# Calculation of the adsorption of rod-like molecules in narrow slit-shaped pores

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The adsorption of rod-like molecules in slit-shaped pores was considered within the framework of the lattice-gas model. This model is applicable over a broad range of fluid concentrations (from the gaseous to the liquid state) and temperatures (including the critical region). In the calculation of the local distributions of mixture components in the equilibrium states, lateral interactions are taken into account. The equations of the model reflect the strong anisotropy of the distribution of mixture components along the normal to the pore wall surface and ordering of the rods along various directions.

**Key words:** isotherm, mixtures, rod-like molecules, monolayer adsorption, slit-shaped pore, lattice gas model, quasichemical approximation.

In many sorption, catalytic, membrane, and other processes occurring in porous solids,[1—3] "working" mixtures consist of components of various shapes and sizes. Porous solids often contain narrow pores, which is usually said to mean pores up to 15 nm wide.[4] In narrow pores, the equilibrium distribution of molecules is substantially affected by the adsorption potential of the wall. The statistic adsorption theory has been mainly developed for mixtures of spherical molecules with commensurable dimensions.[5] In this case, the wall potential gives rise to a highly anisotropic distribution of molecules over the cross-section, which influences the physical state of the fluid and, hence, the mechanism of its transport.

Dissimilar dimensions of molecules complicate the theoretical description of adsorption. Molecules with different spatial orientations interact in different manners with the pore walls; therefore, in this case, the adsorption theory for one sort of molecules becomes analogous to the theory for multicomponent mixtures. The theory of adsorption equilibrium of rectangular parallelepipeds in narrow slit-shaped pores has been developed[6,7] based on the lattice gas model[5] (LGM).

In this communication, we analyze the application of this theory to the simplest case, namely, rod-like molecules, which we will call, for short, rods or particles. The adsorption of rod-like molecules of different lengths in slit-shaped pores with uniform walls was considered. The model takes into account the mutual orientation of the rods of different sizes, the possibility of their ordered state, and intermolecular interactions of components in dense inhomogeneous phases inside the pores. Similar problems are encountered for solutions and liquid crystals in the bulk phase.[8—10] The known potential functions for intermolecular interactions and for interactions of a molecule with the pore walls served as the input information.[8,11—13] The lateral interactions were included in the calculation of the local distributions of mixture components in the equilibrium states using the approximation of isolated contacts. The essence of this approximation is that the energy contributions of the contact pairs of the nearest neighboring molecules are analyzed separately for each contact (without allowance for correlations with the contributions of other contacts of the given molecule). This approximation has been used previously[8] to calculate the equilibrium characteristics for bulk phases and for liquid—vapor interface.

The relationship between the molecule size and the pore width is an important characteristic of the distribution equilibria of molecules in the pores. The notion "narrow" pore for inert gases and spherical simple molecules applies to pores whose size is 30 times greater than the molecule size.[4] If this ratio is retained for rod-like molecules, then for long rod-like molecules the upper limit accepted for the width of "narrow" pores should sharply increase.

**Model.** In the LGM, the space of a slit-shaped pore is split into monoatomic layers with the width $\lambda_c$ parallel to the pore wall and then each layer is split into sites whose size is roughly the volume $v_0 = \lambda_c^3$, where $\lambda_c$ is the linear size of the site (or cell) equal to the linear size of the smallest mixture component.[4] For simplicity, the same size is attributed to a vacancy and to an adsorption site (unit). Apart from volume, each site is characterized by the surface that encloses this site. The number of faces of

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1476—1484, September, 2006.

1066-5285/06/5509-1530 

the site $z$ is equal to the number of adjacent sites in the lattice. For hexagonal and cubic lattices, $z$ = 12 and 6, respectively. Depending on the type of the structure, the area of each site face is $K\lambda_c^2$, where the coefficient $K$ depends on the type of structure. When $z = 6$, then $K = 1$. The surface of site face (or the surface of the contact) is taken as the unit of measurement of the surface of a rod-like molecule.

All linear dimensions of mixture components are expressed in $\lambda_c$ units. Then the pore volume $V_p = Nv_0 = HN_1v_0$, where $N$ is the number of sites in a pore with width $H$, and $N_1$ is the number of sites in the layer. A rod-like molecule of length $L$ occupies $L$ successive sites, and its volume is $Lv_0$. In the case of a mixture of $m$ components, for each $k$ ($1 \le k \le m$), a molecule of the $k$th component has the length $L_k$ and occupies the volume $L_kv_0$, while its full "surface" consists of $\Pi_k = (z-2)L_k + 2$ unit contacts, specifically, two butt contacts and $(z-2)L_k$ side ones, and these contacts can interact only along the normal to their surface. Thus the butt contacts can contact only along the rod axis.

The rod-like molecules can be oriented in space in different ways. The number of possible orientations of a molecule of the $k$th component[6,7] will be designated by $s_k$, and the number (or the index) of its particular orientation will be described by $\lambda$ ($1 \le \lambda \le s_k$). For symmetrical molecules, $s_k = z/2$, and for nonsymmetrical ones, $s_k = z$. The molecule $k$ with orientation $\lambda$ is matched by a pair of indices ($k$, $\lambda$). Each pair can be provided by number $i$, which will be called the sort of the molecule (rod). In what follows, we consider molecules of sort $i$ meaning that its number $k$ as a mixture component and its orientation $\lambda$ are known. The overall number of different sorts of molecules is $\Phi = \sum_{k=1}^{m} s_k$.

For simplicity, we will assume that all $s_k$ are the same and equal to $s$. Hence, $\Phi = ns$. In the case of a one-component system, $\Phi = s$.

Each site can contact through its contact point with either a molecule of sort $i$ ($1 \le i \le \Phi$) or vacancy v. A vacancy v is considered as a rod of sort $\Phi + 1$, $L_{\Phi+1} = 1$, $\Pi_v = z$. It occupies a vacant site. The "surface' of a molecule of sort $i$, except for the face contacting with the pore wall, will be designated by $\Pi_i^w$ and expressed as $\Pi_i^w = \Pi_i - S_{fr}$, where $S_{fr} = 0$, 1, or $L_i$, if the molecule does not contact the pore wall or does contact the pore wall with its butt end or with its lateral surface, respectively.

**Geometric representation of the model.** Let $z = 6$, *i.e.*, let the lattice be cubic. Imagine that a space is split into small unit cubes or cells and that rod molecules are composed of $L$ unit cubes or segments (the segments and the cells will also be called sites meaning that a cell is a space unit and a segment is a rod unit). The contacts of a rod are represented by the outer faces of the segments forming this rod. The number of contacts is $\Pi_k = (z-2)L + 2$. The rods are "embedded" in this space without intersections. Some space remains free, its unit cubes are vacancies.

Rods are considered to be in contact if they touch each other with their contact points, while the contacts that touch each other are called adjoining. For example, rods that touch each other only through a corner are not considered as being in contact. The energy of intermolecular interactions is calculated taking into account the adjoining contacts.

In the three-dimensional case $z = 6$ we consider, the Cartesian coordinates $X$, $Y$, $Z$ are introduced. The slit-shaped pores are described with the assumption that pore walls are parallel to the $XY$ plane, while the $Z$ axis is directed across the pore. The position of the rod is dictated unambiguously by its direction (or orientation) and the position of some fixed segment. The illustration of a slit-shaped pore containing rods of three monomers ($L = 3$) is shown in Fig. 1. Each of these rods has two butt contacts and $4L$ lateral contacts, $2L$ for each of the directions normal to its axis, *i.e.*, totally $\Pi = (z-2)L + 2$ contacts. A somewhat more complicated and less vivid geometric interpretation can also be proposed for the structure with $z = 12$.

In a slit-shaped pore, each site is matched by the number of layer $f$ to which it belongs and the number of site within this layer. Restricting themselves to the case of slit-shaped pores with uniform walls, we assume that all sites within the same layer have identical properties. To distinguish between different positions of the rods, it is sufficient to assume that the number of the site coincides with the number of layer $f$.

In this study, we chose the end segment as the fixed one. For example, for a rod oriented along the $Z$ direction, the lowest segment is the end one. For the rod oriented along the $Y$ direction shown in Fig. 1 this is the

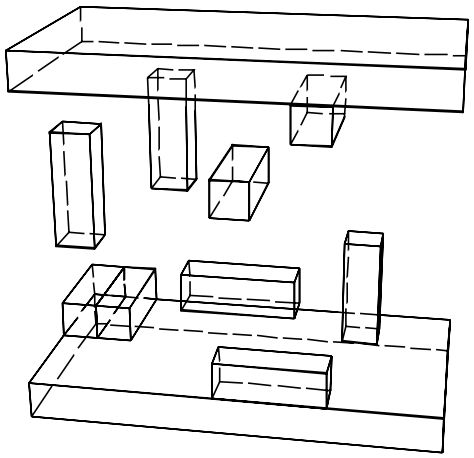

**Fig. 1.** Arrangement of rod-like molecules in a slit-shaped pore for a structure with $z = 6$.

front segment. Thus, the segment with the smallest coordinate value along the direction corresponding to its orientation is taken as the end segment of the rod. The way of choosing the segment that fixes the position of the molecule is not critical, as it can be changed by changing cyclically the segment numbers. From the chosen segment (site), we will count off the other sites occupied by this molecule. Let the end segment of the molecule occupy the site with number $f$. The section of the lattice occupied by this molecule $i$ will be designated by $\{f\}$.

**Henry constants and types of sites.** Each site $f$ occupied by rod $i$ can be characterized by the local Henry constant:[4] $a_{\{f\}}{}^{i} = F_{\{f\}}{}^{i}\beta\exp\{\beta Q_{\{f\}}{}^{i}\}/F_i^0$, $\beta = (k_BT)^{-1}$, where $F_{\{f\}}{}^{i}$ and $F_i^0$ are the statistical sums of the molecule $i$ for the local fragment $\{f\}$ and in a thermostat (where the gas is considered to be ideal), $k_B$ is the Boltzmann constant. The binding energy $Q_{\{f\}}{}^{i}$ of the molecule $i$ with the site $\{f\}$ is determined through the contributions of neighboring walls of the pore: $Q_{\{f\}}{}^{i} = E_i(f) + E_i(H - f + 1)$ $(1 \le f \le t)$, where $E_i(f)$ is the interaction potential for the molecule $i$ with the pore wall.

The lattice sites with equal local Henry constants may be regarded as groups of sites with identical properties. The number of these groups will be designated by $t$. If the walls of a slit-shaped pore are uniform, all sites of the same layer are equivalent; therefore, the number of the layer $f$ coincides with the number of the site located in the layer. Since the pore is symmetric with respect to the walls, then for an even number of monolayers, we assume that $t = H/2$, while for an odd number of monolayers, $t = (H + 1)/2$.

**Distribution equilibrium of molecules in the pore.** The calculation of the distribution equilibrium of molecules is substantially simplified if the approximation of isolated contacts[8,14,15] is used in the equations obtained previously.[6,7] Since the surface of rod $i$ consists of unit contacts, they can be numbered by index $k$, $1 \le k \le \Pi_i$. Then the number of the layer containing a contact and the direction of the contact can always be determined from the number of the contact and the number of the layer $f$ accommodating the end segment of the rod $i$.

The intermolecular interaction will be described by the energy parameter $\varepsilon_{ij}^{kn}$, which characterizes the interaction between $k$ and $n$ contact sites of the neighboring molecules $i$ and $j$, $1 \le k \le \Pi_i$, $1 \le n \le \Pi_j$. Only those pairs of the contacts that are directed toward each other can interact. The attraction of contacts is described by the positive parameter $\varepsilon_{ij}^{kn}$. If one of rods $i$ or $j$ is a vacancy, then $\varepsilon_{ij}^{kn} = 0$.

In this approximation, the equations[6,7] for the distribution equilibrium of molecules in slit-shaped pores assume the form

$$a_f^i p_i \theta_{L_i^v}(f) = x_i(f)\prod_{k=1}^{\Pi_i}\sum_{j=1}^{\Phi+1}\prod_{n=1}^{\Pi_j} t_{ij}^{kn}(fg)\exp(-\beta\varepsilon_{ij}^{kn}), \qquad (1)$$

$$\theta_{ii}^{kk}(fg)\theta_{jj}^{nn}(fg) = [\theta_{ij}^{kn}(fg)]^2\exp\beta(\varepsilon_{ii}^{kk} + \varepsilon_{jj}^{nn} - 2\varepsilon_{ij}^{kn}),$$

$$\theta_{L_i^v}(f) = \theta_v(f)\prod_h t_{hh+1}^{vv}(f), \qquad (2)$$

where $p_i$ is the partial pressure of component $i$; $x_i(f) = N_i(f)/N(f)$ is the mole fraction of component $i$ in layer $f$; $N_i(f)$ is the number of rods $i$ in layer $f$; $N(f) = \sum_{i=1}^{\Phi} N_i(f)$; $t_{ij}^{kn}(fg) = \theta_{ij}^{kn}(fg)/\theta_i^k(f)$ is the conditional probability that contact $n$ of rod $j$ (located in site $g$) occurs near contact $k$ of rod $i$ (located in site $f$); $\theta_{ij}^{kn}(fg)$ is the analogous total probability; $\theta_i^k(f)$ is the probability that contact $k$ of rod $i$ is found in site $f$. The function $\theta_{Liv}(f)$ characterizes the probability of formation of a vacancy in which rod $L_i$ can fit; here $h$ numbers $L_i - 1$ sites blocked by rod $i$; $\theta_v(f)$ is the probability that a site in layer $f$ is vacant; $t_{hh+1}^{vv}(f)$ is the conditional probability that vacant site $h + 1$ occurs near vacant site $h$.

The normalization relationship for the introduced functions is defined in the following way:

$$\sum_{i,k}\sum_{j,n}\theta_{ij}^{kn}(fg) = 1, \qquad \sum_{j,n}\theta_{ij}^{kn}(fg) = \theta_i^k(f)/M(f),$$

$$M(f) = \sum_i x_i(f)\Pi_i, \qquad \sum_{j,n} t_{ij}^{kn}(fg) = 1, \qquad (3)$$

$$\sum_{i,k}\theta_i^k(f) = M(f), \qquad \sum_{i=1}^{\Phi} x_i(f) = 1.$$

Solution of the system of equations (1)—(3) determines the average partial degrees of filling, which are characterized by the volume fraction $\omega_i = L_iN_i/N = L_iC_iv_0$ or the mole fraction of the rods $i$: $x_i = N_i/N = C_iv_0 = \sum_{f=1}^{H} x_i(f)/H$. Here $C_i = N_i/V_p$ is equal to the number of molecules $N_i$ per site volume. The complete filling of the volume is defined as $\omega = \sum_{i=1}^{\Phi}\omega_i$. The relationship between the full concentration of molecule $C$ and the degree of filling $x = \sum_{i=1}^{\Phi} x_i$ is given by the formula $C = x/v_0$. Full isotherms determine the relationship between the partial filling degrees $\{\omega_i\}$ or $\{\theta_i\}$ and pressures in the thermostat $\{p\}$ (the character $\{p\} \equiv p_1, \ldots, p_\Phi$ stands for the full set of all partial pressures of mixture components $p_i$, $1 \le i \le \Phi$). In the case of single-site molecules, the volume and mole fractions coincide.

**Conditions for numerical analysis.** Let us consider a one-component fluid consisting of rod-like molecules of the same length $L$. The lateral interaction parameter for the contacts of neighboring rods $\varepsilon$ will be taken to be constant. The orientation distributions of the rod-like and spherical symmetric molecule are different, the difference being related to an ordered arrangement of the rods. As the key distribution characteristics, we will consider

the volume fractions (partial fillings) $\omega^X$, $\omega^Y$, and $\omega^Z$ for rods with different orientations. If not stated otherwise, the gross density of the fluid, called simply density for short, $\omega = \omega^X + \omega^Y + \omega^Z$, is laid along the abscissa. The density $\omega$ characterizes the degree of filling of a lattice site by the molecules. We are interested, first of all, in the dependence of the partial fillings on the density. This dependence will simply be called distribution.

The distribution provides information on the mutual arrangement of molecules in the fluid at any density. This has an influence on important parameters of the medium such as viscosity in some chosen direction, the diffusion and heat conductivity coefficients, *etc*.

The model parameters were chosen in such a way that an isotropic solution, *i.e.*, a distribution equally probable along the $X$ and $Y$ directions, always exists. This distribution is also equally probable along the $Z$ direction in the absence of walls (bulk phase). In the presence of walls, the distributions only along the $X$ and $Y$ directions will be equally probable (monolayer adsorption and a slit-shaped pore).

The $\varepsilon$ values per contact do not exceed in magnitude 1260 J mol$^{-1}$, which corresponds to the average energy of dispersion type interactions for systems forming no specific bonds. The system temperature is 300 K. Let us consider a cubic lattice with $z = 6$ and three rod orientations along the axes of Cartesian coordinates. This corresponds to the well-known DiMarzio model,[16] which was used to calculate the thermodynamic properties of liquid crystals in the bulk phase.

When the density $\omega$ is low, the system of equations (1)—(3) always has an isotropoc solution, as for spherical molecules. This isotropy implies that the $X$ and $Y$ directions are equally probable, *i.e.*, $\omega^X = \omega^Y$. The main difference of the fluid made of rods from the fluid consisting of single-site molecules is that in addition to the isotropic solution of equation system (1)—(3), more solutions appear for relatively large $L$ and/or $\varepsilon$ values following an increase in the density $\omega$ at some instant $\omega = \omega_{bif}$. These solutions correspond to the predominant arrangement (anisotropy, ordering) of molecules along one of the $X$ and $Y$ axes, while for the bulk phase (see below) also along the $Z$ axis. The ordering along the $X$ direction is manifested as partial filling $\omega^X$ substantially exceeding $\omega^Y$. This means that the molecule will be oriented most likely along the $X$ direction rather than along another direction. The density $\omega_{bif}$ where this phenomenon takes place is called the bifurcation point. The isotropic distribution becomes unstable. Transition into a new phase state with ordering of molecules along the $X$ axis corresponds to a free energy minimum.

We will consider only the solution ordered along the $X$ direction, as it can be transformed into the solution ordered along the $Y$ direction by mere transposition of the variables $X$ and $Y$.

**Bulk phase.** Since we are looking for a solution of the equation system that predicts an ordered arrangement of molecules along the $X$ direction, the $Y$ and $Z$ directions are equally probable, *i.e.*, $\omega^Y = \omega^Z$. The ordering effect of rod-like molecules in the bulk phase in the absence of lateral interactions is shown in the inset in Fig. 2, *a*. The abscissa shows the gross density $\omega = \omega^X + 2\omega^Y$, while the partial fillings are given along the ordinate: $\omega^X$ are upper branches of the curves and $\omega^Y$ are lower branches. In this case, the system solution corresponding to an isotropic arrangement is given by the straight line $\omega^X = \omega^Y = \omega^Z = \omega/3$. The bifurcation point $\omega_{bif}$ depends on both the rod length and the intermolecular interaction.

The inset in Fig. 2, *a* shows the distribution for different rod lengths $L$ varying from 3 to 15 for $\varepsilon = 0$. For $L \le 3$, the only isotropic solution resulting in an isotropic arrangement is given by straight line *3*. For $L > 3$, the

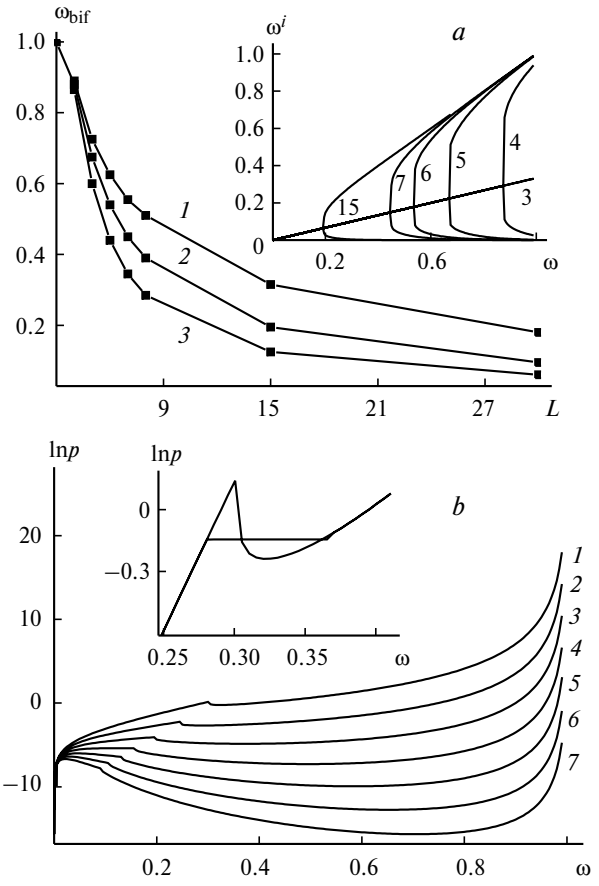


**Fig. 2.** (*a*) Dependence of the bifurcation point $\omega_{bif}$ on the rod length $L$ for the intermolecular interaction parameter $\varepsilon$ = −840 (*1*), 0 (*2*), 840 J mol$^{-1}$ (*3*); bulk phase. The insets show the partial fillings $\omega^X$ (upper branches) and $\omega^Y$ (lower branches) *vs.* density $\omega$ for rods $L$ = 3—7, 15. The numbers of the curves correspond to the lengths $L$. (*b*) Logarithm of the pressure (ln$p$) *vs.* density of molecules $\omega$ for the following values of the lateral interaction parameter $\varepsilon$ = 0 (*1*), 210 (*2*), 420 (*3*), 630 (*4*), 840 (*5*), 1050 (*6*), 1260 L mol$^{-1}$ (*7*); bulk phase.

solution is given by points lying in straight line *3* up to $\omega = \omega_{bif}$. Then this straight line is sharply split into two branches: the $\omega^X$ branch ascends ($\omega^X \to 1$ for $\omega \to 1$), while the $\omega^Y$ branch descends ($\omega^Y \to 0$, $\omega \to 1$). The bifurcation points can clearly be seen because the simultaneous ascending of $\omega^X$ and descending of $\omega^Y$ give rise to an infinite derivative. When the density $\omega > \omega_{bif}$, the molecules tend to become ordered, by tightly lying down side by side along the $X$ direction. This allows them to avoid intersections and to reach a specified fluid density. The greater the rod length $L$, the lower the $\omega$ value at which the ordering appears. Among other reasons, this is due to the fact that a chaotic, equally probable arrangement of long molecules leaves too many free sites between them (see Fig. 1) and for a given fluid density, predominant orientation of molecules along one direction, in our case the $X$ direction, will be energetically favorable. The results are in agreement with early Monte Carlo calculations.[17]

Moreover, even a slight increase in $L$ ($\geq$3.05) results in ordering at about $\omega_{bif}$ values close to unity. In the case of $\varepsilon = 0$, this fact has been noted previously[18] for $L = 3.06$ (Monte Carlo calculations), but situations with nonzero parameter $\varepsilon$ have not been analyzed as yet.

The dependence of the critical density $\omega_{bif}$ on the length of the rod $L$ for three values of the parameter $\varepsilon$ ($-840$, 0, and 840 J mol$^{-1}$) is shown in Fig. 2, *a*. As the rod length $L$ increases, the critical density $\omega_{bif}$ shifts to lower $\omega$ values. Ordered solutions for a specified $\varepsilon$ value exist only in the case where the point $\{L, \omega\}$ occurs above the corresponding curve.

The calculation of isotherms for the rod with $L = 5$ (see Fig. 2, *b*) demonstrates that even at $\varepsilon = 0$ (see the inset), a first-order phase transition takes place in the bulk phase. This transition is manifested as a nonmonotonicity similar to a van-der-Waals loop observed for the attraction of spherical symmetric molecules. The Maxwell rule should be used for the processing of these isotherms.[9] In the case under consideration, the Maxwell rule is used only in the initial section of the isotherm (see the inset in Fig. 2, *b*). As the molecule attraction grows, the position of the bifurcation point shifts to lower density values. The lateral interactions substantially influence the critical density values $\omega_{bif}$. As the $\varepsilon$ value increases, the density jump in the coexisting phases determined by the Maxwell rule takes place between the isotropic distribution existing at low densities and an ordered distribution of rods observed in the condensed state.

**Monolayer adsorption.** Recall that the horizontal axes $X$ and $Y$ are parallel to the surface, the $Z$ axis is directed along the normal to the surface, and the $X$ axis was chosen as the order axis. The adsorption potential (wall potential) affects the distribution of rods, and the distribution along the $Y$ and $Z$ axes becomes nonisotropic, *i.e.*, $\omega^Y \neq \omega^Z$, unlike the bulk phase. Therefore, the situation becomes more complicated. The influence of the wall is described most simply in the case of monolayer adsorption.

We will assume that the binding energy of the rod with the adsorbent surface is proportional to the number of contacts, *i.e.*, in the case of horizontal orientation of the rod, this number is $L$ times greater than for the vertical orientation. Then the Henry constant can be written as follows: $a^i = \exp(\beta L_i \Delta Q)$, where $L_i = L$ if $i = X, Y$; $L_i = 1$ if $i = Z$; $\Delta Q$ is the binding energy between the contact and the adsorbent surface. Now we will investigate the effect of the rod length $L$ and the adsorbate—adsorbent $\Delta Q$ and adsorbate—adsorbate $\varepsilon$ binding energies on the rod ordering process.

The distributions of the rods for different values of the system parameters are presented in Fig. 3. The $\omega^Z$ curves corresponding to vertically oriented rods are marked by the character *z*. The curves corresponding to horizontally oriented rods are marked by digits.

For short, by distribution, we mean the dependence of the partial fillings $\omega^X$, $\omega^Y$, and $\omega^Z$ on the density $\omega$. Now we consider the key features of distribution for the case of monolayer adsorption.

1. The $\omega^Z$ values monotonically increase. This indicates that, unlike the bulk phase, the tendency for vertical orientation of the rods is enhanced as the surface becomes covered and starts to predominate at $\omega \to 1$. Although the binding energy with the adsorbent surface is $L$ times lower for vertical rods than for horizontal rods, this trend is in line with the fact that the rods located in the monolayer plane start to block each other. For rod-like molecules to fill the space with a required density, most of them should be oriented vertically, as with this orientation each molecule occupies only one monolayer site.

2. The curves $\omega^X$ and $\omega^Y$ represent first one curve ($\omega^X = \omega^Y$). In the bifurcation point, this curve is separated into two branches, the upper ($\omega^X$) and the lower ($\omega^Y$) ones. As in the case of the bulk phase, in the $XY$ monolayer plane, the molecules are ordered along the $X$ axis at the expense of their lower proportion along the $Y$ direction ($\omega^X > \omega^Y$). However, when the density $\omega$ is high, these curves approach each other and merge ($\omega^X = \omega^Y$). This fact can be explained as follows. Since most of the molecules are arranged vertically and the required gross density has been nearly attained, the need for ordering in the $XY$ plane is eliminated. Thus, in the case of monolayer adsorption, ordering ($\omega^X > \omega^Y$) covers the range from the beginning to the end of separation of the $\omega^X$ and $\omega^Y$ curves into two branches.

The rod distributions for $L = 4$ (*1*), 5 (*2*), and 6 (*3*) for $\varepsilon = 420$ and $\Delta Q = 840$ J mol$^{-1}$ are shown in Fig. 3, *a*. It can be seen that the ordering region is extended upon an increase in the rod length, the initial ordering point shifting to lower densities and the end point shifting to higher densities. This is due, in particular, to the fact that the longer the molecules, the earlier and the stronger they

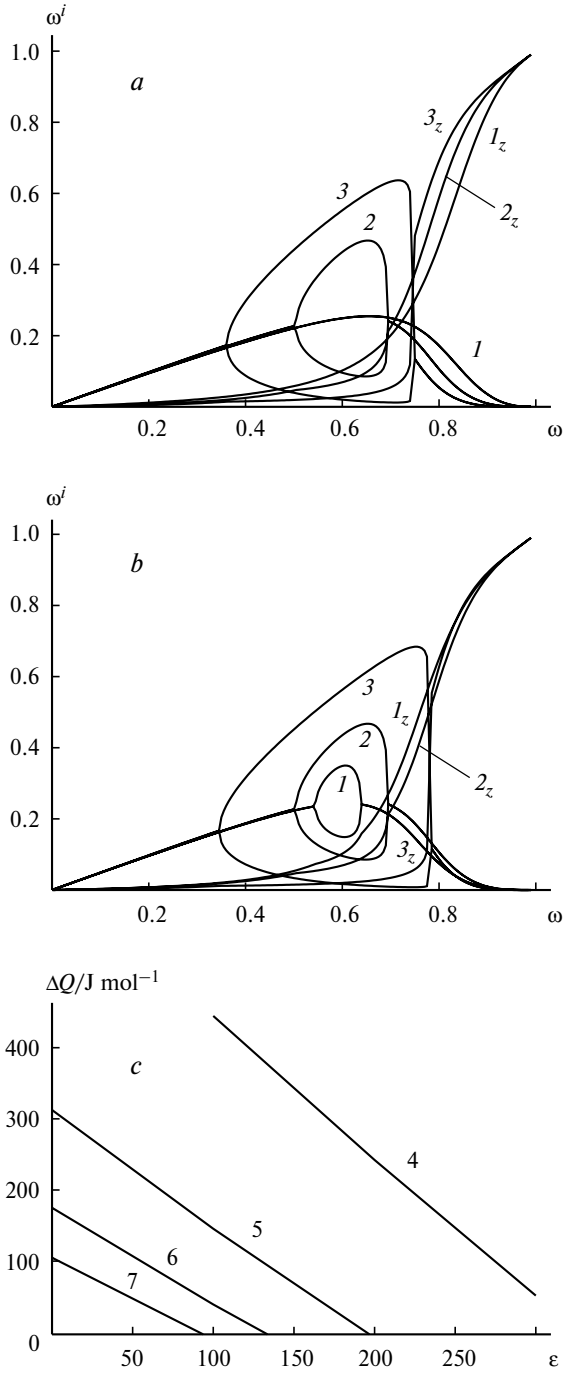


**Fig. 3.** (*a*) Partial fillings $\omega^i$ *vs.* density ω for rods with the lengths $L$ = 4 (*1*), 5 (*2*), 6 (*3*); the character $z$ designates the curves corresponding to $\omega^Z$; monolayer adsorption, ε = 0, $\Delta Q$ = 840 J mol$^{-1}$. (*b*) Partial fillings $\omega^i$ *vs.* density ω for the lateral interaction parameter ε = 315 (*1*), 420 (*2*), 525 J mol$^{-1}$ (*3*) for rods with the length $L$ = 5; the character $z$ the character $z$ designates the curves corresponding to $\omega^Z$; monolayer adsorption, $\Delta Q$ = 840 J mol$^{-1}$. (*c*) Conditions for the existence of the ordered state of the molecules in the monolayer. The abscissa axis shows the lateral interaction parameter ε and the ordinate axis, the lowest $\Delta Q$ value at which rods with the length $L$ = 4—7 become ordered. The numbers of curves correspond to $L$.

start to block each other, while ordering removes this blocking. The longer the rod, the greater the order and the greater the divergence between the branches $\omega^X$ and $\omega^Y$.

The results of analogous calculations for rods with the length $L$ = 5 at $\Delta Q$ = 840 L mol$^{-1}$ and various values of ε (315, 420, 525 J mol$^{-1}$) are shown in Fig. 3, *b*. It can be seen that an increase in the lateral interaction parameter also extends the range of ordering. The rate of increase in the fraction $\omega^Z$ with an increase in the density ω depends on the energetic characteristics of the molecule (the lateral interactions ε and interactions with the wall $\Delta Q$). For weak interactions, the wall potential plays the crucial role. Ordering of the rods in the monolayer plane allows them to cover greater surface than in the absence of ordering; therefore, an increase in the parameter ε retards the growth of $\omega^Z$ in the ordering region and sharply accelerates $\omega^Z$ after this region has been left.

The effect of the parameter $\Delta Q$ largely resembles the effect of the parameter ε. Its increase also extends the region of ordering. It can be seen from the results that ordering of the rods in the monolayer occurs only at particular relationship between the system parameters $L$, ε, and $\Delta Q$. It was found that an increase in any of these parameters extends the ordering region.

The relationship between the energy characteristics of rod-like molecules that ensure ordering of molecules in the monolayer is shown in Fig. 3, *c* for rods with $L$ = 4—7 in the ε and $\Delta Q$ coordinates. The lateral interaction parameter ε is given along the abscissa axis, while the lowest $\Delta Q$ value for which rod ordering is possible is shown in the ordinate axis. For rods of different lengths $L$, the adsorbate—adsorbent binding energy $\Delta Q$ obeys a nearly linear dependence on the adsorbate—adsorbate interaction energy ε, which gives the border line between the regions with and without the molecular ordering. The ordering is possible above the curve and is impossible below the curve. With an increase in $L$, ordering becomes more feasible, *i.e.*, the border curve is lowered being shifted to smaller ε and $\Delta Q$ values due to an increase in the number of contacts per molecule.

**Slit-shaped pore.** Let the binding energy of the rod with the adsorbent surface be the same as in the calculation of monolayer adsorption and $\Delta Q$ be the binding energy of the contact with the adsorbent surface. We will investigate the effect of the adsorbate—adsorbent ($\Delta Q$) and the adsorbate—adsorbate (ε) binding energies on the ordering of rods in various layers of the pore.

The distribution of rods in slits depends additionally on the simultaneous influence of both walls. This is especially evident for narrow pores. For the case of a slit-shaped pore, we will consider a system containing a rod with the length $L$ = 4 in a pore with the width $H$ = 9 monolayers with various molecular parameters $\Delta Q$ and ε. Due to the pore symmetry, we derive the distributions for layers ranging from the first one (near-surface) to the fifth

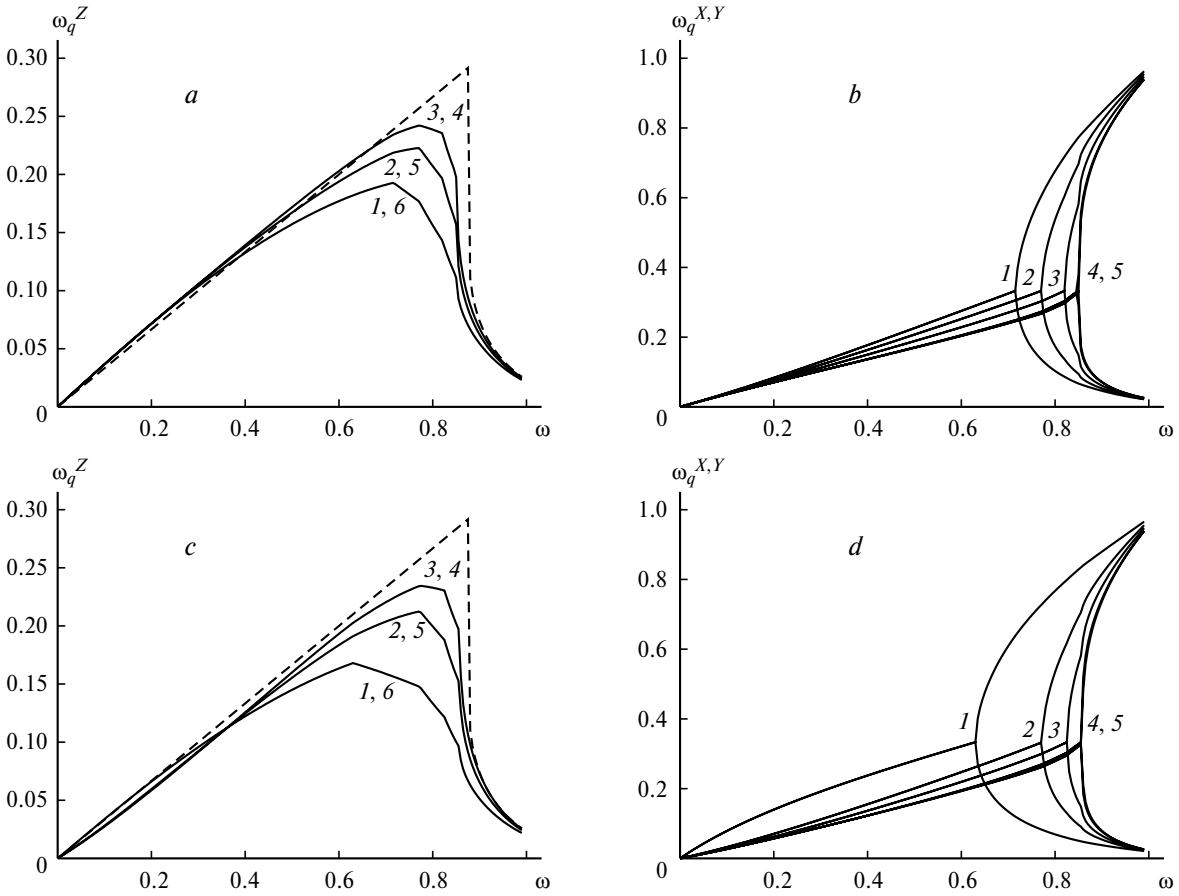


**Fig. 4.** Partial fillings $\omega_q^i$ *vs.* density ω for rods with the length $L = 4$ in various layers of a pore with the width $H = 9$ having symmetrical walls at $\varepsilon = 0$, $\Delta Q = 0$ (*a*, *b*) and 840 L mol$^{-1}$ (*c*, *d*): the filling degrees $\omega_q^X$ and $\omega_q^Y$ (*b*, *d*) are the upper and the lower branches of the curves, respectively, filling degrees $\omega_q^Z$ (*a*, *b*). The numbers of the curves correspond to the number of the layers.

(central) one. The calculation results are shown in Figs 4 and 5. The behavior of the partial fillings $\omega_q^i$ ($q$ is the number of the layer, $i = X, Y, Z$) is largely similar to that for the bulk phase. Note the key features of the distribution in narrow pores.

1. In the initial stage at low densities ω, the distribution of molecules is isotropic in the $XY$ plane, *i.e.*, $\omega_q^X = \omega_q^Y$. The presence of walls hampers the vertical orientation of molecules; therefore, the growth of the partial filling $\omega_q^Z$ lags behind the growth of $\omega_q^X$ (and $\omega_q^Y$). The closer the layer to the wall (the smaller the layer number), the more pronounced this lag.

As the bifurcation point has been attained, the molecules in each layer become ordered along the $X$ axis due to a decrease in the proportion along the $Y$ direction ($\omega_q^X > \omega_q^Y$), as in the bulk phase. The curve is abruptly separated into two branches: the upper $\omega_q^X$ and lower $\omega_q^Y$ ones ($\omega_q^X \to 1$, $\omega_q^Y \to 0$ for $\omega \to 1$). This ordering is not terminated at higher density values ω; in this respect, the distribution resembles more closely that observed in the bulk phase than in a monolayer. The point where ordering appears (bifurcation point) changes monotonically from layer to layer. Following the migration from the near-surface to the central layer, the bifurcation point shifts gradually from its minimum value (in the near-surface layer) to a value close to the bulk $\omega_{bif}$ (in the central layers). The effect of the parameter $\Delta Q$ determining the interaction of a molecule with a surface is similar to that observed in a monolayer: an increase in $\Delta Q$ shifts the bifurcation point in each layer toward lower densities. This effect is most pronounced in the near-surface layer (see Fig. 4, *b*, *d*, curve *1*); it is gradually attenuated on moving away from the surface and nearly vanishes in the central layers (see Fig. 4, *b*, *d*, curves *4*, *5*).

2. The fractions of vertical rods $\omega_q^Z$ are shown in Figs 4, *a*, *b* and in the insets in Figs 5, *a*, *b*. The pattern of these distributions is much closer to the bulk ones than to the monolayer ones. As in the bulk case, in the initial stage of disorder ($\omega_q^X = \omega_q^Y$), they increase to reach a maximum near the bifurcation point and then sharply decrease. Note that for any layer, their values are lower than the corresponding partial fillings $\omega^Z$ for the bulk phase at the same ε value. The smaller the number of the layer, the lower these values.

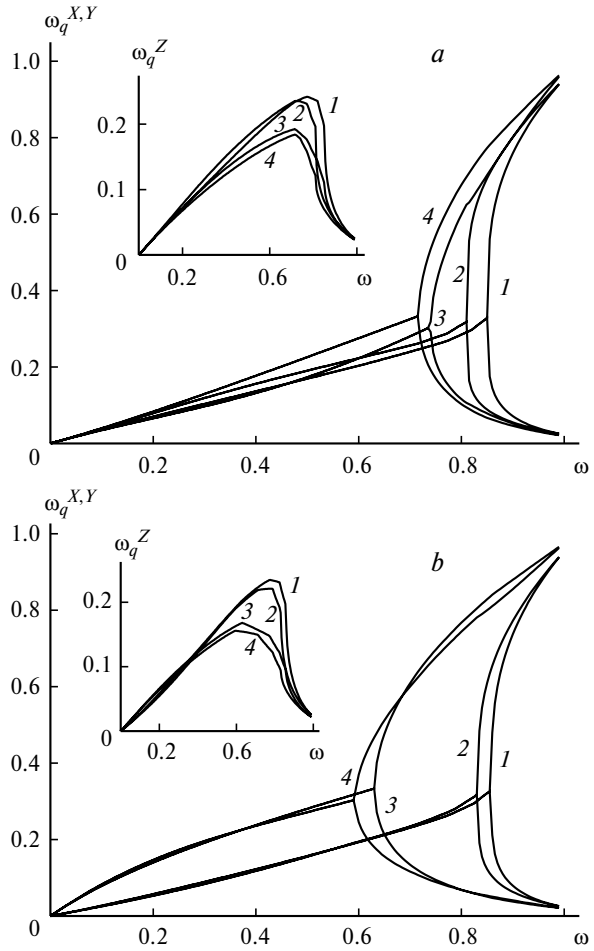


**Fig. 5.** Partial fillings $\omega_q^i$ *vs.* density ω for rods with the lengths $L = 4$ in the central (*1*, *2*) and near-surface (*3*, *4*) pore layers with the width $H = 9$ having symmetrical walls at $\Delta Q = 0$ (*a*) and 840 J mol$^{-1}$ (*b*); $\varepsilon = 0$ (*1*, *3*) and 840 J mol$^{-1}$ (*2*, *4*). The filling degrees $\omega_q^X$ and $\omega_q^Y$ correspond to the upper and lower branches of the curves, respectively. The insets show the fillings $\omega_q^Z$.

The effect of the adsorbate—adsorbent potential $\Delta Q$ on the orientation of molecules in the vertical (*a*, *b*) and horizontal (*c*, *d*) directions is demonstrated in Fig. 4. The numbers of the curves correspond to the number of the layer *q*. One can clearly see the separation of the curves corresponding to $\omega_q^X$ and $\omega_q^Y$ into the upper ($\omega_q^X$) and lower ($\omega_q^Y$) branches. The joint influence of the parameters $\Delta Q$ and ε shifts the bifurcation point to lower densities. The effect of $\Delta Q$ is most pronounced in the near-surface layer; here bifurcation takes place earlier than in other layers. When moving toward the central layer of the pore, the influence of the wall is attenuated, and the distributions in the central layers (4 and 5) differ only slightly from each other and from the bulk one. As the wall potential increases, the fraction of vertical rods ($\omega_q^Z$) becomes higher. A feature common to fields *a* and *b* is the presence of a maximum, which is related to the sharp decrease in $\omega_q^Z$ caused by re-orientation of the rods in a plane parallel to the pore wall at high degrees of filling of the pore space.

The partial fillings of two monolayers (near-surface and central ones) for different values of the energy parameter ε and for two $\Delta Q$ values are shown in Fig. 5. The proportions of vertical rods are shown in the insets in Figs 5, *a*, *b*. As the attraction between molecules grows, the bifurcation point shifts to lower bulk filling degrees of the pore ω. An increase in $\Delta Q$ shifts the border of the ordering region to lower density in the near-surface monolayer, by analogy with the situation observed for the adsorption on an open surface. In the central region, the influence of the parameter $\Delta Q$ is slight.

Thus, the molecular ordering in the layer planes (parallel to the pore walls) differs sharply from the case of adsorption on the open surface where vertical orientation of the molecules becomes favorable at high coverages. This difference is due to the influence of molecules located in the second and further layers. Outside the surface monolayer, the fraction of molecules corresponding to the onset of ordering in each layer increases as the degree of filling of the bulk increases. The mutual influence of the wall and the molecules situated in higher layers rules out the predominant orientation of rods along the *Z* direction in the first monolayer.

Similar dependences for the fraction of rods arranged in the *XY* plane for the central region of slit-shaped pores with different widths and also for the bulk phase are shown in Fig. 6 for a rod with the length $L = 4$.

As the pore width *H* increases, the distributions of rods of different orientations monotonically approach their bulk values. The estimates made for various *H* up to

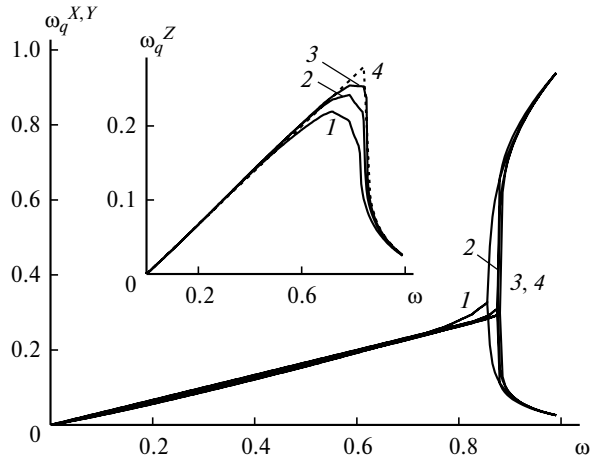


**Fig. 6.** Partial fillings $\omega_q^i$ *vs.* density ω for rods with the length $L = 4$ in the central layer of a pore with $H = 9$ (*1*), 13 (*2*), 15 (*3*), and in the bulk phase (*4*) for $\Delta Q = 840$, $\varepsilon = 420$ J mol$^{-1}$. The filling degrees $\omega_q^X$ and $\omega_q^Y$ are the upper and the lower branches of the curves, respectively. The inset shows the fillings degree $\omega_q^Z$ and the dashed line in the inset is $\omega^Z$ for the bulk phase.

30 monolayers show that a 1% deviation of the partial fillings at the pore center from the corresponding bulk value is attained at $H \approx 30$. The fraction of vertical rods $\omega_q^Z$ approaches the bulk value most slowly. This characteristics was chosen as the criterion of proximity of the distribution in the central layer of the pore to the bulk value.

It follows from the results that the pattern of distribution of molecules in narrow pores is determined by all molecular parameters: the rod length, lateral interactions, and the wall potential. The distribution equilibrium reflects the cooperative behavior of rod-like molecules with specific interactions and their ordering caused by the shape of impermeable "hard cores" of the molecules. The model takes into account that vertically oriented molecules can prohibit the probable filling the probable filling of neighboring layers of the pore with the molecules. The change in the molecule orientation with an increase in the monolayer coverage on an open surface or the filling of the pore bulk is reflected in the shape of isotherms and concentration dependences of the adsorption heats. These dependences differ appreciably from the same concentration dependences in the absence of reorientation of molecules.

The tendency of rods to acquire vertical orientation following an increase in the coverage of the wall surface for a monolayer is replaced by a predominantly horizontal orientation of molecules throughout the whole pore bulk. This is due to the influence of the wall potential, which acts within two to four near-surface monolayers and to the limited pore width. Due to the presence of vertical rods, an increase in the rod length entails an increase in the width of that part of the pore in which the wall has an influence on the distribution of molecules in the near-surface region. The situation largely depends on the relationship between the energy of intermolecular interactions and the energy of interactions with the pore wall. For rods, the notion "narrow pore" covers, most often, more than 10 nm; therefore, detailed analysis of the effect of energy characteristics of the adsorption system on its phase state is required.

The calculation of distribution equilibria is a necessary stage in the calculation of the transfer coefficients of molecules in the pores. Adsorbate ordering should influence all transfer coefficients. The concentration dependences of the dynamic characteristics of rod-like molecules in narrow slit-shaped pores have been considered previously.[19]

This work was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32072a).

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*Received December 21, 2005;*
*in revised form August 31, 2006*