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Abstract

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ON ADSORPTION PEAKS ON DIFFERENTIAL-CAPACITANCE CURVES

(Presented by Academician A. N. Frumkin, 19 I 1962)

It is known that the appearance of sharply expressed maxima (peaks) on the differential-capacitance curves of a mercury electrode in the presence of an organic substance is associated with an additional capacitance which, under equilibrium conditions, according to (^{1}), is expressed as

$$C_{\text{add}} = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_{\varphi} \frac{d\theta}{d\varphi}, \tag{1}$$

where ε is the surface charge, θ is the degree of coverage, and φ is the potential. In order to find C_{add}, it is necessary to know the dependence of θ on φ, which is related to the equation of the adsorption isotherm at the mercury—solution interface.

To explain the S-shaped form of experimental adsorption isotherms, Lorenz (^{2}) used the concept of dimeric association of adsorbed molecules and, on this basis, derived a relation connecting the width of a peak at 1/2 or 3/4 of its height $\left(\Delta\varphi_{1/2}\text{ and }\Delta\varphi_{3/4}\right)$ with the degree of association ν (^{3}):

$$\frac{12.20}{\Delta\varphi_{3/4}} = \frac{3.52}{\Delta\varphi_{1/2}} = \nu|\Phi|, \tag{2}$$

where $\Phi = d\ln K_1/d\varphi$ and K_1 is the adsorption-equilibrium constant.

On the other hand, the S-shaped form of the adsorption isotherm can be expressed by the Frumkin equation (^{4}):

$$Bc = \frac{\theta}{1-\theta} e^{-2a\theta}, \tag{3}$$

where c is the concentration of the adsorbing substance, a is a constant taking into account the interaction of adsorbed particles with one another, and $B = 1/K_1$. In accordance with (^{4},^{5}):

Fig. 1

Figure 1: Fig. 1

$$B = B_0 \exp\left[-\frac{\int_0^{\varphi} \varepsilon_0 \, d\varphi + \varphi C'(\varphi_N - \varphi/2)}{A}\right], \tag{4}$$

where B_0 and A are constants, with $A = RT\Gamma_m$, Γ_m being the limiting value of adsorption; $\varepsilon_0 = \int_0^{\varphi} C_0 \, d\varphi$; 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 are measured from the p.z.c. at $\theta = 0$. Adsorption isotherms calculated from equation (3) are in good agreement with experimental data both in the case of predominance of attractive forces between adsorbed particles ($a > 0$) and in the case where repulsive forces predominate ($a < 0$) (Fig. 1)*. On the other hand, the Lorenz isotherm (^{2}) is applicable only in the first case and, moreover, uses two constants for describing two-dimensional interaction (γ and the association constant K_2) instead of the single constant a in (3).

It follows from equation (3) that, for $a > 2$, part of the theoretical isotherm corresponds to unstable states of the adsorption layer (the dotted part of curve 5 in Fig. 1). The unstable states, for which $d\theta/dc > 0$, can be realized in practice, whereas states for which $d\theta/dc < 0$ (in particular, at $\theta = 0.5$) are not realized.

Fig. 1. Adsorption isotherms calculated from equation (3): 1 $-a = -1$; 2 $-a = 0$ (Langmuir isotherm); 3 $-a = 1$; 4 $-a = 1.6$; 5 $-a = 2.5$; dots –Lorenz’ s experimental data for $[(C_2H_5)_3HN]Cl$ (^{2}); crosses –Lorenz’ s experimental data for tert.-$C_5H_{11}OH$ (^{3}).

Taking the logarithm of (3), and then differentiating with respect to φ, after algebraic transformations we obtain:

$$\frac{d\theta}{d\varphi} = \frac{d \ln B}{d\varphi} h; \quad h = \frac{\theta(1-\theta)}{1 - 2a\theta(1-\theta)}. \tag{5}$$

From (1) and (5) it follows that

* In the present case, however, we did not take into account the change in the activity coefficient with increasing concentration of the organic substance and thus somewhat distorted the form of the adsorption isotherm.

Fig. 2

Figure 2: Fig. 2

$$C_{\text{dop}} = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_{\varphi} \frac{d \ln B}{d\varphi}\, h. \tag{6}$$

Since $\left(\frac{\partial \varepsilon}{\partial \theta}\right)_{\varphi} \frac{d \ln B}{d\varphi}$ varies monotonically with φ, the position of the maximum of C_{dop} is determined by the maximum of h. Finding $dh/d\theta$ from (5) and setting $dh/d\theta = 0$, we obtain:

$$\theta^{\max} = 0.5, \qquad h^{\max} = 1/(4 - 2a). \tag{7}$$

Hence one can find the theoretical dependence of the peak potentials ($\varphi^{\max}$) on c. Indeed, putting $\theta = 0.5$, from equation (3) we find:

$$\ln c = -a - \ln B. \tag{8}$$

A calculation by equations (8) and (4), for $a = 1.6$; $B_0 = 25.4$; $A = 1.045$; $C' = 4.4$; $\varphi_N = 0.5$, using the experimental C_0–φ curve in $0.9\,N$ NaF (^{6}), is compared with Lorenz' s data for tert.-$C_5H_{11}OH$ against a background of $1N$ KF (^{3}) (Fig. 2). The constants A, C', and φ_N were taken from work (^{4}), where they were obtained from electrocapillary measurements, and the value of a was found from the form of the adsorption isotherm of tert.-$C_5H_{11}OH$ (Fig. 1). As can be seen from the figure, Lorenz' s experimental data fit well on the theoretically calculated curve, but contradict the conclusions from the theories of Doss (^{7}) and Breyer (^{8}) on a linear dependence between $\varphi^{\max}$ and $\ln c$.

Fig. 2. Dependence of peak potentials on the concentration of the adsorbing substance: solid line –calculation by equation (8), dots –Lorenz' s experimental data for tert.-$C_5H_{11}OH$ against a background of $1\,N$ KF (^{3}).

If $h \neq h^{\max}$, then, solving (5) with respect to θ and assuming that h constitutes a definite fraction of $h^{\max}$, we obtain, using equation (7):

$$\theta_i = \frac{1}{2}(1 \pm r), \qquad i = 1, 2, \tag{9}$$

where

$$r_{1/4} = \sqrt{\frac{6 - 3a}{8 - 3a}}; \qquad r_{1/2} = \sqrt{\frac{2 - a}{4 - a}}; \qquad r_{3/4} = \sqrt{\frac{2 - a}{8 - a}}; \qquad r_{7/8} = \sqrt{\frac{2 - a}{16 - a}}. \tag{10}$$

(the subscript on the quantity r gives the ratio $h/h^{\max}$). From equation (5), taking into account that $d \ln B/d\varphi = -\Phi$, we obtain:

$$d\varphi = -\frac{1}{\Phi} \frac{1 - 2a\theta(1-\theta)}{\theta(1-\theta)} \, d\theta. \tag{11}$$

Integrating (11) from θ_1 to θ_2, determined by formula (9), we obtain for the widths of the capacitance peaks ($\Delta\varphi$) the general expression:

$$\Delta\varphi = \frac{2}{|\Phi|} \left(\ln \frac{1+r}{1-r} - ar \right), \tag{12}$$

where the quantities r are given by equations (10).

Equations (7) and (12) make it possible to calculate the change in the peak shape with increasing a (Fig. 3). It is seen from Fig. 3 that, as a increases, the peak height increases and its width decreases. At $a = 2$, as follows from (10) and (12), in all cases $\Delta\varphi = 0$, while according to equation (7) $h^{\max} \to \infty$. Thus, at $a = 2$ the peak on the $C - \varphi$ curve degenerates into a vertical line with an indeterminate value of the capacitance. Such data were obtained in a solution of $10^{-3} N[(C_4H_9)_4N]J + 1N\,KJ$ (^{9}). At $a > 2$ the degree of filling changes discontinuously from small θ to θ values close to 1 (Fig. 1). Intermediate, unstable values of θ correspond to unstable values of the capacitance. Since part of the unstable values of θ can be realized, then, by rapidly changing the polarization of the electrode, when recording the $C - \varphi$ curve in different directions one can observe a hysteresis loop. On the other hand, the value $\theta = 0.5$ cannot be realized if $a > 2$, and therefore the capacitance peak corresponding to $\theta = 0.5$ also is not realized under these conditions. It is precisely such phenomena that were discovered by Lorenz in measuring $C - \varphi$ curves in solutions of nonylic acid (^{10}).

Fig. 3. Change in the shape of the adsorption peak as a function of the degree of interaction between adsorbed particles:
1 $-a = 0$; 2 $-a = 0.8$; 3 $-a = 1.2$; 4 $-a = 1.5$; 5 $-a = 1.7$; 6 $-a = 2.0$

From equations (12) and (10), for $a = 0$ we obtain $\Delta\varphi_{1/2} = 3.52/|\Phi|$ and $\Delta\varphi_{3/4} = 2.20/|\Phi|$, in agreement with the conclusion of Lorenz for the case of the Langmuir isotherm (^{3}). If, however, $a \neq 0$, then from equations (2) and (12) we obtain for the quantity v:

$$v_{1/2} = \frac{3.52}{2\left(\ln \frac{1+r_{1/2}}{1-r_{1/2}} - ar_{1/2}\right)}; \qquad v_{3/4} = \frac{2.20}{2\left(\ln \frac{1+r_{3/4}}{1-r_{3/4}} - ar_{3/4}\right)}. \tag{13}$$

Calculation of $v_{1/2}$ and $v_{3/4}$ from equations (13) shows that, for $a > 0$, $v_{3/4} > v_{1/2}$. Table 1 compares Lorenz' s data for $v_{1/2}$ and $v_{3/4}$ in the case of tert-

$C_5H_{11}OH$ (³) with the calculated values of $v_{3/4}$, which correspond to the given values of $v_{1/2}$.

It is seen from the table that equation (13) explains very well the experimental discrepancies between $v_{1/2}$ and $v_{3/4}$, which Lorenz regards as measurement errors.

The quantities ν can be used to find the degree of interaction between adsorbed particles a. Thus, from the values of ν given by Lorenz for tert.-$C_5H_{11}OH$ against a background of $1N$ KF (3), it follows that a varies linearly with potential ($da/d\varphi \simeq 0.25$). Thus, the assumption that a is independent of φ is, as Frumkin pointed out (4), only a first approximation.

Table 1

$\nu_{1/2}$, experiment	5.1	5.4	5.7
$\nu_{3/4}$, experiment	6.0	6.3	6.3 and 6.6
$\nu_{3/4}$, calculation	5.95	6.30	6.60

Let us consider the influence of the concentration of the organic substance on the height of the adsorption peaks. At $C_0 = \text{const}$, using equations (4)–(7), we obtain

$$C^{\max} = \frac{1}{4-2a}\frac{\left[(C_0 - C')\varphi + C'\varphi_N\right]^2}{A}. \tag{14}$$

From equations (8) and (4), under the same condition it follows that

$$(C_0 - C')\varphi^2 + 2\varphi\varphi_N C' = 2A(\ln c + a + \ln B_0) \tag{15}$$

Substituting (15) into (14), we find

$$C^{\max} = \frac{C_0 - C'}{2-a}(a + \ln B_0) + \frac{(C'\varphi_N)^2}{2A(2-a)} + \frac{C_0 - C'}{2-a}\ln c, \tag{16}$$

or, combining all constants:

$$C^{\max} = \text{const}_1 + \text{const}_2 \lg c. \tag{16a}$$

Thus, in contrast to the pseudocapacitance associated with an electrochemical reaction and varying in proportion to the concentration of the reacting substance (11), the height of the adsorption peak, in the first approximation, varies linearly with the logarithm of the concentration of the adsorbed substance.

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