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B. B. Damaskin, G. A. Tedoradze

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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B. B. Damaskin, G. A. Tedoradze

SURFACE COVERAGE BY AN ORGANIC SUBSTANCE AT THE POTENTIALS OF MAXIMA ON DIFFERENTIAL-CAPACITANCE CURVES

(Presented by Academician A. N. Frumkin, May 21, 1963)

It was shown in ([1]) that, when the dependence of the attraction constant a on the electrode potential is taken into account, the differential-capacitance curve in the presence of tert.-$C_5H_{11}OH$ can be interpreted quantitatively by using A. N. Frumkin' s adsorption-isotherm equation ([2])

$$Bc = \frac{\theta}{1-\theta} \exp(-2a\theta), \tag{1}$$

where c is the concentration of the organic substance; $\theta = \Gamma/\Gamma_m$, i.e., the ratio of the adsorption Γ to its limiting value Γ_m, and

$$B =$$

$$= B_0 \exp\left[\frac{\int_0^{\varphi}\int_0^{\varphi} C_0\, d\varphi^2 + C'\varphi\left(\varphi_N - \frac{\varphi}{2}\right)}{A}\right] \tag{2}$$

Fig. 1. Dependence of the coverage at the maximum on the peak potential for different a:
1–$a = 0$; 2–0.5; 3–1.0; 4–1.5; 5–1.9; dashed line–limiting value of $\varphi^{\max}$ as $c \to 0$.

B_0 and A are constants, with $A = RT\Gamma_m$; C_0 and C' are the double-layer capacitances at $\theta = 0$ and $\theta = 1$, respectively; φ is the potential measured from the point of zero charge (p.z.c.) at $\theta = 0$; φ_N is the shift of the p.z.c. on going from $\theta = 0$ to $\theta = 1$. In this case, as follows from ([3]),

$$C = C_0(1-\theta) + C'\theta + \left(\frac{d\ln B}{d\varphi}\right)\left(\frac{\partial\varepsilon}{\partial\varphi}\right)_{\varphi} h, \tag{3}$$

where

$$h = \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \tag{4}$$

To find the dependence of a on φ from experimental data, it was assumed that the position of the peaks on the C,φ-curves is determined mainly by the magnitude h ([3]). In this case the coverage at the maximum is $\theta^{\max} = 0.5$, and the value of a at the peak potentials $\varphi^{\max}$ is determined by the methods described in ([1]).*

Obviously, the position of the peaks on the C,φ-curves corresponds to the maximum of h only for not too small values of a, when a sharp dependence of h on φ is observed ([3]). In the general case the position of the extrema on the C,φ-curves is determined by the condition $dC/d\varphi = 0$, for which the calculation is possible under the assumption $C_0 = \text{const}$ and $a = \text{const}$, when

$$B = B_m \exp[-a(\varphi-\varphi_m)^2], \tag{2a}$$

where $a = (C_0 - C')/2A$, $\varphi_m = -\varphi_N C'/(C_0 - C')$; $B_m = B_0 \exp[(\varphi_N C')^2/2A(C_0 - C')]$.

* A detailed theory is set forth in an article to be published in the *Journal of Physical Chemistry*.

In this case

$$C = C_0(1-\theta) + C'\theta + 4Aa^2(\varphi-\varphi_m)^2 h, \tag{5}$$

$$\frac{dC}{d\varphi} = 12Aa^2(\varphi-\varphi_m)h\left\{1 - \frac{2a}{3}(\varphi-\varphi_m)^2\frac{1-2\theta}{[1-2a\theta(1-\theta)]^2}\right\}. \tag{6}$$

The condition $dC/d\varphi = 0$ is satisfied in the following cases:

1. $h = 0$, i.e., according to (4), $\theta = 0$ or $\theta = 1$. This condition is practically not realized, since it follows from equations (1) and (2a) that $\theta = 0$ at $c \neq 0$ corresponds to $(\varphi - \varphi_m) \to \infty$, and $\theta = 1$ corresponds to $c \to \infty$.
2. $\varphi = \varphi_m$—this is the condition for a minimum on the C,φ-curves at the potential of maximum adsorption.

Figure 2

Figure 2: Figure 2

3. The expression in braces is equal to zero, which gives the conditions for maxima on the C, φ-curve:

$$\varphi^{\max} = \varphi_m \pm \sqrt{\frac{3}{2a}\,\frac{1 - 2a\theta^{\max}(1-\theta^{\max})}{\sqrt{1-2\theta^{\max}}}}. \qquad (7)$$

Fig. 2. Dependence of peak potentials on $\lg c$ for different a:
1—$a = 0$; 2—1.0; 3—1.9; 4—the same under the condition $\theta^{\max} = 0.5$; 5—limiting values of $\varphi^{\max}$ as $c \to 0$.

Calculation by equation (7) of the dependence of $\theta^{\max}$ on $(\varphi^{\max} - \varphi_m)$ for different a at $C_0 = 20$, $C' = 5$, and $A = 1$ is shown in Fig. 1. It is evident from the figure that at $a < 1$ there is a considerable deviation of $\theta^{\max}$ from 0.5. With decreasing concentration of the organic substance, when $\theta^{\max} \to 0$, the position of the maxima for any a tends to the value $\varphi_m \pm \sqrt{3/2a}$, which is obtained under the condition that adsorption of the organic substance obeys the Henry equation (4). Finally, at $a > 0.5$, one and the same position of the maximum corresponds to two values of $\theta^{\max}$. This means that, as the concentration of the organic substance decreases in this case, the peak potentials first approach one another and then diverge again, asymptotically approaching the value $\varphi_m \pm \sqrt{3/2a}$.

Indeed, Fig. 2 gives the dependence of the quantity

$$Q = \lg(B_{mc}) + \frac{a}{2.3} = \frac{a}{2.3}(\varphi^{\max} - \varphi_m)^2 + \lg\frac{\theta^{\max}}{1-\theta^{\max}} + \frac{a}{2.3}(1 - 2\theta^{\max}) \qquad (8)$$

on $\varphi^{\max} - \varphi_m$, calculated from equations (7) and (8) for $a = 0$, $a = 1$, and $a = 1.9$. The parabola, with which the curve for $a = 1.9$ coincides over most of its length, corresponds to the condition $\theta^{\max} = 0.5$ ([3]), when

$$Q = \frac{a}{2.3}(\varphi^{\max} - \varphi_m)^2. \qquad (9)$$

The calculation shows that at $a < 1$, even at high concentrations of the organic substance, a noticeable deviation is observed of the Q–$(\varphi^{\max} - \varphi_m)$ curves from the parabolic dependence corresponding to the condition $\theta^{\max} = 0.5$. Thus, the previously obtained conclusion about the quadratic depend-

dependence of $\varphi^{\max}$ on $\lg c$ ([3]) retains its validity only under the condition $a \gg 1$. At $a = 0$, corresponding to the Langmuir isotherm, as is seen from Fig. 2, over a wide interval of Q (a change of c by 2 orders of magnitude) an approximately linear dependence of $\varphi^{\max}$ on $\lg c$ is obtained, as was pointed out in ([5,6]). Consequently, the conclusion of a quadratic dependence of $\varphi^{\max}$ on $\lg c$, obtained in ([7,8]) from an analysis of the Langmuir equation, cannot be regarded as correct*, and the experimentally found linear relation of $\lg c$ to $(\varphi^{\max} - \varphi_m)^2$ is apparently due to the fact that, for the organic substances studied, $a \gg 1$ and their adsorption on mercury does not obey the Langmuir equation.

From Fig. 2 it is seen that at $a = 1.9$, in a certain rather narrow concentration region, three extrema (two maxima and one minimum) correspond to a single value of Q on each of the branches of the C, φ-curve. The cathodic branch of the C, φ-curve, calculated at $a = 1.9$ and $Q = 0.05$, illustrating this regularity, is shown in Fig. 3. This rather rare effect was observed on the cathodic branch of the C, φ-curve in a solution of $0.5\,N$ CsCl $+10^{-3} M$ $C_{12}H_{25}SO_3Na$ (see Fig. 5 in ([9])).

Fig. 3. Cathodic branch of the C, φ-curve, calculated under the condition $a = 1.9$; $Q = 0.05$; $C_0 = 20$; $C' = 5$; $A = 1$

Using equations (5), (7), and (8), one can calculate the dependence of the peak height $C^{\max}$ on Q and compare it with the linear dependence

$$C^{\max} = \frac{C_0 + C'}{2} + 2.3\,\frac{C_0 - C'}{2 - a}\,Q, \tag{10}$$

Fig. 4. Dependence of the peak height on $\lg c$ for different a:
1—$a = 0$; 2—1.0; 3—1.5. Straight lines—calculation under the condition $\theta^{\max} = 0.5$ for the corresponding values of a

* In principle, a quadratic dependence of $\varphi^{\max}$ on $\lg c$ under the condition $a = 0$ is possible, but only at such high concentrations of the organic substance that $|\varphi^{\max} - \varphi_m| \gg 0.8$ V. In practice this case is not realized.

following from the condition $\theta^{\max} = 0.5$ (3). Such a comparison is made in Fig. 4 for $a = 0$, $a = 1$, and $a = 1.5$. It is seen from the figure that the resulting dependence of $C^{\max}$ on Q, over a considerable range of Q, is well approximated by straight lines, although the slope of these lines at $a < 1$ differs appreciably from the value $2.3\dfrac{C_0 - C'}{2 - a}$, predicted by equation (10).

Table 1

Assigned a	Obtained value of a from the peak width at $h = \frac{1}{2}h^{\max}$	Obtained value of a from the peak width at $h = \frac{3}{4}h^{\max}$	Obtained value of a from the peak height	Obtained value of a from the slope of $C^{\max}$—$\lg c$
1.0	0.93	0.94	0.95	0.98
0.5	0.23	0.29	0.27	0.37

The relations obtained here cannot be compared quantitatively with experimental data, since a necessary condition for the calculation was the assumption $C_0 = \text{const}$ and $a = \text{const}$, which does not correspond to experiment (1). Nevertheless, such a calculation gives the limits of applicability of the methods previously described by one of us (1) for determining the magnitude of a. The values of a found by these methods from theoretically calculated C, φ-curves under the condition $C_0 = 20$, $C' = 5$, $A = 1$, and $\varphi^{\max} - \varphi_m = 0.7$, for $a = 1$ and $a = 0.5$, are given in Table 1. As is seen from the table, the average error in determining a at $a = 1$ is 5%, whereas at $a = 0.5$ it is already 42%. Thus, the noted methods for determining a are applicable only at $a \geqslant 1$; smaller values of a may be found from the form of the adsorption isotherm (10).

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