

Cathodic processes in Cu(II) solutions containing malic acid

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Linear potential sweep voltammetry was applied for the investigation of cathodic processes proceeding in 0.01 M Cu(II) and 0.04 M malic acid (LH₂) solutions at pH ranging from 2.2 to 4.5. The analysis of material balance in the system shows that two species containing Cu(II) are predominant in the acidic medium: CuLH⁺ at pH < 4 and CuL₂²⁻ at pH > 4. Fractions of other species, such as Cu²⁺, CuLH₂²⁺ and CuL, are significantly smaller. Two characteristic current peaks observed on cathodic voltammograms result from Cu(II) reduction and hydrogen evolution, respectively. It is supposed that the protonated ligands generating H⁺ ions take part in the latter process. Peak currents and potentials can be described quantitatively using equations accounting for irreversible character of both processes that are characterized by cathodic charge transfer coefficients equal to 0.4 and 0.55, respectively.

Key words: copper, malic acid, complexes, electroreduction, potential sweep voltammetry

INTRODUCTION

Organic acids containing some OH-groups (oxy-acids) are often used as ligands capable of forming quite stable coordination compounds with Cu(II). Some of them, such as Cu(II)–tartrate complexes have found their practical use in electroless plating of dielectrics. Besides, tartaric and citric acids are also used in plating baths as additives producing compact, fine-grained copper coatings.

However, the kinetics and mechanism of Cu(II) reduction involving oxy-acids are scantily known. Cu(II) reduction [1] as well as Cu and Sn codeposition proceeding in citrate solutions [2–4] have been investigated using the RDE technique. Tafel plots normalized in respect of the surface concentration of electrically active complex (EAC) have been analyzed, and some mechanisms of Cu(II) reduction have been proposed. It was established, however, that the standard rate constant as well as the composition of EAC depend of the solution pH.

Polarographic investigations of Cu(II)–tartaric acid system have shown [5] that the limiting current is of a diffusion nature but nothing has been reported on the character of the polarograms. It should be reasoned that they are reversible since no kinetic parameters have been determined. In contrast, the analysis of quasi-reversible polarograms obtained for Zn(II) solutions involving tartrate complexes made it possible to conclude [6], that

both ion Zn²⁺ and biligand complex ZnL₂²⁻ can be electrically active particles.

A similar conclusion has been settled in the case of the electroreduction of Cu(II) tartrate complexes. An analysis of voltammetric RDE data invoking the normalized Tafel plots have shown [7] that CuL₂²⁻ complexes may be the species that accept the first electron in the consecutive charge transfer process. Besides, the second characteristic current maximum resulting from the hydrogen evaluation has been detected at higher cathodic polarizations.

Two current maxima have also been observed in the case of Cu(II) reduction in solutions containing glycolic acid [8]. The analysis made with an estimation of the surface concentrations of the components have shown that the aqua-complex of Cu(II) takes the immediate place in the charge transfer process in sufficiently acidic media. The second current peak has been attributed to the hydrogen evolution, where glycolic acid assists as a proton donor.

The formation of copper oxides occurring in neutral and alkaline media creates certain complications in the interpretation of the experimental data. This phenomenon is common in ligand-containing systems [9–11]. All-over oxide layers are generally formed, but sometimes other structures are also possible. For instance, the formation of 5–15 nm granules comprised of Cu and Cu₂O has been observed in alkaline Cu(II) solutions containing tartrates and lactates.

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Spare literature data on the reduction of oxy-acid complexes of Cu(II) show that the knowledge in this area is not sound. Therefore, the investigations of the kinetics and mechanism of Cu(II) reduction in such systems still remains a topical problem. This paper presents the main regularities of the processes occurring in Cu(II) solutions containing malic acid.

EXPERIMENTAL

The solutions under investigation contained 0.01 M Cu(II), 0.04 M malic acid and 0.3 M K_2SO_4 as a supporting electrolyte. Analytical grade $CuSO_4 \cdot 5 H_2O$ was purified by means of recrystallization. The required pH was adjusted by adding H_2SO_4 or KOH of high purity. Trice-distilled water was used for the preparation of the solutions. A pure argon stream was passed through the solutions for 0.5 h before the experiments.

A conventional three-electrode cell was used in the experiments. The working electrode was prepared by plating of 5–7 μm thick copper layer onto a Pt disc (1 cm^2 in area) fused into a glass holder. The electrolysis was performed at 10 $mA\ cm^{-2}$ in the solution containing ($g\ dm^{-3}$): $CuSO_4 \cdot 5 H_2O - 125$, H_2SO_4 ($d = 1.84\ g\ cm^{-3}$). A copper plate $\sim 8\ cm^2$ in area served as an auxiliary electrode (anode). Electrode potentials were measured with respect to the $Ag|AgCl|KCl(sat)$ reference electrode and were converted to the standard hydrogen scale.

Cathodic voltammograms were recorded at different potential sweep rates using a PI-50-1 potentiostat, an XY Recorder (Russia) and a freshly prepared copper electrode. All experiments were performed at $20 \pm 1\ ^\circ C$.

RESULTS AND DISCUSSION

Malic acid, $HOOC-CH_2-CH(OH)-COOH$, is usually symbolized as LH_2 to emphasize that its dissociation yields two hydrogen ions. Equilibrium constants of such processes as well as the stability constants of different Cu(II)–malate complexes collected in available catalogues [12–14] relate, in general, to perchlorate or nitrate media. Nevertheless, we have reasoned that these data could be used for the estimation of the composition of sul-

phate solutions. The stability constants conforming to a sufficiently high ionic strength ($\sim 1\ M$) were selected for this purpose. Some of them were averaged or recalculated and expressed in terms of cumulative stability constants β . Molar fractions α_j , defined as the ratio between the concentration of a certain complex and the total concentration of Cu(II), were calculated using the selected data (see Table) and well-known equations [15] accounting for material balance of Cu(II) and the ligand. The obtained results are shown in Fig. 1.

It can be seen that two species containing Cu(II) are predominant in the acidic medium: $CuLH^+$ at $pH < 4$ and CuL_2^{2-} at $pH > 4$. The fractions of other species, such as Cu^{2+} , $CuLH_2^{2+}$ and CuL , are significantly smaller. The content of the first two species increases with the acidity of the solution, whereas the latter complex is observed mainly in moderately acidic media.

A typical example of cathodic voltammograms is shown in Fig. 2. Curves of the same shape were obtained at other pH. Two current peaks, i_{p1} (left) and i_{p2} (right) are observed at ~ 0.0 and $0.9\ V$, respectively. Similar voltammograms have been also obtained in the case of other systems containing tartaric [7] or glycolic [8] acids. It was established using EQCM data that the

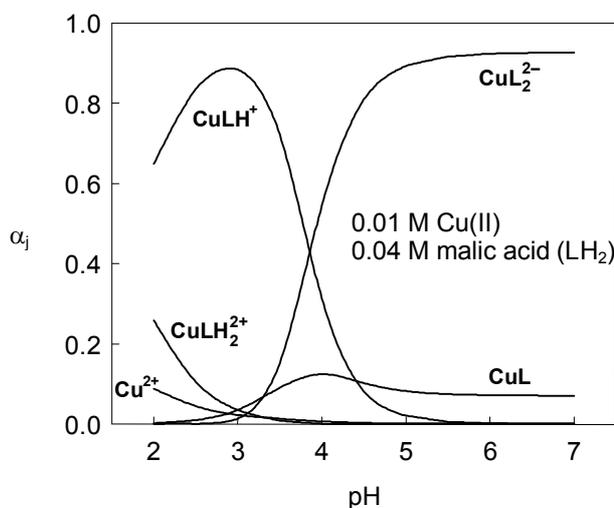


Fig. 1. Distribution of Cu(II) complexes at different pH of solutions containing 0.01 M of Cu(II) and 0.04 M of malic acid

Table. Selected constants of equilibria in Cu(II) solutions containing malic acid

Equilibrium	Equilibrium constant	log β
$L^{2-} + H^+ \rightleftharpoons LH^-$	β_{011}	4.36
$L^{2-} + 2 H^+ \rightleftharpoons LH_2$	β_{012}	7.4
$Cu^{2+} + L^{2-} \rightleftharpoons CuL$	β_{110}	3.4
$Cu^{2+} + 2 L^{2-} \rightleftharpoons CuL_2^{2-}$	β_{120}	6.2
$Cu^{2+} + L^{2-} + H^+ \rightleftharpoons CuLH^+$	β_{111}	7.8
$Cu^{2+} + L^{2-} + 2 H^+ \rightleftharpoons CuLH_2^{2+}$	β_{112}	9.4
$Cu^{2+} + 2 L^{2-} + 2 H^+ \rightleftharpoons CuL_2H_2$	β_{122}	12.0
$2 Cu^{2+} + 2 L^{2-} \rightleftharpoons Cu_2L_2$	β_{220}	8.0

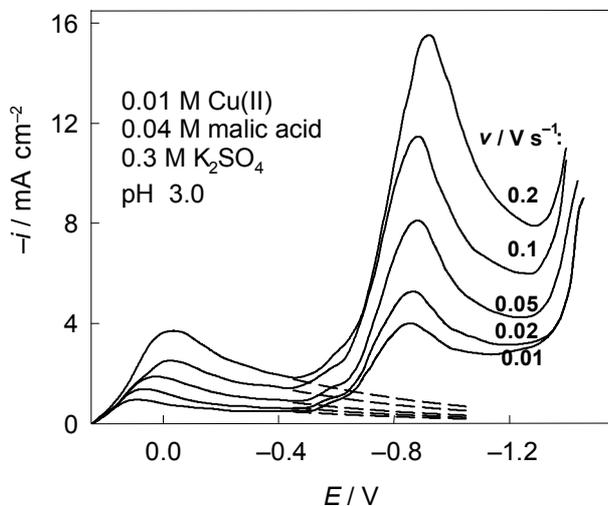


Fig. 2. Typical cathodic voltammograms obtained at different potential sweep rates as indicated in the respective curves. Dotted lines represent an extrapolation of partial Cu(II) reduction

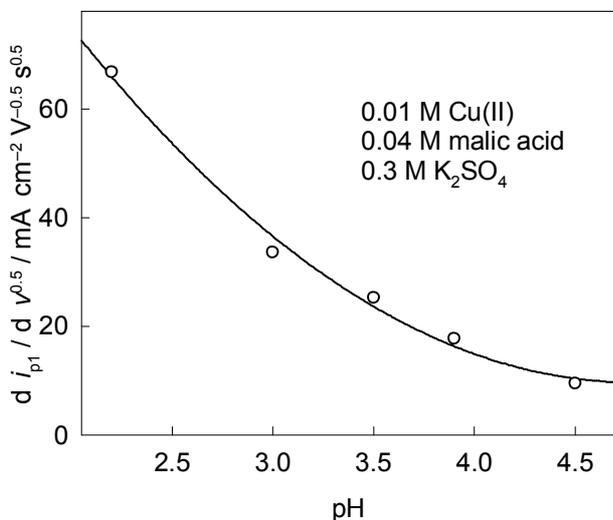


Fig. 4. pH-dependence of slopes of the lines given for i_{p2} in Fig. 3

first current peak arises from the Cu(II) reduction, while i_{p2} results from the hydrogen evolution. Considering the resemblance of these ligands, it seems possible to apply the same statements to malate solutions. Hereafter, we shall use the quantity i_{p2} as the height of the second current maximum measured from the level of Cu(II) reduction (see dotted lines in Fig. 2).

Both current peaks are in a linear dependence on the square root of the potential sweep rate v (Fig. 3). Besides, their potentials (E_{p1} and E_{p2}) also depend on v (vide infra). This is indicative of the irreversible nature of these processes. Based on the regularities of mass transport in labile complex systems [15], the equation derived in [16] can be rewritten as follows

$$i_{p1} = 0.282 n F c_{OB} \sqrt{\frac{\pi F}{RT}} \alpha_{c1} n_{\alpha} v D, \quad (1)$$

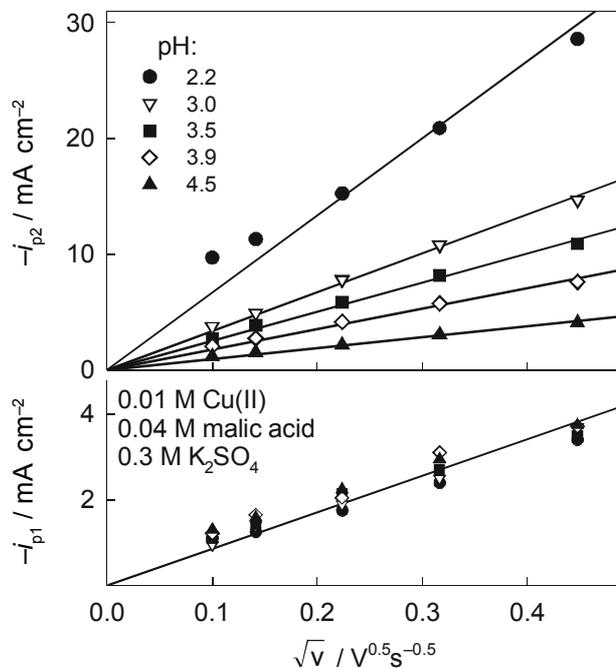


Fig. 3. Variations of the first and second current peaks (i_{p1} and i_{p2} , respectively) vs square root of potential sweep rate

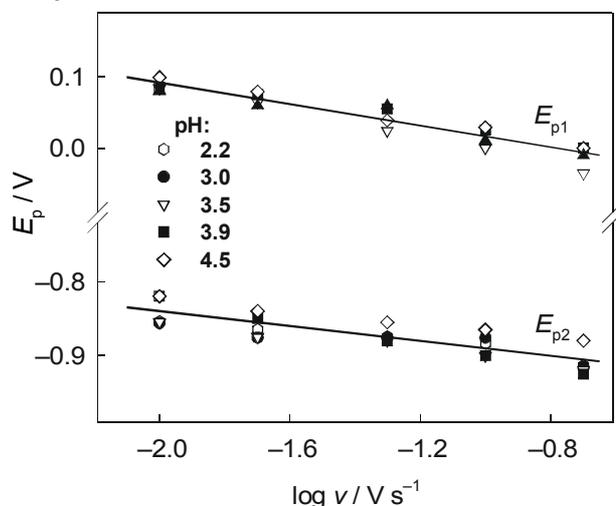


Fig. 5. Variations of potentials corresponding to the first and second current peaks (E_{p1} and E_{p2} , respectively) with the potential sweep rate

where c_{OB} is the total Cu(II) concentration. Eq. (1) can be used accepting that the diffusion coefficient $D = 4.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (the average value obtained for glycolate [8] and tartrate [7] solutions) and considering that the Cu(II) reduction ($n = 2$) proceeds through two consecutive one-electron steps ($n_{\alpha} = 1$). Then the average value of $di_{p1}/d\sqrt{v} = 8.5 \text{ mA cm}^{-2} \text{ V}^{-0.5} \text{ s}^{0.5}$ obtained from the data i_{p1} given in Fig. 3 and Eq. (1) yields the cathodic charge transfer coefficient $\alpha_{c1} = 0.43$.

In contrast to the above case, the dependence of i_{p2} on the solution pH is highly pronounced (Fig. 4). The preliminary analysis shows that the relationship similar to Eq. (1) can be used for a quantitative description of i_{p2} provided that c_{OB} is replaced by the total concentration of proton donors (see [8]). To obtain this quantity,

more faithful β values revised for sulphate solutions are required.

Peak potentials E_{p1} and E_{p2} weakly depend on the solution pH and vary linearly with $\log v$ (Fig. 5). This is in accordance with the theory of irreversible processes [17], asserting that

$$E_p = \text{const} - \frac{RT}{2\alpha_c n_a F} \ln(an_a v). \quad (2)$$

Thus, Eq. (2) and the slopes of the lines in Fig. 5 can be used for the determination of α_c . We obtained 0.39 and 0.55 for Cu(II) reduction and hydrogen evolution, respectively. The first value is consistent with α_{c1} obtained above from i_{p1} characteristics. To determine other kinetic parameters and details concerning the mechanism of charge transfer, more reliable stability constants are required. Literature data available for perchlorate or nitrate media often need corrections accounting for the interactions between Cu^{2+} and sulphate ions [8].

CONCLUSIONS

1. A simulation of the composition of 0.01 M Cu(II) and 0.04 M malic acid (LH_2) solutions shows that CuLH^+ and CuL_2^{2-} species are predominant in acidic media at $\text{pH} < 4$ and $\text{pH} > 4$, respectively. Small fractions (10–20%) of other species (Cu^{2+} , CuL ir CuLH_2^{2+}) can exist at $\text{pH} < 3$.

2. Two characteristic current peaks occurring on the cathodic voltammograms obtained under linear potential sweep conditions are determined by Cu(II) reduction and hydrogen evolution, respectively. Protonated ligands generating H^+ ions take part in the latter process.

3. Specific variations of the peak currents and potentials with the potential sweep rate are indicative of the irreversible character of both processes that are characterized by the cathodic charge transfer coefficients equal to 0.4 and 0.55, respectively.

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KATODINIAI PROCESAI CU(II) IR OBUOLIŲ RŪGŠTIES TIRPALUOSE

Santrauka

Katodiniai procesai, vykstantys 0,01 M Cu(II) ir 0,04 M obuolių rūgšties (LH_2) tirpaluose, kurių pH 2,2–4,5, buvo tiriama, naudojant tiesinio potencialo skleidimo voltamperometrija. Sistemos materialaus balanso analizė rodo, kad rūgščioje terpėje vyrauja du kompleksai: CuLH^+ (pH < 4) ir CuL_2^{2-} (pH > 4). Kitų dalelių (Cu^{2+} , CuL ir CuLH_2^{2+}) kiekiai yra gerokai mažesni (10–20%).

Katodinės voltamperogramos turi du būdingus srovių maksimumus, kuriuos sąlygoja Cu(II) redukcija ir vandenilio skyrimasis. Manoma, kad pastarajame procese dalyvauja protonuoti ligandai, generuojantys H^+ jonus. Taikant negrįžtamųjų procesų lygtis, abiejų maksimumų sroves ir potencialus galima aprašyti kiekybiškai, naudojant katodinius krūvio pernešimo koeficientus, lygius atitinkamai 0,4 ir 0,55.