Electrochemical reduction of $Co(NH_3)_6^{3+}$ on the surface of different metals

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Electrochemical reduction of $Co(NH_3)_6^{3+}$ complex to Co(II) on Pt, Ag, Au electrodes was studied in xNH_4NO_3 + yNH_4OH (x + y = 1.5 M) supporting electrolyte. The rate of the process was shown to be limited by charge transfer and diffusion, the rate constant being dependent on the nature of the solution and the anion of the supporting electrolyte. The process inhibition increased in the range: $Br^- < Cl^- < NO_3^- < SO_4^{2-}$ and the highest effect was observed on Au electrode.

Key words: $Co(NH_3)_6^{3+}$ complex, Pt, Ag, Au electrodes, anions influence

INTRODUCTION

The redox potential of the cobalt(III)–cobalt(II) couple varies in a wide range of values depending on the degree of complexation of cobalt(II) and cobalt(III), which is rather easily controlled by selection of the ligands, changing their concentration and solution pH. Cobalt(II) complexes with amines are the reducing agents sufficiently strong to reduce some metal ions to metallic state and therefore are used in electroless plating systems for deposition of metal coatings. Cobalt(II)-ammonia complex is used for the autocatalytic silver ions reduction (electroless silver deposition) [1–9]. Cobalt(III)-ammonia complex is formed in the plating process, and its reduction to the former divalent state is important for the practical use of the silver plating process as a reducing agent regeneration step.

The cobalt(III)/cobalt(II)-ammonia complex couple is a popular model system for investigation of simple (outer-sphere) heterogeneous charge transfer reactions, and cathodic reduction of Co(III)–ammonia complex was studied on various metals (see a review [10]).

The experimentally observed differences in cobalt(III)–ammonia complex reduction kinetics for various electrode materials (Hg, Ag, Pt, Au) have been found to be compatible with the expected variations in double-layer effects [11]. Such a dependence of the reaction kinetics on the nature of the electrode material is predicted by the charge transfer model used for explaining the simple outer-sphere electrode reactions, which assume the separation of electrode surface from reactant and product particles by a water molecule monolayer. Recently, hexaammine cobalt(III) ion reduction on a single-crystal gold electrode has been used to study double-layer effects and the role of charge distribution in reactant and product [12, 13].

On the other hand, the large variations in the double-layer corrected rate constant for various electrode materials indicate a sensitivity of this process kinetics to the reaction environment, what is more characteristic of electrocatalytic reactions [10].

The electrochemical reduction of chloropentaammino cobalt(III) complex on silver, platinum and gold surfaces has been investigated [14, 15]; these data have been used for analysis of the reaction between *N,N*-dimethyl-*p*-phenylenediamine and the Co(III) complex catalyzed by noble metals, and assuming the catalytic process to consist of two coupled electrochemical reactions.

The electrochemical rate constant of electron transfer in the system $Co(NH_3)_6^{3+/2+}$ on Pt electrode has been measured using the polarization resistance method [16, 17]. The effects of complex hydrolysis and ion pair formation (they decrease the exchange current density) have been studied as well. The exchange current was found to increase while increasing the free ligand concentration. These effects were explained by the different adsorption of the ligand or of the products of its hydrolysis on the electrode surface [16, 18] and on the different electrode material [19]. Other authors explain the differences in the kinetics of $Co(NH_3)_6^{3+}$ by the different anions of supporting electrolyte [20, 21].

In our recent study [22], the rate of electrochemical cobalt(III)–ammonia complex reduction on Pt was found to depend on the supporting electrolyte anion: $Cl^- > NO_3^- > SO_4^{2-}$. This effect was explained by the formation of outer-sphere complexes.

Rotating disc electrode technique and electrochemical quartz crystal microgravimetry were used in the recent study of electrochemical reactions in an uncomplexed Co(III)–Co(II) system [23].

The aim of the present work was the further investigation of $Co(NH_3)_6^{3+}$ electrochemical reduction process on Pt, Au and Ag electrodes and also studies of the solution composition and anion influence on the kinetics of the process. The experiments were carried out in alkaline ammonia salt solutions where the reaction products, cobalt(II)–ammonia complexes, are stable.

EXPERIMENTAL

Potentiodynamic voltammetric curves were obtained on a PI-50 potentiometer (Belarus). The potential sweep was changed from 0.002 to 0.1 V/s. The working electrode was a smooth Pt foil or Au and Ag of 1 cm^2, the auxiliary electrode – a Pt foil of 3 cm^2, as the reference electrode served an Ag/AgCl electrode with saturated KCl solution. All the potential values were referred to the standard hydrogen electrode. Solutions were deoxygenised by Ar. The experiments were carried out at 25 °C.

$[Co(NH_3)_6](NO_3)_3$ salt was used in most experiments. It was prepared from $[Co(NH_3)_6]Cl_3$ solution by adding an equivalent amount of $AgNO_3$ solution, and crystallizing $[Co(NH_3)_6](NO_3)_3$ after filtration. NH_4NO_3 solution was prepared from concentrated ammonia and HNO_3 solutions; $xNH_4NO_3 + yNH_4OH$ was used as the supporting electrolyte, where x + y = 1.5M. The pH of the solutions was as follows: 8.1, 9.5, 10.1. All reagents were of chemical grade. The solutions were prepared using distilled water.

RESULTS AND DISCUSSION

Analysing the influence of $Co(NH_3)_6^{3+}$ concentration on the electrochemical reduction of Co(III) on different electrodes, it was determined that the values of the cathodic current and the cathodic peak potential depended on the nature of the working electrode and also on the composition of the supporting electrolyte.

A comparison of the curves obtained on Pt, Ag and Au electrodes in 1.0 M NH_4NO_3+ 0.5 M NH_4OH solution (pH 9.5), shows that the values of the limiting current on Pt and Au are similar for the same concentrations of Co(III) complex (Fig 1.).

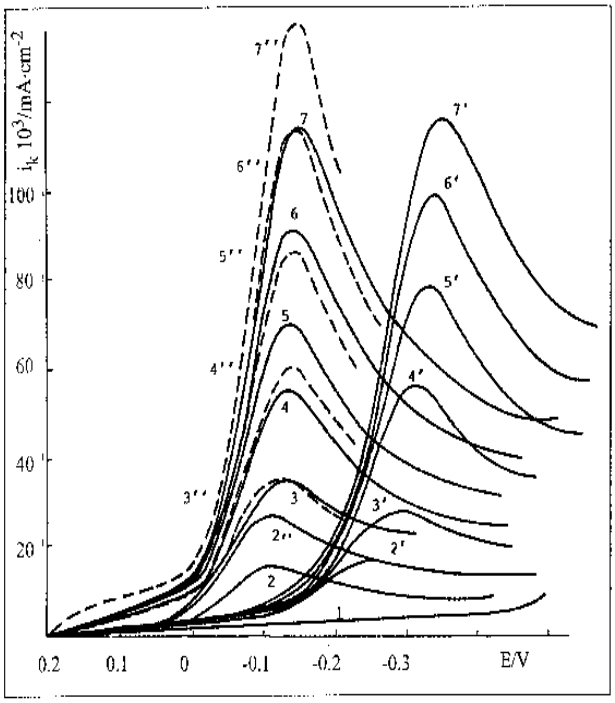

Fig. 1. Influence of $Co(NH_3)_6^{3+}$ concentration on the electrochemical reduction on Pt (1–7), Au (1'–7') and Ag (1''–7'') electrodes in 1.0 M NH_4NO_3 + 0.5 M NH_4OH solution. PH 9.5, $[Co(NH_3)_6](NO_3)_3$ concentrations · $\cdot 10^3$ (M): 1, 1', 1'' – 0; 2, 2', 2'' – 0.1; 3, 3', 3'' – 0.2; 4, 4', 4'' – 0.4; 5, 5', 5'' – 0.6; 6, 6', 6'' – 0.8; 7, 7',7'' – 1.0. v_s = 0.02 V/s

The process on Au occurs at more negative potential values (~ 0.2 V). The currents on Ag electrode are higher compared with those of Pt and Au. This difference could be probably explained by different real surface areas of the electrodes.

The change of the supporting electrolyte composition, as well as higher values of pH increase the influence of the electrode nature. The decrease of NH_4NO_3 and the increase of NH_4OH concentration cause an increase of the current peak and the potential shift to more positive values on Pt electrode (Fig. 2, curves 1–3). This opposite potential shift on Au electrode is observed in the region of pH from 8.1 to 9.5 (Fig. 3, curves 1 and 2), and the further increase in NH_4OH concentration has no influence on the reduction potential (Fig. 3, curve 3), while the current peak becomes slightly higher. The results of similar measurements on Ag electrode showed that in this case the pH change has a minor influence on the current peak and has no influence on the reduction potential values (Fig. 4). When comparing the voltammetric curves on different electrodes under the same conditions, the processes proceed with the similar rate on Pt and Ag electrodes, meanwhile a similar rate on Au electrode is attained at the more negative potential values. The

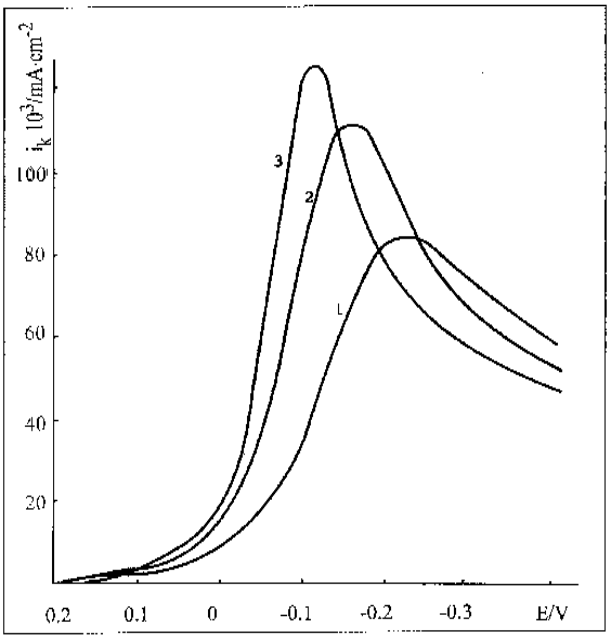

Fig. 2. Influence of the supporting electrolyte composition (and solution pH) on Co(III) reduction on Pt electrode in 10^{-3} M $[Co(NH_3)_6](NO_3)_3$ solution containing: 1 – 1.5 M NH_4NO_3 (pH 8.1); 2 – 1.0 M NH_4NO_3 + 0.5 M NH_4OH (pH 9.5); 3 – 0.5 M NH_4NO_3 + 1.0 M NH_4OH (pH 10.1). v_s = 0.02 V/s

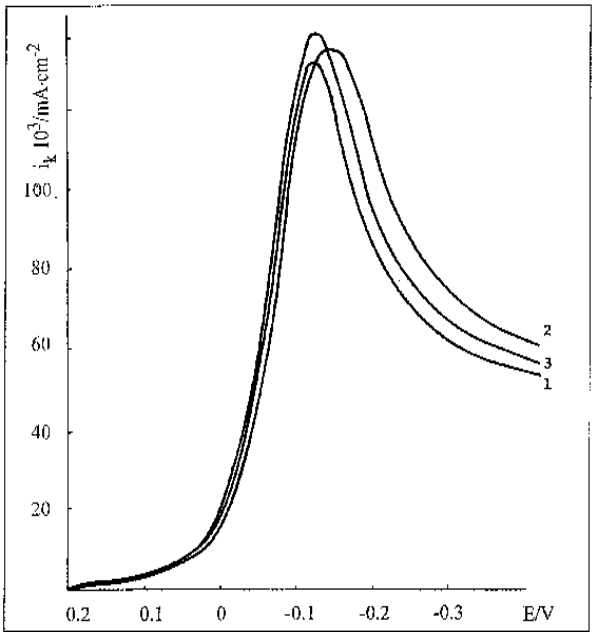

Fig. 4. Influence of the supporting electrolyte composition (and solution pH) on Co(III) reduction on Ag electrode in 10^{-3} M $[Co(NH_3)_6](NO_3)_3$ solution containing: 1 – 1.5 M NH_4NO_3 (pH 8.1); 2 – 1.0 M NH_4NO_3 + 0.5 M NH_4OH (pH 9.5); 3 – 0.5 M NH_4NO_3 + 1.0 M NH_4OH (pH 10.1). v_s = 0,02 V/s

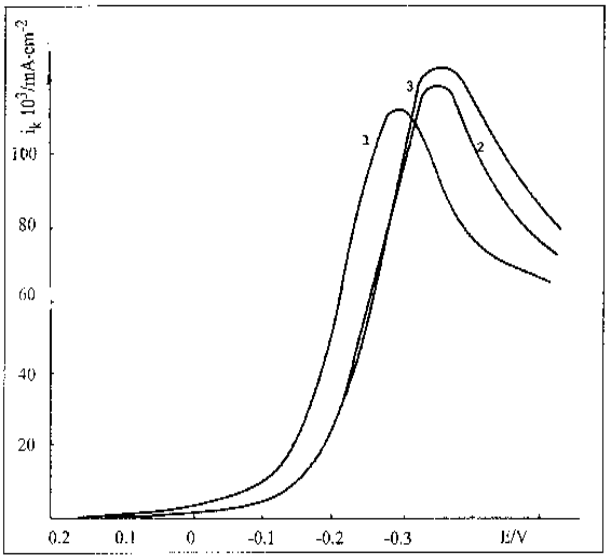

Fig. 3. Influence of the supporting electrolyte composition (and solution pH) on Co(III) reduction on Au electrode in 10^{-3} M $[Co(NH_3)_6](NO_3)_3$ solution containing: 1 – 1.5 M NH_4NO_3 (pH 8.1); 2 – 1.0 M NH_4NO_3 + 0.5 M NH_4OH (pH 9.5); 3 – 0.5 M NH_4NO_3 + 1.0 M NH_4OH (pH 10.1). v_s = 0.02 V/s

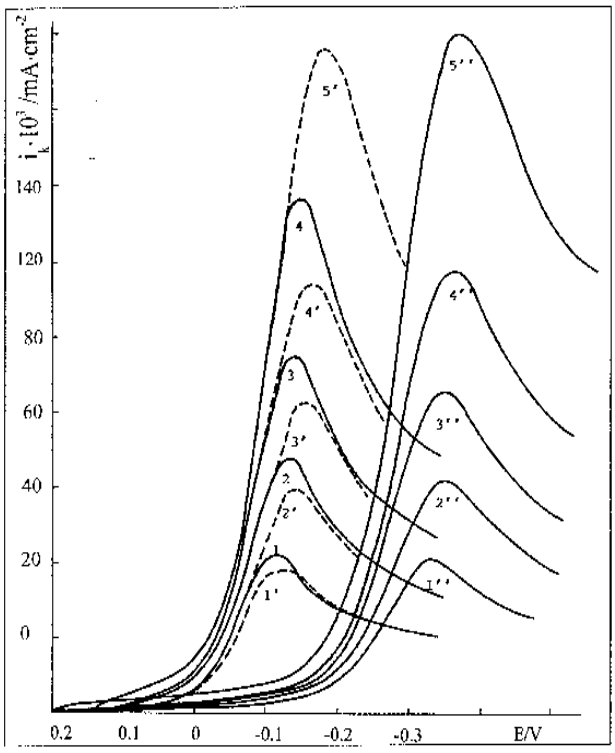

Fig. 5. Influence of the potential sweep rate on the reduction process of Co(III) on Ag (1–4), Pt (1'-5') and Au (1''-5'') electrodes in 10^{-3} M $[Co(NH_3)_6](NO_3)_3$ + 1.0 M NH_4NO_3 + 0.5 M NH_4OH (pH = 9.5) solution. $v_s \cdot 10^3$ (V/s): 1, 1', 1'' – 2; 2, 2', 2'' – 5; 3, 3', 3'' – 10; 4, 4', 4'' – 20; 5', 5'' – 50

values of the current peak potential differ remarkably while the limiting current values are similar. The latter values do not depend on the ratio of x and y of the supporting electrolyte components on

different electrodes when Co(III) concentration is the same and pH is different.

Voltammetric investigations at different potential scan rates (v_s) show that the values of current peaks increase and depend on the electrode metal (Fig. 5). The difference is bigger when v_s is higher. *E.g.*, the values of I_p on voltammetric curves are: 0.038 mA for Pt electrode (curve 4[I]), 0.04 mA – for Au (curve 4[II]), 0.042 mA – for Ag (curve 4), at a scan rate 0.002 V/s and subsequently 0.113 mA – for Pt, 0.117 mA – for Au, 0.137 mA – for Ag when v_s is 0.02 V/s in the solution where the Co(III) concentration is 10^{-3} M (pH 9.5). The difference becomes greater at lower concentrations of NH_4OH when pH is 8.1 (Table). The maximum current on voltammetric curves shifts to more negative potentials with increasing the voltage scan rate. This voltage shift E_p–$E_{p/2}$ is equal to –(0.1÷0.12) V for Pt electrode (pH 8.1) which is characteristic of the irreversible processes and –(0.065÷0.075) V (pH 9.5) along with –(0.06÷0.065) V (pH 10.1), as well as –(0.08÷0.09) V for Au electrode and –(0.06÷0.070)V for Ag electrode (Table).

Table. **Characteristics of the process of $Co(NH_3)_6^{3+}$ electrochemical reduction on electrodes of different metals. Solution composition: pH 8.1 – 10^{-3} M $[Co(NH_3)_6](NO_3)_3$, 1.5 M NH_4NO_3; pH 9.5 – 10^{-3} M $[Co(NH_3)_6](NO_3)_3$, 1.0 M NH_4NO_3, 0.5 M NH_4OH; pH 10.1 – 10^{-3} M $[Co(NH_3)_6](NO_3)_3$, 0.5 M NH_4NO_3, 1.5 M NH_4OH**

pH	v_s, V/s	$v_s^{1/2}$, $V^{1/2}$	ln v_s	E_p, V	$E_{p/2}$, V	$E_{p/2}$–E_p, V	I_p, μA
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
				Platinum electrode			
8.1	0.002	0.044	–6.215	–0.175	–0.075	0.1	29
	0.005	0.070	–5.298	–0.2	–0.095	0.105	44
	0.01	0.10	–4.605	–0.215	–0.105	0.11	61
	0.02	0.141	–3.912	–0.235	–0.120	0.115	85
	0.05	0.224	–2.997	–0.26	–0.140	0.12	132
	0.1	0.316	–1.151	–0.275	–0.150	0.12	181
9.5	0.002	0.045	–6.215	–0.115	–0.05	0.065	38
	0.005	0.071	–5.298	–0.135	–0.065	0.07	58
	0.01	0.10	–4.605	–0.15	–0.085	0.065	81
	0.02	0.141	–3.912	–0.16	–0.085	0.075	113
	0.05	0.224	–2.997	–0.18	–0.1	0.08	175
10.1	0.002	0.045	–6.215	–0.085	–0.02	0.065	39
	0.005	0.071	–5.298	–0.095	–0.035	0.06	62
	0.01	0.10	–4.605	–0.11	–0.05	0.06	89
	0.02	0.141	–3.912	–0.12	–0.06	0.06	127
	0.05	0.224	–2.997	–0.135	–0.075	0.06	199
				Silver electrode			
8.1	0.002	0.045	–6.215	–0.08	–0.015	0.065	40
	0.005	0.071	–5.298	–0.1	–0.045	0.055	61
	0.01	0.10	–4.605	–0.115	–0.05	0.065	75
	0.02	0.141	–3.912	–0.12	–0.05	0.07	129
	0.05	0.224	–2.997	–0.14	–0.06	0.08	194
9.5	0.002	0.045	–6.215	–0.105	–0.04	0.065	42
	0.005	0.071	–5.298	–0.13	–0.06	0.07	67
	0.01	0.10	–4.605	–0.135	–0.07	0.065	94
	0.02	0.141	–3.912	–0.145	–0.08	0.065	137
	0.05	0.224	–2.997	–0.17	–0.09	0.08	210
10.1	0.002	0.045	–6.215	–0.07	–0.1	0.06	44
	0.005	0.071	–5.298	–0.085	–0.025	0.06	69
	0.01	0.10	–4.605	–0.095	–0.035	0.06	96
	0.02	0.141	–3.912	–0.11	–0.04	0.07	142
	0.05	0.224	–2.997	–0.12	–0.05	0.07	210
				Gold electrode			
8.1	0.002	0.045	–6.215	–0.25	–0.175	0.075	37
	0.005	0.071	–5.298	–0.255	–0.175	0.08	59
	0.01	0.10	–4.605	–0.265	–0.18	0.085	82
	0.02	0.141	–3.912	–0.27	–0.195	0.075	120

Table continue

1	2	3	4	5	6	7	8
	0.05	0.224	–2.997	–0.28	–0.205	0.075	186
9.5	0.002	0.045	–6.215	–0.33	–0.25	0.08	40
	0.005	0.071	–5.298	–0.34	–0.26	0.08	59
	0.01	0.10	–4.605	–0.345	–0.255	0.09	84
	0.02	0.141	–3.912	–0.36	–0.275	0.085	117
	0.05	0.224	–2.997	–0.37	–0.275	0.095	182
10.1	0.002	0.045	–6.215	–0.29	–0.21	0.08	40
	0.005	0.071	–5.298	–0.31	–0.23	0.08	61
	0.01	0.10	–4.605	–0.32	–0.235	0.085	70
	0.02	0.141	–3.912	–0.33	–0.245	0.085	128
	0.05	0.224	–2.997	0.35	–0.265	0.085	187

The dependences of Ip – $v_s^{1/2}$ for all electrodes are linear and can be extrapolated to the zero coordinates. Their slopes are different (Fig. 6). The values of Ip and the slope are independent on the ratio of supporting electrolyte components NH_4NO_3/ NH_4OH (correspondingly on solution pH), on gold electrode (curves 1, 1', 1''). On silver electrode the slope is smaller at a lower pH value (pH 8.1) and increases with increasing pH (curves 2, 2', 2''). A remarkable effect is observed on Pt electrode, where changes in solution pH cause an increase of the slope (curves 3, 3' 3"). The dependences E_p – ln v_s are also linear (Fig. 7).

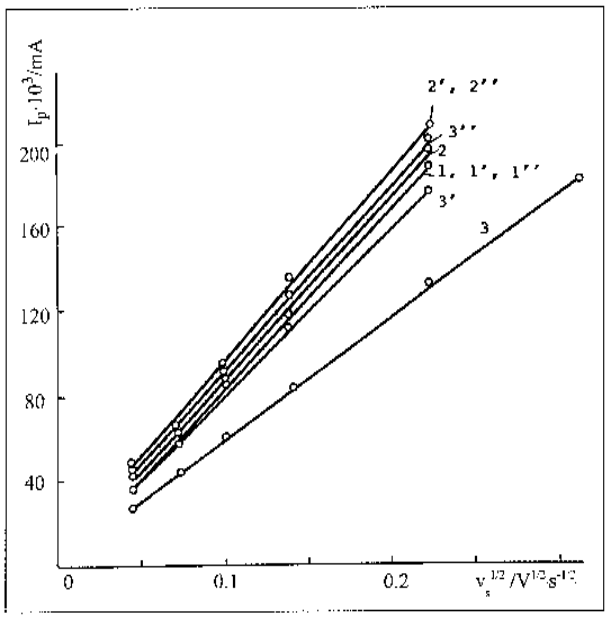

Fig. 6. Dependence of current peak height (I_p) on the potential sweep rate on Au (1), Ag (2) and Pt (3) electrodes in 10^{-3} M $[Co(NH_3)_6](NO_3)_3$ solution containing: 1, 2, 3 – 1.5 M NH_4NO_3 (pH 8.1); 1', 2', 3' – 1.0 M NH_4NO_3 + 0.5 M NH_4OH (pH 9.5); 1'', 2'', 3'' – 0.5 M NH_4NO_3 + 1.0 M NH_4OH (pH 10.1)

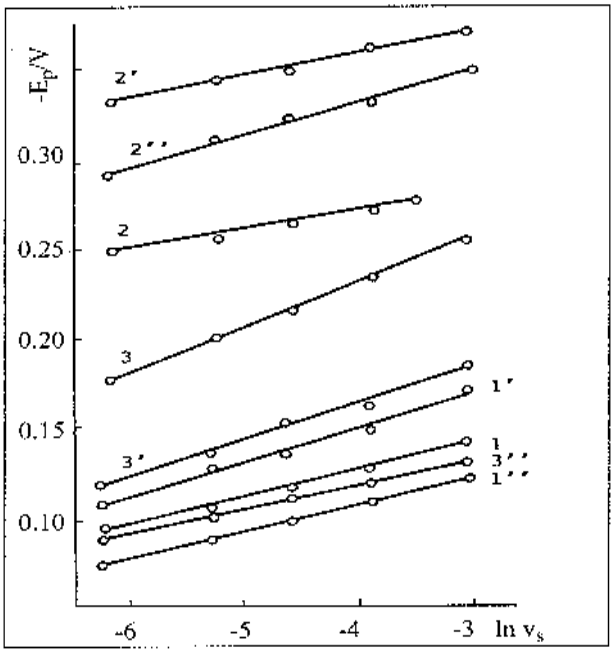

Fig. 7. Dependence of E_p – ln v_s on Au (1), Ag (2) and Pt (3) electrodes in 10^{-3} M $[Co(NH_3)_6](NO_3)_3$ solution containing: 1, 2, 3 – 1.5 M NH_4NO_3 (pH 8.1); 1', 2', 3' – 1.0 M NH_4NO_3 + 0.5 M NH_4OH (pH 9.5); 1'', 2'', 3'' – 0.5 M NH_4NO_3 + 1.0 M NH_4OH (pH 10.1)

Investigation of anion effects on the reduction of $Co(NH_3)_6^{3+}$ complex showed that the kinetics of the process was different on different metals and depended on the composition of the supporting electrolyte. Figue 8 shows the dependence of the reduction of this complex on Pt electrode on Br^- ion concentrations in at the solution pH 8.1. The increase of KBr concentration from 10^{-6} M to 10^{-2} M is followed by an increase of the cathodic process rate – the voltammograms shift to more positive potentials (Fig. 8, curves 1–6), the current peak height

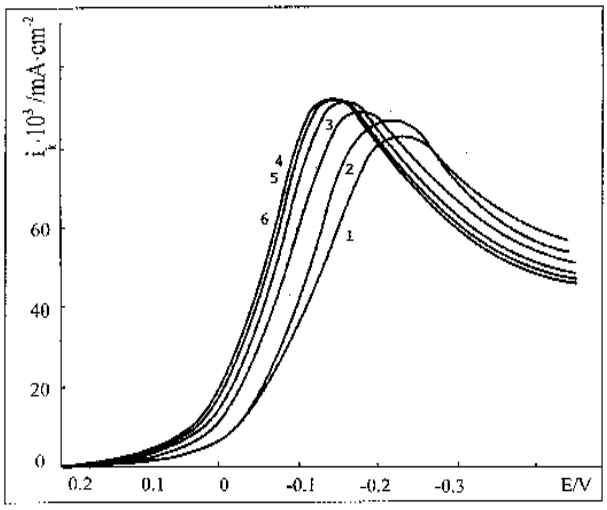

Fig. 8. Influence of Br^- ions concentration on the reduction process of Co(III) on Pt electrode in 10^{-3} M $[Co(NH_3)_6](NO_3)_3$ + 1.5 M NH_4NO_3 (pH 8.1) solution. [KBr] · 10^3 (M): 1 – 0; 2 – 0.001; 3 – 0.1; 4 – 1.0; 5 – 5.0; 6 – 10.0. v_s = 0.02 V/s

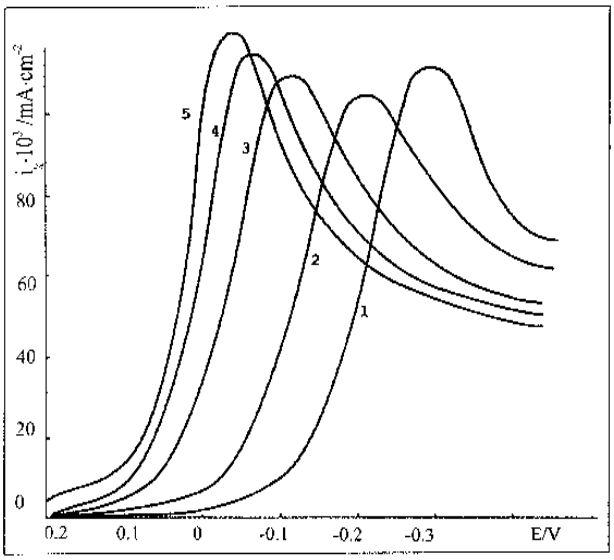

Fig. 9. Influence of Br^- ions concentration on the reduction process of Co(III) on Au electrode in 10^{-3} M $[Co(NH_3)_6](NO_3)_3$ + 1.5 M NH_4NO_3 (pH 8.1) solution. [KBr] · 10^3 (M): 1 – 0; 2 – 0.001; 3 – 0.01; 4 – 1.0; 5 – 5.0. v_s = 0.02 V/s

changing only negligibly with the increase in KBr concentration.

The accelerating effect of Br^- ions is considerably stronger on Au electrode (Fig. 9). The curves shift to more positive potentials by more than 0.25 V. The values of I_p decrease slightly in the KBr concentration range from 10^{-6} M to 10^{-4} M (Fig. 9, curves 1, 2) and then start increasing and reach the values that are higher than in the absence of KBr when the additive concentration is $5 \cdot 10^{-3}$ M (Fig. 9, curve 5).

The bromide effect on the cathodic Co(III) reduction process on Ag electrode is of the same type as that on Au, but the voltammogram shift is smaller (Fig. 10).

A similar effect is observed in at the solutions pH 10.1 (supporting electrolyte 0.5 M NH_4NO_3 + + 1.0 M NH_4OH), but in this case the I_p and E_p shifts are smaller. In the mentioned case an increase in bromide concentration leads to the formation of a forewave on the voltammograms, which is best manifested on Ag electrode.

The sulfate effect on the $Co(NH_3)_6^{3+}$ reduction process is not significant. The height of the limiting current (I_{lim}) decreases on Pt and Ag electrodes with an increase in $(NH_4)_2SO_4$ concentration, while there are almost no changes of I_{lim} on Au electrode. The current peak potential shifts to more negative values with an increase in the concentration of $(NH_4)_2SO_4$ (Fig. 11). The shift is bigger in less basic solutions, where the NH_4NO_3/NH_4OH ratio is higher (change in pH from 10.1 to 8.1). The shift increases when the concentration of SO_4^{2-} exceeds that of $Co(NH_3)_6^{3+}$ or when $(NH_4)_2SO_4$ is used as a supporting electrolyte. In this case both I_p and I_{lim} decrease, and the curve shifts to more negative

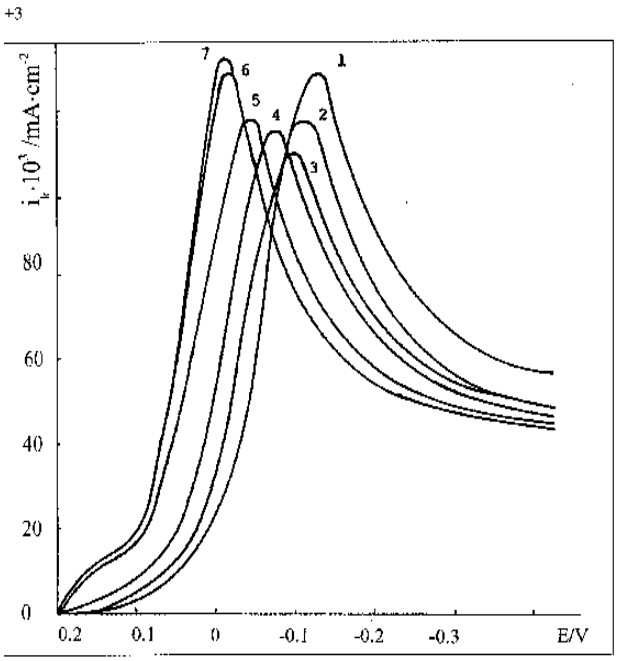

Fig. 10. Influence of Br^- ions concentration on the reduction process of Co(III) on Ag electrode in 10^{-3} M $[Co(NH_3)_6](NO_3)_3$ + 1.5 M NH_4NO_3 (pH 8.1) solution. [KBr] · 10^3 (M): 1 – 0; 2 – 0.001; 3 – 0.01; 4 – 0.10; 5 – 1.0; 6 – 5.0; 7 – 10.0. v_s = 0.02 V/s

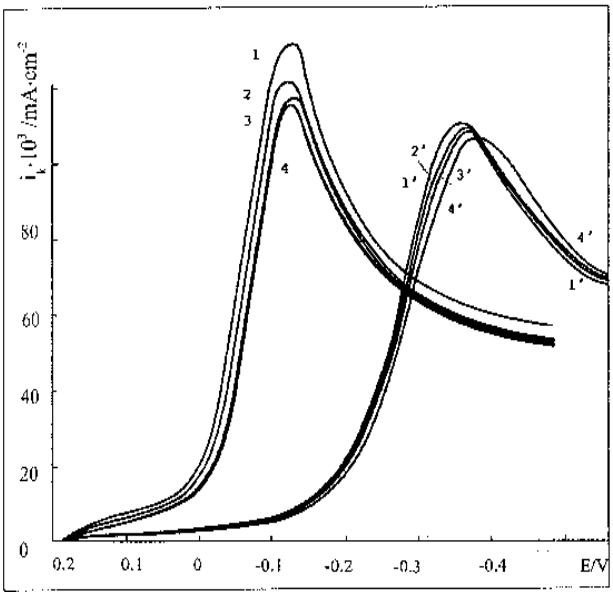

Fig. 11 Influence of SO_4^{2-} ions concentration on the reduction of Co(III) on Ag (1–4) and Au (1'-4') electrodes in 10^{-3} M $[Co(NH_3)_6](NO_3)_3$ + 1.0 M NH_4NO_3 + 0.5 M NH_4OH (pH 9.5) solution. $[(NH_4)_2SO_4] \cdot 10^3$ (M): 1, 1' – 0; 2, 2' – 0.01; 3, 3' – 1.0; 4, 4' – 10.0. v_s = 0.02 V/s

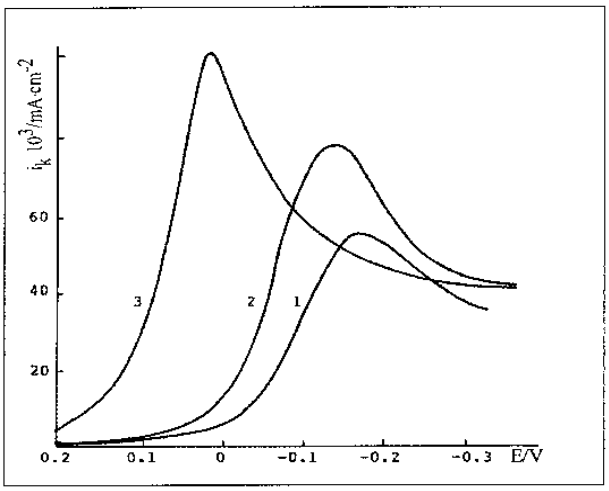

Fig. 12. Influence of the supporting solution on the reduction process of Co(III) on Pt electrode in 10^{-3} M $[Co(NH_3)_6](NO_3)_3$ solution containing: 1 – 1.0 M NH_4Cl; 2 – 1.0 M NH_4NO_3; 3 – 1.0 M $(NH_4)_2SO_4$. v_s = 0.02 V/s

values (Fig. 12, curve 1). This shift could be attributed to the formation of outer–sphere SO_4^{2-} complexes with $Co(NH_3)_6^{3+}$ ion.

The replacement of ammonia nitrate solution by ammonium chloride one, similarly as in the bromide case, leads to an increase of the cathodic reaction rate – the curve shifts to more positive potentials and the height of the $Co(NH_3)_6^{3+}$ reduction peak increases. But it has almost no influence on the limiting current value (Fig. 12, curve 3).

CONCLUSIONS

The rate of the $Co(NH_3)_6^{3+}$ electrochemical reduction process depends on the composition of the supporting solution as well as on the electrode metal applied.

The process of the electrochemical reduction on Au and Pt electrodes is irreversible when the values of the solution pH are comparatively low. The process becomes quasi-reversible with a decrease of the ratio NH_4NO_3/NH_4OH (pH increase) in the solution. The reduction of $Co(NH_3)_6^{3+}$ on Ag electrode proceeds without any great electrochemical limitations and is close to the reversible process.

The magnitude of the anion influence on the process of $Co(NH_3)_6^{3+}$ reduction depends on the nature of electrode. The inhibiting properties of the anion grow in the line: Br^-, Cl^-, NO_3^-, SO_4^{2-} and are most obvious on Au electrode. The anion influence becomes greater when the solution pH is higher.

Received 5 April 2002
Accepted 13 May 2002

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$CO(NH_3)_6^{3+}$ ELEKTROCHEMINĖ REDUKCIJA ANT ĮVAIRIŲ METALŲ PAVIRŠIAUS

S a n t r a u k a

$Co(NH_3)_6^{3+}$ komplekso elektrocheminė redukcija iki Co(II) buvo tirta ant Ag, Au ir Pt elektrodų įvairios anijoninės sudėties x NH_4NO_3 + y NH_4OH (x + y = 1,5 M) foniniuose elektrolituose. Nustatyta, kad proceso greitį riboja krūvio pernešimas bei difuzija, o reakcijos greičio konstanta priklauso nuo foninio elektrolito sudėties bei anijono prigimties. Inhibicinės anijonų savybės didėja eilėje $Br^- < Cl^- < NO_3^- < SO_4^{2-}$ ir ryškiausiai pasireiškia ant Au elektrodo.