Multilayer Adsorption with Multisite Occupancy: An Improved Isotherm for Surface Characterization

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In this work, an improved solution for multilayer adsorption of linear species is presented. The particular case of multilayer dimer adsorption is dealt with in detail, and a new adsorption isotherm is obtained for determination of surface area and adsorption energy from experiments. From the comparison between the new isotherm and the standard Brunauer−Emmett−Teller (BET) formalism, it arises that the monolayer volume, v_m (or the surface area, A), can be up to 1.5 times larger than the one from the BET model. The proposed model is simple and easy to apply in practice and leads to new values of surface area and adsorption heat. Physically, these advantages are a consequence of properly considering the configurational entropy of the adsorbate.

1. Introduction

Multilayer adsorption is an experimentally as well as theoretically relevant field of surface science owing to its importance for the characterization of solid surfaces and to the analytical challenges that are faced in describing the thermodynamics of interacting particles in this regime. Multilayering develops in most practical applications and experiments involving adlayers.

Among the various theories and models that have been proposed to describe multilayer adsorption in equilibrium, the ones of Brunauer−Emmett−Teller (BET)[1] and Frenkel−Halsey−Hill (FHH)[2−4] are the simplest which provided the basis to more elaborate approaches accounting for lateral interaction between the admolecules, differences between the adsorption energy and structure between the first and upper layers, surface heterogeneity, and so forth.[5,6] These leading models, along with more recent contributions, have played a central role in the characterization of solid surfaces by means of gas adsorption.[7]

With regard to multilayer adsorption in the lattice gas approximation, the BET model assumes monomer-like particles occupying one lattice site. Once adsorption in the first layer has taken place, further adsorption can occur on top of the adsorbed particles. No lateral interactions are accounted for, and the adsorption energy of sites in the second layer and upper layers is assumed in general to be constant and different from the one in the first layer. This basic model has been extraordinarily useful in practice for determining the surface area and adsorption energy of solid materials due to the simplicity of its resulting adsorption isotherm, as well as the small number of parameters involved in it and the physical significance of them.

In practical situations, most adsorbates are polyatomic. Hence, a more accurate description of multilayer adsorption should account for the fact that it develops in general with multisite occupancy. Thus, the entropic contribution to the thermodynamic potentials will be appreciably different from the one expected for single-site occupancy. Although many other factors have been considered in multilayer adsorption, multiple occupation of sites has been neglected. It is expected that the entropic contribution of the adsorbate and its shape will be significant as well in the multilayer regime. It has been recently shown that the entropic effects of linear molecules are significant in the monolayer regime when compared with monatomic adsorption.[8−10]

In this work, the rigorous solution for multilayer adsorption thermodynamics of homonuclear linear molecules (k-mers) in the lattice gas model is presented. It is shown that the adsorption isotherm for the simplest polyatomic species (dimer) predicts important differences as compared with BET isotherm in the whole range of the model's parameters. Accordingly, the two parameters that can be inferred from experimental isotherms, namely, the ratio between the partition functions of the molecule in the first and second layer, c (consequently, the adsorption heat), and the monolayer volume, v_m, could also be appreciably distinct from the ones arising from the BET model when the nonspherical character of the adsorbate is considered in a simple fashion.

The present work is organized as follows. In section 2, the general formulation for the grand partition function of homonuclear linear molecules is presented. Section 3 is devoted to a detailed discussion of dimer adsorption within the formalism developed, and a new adsorption isotherm for dimers is obtained. Adsorption isotherms of dimers for various values of c are shown and discussed by

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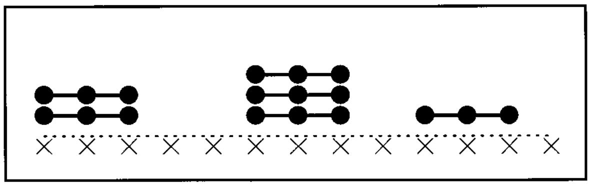

Figure 1. Cartoon representing the lattice gas model of k-mer adsorption in the multilayer regime (the case of trimer adsorption is depicted). Adsorption sites are represented by crosses on the adsorbent's surface. The adsorbate molecule is represented by black beads connected by solid bonds.

comparing with the BET model's predictions. Analysis of standard experimental isotherms is carried out in section 3 as well. Conclusions are drawn in section 4.

2. Multilayer Adsorption of Linear Molecules

Most adsorbates involved in adsorption experiments are polyatomic in the sense that when adsorbed, their typical size is larger than the distance between the nearest-neighbor minima of the gas−solid potential. For instance, this is true for most alkanes.[11] However, even the simplest nonspherical molecules such as N_2 and O_2 may adsorb with partial multisite occupancy depending on the surface structure.[12−17] Furthermore, some monatomic gases such as Kr or Xe may induce some exclusion in neighboring sites upon adsorption because of their large atomic radii. Ultimately, multiple site occupation is the commonest situation in gas adsorption.

To maintain the simplest model that accounts for multisite occupancy in multilayers, we define it in the spirit of the BET's original formulation. The adsorbent is a homogeneous one-dimensional lattice of sites. The adsorbate is assumed to be linear molecules having k identical units (k-mers) each of which occupies an adsorption site. Furthermore, (i) a k-mer can adsorb exactly onto an already adsorbed one; (ii) no lateral interactions are considered; (iii) the adsorption heat in all layers, except the first one, equals the molar heat of condensation of the adsorbate in the bulk liquid phase. Thus, $c = q_1/q_i = q_1/q$ with $q_i = q$ ($i = 2, ..., \infty$) denotes the ratio between the single-molecule partition functions in the first and higher layers. The fact that k-mers can arrange in the first layer leaving sequences of l empty sites with $l < k$, where no further adsorption of a k-mer can occur in such a configuration (as shown in Figure 1), makes the calculation of entropy more elaborate than the one for monomer adsorption.

For a lattice having M adsorption sites, the maximum number of columns that can be grown up onto it is $n_M = M/k$. Let us denote by $\Omega_k(n, M)$ the total number of distinguishable configurations of n columns on M sites. If an infinite number of layers is allowed to develop on the surface, the grand partition function of the adlayer in equilibrium with a gas phase at chemical potential μ and temperature T is given by

$$\Xi(\lambda, M) = \sum_{n=0}^{n_M=M/k} \Omega_k(n, M)\, \xi^n(\lambda) \qquad (1)$$

where $\lambda = \exp(\mu/k_BT)$, μ, and T are the fugacity, chemical potential, and temperature, respectively, and k_B is the Boltzmann constant. In addition, $\Omega_k(n, M)$ can be written as[8]

$$\Omega_k(n, M) = \begin{bmatrix} M - (k-1)n \\ n \end{bmatrix} = \frac{[M-(k-1)n]!}{n!(M-kn)!} \qquad (2)$$

and

$$\xi(\lambda) = \sum_{i=1}^{\infty} q_1 q^{i-1}\lambda^i = c\sum_{i=1}^{\infty} q^i\lambda^i = \frac{c\lambda q}{1-\lambda q} \qquad (3)$$

is the grand partition function of a single column of k-mers having at least one k-mer in the first layer.

The summation in eq 1 cannot be carried out directly for $k > 1$; therefore, we follow the standard procedure of determining the term which makes the maximum contribution.

Thus, by using Stirling's approximation $\ln n! = n \ln n - n$,

$$\ln[\Omega_k(n, M)\, \xi^n] = [M-(k-1)n]\ln[M-(k-1)n] - n\ln n - (M-kn)\ln(M-kn) + n\ln\xi \qquad (4)$$

and

$$\frac{\partial\{\ln[\Omega_k(n, M)\,\xi^n]\}}{\partial n} = -(k-1)\ln[M-(k-1)n] + k\ln(M-kn) + \ln\left(\frac{\xi}{n}\right) = 0 \qquad (5)$$

$$\ln\left\{\left[\frac{M-kn}{M-(k-1)n}\right]^k \frac{\xi}{n}[M-(k-1)n]\right\} = 0 \qquad (6)$$

leads to the following nonlinear equation

$$(M-kn)^k = \frac{n}{\xi}[M-(k-1)n]^{k-1} \qquad (7)$$

By resolving $(M - kn) = (n/\xi)^{1/k}[M - (k - 1)n]^{(k-1)/k}$ from eq 7 and replacing it in eq 1, one obtains

$$\ln\Xi(\lambda, M) = \frac{M}{k}\ln\left\{\frac{\xi}{n}[M-(k-1)n]\right\} \qquad (8)$$

in which it is tacit that n in the right-hand term is the one corresponding to the maximum term of the grand partition function in eq 1. Accordingly, eqs 7 and 8 are the basic relationships from which the thermodynamics of k-mers in the multilayer regime will be derived.

The thermodynamic functions are straightforward from the formalism of the grand canonical ensemble. Therefore,

$$\bar{n} = \lambda\left(\frac{\partial\ln\Xi}{\partial\lambda}\right)_{T,M} \qquad (9)$$

$$s = k_BT\left(\frac{\partial\ln\Xi}{\partial T}\right)_{M,\mu} + k\ln\Xi \qquad (10)$$

$$e = -\left(\frac{\partial\ln\Xi}{\partial\beta}\right)_{M,\lambda} \qquad (11)$$

where $\bar{n}$, s, and e are the number of adsorbed particles,

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entropy, and energy, respectively. From the usual definition of surface coverage of a lattice, θ (the ratio of the occupied sites to the total lattice sites), it arises that

$$\theta = \frac{k\bar{n}}{M} = \frac{k\lambda}{M}\left(\frac{\partial \ln \Xi}{\partial \lambda}\right)_{T,M} \qquad (12)$$

In the case of adsorbed monomers ($k = 1$), $(M\xi/n) = (1 + \xi)$ from eq 7 and

$$\ln \Xi(\lambda, M) = M \ln(1 + \xi) \qquad (13)$$

From eq 9,

$$\bar{n} = \lambda\left(\frac{\partial \ln \Xi}{\partial \lambda}\right)_{T,M} = \frac{\lambda\xi'}{1 + \xi}M \qquad (14)$$

where $\xi' = \mathrm{d}\xi/\mathrm{d}\lambda = cq/(1 - \lambda q)^2$, and finally the surface coverage holds,

$$\theta = \frac{\bar{n}}{M} = \frac{cq\lambda}{(1 - \lambda q)[1 + (c - 1)\lambda q]} \qquad (15)$$

which corresponds to the well-known BET isotherm equation.

3. Multilayer Adsorption of Dimers

Hereforth, we deal with adsorption of the simplest polyatomic model molecule, namely, a homonuclear dimer. On one hand, this case bears theoretical interest because it represents a qualitative advance with respect to the existing lattice gas models of multilayer adsorption, in which the entropic effects of the adsorbate size are explicitly accounted for. On the other hand, since most of the nonporous solid surface characterization is experimentally carried out through nitrogen adsorption, a more accurate description of the adlayer equilibrium may ultimately lead to more reliable values of physical parameters, such as the adsorption energy and surface area, that are determined from experiments.

For dimers, eq 7 reads

$$(M - 2n)^2 = \frac{n}{\xi}(M - n) = \frac{n}{\xi}[(M - 2n) + n] \qquad (16)$$

By denoting $w = (M - 2n)$, eq 16 can be rewritten as

$$w^2 - \frac{n}{\xi}w - \frac{n^2}{\xi} = 0 \qquad (17)$$

Only one of the solutions of eq 17 remains for physical reasons ($w \geq 0$),

$$w = \frac{n}{2\xi} + \frac{1}{2}\sqrt{\frac{n^2}{\xi^2} + \frac{4n^2}{\xi}} = \frac{n}{\xi}\left(\frac{1 + \sqrt{1 + 4\xi}}{2}\right) \qquad (18)$$

From eq 8,

$$\begin{aligned}\ln \Xi(\lambda, M) &= \frac{M}{2}\ln\left[\frac{(M - n)\xi}{n}\right] \\ &= \frac{M}{2}\ln\left[(M - 2n)\frac{\xi}{n} + \xi\right] \qquad (19)\end{aligned}$$

which, from the definition of w and eq 18, gives

$$\ln \Xi(\lambda, M) = \frac{M}{2}\ln\left(\frac{1}{2} + \xi + \frac{\sqrt{1 + 4\xi}}{2}\right) \qquad (20)$$

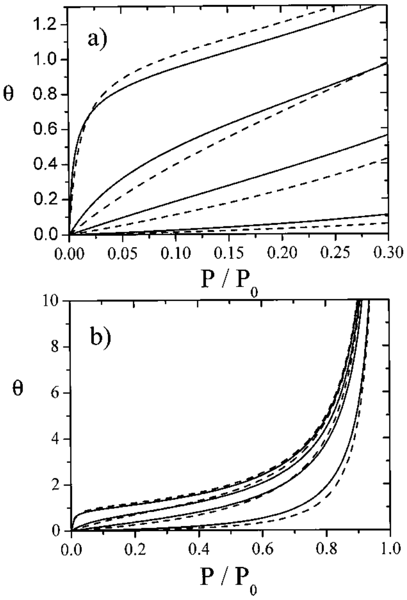

Figure 2. Adsorption isotherms for different values of the parameter c. The solid line represents the isotherm for dimers obtained in the present work [eq 25], and the dashed line represents the BET isotherm (monomers). The pairs of curves from bottom to top correspond to $c = 0.1$, 1, 5, and 100, in the range 0−0.3 of p/p_0 in (a) and 0−1 of p/p_0 in (b).

The mean number of adsorbed particles $\bar{n}$ is [eq 9]

$$\bar{n} = \frac{M}{2}\lambda\frac{\left[\xi' + \dfrac{\xi'}{\sqrt{1 + 4\xi}}\right]}{\left(\dfrac{1}{2} + \xi + \dfrac{\sqrt{1 + 4\xi}}{2}\right)} \qquad (21)$$

Finally, after some algebra the adsorption isotherm becomes

$$\theta = \frac{1}{(1 - \lambda q)}\left\{1 - \left[\frac{(1 - \lambda q)}{(4c - 1)\lambda q + 1}\right]^{1/2}\right\} \qquad (22)$$

Considering that $\lambda q = p/cp_{\mathrm{H}}$ and replacing it in eq 22, p_{H} has the meaning of the Henry law's constant, as it arises from the limit of θ for $p \to 0$.

To compare this isotherm equation with the BET's, we assume that the gas phase is ideal and the state of the adsorbate in the second and higher layers is the same as in the bulk liquid ($q = q_l$, q_l denoting q, the molecular partition function, of the liquid). Thus,

$$\lambda = \Lambda^3 p/k_{\mathrm{B}}T \qquad (23)$$

where $\Lambda^3 = (h^2/2\pi m k_{\mathrm{B}}T)^{1/2}$ and

$$cp_{\mathrm{H}} = \frac{p}{\lambda q} = \frac{k_{\mathrm{B}}T}{\Lambda^3 q} = p_{\mathrm{o}} \qquad (24)$$

m, p, and p_0 being the molecular mass of the adsorbate, the gas pressure, and the saturation pressure of the bulk liquid, respectively. Then,

$$\theta = \frac{1}{(1 - p/p_0)}\left\{1 - \left[\frac{(1 - p/p_0)}{(4c - 1)p/p_0 + 1}\right]^{1/2}\right\} \qquad (25)$$

The adsorption isotherm eq 25 is shown in Figure 2 a,b for small, medium, and large values of the parameter c,

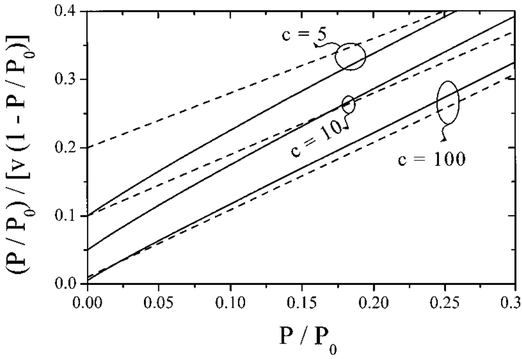

Figure 3. $[p/p_0]/[v(1 - p/p_0)]$ versus p/p_0 for $v_m = 1$ (in arbitrary units) and $c = 100$, 10, and 5 (curves from bottom to top). Solid and dashed curves represent the same models as in Figure 2.

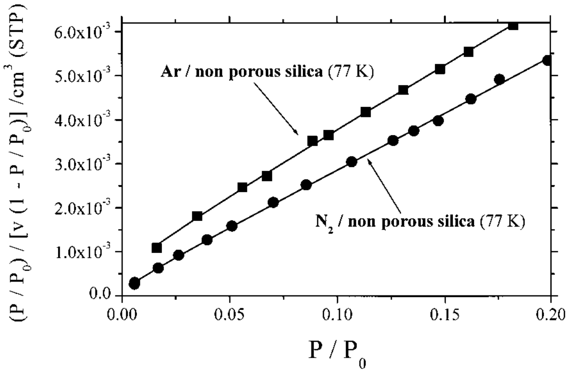

Figure 4. Fitting of experimental adsorption isotherms of the systems N_2/nonporous silica and Ar/nonporous silica, through the dimer isotherm eq 25. The resulting values of the parameters c and monolayer volume v_m are shown in Table 1 along with the ones arising from fitting with the BET model.

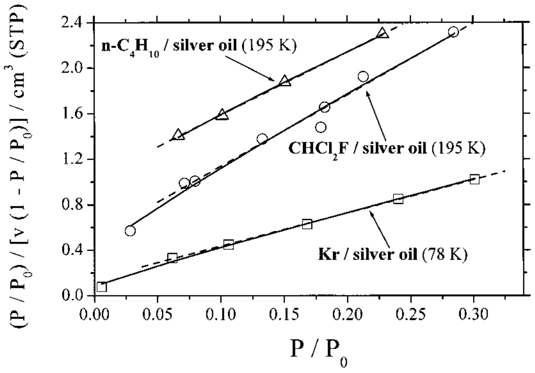

Figure 5. Idem as in Figure 4 for Kr/silver foil, *n*-butane/silver foil, and $CHCl_2F$/silver foil. The resulting values of c and v_m from fitting are shown in Table 2. Solid and dashed curves represent the same models as in Figure 2.

in comparison with the BET isotherm

$$\theta = \frac{c_{\mathrm{BET}}\, p/p_0}{(1 - p/p_0)(1 + (c_{\mathrm{BET}} - 1)p/p_0)} \qquad (26)$$

The predicted isotherm is type II for $c \gg 1$ and type III for $c \ll 1$, as expected. Appreciable quantitative as well as qualitative differences with BET isotherms appear for all values of c (see, for instance, that the isotherms always intersect).

The new adsorption isotherm can be presented similarly to the linearized form of the BET equation. If $\theta = v/v_m$, where v and v_m denote the adsorbed volume and the monolayer volume, respectively, it then follows from eqs 25 and 26 that

$$\frac{p/p_0}{v(1 - p/p_0)} = \frac{p/p_0}{v_m}\left\{1 - \left[\frac{(1 - p/p_0)}{(4c - 1)p/p_0 + 1}\right]^{1/2}\right\}^{-1} \qquad (27)$$

$$\frac{p/p_0}{v(1 - p/p_0)} = \frac{1}{c_{\mathrm{BET}}v_{\mathrm{m,BET}}} + \frac{(c_{\mathrm{BET}} - 1)}{c_{\mathrm{BET}}v_{\mathrm{m,BET}}}p/p_0 \qquad (28)$$

Equation 27 is not a linear function of p/p_0 as is the one arising from the BET isotherm [eq 28]. Equations 27 and 28 are compared in Figure 3. Their behavior shows a significant quantitative disagreement in the range 0–0.3 of relative pressures. These results indicate that the analysis of experimental isotherms of N_2 and larger molecules by means of the dimer isotherm eq 26 would lead to values of the parameters c and v_m appreciably different from the BET ones. By expanding the right-hand of eq 27 in powers of p/p_0 around $p/p_0 = 0$, the first-order approximation leads to

$$\frac{p/p_0}{v(1 - p/p_0)} \approx \frac{1}{2cv_m} + \frac{(3c - 1)}{2cv_m}p/p_0 \qquad (29)$$

Matching the linear forms of eqs 28 and 29 gives $c = c_{\mathrm{BET}}/3$, and $v_m = (3/2)v_{\mathrm{m,BET}}$. In fact, the value $v_m = 1.5v_{\mathrm{m,BET}}$ is consistent with the fact that multiple site occupation of N_2 on graphite would lead to surface areas 1.22 times larger than the BET values, as discussed long ago in ref 18. Ultimately, the rigorous treatment of multilayer adsorption considering the polyatomic nature of the adsorbate is indicating that the surface area that can be obtained by using the isotherm eq 25 would give a result larger than the BET area, consistent with some evidence that the latter generally underestimates the real surface area when nonspherical probe molecules are used. However, the influence of the nonlinear terms of eq 27 will ultimately lead to a different relationship between c, c_{BET}, v_m, and $v_{\mathrm{m,BET}}$, when fitting of experimental data is carried out. The nonlinear behavior of isotherm eq 25 at low pressure matches also a distinctive characteristic of many experimental isotherms. Although there are many potential sources for such a nonlinearity (e.g., lateral interaction and surface heterogeneity), the present results are showing that the entropic contributions coming from the adsorbate structure are not nonnegligible even though lateral interactions and surface heterogeneity are not accounted for in the model. Nevertheless, the physical meaningfulness of the proposed adsorption isotherm for dimers has to be supported by an extensive analysis of experiments. With regard to this purpose, accurate isotherms of N_2, O_2, CO, and light alkanes on nonporous solids, with a significant number of data in the low-pressure regime, are necessary to ascertain the accuracy and applicability of the adsorption isotherm of eq 25 as compared to the BET and other theories of multilayer adsorption.[5] In addition, calorimetric measurements would provide an independent test for the values obtained from adsorption data. Although such a detailed analysis is beyond the main goal and scope of the present work, fitting of standard data for the systems Ar or N_2 on nonporous silica and Kr, *n*-butane, or $CHCl_2F$ on silver foil[11] is displayed in Figures 4 and 5. The corresponding fitting parameters are shown in Tables 1 and 2. The values of v_m and c resulting from the fitting of the isotherm eq

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Table 1. Resulting Values of the Parameters c and Monolayer Volume v_m from the Fitting in Figure 4

	dimer isotherm		BET			
adsorbate/nonporous silica	c	v_m (cm^3 g^{-1})	c_{BET}	$v_{m,BET}$ (cm^3 g^{-1})	$v_m/v_{m,BET}$	c/c_{BET}
N_2	106.9 ± 17.8	40.8 ± 0.5	135.2 ± 20.6	37.7 ± 0.4	1.16	0.56
Ar	23.4 ± 1.6	37.6 ± 0.4	41.5 ± 3.2	32.5 ± 0.5	1.08	0.79

Table 2. Resulting Values of the Parameters c and Monolayer Volume v_m from the Fitting in Figure 5

	dimer isotherm		BET			
adsorbate/silver foil	c	$v_m \times 10^1$ (cm^3 g^{-1})	c_{BET}	$v_{m,BET} \times 10^1$ (cm^3 g^{-1})	$v_m/v_{m,BET}$	c/c_{BET}
Kr	17.34 ± 3.78	3.57 ± 1.19	21.24 ± 1.30	3.26 ± 0.00	1.09	0.82
$CHCl_2F$	7.50 ± 1.63	1.71 ± 0.01	13.33 ± 2.72	1.47 ± 0.01	1.16	0.56
n-C_4H_{10}	2.58 ± 0.10	1.97 ± 0.00	6.35 ± 0.17	1.52 ± 0.00	1.30	0.41

25 differ from those corresponding with BET analysis, and in all cases $c < c_{BET}$ and $v_m > v_{m,BET}$.

4. Conclusions

A general formalism for multilayer adsorption of linear species in the lattice gas approximation was presented. All thermodynamics can be derived from eqs 7 and 8. A rigorous adsorption isotherm of adsorbed dimers was obtained. It was shown that the adsorption isotherm for the simplest polyatomics (dimers) disagrees significantly with the predictions of single-site occupancy (BET) because of the relevant effect of the adsorbate size on the configurational entropy of the adlayer.

A preliminary analysis of polyatomic adsorption data indicates that the values of monolayer volume, v_m, and c arising from using the dimer isotherm equation are more realistic than the ones from BET characterization. The monolayer volume (or equivalently, surface area) and the parameter c resulting from experiments by using the linearized form of the new isotherm could be up to 1.5 and $^1/_3$ times the corresponding ones from BET, respectively. Moreover, the proposed model is simple enough to justify its applicability in determinations of surface area.

Further comprehensive analysis of experimental isotherms involving polyatomics through the proposed formalism appears necessary to discern its reliability and accuracy for the determination of these parameters in comparison with the BET and other models of multilayer adsorption. In addition, theoretical work is in progress to improve our model by including lateral interactions in the adsorbate, the two-dimensional nature of the substrate, and the decrease of the adsorption heat with the number of the layer.

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