Soviet-era science, translated into English

Physical Chemistry

1964

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196401.55998

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

Physical Chemistry

B. B. Damaskin

On the Choice of an Equation for an Adsorption Isotherm

(Presented by Academician A. N. Frumkin, 25 I 1964)

In the quantitative study of the phenomena of adsorption of organic substances on the surface of an electrode, the correct choice of the equation of the adsorption isotherm plays a major role. Besides a theoretical justification of one or another type of equation (^{1}), criteria of an experimental character may also be of importance. Parsons (^{2}) proposed a method for choosing an adsorption isotherm based on studying the dependence of the quantity $(d\theta/d\ln B)_c$ on $\lg c$, where θ is the degree of filling of the surface by the organic substance, c is its volume concentration, and B is the adsorption-equilibrium constant. The Frumkin adsorption isotherm (^{3}), corresponding to the equation of state

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

where $A = RT\Gamma_m$, Γ_m is the limiting adsorption, and a is the attraction constant, leads to a symmetric dependence of $(d\theta/d\ln B)_c$ on $\lg c$, whereas in the case of the equation of state (^{2})

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

corresponding to the Parsons isotherm, this dependence is not symmetric. This criterion is not unambiguous, since the equation of state used by de Boer (^{4}):

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

as well as the equation of state*

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

also lead to an asymmetric dependence of $(d\theta/d\ln B)_c$ on $\lg c$.

Fig. 1. Dependence of $d\ln c/d\theta$ on θ, calculated for different adsorption isotherms: 1 —Parsons (equation 2); 2 —de Boer (equation 3); 3 —for equation (4); 4 —Frumkin (equation 1) and 5 —Temkin (according to equation 10) at $p = 9.2$.

SovietRxiv

Fig. 1. Dependence of $d\ln c/d\theta$ on θ, calculated for different adsorption isotherms: 1 —Parsons (equation 2); 2 —de Boer (equation 3); 3 —for equation (4); 4 —Frumkin (equation 1) and 5 —Temkin (according to equation 10) at $p = 9.2$

Figure 1: Fig. 1. Dependence of $d\ln c/d\theta$ on θ, calculated for different adsorption isotherms: 1 —Parsons (equation 2); 2 —de Boer (equation 3); 3 —for equation (4); 4 —Frumkin (equation 1) and 5 —Temkin (according to equation 10) at $p = 9.2$

Recently G. A. Tedoradze (^{7}) proposed another criterion for choosing an adsorption isotherm, based on determining the dependence of $d\theta/dc$ on θ at constant potential. As was shown in (^{7}), the value of θ at which this curve passes through a maximum (θ_m) varies depending on the magnitude of the attraction constant: when equation (1) is fulfilled, from 0 to 0.5; in the case of equation (2), from 0 to 0.22; and in the case of equation (3), from 0 to 0.33. It is clear that the criterion makes it possible to distinguish one of the three equations considered only under the condition $\theta_m > 0.33$. Adding equation (4) to the three equations considered makes this criterion still more ambiguous, since for equation (4), depending on a and n, any values of θ_m are possible. In addition, it follows from (7) that at small values of a (for example, in the case of the Frumkin isotherm at $a < 0.5$) the dependence $d\theta/dc - \theta$ has no extremum at all and, consequently, the proposed method is not applicable.

In this connection we consider a more general criterion, making it possible, from experimental data, to establish the equation of the adsorption isotherm. As is easy to see, the equations of state (1)—(4) can be written in the following general form:

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

Differentiating (5), we obtain:

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

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

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

* This equation of state was obtained by us by analogy with equation (1), but under the assumption that, upon adsorption of one molecule of organic substance, n water molecules are displaced from the surface of the electrode (^{5,6}). The regularities in the adsorption of organic substances obeying equation (4) will be considered by us in a separate communication.

we find:

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

At a certain $\theta = \theta_{\mathrm{cr}}$, the dependence $d \ln c/d\theta$ on θ at constant electrode potential passes through a minimum, which corresponds to $d^2 \ln c/d\theta^2 = 0$, i.e., to fulfillment of the condition:

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

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

Fig. 2. Dependence of $d \ln c/d\theta$ on θ, obtained from experimental adsorption isotherms: 1 –aniline; 2 –n-$C_5H_{11}NH_2$; 3 –tert-amyl alcohol.

Table 1

Type of isotherm	θ_{cr}	$\Delta\theta$
Frumkin (equation 1)	0.500	0.447
Parsons (equation 2)	0.215	0.158
de Boer (equation 3)	0.333	0.281
Equation (4)	$\frac{1}{1+\sqrt{n}}$	$\frac{\sqrt{4\sqrt{n}+1}}{n+2\sqrt{n}+2}$
Temkin	0.500	0.447 at $p = 2$ 0.472 at $p = 6$ 0.542 at $p = 10$

The values of θ_{cr}, obtained from condition (9) for equations (1)–(4), and also for the Temkin isotherm (*), according to which

$$\frac{d \ln c}{d\theta} = p \, \frac{sh\,(p/2)}{ch\,(p/2) - ch\,[p(0.5-\theta)]}, \tag{10}$$

where p is the factor of repulsive interaction, are presented in Table 1. The dependence of $d \ln c/d\theta$ on θ, calculated from equations (8) and (10) for various adsorption isotherms, is given in Fig. 1.* As is seen from Fig. 1, the difference in the two values of θ under the condition $d \ln c/d\theta - (d \ln c/d\theta)_{\mathrm{min}} = 1$ $(\Delta\theta)$, i.e., the width of the minimum on the curve $d \ln c/d\theta - \theta$, can also serve as a criterion in selecting equation of the adsorption isotherm. The values of $\Delta\theta$ for different isotherms are given in Table 1. From Fig. 1 and Table 1 it follows that, with the aid of this method, practically indistinguishable are only the de Boer equation from equation (4) at $n = 4$, and the Temkin isotherm from the Frumkin isotherm at $a < 0$.

The proposed method was applied to a number of organic compounds whose adsorption we studied jointly with R. Lerch, N. B. Grigor'ev, and I. P. Mishutushkina, and also to tertiary amyl alcohol according to the data of [9]. The dependence $d\ln c/d\theta$ on θ was determined from adsorption isotherms obtained from the equation:

$$C = C_0(1-\theta) + C'\theta, \qquad (11)$$

where C, C_0, and C' are the values of the double-layer capacitance at coverages equal to θ, 0, and 1, respectively. The data obtained are presented in Fig. 2 and in Table 2. As is seen from the data of Table 2, the adsorption of all the compounds studied, except phenol, obeys the Frumkin isotherm with a sufficient degree of accuracy. Adsorption of phenol on mercury can be better described by equation (4) with $n = 2$.

Table 2

System studied	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.-$C_5H_{11}OH$ + $1N\,KF$	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
$C_6H_5NH_2$ + $1N\,KCl$	0.52	0.44
C_6H_5OH + $1N\,Na_2SO_4$	0.45	0.32

As was shown in [10], adsorption of benzenedisulfonate ions on mercury is well described by the Temkin isotherm with $p = 9.2$, and, consequently, the $d\ln c/d\theta$

---

* For convenience of comparison, the attraction constant was chosen in such a way that at the minimum $d\ln c/d\theta = 0$.

curve for these ions can be represented by the θ curve in Fig. 1. Since, as is seen from Fig. 1, the $d \ln c / d\theta$–θ curves for the Parsons and Temkin isotherms differ sharply, the applicability to the adsorption of benzenedisulfonate ions of equation (2) (see [2]) is doubtful.

I express my sincere gratitude to Academician A. N. Frumkin for discussion of the material of the article and to G. A. Tedoradze for acquainting me with his work [7] before its publication.

Moscow State University
named after M. V. Lomonosov

Received
20 I 1964

CITED LITERATURE

[1] A. N. Frumkin, J. Electroanalyt. Chem., **7**, No. 4 (1964).
[2] R. Parsons, J. Electroanalyt. Chem., **7**, No. 4 (1964).
[3] A. N. Frumkin, Zs. Physik, **35**, 792 (1926).
[4] Ya. de Boer, *The Dynamical Character of Adsorption*, IL, 1962.
[5] A. A. Zhukhovitskii, ZhFKh, **18**, 214 (1944).
[6] H. Dahms, M. Green, J. Electrochem. Soc., **110**, 1075 (1963).
[7] G. A. Tedoradze, DAN, **155**, No. 6 (1964).
[8] M. I. Temkin, ZhFKh, **15**, 296 (1941).
[9] W. Lorenz, W. Müller, Zs. phys. Chem., N. F., **25**, 161 (1960).
[10] J. M. Parry, R. Parsons, Trans. Farad. Soc., **59**, 241 (1963).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.