ON SOME REGULARITIES IN THE ADSORPTION OF ORGANIC SUBSTANCES ON MERCURY

The Langmuir equation

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Abstract

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ON SOME REGULARITIES IN THE ADSORPTION OF ORGANIC SUBSTANCES ON MERCURY

(Presented by Academician A. N. Frumkin, 22 I 1964)

At present, various authors have proposed a number of equations relating the degree of coverage of the mercury surface by an organic substance, θ (or the lowering of the interfacial tension $\Delta\sigma$), to the bulk concentration of the adsorbate, c.

The Langmuir equation

$$Bc = \theta(1-\theta)^{-1}, \tag{1}$$

to which there corresponds the equation of state $\Delta\sigma = -RT\Gamma_\infty \ln(1-\theta)$ (B is a constant, Γ_∞ is the surface concentration Γ at $\theta = 1$, and R and T have their usual meanings), which is valid for the adsorption of certain substances with low molecular weight, usually agrees poorly with experiment if aliphatic compounds with a sufficiently large molecular weight are used as adsorbates (^{1}).

A considerably better agreement with experimental results is given by an equation, taking into account the interaction of molecules in the adsorption layer, derived by Frumkin (^{2}):

$$Bc = \theta(1-\theta)^{-1}\exp(-2a\theta). \tag{2}$$

This isotherm corresponds to the equation of state

$$\Delta\sigma = -RT\Gamma_\infty[\ln(1-\theta) + a\theta^2]$$

(where a is the attraction constant).

Parsons (^{3}), on the basis of work (^{4}), considers the equation:

$$\Delta\sigma = RT\Gamma \cdot (1-\theta)^{-2} - A\Gamma^2. \tag{3}$$

Equation (3) corresponds to the isotherm

Figure 1

Figure 1: Figure 1

$$Bc = \theta(1-\theta)^{-1} \exp\left[\theta(1-\theta)^{-1} + (1-\theta)^{-2} - 2g\theta\right], \qquad (4)$$

where $g = A/RT\Gamma_\infty$. This is readily verified by substituting the value of $\dfrac{\partial \Delta\sigma}{\partial c}$ into the Gibbs equation $\Gamma = \dfrac{c}{RT}\dfrac{\partial \Delta\sigma}{\partial c}$ and integrating the resulting expression.

The same experimental data, especially if the measurements are carried out over a narrow concentration interval, may fit quite well curves corresponding to different adsorption isotherms. Therefore, the choice of criteria that make it possible to draw an unambiguous conclusion about the applicability of one or another equation to the adsorption of a given organic substance is of great importance. The solution of this question is the aim of the present work. In doing so we use information that can be obtained by studying the dependence of adsorption on the potential E.

First, let us examine the question of the magnitude of the degree of coverage at the potential of the maximum of the additional capacitance (i.e., the quantity $(q_1 - q_0)\dfrac{\partial\theta}{\partial E}$, where q_1 and q_0 are the values of the electrode charges at $\theta = 1$ and $\theta = 0$, respectively) for various adsorption isotherms.

In the case of equation (2), for $a \geq 1$ the degree of filling corresponding to the adsorption-peak potential (θ^m) is close to 0.5 ([7,6]).

For the Langmuir equation, from the formulas derived in ([7]) it follows that

$$\theta = 0.5 - 1/kE_{\text{max}}^2, \qquad (5)$$

where $k = 2(C_0 - C_1)/3RT\Gamma_\infty$, C_1 and C_0 are the double-layer capacitances at $\theta = 1$ and $\theta = 0$, respectively, and E_{max} is the adsorption-peak potential measured from the potential of maximum adsorption. Thus, for the Langmuir equation θ^m depends on the adsorption-peak potential and takes values from 0.5 to 0. If quantities characterizing, for example, the adsorption of diphenylamine ([5]) from solutions in 0.2 N HCl ($k = 10.7$ V^{-2}, $E_{\text{max}} = -0.65$ V at $c = 2.2 \cdot 10^{-4}\,M$) are substituted into (5), we obtain $\theta^m = 0.28$.

Fig. 1. Dependence of θ_{max} on a for the Frumkin equation

To find θ^m in the case of equation (4), we use the procedure proposed in ([6]): we set the derivative dh/dE equal to zero, where

$$h = \frac{1}{d\ln B/dE}\frac{d\theta}{dE},$$

and E is the potential. In (7) it was shown that this method gives correct values of the filling at the adsorption-peak potential if there is strong attractive interaction between molecules in the adsorption layer.

In the case of equation (4)

$$h = \theta(1-\theta)^3/[1+\theta-2g\theta(1-\theta)^3]$$

and the condition $dh/dE = 0$ is satisfied at $g = 5.9$ (at a larger value of the attraction constant two-dimensional condensation occurs in the adsorption layer and the adsorption peak becomes a vertical line), $\theta^m = 0.22$.

Thus, by measuring the degree of filling at the adsorption-peak potential, one can, at least for substances with a large value of the attraction constant, unambiguously determine the nature of the adsorption isotherm. Because of the large difference in the values of θ^m for different adsorption isotherms, it is sufficient to determine the degree of filling with an accuracy of 10%.

Let us now consider the relation between the derivative $(\partial\theta/\partial c)_E$ and θ at different values of the attraction constant.

In the case of the Langmuir equation

$$\partial\theta/\partial c = \theta/(1-\theta)c.$$

This function has no maximum, decreasing monotonically from the value $\partial\theta/\partial c = B$ (at $\theta = 0$) to $\partial\theta/\partial c = 0$ (at $\theta = 1$).

For the Frumkin equation

$$\partial\theta/\partial c = \theta(1-\theta)/\{c[1-2a\theta(1-\theta)]\}. \tag{6}$$

Equating the second derivative $\partial^2\theta/\partial c^2$ to zero, we obtain the conditions for extrema: $\theta = 0$ and $\theta = 1$ (minima of the curve) and

$$\theta^3 - 2\theta^2 + \theta(1+1/a) - 1/a + 1/2a^2 = 0.$$

This equation gives the condition for a maximum. In the interval $0 \leq \theta \leq 1$ it has only one real root for values $0.5 \leq a \leq 2$. The value of θ corresponding to the maximum of the derivative $\partial\theta/\partial c$ ($\theta_{\max}$) depends

on the value of a. Figure 1 presents the dependence of $\theta_{\max}$ on a. It follows from this graph that at $a \geq 1.8$, $\theta_{\max}$ is close to 0.5. As a decreases, $\theta_{\max}$ falls, especially sharply at $a < 1$. Such a dependence of $\theta_{\max}$ on a makes it possible, if the relation between $\partial\theta/\partial c$ and θ is known, to determine a.

Fig. 2. Dependence of the maximum value $\frac{1}{B}\frac{\partial\theta}{\partial c}$ on a for the Frumkin equation

Figure 2: Fig. 2. Dependence of the maximum value $\frac{1}{B}\frac{\partial\theta}{\partial c}$ on a for the Frumkin equation

It should be noted that the maximum value of $\partial\theta/\partial c$, for a given B, depends on a. Figure 2 gives a plot of this dependence, constructed on the basis of the equation

$$\partial\theta/\partial c = B(1-\theta_{\max})^2 \exp(2a\theta_{\max})/[1-2a\theta_{\max}(1-\theta_{\max})]. \tag{7}$$

Equation (7) is obtained by substituting into (6) the value

$$c = B^{-1}\theta(1-\theta)^{-1}\exp(-2a\theta).$$

For equation (4),

$$\partial\theta/\partial c = \theta(1-\theta)^3/\{c[1+\theta-2g\theta(1-\theta)^3]\},$$

and the condition for a maximum of $\partial\theta/\partial c$ at $g = 5.9$ is

$$1+\theta-2g\theta(1-\theta)^3 = 0,$$

whence $\theta_{\max} = 0.22$. Thus, in the case of applicability of equation (4), $\theta_{\max} \leq 0.22$. A value $\theta_{\max} > 0.22$ means that equations (3) and (4) are inapplicable to the adsorption of the given substance.

Consequently, knowing the θ that corresponds to the maximum of the derivative $(\partial\theta/\partial c)_E$, one can choose among the adsorption isotherms corresponding to the experimental data. $\partial\theta/\partial c$ can be determined either by drawing a tangent to the curve of the dependence of θ on c, or by the method proposed in the work of Tedoradze and Arakelyan ([8]).

With the aim of checking the relations derived, we determined the derivatives $\partial\theta/\partial c$ for the adsorption of aniline (from the experimental data of the diploma thesis of I. P. Mishutushkina), tetrabutylammonium ion (from the experimental data of work ([10])), and isocaproic acid (from the data of works ([2]) and ([11])).*

Fig. 2. Dependence of the maximum value $\dfrac{1}{B}\dfrac{\partial\theta}{\partial c}$ on a for the Frumkin equation.

For aniline, from the adsorption isotherm we obtained $\theta_{\max} = 0.2 \div 0.4$ (mean value 0.3), which corresponds to $a = 0.9$ (in ([9]), $a = 0.95$ was found). For the tetrabutylammonium ion, from the adsorption isotherm at a potential of -1.3 V (N.C.E.) we obtained $\theta_{\max} = 0.4 \div 0.45$ (mean value 0.43), whereas for $a = 1.8$, $\theta_{\max}$ should be close to 0.5.

For the adsorption of isocaproic acid, according to the table in (2), we found that $\theta_{\max} = 0.22 \div 0.31$ (mean value 0.265), which corresponds to $a = 0.82$, whereas Frumkin found in (2) that the adsorption of isocaproic acid obeys isotherm (2) with $a = 0.83$.

In the work of Tedoradze and Arakelyan (8), it was found that in the adsorption of n-amyl alcohol on mercury, the maximum value of $\partial\Gamma/\partial c$ and, consequently, $\partial\theta/\partial c$ is reached when θ is equal to 0.5, as should be the case for $a = 1.6 \div 1.7$, found in that work.

* The latter data refer to the adsorption of isocaproic acid at the water-air interface. The regularities in this case, however, are the same as in adsorption at the mercury-solution interface.

Thus, to describe the dependence of the degree of coverage on concentration in the case of all the substances listed above, judging from the value of $\theta_{\max}$, only the Frumkin equation is suitable.

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