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REDUCTION OF COMPLEX COBALT AMMINES WITH NEGATIVE SUBSTITUENTS IN THE INNER SPHERE AT THE DROPPING MERCURY ELECTRODE

At present, on the basis of extensive experimental material it has been shown that, in the reduction of doubly and more highly charged anions, inhibition of the reaction is observed on the $I - \varphi$ curve in the region of negative surface charges; this inhibition is associated with repulsion of the anions from the negatively charged surface and a decrease in their concentration in the surface layer (^{1}). Upon addition of an indifferent electrolyte, the decrease in current during the reduction of certain anions disappears, which may be explained by the fact that, as the concentration of the background cations increases, the electric field of the negative charges on the electrode surface is weakened.

The described inhibition of the electroreduction reaction is observed not only in the reduction of complex anions, but also in the reduction of neutral molecules. Kivalo and Laitinen observed decreases in current on the $I - \varphi$ curves for the reduction of cis-$Pt(NH_3)_2Cl_2$ (^{2}); inhibition of the reaction in the region of the potential of zero charge of mercury was observed in the reduction of the neutral complex $Pt(OH)_2(NH_3)_2Cl_2$ (^{3}).

The decreases in current during the reduction of neutral particles may be explained by the fact that, at positive charges of the mercury surface, these complexes are bound to the electrode surface through chlorine atoms carrying negative charges; but as the negative charge of the surface increases, adsorption of the complexes on the mercury surface becomes hindered (^{3,4}). The views expressed regarding the cause of inhibition of the reaction at negative surface charges, observed in the reduction of neutral complexes, were used to explain the decrease in current on the $I - \varphi$ curves during the reduction of indium from solutions of its halide salts (^{5}). A decrease in current in the region of the point of zero charge (p.z.c.) during the reduction of indium at the dropping mercury electrode has been observed by a number of authors, and various explanations have been given for this phenomenon ($^{5-7}$). In (^{7}) the appearance of a minimum on the polarization curves for the reduction of indium is explained by the "anionic character of the complex indium ions." In the work of Kh. Z. Brainina (^{5}) it is indicated that, in 0.1-3 N KCl solutions, neutral and positively charged

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

indium complexes exist, and the resulting form of the $I-\varphi$ curves is connected with the reduction of these complexes. Thus, at present there are no unambiguous data on the sign of the charge of the complex indium ion reduced at the mercury electrode.

In studying the reduction of $[Co(NH_3)_6]Cl_3$, Laitinen, Frank, and Kivalo ([8]) observed a decrease in current on the polarographic curve, which they explained by the formation on the electrode surface of a film of cobalt hydroxide. This film is formed as a result of local alkalization of the solution, due to destruction of the ammine complex occurring during its reduction at the electrode surface. We have shown ([9]) that acidification of a $[Co(NH_3)_6]Cl_3$ solution leads to the disappearance of the minimum on the $I-\varphi$

curve for the reduction of this complex; however, a further increase in the HCl concentration leads to the appearance of a minimum at other potentials. This phenomenon was explained by the formation in solution of chloro-substituted complex cobalt ammines, adsorbed on the electrode by means of negatively charged chlorine atoms. As proof, polarograms were taken for a solution of the complex cation $[Co(NH_3)_5Cl]^{2+}$. In the reduction of this cation, just as in the case of anion reduction, retardation of the reaction is observed on the $I-\varphi$ curve in the region of the so-called post-wave. However, the polarization curves for the reduction of $[Co(NH_3)_5Cl]^{2+}$ change with time, which is possibly connected with the slow reaction of inner-sphere substitution in the bulk of the solution ([10]).

Fig. 1

Fig. 2

Fig. 1. Polarization curve for the reduction of $10^{-3}\,N$ $[Co(NH_3)_4CO_3]Cl$ in the presence of $0.1\,N$ KCl

Fig. 2. Polarization curves for the reduction of $10^{-3}\,N$ $[Co(NH_3)_4CO_3]Cl$: 1—without supporting electrolyte, 2—in $1\,N$ KCl medium

To clarify the possibility of reaction retardation in the reduction of positively charged complexes, we investigated on the dropping mercury electrode the reduction of the cation $[Co(NH_3)_4CO_3]^+$, whose solutions are stable. We found no data in the literature on the polarographic reduction of the complex $[Co(NH_3)_4CO_3]Cl$.

As is seen from Fig. 1, in the reduction of $10^{-3}\,N$ $[Co(NH_3)_4CO_3]Cl$ in $0.1\,N$ KCl medium, an ordinary $I-\varphi$ curve is observed, consisting of two waves. The height of the second wave is twice that of the first; therefore the first wave corresponds to the transition Co^{3+} to Co^{2+}, and the second to the reduction

Fig. 3

Figure 2: Fig. 3

of Co^{2+} to the metal. If the complex cation is reduced from dilute solutions, then on the first wave, in the region of the so-called post-wave, a decrease in the current is observed; the current reaches a certain minimum value and then again increases to the values of the limiting diffusion current (Fig. 2). The retardation of the reaction is not associated with formation on the electrode surface of a cobalt hydroxide film, as was observed in the case of reduction of $[Co(NH_3)_6]Cl_3$, since introduction of $10^{-3}\,N$ HCl into the solution does not change the shape of the curve. Addition of $0.1\,N$ KCl or $1\,N$ KCl completely removes the reaction retardation. The limiting current in the presence of $1\,N$ KCl is smaller than in a $10^{-3}\,N$ solution of $[Co(NH_3)_4CO_3]Cl$, owing to removal of the migration effect. Increasing the charge of the background cation increases the effectiveness of the additive. As is seen from Fig. 3, the retardation of the reduction reaction of $[Co(NH_3)_4CO_3]Cl$ is removed upon addition of $BaCl_2$ at a concentration of $10^{-3}\,N$, whereas upon addition of KCl the current drop disappears only in a $0.1\,N$ KCl solution. A change in the radius of the background cations, within the experimental error, has no effect on the reaction rate. Thus, the polarization curves for the reduction of $[Co(NH_3)_4CO_3]Cl$, recorded in the presence of $10^{-3}\,N$ solutions of chlorides of alkali metals, practically coincide. Addition of the organic cation $[(C_2H_5)_4N]^+$, as well as of inorganic cations, leads to an increase in the reaction rate and to complete removal of the retardation (Fig. 4). On passing to cations with a greater length of the organic chain, a sharp retardation is observed

reaction. Introduction of $[(C_5H_{11})_4N]Br$ into the solution leads to a decrease in the reaction rate, but as the negative value of the potential is increased up to the desorption potential of tetraamylammonium cations from the electrode surface, the reaction rate increases.

Thus, in the reduction of the cation $[Co(NH_3)_4CO_3]^+$, as in the case of anion reduction, inhibition of the reaction is observed on going from positive to negative surface charges. The reaction rate depends on the nature, concentration, and charge of the background cations.

Inhibition of the reduction reaction of $[Co(NH_3)_4CO_3]^+$ may be explained by a change in the adsorption conditions when the sign of the charge on the mercury surface changes ($^{3-5}$). The positively charged complex cation $[Co(NH_3)_4CO_3]^+$ is adsorbed at positive surface charges through the negatively charged group CO_3^{2-}. When negative charges appear on the surface—

Fig. 3. Polarization curves for the reduction of 10^{-3} N $[Co(NH_3)_4CO_3]Cl$ in the presence of $BaCl_2$ at concentrations: 1—0, 2—10^{-4} N, 3—10^{-3} N.

Fig. 4. Polarization curves for the reduction of 10^{-3} N $[Co(NH_3)_4CO_3]Cl$, without background (1) and in the presence of: 2—10^{-3} N $[(C_2H_5)_4N]_2SO_4$; 3—

Fig. 4

Figure 3: Fig. 4

10^{-2} N $[(C_2H_5)_4N]_2SO_4$; 4—10^{-4} N $[(C_5H_{11})_4N]Br$; 5—$5{\cdot}10^{-4}$ N $[(C_5H_{11})_4N]Br$.

—the bond with the electrode surface must weaken and the rate of the reduction reaction of $[Co(NH_3)_4CO_3]^+$ falls. Screening of the negative surface charges by background cations leads to an increase in the reaction rate. Strongly adsorbing cations that fill the electrode surface, for example tetraamylammonium, can displace the complex cation from the electrode surface, which leads to a sharp inhibition of the reaction.

Inhibition of the reaction upon a change in the sign of the surface charge, characteristic for the reduction reaction of a series of anions, was observed by us not only in the case of reduction of the positively charged complex ion $[Co(NH_3)_4CO_3]^+$, but also in the reduction of the complex cations trans-$[Co(NH_3)_4Cl_2]^+$, $[Co(NH_3)_5NO_2]^+$, and some others.

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named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.