Reports of the Academy of Sciences of the USSR

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1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1962. Volume 147, No. 1

PHYSICAL CHEMISTRY

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EFFECT OF POTENTIAL ON THE ATTRACTION INTERACTION BETWEEN ADSORBED ORGANIC MOLECULES

(Presented by Academician A. N. Frumkin, June 4, 1962)

In work ([1]), one of us considered the influence of the constant a, characterizing the degree of interaction of adsorbed organic molecules, on the shape of adsorption peaks of the differential capacitance, it being assumed that $a = \text{const}$. In reality, a may vary with the electrode potential both as a result of a change in the area S per adsorbed molecule as the quantity $\theta = \Gamma/\Gamma_m$, i.e., the ratio of adsorption to its limiting value Γ_m ([2]), increases, and as a result of a change with θ in the additional work of adsorption associated with the dipole moment of the adsorbing particles. In the first case, as shown in ([2]), the relation between the surface charge and θ is given by the equation:

$$\varepsilon = \varepsilon_0 \left[1 - k\theta + (k-1)\theta^2\right] + C'(\varphi - \varphi_N)\left[k\theta - (k-1)\theta^2\right], \tag{1}$$

where $k = \dfrac{S_{\theta=0}}{S_{\theta=1}}$; $\varepsilon_0 = \displaystyle\int_0^{\varphi} C_0\, d\varphi$; C_0 and C' are the capacitances, respectively, at $\theta = 0$ and $\theta = 1$; φ_N is the point of zero charge (p.z.c.) at $\theta = 1$; all potentials φ are measured from the p.z.c. at $\theta = 0$. For $k = 1$, from (1) we obtain the equation valid for $a = \text{const}$:

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

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

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

Fig. 1. Curves of differential capacitance in 0.9 N NaF (dashed line), and also with additions of tert.-$C_5H_{11}OH$ at concentrations: 1–0.3 M; 2–0.1 M; 3–0.03 M; 4–0.01 M. I–experimental data, 400 Hz; II–calculation by equation (7) at $A = 1.00$, $B_0 = 25.6$, $C' = 4.4$, $\varphi_N = 0.3$, and constant $a = 1.6$.

Figure 1: Fig. 1. Curves of differential capacitance in 0.9 N NaF (dashed line), and also with additions of tert.-$C_5H_{11}OH$ at concentrations: 1–0.3 M; 2–0.1 M; 3–0.03 M; 4–0.01 M. I–experimental data, 400 Hz; II–calculation by equation (7) at $A = 1.00$, $B_0 = 25.6$, $C' = 4.4$, $\varphi_N = 0.3$, and constant $a = 1.6$.

where $A = RT\Gamma_m$. The dependence of a on φ, corresponding to equation (2), has the form of a parabola and is realized, for example, in the adsorption on mercury of the cations $[(C_4H_9)_4N]^+$ ([3]).

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

$$a = a_0 + \beta\varphi, \tag{3}$$

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

Writing the adsorption isotherm in the form

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

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

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

Thus, in both cases, for $a \neq$ const, the dependence of the electrode charge on θ deviates from the linear dependence corresponding to a constant value of a. Comparing (1a) and (5) and introducing an additional term into equation (5)

in the quantity φ_N, we obtain

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

where φ_N^0 is the value of φ_N at $\theta = 0$. In other words, the linear variation of a with φ observed experimentally can be explained by a change in φ_N with surface coverage. But since the quantity φ_N is associated with the presence, in the

Figure 2

Figure 2: Figure 2

Fig. 1. Curves of differential capacitance in 0.9 N NaF (dashed line), and also with additions of tert.-$C_5H_{11}OH$ at concentrations:
1–0.3 M; 2–0.1 M; 3–0.03 M; 4–0.01 M. I–experimental data, 400 Hz; II–calculation by equation (7) at $A = 1.00$, $B_0 = 25.6$, $C' = 4.4$, $\varphi_N = 0.3$, and constant $a = 1.6$.

adsorbing molecules of a dipole moment, the result obtained means a change in the orientation of the adsorbed molecules with increasing coverage, which leads to a change in the component of the dipole moment normal to the surface and to a corresponding change in the additional adsorption energy ([2]).

We measured C, φ-curves in 0.9 N NaF solutions with various additions of tert.-$C_5H_{11}OH$ (Fig. 1 I), and from the quadratic dependence obtained for the peak potentials ($\varphi^{\max}$) on $\lg c$, the constants used in (1) were refined: $A = 1.00$, $B_0 = 25.6$, $C' = 4.4$, $\varphi_N = 0.3$. Under these conditions the maximum variation of φ_N, and consequently also of the additional energy

adsorption in the case of tert.-$C_5H_{11}OH$ is $\sim 17\%$. However, as follows from (1), the height of the adsorption peaks should in this case change considerably more strongly. Thus, calculation of the C, φ curves from the equation

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

which follows from Frumkin' s theory (2) and is identical to equation (9) in (4), can serve as a sensitive test both of the theory itself and of the existence of a dependence of the quantity a on the electrode potential.

In Fig. 1II the C, φ curves in 0.9 N NaF with various additions of tert.-$C_5H_{11}OH$ are shown, calculated by us with the above constants for constant $a = 1.6$, and in Fig. 2–for a varying linearly with φ according to equation (3). The dependence of θ on φ needed in the calculation was determined graphically with the aid of equation (4). Fig. 2 also gives experimental capacitance data obtained in the corresponding solutions at 400 Hz. As can be seen from Fig. 2, the experimental data agree well with the calculated C, φ curves when the linear change of a with the electrode potential is taken into account. At the same time, it follows from Fig. 1 that the anodic peaks on the C, φ curves calculated for $a = \text{const}$ are considerably smaller than the experimental ones, whereas the cathodic peaks,

Fig. 2. Curves of differential capacitance in 0.9 N NaF (dashed line) and also with additions of tert.-$C_5H_{11}OH$ at concentrations:
1 –0.3 M; 2 –0.1 M; 3 –0.03 M; 4 –0.01 M. Solid lines–calculation by equation (7) with the same A, B_0, C', φ_N as in Fig. 1; a was found from equation (3)

for $a_0 = 1.64$ and $\beta = 0.25$. Points–experimental data in the corresponding solutions, 400 Hz.

on the contrary, are somewhat higher than the experimental ones. This result shows that the forces of interaction between tert.-$C_5H_{11}OH$ molecules adsorbed on mercury do not remain constant when the electrode potential changes. Taking into account the linear dependence of a on φ, Frumkin' s theory (2) makes it possible to convey quantitatively the very complex shape of the differential-capacitance curves in the presence of an organic substance.

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

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

where

$$K_1 = \frac{C_0 + C'}{2} + \frac{C_0 - C'}{2 - a}(a + \ln B_0) + \frac{(C'\varphi_N)^2}{2A} \cdot \frac{a}{(2 - a)};$$

$$K_2 = 2.3 \frac{C_0 - C'}{2 - a}, \tag{9}$$

[Figure 3]

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 concentration of tert.-$C_5H_{11}OH$

Figure 3 gives the experimental dependence of C^{max} on $\lg c$, obtained by us for the cathodic desorption peaks of tert.-$C_5H_{11}OH$, which satisfies relation (8) very well. A comparison of the experimental values of K_1 and K_2 with those calculated for the constants indicated above and for the mean value $C_0 = 16.8\ \mu F/cm^2$ is given in Table 1. As can be seen from the table, the experimental K_1 and K_2 agree considerably better with the calculation at $a = 1.5$ than at $a = 1.6$, corresponding to the potential of maximum adsorption. This result once again indicates a decrease in the attraction constant a for tert.-$C_5H_{11}OH$ with an increase in the negative value of the potential. It should be noted that the change, established by us, in the forces of interaction between adsorbed tert.-$C_5H_{11}OH$ molecules with the electrode potential is in contradiction with the conclusion of Lorenz and Müller ([5]).

Table 1

	Experiment	$a = 1.6$	$a = 1.5$
K_1	135	163	130
K_2	54	71	57

Good agreement of the experimental data with the theory ([1],[2]) makes it possible to determine the value of a from experimental differential-capacitance curves by the following methods:

1) From the height of the adsorption capacitance 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 equation (7) at $\theta = 0.5$ (see ([1])).

2) From the width of the capacitance peaks, respectively at 1/2 or 3/4 of their height, and the value $\Phi \simeq d \ln c / d\varphi^{\max}$, using equation (12) from work ([1]).

3) From the slope of the straight line $C^{\max} - \lg c$, using equations (8) and (9).

4) From the shape of the adsorption isotherm by comparing experimental isotherms with those calculated theoretically at different a (see equation (3) in ([1])).

All these methods, when a is variable, prove to be approximate, but the errors thereby obtained usually do not exceed 2–3%.

We express our deep gratitude to Academician A. N. Frumkin for his attention to the work and for discussion of the experimental data.

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Received
30 V 1962

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* An analogous conclusion was drawn in work ([6]) from an analysis of the Langmuir equation.

Note: Figure translations are in progress. See original paper for figures.