



*J. Serb. Chem. Soc.* 80 (12) 1515–1527 (2015)  
JSCS–4816

## Electrochemistry of cobalt ethylenediamine complexes at high pH

SNEŽANA M. MIULOVIĆ\*, VLADIMIR M. NIKOLIĆ, PETAR Z. LAUŠEVIĆ, DANKA  
D. AČIMOVIĆ, GVOZDEN S. TASIĆ and MILICA P. MARČETA KANINSKI

*Institute of Nuclear Sciences – Vinča, Laboratory of Physical Chemistry, University of  
Belgrade, 11000 Belgrade, Mike Alasa 12–14, Serbia*

(Received 27 March, revised 23 June, accepted 30 June 2015)

**Abstract:** The electrochemical behavior of cobalt ethylenediamine complexes (Co(en)), at pH 12 was investigated by cyclic voltammetry (CV), the potentiostatic pulse technique and polarization curve measurements at stationary and rotating glassy carbon (GC) electrodes. It was shown that sixteen different species could be formed in a solution containing Co(en)<sub>3</sub>, with the most stable one at all pH values being [Co(en)<sub>3</sub>]<sup>3+</sup>. The reduction of [Co(en)<sub>3</sub>]<sup>3+</sup> into [Co(en)<sub>3</sub>]<sup>2+</sup> was shown to be a totally irreversible, one-electron exchange reaction. Further reduction of [Co(en)<sub>3</sub>]<sup>2+</sup> was found to be a complex process leading to cobalt deposition at potentials more negative than –1.45 V vs. SCE. The process of [Co(en)<sub>3</sub>]<sup>2+</sup> oxidation was also complex and most probably coupled with chemical reactions.

**Keywords:** distribution of Co(en)<sub>3</sub>-based complexes; irreversible reduction of [Co(en)<sub>3</sub>]<sup>3+</sup>/[Co(en)<sub>3</sub>]<sup>2+</sup>; reduction of [Co(en)<sub>3</sub>]<sup>2+</sup> to Co.

### INTRODUCTION

The Co(en)<sub>3</sub>Cl<sub>3</sub> was first described and isolated as yellow–gold needle-like crystals by Werner.<sup>1</sup> This was important in the history of coordination chemistry due to its stability and stereochemistry. The cation [Co(en)<sub>3</sub>]<sup>3+</sup> has an octahedral structure with Co–N distance in the range 0.1947–0.1981 nm, with N–Co–N angles of 85° within the chelate rings and 90° between the N atoms on adjacent rings.<sup>2</sup> The acid–base, *cis–trans*, and complex equilibria in the cobalt(III)(en) system was investigated by Bjerrum and Rasmussen.<sup>3</sup> It was shown that in an inert cobalt(III)(en) system, the first hydrolysis constant of the tris(en) ion could be estimated by analytical methods. In the system of diaquobis(en) cobalt(III) ions, *cis–trans* equilibria are established spontaneously. All acidic dissociation and *cis–trans* equilibrium constants were determined. In addition, it was shown

\* Corresponding author. E-mail: snezana.miulovic@vinca.rs  
doi: 10.2298/JSC150327079M

that the partial formation constants could be estimated by glass electrode and spectrophotometric measurements.<sup>3</sup>

It was shown that  $[\text{Co}(\text{en})_3]^{3+}$  became reversibly reduced to the divalent state at a dropping mercury electrode in an excess of (en), while irreversible behavior was detected in the absence of the complexing agent.<sup>4,5</sup> Using the cyclic voltammetry (CV) technique, the formal potential for the reduction of  $[\text{Co}(\text{en})_3]^{3+}$  into  $[\text{Co}(\text{en})_3]^{2+}$  in an aqueous solution of  $0.1 \text{ mol dm}^{-3}$   $\text{LiClO}_4$  was found to be about  $-0.46 \text{ V vs. SCE}$ .<sup>6</sup> It was stated by the same authors that, although  $[\text{Co}(\text{en})_3]^{2+}$  is labile, a small excess ( $0.002\text{--}0.01 \text{ mol dm}^{-3}$ ) of (en) was required in order to prevent dissociation of  $[\text{Co}(\text{en})_3]^{2+}$ .<sup>7</sup> At the same time, the authors claimed that equal cathodic and anodic peak currents were obtained at the CV, with the separation of the peak potentials varying between 60 and 90 mV in the investigated solution.<sup>7</sup> In many electrochemical investigations, the redox reaction  $[\text{Co}(\text{en})_3]^{3+}/[\text{Co}(\text{en})_3]^{2+}$  was examined in order to determine the influence of the outer-sphere effects on the reduction process.<sup>8,9</sup>

One of the important applications of  $\text{Co}(\text{en})_3\text{Cl}_3$  is its use as an ionic activator for the *in situ* activation of the hydrogen evolution reaction (HER) in combination with molybdate ions.<sup>10–12</sup> The addition of small concentrations ( $0.001\text{--}0.01 \text{ mol dm}^{-3}$ ) of ionic activators reduced the overvoltage for HER and the energy needs per mass unit of hydrogen produced.<sup>13</sup> A possible mechanism for the *in situ* activation of the HER has not yet been offered. It is supposed that both metals deposit on the cathode surface producing large surface area of active centers.<sup>14–17</sup> At the same time the catalytic activity of (en), which is present in the electrolyte after decomposition of cobalt complex, has been discussed in the light of Rowland's effect.<sup>18,19</sup> It is assumed that (en) cleans the cathode surface by removing the oxide film and preparing it for deposition of Co and Mo. Since it is found that both metals are present in a very rough deposit formed during the process of *in situ* activation,<sup>14,15</sup> the question arises what is the current efficiency for the deposition of such coatings and how often these chemicals should be added to the electrolyte in order to maintain the same catalytic activity for the HER.

In this work, an attempt was made to better understand the process of  $[\text{Co}(\text{en})_3]^{3+}$  reduction to metallic cobalt in the presence of an excess of (en) at high pH.

#### EXPERIMENTAL

All experiments were performed with extra pure UV water (Smart2PureUV, TKA) and p.a. chemicals in a standard electrochemical cell (EuroCell, Gamry Instruments). The working electrode was a glassy carbon (GC) rotating disc electrode (RDE, Gamry Instruments). A saturated calomel electrode (SCE), connected to the working electrode by means of a Luggin capillary, was used as the reference electrode, while a Pt wire was the counter electrode. Rotating experiments were performed with an RDE710 rotating system (Gamry Instruments). Before the experiments, the GC electrode was polished on polishing cloths impregnated with

polishing alumina (0.05  $\mu\text{m}$ ), kept in an ultrasonic bath for 10 min and rinsed with UV-purified water. CV, pulse experiments and polarization measurements were performed with a Reference 600 potentiostat using PHE 200 software (Gamry Instruments).

The distribution of the  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  complexes in the investigated solutions was obtained with the commercial software HySS2009 (Protonic Software).

## RESULTS AND DISCUSSION

### *Distribution of different cobalt complexes*

In the solution containing excess of ethylenediamine (en) of 0.2 mol  $\text{dm}^{-3}$  and 0.01 mol  $\text{dm}^{-3}$   $\text{Co}^{2+}$  (as  $\text{CoCl}_2$ ), the following species could be formed:<sup>20</sup> (en), (en)H, (en)H<sub>2</sub>,  $\text{Co}^{2+}$ ,  $[\text{Co}(\text{OH})]^+$ ,  $[\text{Co}(\text{OH})_2]$ ,  $[\text{Co}(\text{OH})_3]^-$ ,  $[\text{Co}_4(\text{OH})_4]^{4+}$ ,  $[\text{Co}(\text{en})]^{2+}$ ,  $[\text{Co}(\text{en})_2]^{2+}$  and  $[\text{Co}(\text{en})_3]^{2+}$ . In the same solution of ethylenediamine and 0.01 mol  $\text{dm}^{-3}$   $\text{Co}^{3+}$  (as  $\text{Co}(\text{en})_3\text{Cl}_3$ ), among (en), (en)H and (en)H<sub>2</sub>, additional species,  $\text{Co}^{3+}$ ,  $[\text{Co}(\text{OH})]^{2+}$ ,  $[\text{Co}(\text{en})]^{3+}$ ,  $[\text{Co}(\text{en})_2]^{3+}$  and  $[\text{Co}(\text{en})_3]^{3+}$  could be formed. Hence, if both  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  are present in 0.2 mol  $\text{dm}^{-3}$  (en), sixteen different species could be formed. Taking into account the stability constants for all the above-mentioned species, it is possible to obtain distributions of all species as a function of *pH* (using HySS 2009 software).<sup>20</sup> The results of such an analysis are presented in Fig. 1: a) only  $\text{Co}^{2+}$  is present in the solution, b) only  $\text{Co}^{3+}$  is present in the solution or c) both  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  are present in the solution. As could be seen in Fig. 1a, at *pH* values higher than 10, only the  $[\text{Co}(\text{en})_3]^{2+}$  complex is present in the solution. Figure 1b shows that the  $[\text{Co}(\text{en})_3]^{3+}$  complex is dominant at all *pH* values with its concentration being 0.01 mol  $\text{dm}^{-3}$  (concentration of (en) is also independent of *pH*), while Fig. 1c confirms that at *pH* > 10  $[\text{Co}(\text{en})_3]^{2+}$  and  $[\text{Co}(\text{en})_3]^{3+}$  complexes dominate in 0.2 mol  $\text{dm}^{-3}$  (en). Hence, in an excess of (en) and at *pH* 12 (Fig. 1c), it should be possible to investigate the oxidation of  $[\text{Co}(\text{en})_3]^{2+}$  to  $[\text{Co}(\text{en})_3]^{3+}$ , as well as the reduction of  $[\text{Co}(\text{en})_3]^{3+}$  to  $[\text{Co}(\text{en})_3]^{2+}$ .

### *Electrochemical behavior of $\text{Co}^{3+}$ in 0.2 mol $\text{dm}^{-3}$ ethylenediamine*

The CVs recorded on a GC electrode at a sweep rate of 100  $\text{mV s}^{-1}$  in (a) a solution containing 0.01 mol  $\text{dm}^{-3}$   $\text{Co}(\text{en})_3\text{Cl}_3$  + 0.2 mol  $\text{dm}^{-3}$  (en) and (b) 0.001 mol  $\text{dm}^{-3}$   $\text{Co}(\text{en})_3\text{Cl}_3$  + 0.2 mol  $\text{dm}^{-3}$  (en) are shown in Fig. 2. The CV's were recorded at a stationary (0 r.p.m.) and rotating electrodes (1000 r.p.m. and 2000 r.p.m.). Identical behavior was observed in both solutions, except that the current densities were one order of magnitude lower in the solution containing the lower concentration of cobalt ions (Fig. 2b). The starting potential was set at  $-0.4$  V and electrode was cycled first towards anodic potentials (up to 0.5 V). As expected, no oxidation peak was recorded during the first sweep, since only the  $[\text{Co}(\text{en})_3]^{3+}$  complex was present in the solution. During the reverse sweep down to  $-1.0$  V, well defined reduction peaks at about  $-0.7$  V (a) and  $-0.6$  V (b) were obtained at the stationary electrode. In both cases, reduction of  $[\text{Co}(\text{en})_3]^{3+}$  to

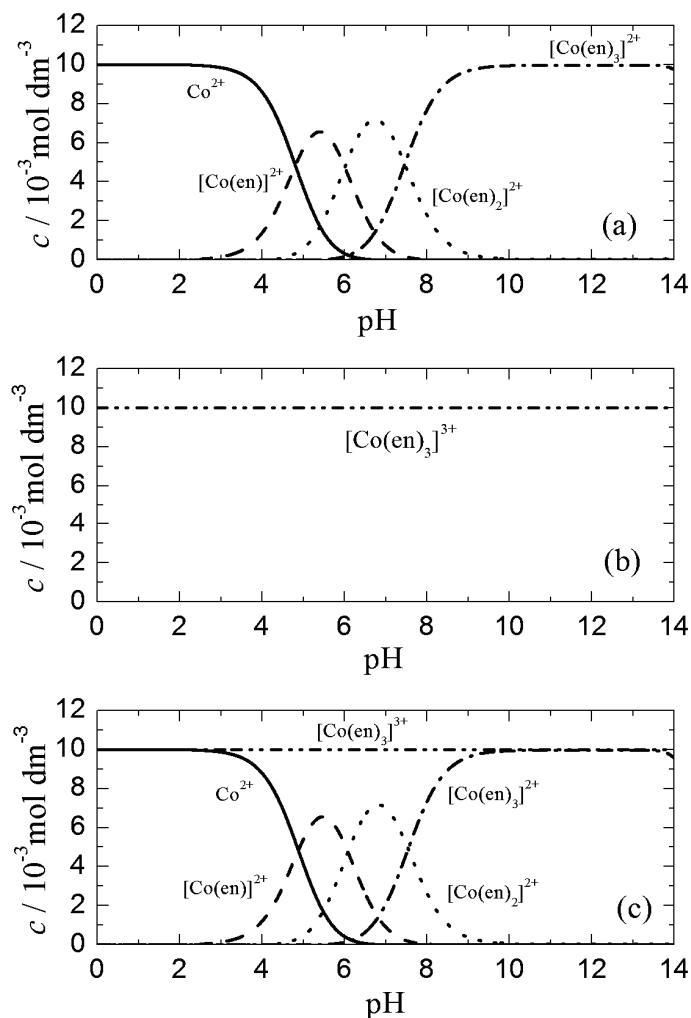


Fig. 1. Distribution of different cobalt complexes in the solution  $0.2 \text{ mol dm}^{-3}$  ethylenediamine, pH 12: (a)  $0.01 \text{ mol dm}^{-3} \text{ Co}^{2+}$ ; (b)  $0.01 \text{ mol dm}^{-3} \text{ Co}^{3+}$ ; (c)  $0.01 \text{ mol dm}^{-3} \text{ Co}^{2+} + 0.01 \text{ mol dm}^{-3} \text{ Co}^{3+}$ .

$[\text{Co(en)}_3]^{2+}$  commenced at about  $-0.45 \text{ V}$ , being defined by cathodic peaks at the stationary electrode (0 rpm) and current density plateaus at the rotating electrode (1000 and 2000 rpm). The oxidation of  $[\text{Co(en)}_3]^{2+}$  to  $[\text{Co(en)}_3]^{3+}$  was evidenced only at the stationary electrode after the formation of the  $[\text{Co(en)}_3]^{2+}$  complex during the first sweep that remained in the vicinity of the electrode surface, being characterized by a broad anodic peak for all subsequent sweeps ( $2^{\text{nd}}-n^{\text{th}}$ ). At the rotating electrode, this reaction did not occur, since all the  $[\text{Co(en)}_3]^{2+}$  complexes formed during the reduction of  $[\text{Co(en)}_3]^{3+}$  were transfer-

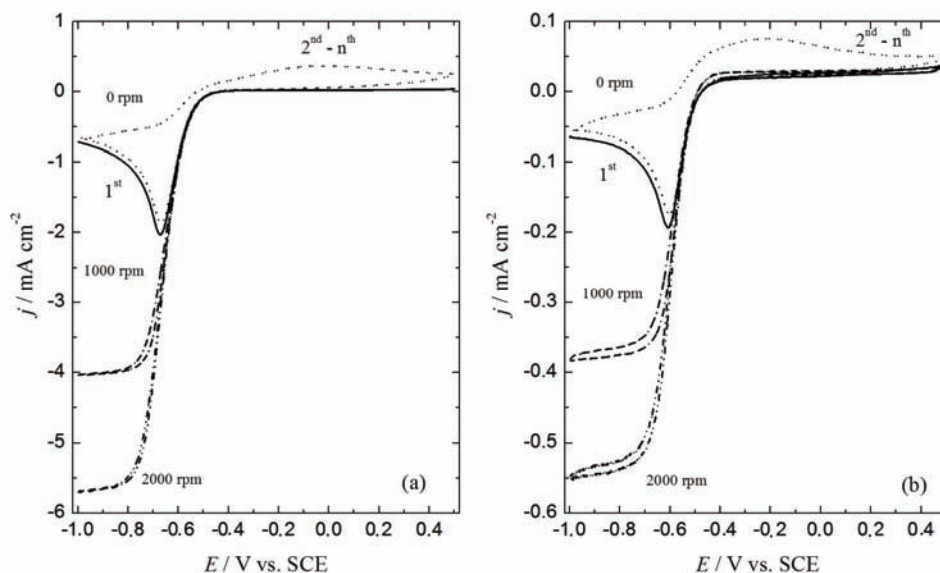


Fig. 2. CVs recorded at  $\nu = 100 \text{ mV s}^{-1}$  at different rotation speeds (marked in the figure) in (a) solutions containing  $0.01 \text{ mol dm}^{-3} \text{ Co(en)}_3\text{Cl}_3 + 0.2 \text{ mol dm}^{-3} \text{ (en)}$  and (b)  $0.001 \text{ mol dm}^{-3} \text{ Co(en)}_3\text{Cl}_3 + 0.2 \text{ mol dm}^{-3} \text{ (en)}$ .

red from the electrode surface to the bulk electrolyte during electrode rotation. Hence, it could be concluded that only a certain amount of  $[\text{Co(en)}_3]^{2+}$ , *i.e.*, that which remained in the vicinity of the surface of the stationary electrode after reduction of  $[\text{Co(en)}_3]^{3+}$  to  $[\text{Co(en)}_3]^{2+}$ , could be oxidized to  $[\text{Co(en)}_3]^{3+}$  during the anodic sweep. Taking into account that the whole amount of cobalt in both solutions is in the form of  $[\text{Co(en)}_3]^{3+}$  complex (Fig. 1b), such behavior could be expected. This finding is in accordance with certain literature data,<sup>5</sup> while some authors claimed that the reduction/oxidation process is reversible with differences in the peak potentials varying from 60 to 90 mV.<sup>7</sup>

Polarization curves for reduction of  $[\text{Co(en)}_3]^{3+}$  to  $[\text{Co(en)}_3]^{2+}$ , recorded at a sweep rate of  $5 \text{ mV s}^{-1}$  at different rotation speeds are presented in Fig. 3a. As can be seen, well-defined diffusion limiting current density plateaus were obtained at potentials more negative than  $-0.7 \text{ V}$  with the shape of the  $j$ - $E$  curves being typical for a totally irreversible reaction. The  $j^{-1}$  vs.  $\omega^{-1/2}$  dependences, obtained by analysis of the polarization curves presented in Fig. 2a, are plotted in Fig. 3b for different potentials and the  $j^{-1}$  vs.  $\omega^{-1/2}$  dependence recorded for  $E = -0.80 \text{ V}$  was the linear one passing through zero. The diffusion coefficient calculated from the slope of this dependence (using the Koutecky–Levich Equation for a one-electron exchange)<sup>21</sup> amounted to  $1.60 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . As expected, in the region of mixed activation–diffusion control of the reduction process (potential range from  $-0.45$  to  $-0.65 \text{ V}$ ), the values of intercepts on the  $j^{-1}$  axes

increased with decreasing cathodic potential, producing higher values of the kinetic current density ( $j_k$ ) and accordingly higher values of the rate constants ( $k_f(E)$ ) at a given potential, since:<sup>21</sup>

$$j_k = Fk_f(E)c_0 \quad (1)$$

where  $c_0$  is the bulk concentration of the  $[\text{Co}(\text{en})_3]^{3+}$  complex. Corresponding values of the rate constants were  $E = -0.60$  V,  $k_f(E) = 0.0497$  cm s<sup>-1</sup>;  $E = -0.55$  V,  $k_f(E) = 0.0122$  cm s<sup>-1</sup> and  $E = -0.50$  V,  $k_f(E) = 0.0022$  cm s<sup>-1</sup>.

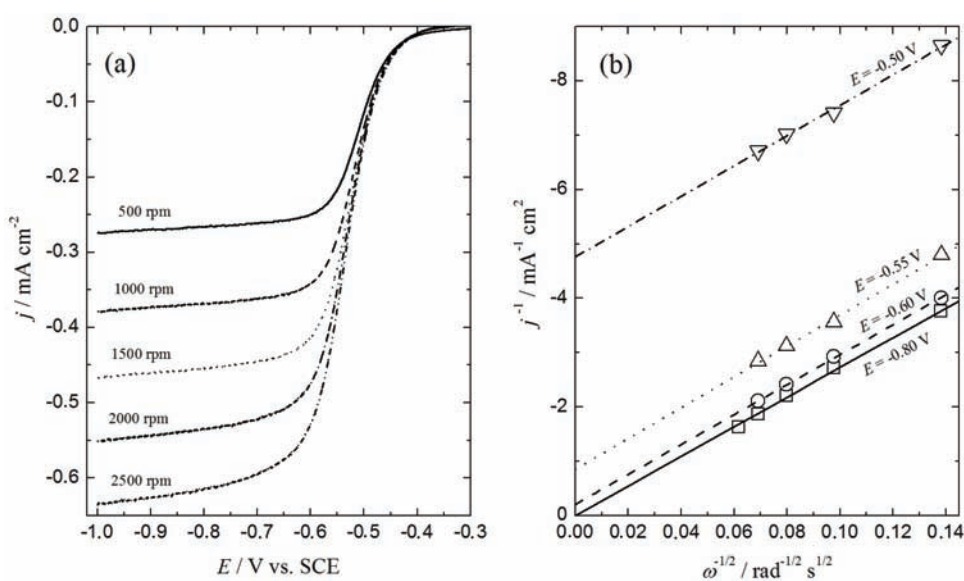


Fig. 3. a) Polarization curves for the reduction of  $[\text{Co}(\text{en})_3]^{3+}$  to  $[\text{Co}(\text{en})_3]^{2+}$ , recorded at  $\nu = 5$  mV s<sup>-1</sup> at different rotation speeds (marked in the figure) in the solution: 0.001 mol dm<sup>-3</sup>  $\text{Co}(\text{en})_3\text{Cl}_3 + 0.2$  mol dm<sup>-3</sup> (en). b) The  $j^{-1}$  vs.  $\omega^{1/2}$  dependences obtained by analysis of the polarization curves presented in (a) for different potentials (marked in the figure).

Similar results were obtained for 0.01 mol dm<sup>-3</sup>  $\text{Co}(\text{en})_3\text{Cl}_3 + 0.2$  mol dm<sup>-3</sup> (en) solution at pH 12. In order to determine the next step in the process of  $[\text{Co}(\text{en})_3]^{3+}$  reduction, the cathodic potential limit was adjusted to  $-1.5$  V and the CV with  $\nu = 20$  mV s<sup>-1</sup> was recorded (Fig. 4a). As can be seen, a stable cathodic current density was detected at potentials more negative than  $-1.0$  V, while it suddenly increases at about  $-1.47$  V. This current density increase reflects simultaneous hydrogen evolution and deposition of cobalt. During the reverse sweep, three anodic peaks appeared on the CV at about  $-0.85$  V ( $\text{I}_a$ ),  $-0.70$  V ( $\text{II}_a$ ) and  $-0.45$  V ( $\text{III}_a$ ), respectively. The first two peaks ( $\text{I}_a$  and  $\text{II}_a$ ) correspond most likely to the dissolution of deposited Co and formation of the  $[\text{Co}(\text{en})_3]^{2+}$  complex, while the third one ( $\text{III}_a$ ) could be ascribed to further oxidation of  $[\text{Co}(\text{en})_3]^{2+}$  to  $[\text{Co}(\text{en})_3]^{3+}$ . Hence, before the deposition of cobalt from this solution occurs,

the reduction of  $[\text{Co}(\text{en})_3]^{3+}$  into  $[\text{Co}(\text{en})_3]^{2+}$  takes place ( $I_c$ ) at potentials about 1.00 V more positive, indicating that the current efficiency for the deposition process (which occurs with simultaneous hydrogen evolution) is very low. At the higher concentration of  $\text{Co}(\text{en})_3\text{Cl}_3$  of  $0.1 \text{ mol dm}^{-3}$ , two more peaks could be detected on the CV recorded at a sweep rate of  $2 \text{ mV s}^{-1}$  (Fig. 4b). The peak (wave)  $II_c$  indicates the commencement of cobalt deposition at about  $-1.25 \text{ V}$ , while peak  $IV_a$  corresponds to the oxidation of deposited cobalt that could not be quantitatively dissolved from the GC surface and its presence could be detected on the GC surface after the experiment.<sup>22</sup>

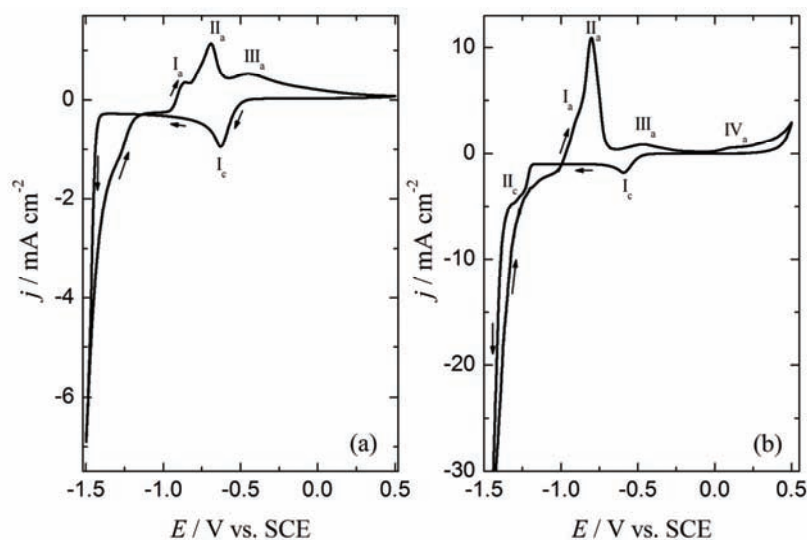


Fig. 4. a) CV with  $\nu = 20 \text{ mV s}^{-1}$  recorded in the solution  $0.01 \text{ mol dm}^{-3} \text{Co}(\text{en})_3\text{Cl}_3 + 0.2 \text{ mol dm}^{-3} (\text{en})$ . b) CV with  $\nu = 2 \text{ mV s}^{-1}$  recorded in the solution  $0.1 \text{ mol dm}^{-3} \text{Co}(\text{en})_3\text{Cl}_3 + 0.2 \text{ mol dm}^{-3} (\text{en})$ , both obtained at a stationary electrode at pH 12.

#### *Electrochemical behavior of $\text{Co}^{2+}$ in $0.2 \text{ mol dm}^{-3}$ ethylenediamine*

The CVs recorded on the GC electrode at a sweep rate of  $100 \text{ mV s}^{-1}$  onto stationary and rotating electrodes (1000 and 2000 rpm) in a solution containing  $0.001 \text{ mol dm}^{-3} \text{CoCl}_2 + 0.2 \text{ mol dm}^{-3} (\text{en})$  are shown in Fig. 5a. The potential was swept in the anodic direction from the starting potential marked with the arrow. Considering the CV obtained at a stationary electrode, it appears that the oxidation of  $[\text{Co}(\text{en})_3]^{2+}$  (dominant complex at pH 12, Fig. 1a) to  $[\text{Co}(\text{en})_3]^{3+}$  did not occur during the first cycle (solid line) and that its reduction takes place at potentials more negative than  $-0.70 \text{ V}$  through a current density wave characterized with the plateau. During the reverse sweep, the oxidation of  $[\text{Co}(\text{en})_3]^{2+}$  to  $[\text{Co}(\text{en})_3]^{3+}$  did occur through a broad anodic peak, while the reduction of  $[\text{Co}(\text{en})_3]^{3+}$  (which is formed during the oxidation process) into  $[\text{Co}(\text{en})_3]^{2+}$

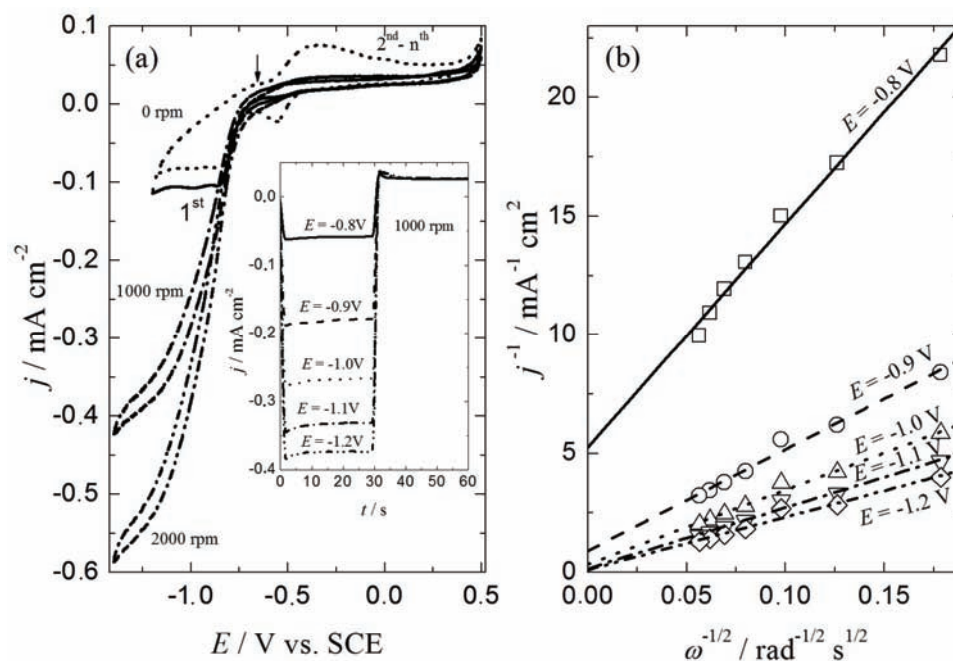


Fig. 5. a) CVs recorded with  $\nu = 100 \text{ mV s}^{-1}$  at different rotation speeds (marked in the figure) in solutions containing  $0.001 \text{ mol dm}^{-3} \text{ CoCl}_2 + 0.2 \text{ mol dm}^{-3} \text{ (en)}$ . Inset: potentiostatic  $j$  vs.  $t$  transients recorded at different cathodic potentials (marked in the figure) and constant anodic potential  $E = -0.2 \text{ V}$  at 1000 rpm. b) The  $j^{-1}$  vs.  $\omega^{1/2}$  dependences obtained from the potentiostatic  $j$  vs.  $t$  transients recorded at different potentials (marked in the figure).

takes place through a sharper cathodic peak positioned between about  $-0.45$  and  $-0.65 \text{ V}$  during the 2<sup>nd</sup> and subsequent cycles. Under the conditions of convective diffusion, oxidation of  $[\text{Co(en)}_3]^{2+}$  to  $[\text{Co(en)}_3]^{3+}$  cannot be detected on the CVs in this solution. The process of reduction of  $[\text{Co(en)}_3]^{2+}$  commenced at about  $-0.75 \text{ V}$ , being expressed by a sudden increase in the cathodic current density without indication of a diffusion limiting current density plateau. The  $j$  vs.  $t$  transients recorded at 1000 rpm, presented in the inset of Fig. 5a, are characterized with a constant current density response at all applied potentials. As can be seen, the values of the cathodic current density increased with increasing cathodic potential, while the values of the anodic current density recorded during the anodic pulse at  $E = -0.2 \text{ V}$  (as well as the amount of anodic charge for the oxidation reaction) was independent of the cathodic potential, *i.e.*, of the amount of reduced  $[\text{Co(en)}_3]^{2+}$ . Taking into account that all reduced species during the cathodic process are removed to the bulk of the solution by electrode rotation, it is reasonable to expect that only a limited amount could be oxidized during the anodic pulse. It should be stated here that even in the case of a stationary electrode only a small amount (about 10 %) of reduced species could be oxidized,



although certain amount of them remain near the electrode surface after the cathodic current density pulse. Hence, it could be concluded that, as in the solution containing only the  $[\text{Co}(\text{en})_3]^{3+}$  complex, the oxidation process of  $[\text{Co}(\text{en})_3]^{2+}$  to  $[\text{Co}(\text{en})_3]^{3+}$  is complex. Considering the results presented in Fig. 5b, it is obvious that the reduction process is complex, since the slopes of the  $j^{-1}$  vs.  $\omega^{-1/2}$  dependences change with the potential, indicating that most likely different species undergo the reduction process in the investigated potential range.<sup>21</sup> It is also possible that some chemical reactions occur, but it is not possible to predict what is really occurring in the system from the presented results.<sup>21</sup>

When the concentration of  $\text{CoCl}_2$  was increased to  $0.01 \text{ mol dm}^{-3}$ , slightly different results were obtained. As can be seen in Fig. 6a, at the stationary electrode, the first and subsequent sweeps were identical, indicating oxidation of  $[\text{Co}(\text{en})_3]^{2+}$  to  $[\text{Co}(\text{en})_3]^{3+}$  immediately at the beginning of cycling (the starting potential is marked with an arrow). It appears that in order to be able to detect this process by CV at  $100 \text{ mV s}^{-1}$ , it is necessary to increase the concentration of  $\text{CoCl}_2$ . During the reverse (cathodic) sweep, a sharp peak of the reduction of  $[\text{Co}(\text{en})_3]^{3+}$  (formed during the oxidation reaction) to  $[\text{Co}(\text{en})_3]^{2+}$  appeared at about  $-0.6 \text{ V}$ , while further reduction of  $[\text{Co}(\text{en})_3]^{2+}$  species was characterized by the presence of an additional, smaller peak at about  $-0.8 \text{ V}$ . As in previous cases, the increase in the anodic current density at the oxidation peak on all the CVs recorded at  $100 \text{ mV s}^{-1}$  was positioned at more negative potentials than expected for a totally irreversible oxidation/reduction mechanism. This could be the consequence of the occurrence of some other reaction, most probably a coupled chemical reaction, during the oxidation process, since the shape of the CVs was similar to those theoretically predicted for such reactions.<sup>21</sup> In the case of electrode rotation, the anodic peak became more pronounced, but practically independent of the rotation speed. During the reverse sweep (from  $0.5$  to  $-1.2 \text{ V}$ ), a first current density plateau appeared between  $0.0$  and  $-0.3 \text{ V}$ , indicating the occurrence of a diffusion controlled oxidation reaction at a current density of about  $0.4 \text{ mA cm}^{-2}$ . An additional, much shorter current density plateau, between  $-0.50$  and  $-0.75 \text{ V}$ , at zero current density indicates that no reduction of  $[\text{Co}(\text{en})_3]^{3+}$  to  $[\text{Co}(\text{en})_3]^{2+}$  occurred under conditions of convective diffusion. The increase in the cathodic current density at potentials more negative than  $-0.75 \text{ V}$  corresponded to further reduction of the  $[\text{Co}(\text{en})_3]^{2+}$  complex. In order to understand better these processes, the potentiostatic pulse experiments were performed and the results are presented in Fig. 6b and c. Figure 6b shows that the species formed during the anodic potential step ( $E = 0.1 \text{ V}$ ) started to be reduced at  $-0.70 \text{ V}$ . The amount of species being reduced during the cathodic potential steps increased with increasing cathodic potential reaching a maximum of about  $12 \%$  at  $E = -1.1 \text{ V}$ . The results presented in Fig. 6c show that about  $28 \%$  of the species formed at  $E = 0.1 \text{ V}$  on the stationary electrode become reduced at

$E = -0.6$  V (peak potential, Fig. 6a), while no reduction could be detected under convective diffusion conditions. Simultaneously, it could be seen that the oxidation process was practically insensitive to the rotation speed. It should be noted here that similar  $j^{-1}$  vs.  $\omega^{-1/2}$  dependences (changing slopes and intercepts as a function of the cathodic potential) compared to those recorded for  $0.001 \text{ mol dm}^{-3} \text{ CoCl}_2$  were obtained.

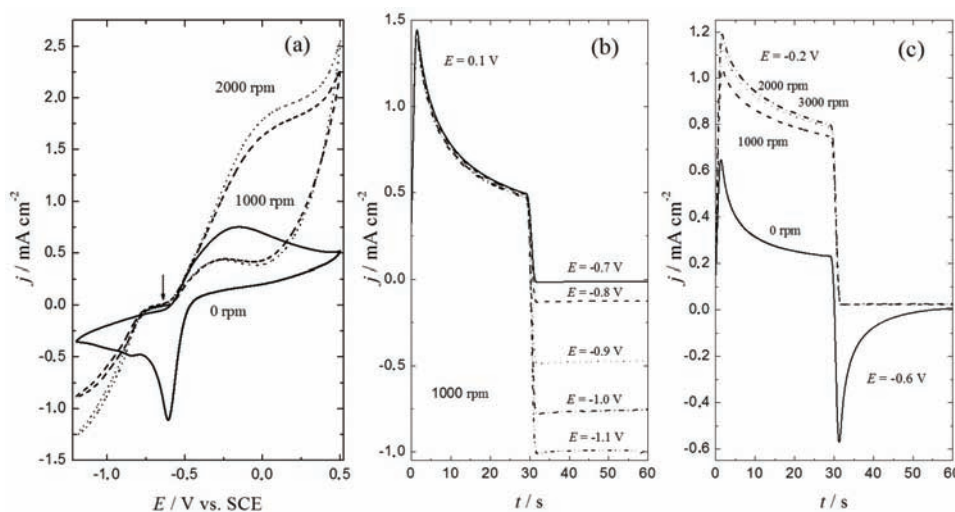


Fig. 6. a) CVs recorded at  $v = 100 \text{ mV s}^{-1}$  for different rotation speeds (marked in the figure) in the solutions containing  $0.01 \text{ mol dm}^{-3} \text{ CoCl}_2 + 0.2 \text{ mol dm}^{-3} \text{ (en)}$ . b) Potentiostatic  $j$  vs.  $t$  transients recorded at different cathodic potentials (marked in the figure) and constant anodic potential  $E = 0.1$  V at 1000 r.p.m. c) Potentiostatic  $j$  vs.  $t$  transients at constant anodic and cathodic potentials (marked in the figure) recorded at different rotation speeds (marked in the figure).

#### *Electrochemical behavior of $\text{Co}^{2+} + \text{Co}^{3+}$ in $0.2 \text{ mol dm}^{-3}$ ethylenediamine*

The CVs recorded at a sweep rate of  $100 \text{ mV s}^{-1}$  on a stationary and rotating electrode (1000 rpm) in a solution containing  $0.001 \text{ mol dm}^{-3} \text{ CoCl}_2 + 0.001 \text{ mol dm}^{-3} \text{ Co(en)}_3\text{Cl}_3 + 0.2 \text{ mol dm}^{-3} \text{ (en)}$  are shown in Fig. 7a. The potential was swept in the anodic direction from the starting potential marked with the arrow. In comparison with the results obtained in the solution containing only  $0.001 \text{ mol dm}^{-3} \text{ CoCl}_2$  (Fig. 5a), a small anodic peak for the 1<sup>st</sup> was detected at the stationary electrode, while for the subsequent sweeps, this peak was identical to that obtained in pure  $0.001 \text{ mol dm}^{-3} \text{ CoCl}_2$  solution. At the same time, the cathodic peak corresponding to the reduction of  $[\text{Co(en)}_3]^{3+}$  to  $[\text{Co(en)}_3]^{2+}$  was much better defined since the  $[\text{Co(en)}_3]^{3+}$  complex was present in the solution at a concentration slightly higher than  $0.001 \text{ mol dm}^{-3}$  (taking into account that a certain amount of the  $[\text{Co(en)}_3]^{3+}$  complex was formed by the oxidation of  $[\text{Co(en)}_3]^{2+}$ ).

Under conditions of convective diffusion, the increase in the anodic current density without a plateau confirmed that the oxidation process was not diffusion controlled, while the shape of cathodic current density wave indicated the occurrence of two processes, the first one corresponding to reduction of  $[\text{Co}(\text{en})_3]^{3+}$  to  $[\text{Co}(\text{en})_3]^{2+}$  (potential range between  $-0.7$  and  $-0.8$  V) and the second one at more negative potentials, which was less pronounced, corresponded to further reduction of  $[\text{Co}(\text{en})_3]^{2+}$ . The potentiostatic pulse responses presented in the inset of Fig. 7a clearly show that only a certain number of species formed during the reduction process could be oxidized during the anodic pulse ( $E = -0.2$  V) and that the oxidation was independent of the rotation speed. The  $j^{-1}$  vs.  $\omega^{-1/2}$  dependences presented in Fig. 7b confirmed, as in the case of  $0.001 \text{ mol dm}^{-3} \text{ CoCl}_2$  solution, that the reduction process was complex in the presence of  $\text{Co}^{2+}$ .

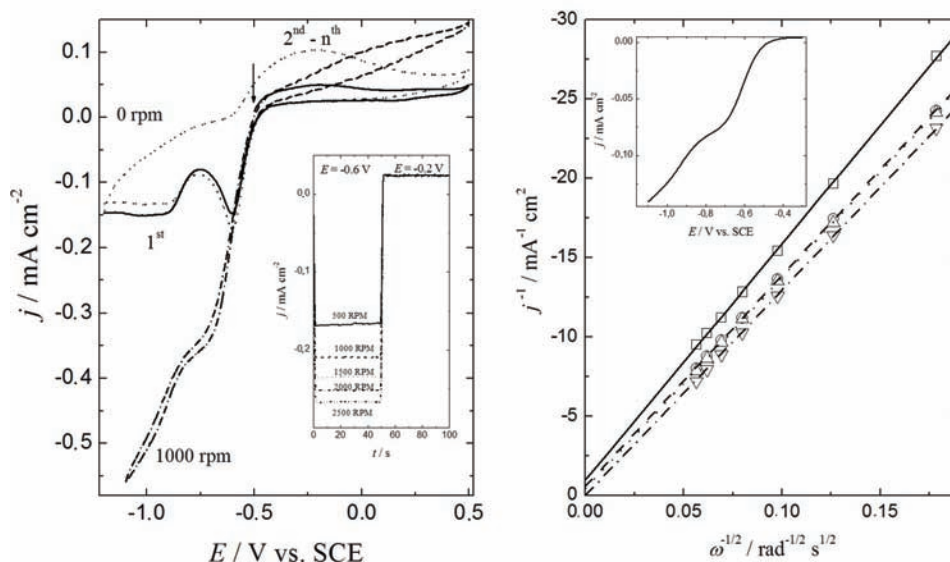


Fig. 7. a) CVs recorded with  $v = 100 \text{ mV s}^{-1}$  at different rotation speeds (marked in the figure) in a solution containing  $0.001 \text{ mol dm}^{-3} \text{ CoCl}_2 + 0.001 \text{ mol dm}^{-3} \text{ Co}(\text{en})_3\text{Cl}_3 + 0.2 \text{ mol dm}^{-3} (\text{en})$ . Inset: potentiostatic  $j$  vs.  $t$  transients recorded at different cathodic potentials (marked in the figure) and constant anodic potential  $E = -0.2$  V at 1000 rpm. b) The  $j^{-1}$  vs.  $\omega^{1/2}$  dependences obtained from the potentiostatic  $j$  vs.  $t$  transients. Inset: polarization curve for the reduction process recorded at a sweep rate of  $1 \text{ mV s}^{-1}$ .

#### CONCLUSIONS

From the results presented in this work, it could be concluded that different cobalt complexes are present in a solution containing  $0.2 \text{ mol dm}^{-3}$  ethylenediamine, with the  $[\text{Co}(\text{en})_3]^{3+}$  complex being the most stable one at all pH values. Its reduction to the  $[\text{Co}(\text{en})_3]^{2+}$  complex represents a totally irreversible,

one electron exchange reaction, while further reduction of  $[\text{Co}(\text{en})_3]^{2+}$  is a complex process leading to cobalt deposition at potentials more negative than  $-1.45$  V. The process of  $[\text{Co}(\text{en})_3]^{2+}$  oxidation is also complex and most probably coupled with a chemical reaction.

*Acknowledgement.* The authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support through Project No. 172045.

## ИЗВОД

ЕЛЕКТРОХЕМИЈА КОБАЛТ–ЕТИЛЕНДИАМИН КОМПЛЕКСА ПРИ ВИСОКИМ  
рН ВРЕДНОСТИМА

СНЕЖАНА М. МИУЛОВИЋ, ВЛАДИМИР М. НИКОЛИЋ, ПЕТАР З. ЛАУШЕВИЋ, ДАНКА Д. АБИМОВИЋ,  
ГВОЗДЕН С. ТАСИЋ и МИЛИЦА П. МАРЧЕТА КАНИНСКИ

*Институт за нуклеарне науке „Винча“, Лабораторија за физичку хемију, Универзитет у Београду,  
Мике Аласа 12–14, 11000 Београд*

Испитивано је електрохемијско понашање кобалта у присуству етилендиаминa у великом вишку при рН 12. Испитивања су извршена методама цикличне волтаметрије, потенциостатског пулса и мерењем поларизационих кривих на стационарној и ротирајућој електроди од стакластог угљеника. Показано је да се у раствору формира шеснаест различитих врста које садрже  $\text{Co}(\text{en})_3$  и да је најстабилнији  $[\text{Co}(\text{en})_3]^{3+}$  при свим рН вредностима. Показано је да је редукција  $[\text{Co}(\text{en})_3]^{3+}$  до  $[\text{Co}(\text{en})_3]^{2+}$  потпуно иреверзибилна једноелектронска реакција. Утврђено је да је даља редукција  $[\text{Co}(\text{en})_3]^{2+}$  сложен процес који води ка таложењу кобалта на потенцијалима негативнијим од  $-1,45$  V у односу на zasiћену каломелову электроду. Процес оксидације  $[\text{Co}(\text{en})_3]^{2+}$  такође је комплексан и највероватније спрегнут са хемијском реакцијом.

(Примљено 27. марта, ревидирано 23. јуна, прихваћено 30. јуна 2015)

## REFERENCES

1. A. Werner, *Ber. Dtsch. Chem. Ges.* **45** (1912) 121
2. D. Witiak, J. C. Clardy, D. S. Martin, *Acta Crystallogr., B* **28** (1972) 2694
3. J. Bjerrum, S. E. Rasmussen, *Acta Chem. Scand.* **6** (1952) 1265
4. H. A. Laitinen, M. W. Grieb, *J. Am. Chem. Soc.* **77** (1955) 5201
5. P. Kivalo, *J. Am. Chem. Soc.* **77** (1955) 2678
6. S. Sahami, M. J. Weaver, *J. Electroanal. Chem.* **122** (1981) 171
7. S. Sahami, M. J. Weaver, *J. Electroanal. Chem.* **122** (1981) 155
8. S. Sahami, M. J. Weaver, *J. Electroanal. Chem.* **124** (1981) 35
9. U. Mayer, A. Kotocova, V. Gutmann, W. Gerger, *J. Electroanal. Chem.* **100** (1979) 875
10. M. M. Jakšić, Č. M. Lačnjevac, *Chem. Tech.* **37** (1985) 257
11. M. M. Jakšić, *Int. J. Hydrogen Energy* **11** (1986) 519
12. M. M. Jakšić, *Mater. Chem. Phys.* **22** (1987) 1
13. M. P. Marceta Kaninski, D. Lj. Stojic, Dj. P. Saponjic, N. I. Potkonjak, S. S. Miljanic, *J. Power Sources* **157** (2006) 758
14. S. Lj. Maslovara, S. M. Miulovic, M. P. Marceta Kaninski, G. S. Tasic, V. M. Nikolic, *Appl. Catal., A* **451** (2013) 216
15. S. M. Miulovic, S. Lj. Maslovara, I. M. Perovic, V. M. Nikolic, M. P. Marceta Kaninski, *Appl. Catal., A* **451** (2013) 220

16. M. P. Marceta Kaninski, V. M. Nikolic, G. S. Tasic, Z. Lj. Rakocevic, *Int. J. Hydrogen Energ.* **34** (2009) 703
17. M. P. Marceta Kaninski, A. D. Maksic, D. Lj. Stojic, S. S. Miljanić, *J. Power Sources* **131** (2004) 107
18. P. R. Rowland, *Nature* **218** (1968) 945
19. P. R. Rowland, *J. Electroanal. Chem.* **32** (1971) 109
20. A. E. Martell, R. M. Smith, *NIST critically selected stability constants of metal complexes: version 8.0*, NIST standard reference database 46, 2004
21. A. J. Bard, L. R. Faulkner, *Electrochemical methods, fundamentals and applications*, Wiley, New York, 2001, pp. 339–343, 471–517
22. H. Gomez Meier, J. R. Vilche, A. J. Arvia, *J. Electroanal. Chem.* **138** (1982) 367.