THE EFFECT OF POTENTIAL ON THE ATTRACTIVE FORCE BETWEEN ADSORBED ORGANIC MOLECULES

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One of us has considered [1] the effect of the constant a, characterizing the degree of attraction between adsorbed organic molecules, on the form of differential capacitance adsorption peaks, on the assumption that a = const. Actually, a can change with electrode potential as a result of a change in area S, of a single adsorbed molecule, with an increase in the quantity $\theta = \Gamma/\Gamma_m$, i.e., the ratio of the adsorption to its limiting value Γ_m [2], and also as a result of a change in θ, the supplementary work of adsorption connected with the dipole moment of the adsorbed particle. In the first case, as shown in [2], the connection between the change on the surface and θ is given by the equation

$$\varepsilon = \varepsilon_0 [1 - k\theta + (k-1)\theta^2] + C'(\varphi - \varphi_N)[k\theta - (k-1)\theta^2], \quad (1)$$

where $k = \frac{S_{\theta=0}}{S_{\theta=1}}$; $\varepsilon_0 = \int_0^{\varphi} C_0 d\varphi$; C_0 and C' are the capacitances at $\theta = 0$ and $\theta = 1$; φ_N is the zero charge point (z.c.p.) at $\theta = 1$; all potentials φ are calculated from the z.c.p. at $\theta = 0$. With k = 1, from (1) we obtain the following equation, which holds true when a = const:

$$\varepsilon = \varepsilon_0 (1 - \theta) + C'(\varphi - \varphi_N)\theta. \quad (1a)$$

If $k \neq 1$, then as shown in [2]

$$a = a_0 + (k-1)P = a_0 + (k-1)\frac{\int_0^{\varphi} \varepsilon_0 d\varphi + \varphi C'(\varphi_N - \varphi/2)}{A}, \quad (2)$$

where $A = RT\Gamma_m$. The dependence of a on φ, from Eq. (2), is parabolic and is realized, for example, with adsorption of the cations $[(C_4H_9)_4N]^+$ on mercury [3].

On the other hand, as noted in [1], during adsorption of tert-$C_5H_{11}OH$ on mercury, a linear dependence of a on φ is observed:

$$a = a_0 + \beta\varphi, \quad (3)$$

where a_0 and β are constants equal, respectively, to 1.64 and 0.25.

Writing the adsorption isotherm in the form

$$Bc = B_0 e^{-P}c = \frac{\theta}{1-\theta}\exp(-2a_0\theta)\exp(-2\theta\beta\varphi), \quad (4)$$

where c is the concentration of the organic substance, and using the properties of the total differential in the Gibbs equation, we obtain after algebraic transformations

$$\varepsilon = \varepsilon_0 (1 - \theta) + C'(\varphi - \varphi_N^0) + \beta A\theta^2. \quad (5)$$

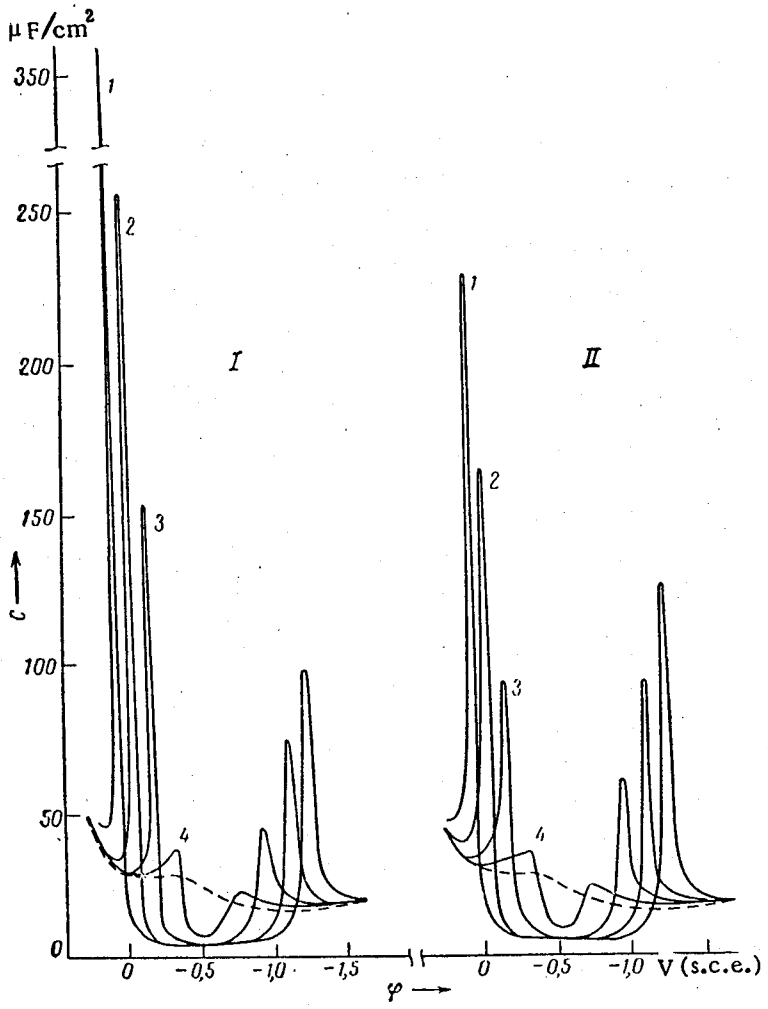

Fig. 1. Differential capacitance curves in 0.9 N NaF (dashed curve) and also with added tert-$C_5H_{11}OH$ in the concentrations: 1) 0.3 M; 2) 0.1 M; 3) 0.03 M; 4) 0.01 M. I refers to experimental data at 400 hertz; II is calculated from Eq. (7) with A = 1.00, B_0 = 25.6; C' = 4.4; φ_N = 0.3 and the constant a = 1.6.

Thus in both cases when a ≠ const, the dependence of electrode charge on θ deviates from the linearity corresponding to a constant value for a. Comparing (1a) and (5) and introducing a supplementary term in Eq. (5) in the quantity φ_N, we obtain

$$\varphi_N = \varphi_N^0 - \frac{\beta A}{C}\theta, \qquad (6)$$

where φ_N^0 is the value of φ_N at θ = 0. In other words the experimentally observed linear variation of a with φ can be explained by changes of φ_N with surface charge. But since the value of φ_N is connected with the presence of adsorbed molecules with dipole moments, then the result obtained indicates a change in orientation of the adsorbed molecules with increased charging, leading to a change in the component of the dipole moment normal to the surface and to a corresponding change in the supplementary adsorption energy [2].

We have obtained C, φ curves in 0.9 N NaF solutions containing added tert-$C_5H_{11}OH$ (Fig. 1, I) and from the observed quadratic dependence of the potential peaks (φ^{max}) on log c have made more precise the constants used in [1]: A = 1.00, B_0 = 25.6, C' = 4.4, φ_N = 0.3. Under these conditions the maximum change in φ_N, and consequently also in the supplementary adsorption energy in the case of tert-$C_5H_{11}OH$, is ~17%. However, as follows from [1], the height of the adsorption peaks in this case should be significantly greater. Thus, calculation of C, φ curves according to the equation

$$C = C_0(1-\theta) + C'\theta + \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)} \frac{[\varepsilon_0 - C'(\varphi - \varphi_N)]^2}{A}, \qquad (7)$$

resulting from Frumkin's theory [2], or from an identical Eq. (9) in [4], may serve as a sensitive test both of the theory itself and of any variation of a with electrode potential.

In Fig. 1, II are given C, φ curves in 0.9 N NaF and different amounts of tert-$C_5H_{11}OH$, calculated from the constants given above and with constant a = 1.6, while in Fig. 2 a changes linearly with φ in accordance with Eq. (3).

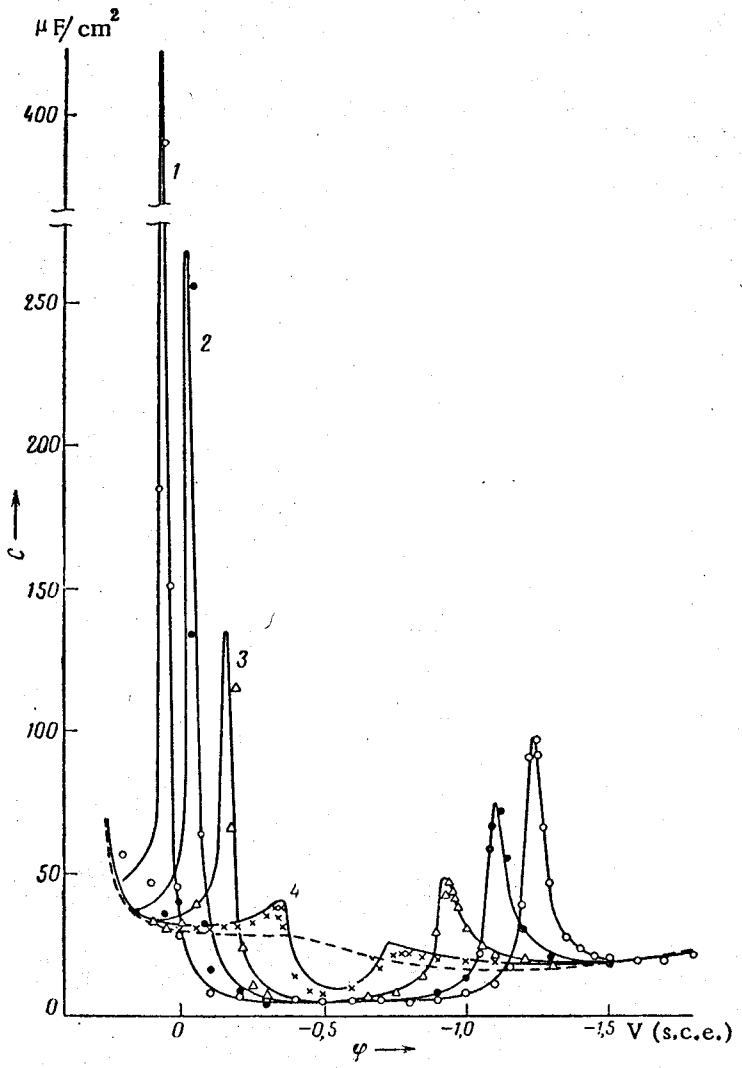

Fig. 2. Differential capacitance curves in 0.9 N NaF (dashed curve) and also with added tert-$C_5H_{11}OH$ in the concentrations: 1) 0.3 M; 2) 0.1 M; 3) 0.03 M; 4) 0.01 M. The continuous line calculated from Eq. (7) with the same A, B_0, C', φ_N, as in Fig. 1; a was found from Eq. (3) with a_0 = 1.64 and β = 0.25. The points represent experimental data in the corresponding solutions, 400 hertz.

The dependence of θ on φ, necessary for the calculation, was determined graphically using Eq. (4). Also shown in Fig. 2 are experimental values of the capacitance obtained in the corresponding solutions at 400 hertz. As seen from Fig. 2, the experimental data agrees well with the calculated C, φ curves. At the same time, from Fig. 1 it is seen that the anodic peaks on the C, φ curves, calculated using a = const, are significantly lower than the experimental

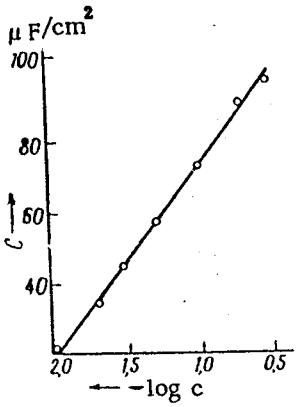

Fig. 3. Dependence of the height of the cathodic capacitance peak in solutions of 0.9 N NaF + tert-$C_5H_{11}OH$ on the logarithm of the alcohol concentration.

peaks while, on the other hand, the cathodic peaks are somewhat higher than those found experimentally. This result shows that the strength of the interaction between tert-$C_5H_{11}OH$ molecules adsorbed on mercury does not remain constant with changes in the electrode potential. By taking a linear dependence of $\underline{a}$ on φ, Frumkin's theory [2] permits a quantitative interpretation of the very complex shapes of the differential capacitance curves in the presence of an organic substance.

In [1] it was shown that the capacitance at the adsorption peak maximum (C^{max}) is probably linearly related to the logarithm of the concentration of the organic substance:*

$$C^{max} = K_1 + K_2 \lg c, \tag{8}$$

where

$$K_1 = \frac{C_0 + C'}{2} + \frac{C_0 - C'}{2 - a}(a + \ln B_0) + \frac{(C'\varphi_N)^2}{2A\,(2-a)};$$
$$K_2 = 2{,}3\,\frac{C_0 - C'}{2 - a}, \tag{9}$$

TABLE 1

	Expt.	a = 1.6	a = 1.5
K_1	135	163	130
K_2	54	71	57

From Fig. 3 it is seen that the experimental dependence of C^{max} on log $\underline{c}$, obtained for cathodic desorption peaks of tert-$C_5H_{11}OH$, is in good agreement with Eq. (8). A comparison of experimental values of K_1 and K_2 with values calculated using the constants mentioned above, and using a mean value for C_0 = 16.8 $\mu F/cm^2$, is given in Table 1. From this table it is seen that the experimental values of K_1 and K_2 are in significantly better agreement with the calculated values when a = 1.5 rather than when a = 1.6, corresponding to the potential at maximum adsorption. This result shows once again the decrease in the attraction constant $\underline{a}$ for tert-$C_5H_{11}OH$ with an increase in the negative value of the potential. It should be noted that the change in the strength of the interaction between adsorbed tert-$C_5H_{11}OH$ molecules with electrode potential is inconsistent with the results of Lorenz and Muller [5].

The better agreement of the experimental data with theory [1, 2] enables the value of $\underline{a}$ to be determined from experimental differential capacitance curves in the following ways:

1) From the heights of capacitive adsorption peaks, using the equation

$$C^{max} = \frac{C_0 + C'}{2} + \frac{[\varepsilon_0 - C'(\varphi - \varphi_N)]^2}{A}\,\frac{1}{4 - 2a}, \tag{10}$$

which follows from Eq. (7) with θ = 0.5 (cf. [1]).

2) From the widths of the capacitance peaks at 1/2 or 3/4 their heights and the quantity $\Phi \approx d \ln c/d\,\varphi^{max}$, using Eq. (12) from reference [1].

3) From the slope of the straight line obtained by plotting C^{max} against log $\underline{c}$, using Eqs. (8) and (9).

4) From the form of the adsorption isotherm by comparing experimental isotherms with those calculated from theory at different values of $\underline{a}$ (cf. Eq. (3) in [1]).

All these methods with variable $\underline{a}$ are approximations, but the errors involved usually do not exceed 2-3%.

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*An analogous result has been given in [6] from an analysis of Langmuir's equation.

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