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Comparative study of equilibrium characteristics of Cu|Cu(II), Cu(I), glycine system containing sulfate or perchlorate as a supporting electrolyte

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The distribution of species in Cu(II)-glycine solutions, containing sulfate or perchlorate as a supporting electrolyte, is considered. Substantial differences are observed at pH < 4.5, where the molar fraction of monoligand complex (associate) $CuSO_4$ reaches up to 20 percent of the total Cu(II) concentration. Cu(I)-containing species are generated at the Cu|solution interface. These are Cu^+ aqua-complexes (acid media) or mono- and bidentate Cu(I)-glycine complexes (alkaline media). The addition of sulfate reduces the content of Cu^+ ions, but practically does not affect the distribution of Cu(I) complexes. The study of acid-base equilibria involving Cu^+ ions shows that the thermodynamic probability of Cu_2O formation remains low in both perchlorate and sulfate media. HSO_4^- ions formed in acid media should be treated as rather labile proton donors. This is quantitatively confirmed by experimental data, according to which the rate of hydrogen evolution increases correspondingly when perchlorate is replaced by sulfate in glycine solutions.

Keywords: copper, glycine, sulfate, lability, hydrogen evolution, LPS voltammetry

INTRODUCTION

Glycine $H_2N\text{-}CH_2\text{-}COOH$ is the simplest amino acid that is widely distributed in nature as an integral part of many vital substances. In addition, this substance and its derivatives are widely used in various fields of human activity, in the practical implementation of which it is often necessary to solve various electrochemical problems. For example, aqueous glycine solutions are known as promising environmentally friendly lixiviates to leach precious metals [1]. Their successful implementation requires extensive knowledge of the electrochemical behaviour of metal-glycine systems. Another example might be the widespread herbicide glyphosate (N-(phosphonometyl) glycine), whose content in the environment must be regularly monitored. Electrochemical methods seem rather attractive for this purpose, but there is some problem in the direct use of electroanalytical devices, since neither glycine nor most of its derivatives show the required electrochemical activity. Recently, an interesting opportunity has emerged to circumvent this obstacle, using the ability of glycine to form coordination compounds with copper ions [2–4]. It was found that anodic peaks on cyclic voltammograms, attributed to the transformations of Cu to Cu^+ and of Cu^+ to Cu^{2+} in the phosphate buffer, increase upon addition of glyphosate. To understand and employ successfully this effect in quantitative analysis, reliable information on the kinetics and mechanism of the processes is required.

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Though a rather extensive material has been accumulated on this subject, it has to be used with some caution, since the data obtained depend on the nature of the supporting electrolyte (see Ref. [5] and references therein). From the theoretical point of view, this component should be electrochemically inert. Perchlorates and nitrates of alkali metals are most closely related to the concept of 'indifferent electrolyte'. The popularity of these substances can be verified by referring, for example, to different databases containing equilibrium characteristics of various processes involving weak acids, bases, metal complexes and protonated ligands. Quite often, the equilibrium constants, determined in perchlorate and nitrate media, differ little, indicating their certain inertness.

Other salts, used as supporting electrolytes, can be considered as inert components only conditionally. First, mention should be made of sulfates, the introduction of which into galvanic baths is often justified for economic reasons. Many researchers, including the authors of the present article, have used these salts, however, interactions involving sulfate ions were not properly considered. In fact, SO_4^{2-} ions are able to compete with ligands, interacting with Cu^{2+} ions. According to the comprehensive study [6], Cu^{2+} and SO_4^{2-} ions form $CuSO_4$ associates containing bridges of water. As in the case of common complexes, their stability can be characterized by a certain constant. Although the stability of such formations is not high, they can constitute an appreciable fraction of copper complexes when sulfate ions are in a large excess. Besides, interactions between SO_4^{2-} and intermediate Cu^+ ions are possible.

In general, observed differences in kinetic parameters could be attributed to the double-layer effects. However, in the first instance, it is necessary to find out what role the sulfate ions play outside the double layer. In this regard, we set out to clarify and quantify the main interactions between the SO_4^{2-} anion and other components of the Cu|Cu(II), glycine system.

EXPERIMENTAL DETAILS

Solutions for investigation were prepared using deionized water and were deaerated before experiments with argon stream over 0.5 h. To prepare the working electrodes, 5–7 μm thick copper layers were coated on a Pt substrate in an acid $CuSO_4$ solution. A polycrystalline layer with well-exhibited crystallographic edges and faces was formed. Detailed characteristics of surface morphology are given elsewhere [7].

Electrode potentials were measured in reference to the Ag|AgCl|KCl (sat) electrode and were converted to the standard hydrogen scale. To enhance the equilibration of the system, cathodic potential scans from the open-circuit potential (E_{oc}) to the hydrogen evolution region were applied until a stable E_{oc} value was established.

Voltammetric measurements were carried out using a potentiostat/galvanostat REF 600 from Gamry Instruments. Linear potential sweep (LPS) rates (v) ranged from 0.01 to 0.2 V s^{-1}. In all cases, cathodic scans were applied, starting with the open-circuit potential. All experiments were performed at 20°C.

RESULTS AND DISCUSSION

Before we start discussing, it is necessary to specify two types of equilibrium states that may occur in the system under study. The first of them (state A) occurs in the solution phase because of chemical interactions producing various Cu(II) complexes and species of protonated ligands. The situation changes when the equilibrated Cu(II) solution is exposed to the metallic phase of the Cu electrode. Intermediate Cu^+ ions, produced by the process

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

are capable of forming Cu(I) complexes and other compounds. This leads to the redistribution of components in the solution phase and to the onset of a new equilibrium (state *B*). Such changes are often ignored as unimportant, but they deserve attention, especially when the intermediate ions form sufficiently stable complexes [8]. The aforementioned phenomena were taken into account employing procedures based on the common material balance equations involving equilibrium constants, which are listed in the Table. Glycine (aminoacetic acid) is symbolized as LH. This species usually takes the form of zwitterion $^{+}H_3N\text{-}CH_2\text{-}COO^{-}$ in aqueous solutions. The reliability of these data appears to be different. In our opinion, the stability of Cu(I) complexes remains to be amended.

Table. **Equilibrium characteristics of Cu|Cu(II), Cu(I), glycine systemx**

Equilibrium	log K	Reference
$H^+ + L^- \rightleftarrows LH$	9.68	[9]
$2\,H^+ + L^- \rightleftarrows LH_2^+$	12.05	[9]
$Cu^{2+} + L^- \rightleftarrows CuL^+$	8.46	[10]
$Cu^{2+} + 2\,L^- \rightleftarrows CuL_2$	15.3	[10]
$H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$	1.477	[9]
$Cu^{2+} + SO_4^{2-} \rightleftarrows CuSO_4$	1.0	[6]
$Cu^{2+} + Cu \rightleftarrows 2\,Cu^+$	–6.345	[11]
$Cu^+ + L^- \rightleftarrows CuL$	6.75	[12]
$Cu^+ + 2\,L^- \rightleftarrows CuL_2^-$	10.16	[13]

Distribution of Cu(II) species

We now return to state *A*. According to the results obtained, the main effect of sulfate on the distribution of Cu(II) species is observed at pH < 4 (Fig. 1). The maximum amount of the $CuSO_4$ associate falls on pH 2, where its fraction reaches ~20% of the total amount of Cu(II). In strongly acidic solutions, the complexing ability of sulfate drops significantly due to its protonation producing inactive HSO_4^- anions. The decrease in the $CuSO_4$ molar fraction, observed at higher pH, arises from other reasons. In this pH region, an increase in the concentration of the competing glycine anion L^- results in the predominant formation of much more stable Cu(II)-glycine complexes (Table). Similar regularities are observed at higher glycine concentrations.

Variations in the complexation degree should manifest themselves in the values of equilibrium potentials (E_{eq}). As has been established earlier [5], the open-circuit potentials, determined in sulfate media, can be described by the Nernst equation with the activity coefficient $\gamma_{Cu^{2+}} = 0.07$. Note that such low values can be also found in reference books. Obviously, they reflect the disregard of the interaction between Cu^{2+} and SO_4^{2-} ions.

In the case of perchlorate media, this anomaly does not occur. Results, obtained using the Nernst equation and the corresponding data presented in Fig. 1, show that the steady-state values of E_{oc} coincide well with E_{eq} calculated at $\gamma_{Cu^{2+}} = 0.4$ (Fig. 2). The latter value is in a good agreement with the well-known Debye–Hückel equation.

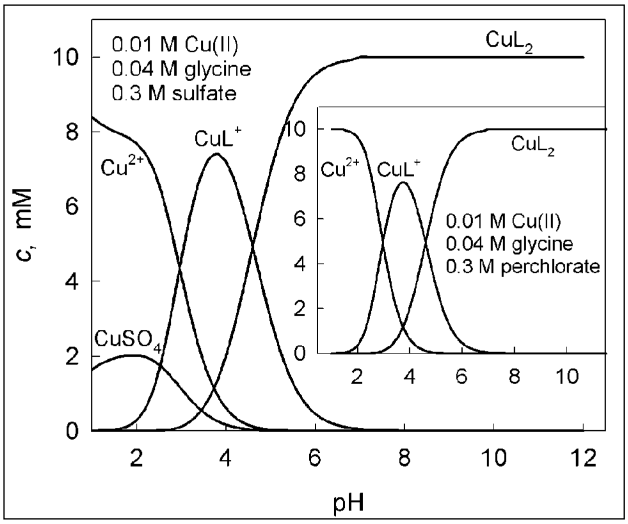

Fig. 1. Distribution of Cu(II) species in the Cu(II)-glycine solutions containing sulfate or perchlorate (inset) as supporting electrolytes (state *A*)

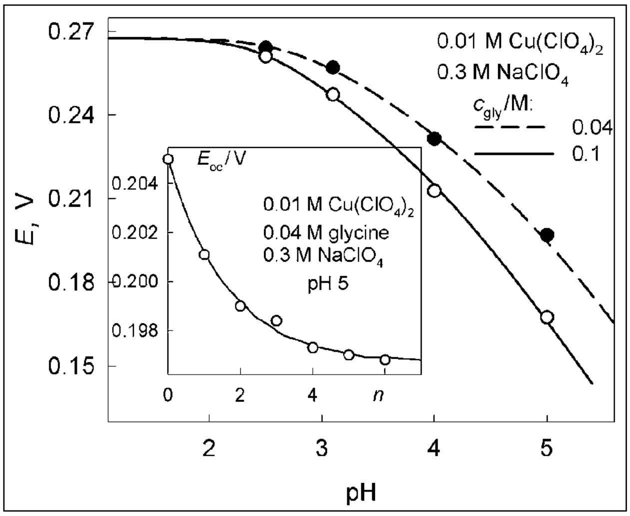

Fig. 2. Comparison between open-circuit (circles) and equilibrium (lines) potentials. Dynamics of the system equilibration is shown in the inset (see the text)

The maximum decrease in E_{eq}, caused by the replacement of 0.3 M perchlorate by 0.3 M sulfate, does not exceed 2.8 mV. With increasing pH, this difference falls and at pH > 2.8 it becomes commensurate with the reproducibility of the experimental results. The equilibration time of the perchlorate system significantly depends on the acidity of solutions and increases with pH. For instance, stable E_{oc} values are established relatively quickly in sufficiently acidic media and there is no need for activation procedures (see the Experimental part). However, at pH 5, more than 6 potential scans are required for equilibration. Open-circuit potentials measured after each cathodic scan are shown in the inset of Fig. 2.

From the above data, we can draw one general conclusion: in the solutions of the indicated concentrations sulfate shows a tangible effect only in acidic media at pH < 4.5. This conclusion is also valid for other properties of the system, considered below.

Distribution of Cu(I) species

We now turn to the equilibrium state *B*, which deals with the appearance of Cu^+ ions generated at the Cu|solution interface. Two pH areas can be distinguished in which a noticeable content of Cu(I)-containing species is observed (Fig. 3). Cu^+ aqua-ions are typical of acid media. Since they are produced by reaction (1), the molar fraction of Cu^+ depends on the same factors that determine the amount of Cu^{2+}, i.e. pH and glycine concentration (Fig. 3). In the sulfate solution, part of Cu^{2+} ions binds to the sulfate complex, so the Cu^+ concentration reduces in line with reaction (1).

In an alkaline medium, the content of Cu^+-glycine complexes increases markedly. The complicated interaction between the components of the system leads to a rather peculiar effect. As the total glycine concentration (c_{gly}) increases from 0.04 to 0.1 M, the fraction of the monoligand complex changes very little, while the amount of the biligand complex increases ~3 times, reaching ~15% of the initial Cu(II) concentration. As follows from the above, the same effects occur both in the perchlorate and sulfate media.

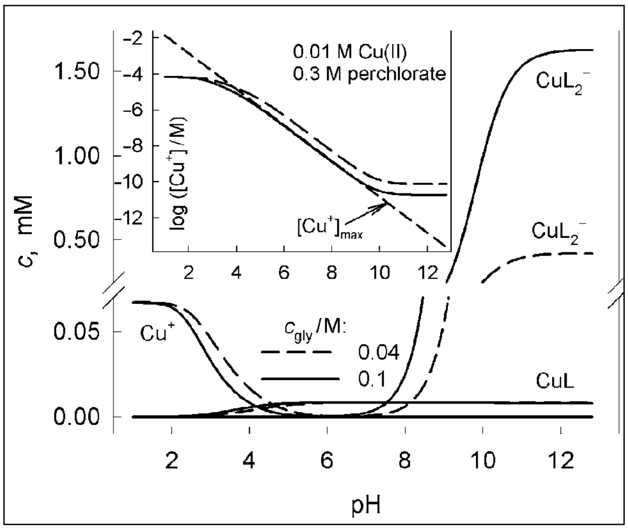

Fig. 3. Distribution of Cu(I) species in the Cu|Cu(II), Cu(I), glycine system (state *B*, perchlorate medium). Comparison of the simulated equilibrium concentrations of Cu^+ ions with their maximum allowable values is given in the inset

The interaction of Cu^+ and OH^- ions is also important, since it can lead to the formation of Cu_2O. A detailed analysis of the stages involved in this process can be found elsewhere [8]. Here we will only indicate that the conditions for the Cu_2O formation are determined by the solubility product of unstable CuOH, i.e. when the concentration of cuprous ions ($[Cu^+]$) exceeds the maximum value, determined by the condition

$$\log\ [Cu^+]_{max} = -0.84 - pH. \qquad (2)$$

The data defined by this condition are given in the inset of Fig. 3 by short dashes. Two rest lines represent the $[Cu^+]$ values resulting from the material balance equations. At sufficiently high concentrations of total glycine (c_{gly} = 0.1 M), the inequality $[Cu^+] < [Cu^+]_{max}$ is valid over a wide range of pH (up to pH 10). At lower c_{gly}, there may be a slight supersaturation of the solution with Cu^+ ions. However, it remains unclear whether this is sufficient for the formation of Cu_2O nucleus. The answer can be obtained from experimental data, since Cu_2O layers have semiconductor properties and are sensitive to light perturbation. For instance, the thermodynamic probability of oxide formation in Cu|Cu(II), β-alanine solutions is much higher. This system is light sensitive and produces a well-defined photopotential, the level of which depends on the quantum energy [8, 14]. In contrast, when a glycine system is disturbed by intense laser radiation, a relatively weak response can be observed, due to apparently thermal phenomena [15]. Given these results, as well as possible inaccuracies of the stability constants, it could be concluded that the formation of Cu_2O layers in the glycine system is unlikely.

Distribution of proton donors

In systems containing protonated species, significant changes in surface pH are often observed [5, 8]. To take into account these changes in establishing the mechanism and kinetic parameters of electrode reactions, it is necessary to determine the concentration of proton donors and acceptors (c_H), as well as to evaluate their lability. The latter property depends on the parameters that determine the rate of chemical stages and that of mass transport. In principle, it also depends on the conditions of the experiment. If chemical reactions are not rated-determining steps, then the system is usually considered labile.

Based on the definition of c_H [8] and using the above data on the distribution of components, the following general expression can be written for sulfate-containing solutions:

$$c_H = [H^+] + [HSO_4^-] + [LH] + 2\,[LH_2^+] - [OH^-]. \quad (3)$$

Then, it is necessary to evaluate the lability of each component and exclude excessive inert particles from consideration. Recombination and dissociation rates in acid equilibria $H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$ are very fast. The rate of HSO_4^- formation is of the same order as the recombination $H^+ + OH^- \rightleftarrows H_2O$ [16]. Hence, an HSO_4^- ion seems to be a rather labile proton donor. However, glycine cannot be ambiguously characterized in this respect. It follows from our analysis [17] that protons attached to different groups in a glycine molecule exhibit different mobility. In contrast to a carboxylic group, the release of an H^+ ion from a protonated amino group proceeds significantly slower. When only the reduction of Cu(II)-glycine complexes takes place, the hydrogen ions are not directly involved in the charge transfer process. Then the dissociation rate of the $-NH_3^+$ group is sufficient to support diffusion flows and Eq. (3) is valid in this case [18]. However, when the protonated glycine species take part in the hydrogen evolution as proton donors, kinetic requirements for mobility increase. Then only protonated $^+H_3N-CH_2-COOH$ species can be treated as labile proton donors, whereas zwitterions $^+H_3N-CH_2-COO^-$ do not fall into this category [17]. Consequently, Eq. (3) transforms into

$$c_H = [H^+] + [HSO_4^-] + [LH_2^+] - [OH^-]. \quad (4)$$

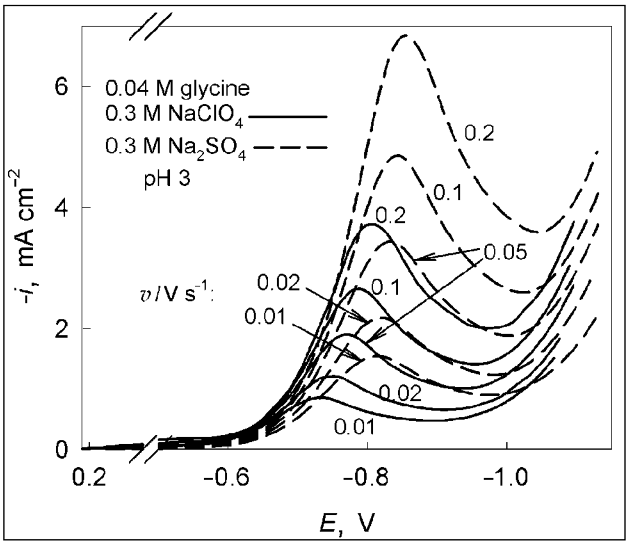

Fig. 4. LPS voltammograms recorded at different potential sweep rates *v* in perchlorate (solid lines) and sulfate (dashed lines) media

To confirm the above assumptions we turn to the LPS voltammetry of hydrogen evolution in this system. LPS voltammograms contain well-defined current maxima (Fig. 4). Current peaks in the sulfate media are higher; this indicates that HSO_4^- ions take part in the hydrogen evolution as proton donors. Peak currents (i_p) and potentials (E_p) vary linearly with $\sqrt{v}$ and log *v*, respectively (Fig. 5), this being indicative that the charge transfer process is irreversible. To quantify the data obtained, we use the equation

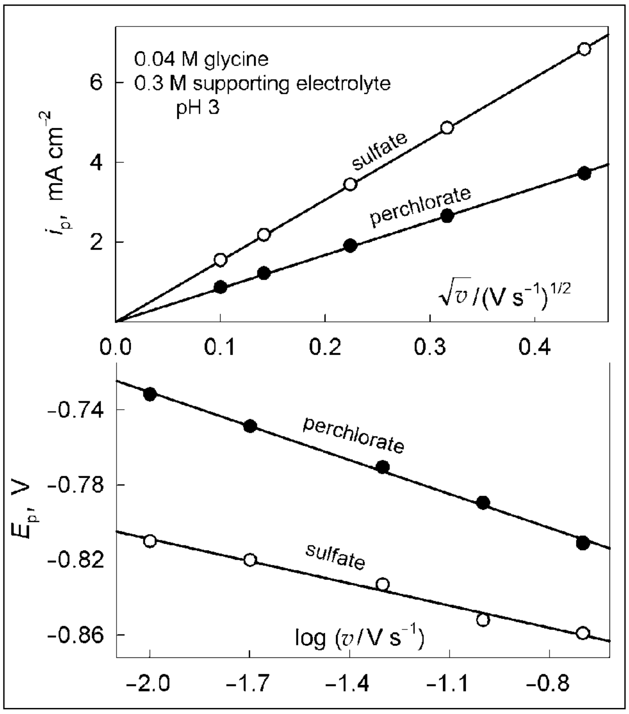

Fig. 5. Variations of current peaks (i_p, the upper part) and peak potentials (E_p, the lower part) with the potential scan rate. Comparison of perchlorate and sulfate media

$$i_p = 0.282\,\mathrm{nF}\sqrt{\frac{\pi F}{RT}\alpha v D}\; c_{\mathrm{H}}, \quad (5)$$

which is valid for charge transfer in the labile system [19]. Simulation of species distribution in Cu(II)-free solutions shows that the addition of 0.3 M sulfate into the 0.04 M glycine solution at pH 3 twice increases the c_H value. This estimate is in a satisfactory agreement with the changes in the slopes of lines in the upper part of Fig. 5: in the sulfate medium, the slope increases 1.84 times.

CONCLUSIONS

1. Substantial differences in the distribution of complexes in Cu(II)-glycine solutions, containing sulfate or perchlorate as an indifferent electrolyte, are observed at pH < 4.5. The molar fraction of the monoligand complex (associate) $CuSO_4$ reaches up to 20 percent of the total Cu(II) concentration.

2. Cu(I)-containing species are generated at the Cu|solution interface. These are Cu^+ aqua-complexes (acid media) or mono- and bidentate Cu(I)-glycine complexes (alkaline media). The addition of sulfate reduces the content of Cu^+ ions, but practically does not affect the distribution of Cu(I) complexes.

3. The study of acid-base equilibria involving Cu^+ ions shows that Cu(II) solutions with an excess of glycine are unlikely to form phase layers of Cu_2O over a wide pH range. The thermodynamic probability of this process remains low in both perchlorate and sulfate media.

4. When replacing perchlorate to sulfate in glycine solutions, the rate of hydrogen evolution in an acidic medium increases significantly. A good agreement between simulated and experimental data suggests that HSO_4^- ions are rather labile proton donors.

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SISTEMOS CU | CU (II), CU (I), GLICINO SU FONINIU SULFATO AR PERCHLORATO ELEKTROLITU PUSIAUSVYROS CHARAKTERISTIKŲ PALYGINAMASIS TYRIMAS

Santrauka

Analizuojamas kompleksų ir ligandų pasiskirstymas Cu(II)-glicino tirpaluose su foniniu sulfato arba perchlorato elektrolitu. Didžiausi pasiskirstymo nevienodumai aptinkami rūgščioje terpėje ($pH < 4,5$). Tada monoligandinio komplekso (asociato) $CuSO_4$ molinė dalis pasiekia iki 20 proc. visos Cu(II) koncentracijos. Cu ir tirpalo tarpfazyje susidaro Cu(I) junginiai: Cu^+ akva-kompleksai (rūgštinėse terpėse) arba mono ir bidentatiniai Cu(I)-glicino kompleksai (šarminėse terpėse). Pridėjus sulfato, Cu^+ jonų kiekis sumažėja, tačiau Cu(I) kompleksų pasiskirstymas iš esmės nepakinta.

Pusiausvyrų tarp rūgščių ir bazių bei Cu^+ jonų tyrimai rodo, kad Cu_2O susidarymo termodinaminė tikimybė yra maža ir perchlorato, ir sulfato terpėse.

Susidarančius rūgščioje terpėje HSO_4^- jonus reikėtų laikyti gana labiliais protonų donorais. Tai kiekybiškai patvirtina eksperimentiniai duomenys: pakeitus glicino tirpaluose perchloratą į sulfatą, vandenilio išsiskyrimo greitis juose atitinkamai padidėja.