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Impedance of copper electrode in slightly acid Cu(II)-glycine solutions

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Electrochemical impedance spectroscopy was used to study the kinetics of reduction of Cu (II) in weakly acidic (pH 4 and 5) solutions of Cu (II) containing glycine (0.04 or 0.1 M) as a complexing agent. A rather slow equilibration was observed at pH 4 and glycine concentration $c_L = 0.04$ M. With increasing pH or c_L, the total concentration of intermediate Cu(I) decreases. At the same time, impedance increases over the entire range of frequencies applied. An equivalent circuit with two parallel sub-circuits, each containing the charge transfer resistance and Warburg impedance in series, was used to quantify the impedance spectra. The exchange current densities of two consecutive one-electron transfers were estimated. Their average values are ~1 μA cm^{-2} and ~0.1 mA cm^{-2}.

Keywords: copper, electroreduction, glycine, impedance, equivalent circuit

INTRODUCTION

Glycine $H_2N\text{-}CH_2\text{-}COOH$ is widely distributed in the nature as an integral part of many vital substances. The ability of glycine to form complexes with metal ions has found its application in various fields of human activity. For example, in recent years, aqueous glycine solutions have shown themselves to be promising environment-friendly lixiviates for leaching precious metals [1]. In addition, glycinate complexes are often used in galvanic baths, the practical implementation of which from time to time encounters certain electrochemical problems. Besides, electrochemical systems containing metal complexes are also interesting from a theoretical point of view. The abundance of various chemical stages accompanying a charge transfer step makes them an attractive object for experimental studies.

The above also applies to the Cu|Cu (II)-glycine system, whose electrochemical properties have been investigated quite intensively until now. According to Aksu et al. [2], about 30 processes involving various species of ligands and complexes, as well as insoluble oxygen compounds, are possible in this system. The research conducted at our research institute has shown [3] that the reduction of Cu(II)-glycine complexes proceeds via two one-electron transfers, and CuL^+ is an electrochemically active complex (EAC) on which the first electron is transferred (here and below, to shorten the entries, glycine is symbolized as LH). Further studies using a rotating disk electrode [4] confirmed the conclusion about the EAC composition. Besides, they showed that the nature of the charge transfer step changes in the presence

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of surface oxides. Then, the transfer of the second electron to the intermediate complex of Cu(I) becomes a rate-determining step. It also turned out [3] that the kinetic data depend on the nature of the foreign (supporting) ions. Therefore, a rather extensive experimental material accumulated to date should be used with some caution, taking into account the nature of the supporting electrolyte. Some aspects of this problem are discussed elsewhere [5]. Finally, we point out an interesting, in our opinion, result. It turned out [6] that the glycine system can be successfully used to simulate the electrochemical behaviour of some herbicides in the environment.

Though a significant progress in the study of this system has been reached, some of its electrochemical properties require further investigations. In particular, this applies to solutions with the so-called 'hidden' ligand deficiency. This category includes slightly acidic media, where the amount of the active deprotonated ligand L^{-1} is very low, despite the apparent large excess of the total glycine.

Recently, studies of Cu(II)-glycine complexes in perchlorate media have been performed [7] employing more advanced experimental techniques, such as linear potential sweep (LPS) voltammetry, electrochemical quartz crystal microgravimetry, and appropriate methods of quantitative analysis of experimental data. LPS voltammograms obtained at pH 4 contained two current peaks. In spite of this, it turned possible to construct linear Tafel dependences in the entire region of cathodic overvoltages. Their analysis made it possible to determine the kinetic characteristics of charge transfer, which is desirable to compare with the results obtained by other methods.

In this regard, we turned to electrochemical impedance spectroscopy (EIS), since it makes possible to obtain information both on faradaic processes and on a double electric layer. Impedance characteristics of the copper electrode, obtained for slightly acid Cu(II)-glycine solutions, are analysed in the present paper.

EXPERIMENTAL

Solutions were prepared using deionised water, $Cu(ClO_4)_2 \cdot 6\,H_2O$ and glycine (both from Aldrich), and $NaClO_4 \cdot H_2O$ (Fluka) as a supporting electrolyte. Specified values of pH were adjusted by addition of $HClO_4$ or NaOH. Solutions were deaerated before experiments with argon stream over 0.5 h.

To prepare the working electrodes, a 0.4 cm^2 platinum wire was coated with ~5 μm thick copper in the solution containing (g dm^{-3}) $CuSO_4 \cdot 5\,H_2O$ – 250, H_2SO_4 – 50. A polycrystalline layer with well-exhibited crystallographic edges and faces was formed. The roughness factor, estimated by scanning probe microscopy measurements, was ~1.1. More data on surface morphology is given elsewhere [8]. The prepared electrodes were rinsed with water and immersed immediately into the solution under investigation.

Impedance measurements were carried out using an Autolab PGSTAT302 potentiostat. Nyquist plots (relations between the real (Z') and the imaginary (Z'') components of the impedance) were obtained within the frequency (f) range from 0.1 to 3 × 10^4 Hz at the open-circuit potential. The amplitude of the imposed sinusoidal perturbation of the electrode potential was 5 mV. The electrode potential was measured in reference to the Ag | AgCl | KCl (sat) electrode and was converted to the standard hydrogen scale. All experiments were performed at 20°C.

Computer programs elaborated by Boukamp [9] were used for analysing impedance spectra. When presenting the impedance values, no corrections for surface roughness were done.

RESULTS AND DISCUSSION

A general view of the data obtained is given in Figs. 1 and 2. At not too low frequencies (the left part of the curves), Nyquist plots represent the arcs whose centres are below the abscissa axis. With a decrease in frequency, deviations from this dependence are observed, but the plots do not go over to explicit lines, which usually occur in the case of simpler redox processes controlled by mass transport and charge transfer.

At least three main factors affect the impedance spectra. These include, in the first place, the pH of the solutions. With a decrease in acidity, the impedance of Cu electrodes increases in the entire frequency range (cf. Figs. 1, 2). Similar phenomena were also observed with a change in the total ligand concentration (c_L): a significant increase in impedance with c_L occurs both at pH 4 (Fig. 1) and at pH 5 (Fig. 2). Finally, the third factor, which

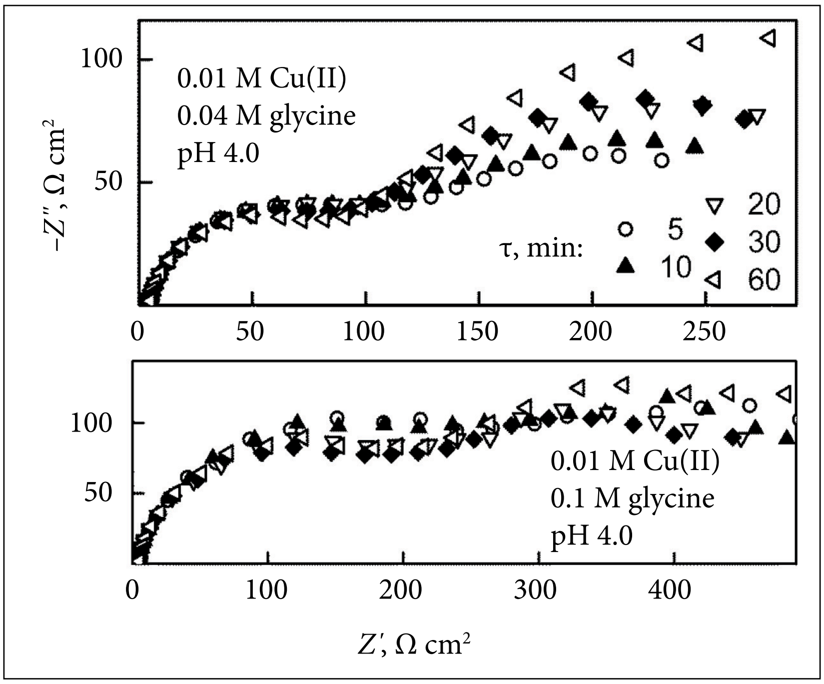

Fig. 1. Variations of Nyquist plots with exposure time. The data obtained at pH 4 and different ligand concentrations as indicated

should be considered, is the exposure time (τ) of the freshly prepared electrode in the test solution. Its influence is especially pronounced at pH 4 and $c_L = 0.04$ M. In this case, an increase in impedance with exposure time is clearly visible, especially in the region of lower frequencies (upper part of Fig. 1). In other solutions studied by us, this effect is less pronounced. It is most likely that some data scatter might be qualified as insufficient measurement reproducibility.

The reasons for such behaviour seem to lie in the equilibration processes that occur when

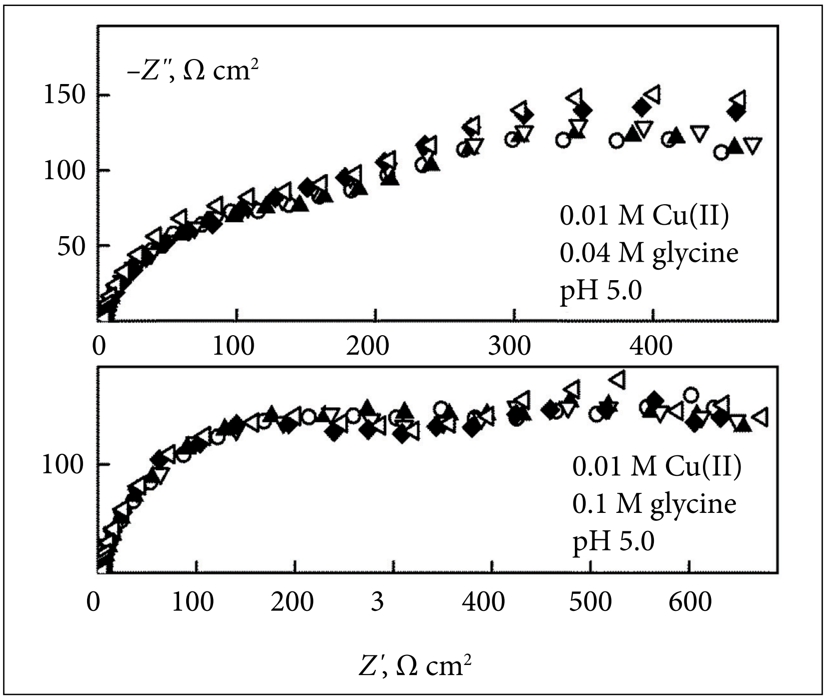

Fig. 2. The same as on Fig. 1 at pH 5

the Cu electrode is immersed in the Cu(II)-glycine solution. Then, Cu(I)-containing species are generated at the Cu|solution interface by the process Cu + $Cu^{2+} \rightarrow 2\ Cu^+$. This leads to the redistribution of components in the solution phase and to the onset of a new equilibrium. The aforementioned phenomena were quantified employing procedures based on the material balance equations [5, 7]. It was found that the total amount of Cu(I) species formed in slightly acidic media ($c_{\mathrm{Cu(I)}}$) falls with both pH and c_{L}. It is reasonable to assume that the equilibration time will also change in accordance with the $c_{\mathrm{Cu(I)}}$ value. Therefore, such an interpretation is consistent with the experimental phenomena noted above.

Quantitative analysis of experimental data is conveniently carried out using equivalent circuits (EC) if they adequately reflect the basic properties of the electrochemical system. When choosing them, we completely sustain Sluyters' position [10], according to which 'it is preferable to analyse the impedance data according to the appropriate theoretical models for which the mathematical expressions are derived'. It is well known that Cu^{2+} reduction proceeds via formation of a stable intermediate Cu^+, which is capable of leaving the reaction zone by diffusion; this was confirmed experimentally using a rotating ring-disk electrode. Therefore, we focused on such theoretical developments.

In previous studies, a theoretical analysis of the faradaic impedance has been performed provided that the final product is also soluble [11–13]. Next, the relationships obtained in Ref. [11] have been extended for the case when an insoluble final product (e.g. metal deposit) is formed [14]. No EC was proposed in the previous investigations [11, 12] until it was found [13] that the general impedance expression corresponds to an equivalent circuit that contains 5 elements, including resistances (R), Warburg impedances (W) and capacitance (C). Its description code is as follows: $R_\infty(R_1W_1)(C_2W_2)$. Here, elements in series are given in square brackets, and elements in parallel are enclosed in parentheses. According to the authors [13], most elements of this EC 'have no sensible physical meaning'. At the same time, another faradaic EC, viz. $([R_1W_1][R_2W_2])$, has been suggested [15], which rigorously followed from the same analytical expressions, but contained less elements. So, two different EC have been suggested for description of the same mechanism. Analysis has shown [16] that both ECs are indistinguishable. Upon a proper choice of elements, they display the same impedance spectrum over the entire frequency range. Our choice falls on the latter EC, because it is simpler, the elements have a clear physical meaning, and, most importantly, there are analytical expressions that relate the values of the elements to the kinetic parameters of the process (exchange current densities i_{01} and i_{02}):

$$i_{01} + i_{02} = \frac{RT}{F}\left(\frac{1}{R_1} + \frac{1}{R_2}\right), \tag{1}$$

$$\frac{1}{i_{01}} + \frac{1}{i_{02}} = \frac{R_1 + R_2}{\sigma_1 + \sigma_2}\frac{1}{F\sqrt{D}}\left(\frac{1}{[\mathrm{Cu}^{2+}]} + \frac{4}{[\mathrm{Cu}^{+}]}\right). \tag{2}$$

Here Warburg coefficients (σ) have their common meaning [17]. By definition, the Warburg admittance $Y_{\mathrm{W}} = 1/Z_{\mathrm{W}} = Y_0(j\omega)^{1/2}$, where j is an imaginary unit and $\omega = 2\pi f$; then $\sigma = 1/\sqrt{2}\,Y_0$.

These equations were derived for the two one-step electron transfers in the system containing simple metal ions [14, 15]. It seems possible to apply such relations to processes involving metal complexes if the chemical stages in a complex system are sufficiently fast. Then, concentrations of simple ions (i.e. $[Cu^{2+}]$ and $[Cu^+]$) should be replaced by the corresponding total concentrations $c_{\mathrm{Cu(II)}}$ and $c_{\mathrm{Cu(I)}}$ [18]. The above EC was supplemented by two non-faradaic elements: the solution resistance R_Ω and the impedance of the double electric layer. Since the structure of the double layer is not known in detail, its impedance is best represented by the constant phase element Q_{dl}, the admittance of which is expressed by the relation $Y = Y_0(j\omega)^n$. This generalized EC is shown in Fig. 3.

When comparing the EC impedance with the experimental data, the following procedures were carried out. First, extrapolating the impedance to an infinite frequency, the resistance of the solution R_Ω was determined and eliminated from the experimental data. Then, the data were transformed to the admittance spectrum. Again, the high-frequency limit provided parameters of Q_{dl}, which was also subtracted from the admittance spectrum. The rest was fitted to a sub-circuit containing faradaic elements R and W. In most cases, a satisfactory agreement was obtained

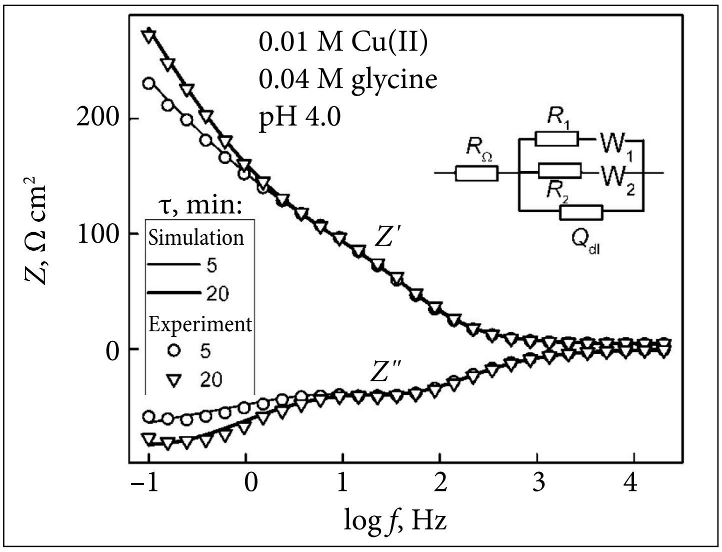

Fig. 3. Comparison of experimental impedance spectra (symbols) with those simulated for a given equivalent circuit (lines)

between the EC impedance and experimental data, and the frequency error did not exceed 3–4%. Such data are presented below.

Table 1 contains data obtained for pH 4. We have already noted that the impedance in this solution depends on the exposure time τ. It can be seen that this effect is caused by changes in the subcircuit [R_1W_1]. Both the charge transfer resistance R_1 and the complex conductance of Warburg impedance Y_0 increase with exposure time. Initially, the latter element is determined with a sufficient degree of reliability, but later it is possible to determine only the order of conductivity (data marked with an asterisk). However, this circumstance does not prevent the determination of the exchange current density i_{01}, which also decreases with time.

Other parameters do not correlate with τ. This also applies to the CPE Q_{dl}, which transforms into electrical capacitance at $n = 1$. The average value of n for Q_{dl} is ~0.85, and this shows the capacitive nature of the double layer impedance. Assuming that the parameter Y_0 approximately represents the double-layer capacitance we obtain the order of C_{dl} ~70 μF cm^{-2}. Relatively high values of C_{dl}, typical of a Cu electrode, were observed both in solutions of simple salts and in the presence of ligands [15, 16, 19, 20].

Using the data of Table 1, we calculated the spectra of the equivalent circuit, which were compared with the corresponding experimental data. The examples of such comparison are presented in Figs. 3 and 4. A suitable agreement between the compared data is observed at $f > 1$ Hz. Some discrepancies observed at the lowest frequencies seem to arise from an insufficiently accurate representation of the imaginary part of the impedance. This is most

Table 1. **Parameters of the equivalent circuit R_Ω(Qdl [R_1W$_1$] [R_2W$_2$]) obtained for 0.01 M Cu(II) solution containing 0.04 M glycine at pH 4.0. $R_\Omega = 4.2 \pm 0.04\ \Omega\ \mathrm{cm}^2$**

τ, min	Q_{dl}		R_1, Ω cm²	W_1	R_2, Ω cm²	W_2	i_{01}, μA cm^{-2}	i_{02}, mA cm^{-2}
	$Y_0 \cdot 10^6$, Ω^{-1} cm^{-2} s^n	n		$Y_0 \cdot 10^2$, Ω^{-1} cm^{-2} s$^{0.5}$		$Y_0 \cdot 10^3$, Ω^{-1} cm^{-2} s$^{0.5}$		
2	67.3	0.858	153	1.35	76	0.46	7.0	0.48
5	83.8	0.832	294	2.83	125	1.79	1.0	0.28
10	77.2	0.840	346	4.10	114	1.91	0.8	0.29
20	75.2	0.840	460	23	100	2.14	0.6	0.30
30	54.9	0.870	460	33	86	2.15	0.6	0.34
60	62.1	0.856	700	~	84	2.90	0.3	0.33

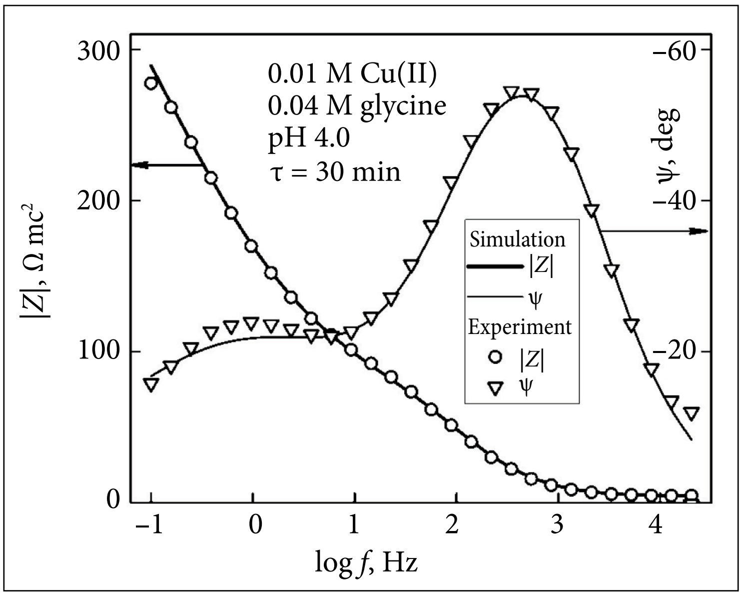

Fig. 4. Bode plots obtained at pH 4 for the impedance module $|Z|$ (ordinate to the left) and phase angle ψ (ordinate to the right). Comparison of experimental (symbols) and simulated (lines) data

clearly seen when considering the phase angle $\psi = \arctan(Z''/Z')$. Discrepancies in ψ are most pronounced at ~1 Hz (Fig. 4).

Similar phenomena were discovered during the study of the Cu|Cu(II), glycolic acid system [19]. It was established that the matching could be significantly improved if the Gerischer impedance G [21] was introduced into the $[R_1W_1]$ sub-circuit. This element imitates the kinetics of the first-order chemical step, which is not so easy to find in a complex system involving various chemical interactions. The formation of Cu(II)-glycine complexes was found to be rather fast [22]. Some ambiguity concerns the mobility of the NH_2-group protonization in the glycine molecule. Glycine in aqueous solutions promotes formation of a zwitterion $^{+}H_3N–CH_2–COO^{-}$, which together with its protonated form $^{+}H_3N–CH_2–COOH$ dominates in acid media. Both species are capable of splitting protons. During the reduction of Cu (II) complexes, they behave as mobile proton donors [7]. However, zwitterions do not fall into this category when protonated species support the electrochemical evolution of hydrogen [23]. The data obtained do not allow an unambiguous choice in this dilemma, because the differences between the compared spectra are not significant. At the same time, there is a reason to believe that a preliminary analysis of impedance is possible without a quantitative assessment of the system lability.

A similar behaviour is shown by other solutions. Some differences in their impedance characteristics have already been discussed above. Below, we present the data obtained for the 0.01 M Cu(II) solution containing 0.1 M glycine at pH 5. Unlike pH 4, lower double layer admittance is observed in this case (see Table 2). Besides, there is a tendency to decrease the capacitance of the double layer with time, this being indicative of the adsorption of glycine or glycine-containing species. As in the previous case, a satisfactory agreement is observed between the impedance spectrum of the equivalent circuit and the experimental data (Fig. 5). Qualitatively, the impedance spectra of the systems studied are similar. So, for example, the position of the maximum on the ψ spectra falls at a frequency of ~400 Hz and weakly depends on the solution composition (cf. Figs. 4, 5).

Tables 1 and 2 contain the values of the exchange current densities calculated according to Eqs. (1) and (2) with the following parameters: $D = 6.6 \times 10^{-6}$ cm² s⁻¹ [7], $c_{Cu(II)} = 10^{-5}$ mol cm^{-3}, $c_{Cu(I)} = 2 \times 10^{-8}$ mol cm^{-3} (pH 4) and $c_{Cu(I)} = 10^{-8}$ mol cm^{-3} (pH 5) [5]. Since a number of assumptions were made for the validity of this approach (see above), an estimate of i_0 should be considered approximate, determining the order of these values. The condition $i_{01} << i_{02}$ is characteristic of the Cu(II) reduction. Note that similar values

Table 2. **Parameters of the equivalent circuit $R_\Omega(Q_{dl}\,[R_1W_1]\,[R_2W_2])$ obtained for 0.01 M Cu(II) solution containing 0.1 M glycine at pH 5.0. $R_\Omega = 4.25 \pm 0.03\ \Omega\ \text{cm}^2$**

τ, min	Q_{dl}		R_1, Ω cm²	W_1	R_2, Ω cm²	W_2	i_{01}, μA cm⁻²	i_{02}, mA cm⁻²
	$Y_0 \cdot 10^6$, Ω^{-1} cm^{-2} s^n	n		$Y_0 \cdot 10^2$, Ω^{-1} cm^{-2} s$^{0.5}$		$Y_0 \cdot 10^4$, Ω^{-1} cm^{-2} s$^{0.5}$		
2	51.0	0.877	573	1.17	285	3.80	1.3	0.13
5	38.3	0.904	621	0.72	266	3.32	1.3	0.13
10	40.8	0.893	800	1.98	373	5.28	0.7	0.10
20	34.8	0.908	852	3.60	345	5.95	0.6	0.10
30	33.0	0.912	920	~	348	7.15	0.5	0.10
60	29.5	0.919	1030	~	342	7.35	0.4	0.10

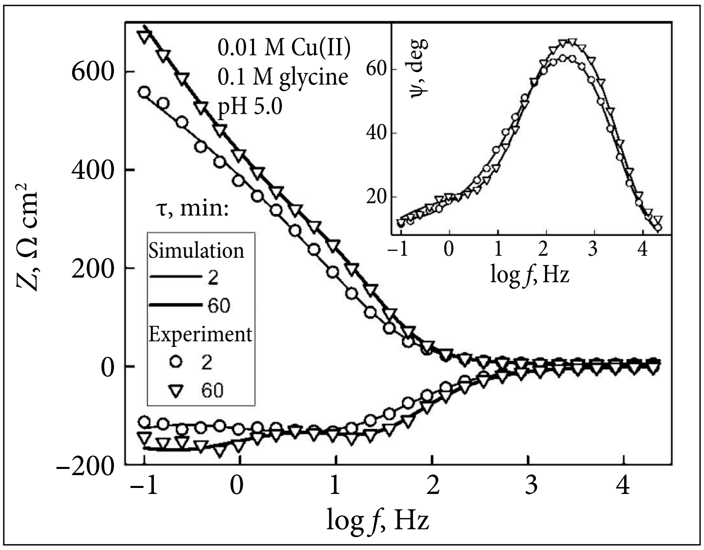

Fig. 5. Impedance and phase angle (inset) spectra obtained at pH 5. Comparison of experimental (symbols) and simulated (lines) data

of i_{01} and i_{02} were obtained for Cu(II) solutions containing gluconic acid [20, 24]. In addition, the i_{02}values defined in this article are in line with the current density obtained from voltammetric data for similar solutions [7].

CONCLUSIONS

In weakly acidic solutions (pH 4 and 5), the impedance of Cu|Cu(II)-glycine system increases with ligand concentration (c_L) and solution pH. The third factor affecting the impedance is the exposure time of Cu electrode in the test solution. Its effect is especially noticeable at pH 4 and c_L = 0.04 M when a rather slow equilibration of the system is observed.

Nyquist plots of the Cu electrode present the arcs centred below the abscissa axis. They are typical of electrochemical reactions proceeding via two consecutive one-electron transfers. An equivalent circuit with two parallel sub-circuits, each of which contains the charge transfer resistance and the Warburg impedance in series, is suitable for the quantitative estimation of impedance spectra.

Two exchange current densities determined from the impedance spectra differ by 2 orders of magnitude. Their average values (~1 μA cm^{-2} and ~0.1 mA cm^{-2}) are in line with respective literature data.

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VARIO ELEKTRODO IMPEDANSAS SILPNAI RŪGŠČIUOSE Cu(II)-GLICINO TIRPALUOSE

Santrauka

Cu(II) redukcijos kinetikos tyrimams silpnai rūgščiuose (pH 4 ir 5) Cu(II)-glicino tirpaluose panaudota elektrocheminio impedanso spektroskopija. Nustatyta, kad Cu elektrodo impedansas auga didinant ligando koncentraciją ir tirpalo pH. Trečiasis veiksnys, turintis įtakos impedanso spektrams, yra Cu elektrodo ekspozicijos trukmė tiriamajame tirpale.

Gautos lankų pavidalo Naikvisto kreivės, kurių centras yra žemiau abscisės ašies. Jos yra būdingos elektrocheminėms reakcijoms, vykstančioms nuosekliai pernešant kiekvieną elektroną. Impedanso spektrams kiekybiškai įvertinti panaudota adekvati ekvivalentinė grandinė. Ji susideda iš dviejų lygiagrečių subgrandinių, kuriose krūvio pernašos varža yra nuosekliai sujungta su Varburgo impedansu.

Nustatyti dviejų elektronų nuoseklios pernašos mainų srovės tankiai, kurie skiriasi ~100 kartų. Jų vidutinės vertės (~1 μA cm^{-2} ir ~0,1 mA cm^{-2}) sutampa su atitinkamais literatūros šaltiniuose pateikiamais duomenimis.