ADSORPTION OF ORGANIC SUBSTANCES AS FUNCTION OF BASE-ELECTROLYTE CONCENTRATION IN ABSENCE OF A SALTING- OUT EFFECT

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It has been noted in [1-4] that there are two factors determining how the adsorption of an organic substance depends on the concentration of a surface-inactive base electrolyte: the change in electrode charge density at the given potential and the salting-out effect. With the base-electrolyte concentrations usually employed ($c = 0.1$-1 N), the salting-out effect is very substantial, so that one can, more particularly, determine the salting-out coefficient k from the log c dependence of the desorption potential [3, 5], or find the electrode charge density from the same dependence when k is known [4, 6].

It is of interest to investigate how base-electrolyte concentration will influence the adsorption of an organic substance under conditions where the salting-out effect can be neglected. However, until recently such an investigation was not feasible, as it is impossible to measure electrocapillary (σ-φ) curves in dilute (≤ 0.01 N) electrolyte solutions with the usual Gouy electrometer (because of sticking to the glass or of incomplete wetting of the glass in the capillary [7-9]). In order to overcome this difficulty we decided to use the method of measuring σ with the aid of a U-shaped capillary as proposed by Schiffrin [10]. This method had been successfully employed before for recording $\sigma-\varphi$ curves both in dilute electrolyte solutions [10, 11] and in the presence of organic substances causing the mercury to stick to the glass in the Gouy electrometer [12, 13].

In the present work we have used a U-shaped capillary to record $\sigma-\varphi$ curves in ethyl acetate solutions in 0.007, 0.05, and 0.1 N NaF. Figure 1 shows the location of $\sigma-\varphi$ curves measured at different base-electrolyte concentrations but the same ethyl acetate concentration (0.1 M). The influence of base-electrolyte concentration can be demonstrated more clearly by plotting as a function of φ the depression in interfacial tension $\Delta\sigma$ caused by the surface-active additive (Figs. 2 and 3). It can be seen from these plots that at NaF concentrations ≤ 0.05 N the $\Delta\sigma-\varphi$ curves have a common point of contact at the potential of maximum adsorption, but they intersect when the base-electrolyte concentration is raised to 0.1 N. We have observed similar behavior at other ethyl acetate concentrations.

It is easy to show that the intersecting of the $\Delta\sigma-\varphi$ curves (and thus that of the $\Gamma-\varphi$ curves as well, where Γ is the adsorption of the organic substance) is due to the salting-out effect.* In fact, by starting from the equation [5]

$$\lg B_0 = \lg B_0^0 + kc, \tag{1}$$

where B_0^0 is the adsorption equilibrium constant in pure water, and from the adsorption isotherm [16]

$$B_0 c_{\text{org}} = \frac{\theta}{1-\theta} \exp(-2a\theta), \tag{2}$$

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* It can be seen from Fig. 3 that neither of these intersection points corresponds to the potential of zero charge (pzc) in the pure base-electrolyte solution. This again disproves the method of Green and Dahms [14], which has been criticized in [4] but recently was again used for determining the pzc of the copper electrode [15].

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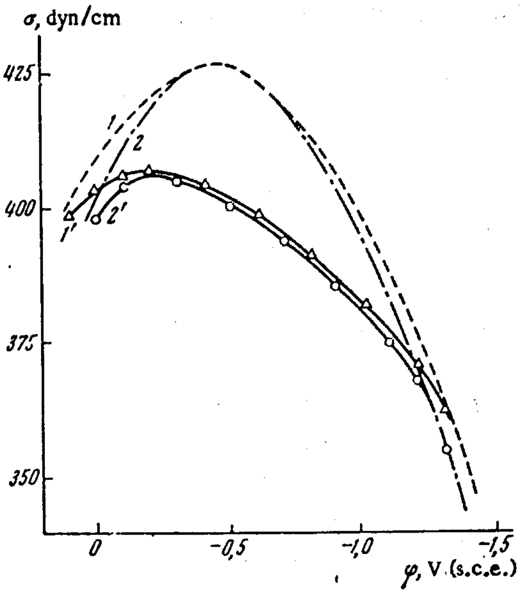

Fig. 1. Electrocapillary curves for a mercury electrode in the solutions: 1) 0.007 N NaF; 1') 0.007 N NaF + 0.1 M ethyl acetate; 2) 0.1 N NaF; 2') 0.1 N NaF + 0.1 M ethyl acetate.

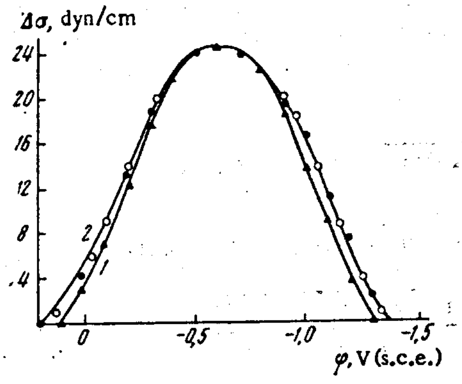

Fig. 2

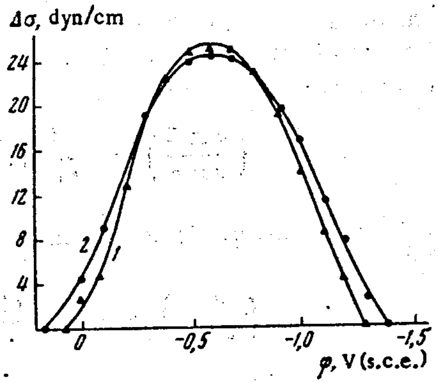

Fig. 3

Fig. 2. Depression of interfacial tension as a function of potential in 0.1 M ethyl acetate solution: 1) in 0.05 N NaF; 2) in 0.007 N NaF. Open circles on curve 2 are points calculated with the aid of Eqs. (9) and (10).

Fig. 3. Depression of interfacial tension as a function of potential in 0.1 M ethyl acetate solutions: 1) in 0.1 N NaF; 2) in 0.007 N NaF.

where c_{org} is the concentration of organic substance and a is the attraction constant, one can estimate the change in the degree of surface coverage θ which occurs under the influence of the salting-out effect, and then with the aid of the equation

$$\Delta\sigma = -RT\Gamma_\infty[\ln(1-\theta)+a\theta^2], \tag{3}$$

where Γ_∞ is the limiting adsorption at $\theta = 1$, one can estimate the corresponding change in $\Delta\sigma$. A calculation following Eqs. (1) to (3) shows that with $a = 1.15$, $RT\Gamma_\infty = 1\ \mu J/cm^2 = 10$ dyn/cm, and $k = 0.3$ liter/mole, a given coverage $\theta_0 = 0.80$ (at $c = 0$) has its counterpart $\theta_{0.1} = 0.83$ (at $c = 0.1$ N) and $\Delta(\Delta\sigma) = \Delta\sigma_{0.1} - \Delta\sigma_0 = 1.4$ dyn/cm, and this practically coincides with the experimental $\Delta(\Delta\sigma)$ value in the maximum of the $\Delta\sigma - \varphi$ curves (Fig. 3). At the base-electrolyte concentration $c = 0.05$ N, a similar calculation gives the value

$\Delta(\Delta\sigma) = 0.3$ dyn/cm, which is already close to the experimental accuracy with which this quantity can be determined. Thus, the influence of base-electrolyte concentration on the adsorption of an organic substance can only be observed without a salting-out effect when the NaF concentration is less than 0.05 N.

Under these conditions the concentration effect of the base electrolyte can be described by employing the model of two parallel capacitors [17] while allowing for the dependence of capacitances C_0 (at $\theta = 0$) and C' (at $\theta = 1$) on electrolyte concentration according to the Gouy–Chapman–Grahame theory [18]. As in [4], such an approach rests on the general equation for the congruent isotherm

$$B(\varphi, c) \cdot c_{\text{org}} = f(\Gamma), \tag{4}$$

but in contrast to [4] it takes into account that C' depends on c, which becomes necessary in dilute base-electrolyte solutions ($c \leq 0.05$ N). At $c_{\text{org}} = \text{const}$ it follows from Eq. (4) that

$$\left(\frac{\partial \ln B}{\partial \varphi}\right)_c d\varphi + \left(\frac{\partial \ln B}{\partial \ln c}\right)_\varphi d\ln c = d\ln f(\Gamma), \tag{5}$$

whence at $\Gamma = \text{const}$ we obtain

$$\left(\frac{\partial \ln B}{\partial \varphi}\right)_c \left(\frac{\partial \varphi}{\partial \ln c}\right)_\Gamma = -\left(\frac{\partial \ln B}{\partial \ln c}\right)_\varphi . \tag{6}$$

Equation (6) shows that B, and hence Γ and $\Delta\sigma$, do not depend on c when $(\partial \ln B/\partial\varphi)_c = 0$, i.e., at the potential of maximum adsorption. Figure 2 confirms this result.

It follows further from the model of two parallel capacitors [17] that

$$\left(\frac{\partial \ln B}{\partial \varphi}\right)_c = -\frac{\varepsilon_0 - \varepsilon'}{RT\Gamma_\infty} , \tag{7}$$

where ε_0 and ε' are the surface charge densities at $\theta = 0$ and $\theta = 1$, respectively. On the other hand, we obtain from the same model and from diffuse-layer theory, under the condition $k = 0$ but allowing for the dependence of C' (and hence of ε') on c, by analogy with the result reported in [4], the following equation for a 1:1 base electrolyte:

$$\left(\frac{\partial \ln B}{\partial \ln c}\right)_\varphi = -\frac{1}{F\Gamma_\infty}\left[\sqrt{4A^2c + \varepsilon_0^2} - \sqrt{4A^2c + (\varepsilon')^2}\,\right], \tag{8}$$

where $A = \sqrt{DRT/2\pi}$. On substituting (7) and (8) into (6) and solving for the derivative $(\partial\varphi/\partial \ln c)_\Gamma$ we find

$$\left(\frac{\partial \varphi}{\partial \ln c}\right)_\Gamma = -\frac{RT}{F} \cdot \frac{\sqrt{4A^2c + \varepsilon_0^2} - \sqrt{4A^2c + (\varepsilon')^2}}{\varepsilon_0 - \varepsilon'} . \tag{9}$$

Expression (9) shows that for $\varepsilon_0^2 \gg 4A^2c$ and $(\varepsilon')^2 \gg 4A^2c$*

$$\left(\frac{\partial \varphi}{\partial \ln c}\right)_\Gamma \approx \left(\frac{\partial \varphi}{\partial \ln c}\right)_{\Delta\sigma} \approx \pm\frac{RT}{F}$$

(the plus sign for $\varepsilon_0 - \varepsilon' < 0$ and the minus sign for $\varepsilon_0 - \varepsilon' > 0$). Therefore, at large densities ε_0 and ε' and at $\Delta\sigma = \text{const}$, a change in the concentration of a 1:1 base electrolyte by one order of magnitude produces a shift in potential of about 58 mV.

With the aid of expression (9) we have calculated the average value of the derivative $(\partial\varphi/\partial \ln c)_\Gamma$ in the interval of base-electrolyte concentrations from 0.007 to 0.05 N, and then with the expression

$$\Delta\varphi = \overline{\left(\frac{\partial \varphi}{\partial \ln c}\right)_\Gamma} \cdot \Delta \ln c \tag{10}$$

we calculated the potential shift which, at $\Delta\sigma = \text{const}$, corresponds to a transition from 0.05 N to 0.007 N NaF. Then, we calculated the $\Delta\sigma - \varphi$ curve for 0.1 M ethyl acetate solution in 0.007 N NaF as base electrolyte by using as a basis the $\Delta\sigma - \varphi$ curve in 0.1 M ethyl acetate solution in 0.05 N NaF and employing the

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* In aqueous solutions at 25°C and $c = 0.01$ N, the quantity $4A^2c$ constitutes approximately 1.4 $\mu C^2/cm^4$.

theoretical $\Delta\varphi$ values. It can be seen from Fig. 2 that the $\Delta\sigma - \varphi$ curve for 0.007 N base-electrolyte solution thus calculated agrees well with the experimental curve.

Thus, the influence of the concentration of a surface-inactive base electrolyte upon the adsorption of an organic substance in the absence of a salting-out effect (at NaF concentrations ≤ 0.05 N) can be satisfactorily described (as suggested previously [3, 4]) on the basis of the model of two parallel capacitors and of diffuse-layer theory.

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