak appears at –461 mV (III) followed by a peak at –273 mV (IV). The appearance of two cathodic peaks separated by ~ 300 mV suggests that: (a) stepwise electronation of the divalent copper complex takes place and the reduction of monovalent copper complex becomes increasingly difficult, or that (b) electronation may take place via hydroxy complex and also via copper (II) hydroxy complexes.

The anodic peaks suggest stepwise dissolution of copper and the stabilization of monvalent copper by TEA ligands. On cycling, the cathodic peak becomes more negative suggesting that electronation becomes sluggish; the anodic peak potential (III) does not vary with TEA concentration suggesting that not all hydroxy groups are replaced by TEA ligands. Cathodic peak potentials vary linearly with log v with a slope of 120 mV/decade. $\Delta E_p = E_{p,c}$ (I) – $E_{p,a}$ (III) vary with log [TEA] concentration linearly.

3.3 *Trisodium citrate and triethanolamine solutions*

Figure 3 presents the cyclic voltammogram obtained from 10^{-2} M $CuSO_4$ + 1 M NaOH + 4×10^{-2} M TEA. Cathodic peaks appear at –705 mV and –1026 mV during the forward

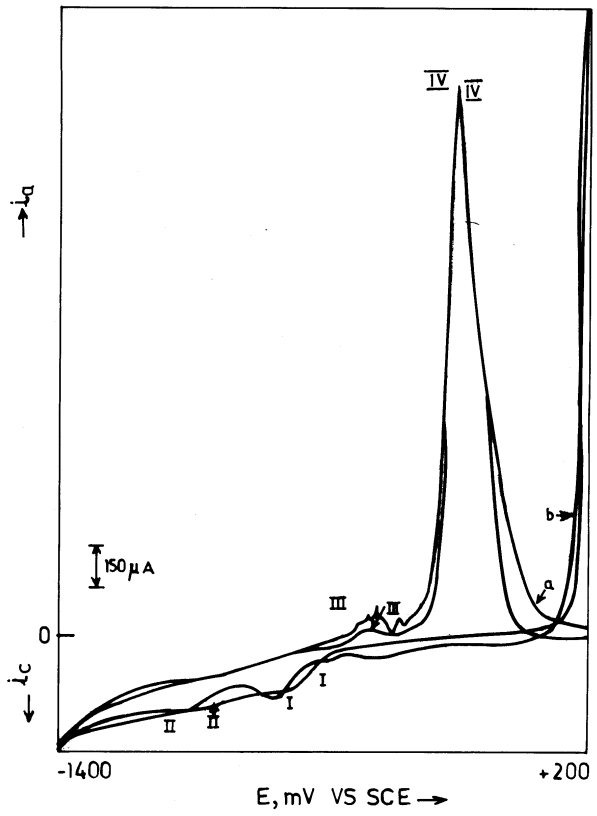

Figure 3. Typical voltammogram in copper sulphate + TEA + TSC solutions: (a) 0·01 M copper sulphate + 0·04 M TEA, (b) 0·01 M copper sulphate + 0·04 M TEA + 0·04 M TSC. $E_{\lambda,a}$ = 0 mV; $E_{\lambda,c}$ = – 1400 mV; v = 50 mV/s.

scan, anodic peaks at –436 mV and –205 mV in the reverse scan. Introduction of 4×10^{-2} M TSC to the solution modifies the electrochemical spectrum; in the forward scan an additional cathodic peak suggests: (a) electronation of two types of copper complexes, (b) stepwise electronation or, (c) the presence of TEA favours the reduction of TSC complex

Anodic peak potentials (I and II) vary with log *v* by 60 mV/decade and cathodic peak potentials (III and IV) by 120 mV/decade changes.

4. Discussions

The divalent copper exhibits coordination numbers of 4, 5 and 6. The divalent copper complexes undergo stepwise electronation (I). In strong alkaline solutions the formation of $Cu(OH)_2$ decreases the free Cu^{2+} ions concentration [6]. The free Cu^{++} ion concentration in equilibrium with $Cu(OH)_2$ at a hydroxyl ion concentration of 10^{-2} M is $1{\cdot}6 \times 10^{-7}$ M. The equilibrium potential of cupric ion reduction is

$$E_{Cu++/Cu} = 0{\cdot}337 - 0{\cdot}059/2 \log (1{\cdot}6 \times 10^{-17})$$
$$= -0{\cdot}40 \text{ volt vs SCE.}$$

Reduction of $Cu(OH)_2$ to Cu_2O occurs as $2Cu(OH)_2 + 2e \rightarrow Cu_2O + H_2O + 2OH^-$ with a reversible potential of –284 mV vs SCE at *p*H 12. The reduction of Cu_2O to copper occurs as $Cu_2O + e \rightarrow 2Cu + 2OH^-$ with a reversible potential of –482 mV vs SCE. Reduction of water to liberate hydrogen occurs at potentials more negative to the reversible potential of –895 mV vs SCE.

Figure 4 presents the UV/Vis absorption spectra of copper and its complexes. For $CuSO_4$ solution the absorption peak appears at 836·9 nm. In the presence of TEA and NaOH, the absorption peak is shifted to 720 nm. Greater shift is seen in $CuSO_4$ solution containing TSC and NaOH [690·5 nm]. In the presence of both, the absorption peak appears at 720 nm suggesting preferential complexation of TEA.

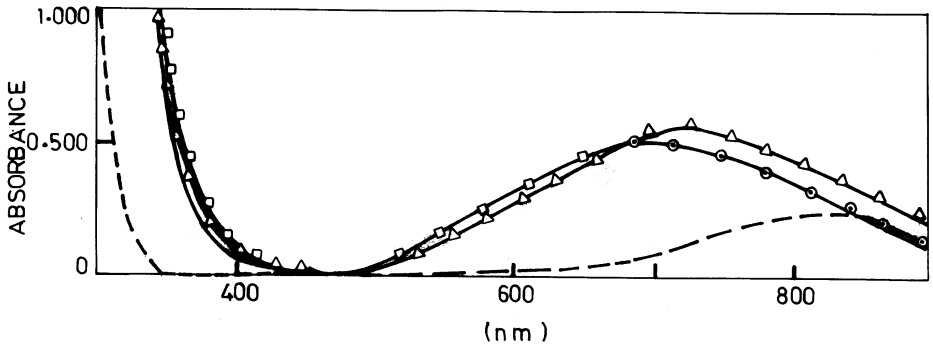

Figure 4. UV/Vis spectra of copper and its complexes: - - - - copper sulphate; -Δ-Δ-Δ copper sulphate + TEA + TSC + sodium hydroxide; O–O–O–O copper sulphate + TSC + sodium hydroxide; ———— copper sulphate + TEA + sodium hydroxide.

4.1 *Trisodium citrate solutions*

Under transient polarisation conditions [5–100 mV/s] the deposition of copper may involve the formation of monovalent copper and the citrate ligand, X, as

$$[Cu(OH)_3X]^{2-} \rightleftharpoons [Cu(OH)_2X]^- + OH^-,$$

$$[Cu(OH)_2X]^- \rightleftharpoons [Cu(OH)X] + OH^-,$$

$$[CuOHX] + e \rightarrow CuOH + OH^-,$$

$$[CuOH] + e \rightleftharpoons Cu + OH^-.$$

The cathodic current is under Langmuir adsorption conditions,

$$I_c = \overrightarrow{k_3} K_2K_1 [Cu(OH)_3X]^{2-}/[OH^-]^2 \exp - \beta\Delta\Phi_C F/RT,$$

where β is the symmetry factor

$$\Delta\Phi_C = [2{\cdot}303RT/ - \beta F] \log K + [2{\cdot}303RT/ - \beta F] \frac{\log[Cu(OH)_3X]^{2-}}{[OH^-]^2},$$

and $[dE_{p,c}/d \log c_X]$ should be 120 mV. The observed value confirms this.

For an irreversible process [7,8],

$$E_{p,c} = E'_0 - RT/\alpha_c F\{0{\cdot}78 + \ln (D_0/k_0)^{1/2} + \ln (\alpha_c Fv/RT\}^{0{\cdot}5}\},$$

where k_0 is the standard rate constant; D_0 is the diffusion coefficient of the species; E'_0 is the formal potential of the electrode. $[dE_{p,c}/d \ln v]$ gives a slope of $[2{\cdot}303RT/\alpha_c F]$. The observed value of 120 mV/decade confirms this. $[d \log I_{p,a}/d \log C_{TSC}] = 0$ and $[d \log I_{p,c}/d \log C_{TSC}] = 0$ suggest that the first electron transfer is slow in the deposition process.

4.2 *Triethanol amine solutions*

In alkaline copper sulphate solutions, TEA may form a complex $[Cu(OH)_3x]^{2-}$ where X is the TEA ligand. Under transient polarisation conditions [5–100 mV/S],

$$[Cu(OH)_3X]^{2-} \rightleftharpoons [Cu(OH)_3]^- + X^-, \quad (1)$$

$$[Cu(OH)_3]^- \rightleftharpoons Cu(OH)_2 + OH^-, \quad (2)$$

$$[Cu(OH)_2] + e \rightleftharpoons CuOH + OH^-, \quad (3)$$

$$CuOH + e \rightleftharpoons Cu + OH^-. \quad (4)$$

Under Langmuir adsorption conditions with step (3) being slow,

Table 1. Parameters derived from cyclic voltammograms

Parameter	TSC solution (mV/decade)	TEA solution (mV/decade)
[d$E_{p,c}$ (I)/d log v]	122	120
[d log $I_{p,a}$ (III)/d log C_x]	0	0
[d log$I_{p,c}$ (I)/d log C_x]	0	0
[d log ΔE_p/d log C_x]	120	110

$$I_c = \overrightarrow{k_3}\, k_2 k_1 \left\{\frac{[\mathrm{Cu(OH)_3X}]^{2-}}{(\mathrm{X})(\mathrm{OH^-})}\right\} \exp -\beta\Delta\Phi_C F/RT,$$

would result, {d$E_{p,c}$/d log v} = 120 mV; {d log $I_{p,c}$/d log v} = –1, {d log $I_{p,a}$/d log X} = 0.

Under non-activated Temkin conditions, step (3) is

$$I_c = \overrightarrow{k_3}\, k_2 k_1 \left\{\frac{(\mathrm{CuOH})_3(\mathrm{X})}{(\mathrm{OH^-})(\mathrm{X})}\right\}^{2-} \exp -\beta\Delta\Phi_C F/RT \exp (1-\beta) r\eta F/RT,$$

$I_a = k_4\{\mathrm{Cu}\}\{\mathrm{OH^-}\}^2 \exp (1-\beta)\Delta\Phi_C\, F/RT \exp (-\beta)\eta rF/RT$. This results {dlog $I_{p,c}$/d log C_x} = –0·5;{d$E_{p,c}$/d log v} = 60 mV/decade; {d log $I_{p,a}$/d log C_x} = 0. The observed experimental values confirm these (see table 1).

4.3 *Trisodium citrate and triethanol amine solutions*

UV/Vis absorption spectra show absorption peaks at 720 nM which coincide with the absorption peak obtained in the absence of TSC. Hence, in these solutions the predominant species is $\{\mathrm{Cu(OH)_3X}\}^{2-}$ where X is the TEA ligand. The observed values {d$E_{p,c}$/d log v} of 60 mV/decade and {d$E_{p,a}$ {III}/d log v} of 120 mV decade suggest that reduction of $[\mathrm{Cu(OH)_3X}]^{2-}$ follows the first electron transfer which is slow.

5. Conclusions

Voltammetric studies carried out on platinum indicate that under transient polarisation conditions in the *p*H range of 10·5 to 11·5, the deposition of copper from alkaline copper solutions containing trisodium citrate involves the formation of adsorbed monovalent copper obeying the Langmuir isotherm. The conversion of divalent copper to monovalent is thus slow. In alkaline triethanol amine solutions, the deposition of copper involves the adsorption of monovalent copper species obeying the non-activated Temkin adsorption isotherm and conversion of divalent copper to monovalent is again slow. In the presence of TSC and TEA, the predominant species contains only TEA ligands, which undergo stepwise reduction.

References

1. Kolthoff M and Lingane J J 1952 *Polarography* (New York: Interscience)
2. Vonstackelberg M and Vonfreyhald H 1940 *Z. Electrochem.* **46** 120

3. Khan S H and Khan A A 1969 *J. Electroanal. Chem.* **22** 424
4. Furness W, Crawshaw P and Daview W C 1949 *Analyst* **74** 629
5. Mayanna S M and Maruthi B N 1996 *Metal Finishing* **46** 42
6. Bard A J 1976 *Encyclopedia of electrochemistry of the elements* (New York: Marcel)
7. Nicholson R S and Shain I 1964 *Anal. Chem.* **36** 706
8. Macdonald D D 1977 *Transient techniques in electrochemistry* (New York: Plenum) p. 193