

# Effect of the nature of supporting electrolyte on the electroreduction kinetics of Cu(II)–glycine complexes in slightly alkaline medium

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Voltammetry and electrochemical impedance spectroscopy were used to investigate the effect of the nature of a supporting electrolyte (lithium, sodium, potassium and caesium sulphates) on the electroreduction kinetics of Cu(II)–glycine complexes at pH 8.3. An analysis of normalized Tafel plots shows that voltammograms may be treated quantitatively provided that a mono-ligand complex  $\text{CuL}^+$  ( $\text{L}^-$  is the anion of glycine) is the electrically active complex taking part in the consecutive transfer of two electrons. With an increase in the radius of the alkaline metal ion there is a rise in the cathodic charge transfer coefficient accompanied by a fall in the exchange current density. Surface oxides may be formed in the system and the most pronounced effect of the surface oxidation is observed in solutions containing  $\text{K}_2\text{SO}_4$ .

**Key words:** copper, glycine, complexes, electroreduction, cuprous oxide, voltammetry, impedance spectroscopy

## INTRODUCTION

Cathodic processes involving Cu(II) complexes are often complicated due to the formation of surface oxides as a rule containing  $\text{Cu}_2\text{O}$ . This side process affects not only the kinetics of Cu(II) reduction but is also capable of changing its mechanism [1]. In the case of sufficiently thin oxide layers, basic relationships of formal electrode kinetics are still appropriate, but their employment becomes problematic when tens of  $\text{Cu}_2\text{O}$  monolayers are formed [2]. The thermodynamic probability of copper oxidation mainly depends on solution pH, but the kinetics of this process is also of great importance. The investigations of Cu|Cu(II) systems containing different ligands have shown [3] that the formation of photosensitive oxide layers on copper electrode is most pronounced when the complexation degree of Cu(II) is sufficiently low.

From this point of view, systems containing such simple amino acids as glycine,  $\alpha$ - or  $\beta$ -alanine are of a certain interest. The analysis of the interactions proceeding at the interface Cu|solution has shown [4] that  $\text{Cu}_2\text{O}$  layers become thermodynamically stable when the pH of these solutions exceeds 4, 3.5 and 3.3, respectively. However, due to the fact that two former ligands give rise to more stable Cu(II) complexes, the oxidation degree of Cu electrode in this case is low and, consequently, the photo-effects are considerably weaker as compared with these observed in  $\beta$ -alanine system [1–3, 5–7].

It was also found [8] that the kinetic parameters of the reduction of Cu(II)–glycine complexes in an acidic medium (pH 3.5)

significantly depend on the nature of the supporting electrolyte. While moving from  $\text{Li}_2\text{SO}_4$  to  $\text{Cs}_2\text{SO}_4$ , the cathodic charge transfer coefficient increases from 0.16 to 0.7, and the exchange current density falls from 0.3 to 0.06  $\text{mA cm}^{-2}$ . The obtained results show that the cations of alkaline metals are capable of interacting with Cu(II) complexes in the double electric layer and, therefore, they cannot be treated as ‘inactive’ components.

It is important to determine whether these regularities are obeyed in slightly acidic media, where the formation of oxide layers is possible. In this connection, voltammetric and impedance measurements were performed at pH 8.3 in Cu(II)–glycine solutions containing sulphates of different alkaline metals.

## EXPERIMENTAL

The solutions under investigation contained 0.01 M  $\text{CuSO}_4$ , 0.04 M  $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$  (both *Peaxum* (Russia), analytical grade) and 0.3 M  $\text{Me}_2\text{SO}_4$  (Me is any alkaline metal except rubidium). A specified value of pH, equal to 8.3, was adjusted by adding respective hydroxides. Thrice-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 measurements.

A conventional rotating disc electrode (RDE) technique was used in voltammetric measurements. For the preparation of the working electrodes, a platinum disc (3 mm in diameter) was coated at 10  $\text{mA cm}^{-2}$  with 5–7  $\mu\text{m}$  thick copper layer in the solution containing ( $\text{g dm}^{-3}$ ):  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O} - 200$ ,  $\text{H}_2\text{SO}_4 - 50$ . The working electrode was rinsed with water, immediately immersed into the solution under investigation and kept in it for ~10 min.

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A similar procedure was applied to prepare the electrodes for impedance measurements. A platinum wire with  $0.36 \text{ cm}^2$  surface area fused into a glass holder was used as a substrate in this case. An additional electrode (platinum cylinder) was embedded for the perturbation by an alternating current. Electrode potentials were measured with respect to Ag | AgCl | KCl(sat) reference electrode and were converted to the standard hydrogen scale.

Voltammetric characteristics were recorded at potential sweep rates  $v = 5 \text{ mV s}^{-1}$  using AUTOLAB (ECO Chemie, the Netherlands) and the rotating disc electrode. The same equipment was used to obtain the impedance spectra within a frequency  $f$  range from 0.05 to 40 000 Hz. Each record took about 5 min and was repeated for 3–4 times. All experiments were performed at  $20 \text{ }^\circ\text{C}$ . Computer programs elaborated by Boukamp [9] were used for analyzing the impedance data.

## RESULTS AND DISCUSSION

The voltammograms of Cu(II) reduction obtained for the solutions containing different supporting electrolytes are shown in Fig. 1. It is clearly seen that the cathodic current density  $i$  to a marked extent depends on the intensity of forced convection, i. e. on the rotating velocity  $\Omega$  of RDE. This means that the dif-

fusive mass transport is one of the main factors that control the kinetics of the cathodic process. In general, it may be considered that the limiting current  $i_{\text{lim}}$  is of a diffusive nature ( $i_d$ ), but this is strictly true only for solutions containing lithium, sodium or caesium sulphates as electrochemically inactive electrolytes. In this case,  $i_{\text{lim}}$  dependences on  $\sqrt{\Omega}$  may be approximated by a single line passing through the origin of the Levich coordinates (Fig. 2). Quite an acceptable value of the average diffusion coefficient, namely,  $D = 5.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  is obtained from these data and the Levich equation:

$$i_d = 0.62 nFD^{2/3}v^{-1/6}\Omega^{1/2}c_{\text{OB}}, \quad (1)$$

where  $c_{\text{OB}}$  is the total concentration of Cu(II).

However, similar data obtained for solutions containing  $\text{K}_2\text{SO}_4$  are elevated by  $\sim 1.7 \text{ mA cm}^{-2}$ . An examination of respective voltammograms (Fig. 1) shows that certain pre-waves occur at low cathodic polarizations. The rudiments of such irregularities may be also detected in the presence of  $\text{Cs}_2\text{SO}_4$ , but the height of the pre-waves under discussion is significantly lower in the latter case. The reasons for such behaviour are discussed below, and here we begin with the analysis of the voltammograms obtained in the presence of the rest supporting electrolytes.

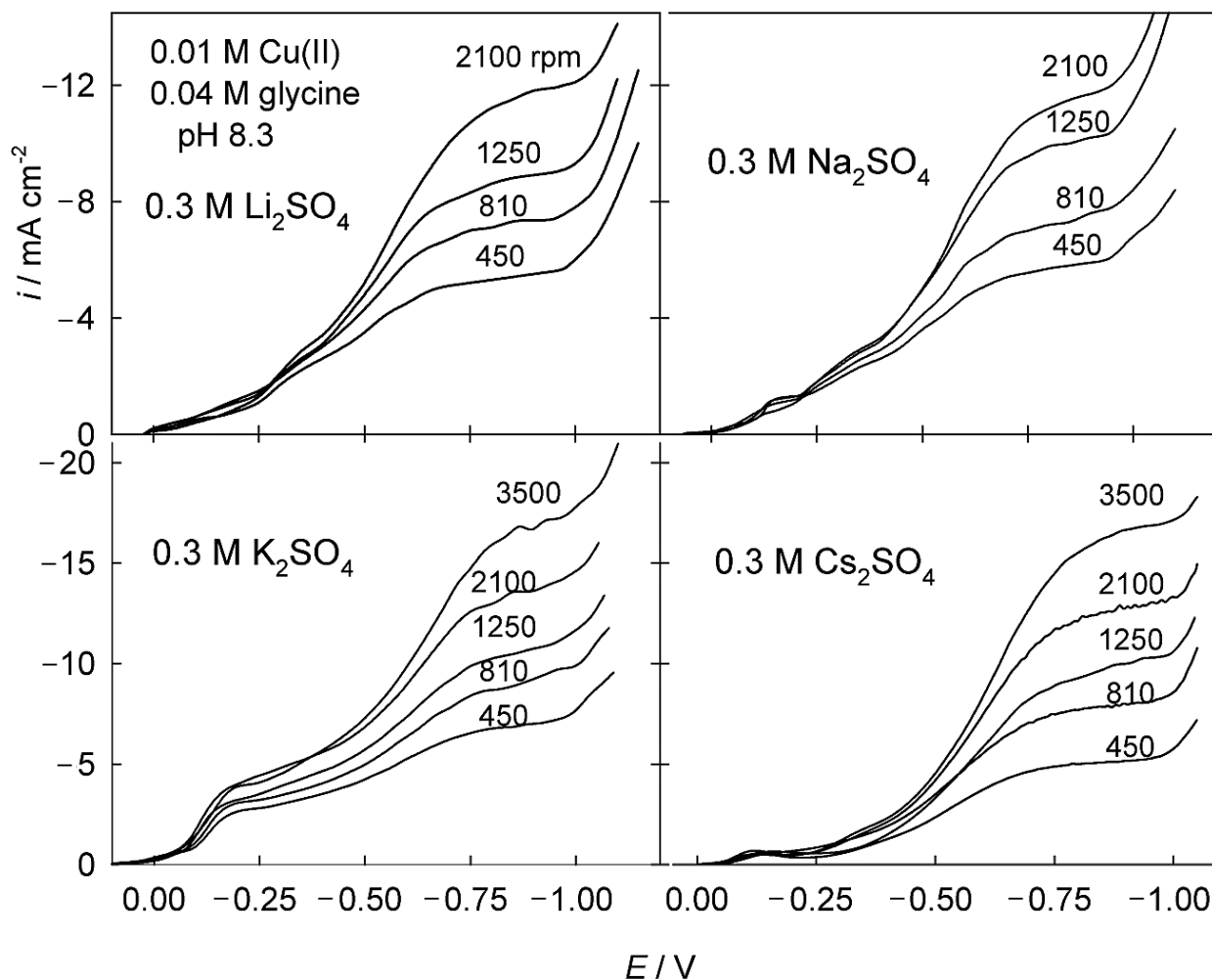


Fig. 1. Voltammograms of Cu(II) reduction obtained in the solutions containing different supporting electrolytes as indicated. The rotating velocities of RDE (revolutions per minute) are given at respective curves

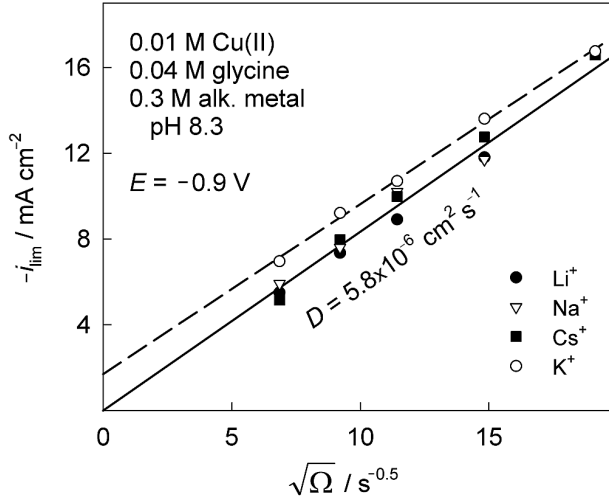


Fig. 2. Variations of the limiting current density with square root of angular rotating velocity of RDE

According to [10], glycine  $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$  may be expressed as LH to indicate that this substance is a weak acid containing one mobile proton and capable of generating the active deprotonated form  $\text{L}^-$ . The latter species form complexes  $\text{CuL}^+$  and  $\text{CuL}_2$ . Depending on the solution pH, there may exist three species of the free ligand:  $\text{L}^-$ , LH and  $\text{LH}_2^+$ . The compositions of the solutions under investigation can be calculated using material balance equations written for total metal and total ligand concentrations [8]:

$$c_{\text{OB}} = [\text{Cu}^{2+}] \left( 1 + \sum_{p=1}^2 \beta_p [\text{L}^-]^p \right), \quad (2)$$

$$c_{\text{LB}} = [\text{Cu}^{2+}] \sum_{p=1}^2 p \beta_p [\text{L}^-]^p + [\text{L}^-] \left( 1 + \sum_{q=1}^2 \beta_q^{\text{H}} [\text{H}^+]^q \right), \quad (3)$$

where  $\beta_p$  and  $\beta_q^{\text{H}}$  are stability constants of  $\text{CuL}^{2-p}$  and  $\text{LH}_q^{q-1}$ , respectively. The last two relationships may be also used to evaluate the distribution of the components at the electrode surface. Then, the surface concentration of the total metal depends on  $i$ :

$$c_{\text{OB},s} = c_{\text{OB},b} (1 - I / i_d), \quad (4)$$

(here additional subscripts  $s$  and  $b$  denote the surface and bulk concentrations) and the relationship, accounting for the material balance of proton donors and acceptors

$$c_{\text{HB}} = [\text{H}^+] + [\text{L}^-] \sum_{q=1}^2 q \beta_q^{\text{H}} [\text{H}^+]^q - [\text{OH}^-], \quad (5)$$

should be used in addition to [8].

The quantitative analysis of the voltammetric data is based on the following statements. According to [1, 8], monoligand complexes of Cu(II), viz  $\text{CuL}^+$ , are the electrically active species that take part in the charge transfer process. The latter is known to proceed by two one-electron transfers

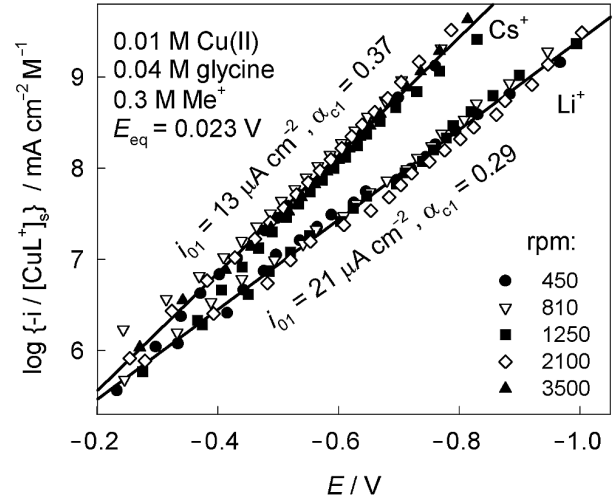


Fig. 3. Normalized Tafel plots obtained from the data in Fig. 1. Kinetic parameters obtained from the linear regions of the plots are also listed



that are characterized by the respective exchange current densities ( $i_{01}$  and  $i_{02}$ ) and cathodic charge transfer coefficients ( $\alpha_{c1}$  and  $\alpha_{c2}$ ). When  $i_{01} \ll i_{02}$ , the kinetic equation takes the following form:

$$i = 2i_{01} \left\{ \exp \left( \frac{(2 - \alpha_{c1})F}{RT} \eta \right) - \frac{[\text{CuL}^+]_s}{[\text{CuL}^+]_b} \exp \left( -\frac{\alpha_{c1}F}{RT} \eta \right) \right\}. \quad (8)$$

Then, the next relationship is valid for sufficiently high cathodic overvoltages  $\eta$ :

$$\log \frac{|i|}{[\text{CuL}^+]_s} = \log 2i_{01} - \log [\text{CuL}^+]_b - \frac{\alpha_{c1}F}{2.303 RT} \eta. \quad (9)$$

The graphs, constructed according to eq. (9), are known as Tafel plots normalized with respect to the surface concentration of the electrically active complex (NTP, in short).

The experimental voltammograms were transformed into NTP using simulated  $[\text{CuL}^+]_s$  values as functions of  $i$  (for details see [2, 3]). Calculations were performed with  $\beta$  values as follows [1, 10]:  $\log \beta_1 = 8.46$ ,  $\log \beta_2 = 15.3$ ,  $\log \beta_1^{\text{H}} = 9.68$ ,  $\log \beta_2^{\text{H}} = 2.05$ . The obtained results show (Fig. 3) that a single line in a wide region of the cathodic overvoltages may approximate NTP constructed for different rotating velocities. Kinetic parameters  $\alpha_{c1}$  and  $i_{01}$  were obtained, respectively, from the slopes of NTP and  $i$  values extrapolated to equilibrium potential; they are listed in Fig. 3. Similar results obtained for solutions containing  $\text{Na}_2\text{SO}_4$  are close to these established in the presence of  $\text{Li}_2\text{SO}_4$ :  $i_{01} = 20 \mu\text{A cm}^{-2}$  and  $\alpha_{c1} = 0.27$ . Certain pre-waves are observed on the voltammograms recorded in the solutions containing potassium sulphate. For this reason, linear NTP were not obtained and the kinetic parameters were not determined in this case.

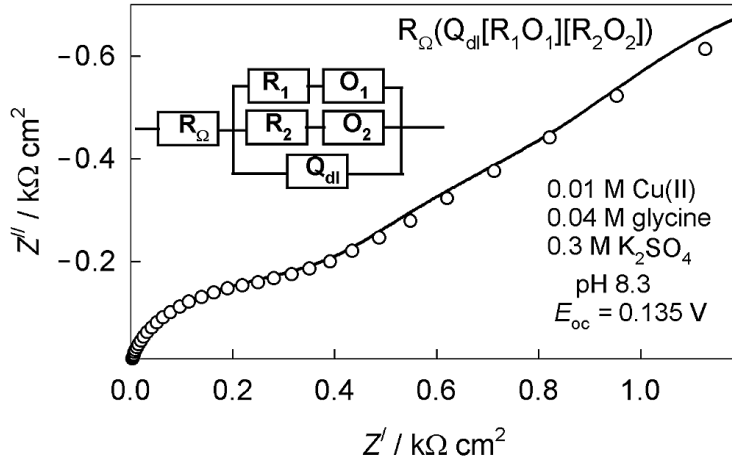


Fig. 4. Nyquist plot obtained for the solution of indicated composition at the open-circuit potential. Experimental data (circles) are compared with spectra (solid line) simulated for given equivalent circuit at  $R_{\Omega} = 1.96 \Omega \text{ cm}^2$ ,  $R_1 = 502 \Omega \text{ cm}^2$ ,  $R_2 = 203 \Omega \text{ cm}^2$ . The rest parameters are:  $Y_0 = 2.6 \times 10^{-5} \Omega^{-1} \text{ cm}^{-2} \text{ s}^n$  and  $n = 0.909$  (element  $Q_{dl}$ ),  $Y_0 = 1.2 \times 10^{-3} \Omega^{-1} \text{ cm}^{-2} \text{ s}^{0.5}$  and  $B = 3.73 \text{ s}^{0.5}$  (element  $O_1$ ),  $Y_0 = 2.1 \times 10^{-4} \Omega^{-1} \text{ cm}^{-2} \text{ s}^{0.5}$  and  $B = 1.21 \text{ s}^{0.5}$  (element  $O_2$ ).

Some additional information on the kinetic and double layer parameters may be obtained from the impedance measurements. According to [11], when the step-wise reduction of  $\text{Cu}^{2+}$  proceeds in the absence of a ligand on ideally smooth electrodes, the equivalent circuit contains two parallel Faradaic subcircuits, each of them involving charge transfer resistance  $\mathbf{R}$  and Warburg impedance  $\mathbf{W}$  in series. This set of elements is shunted with double layer capacitance  $\mathbf{C}_{dl}$  and, finally, an ohmic resistance of the solution  $\mathbf{R}_{\Omega}$  should be added [11]. In terms of Boukamp's notation [9], the description code of such circuit is  $\mathbf{R}_{\Omega}(\mathbf{C}_{dl}[\mathbf{R}_1\mathbf{W}_1][\mathbf{R}_2\mathbf{W}_2])$ . In this case, Nyquist plots (relations between real ( $Z'$ ) and imaginary ( $Z''$ ) components of the impedance) are composed of arcs centred below the abscissa axis (high frequency region) and of the lines with the unit slope (low frequency region).

Since these features are, in general, characteristic of the experimental data (Fig. 4), the above equivalent circuit may be used as a basis for a quantitative description of the impedance spectra. However, certain modifications of the electric analogues are necessary. Primarily, due to the deviations from the ideal behaviour that are typical of solid electrodes,  $\mathbf{C}_{dl}$  should be replaced by the constant phase element  $\mathbf{Q}_{dl}$ . Besides, the analysis has also shown that the model of the semi-infinite diffusion is not the best approximation and an appropriate account for the finite-length diffusion is required. In this connection, the concept of the so-called "transmissive boundary" [12] was used. According to this model, the diffusive mass transport takes place within the surface layer, located at the distance  $x \leq l$  from the electrode surface. Farther to the bulk of the solution, a fixed concentration for the diffusing species is maintained and the boundary at  $x = l$  is permeable for them. This type of mass transport is generally observed for the rotating disc electrode, where the thickness of the diffusion layer is determined by the rotation rate, or in oxygen conducting electrodes, as well as in the corrosion related diffusion. To account for the above phenomena, element  $\mathbf{O}$  was introduced with impedance [12]

$$Z_w = \frac{\sigma}{\sqrt{\omega}} \tanh\left(\sqrt{\frac{j\omega}{D}} l\right) (1-j), \quad (10)$$

where  $\omega = 2\pi f$ ,  $j = \sqrt{-1}$  and  $\sigma$  is the well-known Warburg constant following from (10) at  $l \rightarrow \infty$ .

Thus, the modified equivalent circuit transforms into  $\mathbf{R}_{\Omega}(\mathbf{Q}_{dl}[\mathbf{R}_1\mathbf{O}_1][\mathbf{R}_2\mathbf{O}_2])$ . Its impedance spectrum is in good

agreement with the experimental data (Fig. 4). The established parameters of the circuit are given in Fig. 4 following the Boukamp's notation [9], according to which the admittance of element  $\mathbf{O}$  is:

$$Y = Y_0 \sqrt{j\omega} \coth(B\sqrt{j\omega}). \quad (11)$$

Equations (10) and (11) become identical at  $Y_0 = 1/\sigma$  and  $B = 1/\sqrt{D}$ . The insertion of  $B$  and  $D$  values obtained from the impedance and voltammetric data (see above) into the last relationship shows that the thickness of the limited diffusion space is in the range of 30–50  $\mu\text{m}$ . This quantity could not be attributed to the thickness of the Nernst-type diffusion layer formed in the solution under natural convection conditions (it should be at least 5 times larger). Another alternative is the concept according to which copper ions pass the oxide layer, where  $D$  is commonly by 2–3 orders of magnitude lower and, consequently, the thickness of this layer might be respectively thinner. There are grounds to assume that both types of diffusion are responsible for the obtained  $B$  values. The attempts to install the subcircuit accounting for the existence of the oxide layer failed due to a significant complication of the basic equivalent circuit resulting in its ambiguity. Therefore, more definite conclusions are not available yet. It should be noted that very close  $B$  values equal to  $3.37 \text{ s}^{0.5}$  have been obtained for Cu(II) acetate solutions [13]. Besides, somewhat similar equivalent circuit  $\mathbf{R}_{\Omega}(\mathbf{Q}_{dl}\mathbf{R}_1[\mathbf{R}_2\mathbf{O}_2])$  with  $B = 3.53 \text{ s}^{0.5}$  was found to be applicable in the case of 0.01 M  $\text{CuSO}_4$  solutions at pH 5 when the formation of the surface oxides is also possible.

The impedance obtained for the system under investigation is almost by 100 times higher as compared with the ligand-free solutions, though the spectra of electrical phase angle  $\psi = \arctan(Z''/Z')$  are similar in shape (Fig. 5). This means that the chemical reactions preceding the charge transfer steps, as well as the weak surface oxidation, do not change radically the overall electrochemical reaction. Cu(II)–glycine complexes should be categorized as quite labile compounds. This is evident from high rate constants of the processes  $\text{CuL}_{n-1}^{3-n} + \text{L}^- \rightarrow \text{CuL}_n^{2-n}$  that are equal to  $4 \times 10^9$  ( $n = 1$ ) and  $4 \times 10^8$  ( $n = 2$ )  $\text{M}^{-1} \text{ s}^{-1}$  [14].

Returning to the voltammetric data, it might be concluded that the kinetics of the reduction of Cu(II)–glycine complexes in a slightly alkaline medium can be described quantitative within the

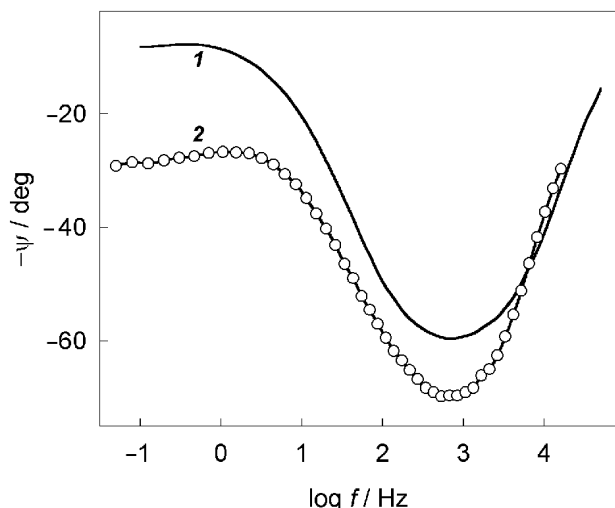


Fig. 5. Spectra of the electrical phase angle obtained for 0.01 M Cu(II) solution containing 0.6 M  $\text{H}_2\text{SO}_4$  (curve 1) and for Cu(II)–glycine system containing 0.3 M  $\text{K}_2\text{SO}_4$  at pH 8.3 (curve 2)

framework of the formal electrochemical kinetics provided that the surface oxidation is not too intensive. As in the case of acidic media, the kinetic parameters also depend on the nature of the supporting electrolyte, but these effects are less pronounced. Potassium sulphate somehow stands out from other cations: the surface oxidation is most pronounced in the presence of  $\text{K}^+$ . It should be mentioned that it is possible to intensify this process under certain experimental conditions. Then the voltammograms containing areas with negative slopes can be obtained and the nature of the rate-determining step becomes different for bare and oxidized surfaces [1].

## CONCLUSIONS

1. Limiting currents observed at pH 8.3 on the cathodic voltammograms of Cu|Cu(II)–glycine system with different supporting electrolytes obey the Levich equation, except the solutions containing  $\text{K}^+$ . In this case, limiting currents are elevated due to the appearance of the pre-wave at low cathodic polarizations.

2. The normalization of the voltammograms with respect to the surface concentration of the electrically active complex  $\text{CuL}^+$  ( $\text{L}^-$  is an anion of glycine) yields Tafel plots that are linear in a large region of cathodic overvoltages and rotating velocities of the disc electrode, when  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Cs}^+$  are present in the solution. In this sequence, the cathodic charge transfer coefficient increases and the exchange current density falls down.

3. The development of surface oxides is the most pronounced process in the solutions containing  $\text{K}_2\text{SO}_4$ . In this case, experimental impedance spectra match the equivalent circuit that contains the elements characterizing finite-length diffusion.

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## References

1. A. Survila, V. Uksienė, *Electrochim. Acta*, **37**, 745 (1992).
2. A. Survila, V. Uksienė, *Sov. Electrochem.*, **29**, 202 (1993).
3. A. Survila, P. Kalinauskas, I. Valsiūnas, *Russ. J. Electrochem.*, **38**, 1068 (2002).
4. A. Survila, V. Uksienė, *Sov. Electrochem.*, **25**, 856 (1989).
5. A. Survila, P. Kalinauskas, V. Uksienė, *Electrochim. Acta*, **38**, 2733 (1993).
6. A. Survila, P. Kalinauskas, E. Ivaškevič, W. Kutner, *Electrochim. Acta*, **42**, 2935 (1997).
7. A. Survila, A. Survilienė, S. Kanapeckaitė, J. Būdienė, P. Kalinauskas, G. Stalnionis, A. Sudavičius, *J. Electroanal. Chem.*, **582**, 221 (2005).
8. A. Survila, *Electrode processes in systems of labile complexes of metals*, Vilnius, Mokslas (1989).
9. B. B. Boukamp, *Equivalent Circuit (EQUIVCRT.PAS). User's Manual*. University of Twente (1989).
10. L. G. Sillen, A. E. Martel (eds.), *Stability Constants of Metal-Ion Complexes*, Special Publications N 17 and 25, Chemical Society, London, Vol. 1 (1964), Vol. 2 (1971).
11. A. Survila, V. Baliukienė, *Chemija*, **12**, 195 (2001).
12. A. Lasia, *Electrochemical impedance spectroscopy and its applications*, in *Modern aspects of electrochemistry*, B. E. Conway, J. Bockris, R. E. White (eds.), Kluwer Academic / Plenum Publishers, New York, Vol. 32, p. 143 (1999).
13. M. Metikoš-Huković, R. Babić, I. Paić, *J. Appl. Electrochem.*, **30**, 617 (2000).
14. A. F. Pearlmutter, J. Stuehr, *J. Amer. Chem. Soc.*, **90**, 858 (1968).

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## FONINIO ELEKTROLITO PRIGIMTIES ĮTAKA Cu(II)–GLICINO KOMPLEKSŲ ELEKTROREDUKCIJOS KINETIKAI SILPNAI ŠARMINĖJE TERPĖJE

### Santrauka

Voltamperometrijos ir elektrocheminio impedanso spektroskopijos metodais ištirta foninio elektrolito (ličio, natrio, kalio ir cezio sulfatų) prigimties įtaka Cu(II)–glicino kompleksų elektroredukcijos kinetikai silpnai šarminėje terpėje (pH 8,3). Normalizuotų Tafelio priklausomybių analizė parodė, kad eksperimentines voltamperogramas galima kiekybiškai aprašyti formaliosios elektrocheminės kinetikos lygtimis, darrant prielaidą, kad monobranduolinis kompleksas  $\text{CuL}^+$  ( $\text{L}^-$  yra glicino anijonas) yra elektriškai aktyvi dalelė, į kurią yra nuosekliai pernešami du elektronai. Didėjant šarminio metalo jono spinduliui, didėja katodinis krūvio pernašos koeficientas, kurį lydi mažėjantis mainų srovės tankis. Nagrinėjamoje sistemoje gali susidaryti paviršiniai oksidai. Šis procesas ypač pasireiškia tirpaluose su  $\text{K}_2\text{SO}_4$ .

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