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The electrochemical behaviour of cobalt(II)–amine complexes on Au electrode in alkaline solutions

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The effect of three amines on the electrochemical parameters of the Au rotating disk electrode in alkaline Co(II)–glycine solutions was studied. Addition of 1,2-cyclohexanediamine (*chn*), diethylenetriamine (*dien*) in mM levels shifts the open-circuit potential to more negative values by 0.5 V and enhances dramatically the anodic Co(II) oxidation current as a result of Co(II) complex transformation into more stable and electrochemically active Co(II)–amine species, while 1,4-butanediamine (*bn*) has no appreciable effect on the Au electrode. The effect of amines on the anodic current changes in the sequence *dien* > *chn* >> *bn.* The effects of amines on the electrochemical behaviour of Co(II) may have analytical applications.

Key words: cobalt(II) complexes, amines, 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 ligands selection, their concentration and the solution pH. Many cobalt(II) complexes with amines are rather strong reducing agents capable of reducing some metal ions to the metallic state [1] and therefore used in electroless plating systems for the deposition of metallic coatings: the cobalt(II)–ammonia complex is used for electroless silver deposition [1, 2], the cobalt(II)–ethylenediamine complex – for electroless copper deposition [1, 3], and cobalt(II)–propylenediamine complexes with different amine isomers – for both silver and copper plating [4].

The anodic oxidation of the reducing agent, a cobalt(II) complex with amine in our case, is one of the 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 the cobalt(II)–ammonia complex on a rotating Pt electrode was shown to be very slow, and the oxidation currents were only of the order of 1% of the expected value [5]. Recently [6] the ligand effect on the oxidation rate of Co(II) has been demonstrated: the oxidation rate of Co(II)–ethylenediamine complexes was shown to be higher than that of Co(II)–ammonia species under comparable conditions by a factor of 10–40.

The electrochemical oxidation of cobalt(II) complexes has not been studied in detail 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 to 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 [7–9] and Hg [10] electrodes, and the anodic oxidation of the Co(II)–ethylenediamine complex on Cu was investigated in relation to autocatalytic copper deposition [11].

In this work, in continuing the investigation of electrochemical response of Au electrode in alkaline Co(II)–glycine (Gly, aminoacetic acid) solution to ethylenediamine (*en*), 1,2-propylenediamine (*pn*), 1,3-propylenediamine (*tmda*) [12], the effect of three amines of a more complicated structure, 1,2-cyclohexanediamine (*chn*), 1,4-butanediamine

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(*bn*) and diethylenetriamine (*dien*), was studied. The Au–*Gly* system was selected for several reasons: 1) the gold electrode is more stable in amine solutions compared with silver and copper used in the recent investigations [6, 11], 2) Co(II) forms complexes with glycine, stable enough to prepare alkaline solutions in a wide pH range, 3) the anodic oxidation of the 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 cm^2 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, the 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 using a $Ag|AgCl|KCl_{sat}$ reference electrode, its values are given with respect to the standard hydrogen electrode.

The main solution contained (M): $CoSO_4$ – 0.01, *Gly* – 0.04; the 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

In the previous investigation [12] the cobalt(II)–glycine complex was shown to be electrochemically inactive in anodic oxidation on a gold electrode: no appreciable current was observed at anodic potential scan in a wide potential interval from *ca.* 0V (open-circuit value) up to 0.8 V for the main solution at pH 6–11.

The electrochemical response to the three amines studied was different. Addition of 1,4-butanediamine (*bn*) 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, *bn* does not form electrochemically active cobalt(II) complexes or forms too weak complexes and cannot compete with glycine for cobalt(II) ions.

A great electrochemical response of the Au electrode was observed in the presence of **1,2**-cyclohexanediamine (*chn*) and diethylenetriamine (*dien*): the open-circuit potential shifted to more negative values and considerable anodic currents appeared at the positive potential scan.

The open-circuit potential. The open-circuit potential shift to more negative values for *chn* and *dien* additions reaches 0.5 V, while the effect of *bn* is limited to 10–20 mV (Fig. 1). The greatest effects on electrode potential are observed for the *chn* and *dien* concentrations up to 0.015 M, and at the amine concentrations over 0.03 M there were practically no changes in the electrode potential (Fig. 1). The electrode potential changes are compatible with the formation of cobalt(II) complexes with *chn* and *dien* added, these complexes being more stable than those with glycine, and electrochemically active. Indeed, the stability 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 of *chn* complexes are 13.2 (for *cis*-isomer) and 15.2 (for *trans*-isomer), and $\log\beta_2$ of *dien* complex is 14.1 [13].

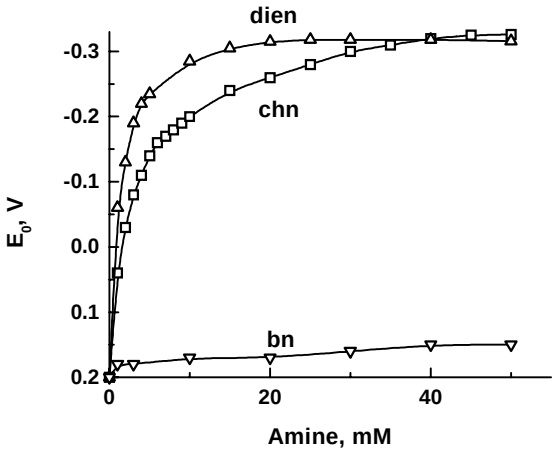

Fig. 1. Effect of amines on Au RDE open-circuit potential. Solution contained (M): $CoSO_4$ – 0.01; Gly – 0.05; pH 11

The transformation of cobalt(II) complexes occurring in the solution upon addition of *chn* and *dien* can be described by the following equations:

$$CoGly_n^{2+} + m chn \rightarrow Co(chn)_m^{2+} + nGly, \quad (1)$$

$$CoGly_n^{2+} + p dien \rightarrow Co(dien)_p^{2+} + nGly, \quad (2)$$

where n, m = 1 – 3, p = 1, 2.

The open-circuit potential shift appears at a solution pH *ca.* 6.0 and increases with rising the pH (Fig. 2); the most negative open-circuit potential values are reached at pH *ca.* 9 with almost constant potential values at a higher solution alkalinity. The

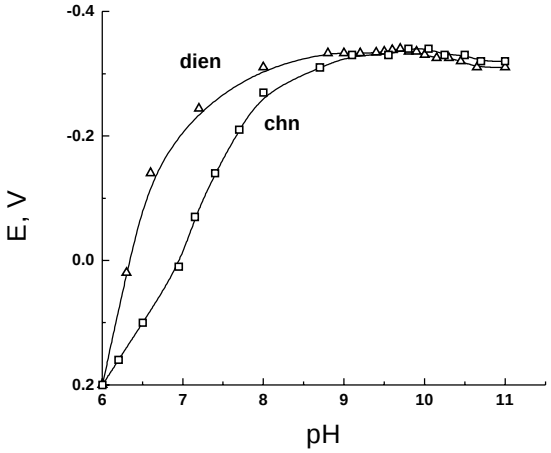

Fig. 2. Effect of solution pH on Au RDE open-circuit potential. Solution contained (M): $CoSO_4$ – 0.01; Gly – 0.05; amine – 0.1

dependence "open-circuit potential – pH" is practically the same for both *chn* and *dien,* but at lower pH values the potential is considerably more negative in *dien* solutions; *e.g.*, at pH 7 the difference between the Au electrode potential in the presence of *chn* and *dien* is more than 0.2 V (Fig. 2). Differences in open-circuit potential values for these two amines are observed also at their concentrations lower than 0.04 M (Fig. 1), while at higher concentrations the potentials are the same.

The differences in open-circuit potentials apparently reflect differences in redox potentials of the cobalt(III)/cobalt(II) couple in the presence of various amines; the influence of the difference in kinetic activity of the corresponding cobalt species is also possible. It is impossible to calculate the Co(III)/Co(II) redox potentials for *chn* and *dien* solutions because of the lack of stability data for their cobalt(III) 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 *chn* and *dien* solutions are similar. Comparison of these data with those of our previous work [12] shows a similarity of the redox potentials of Co(III)/Co(II) in the presence of four amines – *en, pn, chn* and *dien*.

The anodic oxidation of Co(II). The introduction of *chn* or *dien* into Co(II)–glycine solution even at mM level, alongside with the shift of the open-circuit potential of Au electrode to more negative values, gives rise to the anodic current in a wide potential range beginning from *ca.* –0.3 V, the negative limit of this potential range depending on the amine and solution pH. The shape of voltammograms depends on the amine concentration: the current maximum is observed in the potential range from 0 to 0.2 V at the higher concentrations – the typical curves (the initial parts of voltammograms) for *dien* additions are shown in Fig. 3. The entire voltammogram of a rotating Au electrode in this and similar cases of alkaline Co(II)–amine solutions contains a current minimum at more positive potential values and a second current maximum at 0.6–0.7 V; a more detailed study of Co(II) anodic oxidation on a rotating Au electrode for ammonia-*en* solutions is presented in [14]. In this work, only the initial part of the voltammogram was analysed – the maximum anodic currents at 0–0.1 V were measured.

The anodic current increases with an increase in amine concentration (Fig. 3), but the current response is different for different amines: the highest currents are obtained in *dien* solutions, and considerably lower in *chn* solutions (Fig. 4). In *bn* solutions only residual currents are observed, and this is in agreement with the absence of Au potential response to *bn* additions.

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) and (2)). More readily oxidizable, both thermodynamically and kinetically, Co(II)–*dien* and Co(II)–*chn* complex species are formed due to their higher stability compared to Co(II)–glycine complexes.

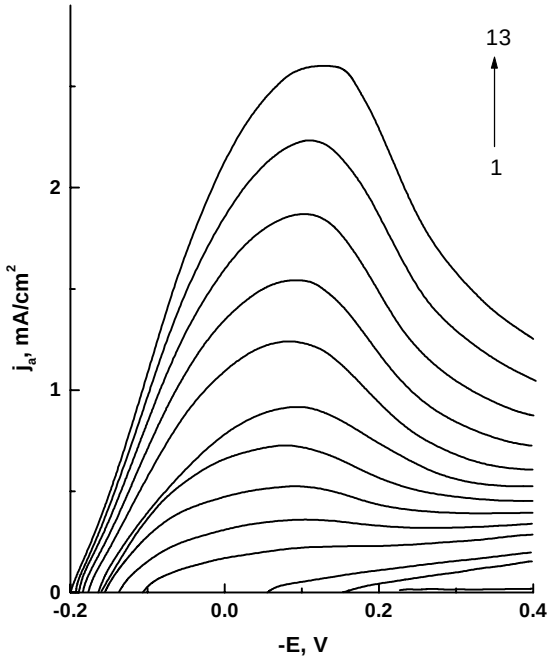

Fig. 3. Effect of diethylenetriamine on Co(II) oxidation on Au RDE. Solution contained (M): $CoSO_4$ – 0.01; Gly – 0.05; *dien* (mM): *1* – 0, *2* – 2, *3* – 4, *4* – 6, *5* – 8, *6* – 10, *7* – 12, *8* – 15, *9* – 18, *10* – 21, *11* – 24, *12* – 27, *13* – 30; pH 11

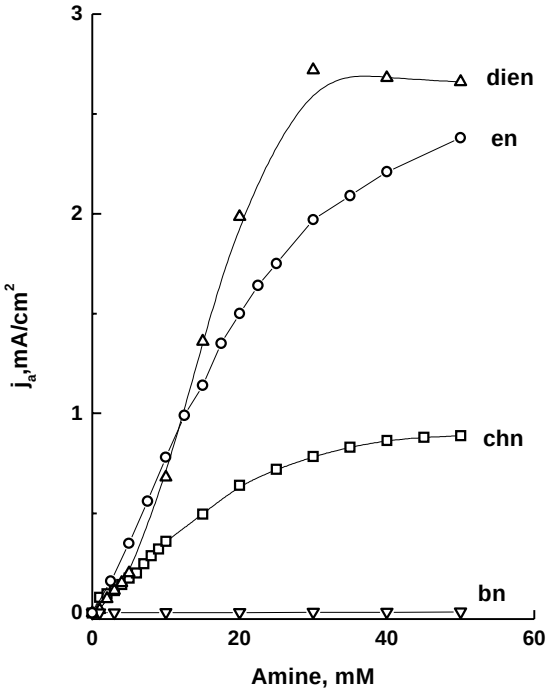

Fig. 4. Effect of amines on Co(II) oxidation current on Au RDE. Solution contained (M): $CoSO_4$ – 0.01; *Gly* – 0.05; pH 11

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

$$Co(dien)_m^{2+} + (2\text{-m})dien - e \rightarrow Co(dien)_2^{3+}, \quad (3)$$

$$Co(chn)_n^{2+} + (3\text{-n})chn - e \rightarrow Co(chn)_3^{3+}, \quad (4)$$

where m = 1, 2 and n = 1–3.

Cobalt(II) complex species with a different number of coordinated ligand molecules are of different activity regarding the oxidation process both for the thermodynamic and kinetic reasons; the higher coordinated Co(II) complexes are stronger and more active reducing agents. An analysis of calculation and experimental data for the Co(II)-*en* solutions [3, 6] allowed to presume participation of complexes with n = 2 and 3 in the oxidation reaction similar to (4).

The Co(II) oxidation current in the initial part of the dependence "anodic current – amine concentration" is linear (Fig. 4). At higher amine concentrations (over 0.03 M for *chn* and *dien*) the current reaches constant values; it corresponds to a complete transformation of the Co(II)–glycine complexes into active complexes with the amines added. The current response strongly depends on the amine and changes in the sequence *dien* > *en* > *chn* >> *bn* (Fig. 4). The effect of the earlier studied amine, *en*, is presented in Fig. 4; ethylenediamine was the most active enhancing agent among compounds studied in [12], and a comparison with amines used in this work indicates *dien* as the most effective cobalt(II) ligand regarding to Co(II) oxidation in alkaline solutions (pH 11).

The electrochemical response to amines depends on solution pH: the anodic current appears at pH 6.2–7 (Fig. 5) and increases with increasing the pH values up to the maximum at pH 9.5–10 for both *dien* and *chn*. The additions of *dien* are effective at a low solution pH where other amines studied have no influence on Co(II) oxidation (Fig. 5).

The pH effects on Co(II) oxidation are compatible with the amine protonation and cobalt(II) com-

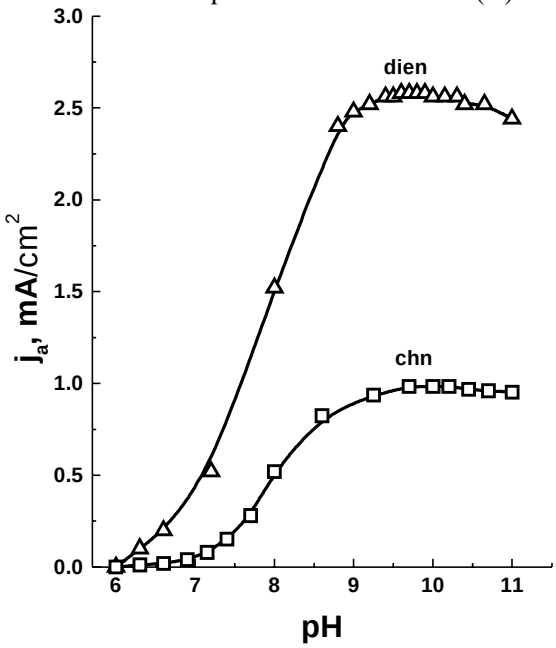

Fig. 5. Effect of solution pH on Co(II) oxidation on Au RDE in the presence of amines.
Solution contained (M): $CoSO_4$ – 0.01; *Gly* – 0.05; amine – 0.1.

plex equilibria in the solutions under study; the rise of the anodic current with solution pH is related to the increase of 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, 6].

The effects of amines on the electrochemical behaviour of Co(II) (the linear dependence of the anodic current on amine concentration in a wide concentration range and the great changes of electrode potential) may have analytical applications.

CONCLUSIONS

1. The effects of 1,2-cyclohexanediamine (*chn*), 1,4-butanediamine (*bn*), diethylenetriamine (*dien*) on the 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)–amine species.

2. The effect of amines on the open-circuit potential changes in the line *dien ~ chn >> bn* and on the anodic current in the sequence *dien > chn >> >> bn.*

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KOBALTO(II) KOMPLEKSŲ SU AMINAIS ELEKTROCHEMINĖ ELGSENA ANT AU ELEKTRODO ŠARMINIUOSE TIRPALUOSE

S a n t r a u k a

Ištirta trijų aminų įtaka elektrocheminiams Au sukamo disko elektrodo parametrams šarminiuose Co(II)-glicino tirpaluose. Parodyta, kad dietilentriamino (*dien*) ir 1,2-cikloheksandiamino (*chn*) mM eilės priedai pastumia atviros grandinės elektrodo potencialą 0,5 V į neigiamesnių verčių pusę ir labai padidina anodinės Co(II) oksidacijos srovę, o 1,4-butandiaminas (*bn*) neveikia Au elektrodo. Aminų įtaka paaiškinama Co(II) kompleksų su glicinu transformacija į stabilesnius ir elektrochemiškai aktyvesnius Co(II)-amino junginius. Aminų poveikis anodinei srovei mažėja eilėje: *dien > > chn >> bn*.

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