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Abstract

Full Text

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THE INFLUENCE OF ADSORBED HYDROGEN AND OXYGEN ON ADSORPTION SHIFTS OF POTENTIAL AT A PLATINIZED ELECTRODE

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Earlier it was shown ([1,2]) that shifts of the potential of a platinum electrode, observed in the absence of oxidizing and reducing agents when a surface-inactive electrolyte, for example 1 N H_2SO_4, is replaced by an electrolyte containing surface-active ions, make it possible to draw conclusions about the adsorption of the latter. The observed potential shifts may be interpreted, with some approximation, as adsorption potentials, if adsorbed hydrogen and oxygen are absent from the surface, since their ionization distorts the results obtained ([1]). In connection with this, the initial values of the potentials φ were chosen in the potential range lying approximately between 0.3 and 0.7 V. However, in the case of anion adsorption the final values of the potentials fall into the hydrogen region, while adsorption of cations shifts the potential into the region of the onset of oxidation.

In the present work, the influence of adsorbed hydrogen and oxygen on the potential shift caused by the specific adsorption of ions was investigated. The conditions for carrying out the experiments were somewhat modified in comparison with those described earlier; namely, the volume of solution was brought to 1.2 cm^3, and the purification of the initial solution and of the solution containing the adsorbing ion was made more prolonged. These measures led to certain changes in the observed adsorption shifts of the potential. Thus, in the case of 10^{-1} N KJ, at an initial value of 0.6 V, $\Delta\varphi$ was from -0.49 to -0.51 V, instead of -0.46 V obtained under the former experimental conditions; for 10^{-1} N KBr, -0.38 instead of -0.35 V. The difference was more significant in the case of thallium sulfate. At an initial value $\varphi = 0.3$ V, $\Delta\varphi$ was 0.465 V instead of 0.6 V in the former experiments. It is possible that complete reduction of impurities—trivalent thallium or other oxidizing agents that could somewhat increase the potential shift in the anodic direction—was achieved only with more prolonged purification on the platinized electrode.

The first series of experiments was devoted to studying the influence of introducing surface-active ions into the solution on the potential of the hydrogen electrode. The electrode under investigation in 1 N H_2SO_4 solution was brought by polarization to the value of the reversible hydrogen potential. The same solution, containing a surface-active ion and saturated with hydrogen, was transferred under hydrogen pressure into the vessel with the test electrode, after which the

displacement of the potential was observed with time while hydrogen was passed through. Fig. 1a gives the results for 0.1 N KJ. All potentials are referred to the normal hydrogen electrode. As can be seen, in the presence of KJ the potential shifted in the cathodic direction by 0.018 V, but after 15–20 min returned to the initial value of the reversible hydrogen potential. Similar phenomena were previously observed in the case of a Pd electrode ([3]). The observed shift may be partly caused directly by adsorption of the J^- ion, which shifts the potential in the negative direction, but part of the shift is undoubtedly connected with desorption of hydrogen adsorbed on platinum under the influence of adsorbed J^-. The desorbing action of J^- on hydrogen adsorbed on platinum follows from the shortening of the hydrogen hold-up length on charging curves

in KI solutions (1). On desorbing, the hydrogen atoms pass into molecular hydrogen and partly into H^+ ions, which causes a shift of the potential in the cathodic direction. After some time, the increase in the concentration of dissolved hydrogen in the near-electrode layer is equalized, and the electrode potential returns to the normal hydrogen potential, which is the equilibrium value for this system, through discharge of hydrogen ions from the solution. In the case of iodine, the effects associated with hydrogen desorption and with the direct action of adsorption of the ion J^- have the same sign. From this point of view it was of interest to consider the case of the Tl^+ ion. Previously obtained charging curves in a thallium sulfate solution indicate hydrogen desorption during adsorption of Tl^+, as also during adsorption of J^-, whereas the adsorption potential of Tl^+ has a sign opposite to that of the adsorption potential of J^-. Experiment shows (Fig. 1b) that, at the reversible hydrogen potential, Tl^+ ions, like J^- ions, initially shift the potential of the hydrogen electrode in the cathodic direction, after which, after 15–20 min, the potential returns to its initial value. Since specific adsorption of Tl^+ should raise the potential, the described shift can be explained only by desorption of hydrogen from the platinum surface, which, consequently, has the predominant significance under the experimental conditions.

Fig. 1. *a* —displacement of the potential with time under the influence of the iodine ion at the reversible hydrogen potential; *b* —the same under the influence of the thallium ion at various initial potentials.

By varying the values of the initial potential in the interval from the reversible hydrogen potential to 0.8 V, we obtain a series of curves of the change of potential with time after replacing 1 N H_2SO_4 by 1 N $H_2SO_4 + 10^{-1}$ N Tl_2SO_4. In the case of positive initial potentials (Fig. 1b), the measurements were carried out while passing carefully purified nitrogen through the cell. At initial values of 0.06 V and 0.1 V, an initial shift in the cathodic direction is observed, after which the potential returns to more positive values. Evidently, the decrease in the adsorption energy of atomic hydrogen caused by adsorption of Tl^+ must lead to its partial ionization, and also (at initial values of φ that are not too positive) to desorption in the form of H_2. Superposed on the shift of φ in the cathodic direction associated with ionization of adsorbed hydrogen is the ad-

Fig. 3. Dependence of $|\Delta\varphi|$ on the initial φ for the ion Br^-

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sorption shift of the potential of the Tl^+ ion, which has the opposite sign; in addition, the liberated H_2 is removed by nitrogen. The last two circumstances lead to a gradual return of the potential to more anodic values.

Fig. 2. Dependence of $\Delta\varphi$ on the initial φ for the Tl^+ ion (I) and for the Cd^{2+} ion (II).

Beginning with an initial potential of 0.2 V, a shift of φ in the anodic direction is observed; in other words, the adsorption shift of the potential overlaps the effect associated with hydrogen desorption, which can be neglected. At

Upon reaching the value $\varphi = 0.3$ V, a maximum value $\Delta\varphi = 0.48$ V is observed, which directly reflects the change in the structure of the double layer under the influence of the specific adsorption of the ion Tl^+. With a further increase in the initial values of φ, the magnitude $\Delta\varphi$ decreases, both as a result of the decrease in adsorption of the cation at more positive φ, and especially because the final values of φ in this case fall in the region of potentials corresponding to considerable oxidation of the electrode surface, which is facilitated in the presence of the surface-active cations Tl^+ and Cd^{2+} (2). The appearance on the surface of adsorbed OH groups or O atoms is accompanied by donation of electrons to platinum and stops the displacement of the potential in the positive direction. As a result, the curve expressing the dependence of $\Delta\varphi$ on the initial potential φ with increasing φ (Fig. 2, I) passes through a maximum. Similar curves were obtained for cadmium ions (Fig. 2, II) and bromine (Fig. 3). For Tl^+ the maximum lies at 0.36 V, for Cd^{2+} at 0.32 V, and for Br^- at 0.7 V.

Fig. 3. Dependence of $|\Delta\varphi|$ on the initial φ for the ion Br^-

In interpreting the character of the observed $|\Delta\varphi|$, φ curves, it is necessary to keep the following circumstance in mind. If adsorbed hydrogen and oxygen were absent from the platinum surface, the magnitude $|\Delta\varphi|$ would have to increase monotonically with increasing φ in the case of surface-active anions, and decrease monotonically in the case of cations. When the influence of adsorbed hydrogen and oxygen is taken into account, somewhat different conclusions are obtained under two different assumptions.

1. Adsorption of the surface-active ion does not affect the adsorption of hydrogen at constant potential. As was shown in (1) for the example of the ion J^-, under this assumption the presence of adsorbed hydrogen should reduce the absolute magnitude of $\Delta\varphi$. It is easy to verify that this conclusion is equally applicable to the adsorption of cations in the hydrogen region.

2. Adsorption of the surface-active ion decreases the adsorption of hydrogen

at constant potential. As was discussed at the beginning of the present article, such desorption should increase the magnitude of $|\Delta\varphi|$ in comparison with what would be expected in the first case for anions, and still further decrease the expected effect for cations. This explains the very sharp fall of the $|\Delta\varphi|$, φ curve in the case of Tl^+ on approaching the hydrogen potential. In the case of the ion Cd^{2+}, which does not shorten the hydrogen arrest on the charging curves (2) and, consequently, does not desorb hydrogen, this decrease occurs much more slowly. The same reasoning explains the relatively slow decrease of $|\Delta\varphi|$ on approaching the hydrogen potential in the case of the ion Br^-. Similar conclusions may also be drawn with respect to the action of adsorbed oxygen.

The features of the process at such small initial values of φ, at which the hydrogen content in the bulk of the electrolyte becomes comparable to or exceeds its content on the surface, were considered at the beginning of the present communication.

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