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Application of a Partially Mobile Model of Monolayer Adsorption to Multilayer Phenomena

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Two multilayer adsorption models are discussed, assuming partially mobile adsorption in the first layer, and the *BET* or *Kim-Oh* (*KO*) mechanisms for formation of higher layers. The theoretical multilayer adsorption isotherms corresponding to these models have been calculated for differing degrees of mobility of the first layer.

(Keywords: BET adsorption model; Multilayer adsorption; Partially mobile adsorption)

Anwendung eines partiell mobilen Modells der Adsorption der ersten Schicht bei Mehrschicht-Phenomenen

Zwei Mehrschicht-Modelle, bei der Annahme einer partiell mobilen Adsorption der Erst-Schicht, und des *BET*, bzw. *Kim-Oh* (*KO*) Mechanismus für die Ausbildung höherer Schichten, werden diskutiert. Die theoretischen Mehrschicht-Adsorptionsisothermen, die diesen Modellen entsprechen, werden für verschiedene Grade von Mobilität der ersten Schicht berechnet.

Introduction

Many attempts have been made to explain the phenomena observed in the field of multilayer adsorption of gases on solid surfaces[1–5]. One of the most popular equations describing the formation of multilayers is the *BET* adsorption isotherm[1]. Nevertheless, the *BET* equation is frequently modified in order to achieve a better fitting of experimental data. These modifications usually concern the effects of lateral

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interactions[6], surface heterogeneity[7,8], as well as the influence of the adsorbent force field on the formation of the finite number of adsorbed layers[9,10]. The customary *BET* equation predicts too large adsorption at relative pressures greater then 0.35[9]. The purpose of many modifications of the *BET* equation is the decrease of adsorption at higher relative pressures.

In this paper we shall discuss the model of multilayer adsorption in which the first layer is partially mobile (for this layer we assume the model of *Lee* and *O'Connell*[11]) and higher layers are formed according to the *BET*[1] or *Kim-Oh* (*KO*)[5] assumptions. The assumption of the partially mobile adsorption model in the first layer decreases the adsorption in higher layers.

Theory

First, let us establish the main assumptions of the simplified *Lee—O'Connell* model of monolayer adsorption. These may be summarized as follows:

(i) B equivalent sites are available for localized adsorption, with the restriction that only one molecule can be adsorbed on a single adsorption site;

(ii) mobile molecules behave as a two-dimensional imperfect gas;

(iii) lateral attractive interactions between adsorbed molecules are neglected; and

(iv) the fraction of molecules which are localized on particular sites, is determined by temperarure and properties of adsorbate and solid adsorbent.

Thus, localized adsorption is treated in the same way as in the *Langmuir* model, whereas mobile adsorption according to the *Volmer* model.

Next, for the molecules which form the second and higher layers the same assumptions as in the *BET*[1] or *KO*[5] models will be made. However, when the *BET* mechanism for the formation of multilayer is applied the additional assumption that only localized molecules in monolayer can be considered as possible sites able to form the second layer must be adopted. But, when the *KO* model is used the second layer can be formed on all molecules adsorbed in the first layer. The above restrictions are connected with the fact that the *BET* theory assumes that adsorbed molecules form molecular piles and it is rather difficult to imagine that such a pile can be formed on a mobile molecule. On the other hand the *KO* theory assumes that the second layer of adsorbate is a two-dimensional ideal gas and thus it is completely mobile. For this case we have no reason to favor any kind of molecules adsorbed in monolayer so that all of them should be considered equaly.

Now, according to the assumptions (i—iv), the canonical partition function for N molecules adsorbed in the first layer may be written as follows.

$$Q_{\mathrm{I}}(N,B,T) = \frac{B!\,q_l^{Nf_l}}{(Nf_l)!\,(B-Nf_l)!}\;\frac{(B-\gamma N)^{Nf_m} q_m^{Nf_m}}{(Nf_m)!} \tag{1}$$

In the above equation f_m and f_l denotes the fractions of mobile and localized molecules respectively, q_m and q_l are the molecular partition functions of a single mobile and localized molecule, and finally, γ is a parameter which is a measure of the effective area occupied by a single adsorbed molecule. In the following discussion we confine ourselves to the very special case of $\gamma = 1$. If the total number of adsorbed molecules is M, then the number of molecules in the second and higher layers is equal to $M-N$. Thus, the canonical partition functions for these molecules assume the following forms:

$$Q_{BET}(M,N,T) = \frac{(M-Nf_m-1)!\,q_2{}^{(M-N)}}{(M-N)!\,(Nf_l-1)!} \tag{2}$$

and

$$Q_{KO}(M,N,T) = \frac{(Nq_2)^{(M-N)}}{(M-N)!} \tag{3}$$

for BET and KO models, q_2 is the molecular partition function for a single molecule in the second and higher layers. We made the assumption that molecules in all layers, beyond the first one, have the same properties. The complete canonical partition function for the whole adsorbed phase is then

$$Q = \sum_{N=1}^{k} Q_{\mathrm{I}} Q_{\mathrm{II}};\; k = M\ (M < B),\; k = B\ (M > B) \tag{4}$$

and Q_{II} may be described by Eq. (2) for the BET model, or by Eq. (3) for the KO model.

We make the usual approximation of setting ln $\mathbf{Q}$ equal to the logarithm of the largest term in the summation (4). The value of N which gives this term is determined from

$$\left(\frac{\partial \ln Q_{\mathrm{I}} Q_{\mathrm{II}}}{\partial N}\right)_{M,T} = 0 \tag{5}$$

The chemical potential of the adsorbed molecules is

$$\mu_s/kT = -\left(\frac{\partial \ln Q_{\mathrm{I}} Q_{\mathrm{II}}}{\partial M}\right) \tag{6}$$

and in the state of equilibrium it must be equal to the chemical potential of bulk phase (assumed ideal), for which we have

$$\mu_g/kT = \mu_g{}^0/kT + \ln p \tag{7}$$

where $\mu_g{}^0$ is the standard chemical potential of the bulk phase and p is an equilibrium pressure.

The adsorption isotherm equations for the *BET* and *KO* models of multilayers [after performing the differentiations in (5) and (6) and after considerable algebra] takes the forms:

$$\eta = \frac{\Theta y}{(1-\Theta y)^{f_m}(1-f_l\Theta y)^{f_l}} \exp\left(\frac{\Theta y f_m}{1-\Theta\cdot y}\right) \tag{8}$$

with

$$\eta = \begin{cases} A_{BET}\dfrac{1-y}{y^{f_l}(1-f_m y)^{f_m}} & \text{for the } BET \text{ model} \\[2ex] A_{KO}\dfrac{1-y}{y}\exp\left(\dfrac{1-y}{y}\right) & \text{for the } KO \text{ model} \end{cases} \tag{9}$$

where

$$y = \begin{cases} \dfrac{1-x}{1-f_m x} & \text{for the } BET \text{ model} \\[2ex] \dfrac{1}{1-x} & \text{for the } KO \text{ model} \end{cases} \tag{10}$$

and

$$\begin{gathered} c_l = q_l/q_2;\; c_m = q_m/q_2;\; x = p/p_0; \\ 1/p_0 = q_2 \exp(\mu_g{}^0/kT); \\ A_{BET} = c_l{}^{f_l} c_m{}^{f_m} f_l{}^{-2f_l} f_m{}^{-f_m}; \\ A_{KO} = c_l{}^{f_l} c_m{}^{f_m} f_l{}^{-f_l} f_m{}^{-f_m}; \end{gathered} \tag{11}$$

The surface coverage Θ is defined as

$$\Theta = M/B \tag{12}$$

The interesting feature of equation (8) is that upon introducing the following definition of "reduced" surface coverage $\vartheta = \Theta y$, the right hand side of Eq. (8) becomes formally identical with the equation of monolayer adsorption corresponding to the canonical partition function (1).

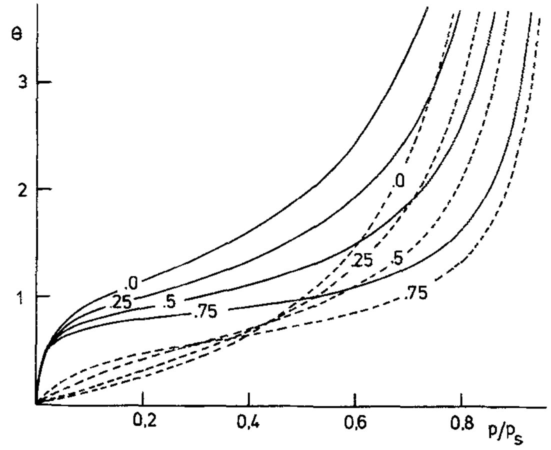

Fig. 1. Theoretical adsorption isotherms calculated according to Eq. (8) for the *BET* model of multilayers. The solid lines were calculated for $c_m = 100$ and $c_l = 50$, whereas the dashed lines were calculated for $c_m = 10$ and $c_l = 1$. The contributions of mobile adsorption in the first layer are indicated in the figure

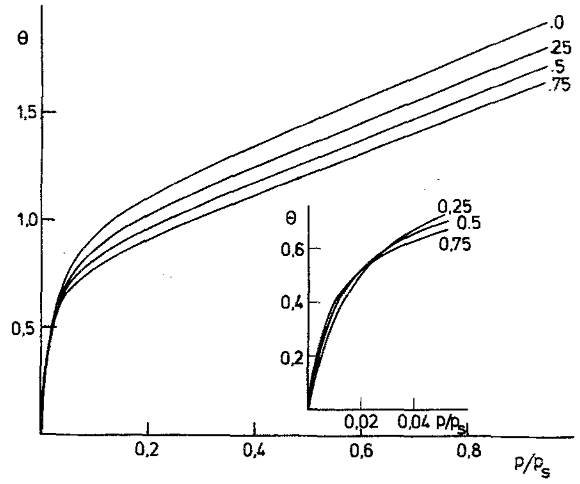

Fig. 2. Theoretical adsorption isotherms calculated according to Eq. (8) for the *KO* model of multilayers for $c_m = 100$ and $c_l = 50$, and for different degrees of mobility of the first layer

Model Calculations

Mathematical analysis of Eq. (8), shows, that the complex expression (8) has one solution with respect to Θ for $x \in (0,1)$. This value of Θ belongs to the interval $(0,1/y)$ which in the case of the *KO* model becomes (0,2), whereas for the *BET* model this interval transforms to $(0, \infty)$.

Figs. 1 and 2 present the theoretical multilayer adsorption isotherms calculated according to Eq. (8). The solid lines in Fig. 1 denote the multilayer adsorption isotherms for the *BET* model calculated for $c_m = 100$, $c_l = 50$ and differing values of f_m. However, the dashed lines in Fig. 1 were calculated according to Eq. (8) (*BET* adsorption model) for $c_m = 10$ and $c_l = 1$. Fig. 2 shows the multilayer adsorption isotherms for the *KO* model obtained for $c_m = 100$ and $c_l = 50$. From the results presented in Figs. 1 and 2 the following conclusions can be drawn:

(a) an increase of mobility parameter f_m caused a decrease of adsorption in multilayer pressure region, however, in the submonolayer region a contrary effect is observed;

(b) high influence of the parameters c_m and c_l on adsorption is observed in the submonolayer pressure region, whereas this influence decreases with the increasing of the relative adsorbate pressure.

Increase of the f_m value denotes the number of mobile molecules in the first layer increases; then the number of localized molecules on which the multilayer forms decreases. These arguments explain conclusion (a). As for conclusion (b), the parameters c_m and c_l are associated with the adsorption energy, therefore they mainly influence the formation of the first layer.

The main advantage of Eq. (8) (*BET* model) is the fact that this equation predicts smaller adsorption for $f_m \neq 0$ than the customary *BET* isotherm. This makes Eq. (8) an attractive equation for the study of multilayer adsorption on solids. Also, the physical grounds of the partially mobile adsorption model are close to reality[11].

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