Physical Chemistry

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1962

SovietRxiv

Abstract

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MEASUREMENT OF ADSORPTION POTENTIALS ON SMOOTH PLATINUM

(Presented by Academician A. N. Frumkin on 16 IX 1961)

In earlier works ($^{1-3}$), potential shifts caused by the adsorption of surface-active anions and cations on platinized platinum were determined. In the present work an attempt was made to determine adsorption potentials on a smooth platinum electrode. In this case, the application of the method developed is made difficult by the fact that, because of the small surface area of the electrode, the presence of even traces of incidental depolarizers distorts the measurement results. In studying the polarization capacitance of a smooth platinum electrode, Ershler used a capillary cell with an insignificant volume of solution, in which the influence of depolarizers was almost eliminated (^{4}). However, since in measuring adsorption potentials it is necessary to replace an inactive solution with an active one, the capillary cell could not be used in the present work. We used the cell described in (^{3}), with a solution volume not exceeding 1.2 cm^3. An electrode made of platinum foil 0.1 mm thick, with a visible surface area of 18–20 cm^2, rolled into a cylinder, surrounded a glass finger sealed into the bottom of the cell. In this cell the same ratio between the electrode surface and the solution volume was achieved as in (^{4}), and measurement of the charging curve of smooth platinum gave results coinciding with those obtained in the cited work.

Measurements with smooth platinum were carried out as follows: before each experiment the platinum was etched in hot aqua regia; traces of acid were repeatedly washed off in hot bidistilled water. After this the electrode was annealed for 3 min in a quartz tube at a pink heat. The latter operation facilitates stabilization of the initial potential by delaying the emergence onto the surface of hydrogen and oxygen dissolved in the metal (^{5,6}). The solutions were prepared with twice-distilled water from twice-distilled acid. After double crystallization, the salts were calcined in an atmosphere of hydrogen at 400°. A 1 N H_2SO_4 solution was purified for 20 h on a large platinized platinum electrode in an atmosphere of air purified by passage through a trap with liquid nitrogen and in an atmosphere of hydrogen purified in the same way. In this solution, which was freed from hydrogen and oxygen by prolonged passage of purified nitrogen, the electrode was brought by polarization to the desired value of the potential, after which the magnitude of the polarizing current was reduced to the values necessary to maintain constancy of the potential attained. Under these conditions, after approximately an hour complete stabilization of the electrode potential

Fig. 1-3

Figure 1: Fig. 1-3

was observed; it retained a constant value after cessation of polarization even with hourly passage of purified nitrogen. The latter also served as a check on the purity of the nitrogen. With the electrode prepared in this way, the adsorption shift of the potential arising when 1 N H_2SO_4 was replaced by a 1 N H_2SO_4 solution containing surface-active ions J^- was measured. However, the values of the adsorption potentials obtained on smooth platinum were

lower than those obtained earlier on platinized platinum, and the measurement results were poorly reproducible.

Fig. 1 shows a typical curve of the change in potential on smooth platinum with time at an initial potential of 0.6 V vs. n.h.e. As in the case of the platinized electrode, a sharp shift of the potential toward more negative values is observed; however, it amounted not to 0.49–0.51 V (as on platinized platinum), but varied within the range 0.15–0.4 V. After the initial shift in the cathodic direction, a reverse displacement toward the initial values was observed. The same irreproducibility of adsorption potentials on smooth platinum was also observed in thallium sulfate solutions. To clarify the cause of the phenomena described, experiments were carried out with electrodes of different degrees

Fig. 1. Shift of the potential on smooth platinum with time under the influence of adsorption of iodide ion from $0.1\,N$ KI $+ 1\,N$ H_2SO_4

Fig. 2. Shift of the potential with time in $0.1\,N$ Tl_2SO_4 $+ 1\,N$ H_2SO_4 at different degrees of platinization: a—hydrogen-retention length 0.04 coul/cm^2, b—0.07 coul/cm^2, c—0.12 coul/cm^2

Fig. 3. Shift of the potential with time on smooth and platinized platinum in a previously purified solution of $0.1\,N$ KI $+ 1\,N$ H_2SO_4: a, b—smooth, c—platinized platinum

of platinization, i.e., with different surface areas. The latter was estimated from the hydrogen-retention length on the anodic charging curve (from the reversible hydrogen potential to the beginning of the double-layer region). Curves of the change in potential with time during adsorption of Tl^+ ion from $0.1\,N$ $Tl_2SO_4 +$ $1\,N$ H_2SO_4 for electrodes with increasing degrees of platinization are plotted in Fig. 2.

The behavior of the electrode with the smallest coating approaches that of a smooth electrode—the initial jump is small and a return of the potential toward the initial values is observed, despite the fact that the surface of the electrode was two orders of magnitude larger than the surface of the smooth electrode. As the surface area increases, the potential shift increases and, at the same time, the reproducibility of the experiments improves.

Fig. 4. Potential displacement with time in highly 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

Figure 2: Fig. 4. Potential displacement with time in highly 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 led to the supposition that the dependence of the potential on time observed on smooth platinum is connected with the presence in the solution of small amounts of impurities that can be oxidized or reduced. When the electrode potential is brought by polarization to the initial value, a certain oxidation-reduction system is created in the solution, which tends to return the electrode potential to its initial value after the initial potential shift caused by adsorption. The kinetics of the return are probably determined by diffusion of the components of the formed oxidation-reduction system from the volume of the solution to the electrode surface. These effects must, evidently, be the more will appear less, the larger the electrode surface (for a given volume of solution). It followed from this that, in order to obtain correct values of the adsorption potentials on smooth platinum, a higher degree of purification of the solutions is required. For this purpose, the duration of purification of the solution on platinized platinum in a hydrogen atmosphere was brought up to 60–100 h. In addition, secondary purification was introduced on platinized platinum in a hydrogen atmosphere for a small volume of solution, used in a single experiment, in the part of the cell directly adjacent to the electrode space; this reduced the danger of contamination of the solution along its path. During the experiment it turned out that such purification shortens the time required for stabilization of the initial value of the electrode potential.

Fig. 4. Potential displacement with time in highly 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.

Figure 3 gives the results obtained after such purification during adsorption of J^- from a $0.1\,N$ KJ solution against a background of $1\,N$ H_2SO_4. Curves *a* and *b* refer to smooth platinum, and curve *c* to platinized platinum. As can be seen, the adsorption shifts of potential obtained in this solution on smooth and platinized platinum almost coincide, although adsorption equilibrium is established, in the case of smooth platinum, as if somewhat more slowly. Curve 1 in Figs. 4*a* and *b* gives the dependence of the potential on time during adsorption, respectively, of Tl^+ ions from $0.1\,N$ $Tl_2SO_4 + 1\,N$ H_2SO_4 and Cd^{2+} ions from $0.1\,N$ $CdSO_4 + 1\,N$ H_2SO_4 on smooth platinum. Curve 2 in the same figures represents the same dependences for platinized platinum. Taking into account that the initial potential for curve 1 was 0.27 V, and for curve 2, 0.3 V, the adsorption shifts of potential on smooth and platinized platinum may be regarded as practically coincident. On curve 1 of Fig. 4*a* some oscillations of the potential with time are visible, the cause of which is not yet clear. It is possible that these oscillations are connected with the emergence at the surface of hydrogen and oxygen dissolved in platinum from the interior of the electrode.

The coincidence of the adsorption shifts of potential on smooth and on platinized platinum, the surface of which exceeds that of smooth platinum by three orders of magnitude, confirms the correctness of the interpretation of the physical meaning of the indicated quantities. It should, however, be noted that in the case of smooth platinum we are approaching the limit of applicability of the method developed, because of the increased requirements on the degree of purity of the solution.

I express my gratitude to Academician A. N. Frumkin for valuable guidance in carrying out the present work.

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Received
10 IX 1961

CITED LITERATURE

1. A. D. Obrucheva, ZhFKh, **32**, 2155 (1958).
2. A. D. Obrucheva, DAN, **120**, 1072 (1958).
3. A. D. Obrucheva, DAN, **141**, No. 6 (1961).
4. B. V. Ershler, *Acta Physicochimica URSS*, **7**, 327 (1937).
5. G. A. Deborin, B. V. Ershler, ZhFKh, **14**, 708 (1940).
6. A. D. Obrucheva, ZhFKh, **26**, 1472 (1952).

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