STATE OF THE SURFACE OF THE PLATINIZED PLATINUM ELECTRODE IN SULFATE SOLUTIONS AT POTENTIALS IN THE "DOUBLE LAYER" REGION

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When the potential of a platinum electrode in sulfuric acid solution lies within the interval 350-750 mV, relative to the reversible hydrogen electrode in the same solution (φ_r), the electrode is said to be in the "double layer" region. However, according to data in [1], adsorbed gases may be present on the surface of the electrode in this region of potentials. This is confirmed by the results of Kazarinov and Balashova, whereby the double layer capacity calculated from data on the adsorption of SO_4^{2-} ions in the 0.3-0.8 V interval, is 36 ±5 $\mu F/cm^2$, while a calculation from the charging curve slope for 0.3-0.5 V gives about 70 $\mu F/cm^2$ [2]. These measurements, however, do not allow one to determine whether the increase in the charging curve slope is associated with the ionization of the last portion of adsorbed hydrogen, or whether it is caused by simultaneous adsorption of oxygen.

To resolve this question, we performed experiments using a method proposed by Frumkin and Shlygin [3]. Experiments were performed on a Pt/Pt electrode at room temperature. Preparation of the electrode, construction of the electrolytic cell, and the experimental procedure are described in detail in [4].

The change in the open-circuit potential of the Pt/Pt electrode was determined when the solution 1N Na_2SO_4 + 0.01 N H_2SO_4 was replaced by 1N KCl + 0.01 N HCl.

While the change from one solution to the other is made, without passage of current, a constant surface density of hydrogen, in the Gibbs thermodynamic sense, or, differently, the total electrode surface charge, Γ_H, is conserved [3, 5]. Thus we find on the charging curves points which correspond to identical values of Γ_H for the solution being studied.

These points are connected in Fig. 1 by arrows, which are practically vertical for our arrangement of charging curves along the abscissa. Also shown in Fig. 1 are Γ_{H^+}, φ_r curves (Γ_{H^+} is the surface density of hydrogen ions), constructed from data from [1] and [4], and the dependence on potential of the amount of adsorbed hydrogen, A_H, on the electrode. The latter was calculated according to the equation $\Gamma_H = A_H - \Gamma_{H^+}$ [3]. If, in the 1N KCl + 0.01 N HCl solution, there is a vertical region on the A_H, φ_r curve, corresponding to A_H [3], then the $A_H \varphi_r$-curve in the interval of φ_r = 350-750 mV in the 1N Ha_2SO_4 + 0.01 N H_2SO_4 solution has a considerable slope. This is in agreement with the results of [1] and [2], on the presence of gases adsorbed on the electrode in the "double layer" region.

The intersection of the line $A_H = 0$ with the A_H, φ_r curve in the solution 1N Na_2SO_4 + 0.01 N H_2SO_4 occurs at φ_r near 350 mV. This is the same potential at which $A_H = 0$ in the solution under study. Consequently, one can expect the appearance of adsorbed oxygen on a platinized platinum electrode at such low potentials in a sulfuric acid solution. That is, in sulfuric acid, as in basic solution [3], the regions of hydrogen and oxygen adsorption overlap. A similar phenomenon probably occurs in the case of solutions of other acids which contain anions with low surface activities (e.g., ClO_4^-, HPO_4^{2-}, etc.). It should be noted that the first portion of oxygen appears on platinized platinum in sulfuric acid solutions at potentials lower than φ_r, at which the electrooxidation of a series of organic substances in steady state conditions begins at an appreciable rate (e.g., methanol [6]). This supports the possibility of electrooxidation of organic substances in which OH_{ads} particles participate, as proposed in the series of work [7, 8, 9].

The data in Fig. 1 show also that a correction for the charging of a double layer on the platinum electrode by a linear extrapolation of the double layer region of the charging curve may introduce errors in the determination of the amount of hydrogen adsorbed on the electrode. Thus it is found that, with extrapolation, the amount of adsorbed hydrogen is larger by 10% in the solution 1N KCl + 0.01 N HCl, while the magnitudes 1N Na_2SO_4 + 0.01 N H_2SO_4 turn out to be identical in a correction account of the amount of charge expended charging the double layer.

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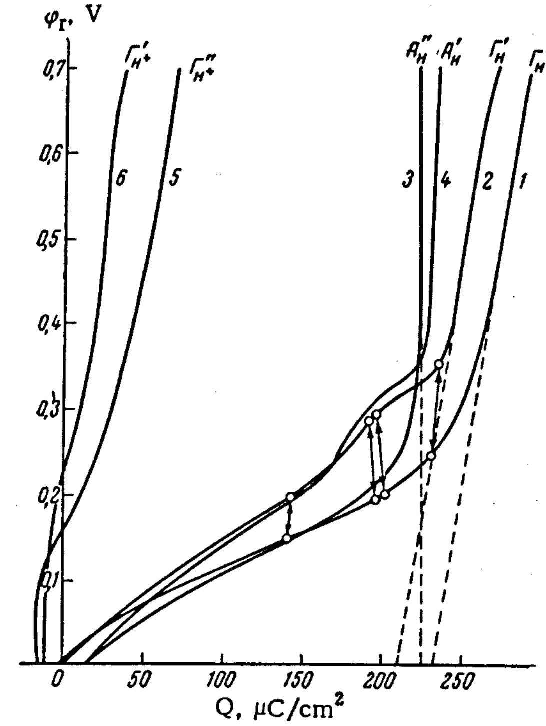

Fig. 1. Charging curves (1, 2) dependence of A_H on φ_r (3, 4) and adsorption curves (5, 6) for 1 N Na_2SO_4 + 0.01 N H_2SO_4 solutions (2, 4, 6) and for 1 N KCl + 0.01 N HCl solutions (1, 3, 5). Curve 6 is taken from [1].

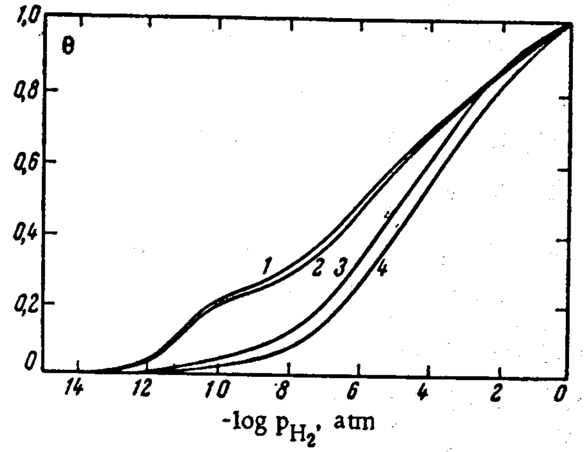

Fig. 2. Hydrogen adsorption isotherms, calculated from A_H, φ_r-curves (2, 4) and from charging curves with linear extrapolation in the double layer region (1, 3) in 1 N Na_2SO_4 + 0.01 N H_2SO_4 (1, 2) and in 1 N KCl + 0.01 N HCl (3, 4).

In the determination of the amount of adsorbed hydrogen in sulfuric acid solutions, errors associated with extrapolation of the double layer region are insignificant, while they reach about 10% in hydrochloric acid solution.

Hydrogen adsorption isotherms, calculated from A_H, φ_r-curves and from charging curves, with linear extrapolation of the curve in the double layer region, are shown in Fig. 2. The results shown allow an evaluation of the errors introduced into the calculations by the estimate of the double layer charge. These errors may reach significant magnitudes in the case of HCl solutions.

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LITERATURE CITED

1. A. Shlygin, A. Frumkin, and V. Medvedovskii, Acta Physicochem. URSS, 4, 911 (1936).
2. V. Ye. Kazarinov and N. A. Balashova, Coll. Czech. Chem. Comm., 30, 4184 (1965).
3. A. Frumkin and A. Shlygin, Izv. AN SSSR, Ser. Khim., 773 (1936); Acta Physicochem. URSS, 5, 819 (1936).
4. O. A. Petrii, R. V. Marvet, and A. N. Frumkin, Élektrokhimiya, 3, 116 (1967).
5. A. N. Frumkin, O. A. Petrii, and R. V. Marvet, J. Electroanalyt. Chem., 12, 504 (1966).
6. Khira Lal, O. A. Petrii, and B. I. Podlovchenko, Élektrokhimiya, 1, 316 (1965).
7. A. N. Frumkin and B. I. Podlovchenko, Dokl. AN SSSR, 150, 349 (1963); O. A. Petrii, B. I. Podlovchenko, A. N. Frumkin, and Khira Lal, J. Electroanalyt. Chem., 10, 253 (1965).
8. J. O'M. Bockris and H. Wroblowa, J. Electroanalyt. Chem., 7, 428 (1964).
9. V. S. Bagotskii and Yu. B. Vasil'eva, Electrochim. Acta, 9, 869 (1964).