ADSORPTION PEAKS ON DIFFERENTIAL CAPACITY CURVES

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The appearance of sharply expressed maxima (peaks) on differential capacity curves of a mercury electrode in the presence of an organic substance is connected with the additional capacity, which, according to [1], is expressed by the following equation under equilibrium conditions:

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

where ε is the surface charge, θ the degree of filling, and φ the potential. In order to find C_{add} it is necessary to know the relation of θ to φ, which is connected with the isotherm equation for adsorption at the mercury–solution interphase.

To explain the sigmoid form of the experimental adsorption isotherms, Lorenz [2] used the idea of two-dimensional association of adsorbed molecules and on this basis, derived a relation between the width of the peak at $^1/_2$ or $^3/_4$ of its height ($\Delta\varphi^1/_2$ and $\Delta\varphi^3/_4$) and the degree of association ν [3]:

$$\frac{|2{,}20}{\Delta\varphi_{3/4}} = \frac{3{,}52}{\Delta\varphi_{1/2}} = \nu\,|\,\Phi\,|, \quad (2)$$

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

On the other hand, the sigmoid form of the adsorption isotherm may be represented by Frumki's equation [4]:

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

where c is the concentration of the substance adsorbed, a is a constant allowing for the interaction of the adsorbed particles, and $B = 1/K_1$. According to [4, 5]:

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

where B_0 and A are constants and $A = RT\Gamma_m$, Γ_m is the limiting adsorption; $\varepsilon_0 = \int_0^{\varphi} C_0\, d\varphi$; C_0 and C' are the capacities at $\theta = 0$ and $\theta = 1$, respectively; φ_N is the zero-charge point (z.c.p.) when $\theta = 1$; the zero for all the potentials is the z. c. p. at $\theta = 0$. The adsorption isotherms calculated from equation (3) agree well with experimental data both when repulsive forces between the adsorbed particles predominate ($a > 0$) and when repulsive forces predominate ($a < 0$)(Fig. 1).* On the other hand, Lorenz's isotherm [2] only applies in the first case and, moreover, uses two constants to describe the two-dimensional interaction (ν and the association constant K_2) instead of the one constant as in (3).

From equation (3) it follows that where $a > 2$ part of the theoretical isotherm corresponds to unstable states of the adsorption layer (the broken part of curve 5 in Fig. 1). The unstable states for which $d\theta/dc > 0$ may be realized practically, while the states for which $d\theta/dc < 0$ (in particular, when $\theta = 0.5$) cannot be realized.

* However, in this case we did not allow for the change in the activity coefficient with an increase in the concentration of the organic substance and thus, the form of the adsorption isotherm is slightly distorted.

By taking logarithms of (3) and then differentiating with respect to φ, after algebraic rearrangements 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:

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

As $\left(\frac{\partial \varepsilon}{\partial \theta}\right)_{\varphi} \frac{d\ln B}{d\varphi}$ changes monotonically with φ, the position of the maximum of C_{add} is determined by the maximum of h. By finding $dh/d\theta$ from (5) and letting $dh/d\theta = 0$, we obtain:

$$\theta^{max} = 0{,}5, \quad h^{max} = 1/(4-2a). \tag{7}$$

Hence, it is possible to find the theoretical relation of the peak potentials (φ^{max}) to c. In actual fact, by letting $\theta = 0.5$, from equation (3) we find:

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

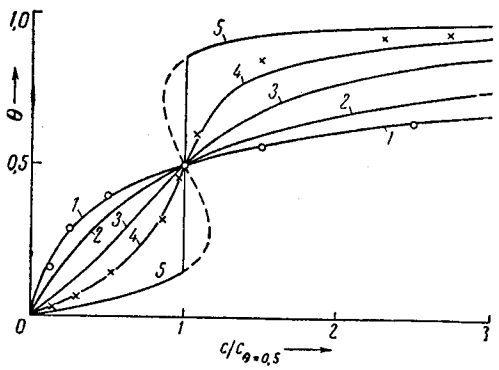

Fig. 1. Adsorption isotherms calculated from equation (3): 1) a = -1; 2) a = 0 (Langmuir isotherm); 3) a = 1; 4) a = 1.6; 5) a = 2.5; the points represent Lorenz's experimental data for $[(C_2H_5)_3HN]Cl$ [2]; the crosses represent Lorenz's experimental data for neopentanol [3].

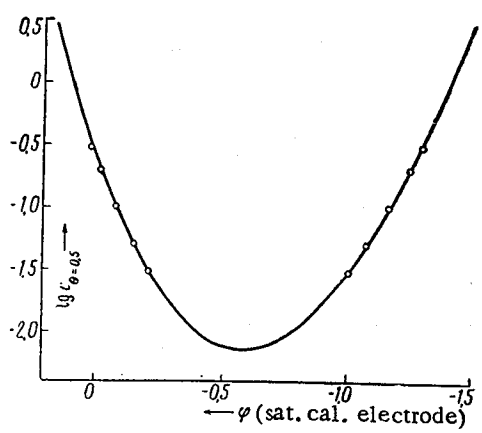

Fig. 2. Relation of the peak potentials to the concentration of the adsorbed substance: solid line—calculated from equation (8); points—Lorenz's experimental data for neopentanol in a base electrolyte of 1 N KF [3].

The calculation from equations (8) and (4) with a = 1.6; $B_0 = 25.4$; A = 1.045; C' = 4.4; $\varphi_N = 0.5$, using the experimental curve of C_0 against φ in 0.9 N NaF [6] is compared with Lorenz's data for neopentanol in a base electrolyte of 1 N KF [3] (Fig. 2). The constants A, C', and φ_N were taken from [4], where they were obtained from electrocapillary measurements, and the value of a was taken from the form of the adsorption isotherm of neopentanol (Fig. 1). As the figure shows, Lorenz's experimental data lie well on the theoretical curve, but contradict the conclusions from Doss [7] and Breyer's [8] theories on the linear relation between φ^{max} and ln c.

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

$$\theta_i = {}^1/_2(1 \pm r), \quad i = 1,2, \tag{9}$$

where

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

(the index at r gives the ratio h/h^{max}). By taking in account the fact that $d\ln B/d\varphi = -\Phi$, from equation (5) we obtain:

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

By integrating (11) from θ_1 to θ_2, determined from formula (9), we obtain the following general expression for the widths of the capacity peaks ($\Delta\varphi$):

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

where the values of r are given by the equations (10).

The equations (7) and (12) make it possible to calculate the change in the form of the peak with an increase in a (Fig. 3). Figure 3 shows that with an increase in a

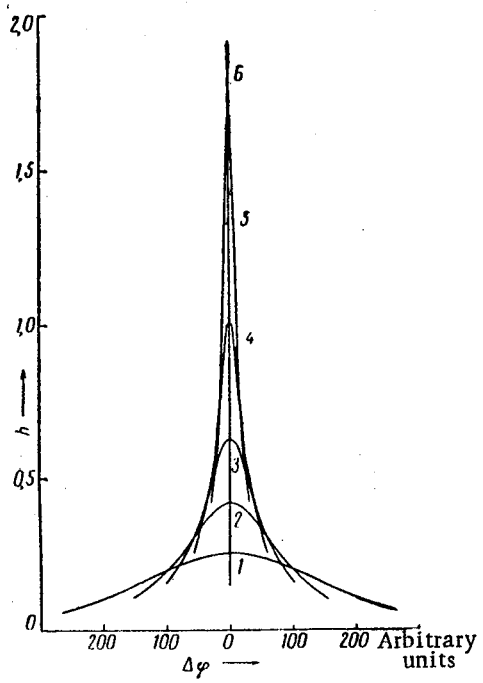

Fig. 3. Change in form of the adsorption peak in relation to the degree of interaction of the adsorbed particles: 1) a = = 0; 2) a = 0.8; 3) a = 1.2; 4) a = 1.5; 5) a = 1.7; 6) a = 2.0.

there is an increase in the height of the peak and a decrease in its width. When a = 2, as follows from (10) and (12), in all cases $\Delta\varphi = 0$, while from equation (7), $h^{max} \to \infty$. Thus, when a = 2, the peak on the curve of C against φ degenerates into a vertical line with an indeterminant capacity. Such data were obtained with the solution 10^{-3} N$[(C_4H_9)_4N]$ I + 1N KI [9]. When a > 2, the degree of filling changes in a jump from small values of θ to θ close to 1 (Fig. 1). Unstable capacity values correspond to the intermediate, unstable values of θ. As some of the unstable values of θ may be realized by changing the polarization of the electrode rapidly in plotting a curve of C against φ in different directions it is possible to observe a hysteresis loop. On the other hand, the value $\theta = 0.5$ cannot be realized if a > 2 and therefore the capacity peak corresponding to $\theta = 0.5$ is not realized under these conditions either. Precisely these phenomena were observed by Lorenz in measuring curves of C against φ in solutions of pelargonic acid [10].

From equations (12) and (10), when a = 0 we obtain $\Delta\varphi_{1/2} = 3.52/|\Phi|$ and $\Delta\varphi_{3/4} = 2.20/|\Phi|$ in accordance with Lorenz's conclusion for the Langmuir isotherm [3]. If $a \neq 0$, then from equations (2) and (12), we obtain for the value ν:

$$\nu_{1/2} = \frac{3{,}52}{2\left(\ln\frac{1+r_{1/2}}{1-r_{1/2}} - ar_{1/2}\right)}; \quad \nu_{3/4} = \frac{2{,}20}{2\left(\ln\frac{1+r_{3/4}}{1-r_{3/4}} - ar_{3/4}\right)}. \tag{13}$$

Calculation of $\nu_{1/2}$ and $\nu_{3/4}$ from the equations (13) shows that when a > 0, $\nu_{3/4} > \nu_{1/2}$. In Table 1 we compare Lorenz's data for $\nu_{1/2}$ and $\nu_{3/4}$, which correspond to the given values of $\nu_{1/2}$.

The table shows that equation (13) explains very well the experimental discrepancies between $\nu_{1/2}$ and $\nu_{3/4}$, which Lorenz regarded as experimental errors.

The values of ν may be used to find the degree of interaction between the adsorbed particles a. Thus, from the values of ν given by Lorenz for neopentanol in a base electrolyte of 1 N KF [3] it follows that a changes linearly with potential ($da/d\varphi \cong 0.25$). Thus, the assumption that a is independent of φ is, as Frumkin pointed out [4], only a first approximation.

TABLE 1

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

Let us examine the effect of the concentration of the organic substance on the height of the adsorption peaks. When C_0 = const, by using equations (4)-(7), we obtain

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

From equations (8) and (4) with the same condition it follows that:

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

By introducing (15) into (14), we find

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

or combining all the constants:

$$C_{add}^{max} = const_1 + const_2 \lg c. \quad (16a)$$

Thus, in contrast to the pseudocapacity connected with the electrochemical reaction, which is proportional to the concentration of the reacting substance [11], the height of the adsorption peak in the first approximation changes linearly with the logarithm of the concentration of the substance adsorbed.

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