The fundamentals of adsorption theory for a mixture of bulky molecules in slit-shaped pores with heterogeneous wall surfaces

Yu. K. Tovbin, L. K. Zhidkova, and V. N. Komarov*

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

The fundamentals of the adsorption theory for a mixture of bulky molecules blocking more than one adsorption site on the surface in slit-shaped pores with heterogeneous wall surfaces are outlined. The adsorbate—adsorbate lateral interactions are taken into account in the quasi-chemical approximation and in the mean-field approximation. The expressions for the partial adsorption isotherms and for the binary coefficients of mixture separation and the way of isolation of the partial contributions of molecules on heterogeneous adsorption sites on pore walls are discussed. A simplified variant of adsorption theory for a binary mixture of molecules of different sizes in two-layer pores with the assumption of complete coverage of the pores is considered. The influence of the energy of binding of molecules to pore walls, lateral interactions, and the ratio of the component sizes on the shape of adsorption isotherms is analyzed. The results of calculations are compared with the experimental data for the benzene—CCl_4—microporous AC carbon adsorbent system.

Key words: benzene, CCl_4, microporous carbon adsorbent, component mixture, adsorption, heterogeneous surface, slit-shaped pores, blocking of adsorption sites, lattice-gas model, isotherm.

Bulky molecules are capable of blocking several neighboring adsorption sites on the adsorbent surface. This complicates dramatically counting of the number of possible configurations of adsorbed molecules; therefore, the theory of adsorption of such molecules is much less developed than that for molecules that occupy only one site. A theory of adsorption of bulky molecules on open surfaces and in slit-shaped pores taking into account the joint influence of lateral interactions and surface heterogeneity has been considered in the literature in relation to one-component systems.[1—3] In the present study, we extend the adsorption theory to the case of mixtures of bulky molecules in slit-shaped pores. To construct the equations describing the adsorption equilibrium, the cluster approach was used.[4] If the pore is so wide that the influence of its walls on the state of the adsorbate in its center can be neglected, one has to consider multilayer adsorption on an open surface of the adsorbent. The theory of adsorption of mixtures of bulky molecules for this situation has not yet been developed either.

The purpose of the present work is to derive macroscopic expressions for partial adsorption isotherms and for binary coefficients of mixture separation, to derive a method for isolation of the partial contributions of molecules on heterogeneous adsorption sites on the pore wall and within the pore volume, and to construct a simplified version of the theory for the description of adsorption of a binary mixture consisting of molecules of different sizes located in pores with a diameter equal to two monolayers provided that the pore is completely filled. We planned to use this simplified approach to perform parametric analysis of adsorption isotherms, based on the study of the shape of isotherms as a function of the energy of binding of a molecule to the pore walls, lateral interactions, and the ratio of the sizes of component molecules. The simplified variant of the theory is used to describe the experimental data for the benzene—CCl_4—microporous adsorbent (AC) system.[5]

Model. The adsorbed molecules are represented as rectangular parallelepipeds $b \cdot d \cdot n$ with a solid core, where b, d, n are the linear dimensions of the molecule. The theory takes into account different possible orientations of the adsorbate molecule at the planar surface. A significant feature of the adsorption of bulky molecules is that the horizontal orientation of the long axes of the molecules can switch to the vertical orientation with the change in the surface coverage.[1,2,6] As the adsorbate concentration increases, an ordered arrangement of molecules with identical orientations of their long axes can become preferable under certain conditions, *i.e.*, an analog of three-dimensional phase transitions of the disordered phase—nematic (or smectic) type takes place.[7,8]

The adsorption of a mixture is described in terms of the lattice-gas model, which has previously been used[1—3] to describe one-component adsorption. The volume of a slit-shaped pore is separated into unit volumes. This approach provides a lattice structure with the number z of closest neighbors. The lattice constant is equal to the size of an adsorption site (unit), which is determined by

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 752—758, May, 2001.

1066-5285/01/5005-786 $25.00

the size of the local minimum of the adsorbent—adsorbate potential energy for one of the mixture components.

Let all the components occupy an integer number of units equal to M_m in the pore bulk, where $1 \le m \le \psi$, ψ is the number of components in the mixture. The orientation of each adsorbed molecule m is described by specific energetic characteristics; hence, in the statistical description of adsorption, a molecule with a specific orientation can be regarded as an individual sort of particles. Therefore, the allowance made for different orientations of molecules, even for a one-component system, is reduced to the problem of adsorption of a mixture of molecules with different sizes, each of them having a strictly fixed orientation. We consider that the orientation of the molecule is determined with respect to a chosen direction in the plane of the adsorbent near-surface layer. Let us designate the number of possible directions of the orientation axes of an adsorbed molecule by L_m; the index λ, $1 \le \lambda \le L_m$, is the ordinal number of a particular orientation axis of the molecule. For the sake of simplicity, L_m is taken to be the same for each surface site.

A "molecule m in orientation λ" will be referred to as "particle i" (m, $\lambda \leftrightarrow i$, *i.e.*, each pair of indices, m and λ, is matched by one index i), $M_i \equiv M_m$. Let us arrange the pair of indices m and λ in the following way. We wll consider that the first values of index i (from 1 to L_1) refer to the first component, the next values of index i (from $L_1 + 1$ to L_2) refer to the second component, and so on; then $1 \le i \le S$, where $S = \sum_{m=1}^{\psi} s_m$. Here s_m is the number of distinguishable variants of orientation of molecule m in which its long axis coincides with one of the axes of possible directions. For nonsymmetric molecules, one should distinguish the cases where the direction of the long axis of the molecule is the same as or the opposite to the direction of the orientation axis. In this case, $s_m = 2L_m$. For symmetric molecules, both cases correspond to the same states, then $s_m = L_m$.

Let us consider a lattice structure with $z = 6$ and $L_m = 3$. For molecules shaped like rectangular parallelepipeds $(b \cdot d \cdot n)_m$, the number of possible orientations s_m is 6, because each of the three fixed directions of the long axis b_m of molecule m allows two variants of arrangement of a molecule along two other axes for $d_m \ne n_m$. The different types of orientation of the $(b \cdot d)_m$ face where the third axis of the molecule m is stretched along the third axis of coordinates are shown in Fig. 1. The parameter n_m can assume any value but the conditions $n_m = d_m$ or $n_m = b_m$ correspond to spatially degenerate states of the molecule and, as in the case of a rod, $s_m = 3$. For a $(b \cdot d \cdot n)_m$ parallelepiped, we obtain the following sizes for particle i ($b_i(\alpha)$) along the axes $\alpha = x, y, z$:

λ	1	2	3	4	5	6
x	b_m	b_m	d_m	d_m	n_m	n_m
y	d_m	n_m	b_m	n_m	b_m	d_m
z	n_m	d_m	n_m	b_m	d_m	b_m

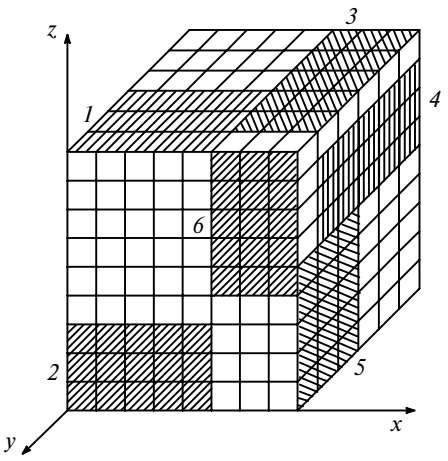

Fig. 1. Six types of orientation of the parallelepiped "hard sphere" taken into account in the description of adsorption of bulky molecules in slit-shaped pores at $z = 6$ and $L = 3$ (axes x and y are parallel to the pore walls, the pore width varies along the z axis).

Depending on the orientation, a given molecule m will block different numbers of points on the pore walls and in other layers. Let us denote the number of units occupied by particle i ($1 \le i \le S$) in each layer of a slit-shaped pore by I_i; it is equal to $I_i \equiv I_{m,\lambda} = b_i(x)b_i(y)$, where $I_{m,1} = I_{m,3} = (bd)_m$, $I_{m,2} = I_{m,5} = (bn)_m$, $I_{m,4} = I_{m,6} = (dn)_m$. The perimeter of particle i in the layer will be designated by P_i : $P_i = P_{m,\lambda} = 2[b_i(x) + b_i(y)]$, where $P_{m,1} = P_{m,3} = 2(b + d)_m$, $P_{m,2} = P_{m,5} = 2(b + n)_m$, $P_{m,4} = P_{m,6} = 2(d + n)_m$.

Let us formulate the rule for determining the position of a bulky molecule that blocks M_m neighboring units of the lattice structure in a particular unit. We chose one segment of particle i, for example an angle segment for a parallelepiped (plate or rod), and reckon from it the other units occupied by the same particle. It will be considered that the given particle occupies a unit with the number f ($1 \le f \le N$, where N is the number of units of the lattice structure in the pore volume) in which the chosen segment of the particle i, while the section of the lattice occupied by this particle i will be denoted by $\{f\}$. (In a slit-shaped pore, the number of unit f is matched by the number of layer k and the number of the unit in a given layer l: $f \leftrightarrow (k,l)$; hence, a section $\{f\}$ is characterized by a particular set of values $\{k,l\}$.)

On a heterogeneous lattice structure, each adsorption site $\{f\}$ can be characterized by a local Henry constant[4,9,10] $a^i_{\{f\}}$ for the adsorption of particle i on it: $a^i_{\{f\}} = a^{0i}_{\{f\}}\exp(\beta E^i_{\{f\}})$, where $\beta = (k_B T)^{-1}$; $a^{0i}_{\{f\}} = F^i_{\{f\}}\beta/F^0_i$ is the pre-exponent of the Henry constant; $F^i_{\{f\}}$ and F^0_i are statistic sums of the adsorbate in orientation i on a local fragment $\{f\}$ and in the gas phase, respectively (we are considering adsorption without dissociation of the adsorptive); $E^i_{\{f\}}$ is the bonding energy of the particle i with the unit $\{f\}$.

The lateral interactions should be taken into account for the nearest neighbors. The intermolecular interactions of the neighboring particles i and j located in units $\{f\}$ and $\{g\}$ are characterized by energetic parameters $\varepsilon^{ij}_{\{f\}\{g\}}$. Let us agree that positive values for the interaction parameters correspond to attraction.

If we assume that the energy of intermolecular interactions is calculated in the atom-atom approximation,[11] the $E^i_{\{f\}}$ and $\varepsilon^{ij}_{\{f\}\{g\}}$ parameters are represented by the sums of the contributions of pairwise interactions.

In addition, the notion of energetic contacts of the molecule can be introduced, the overall potential energy of interaction of the neighboring particles being represented by the sum of the contributions of these contacts.[12,13] The surface area of the molecule will be expressed in unit contacts whose area is assumed to be equal to the lattice constant squared. The surface of particle i is designated by $Q_i = P_i b_i(z) + 2I_i$. The number of class φ contacts of particle i is designated by Q_i^{φ}; $Q_i = \sum_{\varphi=1}^{\tau_i} Q_l^{\varphi}$, where the sum over φ from 1 to τ_i implies summation over all classes of contacts of particle i. The contact area of the neighboring particles i and j located in units $\{f\}$ and $\{g\}$ will be designated by σ^{ij}_{fg}. For any *particular complete set* of neighboring particles j with a specified order of arrangement and orientation relative to the central particle, which is designated by $\alpha(j)$, we have $Q_i = \sum_j \sigma^{ij}_{fg}$, where the sum over j involves all the neighboring particles surrounding the particle i. Then the parameter $\varepsilon^{ij}_{\{f\}\{g\}}$ can be represented as a sum of contributions $\varepsilon^{ij}_{\{f\}\{g\}}(\varphi\xi)$ between the neighboring contacts φ and ξ, which correspond to the unit contact surface area:

$$\varepsilon^{ij}_{\{f\}\{g\}} = \sum_{(\varphi\xi)} \varepsilon^{ij}_{fg}(\varphi\xi).$$

Here, the summation of the pairs of neighboring contacts $(\varphi\xi)$ is performed over a section with the area σ^{ij}_{fg}. The contact φ refers to particle i that occupies section $\{f\}$, while the contact ξ corresponds to particle j that occupies section $\{g\}$.

Each unit of the lattice structure can either be blocked by the adsorbate or be free. A free unit v is considered to be a particle of sort $S + 1$, all its contacts are equivalent, and $Q_v \equiv Q_{S+1} = z$; $m_{S+1} = 1$. The interactions of a particle with free units are equal to zero. The adsorbate—adsorbate lateral interactions between the nearest neighbors are taken into account in the quasi-chemical approximation, which retains the effects of direct correlations, and in the mean-field approximation in the absence of correlation effects.

Set of equations. The above-formulated model makes it possible to generalize the equations derived previously for a one-component adsorption.[1–3] Let us introduce functions $\theta^i_{\{f\}}$ and $\theta^{ij}_{\{f\}\{g\}}$ describing the distribution of particles over the lattice; $\theta^i_{\{f\}}$ is the probability that unit f is occupied by particle i; the symbol M_i^v means a free section of the lattice with size M_i in which particle i can be placed, and function $\theta_{\{f\}}{}^{M_i^v}$ is the probability that section $\{f\}$ of size M_i is free; and $\theta^{ij}_{\{f\}\{g\}}$ is the probability that particle i in unit $\{f\}$ is located near particle j in section $\{g\}$, where $1 \le j \le (S + 1)$. The local isotherm equation relates the probabilities of the occupied and vacant states of this section $\{f\}$ to each other. For each unit f of this structure, the following expression for the local adsorption isotherm can be written:

$$a^i_{\{f\}} p_i \theta^{M_i^v}_{\{f\}} = \theta^i_{\{f\}} \Lambda^i_{\{f\}} / M_i, \qquad (1a)$$

where $p_i \equiv p_m$ is the partial pressure of adsorptive m. The function $\Lambda^i_{\{f\}}$ takes into account the non-ideal character of the adsorption system; it depends on the way of accounting the lateral interactions between the neighboring molecules.

$$\Lambda^i_{\{f\}} = \exp\left(-\beta \sum_{\alpha(j)} \sum_j \varepsilon^{ij}_{\{f\}\{g\}} \theta^j_{\{g\}}\right), \qquad (1b)$$

$$\Lambda^i_{\{f\}} = \sum_{\alpha(j)} \prod_j t^{ij}_{\{f\}\{g\}} \exp\left(-\beta \varepsilon^{ij}_{\{f\}\{g\}}\right), \qquad (1c)$$

where summation over $\alpha(j)$ implies the sum over all the possible arrangements of all the neighboring molecules j. The variants of arrangement change upon changes in the number, the order of arrangement, and the orientation of neighboring molecules with respect to the central particle. In Eq. (1b), the lateral interactions are taken into account in the mean-field approximation, while in Eq. (1c), they are included in the quasi-chemical approximation. The function $t^{ij}_{\{f\}\{g\}}$ is the conditional probability that a particle i in section $\{f\}$ is found near particle j in section $\{g\}$, where $1 \le j \le (S + 1)$. It is these functions that reflect the correlation effects in the quasi-chemical approximation in which they are found by solving the following set of equations:

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

$$t^{ij}_{\{f\}\{g\}} = \theta^{ij}_{\{f\}\{g\}} / \theta^i_{\{f\}}. \qquad (2)$$

The condition of normalization to pair probabilities is written as

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

If the lateral interactions can be neglected, then $\Lambda^i_{\{f\}} = 1$ and $a^i_{\{f\}} p_i = \theta^i_{\{f\}} / (M_i \theta_{\{f\}}{}^{M_i^v})$. This case correspond to extremely low degrees of coverage (the Henry region).

To close Eqs. (1) and (2), conditions of normalization to the local occupation of units should be added and a method for calculation of the $\theta_{\{f\}}{}^{M_i^v}$ functions should be found. The probability of finding a free

section of the lattice $\theta_{\{f\}}^{M_i^v}$ on the surface, in which adsorption of particle i is possible, is given, as in previous publications,[1–3] by the relation

$$\theta_{\{f\}}^{M_i^v} = \rho_f^v \prod_h t_{hh+1}^{vv}, \qquad (3)$$

where the index h numbers $(M_i - 1)$ units blocked by particle i with size M_i; ρ_f^v is the probability that unit f is free ; t_{hh+1}^{vv} is the conditional probability that a free unit with the number $(h + 1)$ is found near a free unit with the number h. In the mean-field approximation, the functions t_{hh+1}^{vv} in relation (3) can be directly expressed in terms of the local densities (as it is done for the case of absence of lateral interactions) in the form

$$t_{hh+1}^{vv}(k) = \rho_{h+1}^v \left[\rho_{h+1}^v + \sum_{i=1}^{S} \sum_{\varphi} \rho_{h+1}^{\varphi} Q_i^{\varphi}(k)/z \right]^{-1}, \qquad (4)$$

where the pair of indices h and $h + 1$ specifies the orientation (k) of a pair of free units; $Q_i^{\varphi}(k)$ is the number of contacts of class φ of the neighboring particle i in the direction specified by the k value.

The local condition for normalization of the probabilities of occupation of a unit with the number f is written as

$$\rho_f^v + \sum_{i=1}^{S} \sum_{\xi} \rho_{f-\xi}^i = 1, \qquad (5)$$

where

$$\rho_f^i = \theta_{\{f\}}^i / M_i.$$

Here, the index ξ numbers any possible shift of the particle i in any direction without changing its orientation: $0 \le \xi \le (M_i - 1)$; the value $\xi = 0$ corresponds to unit f. The normalization condition (5) reflects the whole set of different modes in which a given particle i can block a given unit f.[3]

The particular cases of equations describing rigid rods of length n or $b \cdot d$ plates are derived from the equations for the three-dimensional case $b \cdot d \cdot n$ upon simplifications $b = d = 1$ and $n = 1$, which reduce the size and the number of dimensions of the molecule in the former and in the latter case, respectively. The equations constructed provide, in the general case, a more detailed description of the orientation of a molecule if the condition $L_m > z/2$ is used instead of $L_m = 3$ for $z = 6$.

Solution of the set of equations (1)—(3), (5) for $\theta_{\{f\}}^i$ makes it possible to find all the partial isotherms

$$\theta_m(\{p\}) = \sum_{i=1}^{s_m} \sum_{f=1}^{N} \theta_{\{f\}}^i(\{p\})/N,$$

where $i \in (m, \lambda)$, $\{p\}$ is the list including the pressures of mixture components as well as the full adsorption isotherm

$$\theta(\{p\}) = \sum_{m=1}^{\Psi} \theta_m(\{p\}).$$

This solution provides a detailed description of the local occupancies of individual units in a three-dimensional fragment of the lattice and, in the general case, it requires the use of numerical methods of analysis. The dimensionality of the set of equations in the quasi-chemical approximation can be markedly decreased by introducing new variables, $X_{\{f\}\{g\}}^i$, using the relation $\theta_{\{f\}\{g\}}^{ij} = X_{\{f\}\{g\}}^i X_{\{g\}\{f\}}^j \exp(\beta\varepsilon_{\{f\}\{g\}}^{ij})$ because Eqs. (2) are thus transformed into the identity $1 \equiv 1$. Nevertheless, analytical solutions of this set of equations are also possible for the simplest limiting cases regarding the component densities or molecular parameters.

Macroscopic systems. The occupancy of individual units can be described only for small fragments of porous systems containing ~10^3 units. The properties of porous macro objects can be described adequately in terms of adsorption on small fragments only in the case where they have homogeneous wall surfaces or a strictly regular arrangement of the heterogeneous adsorption sites on pore walls. In the general case, it is necessary to take into account all possible variants of mutual arrangement of adsorption sites. Therefore, to describe macroscopic porous systems with heterogeneous wall surfaces, it is necessary to introduce distribution functions of units of different types and to use them for averaging the resulting solutions. In turn, to take into account a broad spectrum of variations of mutual positions of different adsorption sites, one should employ the procedure of averaging the contributions to local isotherms from each type of adsorption sites over different types of local structures. To this end, it is necessary to formulate a method for the separation of partial contributions of heterogeneous adsorption sites on the lattice structure. The same is needed in the case of a one-component adsorption of bulky molecules.[1–3] This procedure is also required to compare the theory and the numerical results obtained by the Monte Carlo and molecular dynamics methods.

As a result, we get the known expression for the overall adsorption isotherm[4,9,15,16]

$$\theta(p) = \sum_{i=1}^{S} \sum_{q=1}^{T} f_q \theta_q^i, \qquad (6)$$

where

$$\sum_{q=1}^{T} f_q = 1.$$

Here, f_q is an unitary distribution function of units of the lattice structure over adsorption capacity; T is the number of unit types in this structure. For large T values, an integral over the energy states of the molecule is often used in Eq. (6) instead of the sum over the types of units q.[14,15] Without summation over the sorts of molecules, Eq. (6) gives the relation for the partial adsorption isotherm. The local degrees of coverage θ_q^i are found from the set of equations (1)—(3), (5) using the following procedure.[1–3]

Let unit with a number f be a type q unit surrounded by a particular set of units. For another unit of type q, for example, for the unit with the number h, a different type of surrounding by neighboring units exists. The function f_q in Eq. (6) takes into account the fraction of units of type q but does not characterize the types of units surrounding the units with numbers f and h. Thus, the function f_q does not reflect the surface structure and does not indicate what neighboring units can be blocked by large particles. In a slit-shaped pore, when particle i is located in a type q unit, the neighboring units of different types blocked by this particle can be located in different layers. All the possible variants of this blocking are reflected in Eq. (5). For a particular sort of particles i, in deriving the expression for θ_q^i, it is necessary to perform averaging over the probabilities of realization of different ways of arrangement of neighboring $(M_i - 1)$ units around a type q unit blocked by a given particle i. As a consequence, the function θ_q^i is found as

$$\theta_q{}^i = \sum_{q_1=1}^{T} \cdots \sum_{q_{M-1}=1}^{T} F_{q_1 \ldots q_{M-1}}(f)\theta_f^i, \qquad (7)$$

here q is the type of unit from which the region blocked by particle i is reckoned; the sums are taken successively over the types of all units in the blocked region from $q = 1$ to $q = M - 1$; F is the conditional probability that a section of units of the type q_1, ..., q_{M-1} falls in the blocked region; the index f numbers the position of the "origin" of the molecule in a type q unit. The function θ_f^i refers to the corresponding local probability of the presence of particle i in unit f determined in terms of Eqs. (1).

Let us write the so-called "binary separation coefficient"[16—19] as $\alpha_{ij} = \theta_i p_j/(\theta_j p_i)$ (the gas phase is assumed to be ideal). This coefficient makes it possible to characterize the efficiency of purification of liquid and gas mixtures. It relates the equilibrium concentrations of components i and j in the gas—adsorbate system for a multicomponent mixture. By analogy with relation (7), this extends the relations derived previously[19] to the case of adsorption of a mixture of bulky molecules.

$$\alpha_{ij} = \sum_{q=1}^{T} f_q U_q^i \Big/ \sum_{q=1}^{T} f_q U_q^j,$$

$$U_q{}^i = \sum_{q_1=1}^{T} \cdots \sum_{q_{M-1}=1}^{T} F_{q_1 \ldots q_{M-1}}(f) a_{\{f\}}^i \theta_f^{M_i^{\nu}} / \Lambda_f^i, \qquad (8)$$

where U_q^i is the partial contribution made by particle i located in a unit of type q to the binary separation coefficient. It is expressed in terms of the local Henry constant, the probability of finding a free section (Eq. (3)) in which adsorption of a given molecule i is possible, and *via* the non-ideality function of the adsorption system (Eqs. (1b), (1c)).

Binary mixture of planar molecules in two-layer pores. Using general equations (1)—(3), (5), one can construct simpler equations reflecting particular properties of the adsorbents studied. As a simple example, we will consider the model situation when molecule i (i = A, B) is adsorbed from a binary solution by a microporous adsorbent with a pore size of about two monolayers. The difference between sizes of molecules M_i is related to the difference between their areas $S_i \equiv I_i$ for a thickness of a single monolayer $h = 1$ ($M_i = I_i = S_i h$). In this case, no effects of molecule reorientation are involved. We will take into account only lateral interactions in the molecular-field approximation; this gives the following equation describing the pore coverage by molecules A:

$$U_A = U_B^n (\xi_{vv}^{bulk}/\xi_{vv})^{n^*},$$

$$U_i = \Lambda_i^* \theta_i \exp(-\beta E_i)/\theta_i^{bulk},$$

$$\Lambda_i^* = \exp\left\{\beta \sum_{j=A}^{B} \varepsilon_{ij}\left[P_i(\theta_j^{bulk} - \theta_j)\right] + I_i(2\theta_j^{bulk} - \theta_j)\right\},$$

where $n = M_A/M_B$; $n^* = n(M_B - 1)/(M_A - 1)$; ξ_{vv} are determined by relation (4); the superscript "bulk" means that the given value refers to the bulk phase. This expression was derived from Eqs. (1) from which the contribution of vacancies has been eliminated because their fraction in a liquid binary solution is low. Here, the U_i value is the ratio of the right-hand parts of Eqs. (1) for component i located in the adsorbent and in the bulk phase of the binary solution outside the adsorbent.

Now we consider the influence of molecular parameters on the pattern of adsorption isotherms (Fig. 2). It was assumed in the calculations that $I_i = L_i^2$, where L_i is the linear size of the molecule i; $\varepsilon_{AB} = (\varepsilon_{AA}\varepsilon_{BB})^{1/2}$. The parameters varied included the ratio of linear dimensions of molecules L_A/L_B, the energy of binding of molecules to the pore surface E_i, and the adsorbate—adsorbate lateral interactions ε_{ij}.

With zero lateral interaction parameters and with equal interaction of the components with the pore walls, adsorption of bulky molecules decreases (see Fig. 2, *a*, curve *6*), while that of small molecules increases (see. Fig. 2, *a*, curve *5*) with an increase in the concentration of molecules A in the solution bulk. For comparison, we show curves *3* and *4* corresponding to the selective adsorption of components A and B, respectively. It can be considered that an increase or decrease in the linear size of molecule A by 25% is matched by a ~$3kT$ decrease or increase in the energy of its binding to the pore walls.

The influence of lateral interactions on the pattern of adsorption isotherms of component A with equal interactions of molecules A and B with the pore walls is presented in Fig. 2, *b*. When the component sizes are equal, an increase in the ε_{AA} parameter (see Fig. 2, *b*, curve *7—9*) induces an increase (decrease) in the adsorption of component A for small (great) densities of A in the the solution bulk. Curve *9* describes the separation of the mixture into components in the pores (in this case, the position of the density step in the isotherm

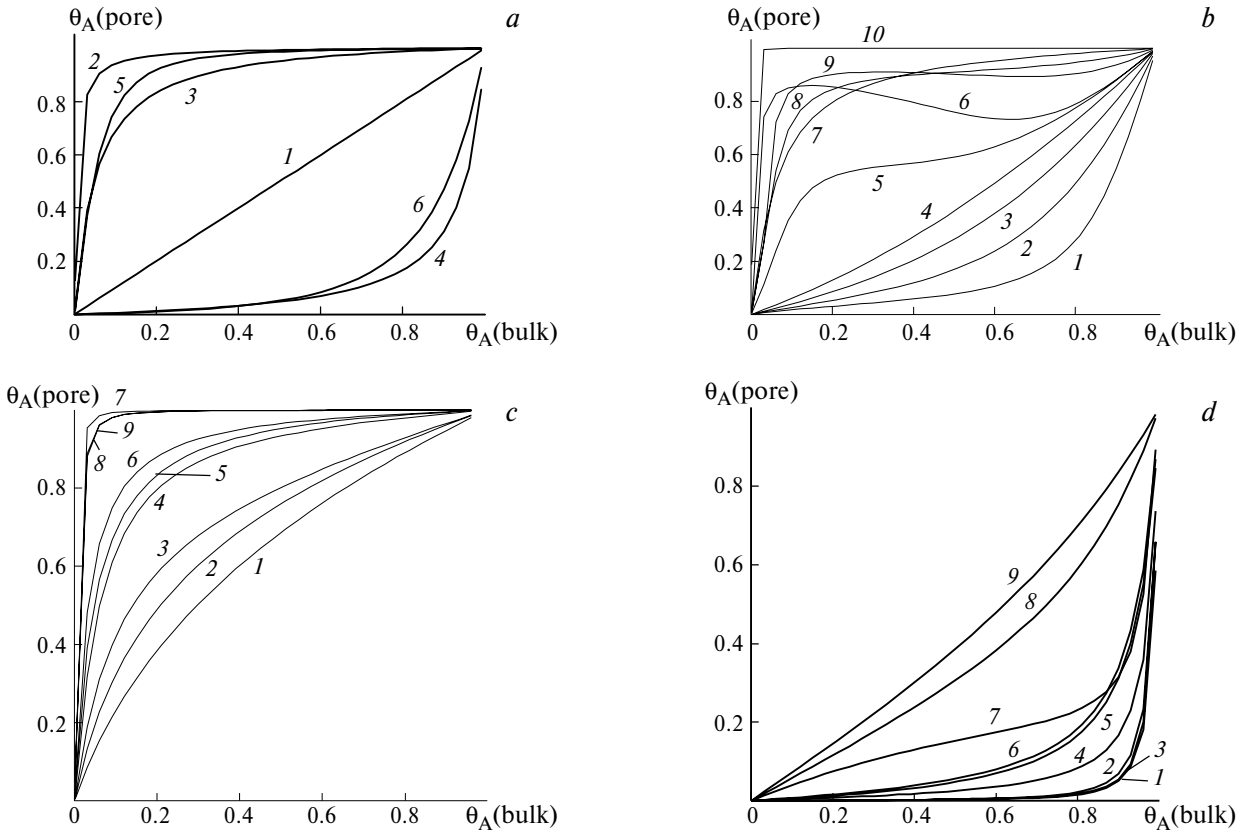

Fig. 2. Influence of molecular (ε_{ij}, ε_{AA}, ε_{BB}) and energetic (L_A/L_B, $E_A - E_B$) parameters on the pattern of adsorption isotherms of component A from a binary mixture at $T = 300$ K (the energy parameters are expressed in the kT units): *a*: $\varepsilon_{ij} = 0$; $L_A/L_B = 0.75$ (*5*), 1.0 (*1—4*), 1.25 (*6*); ($E_A - E_B$) = 5 (*2*), 3 (*3*), 0 (*1*, *5*, 6), −3 (*4*); *b*: ($E_A - E_B$) = 0; $L_A/L_B = 1.25$ (*1—6*), 1 (*7—9*), 0.75 (*10*); $\varepsilon_{BB} = 1.5$ (*6*) and 1.0 (other curves); ε_{AA} = 5 (*1*, *9*), 4 (*2*, *8*), 3 (*3*), 2 (*4*, *7*), 0 (*5*, *6*); *c*: ($E_A - E_B$) = 3; $\varepsilon_{BB} = 1.0$; $L_A/L_B = 1.25$ (*1—3*), 1.0 (*4—6*), 0.75 (*7—9*); ε_{AA} = 2 (*1*, *4*, *7*), 1 (*2*, *5*, *8*), 0.5 (*3*, *6*, *9*); *d*: ($E_A - E_B$) = −3; $\varepsilon_{BB} = 1.0$; $L_A/L_B = 1.25$ (*1—3*), 1.0 (*4—6*), 0.75 (*7—9*); ε_{AA} = 2 (*1*, *4*, *7*), 1 (*2*, *5*, *8*), 0.5 (*3*, *6*, *9*).

is found, as usual, using the Maxwell rule[4]). An increase in the ε_{AA} parameter (for ε_{BB} = const) entails a decrease in the adsorption of bulky molecules A in the pores (see Fig. 2, *b*, curves *1—5*), because for these molecules, it is more favorable for energetic or thermodynamic reasons to occur in the bulk phase in which they are surrounded on all sides by like molecules. In this case, the mixture in the solution is separated into layers. As the ε_{BB} parameter increases (see Fig. 2, *b*, curve *6*), the mixture in the pores is also separated. Conversely, when the size of molecule A is small, the pore is covered virtually completely at any ε_{AA} (see Fig. 2, *b*, curve *10*).

This effect of adsorbate separation is a result of using the model of an infinite slit with homogeneous walls. It should be noted that the problem of segregation of one- and two-component systems into layers in micropores has long been discussed. Substantial heterogeneities on the "surfaces" of active carbons and zeolites change markedly the adsorbate properties. However, if the micropores form an interconnected system, separation of the adsorbate is not eliminated completely but occurs at much lower temperatures even in the presence of strong heterogeneous potential fields of the adsorbent walls.[20]

The pattern of isotherms changes if the wall potential affects selectively some component in the solution. If $E_A > E_B$ (adsorption of molecules A becomes more selective with a decrease in the ε_{AA} parameter), the adsorption of these molecules increases and the isotherms become convex even when $L_A/L_B = 1.25$ (see Fig. 2, *c*). However, with strong attraction ($\varepsilon_{AA} > 3kT$), the isotherms remain concave (*cf.* Fig. 2, *b*). The general trend of acceleration of the adsorption of a component in the pores with a decrease in the pore size is retained: curves *7—9* in Fig. 2, *c* are located above curves *4—6*, which are, in turn, located above curves *1—3*.

If $E_B > E_A$ (high selectivity in adsorption of molecules B), all the isotherms of component A are concave (see Fig. 2, *d*), although the sequence of their arrangement for mixture components having different sizes is retained as shown in Fig. 2, *c*: curves *9* and *8* coincide and are located below curve *7*; similarly, in Fig. 2, *d*, curves *1* and *3* virtually coincide and are arranged below curve *2*.

The model described here was used to treat experimental data on adsorption of benzene molecules in the micropores of the AC activated carbon from a

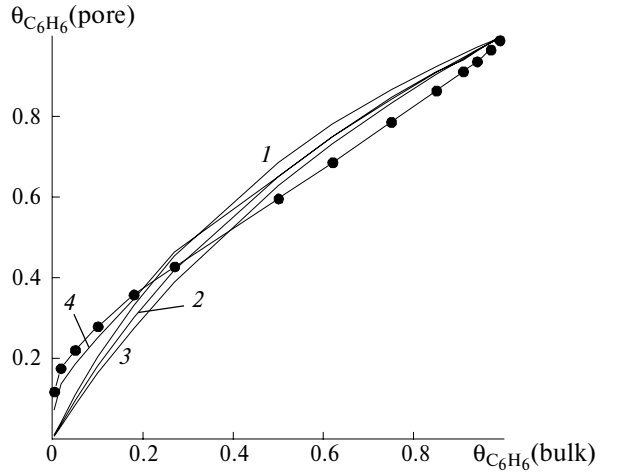

Fig. 3. Adsorption of benzene molecules by the microporous active carbon AC from a benzene—CCl_4 solution at 300 K[5] ($L_{C_6H_6}/L_{CCl_4}$ = 1.04): (*1*) E_A = 11, E_B = 8.8, ε_{AA} = 1.0, ε_{BB} = 0.76; (*2, 4*) E_A = 17, E_B = 14, ε_{AA} = 1.5, ε_{BB} = 0.76; (*3*) E_A = 17, E_B = 14.5, ε_{AA} = 1.5, ε_{BB} = 2.0; the dots are experimental values.[5] The energy parameters are expressed in the kT units.

C_6H_6—CCl_4 solution at 300 K.[5] In terms of the theory of volume filling of micropores, this adsorbent has a volume of 0.39 $cm^3\ g^{-1}$ and a pore width of ~1.2 nm.[5] With the given component dimensions, ~0.68 nm (CCl_4) and 0.34—0.73 nm (benzene), the two-layer pore model corresponds qualitatively to experimental data. The excess adsorption values found experimentally were converted to total contents using known equations.[5,21] Typical isotherms are shown in Fig. 3 for three sets of parameters (curves *1*—*3*). The two-layer pore model provides a qualitatively correct description of experimental results in a broad range of concentrations. However, for low degrees of coverage of pores with benzene ($\theta_{C_6H_6} < 0.2$), this model does not provide a qualitative agreement with the experiment. The use of this model results in overestimation of the calculated isotherms for high degrees of pore coverage with benzene ($\theta_{C_6H_6} > 0.5$). To improve the description of the experiment (see Fig. 3, curve *4*), it is necessary to reject the condition of homogeneity of the pore walls and to introduce strongly adsorbing sites for molecules A present in a low concentration (~2%) with a binding energy greater than that for the rest of units on the surface by $10kT$ (for the values of parameters corresponding to curve *2* in Fig. 3).

Thus, the theory for adsorption of a mixture of bulky molecules proposed here, on the one hand, provides a fairly detailed description of the state of a molecule in slit-shaped pores with heterogeneous wall surfaces, which is obtained by the numerical Monte Carlo and molecular dynamics methods, and, on the other hand, makes it possible to design different variants of simplified models with clearly formulated assumptions at the molecular level for the description of experimental data on multicomponent adsorption.

The authors are grateful to A. M. Tolmachev for useful discussions.

This work was financially supported by the INTAS (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. Fizika* [*Chem. Phys.*], 1998, **17**, 140 (in Russian).
3. Yu. K. Tovbin, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1467 [*Russ. Chem. Bull.*, 1999, **48**, 1450 (Engl. Transl.)].
4. Yu. K. Tovbin, *Teoriya fiziko-khimicheskikh protsessov na granitse gaz—tverdoe telo* [*Theory of Physicochemical Processes on the Gas—Solid Interface*], Nauka, Moscow, 1990, 288 pp. (in Russian).
5. O. G. Larionov, Sc.D. Thesis (Chemistry), *Institute of Chemical Physics of the USSR Acad. Sci.*, Moscow, 1975, 378 pp. (in Russian).
6. B. E. Boehm and D. E. Martire, *J. Chem. Phys.*, 1977, **67**, 1961.
7. S. Chandrasekar, *Liquid Cristalls*, Cambridge University Press, Cambridge—London—New York—Melburn, 1977.
8. I. P. Bazarov and E. V. Gevorkyan, *Statisticheskaya teoriya tverdykh i zhidkikh kristallov* [*Statistical Theory of Solid and Liquid Crystals*], Izd-vo MGU, Moscow, 1983, 262 pp. (in Russian).
9. Yu. K. Tovbin, *Zh. Fiz. Khim.*, 1990, **64**, 958 [*Russ. J. Phys. Chem.*, 1990, **64** (Engl. Transl.)].
10. Yu. K. Tovbin, *Langmuir*, 1997, **13**, 979.
11. A. V. Kiselev, *Mezhmolekulyarnye vzaimodeistviya v adsorbtsii i khromatografii* [*Intermolecular Interactions in Adsorpton and Chromatography*], Vysshaya shkola, Moscow, 1986, 360 pp. (in Russian).
12. J. A. Barker, *J. Chem. Phys.*, 1952, **20**, 1526.
13. E. A. Guggenheim, *Mixtures*, Clarendon Press, Oxford, 1952, 271 pp.
14. I. Z. Roginskii, *Adsorbtsiya i kataliz na neodnorodnykh poverkhnostyakh* [*Adsorption and Catalysis on Inhomogeneous Surfaces*], Izd-vo Akad. Nauk SSSR, Moscow—Leningrad, 1948, 643 pp. (in Russian).
15. S. L. Kiperman, *Vvedenie v kinetiku geterogennykh kataliticheskikh reaktsii* [*Introduction to the Kinetics of Heterogeneous Catalytic Reactions*], Nauka, Moscow, 1964, 607 pp. (in Russian).
16. D. M. Ruthven, *Principles of Adsorption and Adsorption Processes*, J. Wiley, New York, 1984.
17. A. M. Tolmachev, *Usp. Khim.*, 1981, **50**, 769 [*Russ. Chem. Rev.*, 1981, **50** (Engl. Transl.)].
18. M. F. Gilyazov, A. A. Lopatkin, and A. M. Tolmachev, *Vysokochist. Veshchestva* [*High-Purity Compounds*], 1987, No 6, 40, 48 (in Russian).
19. Yu. K. Tovbin, M. F. Gilyazov, and A. M. Tolmachev, *Vysokochist. Veshchestva* [*High-Purity Compounds*], 1990, No. 1, 76, 83 (in Russian).
20. Yu. K. Tovbin, *Dokl. Akad. Nauk SSSR*, 1981, **260**, 679 [*Dokl. Chem.*, 1981 (Engl. Transl.)].
21. A. M. Tolmachev, *Zh. Fiz. Khim.*, 1994, **66**, 190 [*Russ. J. Phys. Chem.*, 1994, **66** (Engl. Transl.)].

Received August 18, 2000;
in revised form January 19, 2001