ADSORPTION OF BENZENE, PHENOL, AND NAPHTHALENE ON PLATINUM

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The adsorption of benzene, phenol, and naphthalene on smooth and platinized platinum was studied by the method of radioactive tracers in conjunction with electrochemical methods. The kinetics of the adsorption of these substances at various pH of the solution, the dependences of adsorption on the electrode potential, and the concentration of the adsorbate in solution were measured. The irreversible nature of the adsorption of benzene, phenol, and naphthalene on platinum was demonstrated. It was established that in the case of phenol and naphthalene at $\varphi_r \leq 0.05$ V, there is an accumulation of hydrogenation products on the electrode.

A number of studies have been devoted to the investigation of the adsorption behavior of benzene, phenol, and naphthalene on smooth and platinized platinum [1-7]. According to [1-3, 7], the adsorption of these substances is reversible. The bell-shaped dependence of the values of the adsorption of benzene, naphthalene, and phenol on the potential with a maximum at $\varphi_r \approx 0.5$ V is explained by the equilibrium competitive adsorption of water molecules and the organic substance, while the potential of the maximum of adsorption is related to the zero charge potential [8-10]. Analogous representations were also used in a later study [11]. This viewpoint was criticized in [6, 12]. However, there were no direct experimental data, confirming the irreversible nature of adsorption of the indicated substances.

To clarify the adsorption behavior of benzene, naphthalene, and phenol on smooth and platinized platinum, in this work we used a radiochemical method, proposed in [13-17], in conjunction with electrochemical methods. The true surface of the electrodes was determined according to the adsorption of hydrogen: In the case of smooth platinum (Pt) the method of rapid i versus φ curves was used,* and in the case of platinized platinum (Pt/Pt) the method of charging curves was used. The true surface exceeded the visible surface by approximately fivefold in the case of Pt and 1000-fold in the case of Pt/Pt. The platinizing of the electrodes was conducted at room temperature from solutions of 3% H_2PtCl_6 in a cell with unseparated anodic and cathodic spaces with a current of 2 mA/cm^2 of visible surface. After electrodeposition, the electrodes were subjected to cathodic polarization in 0.1 N H_2SO_4 at 50°C for 2 h to obtain stable (resistant to "aging") Pt/Pt electrodes [15].

We used radioactive preparations of benzene (1-6-C^{14}; MRTU 6-02-356-66; specific activity 1.1 mCi/mmole), phenol (1-C^{14}; MRTU 6-02-356-66; specific activity 0.4 mCi/mmole) and naphthalene (1-C^{14}; produced by the radiochemical center at Amersham, England; specific activity 2 mCi/mmole†). The absolute values of the adsorption of benzene, phenol, and naphthalene were calculated by comparison with a standard consisting of the limiting value of the adsorption of methanol ($3.6 \cdot 10^{14}$ particles/cm^2) on the same electrode [15]. The concentration of benzene and phenol was 10^{-2} M in all the experiments, while that of naph-

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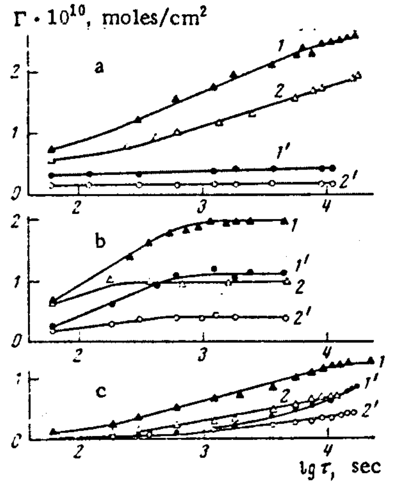

Fig. 1

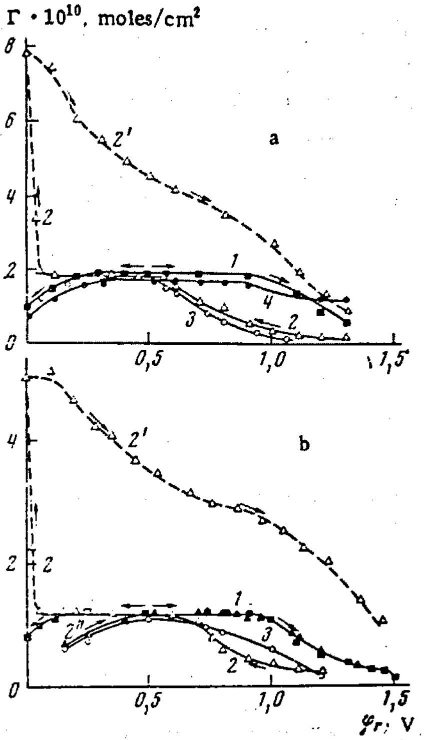

Fig. 2

Fig. 1. Kinetics of the adsorption on Pt/Pt of phenol (a), benzene (b), and naphthalene (c) in 0.1 N H_2SO_4 (1, 2) and in 0.1 N NaOH (1', 2') at potentials 0.5 V (1, 1') and 0.15 V (2, 2').

Fig. 2. Dependence of the values of the adsorption of naphthalene on the potential (in Figs. 2-4 the direction of the change in the potential is indicated by arrows; explanations in text). a) Pt: 1) in 0.1 N H_2SO_4 (behavior in the chemisorbed layer), 2, 2') in a solution of $4 \cdot 10^{-5}$ M $C_{10}H_8$ + 0.1 N H_2SO_4; 3) constructed according to the limiting values of the adsorption reached at a constant potential in the same solution as curve 2; 4) in a solution of $4 \cdot 10^{-5}$ M $C_{10}H_8$ + 0.1 N NaOH with an arbitrary direction of variation of the potential. b) Pt/Pt: 1) in 0.1 N H_2SO_4 (behavior in the chemisorbed layer); 2, 2') in a solution of $2 \cdot 10^{-4}$ M $C_{10}H_8$ + 0.1 N H_2SO_4; 3) constructed according to the values of the adsorption reached in 5 h at a constant potential in the same solution as curve 2.

thalene was $2 \cdot 10^{-4}$ M in the case of Pt/Pt and $5 \cdot 10^{-5}$ M in the case of Pt. To maintain a constant concentration of aqueous solutions of benzene and naphthalene, the solution was periodically replaced with new portions.

The kinetics of the adsorption of benzene, naphthalene, and phenol in 0.1 N H_2SO_4 and 0.1 N NaOH was studied in the region of φ_r = 0.0-1.2 V. Equilibrium values of the adsorption of benzene, naphthalene, and phenol on smooth platinum in the region of potentials 0.05-1.2 V were reached within 10-15 min.

The reaching of equilibrium values of the adsorption on Pt/Pt requires a substantially longer time: in the case of benzene 20-30 min; phenol and naphthalene more than 5 h (Fig. 1). From the figure it is also evident that the kinetics of the adsorption of benzene, naphthalene, and phenol obeys the principles characteristic of processes of adsorption on a uniformly inhomogeneous surface. For calculations of the kinetic parameters of such processes, the Roginskii–Zel'dovich equation can be used:

$$V_{ads} = \frac{d\theta}{d\tau} = K_{ads} c \exp(-\alpha/\theta),$$

where V_{ads} is the rate of adsorption; θ is the degree of surface coverage, equal to Γ/Γ_{max}; τ is the time of adsorption; K_{ads} is the rate constant of adsorption; c is the concentration of the substance to be ad-

TABLE 1. Dependence of the Values of αf and K_{ads} of Benzene, Phenol, and Naphthalene on the Potential of a Pt/Pt Electrode and the pH of the Solution

Substance	pH	φ_r	K_{ads}	αf	Substance	pH	φ_r	K_{ads}	αf
Naphthalene	1	0,15	2,4	9	Benzene	1	0,15	0,3	8
		0,25	4,5	8			0,5	1,4	4
		0,50	8	5		2,7	0,15	0,4	6
		0,8	7	8			0,5	0,5	5
		1,2	0,4	34			0,15	0,3	18
	2,7	0,15	1,2	10		13	0,5	0,5	5
		0,5	3,3	5	Phenol	1	0,15	0,3	15
		0,15	0,5	10			0,5	1	8
	13	0,5	0,7	5					

sorbed; α is a coefficient, equal to the ratio of the change in the activation energy of adsorption to the change in the characteristic heat of adsorption ($0 \leq \alpha \leq 1$); f is a coefficient characterizing the degree of surface inhomogeneity.

We calculated the coefficients αf and the rate constants of adsorption entering into this equation for various potentials of the Pt/Pt electrode and various pH of the solution (Table 1). The values of the adsorption of benzene, naphthalene, and phenol from saturated solutions of them at $\varphi_r = 0.5$ V in 0.1 N H_2SO_4 ($2 \cdot 10^{-10}$, $1.2 \cdot 10^{-10}$, and $2.6 \cdot 10^{-10}$ moles/cm², respectively) were arbitrarily taken as Γ_{max}. In the case of naphthalene and phenol, these values are actually close to the limiting balues of the adsorption, while in the case of benzene they are smaller than Γ_{max}, as will be evident from the data presented below.

The dispersion of the values of the adsorption to be determined for various electrodes is ±5%. Analogous calculations were made of αf at other potentials in the region $\varphi_r = 0.1$–1.2 V. It was found that the values of αf depend little on the potential within the interval $\varphi_r = 0.2$–0.7 V and increase sharply at $\varphi_r < 0.2$ and $\varphi_r > 0.7$ V.

Such a change in the values of αf cannot be explained only by the fact that the calculation of αf was performed without considering the fraction of the surface occupied by adsorbed hydrogen and oxygen. If we calculate the free surface, considering this circumstance, then αf is decreased, but still remains more than eight. The fraction of the surface occupied by adsorbed hydrogen and oxygen was determined on the basis of the assumption that each adsorbed hydrogen or oxygen atom binds one platinum atom. The variations of αf beyond the limits of the potential interval 0.2–0.7 V are evidently explained by the substantial increase in the activation energy of the adsorption of organic substances on the surface partially occupied by chemisorbed hydrogen and especially oxygen.

A comparison of the data on the kinetics of adsorption from acid and alkaline solutions shows that the rate constant of the adsorption of benzene, naphthalene, and phenol on Pt/Pt in alkaline solutions as a function of the potential is 2–10 times lower than in acid solution, which was observed earlier in the adsorption of other organic compounds as well [16].

To determine the nature of the adsorption of naphthalene, benzene, and phenol on Pt and Pt/Pt, we studied the dependence of the value of the adsorption on the electrode potential. The shape of this dependence is determined by the experimental conditions. Curves 1 in Figs. 2–4 reflect the behavior of naphthalene, benzene, and phenol in the adsorption layer when the potential is varied from 0.5 V in the anodic or cathodic direction in 0.1 N H_2SO_4. The adsorption of the organic substance was conducted at $\varphi_r = 0.5$ V. The absence of variation of the radioactivity of the adsorbed substance (at a constant electrode potential) in the case of replacement of the solution of the organic substance by 0.1 N H_2SO_4 indicates a strong chemisorption of naphthalene, benzene, and phenol. The decrease in the degree of coverage of the surface by chemisorption products at $\varphi_r < 0.2$ V can be attributed to hydration of the adsorption products of naphthalene, benzene, and phenol, while at $\varphi_r > 0.8$ V, as will be shown below, it occurs as a result of their oxidation.

Curves 2, 2', and 2" (Figs. 2–4), obtained by variation of φ_r from 1.3 to 0.0 V (curve 2) and from 0.0 (curve 2') or 0.15 (curve 2") to 1.3 V, show Γ versus φ_r dependence in a solution with an organic substance (rate of change of the potential 3 mV/min). Curves 3 (Figs. 2–4) reflect the Γ versus φ_r dependence, constructed according to the limiting values of the adsorption, reached at set values of the potential. A comparison of the Γ versus φ_r dependences obtained by variation of the electrode potential in

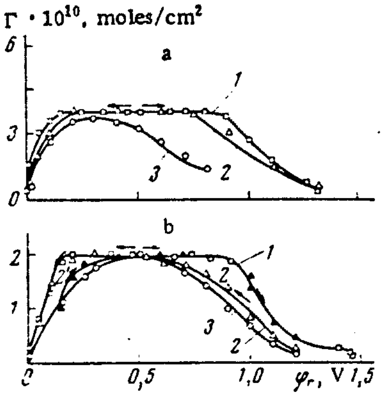

Fig. 3

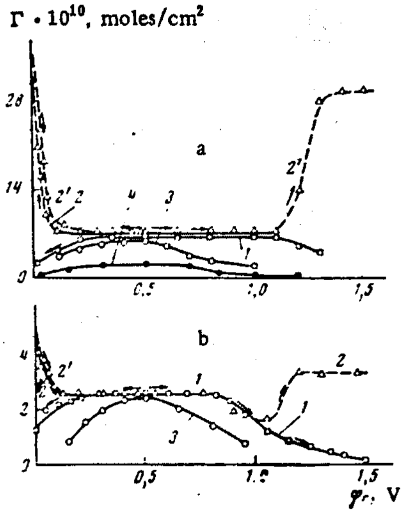

Fig. 4

Fig. 3. Dependence of the values of the adsorption of benzene on the potential: a) Pt: 1) in 0.1 N H_2SO_4 (behavior in the chemisorbed layer); 2) in a solution of 10^{-2} M C_6H_6 + 0.1 N H_2SO_4 with an arbitrary direction of variation of the potential; 3) constructed according to the limiting values of the adsorption reached at a constant potential in the same solution as curve 2. b) Pt/Pt: 1) in 0.1 N H_2SO_4 (behavior in the chemisorbed layer); 2, 2') in a solution of 10^{-2} M C_6H_6 + 0.1 N H_2SO_4; 3) constructed according to the limiting values of the adsorption reached at a constant potential in the same solution as curve 2.

Fig. 4. Dependence of the adsorption of phenol on the potential: a) Pt: 1) in 0.1 N H_2SO_4 (behavior in the chemisorbed layer); 2, 2') in a solution of 10^{-2} M C_6H_5OH + 0.1 N H_2SO_4; 3) constructed according to the limiting values of the adsorption reached at a constant potential in the same solution as curve 2; 4) in a solution of 10^{-2} M C_6H_5OH + 0.1 N NaOH with an arbitrary direction of variation of the potential. b) Pt/Pt: 1) in 0.1 N H_2SO_4 (behavior in the chemisorbed layer); 2, 2') in a solution of 10^{-2} M C_6H_5OH + 0.1 N H_2SO_4, after reaching of the limiting value of the adsorption of phenol at $\varphi_r = 0.5$ V; 3) constructed according to the limiting values of the adsorption reached in 5 h at a constant potential in the same solution as curve 2.

solution with the organic substance with the Γ versus φ_r dependence reflecting the behavior of benzene, naphthalene, and phenol chemisorbed at $\varphi_r = 0.5$ V in the case of variation of the electrode potential in the solution of the supporting electrolyte shows that within the interval of potentials 0.2-0.7 V the values of the adsorption do not depend on the potential. The Γ versus φ_r dependence constructed according to the limiting values of the adsorption reached at a constant potential takes a more bell-shaped form. This can be explained by the influence of chemisorbed hydrogen and oxygen on the value of the adsorption of organic substances.

In the recording of the Γ versus φ_r dependence in a solution of naphthalene at $\varphi_r < 0.05$ V, a sharp increase is observed in the radioactivity of the electrode, corresponding to several monolayers in a formal calculation. This is evidently associated with the accumulation of the hydrogenation product of naphthalene. The values of the amount of this product on the electrode at $\varphi_r = 0.05$ V, cited in Fig. 2, were reached on Pt in 60-70 min and on Pt/Pt in ~7 h. When the concentration of naphthalene in solution is decreased, or in the case of more intense purging of the cell with argon, the radioactivity of the electrodes drops sharply. The amount of the product of adsorption of naphthalene remaining on the electrode after washing of the cell with 0.1 N H_2SO_4 at $\varphi_r = 0.0$ V, corresponds to the value of the adsorption of naphthalene at this potential according to curves 1 of Fig. 2. When the electrode potential is shifted in a naphthalene solution from $\varphi_r = 0.0$ V in the anodic direction without purging of the solution with gas, there is a gradual removal

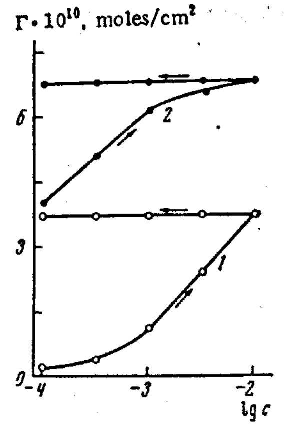

Fig. 5

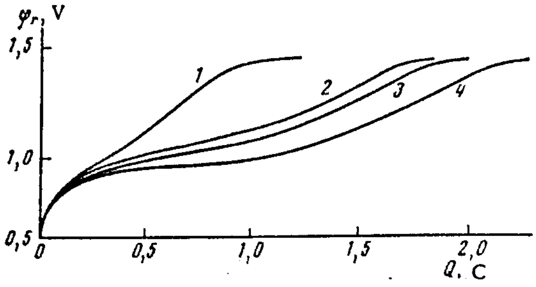

Fig. 6

Fig. 5. Dependence of the adsorption of benzene (1) and phenol (2) on Pt on their concentration in solution at $\varphi_r = 0.3$ V. The arrows indicate the direction of the variation of the concentration. Supporting electrolyte 0.1 N H_2SO_4.

Fig. 6. Curves of the charging of a Pt/Pt electrode in 0.1 N H_2SO_4: 1) in the absence of chemisorbed organic substances on the electrode; 2) in the presence of chemisorbed benzene on the electrode; 3) in the presence of chemisorbed naphthalene on the electrodes; 4) in the presence of chemisorbed benzene on the electrode.

of the product found on the electrode all the way up to 1.4 V. The rate of removal of this product does not depend on the rate of application of the potential (V = 0.001-0.1 V/min). These facts give a basis for believing that the product formed on the electrode at $\varphi_r < 0.05$ V is a sparingly soluble reduction product of naphthalene.

Analogous phenomena are observed on platinum electrodes in the presence of benzene as well (Fig. 4, curves 2). When the potential of a platinum electrode in a solution of phenol was displaced from $\varphi_r = 1.2$ V in the direction of positive values, an increase in the amount of the product found on the electrode was observed (Fig. 4). The particles adsorbed at $\varphi_r > 1.1$ V cannot be removed from the surface either by cathodic or by anodic polarization in a solution of 0.1 N H_2SO_4, in contrast to the particles chemisorbed at $\varphi_r < 1.1$ V. A sharp change in the adsorption behavior of the platinum electrode at $\varphi_r > 1.1$ V in the presence of phenol was observed earlier in [5, 18, 19], and for p-nitrophenol in [20], conducted by the method of radioactive tracers. In [5] it was shown that the products of the adsorption of phenol on Pt at $\varphi_r > 1.1$ V was removed from the electrode surface only by calcination. Probably at $\varphi_r > 1.1$ V there is a formation of a polymer product, firmly bound to the electrode surface.

We also studied the dependence of the value of the adsorption of benzene and phenol on smooth platinum on the concentration at a constant potential. This dependence was determined as follows. Since the adsorption did not increase after the reaching of an equilibrium value of the adsorption of benzene and phenol at $\varphi_r = 0.3$ V in a 10^{-4} M solution of the organic substance in 0.1 N H_2SO_4, when the solution was replaced with a new portion of the same concentration, the concentration of the corresponding substance in solution was increased to $3 \cdot 10^{-4}$ M and reached the equilibrium value of the adsorption at this concentration. Then the concentration was again increased to 10^{-3} M and the variation of the amount of the adsorbed substance was followed until a constant value was reached, etc., up to a concentration of 10^{-2} M (Fig. 5). After this the electrode was placed in contact with solutions more dilute with respect to benzene (or phenol). No change in the radioactivity of the electrode was observed down to a practically zero content of benzene or phenol in solution. From Fig. 5 it is evident that the dependence of the value of the adsorption of benzene and phenol on the volume concentration is formally described by the equation of the Temkin isotherm. In the case of benzene the value of $\Gamma_{\lim}$ is not reached at a concentration of 10^{-2} M, close to a saturated solution. According to the data of Bockris et al. [1], the adsorption isotherm of benzene already reaches a limit at a concentration of $2 \cdot 10^{-5}$ M. The cause of such a discrepancy is unclear.

To determine the mechanism of desorption in the region of anodic potentials we conducted the electrooxidation of organic substances in the adsorbed layer with a simultaneous determination of the number of desorbed particles according to the decrease in the radioactivity of the adsorbed substance. On the anodic charging curves of the Pt/Pt electrode with chemisorbed benzene, phenol, and naphthalene (Fig. 6) there are plateaus corresponding to the electrooxidation of chemisorbed particles, which are oxidized at potentials of the deposition of oxygen on the surface of platinum (0.85-1.25). A comparison of the amount of electricity consumed for the oxidation of the organic substance with the number of desorbed particles leads to the conclusion that in the case of benzene 26 ± 4, phenol 25 ± 8, and naphthalene 45 ± 6 electrons are consumed per particle. These values are close to the values calculated from the stoichiometry of the conversions of benzene, phenol, and naphthalene to CO_2, namely, 30, 28, and 48 electrons, respectively. The conclusion of complete oxidation of the chemisorbed benzene to CO_2 agrees with the data of [2].

The absolute amounts of chemisorbed benzene, phenol, and naphthalene on Pt/Pt are equal to $2 \cdot 10^{-10}$, $2.6 \cdot 10^{-10}$, and $1.2 \cdot 10^{-10}$ g-mole/cm², respectively. This indicates that molecules of benzene, phenol, and naphthalene occupy 9, 7, and 15 adsorption sites on the surface of platinum, respectively. On smooth platinum the absolute amounts of chemisorbed benzene, phenol, and naphthalene are equal to $3.8 \cdot 10^{-10}$, $7 \cdot 10^{-10}$, and $2 \cdot 10^{-10}$ g-mole/cm², respectively. This is equivalent to the fact that the molecules of these substances occupy 5, 3, and 9 adsorption centers on the surface of Pt, respectively. The cause of the difference in the values of the maximum adsorption on smooth and platinized platinum, ~twofold, is not entirely clear. The elucidation of this question is of interest, since this would permit a conclusion on the orientation of the organic substance on the surface of platinum. On the basis of the data cited above on the values of Γ_{max} on Pt/Pt, it can be assumed that the molecules of the organic substance are arranged flat on the surface of the latter. In the case of smooth Pt, evidently there is a vertical orientation of the organic molecules on the surface. It must be noted that the difference obtained above in the nature of the arrangement of the organic molecules on the surface of Pt and Pt/Pt was obtained under the condition of the same accessibility of the adsorption sites to the molecules of the organic substance on smooth Pt and Pt/Pt and the same value of the maximum degree of coverage of the surface of smooth and platinized platinum by methanol, equal to 0.8.* However, as will be shown below, these conditions are not always fulfilled, i.e., the calculation of the number of adsorption sites occupied by a molecule of the organic substance is formal. The effect of inaccessibility of most of the hydrogen adsorption sites (surface platinum atoms) for the adsorption even of a comparatively small molecules of N_2, O_2, H_3COH, etc., was observed earlier on electrolytic deposits on Pt, obtained at negative deposition potentials φ_r^{dep}[21, 22] and on certain chemically precipitated samples of platinum blacks [23]. The results cited permit us to assume that an analogous phenomenon also occurs on Pt deposits with positive φ_r^{dep}, but only in the case of the adsorption of substantially larger organic particles.

The aggregate of experimental data obtained is evidence of an irreversible nature of the adsorption of naphthalene, benzene, and phenol on platinum. Consequently, the theoretical concepts developed by Bockris et al. [8-11] and used by them for the interpretation of the data obtained in [1-3, 7], and the Frumkin thermodynamic theory of adsorption on a hydrogen electrode cannot be applied to these systems.

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*If Pt/Pt obtained at sufficiently positive potentials of deposition is used [21].

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