

# DIRECT EVIDENCE OF THE ADSORPTION OF NEUTRAL ORGANIC COMPOUNDS ON PLATINUM AT HIGH POSITIVE POTENTIALS

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The adsorption of neutral organic compounds on platinum detected earlier [1, 2] at high positive potentials ( $\varphi$ ) is of interest for a number of fields of electrochemistry [3]. The investigation of this phenomenon had been conducted up to the present time only by indirect methods; thus far there had been no direct evidence of the adsorption of organic substances in the region of the potentials of liberation of oxygen. To obtain such data, in this work we studied the dependence of the adsorption  $\Gamma$  of benzene and naphthalene on the potential of a smooth platinum electrode in the range  $\varphi_r = 1.2$ -2.3 V ( $\varphi_r$  is the value of the potential relative to a reversible hydrogen electrode in the same solution) by the method of radioactive tracers. We also investigated the influence of these substances on the adsorption of anions of sulfuric acid in this potential region.

The measurements were performed in a thermostatically controlled ( $t = 20 \pm 1^\circ$ ) cell on a rotating platinum disc electrode, pressed into Teflon, with a geometrical surface of  $0.68 \text{ cm}^2$ . The rate of rotation was 6500 rpm. The potential was set with a P-5827 potentiostat. The following reagents were used in the work: sulfuric acid redistilled twice; cryoscopic benzene redistilled twice; cp naphthalene sublimed twice; labeled sulfuric acid  $\text{H}_2\text{S}^{35}\text{O}_4$  ( $I_{sp} \approx 200 \text{ mCi/mmole}$ ); labeled ( $1 \text{ C}^{14}$ ) benzene ( $I_{sp} \approx 0.5 \text{ mCi/mmole}$ ); labeled ( $1 \text{ C}^{14}$ ) naphthalene ( $I_{sp} \approx 2 \text{ mCi/mmole}$ ). \* The solutions were prepared in double-distilled water.

Before each measurement the electrode was activated by a single anodic-cathodic polarization ( $i_a = 30 \text{ mA}$ , 10 min;  $i_c = 30 \text{ mA}$ , 10 min), washed in double-distilled water in air, and exposed at the adsorption potential in the investigated solution for 5 min. Then it was removed from the cell, washed with rotation in three portions of double-

distilled water for 10 sec each, and dried with filter paper. The radioactivity was measured on a gas-flow counter. The amount of adsorbed radioactive substance was calculated by the usual method [4]. The average deviation in three parallel determinations did not exceed  $\pm 7\%$ . The values of the adsorption are given calculated per  $\text{cm}^2$  of visible surface.

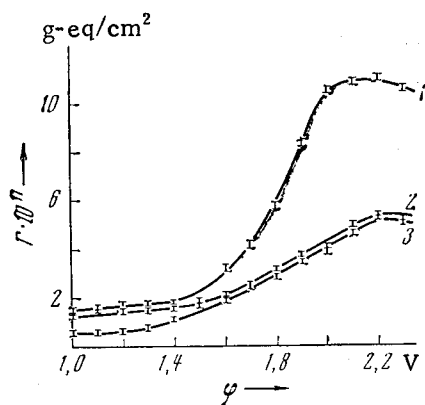


Fig. 1. Dependence of the adsorption of sulfuric acid on the potential of a platinum electrode from a solution of 0.01 N  $\text{H}_2\text{SO}_4$  (1) and with additions of  $2 \cdot 10^{-2} \text{ M}$  benzene (2) or  $2 \cdot 10^{-4} \text{ M}$  naphthalene (3).

The results of the measurements with labeled sulfuric acid are presented in Fig. 1. At the potentials 1.0-1.5 V the adsorption of sulfate ions is small ( $1.2$ - $1.6 \cdot 10^{-11} \text{ g-eq/cm}^2$ ). Then, beginning with  $\varphi_r = 1.6 \text{ V}$  it increases, reaching a value of  $\Gamma = 1.1 \cdot 10^{-10} \text{ g-eq/cm}^2$  at  $\varphi_r = 2.2 \text{ V}$ . The results of measurements at  $\varphi \leq 1.8 \text{ V}$  agree with those published earlier [5]. The higher values of the adsorption cited in [6] at  $\varphi = 2.3 \text{ V}$  are evidently due to substantial differences in the experimental conditions, namely, substantially higher concentrations of the solutions and low temperatures.

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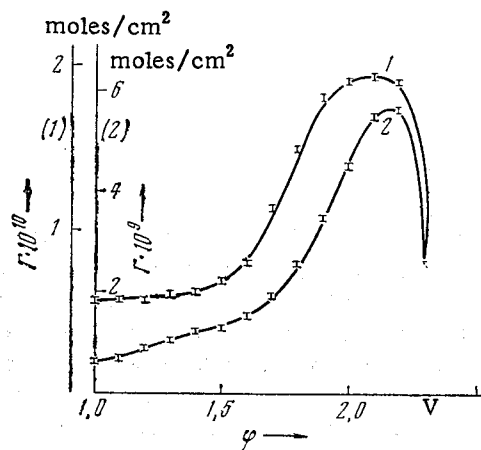


Fig. 2

Fig. 2. Dependence of the adsorption of benzene (1) and naphthalene (2) on the potential of a platinum electrode from solutions of  $2 \cdot 10^{-2}$  M benzene and  $2 \cdot 10^{-4}$  M naphthalene, respectively. Background 0.1 N  $\text{H}_2\text{SO}_4$ .

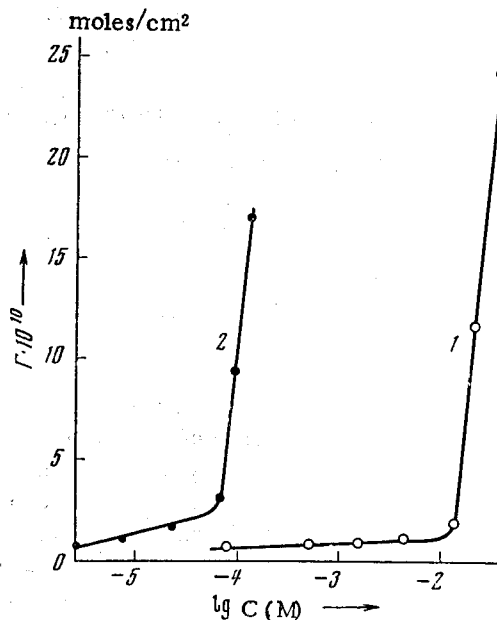


Fig. 3

Fig. 3. Dependence of the adsorption of benzene (1) and naphthalene (2) on their concentration on a platinum electrode at  $\varphi_r = 2.0$  V. Background 0.1 N  $\text{H}_2\text{SO}_4$ .

When benzene is added to the solution ( $C = 2 \cdot 10^{-2}$  M), there is a substantial decrease in the adsorption of sulfate ions in the range 1.6-2.3 V (curve 2) as a result of their displacement from the surface by organic molecules. An analogous effect is also produced by the addition of naphthalene ( $C = 2 \cdot 10^{-4}$  M); in this case a decrease in the adsorption is observed in the entire range of potential studied (curve 3). Despite the substantial differences in concentrations the degree of displacement of anions is practically the same for both substances at  $\varphi_r > 1.6$  V. It should be kept in mind that the solution of naphthalene is close to saturated. As will be shown below, this circumstance substantially influences the adsorption of the organic substance.

Figure 2 presents the dependence of the adsorption of benzene and naphthalene on the electrode potential from  $2 \cdot 10^{-2}$  and  $2 \cdot 10^{-4}$  M solutions, respectively. As can be seen, curves of  $\Gamma$  vs  $\varphi_r$  have a maximum in the region of  $\varphi_r = 2.1-2.2$  V. The adsorption reaches extremely high values ( $\Gamma_{\text{C}_{10}\text{H}_8} = 5.7 \cdot 10^{-9}$  mole/cm<sup>2</sup>,  $\Gamma_{\text{C}_6\text{H}_6} = 1.9 \cdot 10^{-10}$  mole/cm<sup>2</sup>).

When the potential is varied from  $\varphi_{\text{max}}$  in the negative direction, a substantial hysteresis is observed between the "forward" and "reverse" paths of the  $\Gamma$  vs  $\varphi_r$  curves (the values of  $\Gamma$  corresponding to the reverse path are higher than in the case of the direct path); there is no appreciable desorption of hydrocarbons even at low potentials, all the way to  $\varphi_r = 0$ . It should be noted that preliminary oxidation of platinum in a solution of 1 N  $\text{H}_2\text{SO}_4$  at  $\varphi_r = 2.2$  V only slightly (by 20-25%) decreases the adsorption activity of the electrode with respect to the indicated compounds.

In the range of potentials of the extreme, the dependence of the adsorption of both hydrocarbons on their concentration  $C$  (at  $C \ll C_{\text{sat}}$ ) is approximated in a first approximation by the equation of a logarithmic isotherm (Fig. 3). On the basis of potentiodynamic measurements it was established earlier that in solutions of hydrocarbons at concentrations  $C \geq 0.2 C_{\text{sat}}$  there is a sharp, almost abrupt increase in the degree of coverage [8]. As can be seen from Fig. 3, direct adsorption measurements confirm this effect. In the indicated concentration interval, regardless of the absolute value of  $C_{\text{sat}}$  a sharp increase in the value of  $\Gamma$  is observed, all the way up to values corresponding to tens of monolayers. (In a saturated solution of benzene, for example,  $\Gamma = 5.3 \cdot 10^{-8}$  mole/cm<sup>2</sup>.) Adsorbed benzene and naphthalene are not removed by repeated washing of the electrode in double-distilled water or sulfuric acid. Purification of the surface occurs only after prolonged cathodic-anodic polarization.

Thus, in this work direct evidence of the substantial irreversible adsorption of organic compounds on platinum at potentials all the way up to 2.3 V was obtained for the first time. The interpretation of the adsorption phenomena observed on oxidized platinum will require new approaches. The nature of the phenomenon is scarcely exhausted by the hypotheses of the ligand theory of chemisorption [7] or  $\pi$ -electronic interaction of the adsorbate with the positively charged surface of the electrode [1], on the basis of which we should have expected a higher adsorbability of unsaturated or aromatic compounds, which is not confirmed experimentally [8]. It is characteristic that the extreme dependence of the adsorption of an organic substance on the potential of oxidized platinum, the existence of which was detected in [9] and recently confirmed in [7], coincides with the region of potentials of reaching the maximum coverage of the surface by chemisorbed oxygen [10] as well as anions of sulfuric acid [5, 6]. The energy of the bond of platinum to the organic adsorbate is so high that neutral molecules displace the chemisorbed oxygen firmly bound to the metal [1, 7] and specifically adsorbed sulfate anions. The adsorption is irreversible, which is evidently associated with deep insertion of the organic molecule into the oxide and the formation of extremely stable surface compounds. The possibility remains that at concentrations of the adsorbate close to saturation a polymer film with high conductivity is formed on the surface of the electrode. From the results cited it also follows that in quantitative investigations of adsorption under the conditions considered, the contribution of anions of the electrolyte cannot be ignored [11].

In the electrochemical literature the idea is widespread that the anodic polarization of platinum metals at potentials  $\varphi_F \geq 1.2$ -1.4 V, when the coverage of the surface with  $O_{ads}$  reaches substantial values, leads to complete desorption and oxidation of the adsorbed organic molecules. "Cleaning" of the surface by oxidation of the electrode at these potentials is widely used (see, for example, [12]). The material presented shows that this viewpoint cannot be considered sufficiently substantiated.

To determine the nature of the phenomena described, a detailed investigation of the state of the electrode surface as well as the composition of desorption and oxidation products of neutral substances is essential.

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