THE ADSORPTION POTENTIALS AT A MERCURY/ELECTROLYTE BOUNDARY, AS A FUNCTION OF THE AMOUNT OF NEUTRAL MOLECULES ADSORBED

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In view of the discussion going on at the present time [1-3], it was of interest to find a unique criterion, which, on the basis of the experimental data, would make it possible to decide which of the electrical variables, the potential (φ) or the charge (ε), is the better one to use in investigating the adsorption of various organic compounds. This is the purpose of the present paper.

Assume that the experimental curve of the adsorption of an organic substance (Γ) as a function of its concentration by volume (c) and φ may be written in the form:

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

where B is some function of φ alone, and $f(\Gamma)$ is a function of Γ alone. Under these conditions, it is obvious that it is well to use the potential as the independent electrical variable. It follows from (1), 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 equation follows from the basic equation of electrocapillarity. 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 maximum value of Γ, ε_0 is the value of ε for $\theta = 0$, and $A = RT\Gamma_m$. We write the charge at $\theta = 1$ and a fixed potential, in terms of ε', and then:

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

It follows from Eqs. (3) and (3a) that:

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

differentiating (4) with respect to φ for θ =const, we obtain:

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

where C, C_0, and C' are the capacities of the double layer for surface fillings respectively equal to θ, 0, and 1.

Thus, writing the adsorption isotherm in the form of Eq. (1) corresponds to the model of the double layer proposed by Frumkin [4], in which the double layer, with an organic substance present, may be represented by two condensers connected in parallel. Between the plates of one of the condensers, we have only the solvent (water),

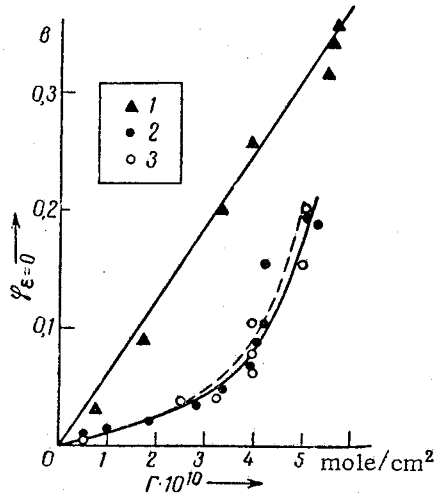

Fig. 1. The shift in the z.c.p. as a function of n-C_4H_9COOH adsorption: 1) At the solution/air interface, background 0.01 n-H_2SO_4; 2 and 3) At the mercury/solution interface (2-background 0.01 n-H_2SO_4; 3) background 1 n-Na_2SO_4 + 0.01 n-H_2SO_4). The dotted line is calculated from Eq. (6) for $\varphi_N = 0.2$ V, $\Gamma_m = 5 \cdot 10^{-10}$ M/cm², and $C_0/C' = 5$.

while between the plates of the other condenser, we have only molecules of the organic substance.

If the capacities C_0 and C' are independent of φ, and if the shift of the zero charge point (z.c.p.) on going from $\theta = 0$ to $\theta = 1$ is equal to φ_N, it is obvious that $\varepsilon_0 = C_0 \varphi$, and $\varepsilon' = C'(\varphi - \varphi_N)$ (the potentials here, and in the rest of the paper, are read from the z.c.p. for θ 0). In this case, Eq. (4) may be rewritten in the form:

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

Setting $\varepsilon = 0$ in (4a), we obtain the z.c.p. ($\varphi_\varepsilon = 0$) as a function of θ:

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

It may be seen from Eq. (6) that the curve of the z.c.p. as a function of θ (or Γ) is not linear when the potential is used as the electrical variable, the departure from linearity being greater, the greater the value of C_0/C'.

Assume now that the experimental data may be described by an equation of the form:

$$Gc = f(\Gamma), \quad (7)$$

where G is some function of ε alone, and $f(\Gamma)$ is a function of Γ alone. In this case, it is well to use the charge on the electrode as the independent electrical variable. It follows from (7) that:

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

where the second equation follows from the fundamental equation of electrocapillarity, written for ε = const [5]. Integrating (8), we find:

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

where φ_0 is the value of φ at $\theta = 0$, corresponding to a given charge ε. If we let the potential at a given value of ε, and $\theta = 1$, be φ', we have:

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

It follows from Eq. (9) and (9a) that:

$$\varphi = \varphi_0(1-\theta) + \varphi'\theta. \quad (10)$$

Differentiating (10) with respect to ε for θ = const, we obtain:

$$1/C = (1-\theta)/C_0 + \theta/C'. \quad (11)$$

Thus, writing the adsorption isotherm in the form of Eq. (7) corresponds to connecting in series two condensers with the capacity $C_0/(1-\theta)$, and C'/θ. Any physical interpretation of this model seems difficult to us.

If the capacities C_0 and C' are independent of ε, it is obvious that $\varphi_0 = \varepsilon/C_0$, and $\varphi' = \varepsilon'/C' + \varphi_N$. In this case, Eq. (10) may be rewritten in the form:

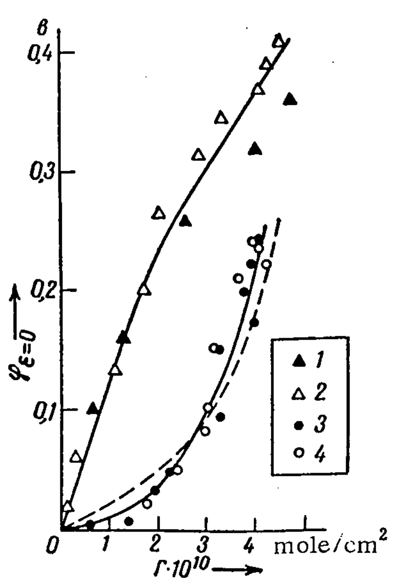

Fig. 2. The shift in the z.c.p. as a function on n-$C_5H_{11}NH_2$ adsorption: 1 and 2) At the solution/air interface (1 – background 0.05 n-KOH, 2 – background 1 n-Na_2SO_4 + 0.05 n-KOH); 3 and 4) At the mercury/solution boundary (3 – background 0.05 n-KOH, 4 – background 1 n-Na_2SO_4 + 0.05 n-KOH). The dotted line is calculated from Eq. (6) for φ_N = 0.4 V, $\Gamma_m = 5 \cdot 10^{-10}$ M/cm², and C_0/C' = 5.

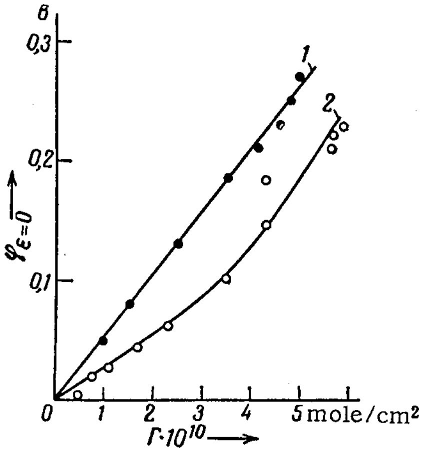

Fig. 3. The shift in the z.c.p. as a function of n-C_3H_7OH adsorption: 1) At the solution/air interface; 2) at the mercury/solution interface. Background 0.01 n-H_2SO_4.

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

Setting ε = 0 in (10a), we obtain a linear relation between φ_ε = 0 and θ (or Γ), thus:

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

Thus, the relation between the z.c.p. and Γ makes it possible to decide whether condition (1) or (7) is realized and hence to decide which of the variables (φ or ε) is better when making a study of the adsorption of an organic substance at an interface.

Figures 1-3 give curves of φ_ε = 0 as a function of Γ for 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, we found the values of φ_ε = 0 and Γ from the electrocapillarity curves. At the solution/air interface, the values of φ_ε = 0 were measured by Kenrik's method, and the values of Γ were calculated from the values of the surface tension, measured by the method of maximum pressure in a bubble. The values of φ_ε = 0 for different concentrations of n-C_4H_9COOH and n-C_3H_7OH on a background of 0.01 n-H_2SO_4 were taken from [6].

It may be seen from the figures that in the case of n-C_4H_9COOH and n-$C_5H_{11}NH_2$, the relation between φ_ε = 0 and Γ at the mercury/solution interface is in good agreement with Eq. (6), independently of the concentration of the background, and departs greatly from the linear relation predicted by Eq. (12). At the same time, at the solution/air interface, the relation approximately follows Eq. (12).† We have also obtained similar results in the system 3nKCl + n-C_4H_9OH using the data of [7] for the mercury/solution interface. A somewhat smaller difference in the relationship between φ_ε = 0 and Γ at the two interfaces is observed in the case of n-C_3H_7OH (Fig. 3). This may be partially due to the increase in C' on going to n-C_3H_7OH, since it is easily seen that Eq. (6) reduces to (12) when $C' = C_0$. Accordingly, in the case of n-C_3H_7OH, good agreement between theory and experiment is to be expected when either φ or ε is used as the electrical variable. At the same time, in the case of n-C_4H_9COOH and n-$C_5H_{11}NH_2$, as well as n-C_4H_9OH, Frumkin's model gives considerably better agreement with experiment at the mercury/solution interface, so that the potential should be used as the electrical variable in these systems.

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*For a solution/air interface, φ_ε = 0 means the adsorption potential jump.

†Here we are not considering departures from a linear relationship between φ_ε = 0 and Γ at the solution/air boundary, resulting, for example, from change in orientation of the adsorbed molecules with increase in Γ.

It was noted in [8], in referance to Overbeek, that although the conclusions from Eq. (4) are well supported by experiment, the following fact raises some doubt. At $\varepsilon = 0$, $\varepsilon_0(1-\theta)$ and $\varepsilon'\theta$ are not equal to zero separately, i.e., parts of the surface are charged. Let us point out in this connection that the model discussed above is quantatively correct, if the adsorbed layer is bounded on both sides by strictly equipotential planes, and the lines of force are perpendicular to it over its whole extent. These conditions may be satisfied approximately, if the dipoles of water and the organic substance oriented perpendicular to the surface are located between two phases having quite high dielectric constants. This is the reason why this model is not satisfied at the solution/air interface. The fact that the relation between $\varphi_\varepsilon = 0$ and Γ remains the same when the concentration of the background is changed (Fig. 1, 2) shows that the equalization of the potential in the water phase is not determined by the concentration of ions in the diffuse layer, but by the high dielectric constant of the water itself (see [9]). For this reason, it does not depend on the relation between the Debye length and the distance between the centers of the water molecules and the organic substance in the adsorbed layer. It should also be kept in mind that the increase in this distance, which probably occurs with increase in θ as a result of partial segregation of the organic substance and the water in the surface layer, will help to satisfy the condition (4).

If this explanation is correct, then, with a weakly absorbing substance present, the adsorption of which is only appreciable at high concentrations by volume, and which lowers the dielectric constant of the water, departures are to be expected from the model proposed. An example of such a system is probably provided by solutions of n-C_3H_7OH Further investigations are, however, required to get any more deeply into the reasons why Eq. (4) is satisfied at the mercury/solution interface.

LITERATURE CITED

1. R. Parsons, J. Electroanalyt. Chem., 7, 136 (1964).
2. B. B. Damaskin, J. Electroanalyt. Chem., 7, 155 (1964).
3. R. Parsons, Transactions of the Fourteenth Conference of the CITCE (in press).
4. A. N. Frumkin, Transactions of the L. Yu. Karpov Institute [in Russian], No. 5, 3 (1926); A. N. Frumkin, Zs. Phys., 35, 792 (1926).
5. R. Parsons, Trans. Farad. Soc., 55, 999 (1959).
6. A. N. Frumkin, Transactions of the L. Yu. Karpov Institute [in Russian], No. 3, 3 (1924); A. N. Frumkin, Zs. phys. Chem., 111, 190 (1924).
7. T. A. Kryukova and A. N. Frumkin, ZhFKh, 23, 819 (1949).
8. R. S. Hansen, D. J. Kelsh, and D. H. Grantham, J. Phys. Chem., 67, 2316 (1963).
9. N. F. Mott, R. Parsons, and R. J. Watts-Tobin, Phil. Mag., 7, No. 75, 483 (1962).