
Peculiarities of cathodic processes in ligand-deficient Cu|Cu(II), ethylenediamine

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A plateau of limiting current observed in ligand-deficient Cu|Cu(II), ethylenediamine system is a prewave resulting from abrupt changes in solution composition at the electrode surface. Voltammograms may be quantitatively described by equations of formal kinetics accounting for two consecutive one-electron steps and involving aqua-complexes of Cu(II) as electrically active species. The process of $\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$ seems to be a rate-determining step.

Key words: copper, ethylenediamine, deficit of ligand, mechanism

INTRODUCTION

Cathodic processes proceeding in ligand-deficient systems offer some peculiarities which are mostly interesting from the theoretical point of view. Early studies in this field deal with reversible processes, as applied to polarography [1] or voltammetry [2]. According to a more general approach describing mass transfer in labile complex systems [3], prewaves in voltammetry, two transition times in chronopotentiometry, two current peaks in potential sweep voltammetry [4] are expected. The systems under discussion are still not clearly understood; among these is Cu|Cu(II), ethylenediamine system.

Although solutions of Cu(II)-ethylenediamine complexes were used as plating baths more than 60 years ago, only much later a start has been made to investigate the kinetics and mechanism of cathodic processes. Delahay and Berzins [5] have established by means of chronopotentiometry that an electrically active complex (EAC) of CuL_2^{2+} (L is ethylenediamine) takes part in a charge transfer step on mercury electrode. The same conclusion has been arrived at in the case of copper electrode in solutions containing an excess of ligand [6–8]. Nevertheless, some other complexes have been also referred to as possible EAC: aqua-complexes of Cu^{2+} [6], CuL^{2+} [8, 9]. Two consecutive charge transfer steps generating intermediate product of CuL^+ have been considered in [9].

Ambiguous judgments on EAC composition seem to result from the fact that it depends on the amount of ligand. Peculiarities of ligand-deficient systems are also insufficiently studied. This paper aims to fill some gaps in these problems.

MODEL OF THE SYSTEM

The model of labile complex system [3] is used in the present paper. It allows to estimate the distribution of complexes and protonated species of ligand both in the bulk of solution and at the electrode surface. This model has proved itself in investigations of some complex systems and has made it possible to describe quantitatively voltammograms involving prewaves [3, 10]. The determination of surface concentrations of species is based on the following regularities of diffusive mass transfer:

- i) the concentration profile of total metal is linear over the whole area of Nernst-type diffusion layer;
- ii) the gradient of total ligand concentration is absent in it;
- iii) the latter statement is also valid for proton donors and acceptors.

A deficit of ligand narrows the pH range of solutions under investigation because of the precipitation of $\text{Cu}(\text{OH})_2$ at $\text{pH} > 5.3$. An analysis of solution composition based on cumulative stability constants of Cu(II)-ethylenediamine complexes (β_j) and those of protonated species of ligand (β_m^H) available in literature [11] has shown that it is essential to account for such species as Cu^{2+} , CuL^{2+} , CuL_2^{2+} , L, LH^+ , LH_2^{2+} . Concentrations of other possible particles (CuL_3^{2+} , hydroxo-complexes) are negligible in acid media. The material balance equations for electrode surface take the form

$$[\text{Cu}^{2+}] (1 + \beta_1 [\text{L}] + \beta_2 [\text{L}]^2) = c_M (1 - i/i_d), \quad (1)$$

$$[\text{Cu}^{2+}] (\beta_1 [\text{L}] + 2 \beta_2 [\text{L}]^2) + [\text{L}] (1 + \beta_1^H [\text{H}^+] + \beta_2^H [\text{H}^+]^2) = c_L, \quad (2)$$

$$[L](\beta_1^H[H^+] + 2\beta_2^H[H^+]^2) + [H^+] - [OH^-] = c_H \quad (3)$$

where c_M , c_L , c_H are total bulk concentrations of Cu(II), ethylenediamine, proton donors and acceptors respectively, i_d is a limiting current density. Contrary to c_M or c_L which have real physical meaning, the quantity c_H is somewhat formal and is necessary for determination of surface pH under electrolysis conditions.

The relation between current density and overvoltage may be specified by kinetic equation accounting for the consecutive transfer of two electrons: $\text{Cu(II)} + e \rightarrow \text{Cu(I)} + e \rightarrow \text{Cu}$. The steps of this process are characterized by respective values of exchange densities, namely, i_{o1} and i_{o2} . The special case of kinetic relationship is discussed below.

Simulations were carried out using the following values of stability constants [11]: $\log \beta_1 = 10.7$, $\beta_2 = 19.9$, $\log \beta_1^H = 10.2$, $\log \beta_2^H = 17.7$. At $i = 0$, equations 1–3 involve the bulk concentrations of species. Since the bulk pH is known in this case, it is essential to solve equations 1 and 2 with $[H^+] = 10^{-\text{pH}}/\gamma_{H^+}$, where the activity coefficient of H^+ ions $\gamma_{H^+} \approx 0.5$ [10]. Once the value of c_H is determined by equation 3, this value is used further at $i \neq 0$. The formal potential of Cu|Cu²⁺ couple was taken to be equal to 0.307 V at $\gamma_{\text{Cu}^{2+}} \approx 0.07$ [12].

Results of theoretical analysis show that the system is very simple at a sufficiently low pH. Only aqua-complexes of Cu²⁺ and LH₂²⁺ species incapable of forming coordination bonds prevail at pH < 3. Such a situation leaves unchanged under cathodic polarization conditions (Fig. 1). Consequently, the protonated ligand acts as supporting electrolyte in this case. The complexation degree of the system increases with pH and *ca* 40% of total Cu(II) is in form of CuL²⁺ at pH 5.3, while the free ligand holds a form of LH₂²⁺ (see data for $i = 0$ in Fig. 2).

A certain amount of ligand is released during cathodic reaction resulting in an increase in complexation degree at the electrode surface. A redistribution of surface species is shown in Fig. 2. Although the total concentration of Cu(II) varies linearly with i , variations of concentrations of individual species are obviously non-linear. Abrupt changes in surface concentrations occur at $i/i_d \approx 0.8$ due to a transition from ligand-deficient state to that with an excess of ligand. The latter effect manifests itself as a prewave on a voltammogram (Fig. 3). This is a characteristic property of so-called “partially complexed systems”; prewaves disappear when an excess of ligand in the bulk is attained [3].

Similar considerations can be applied to quasi-reversible processes. The height of prewave remains the same in this case, but the range of its potentials

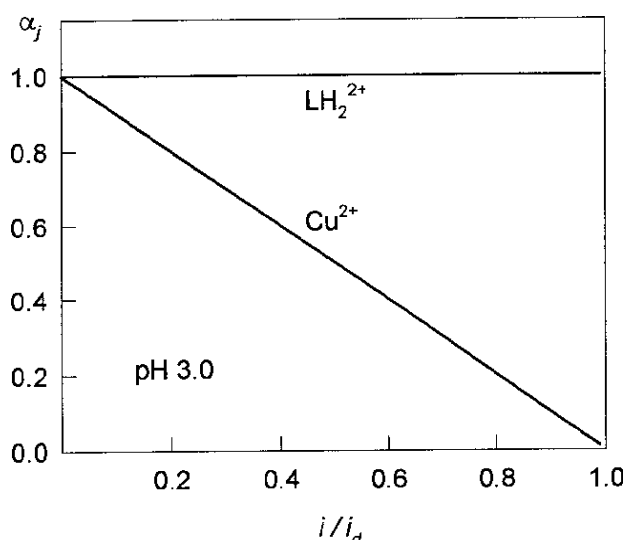


Fig. 1. Variation of surface concentrations of species indicated at the curves with normalized cathodic current density. The molar fraction α_j is equal to $[\text{CuL}_j^{2+}] / c_M$ or to $[\text{LH}_m^{m+}] / c_L$ for species involving Cu(II) or ligand, respectively. $c_M = 0.01$ M, $c_L = 0.005$ M, pH 3.0

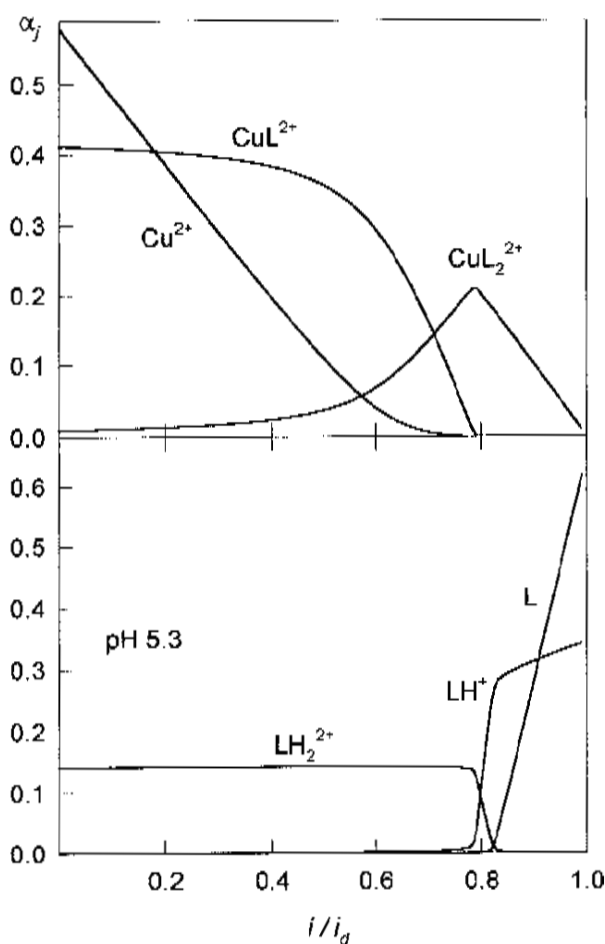


Fig. 2. The same as in Fig. 1 at pH 5.3

becomes dependent on kinetic parameters of charge transfer process. This information may be obtained from experimental data.

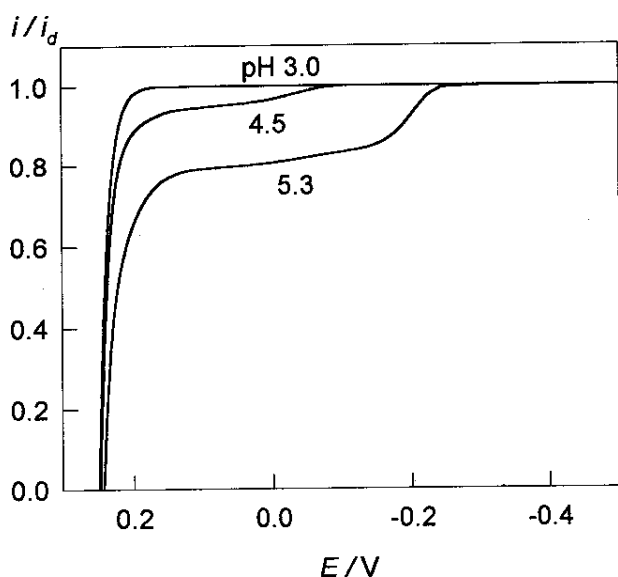


Fig. 3. Simulated cathodic voltammograms for reversible process at $c_M = 0.01$ M, $c_L = 0.005$ M and various bulk pH indicated at the curves. Development of pre-waves is seen with increase in pH

EXPERIMENTAL

A conventional technique of rotating disc electrode was used. Solutions under investigation contained, as a rule, 0.01 M of CuSO_4 , 0.005 M of ethylenediamine and 0.3 M of K_2SO_4 as a supporting electrolyte. Analytical grade salts were purified additionally by means of recrystallization and heating; ethylenediamine was distilled at reduced pressure. Some experiments with 0.04 M of ligand were carried out at pH 8.2. Solutions were deaerated by argon stream over 0.5 h. Triple-distilled water was used for preparation of solutions.

A 5–7 μm thick copper layer was coated on Pt substrate in acid sulphate solution at a current density of 10 mA cm^{-2} . This electrode was exposed to the solution for less than 3 min. A saturated $\text{Ag}|\text{AgCl}$, KCl couple served as a reference electrode. A potential sweep rate was equal to 5 mV s^{-1} . Potentials of the electrode are converted to the standard hydrogen scale. All experiments were carried out at 20 ± 0.5 °C.

RESULTS AND DISCUSSION

Voltammograms recorded using RDE technique exhibit a well-defined plateau of limiting current density (i_l) which varies linearly with $\omega^{0.5}$ (Fig. 4). Lines approximating experimental data pass through the origin. Data obtained at pH 3 with $c_L = 0.005$ M (system involving only aqua-complexes) and those at pH 8.2 with $c_L = 0.04$ M (excess of ligand) coincide very closely, while the data for pH 5.3 are dis-

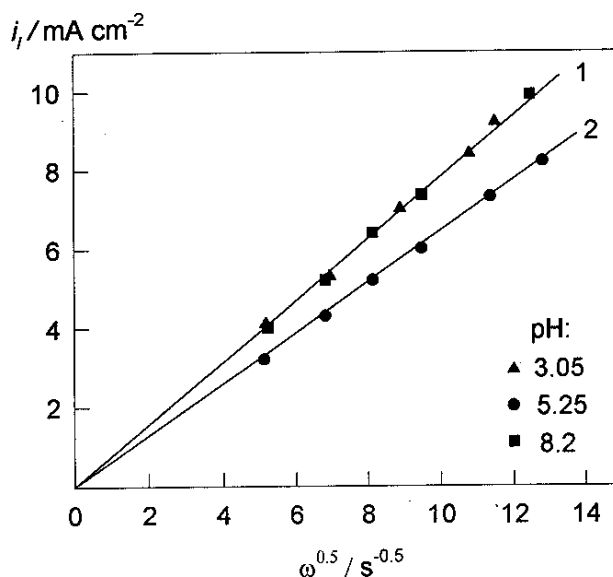


Fig. 4. Variation of current density in the region of voltammogram plateau with $\omega^{0.5}$ (ω is the angular velocity of electrode rotation). Data for pH 8.2 were obtained at $c_L = 0.04$ M.

posed significantly lower. It is reasonable that diffusion coefficients determined by Levitch equation differ as well: $D = 5.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (line 1) and $D = 4.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (line 2). The first value is in good agreement with data obtained in [13, 14] for an excess of ligand. It is particularly remarkable that the ratio of two limiting currents at fixed ω is equal to 0.8 and gives an excellent agreement with the ratio between i_l and i_d at pH 5.3. This result suggests that the current plateau could be treated as a prewave. According to the analysis that follows, a true limiting current of diffusive nature is expected to arise at significantly more negative potentials where the evolution of hydrogen is very intensive. Therefore, it cannot be detected experimentally.

To determine the composition of EAC, we used the method of normalized Tafel plots (NTP) [3]. It accounts for redistribution effects at the electrode surface and requires to normalize the cathodic current density (i_c) to the surface concentration of EAC (c_s). A special feature of such plots lies in the fact that experimental data can be fitted by the same line at various compositions of solutions (different i_0), if the EAC remains the same, provided that effective standard rate constant and charge transfer coefficients do not change noticeably (double layer effects are weak). An example of NTP is shown in Fig. 5 for two possible EAC: Cu^{2+} and CuL_2^{2+} (in the case of CuL_2^{2+} as EAC, the plot passes the maximum, and therefore it cannot be interpreted in terms of formal kinetics). Data for pH 3.0 and 5.3 fall actually on the same line when a reduction of Cu^{2+} ions is suggested. It is evident (see Fig. 1)

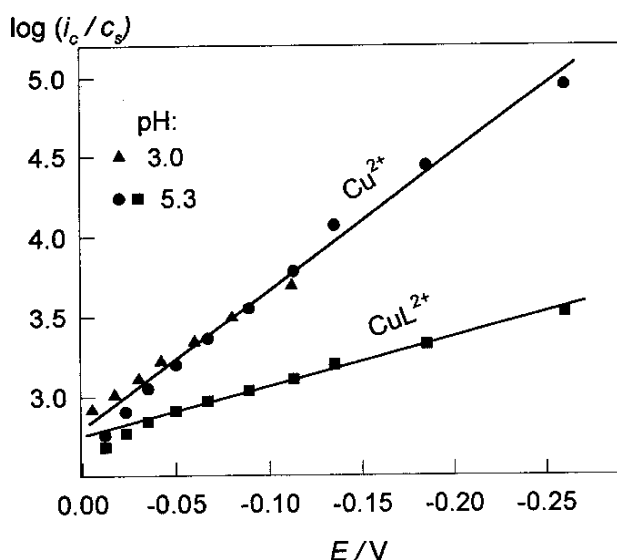


Fig. 5. Normalized Tafel plots at various pH. The composition of postulated EAC is given at the curves

that there is no other alternative at pH 3.0. So, aqua-ions of Cu^{2+} seem to remain as electrically active complexes at pH 5.3 as well.

When the charge transfer process proceeds by two steps,



and the transfer of the first electron is a rate-determining step ($i_{o1} \ll i_{o2}$), the kinetic equation takes the form

$$i = 2i_{o1} \left\{ \exp \left[\frac{(1 + \alpha_{a1})F}{RT} \eta \right] - \frac{[\text{Cu}^{2+}]_s}{[\text{Cu}^{2+}]_b} \exp \left(-\frac{\alpha_{c1}F}{RT} \eta \right) \right\}, \quad (6)$$

where subscripts s and b denote surface and bulk concentrations, α_{a1} and α_{c1} are anodic and cathodic charge transfer coefficients of the process (4), respectively, η is an overvoltage.

Relationship (6) is derived on the assumption proposed by Vetter [15] that partial current densities of consecutive transfer of two electrons (i_1 and i_2) are equal. This is approximately valid at sufficiently high cathodic overvoltages (η_c) under steady-state conditions [16]. At high η_c , equation reduces to

$$\log \frac{i_c}{[\text{Cu}^{2+}]_s} = \log(2i_{o1}) - \log[\text{Cu}^{2+}]_b + \frac{\alpha_{c1}F}{2.3RT} \eta_c, \quad (7)$$

where cathodic i and η are taken as positive. Equation 7 serves as a basis for analysis of experimental data presented in Fig. 5.

The kinetic parameters determined were used to calculate voltammograms by equation. A comparison of simulated and experimental data is given in Fig. 6. An exchange current density at pH 3.0 agrees quite well with that ($24 \mu\text{A cm}^{-2}$) obtained from impedance data for a similarly prepared electrode [17]. Simulated voltammogram attains the true diffusion limiting current at significantly negative potentials ($\text{ca} -1.7 \text{ V}$), where an evaluation of hydrogen is very intensive.

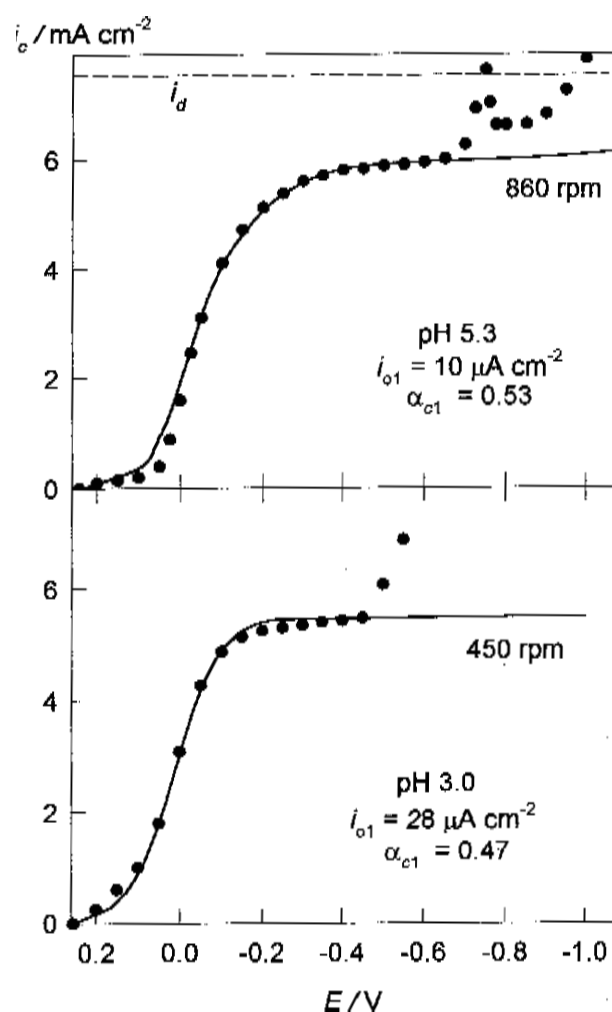


Fig. 6. Comparison between experimental and simulated voltammograms at given values of kinetic parameters. The case of consecutive transfer of two electrons to $\text{Cu}^{2+}(\text{aq})$ as an electrically active complex. The level of true limiting current density, i_d , is shown in the upper part

At pH 5.3, i_{o1} is lower due to lower $[\text{Cu}^{2+}]_b$ in this case; but it has the same order of magnitude as determined in [14, 18]. A weak maximum observed at $E \approx -0.75 \text{ V}$ (Fig. 6) seems to be conditioned by reduction of a small amount of surface Cu_2O . Such an effect may be strongly pronounced under certain conditions; this problem will be discussed in our next communication.

CONCLUSIONS

A good agreement between simulated and experimental voltammograms allows to conclude that the current plateau observed at pH 5.3 is in fact a pre-wave amounting to *ca* 0.8 of the true limiting current density. It is conditioned by abrupt changes in solution composition at the electrode surface where the transition from a ligand-deficient system to that with an excess of ligand occurs.

Voltammograms may be quantitatively described by equations of formal kinetics accounting for two consecutive one-electron steps and involving aqua-complexes of Cu(II) as electrically active species. The process of $\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$ seems to be a rate determining step.

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References

1. J. Koryta, *Progress in Polarography*, Interscience, NY, 1962. Vol. 1 P. 295.
2. J. E. Spell and R. H. Philp Jr., *J. Electroanal. Chem.*, **112**, 281 (1980).
3. A. Survila. *Electrode Processes in Systems of Labile Complexes of Metals* (in Russian), Mokslas, Vilnius, 1989.
4. A. Survila and P. V. Stasiukaitis, *Electrochim. Acta*, **42**, 1113 (1997).
5. P. Delahay and T. Berzins, *J. Amer. Chem. Soc.*, **75**, 2486 (1953).
6. V. Kiselevich and N. N. Zverev, *Khim. Tekhnol. (Khar'kov)*, **8**, 87 (1967).
7. S. I. Berezina, G. A. Gorbachuk, N. V. Gudin and R. L. Achmetova, *Zashchita Metallov*, **4**, 532 (1968).
8. V. L. Kheifets and P. A. Cokolskaya, *Zh. Prikl. Khim.*, **45**, 792 (1972).
9. Ya. D. Zytner, E. A. Maksimyuk and I. D. Talte, *Zh. Prikl. Khim.*, **45**, 116 (1972).
10. A. Survila and V. Uksienė, *Electrochim. Acta*, **37**, 745 (1992).
11. L. G. Sillen and A. E. Martel, *Stability Constants of Metal-Ion Complexes. Special Publications N 17 and 25*. Chemical Society, London, Vol. 1, 1964; Vol. 2., 1971.
12. A. A. Survila and L. B. Spudas, *Lietuvos TSR MA Darbai. B serija*, **5(126)**, 27 (1981).
13. N. V. Gudin, M. S. Shapnik and E. M. Gamburg, *Zashchita metallov*, **4**, 539 (1968).
14. K. Leinartas, *Role of phase layers in kinetics of electrodeposition of copper from ethylenediamine solutions*. Doct. Thesis, Vilnius, 1987.
15. K. J. Vetter, *Z. Naturforsch.*, **8a**, 823 (1953).
16. A. Survila and P. V. Stasiukaitis, *Chemija (Vilnius)*, **3**, 31 (1997).
17. A. Survila and P. V. Stasiukaitis, *Chemija (Vilnius)*, **1**, 23 (1997).
18. M. S. Shapnik, T. P. Petrova and K. A. Zinkicheva, *Prikl. elektrokhim.*, **5**, 39 (1975).

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KATODINIŲ PROCESŲ YPATUMAI SISTEMOJE Cu|Cu(II), ETILENDIAMINAS SU LIGANDO TRŪKUMU

S a n t r a u k a

Ribinės srovės plato, stebima sistemoje Cu|Cu(II), etilendiaminas su ligando trūkumu, yra priešbangis, sąlygojamas staigių tirpalo sudėties pokyčių prie elektrodo paviršiaus. Voltamperogramas galima kiekybiškai aprašyti formaliosios kinetikos lygtimis, įvertinančiomis nuoseklų dviejų elektronų pernešimą į elektriškai aktyvius Cu(II) akva-kompleksus, tariant, kad procesas $\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$ yra limituojanti stadija.

A. Сурвила, С. Канапецкайте

ОСОБЕННОСТИ КАТОДНЫХ ПРОЦЕССОВ В СИСТЕМЕ Cu|Cu(II), ЭТИЛЕНДИАМИН С НЕДОСТАТКОМ ЛИГАНДА

Р е з ю м е

Плато предельного тока, наблюдаемое в системе Cu|Cu(II), этилендиамин с недостатком лиганда, является предволной, обусловленной резкими изменениями состава раствора у поверхности электрода. Вольтамперограммы могут быть количественно описаны уравнениями формальной кинетики, учитывающими последовательный перенос двух электронов на электрически активные аква-комплексы Cu(II), считая, что процесс $\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$ является скоростью определяющей стадией.