DETERMINATION OF THE ZERO-CHARGE POTENTIAL OF RHODIUM IN ACID SOLUTION BY MEANS OF RADIOACTIVE TRACERS

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UDC 541.13

To understand the adsorption behavior of rhodium in various solutions, we need to know its zero-charge potential in these solutions. So far there is only publication [1] on this subject: it gives data on the adsorption of ions from acid sodium chloride solution (1 N, pH 2), giving an idea of the way in which the adsorption of Cl^- ions by rhodium depends on the potential, and estimating the zero-charge point. For solutions of surface-active ions, we know of some unpublished work by Lunev, who studied the way in which adsorption of ions depends on the potential of a rhodium electrode in acid sodium sulfate solution (1 N, pH 1.7) [2]. These two authors obtained their results by titrating solutions in which adsorption of ions caused variation in the hydrogen-ion concentration. This method, of course, gives the difference between the adsorption of cations and anions.

Our aim in this work was to study the dependence of adsorption of Na^+ and SO_4^{2-} ions on the rhodium potential and to determine the zero-charge point of the rhodium surface in acidified solutions of sodium sulfate. The amount of adsorption was measured by means of radioactive tracers – a direct quantitative method.

The radioactive tracers were the isotopes Na-22 and S-35, added to the solution in the form of sodium sulfate. In all the experiments, the initial potential was that of a reversible hydrogen electrode in the given solution. The rhodium electrode was first cathodically reduced in sulfuric acid, and then immersed in the experimental solution and brought to the initial potential in an atmosphere of hydrogen. Dissolved hydrogen was then removed in an atmosphere of argon or nitrogen, and by means of a decreasing anode current the electrode was given a definite potential at which it was held without current long enough to attain a constant adsorption of ions. The electrode was then taken out, weighed to determine the amount of solution adhering to it, dried, and placed in a counter apparatus to measure its radioactivity. After washing off adsorbed ions with water and cathodic-anodic polarization in sulfuric acid, we again immersed the electrode in the same solution and repeated all the above operations, so as to determine the adsorption of anions and cations at all the required potentials. The number of ions adsorbed was calculated from the measured radioactivity of the whole electrode surface, with a correction for the adherent layer of solution by the method described in [3].

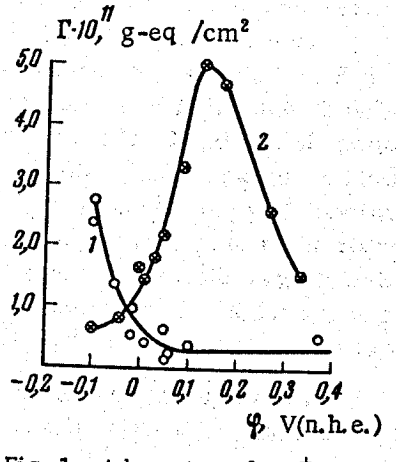


Fig. 1. Adsorption of Na^+ cations (1) and SO_4^{2-} anions (2) versus potential of rhodium in solution of $1 \cdot 10^{-2}$ N Na_2SO_4 + $1 \cdot 10^{-2}$ N H_2SO_4. Potentials are referred to normal hydrogen electrode.

The electrodes were electrolytic rhodium deposits obtained by coating a platinum sheet (2 × 2 cm) in a solution of rhodium chloride in the usual conditions for platinizing. The weight of the coating was about 0.03 g. The true electrode surface was calculated from the amount of adsorbed hydrogen, in a way similar to that used in the case of platinized platinum [4], with the aid of charging curves measured in sulfuric acid. For this purpose, by extrapolation of the double-layer part of the charging curve on to the axis of abscissas, we determined the quantity of electricity expended on ionization of the hydrogen adsorbed on the rhodium. In calculating the surface area it was assumed that each rhodium atom adsorbs one hydrogen atom, and that the number of rhodium atoms per square cm is $1.39 \cdot 10^{15}$ [2]. The true electrode surface was 2-2.5 thousand times the apparent surface.

Figure 1 plots the adsorption of Na^+ cations (curve 1) and SO_4^{2-} anions (curve 2) versus the potential of the rhodium electrode. As will be seen from

Electrochemistry Institute, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 3, No. 5, pp. 656-659, May, 1967. Original article submitted December 22, 1966.

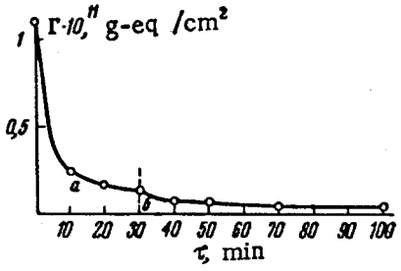


Fig. 2. Elution of Na^+ ions, adsorbed at reversible hydrogen potential, from rhodium surface: section a) water; section b) 0.1-1.0 N sulfuric acid with or without anode polarization.

this figure, the adsorption of cations is equal to the adsorption of anions at −0.03 V. This is therefore the zero-charge potential of the rhodium surface in an acid solution of sodium sulfate. The value obtained for the zero-charge potential of rhodium in 0.01 N Na_2SO_4 is close to the value obtained with a 1 N concentration of the same salt and the same solution pH [2].

On comparing this result with the data in [1], we see that the zero-charge potential of rhodium in sodium chloride solution is about 70 mV more negative than that in a sulfate solution. Thus, as we observe for other metals, the Cl^- anion is surface-active towards rhodium, and displaces its zero-charge point towards the negative. The zero-charge potential of rhodium in acidified sodium sulfate is about 200 mV more negative than the zero-charge potential of platinum in the same conditions [5].

Corresponding with the change of sign and value of the surface charge on rhodium when the potential shifts towards the negative from the zero point, we observe an increased adsorption of cations; while when it shifts towards the positive, we observe an increased adsorption of anions. However, the latter phenomenon goes on only up to 0.12 V. At more positive potentials we find a decrease in adsorption of anions: this may be explained by adsorption of oxygen which displaces the anions from the rhodium surface. This agrees with the charging curves, which show that adsorption of oxygen on rhodium takes place at less positive potentials than on platinum at the same pH [2].

In the sodium sulfate solutions under study, the concentrations of Na^+ and H^+ ions were equal. Reduction of the H^+ concentration by an order of magnitude does not cause an appreciable change in the adsorption of Na^+ anywhere in the potential range. At reversible hydrogen potential, the adsorption of Na^+ ions in a solution with pH 2 is $2.7 \cdot 10^{-11}$ g · equ/cm², and in a solution of pH 3 it is $4.1 \cdot 10^{-11}$ g · equ/cm² true electrode surface. Thus the Na^+ adsorption increases as the H^+ concentration decreases: this may be due either to increase in the negative surface charge, or to reduction in the competing adsorption of H^+ ions. Our results indicate that Na^+ ions are adsorbed in preference to H^+ ions. This is also confirmed by the slowness of desorption of Na^+ ions adsorbed on rhodium in solutions of sulfuric acid of various concentrations up to 1 N. The adsorption on rhodium of ions by a surface of like charge is evidence for specific adsorption of Na^+ ions and SO_4^{2-} ions. This adsorption reaches its maximum value at the zero-charge potential of rhodium, where it is about $0.9 \cdot 10^{-11}$ g · equ/cm².

Figure 2 plots the quantity of Na^+ adsorbed by a rhodium surface versus the time required to wash it off by means of water or sulfuric acid: it will be seen that Na^+ is only very slowly desorbed. When the electrode is washed with double-distilled water in air or hydrogen, there remains after 10 min more than 20% of the amount adsorbed at hydrogen potential. Further washing in water takes place even more slowly, and after 30 min only 88% is washed off. If the water is replaced by sulfuric acid (0.1 N), with or without anodic polarization, desorption of Na^+ is at first somewhat accelerated (apparently owing to exchange of Na^+ with H^+ cations), but then desorption again slows down. About 5% of the initial quantity remains practically unaffected in these conditions. This phenomenon may be due to the formation of a strong bond between the cations and oxygen, which is easily adsorbed by rhodium, especially at potentials acquired by the electrode in an atmosphere of hydrogen, in which all the radioactivity measurements were carried out. Subsequent treatment of the rhodium surface with hydrogen in a sulfuric acid solution, even with cathode polarization, did not lead to appreciable reduction of the amount of Na^+ remaining.

Thus the adsorption of cations is much greater than that of anions in the region of negative surface charges on rhodium, and the adsorption of anions exceeds that of cations even more strongly at positive surface charges: this indicates that specific adsorption of both types of ion by rhodium, accompanied by adsorption of the oppositely-charged ion, occurs to a very limited extent. A similar phenomenon occurs for platinum [3].

We would like to thank Academician A. N. Frumkin for valuable comments on our work.

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