DEPENDENCE OF THE ADSORPTION OF ORGANIC SUBSTANCES ON THE POTENTIAL ON METALS ADSORBING HYDROGEN

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The problems of the adsorption of organic substances on metals of the iron group and platinum group, as well as on gold, have recently begun to attract attention, primarily as a result of a desire to analyze the mechanisms of the action of inhibitors of corrosion and anode oxidation of organic compounds. The processes of adsorption of organic compounds on these metals, accompanied in many cases by profound chemical changes of the adsorbed molecules, naturally differ from the relatively well-studied processes of absorption on mercury. In the consideration of this question, however, it is usually not considered that in the case of complete reversibility of the adsorption process, the ability of the metal to adsorb hydrogen, characteristic to one degree or another of all the enumerated metals, leads to a substantial difference in the character of the dependence of the adsorbability of the organic substance on the electrode potential.

For simplicity we shall consider the behavior of a metal functioning as a hydrogen electrode, i.e., the ionization of which can be neglected and the electrode potential of which, φ is determined by the equation:

$$\varphi = -\frac{1}{F}(\mu_H - \mu_{H^+}) + \text{const}, \tag{1}$$

where μ_H and μ_{H^+} are the chemical potentials of the adsorbed atomic hydrogen and hydrogen ions, respectively. Let us assume, further, that the electrode exists in equilibrium with a solution of definite pH and definite concentration of the background electrolyte, so that the state of the system is entirely set by the quantities μ_H and μ_{org}, where μ_{org} is the chemical potential of the adsorbed organic substance. We shall consider the concentration of the latter as so small that changes in it exert no influence on the chemical potentials of the other components of the solution. Then, applying the Gibbs adsorption equation to the metal-solution boundary of separation and selecing its position such that the surface density of water Γ_{H_2O} can be assumed equal to zero, we obtain

$$d\sigma = -\Gamma_H\, d\mu_H - \Gamma_{org}\, d\mu_{org}, \tag{2}$$

where σ is the boundary tension, Γ_H and Γ_{org} are the surface densities of hydrogen and the organic substance, respectively, i.e., the amounts that should be added to a closed system in order for the quantities μ_H and μ_{org} to remain constant with an increase in the surface of separation by one. If the entire consumption of hydrogen when the surface of separation is increased depended on the process of its ionization, related to the appearance of a charge on the boundary of separation, then Γ_H would be equal to $-q/F$, where q is the charge density of the metallic lining of the double layer. In this case, according to (1) and (2),

$$d\sigma = -q\, d\varphi - \Gamma_{org}\, d\mu_{org}, \tag{3}$$

i.e., we arrive at the usual equation of electrocapillarity, upon which the theory of the influence of an electric field on the adsorption of organic substances is based [1]. In the case of a metal adsorbing hydrogen,

$$\Gamma_H = A_H - q/F, \tag{4}$$

where A_H is the number of gram atoms of hydrogen adsorbed on 1 cm^2 of surface, not entering the volume of the solution in the form of ions. Equation (4) has already been used in conjunction with the Gibbs adsorption formula in a consideration of other aspects of the adsorption behavior of hydrogen electrodes [2, 3].

From (1), (2), and (4) it follows that

$$\left(\frac{\partial A_H}{\partial \mu_{org}}\right)_\varphi - \frac{1}{F}\left(\frac{\partial q}{\partial \mu_{org}}\right)_\varphi = -\frac{1}{F}\left(\frac{\partial \Gamma_{org}}{\partial \varphi}\right)_{\mu_{org}}, \quad (5)$$

$$\left(\frac{\partial \mu_{org}}{\partial \varphi}\right)_{\Gamma_{org}} = -\left(\frac{\partial \mu_{org}}{\partial \Gamma_{org}}\right)_\varphi \left(\frac{\partial \Gamma_{org}}{\partial \varphi}\right)_{\mu_{org}} = F\left(\frac{\partial A_H}{\partial \Gamma_{org}}\right)_\varphi - \left(\frac{\partial q}{\partial \Gamma_{org}}\right)_\varphi. \quad (6)$$

Since

$$\left(\frac{\partial \mu_{org}}{\partial \varphi}\right)_{\Gamma_{org}} = \left(\frac{\partial \Delta G_{org}}{\partial \varphi}\right)_{\Gamma_{org}},$$

where ΔG_{org} is the standard free energy of the process of adsorption of the organic substance, then Eq. (6) can also be rewritten in the following way:

$$\left(\frac{\partial \Delta G_{org}}{\partial \varphi}\right)_{\Gamma_{org}} = -\left(\frac{\partial q}{\partial \Gamma_{org}}\right)_\varphi + F\left(\frac{\partial A_H}{\partial \Gamma_{org}}\right)_\varphi. \quad (6a)$$

The change in the adsorbability of organic substances with the potential on a mercury electrode is determined by the first factor in the right-hand portion of Eq. (6a). To compare the magnitude of the first and second members, it is more convenient to proceed not from the values of the derivatives, but from the variations of the quantities $-q$ and FA_H in the case of coverage of the surface by the adsorbed organic substance. Let us assume that the adsorption of the organic substance is being investigated at a potential 0.4 more negative than the point of zero charge of the electrode, which approximately corresponds to the limit of th potential range within which the potential dependence of the adsorption of naphthalene on gold was investigated in [4]. Under these conditions the initial value of $-q$ (in the absence of the organic substance), judging by the analogy with mercury, can constitute $\sim 8 \cdot 10^{-6}$ C/cm^2, and $|\Delta q|$, i.e., the change in $-q$, can be no more than $6 \cdot 10^{-6}$ C/cm^2. Data pertaining to the second factor of the right-hand portion are available only for the platinum electrode. In the case of the reversible hydrogen potential, the quantity FA_H is equal to $\sim 2.1 \cdot 10^{-4}$ C/cm^2 [3], and in the presence of adsorbed methanol it is reduced approximately three to four-fold* [7, 8]. Thus, $|\Delta FA_H| \sim 10^{-4}$ C/cm^2 and is more than an order of magnitude greater than the maximum value of $|\Delta q|$. From this it follows that the influence of adsorbed hydrogen on the adsorption of an organic substance cannot be neglected even when the coverage of the surface by adsorbed hydrogen does not exceed several percent, as in the case of the gold electrode [6].

In view of the irreversibility of the process of adsorption of oxygen, an analogous thermodynamic treatment cannot be applied to the question of the influence of adsorbed oxygen; however, there is no doubt that here analogous effects should be observed, and that the position of the maximum adsorbability of organic substances on electrodes adsorbing hydrogen and oxygen is determined not so much by the potential of the point of zero charge of the double electric layer as by the position of the potential range within which the adsorption of hydrogen and oxygen is a minimum.

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* The presence of chemosorbed hydrogen also reduces the adsorption of ethylene on nickel [5].