Concentration relationships of coefficients of self-diffusion and viscosity of the adsorbate in narrow slit-like pores

Yu. K. Tovbin★ and N. F. Vasyutkin

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

Concentration relationships of dynamic characteristics of the adsorbate (coefficients of self-diffusion and shear viscosity) in narrow slit-like pores with different widths were considered. These coefficients were calculated using the simplest molecular model (lattice-gas model), which takes into account the intrinsic volume of molecules and their interactions in the quasi-chemical approximation. The values of coefficients of self-diffusion and shear viscosity of the adsorbate depend strongly on the distance to the pore wall.

Key words: slit-like pores, adsorption, isotherm, coefficient of self-diffusion, coefficient of shear viscosity, lattice-gas model, quasichemical approximation

Transport of molecules adsorbed in porous materials plays an important role in catalytic and adsorption processes.[1—4] In narrow pores with a width of 7 to 10 nm,[5] the potential of walls affects the aggregate state of the fluid and, correspondingly, the mechanism of its transport. When moving in these pores, all transport characteristics of the adsorbate differ from their values in bulk vapor and liquid phases. Coefficients of self-diffusion and shear viscosity belong to the most important dynamic characteristics.[1—4] It is difficult to theoretically calculate these values in a wide range of fillings and temperatures, although the first results have already been obtained[6] for rarefied gases. In the present time, coefficients of self-diffusion and shear viscosity of the adsorbate are calculated predominantly by the molecular dynamics methods but the obtained results are scarce.[7—9] Available experimental methods for measuring coefficients of self-diffusion (NMR and isotope method) give values that differ considerably from flow characteristics,[10,11] whereas estimations of the shear viscosity are completely based only on measurements performed in bulk phases.

In this work, we calculated the concentration relationships of coefficients of self-diffusion and shear viscosity of the adsorbate in a wide region of pore fillings at different adsorbent—adsorbate potentials. With this purpose, we used the lattice-gas model,[12] which takes into account the intrinsic volume and interaction of atoms in the quasichemical approximation. This model makes it possible to find self-consistent characteristics of the vapor-liquid system and transfer coefficients of molecules in the volume phase using a single set of energy parameters. It is applicable in wide ranges of fluid concentrations and temperatures. The phase diagrams obtained by this model agree well with those found by the Monte Carlo and molecular dynamics method.[13,14]

Lattice-gas model

In the lattice-gas model,[15] the volume of a slit-like pore V_p is mentally divided into monoatomic layers with the linear size (width) λ arranged in parallel to the pore wall, and each layer is divided into cells with a size of an order of the volume of one molecule $v_0 = \lambda^3$. Then $V_p = Nv_0$, where N is the number of cells in the system. Each cell can contain only one particle: either molecule A (if the center of gravity of the molecule is inside the cell) or vacancy v. If the cell with number f ($1 \le f \le N$) is occupied by molecule A, the index of this cell i = A, and if it is occupied by the vacancy, then i = v. Let us designate the number of f-cells neighboring to the cell in this imaginary lattice structure through z. The concentration of molecules is usually expressed by the number of these molecules N_m per unit volume: $C = N_m/V_p$. In the lattice-gas model, the concentration of the fluid (*i.e.*, molecules A) is characterized by the value $\theta = N_m/N_{den}$ equal to the ratio of the number of real particles in some volume to the highest possible number of close-packed particles N_{den} in the same volume (in the considered case, $N_{den} = N$). Then $\theta = Cv_0$. Let us designate the local density of particles i in the cell with number f through θ_f^i, keeping in mind that $\theta_f^A + \theta_f^v = 1$, $\theta_f^A \equiv \theta_f$. The average concentration of the fluid θ is determined through the local concentrations as $\theta = \sum_{f=1}^{N} F_f \theta_f / N$, where F_f is the fraction of cells of type f.

Each cell f is characterized by a specific energy of interaction of molecules with the walls and, correspondingly, by its Henry′s constant. Using the latter value, all

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cells of the lattice can be divided into groups with the same properties. Designate the number of these groups through t. When the walls of a slit-like pore are uniform, all cells of the same layer are equivalent and, therefore, the layer number f coincides with the number of the cell contained in this layer. For the even number of monolayers (H) $t = H/2$, and for the odd H $t = (H + 1)/2$. Local Henry's constant is $a_f = \beta F/F_0 \exp(\beta Q_f)$, where $\beta = (kT)^{-1}$; F and F_0 are the statistical sums of the state of particles in the lattice system and out of it (in the gas phase), respectively; Q_f is the bond energy of the molecule in the layer f with the pore walls, and $Q_f = u(f) + u(H - f + 1)$, $1 \le f \le t$, and the potential of interaction of the molecule with the pore wall $u(f) = \varepsilon_a/f^3$ corresponds to the attracting branch of the Mi potential (3—9),[16] and ε_a is the energy parameter of the potential.

Let us consider interactions of the nearest neighboring molecules and designate through ε_{ij} the energy of interaction of particles i and j (j = A or v). Here $\varepsilon_{AA} \equiv \varepsilon$, $\varepsilon_{iv} = 0$, *i.e.*, the energy of interaction of particle i with the vacancy is equal to zero. The mutual distributions of molecules are described by pairwise distribution functions θ_{fg}^{ij}, which determine a probability for a pair of particles ij to occupy adjacent cells f and g. The following norming correlations are valid for them: $\theta_{fg}^{AA} + \theta_{fg}^{Av} = \theta_f$ and $\theta_{fg}^{vA} + \theta_{fg}^{vv} = \theta_f^v$.

The local adsorption isotherms relating the values of local filling of cells to the external pressure p outside the pore are described by the following equations[12,15]:

$$a_f P(1 - \theta_f) = \theta_f \prod_{g \in z_f} (1 + x_{fg} t_{fg}), \; x_{fg} = \exp(-\beta\varepsilon) - 1, \quad (1)$$

$$t_{fg} = 2\theta_g/[\delta_{fg} + b_{fg}],$$

$$\delta_{fg} = 1 + x_{fg}(1 - \theta_f - \theta_g), \; b_{fg} = \{[\delta_{fg}]^2 + 4x_{fg}\theta_f\theta_g\}^{1/2}.$$

Index g runs over all adjacent cells z_f around the central cell in the layer f; $t_{fg}^{AA} \equiv t_{fg} = \theta_{fg}^{AA}/\theta$ is the conventional probability molecule A is located in cell g near the "central" molecule A in cell f. The equilibrium particle distribution over cells of different types can be found solving the system of equations (1) using the iteration method.

Consider adsorption of Ar atoms in slit-like pores of graphite. The energy characteristics of the lattice model for this system are: $Q_1 = 9.24\varepsilon$, where $\varepsilon = 0.238$ kcal mol^{-1} (see Refs. 16, 17), $Q_2 = Q_1/8$ (in agreement with the Lennard-Jones potential), while other $Q_f = 0$. In calculations conducted for adsorption at $T = 200$ K, the $\beta\varepsilon$ value (0.595) is dimensionless, and for Ar atoms $z = 6$ is accepted. Figure 1, *a* shows the adsorption isotherms of argon in graphite pores with different widths, and Fig. 1, *b* demonstrates the distribution of local adsorbate concentrations at the mean fraction of filling of the pore volume $\theta = 0.5$. In all cases, the density of atoms near the pore wall is much higher than in its central part, except for the case when the number of monolayer is two. At $H = 2$ the character

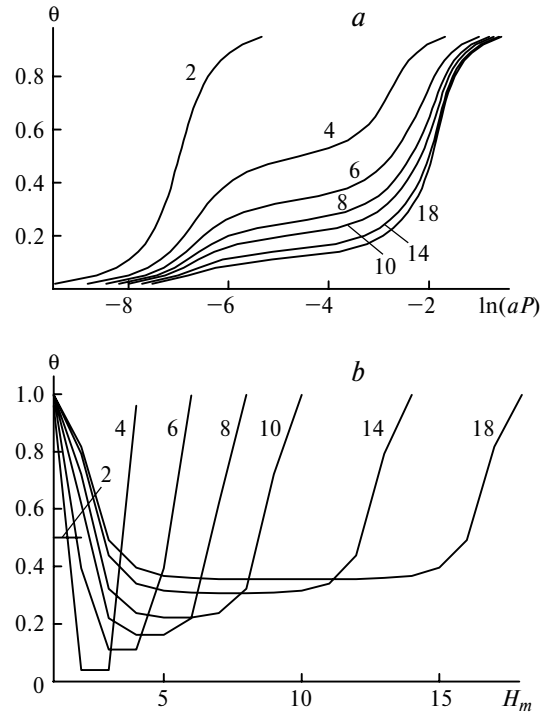

Fig. 1. Equilibrium adsorption of argon in slit-like pores of graphite (numbers of curves correspond to pore widths expressed in the number of monolayers): *a*, adsorption isotherms (the product aP is dimensionless, here a is the mean value of local Henry's constants); *b*, concentration profiles of the adsorbate for an average pore filling of 0.5 (numbers of monolayers H_m are put on the abscissa).

of filling of both pores is the same. Nonuniformity of the local densities of the adsorbate influences the character of its motion in this or another direction relatively to the pore walls.

Migration rate of molecules

It is difficult to use the free path of molecules for the description of migration in adsorbent pores because the values in the rarefied gas and compact liquid phases can differ strongly ($10^4\lambda$ and λ, respectively). In the lattice-gas model, as in the kinetic theory of liquids,[18,19] the idea of the probability of jump (or shear) of a molecule $W(\rho)$ at the distance ρ is used instead of the free path: $W(\rho) = U_{fg}(\rho)/\theta_f$, where $U_{fg}(\rho)$ is the rate of jump of molecules from the cell f into the empty cell g at the distance ρ. As follows from the ratio of dimensionalities, the mean thermal velocity of motion of molecules is $w_{fg} = \rho U_{fg}(\rho)/\theta_f$.

The transition state model developed by Eyring[20] is used for the calculation of the rate of particle jump. In this model, the shear of molecules is considered as an activation process needed to surmount an energy barrier. In nonideal reaction systems, the barrier is created by potentials of adjacent particles and the solid sur-

face.[21–23] For the simplest case of the jump into the nearest neighboring cells at ρ = 1 in the nonuniform lattice system that exists at the state of equilibrium the $U_{fg}(\rho)$ value is described by the following formula:

$$U_{fg} = k_{fg}V_{fg},\ k_{fg} = F^*\exp(-\beta E_{fg})/(\beta hF),\ V_{fg} = \theta_{fg}^{Av}T_{fg}, \quad (2)$$
$$\theta_{fg}^{Av} = \theta_{fg(1)}{}^{Av},\ T_{fg} = \prod_{\xi\in z_f-1} S_{f\xi}^{A} \prod_{\xi\in z_g-1} S_{g\xi}^{v},$$

where k_{fg} is the rate constant of jump of a particle from the cell f to an empty cell g at the distance ρ in the vacated lattice; F^* and F are the statistical sums of the states of particles in the transition and ground states, respectively; E_{fg} is the activation energy of jump ($E_{fg} = 0$ for cells remote from the pore wall and $E_{fg} \neq 0$ near the walls with the adsorption potential); and h is Planck's constant. The concentration relationship of the migration rate of a molecule is expressed by the cofactor V_{fg}, which, in turn, consists of the cofactors θ_{fg}^{Av} and T_{fg} (The cofactor θ_{fg}^{Av} reflects a probability of the adjacent cell to be vacated, and the cofactor T_{fg} takes into account the influence of interactions of molecules surrounding the central particle A and present in the adjacent empty cell). The cofactor $S_{f\xi}^{A} = 1 + t_{f\xi}x^*$ in T_{fg} relates to $(z - 1)$ nearest neighbors ξ of molecule A, which exists in the initial state in cell f (cell g is excluded), and the cofactor $S_{g\zeta}^{v} = 1 + t_{g\zeta}{}^{vA}y^*$ is attributed to the neighbors of the empty cell. Here $x^* = \exp[\beta(\varepsilon^* - \varepsilon)] - 1$, $y^* = \exp(\beta\varepsilon^*) - 1$, where ε^* is the energy parameter of the interaction of particles in the transition and ground states. The dimensionless parameter $\alpha = \varepsilon^*/\varepsilon$ was used in calculations.

In the absence of lateral interactions, formula (2) takes the form $U_{fg} = k_{fg}\theta_f(1 - \theta_g)$. When a particle is far from the pore walls the F/F^* ratio corresponds to the translatory degree of freedom in the direction of particle motion and equals $(2\pi m\beta^{-1})^{1/2}\rho/h$, where m is the weight of the molecule. Then the rate constant of jump in the bulk phase can be expressed as $k_\rho = (2\pi m\beta\rho)^{-1}$ or $w/4\rho$ containing the well-known velocity of thermal motion of molecules in the gas phase $w = (8/\pi m\beta)^{1/2}$ (see Ref. 24).

Knowing the jump rates U_{fg}, one can calculate coefficients of self-diffusion and shear viscosity.

Coefficient of self-diffusion

It follows from the equations derived for the calculation of coefficients of self-diffusion in nonuniform media[12,21,22] that the coefficient of self-diffusion depends on the direction of particle motion. The expression for the local coefficient of self-diffusion, which characterizes the redistribution of molecules between adjacent cells, has the form

$$D_{fg}^* = z_{fg}^* U_{fg}/\theta_f, \quad (3)$$

where z_{fg}^* is the number of possible jumps of the particle from the cell f into adjacent cells at the distance ρ. The averaged parameter of motion of "labeled" (for example, isotopic) molecules along the pore axis is the coefficient of self-diffusion described by the expression

$$D^* = \lambda^2 \sum_{q=1}^{t} F_q \sum_{p=1}^{t} z_{qp}U_{qp}/\theta_q \frac{d\theta_q^*}{d\theta^*}, \quad (4)$$

where z_{qp} is the number of bonds of the cells in the layer q with adjacent cells in the layer p, $d\theta_q^*/d\theta^* = d\theta_q/d\theta$. All possible jumps of the migrating molecule to adjacent cells of different types are taken into account in this expression. Averaging was performed by the contributions from both cells into which the migrating molecule jumps (cell of the p type) and cells from which it migrates (cell of the q type) to the overall flow of molecules. Rate constants of jumps for different cells obey the condition that a deepening in the energy well decreases a probability of ejection of the particle from this well. The relation between the rate constants of jumps and local Henry's constants is described by the equation $a_q{}^i k_{qp}{}^{iv} = a_p{}^i k_{pq}{}^{iv}$, where $a_q{}^i = a_q{}^{0i}\exp(\beta Q_q{}^i)$ is taken into account.

Coefficients of self-diffusion were calculated for several values of the dimensionless parameter $\alpha_{11} = E_{11}/Q_1$, which characterizes the ratio of the activation barrier of the surface migration of the molecule to the bond energy of the molecule with the surface ($E_{12} = Q_1$, others $E_{qp} = 0$). The first figure in the subscript designates the number of the layer from which the motion begins, and indices 11, 22, 33, *etc.* indicate the migration over the layer. If the second figure differs from the first figure, this indicates the transportation from layer into layer, *e.g.*, 12. All concentration curves presented below were plotted in the normalized form. Normalization was performed to the corresponding values of coefficients of self-diffusion at θ = 0 and $Q_1 = 0$.

Figure 2 presents the plots of the local coefficients of self-diffusion for argon *vs.* degree of filling of the graphite pore with the width $H = 6$ and 18 monolayers and their average values over the pore cross sections. At $f = g$ the curves show the motion of atoms inside the layer, and at $f \neq g$ they show the motion of atoms between the layers. Curve *1* corresponds to the motion of Ar atoms along the pore surface when they cross the activation barrier with the height E_{11}. At low fillings curve *1* lies above curve *2* because for the transition from the first layer into the second layer the barrier $E_{12} > E_{11}$ has to be crossed. However, with filling of the first monolayer (at θ > 0.4) the fraction of empty cells, which provide a possibility of argon motion, decreases sharply, and the transition of the atom into the second layer becomes more favorable (curve *2* lies above curve *1*). For the transition from the second layer to the first layer an activation barrier does not need to be crossed, and the decrease in D^*_{21} (curve *3*) is also explained by the filling of the surface monolayer. The coefficients of self-diffusion of argon in the second and third layers (curves *4*

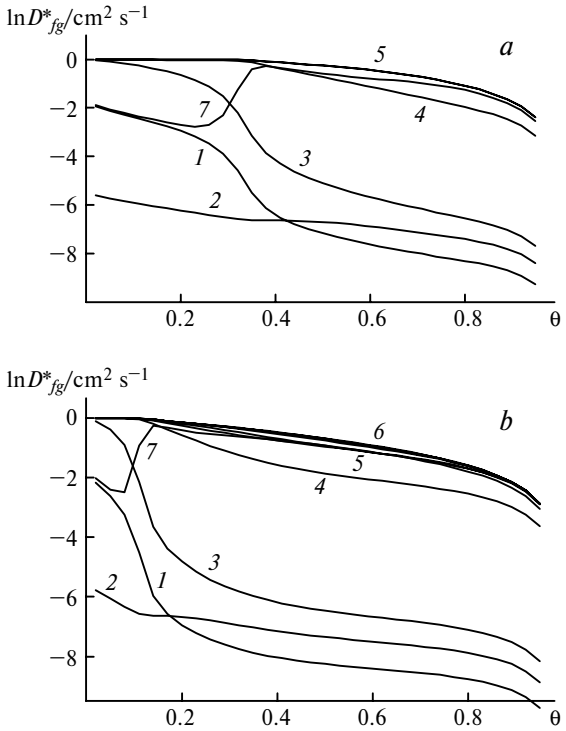

Fig. 2. Coefficients of self-diffusion of argon in slit-like graphite pores with the width $H = 6$ (*a*) and 18 (*b*) of monolayers at $\alpha = 0.5$, $\alpha_{11} = 0.333$. *a*, curves correspond to the local D^*_{fg} values of the following pairs of adjacent layers *fg*: 11 (*1*), 12 (*2*), 21 (*3*), 22 (*4*), 33 (*5*), 99 (*6*), and curve *7* represents the mean value of D^*.

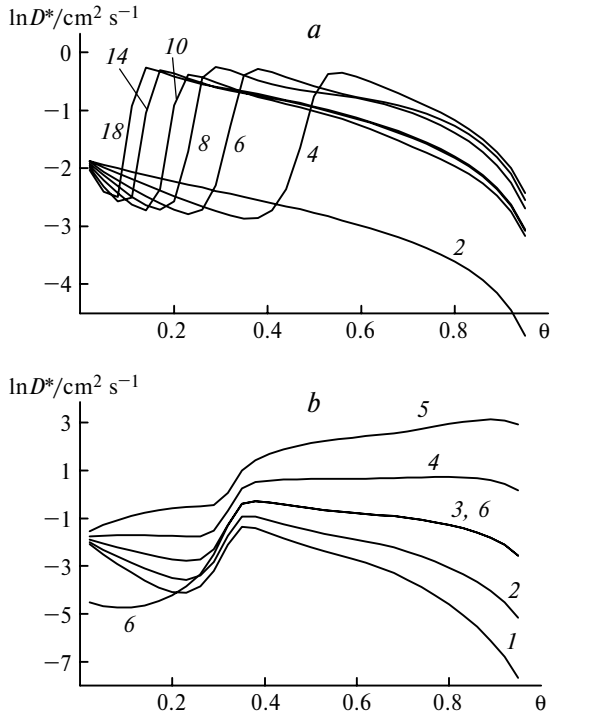

Fig. 3. Concentration relationships of mean normalized values of coefficients of self-diffusion of argon D^*: *a*, in pores with different widths (numbers of curves correspond to the pore width expressed as a number of monolayers); *b*, in pores with a width of 6 monolayers at $\alpha = -0.5$ (*1*), 0.0 (*2*), 0.5 (*3*, *6*), 1.0 (*4*), 1.5 (*5*), and $\alpha_{11} = 0.33$ (*1*—*5*) or 1.33 (*6*).

and *5*) change slightly at low fillings and somewhat decrease with further pore filling. These values are rather close even at high degrees of filling.

Figure 2, *b* shows similar curves for the pore with a width of 18 monolayers. Almost all coefficients of self-diffusion in the third and subsequent layers (see Fig. 2, curves *5* and *6*) have the same values: the influence of the pore volume in these layers is weak and the coefficient values are close to those in the bulk at the corresponding concentrations of argon.

The nonmonotonic character of changing the average values of coefficients of self-diffusion calculated using formula (4) (curve *6* in Fig. 2, *a* and curve *7* in Fig. 2, *b*) is explained as follows. Initially the D^* value decreases due to the filling of the surface monolayer, which provides the main contribution to this value at low gas densities, and then the motion of Ar atoms in the second and subsequent layers becomes more favorable and that increases D^*. Finally, at high degrees of filling when the fraction of empty cells is low, the D^* coefficient decreases monotonically. Pores with any width are characterized by these regularities (Fig. 3, *a*) (here $\alpha = 0.5$, $\alpha_{11} = 0.333$). The case of $H = 2$ is special because all cells are filled in the same manner and D^* decreases monotonically in the whole region of θ.

The concentration plots of the D^* values for pores with medium cross sections at different molecular parameters of the adsorption system are presented in Fig. 3, *b*. Curves *1*—*5* were obtained varying the α parameter, which characterizes the interactions of Ar atoms in the transition and ground states (at $\alpha_{11} = 0.333$). The calculations show that these interactions substantially affect the numerical values of coefficients of self-diffusion. The stronger the mutual attraction of Ar atoms in the transition state, the higher the D^* value. However, in all cases, the interaction with the pore wall makes a substantial contribution, and an increase in θ results in a decrease in D^*.

The increase in the activation barrier of the surface migration (see Fig. 3, *b*, curve *6*) sharply decreases the coefficient of self-diffusion at low densities. However, with filling of the surface monolayer the influence of the wall potential decreases and the coefficients of self-diffusion in subsequent layers become virtually independent of the properties of the wall.

Coefficient of shear viscosity

Shear viscosity was calculated using the modified model, which allows the extension of the Eyring model[20] over the whole interval of densities of the fluid. The initial Eyring model, which assumed the cellular structure of the liquid phase (without vacancies), correctly describes the temperature relationship of the shear vis-

cosity of the liquid but it is not applicable to rarefied fluids. The lattice-gas model is considered instead of the cellular structure in the modified Eyring model.[25] The viscosity coefficient of the gas η_{fg} corresponding to the shear of the fluid in the cell g relative to the cell f is described by the expression

$$\eta_{fg} = \eta_0\theta_f\exp(\beta E_{fg})/V_{fg}, \quad (5)$$

where $\eta_0 = (mkT/\pi)^{1/2}/(\pi\sigma^2)$ is the viscosity of the ideal rarefied gas, m is the mass of the atom, and σ is the diameter of the molecule. At low densities the viscosity depends linearly on the pore filling as in the case of the ideal gas, and with increasing θ the ratio of the ε and ε^* parameters begin to influence the pattern of the $\eta(\theta)$ curve. At low densities viscosity η is a function of the $T^{1/2}$ value, whereas at high densities it depends exponentially on the temperatures as in the traditional Eyring model.[20] The volume viscosities calculated using formula (5) (at $E_{fg} = 0$) for several gases (Ar, He, H_2, N_2, NH_3, CO_2) coincide well with experimental data.[26,27]

Coefficients of viscosity were calculated at the same molecular parameters that were used for the estimation of coefficients of self-diffusion. As in the previous Section, the concentration plots were normalized to the corresponding values of coefficients of viscosity at $\theta = 0$ and $Q_1 = 0$. Figure 4, *a* presents the layer coefficients of shear viscosity of argon in a pore with the width $H = 8$. As the layer moves away from the pore wall, the coefficients of viscosity η_{qq} decreases, whereas they increase monotonically with an increase in the degree of pore filling. The concentration of the adsorbate has the strongest effect on the viscosity in the surface layer, and the effect is weakest on the viscosity of the layer arranged in the center of the pore.

The influence of the pore width on the viscosity in the surface layer and in the layer in the center of the pore is seen in Fig. 4, *b*. The viscosity of the adsorbate in the central layer depends rather weakly on the pore width, although its influence cannot completely be neglected. The viscosity in the surface layer at the unchanged θ increases with an increase in the pore width H because at θ = const a better filling of the surface layer θ_1 is achieved. Figure 4, *c* shows the influence of the molecular parameters of the adsorption system on the viscosity of the adsorbate in the surface layer. Curves in Fig. 4, *c* can be considered as inverse to curves for the coefficient of self-diffusion (see Fig. 3, *b*). An increase in the activation barrier of argon migration along the surface increases the viscosity of the adsorbate in the surface layer, while an increase in the mobility of atoms decreases it.

The method for calculation of concentration characteristics of the transfer parameters of compact adsorbates in narrow pores described above is based on the concept that the local rates of molecules are at equilibrium. This approach is justified only in the case of sufficiently high densities of the adsorbate: it is applicable to liquid-like systems[18,19] in the interval

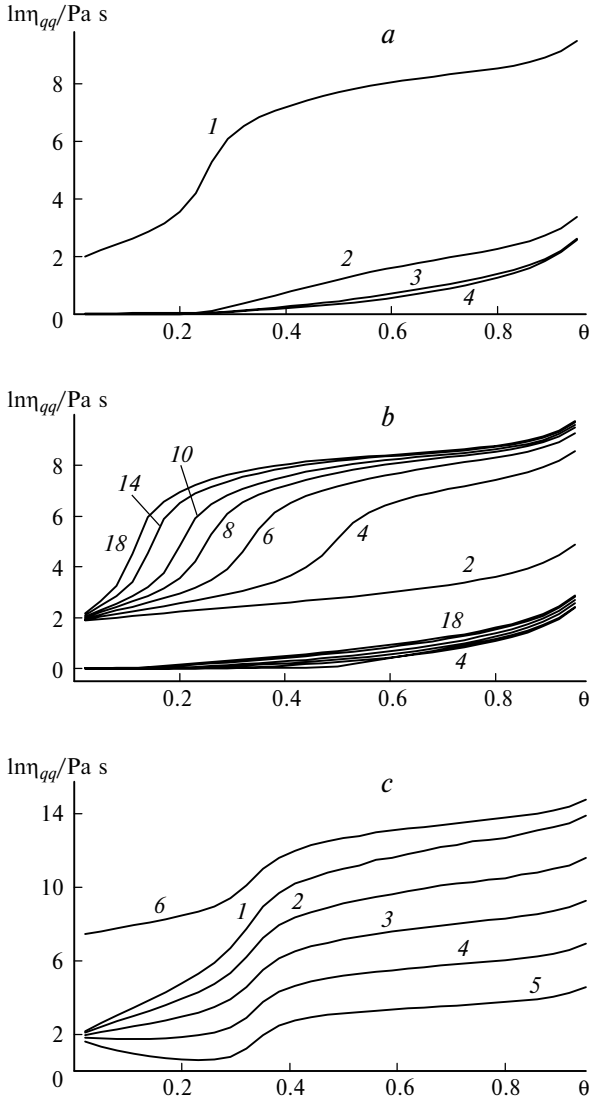

Fig. 4. *a*, Concentration relationships of local normalized coefficients of shear viscosity of argon η_{qq} at $H = 8$, $\alpha = 0.5$, $\alpha_{11} = 0.33$, $Q_1 = 9.24\varepsilon$. Numbers of curves correspond to the numbers of layers (beginning from the pore wall); *b*, concentration relationships of argon in the surface layer (upper group of curves *2—18*) and in the central layer (bottom group of curves *4—18*) at different pore widths. Number of curves correspond to the pore width expressed as a number of monolayers; *c*, influence of molecular parameters of the adsorbate on the fluid viscosity in the surface layer of the pore with a width of 6 monolayers (for numbers of curves and parameters, see Fig. 3, *b*).

$(0.01—0.03) < \theta < 1.0$. However, at $\theta < 0.01$ this model needs to be refined. Nevertheless, the following estimation indicates the important role of the width. It follows from the elementary kinetic theory of gases[24] that in pores with the width to 7.0 nm the collision frequency of Ar atoms with the walls is by approximately two orders of magnitude higher than the frequency of their collisions between each other in the gas phase (at 300 K

and a pressure of 1 atm). This implies that in narrow pores the effective density of the rarefied system is by two orders of magnitude higher than that in the gas volume. Correspondingly, the equilibrium is more rapidly established in narrow pores due to various collisions. Therefore, this model provides a reasonable estimation of dynamic characteristics, although it ignores effects associated with the dispersion of the rate of molecules.

Our calculations show that the dynamic characteristics of the adsorbate depend strongly on the anisotropic distribution of molecules over the cross section of the slit-like pore. Coefficients of self-diffusion and shear viscosity change especially strongly near the pore walls. In the center of the pore these values depend on the contribution of the potential of the wall and the total concentration of the adsorbate. It follows from the results obtained that traditional assumptions about the constant character of coefficients of self-diffusion[1,4] and shear viscosity[2] are not valid in the general case. Analyzing experimental data, one should take into account a relatively strong concentration relationship of the dynamic characteristics of the adsorbate in narrow pores resulted from both the influence of the potential of the pore walls and the intermolecular interactions.

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