

DEPENDENCE OF THE ADSORPTION OF IONS ON THE POTENTIAL OF PLATINUM

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The relationship between the structure of the electric double layer and the potential of platinum was first experimentally established and theoretically substantiated within a broad region of potentials [1]. In these studies, the difference in the values of the adsorption of anions and cations was measured according to the change in the hydrogen ion concentration in solution.

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

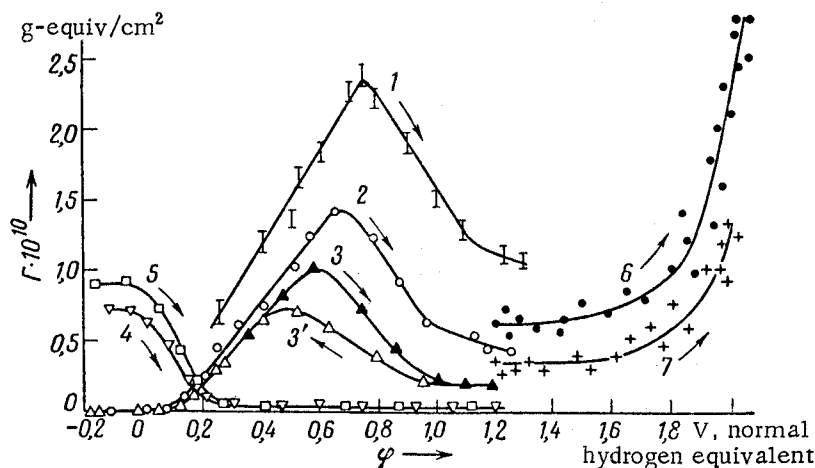
The purpose of this work was to obtain such data for the example of acidified solutions of Cs_2SO_4 and solutions of H_2SO_4 within a broad range of concentrations, as well as to study the adsorption properties of platinum in H_2SO_4 at high anode potentials.

The dependence of the adsorption of the ions Cs^+ and SO_4^{2-} on the potential φ was measured on platinized platinum according to the following procedure. After taking the charging curve in 0.1 N H_2SO_4 to determine the true value of the surface,* the electrode was washed in double-distilled water in an atmosphere of hydrogen, and then for 16 h in air. The electrode prepared in this way was lowered into a solution containing H_2SO_4 , labeled with S^{35} , or Cs_2SO_4 , labeled with Cs^{134} . By creating a hydrogen atmosphere and cathode polarization, the electrode potential was brought up to the reversible hydrogen potential; then it was lowered to a set value in an atmosphere of nitrogen with an anode current of decreasing density, and the electrode was maintained at this potential for 15 min in the absence of polarization. The displacement 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 that it carried out, and then dried. Then the radioactivity of the electrode was measured on an end-window counter. The value of the adsorption was calculated according to its value with a correction for the radioactivity of the solution carried out [3]. Then the electrode was lowered into the solution, and all the operations were repeated in the same order; the final values of the potential lay within the range from the reversible hydrogen potential to +1.2 V.

The reproducibility of the values of the adsorption on the same electrode was $\pm 5\%$, while on different electrodes it is $\pm 15\%$. Increasing the exposure of the electrode at set φ from 15 min to one hour did not lead to any increase in the value of the adsorption. This indicates that it possesses an equilibrium value under such conditions. The results obtained are presented in Fig. 1. The dependence of the value of the adsorption of SO_4^{2-} anions on φ in a solution of 10^{-2} N Cs_2SO_4 + 10^{-2} N H_2SO_4 coincides with that for pure H_2SO_4 within the limits of reproducibility of the results (curve 2).

A joint consideration of curves 2 and 4 shows that equality of the values of the adsorption of anions and cations occurs when $\varphi = 0.17$ V, normal hydrogen equivalent. This potential corresponds to the point of zero charge and agrees with its determination by other methods. An electrode more negative than the point of zero charge adsorbs predominantly cations. The value of their adsorption close to the reversible hydrogen potential is practically constant. This means that the change in φ at high degrees of coverage of the surface by adsorbed hydrogen occurs either

*The true value of the surface was determined from the length of the hydrogen portion of the charging curve, considering that each surface platinum atom ($1 \cdot 31 \cdot 10^{15}$ at/cm²) adsorbs one hydrogen atom [2]. The true surface, calculated in this way, was 2-4 thousand times as great as the geometrical surface.



Dependence of the adsorption of ions on the 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).

on account of a change in the amount of the latter, or on account of a change in the capacitance of the electrical double layer [1]. A comparison of the values of the adsorption of Cs^+ at these potentials (curves 4 and 5) shows that Cs^+ is adsorbed predominantly before H^+ .

In the case of displacement of φ in the positive direction from the point of zero charge, a linear increase occurs in the value of the adsorption of SO_4^{2-} , all the way up to the potential of the beginning of the adsorption of oxygen. The value of 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 value of the adsorption of Cs^+ on φ in the presence of a practically 10 fold excess of Cs^+ in comparison with the H^+ concentration in solution (curve 5) takes the same form as at a 1:1 concentration ratio (curve 4). From this it follows that on a positively charged surface, in the first place, there is no specific adsorption of Cs^+ , in agreement with [4]; in the second place, no predominant adsorption of H^+ in comparison with Cs^+ is observed; in the third place, there is no appreciable adsorption of SO_4^{2-} above the equivalent charge of the surface. The latter conclusion is confirmed by a comparison of the values of the capacitance, calculated, on the one hand, from adsorption data, and, on the other, on the charging curve, as was done in [5]. Such a comparison for 0.1 N H_2SO_4 shows that in the region of potentials 0.3-0.8 V, according to the adsorption data, the capacitance is $36 \pm 5 \mu\text{F/cm}^2$, while according to the charging curve, large values are obtained namely $70 \pm 7 \mu\text{F/cm}^2$ for φ 0.3-0.5 V, and $150 \pm 15 \mu\text{F/cm}^2$ for φ 0.5-0.8 V. The large values of the capacitance, obtained according to the charging curves, are also evidence that, in addition to the adsorption of SO_4^{2-} in the double layer region of potentials, part of the charges communicated to the electrode are consumed for other processes. Such, for example, are the ionization of the 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 maximum adsorption of SO_4^{2-} in 0.1 N H_2SO_4 corresponds to the potential of the beginning of the oxygen portion of the charging curve. Further adsorption of oxygen leads to a partial displacement of the adsorbed SO_4^{2-} ions, which is more strongly pronounced, the lower the oxygen concentration. The nature of the bond of the SO_4^{2-} adsorbed on oxidized platinum is different from that in the absence of adsorbed oxygen and is apparently chemisorbed. This is indicated by the slowness of their exchange with the same anions of the solution, as well as by the slowness of the reaching of an equilibrium value of the adsorption on preliminarily oxidized platinum.

In the reverse path of the curves 1-3 (the figure gives curve 3' for 0.001 N H_2SO_4), there is a hysteresis, expressed more distinctly, the lower the acid concentration. The cause of the hysteresis is the mutual influence of the anions and oxygen during adsorption [7]. The conclusion of the chemisorption character of the bond of SO_4^{2-} to oxidized platinum agrees with a number of other studies [8].

Comparing the position of the potential of the maximum with respect to the reversible hydrogen potential in the same solution, we can see that the oxidation of platinum in more dilute solutions of acid begins at less positive potentials. Such a conclusion, however, requires supplementary confirmation, in view of the small number of points close to the maxima.

From the figure, we can see that at φ more positive than 0.8 V, no increase in the adsorption of Cs^+ is observed, while the value of the adsorption of SO_4^{2-} is greater than that for Cs^+ . This means that under equilibrium conditions, in solutions of H_2SO_4 (> 0.001 N), the 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 this 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 causes of the existing differences will be discussed in a separate article.

The adsorption of SO_4^{2-} at high anode φ was studied on smooth platinum electrodes, prepared in the same way as in [6]. After exposure for 15 min at set φ in labeled H_2SO_4 they were removed, rinsed with three portions of water for 30 sec each, and dried. Increasing the exposure to 30 min did not lead to any appreciable increase in the value of the adsorption. The value of the adsorption, which, of course, is not the equilibrium value, but comprises a certain portion of it, was calculated according to the radioactivity of the electrode, measured on a 4π -counter.

Thus, information can be obtained on the relative change in the value of the adsorption and strength of the bond of SO_4^{2-} to the surface in the case of variation of φ . The experimental results are represented by curves 6 and 7. The value of the adsorption is given, calculated per unit geometrical surface. It is evident that at potentials higher than 1.5 V, a sharp increase in the adsorption is observed, which was first indicated by Schwabe [10]. Sulfuric acid adsorbed under these conditions is very slowly washed off in water, alkali, and acid in air, but is readily desorbed in the case of cathodic polarization in the same solution ($> 99.5\%$ is desorbed in 3 min at $i = 20$ mA/cm²). Apparently the SO_4^{2-} anions are contained in the oxides, and for this reason are stably retained by the surface. These data confirm the observations of other authors on the change in surface properties of platinum at potentials higher than 1.5 V [11].

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LITERATURE CITED

1. A. N. Frumkin, *Phys. Zs. Sowjetunion*, **4**, 246 (1933); A. Shlygin, A. Frumkin, and V. Medvedovskii, *Acta physicochim. URSS*, **4**, 911 (1936); A. Frumkin and A. Shlygin, *Acta physicochim. URSS*, **6**, 819 (1936).
2. B. V. Ershler, *Acta physicochim. URSS*, **7**, 327 (1937); M. Breiter, C. Knorr, and W. Völkl, *Zs. Elektrochem.*, **59**, 681 (1955); A. I. Pletyushkina, G. P. Khomchenko, and G. D. Vovchenko, *Collection: Catalytic Reactions in the Liquid Phase* [in Russian], Alma-Ata (1963), p. 295.
3. N. A. Balashova and N. S. Merkulova, *Collection: New Methods of Physicochemical Investigation, Transactions of the Institute of Physical Chemistry, Academy of Sciences, USSR* [in Russian], Moscow (1957), p. 12; V. E. Kazarinov and N. A. Balashova, *Advanced Scientific-Technical and Industrial Experience* [in Russian], No. 17-62-883/7, Moscow (1963), p. 18.
4. A. D. Obrucheva, *DAN*, **120**, 1072 (1958).
5. A. Frumkin and A. Shlygin, *DAN*, **2**, 173 (1934).
6. V. E. Kazarinov and N. A. Balashova, *DAN*, **139**, 614 (1961).
7. Ch. Wessmantel, *Dissertation, Tech. Hochschule Dresden, Inst. Elektrochem. u. phys. Chem.*, (1958); J. Belloni-Cofler, *Theses, Paris* (1961).
8. N. A. Balashova and A. N. Frumkin, *DAN*, **20**, 449 (1938); N. A. Balashova, *Wiss. Zs. Tech. Hochschule Dresden*, **12**, 1177 (1963).
9. N. A. Balashova, *DAN*, **103**, 639 (1955); N. A. Balashova, *Zs. phys. Chem.*, **207**, 340 (1957); N. A. Balashova, V. A. Ivanov, and V. E. Kazarinov, *DAN*, **115**, 336 (1957); N. A. Balashova and N. S. Merkulova, *Transactions of the Fourth Conference on Electrochemistry* [in Russian], *Izd. AN SSSR* (1959), p. 48.
10. K. Schwabe, *Elektrochim. acta*, **6**, 223 (1962).
11. V. I. Ginzburg and V. I. Veselovskii, *ZhFKh*, **24**, 336 (1950); T. I. Borisova, *Transactions of the Third Conference on Electrochemistry* [in Russian], *Izd. AN SSSR* (1953), p. 386; M. Breiter and B. Kennel, *Zs. Elektrochem.*, **64**, 1180 (1960).