

MOLECULAR DIMERISATION IN A MULTILAYER ADSORPTION PHASE ON HOMOGENEOUS SURFACES OF A SOLID ADSORBENT

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ABSTRACT

Continuing the discussion on the description of adsorbate-adsorbate association on homogeneous surfaces of solids, an attempt was made to formulate an analytical form of adsorption equation for a multilayer adsorption phase. The validity of Berezin's and Kiselev's assumptions concerning the independence of adsorption in further layers from the model of the phenomenon in the first of them was discussed. The fundamental validity of this assumption has been demonstrated, simultaneously ridding it of its arbitrary character. The main aim of the study was to demonstrate the possibility of formulating a description assuming molecule association in the entire adsorption phase (and not only in the first layer). Theoretical considerations are confined to the case of dimerisation in the concentration range thus warranting the approximation characteristic of the Berezin and Kiselev model. The obtained final adsorption equation exhibits physically acceptable boundary properties; with adequate assumptions it amounts to the Brunauer, Emmett and Teller equation, the equation formulated earlier by one of the authors of this paper or the Langmuir equation.

Keywords: adsorption, association, homogeneous surfaces, multivalence.

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INTRODUCTION

The description of association of adsorbed molecules on the surface of a solid body, initiated more than half a century ago by Kiselev, has a number of valuable solutions for both localised [1-3], mobile [4] and mixed (in the sense of partial mobility) [5] adsorption layers. These proposals assumed, in general, energetic homogeneity of the solid body surface, and in order to formulate appropriate adsorption equations, the formalism of phenomenological and statistical thermodynamics was applied.

In the evaluation of the solutions in question, their undisputed cognitive value should be emphasised, as well as their usefulness for describing the experimental adsorption data [1,6], particularly in the range of low pressure of the adsorptive. However, one of the important aspects of the discussed problem has not yet been taken into account to a degree similar to the rest. It is the possibility of creating "horizontal", i.e. parallel to the surface of the adsorbent, adsorbate-adsorbate associations in further adsorption layers than the first one. Although, from a physical point of view, this effect should cover the entire adsorption phase, due to mathematical complexity it was limited to the assumption that, regardless of the mechanism of the phenomenon in the first layer, the creation of further adsorption layers proceeds according to the Brunauer, Emmett, Teller (BET) model [7].

This means that starting from the second layer, adsorption was treated as adsorptive condensation on the molecules of the layer directly below, and all intermolecular interactions were limited to the formation of interlayer complexes. Undoubtedly, this assumption increased the effectiveness of the description of the experimental data in the range of pressures close to the saturated vapour pressure of the adsorptive, however, by drastically differentiating the status of further adsorption layers in relation to the first one, it simultaneously left a significant theoretical deficiency.

This aspect of adsorption on a homogeneous solid surface is referred to in this paper by considering adsorbate-adsorbate associations also in further adsorption layers. Without prejudging the possibility (or lack thereof) of formulating a complete model for any factor of emerging associates and any (finite) number of layers, the considerations were limited to the case of adsorbate-adsorbate dimerisation in the phase formed by an infinite number of adsorption layers. The aim of the study was to demonstrate the possibility of obtaining an open solution for such a variant of the discussed phenomenon.

PROPOSAL FOR THE DESCRIPTION OF MOLECULAR DIMERIZATION IN THE WHOLE ADSORPTION PHASE

In the multi-layered variant of Berezin's and Kiselev's model [1] it is assumed that the amount of adsorption in further layers depends, at given values of temperature and pressure, only on the number of molecules in the first layer, but does not depend on the state of these molecules, i.e. on the effects of their mutual interactions, including the adsorbate-adsorbate

association.

The authors cited above accept this assumption as a certainty not requiring justification. It seems, however, that such a position may, regardless of its ultimate validity, cause uncertainty as to the general character of the assumption. With this aspect in mind, we will present below what we believe to be the necessary comment.

In order to do so, let us mark any molecule of the first adsorption layer with the symbol A. Let the expression of the diversity of the state of particular A molecules be their division into single A₁ complexes and horizontal i-factor associations, A_i, where i ≥ 2. If N_{A1} and N_{Ai} are numbers A₁ and A_i respectively, then the number of molecules in the first adsorption layer, N' ≡ N_A, amounts to

$$N' = N_{A_1} + \sum_{i \geq 2} i N_{A_i}$$

Because, according to the BET model, the only adsorption centres for layer two molecules are molecules A, part of molecules A is in a state of adsorption equilibrium, covered "from above". Let N_{A*}, N_{A1*} and N_{Ai*} be equivalent to N_A (i.e. N'), N_{A1} and N_{Ai} in the uncovered part of the first layer. According to the concept of Berezin and Kiselev, the following scheme characterises primary adsorbate-adsorbent interactions:

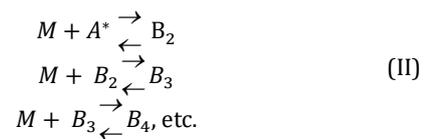


where M and S are respectively the adsorptive molecule and the binding site of the adsorbent surface. The K₁ equilibrium constant corresponding to this scheme has the following form:

$$K_1 = \frac{N_{A_1^*}}{p(Y - N')} \tag{1}$$

Where p and Y are the pressure of the adsorptive and the number of binding points on the adsorbent surface respectively.

In turn, the formation of further adsorption layers follows the scheme:



where B_{i≥2} means vertical, i.e. perpendicular to the surface of the adsorbent complex whose peak molecule belongs to the i-th adsorption layer.

The BET model identifies individual stages of the scheme (II) as three-dimensional adsorptive condensation, and therefore assigns to the subsequent equilibrium constants an equal value equal to the inverse pressure of the saturated vapour of the adsorptive, p_s.

Hence, we have:

$$\frac{1}{p_s} = \frac{N_{B_2}}{p N_{A^*}} \tag{2}$$

$$\frac{1}{p_s} = \frac{N_{B_3}}{p N_{B_2}} \tag{3}$$

$$\frac{1}{p_s} = \frac{N_{B_4}}{p N_{B_3}}, \text{ etc.} \tag{4}$$

Therefore:

$$N_{B_2} = hN_{A^*} \quad (5)$$

$$N_{B_3} = h^2N_{A^*} \quad (6)$$

$$N_{B_4} = h^3N_{A^*}, \text{ etc.} \quad (7)$$

Where $h (=p/p_s)$ is the relative pressure of the adsorptive (note that for a gas below critical temperature, $0 < h < 1$, while $h > 1$ means compression of liquid under pressure $p > p_s$).

In view of the obvious dependencies:

$$N' = N_{A^*} + N_{B_2} + N_{B_3} + \dots \quad (8)$$

and

$$N = N_{A^*} + 2N_{B_2} + 3N_{B_3} + \dots \quad (9)$$

For n adsorption layers we have:

$$N' = N_{A^*} \frac{1 - h^n}{1 - h} \quad (10)$$

and

$$N = N_{A^*} \frac{1 - (n+1)h^n + nh^{n+1}}{(1-h)^2} \quad (11)$$

Dividing the last two equations by themselves gives:

$$N = N_{A^*} \frac{(1-h)(1-h^n)}{1 - (n+1)h^n + nh^{n+1}} \quad (12)$$

The amount of adsorbate in further layers, N'' , is of course the difference between N and N' , which in relation to equation (12) means that

$$N'' = N' h \frac{1 - nh^{n-1} + (n-1)h^n}{(1-h)(1-h^n)} \quad (13)$$

For an infinite number of adsorption layers ($n \rightarrow \infty$):

$$N'' = N' \frac{h}{1-h} \quad (14)$$

Equation (13), as well as its boundary form (14) prove that for the established values of pressure and temperature (remember that $h = h(p, p_s(T))$) and for the BET-type course of adsorption in further layers, the amount of adsorbate in this part of the adsorption phase does not depend on the phenomenon pattern in the first layer, but solely on the concentration of this layer. This conclusion confirms the validity of Berezin and Kiselev's assumption and, together with the commentary preceding it, releases this assumption from its largely arbitrary character.

The realisation of the main goal of this paper is based on the following description of the adsorption phase:

- the surface of the solid adsorbent contains Y identical binding sites,
- the adsorption of a single gas component is multilayer in nature, where:

- the first adsorption layer is filled according to the Berezin-Kiselev model with limited adsorbate-adsorbate adsorption at most to dimers,
- the binding sites for molecules of any of the further adsorption layers are exclusively those of the immediately lower layer,
- the equilibrium constant of the adsorptive-adsorbate interaction is equal to $1/p_s$,
- Further adsorption layer molecules, like layer 1 molecules, may be subject to horizontal dimerisation,
- the equilibrium constant of this dimerisation K_2 is common to the entire adsorption phase,
- the number of adsorption layers is unlimited ($n \rightarrow \infty$),
and
- the adsorptive is an ideal gas.

The types of complexes constituting the adsorption phase corresponding to the above description are shown in Figure 1. Each of the three levels of illustration is supplemented with the symbols of these complexes - (a), and the general code of their number of molecules - (b).

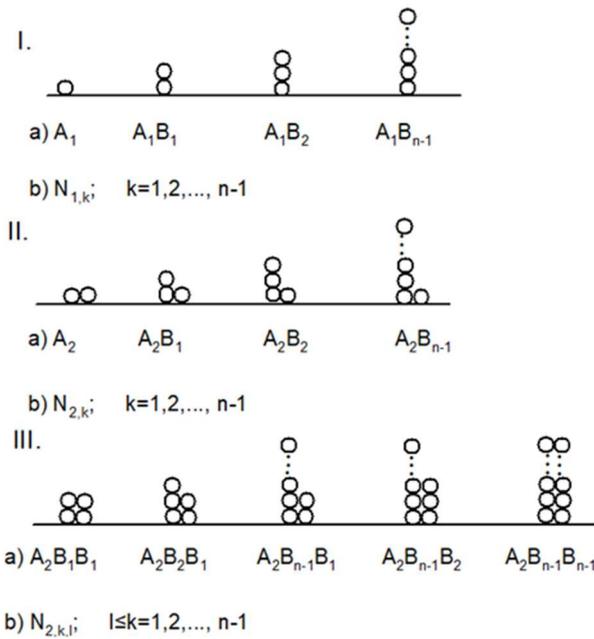
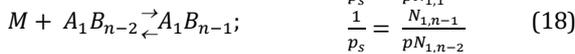


Fig. 1 Types of adsorption complexes and corresponding symbols.

The thermodynamic equilibrium of the system is represented by the following diagrams and corresponding equilibrium constant expressions:

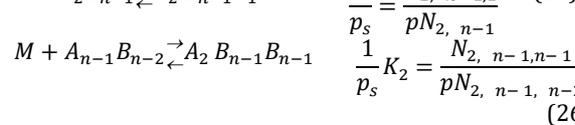
Level (I)



Level II



Level III



The presence of the number of binding sites, Y in equation (15) ensures the equilibrium constant K_2 the character of intensive quantity. The need to take this aspect into account was explained in our previous publication [8].

Equations (19)-(26) lead to the following expressions for the number of molecules of particular adsorption complexes.

$N_{1,1} = hN_1 \quad (27)$

$N_{1,2} = h^2N_1 \quad (28)$

$N_{1,3} = h^3N_1 \quad (29)$

$N_{1,n-1} = h^{n-1}N_1 \quad (30)$

$N_{2,1} = hN_2 \quad (31)$

$N_{2,2} = h^2N_2 \quad (32)$

$N_{2,3} = h^3N_2 \quad (33)$

$N_{2,n-2} = h^{n-1}N_2 \quad (34)$

$N_{2,1,1} = K_2h^2N_2 \quad (35)$

$N_{2,2,1} = K_2h^3N_2 \quad (36)$

$N_{2,n-1,1} = K_2h^nN_2 \quad (37)$

$N_{2,n-1,n-1} = K_2^{n-1}h^{2(n-1)}N_2 \quad (38)$

and moreover, in accordance with equation (19),

$N_2 = \frac{K_2}{Y} N_1^2 \quad (39)$

As is evident from equation (15), the formulation of the adsorption equation requires explicit forms of $N_1(N)$ and $N'(N)$ functions. For this purpose, using the above dependencies, we will write:

$N' = N_1(1 + h + h^2 + h^3 + \dots) + 2N_2(1 + h + h^2 + h^3 + \dots)[1 + K_2h^2 + (K_2h^2)^2 + (K_2h^2)^3 + \dots] \quad (40)$

For an infinite number of adsorption layers and assuming that $K_2h^2 < 1$, we obtain:

$N' = \frac{N_1}{1-h} + \frac{2N_2}{(1-h)(1-K_2h^2)} \quad (41)$

where N_2 is defined with equation (39),

$$N = N_1(1 + 2h + 3h^2 + 4h^3 + \dots) + N_2[(2 + 3h + 4h^2 + 5h^3 + \dots) + K_2h^2(4 + 5h + 6h^2 + 7h^3 + \dots) + (K_2h^2)^2(6 + 7h + 8h^2 + 9h^3 + \dots) + (K_2h^2)^3(8 + 9h + 10h^2 + 11h^3 + \dots) + \dots], \quad (42)$$

which once again for $n \rightarrow \infty$ and $Kh^2 < 1$, gives:

$$N_1 = \frac{2N(1-h)^2}{\beta + 1} \quad (43)$$

where

$$\beta = \sqrt{4K_2 \frac{N}{Y} \frac{2-h(1+Kh^2)}{(1-Kh^2)^2} + 1} \quad (44)$$

By combining equations (39), (41) and (43) we receive:

$$N' = N \frac{2(1-h)}{\beta+1} \left[1 + 4 \frac{K_2}{Y} \frac{N(1-h)^2}{(1-K_2h^2)(\beta+1)} \right] \quad (45)$$

The substitution of dependencies (43) and (45) to equation (15) gives, after a simple transformation, the final adsorption equation in the form:

$$h = \frac{\theta(1-h)^2 \frac{2}{\beta+1}}{C_{BET} \{ 1 - 2\theta(1-h) \frac{(\beta+1)(1-K_2h^2) + K_2h^2(2-h)-h}{(\beta-1)[2-h(1+K_2h^2)]} \}} \quad (46)$$

where

$$\beta = \sqrt{4K_2 \frac{2-h(1+K_2h^2)}{(1-K_2h^2)^2} \theta(1-h)^2 + 1} \quad (47)$$

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