THE CHOICE OF AN EQUATION FOR THE ADSORPTION ISOTHERM

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The correct choice of an equation for the adsorption isotherm is a matter of importance in quantitative studies of the adsorption of organic substances on electrode surfaces. Experimental criteria can be as significant here as theoretical considerations favoring the one or the other of the equations [1]. Parsons [2] has proposed a method for selection of the equation of the adsorption isotherm based on a study of the $(d\theta/d \ln B)_c$, log c relation (θ is the degree of surface coverage by the organic material, c the bulk concentration of this substance, and B the equilibrium constant for the adsorption). The equation of state for the Frumkin adsorption isotherm [3]

$$\Delta\sigma = A\,[-\ln(1-\theta) - a\theta^2], \tag{1}$$

($A = RT\Gamma_m$, Γ_m is the limiting adsorption, and a is the attraction constant) leads to a symmetrical $(d\theta/d \ln B)_c$, log c relation, while the equation of state for the Parsons isotherm [2]

$$\Delta\sigma = A\,[\theta/(1-\theta)^2 - a\theta^2], \tag{2}$$

leads to an unsymmetrical relation. These criteria are not unique, however, both the deBoor equation of state [4]

$$\Delta\sigma = A\,[\theta/(1-\theta) - a\theta^2], \tag{3}$$

and the equation of state*

$$\Delta\sigma = A\,[-n\ln(1-\theta) - (n-1)\theta - a\theta^2] \tag{4}$$

lead to unsymmetrical $(d\theta/d \ln B)_c$, log c relations.

G. A. Tedoradze [7] has recently proposed another criterion for the selection of the adsorption isotherm, this based on the $d\theta/dc$, θ relation at fixed potential. It has been shown in [7] that the θ value at which the curve passes through a maximum (θ_m) varies with the attraction constant, the variation being from 0 to 0.5 in the case of Eq. (1), from 0 to 0.22 in the case of Eq. (2) and from 0 to 0.33 in the case of Eq. (3). It is clear that selection can be made between these three equations only when the situation is such that $\theta_m > 0.33$. The criterion becomes even less significant when the set of equations is augmented by (4), the latter being of such form that θ_m can be made to assume any desired value by adjustment of a and n. It also follows from [7] that the criterion will not be applicable to cases such as that of the Frumkin isotherm with $a < 0.5$, and the $d\theta/dc$, θ curve failing to pass through a maximum when a is low.

We have therefore turned to a still more general criterion for determining the equation of the adsorption isotherm from the experimental data. It can be readily shown that the equations of state (1) - (4) can all be written in one general form, namely:

$$\Delta\sigma = A\,[f(\theta) - a\theta^2]. \tag{5}$$

Differentiation of (5) leads to:

$$d(\Delta\sigma) = -d\sigma = A\,[f'(\theta) - 2a\theta]\,d\theta, \tag{6}$$

*Our derivation of this equation is analogous to that of Eq. (1), the difference being that the adsorption of one molecule of the organic substance is assumed to involve the displacement of n molecules of water from the electrode surface [5, 6]. Details concerning the adsorption of organic substances predicted by Eq. (4) will be considered in a separate communication.

where $f'(\theta) = df(\theta)/d\theta$. Substitution from (6) into the Gibbs equation:

$$d\sigma = -RT\Gamma\, d\ln c = -A\theta\, d\ln c, \tag{7}$$

gives

$$d\ln c/d\theta = f'(\theta)/\theta - 2a. \tag{8}$$

The curve showing the dependence of d ln c/d θ on θ at fixed electrode potential passes through a minimum at a certain critical value, θ_{cr}; here $d^2 \ln c/d\theta^2 = 0$, i. e., which is to say that

$$\theta f''(\theta) = f'(\theta), \tag{9}$$

with $f''(\theta) = d^2 f(\theta)/d\theta^2$. The essential point is that the value of θ_{cr} proves to be independent of the attraction constant and can therefore be made to serve as a criterion for the selection of the equation for the adsorption isotherm.

Table 1 gives values of θ_{cr} for Eqs. (1) - (4) and for the Temkin isotherm [8] with

$$\frac{d\ln c}{d\theta} = p\,\frac{sh\,(p/2)}{ch\,(p/2) - ch\,[p\,(0{,}5 - \theta)]}, \tag{10}$$

(p is the factor for repulsive interaction) these values having been obtained from Eq. (9). Curves showing the d ln c/d θ, θ relations for various adsorption isotherms were developed from Eqs. (8) and (10) and are reproduced in Fig. 1*. It is seen that the difference in θ values satisfying the condition d ln c/d θ − (d ln c/d θ) min = 1 (Δθ), (i. e., the width of the curve minimum) can also serve as a criterion for the selection of the equation of the adsorption isotherm. Values of Δθ for the various isotherms are presented in Table 1. It is seen from this table and Fig. 1 that the method in question distinguishes all cases with the exception of the de Boor equation and Eq. (4) with n = 4 and the Temkin isotherm and the Frumkin isotherm with a < 0.

The method has been tested on certain organic compounds whose adsorption we have studied in collaboration with R. Lerkkh, N. B. Grigor'ev, and I. P. Mishutushkina; application has also been made to tertiary amyl alcohol, using the data of [9]. The d ln c/d θ, θ relations were developed from adsorption isotherms based on the equation:

$$C = C_0(1 - \theta) + C'\theta, \tag{11}$$

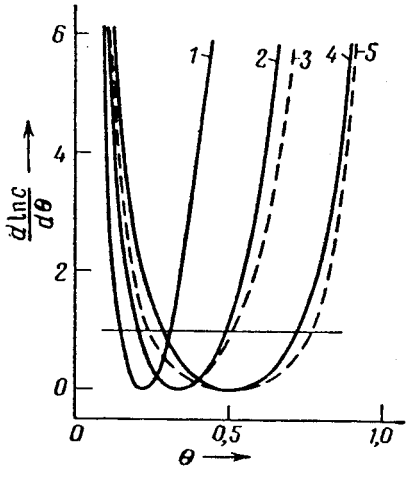

Fig. 1. The d ln c/d θ, θ relations for various adsorption isotherms: 1) Parsons (Eq. (2)); 2) deBoor (Eq. (3)); 3) Eq. (4); Frumkin (Eq. (1)); 5) Temkin (Eq. (10) with p = 9.2).

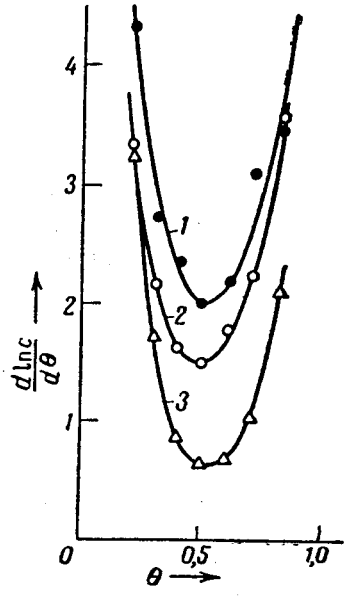

Fig. 2. d ln c/d θ, θ relations for various experimentally developed adsorption isotherms: 1) analine; 2) n-$C_5H_{11}NH_2$; 3) tert. amyl alcohol.

*For ease of comparison, the attraction constant was so chosen that d ln c/d θ = 0.

TABLE 1

Type of isotherm	θ_{cr}	$\Delta\theta$
Frumkin (eq. (1))	0,500	0,447
Parsons (Eq. (2))	0,215	0,158
de Boor (Eq. (3))	0,333	0,281
Eq. (4)	$\frac{1}{1+\sqrt{n}}$	$\frac{\sqrt{4\sqrt{n}+1}}{n+2\sqrt{n}+2}$
Temkin	0,500	0,447 min $p=2$ 0,472 min $p=6$ 0,542 min $p=10$

TABLE 2

System	θ_{cr}	$\Delta\theta$
n-C_3H_7OH + 1N Na_2SO_4	0,48	0,48
n-$C_5H_{11}OH$ + 1N Na_2SO_4	0,53	0,45
tert-$C_5H_{11}OH$ + 1NKF	0,54	0,46
n-$C_5H_{11}NH_2$ + 1N Na_2SO_4	0,49	0,45
iso-$C_5H_{11}NH_2$ + 1N Na_2SO_4	0,49	0,46
$[(C_4H_9)_4N]_2SO_4$ + 1N Na_2SO_4	0,55	0,50
$C_6H_5NH_2$ + 1NKCl	0,52	0,44
C_6H_5OH + 1N Na_2SO_4	0,45	0,32

C, C_0, and C' being the double layer capacitances corresponding to surface coverages of θ, 0, and 1, respectively. Values obtained in this manner are shown in Fig. 2 and in Table 2. The figures of Table 2 make it clear that the Frumkin isotherm gives a rather exact description of the adsorption of all the compounds used in this study with the exception of phenol. The adsorption of phenol on mercury can best be described by Eq. (4) with n = 2.

It has been shown in [10] that the adsorption of benzenedisulfonate ions on mercury can be satisfactorily described by a Temkin isotherm with p = 9.2 and the d ln c/d θ curve for these ions is therefore shown as one of the curves in Fig. 1. The use of Eq. (2) (see [2]) to describe the adsorption of benzenedisulfonate ions is questionable since Fig. 1 indicates a pronounced difference in the d ln c/d θ, θ curves for Parsons and Temkin isotherms.

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