Electroreduction of Cu(II)-tartrate complexes in acid media

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Cathodic processes proceeding in 0.01 M Cu(II) solutions involving 0.04 M tartaric acid at $2.8 < pH < 4.2$ have been investigated. Voltammograms obtained under forced convection conditions may be quantitatively described by equations of formal electrode kinetics provided that the transfer of the first electron to CuL_2^{2-} (L^{2-} is an anion of tartaric acid) is the rate-determining step. Kinetic parameters were found to be different for direct and reverse scan of the electrode potential. Changes in the surface activity of Cu electrode caused by the formation/destruction of Cu_2O layers are supposed to be responsible for such an effect. The characteristic current peak observed at ca -0.7 V might be attributed to the reduction of tartaric acid.

Key words: copper, plating, tartaric acid

INTRODUCTION

Tartaric acid (HOOC-CH(OH)-CH(OH)-COOH) and its salts are widely used in electrochemical and electroless plating of copper [1, 2]. It is known as a bidentate ligand [3, 4] capable of forming Cu(II) chelates in a wide pH region. Since this acid contains two mobile protons in carboxylic groups, it is usually symbolized as LH_2 [5, 6]. Besides, a release of the third proton is also known to occur due to a dissociation of OH-group in strongly alkaline media [6, 7].

Equilibrium characteristics of Cu(II)–tartrate complexes have been investigated by means of various methods including pH-metry [8, 9], potentiometry [9], polarography [10], NMR [8], EPR [4], spectrophotometry [8, 10], optical rotation [7]. Mercury and amalgam electrodes have been used in electrochemical methods. The determined stability constants are generalized in [5, 6]. However, the mechanism of electrochemical processes remains an open question as yet. In this connection, we have made an attempt to investigate the kinetics of electroreduction of Cu(II)-tartrate complexes in acid media.

EXPERIMENTAL

Solutions were prepared using thrice-distilled water, analytical grade $CuSO_4 \cdot 5 H_2O$ (0.01 M), L(+)-tartaric acid (0.04 M) and $Na_2SO_4 \cdot 10 H_2O$ (0.3 M) as a supporting electrolyte. Inorganic salts were recrystallized and heated. Solutions were deaerated by an argon stream for 0.5 h before each experiment.

The conventional three-electrode cell was used. A 5 µm thick copper layer plated on 1 cm^2 Pt substrate in acid Cu(II) sulphate solution at 10 mA cm^{-2} served as a working electrode. Electrode potentials (E) were measured with respect to the saturated Ag|AgCl, KCl reference electrode and converted to the hydrogen scale.

Experiments were carried out under natural or forced convection conditions, using rotating disc electrode (RDE). Voltammograms were recorded using the potentiostat PI-50-1 (Belarus) at 2 mV s^{-1} potential sweep rate, unless otherwise noted. All experiments were carried out at 20 ± 0.5 °C.

RESULTS AND DISCUSSION

Typical cyclic voltammograms recorded under forced convection conditions are shown in Fig. 1. Cathodic current densities (i_c) obtained with direct and reverse scans of the potential do not coincide and differ by *ca* 0.15 V. The reason for such a behaviour will be discussed below. The well-defined plateau of the limiting current density (i_d) is observed at $-0.4 < E < -0.2$ V. It slightly depends on pH, but is strongly controlled by the intensity of forced convection. Experimental plots of i_d *vs* $\sqrt{\omega}$ (ω is the angular velocity of electrode rotation) may be well approximated by the line passing the origin (Fig. 2). It follows from these data and Levich equation that an effective diffusion coefficient $D = 3.7 \times 10^{-6}$ cm^2 s^{-1}. Similar D values have also been obtained for Zn–tartrate complexes [11].
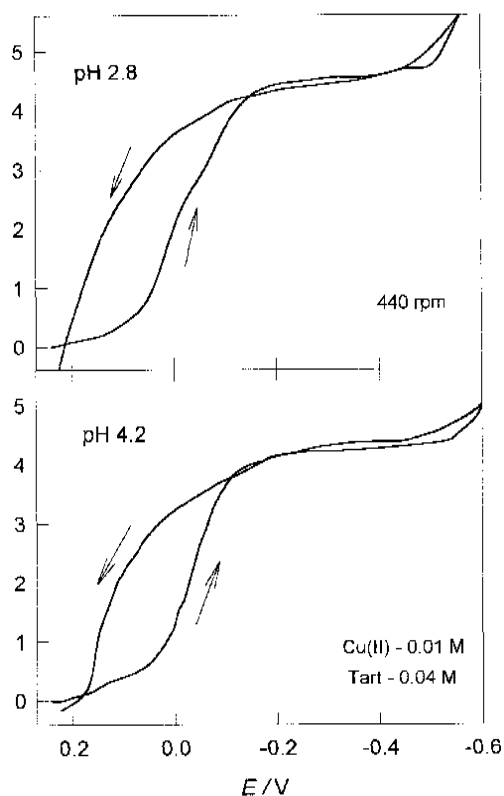
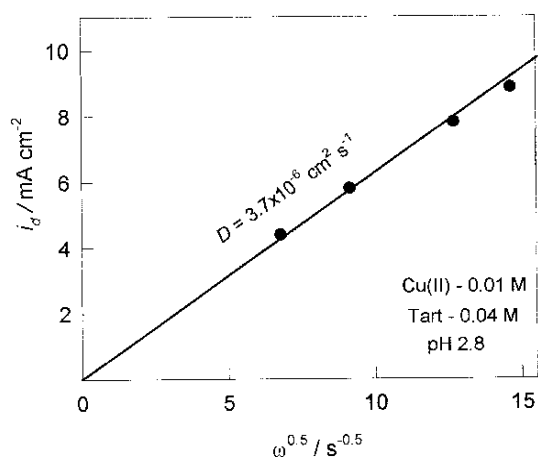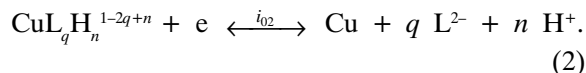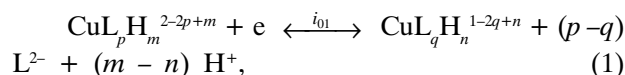Fig. 1. Examples of cyclic voltammograms obtained under forced convection conditions (RDE at 440 rev min⁻¹)

Fig. 2. Variation of limiting current density with $\sqrt{\varpi}$ (ϖ is an angular rotating velocity of RDE). Experimental data (symbols) and Levich approximation (line) obtained with $D = 3.7\times10^{-6}$ cm^2 s^{-1}

$$CuL_pH_m^{2-2p+m} + e \xrightleftharpoons{i_{01}} CuL_qH_n^{1-2q+n} + (p-q)$$
$$L^{2-} + (m-n)\ H^+, \tag{1}$$

$$CuL_qH_n^{1-2q+n} + e \xrightleftharpoons{i_{02}} Cu + q\ L^{2-} + n\ H^+. \tag{2}$$

Both steps are characterized by exchange current densities (i_{01} and i_{02}) and respective anodic (α_{a1}, α_{a2}) and cathodic (α_{c1}, α_{c2}) charge transfer coefficients. General kinetic equations for such processes may be found, e.g., in [12]. The following simplified relationship is valid at sufficiently high cathodic overvoltages provided that the transfer of the first electron is the rate-determining step ($i_{01} << i_{02}$):

$$i_c = 2i_{01}\frac{c_s}{c_b}\exp\left(\frac{\alpha_{c1}F}{RT}\eta_c\right), \tag{3}$$

where c_s and c_b are surface and bulk concentrations of the electrochemically active complex (EAC) given in the left side of Eqn. (1). The cathodic current density (i_c) and overvoltage (η_c) are assumed to be positive. Since c_s depends on i_c, linear Tafel plots can be obtained with i_c normalized to c_s. Actually, it follows from (3) that

$$\log (i_c/c_s) = \log (2\,i_{01}) - \log c_b + \alpha_{c1}\,F\eta_c/\,2.303\,RT. \tag{4}$$

The c_s, as a function of i_c, can be obtained from the relationships describing the mass balance at the electrode surface. This procedure is given in detail in [12]. The analysis shows that the equilibria listed in Table are sufficient to be accounted for in the case of acid media.

Normalized Tafel plots (NTP) were constructed for all complex species whose bulk concentrations were not negligible. The experimental data obtained with direct scan of the potential and simulated for c_s, and c_b data were used for this purpose. Linear NTP (with the correlation coefficient equal to 0.998) was obtained only for CuL_2^{2-} (Fig. 3). This gives grounds to suppose that CuL_2^{2-} is the EAC taking part in the charge transfer step (1). The EAC of similar composition have been determined for electroreduction of Zn(II) on Hg [11].

Before proceeding to the quantitative description of the experimental data, some preliminary notes should be made. Two consecutive one-electron transfers are typical of Cu(II) reduction. As applied to the system under discussion, they may be given by the following generalized reactions:

Table. **Equilibrium characteristics of Cu(II)-tartrate system**

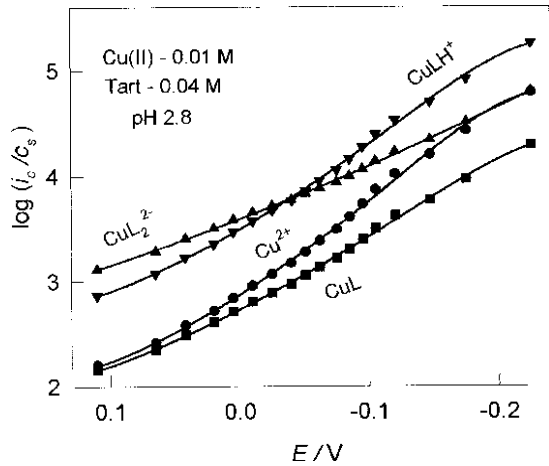| Equilibrium	Constant	Logarithm of constant	Reference
$L^{2-} + H^+ \Leftrightarrow LH^-$	β_1^H	4.24	[5, 6]
$L^{2-} + 2\ H^+ \Leftrightarrow LH_2$	β_2^H	7.24	[5, 6]
$Cu^{2+} + L^{2-} \Leftrightarrow CuL$	β_{10}	3.34	[5]
$Cu^{2+} + 2\ L^{2-} \Leftrightarrow CuL_2^{2-}$	β_{20}	5.68	[5]
$Cu^{2+} + L^{2-} + H^+ \Leftrightarrow CuLH^+$	β_{11}	5.45	[5]

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Fig. 3. Normalized Tafel plots constructed for different species (indicated on the curves) as possible electrically active complexes

The use of Eqn. (4) yields:

$$\alpha_{c1} = 0.295, \quad i_{o1} = 0.06 \text{ mA cm}^{-2}. \tag{5}$$

According to [12], the value of $\alpha_{c1} < 1$ supports the above assumption that the transfer of the first electron is the rate-determining step (otherwise an effective α more than 1 should be obtained). Then the complete kinetic equation takes the form

$$i_c = 2i_{o1}\left\{\frac{[CuL_2^{2-}]_s}{[CuL_2^{2-}]_b}\exp\left(\frac{\alpha_{c1}F}{RT}\eta_c\right) - \frac{[L^{2-}]_s^2}{[L^{2-}]_b^2}\exp\right.$$

$$\left.\left[-\frac{(2-\alpha_{c1})F}{RT}\eta_c\right]\right\}. \tag{6}$$

Kinetic parameters (5) and Eqn. (6) were used to simulate entire voltammograms that fairly coin-
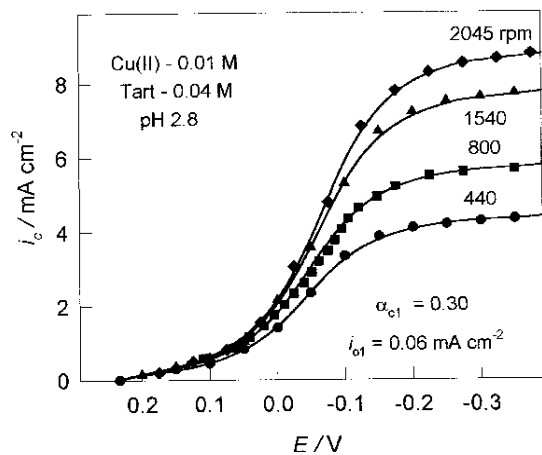

Fig. 4. Comparison of simulated (full lines) and experimental (symbols) voltammograms obtained with direct scan of electrode potential at different rotating velocities (rev min^{-1}) indicated on the curves

cide with experimental data obtained at different intensities of forced convection (Fig. 4).

Preliminary XRD investigations have shown that Cu$_2$O layers may be formed on the electrode surface in the system under discussion. Such an effect is typical of most electrochemical systems involving Cu(II) [13–20]. Cu$_2$O layers may affect not only the kinetics of Cu(II) reduction, but also its mechanism [13]. NTP obtained for direct and reverse scans do not coincide (Fig. 5), and higher exchange current densities follow from the analysis of presented data at the reverse scan. At the same time, the mechanism of Cu(II) reduction seems to remain the same, since linear NTP are obtained for CuL$_2^{2-}$ as an electrochemically active complex. An increase in α_{c1} with solution pH is also observed.

These phenomena make it possible to suppose that the activity of Cu electrode is increased at sufficiently high cathodic overvoltages due to the
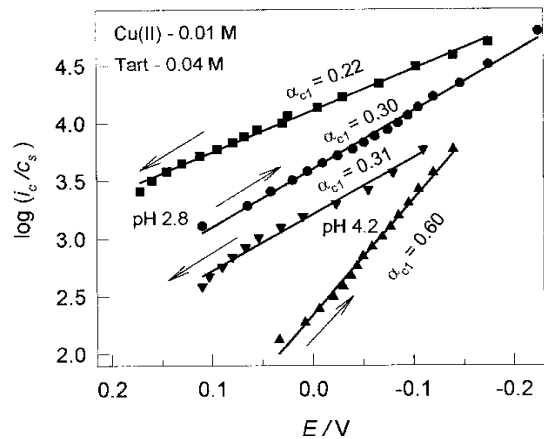

Fig. 5. Normalized Tafel plots obtained at different pH. The direction of potential scan is indicated by arrows
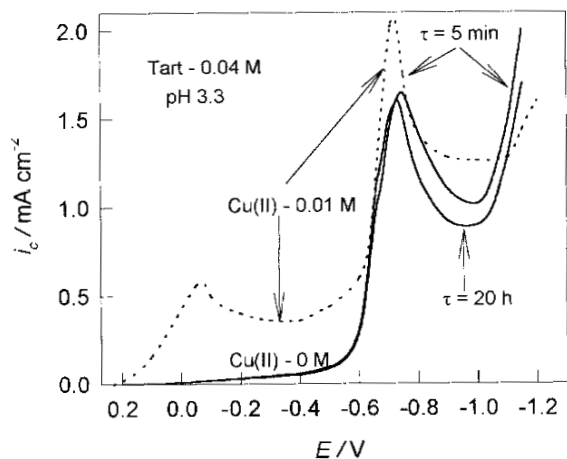

Fig. 6. Voltammograms obtained under natural convection conditions for copper-free (full lines) and Cu(II) containing (dotted line) solutions at 5 mV s^{-1} potential scan rate. Cu electrodes were exposed to the solutions for indicated time τ before measurements

reduction of Cu_2O. This process usually begins at a certain potential which depends on the ligand nature. The kinetic stability of Cu_2O has been discussed in [14, 17–20]. In the case of Cu|Cu(II), ethylenediamine system [20], Cu_2O reduction manifests itself as a well-defined peak of cathodic current whose height (i_p) varies linearly with the potential scan rate (v). Similar effects were also found to occur in Cu(II) solutions involving β-alanine, but no specific current peaks were observed in Cu|Cu(II), glycine system [13].

Cathodic current peaks are also observed at sufficiently high electrode potentials (*ca* –0.75 V) for the system under discussion (Fig. 6), but they cannot be attributed to Cu_2O reduction. Firstly, their height varies linearly with $\sqrt{v}$, this being indicative of a diffusion-controlled process. Secondly, i_p does not depend on the time (τ) of Cu electrode exposure to the solution. Finally, such peaks may be detected in Cu(II)-free solutions for both Cu (Fig. 6) and Pt (not shown) electrodes. Therefore, it may be assumed that the reduction of tartaric acid is responsible for a rise in i_p. The rate of such process is known to be reduced in less acid media where deprotonated species (anions of acids) begin to prevail. Such is indeed the case: the obtained experimental data have shown that i_p decreases with alkalization of the solutions.

CONCLUSIONS

1. Cathodic voltammograms obtained under forced convection conditions for 0.01 M Cu(II) solutions involving 0.04 M tartaric acid at 2.8 < pH < 4.2 have been quantitatively described in terms of formal kinetics provided that the transfer of the first electron to CuL_2^{2-} (L^{2-} is an anion of tartaric acid) is the rate-determining step.

2. Kinetic parameters of the charge transfer process are found to be different for direct and reverse scans of the electrode potential. Changes in the surface activity of Cu electrode caused by the formation/destruction of Cu_2O layers are supposed to be responsible for such an effect.

3. The characteristic current peak observed at *ca* –0.7 V might be attributed to the reduction of tartaric acid.

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TARTRATINIŲ Cu(II) KOMPLEKSŲ ELEKTROREDUKCIJA RŪGŠČIOSE TERPĖSE

S a n t r a u k a

Ištirti katodiniai procesai, vykstantys 0.01 M Cu(II) ir 0.04 M vyno rūgšties tirpaluose, kai 2.8 < pH < 4.2. Voltamogramas, gautas priverstinės konvekcijos sąlygomis, galima kiekybiškai aprašyti formaliosios elektrodinės kinetikos lygtimis, priimant, kad pirmojo elektrono pernešimas į CuL_2^{2-} (L^{2-} yra vyno rūgšties anijonas) yra greitį limituojanti stadija. Tiesioginio ir priešingos krypties potencialo skleidimo metu yra gaunami skirtingi kinetiniai parametrai. Manoma, kad šio efekto priežastimi yra Cu elektrodo paviršiaus aktyvumo pokyčiai, kuriuos sukelia Cu_2O sluoksnių susidarymas ar irimas. Charakteringą srovės smailę –0.7 V aplinkoje galima būtų priskirti vyno rūgšties redukcijai.

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ЭЛЕКТРОВОССТАНОВЛЕНИЕ ТАРТРАТНЫХ КОМПЛЕКСОВ Cu(II) В КИСЛЫХ СРЕДАХ

Р е з ю м е

Исследованы катодные процессы, протекающие в 0,01 М растворах Cu(II), содержащих 0,04 М винной кислоты при 2,8 < pH < 4,2. Вольтамперо-граммы, полученные в условиях принудительной конвекции, могут быть количественно описаны уравнениями формальной электродной кинетики в предположении, что перенос первого электрона на CuL_2^{2-} (L^{2-}-анион винной кислоты) является скорость определяющей стадией. Обнаружено, что кинетические параметры, установленные при прямой и обратной развертке потенциала, различаются. Предполагается, что этот эффект может быть обусловлен изменением активности поверхности электрода из-за образования или разрушения слоев Cu_2O. Характерный пик тока, наблюдаемый при –0,7 В, может быть вызван восстановлением винной кислоты.