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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE EFFECT OF ADSORPTION ON THE RATE OF PROCESSES AT A PLATINUM ELECTRODE IN THE QUINONE–HYDROQUINONE SYSTEM

(Presented by Academician A. N. Frumkin on 18 III 1963)

The aim of the present work was to establish a quantitative relationship between the kinetics of the electrochemical process and adsorption phenomena on a platinum electrode, which, as is known, has a high capacity for chemisorption of ions and molecules in the presence of a heterogeneous surface ([1–5]).

We studied the effect of the anions F^-, Cl^-, Br^-, J^-, the cations $(CH_3)_4N^+$, Cs^+, Rb^+, NH_4^+, K^+, and the organic substances hexanol, isoamyl alcohol, and phenylsuccinic acid on the rate of electrochemical oxidation of hydroquinone and reduction of quinone at a rotating platinum electrode. In order to eliminate diffusion limitations, we used not only the usual disk electrode, but also Z- and S-shaped rotating electrodes ([6]), providing stirring equivalent to 30,000-180,000 rpm of an ordinary disk electrode. The study was carried out in a solution of quinone $5 \cdot 10^{-3}$ M in a background of 0.12 M $HClO_4 + 0.1$ M NaH_2PO_4 by recording polarization curves by the usual compensation method and on a PO-5122 oscillographic polarograph. To study the influence of the nature of the cation, the perchloric acid of the background was replaced by sulfuric acid. The high purity of the starting reagents and preliminary cathodic–anodic activation of the surface made it possible to obtain a time-stable exchange current and good reproducibility of the results (±2 mV). Preliminary treatment of the electrode in the background solution, replacement of the background by the solution under investigation, and all polarization measurements were carried out in an atmosphere of purified nitrogen with solutions freed of oxygen.

Figure 2

Figure 2: Figure 2

Fig. 1. Dependence of the relative rate of quinone reduction and hydroquinone oxidation on cation concentration:
1 –K^+; 2 –NH_4^+; 3 –Rb^+; 4 –Cs^+; 5 –$(CH_3)_4N^+$.

Measurements of the adsorption of iodine and bromine anions were carried out by the radioactive tracer method (J^{131}, Br^{82}) according to a procedure described earlier (^{7,8}). Smooth platinum plates 20 × 20 mm served as electrodes; the solution was stirred with nitrogen. All experimental conditions and preliminary preparation of the platinum electrode in the electrochemical and adsorption studies were kept the same.

Electrochemical studies show that the introduction into the solution of both cations K^+, NH_4^+, Rb^+, Cs^+, $(CH_3)_4N^+$, and anions F^-, Cl^-, Br^-, J^-, as well as organic molecules, leads to a decrease in the exchange current in the quinone –hydroquinone system. From Fig. 1, which shows the decrease in the relative rate of the electrochemical process as a function of the concentration of the introduced cation at φ-const, it is seen that the dependence in its form resembles an adsorption isotherm. The identical sign of the effect upon ad–

adsorption of anions and cations does not allow their action to be explained solely by a change in the ψ_1-potential. Analysis of the results shows that, upon introduction of both anions and organic molecules, beginning with a certain concentration of the additive, a general regularity is observed: a decrease in the rate of the process,

Fig. 2. Dependence of the relative rate of electrochemical processes on the logarithm of the concentration of NaF (1), NaCl (2), NaBr (3), and on the adsorption value of bromine ions (3): *a*–at φ_p; *b*–at $\eta_A = 40$ mV; *c*–at $\eta_k = 40$ mV; *d*–at $\eta_k = 100$ mV; *e*–at $\eta_A = 100$ mV

$$i' = i \left(a - b \lg c_{\text{additive}}\right), \tag{1}$$

where i' is the rate of the process upon introduction of the additive, i is the rate in the absence of the additive, and a and b are certain constants depending on the nature and concentration of the background and on the nature of the additive.

As follows from Fig. 2, the dependence of the decrease in the relative rate of the electrochemical process of hydroquinone oxidation and quinone reduction on the logarithm of the bulk concentration of bromine ions is linear over a wide range of concentrations. The decrease in the rate at one and the same bulk concentration of additive increases in the series $F^- < Cl^- < Br^-$. Upon introduction of J^-, the picture is complicated by side processes. For cations the

Figure 3

Figure 3: Figure 3

series has the following form: $K^+ < NH_4^+ < Rb^+ < Cs^+ < (CH_3)_4N^+$. Among the organic molecules studied, phenylacetic acid had the greatest inhibiting efficiency, followed by isoamyl alcohol and hexyl alcohol.

To understand the nature of the influence of anions on the rate of electrochemical processes, it is necessary to establish the connection of this effect not with the bulk concentration, but with the amount of adsorbed additive. Figure 3 shows the dependence of the amount of adsorbed Br^- and J^- anions on their bulk concentration in the quinone-hydroquinone solution. It is seen that the amount of adsorbed anions increases linearly with the change in the logarithm of the bulk concentration over a wide concentration range. Thus, the adsorption isotherm of iodine and bromine at φ-const is the logarithmic Temkin–Frumkin isotherm. From a comparison of the adsorption values of iodine and bromine ions at equal bulk concentrations it follows that iodine adsorption is twice as large as bromine adsorption. For iodine, when the bulk concentration is increased above $10^{-3}\,M$, surface saturation is observed. For bromine, saturation is not reached even at a concentration of $10^{-1}\,M$. In Fig. 3, for comparison, the adsorption curve of iodine in the absence of quinone and hydroquinone in $0.1\,N\,H_2SO_4$ solution is given. Under these conditions adsorption

Fig. 3. Amount of adsorbed iodine (2, 3) and bromine (4, 5) anions as a function of the logarithm of their bulk concentration in a quinone-hydroquinone solution; 2, 4—measured after removal of the wetting solution with filter paper; 3, 5—after rinsing the electrode in bidistilled water; 1—adsorption of iodine ions in $0.1\,N\,H_2SO_4$

of iodine is twice as large and reaches saturation at bulk concentrations above $10^{-4}M$. This indirectly indicates strong adsorption of quinone and hydroquinone on platinum. Both the electrochemical data and the study of the adsorption kinetics of iodine and bromine show that establishment of the equilibrium adsorption value in our system occurs rapidly (for bromine-ion concentrations of $10^{-4}M$, in less than 1 min). The adsorption values presented in Fig. 3 were measured after the electrode had been in the solution for 30 min, which is sufficient for establishment of the equilibrium adsorption value at lower concentrations.

From comparison of the electrochemical data with the adsorption data (Fig. 2), it follows that the decrease in the rate of the electrochemical process is proportional to the filling of the surface by the anion, i.e.,

$$i' = i\left(a_0 - b_0\frac{\Gamma}{\Gamma_\infty}\right) = ki(1 - \nu\theta), \tag{2}$$

where Γ is the adsorption value of the anion, Γ_∞ is the adsorption value corre-

Fig. 4. Dependence of the relative rate of electrochemical processes on the filling of the surface by bromide ions at different potentials. Symbols are as in Fig. 2

Figure 4: Fig. 4. Dependence of the relative rate of electrochemical processes on the filling of the surface by bromide ions at different potentials. Symbols are as in Fig. 2

sponding to monolayer filling, and θ is the degree of filling of the surface by the anion.

The fact that very small concentrations of bromide ions (down to $10^{-5} M$) do not cause a noticeable decrease in electrode activity is explained by the fact that in a solution of $0.12\, HClO_4 + 0.1\, M\, NaH_2PO_4$ the surface of the platinum electrode is not completely free. Thus, according to the data of Kazarinov (7), in $0.1\, M\, H_3PO_4$, $1.7 \cdot 10^{-10}$ g-ion/cm^2 of $H_2PO_4^-$ anion is adsorbed on the surface of the platinum electrode (filling $\theta H_2PO_4^- \sim 0.18$).

Fig. 4. Dependence of the relative rate of electrochemical processes on the filling of the surface by bromide ions at different potentials. Symbols are as in Fig. 2.

It may be assumed that at $NaBr$ concentrations $< 10^{-5} M$ the total adsorption value of the $H_2PO_4^-$ anion and bromide ions differs little from the adsorption value of pure phosphoric acid. Thus, expression (2) must be written taking into account the adsorption of all components of the solution that do not participate in the electrochemical process:

$$i' = i^0 \left(1 - \sum \nu_i \theta_i\right), \tag{3}$$

where i^0 is the rate of the process on a free surface; $\sum \nu_i \theta_i$ is the sum of the products of the filling (θ_i) by the coefficient (ν_i), which takes into account over how many radii of the adsorbed ion its action extends.

To pass from the quantity i^0, which cannot be measured, to the rate of the process in a solution without additive (i), we must also apply an expression analogous to expression (3):

$$i = i^0 \left(1 - \sum \nu_0 \theta_0\right), \tag{4}$$

where $\sum \nu_0 \theta_0$ is the total filling in the solution without additive.

Thus, the general expression for the rate of the electrochemical process upon adsorption of an anion has the form:

$$i' = \frac{i\,(1 - \sum \nu_i \theta_i)}{(1 - \sum \nu_0 \theta_0)} = ki \left(1 - \sum \nu_i \theta_i\right). \tag{5}$$

At concentrations of bromide ions at which the adsorption of phosphoric acid ions may be neglected in comparison with the adsorption of bromide ions, expression (5) coincides with expression (2).

The dependence, presented in Fig. 4, of the relative rate of the processes at various potentials on the coverage by bromide ions indicates the absence of long-range forces in the poisoning of a platinum electrode by bromide anions ($\nu_{\mathrm{Br}} \simeq 0.9$), as well as the small influence of changes in the Ψ_1-potential. It follows from expression (3) that the rate of the electrochemical process is proportional to the fraction of the surface free from the adsorbed poison. Such a conclusion, obvious for microblocking of a homogeneous surface, may nevertheless remain valid for a heterogeneous surface as well, as follows from the theory of catalytic processes ([10]). The heterogeneity of the electrode surface is taken into account only when substituting the adsorbed amount of poison from its bulk concentration.

Breiter’ s data ([9]) on the dependence of the adsorption of organic substances on a platinum electrode on the bulk concentration, and the data of Balashova and co-workers ([7,8]) on the adsorption of anions on platinum, make it possible to suppose that expression (3), like (1), will be valid both for all anions and for organic molecules.

Thus, the results obtained by us show that the decrease in the rate of the electrochemical reaction in the presence of adsorbing anions and organic molecules occurs mainly as a result of microblocking of the surface. Taking into account the small magnitude of cation adsorption ([7]), it should be assumed that their action is connected with a change in the structure of the electrical double layer.

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