THE SURFACE COVERAGE BY ORGANIC SUBSTANCES AT THE POTENTIAL MAXIMUM ON THE DIFFERENTIAL CAPACITY CURVE

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It has been shown in [1] that a quantitative interpretation of the differential capacity curve developed in the presence of ter-$C_5H_{11}OH$ can be obtained from the isothermal equation of A. N. Frumkin [2] by making allowance for the variation of the attraction constant, a, with the electrode potential. This equation has the form

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

c being the concentration of the organic material, $\theta = \Gamma/\Gamma_m$ being the ratio of the actual adsorption, Γ, to the limiting value, Γ_m, and

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

B_0 and A being constants and $A = RT\Gamma_m$. C_0 and C' are the capacities of the double layer at $\theta = 0$ and $\theta = 1$, respectively, φ is the potential referred to the null-point potential at $\theta = 0$, and φ_N is the displacement of the null-point potential due to passage from $\theta = 0$ to $\theta = 1$. It follows from [3] that

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

where

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

The relation between a and φ was developed from the experimental data by assuming the position of the peak on the $C-\varphi$ curve to be essentially determined by the value of h [3]. The coverage at maximum, θ^{max} is then 0.5 and the value of a at the peak potential, φ^{max}, can be determined by the method described in [1]. *

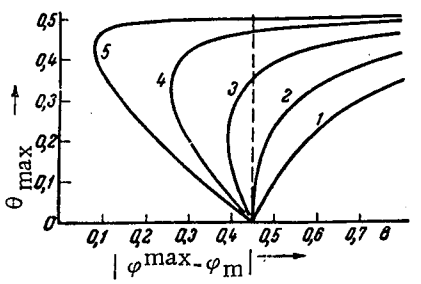

Fig. 1. Relation between the maximum coverage and the peak potential for various values of a: 1) a=0; 2) 0.5; 3) 1.0; 4) 1.5; 5) 1.9; the dotted curve gives the limiting value approached by φ^{max} as $c \to 0$.

It is clear that the peak on the $C-\varphi$ curve will correspond to a maximum in h only when the value of a is small and h itself varies markedly with φ [3]. The general case is that in which the position of the extremum on the $C-\varphi$ curve is determined through the condition $dC/d\varphi = 0$. Calculation of this position can be made for the case $C_0 = \text{const}$ and $a = \text{const}$, if

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

where $\alpha = (C_0 - C')/2A$, $\varphi_m = -\varphi_N C'/(C_0 - C')$;

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

Here

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

* The theory is presented in detail in an article to be published in the Zhurnal fizicheskoi khimii.

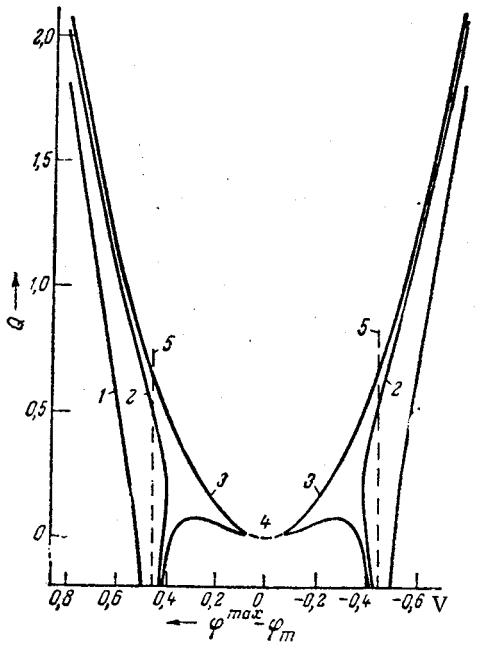

Fig. 2. Relation between the peak potential and log c for various values of a: 1) a = 0; 2) 1.0; 3) 1.9; 4) the same, but with the condition that $\theta^{max} = 0.5$; 5) limiting values of φ^{max} as $c \to 0$.

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

The condition $dC/d\varphi = 0$ will be satisfied if:

1. h = 0, i.e., according to (4), if $\theta = 0$, or $\theta = 1$. This condition is actually never realized since Eqs. (1) and (2a) require $(\varphi - \varphi_m) \to \infty$ in order that $\theta = 0$ with $c \neq 0$ and $c \to \infty$ in order that $\theta = 1$.

2. $\varphi = \varphi_m$, this being the condition for a minimum on the C–φ curve at the potential corresponding to maximum adsorption.

3. The expression in brackets is equal to zero, this giving the condition for the maximum on the C–φ curve in the form:

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

Equation (7) was used to develop the relation between θ^{max} and $(\varphi^{max} - \varphi_m)$ for various values of a with $C_0 = 20$, $C' = 5$, and A = 1, the results being as shown in Fig. 1. It is seen from this figure that the deviation of θ^{max} from 0.5 is quite marked when $a < 1$. When the adsorption of the organic material follows Henry's Law [4] the position of the maximum tends toward $\varphi_m \pm \sqrt{3/2\alpha}$, for all values of a as the concentration of the organic material is diminished and $\theta^{max} \to 0$. Finally, two values of θ^{max} are associated with each position of the maximum when $a > 0.5$. This indicates that a reduction of the concentration of the organic material causes the peak potentials to first approach and then once more diverge, moving asymptotically toward the values $\varphi_m \pm \sqrt{3/2\alpha}$.

Figure 2 shows the relation between

$$Q = \log(B_m c) + \frac{a}{2{,}3} = \frac{\alpha}{2{,}3}(\varphi^{max} - \varphi_m)^2 + \log\frac{\theta^{max}}{1-\theta^{max}} + \frac{a}{2{,}3}(1 - 2\theta^{max}) \quad (8)$$

and $\varphi^{max} - \varphi_m$ as developed from Eqs. (7) and (8) for a = 0, a = 1, a = 1.9. A parabola representing the two branches of the curve for a = 1.9 will correspond to the condition $\theta^{max} = 0.5$ [3] if

$$Q = \frac{\alpha}{2{,}3}(\varphi^{max} - \varphi_m)^2. \quad (9)$$

Calculation shows the $Q-(\varphi^{max} - \varphi_m)$ relation to depart markedly from the parabolic function corresponding to $\theta^{max} = 0.5$ when $a < 1$, even when the concentration of the organic material is high. Thus, the earlier reported second-power relation between φ^{max} and log c [3] is valid only when $a \geq 1$. The case in which a = 0 and adsorption follows the Langmuir isotherm is seen from Fig. 2 to be one in which the φ^{max}– log c relation is almost linear over a wide interval of Q values embracing a two-order alteration in c, a fact pointed out earlier in [5, 6]. Thus, the second-power φ^{max} – log c relation deduced in [7, 8] on the basis of an analysis of the Langmuir Equation cannot be considered as valid, * the experimentally developed linear relation between log c and $(\varphi^{max} - \varphi_m)^2$ clearly arising from the fact that the adsorption on mercury of the organic materials under study failed to follow the Langmuir Equation and a was ≥ 1.

The case of a = 1.9 is seen from Fig. 2 to be such that over a narrow concentration interval three extrema (two maxima and one minimum) appear on each branch of the C–φ curve for each value of Q. The cathodic branch of the C–φ curve was developed for a = 1.9 and Q = 0.05 to illustrate this point and is shown in Fig. 3. This rather rare effect is observed on the cathodic branch of the C–φ curve for a 0.5 N CsCl + 10^{-3}M $C_{12}H_{25}SO_3Na$ solution (see Fig. 5 of [9]).

Equations (5), (7), and (8) can be used to develop a relation between the peak height, C^{max}, and Q that can be compared with the linear relation,

$$C^{max} = \frac{C_0 + C'}{2} + 2{,}3\,\frac{C_0 - C'}{2 - a}\,Q, \quad (10)$$

* It is possible in principle to have a second-power relation between φ^{max} and log c with a = 0, but only if the concentration of the organic material is so high that $|\varphi^{max} - \varphi_m| \gg 0.8$ v. This case is not realized in practice.

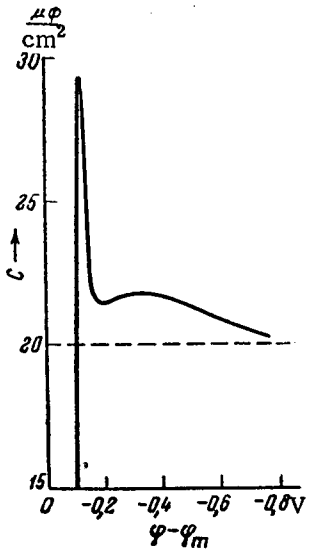

Fig. 3. Cathodic branch of the C–φ curve as developed for a = 1.9; Q = 0.05; C_0 = 20; C' = 5; A = 1.

following from the condition θ^{max} = 0.5 [3]. A comparison of this type has been made in Fig. 4 for the case in which a = 0, a = 1, and a = 1.5. The figure makes it clear that the C^{max}, Q relation developed here is very nearly linear over a wide interval of Q values, and this despite the fact that the curve slope for a < 1 is considerably different from the $2{,}3(C_0-C')/(2-a)$ predicted by Eq. (10).

The relations developed here cannot be quantitatively compared with the experimental results since the conditions on which the calculations are based namely, C_0 = const and a = const, are not fulfilled in practice [1]. Nevertheless, these calculations do mark out limits of applicability for methods described by one of us for the determination of a [1]. Values of a calculated by these methods from theoretical C–φ curves developed for the conditions C_0 = 20; C' = 5; A = 1 and $\varphi^{max}-\varphi_m$ = 0.7 with a = 1 and a = 0.5 are shown in the table. This table

Given value of a	Value of a calculated			
	from peak width at $h=1/2h^{max}$	from peak width at $h=3/4h^{max}$	from peak height	from slope of C^{max} – log c curve
1.0	0.93	0.94	0.95	0.98
0.5	0.23	0.29	0.27	0.37

shows that the mean error in the determination of a is 5% for a = 1 and 42% for a = 5. Thus, the methods in question are applicable only when $a \geq 1$; lower values of a can be determined from the adsorption isotherm [10].

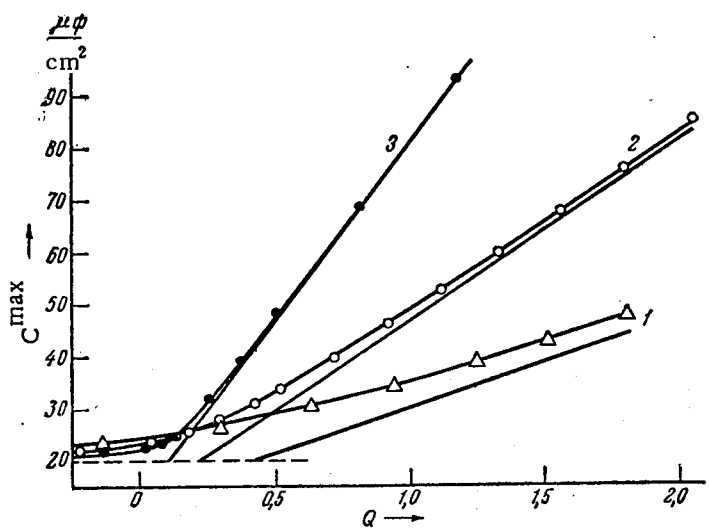

Fig. 4. Relation between the peak height and log c for various values of a; 1) a = 0; 2) 1.0; 3) 1.5. The straight lines were developed for the various values of a and the condition that θ^{max} = 0.5.

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