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COMMENTS ON THE PAPER OF R. G. BARRADAS AND J. M. SEDLAK: SOME OBSERVATIONS ON RECENT THEORIES OF ADSORPTION OF ORGANIC COMPOUNDS IN THE DOUBLE LAYER

B. B. Damaskin and A. N. Frumkin

Institute of Electrochemistry of the Academy of Sciences, Moscow State University, Moscow, U.S.S.R.

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vo theories describing the effect of electric field on sorption of organic molecules on electrodes are ailable at present: the theory developed by Frumkin–imaskin[1–4] and that of Bockris–Devanathan–üller[5] developed further in [6]. In Refs. [7–12] the sitive and negative aspects of these theories were mpared. When Refs. [11–12] appeared we thought that e discussion on this problem had been finished. How- er the paper of Barradas and Sedlak[13] compels us to ke it up once more.

The common features of the two theories are: they both ke into account, although in a different way, the placement of solvent by adsorbed molecules of organic bstance, are model theories (a macromodel in the FD eory and a micromodel in the BDM theory) and, ally, they are to a greater or lesser degree semi- pirical. An advantage of the FD theory is that it ows to describe quantitatively the electrocapillary E-curves) and the differential capacity (C, E-curves) rves in the presence of organic substances. The limita- n of this theory lies in the difficulties involved in lecular interpretation of the adsorption parameters tained. On the other hand, the BDM theory is a lecular one, it takes explicit account of the competi- n between water molecules and organic substance on electrode surface, but it contains some incorrect umptions, considered by us in detail earlier[7, 8, 11]. ese are: 1. the BDM theory does not take into con- eration the energy of the ionic double layer; 2. it regards the polar nature of adsorbed organic mole- es or underestimates its importance; 3. it does not take o account the interaction between adsorbed organic lecules. The BDM theory can not offer a quantita- e description of the σ, E- and C, E-curves.

According to Barradas and Sedlak[13] the BDM ory was confirmed by new experimental data on nol adsorption on platinum[14] and on adsorption cyclopentanone and furan derivatives on mercury[15]. wever, Horanyi's measurements[16] by means of the ioactive tracers method testify to a completely eversible nature of phenols adsorption on a platinum ctrode. Independently, Kazarinov[17] showed that orption even of such compounds as benzene and hthalene on platinum is also irreversible. Therefore, data of Gileadi *et al*[14] can not serve as a criterion verification of an equilibrium adsorption theory.

Let us analyze some results obtained by Barradas and Sedlak in [15]. On the basis of the BDM theory the authors calculated from the position of the charge corresponding to maximum adsorption of organic substance ($q = q^*$) the dielectric constant in the dense layer (ε) and pointed out that the interaction parameter between adsorbed water molecules β can be found from the slope of the adsorption vs charge curves. The values of ε are given in [15], whereas the values of β are absent. Let us calculate the value of β, for instance for tetrahydrofurane. Since the coefficient of displacement of adsorbed water molecules according to Barradas and Sedlak $n = 3$, at the area per water molecule equal to 10 Å^2, the limiting adsorption of hydrofurane $\Gamma_\infty = 5{\cdot}56 \times 10^{-10}$ mole/cm^2. It follows from Fig. 6a in [15] that at $q = q^*$ $\Gamma = 4 \times 10^{-10}$ and at $q - q^* = 6$ $\Gamma = 2 \times 10^{-10}$ mole/cm^2. Thus at these electrode charges $\theta^* = 0{\cdot}72$ and $\theta = 0{\cdot}36$, and the function $f(\theta) = [\theta/n(1-\theta)^n] \times [1 - \theta + (\theta/n)]^{n-1}$ is equal to 2·96 and 0·265, respectively. Since according to the BDM theory $f(\theta^*)/f(\theta) = \exp(nz\,\mathrm{th}\,z)$, where $z = (4\pi\mu_w/\varepsilon kT)(q - q^*) - \beta\,\mathrm{th}\,z$, from the ratio $f(\theta^*)/f(\theta) = 11{\cdot}15$ we find first $z = 1{\cdot}04$ and then $\beta = 0{\cdot}05$ (at $\mu_w = 1{\cdot}84D$; $T = 298°$ and $\varepsilon = 9{\cdot}4$). Now if using the BDM theory at the same values of ε and β, we shall calculate the capacity arising from the reorientation of adsorbed water dipoles, at $q = q^*$ we shall obtain $C_{\mathrm{dip}} = (\varepsilon^2 kT/16\pi^2\mu_w^2 N_w)(1 + \beta) = 7{\cdot}9$ μf/cm^2. Since the overall capacity in the supporting electrolyte solution $C_0 > 0$ and

$$\frac{1}{C_0} = \frac{1}{K_0} - \frac{1}{C_{\mathrm{dip}}},$$

the integral capacity of the dense layer K_0 must be less than 7·9 μf/cm^2. But this is obviously at variance with the experimental data, according to which for aqueous solutions $K_0 \geqslant 15$ μf/cm^2.

Thus, analysis of the data of [15] shows that the calculations by means of the BDM theory, while allowing to interpret some properties of the surface layer, at the same values of parameters are at variance with other experimental results. To eliminate these contradictions it would be necessary to take into account the energy of the ionic double layer.

According to Barradas and Sedlak[13], the limitation of the FD theory is that the equation of the two parallel capacitors model

$$q = q_0(1-\theta) + q'\theta \tag{1}$$

(q is the electrode charge and q_0 and q'—its values at the surface coverage $\theta = 0$ and $\theta = 1$, respectively) is supposedly compatible only with the Henry and Freundlich isotherms. Barradas and Sedlak corroborate this conclusion referring the reader to Parsons[18]. However, the problem considered in [18] is entirely different, *viz* at what conditions the differential capacity $C = \mathrm{d}q/\mathrm{d}E$ is a linear function of θ. Differentiating (1), we obtain

$$C = C_0(1-\theta) + C'\theta + (q'-q_0)\frac{\mathrm{d}\theta}{\mathrm{d}E}, \tag{2}$$

where C_0 and C' are the values of C at $\theta = 0$ and $\theta = 1$, respectively. As it follows from (2), in the region of maximum adsorption of organic substance, where $\mathrm{d}\theta/\mathrm{d}E = 0$,

$$C = C_0(1-\theta) + C'\theta \tag{3}$$

and the differential capacity varies linearly with θ, irrespective of the kind of the adsorption isotherm. As was shown by Parsons[18], in the case of the Henry and Freundlich adsorption isotherms, the third term in (2) also varies linearly with θ. This conclusion, however, has nothing to do with (1), which, as it follows from (3.7) in [18] holds for any isotherm of the kind $B(E)\alpha = f(\Gamma)$, where α is the activity of organic substance and Γ its amount adsorbed.

Also incorrect is another statement of Barradas and Sedlak, *viz* that in [8] one of the authors of this paper proposed a new theory of the effect of electric field on adsorption or organic molecules. In fact, since in [6] it was affirmed that the FD theory does not take into account the reorientation of adsorbed dipoles of the solvent, it seemed reasonable to show qualitatively the erroneousness of this statement using a simplest model. This was done in [8], where a simplified version of the three parallel capacitors model was considered: a layer of organic molecules and two layers of water with opposite dipoles orientation. For additional simplification it was assumed that there was no interaction of adsorbed water molecules with one another and that two states of these molecules ↑ and ↓ had the same integral capacity K_0 and equal in value, but opposite in sign adsorption potentials $E_N{}^{w}(\uparrow) = -E_N{}^{w}(\downarrow)$. This model showed clearly that the reorientation of adsorbed solvent dipoles is taken account of by the FD theory through the potential dependence of the differential capacity in the supporting electrolyte solution C_0. What is particularly important and was several times stressed in [8], is that the taking account of the reorientation of adsorbed solvent dipoles is rigorous if we do it on the basis of the experimental C_0, E-curves, as was the case in all quantitative calculations for the two parallel capacitors model. Therefore, in the FD theory there is no necessity of making any model assumptions concerning the reorientation of adsorbed water dipoles. Consequently, all critical remarks of Barradas and Sedlak[13] about the approximate nature of the three parallel capacitors model described in [8] have nothing to do with the FD theory.*

Thus, it can be said that the paper of Barradas and Sedlak[13] misrepresents the main statements of the FD theory and contains a number of erroneous assertions.

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* It should be noted only that there is no contradiction in the determination of K_0. In fact, under the assumptions made, $E_N{}^{w}(\downarrow) = -E_N{}^{w}(\uparrow)$ and $K_0 = \text{const.}$, the condition $\theta_\downarrow = \theta_\uparrow = 0{\cdot}5$ is realized at $q_0 = 0$, *ie* the corresponding potential $E_h = 0$. Therefore, at $E - E_h = 0$, the equation $q_0 = K_0 E_h$ becomes an identity $0 = K \times 0$, valid at any value of K_0, which Barradas and Sedlak[13] apparently overlooked.

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