Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1964

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 154, No. 6

PHYSICAL CHEMISTRY

Academician A. N. FRUMKIN

ON THE DEPENDENCE OF THE ADSORPTION OF ORGANIC SUBSTANCES ON THE POTENTIAL ON METALS THAT ADSORB HYDROGEN

Recently, questions concerning the adsorption of organic substances on metals of the iron group and the platinum group, as well as on gold, have begun to attract attention; this is connected primarily with the desire to understand the mechanisms of action of corrosion inhibitors and of the anodic oxidation of organic compounds. The processes of adsorption of organic compounds on these metals, accompanied in many cases by profound chemical changes in the adsorbing molecules, naturally differ from the relatively well-studied processes of adsorption on mercury. In considering this question, however, it is usually not taken into account that, even when the adsorption process is completely reversible, the ability of a metal to adsorb hydrogen—an ability characteristic, to one degree or another, of all the metals listed—leads to a substantial difference in the character of the dependence of the adsorbability of an organic substance on the electrode potential.

For simplicity, let us consider the behavior of a metal functioning as a hydrogen electrode, i.e., one whose ionization may be neglected, and whose electrode potential 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, respectively, the chemical potentials of adsorbed atomic hydrogen and hydrogen ions. Let us further assume that the electrode is in equilibrium with a solution of definite pH and definite concentration of the background electrolyte, so that the state of the system is completely specified by the quantities μ_H and μ_{org}, where μ_{org} is the chemical potential of the adsorbing organic substance. We shall regard the concentration of the latter as so small that changes in it do not affect the chemical potentials of the other components of the solution. Then, applying the Gibbs adsorption equation to the metal-

solution interface and choosing its position so that the surface density of water Γ_{H_2O} may be taken equal to zero, we obtain

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

where σ is the interfacial tension, and Γ_H and Γ_{org} are, respectively, the surface densities of hydrogen and of the organic substance, i.e., the amounts that must be added to the closed system in order that the quantities μ_H and μ_{org} remain constant when the area of the interface is increased by unity. If the entire expenditure of hydrogen upon increasing the area of the interface depended on the process of its ionization, associated with the appearance of charge at the interface, then Γ_H would be equal to $-q/F$, where q is the charge density of the metallic plate 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 electrocapillary equation, on which the theory of the influence of the electric field on the adsorption of organic substances is based ([1]). In the case of a metal that adsorbs 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 and not entering the bulk of the solution in the form of ions. Equation (4), in combination with the Gibbs adsorption formula, has already been used

earlier in considering other aspects of the adsorption behavior of hydrogen electrodes ([2,3]).

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

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

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

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 adsorption process of the organic substance, equation (6) can also be rewritten as follows:

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

The change in the adsorbability of organic substances with potential on a mercury electrode is determined by the first term on the right-hand side of equation (6a). For comparing the magnitudes of the first and second terms, it is more convenient to proceed not from the values of the derivatives but from the changes in the quantities $-q$ and FA_H upon filling the surface with the adsorbed organic substance. Suppose that the adsorption of an organic substance is studied at a potential 0.4 V more negative than the point of zero charge of the electrode, which approximately corresponds to the limit of the range of potentials in which the dependence of naphthalene adsorption on gold on potential was investigated ([4]). Under these conditions the initial value of $-q$ (in the absence of organics), judging by analogy with mercury, may be $\sim 8 \cdot 10^{-6}$ coul/cm^2 and $|\Delta q|$, i.e., the change in $-q$, no more than $6 \cdot 10^{-6}$ coul/cm^2. Data relating to the second term on the right-hand side are available only for a platinum electrode. At the reversible hydrogen potential the value FA_H is $\sim 2.1 \cdot 10^{-4}$ coul/cm^2 ([3]), and in the presence of adsorbed methyl alcohol it decreases by approximately a factor of 3-4* ([7],[8]). Thus, $|\Delta FA_H| \sim 10^{-4}$ coul/cm^2 and exceeds the maximum value of $|\Delta q|$ by more than an order of magnitude. It follows from this that the effect of adsorbed hydrogen on the adsorption of an organic substance cannot be neglected even when the filling of the surface by adsorbed hydrogen does not exceed a few percent, as in the case of a gold electrode ([6]).

In view of the irreversibility of the process of oxygen adsorption, an analogous thermodynamic treatment cannot be applied to the question of the influence of adsorbed oxygen; however, there is no doubt that analogous effects must be observed here as well, 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 electrical double layer as by the position of the interval of potentials in which the adsorption of hydrogen and oxygen is minimal.

Received
6 XII 1963

CITED LITERATURE

[1] A. Frumkin, *Zs. Phys.*, **35**, 792 (1926); *Tr. Khim. inst. im. Karpova*, **5**, 3 (1926).
[2] A. Frumkin, A. Shlygin, *Izv. AN SSSR, ser. khim.*, 773 (1936); A. Frumkin, A. Slygin, *Acta physicochim. USSR*, **5**, 819 (1936).
[3] A. Frumkin, *Advances in Electrochemistry*, **3**, Interscience, N. Y., 1963, p. 287.

[4] H. Dahms, M. Green, *J. Electrochem. Soc.*, **110**, 1075 (1963).
[5] B. Bruns, K. Ablezova, *Acta physicochim. USSR*, **1**, 90 (1934).
[6] M. Breiter, C. A. Knorr, W. Völkl, *Zs. Elektrochem.*, **59**, 681 (1955).
[7] M. Breiter, S. Gilman, *J. Electrochem. Soc.*, **109**, 622 (1962).
[8] K. N. Kombarov, D. V. Sokolsky, *Khimiya i khim. tekhnol.*, Collection of Scientific Works of the Ministry of Higher and Secondary Specialized Education of the Kazakh SSR, **1**, Alma-Ata, 1963, p. 25.

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

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