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Abstract

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On the Dependence of Adsorption Potentials at the Mercury/Electrolyte Interface on the Magnitude of Adsorption of Neutral Molecules

In connection with the recent discussion ($^{1-3}$), it was of interest to find an unambiguous criterion that would make it possible, on the basis of experimental data, to establish which of the electrical variables—the potential (φ) or the charge (ε)—is more appropriate to choose in studying the adsorption of various organic compounds. The present work is devoted to this purpose.

Let the experimental dependence of the adsorption of an organic substance (Γ) on its bulk concentration (c) and φ be written in the form

$$Bc = f(\Gamma), \tag{1}$$

where B is a function only of φ, and $f(\Gamma)$ is a function only of Γ. Under these conditions, evidently, the potential should be chosen as the independent electrical variable. From (1) it follows that

$$\frac{d\ln B}{d\varphi} = -\left(\frac{\partial \ln c}{\partial \varphi}\right)_\Gamma = \frac{1}{RT}\left(\frac{\partial \varepsilon}{\partial \Gamma}\right)_\varphi, \tag{2}$$

where the second equality follows from the fundamental electrocapillary equation. Integrating (2), we find

$$\varepsilon = RT\left(\frac{d\ln B}{d\varphi}\right)\Gamma + \varepsilon_0 = A\left(\frac{d\ln B}{d\varphi}\right)\theta + \varepsilon_0, \tag{3}$$

where $\theta = \Gamma/\Gamma_m$, Γ_m is the limiting value of Γ, ε_0 is the value of ε at $\theta = 0$, and $A = RT\Gamma_m$. Denote the charge at $\theta = 1$ and a given potential by ε'; then

$$\varepsilon' = A\left(\frac{d\ln B}{d\varphi}\right) + \varepsilon_0. \tag{3a}$$

From equations (3) and (3a) it follows that

$$\varepsilon = \varepsilon_0(1-\theta) + \varepsilon'\theta. \tag{4}$$

Differentiating (4) with respect to φ at $\theta = \text{const}$, we obtain

$$C = C_0(1-\theta) + C'\theta, \tag{5}$$

where C, C_0, and C' are the capacitances of the double layer at surface coverages equal to θ, 0, and 1, respectively.

Thus, writing the adsorption isotherm in the form of equation (1) corresponds to the model of the double layer proposed by Frumkin (^{4}), according to which the double layer in the presence of an organic substance may be represented as two capacitors connected in parallel. Between the plates of one of them there is only the solvent (water), while between the plates of the other there are only molecules of the organic substance.

If the capacitances C_0 and C' do not depend on φ, and if the shift of the point of zero charge (p.z.c.) on going from $\theta = 0$ to $\theta = 1$ is equal to φ_N, then it is evident that $\varepsilon_0 = C_0\varphi$ and $\varepsilon' = C'(\varphi - \varphi_N)$ (the potentials here and below are measured from the p.z.c. at $\theta = 0$). In this case equation (4) can be rewritten as

$$\varepsilon = C_0\varphi(1-\theta) + C'(\varphi - \varphi_N)\theta. \tag{4a}$$

Setting $\varepsilon = 0$ in (4a), we obtain the dependence of the p.z.c. ($\varphi_{\varepsilon=0}$) on θ

$$\varphi_{\varepsilon=0} = \varphi_N\theta \Big/ \left[\frac{C_0}{C'}(1-\theta) + \theta\right]. \tag{6}$$

As is seen from equation (6), the dependence of the p.z.c. on θ (or Γ) when the potential is chosen as the electrical variable is not linear, and deviates from linearity the more strongly, the larger C_0/C' is.

Let now the experimental data be describable by an equation of the form:

$$Gc = f(\Gamma), \tag{7}$$

where G is some function only of ε, and $f(\Gamma)$ is a function only of Γ. In this case it is expedient to choose the electrode charge as the independent electrical variable. From (7) it follows that

$$\frac{d\ln G}{d\varepsilon} = -\left(\frac{\partial \ln c}{\partial \varepsilon}\right)_\Gamma = -\frac{1}{RT}\left(\frac{\partial\varphi}{\partial\Gamma}\right)_\varepsilon, \tag{8}$$

where the second equality follows from the fundamental equation of electrocapillarity, written for $\varepsilon = \text{const}$ (^{5}). Integrating (8), we find

$$\varphi = -RT\left(\frac{d\ln G}{d\varepsilon}\right)\Gamma + \varphi_0 = -A\left(\frac{d\ln G}{d\varepsilon}\right)\theta + \varphi_0, \tag{9}$$

where φ_0 is the value of φ at $\theta = 0$, corresponding to the given charge ε. If the potential at the given ε and at $\theta = 1$ is denoted by φ', then

$$\varphi' = -A\left(\frac{d\ln G}{d\varepsilon}\right) + \varphi_0. \tag{9a}$$

From equations (9) and (9a) it follows that

$$\varphi = \varphi_0(1-\theta) + \varphi'\theta. \tag{10}$$

Differentiating (10) with respect to ε at $\theta = \text{const}$, we obtain

$$1/C = (1-\theta)/C_0 + \theta/C'. \tag{11}$$

Thus, writing the adsorption isotherm in the form of equation (7) corresponds to the series connection of two capacitors with capacitances $C_0/(1-\theta)$ and C'/θ. The physical interpretation of such a model appears difficult to us.

If the capacitances C_0 and C' do not depend on ε, then it is obvious that $\varphi_0 = \varepsilon/C_0$ and $\varphi' = \varepsilon/C' + \varphi_N$. In this case equation (10) can be rewritten as:

$$\varepsilon = (\varphi - \theta\varphi_N)\Big/\left(\frac{1-\theta}{C_0} + \frac{\theta}{C'}\right). \tag{10a}$$

Setting $\varepsilon = 0$ in (10a), we obtain a linear dependence of $\varphi_{\varepsilon=0}$ on θ (or on Γ)

$$\varphi_{\varepsilon=0} = \theta\varphi_N. \tag{12}$$

Thus, the dependence of the p.z.c. on Γ makes it possible to decide whether condition (1) or (7) is fulfilled, and, consequently, which of the variables (φ or ε) is more expedient to choose in studying the adsorption of an organic substance at a phase boundary.

Figures 1–3 show the dependences of $\varphi_{\varepsilon=0}$ on Γ in the case of adsorption of n-C_4H_9COOH, n-$C_5H_{11}NH_2$, and n-C_3H_7OH at mercury/solution and solution/air interfaces*. At the mercury/solution interface, the values of $\varphi_{\varepsilon=0}$ and Γ were determined by us from electrocapillary curves. At the solution/air interface, the values of $\varphi_{\varepsilon=0}$ were measured by the Kenrick method, and the quantities Γ were calculated from the values of surface tension measured by the

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

maximum bubble pressure method. The values of $\varphi_{\varepsilon=0}$ for various concentrations of n-C_4H_9COOH and n-C_3H_7OH in the presence of 0.01 N H_2SO_4 were borrowed from work (^{6}).

As is seen from the figures, in the case of n-C_4H_9COOH and n-$C_5H_{11}NH_2$, the relation between $\varphi_{\varepsilon=0}$ and Γ at the mercury/solution interface is independent of the concentration

* For the air interface, $\varphi_{\varepsilon=0}$ denotes the adsorption potential jump.

of the background agrees well with equation (6) and deviates sharply from the rectilinear dependence predicted by equation (12). At the same time, at the solution/air interface the indicated dependence approximately follows equation (12)*. Analogous results were also obtained by us in the system 3 N KCl + n-C_4H_9OH, using for the mercury/solution interface the data of [7]. A somewhat smaller difference in the dependence of $\varphi_{\varepsilon=0}$ on Γ at the two interfaces is observed in the case of n-C_3H_7OH (Fig. 3). This is partly

Fig. 1. Dependence of the shift of the p.z.c. on the adsorption of n-C_4H_9COOH:
1 –at the solution/air interface, background 0.01 N H_2SO_4;
2 and 3 –at the mercury/solution interface (2 –background 0.01 N H_2SO_4, 3 –background 1 N Na_2SO_4 + 0.01 N H_2SO_4).
The dashed line is the calculation by equation (6) at $\varphi_N = 0.2$ V; $\Gamma_m = 5 \cdot 10^{-10}$ M/cm^2 and $C_0/C' = 5$.

Fig. 2. Dependence of the shift of the p.z.c. on the adsorption of n-$C_5H_{11}NH_2$:
1 and 2 –at the solution/air interface (1 –background 0.05 N KOH; 2 –background 1 N Na_2SO_4 + 0.05 N KOH);
3 and 4 –at the mercury/solution interface (3 –background 0.05 N KOH; 4 –background 1 N Na_2SO_4 + 0.05 N KOH).
The dashed line is the calculation by equation (6) at $\varphi_N = 0.4$ V; $\Gamma_m = 5 \cdot 10^{-10}$ M/cm^2 and $C_0/C' = 5$.

may be associated with an increase in C' on passing to n-C_3H_7OH, since, as is easy to see, at $C' = C_0$ equation (6) becomes (12). Therefore, in the case of n-C_3H_7OH one may expect good agreement between theory and experiment when either φ or ε is chosen as the electrical variable. At the same time, in the case of n-C_4H_9COOH, n-$C_5H_{11}NH_2$, and also n-C_4H_9OH at the mercury/solution interface, the Frumkin model agrees with experiment significantly better; consequently, in these systems the potential should be used as the electrical variable.

It was noted in [8], with reference to Overbeek, that although the conclusions from equation (4) are well confirmed by experiment, the following circumstance raises doubt. At $\varepsilon = 0$, $\varepsilon_0(1-\theta)$ and $\varepsilon'\theta$ separately are not equal to zero, i.e.,

Figure 3

Figure 2: Figure 3

portions of the surface turn out to be charged. In this connection we point out that the model considered above is quantitatively justified if the adsorbed layer is bounded on both sides by strictly equipotential planes and the lines of force are perpendicular to them throughout. These conditions may be approximately fulfilled if perpendicularly oriented—the water and organic-substance dipoles adjacent to the surface are located between two phases with sufficiently large dielectric constants. It is precisely for this reason that this model is not fulfilled at the solution/air boundary. The invariance of the dependence of $\varphi_{\varepsilon=0}$ on Γ upon changing the background concentration (Figs. 1, 2) indicates that potential equalization in the aqueous phase is determined not by the concentration of ions in the diffuse layer, but by the high dielectric constant of the water itself (cf. (9)). Therefore it does not depend on the ratio between the Debye length and the distance between the centers of the molecules of water and of the organic substance in the adsorption layer. It should also be borne in mind that an increase in this distance, which probably occurs with increasing θ owing to partial segregation of the organic substance and water in the surface layer, should promote fulfillment of condition (4).

Fig. 3. Dependence of the shift of the p.z.c. on adsorption of n-C_3H_7OH: 1 —at the solution/air boundary; 2 —at the mercury/solution boundary. Background: 0.01 N H_2SO_4.

If this explanation is correct, then in the presence of a weakly adsorbing substance, whose adsorption becomes appreciable only at high bulk concentrations and which lowers the dielectric constant of water, deviations from the proposed model may be expected. An example of such a system may probably be solutions of n-C_3H_7OH. For a deeper elucidation of the reasons leading to fulfillment of equation (4) at the mercury/solution boundary, however, additional investigation is required.

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* We do not consider here deviations from the linear dependence of $\varphi_{\varepsilon=0}$ on Γ at the solution/air interface, for example, as a result of changes in the orientation of adsorbed molecules with increasing Γ.

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