MEASUREMENT OF ADSORPTION POTENTIALS ON SMOOTH PLATINUM

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Shifts in potentials caused by adsorptions of surface active anions and cations on platinized platinum were detected earlier [1-3]. In the current work an attempt was made to determine the adsorption potentials on a smooth platinum electrode. In this case it is inconvenient to use the method developed earlier since, because of the small surface area of the electrode, the presence, if only of traces, of unpremeditated depolarizers distorts the results of the measurements. During a study of the polarization capacity of a smooth platinum electrode Ershler used a capillary cell containing a very small volume of solution, in which the effect of depolarizers was almost eliminated [4]. However, since in order to measure the adsorption potentials it is necessary to replace an inactive solution by an active one, a capillary cell could not be used in this work. We used a cell, described in [3], with a volume of solution not exceeding 1.2 cm^3. The electrode was prepared from platinum sheet of thickness 0.1 mm and apparent surface area 18-20 cm^2, which was rolled into a cylindrical shape and surrounded a glass peg which was sealed to the cell bottom. The same relationship between the electrode surface and the volume of solution as was the case in [4] was attained in this cell, and measurement of the charging curve for smooth platinum produced results matching those produced in the cited work.

The measurements with smooth platinum were carried out in the following manner: before each experiment the platinum was pickled in hot aqua regia; traces of acid were removed by repeated washing in hot bidistillate. After this the electrode was annealed for three minutes, in a quartz tube, at rose-heat. The last operation facilitates stabilization of the initial potential, retarding the discharge on the surface of hydrogen and oxygen dissolved in the metal [5, 6]. The acid solutions were prepared by dissolving twice-distilled acid in twice-distilled water. The salts, after double crystallization, were heated in a hydrogen atmosphere at 400°. A 1 N H_2SO_4 solution was purified for 20 hr over a large platinized platinum electrode in an atmosphere of air, purified by passage through a liquid nitrogen trap, and in an atmosphere of hydrogen, purified by the same means. In this solution, which was freed from hydrogen and oxygen by prolonged passage of purified nitrogen, the electrode was polarized up to the desired potential, after which the polarizing current strength was reduced to values necessary in order to maintain constant the attained potential.[1] Under these conditions complete stabilization of the electrode potential was observed after approximately one hour, and the electrode potential remained constant after stopping the polarization, even when purified nitrogen was passed for one hour. The latter was also a check of the nitrogen purity. The adosorption potential shift, arising from replacement of the 1 N H_2SO_4 by a 1 N H_2SO_4 solution containing surface active I^- ions, was measured with the aid of an electrode prepared in this way. However, the adsorption potentials obtained on smooth platinum were lower than those obtained earlier on platinized platinum, and the results of the measurements were poorly reproducible.

A typical potential shift with time curve is plotted in Fig. 1 for smooth platinum with initial potential 0.6 v, referred to a normal hydrogen electrode. Just the same as in the case of the platinized electrode, a sharp potential shift in the direction of more negative values was observed, the potential reducing, however, not to 0.49-0.51 v (as on platinized platinum), but to a value fluctuating within the limits 0.15-0.4 v. After the first shift in the cathodic direction a reverse shift in the direction of the initial potential was observed. A similar irreproducibility of the adsorption potentials on smooth platinum was also observed in thallous sulfate solutions. Experiments with electrodes platinized to different extents, i.e., having different surface areas, were carried out in order to clarify the causes of the described effects. The electrode surface area was estimated from the length of the hydrogen delay on the anodic

charging curve (from the reversible hydrogen potential to the start of the double layer region). Potential shift with time curves, in the case of Tl^+ ion adsorption from 0.1 N Tl_2SO_4 + 1 N H_2SO_4 solutions, are plotted in Fig. 2 for electrodes having increasing degrees of platinization.

The behavior of the least platinized electrode approaches that of the smooth electrode– the first jump is small and then the potential is observed to return in the direction of the original value– in spite of the fact that the electrode surface area is of the order of twice the surface area of the smooth electrode. The potential shift increases in proportion to the increase in the surface area, at the same time, the reproducibility of the experiments improves.

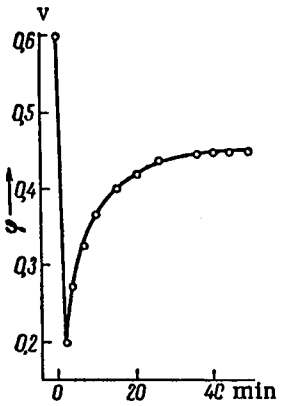

Fig. 1. Potential shift with time on smooth platinum under the influence of iodine ion adsorption from 0.1 N KI + 1 N H_2SO_4 solutions.

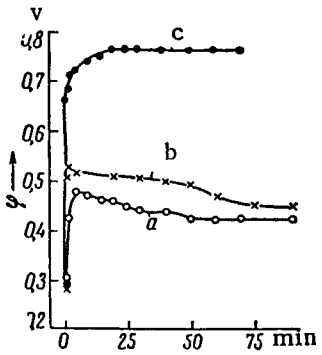

Fig. 2. Potential shift with time in 0.1 N Tl_2SO_4 + 1 N H_2SO_4 with different degrees of platinization. Length of hydrogen delay: a) 0.04 coul/cm^2; b) 0.07 coul/cm^2; c) 0.12 coul/cm^2

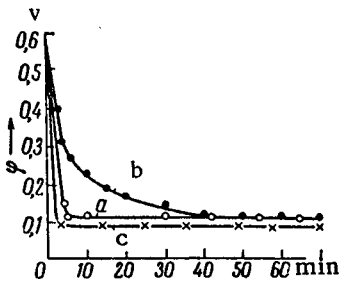

Fig. 3. Potential shift with time on smooth and platinized platinum in rigorously purified 0.1 N KI + + 1 N H_2SO_4 solution. a,b) Smooth platinum; c) platinized platinum.

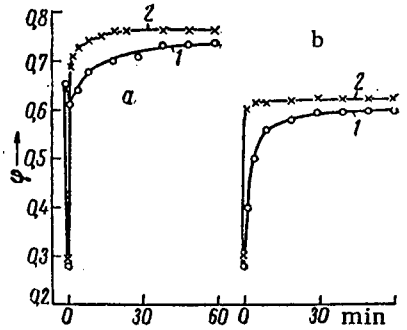

Fig. 4. Potential shift with time in rigorously purified solutions. a) 0.1 N Tl_2SO_4 + 1 N H_2SO_4; b) 0.1 N $CdSO_4$ + 1 N H_2SO_4; 1) smooth platinum; 2) platinized platinum.

These experiments caused us to assume that the potential-time relationship which was observed on smooth platinum is connected with the presence in the solution of small amounts of impurities which can be oxidized or reduced. At the potential attained by the electrode, which had been polarized to an initial potential, a certain oxidation-reduction system is established in the solution, which tends, after the first potential shift caused by adsorption, to return the electrode potential to its initial value. The kinetics of the return are established, probably, by diffusion of the components forming the oxidation-reduction system from the bulk of solution to the electrode surface. These effects, evidently, must be less apparent the larger the electrode surface area (for a fixed volume of solution). Hence, it follows that the solutions are required to be purified to the highest degree in order to obtain

accurate values of the adsorption potentials on polished platinum. With this object the time for which the solution was purified over platinized platinum in a hydrogen atmosphere was increased to 60-100 hr. Besides this, a small volume of the solution was purified for a second time over platinized platinum in a hydrogen atmosphere, this being used in one experiment, in the section of the cell adjoining the electrode compartment, which decreased the risk of contamination of the solution. It was shown during the experiment that such purification shortens the time necessary for stabilization of the initial electrode potential.

The results obtained after such purification are shown in Fig. 3 for the case when I^- ions are adsorbed from 0.1 N KI in 1 N H_2SO_4 solution. Curves a and b refer to smooth platinum and curve c to platinized platinum. As is evident, the potential shifts caused by adsorption which were obtained in this solution on smooth and on platinized platinum were almost identical, although the adsorption equilibrium was established somewhat more slowly in the case of smooth platinum. Curves 1 in Figs. 4a and b show the potential-time relationships affiliated with adsorption respectively of Tl^+ ions from 0.1 N Tl_2SO_4 + 1 N H_2SO_4 solution and Cd^{2+} ions from 0.1 N $CdSO_4$ + 1 N H_2SO_4 solution on smooth platinum. Curves 2 show the equivalent relationships for platinized platinum. Taking into account the fact that the initial potentials were 0.27 v for curves 1 and 0.3 v for curves 2, the potential shifts caused by these adsorptions on smooth and platinized platinum can be assumed to be practically identical. Some potential fluctuations with time can be seen on curve 1 in Fig. 4a, the reason for which is still not clear. It is possible that these fluctuations are connected with liberation on the surface of hydrogen and oxygen which was dissolved deeply in the platinum electrode.

The conformity of the potential shifts caused by adsorption on smooth and platinized platinum, the surface area of the latter electrode being of the order of three-times that of the smooth platinum, confirms the accuracy of the interpretation of the physical meaning of the stated quantities. However, it should be noted that in the case of smooth platinum we approached the limit to which the developed method can be applied on account of the need to increase the extent to which the solution must be purified.

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