

VILNIUS UNIVERSITY
INSTITUTE OF CHEMISTRY

Julija Uljanionok

**ROLE OF Cu(I) COMPLEXES IN THE
ELECTROCHEMICAL REDUCTION OF GLYCINATE
AND MALEATE Cu(II) COMPLEXES**

Summary of Doctoral Dissertation
Physical Sciences, Chemistry (03 P)

Vilnius, 2009

Doctoral dissertation was prepared at Institute of Chemistry in 2006-2009.

Scientific Supervisor

Prof. habil. dr. Arvydas Survila (Institute of Chemistry, Physical Sciences,
Chemistry - 03 P)

Vilnius University Doctoral Dissertation Committee in Chemistry:

Chairman

Habil. dr. Rimantas Ramanauskas (Institute of Chemistry, Physical Sciences,
Chemistry – 03 P)

Members:

Doc. dr. Henrikas Cesiulis (Vilnius University, Physical Sciences, Chemistry –
03 P)

Dr. Konstantinas Leinartas (Institute of Chemistry, Physical Sciences,
Chemistry –03 P)

Dr. Julija Razumienė (Institute of Biochemistry, Physical Sciences,
Biochemistry – 04 P)

Prof. habil. dr. Algimantas Undzėnas (Physics Institute, Physical Sciences,
Chemistry – 03 P)

Opponents:

Prof. habil. dr. Kęstutis Juodkazis (Institute of Chemistry, Physical Sciences,
Chemistry – 03 P)

Doc. dr. Gintaras Valinčius (Institute of Biochemistry, Physical Sciences,
Biochemistry – 04 P)

The official defense of the dissertation will be held at 11 a.m. on January 21, 2010 at the conference hall of Institute of Chemistry.

Address: Goštauto 9, LT-01108 Vilnius, Lithuania.

The summary of the doctoral dissertation was distributed on December 15, 2009.

The copy of the doctoral dissertation is available for review at the Library of Institute of Chemistry and Vilnius University.

VILNIAUS UNIVERSITETAS
CHEMIJOS INSTITUTAS

Julija Uljanionok

**Cu(I) KOMPLEKSŲ VAIDMUO GLICINATINIŲ
IR MALEATINIŲ Cu(II) KOMPLEKSŲ
ELEKTROCHEMINĖS REDUKCIJOS PROCESUOSE**

Daktaro disertacijos santrauka
Fiziniai mokslai, chemija (03 P)

Vilnius, 2009

Disertacija rengta 2006-2009 metais Chemijos institute.

Mokslinis vadovas:

Prof. habil. dr. Arvydas Survila (Chemijos institutas, fiziniai mokslai, chemija - 03 P)

Disertacija ginama Vilniaus Universiteto Chemijos mokslo krypties taryboje:

Pirmininkas

Habil. dr. Rimantas Ramanauskas (Chemijos institutas, fiziniai mokslai, chemija - 03 P)

Nariai:

Doc. dr. Henrikas Cesiulis (Vilniaus universitetas, institutas fiziniai mokslai, chemija - 03 P)

Dr. Konstantinas Leinartas (Chemijos institutas, fiziniai mokslai, chemija – 03 P)

Dr. Julija Razumienė (Biochemijos institutas, fiziniai mokslai, biochemija - 04 P)

Prof. habil. dr. Algimantas Undzėnas (Fizikos institutas, fiziniai mokslai, chemija - 03 P)

Oponentai:

Prof. habil. dr. Kęstutis Juodkazis (Chemijos institutas, fiziniai mokslai, chemija - 03 P)

Doc. dr. Gintaras Valinčius (Biochemijos institutas, fiziniai mokslai, biochemija - 04 P)

Disertacija bus ginama viešame Chemijos mokslo krypties tarybos posėdyje 2010 m. sausio mėn. 21 d. 11 val. Chemijos instituto aktų salėje.

Adresas: Goštauto 9, LT-01108 Vilnius.

Disertacijos santrauka išsiuntinėta 2009 m. gruodžio mėn. 15 d.

Su disertacija galima susipažinti Chemijos instituto ir Vilniaus Universiteto bibliotekose.

Introduction

Compounds containing Cu(I) are often formed as intermediate products of different chemical reactions. Spontaneous metabolic processes involving this microelement are rather common in the nature. Various ligands that are capable of forming stable Cu(I) complexes play an important role in the environment. Consequently, they are responsible for stabilization and detoxification of the excess of Cu^+ ions. Similar processes involving complexation of Cu(I) are also employed in industry, including plating and metal finishing. Accumulation of knowledge concerning electrochemical characteristics of the intermediates creates backgrounds for further improvements in different technologies and for control of commercial processes. Besides, investigations in this field promote better understanding of mechanism of step-wise electrochemical reactions and might be expedient for further development of electrochemical kinetics. The aforesaid gives grounds to consider that the present dissertation is concerned with **actual problems** and the results obtained could find **practical use**.

Processes of electrochemical reduction of glycinate and maleate complexes of Cu(II) are the main **subject of the research**. The main difference between the two systems lies in the fact that, in contrast with glycinate system, a large amount of stable Cu(I) complexes may be formed in maleate solutions. The **major goal of the work** consists in the comparative analysis of electrochemical characteristics of the systems focusing on the role of intermediates. To execute a purpose, the following tasks were scheduled:

- determination of equilibrium characteristics of Cu(II) and maleic acid solutions;
- derivation of the back-ground theoretical model accounting for step-wise charge transfer processes in the labile complex systems;
- evaluation of the effect of the alkali metal cations on the reduction kinetics of Cu(II) glycinate complexes;
- investigation of electrochemical reduction of Cu(II) maleate complexes;
- analysis of mechanism and kinetics of Cu(I) generation in maleic acid system.

Novelty of scientific investigation:

- new modifications based on the quantitative description of pH-metric and spectrophotometric data are proposed for the analysis of experimental data;

- equilibrium characteristics of Cu(II) and maleic acid solutions containing supporting sulphate electrolyte are determined;
- effect of the nature of supporting electrolyte on the reduction of Cu(II) glycinate complexes is established;
- regularities of Cu(I) formation in the Cu|Cu(II), maleic acid system are analyzed;
- peculiarities of pre-electrolysis of maleate solutions are investigated.

Statements carried out for defense:

- The equation accounting for mass and charge balance and dilution effects is derived. It well fits experimental pH-metric data with the following values of maleate protonization constants: $\log\beta_1^H = 6.05$, $\log\beta_2^H = 7.48$. Addition of sulphate weakens the interaction between maleate and hydronium ions.
- The distribution law following from the theory of driven harmonic oscillator is applied for analysis of spectrophotometric data. The stability constant of monoligand Cu(II) maleate complex equal to $10^{2.2}$ is obtained using special procedure.
- The basic statements of formal electrochemical kinetics and regularities of mass transport of chemically interacting particles are sufficient for characterization of the processes occurring in Cu|Cu(II), glycine system. Kinetic parameters of the reduction process depend on the nature of supporting electrolyte. The exchange density decreases and the cathodic charge transfer coefficient increases in the sequence: $\text{Li}^+ - \text{Na}^+ - \text{K}^+ - \text{Cs}^+$.
- Formal electrochemical kinetics describes satisfactorily steady-state voltammograms obtained for Cu|Cu(II), maleic acid system. However, in the case of time-dependent processes, contradictory kinetic data are obtained.
- According to the results of thermodynamic analysis, up to 90 % of Cu(II) can be transformed into Cu(I) in the Cu|Cu(II), maleic acid system.
- Effect of pre-electrolysis of Cu(II) and maleic acid solutions depends on their pH. The balance of cathodic and anodic processes can be disordered in slightly acid (pH 3.9) media due to the passivation of electrodes.

Publication and approbation of scientific results

Major results of the thesis are published in 3 referred scientific papers; the report at international conference was also presented.

Content of the thesis

The thesis is divided into five chapters including short introduction and conclusions. Main goals of the investigations, scientific novelty, practical importance and main statements are given in the **Introduction**. The main goals and tasks of the research have been also formulated. Short introduction of the problems to be solved and structure of the thesis are also presented.

The second chapter presents a review of publications related to the problem under investigation. Theoretical concepts regarding consequent transfer of several electrons are introduced. Considerable attention is paid to the literature data concerning electrochemical processes in Cu|Cu(II), glycine system. Further, some phenomena that accompany the reduction of metals (hydrogen evolution, oxide formation at the electrode surface) are overviewed. At the end, the data concerning properties of ligands, which form Cu (I) complexes, are collected.

Experimental procedures used in the work are described in **the third chapter**. The main details concerning the preparation of solutions and electrodes, as well as the general description of pre-electrolysis is given. The methods applied are: pH-metry, spectrophotometry, voltammetry (rotating disc electrode and measurements with linear potential sweep), electrochemical quartz crystal microgravimetry (EQCM) and electrochemical impedance spectroscopy (EIS).

The fourth chapter presents the results of investigations and discussion. It is subdivided into some parts the essence of which is presented below. Then, the results obtained are summarized and the problems to be solved are formulated.

Conclusions that follow from the analysis of the experimental results and literature data are itemized in **the fifth chapter**. Further, **references** containing 127 positions are listed separately. The **list of articles**, published on the topic of the dissertation, is included at the end.

Equilibrium characteristics of Cu(II) and maleic acid solutions

Literature data on stability constants of maleic acid LH_2 and maleate anion LH^- (β_1^{H} and β_2^{H} respectively) concerns, as a rule, perchlorate media whereas the data concerning sulphate solutions are absent at all. At the same time, the analysis of some Cu(II)-ligand systems has shown that the substitution of sulphates for perchlorates results in the certain diminution of protonization and stability constants. In this connection, it seemed expedient to carry out the experiments offering a clearer view on the equilibrium characteristics of the solutions containing maleic acid and supporting sulphate electrolyte. Spectrophotometry of the solutions and titration methods were chosen for this purpose.

Consideration of ligand protonization and an account for dilution effects made it possible to perform a rigorous quantitative description of experimental titration curves. The following equation was obtained and fitted to the experimental data:

$$\frac{V_{\text{alk}}}{V_{\text{ac}} + V_{\text{alk}}} = \frac{P c_{\text{ac}} - Q \left([\text{H}^+] - \frac{K'_w}{[\text{H}^+]} + \frac{K [\text{H}^+] c_{\text{F}}}{1 + K [\text{H}^+]} \right)}{P c_{\text{ac}} + Q c_{\text{alk}}}, \quad (1)$$

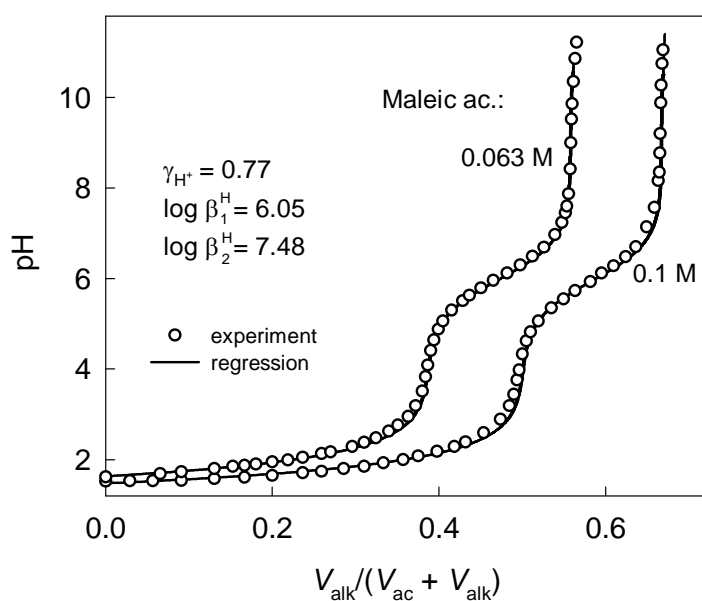


Fig. 1. Experimental titration curves of maleic acid solutions with 0.1 M KOH (symbols). Solid lines represent regression results with listed parameters.

where $P = 2 + \beta_1^{\text{H}} [\text{H}^+]$, $Q = 1 + \beta_1^{\text{H}} [\text{H}^+] + \beta_2^{\text{H}} [\text{H}^+]^2$, V_{alk} , c_{alk} , V_{ac} , c_{ac} are the volume and the concentration of alkali and acid solutions respectively, K'_w is the ionic product of water, K is the stability constant of HSO_4^- ions. The results obtained are listed in Table 1. Figure 1 shows the fitting results and demonstrates the reliability of the constants.

Table 1. Cumulative stability constants of protonated species of ligand

| Logarithm of stability constant | Sulphate concentration | |
|---------------------------------|------------------------|-----------------|
| | 0 | 0.3 M |
| $\log \beta_1^H$ | 6.05 ± 0.07 | 5.75 ± 0.09 |
| $\log \beta_2^H$ | 7.48 ± 0.07 | 7.30 ± 0.08 |

Cumulative stability constants of protonated species of ligand, established in the presence of 0.3 M K_2SO_4 are lower as compared with solutions containing no supporting electrolyte. This effect seems to arise from the higher ionic strength of the former solutions.

Absorption spectra of $CuSO_4$ solutions show maxima at $\lambda_{max} = 806-808$ nm and their height (A_{max}) linearly depends on the concentration of Cu^{2+} aqua-ions with the extinction coefficient $\epsilon = 11.4 M^{-1}cm^{-1}$. Maleic acid solutions do not absorb in the visible region of spectrum, but addition of this substance into $Cu(II)$ solutions results in the gradual rise of A_{max} and its shift towards shorter wavelengths (from 806 up to 722 nm.). Similar tendencies were also observed when solution pH increases, i.e. when the more favorable conditions emerge for complex formation.

Two species, viz. Cu^{2+} aqua-complexes and CuL , were supposed to be responsible for absorption in the visible part of spectrum. Individual absorption characteristics of these species were obtained from the results of experiments carried out in ligand-free $Cu(II)$ solutions and at the large excess of ligand. Congruency their asymmetric spectra made it possible to apply the modified Lorentz distribution that follows from description of driven harmonic oscillator. It was established that the relationship, written as follows:

$$y \equiv \frac{A}{A_{max}} = \frac{a}{(x^2 - x_0^2)^2 + 4x^2 g^2} + g_0, \quad (2)$$

fits experimental data quite well (Fig. 2). Here x is a frequency or other adequate term, x_0 , a , g and g_0 are fitting parameters.

Using established fitting parameters, absorption spectra were simulated, provided that they may be obtained by simple addition of two spectra related to Cu^{2+} and CuL . In so doing, the condition $[Cu^{2+}] + [CuL] = 0.01$ M was also fulfilled. As the result, functions representing the correlation between A_{max} (or λ_{max}) and $[Cu^{2+}]$ were obtained as calibration curves for experimental spectra. Finally, the value of CuL stability constant

$$\beta_1 = [CuL] / [Cu^{2+}][L^{2-}] \quad (3)$$

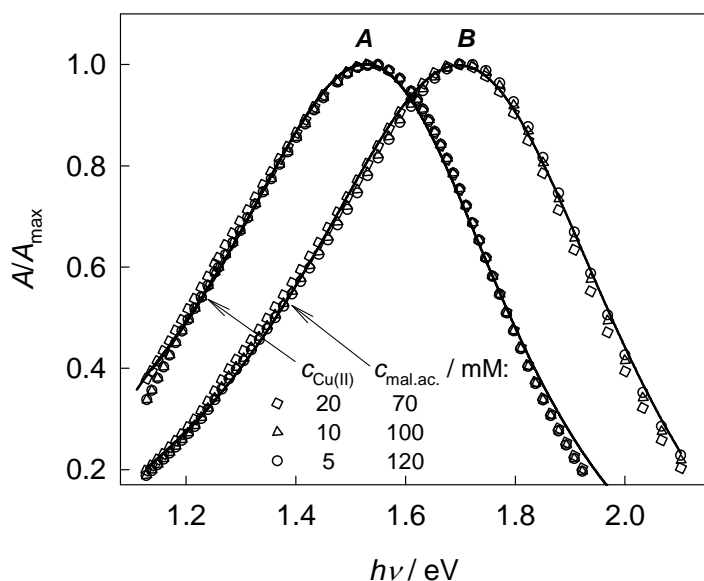


Fig. 2. Normalized absorption spectra obtained for ligand-free Cu(II) solutions (A) and for 0.01 M Cu(II) solutions with high excess of ligand (B). Fitting results are shown by lines.

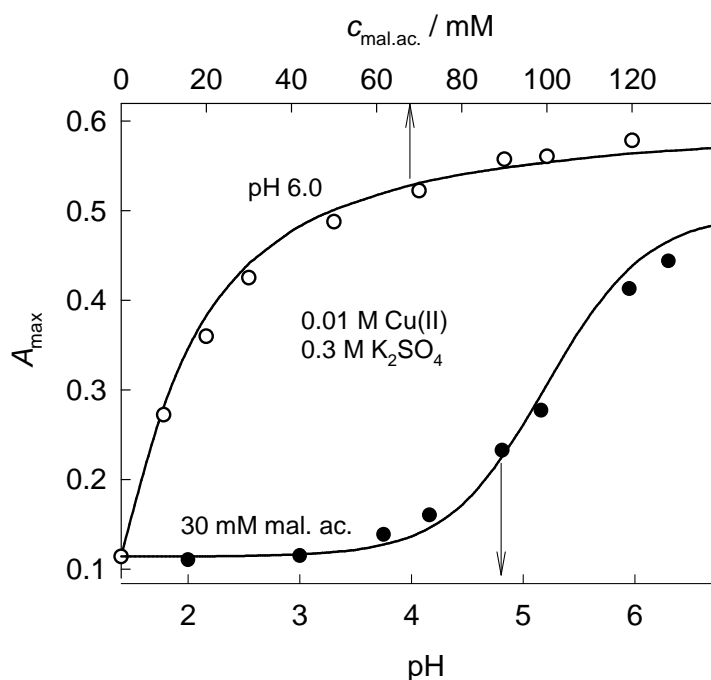


Fig. 3. Absorption maxima of 0.01 M Cu(II) solutions vs. maleic acid concentration at pH 6 (white circles) and vs. pH of the solutions containing 0.03 M of maleic acid (black circles). Solid lines represent results of simulation.

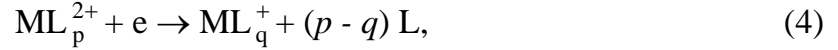
was obtained using material balance equations for the solution containing 0,3 M K_2SO_4 . Expressed in concentration terms, $\log \beta_1 = 2.2 \pm 0.07$. The activity-corrected quantity β_1^T could be also estimated, provided that activity coefficients of CuL and L^{2-} are similar and γ for Cu^{2+} is rather low (~ 0.07). Then, substitution of activities for concentrations in Eq. (3) yields $\log \beta_1^T \approx 3.35$.

To check correctness of the method applied, absorption spectra were simulated and compared with experimental data (Fig. 3). Quite good agreement between simulated and experimental values of A_{max} is observed for a large scale of solutions.

Absorption spectra obtained for $CuSO_4$ and $Cu(ClO_4)_2$ solutions are very similar. These results provide no data on the characteristics of interaction between Cu^{2+} and SO_4^{2-} ions.

Theoretical background

Experimental data are analyzed within the framework of formal electrochemical kinetics. The general scheme of charge transfer process involves two steps



with current densities i_1 and i_2 respectively. At $i_1 = i_2 = i/2$ (steady state conditions), the main kinetic equation takes the form:

$$i = \frac{\frac{[L]_s^p}{[L]_b^p} \exp\left[\frac{(1 + \alpha_{a1})F}{RT} \eta\right] - \frac{[ML_p^{2+}]_s}{[ML_p^{2+}]_b} \exp\left(-\frac{\alpha_{c1}F}{RT} \eta\right)}{\frac{1}{2i_{01}} + \frac{1}{2i_{02}} \frac{[L]_s^{p-q}}{[L]_b^{p-q}} \exp\left[\frac{(\alpha_{a1} + \alpha_{c2})F}{RT} \eta\right]}, \quad (6)$$

where i_0 is an exchange current density, α_a and α_c are anodic and cathodic charge transfer coefficients, η is an overvoltage. Additional subscripts 1 and 2 assign the kinetic parameters to steps (4) and (5), and indexes s and b designate surface and bulk concentrations respectively.

Non-steady-state electrolysis is characterized by the second Flick's law and regularities of mass transport of labile complexes. Then, the surface concentrations of total Cu(II) and total Cu(I) are time-dependent functions of partial current densities:

$$c_{M(II),s} = c_{M(II),b} + \frac{1}{F\sqrt{\pi D}} \int_0^t \frac{i_1(t-u)}{\sqrt{u}} \psi(u) du, \quad (7)$$

$$c_{M(I),s} = c_{M(I),b} + \frac{1}{F\sqrt{\pi D}} \int_0^t \frac{i_2(t-u) - i_1(t-u)}{\sqrt{u}} \psi(u) du, \quad (8)$$

where u is an auxiliary variable and function $\psi(u)$ accounts for the existing of Nernst-type diffusion. layer. Finally, the coordinates of voltammetric maxima (E_p , i_p) arising in the case of linear potential sweep, depend on sweep rate v according to the relationships:

$$\frac{\partial i_p}{\partial \sqrt{v}} = 0,282nF \sqrt{\frac{\pi F}{RT} \alpha n_a D} c, \quad (9) \quad \frac{\partial E_p}{\partial \ln v} = \frac{RT}{2\alpha n_a F}. \quad (10)$$

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

Voltammograms of Cu(II) reduction obtained for the solutions containing different supporting electrolytes (lithium, sodium, potassium and caesium sulphates) show that cathodic current density i depends to a marked extent on the intensity of forced convection. Limiting current density obeys the well-known Levich equation with diffusion coefficient $D = 5.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

Glycine $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$, symbolized as LH, forms complexes CuL^+ and CuL_2 . Simulation procedure using material balance equations made it possible to obtain surface concentrations of electrically active complex CuL^+ at any point of voltammogram. Then, the experimental data were transformed into normalized Tafel plots (NTP) according to the equation:

$$\log \frac{|i|}{[\text{CuL}^+]_s} = \log 2i_{01} - \log [\text{CuL}^+]_b - \frac{\alpha_{c1} F}{2.303 RT} \eta, \quad (11)$$

that follows from Eq. (6) at sufficiently high cathodic overvoltages and describes the case according to which the process $\text{CuL}^+ + e \rightarrow \text{CuL}$ is the rate-determining step ($i_{01} \ll i_{01}$).

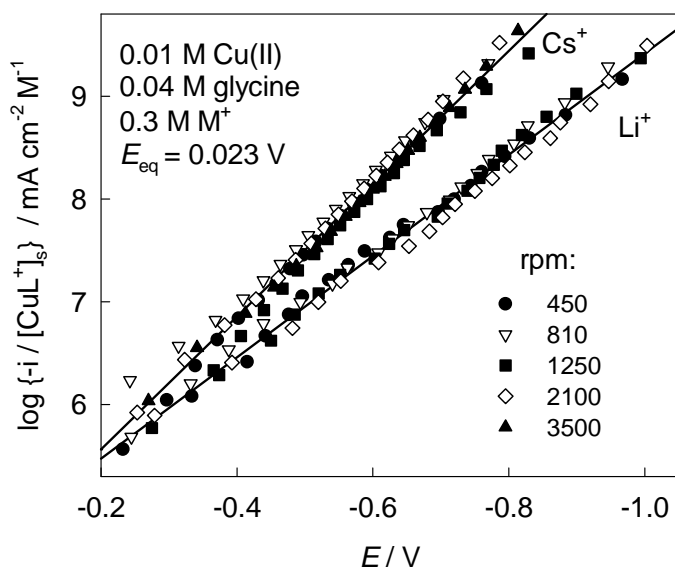


Fig. 4. Normalized Tafel plots obtained at equilibrium potential and indicated rotating velocities of the electrode. pH 8.3.

An example of NTP obtained is shown in Fig. 4. Single lines in a wide region of cathodic overvoltages approximate NTP constructed for different rotating velocities. Kinetic parameters α_{c1} and i_{01} were obtained, respectively, from slopes of NTP and i values extrapolated to equilibrium potential. They are compared with literature data in Table 2.

Table 2. Kinetic parameters of the rate-determining charge transfer step $\text{CuL}^+ + e \rightarrow \text{CuL}$ obtained for different supporting electrolytes.

| Supporting electrolyte | $i_{01} / \text{mA cm}^{-2}$ | | α_{c1} | |
|--------------------------|------------------------------|--------|---------------|--------|
| | pH 3.5 | pH 8.3 | pH 3.5 | pH 8.3 |
| Li_2SO_4 | 0.3 | 0.021 | 0.16 | 0.29 |
| Na_2SO_4 | | 0.020 | | 0.27 |
| K_2SO_4 | 0.18 | | 0.25 | |
| Cs_2SO_4 | 0.06 | 0.013 | 0.70 | 0.37 |

Data for pH 3.5 are taken from:
A. Survila. Electrode processes in systems of labile complexes of metals. Vilnius: Mokslas, 1989. P. 101.

Some additional information on kinetic and double layer parameters was obtained from impedance measurements. Optimal equivalent circuit (Fig. 5) reflects the step-wise reduction of Cu^{2+} and contains two parallel Faradaic subcircuits each of which involves charge transfer resistance \mathbf{R} and diffusion impedance \mathbf{O} in series. This set of elements is shunted with double layer impedance \mathbf{C}_{dl} and, finally, an ohmic resistance of the solution \mathbf{R}_Ω is added. Impedance spectrum of this circuit is in a good agreement with experimental data. Some special features of the electrical analogues \mathbf{O} (they account for the finite-length diffusion) may be attributed to the existence of oxide layers on the electrode surface. Surface oxidation is most noticeable in the solutions containing K_2SO_4 . The impedance obtained for glycine-containing solutions is almost 100 times

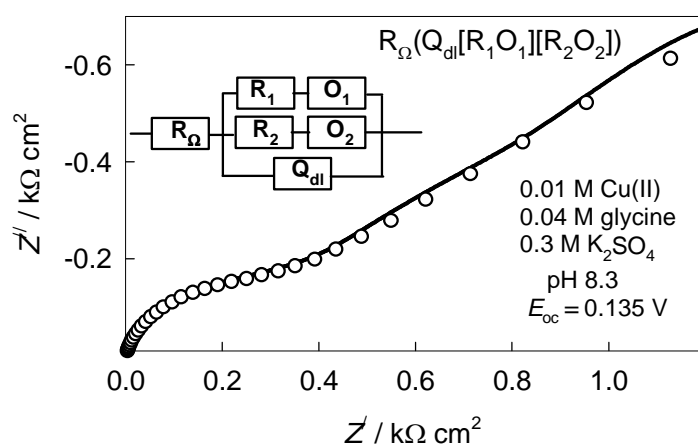


Fig. 5. Nyquist plot (relation between real, Z' , and imaginary, Z'' , components of the impedance) and the equivalent circuit of the electrode. Experimental data are compared with these simulated for the circuit.

higher as compared with ligand-free solutions. Although, the spectra of electrical phase angle $\psi = \arctan(Z''/Z')$ are similar in shape. This means that the chemical reactions preceding charge transfer steps, as well as a weak surface oxidation, do not change radically the overall electrochemical reaction. Cu(II) -glycine complexes should be categorized as quite labile ones.

Electroreduction kinetics of Cu(II)-maleate complexes

Voltammograms in this case are similar to those obtained for glycinate system. Cathodic polarization increases with ligand concentration and pH. Diffusive limiting current obeys Levich equation and yields D equal to $5.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. In contrast with

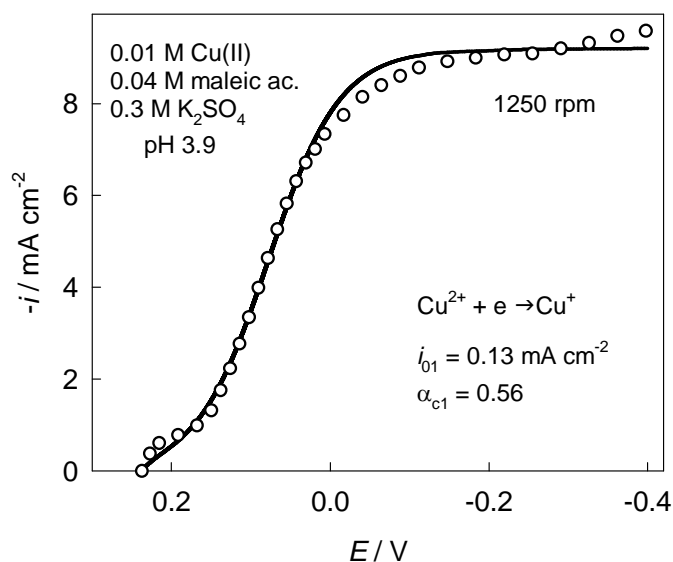


Fig. 6. Comparison of simulated (line) and experimental (symbols) voltammograms.

previous system, NTP obtained from RDE data contain breaks. However, some their portions are amenable to approximation by lines. Simulations of entire voltammograms using established kinetic parameters and Eq. (6) give satisfactory results (Fig. 6). Some deviations are observed at low cathodic polarizations and in the region of limiting current plateau.

Voltammograms obtained with linear potential sweep technique are more complicated and their shape depends on solution pH to a great extent. Two current peaks observed at pH 3.9 (left i_{p1} and right i_{p2}) are conditioned by the reduction of Cu^{2+} and

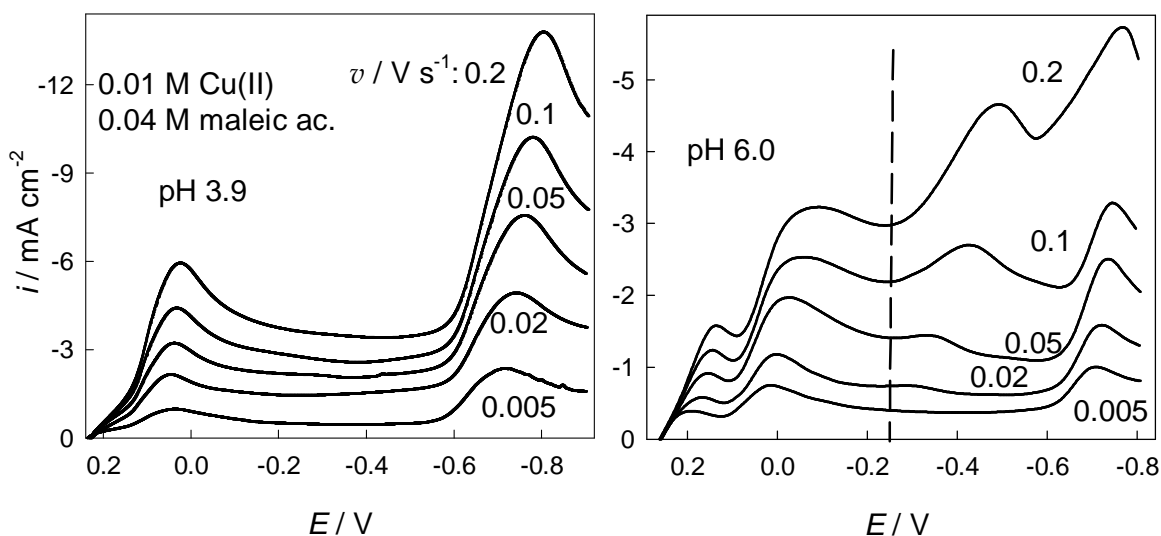


Fig. 7. LSV data obtained at different potential sweep rates v indicated at the curves. Reduction of hydrogen takes place to right of the dotted line (data for pH 6).

H_3O^+ respectively. To establish the regions of partial processes at pH 6, special analysis was performed, using Eqns (7) and (8). According to the results obtained, voltammograms may be divided into two parts (Fig. 7). Only Cu(II) reduction occurs at $E > -0.25$, and hydrogen evolution is observed at more negative potentials.

Eqns (9) and (10) were employed to analyze current peaks at pH 3.9. It was found that the linearity of $i_{p1} - \sqrt{v}$ and $E_{p1} - \log v$ dependences is supported, but the former do not pass the origin. Moreover, both equations produce different kinetic parameters. Such inconsistencies are not typical of right peaks. The values of $\alpha n_\alpha = 0.58$ and $D = 1,2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ were established for hydrogen evolution.

Formation of Cu(I) compounds in the Cu/Cu(II), maleic acid system

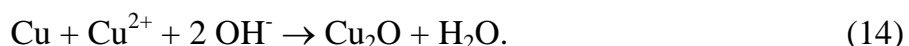
Generation of Cu^+ ions in the system is possible when the reversible process



occurs. It may be performed by the electrolysis of Cu(II) solutions or under open-circuit conditions when Cu(II) solution comes into contact with Cu electrode. Three equilibrium states and the transitions between them are analyzed in the dissertation. The initial state A concerns the solution containing only Cu(II) complexes. Copper, in contact with this solution, produces Cu(I) until the new equilibrium (state B) is established. However, if the process (12) generates more Cu^+ ions than this is permitted by the equation

$$\log [\text{Cu}^+]_{\text{max}} = -0.84 - \text{pH}, \quad (13)$$

the formation of unstable intermediate CuOH originates with its following decomposition into Cu_2O :



Again, further shifts in the chemical equilibria are observed resulting in the establishment of the final equilibrium state C.

The depth of Cu(II) transformation into Cu(I) is analyzed theoretically using material balance equations and constants characterizing all the equilibria possible in the system. The results are presented as distribution of Cu(II) and Cu(I) complexes vs pH in all aforementioned states. They show (see also the example in Fig. 8) that rather deep

chemical changes are possible in the system and formation of Cu_2O at the electrode surface stimulates this process, when the certain critical pH is exceeded. At sufficiently

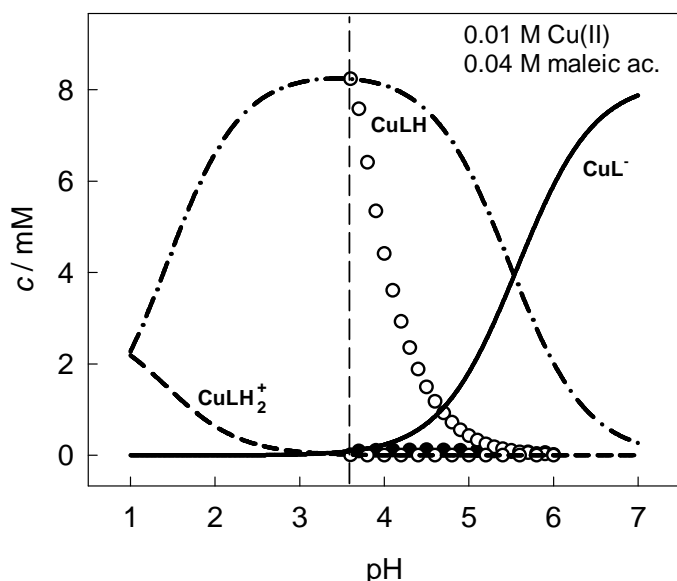


Fig. 8. Quantities of Cu(I) complexes formed in the solution containing initially 0.01M of Cu(II) and 0.04 M of maleic acid. Lines and symbols present states B and C respectively.

high ligand concentrations, ~90 % of Cu(II) can be converted into Cu(I).

Results of simulations were checked by experiments performed using electrochemical quartz crystal microgravimetry (EQCM) and spectrophotometry. It follows from EQCM data obtained under open-circuit conditions that Cu electrode mass decreases in sufficiently acidic Cu(II)-maleic acid solutions ($\text{pH} \leq 5$) due to the heterogeneous reaction (12). Conditions favorable for Cu_2O formation emerge in less acidic

media ($5.5 < \text{pH} < 6.0$). Considering simple relationship between changes in quartz mass and oscillation frequency ($\Delta m = -k \Delta f$), the rate of heterogeneous process may be given as follows:

$$v = \frac{k}{M} \left| \frac{d\Delta f}{dt} \right|, \quad (15)$$

where M is the molar mass of the chemical element that is responsible for the occurrence mass changes. The rate of electrochemical dissolution of copper electrode was found to fall into the region from 0.4 to 0.8 $\text{nmol cm}^{-2} \text{s}^{-1}$ depending on solutions pH. Similar quantities were obtained for oxide formation: its rate accounts for some $\text{nmol cm}^{-2} \text{s}^{-1}$.

In agreement with theoretical predictions, spectrophotometric data showed the respective diminution of Cu(II) content in the solutions caused by the above processes. Some kinetic aspects concerning practical establishment of different equilibrium states are also discussed in the thesis.

Effect of pre-electrolysis

To saturate the solution with the intermediate product, a pre-electrolysis procedure is often applied. For this purpose, we utilized hermetic cell with copper electrodes (surface area $\sim 8 \text{ cm}^2$). Direct current of $\sim 0.1 \text{ mA cm}^{-2}$ passed through the deaerated solution for a controlled time τ . When only copper-containing particles take

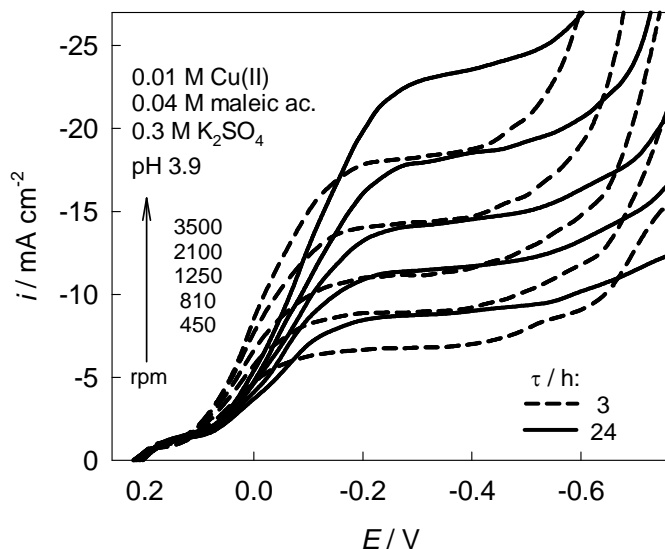


Fig. 9. RDE voltammograms obtained for solutions pre-electrolyzed for 3 (solid lines) 24 (dashed lines) hours. Rotation velocities increase from bottom to top as indicated.

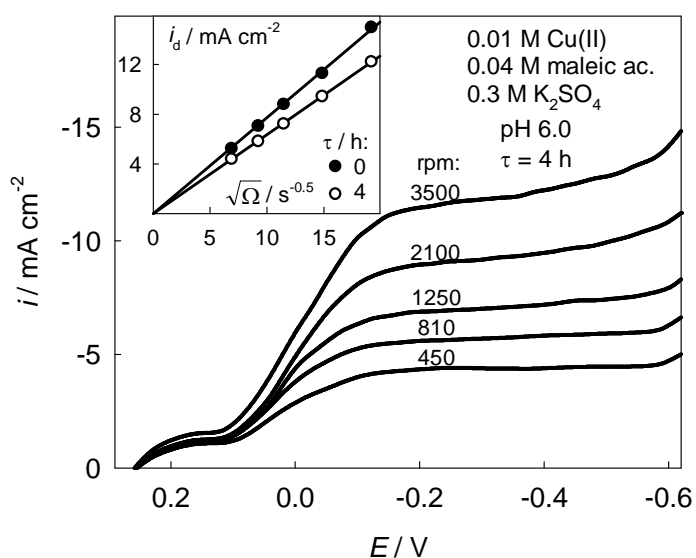


Fig. 10. RDE voltammograms obtained at pH 6. Effect of pre-electrolysis is seen from the data given in the inset.

part in electrochemical processes, the relationship follows from mass and charge conservation law:

$$c_{\text{Cu(I)}/2} + c_{\text{Cu(II)}} = \text{const.} \quad (16)$$

It is also valid when copper electrode is kept in contact with solution under open-circuit conditions. In any case, limiting current density should remain unchanged. Some deviations from this rule are possible, when effective D of Cu(I) and Cu(II) differ significantly.

Typical result, obtained at pH 3.9, is shown in Fig. 9. Pre-electrolysis increases both cathodic polarization and current density. Similar effects were also observed in the case of linear sweep voltammetry. However, this is not the case of less acidic solutions (Fig. 10).

It was established that that maleic acid is electrically inactive component and can take part only in hydrogen evolution as proton donor. Passivity of electrodes was observed at pH 3.9, giving rise to the reduction of H_3O^+

ions and, as a consequence, to the accumulation of Cu(II) in the solution. Results of other experiments support the conclusions made above. An increase in solution pH was observed during the electrolysis. Spectrophotometric investigations have shown that the absorption maximum of the solutions grows and shifts to shorter waves. By the way, A_{\max} is able to triple its height in 24 hours. The main peculiarities may be seen from the

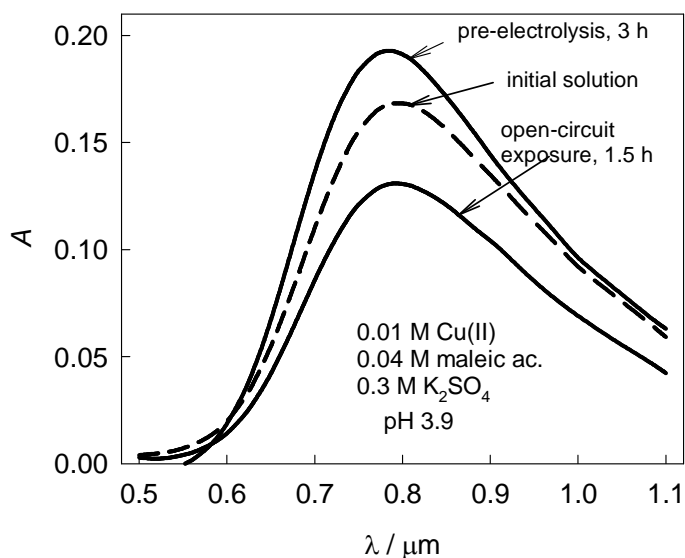


Fig. 11. Absorption spectra of the solution in the initial state, after exposure for 1.5 hours in contact with copper electrodes and after 3 hours of pre-electrolysis.

data given in Fig. 11. Initially, the solution was kept for 1.5 hours in contact with copper electrodes under open-circuit conditions. It can be seen that the concentration of Cu(II) is lowered. Then, the direct current was applied for 3 hours and this promoted the generation of Cu(II) to a significant extent. These results not only explain the experimental results, but they are also indicative of possible side effects that cause some shortcomings of pre-electrolysis.

Comparison of the results obtained for two different systems makes it possible to draw some general conclusions. The above theoretical model fits well for description of electrochemical transforms, if the quantity of generated Cu(I) complexes is low. Then, the concept of overvoltage may be used of, since the equilibrium state can be achieved under open-circuit conditions. Besides, the equality of partial current densities ($i_1 = i_2$), may be also assumed. Ultimately, most of classical fundamental kinetic equations may be used with substitution of concentration of free metal ions (metal aqua-complexes) for the total metal concentration. All these expedients were applied successfully in the case of Cu|Cu(II), glycine system.

Application of the same approach for system with high content of Cu(I) is limited. The concept of overvoltage and the assumption that $i_1 = i_2$ should be revised. Besides, experimental data concerning voltammograms of partial processes are requested. To achieve progress in this field, further investigations are required.

Conclusions

1. The equation derived for quantitative description of pH-metric data, was applied for the analysis of the entire titration curve. Protonization constants of maleate anions, obtained with fitting procedures, are as follows: $\log\beta_1^H = 6.05$, $\log\beta_2^H = 7.48$. It was established that the addition of 0.3 M K_2SO_4 results in the diminution of stability constants ($\log\beta_1^H = 5.75$, $\log\beta_2^H = 7.30$).
2. To obtain equilibrium characteristics of Cu(II) maleate complexes from spectrophotometric data, the method, based on the driven harmonic oscillator theory, was proposed. Stability constant of monoligand complex was found to be equal to $10^{2.2} M^{-1}$.
3. Basic equations of formal electrochemical kinetics are applicable for interpretation of experimental data obtained for Cu|Cu(II), glycine system. According to the results of analysis, kinetic parameters of Cu(II) glycinate reduction depend on the nature of the supporting electrolyte. Exchange current density decreases and cathodic charge transfer coefficient increases in the sequence: $Li^+ - Na^+ - K^+ - Cs^+$.
4. Thermodynamic analysis shows that deep changes are possible in this system resulting in 90 % transform of Cu(II) into Cu(I). It follows from EQCM data, that the rates of Cu corrosion and Cu_2O formation are estimated to be of the same order ($nmol\ cm^{-2}\ s^{-1}$).
5. The theoretical model applied describes satisfactorily the steady-state voltammetric characteristics of Cu|Cu(II), maleic acid system, but it yields some contradictory results in the case of time-dependent processes.
6. To enhance the Cu(I) generation in maleic acid system, the pre-electrolysis procedure was applied. It was found that its effect depends on solution pH. Passivity of electrodes, observed at pH 3.9, gives rise to the reduction of H_3O^+ ions and, as a consequence, to the accumulation of Cu(II) in the solution.

List of the published works on the topic of the dissertation

1. Julija Uljanionok, Arvydas Survila. *Effect of the nature of supporting electrolyte on the electroreduction kinetics of Cu(II)-glycine complexes in slightly alkaline medium*. Chemija (Vilnius). 2008. Vol. 19. No. 1. P. 20-24.
2. Julija Uljanionok, Arvydas Survila. *Effect of supporting sulphate electrolyte on equilibrium characteristics of Cu(II) and maleic acid solutions*. Chemija (Vilnius). 2009. Vol. 20. No. 2. P. 84-88.
3. Julija Uljanionok, Aldona Jagminienė, Arvydas Survila *Spectrophotometric investigation of the formation of Cu(II)-maleic acid complexes*. Chemija (Vilnius). 2009. Vol. 20. No. 2. P. 89-92.

Conference thesis

1. J. Uljanionok, A. Survila. *Redox processes in the Cu/Cu(II), Cu(I), maleic acid system*. 10-th Conference "Advanced Materials and Technologies". 27- 31 August 2008, Palanga, Lithuania.

REZIUMĖ

Atliktas palyginamasis dviejų kompleksinių sistemų - Cu|Cu(II), glicinas ir Cu|Cu(II), maleino rūgštis – elektrocheminių charakteristikų tyrimas.

Nustatytos maleino rūgšties tirpalų pusiausvyrinės charakteristikos. Kiekybiniam titravimo kreivių aprašymui išvestos lygtys, kuriose įvertinti medžiagų bei krūvių balansai bei atsižvelgta į praskiedimo efektus. Jų taikymas pH-metrinių duomenų analizei davė tokias maleato anijonų protonizacijos konstantų reikšmes: $\log \beta_1^H = 6,05$, $\log \beta_2^H = 7,48$. Nustatyta, kad tirpaluose su 0,3 M K_2SO_4 priedu protonizuotų ligando formų stabilumas sumažėja ($\log \beta_1^H = 5,75$, $\log \beta_2^H = 7,30$).

Cu(II) maleatinių kompleksų stabilumui nustatyti panaudotas spektrofotometrijos metodas ir pasiūlyta duomenų analizės procedūra. Ji remiasi kiekybiniu absorbcijos spektrų aprašymu, taikant lygtis, išplaukiančias iš valdomo harmoninio oscilatoriaus teorijos. Išanalizavus įvairių sudėčių tirpalų absorbcijos maksimumo dydžius, prieita išvados, kad rūgščiose terpėse vyrauja monoligandinis kompleksas, kurio koncentracinė stabilumo konstanta $\log \beta_1 = 2,2$.

Atlikta sistemos Cu|Cu(II), maleino rūgštis pusiausvyrų termodinaminė analizė. Nustatyta, kad esant metalinio vario ir tirpalų sąlyčiui, sistemoje galimi gilūs virsmai, kurių metu iki 90 % Cu(II) transformuojasi į Cu(I). Teorines išvadas patvirtina eksperimentiniai duomenys, gauti spektrofotometrijos ir elektrocheminės kvarco kristalo mikrogravimetrijos metodais. Įvertinti Cu korozijos bei fazinių Cu_2O sluoksnių susidarymo greičiai, kurie abu yra tos pačios eilės ($nmol\ cm^{-2}\ s^{-1}$) dydžiai.

Suformuluotas bazinis teorinis modelis, kuris panaudoti pagrindiniai formaliosios elektrocheminės kinetikos dėsniumai bei atsižvelgta į chemiškai sąveikaujančių dalelių masės transporto ypatumus. Nustatyta kad šis modelis gerai tinka sistemos Cu|Cu(II), glicinas voltamperometrinių duomenų interpretacijai. Šių duomenų transformacija į normuotas Tafelio priklausomybes (NTP) parodė, kad plačiame katodinių viršįtampių intervale tiesinės NTP praktiškai nepriklauso nuo priverstinės konvekcijos intensyvumo. Jų analizė parodė, kad monoligandinio Cu(II) komplekso redukcijos kinetiniai parametrai priklauso nuo foninio elektrolito prigimties: sekoje $Li^+ - Na^+ - K^+ - Cs^+$ mainų srovės tankis mažėja, o katodinis krūvio pernašos koeficientas auga.

Bazinis teorinis modelis patenkinamai aprašo sistemos Cu|Cu(II), maleino rūgštis stacionariąsias voltamperines charakteristikas. Nedideli skirtumai tarp eksperimentinių ir teorinių voltamperogramas, aptikti mažų katodinių poliarizacijų srityje ir perėjime į ribinės srovės plato. Chronovoltamperogramose, kurios charakterizuoja nestacionarius procesus, rūgščių tirpalų (pH 3,9) atveju aptikti du srovės maksimumai, kuriuos sąlygoja Cu(II) redukcija ir vandenilio skyrimasis. Abiejų maksimumų koordinatės (E_p ir i_p) priklauso nuo potencialo skleidimo greičio pagal bazinės teorijos dėsnius. Tačiau tik antrojo maksimumo analizė duoda patikimas H_3O^+ redukcijos kinetinių parametru reikšmes, o Cu(II) redukcijos proceso atveju gaunami prieštaringi rezultatai. Mažiau rūgščiose terpėse užregistruoti keturi srovės maksimumai, iš kurių du pirmieji priklauso Cu(II) redukcijai.

Cu(I) generacijos intensifikacijai maleino rūgštis sistemoje panaudota parengiamosios elektrolizės procedūra. Nustatyta, kad jos efektas priklauso nuo tirpalo pH. Rūgščioje terpėje (pH 3,9) aptikta elektrodų pasyvacija, dėl kurios suintensyvėja vandenilio skyrimasis. Dėl to išsibalansuoja anodinis ir katodinis procesai ir sistemoje kaupiasi Cu(II).

Apibendrinant gautus rezultatus, aptartos spręstinios teorinės ir eksperimentinės problemos.

Darbo metu gauti ir disertacijoje aprašomi rezultatai atspausdinti 3-juose moksliniuose straipsniuose ir pristatyti tarptautinėje konferencijoje.

CURRICULUM VITAE

Brief information about the author:

Name: Julija

Surname: Uljanionok

Date of birth and place: 1970 January 21, Kaliningrad, Russia

Email: uljanionok@mail.ru

Education:

1987 graduated 51st Secondary school, Vilnius

1987-1992 studies at the Vilnius University, for a Master's degree. Completed with a work "Investigation of NO₃⁻ ions electric resolution and their influence on the cathode polarization in the sulfitic silvering electrolytes." Supervisor doc.V.Skučas

2003-2005 studies at the Vilnius Pedagogical University, for a Master's degree.

Completed with a work "Effect of polypropylenglycol electrochemically synthesized polyaniline." Supervisor: Dr. V. Kapočius.

2005-2009 studies at the Institute of Chemistry for a Doctor degree.

Professional experience:

Since 1994 "Žara" Secondary school. Teacher of Physics

Since 1995 "Žara" Secondary school. Teacher of Chemistry

GYVENIMO APRAŠYMAS

Vardas: Julija

Pavardė: Uljanionok

Gimimo data ir vieta: 1970 sausio 21, Kaliningradas, Rusija.

El Paštas: uljanionok@mail.ru

Išsilavinimas:

1987 m. baigė Vilniaus m. 51-ją vidurinę mokyklą.

1987-1992 m. aukštosios studijos Vilniaus universitete, baigė Chemijos fakulteto chemijos specialybės mokslus ir jai suteikta diplomuoto chemiko kvalifikacija.

Diplominio darbo tema "NO₃⁻ jonų elektoredukcijos ir jų įtakos katodinei poliarizacijai sulfitinuose sidabravimo elektrolituose tyrimas." Darbo vadovas doc. V.Skučas.

2003-2005 m. baigtos magistrantūros studijos Vilniaus pedagoginiame universitete, įgytas chemijos magistro laipsnis ir mokytojo kvalifikacija. magistrinio darbo tema „Polipropilenglikolio poveikis elektroccheminei polianilino sintezei“. Mokslinis vadovas: dr.V.Kapočius.

2005-2009 m. doktorantūros studijos Chemijos institute.

Julija Uljanionok

**ROLE OF Cu(I) COMPLEXES IN THE ELECTROCHEMICAL REDUCTION
OF GLYCINATE AND MALEATE Cu(II) COMPLEXES**

**Summary of Doctoral Dissertation
Physical Sciences, Chemistry (03 P)**

Julija Uljanionok

**Cu(I) KOMPLEKSŲ VAIDMUO GLICINATINIŲ IR MALEATINIŲ Cu(II)
KOMPLEKSŲ ELEKTROCHEMINĖS REDUKCIJOS PROCESUOSE**

**Daktaro disertacijos santrauka
Fiziniai mokslai, chemija (03 P)**