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Abstract

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DEPENDENCE OF CATION ADSORPTION ON THE POTENTIAL OF A PLATINUM ELECTRODE

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For most metals, the study of cation adsorption on their surface is complicated by the phenomenon of exchange between the metal cations and the intrinsic or foreign cations of the solution. Such exchange is not observed on platinum (1), which makes it convenient to compare its electrochemical and adsorption properties. Up to the present time no special studies have been known on the adsorption of cations on platinum. Certain results of the work of Erbacher (2) and Lorenz (3), relating to the adsorption of ions on platinum, do not make it possible to draw conclusions about the connection between adsorption phenomena and the structure of the electrical double layer at the metal surface. From a number of studies carried out with a mercury electrode, it followed that inorganic cations, with the exception of the thallium ion (4), do not possess specific adsorbability. For monovalent cations it was shown that they exhibit even a certain negative adsorption on mercury from concentrated solutions (5). Only for polyvalent lanthanum and thorium cations, from capacitance measurements, was an effect of their superequivalent adsorption with respect to a weak negative charge discovered, which was explained by the formation of anion–cation pairs adsorbed on the mercury surface in such a way that the anion is directed toward the solution (6).

To study the structure of the electrical double layer on metals, it was of interest to determine the dependence of cation adsorption on the potential of a platinized platinum electrode, which was done in the present work by the tracer-atom method. Cation adsorption was measured from the change in radioactivity of a solution labeled with the corresponding radioactive isotope. The method is described in detail in work (7). The electrode potential was varied over the interval from the reversible hydrogen value to the oxygen value by polarization. At each value of the potential the electrode was held for 10 min. The experiments were carried out in acidified perchloric and sulfuric acid solutions of cesium, strontium, and lanthanum salts. Radioactive isotopes of cesium Cs^{-134}, strontium Sr^{-89}, and lanthanum La^{-140} served as indicators. The solutions were prepared from twice-distilled acids and recrystallized salts. In the work,

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

the conditions of all preliminary operations in the preparation of the electrodes were strictly taken into account, since the reproducibility of the results depends strongly on this. The electrodes were platinized by the method described in work ([8]). All experiments were carried out with stirring by purified nitrogen at room temperature.

Figure 1 shows a typical curve of the dependence of the adsorption of cesium cations from a sulfuric acid solution ($2 \cdot 10^{-2}$ N Cs_2SO_4, pH 2.5) on the platinum potential. All potentials are referred to the normal hydrogen electrode. Adsorption is expressed in gram-equivalents per 1 cm^2 of true surface, determined in each experiment by comparing the length of the hydrogen portion of the charging curves with the corresponding value for smooth platinum, whose roughness factor was taken as 1.5. Figure 2 gives an analogous curve for strontium cations adsorbed from a perchloric acid solution.

From the literature data it is known that the point of zero charge of unoxidized platinum lies at potentials of 0.11-0.27 V ([8,10]). Consequently, electrostatic adsorption of cations, directly caused by attraction to the charges on the platinum surface, should be observed only at negative surface charges.

The results presented show that the dependence of cation adsorption on potential has a more complex form than corresponds to such a simple picture. As is seen from Figs. 1 and 2, in the region of the largest negative charges there is a maximum value of cation adsorption which, even without allowing for possible adsorption of H^+ ions, apparently somewhat exceeds the value required for the construction of the double layer on the surface, calculated as explained above.

Fig. 1. Dependence of the adsorption of cesium cations on potential. Solution $Cs_2SO_4(2 \cdot 10^{-1} N,\ \text{pH } 2.5)$

With a shift of the potential in the positive direction, a rapid decrease in cation adsorption is observed, corresponding to a decrease in the negative charge of the surface; however, at the zero point the adsorption of cations is not equal to zero. In the range of potentials from 0.20 to 0.45 V, corresponding to an increase in the positive charge of the surface, an increase in cation adsorption is observed.

Fig. 2. Dependence of the adsorption of strontium cations on potential. Solution $Sr(ClO_4)_2(5 \cdot 10^{-3} N,\ \text{pH } 1.85)$

The dependence of the adsorption of cations on the potential of platinum found in this region can be explained by taking into account the specific adsorption of anions. We explain the adsorption of cations on positively charged platinum by the over-equivalent adsorption of the anions SO_4^{2-} and ClO_4^- at these potentials, which was proved by direct experiments for the case of SO_4^{2-} by the tracer-atom method ([11]). It was also shown there that even at negative and zero charges of platinum there is appreciable adsorption of anions. The presence of specifically adsorbed anions at negative charges should lead to adsorption of cations exceeding that which would correspond to the negative charge of the surface. As is known, over-equivalent adsorption of anions leads to adsorption of cations on a positively charged surface also in the case of mercury ([5]). At not too high concentrations near the point of zero charge, adsorption of cations in the presence of most anions passes through a minimum ([12]).

The course of the curves in Figs. 1 and 2, which is observed at potentials more positive than 0.45 V, is, in all probability, connected with the appearance of adsorbed oxygen on the surface. As was shown earlier ([8,11]), with the onset of oxygen adsorption on platinum there is observed desorption of anions adsorbed at positive surface charges, explained

the appearance of negative charges caused by oxygen—platinum dipoles whose negative end is turned toward the solution. According to what was stated above, desorption of anions should lead to a decrease in the adsorption of cations, so long as the surface charge remains positive. This may explain the decrease in cation adsorption in the potential range 0.45–0.55 V. With a further increase in the amount of adsorbed oxygen, the charge of the platinum surface becomes negative and electrostatic adsorption of cations increases. After the potential reaches 0.7 V, the increase in the amount of adsorbed oxygen can no longer compensate for the effect of the increase in the positive jump in potential, and cation adsorption again begins to fall. At more positive potentials one can observe still further minima and maxima on the adsorption curves, possibly also connected with the appearance of surface oxides studied by V. I. Veselovsky [13]. However, definite conclusions cannot yet be drawn on this point, since with the rapid change in potential that took place in our experiments, poorly reproducible results are obtained with oxidized platinum, which is probably connected with the nonequilibrium state of the surface. A special study of the adsorption properties of oxidized platinum is necessary; this has not yet been carried out.

In the present work, some results have been obtained on the adsorption of cations on oxidized platinum at high anodic potentials. In acid solutions of various concentrations, at potentials above 1.9 V one can observe practically complete desorption of the cations Cs^+ and Sr^{2+} adsorbed at negative platinum charges. Adsorption of these cations at 1.9 V is not observed. On the basis of these results, it may be supposed that at potentials close to the potential of oxygen evolution the platinum surface is positively charged. Under these conditions, however, lanthanum and yttrium cations do not desorb completely. This can presumably be explained by their adsorption on platinum oxides, which is confirmed by the increase in desorption of these cations under cathodic polarization, which destroys the platinum oxides.

The large magnitude of cation adsorption obtained at all values of the potential is probably connected with the penetration of ions into the depth of the platinum through pores and microcracks and with their adsorption on a surface larger than that determined from charging curves. Penetration into the depth of platinum has been demonstrated by the tracer-atom method for the anions SO_4^{2-} [11], J^-, and Br^-.

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