THE INFLUENCE OF INORGANIC AND ORGANIC CATIONS ON THE REDUCTION OF THE ANION $\mathrm{PtCl}_4^{\prime\prime}$ AT THE DROPPING MERCURY ELECTRODE

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Abstract

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N. V. NIKOLAEVA-FEDOROVICH, L. A. FOKINA, and O. A. PETRII

THE INFLUENCE OF INORGANIC AND ORGANIC CATIONS ON THE REDUCTION OF THE ANION $PtCl_4''$ AT THE DROPPING MERCURY ELECTRODE

(Presented by Academician A. N. Frumkin, April 17, 1958)

In the case of the electroreduction of certain anions, for example, S_2O_8'', $FeCy_6'''$, $HgCy_4''$, and others, a sharp inhibition of the reaction is observed in dilute solutions; this is associated with electrostatic repulsion of anions by the negatively charged electrode surface upon transition from positive charges of the electrode surface to negative ones at the point of zero charge (^{1}). Increasing the concentration of the indifferent electrolyte causes an increase in the reaction rate and, in some cases, complete removal of the inhibition. This influence of the supporting background can be explained by the fact that, as the concentration of background cations is increased, the electric field of the negative charges of the electrode surface is screened and the repulsion of anions by the electrode surface decreases. The action of organic cations $[(CH_3)_4N]^+$, $[(C_4H_9)_4N]^+$, tribenzylamine, and others is analogous to the action of inorganic cations and is manifested in the region of potentials of their adsorption (^{2}).

However, different anions show different sensitivity to the influence of additions of indifferent electrolyte (^{1}). Thus, the addition of KCl at a concentration of $1N$ completely removes the inhibition of the reduction reaction of the anion S_2O_8'', whereas in the reduction of $PtCl_4''$, in the presence of the same concentration of KCl, inhibition of the reaction is preserved, although it is observed over a narrower interval of potentials. It was therefore of interest to investigate the action of the most active inorganic and organic cations on the electroreduction of the anion $PtCl_4''$.

As is known, the effectiveness of the action of background cations on electroreduction reactions increases in the series $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ and $Ca^{++} < Sr^{++} < Ba^{++}$; for example, in the case of the electroreduction of S_2O_8'', the reaction rate on going from $0.01\,N$ LiCl to $0.01\,N$ CsCl increases by a factor of 40 ($\varphi = -1.0$ V versus the normal calomel electrode) (^{3}). Figure 1* gives the polarization curves for the reduction of the anion $PtCl_4''$ in the presence of $1N$ chlorides of the alkali metals. As can be seen from the figure presented, the addition of indifferent electrolyte leads to an increase in the reaction rate

Fig. 1 and Fig. 2: polarization curves

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over the entire range of potentials of adsorption of the background cations (^{4}). The reaction rate, as in the case of reduction of S_2O_8'', depends on the nature of the background cation, but even in the presence of 1N CsCl the inhibition of the reaction is not completely removed. The organic cations $[(CH_3)_4N]^+$ and $[(C_2H_5)_4N]^+$ also accelerate the electroreduction reaction of $PtCl_4''$. With increasing concentration of the additive and increasing length of the organic chain, for example, upon addition of $[(C_2H_5)_4N]^+$, the effectiveness of the action of orga- the inorganic cations increases (Fig. 2). Organic cations are more effective additives than even the most effective of the singly charged inorganic cations, Cs^+, taken at the same concentration. However, the effectiveness of the action of cations on the electroreduction of anions is determined not only by their adsorbability but, apparently, by the relation between the size of the cation and the position of the center of the activated complex of the discharging anion. Thus, the cation $[(C_4H_9)_4N]^+$, which increases the rate of the reduction reaction of S_2O_8'' (^{2}), $HgCy_4''$ (^{2}) over the entire range of cation adsorption potentials, in the case of the reduction of the $PtCl_4''$ anion accelerates the reaction only at potentials more negative than −1.2 V versus the N.C.E. (Fig. 3). The acceleration of the process disappears completely at still more negative potentials, owing to desorption of the organic cation from the electrode surface. The potential at which the accelerating action of $[(C_4H_9)_4N]^+$ on the reduction reaction of $PtCl_4''$ ceases coincides with the desorption potential determined from curves of differential capacitance versus potential in the case of a mercury electrode (^{2}). In the potential region where acceleration of the reaction is observed in the presence of $[(C_4H_9)_4N]^+$, the polarization curves are distorted by the catalytic wave of hydrogen evolution, which appears in the presence of traces of platinum. At potentials more positive than −1.2 V versus the N.C.E., a decrease in the rate of reduction of

Fig. 1. Polarization curves for the reduction of $10^{-3}N$ K_2PtCl_4 at a dropping mercury electrode in the presence of: 1N NaCl (a), 1N KCl (b), 1N CsCl (c), and without additive (d)

Fig. 2. Polarization curves for the reduction of $10^{-3}N$ K_2PtCl_4 at a dropping mercury electrode in the presence of $10^{-3}N$ $[(C_2H_5)_4N]Br$ (a), $10^{-3}N$ $[(CH_3)_4N]_2SO_4$ (b), and without additive (c)

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* In all figures only that part of the polarization curve corresponding to negative surface charges is shown, since at positive charges a sharp distortion of the curve by polarographic maxima is observed.

Fig. 3 and Fig. 4: polarization curves

Figure 2: Fig. 3 and Fig. 4: polarization curves

$PtCl_4''$ is observed. With increasing concentration of $[(C_4H_9)_4N]^+$ and increasing concentration of the supporting electrolyte, the relative inhibition of the reaction is manifested more strongly (Figs. 3 and 4).

Such an action of the cation $[(C_4H_9)_4N]^+$ on the reduction of $PtCl_4''$ may be explained as follows. The anion $PtCl_4''$ has a planar configuration and is strongly adsorbed on the mercury surface. As a result, electron transfer during its reduction occurs at distances closer to the electrode than in the reduction of the anions S_2O_8'', $HgCy_4''$. Inorganic cations, having small sizes and relatively small

organic cations, for example $[(CH_3)_4N]^+$, can approach the electrode so closely that the electric field of these cations affects the reduction of $PtCl_4''$. The positive charge of the cation $[(C_4H_9)_4N]^+$, located at a large distance from the electrode surface, proves ineffective up to a potential of -1.2 V versus the SCE. The inhibition of the reaction in this potential region is associated with the removal of the accelerating action of inorganic cations, owing to their displacement, at these potentials, by the

Fig. 3. Polarization curves for the reduction of $10^{-3}N$ K_2PtCl_4 at a mercury dropping electrode in the presence of: without additives (a), $10^{-5}N$ $[(C_4H_9)_4N]_2SO_4$ (b), $10^{-4}N$ $[(C_4H_9)_4N]_2SO_4$ (c), $5 \cdot 10^{-4}N$ $[(C_4H_9)_4N]_2SO_4$ (d), $10^{-3}N$ $[(C_4H_9)_4N]_2SO_4$ (e), $5 \cdot 10^{-3}N$ $[(C_4H_9)_4N]_2SO_4$ (f).

Fig. 4. Polarization curves for the reduction of $10^{-3}N$ K_2PtCl_4 at a mercury dropping electrode in the presence of: $0.1N$ Na_2SO_4 (a), $0.1N$ $Na_2SO_4 + 10^{-3}N$ $[(C_4H_9)_4N]_2SO_4$ (b), $1N$ Na_2SO_4 (c), $1N$ Na_2SO_4 + $10^{-3}N$ $[(C_4H_9)_4N]_2SO_4$ (d).

inorganic cations, tetrabutylammonium. Comparison of the polarization curves in a solution of $10^{-3}N$ K_2PtCl_4 + $0.1N$ Na_2SO_4 and $10^{-3}N$ K_2PtCl_4 + $0.1N$ Na_2SO_4 + $10^{-3}N[(C_4H_9)N]_2SO_4$ with the $I - \varphi$ curves in the same solutions without the addition of $0.1N$ Na_2SO_4 shows that an increase in the concentration of the inorganic cation leads to an increase in the effect of relative inhibition of the reduction reaction of $PtCl_4''$ (Fig. 4). With a further increase in the concentration of Na_2SO_4 to $1N$, the potential region in which inhibition of the reaction is observed remains the same as upon addition of $0.1N$ Na_2SO_4; however, the inhibition at the minimum of the curve decreases somewhat, because at this ratio of the concentrations of the tetrabutylammonium cation ($10^{-3}N$) and the Na^+ cation ($1N$), the accelerating action of the inorganic cation begins to appear (Fig. 4). If Na^+ is replaced by a singly charged cation of larger size, for example Cs^+, then the inhibition associated with displacement of the inorganic cation from the electrode surface by the cation $[(C_4H_9)_4N]^+$ decreases. However, this difference between Na^+ and Cs^+ is smoothed out with increasing concentration of $[(C_4H_9)_4N]^+$, and in the case of addition of $10^{-3}N[(C_4H_9)_4N]^+$ to solutions of $10^{-3}N$ $K_2PtCl_4 + 0.1N$ NaCl and $10^{-3}N$ $K_2PtCl_4 + 0.1N$ CsCl, the $I - \varphi$ curves for the reduction of $PtCl_4''$ coincide completely.

The increase in the reaction rate observed at potentials more negative than -1.2 V versus the N.C.E. apparently occurs as a result of a certain deformation of the cation $[(C_4H_9)_4N]^+$ at the electrode, owing to which the center of gravity of its charge approaches the electrode surface. This is confirmed by the change in the capacitance of the mercury electrode in the presence of the cation $[(C_4H_9)_4N]^+$: up to the potential at which desorption of $[(C_4H_9)_4N]^+$ occurs, beginning with $\varphi = -1.2$ V versus the N.C.E., an increase in capacitance is observed, which may be associated with deformation of the large organic cation at the electrode surface (2). A confirmation of the correctness of the explanation given is also the fact that, in the reduction of the anion $PtCl_6''$, which has not a planar but an octahedral structure, the cation $[(C_4H_9)_4N]^+$ accelerates the first stage of the reduction reaction of $PtCl_6''$ throughout the entire range of adsorption potentials of this cation.

In connection with the experimental data we have obtained on the influence of inorganic and organic cations on the electroreduction reaction of the anion $PtCl_6''$, it is necessary to make several comments concerning the work of P. Kivalo and H. Laitinen (5), in which the theory explaining the anomalous decrease of current on the $I-\varphi$ curves for the reduction of anions by electrostatic repulsion of a negatively charged particle from a negatively charged electrode surface is criticized. P. Kivalo and H. Laitinen believe that the reduction of $PtCl_4''$ at the dropping mercury electrode is not an electrochemical process, but a purely chemical one: in the first stage of reduction, $PtCl_4''$ reacts with mercury with the formation of Hg_2^{++}, then Hg_2^{++} oxidizes $PtCl_4''$ to Hg^{++}, which again forms Hg_2^{++} by the reaction $Hg^{++} + Hg \rightarrow Hg_2^{++}$. This catalytic cycle is disrupted at more negative potentials owing to the rapid electroreduction of Hg_2^{++}, formed in the first stage at the electrode surface. The incorrectness of the assumption of a purely chemical reduction of $PtCl_6''$ by mercury has already been pointed out in the literature (6). We wish to note that the dependences we obtained for the rate of reduction of $PtCl_6''$ on the radius of the background cation, as well as the influence of organic cations on this reaction, cannot be explained by adopting the scheme of P. Kivalo and H. Laitinen. Direct proof of the correctness of the electrochemical process of reduction of $PtCl_4''$ is the fact that the action of cations on the reduction reaction of $PtCl_4''$ is observed only in the region of adsorption potentials of the organic cation (Figs. 3 and 4). These data indicate that the reduction of $PtCl_4''$ is a surface process and does not occur in the bulk of the solution.

In conclusion, we consider it our pleasant duty to express our gratitude to Academician A. N. Frumkin for constant consultation and attention to the work.

Moscow State University

named after M. V. Lomonosov

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