

Polarographic Behaviour of Some Cobalt(III) Complexes with Neutral and Ionic Ligands in the Presence of Tetrabutylammonium Ion

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The electroreduction $\text{Co(III)} + \text{e}^- \rightleftharpoons \text{Co(II)}$ of Co(III) complexes with neutral and anionic ligands (NH_3 , H_2O , CO_3^{2-} , HCO_3^- , OH^-) recorded as one polarographic wave is split into two waves in the presence of tetrabutylammonium ion. The first wave corresponds to the reduction of the Co(III) complexes only with neutral ligands and the second one (more negative) to the reduction of the Co(III) complexes with anionic ligands as well.

The complex ions with anionic ligands are adsorbed in the electroreduction on the positively charged surface of the metallic electrode [1]. The surface-active ions as tetrabutylammonium cation (TBA^+) [2–6] can displace the complex ion on the electrode surface and cause an intense inhibition of the electrode reaction. The above phenomenon can be observed as the shift of the electroreduction to the more negative potentials.

This paper contains the results obtained by an investigation of two complex ions $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ in aqueous solutions.

EXPERIMENTAL

The complex compounds $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$ and $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ were prepared according to a literature method [7]. Tetrabutylammonium perchlorate was synthesized from perchloric acid and tetrabutylammonium hydroxide and then recrystallized.

Polarographic measurements were done on a OH-105 polarograph (Radelkis, Budapest). A three-electrode configuration was used consisting of a dropping mercury working electrode, a platinum foil auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE).

The solutions of the complexes were prepared by dissolution of the solid compounds in an airless 1 M- NH_4HCO_3 solution. After addition of the solid compound to the solution this was mechanically stirred until the solid was dissolved and then immediately electrolyzed.

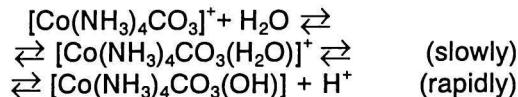
The depolarizer concentration was in the range 10^{-4} – 10^{-3} mol dm $^{-3}$ and the TBA^+ ion concentration was 2.4×10^{-4} mol dm $^{-3}$. All polarograms were made at the temperature 20 °C and were reproducible.

RESULTS AND DISCUSSION

$[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$

The one-electron electroreduction of the complex in the presence of TBA^+ ion was split into two waves, the half-wave potentials of which had more negative values than that in the case without TBA^+ (Fig. 1). The difference between the half-wave potentials of the separated waves was constant at the same concentration of TBA^+ and an increased concentration of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ ion.

The sum of heights of the split reduction wave was one half of a height of a two-electron electroreduction wave. The height of the first wave increased with the addition of $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion into the solution. Hence it follows that the complexes which are reduced as the first should not contain the anionic ligands. This was confirmed by observations obtained by electrolysis of the solution after a certain time from its preparation. The observations showed a decrease of the first wave and increase of the second one as a result of substitution and hydrolytic equilibria that cannot be neglected in this time interval. This is also consistent with the results obtained by investigation of the hydrolytic equilibria of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ ion [8]



The chelate-bonded group CO_3^{2-} does not demonstrate the properties of the negative ligands.

$[\text{Co}(\text{NH}_3)_6]^{3+}$

The splitting of the one-electron electroreduction wave in the presence of TBA^+ ion was not in such

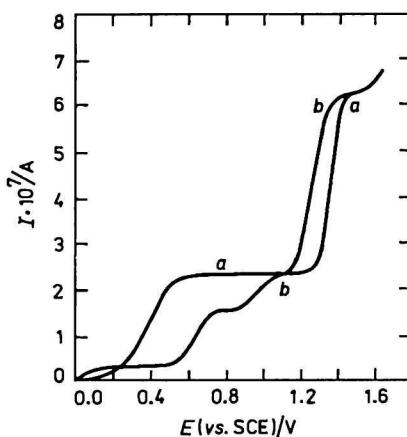


Fig. 1. Reduction of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ ion ($c = 1.0 \text{ mmol dm}^{-3}$) without (a) and with (b) TBA^+ ion ($c = 2.4 \times 10^{-4} \text{ mol dm}^{-3}$).

an extent as with $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ ion (Fig. 2), which is due to the kinetic stability of this ion. It was possible to observe on the polarogram the second but less expressive wave. As in the above case the electroreduction in the presence of TBA^+ ion was shifted to the negative potentials. The polarogram was changed with time and the increase of the second wave was observed as a consequence of hydrolytic and substitution equilibria the products of which were the complexes with the anionic ligands.

The obtained results showed that in the studied solutions two types of the Co(III) complexes were present which differentiated in the anionic ligands. The complexes are reduced at nearly same potentials* when TBA^+ ion is not present. In the presence of the surface-active cation (TBA^+) the electroreduction of the Co(III) complexes was observed at other potentials. The surface-active cations displace from the surface of the electrode the complex cations and in this way inhibit the course of the electroreduction and shift it to the negative potentials. They make the course of the electroreduction difficult in the case of the specific electrostatic interactions, i.e. the electron transfer from the electrode surface to the negative particle is the rate-determining step.

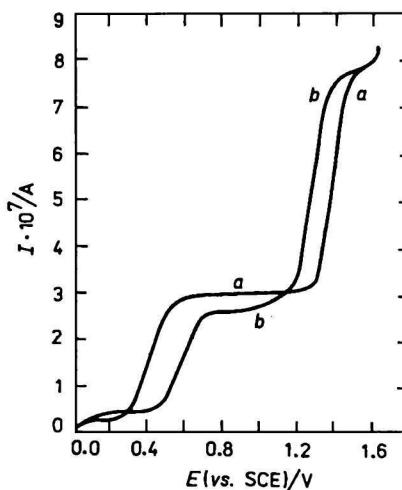


Fig. 2. Reduction of $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion ($c = 1.0 \text{ mmol dm}^{-3}$) without (a) and with (b) TBA^+ ion ($c = 2.4 \times 10^{-4} \text{ mol dm}^{-3}$).

This was confirmed by the results of the experiment. The studied Co(III) complexes with the anionic ligands are reduced (except $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ complex ion with the chelate-bonded carbonato group) in the presence of TBA^+ ion at the more negative potentials than the complexes in which the anionic ligands are not supposed.

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*Half-wave potentials of these complexes lie very close to one another so that only a single wave is observed.