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V. E. KAZARINOV, N. A. BALASHOVA

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Abstract

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V. E. KAZARINOV, N. A. BALASHOVA

ON THE DEPENDENCE OF ION ADSORPTION ON THE POTENTIAL OF PLATINUM

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The connection between the structure of the electrical double layer and the potential of platinum over a wide range of potentials was first established experimentally and substantiated theoretically in works ([1]). In them, the difference between the adsorption values of anions and cations was measured from the change in the concentration of hydrogen ions in solution.

For a more detailed study of the structure of the electrical double layer, data are needed on the dependence of the adsorption values of anions and cations on the potential, obtained by an independent method.

The purpose of the present work was to obtain such data using acidified solutions of Cs_2SO_4 and solutions of H_2SO_4 over a broad concentration range as examples, and also to study the adsorption properties of platinum in H_2SO_4 at high anodic potentials.

The dependence of the adsorption value of Cs^+ and ${SO_4}^{2-}$ ions on the potential ϕ was measured on platinized platinum by the following procedure. After recording a charging curve in 0.1 N H_2SO_4 to determine the true surface area,* the electrode was washed in twice-distilled water in a hydrogen atmosphere, and then for 16 hours in air. The electrode thus prepared was immersed in a solution containing H_2SO_4 labeled with S^{35}, or Cs_2SO_4 labeled with Cs^{134}. By creating a hydrogen atmosphere and cathodic polarization, the electrode potential was brought to the reversible hydrogen potential; then, in a nitrogen atmosphere, by an anodic current of decreasing density it was shifted to the specified value, at which, in the absence of polarization, the electrode was held for 15 min. The shift of ϕ during this time did not exceed 20 mV. After this the electrode was removed from the cell, weighed to determine the amount of solution carried out, and then dried. Next, the radioactivity of the electrode was measured on an end-window counter. From its magnitude, with a correction for the radioactivity of the solution carried out, the adsorption value was calculated ([3]). The electrode was then immersed in the solution, and all operations were repeated in the same order; the final values of the potential lay in the range from the reversible hydrogen potential to +1.2 V.

Figure 1

Figure 1: Figure 1

The reproducibility of adsorption values on one and the same electrode is $±$5%, and on different electrodes $±$15%. Increasing the holding time of the electrode at a given ϕ from 15 minutes to 1 hour did not lead to an increase in the adsorption value. This indicates its equilibrium value under these conditions. The results obtained are presented in Fig. 1. The dependence of the adsorption value of $SO_4{}^{2-}$ anions on ϕ in a solution of 10^{-2} N Cs_2SO_4 + 10^{-2} N H_2SO_4, within the reproducibility of the results, coincides with that for pure H_2SO_4 (curve 2).

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* The true surface area was determined from the length of the hydrogen part of the charging curve, assuming that each surface atom of platinum ($1 \cdot 31 \cdot 10^{15}$ atoms/cm^2) adsorbs one hydrogen atom ([2]). The true surface area calculated in this way exceeded the geometric area by 2-4 thousand times.

Joint consideration of curves 2 and 4 shows that equality of the adsorption values of anions and cations occurs at $\varphi = 0.17$ V vs. N.H.E. This potential corresponds to the point of zero charge (p.z.c.) and agrees with its determinations by other methods. At potentials negative with respect to the p.z.c., the electrode adsorbs predominantly cations. Their adsorption near the reversible hydrogen potential is practically constant. This means that the change in φ, at a high degree of surface coverage by adsorbed hydrogen, occurs either through a change in the amount of the latter, or through

Fig. 1. Dependence of the magnitude of ion adsorption on potential: 1 –SO_4^{2-} in 0.1 N H_2SO_4; 2 –SO_4^{2-} in 0.01 N H_2SO_4 or 0.01 N Cs_2SO_4 + 0.01 N H_2SO_4; 3 and 3′ –SO_4^{2-} in 0.001 N H_2SO_4; 4 –Cs^+ in 0.01 N Cs_2SO_4 + 0.01 N H_2SO_4; 5 –Cs^+ in 0.018 N Cs_2SO_4 + 0.002 N H_2SO_4 (1-5 –platinized platinum); 6 –SO_4^{2-} in 0.1 N H_2SO_4 and 7 –SO_4^{2-} in 0.01 N H_2SO_4 (6-7 smooth platinum)

a change in the capacitance of the electrical double layer ([1]). Comparison of the adsorption values of Cs^+ at these potentials (curves 4 and 5) shows that Cs^+ is adsorbed preferentially over H^+.

When φ is shifted in the positive direction from the p.z.c., there is a linear increase in the adsorption of SO_4^{2-} up to the potential at which oxygen adsorption begins. The adsorption of Cs^+ in this region of φ is many times smaller than that of SO_4^{2-}. Its nature cannot be established on the basis of these data. The dependence of the adsorption of Cs^+ on φ, with an almost tenfold excess of Cs^+ compared with the concentration of H^+ in the solution (curve 5), has the same form as when their concentration ratio is 1:1 (curve 4). It follows from this that, on a positively charged surface, first, there is no specific adsorption of Cs^+, in agreement with ([4]); second, no preferential adsorption of H^+ compared with

Cs^+ is observed; and, third, there is no appreciable superequivalent charge of the adsorption surface of SO_4^{2-}. The last conclusion is confirmed by comparing capacitance values calculated, on the one hand, from adsorption data and, on the other, from the charging curve, in the same way as was done in ([5]). Such a comparison for 0.1 N H_2SO_4 shows that in the potential range 0.3-0.8 V, according to the adsorption data, the capacitance is 36 ± 5 $\mu F/cm^2$, whereas the charging curve gives larger values, namely 70 ± 7 $\mu F/cm^2$ for φ = 0.3-0.5 V and 150 ± 15 $\mu F/cm^2$ for φ = 0.5-0.8 V. The larger capacitance values obtained from the charging curve also indicate that, alongside the adsorption of SO_4^{2-} in the double-layer potential region, part of the charges delivered to the electrode is consumed in other processes. These, apparently, are

are the ionization of firmly bound hydrogen at φ 0.3-0.5 V and the adsorption of small amounts of oxygen at φ 0.5-0.8 V.

The potential of the adsorption maximum of SO_4^{2-} in 0.1 N H_2SO_4 corresponds to the potential at the beginning of the oxygen part of the charging curve. Further adsorption of oxygen leads to partial displacement of adsorbed SO_4^{2-} ions, which is expressed the more strongly the lower the acid concentration. The nature of the bond of SO_4^{2-} adsorbed on oxidized platinum is different from that in the absence of adsorbed oxygen and is, apparently, chemisorptive. This is indicated by the slowness of their exchange with the same anions of the solution, as well as by the slowness with which the equilibrium value of adsorption is attained on preliminarily oxidized platinum.

On the reverse run of curves 1-3 (Fig. 1 gives curve 3′ for 0.001 N H_2SO_4) hysteresis is observed, the more pronounced the lower the acid concentration. The cause of the hysteresis is the mutual influence of anions and oxygen during adsorption ([7]). The conclusion regarding the chemisorptive nature of the bond of SO_4^{2-} with oxidized platinum is consistent with a number of other works ([8]).

Comparing the positions of the potential of the maximum relative to the reversible hydrogen potential in the same solution, one can see that oxidation of platinum in more dilute acid solutions begins at less positive potentials. This conclusion, however, requires additional confirmation because of the small number of points near the maxima.

From Fig. 1 it is seen that at φ positive by 0.8 V no increase in the amount of adsorption of Cs^+ is observed, while the amount of adsorption of SO_4^{2-} is greater than that for Cs^+. This means that, under equilibrium conditions in H_2SO_4 solutions (> 0.001 N), adsorption of oxygen leads only to a decrease in the positive charge of the surface, and not to its overcharging (in contrast to acids of lower concentrations ([8]) and neutral solutions ([1])).

The results obtained in the present work on the adsorption of ions on platinized platinum are in good agreement with the data of ([1], [5]), but differ from other data ([9]). The reasons for the existing differences will be considered in a separate article.

Adsorption of SO_4^{2-} at high anodic φ was studied on smooth platinum electrodes prepared in the same way as in ([6]). After being held for 15 min at a given φ in labeled H_2SO_4, they were removed, rinsed in three portions of water for 30 sec each, and dried. Increasing the holding time to 30 min did not lead to a noticeable increase in the amount of adsorption. From the radioactivity of the electrode, measured on a 4π-counter, the amount of adsorption was calculated, which, of course, is not the equilibrium value, but constitutes only a certain part of it.

Thus, one can obtain information on the relative change in the amount of adsorption and in the strength of the bond of SO_4^{2-} with the surface upon changing φ. The results of the experiments are represented by curves 6 and 7. The amount of adsorption is given per unit geometric surface area. It is seen that at potentials above 1.5 V a sharp increase in adsorption is observed, as was first pointed out by Schwabe ([10]). The sulfuric acid adsorbed under these conditions is washed off only very slowly in water, alkali, and acid in air, but is readily desorbed during cathodic polarization in the same solutions (in 3 min at $i = 20$ mA/cm^2, $> 99.5\%$ is desorbed). Apparently, SO_4^{2-} anions enter into the composition of oxides and for this reason are strongly retained by the surface. These data confirm the observations of other authors on changes in the surface properties of platinum at potentials above 1.5 V ([11]).

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Institute of Electrochemistry
Academy of Sciences of the USSR

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