

## Electrochemical behaviour of Cu–NTA complexes

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**Abstract.** The deposition of copper was found to involve adsorbed monovalent copper which follows nonactivated Temkin isotherm. The presence of nitrilotriacetic acid stabilises it and the second electron transfer is slow.

**Keywords.** Cyclic voltammetry; copper complexes; nitrilotriacetic acid.

### 1. Introduction

The electrochemical behaviour of copper is determined by its nobility with respect to most other metals and the existing divalent copper ions in a solution. The study of this behaviour is of great interest from the view points of technology as well as copper deposition from simple and complex baths. In noncomplexing baths such as perchlorates, nitrates and sulphates, copper exists in the divalent state and polarograms reveal only one wave corresponding to the two-electron reduction from  $\text{Cu}^{++}$  to Cu (Kolthoff and Lingane 1952). However in the presence of a variety of complexing agents, solutions containing  $\text{Cu}^{++}$  ion exhibit two polarographic waves corresponding to the stepwise reduction. The use of acetonitrile has been found to cause a splitting of the anodic and cathodic waves (Altermatt and Manahan 1968). Ammonia, a number of amines and nitrogen-containing heterocyclic compounds give rise to a stepwise reduction of copper from the complexes (Vonstacelberg and Von Freyhald 1940).

Salicylamide and malonamide complexes in alkaline media are reported to exhibit two reversible one-electron waves (Khan and Khan 1969). In ethylene diamine tetra acetic acid complexes in ammonia solution, a single two-electron wave at a potential more negative than that of the ammonia complex doublet has been observed. (Furness *et al* 1949). Though many complexing agents have been examined, no detailed study has been made on the electrochemical behaviour of copper nitrilo triacetic acid (Cu–NTA) complexes.

### 2. Experimental

A three-electrode cell assembly was used. A glassy carbon electrode (Tokai carbon company, Japan) with an area of  $23.6 \text{ mm}^2$  embedded in a Teflon gasket was used

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as a working electrode. The electrical connections were provided by a screw and thread arrangement. The electrode was polished successively with 1/0, 2/0, 3/0, 4/0 and 5/0 emery papers. It was degreased with trichloroethylene and immersed in the solution under study. A platinum foil  $25 \times 25$  nm size was used as an auxiliary electrode. A saturated calomel electrode served as a reference electrode.

The solutions under study were deoxygenated for one hour using purified hydrogen. The temperature of the cell was kept at  $30 \pm 0.01^\circ\text{C}$ .

Solutions were prepared using analar chemicals.  $\text{CuSO}_4$  solutions ( $10^{-3} \text{ M} \langle x \rangle 10^{-1} \text{ M}$ ), with  $10^{-1} \text{ M}$   $\text{Na}_2\text{SO}_4$  concentration to keep the ionic strength constant, were used. For the above solutions different concentrations of sodium salt of NTA ( $5 \times 10^{-4} \langle x \rangle 5 \times 10^{-2} \text{ M}$ ) were used. The pH of the solution was monitored using a digital pH meter by adding drops of dilute NaOH solutions. The working electrode was perturbed with triangular potential sweeps between  $+400$  and  $-400$  mV or  $-1000$  mV as the case may be. The sweep rates were resorted to at  $2.5 \text{ mVs}^{-1}$  to  $50 \text{ mVs}^{-1}$ .

### 3. Results

#### 3.1 $\text{CuSO}_4$ solutions

Figure 1 presents the electrochemical spectrum corresponding to polarisation from  $+400$  to  $-400$  mV. A single cathodic peak was formed at  $-10$  mV during the forward scan whose peak potential did not vary with  $v$ . The reverse scan exhibited an anodic peak at  $-10$  mV followed by another anodic peak at  $50$  mV. The anodic peak potentials did not vary with  $v$ . On repetitive cycling, the cathodic peak potential shifted towards more negative values indicating that the reduction of the species formed during the anodic cycle became difficult and needed higher over voltages. The charges flowed under the peaks increased suggesting they were consecutive.

When the copper concentration was increased further the forward scan revealed two cathodic peaks ( $-40$  and  $-125$  mV respectively) followed by a single anodic peak ( $60$  mV) in the reverse scan (figure 2). On subsequent cycling the charges ( $Q_a$ ) flowing under the anodic peak increased while that due to the cathodic peak decreased. This suggests that the amount of species formed at  $60$  mV diffuse away and a portion of the species formed undergo reduction during the cathodic cycle.

A still further increase in copper concentration (figure 3) resulted in the appearance of a single cathodic peak followed by an anodic peak with a split at  $+10$  mV. Both

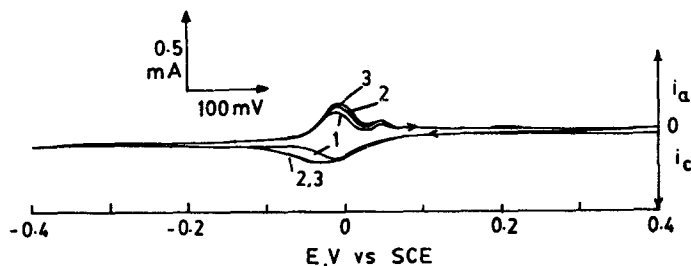
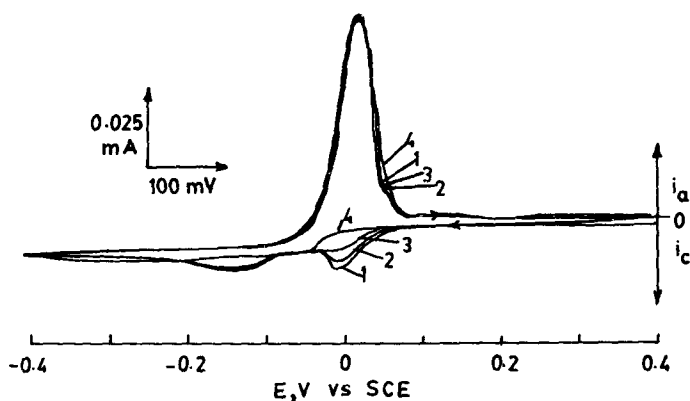
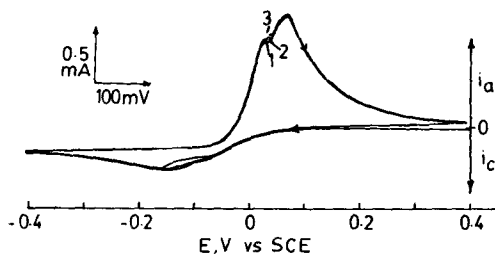


Figure 1. Cyclic voltammogram in  $10^{-3} \text{ M}$   $\text{CuSO}_4 + 10^{-1} \text{ M}$   $\text{Na}_2\text{SO}_4$  solution:  $E_{\lambda,a} = 400 \text{ mV}$ ;  $E_{\lambda,c} = -400 \text{ mV}$ ;  $v = 2.5 \text{ mVs}^{-1}$ .



**Figure 2.** Cyclic voltammogram in  $2 \times 10^{-3}$  M  $\text{CuSO}_4 + 10^{-1}$  M  $\text{Na}_2\text{SO}_4$  solution:  $E_{\lambda,a} = 400$  mV;  $E_{\lambda,c} = -400$  mV;  $v = 2.5$  mV s $^{-1}$ .



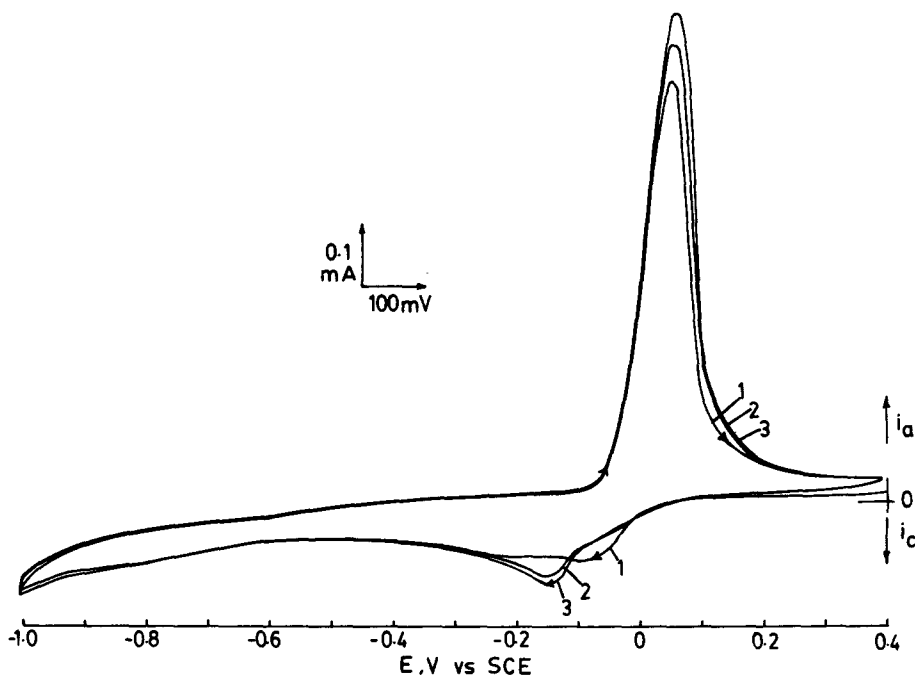
**Figure 3.** Cyclic voltammogram in  $5 \times 10^{-3}$  M  $\text{CuSO}_4 + 10^{-1}$  M  $\text{Na}_2\text{SO}_4$  solution:  $E_{\lambda,a} = 400$  mV;  $E_{\lambda,c} = -400$  mV;  $v = 2.5$  mV s $^{-1}$ .

the anodic and cathodic peak potentials moved towards the negative direction with an increase in copper concentration. There was no marked change in  $\Delta E_p (E_{p,c} - E_{p,a})$  with copper concentration. The appearance of a single cathodic peak may be due to the reduction of cupric ions to copper while the dissolution may involve stepwise electron transfer.

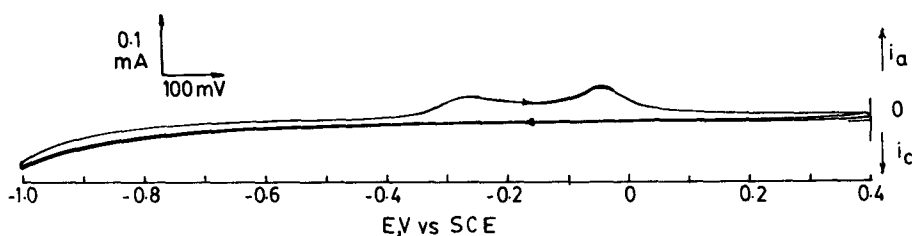
### 3.2 NTA added $\text{CuSO}_4$ solution

**3.2a  $3 \times 10^{-3}$  M  $\text{CuSO}_4$  solutions:** In the presence of the complexing anions, the electrochemical spectra exhibited certain interesting features. With the  $1.5 \times 10^{-3}$  M NTA solution, excursion from +400 to -1000 mV revealed a single cathodic peak at -50 mV which shifted to -150 mV on subsequent cycling followed by a sharp anodic peak at +50 mV in the reverse scan. The charges corresponding to the peaks increased with cycling but the peak potentials were not affected by scan rate (2.5 to 50 mV s $^{-1}$ ) (figure 4).

With increase of NTA concentration ( $1.5 \times 10^{-2}$  M) the cathodic peak disappeared leading to copper deposition along with hydrogen evolution. The dissociation of NTA resulted in the generation of more protons which were subsequently discharged at high negative potentials (figure 5). The anodic peaks were formed at -275 and -50 mV respectively suggesting that dissolution took place with stepwise electron transfer.



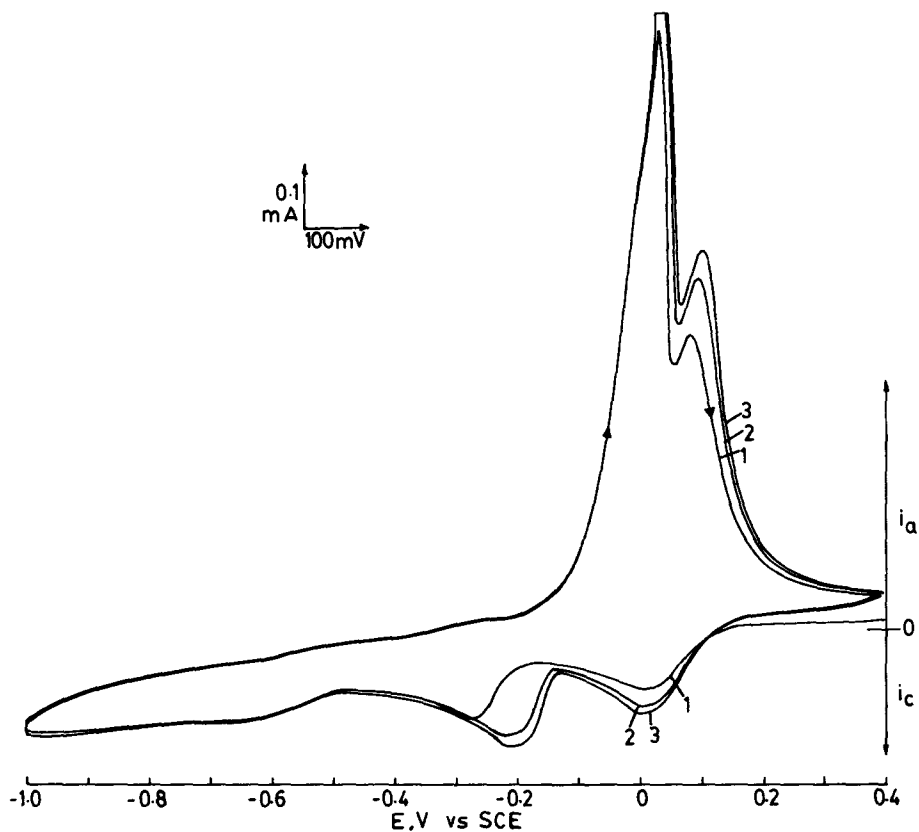
**Figure 4.** Cyclic voltammogram in  $3 \times 10^{-3}$  M  $\text{CuSO}_4 + 10^{-1}$  M  $\text{Na}_2\text{SO}_4 + 1.5 \times 10^{-3}$  M NTA;  $E_{\lambda,a} = 400$  mV;  $E_{\lambda,c} = -1000$  mV;  $\nu = 50$  mV s $^{-1}$ .



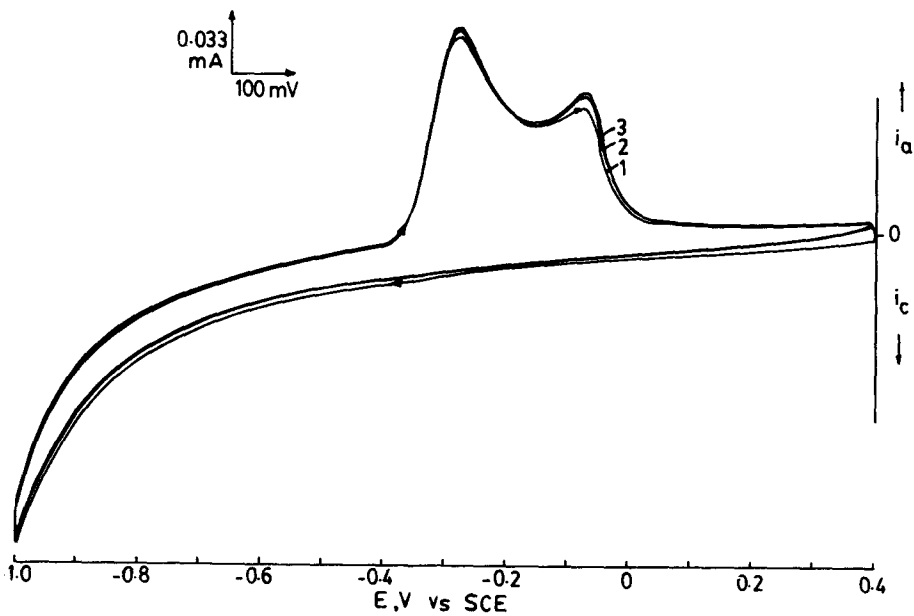
**Figure 5.** Cyclic voltammogram in  $3 \times 10^{-3}$  M  $\text{CuSO}_4 + 10^{-1}$  M  $\text{Na}_2\text{SO}_4 + 1.5 \times 10^{-3}$  M NTA;  $E_{\lambda,a} = 400$  mV;  $E_{\lambda,c} = -1000$  mV;  $\nu = 50$  mV s $^{-1}$ .

**3.2b  $5 \times 10^{-3}$  M  $\text{CuSO}_4$  solutions:** The electrochemical spectrum revealed (figure 6) three cathodic peaks in the forward scan at 25, -275 and -560 mV respectively. The reverse scan exhibited a shoulder followed by two anodic peaks at 25 and 100 mV, respectively. The peak potentials were invariant with  $\nu$  while the charges corresponding to the peaks increased with scan number. The  $E_{p,c}$  (-275 mV) shifted towards the more positive direction with an increase in scan number suggesting that the species formed in the reverse scan were getting reduced even at less negative potentials. The origin of the appearance of a shoulder and the invariance of peak potentials with  $\nu$  are not easy to unravel.

As the NTA concentration increased the cathodic peak potentials were shifted towards more negative values and finally they disappeared. During the reverse scan, at all NTA concentrations two anodic peaks appeared at -275 and -70 mV respectively indicating stepwise dissolution of copper (figure 7). The disappearance



**Figure 6.** Cyclic voltammogram in  $5 \times 10^{-3}$  M  $\text{CuSO}_4 + 10^{-1}$  M  $\text{Na}_2\text{SO}_4 + 2.5 \times 10^{-3}$  M NTA;  $E_{\lambda,a} = 400$  mV;  $E_{\lambda,c} = -1000$  mV;  $v = 50$  mV s $^{-1}$ .



**Figure 7.** Cyclic voltammogram in  $5 \times 10^{-3}$  M  $\text{CuSO}_4 + 10^{-1}$  M  $\text{Na}_2\text{SO}_4 + 2.5 \times 10^{-2}$  M NTA;  $E_{\lambda,a} = 400$  mV;  $E_{\lambda,c} = -1000$  mV;  $v = 50$  mV s $^{-1}$ .

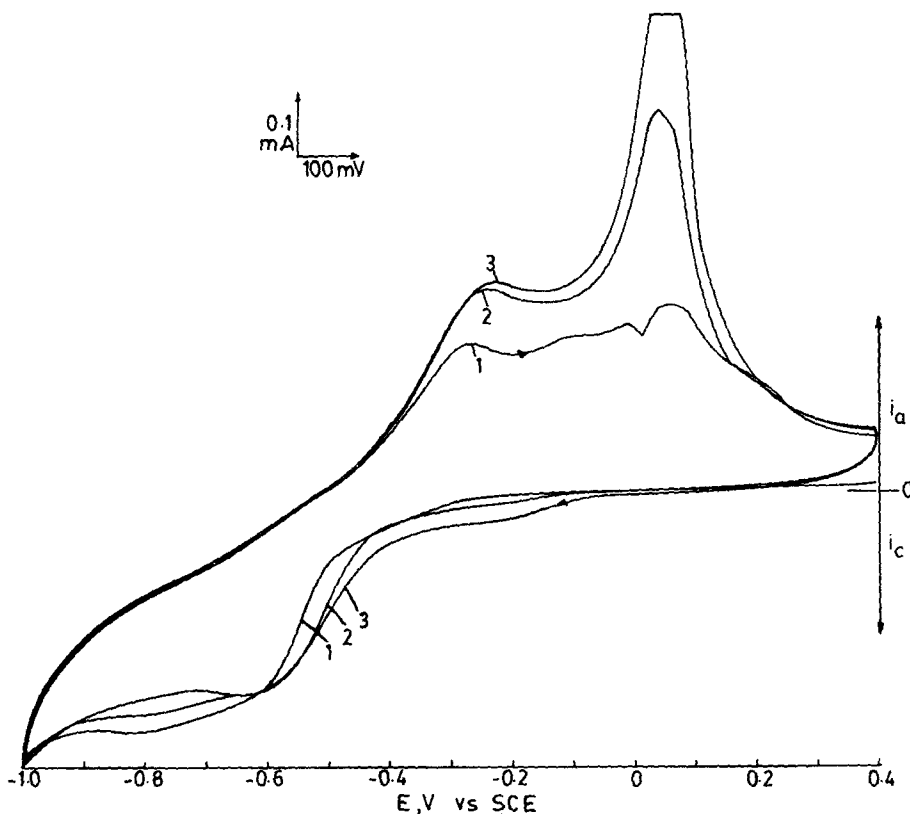


Figure 8. Cyclic voltammogram in  $10^{-2}$  M  $\text{CuSO}_4$  +  $10^{-1}$  M  $\text{Na}_2\text{SO}_4$  +  $10^{-2}$  M NTA;  $E_{\lambda,a} = 400$  mV;  $E_{\lambda,c} = -1000$  mV;  $v = 50$  mV s $^{-1}$ .

of cathodic peaks may be due to the reduction of the divalent copper complex along with hydrogen. This must be attributed to the discharge of the Cu-NTA complex at more negative potentials. Increase of scan number resulted in the increase in the charges corresponding to the anodic peaks because of the oxidation at high positive potentials of all species formed in the anodic peak region.

**3.2c  $10^{-2}$  M  $\text{CuSO}_4$  solution:** When polarised from  $-400$  to  $+1000$  mV the forward scan revealed a small peak around  $-270$  mV followed by two cathodic peaks at  $-625$  and  $-800$  mV. The reverse scan revealed two anodic peaks at  $-275$  and  $+70$  mV whose charges increased enormously with subsequent sweeping (figure 8). All the peak potentials were invariant with sweep rates. The cathodic peak potential ( $-625$  mV) shifted towards the more negative end on subsequent sweeping thereby suggesting that the copper species that were formed during the anodic cycle required higher overpotentials to undergo reduction.

An increase of NTA concentration resulted in the disappearance of the cathodic peak and a single broad anodic peak around  $-340$  mV on the reverse scan (figure 9). On subsequent cycling, the charge flowing under the anodic peak region decreased while the  $E_{p,a}$  was not shifted.

The appearance of a single anodic peak should be ascribed to the formation of

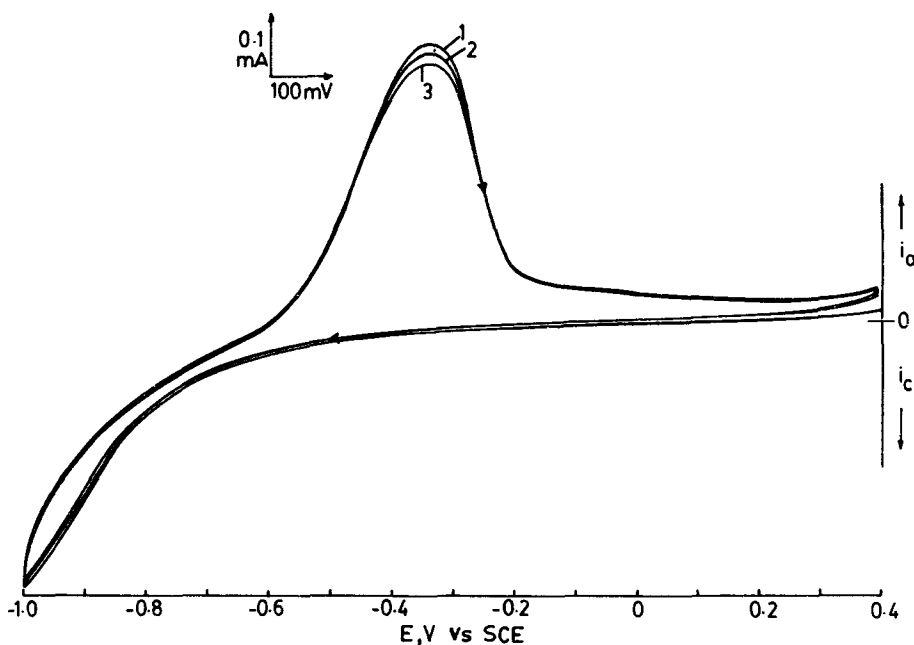
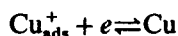
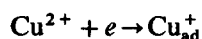


Figure 9. Cyclic voltammogram in  $10^{-2}$  M  $\text{CuSO}_4$  +  $10^{-1}$  M  $\text{Na}_2\text{SO}_4$  +  $5 \times 10^{-2}$  M NTA;  $E_{\lambda,a} = 400$  mV;  $E_{\lambda,c} = -1000$  mV;  $v = 50$  mV s $^{-1}$ .

monovalent copper species (cf. figure 2) and the presence of NTA stabilises it. Monovalent copper conversion to solution soluble divalent copper occurs at higher anodic potentials with its surface concentration decreasing on subsequent on sweeping.

#### 4. Discussion

The deposition of copper under transient conditions (20–100 mVs $^{-1}$ ) may involve the formation of  $\text{Cu}^+$  and



$$i_c = K_1(\text{Cu}^{2+}) \exp[-\alpha_c F \Delta\phi / RT]$$

where  $\alpha_c$  is the cathodic transfer coefficient and  $\Delta\phi$  is the interfacial potential difference. This suggests that

$$\left\{ \frac{d \log i}{d \log \text{Cu}^{2+}} \right\}_E = \text{order with respect to } \text{Cu}^{2+} \text{ ions} = 1.0.$$

The observed value of 0.5 (figure 10) suggests that the adsorbed monovalent ( $\text{Cu}^+$ ) $_{\text{ads}}$  may have a surface coverage  $\gg 0.1$ , the interaction between the monovalent species becomes appreciable and different sites on the metal may have different free energies

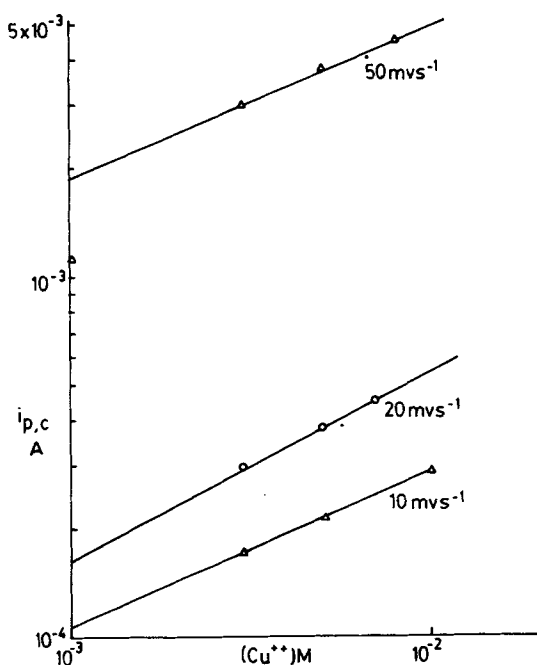


Figure 10. The variation of log cathodic peak current with log Cu(II) concentration for different  $v$  at constant pH.

of adsorption. Hence in terms of the Temkin isotherm

$$i_c = K_1(\text{Cu}^{2+}) \exp[-\alpha_c F \Delta \phi / RT] \exp[(1 - \beta)r\theta / RT]$$

The term ' $\beta$ ' is the symmetry factor and ' $r$ ' is the interaction parameter.

$$\exp(r\theta / RT) = [\bar{K}_1 / \bar{K}_1](\text{Cu}^{2+}) \exp[-F \Delta \phi / RT],$$

$$\exp[(1 - \beta)r\theta / RT] = [\bar{K}_1 / \bar{K}_1]^{(1 - \beta)} (\text{Cu}^{2+})^{(1 - \beta)} \exp(1 - \beta) F r \phi / RT$$

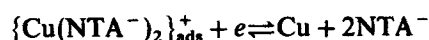
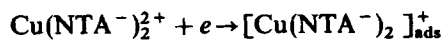
If  $\beta = 0.5$ , under transient conditions, the

$$\left\{ \frac{d \log i_{p,c}}{d \log \text{Cu}^{2+}} \right\}_v = 0.5$$

agrees well with the observed value.

The variations of cathodic peak current with (NTA) for constant  $\text{Cu}^{2+}$  ion concentration and pH at different sweep rate and  $(\text{Cu}^{2+})$  at constant (NTA) and pH at different sweep rates (figures 11 and 12) suggest the participation of NTA in the reaction sequence. Table 1 presents the parameters derived for the deposition of copper from NTA complexes.

In the presence of NTA,





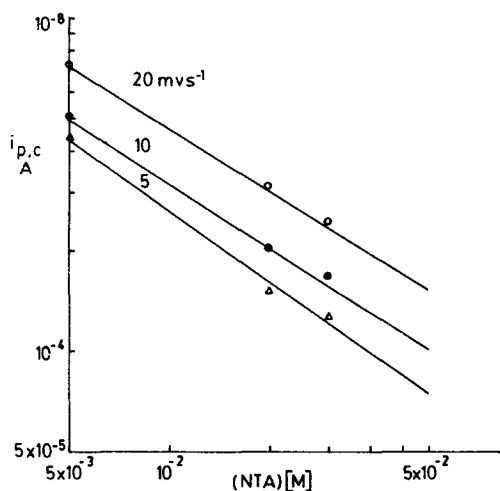


Figure 11. The variation of log cathodic peak current with log (NTA) concentration at  $10^{-2}$  M  $\text{CuSO}_4$  at different  $v$ .

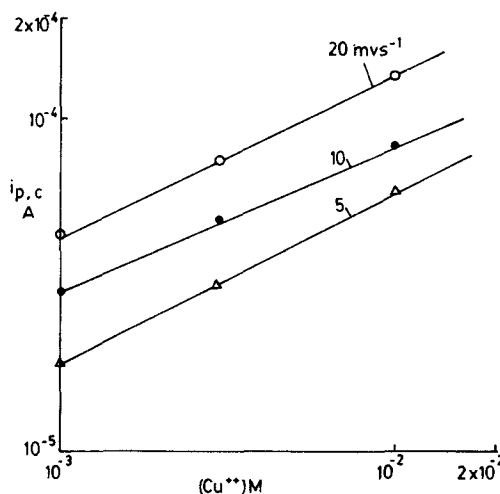
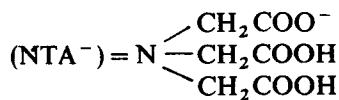


Figure 12. The variation of log cathodic peak current with log Cu(II) concentration at different  $v$  in  $5 \times 10^{-3}$  M NTA.

where



If the conversion of the divalent complex to the monovalent one is slow,

$$i_c = \bar{K}_1 [(\text{Cu}(\text{NTA}^-)_2)^{2+}] \exp [(-\beta F \Delta \phi)] / RT.$$

Under Langmuir conditions the slow second electron transfer will give

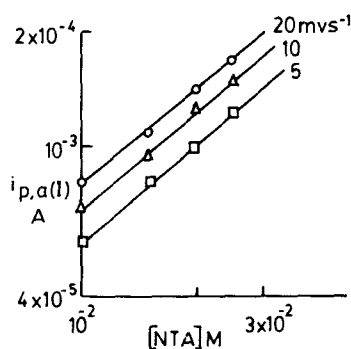
$$i_c = \bar{K}_2 K_1 \{ \text{Cu}(\text{NTA}^-)_2 \}^{2+} \exp [-(1 + \beta)(F \Delta \phi / RT)]$$

**Table 1.** Possible schemes and expected values for the deposition of copper from Cu-NTA complexes.

No. Scheme	$[d \log i_{p,c}/d \log \text{Cu(II)}]_{\text{NTA},v} [d \log i_{p,c}/d \log (\text{NTA})]_{\text{Cu(II)},v}$			
	Nonactivated		Nonactivated	
	Langmuir	Temkin	Langmuir	Temkin
A) $[\text{Cu}(\text{NTA})_2]^{++} + e \rightarrow [\text{Cu}(\text{NTA}^-)_2]_{\text{ads}}^+$ $[\text{Cu}(\text{NTA}^-)_2]_{\text{ads}}^+ + e \rightleftharpoons \text{Cu} + 2\text{NTA}^{(-)}$	1.0	+ 1.5	0.0	- 0.5
B) $[\text{Cu}(\text{NTA})_2]^{++} + e \rightleftharpoons [\text{Cu}(\text{NTA}^-)_2]_{\text{ads}}^+$ $[\text{Cu}(\text{NTA}^-)_2]_{\text{ads}}^+ + e \rightarrow \text{Cu} + 2\text{NTA}^{(-)}$	1.0	+ 0.5	0.5	- 0.5

$\text{NTA}^- = \text{N} \begin{cases} \text{CH}_2\text{COO}^- \\ \text{CH}_2\text{COOH} \\ \text{CH}_2\text{COOH} \end{cases}$

Experimental:  $[d \log i_{p,c}/d \log \text{Cu(II)}]_{\text{NTA},v} = + 0.45$   
 $[d \log i_{p,c}/d \log \text{NTA}]_{\text{Cu(II)},v} = - 0.5$

**Figure 13.** The variation of first anodic peak current  $i_{p,a}(I)$  with NTA concentration for different  $v$ .

If  $\theta > 0.1$ , and for the nonactivated Temkin isotherm with the second electron being slow,

$$i_c = \bar{K}_2 K_1 \{ [\text{Cu}(\text{NTA}^-)]^{2+} \}^{0.5} \exp[-\beta F \Delta \phi / RT]$$

The formation of the monovalent copper complex is further confirmed by the  $i_{p,a}(I)$  dependencies on (NTA) concentration (figure 13) and excess  $\text{Cu}^{2+}$  ions would increase the first anodic peak current (figure 14) with the formation of monovalent complex stabilised by  $\text{Cu}^{2+}$  ions. The second anodic peak current corresponding to the formation of Cu(II) complex was diminished by the presence of excess  $\text{Cu}^{2+}$  ions (figure 15).

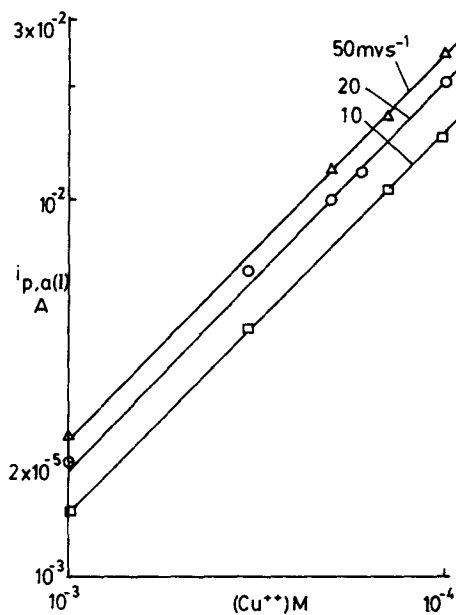


Figure 14. The variation of log first anodic peak current  $i_{p,a}(I)$  with  $\log(Cu^{2+})$  concentration in  $5 \times 10^{-3}$  M NTA for different  $v$ .

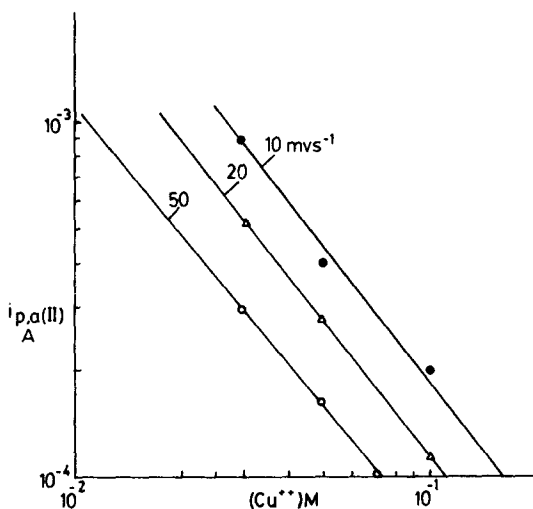


Figure 15. The variation of log second anodic peak current  $i_{p,a}(II)$  with  $\log(Cu^{2+})$  ion concentration at different  $v$ .

### Conclusions

Voltammetric studies revealed that under transient conditions, the deposition of copper from cupric ions involves the formation of adsorbed monovalent copper whose adsorption obeys the nonactivated Temkin isotherm. The conversion of  $Cu^{++}$  to

$\text{Cu}^+$  is a slow step. In presence of NTA ( $10^{-3}$  M to  $10^{-2}$  M) the formation of the monovalent copper complex obeys nonactivated Temkin adsorption. The presence of NTA changes the mechanism of deposition and the second electron transfer is slow.

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