# Equilibration processes in alkaline Cu | Cu(II), glycine system

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The nature and kinetics of the equilibrium processes at the interface between the copper electrode and the alkaline solution containing glycine complexes of Cu(II) have been studied. The material balance equations that consider the formation of Cu(I) complexes were used to calculate the composition of the equilibrium system. It was found that the amount of Cu(I) compounds increases with increasing the pH and ligand concentration. Using the EQCM method it was found that the electrochemical dissolution of Cu electrode proceeds under open circuit conditions at potentials 60–70 mV higher than their equilibrium values. The generation of Cu$^+$ ions obeys the laws of pseudo-first order processes at a rate constant of $\sim 2 \times 10^{-4}$ s$^{-1}$. It is assumed that the final product of the equilibration is a monoligand complex of CuL (L$^-$ is a glycinate anion). Besides, there is a thermodynamic probability of the formation of cuprous oxide in the system.

**Keywords:** copper, glycine, intermediate complexes, equilibration

## INTRODUCTION

The electroreduction of Cu(II) compounds usually involves two consecutive one-electron stages during which stable intermediate products containing Cu(I) are formed. These species are also formed under open circuit conditions when the copper electrode comes into a contact with Cu(II) solution. The formation of Cu(I) in the Cu | Cu(II) system will continue until an equilibrium of $Cu^{2+} + Cu \rightleftarrows 2\,Cu^+$ is established at the interface. If the system contains simple Cu(II) salts, the fraction of Cu$^{2+}$ ions converted to Cu$^+$ ions is small ($\sim$1%), therefore this process is often not considered. However, the situation can significantly change in the case of systems containing ligands that form complex compounds with both Cu$^{2+}$ and Cu$^+$. At certain ratios between stability constants of these complexes, the molar fraction of Cu(II) transformed into Cu(I) can reach significant values [1]. Consequently, equilibration processes can proceed quite intensively, significantly affecting

characteristics of the Cu | solution interface and causing certain deviations of the open-circuit potential ($E_{oc}$) from its equilibrium ($E_{eq}$) value. In a quantitative interpretation of the experimental data aimed at determining the mechanism and kinetic parameters of electrochemical steps, these phenomena must be considered.

The above is fully applicable to Cu(II) solutions containing aminoacetic acid (glycine) as a ligand, hereinafter referred to as LH. Various studies showed [2–13] that electrically active Cu(I)-glycine complexes can be formed, but data concerning their characteristics are scarce. Only two references concerning the stability constants (β) of Cu(I)-glycine complexes are presented in various databases. 60 years ago, James and Williams [14] analysed the redox potentials of cuprous-cupric pairs. To avoid Cu(I) disproportionation, a thousandfold excess of the ligand was used, and a log β$_2$ value of $\sim$10.0 was attributed to the diligand Cu(I)-glycine complex. Another recent study was based on zero-current potentiometry [15]. Cu$^+$ or Cu$^{2+}$ ions were selectively generated on the surface of a copper

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electrode, and zero-current potentials were measured. For the Cu(I)-glycine monoligand complex, the stability constant $\beta_1 = 10^{6.75}$ was obtained. We used these $\beta$ values to estimate the composition of the equilibrium Cu | Cu(II), Cu(I), glycine system [16]. It was found that depending on the pH, different Cu(I)-containing species can be formed. Cu$^+$ aqua-ions are characteristic of acidic solutions, while the formation of the above Cu(I)-glycine complexes occurs in alkaline media.

As far as we know, the equilibration in this system has not been studied in more detail. To fill this gap, we carried out studies comparing theoretical calculations with the results of electrochemical experiments, conducted in combination with electrochemical quartz crystal microgravimetry (EQCM). The present work also deals with some parameters of voltammetric characteristics [17, 18], which have not yet been discussed.

## EXPERIMENTAL DETAILS

Basic information about the preparation of deaerated solutions, the electrodeposition of copper coatings and their morphological characteristics is available elsewhere [17, 18]. The EQCM measurements were performed using Parstat 2273 electrochemical measurement systems from Princeton Applied Research (USA) equipped with a QCM922 module. 50 cm$^3$ of the solution was placed in the measuring cell. The active element was a gold-coated quartz crystal with an active area $A = 0.5$ cm$^2$ and a resonance frequency of 6 MHz. Additionally, it was covered by a layer of copper with a thickness of ~1 μm. The specifics of the measurements did not allow the use of thicker coatings. The constant relating the variations in quartz crystal mass ($\Delta m$) with its oscillation frequency ($\Delta f$) was determined by a special calibration according to the EQCM data obtained for acidic CuSO$_4$ solutions at controlled current density (for details see Ref. [10]). This value was in line with the quantity $k = 12.35 \times 10^{-6}$ g Hz$^{-1}$ cm$^{-2}$ obtained by the well-known Sauerbrey equation. To eliminate traces of chloride ions, the Ag | AgCl | KCl (sat) reference electrode used in voltammetry was replaced with a Hg | Hg$_2$SO$_4$ | K$_2$SO$_4$ (sat) electrode. In the present article, potential values converted to the standard hydrogen scale are given. All experiments were performed at 20°C.

## RESULTS AND DISCUSSION

Material balance equations containing expressions of the constants of various equilibria make it possible to determine the degree of conversion of Cu(II) to Cu(I) in systems containing ligands [1]. The list of the considered equilibrium processes and their characteristics are presented in the article published earlier [16]. The amount of Cu(I) formed in alkaline media increases with pH, tending to a certain limit (Fig. 1). The concentration of glycine ($c_{gly}$) has a significant effect on the extent
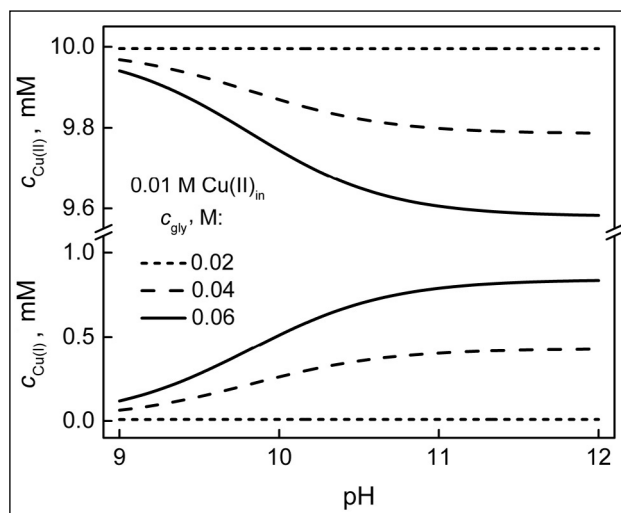


**Fig. 1.** Total amounts of Cu(II) and Cu(I) species in the equilibrated Cu | Cu(II), Cu(I), glycine system. Initial Cu(II) concentration is equal to 0.01 M

of this process. In the absence of an excess of ligand ($c_{gly} = 0.02$ M), the amount of the generated Cu(I) is extremely minor, but this quantity rises strongly with increasing the ligand concentration. For instance, at $c_{gly} = 0.06$ M, about 4% of the initial Cu(II) can be partially reduced at the interface, that is unlikely for ligand-free solutions. As might be expected, the fraction of the diligand complex CuL$_2^-$ increases with the ligand concentration (Fig. 2), whereas the content of the monoligand complex CuL decreases correspondingly (inset in Fig. 2).

The above amounts of Cu(I) are formed through the heterogeneous reaction

$$Cu^{2+} + Cu \rightarrow 2\,Cu^+, \qquad (1)$$

occurring at the interface between copper and solution, with further formation of Cu(I) complexes:
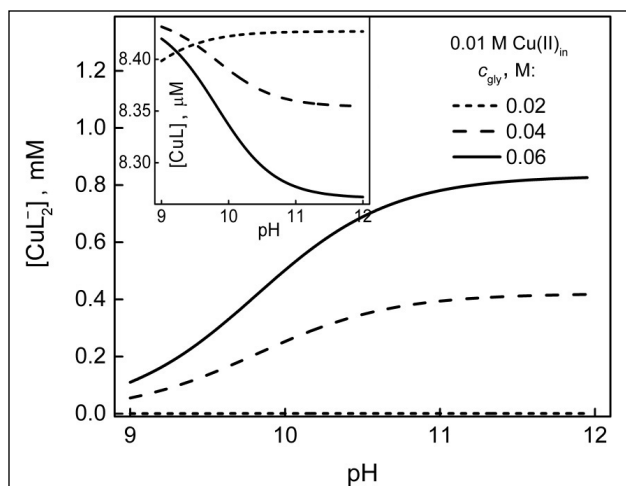
**Fig. 2.** Equilibrium distribution of Cu(I) complexes in the alkaline Cu | Cu(II), Cu(I), glycine system

$$Cu^+ + L^- \rightarrow CuL, \tag{2}$$

$$CuL + L^- \rightarrow CuL_2^-. \tag{3}$$

Obviously, an equilibrium state is not possible at the initial moments of copper contact with Cu(II) solution. Due to the anodic dissolution of copper, the open-circuit potentials are 60–70 mV higher than the equilibrium potentials (Fig. 3). The reproducibility of $E_{oc}$ values is weak and depends on the procedures preceding the measurements. Besides, $E_{oc}$ change over time to a certain extent. A good illustration of these effects can be the data in Fig. 4 obtained from the EQCM experiments.
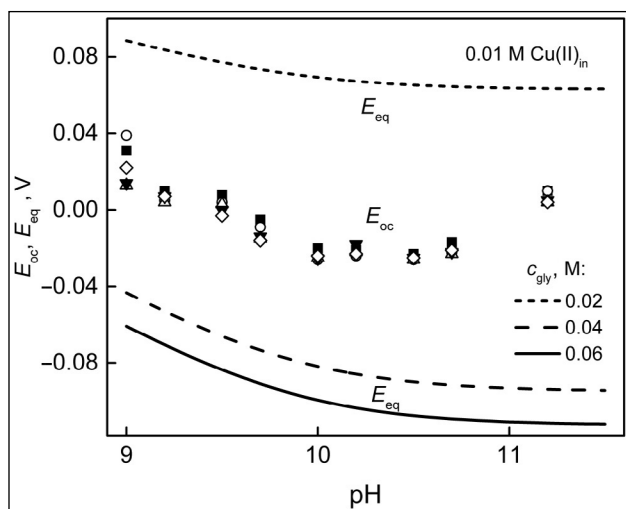


**Fig. 3.** Comparison of the equilibrium potentials ($E_{eq}$) calculated at different pH and glycine concentrations ($c_{gly}$) with the open-circuit potentials ($E_{oc}$) observed at $c_{gly} = 0.04$ M
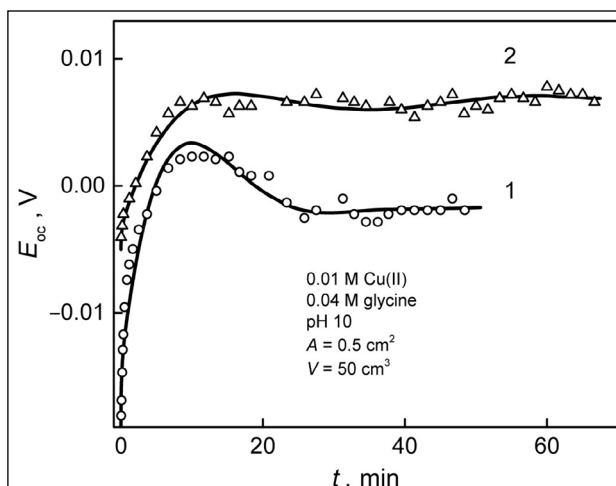


**Fig. 4.** An example of the potential control in EQCM experiments. Two consecutive recordings of $E_{oc}$ dynamics in a solution of the specified composition

Despite a certain difference in the open-circuit potentials recorded during the individual experiments, the shape of $E_{oc}$–$t$ dependence is similar. After a certain transient time, $E_{oc}$ acquires a more or less constant value. At the same time, the mass of copper electrode decreases monotonically over the entire time region (Fig. 5). It is of interest to conduct a quantitative analysis of these data. If Cu(I)-glycine complexes are sufficiently labile, the stage determining the rate of electrochemical copper corrosion is the reaction (1) given above,
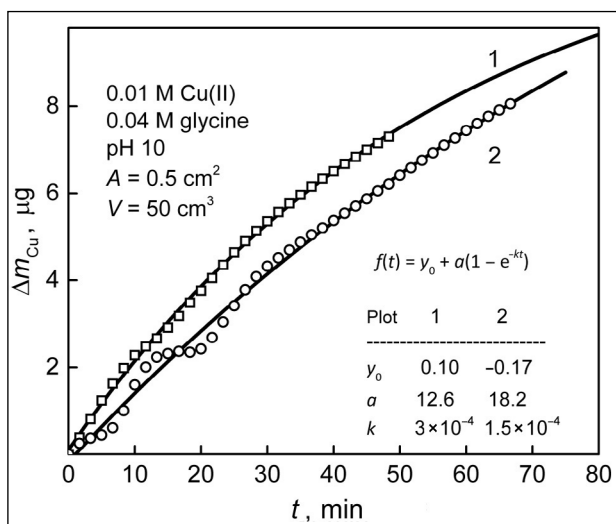


**Fig. 5.** Changes in the mass of the Cu electrode with a surface area of 0.5 cm² during two EQCM experiments (1 and 2). The volume of the solution in the measuring cell was 50 cm³. The simulation results obtained with the function $f(t)$ (lines) are fitted to the experimental data (symbols)

which belongs to the pseudo-first-order reaction and is characterised by the kinetic equation

$$\Delta m \approx f(t) = y_0 + a(1 - e^{-kt}). \qquad (4)$$

Certainly, the experimental values of $\Delta m$ are well described by this equation at the parameters shown in Fig. 5. It follows from the data obtained that the heterogeneous reaction (1) proceeds slowly with an average rate constant $k \sim 2 \times 10^{-4}$ s$^{-1}$. At this value, the half-life of the reaction is one hour. The extrapolation of simulated data to $t \to \infty$ allows us to determine the limiting value of $\Delta m$ corresponding to the equilibrium state of the system. A simple further recalculation for an electrode with a surface area $A = 1$ cm$^2$ and a solution volume $V = 1$ dm$^3$ shows that the final concentration of Cu(I) compounds should be 8–12 μM. This value is consistent with the equilibrium concentration of the monoligand complex CuL and differs significantly from the value obtained for the diligand complex Cu L$_2^-$ (see Fig. 2).

As follows, the data obtained show no indication that this complex can form within the first hour. To speed up the saturation of the Cu(II) solution with the products of electrochemical transformations, we conducted a series of experiments with much smaller its volume (2 cm$^3$). However, reliable data were not obtained due to the uneven nature of the electrochemical dissolution of copper. In some cases, the pitting corrosion and the formation of areas covered by insoluble compounds was observed on the copper surface. Similar phenomena were observed in the alkaline leaching of copper in glycine solutions [12]. The retardation of the process at pH > 10 was attributed to the effect of surface oxides. We also found passivation phenomena when studying the anodic processes in this system using a rotating disk electrode [18].

In connection with these observations, it is of interest to evaluate the formation of cuprous oxide on the electrode surface as the most likely insoluble compound of Cu(I). According to Pourbaix diagrams [19], the formation of Cu$_2$O is thermodynamically possible if the concentration of Cu$^+$ ions exceeds the critical value [Cu$^+$]$_{max}$, defined by the ratio

$$\log [\mathrm{Cu}^+]_{max} = -0.84 - \mathrm{pH}. \qquad (5)$$
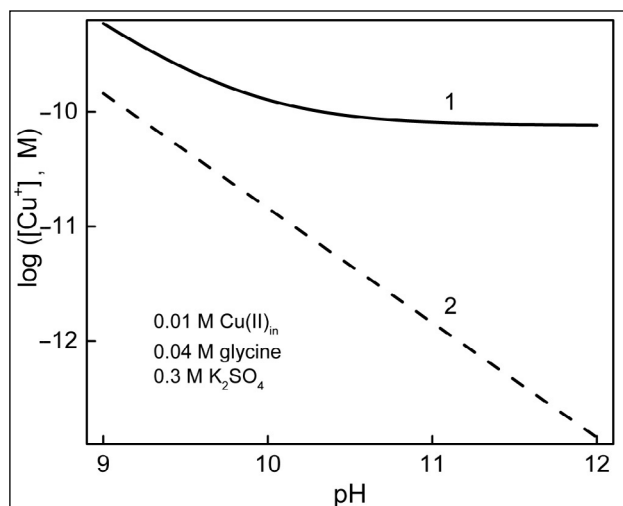


**Fig. 6.** Comparison of the dependences of Cu$^+$ concentration on pH determined by the material balance equations (a solid line 1) and determined by condition (5) (a dashed line 2)

The distribution of Cu$^+$ ions in the equilibrium Cu | Cu(I), Cu(II), glycine system obtained with material balance equations (see above) is compared with the data following from Eq. (5) in Fig. 6. It can be seen that the concentration of Cu$^+$ ions is higher than [Cu$^+$]$_{max}$ in the entire pH range. Considering that Cu$^+$ ions accumulate gradually, the thermodynamic stability of Cu$_2$O should come within a certain time. Furthermore, for the initial formation of cuprous oxide some oversaturation of the solution with Cu$^+$ ions is necessary. So, passivation of the copper surface may be absent for a certain time, but strictly speaking, this state cannot be considered an equilibrium state.

## CONCLUSIONS

The nature and kinetics of the equilibrium processes at the interface between the copper electrode and the alkaline solution containing glycine complexes of Cu(II) have been studied. The material balance equations that consider the formation of Cu(I) complexes were used to calculate the composition of the equilibrium system. It was found that the amount of Cu(I) compounds increased with increasing the pH and ligand concentration. Using the EQCM method it was found that the electrochemical dissolution of Cu electrode proceeds under open circuit conditions at potentials 60–70 mV higher than their equilibrium values. The generation of Cu$^+$ ions obeys the laws of pseudo-first order processes at a rate constant of $\sim 2 \times 10^{-4}$ s$^{-1}$. It is

assumed that the final product of the equilibration is a monoligand complex of CuL (L⁻ is a glycinate anion). Besides, there is a thermodynamic probability of the formation of cuprous oxide in the system.

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### PUSIAUSVYROS NUSISTOVĖJIMO PROCESAI ŠARMINĖJE CU | CU(II), GLICINO SISTEMOJE

*S a n t r a u k a*

Ištirtas pusiausvyros procesų, vykstančių sąsajoje tarp vario elektrodo ir šarminio Cu(II)-glicino kompleksų tirpalo, pobūdis ir kinetika. Apskaičiuojant pusiausvyrosios sistemos sudėtį, naudotos medžiagų balanso lygtys, kuriose atsižvelgiama į Cu(I) kompleksų susidarymą. Nustatyta, kad Cu(I) junginių kiekis auga, didėjant pH ir ligando koncentracijai. Naudojant EQCM metodą nustatyta, kad atviros grandinės sąlygomis, kai potencialai yra 60–70 mV didesni už jų pusiausvyrąsias vertes, vyksta elektrocheminis Cu elektrodo tirpimas. Cu⁺ jonų susidarymas vyksta pagal pseudo-pirmojo laipsnio procesų dėsningumus, kai greičio konstanta yra ~2 × 10⁻⁴ s⁻¹. Daroma prielaida, kad galutinis pusiausvyros produktas yra monoligandinis CuL kompleksas (L⁻ yra glicinato anijonas). Be to, atsiranda termodinaminė tikimybė ir vario(I) oksidui susidaryti.