
Electrochemical response of Au electrode to organic diamines in alkaline cobalt(II) solutions

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The effect of various amines on the electrochemical parameters of the Au rotating disk electrode in alkaline Co(II)-glycine solutions was studied. Addition of ethylenediamine (*EN*), 1,2-propylenediamine (*PDA*), 1,3-propylenediamine (*TMDA*) in mM levels shifts the open-circuit potential to more negative values by 0.3–0.5 V and enhances dramatically the anodic Co(II) oxidation current, as a result of Co(II) complex transformation to more stable and electrochemically active Co(II)-diamine species. The effect of diamines on the open-circuit potential changes in the line $PDA > EN > TMDA$ and on the anodic current – in the sequence $EN > PDA > TMDA$. The anodic oxidation of cobalt(II) complexes with diamine is accelerated by the bromide ion. The effects of diamines on the electrochemical behaviour of Co(II) may have analytical applications.

Key words: cobalt(II) complexes, diamines, Au rotating disk electrode, anodic oxidation

INTRODUCTION

The redox potential of the cobalt(III)–cobalt(II) couple varies in a wide range of values (from 1.8 to ca. –0.6 V), depending on the degree of complexation of cobalt(II) and cobalt(III) which is controlled by selection of ligands, changing their concentration and the solution pH. Many cobalt(II) complexes with amines are rather strong reducing agents and are capable of reducing some metal ions to the metallic state [1] and therefore are used in electroless plating systems for the deposition of metallic coatings: cobalt(II)–ammonia complex is used for electroless silver deposition [1–3], and cobalt(II)–ethylenediamine complex for electroless copper deposition [1, 4, 5].

The anodic oxidation of a reducing agent – a cobalt(II) complex with amine in our case – is one of two partial electrochemical reactions of the autocatalytic electroless metal deposition process, and its rate is usually the main factor determining the overall electroless process rate.

The rate of anodic oxidation of various Co(II)–amine complexes is known to be different. For example, the oxidation of cobalt(II)–ammonia complex on a rotating Pt electrode was shown to be very slow, the oxidation currents were only of the order of 1% of the expected value for the Co(II) concentrations [6]. Recently [7] the ligand effect on the oxidation rate of Co(II) has been demonstrat-

ed – the oxidation rate of Co(II)–ethylenediamine complexes was shown to be higher than that of Co(II)–ammonia species at comparable conditions by a factor of 10–40.

The electrochemical oxidation of cobalt(II) complexes has not been given thorough studies until now, possibly because of the lability of these complexes. They exist only in the alkaline solutions containing rather high free ligand concentrations, in contrast with inert cobalt(III) species, which are stable enough in various acidic and alkaline solutions and whose cathodic reduction was extensively studied. Besides the mentioned investigations, the charge transfer kinetics for several Co(II)–Co(III)–amine systems was studied on Pt electrode [8–11], and the anodic oxidation of the Co(II)–ethylenediamine complex on Cu was investigated in relation to autocatalytic copper deposition [12, 13].

In this work, the electrochemical response of Au electrode in alkaline Co(II)-glycine (*Gly*, aminoacetic acid) solution to various amines was studied. This system was selected for several reasons: 1) gold electrode is more stable in amine solutions compared with silver and copper used in the recent investigations, 2) Co(II) forms complexes with glycine, stable enough to prepare alkaline solutions in a wide pH range, 3) the anodic oxidation of cobalt(II)–glycine complex is very slow and the effect of various amines added can be compared easily.

EXPERIMENTAL

The voltammetry with a rotating disk electrode and standard electrochemical equipment was used to study the Au–Co(II)–amine system in glycine solutions.

Voltammetric measurements were carried out using a 1 cm² platinum disc electrode which was electroplated with gold (10 μm) from a standard cyanide bath before each series of measurements. The disc rotation rate in the main experiments was 930 rpm. A closed cell was used, solutions were purged with Ar before introducing Co(II) to avoid oxidation by atmospheric oxygen; the Ar atmosphere was maintained over the solution during the measurements. The potential sweep rate was 10 mV s⁻¹, the potential was measured and its values are given with respect to the Ag|AgCl|KCl_{sat} reference electrode.

The main solution contained (M): CoSO₄ – 0.01, Gly – 0.04; solution pH was changed by adding NaOH solution. Reagent grade chemicals and bidistilled water were used to prepare the solutions, amines were from Aldrich. All experiments were carried out at 20 ± 1 °C.

RESULTS AND DISCUSSION

The open-circuit potential of the Au electrode in the main solution containing cobalt(II)–glycine complex depends on solution pH and its values are not far from 0 V (*ca.* 0.05 V at pH 6 and –0.05 V at pH 11). At the anodic potential scan no appreciable current was observed in a wide potential interval of the Au electrode up to 0.8 V. The conclusion can be drawn that the cobalt(II)–glycine complex is not electrochemically active in anodic oxidation on a gold electrode.

The electrochemical response to various amines added to the main solution was different. The addition of ammonia, monoethanolamine, triethanolamine, Quadrol (*N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine), tris-hydroxymethylamine ethane to the Co(II)–glycine solution changed little the open-circuit potential of the Au electrode and no appreciable current was measured at the anodic potential scan in a wide range of potential values. Evidently, all these amines do not form electrochemically active cobalt(II) complexes or form too weak complexes and cannot compete with glycine for cobalt(II) ions.

Great changes in the electrochemical behaviour of the Au electrode were observed in the presence of diamines: ethylenediamine (*EN*), 1,2-propylenediamine (*PDA*), 1,3-propylenediamine (*TMDA*) – the open-circuit potential shifted to more negative values by 0.1–0.5 V (Figs. 1, 2) and the considerable

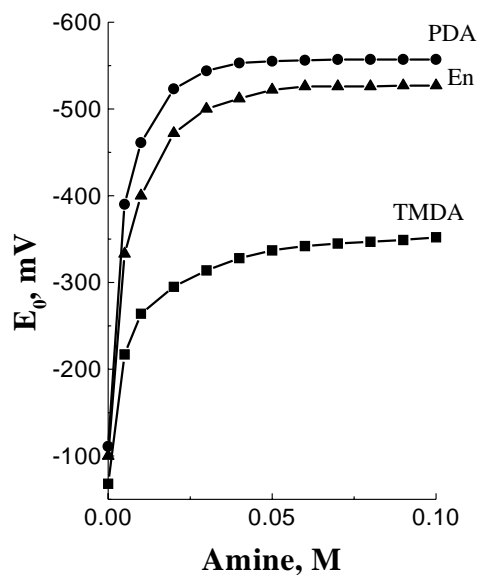


Fig. 1. Effect of amines on Au RDE open-circuit potential. Solution contained (M): CoSO₄ – 0.01; Gly – 0.05; pH 11

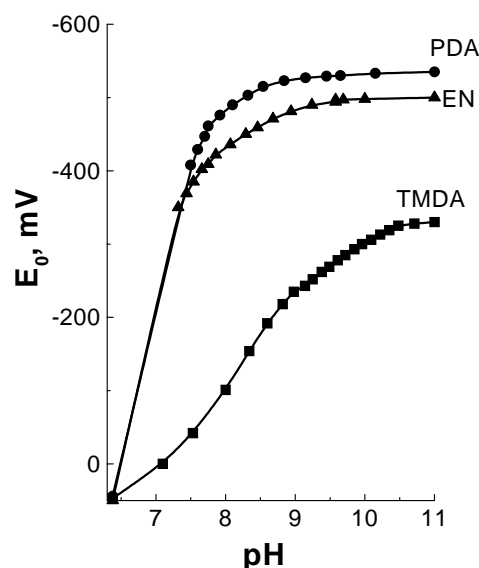


Fig. 2. Effect of solution pH on Au RDE open-circuit potential. Solution contained (M): CoSO₄ – 0.01; Gly – 0.05; KBr – 0.01; amine – 0.1

anodic currents appeared at positive potential scan (Figs. 3–5).

The open-circuit potential. The greatest effects on the electrode potential are observed for the amine concentrations up to 0.015 M (Fig. 1). At the amine concentrations over 0.05 M there were practically no changes in the electrode open-circuit potential. These facts are compatible with the formation of cobalt(II) complexes with the diamines added, these complexes being more stable than those with glycine, and electrochemically active. Indeed, the sta-

bility of the cobalt(II) complex with glycine CoGly_3^{2-} is characterized by the stability constant $\log\beta_3 = 10.76$, while the corresponding $\log\beta_3$ values for *EN* and *PDA* complexes are 14.9 and 14.7 (for *TMDA* there are no such data available).

The transformation of cobalt(II) complexes occurring in the solution upon addition of diamines in the general form can be described by the following equation (for *EN* addition, the equations of the same type are valid for the other two diamines):



where $n, m = 1-3$.

The open-circuit potential changes are largest for *PDA* with *EN* effects being close to it, and considerably lower for *TMDA* (Fig. 1). The open-circuit potential shift appears at solution pH *ca.* 6.5 and increases with rising the pH (Fig. 2); the most negative open-circuit potential values are reached at pH 9–10 with constant potential values at a higher solution alkalinity in the case of *PDA* and *EN*, and at pH values close to 11 in the case of *TMDA*.

The differences in open-circuit potential values for diamines under study apparently reflect differences in redox potentials of the cobalt(III) | cobalt(II) couple in the presence of those compounds; neither the influence of the difference in the kinetic activity of the corresponding cobalt complexes can be excluded. It is impossible to calculate the Co(III)/Co(II) redox potentials for *PDA* and *TMDA* solutions because of the lack of stability data for their cobalt complexes; from the open-circuit potential measurements it is possible to conclude that in the simplest case the redox potentials of Co(III) | Co(II) in *PDA* and *EN* solutions are similar (the difference in open-circuit potential values are 30–40 mV), while the redox potential in *TMDA* solutions is considerably more positive (by 150–180 mV). This is in agreement with the behaviour of the corresponding cobalt(II) complexes as reducing agents: the complexes with *TMDA* are not as strong reducing agents as the complexes with *PDA* and *EN* and are able to reduce to metallic state only Ag(I), in contrast to other two amines – their cobalt(II) complexes reduce copper(II) to metal also (this process takes place at more negative potentials compared to silver deposition) [14].

The observed great changes of the open-circuit potential of the Au electrode upon addition of diamines to alkaline cobalt(II) solutions (they reach 500–550 mV for *EN* and *PDA* and 350 mV for *TMDA*) can be used for determination of these amines, e.g. by potentiometric titration.

Anodic oxidation of Co(II). The introduction of diamines (*EN, PDA* or *TMDA*) into Co(II)–glycine

solution even at mM level, alongside with the shift of the open-circuit potential of the Au electrode to more negative values, gives rise to the anodic current in the potential range from –0.55 to 0.2 V, this potential range negative limit depending on the diamine, – the largest potential range is observed for *PDA* and the most narrow for *TMDA* (Figs. 3–5). The anodic current increases with an increase in amine concentration, but the current response is different for different amines – the highest currents are obtained in *EN* solutions (Fig. 4), slightly lower – in *PDA* solutions (Fig. 3),

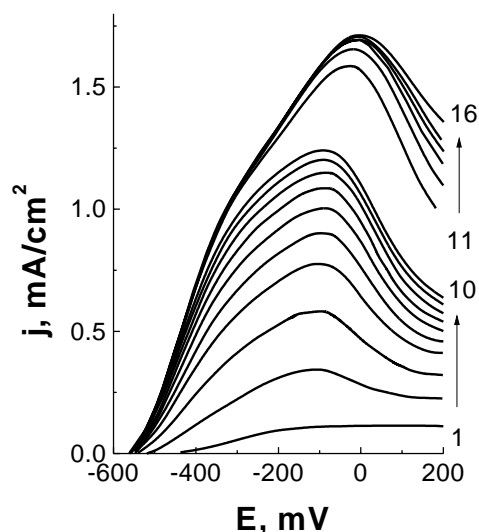


Fig. 3. Effect of propylenediamine on Co(II) oxidation on Au RDE. Solution contained (M): CoSO_4 – 0.01; *Gly* – 0.05; *PDA* – from 0.01 to 0.1 (curves 1–10) and 0.1 (curves 11–16); *KBr*: 11 – 0.001; 12 – 0.002; 13 – 0.003; 14 – 0.004; 15 – 0.007; 16 – 0.01; pH = 11

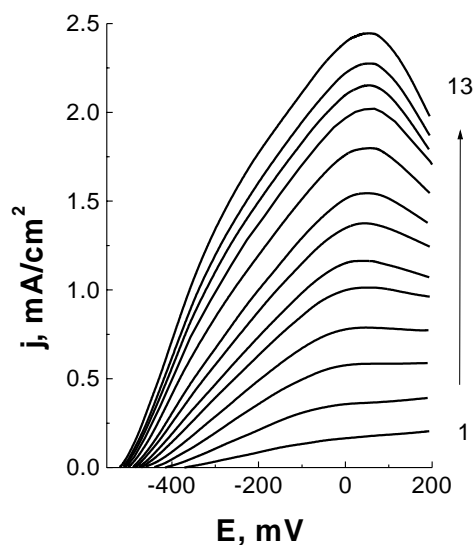


Fig. 4. Effect of ethylenediamine on Co(II) oxidation on Au RDE. Solution contained (M): CoSO_4 – 0.01; *Gly* – 0.05; *KBr* – 0.01; pH=11. *EN* (mM): 1 – 2.5; 2 – 5; 3 – 7.5; 4 – 10; 5 – 12.5; 6 – 15; 7 – 17.5; 8 – 20; 9 – 25; 10 – 30; 11 – 35; 12 – 40; 13 – 50

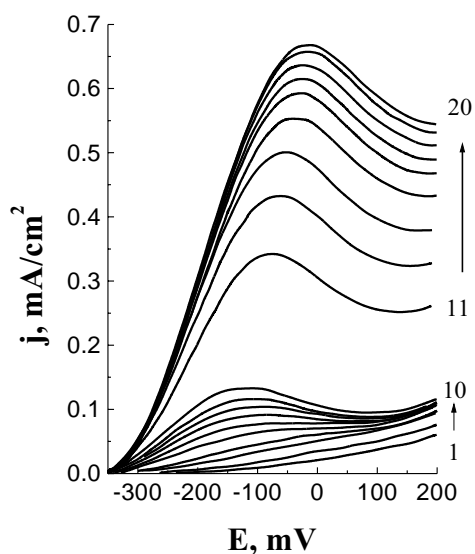


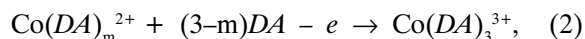
Fig. 5. TMDA and bromide effects on Co(II) oxidation on Au RDE.

Solution contained (M): CoSO_4 – 0.01; Gly – 0.05; TMDA – from 0.01 to 0.1 (curves 1–10) and 0.1 (curves 11–19); KBr – from 0.001 to 0.009 (curves 11–19); pH 11

and much lower – in the solutions of TMDA (Fig. 5). The shape of voltammograms depends on diamine concentration: the current maximum is observed in the potential range from -0.2 to 0 V at higher amine concentrations.

The observed amine effects on the anodic current are obviously related to Co(II) complex redistribution in the solution: cobalt(II)-glycine complexes transform into cobalt complexes with amines added (see eq. (1)). The more readily oxidizable, both thermodynamically and kinetically, Co(II)- EN , Co(II)- PDA and Co(II)- TMDA complex species are formed due to their higher stability as compared to Co(II)-glycine complexes.

Therefore, the anodic current observed should be a result of the anodic oxidation of cobalt(II) complexes with diamines:



where DA is diamine (EN , PDA or TMDA), $m = 1-3$.

Cobalt(II) complex species with a different number of coordinated ligand molecules are of different activity regarding oxidation process both by thermodynamic and kinetic reasons. An analysis of calculation and experimental data for Co(II)- EN solutions [7] allowed to presume participation of complexes with $m = 2,3$ in reaction (2).

The Co(II) oxidation current in the initial part of the dependence “anodic current–amine concentration” is linear (Fig. 6). At higher amine concen-

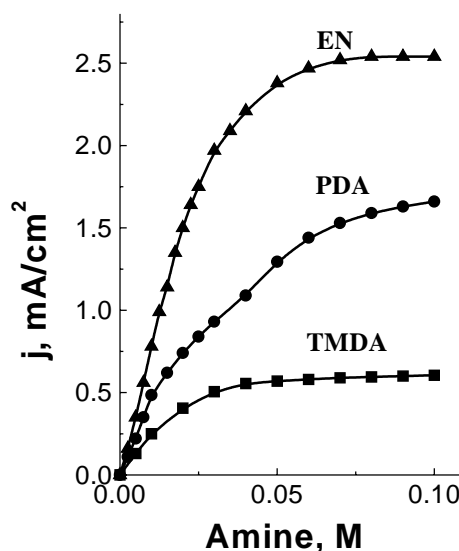


Fig. 6. Effect of amines on Co(II) oxidation current on Au RDE. Solution contained (M): CoSO_4 – 0.01; Gly – 0.05; KBr – 0.01. pH = 11

trations (over 0.05 M) the current reaches the constant values; it corresponds to a complete transformation of the Co(II)-glycine complexes into active complexes with diamines. The current response strongly depends on the diamine and changes in the sequence $\text{EN} > \text{PDA} > \text{TMDA}$ (Fig. 6).

The data of Figs. 3 and 5 demonstrate also the enhancing effect of the bromide ion: addition of only 1 mM KBr increases the anodic current considerably. An especially great current enhancement is observed for TMDA solutions, where 1 mM bromide addition leads to a more than twofold increase of the anodic current and the current rise continues at the further increase of bromide concentration – at 9 mM the enhancement is *ca.* fivefold (Fig. 5).

The current enhancement by bromide is a rather universal phenomenon in the systems under study: it is observed in the whole range of amine concentrations (Fig. 7), and in the entire solution pH interval where the anodic currents are measured (Fig. 8). Acceleration of cobalt(II) complex oxidation by bromide ion is most impressive for the system where Co(II) ligand is TMDA ; in that case, cobalt(II) oxidation in the absence of accelerator is rather slow, and the accelerator – bromide ion – apparently removes some important kinetic barriers. In the case of kinetically more easy cobalt(II) oxidation of PDA complexes, the oxidation process enhancement by bromide is more modest – only 20–30% (Fig. 3, curves 10–16). The effect of bromide ion on cobalt(II) oxidation in the presence of EN is lower than in TMDA solutions, but it is rather high (Fig. 8).

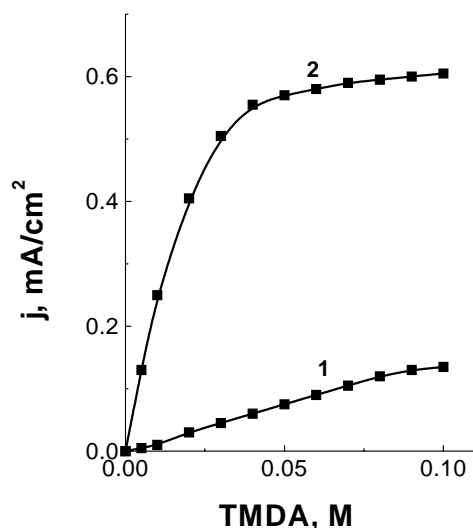


Fig. 7. Effect of *TMDA* on Co(II) oxidation current on Au RDE in the solution containing (M): $\text{CoSO}_4 - 0.01$; $\text{Gly} - 0.05$; pH 11. KBr (M): 1 - 0; 2 - 0.01

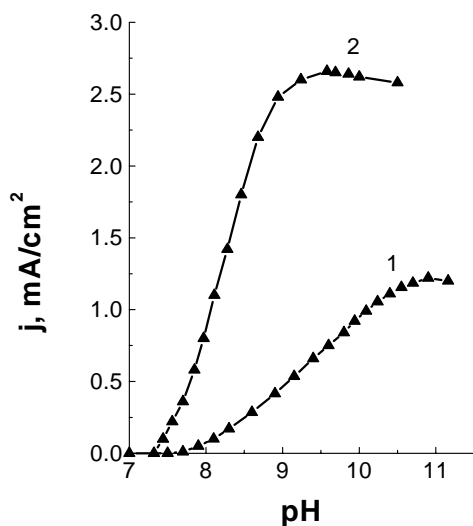


Fig. 8. Effect of solution pH on Co(II) oxidation on Au RDE in the presence of *EN*. Solution contained (M): $\text{CoSO}_4 - 0.01$; $\text{Gly} - 0.05$; *EN* - 0.1. KBr: 1 - 0; 2 - 0.01

The considerable enhancement of the anodic Co(II) oxidation current by bromide ion allows to achieve a higher sensitivity of our system to amines, and addition of KBr in mM levels was applied in most experiments.

The electrochemical response to diamines depends on solution pH: the anodic current appears at pH *ca.* 7.5–8 (Figs. 8, 9) and increases with increasing the pH values, reaching the maximum values at pH 9.5 for *EN* and 10–11 for *PDA* and *TMDA*. The pH effects are compatible with the diamine protonation and cobalt(II) complex equilibria in the solutions under study; the rise of the anodic current with solution pH is related to the increase of

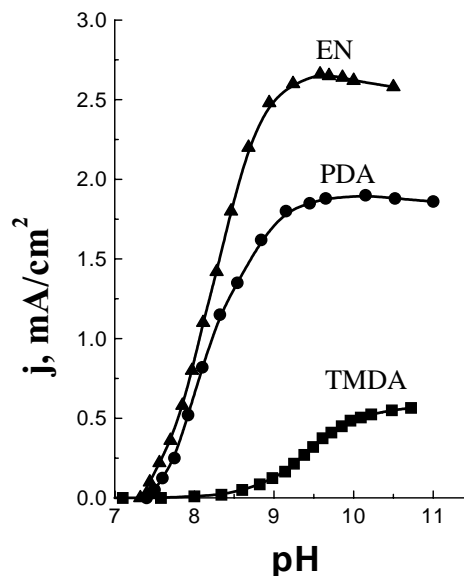


Fig. 9. Effect of solution pH on Co(II) oxidation on Au RDE in the presence of *TMDA*, *PDA* and *EN*. Solution contained (M): Co(II) - 0.01; $\text{Gly} - 0.05$; amine - 0.1; KBr - 0.01

the concentration of the free (unprotonated) amine and of the higher-coordinated cobalt(II) complex species. A detailed analysis of solution pH effects was done for the Co(II/III)–*EN* solutions [1,7].

CONCLUSIONS

1. The effects of ethylenediamine (*EN*), 1,2-propylenediamine (*PDA*), 1,3-propylenediamine (*TMDA*) on electrochemical parameters of the Au rotating disk electrode in alkaline Co(II)–glycine solutions: the shift of the open-circuit potential and enhancement of the anodic Co(II) oxidation current are a result of Co(II) complex transformation to more stable and electrochemically active Co(II)-diamine species.

2. The effect of diamines on the open-circuit potential changes in the line *PDA* > *EN* > *TMDA* and on the anodic current – in the sequence *EN* > *PDA* > *TMDA*.

3. The anodic oxidation of cobalt(II) complexes with diamine is accelerated by a bromide ion.

4. The effects of diamines on the electrochemical behaviour of Co(II) may have analytical applications.

Received 14 November 2002

Accepted 29 January 2003

References

1. A. Vaškelis and E. Norkus, *Electrochim. Acta* **44**, 3667 (1999).

2. A. Vaškelis and O. Diemontaitė, *Trans. Lithuanian Acad. Sci. B* **1**(116) 3, (1980).
3. A. Vaškelis, E. Norkus, A. Jagminienė and L. Tamašauskaitė-Tamašiūnaitė, *Galvanotechnik* **91** (2000) 2129, 3395.
4. A. Vaškelis, J. Jačiauskienė and E. Norkus, *Chemija* (Vilnius), N 3, 16 (1995).
5. A. Vaskelis, E. Norkus, J. Jačiauskienė and J. Reklaitis, *Galvanotechnik* **90**, 1556 (1999).
6. H. A. Laitinen and P. Kivalo, *J. Amer. Chem. Soc.* **75**, 2198 (1953).
7. A. Vaškelis, A. Jagminienė and L. Tamašauskaitė-Tamašiūnaitė, *J. Electroanal. Chem.* **521**, 137 (2002).
8. H. Bartelt and S. Landazury, *J. Electroanal. Chem.* **22**, 105 (1969).
9. H. Bartelt, *Electrochim. Acta* **16**, 307 (1971).
10. H. Baetelt and H. Skilandat, *J. Electroanal. Chem.* **23**, 407 (1969).
11. H. Bartelt and H. Skilandat, *J. Electroanal. Chem.* **24**, 207 (1970).
12. A. Vaškelis, G. Stalnionis and Z. Jusys, *J. Electroanal. Chem.* **465**, 142 (1999).
13. Z. Jusys and G. Stalnionis, *Electrochim. Acta* **45**, 3675 (2000).
14. A. Vaškelis, J. Jačiauskienė, A. Jagminienė and E. Norkus, *Solid State Sci.* **4**, 1299 (2002).

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ORGANINIŲ DIAMINŲ POVEIKIS Au SUKAMO DISKO ELEKTRODO ELGSENAI ŠARMINIUOSE KOBALTO(II) TIRPALUOSE

S a n t r a u k a

Ištirta įvairių aminų įtaka elektrocheminiams Au sukamo disko elektrodo parametrams šarminiuose Co(II)-glicino tirpaluose. Parodyta, kad diaminų: etilendiamino (EN), 1,2-propilendiamino (PDA), 1,3-propilendiamino (TMDA) mM eilės priedai pastumia atviros grandinės elektrodo potencialą 0,3–0,5 V į neigiamesnių verčių pusę ir labai padidina anodinės Co(II) oksidacijos srovę. Šie pokyčiai paaiškinami Co(II) kompleksų su glicinu transformacija į stabilesnius ir elektrochemiškai aktyvesnius Co(II)-diamino junginius. Diaminų poveikis elektrodo atviros grandinės potencialui mažėja eilėje: PDA > EN > TMDA, o anodinei srovei – eilėje: EN > PDA > TMDA. Kobalto(II) kompleksų su diaminais anodinę oksidaciją gerokai greitina bromido jonai, kurių veikimas yra kitokios prigimties, negu aminų, ir susijęs su procesais elektrodo paviršiuje, o ne tirpalo tūryje.

Gana plačiame diaminų koncentracijų intervale anodinės Co(II) oksidacijos srovė tiesiškai priklauso nuo amino koncentracijos; šis dėsningumas ir selektyvus diaminų poveikis Au potencialui sudaro galimybę panaudoti rastus efektus cheminėje analizėje.