Principles of the theory of adsorption of large molecules in pores with nonuniform walls

Yu. K. Tovbin

State Research Center of the Russian Federation "L. Ya. Karpov Institute of Physical Chemistry,
10 ul. Vorontsovo pole, 103064 Moscow, Russian Federation.
Fax: +7 (095) 975 2450. E-mail: tovbin@cc.nifhi.ac.ru

Principles of the theory of adsorption of large molecules blocking more than one adsorption center on a surface in slit-like pores are proposed. The theory takes into account lateral adsorbate—adsorbate interactions and nonuniformity of the pore walls. The equations of adsorption isotherms are derived using the cluster approach. The lateral interactions are taken into account in the quasi-chemical approximation, preserving effects of direct correlations, and in the mean field approximation without effects of correlations. The following problems are discussed: 1) distinguishing of partial contributions of nonuniform adsorption centers on the pore walls; 2) exact solution for dimer adsorption in a two-layer pore with uniform walls; 3) basic types of adsorption isotherms, for which the differences are due to various orientations of the adsorbate in micropores with uniform walls; 4) estimates of the pressure responsible for volume filling of micropores; and 5) the effect of nonuniformity of the pore walls on the pressure values.

Key words: adsorption, isotherm, slit-like pores, nonuniform surface, blocking of adsorption centers, lattice-gas model, cluster approach, quasi-chemical approximation, model of contacts.

One of the important problems of modern adsorption theory is associated with the fact that blocking of several neighboring adsorption centers by adsorbed molecules strongly affects and makes more difficult calculations of the number of realizable molecular configurations. Therefore, the adsorption theory for this type of molecules is much less developed than for those occupying one center. The current state-of-the-art in the theory of adsorption of large molecules on open uniform and nonuniform surfaces has been considered previously.[1] Currently, this theory, which takes into account the joint effect of lateral interactions (necessary for the description of experimental data over a wide range of fillings and temperatures) and nonuniformity of the surface, is only at its beginning.[2] In this theory various possible orientations of adsorbate in the surface plane are considered, since under certain conditions an ordered arrangement of the molecules with the same orientation of long molecular axes becomes more favorable as the filling with adsorbate increases, *i.e.*, a two-dimensional analog of three-dimensional phase transitions of the type nematic (and/or smectic)—disordered phase is realized.[3,4] Another important feature of the adsorption of large molecules is the possibility of changing the horizontal orientation of long molecular axes so that it becomes vertical (along the normal to the surface) as the surface coverage increases.[2,5]

Most adsorption processes occur in porous systems.[6,7] Depending on the pore width, the joint effect of both pore walls can differently affect the type of adsorbate distribution. This factor is of particular importance for micropores. In this case the conditions for capillary condensation can be dependent on the degree of nonuniformity of the walls.[8,9] In this work the theory of adsorption of large molecules in pores is considered for the first time. The cluster approach[10] was used to derive the equations describing the adsorption equilibrium. Previously, this approach was used in the adsorption theory to take into account lateral interactions between one-center molecules on open surfaces and in porous systems with nonuniform walls,[8,9] as well as for the adsorption of large molecules on open nonuniform surfaces.[1] We shall restrict our consideration to the case where the adsorbate has the shape of a rectangular parallelepiped $b \times d \times n$ with the sides b, d, and n. Particular cases of equations for rigid rods of length n and plates of size $b \times d$ are easily obtained from equations for a three-dimensional model of molecules with a hard core. If the pore size becomes so large that the effect of the pore walls on the states of the adsorbate at the pore center can be neglected, we virtually have multilayer adsorption on the open surface of the adsorbent. Such a situation has never been considered in the theory of adsorption of large molecules.

Model

We shall describe adsorption using a lattice model in which the volume of a slit-like pore is represented as a

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1467—1478, August, 1999.

lattice structure with the number of nearest neighbors equal to z. The lattice constant is equal to the linear dimension of the adsorption center (site), whose surface area is determined by the value of the potential energy of adsorbate—adsorbent interaction at a local minimum. Let the adsorbate occupy M sites (M is an integer) in the pore volume. Each orientation of adsorbed molecules is characterized by its energetics, which makes it possible to consider it as an individual sort of particles in the case of statistical description of adsorption. Therefore, consideration of different molecular orientations even for a single-component system is reduced to the problem of adsorbing a mixture of molecules of different sizes with a fixed orientation for each of them. We shall begin with finding (1) the number of "sorts" of particles with different orientations for a single-component system (extension to multicomponent mixtures is obvious) and (2) a procedure for establishing a one-to-one relation between the molecular position and the number of lattice sites occupied by the molecule (since it blocks more than one site).

Let us denote the number of possible orientations of the axes of an adsorbed molecule as L. This number, characteristic of a given molecule, is determined by the nature of bonds formed between the molecule and the adsorption centers of the adsorbent. For simplicity, we shall assume that it is a constant for all surface centers (otherwise, the number of possible molecular orientations becomes dependent on the type of adsorption centers). Let us call a "molecule with orientation i" "particle i"; $1 \le i \le s$, where s is the number of discernible molecular orientations in the case where the long molecular axis coincides with one of the possible orientations of the axes. If an external field (in the bulk phase) or an adsorbent field (in the near-surface area) is applied to a molecule, then two situations, where the direction of the long molecular axis coincides with or is opposite to the direction of the orientation axis, should be distinguished for asymmetric molecules; therefore, $s = 2L$. For symmetric molecules, both these cases correspond to the same states and $s = L$.

Let us consider a lattice structure with $z = 6$ and $L = 3$ (though, in the general case, molecular orientations can be described in more detail and then $L > z/2$). A scheme of a slit-like pore filled with a rigid linear trimer is shown in Fig. 1: s is equal to 3 and 6 for a symmetric and asymmetric trimer, respectively. For a rectangular parallelepiped of dimensions $b \times d \times n$, the number of "sorts" $s = 6$, since for each of the three fixed directions of the long molecular axis b, two molecular orientations with respect to each of the remaining two axes are possible at $d \ne n$. Different orientations of the $b \times d$ face are shown in Fig. 2; the third molecular axis is directed along the third orientation axis. The n value can be arbitrary; however, the cases $n = d$ or $n = b$ correspond to spatially degenerate molecular states, so $s = 3$ as for a rod. For the $b \times d \times n$ parallelepiped, there are the following dimensions $b_i(\alpha)$ of particle along the α (x, y, z) axes:

i	1	2	3	4	5	6
x	b	b	d	d	n	n
y	d	n	b	n	b	d
z	n	d	n	b	d	b

The above-mentioned molecular orientations were defined with respect to the surface layer of adsorbent; however, different numbers of sites will also be blocked

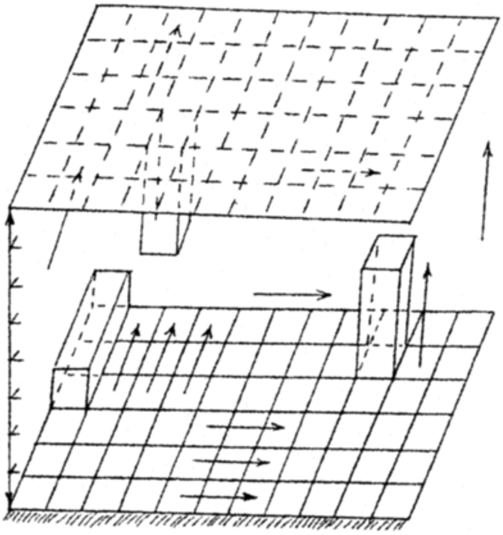

Fig. 1. Scheme of a slit-like pore filled with a rigid linear trimer. $L = 3$, $z = 6$. The trimer has three types of orientations, two in the surface plane and one perpendicular to the surface plane. The trimers are schematically shown by arrows. H is the pore width in monolayers.

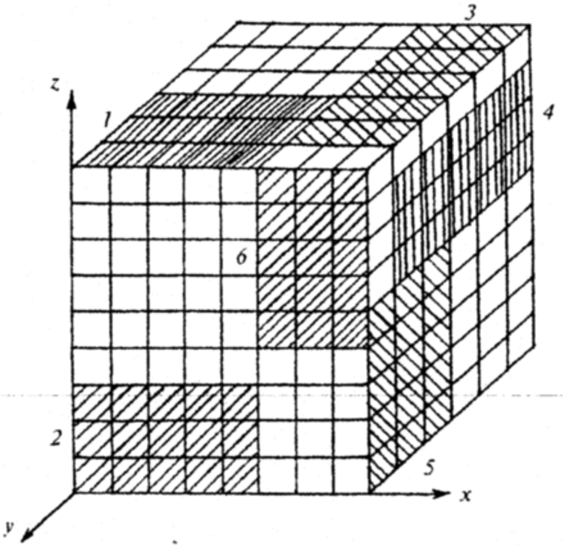

Fig. 2. Six types of orientations of the "hard sphere" of a parallelepiped (*1—6*) that are taken into account when describing the adsorption of large molecules in slit-like pores at $z = 6$ and $L = 3$. The x and y axes are parallel to the pore walls; the pore width changes along the z axis.

in other layers depending on the orientation of a given molecule. For a parallelepiped, let us denote the number of sites in each layer of the slit-like pore for particle i ($1 \le i \le s$) as $l_i = b_i(x)b_i(y)$, where $l_1 = bd$; $l_2 = bn$; $l_3 = db$; $l_4 = dn$; $l_5 = nb$; and $l_6 = nd$, and the perimeter of particle i in the layers as $P_i = 2[b(x) + b(y)]$, where $P_1 = P_3 = 2(b + d)$; $P_2 = P_5 = 2(b + n)$; and $P_4 = P_6 = 2(d + n)$. (It is convenient to use these numbers for averaging over the occupation states of neighboring sites; in particular, they will be used below to estimate the pressures corresponding to filling the pore volumes.)

Large molecules are adsorbed on several neighboring adsorption centers. To perform a correct averaging over all configurations of large particles, it is necessary that none of the occupation states of each site be bypassed or counted more than once. To this end, let us state the rule defining the relation between the position of the molecule blocking M neighboring sites of the lattice structure and a given site. Let us choose a segment of particle i, for instance, a corner segment of a parallelepiped (plate or rod) as the "origin" for numbering other sites occupied by the same particle. The number of site f ($1 \le f \le N$, N is the number of sites in the lattice structure) in which the chosen segment of particle i is located will be considered to be occupied by a given particle and the lattice fragment (the list of site numbers) occupied by the given particle i will be denoted as $\{f\}$. In a slit-like pore, the layer number k and the number of the site in a given layer q correspond to the site number f. $f \Leftrightarrow (k, q)$; correspondingly, the lattice fragment $\{f\}$ is characterized by its own set of $\{k, q\}$ values. (In the general case, any (but not the same) segment number can be chosen as the "initial" segment of the particle. In particular, the "central" segment can be chosen as the "initial" one for symmetric particles; however, in this case one should prevent possible inconsistency between the position of the geometric center of the particle and the center of the "initial" site of the lattice structure.)

Adsorption capacity of a system is characterized by the Henry constant. Each adsorption center on a nonuniform surface can be characterized by the local Henry constant.[10] Let us denote the local Henry constant of particle i at the site f as $a_{\{f\}}^i$: $a_{\{f\}}^i = a^0{}_{\{f\}}^i\exp(\beta E_{\{f\}}^i)$; $\beta = 1/(k_\mathrm{B}T)$, where $a^0{}_{\{f\}}^i$ is its pre-exponent; $a^0{}_{\{f\}}^i = F_{\{f\}}^i\beta/F_i^0$; $F_{\{f\}}^i$ and F_i^0 are respectively statistical sums of the adsorbate with orientation i on the local fragment $\{f\}$ and in the gas phase (adsorption without adsorptive dissociation is considered); $E_{\{f\}}^i$ is the energy of the bond between particle i and the site $\{f\}$. In the atom-atom approximation,[7] this value is obtained by summation of all contributions from the interactions of the atoms constituting the molecule with the atoms of both walls of the slit-like pore.

Let us take into account lateral interactions between the nearest neighbors. We shall characterize intermolecular interactions between neighboring particles i and j occupying the sites f and g, respectively, by energy parameters $\varepsilon^{ij}_{\{f\}\{g\}}$. The value of this parameter depends on the mutual orientation of the molecules. If the energy of intermolecular interaction is calculated in the atom-atom approximation, the value of parameter $\varepsilon^{ij}_{\{f\}\{g\}}$ is the sum of the contributions of pair interactions. Let us agree that positive values of the interaction parameters correspond to attraction.

By analogy with the studies reported earlier[11,12] it is possible to introduce the idea of the energy contacts between the molecules and represent the total potential energy of the interaction between neighboring particles as the sum of contributions from these contacts. We shall measure the surface area of a molecule in elementary contacts whose surface area is equal to the squared lattice constant. Let us denote the surface area of particle i as Q_i, the number of its contacts belonging to class φ as Q_i^φ ($Q_i = \sum_{\varphi=1}^{\tau_i} Q_i^\varphi$, where the sum over φ from 1 to τ_i means summation over all classes of contacts of particle i), and the surface area of the contact of neighboring particles i and j occupying the sites f and g, respectively, as σ_{fg}^{ij}. (All contact fragments belonging to the same class are energetically equivalent.) For any *complete particular* set of neighboring particles $\{j\}$, taking into account the sequence of their positions and orientations with respect to the central particle (we denote this set as $\alpha(j)$), we have $Q_i = \sum_j \sigma_{fg}^{ij}$, where summation over j is performed for all neighboring particles surrounding particle i. Then the values of parameter $\varepsilon^{ij}_{\{f\}\{g\}}$ can be represented as the sum of contributions $\varepsilon^{ij}_{\{f\}\{g\}}(\varphi\xi)$ from neighboring contacts φ, corresponding to particle i occupying the lattice fragment $\{f\}$, and ξ, corresponding to particle j occupying the lattice fragment $\{g\}$, per surface area of the elementary contact: $\varepsilon^{ij}_{\{f\}\{g\}} = \sum_{(\varphi\xi)} \varepsilon^{ij}_{\{f\}\{g\}}(\varphi\xi)$, where summation over pairs of neighboring contacts ($\varphi\xi$) is performed for a lattice fragment with surface area σ_{fg}^{ij}. It is more convenient to use $\varepsilon^{ij}_{\{f\}\{g\}}$ values for deriving general equations and $\varepsilon^{ij}_{\{f\}\{g\}}(\varphi\xi)$ parameters for performing particular calculations.

Each site of the lattice structure can be either unoccupied or blocked by adsorbate. We consider an unoccupied site v a particle of the sort $s + 1$. All contacts of this particle are equivalent, $Q_v \equiv Q_{s+1} = z$, and $m_{s+1} = 1$. Particles do not interact with unoccupied sites.

The total energy (E) of the adsorption system can be written in the form

$$E = \sum_{f=1}^{N}\sum_{i=1}^{s} u^i_{\{f\}}\Gamma^i_{\{f\}} - \frac{1}{2}\sum_{f,g}\sum_{i,j}\varepsilon^{ij}_{\{f\}\{g\}}\Gamma^i_{\{f\}}\Gamma^j_{\{g\}},$$

$$\Gamma^i_{\{f\}} = \gamma^i_f\prod_h \gamma^i_h, \qquad (1)$$

where $u_{\{f\}}^i = -\beta^{-1}\ln(a_{\{f\}}^i p)$, p is the adsorptive pressure; the index h in the formula for $\Gamma_{\{f\}}^i$ runs over $M - 1$ sites blocked by a given particle i occupying the site f; γ_f^i is a random variable: if site f is occupied by particle i, then $\gamma_f^i = 1$; otherwise $\gamma_f^i = 0$. Index f and a set of

$M_i - 1$ indices h unambiguously define the position of particle i.

Our first major problem is to derive equations describing the process of covering the local fragments of a nonuniform surface; further, we shall consider macroscopic fragments of the adsorbent surface.

System of equations

We shall derive the system of equations corresponding to the adsorption of large molecules on nonuniform adsorbents using the cluster approach to description of the distribution of laterally interacting molecules over nonuniform sites of a lattice system.[10] The cluster approach consists in analyzing a complete set of all possible local configurations of the molecules surrounding the central particle (all components of the system are considered the "central" ones) on all types of adsorption centers and deriving approximate expressions for many-particle probabilities of realization of different configurations (*i.e.*, in deriving a complete system of equations for the cluster distribution functions and introducing a unified procedure for disjunction of higher correlation functions). This approach is more convenient than calculations of the statistical sum of a system, especially for nonuniform systems. Using the cluster approach, it is possible to express the complete set of realized particle distributions (both one-center and multicenter ones) through many-particle probabilities.

The above model makes it possible to use the equations[1] derived for monolayer adsorption by modifying them to take into account filling of the volume element $\{f\}$ of the lattice structure by large molecules. To construct a local equation for the adsorption isotherm, it is necessary to relate the probability of the filled state to that of the unfilled state of a given volume element $\{f\}$. To this end, let us introduce the functions $\theta_{\{f\}}{}^i$ and $\theta^{ij}{}_{\{f\}\{g\}}$: $\theta_{\{f\}}{}^i$ is the probability of filling site f by particle i; the symbol $M_i v$ denotes an unfilled volume element of size M_i, which can be filled with particle i (despite the fact that all particles are uniform in size, equal to M, the number of sites in different layers of the pore blocked by particle i can be different for different orientations of particles). The function $\theta_{\{f\}}{}^{M_i v}$ is the probability of the unfilled state of a given volume element $\{f\}$ of size M_i; $\theta^{ij}{}_{\{f\}\{g\}}$ is the probability of finding neighboring volume elements $\{f\}$ and $\{g\}$ of particles i and j, respectively (here $1 \le j \le (s+1)$). For each site f of this structure, it is possible to derive the following expression for the local adsorption isotherm, in which lateral interactions between neighboring molecules are taken into account in the quasi-chemical approximation with retention of the effects of direct short-range correlations:

$$a^i_{\{f\}} p \theta^{M_i v}_{\{f\}} = \theta^i_{\{f\}} \Lambda^i_{\{f\}} / M ,$$

$$\Lambda^i_{\{f\}} = \sum_{\alpha(j)} \prod_j t^{ij}_{\{f\}\{g\}} \exp\left(-\beta \varepsilon^{ij}_{\{f\}\{g\}}\right), \qquad (2)$$

$$\theta^{ij}_{\{f\}\{g\}} \theta^{M_i v, M_j v}_{\{f\}\{g\}} = \theta^{i, M_j v}_{\{f\}\{g\}} \theta^{M_i v, j}_{\{f\}\{g\}} \exp\left(-\beta \varepsilon^{ij}_{\{f\}\{g\}}\right), \qquad (3)$$

$$t^{ij}_{\{f\}\{g\}} = \theta^{ij}_{\{f\}\{g\}} / \theta^i_{\{f\}} .$$

Let us write the condition for normalization to pair probabilities as $\sum\limits_j \theta^{ij}{}_{\{f\}\{g\}} = \theta_{\{f\}}{}^i$. The function $\Lambda_{\{f\}}{}^i$ takes into account nonideality of the adsorption system and is dependent on the lateral interactions between neighboring molecules. Summation over $\alpha(j)$ in formula (2) means the sum over all possible positions of all neighboring molecules j (*i.e.*, in the case of changing the number, order, and orientation of neighboring molecules with respect to the central particle). The function $t^{ij}{}_{\{f\}\{g\}}$ is the conditional probability of finding neighboring volume elements $\{f\}$ and $\{g\}$ of particles i and j, respectively (here $1 \le j \le (s+1)$); it is those functions that are responsible for reproducing correlation effects. If lateral interactions can be neglected, then $\Lambda_{\{f\}}{}^i = 1$ and $a_{\{f\}}{}^i p = \theta_{\{f\}}{}^i / (M \theta_{\{f\}}{}^{M_i v})$. This corresponds to low fillings (Henry's law region).

By complementing Eqs. (2) and (3) with the conditions for normalization to local site coverages and the procedure for calculating the $\theta_{\{f\}}{}^{M_i v}$ functions it is possible to calculate local isotherms. The probability of finding an unoccupied lattice fragment $\theta_{\{f\}}{}^{M_i v}$, on which particle i can be adsorbed, is a complicated distribution function of adsorbed particles blocking unoccupied sites. For adsorption of particle M_i to occur, the lattice fragment $\{f\}$ should consist of only unoccupied sites. The probability of such an event can be expressed as the product of the probability of finding an unoccupied site with number f by the probability of finding a neighboring unoccupied site from a lattice fragment of size $M_i - 1$ and appropriate shape, *etc.*, searching analogously through all the sites of fragment $\{f\}$ until the last unoccupied site. As a result, the expression for the function $\theta_{\{f\}}{}^{M_i v}$ can be written as follows:

$$\theta^{M_i v}_{\{f\}} = \rho^v_f \prod_h t^{vv}_{hh+1} , \qquad (4)$$

where the index h corresponds to the numbering of $M_i - 1$ sites blocked by particle i of size M_i; $\rho_f{}^v$ is the probability of finding an unoccupied site f; $t^{vv}{}_{hh+1}$ is the conditional probability of finding neighboring unoccupied sites with numbers h and $h + 1$.

In the mean field approximation, the effects of correlation between interacting particles are neglected. This simplifies the system of equations (2)—(4), since Eqs. (3) become unnecessary and functions $t^{vv}{}_{hh+1}$ in the formula for $\theta_{\{f\}}{}^{M_i v}$ can be directly expressed through local densities. In this approximation, the function of nonideality of the adsorption system $\Lambda_{\{f\}}{}^i$ is given as $\Lambda_{\{f\}}{}^i = \exp[-\beta \sum\limits_{\alpha(j)} \sum\limits_j \varepsilon^{ij}{}_{\{f\}\{g\}} \theta_{\{g\}}{}^j]$. As in the case of neglecting lateral interactions, the functions $t^{vv}{}_{hh+1}$ in formula (4) have the form

$$t^{vv}_{hh+1}(k) = \rho^{v}_{h+1}\left(\rho^{v}_{h+1} + \sum_{i=1}^{s}\sum_{\varphi}\rho^{\varphi}_{h+1}Q_i^{\varphi}(k)\Big/z\right)^{-1}, \qquad (5)$$

where two indices, h and $h + 1$, define the orientation (k) of two unoccupied sites, and $Q_i{}^{\varphi}(k)$ is the number of contacts of neighboring particle i, belonging to class φ, in the direction defined by the index k.

The local normalization condition for the probabilities of occupation of the site f has the form

$$\rho^{v}_{f} + \sum_{i=1}^{s}\sum_{\xi}\rho^{i}_{f-\xi} = 1\,, \qquad \rho_f^{i} = \theta_{\{f\}}{}^{i}/M_i, \qquad (6)$$

where the index ξ corresponds to the numbering of all possible displacements of particle i in all directions without changing its orientation: $0 \le \xi \le (M_i - 1)$; the case $\xi = 0$ corresponds to the site f. The normalization condition (6) takes into account all variants of blocking a given site f by a particular particle i. Expression (6) differs from the analogous equation for a surface monolayer[1]: in the latter case, M_i is the projection of particle i on the monolayer plane. In calculations of the phase and orientational states of the molecules in the bulk or in pores, the M_i value ($M_i = M$), which defines the total number of occupied lattice sites (the molecular volume), is independent of the molecular orientation. Formula (6) can be specified for the following five cases:

1. Bulk gaseous or liquid phases: $\theta_f^{v} + \sum_{i=1}^{s} \theta_{\{f\}}{}^{i} = 1$.

2. Multilayer adsorption on an open uniform surface — all sites in the layer k are equivalent and the layers are numbered from the surface layer ($k_{\min} = 1$) to the last bulk one ($k = k_{\max}$, $k_{\max}$ corresponds to a certain fixed k value for which the characteristics of particle distributions (*e.g.*, densities of particular orientations) differ from analogous three-dimensional distributions by no more than a prescribed small value, which usually varies from 0.1 to 1%):

$$\rho_k^{v} + I_1\sum_{\varphi=0}^{n-1}\rho^{1}_{k-\varphi} + I_2\sum_{\varphi=0}^{d-1}\rho^{2}_{k-\varphi} + I_3\sum_{\varphi=0}^{n-1}\rho^{3}_{k-\varphi} + {}$$
$$+ I_4\sum_{\varphi=0}^{b-1}\rho^{4}_{k-\varphi} + I_5\sum_{\varphi=0}^{d-1}\rho^{5}_{k-\varphi} + I_6\sum_{\varphi=0}^{b-1}\rho^{6}_{k-\varphi} = 1. \qquad (6a)$$

Here $k_{\min} \le k \le k_{\max}$; the index φ is used for numbering displacements of particles i with respect to the layer k; $0 \le \varphi \le b_i(z) - 1$; physically realizable are those positions of the particles for which the condition $k - \varphi \ge k_{\min}$ holds.

3. Multilayer adsorption on an open nonuniform surface — in this case it is necessary to specify the type of particle distributions in the layer k

$$\rho^{v}_{k,q} + \sum_{i=1}^{s}\sum_{\varphi=0}^{b_i(z)-1}\sum_{g}\rho^{i}_{k-\varphi,q,g} = 1, \qquad g \in I_i, \qquad (6b)$$

where the range of values of index φ is indicated above and the index g corresponds to the number of sites in a given layer $k - \varphi \ge k_{\min} = 1$; the number of such sites is I_i.

4. Adsorption in a slit-like pore with uniform walls — the equation for local normalization has the form (6a); here $1 \le k \le k_{\max} = H - b_i(z) + 1$. Because of the symmetry of the properties of the system, $\rho_k{}^{v} = \rho^{v}{}_{H-k+1}$, $\rho_k{}^{i} = \rho^{i}{}_{H-b(z)-k+2}$, and it is sufficient to consider the equations for $H/2$ (at even H) and $(H + 1)/2$ layers (at odd H). As in the case 2, physically realizable are those positions of the particles for which the condition $k - \varphi \ge k_{\min} = 1$ holds.

5. Adsorption in a slit-like pore with nonuniform walls; the equation for local normalization has the form (6b), where $k - \varphi \ge k_{\min} = 1$ and $k_{\max} = H - b_i(z) + 1$; in the general case, the molecular distribution over the pore width is asymmetric.

As follows from the structure of the expressions obtained, the derived system of equations is nonlinear. Links between the occupation states of different sites are due to lateral interactions (formulas (2) and (3)) (this factor is also the major one for interacting one-center particles) and to blocking of several neighboring sites by one molecule (formulas (4) and (6)), which occurs also in the absence of lateral interactions. Solving the equations with respect to local coverages $\theta_{\{f\}}{}^{i}$ makes it possible to find the dependence of the overall surface coverage on pressure, *i.e.*, the adsorption isotherm:

$$\theta(p) = \sum_{i=1}^{s}\sum_{f=1}^{N}\theta^{i}_{\{f\}}(p)/N\,.$$

Analysis of the system of equations (2)—(4), (6) requires numerical methods. Dimensionality of the system of equations is substantially reduced after introducing new variables $X^{i}{}_{\{f\}\{g\}}$ using the relation $\theta^{ij}{}_{\{f\}\{g\}} = X^{i}{}_{\{f\}\{g\}}X^{j}{}_{\{g\}\{f\}}\exp(\beta\varepsilon^{ij}{}_{\{f\}\{g\}})$ (this turns Eqs. (3) into identities $1 \equiv 1$). Analytical expressions can be obtained only for the simplest limiting cases of low densities or other molecular parameters of the system (the case $H = 2$ is discussed below). It should be noted that the case where molecules located at different adsorption centers can have different numbers of orientations is described by analogous Eqs. (1)—(6), in which the index (the number of "sorts" of particles occupying a given site) is dependent on the type of this site. This means that the index s in Eqs. (2)—(6) should be replaced by the index s_f. Otherwise the structure of the equations derived remains unchanged.

Macroscopic systems

The system of equations (2)—(4) and (6) gives a site-by-site description of local populations of a three-dimensional lattice fragment. This can be done only for small pore fragments. The properties of porous macroscopic objects can be adequately described using the description of small pore fragments only if the latter have uniform walls or the arrangement of heterogeneous centers is ordered. In the general case, constructing a complete isotherm implies taking account of versatile types of mutual arrangement of different adsorption centers. The same situation is also observed in the case of adsorption on nonuniform surfaces of one-center particles, for which this problem has been considered in detail previously[10,13,14]; basic ideas reported in Refs. 10, 13, and 14 are also valid for multicenter particles.

To describe macroscopic porous systems with nonuniform walls, it is necessary to introduce the distribution functions of different types of sites and average the solutions for local adsorbate distributions, obtained on the basis of Eqs. (2)—(4) and (6), using these functions. In turn, taking account of a large set of mutual arrangements of different adsorption centers requires using a procedure for averaging the contributions from each adsorption center to local isotherms over different types of local structures. To this end, it is necessary to state a procedure for separating partial contributions from heterogeneous adsorption centers on the pore walls. (It should be noted that this procedure is also required for comparing the theories and numerical results obtained using the Monte Carlo and molecular dynamics methods.)

As a result, we get the known expression for the adsorption isotherm[10,15,16]:

$$\theta(p) = \sum_{i=1}^{s}\sum_{q=1}^{T} f_q\theta_q^i, \qquad \sum_{q=1}^{T} f_q = 1. \tag{7}$$

Here f_q is the unary distribution function of sites over adsorption capacity, characterizing the surface composition of pore walls; T is the number of types of sites on the whole nonuniform surface (at large T values, the integral over the energies of bonding of the molecules to the surface[15,16] is very often used instead of the sum over the types of sites q in Eq. (7)); and local coverages $\theta_q{}^i$ are determined by solving the system of equations (2)—(4) and (6) using the following procedure.

Let the site f belong to the type q. It is surrounded by sites belonging to certain particular types. Another site of type q is surrounded by another set of sites of different types. Function f_q takes into account the fraction of sites of type q without indicating the types of sites in their surroundings (*i.e.*, the surface structure), which can be blocked by large particles. In a slit-like pore, where particle i is located at a site of type q and blocks neighboring sites of different types, the latter can be located in different layers. All possible variants of such blocking can be taken into account using Eq. (6). For a specified sort to which particle i belongs, the expression for $\theta_q{}^i$ is obtained by averaging over the probabilities of various types of arrangement of neighboring $M - 1$ sites, blocked by the specified particle i, with respect to the site of type q. As a result, the function $\theta_q{}^i$ is defined as

$$\theta_q^i = \sum_{q_1=1}^{T}\sum_{q_2=1}^{T} \dots \sum_{q_{M-1}=1}^{T} F_{q_1q_2\dots q_{M-1}}(f)\theta_f^i, \tag{8}$$

where q_n is the type of the site from which the fragment blocked by a particle with orientation i is measured; F is the conditional probability of finding a fragment of sites of the types q_1, ..., q_{M-1} in the blocked fragment; and the index f numbers the position of the "origin" of the molecule in a site of type q. Function $\theta_{f-\xi}{}^i$ is the local probability of finding the particle i defined in Eqs. (2).

For instance, in the case of horizontal orientation of a trimer, it is possible to introduce the total probability of finding any three sites on a given nonuniform surface $f(q,\xi,\eta)$ and the conditional probability of finding two other neighboring sites of types ξ and h in a certain configuration $F(q,\xi,\eta) = f(q,\xi,\eta)/f_q$ near a site of the type q. Such distribution functions describe the local structure of a surface with arbitrary correlation in the arrangement of sites belonging to different types. For chaotic site distribution, we have $f(q,\xi,\eta) = f_qf_\xi f_\eta$ and $F(q,\xi,\eta) = f_\xi f_\eta$. For the vertical orientation of the trimer, averaging along the third axis z is considered. In the general case,[13,14] the conditional distribution functions F are of dimensionality $M_i - 1$.

Adsorption of dimers in two-layer pore with uniform walls

Analytical expressions for the system of equations (2)—(4) and (6) can be derived only for several simplest cases. In particular, this is possible for adsorption of symmetric dimeric molecules in a two-layer pore ($H = 2$) with uniform walls neglecting lateral interactions and assuming that the dimers are ordered in the wall plane (isotropic adsorbate phase with $L = 2$ and $z = 6$, *i.e.*, a three-dimensional system). In this case, there is only one type of sites, *viz.*, a surface monolayer on both sides of the pore. Considering the pore volume, let us denote the fraction of sites filled with dimers in horizontal and vertical orientation as $\theta_{\rm hor}$ and $\theta_{\rm ver}$, respectively. Let us write the system of equations in the form

$$a_{\rm hor}p\theta_{\rm hor}{}^{2v} = 2\theta_{\rm hor}/mz_s,$$

$$a_{\rm ver}p\theta_{\rm ver}{}^{2v} = \theta_{\rm ver}/m,$$

$$\theta_{\rm hor} + \theta_{\rm ver} + \theta_v = 1,$$

$$\theta_{\rm hor}{}^{2v} = \theta_v t_{vv}(g),$$

$$\theta_{\rm ver}{}^{2v} = \theta_v t_{vv}(v),$$

$$t_{vv}(j) = \theta_v/[\theta_v + (Q_{\rm ver}(j)\theta_{\rm ver} + Q_{\rm hor}(j)\theta_{\rm hor})/zm].$$

Here $z_s = 4$ is the number of neighboring sites in the monolayer plane; $m = 2$; $Q_{\rm hor}(g) = 2(z - 1)$; $Q_{\rm ver}(g) = z$; $Q_{\rm hor}(v) = 0$; $Q_{\rm ver}(v) = 0$; $a_{\rm hor}$ and $a_{\rm ver}$ are the local Henry constants for horizontally and vertically oriented dimers, respectively; $\theta_{hor}{}^{2v}$ and $\theta_{ver}{}^{2v}$ are the probabilities of finding two vacancies in horizontal and vertical orientations, respectively; $t_{vv}(g)$ and $t_{vv}(v)$ are the conditional probabilities of finding an unoccupied site next to another unoccupied site in their horizontal and vertical orientations, respectively; and θ_v is the probability of finding an unoccupied site.

If the fraction of vertically oriented dimers is denoted as γ ($\theta_{ver} = \gamma\theta$, where θ is the total filling of pore volume with differently oriented dimers), the dependence of γ on θ has the form

$$\gamma = 4(z - \theta)/(B + C),$$

$$B = Azz_s(1 - \theta) + z(2 + \theta) - 4\theta,$$

$$C = [B^2 - 8\theta(z - \theta)(z - 2)]^{1/2},$$

where $A = a_{hor}/a_{ver} = (a_{hor}{}^0/a_{ver}{}^0)\exp(\beta\Delta)$ and $\Delta = E_{hor} - E_{ver}$. For a dimer with all equal contacts, the energies of bonding with the surface of lateral and face contacts are equal to $E_{hor} = 2E$ and $E_{ver} = 2E$, where E is the energy of bonding of one contact with the surface (it will be recalled that all $E > 0$ correspond to attraction), and $\Delta = 0$. Assuming that the dimer has different lateral and face contacts, only the energy of interaction between the particle and the surface of pore walls is changed, *i.e.*, $\Delta \neq 0$. At low fillings of the pore, we get $\gamma = 1/(1 + z_sA/2)$. If $E_{hor} > E_{ver}$, then $A \gg 1$ at $a_{hor}{}^0/a_{ver}{}^0 \approx 1$ and in this case the fraction of vertically oriented dimers is always small and decreases as A increases. If $E_{hor} < E_{ver}$ so that $z_sA/2 < 1$, then vertical orientation is predominant at low fillings. In this case, the fraction of horizontal dimers will decrease as filling θ increases. (The case in question is usually interpreted as adsorption with the only orientation of the adsorbed molecule.) At high fillings ($\theta \to 1$), $\gamma \to 1$ at any A and the dimers are always vertically oriented (the A value affects the range of pressures at which $\theta \to 1$). The equilibrium pressure p is expressed through the degree of pore filling θ as $p = \gamma\theta/[2(1 - \theta)^2a_{ver}]$ and the formula for the isosteric heat of adsorption of a dimeric molecule is obtained in the form $E_{is} = E_{ver} + Azz_s(1 - \theta)(E_{hor} - E_{ver})/C$. From this it follows that at $\theta \to 1$ at any A and z we have $E_{is} = E_{ver}$, whereas at $\theta \to 0$ we get $E_{is} = E_{ver} + Az_s(E_{hor} - E_{ver})/[2(1 + Az_s/2)]$, *i.e.*, the heat of adsorption at zero fillings depends on all molecular properties of the system. If $Az_s/2 \gg 1$, we get $E_{is} = E_{hor}$ since all dimers adsorbed are horizontally oriented.

It should be noted that at $M > 2$, the relationship between the "specific" energies per surface center, E_{hor}/m_{hor} and E_{ver}/m_{ver}, where m_{hor} and m_{ver} are the surface areas (the numbers of centers) occupied by molecules with a given orientation ($m_{hor} > m_{ver}$), should be considered as a measure of the strength of the adsorbent—particle bonding instead of the relationship between E_{hor} and E_{ver}. If $Q_{hor}/m_{hor} < Q_{ver}/m_{ver}$, then the vertical orientation of the molecules is preferable at any surface coverages (this case is of the least interest). If $Q_{hor}/m_{hor} > Q_{ver}/m_{ver}$, then the horizontal orientation of the molecules is preferable at low coverages, whereas the vertical one is preferable at high coverages. Nonuniformity of the surface and lateral interactions make these relationships more complicated.

Isotherms of filling of micropores with uniform walls

For simplicity, we consider the main types of isotherms for adsorption of rigid linear trimers ($M = 3$) in narrow pores (according to M. M. Dubinin, they belong to micropores) under the following conditions: 1) all surface contacts of trimers have equal energies of interaction with the uniform surface of the pore walls; therefore, the energy of bonding of a horizontal trimer to the surface is by a factor of 3 higher than that of a vertical trimer, 2) Henry's constants for different orientations of the trimer have equal pre-exponents, 3) horizontal trimers are disordered, and 4) the effect of the wall potential is confined to the nearest layer.

The total ($\theta(p)$) and partial ($\theta_i(p)$) adsorption isotherms are plotted in the θ (or θ_i)—ln$p$ coordinates, where θ is the fraction of the pore volume filled with adsorbate and measured in monolayers; the maximum θ value is H. Partial isotherms are denoted as θ_{hor} and θ_{ver} for horizontal (i = hor) and vertical (i = ver) orientations, respectively, and $\theta = \theta_{hor} + \theta_{ver}$. In the case of condensation of the molecules, the position of the filling jump (the secant line) for the isotherm is determined conventionally using the Maxwell rule.[10,17]

Typical isotherms for one- and two-layer micropores are shown in Fig. 3. In the case of capillary condensation, the isotherms (curves *1*—*4*) are always to the left of those obtained in the absence of capillary condensation (curves *5*—*8*). This is due to the fact that the former correspond to larger values of the dimensionless parameter $\beta\varepsilon$ (ε is the parameter of interaction between the contacts of neighboring trimers). Curves *1*, *2*, *5*, and *6* correspond to $H = 1$, while curves *3*, *4*, *7*, and *8* correspond to $H = 2$. Since the width H is less than the long axis of the trimer ($M = 3$), only horizontal orientation of adsorbate is possible in this case. For comparison with the trimer isotherms (curves *1*, *3*, *5*, and *7*), those of one-center particles (curves *2*, *4*, *6*, and *8*) are also shown. On these isotherms, at low fillings the increase in the θ values with increasing pressure begins for trimers earlier than for one-center particles (since the energy of bonding with the walls is higher for trimers). At high fillings, the θ values for trimers increase more slowly than for one-center particles (because of steric hindrances to adsorption of closely packed trimers).

Typical isotherms for $M = H = 3$ are shown in Fig. 4. In this case, where the length of the molecule is equal to the pore width, two types of isotherms are possible depending on the ratio between the Henry constants for vertical and horizontal orientations of the

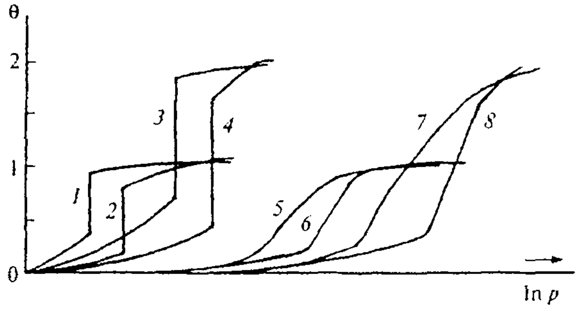

Fig. 3. Main types of isotherms (*1—8*) for adsorption of rigid linear trimeric molecules (trimers) in the region of capillary condensation (*1—4*) and without condensation (*5—8*) for slit-like pores of width $H = 1$ (*1, 2, 5, 6*) and 2 (*3, 4, 7, 8*).

trimers and the contribution of lateral interactions. At low densities, the Henry constant for vertical orientation is smaller than that for the horizontal one, and a layer-by-layer coverage of both pore walls occurs first. At high densities (among these always is the region of density jump upon condensation, especially for the dense phase), the ratio of the different orientations of dimers is dependent on both the ratio of the Henry constants and lateral interactions. The contribution of the latter is determined by the fraction of contact pairs between the trimers having different orientations and located in different layers. Here, these are vertical orientations, which completely cover the whole pore, and layer-by-layer orientations of the trimer in the vicinity of both pore walls and at its center. Depending on temperature (at fixed Henry's constants and parameters of lateral interaction), the type of the jump can be changed because of the competition of "contact pairs" (in the case of horizontal orientation, each trimer has 6 contacts with identical neighboring particles, whereas in the case of vertical orientation, the number of contacts is 12).

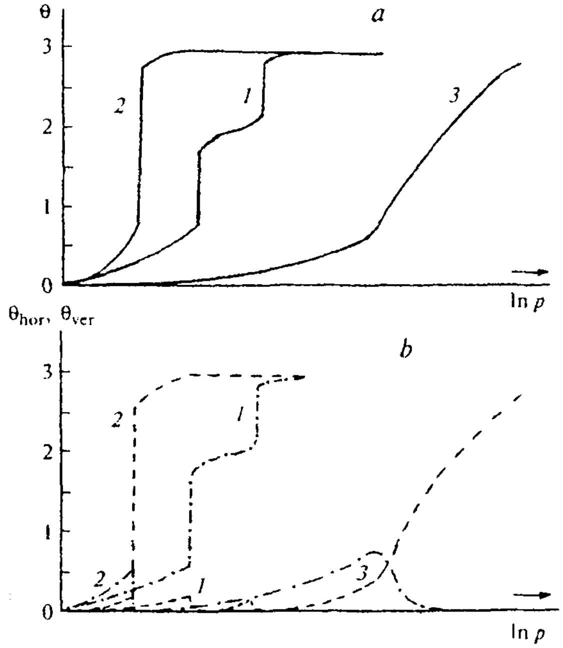

Fig. 4. Main types of isotherms (*1—3*) for adsorption of rigid linear trimers in the region of capillary condensation and without condensation for slit-like pores of width $H = 3$: *a*, total isotherms, *b*, partial isotherms for horizontally (dash-and-dot line) and vertically (dashed line) oriented adsorbate molecules.

Thus, if horizontal orientation of adsorbate is predominant, monolayer coverage of both surface layers occurs first, followed by filling the pore volume. At low temperatures, two steps corresponding to these two types of fillings are observed (see Fig. 4, curve *1*). In practice, it can be assumed that $\theta = \theta_{hor}$, since the fraction of vertically oriented trimers is small. Two small peaks in the vicinity of both density jumps θ_{hor} correspond to vertically oriented trimers.

If reorientation of trimers occurs as the adsorbate density increases, a phase transition is observed (see Fig. 4, curve *2*). A small peak of θ_{hor} and substantial increase in the density θ_{ver} upon capillary condensation are observed before this transition. If reorientation of trimers occurs as temperature increases, the total isotherm (see Fig. 4, curve *3*) has a shape similar to that of curves *5* and *7* for $H = 1$ and 2; however, partial contributions to the total isotherm indicate that horizontal trimers are replaced by vertical ones, whose fraction passes through a maximum and decreases as the pressure increases. Taking account of ordered horizontal trimers makes the shape of partial adsorption isotherms more complicated; however, it has little effect on the ratios between the sum of both partial ordered horizontal isotherms and the partial isotherm for vertically oriented molecules.

The case where the pore width exceeds the long molecular axis is illustrated in Fig. 5. Curves *1—4* describe the capillary condensation, while curves *5* and *6* correspond to its absence. At $H > M$, the total isotherms (curves *1* and *2*; *3* and *4*; and *5* and *6*, respectively) are qualitatively similar. However, the mechanism of the pore filling is different, since it is dependent on the possibility of pore filling with closely packed, differently oriented trimers. In a particular case, a layer-by-layer coverage of both pore walls with horizontal trimers (see Fig. 5, curves *1* and *3*) is followed by an analogous layer-by-layer filling of the remaining pore volume (curve *1*) or filling with vertically oriented trimers (curve *3*). In another case, initial coverage of one wall with vertical trimers (see Fig. 5, curves *2* and *4*) is followed by filling of the remaining pore volume with horizontal trimers on one wall (curve *2*) or on two walls (curve *4*).

With the availability of different types of contacts other types of partial dependences are possible due to competition between lateral interactions.

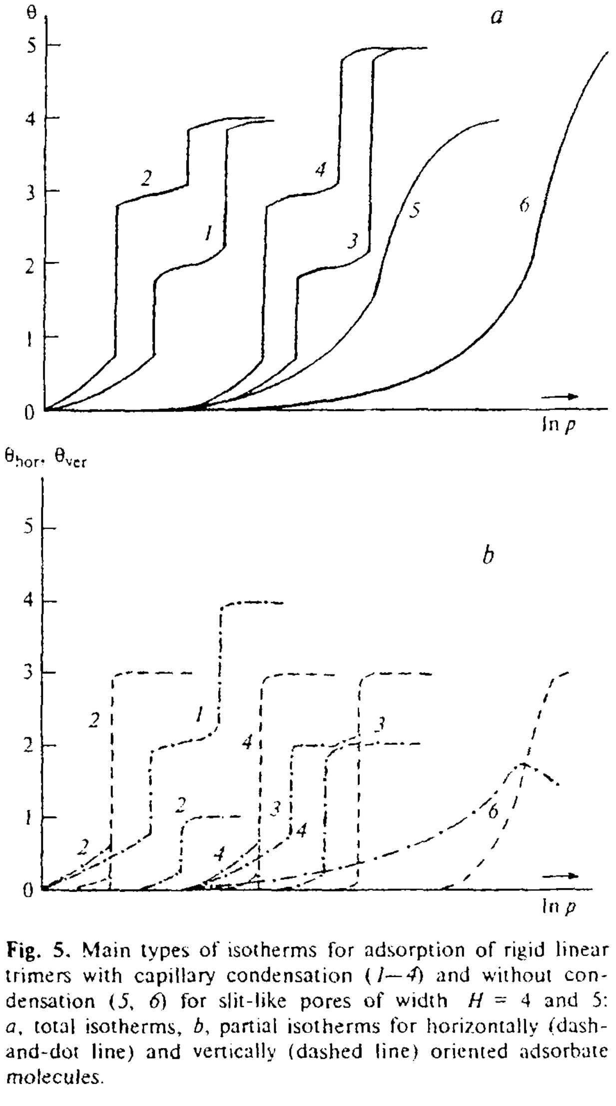

Fig. 5. Main types of isotherms for adsorption of rigid linear trimers with capillary condensation (*1—4*) and without condensation (*5, 6*) for slit-like pores of width $H = 4$ and 5: *a*, total isotherms, *b*, partial isotherms for horizontally (dash-and-dot line) and vertically (dashed line) oriented adsorbate molecules.

Estimates of pressures corresponding to volume filling of micropores

Usually, the volume of micropores (W_0) of different sorbents is determined using the Dubinin—Radushkevich equation[18]

$$W = W_0\exp(-k\varepsilon^2/\gamma^2), \tag{9}$$

where k is a parameter of the equation; γ is the coefficient of affinity, relating the "adsorption potential" of a given adsorbate to that of the standard adsorbate (for benzene, $\gamma = 1$); $\varepsilon = -RT\ln x$, $x = p/p_s$, ε is the "adsorption potential," *i.e.*, the work necessary for compressing the vapor from the equilibrium pressure p to the saturation vapor pressure p_s under isothermal conditions. According to Eq. (9), the W_0 value can be determined by linear extrapolation of the dependence of $\ln W$ on $(\varepsilon(x))^2$ to $x = 1$; at this x value, the p_s value is found from the data of independent non-adsorption experiments for the bulk phase, performed at temperature T. It was shown[19] that formula (9) gives an overestimated W_0 value, since the saturation vapor pressure $p_s(H)$ in micropores is dependent on the pore width H and $p_s(H) \le p_s$. For obtaining a more accurate W_0 value one should use the equation[19]

$$\ln[W/W_0(H)] = -k(RT/\gamma)^2\{\ln[p_s(H)/p]\}^2, \tag{10}$$

where the actual pressure $p_s(H)$, corresponding to the filling of micropores, was used for the volume of micropores $W_0(H)$ with characteristic pore width H. Formula (10) is as simple as formula (9) and differs from the latter only by $p_s(H)$ instead of p_s being in the numerator. If the experimental curve is rectified in the coordinates of Eq. (10), the point of its intersection with the ordinate axis determines the volume of micropores $W_0(H)$ of characteristic size H. The advantage of dependence (10) is that it cannot be extrapolated to the range of pressures higher than $p_s(H)$. In this case all uncertainties in the interpretation, associated with deviation of the experimental curve from linear dependence at higher pressures, disappear. At the same time, deviation of the experimental curve, constructed in the coordinates of Eq. (10), from linear dependence indicates that the density of distribution function differs from the $\Phi(\varepsilon) = 2k\varepsilon\exp(-k\varepsilon^2)$ distribution corresponding to Eq. 10.[20]

For microporous systems, there are no methods for determination of $p_s(H)$ values, except for the analysis of the results of adsorption measurements. Estimates of $p_s(H)$ for the adsorption of one-center particles were obtained,[19] *viz.*, the pressures $p_1(H)$ and $p_2(H)$, corresponding to two types of volume filling of micropores of width H (capillary condensation in the pore and pore filling without capillary condensation, respectively), were introduced. Analogous estimates for the adsorption of large plate-shaped molecules A ($M = b \times d$) are listed below. For these molecules, a horizontal packing (parallel to pore walls) is predominantly realized in the slit. These estimates make it possible to analyze the size effect of large molecules on the conditions of volume filling of micropores. As in the previously published study,[19] we shall use the previously derived[21] Eq. (10), which defines the pressure $p_s(k)$ at which two-dimensional condensation of the molecules in each layer k occurs in the course of multilayer adsorption on an open surface:

$$\ln[a_0 p_s(k)] = \int_0^1 \ln \Lambda_k^A d\theta_k - \beta E_k^A. \tag{11}$$

This equation is based on using the condensation approximation[15,22] for calculating the isotherms.

For the adsorption of plate-shaped molecules, the expression for the local isotherm of adsorption in the layer k can be written as

$$a_k^A p \theta_k^{M_1} = \theta_k^A \Lambda_k^A / M \; ,$$

$$\theta_k^{Mv} = \left(\rho_k^v\right)^M \left(\xi_{kk}^{vv}\right)^{(2M-b-d)},$$

$$\Lambda_k^{A} = \prod_{n=k-1}^{k+1} \left(1 + t_{kn}^{AA} x\right)^{R_n}, \qquad (12)$$

where the function $\Lambda_k{}^A$ is given in the quasi-chemical approximation; $x = \exp(-\beta\varepsilon) - 1$, ε is the parameter of interaction between contacts in the approximation of isolated contacts[11]; $R_{k\pm1} = P_A = 2(b + d)$, $R_k = I_A = M$; and the functions $\xi_{kk}{}^{vv} = t_{kk}{}^{vv}/\theta_k{}^v$ are given by formulas (3) and (4).

In the mean field approximation, correlation effects are ignored and these formulas have a simpler form (here, $Q_A = 2M + P_A$).

$$\xi_{kk}{}^{vv} = (\rho_k{}^v + Q_A\rho_k{}^A/z)^{-1} = [1 - \theta_k{}^A(1 - Q_A/zM)]^{-1},$$

$$\Lambda_k{}^A = \exp[-\beta\varepsilon(M\theta_{k+1} + P_A\theta_k + M\theta_{k-1})]. \qquad (12a)$$

It should be noted that, in the framework of the condensation approximation, consideration of lateral interaction in both the quasi-chemical and the mean field approximation leads to the same results, though the formulas for $\Lambda_k{}^A$ are different. For this reason, below we shall use simpler expressions obtained in the mean field approximation. In the condensation approximation, the saturation vapor pressure of plate-shaped molecules in the bulk phase can be estimated from Eq. (12) at $a_g p_s = \exp(-\beta\varepsilon Q_A/2)/M$.

Let us estimate the $p_{1,2}(H)$ values using Eqs. (11) and (12). Let us determine the $p_1(H)$ value under the assumption of capillary condensation in the pore volume. As a rule, the first monolayer in the sorbents is covered from each side of the pore, *i.e.*, $\theta_1 = \theta_H \approx 1$. We shall consider the remaining $H - 2$ layers of the pore for $H > 2$ as a uniform phase of density θ_{pore}. Then, the total pore filling (7) can be represented in the form $\theta = f_1\theta_1 + f_{pore}\theta_{pore}$, where $f_1 = 2/(H - 2)$ and $f_{pore} = 1 - f_1$. Let us write Eq. (12a) for θ_{pore} in the form

$$a_{pore}p\theta^{Mv}{}_{pore} = \theta_{pore}\Lambda_{pore}/M,$$

$$\Lambda_{pore} = \exp(-\beta\varepsilon Q_{pore}\theta_{pore}), \qquad (13)$$

where the Q_{pore} and E_{pore} values ($a_{pore} = a_0\exp(\beta E_{pore})$) are determined by averaging the contributions of lateral interactions and E_k over $H - 2$ layers of the pore, $Q_{pore} = [P_A(H - 2) + 2M(H - 3) + 2M\theta_1/\theta_{pore}]/(H - 2)$. To calculate the θ_1/θ_{pore} ratio for capillary condensation, let us use the $\theta_1/\theta_{pore} = (M^{1/D} + 1)/M^{1/D}$ approximation based on the following statements: 1) $\theta_1 = \theta_H \approx 1$; 2) according to the exact result[23] obtained for the one-dimensional lattice ($D = 1$), the value $\theta^* = M/(M + 1)$ is an analog of the critical density (no condensation of the molecules occurs on the one-dimensional lattice itself); 3) in the case of isotropic packing of large molecules in the vicinity of the critical point $\theta^* = M^{1/D}/(M^{1/D} + 1)$, the formula from item 2 can be extrapolated to planar ($D = 2$) and three-dimensional ($D = 3$) lattices.

Let us express the E_{pore} value as $E_{pore} = 2E_1\varphi(H)/(H - 2)$, where $\varphi(H) = \sum_{k=2}^{H-1} k^{-3}$, $E_1 = ME$ is the heat of adsorption of the molecules at low coverages of the monolayer on an open surface of analogous adsorbent, and E is the bonding energy per molecule—surface contact. Finally, we get the desired formula

$$p_1(H) = p_s\exp(-b_1),$$

$$b_1 = \beta[\varepsilon(M + M^{1/2}) + 2ME\varphi(H)]/(H - 2) - \ln(3/2), \qquad (14)$$

where it is considered that the molecules in the pore are horizontally packed ($D = 2$) and that in an isotropic bulk phase all molecular orientations are equiprobable ($a_g = 3a_0/2$). As for one-center particles, the b_1 value decreases as the slit width H increases and the pressure $p_1(H)$, corresponding to pore filling, exponentially approaches its bulk-phase value p_s. The b_1 value increases while the pressure, corresponding to volume filling of micropores, decreases as the size of the molecules increases. At the same time, distinctions in realization of different orientational states of the molecules in the bulk phase and in the slit-like pore result in a decrease in the b_1 value by ln(3/2).

To find the $p_2(H)$, value let us consider the last stage of the layer-by-layer filling of a pore when preceding layers have been filled. Here, two estimates (the lower and the upper bounds) of the pressure, corresponding to filling of the last layer, can be obtained. To obtain the upper bound, let us assume that two-dimensional condensation occurs in the last layer. Then, (after substituting the subscript "pore" by "layer") Eq. (13) can be rewritten as

$$a_0\exp(\beta E_{layer})p_2{}^+(H) = \theta_{layer}\Lambda_{layer}/(\theta^{Mv}{}_{layer}M). \qquad (15)$$

Here we introduced the quantities $\Lambda_{layer} = \exp(-\beta\varepsilon P_A\theta_{layer})$ and $Q_{layer} = [2M\varepsilon + MED(H)]$; $D(H)$ is equal to $[1/(H/2)^3 + 1/(1 + H/2)^3]$ for even H and $2/((H + 1)/2)^3$ for odd H. From a formula of the type (11) we have

$$p_2{}^+(H)/p_s = \exp[-b_2{}^+(H)],$$

$$b_2{}^+(H) = \beta[M\varepsilon C(H) + MED(H)] - \ln(3/2), \qquad (16)$$

where $C(H)$ equals 1 for odd H and 1/2 for even H.

The lower bound $p_2{}^-(H)$ is obtained if the case $\theta_{layer} \to 1$ is considered for Eq. (12). To calculate the probability of finding an unoccupied area of size M in the last layer of the dense phase $\theta^{Mv}{}_{layer}$, we shall successively add vacancies to one another and consider the number of bonds between the vacancies ("internal," "external," and "corner" for a plate of size M) in this layer and between the above-mentioned vacancies and neighboring plate-shaped molecules. As a result, we get $\theta^{Mv}{}_{layer} \approx \exp(-\beta Q_A\varepsilon)$ and

$$p_2{}^-(H)/p_s = \exp[-b_2{}^-(H)],$$

$$b_2{}^-(H) = \beta[Q_A\varepsilon/2 + MED(H)] - \ln(3/2) \qquad (17)$$

From here it follows that the inequality $p_2^-(H) < p_2^+(H)$ always holds. Formulas (16) and (17) contain equal contributions from the interaction between the molecules and the pore walls. As for one-center particles, it can easily be shown that these contributions are analogous to extension of the Frenkel—Halsey—Hill[6,24] equation for multilayer adsorption to porous systems; in this case, it should be rewritten as follows: $\ln[p(H)/p_s] = -\beta ME[k^{-3} + (H - k + 1)^{-3}]$, $1 \le k \le H$. Because of limited size of the pore, the minimum value of the right side of the equation is reached at $k = H/2$ (for even H) or $k = (H + 1)/2$ (for odd H), which makes it possible to find the ratio of pressures, $p_2^+(H)/p_s = \exp[-\beta MED(H)]$ at which the pores are completely filled (neglecting the contributions from lateral interactions).

In all cases, micropores are filled at pressures that are lower than the saturation vapor pressure in the bulk phase at a given temperature. For temperatures below and above the critical temperature in the pore, the contributions from the interaction of adsorbate molecules with the pore walls and between one another manifest themselves differently. From the formulation of the models it follows that $D(H) = \varphi(H)/(H - 2)$ at $H = 3$ and 4; therefore, $b_1 = b_2^+$, whereas $D(H) < \varphi(H)/(H - 2)$ at $H > 4$. In this case, the contribution from the walls to $p_2(H)$ is smaller than to $p_1(H)$ at $H =$ const. The contribution of lateral interactions to the $b_{1,2}(H)$ coefficients decreases as H increases in the case of capillary condensation and remains equal to 1 or 1/2 depending on the H parity in the absence of condensation.

Previously,[19] the following estimates of $b_{1,2}(H)$ have been obtained for spherically symmetric particles in the absence of specific interactions (inert gases, CH_4, N_2, O_2, and like molecules): the b_1 value is varied from 1.7 at $H = 6$ to 4.9 at $H = 3$. Analogously, the b_2^+ and b_2^- values are respectively changed from 1.2 to 4.9 and from 2.8 to 7.7 at the same H values. An increase in the size of the molecules leads to an increase in the above coefficients due to interaction between the molecules and with the pore walls and to their decrease (by about 0.4) due to predominant horizontal orientation of the molecules. Therefore, the above intervals of the values of the $b_{1,2}(H)$ coefficients are slightly changed for relatively small polyatomic molecules. This conclusion is in good agreement with experimental data for CCl_4, benzene, cyclohexane (at 25 °C for all systems), and isopentane (at 0 °C) on ammonium phosphomolybdate,[25] benzene on anthracite,[26] propane on zeolite 5A (at $T =$ 273, 323, and 398 K),[27] and argon on chabasite (at T from 138 to 195 K).[28] Isotherms of these systems become flattened in the θ—p/p_s coordinates in the region from 0.1 to 0.3 p/p_s. These data correspond to b values lying in the range from 2.3 to 1.1. After appropriate correction of experimental adsorption isotherms for filling of the mesopores considered, the above b values should be of the order of 1.3—2.5. However, the energy contribution will be predominant for large polyatomic molecules and the pressure corresponding to volume filling of micropores will decrease. The estimates obtained for plate-shaped molecules provide a correct dependence of the pressure of the volume filling of micropores on the number of layers blocked by a "nonplanar" adsorbate at a fixed pore width, *viz.*, the number of monolayers H decreases as the plate width increases. This leads to an increase in the $b_{1,2}(H)$ values and, correspondingly, to a greater decrease in the pressure of the pore filling. As a result, if intersection[29] of the curves at one point W_0 is the condition for applicability of Eq. (9), then, in the case of Eq. (10), the curves of isotherms have to be terminated at the same W_0 value but at different pressures $p_s(H)$.

Effect of nonuniformity of the pore walls

Nonuniformity of the pore walls changes the local distribution of molecules as compared with that for uniform walls. Numerical solution of the system of equations (2)—(4) and (6) gives a detailed description of such distributions. However, it is possible to qualitatively analyze the effect of nonuniformity of the pore walls on the obtained estimates of pressures corresponding to the volume filling of micropores without solving these equations.

Conventionally, two types of nonuniformities, chemical and structural ones, can be distinguished. Chemical nonuniformities modify the energetics of the surface layer without changing the adsorbent structure. Structural nonuniformities have no effect on the chemical composition of the adsorbent; however, they change the structure of the surface layer, thus forming a rough surface at the atomic level. The effects of chemical and structural nonuniformities, respectively, manifest themselves as changes in the energies of adsorbent—adsorbate bonding E and changes in the local widths H of slit-like pores. Each of these factors changes the local adsorbate distributions and, thus, macroscopic characteristics of the system under study. When analyzing the estimates of pressures corresponding to volume fillings of micropores, it is possible, to a first approximation, to restrict ourselves to consideration of the $b_{1,2}$ coefficients in Eqs. (14), (16), and (17) and compare their values for uniform and nonuniform pore walls. For chemical nonuniformity of the walls (at $H =$ const), the difference $\Delta b_{1,2}(E) = \langle b_{1,2}\rangle_E - b_{1,2}$ (where $\langle b_{1,2}\rangle_E$ corresponds to averaging of the $b_{1,2}$ coefficient over the adsorbate—adsorbent bonding energy E) can be represented as $\Delta b_{1,2}(E) = K_E(\langle E\rangle_E - E)$, $\langle E\rangle_E = \sum_{q=1}^{T} E(q)f_q$, and $E(q)$ is the adsorbate—adsorbent bonding energy for the adsorption center of type q, where $K_E = 2\beta M\varphi(H)/(H - 2)$ for b_1 and $K_E = \beta MD(H)$ for b_2. It is thus seen that an increase in the fraction of strongly adsorbing centers compared to the contribution of the uniform surface leads to an increase in the $\Delta b_{1,2}(E)$ value and, hence, to a decrease in the pressure at which volume filling of micropores occurs. Increase in the fraction of weakly adsorbing centers has the opposite effect.

For structural nonuniformity (at E = const), let us consider the $\Delta b_{1,2}(H) = \langle b_{1,2}\rangle_H - b_{1,2}$ difference, where $\langle b_{1,2}\rangle_H$ corresponds to averaging over the width H of a slit-like pore, $\langle b_{1,2}\rangle_H = \sum_H f(H) b_{1,2}(H)$, where the $b_{1,2}(H)$ values are defined by formulas (14), (16), and (17), and $f(H)$ is the distribution function of the pores over the widths, the sum over H is taken from $H_{\min} = 2$ to $H_{\max}$. Analysis of these expressions leads to a simple conclusion: the presence of a macroscopic fraction of the narrowings of a pore of width H compared to its ideal geometry and $\langle H\rangle < H$, where $\langle H\rangle$ is the average value, leads to an increase in the $\Delta b_{1,2}(H)$ value and to a decrease in the pressure at which the volume filling of micropores occurs. Increase in the average pore size has the opposite effect.

Under actual conditions, simultaneous existence of both types of nonuniformities of the pore walls is possible. Then, to a first approximation, it can be accepted that the estimates (14), (16), and (17) indicate changes in the $b_{1,2}$ values due to the effect of chemical and structural nonuniformities of the pore walls, if averaged values for the bonding energies $\langle E\rangle$ and pore widths $\langle H\rangle$ are used in these formulas.

This work was financially supported by the INTAS Foundation (Grant 96-1186).

References

1. Yu. K. Tovbin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 458 [*Russ. Chem. Bull.*, 1997, **46**, 437 (Engl. Transl.)].
2. Yu. K. Tovbin, *Khim. Fiz.*, 1998, **17**, 140 [*Sov. Chem. Phys.*, 1998, **17** (Engl. Transl.)].
3. S. Chandrasekhar, *Liquid Crystals*, Cambridge University Press, Cambridge, 1977.
4. I. P. Bazarov and E. V. Gevorkyan, *Statisticheskaya teoriya tverdykh i zhidkikh kristallov* [*Statistical Theory of Solid and Liquid Crystals*], Izd. Mosk. Univ., Moscow, 1983, 262 pp. (in Russian).
5. B. E. Boehm and D. E. Martire, *J. Chem. Phys.*, 1977, **67**, 1961.
6. S. J. Gregg and K. G. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982.
7. A. V. Kiselev, *Mezhmolekulyarnye vzaimodeistviya v adsorbtsii i khromatografii* [*Intermolecular Interactions in Adsorption and Chromatography*], Vysshaya Shkola, Moscow, 1986, 360 pp. (in Russian).
8. Yu. K. Tovbin and E. V. Votyakov, *Langmuir*, 1993, **9**, 2652.
9. E. V. Votyakov and Yu. K. Tovbin, *Zh. Fiz. Khim.*, 1994, **68**, 287 [*Russ. J. Phys. Chem.*, 1994, **68** (Engl. Transl.)].
10. Yu. K. Tovbin, *Teoriya fiziko-khimicheskikh protsessov na granitse gaz—tverdoe telo* [*Theory of Physicochemical Processes at a Gas—Solid Interface*], Nauka, Moscow, 1990, 288 pp. (in Russian).
11. J. A. Barker, *J. Chem. Phys.*, 1952, **20**, 1526.
12. E. A. Guggenheim, *Mixtures*, Clarendon Press, Oxford, 1952, 271 pp.
13. Yu. K. Tovbin, *Zh. Fiz. Khim.*, 1990, **64**, 958 [*J. Phys. Chem. USSR*, 1990, **64** (Engl. Transl.)].
14. Yu. K. Tovbin, *Langmuir*, 1997, **13**, 979.
15. I. Z. Roginskii, *Adsorbtsiya i kataliz na neodnorodnykh poverkhnostyakh* [*Adsorption and Catalysis on Nonuniform Surfaces*], Izd. Akad. Nauk SSSR, Moscow—Leningrad, 1948, 643 pp. (in Russian).
16. S. L. Kiperman, *Vvedenie v kinetiku geterogennykh kataliticheskikh reaktsii* [*Introduction to Kinetics of Heterogeneous Catalytic Reactions*], Nauka, Moscow, 1964, 607 pp. (in Russian).
17. T. L. Hill, *Statistical Mechanics*, McGraw-Hill, New York, 1956.
18. M. M. Dubinin and V. L. Radushkevich, *Dokl. Akad. Nauk SSSR*, 1947, **55**, 331 (in Russian).
19. Yu. K. Tovbin, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 659 [*Russ. Chem. Bull.*, 1998, **47**, 637 (Engl. Transl.)].
20. V. L. Radushkevich, *Zh. Fiz. Khim.* [*J. Phys. Chem.*], 1949, **23**, 1410 (in Russian).
21. Yu. K. Tovbin and E. V. Votyakov, *Zh. Fiz. Khim.*, 1992, **66**, 1597 [*Russ. J. Phys. Chem.*, 1992, **66** (Engl. Transl.)].
22. I. Z. Roginskii, *Dokl. Akad. Nauk SSSR* [*Dokl. Chem.*], 1944, **45**, 61; 194 (in Russian).
23. Yu. K. Tovbin, *Teor. Eksp. Khim.* [*Theor. Exp. Chem.*], 1976, **12**, 196 (in Russian).
24. Ya. I. Frenkel', *Statisticheskaya fizika* [*Statistical Physics*], Izd. Akad. Nauk SSSR, Moscow, 1948, 760 pp. (in Russian).
25. S. J. Gregg and R. Stock, *Trans. Faraday Soc.*, 1957, **53**, 1355.
26. D. A. Cadenhead and D. H. Everett, *Conf. on Industrial Carbon and Graphite*, Soc. Chem. Industry, 1958, 272.
27. D. M. Ruthven and K. F. Loughlin, *J. Chem. Soc., Faraday Trans. I*, 1972, **68**, 690.
28. T. A. Egerton and F. S. Stone, *Trans. Faraday Soc.*, 1970, **66**, 2364.
29. M. M. Dubinin, *Zh. Fiz. Khim.*, 1965, **39**, 1305 [*J. Phys. Chem. USSR*, 1965, **39** (Engl. Transl.)].

Received December 4, 1998;
in revised form January 29, 1999