Journal of Engineering Physics and Thermophysics, Vol. 79, No. 1, 2006

VISCOSITY OF A BINARY FLUID IN NARROW SLOT-LIKE PORES

Yu. K. Tovbin, E. E. Gvozdeva,
and L. K. Zhidkova

UDC 533.7 + 541.183

The concentration dependences of the shear-viscosity coefficient of a fluid, representing a binary mixture of components with molecules of approximately equal sizes, in narrow slot-like pores filled to a different degree (from a rarefied gas to a liquid) have been theoretically investigated with the use of a lattice-gas model accounting for the characteristic volume of atoms and interactions between them in the quasichemical approximation. This model allows one to determine the self-consistent equilibrium characteristics of a vapor-liquid system and the shear-viscosity coefficients of molecules with the use of a unique set of energy parameters. The influence of the activation energy of the surface migration of molecules on the local coefficients of viscosity has been considered. A molecular interpretation of the sliding friction of a fluid near the walls of pores has been given; this effect was explained by the surface migration of the mixture components.

The transport of molecules in porous bodies determines the dynamic characteristics of gas and liquid flows in them. The sizes of the pores of disperse materials determine the catalytic, adsorption, and membrane processes occurring in them as well as the processes of their cleaning, wetting, impregnation, and drying [1–6]. The maximum width of narrow pores is equal to ~10 nm for a short-range, nonspecific, Lennard-Jones interaction potential between molecules (6–12), which corresponds to 25–30 monolayers [7–9]. This value was obtained from analysis of the conditions under which the surface potential influences the capillary condensation (for a long-range interaction potential, it increases with increase in the radius of the potential).

In a narrow pore, the surface potential significantly influences the mobility of molecules and their distribution over the cross section of the pore. All transport characteristics of an adsorbate in such pores differ from those in the bulk of vapor and liquid phases. Among the most important dynamic characteristics of a substance is its shear viscosity. It should be noted that the Navier–Stokes equation cannot be used for narrow pores. In this case, kinetic transport equations for condensed media should be used. For organization and simulation of flows in narrow pores, it is necessary to know the transport characteristics of the system of these pores at the molecular level. In [10, 11], a new molecular approach to representation of flows in narrow pores of one-component fluids with densities and temperatures varying in wide ranges has been proposed. It is based on the simplest molecular model of condensed media — the lattice-gas model that accounts for the characteristic volume of molecules and their interaction with each other [12, 13]. This model can be used for fluids with concentrations changing in a wide range (from the gaseous to the liquid state) at widely varying temperatures, including the critical one, which allows one to investigate the dynamics of a fluid flow in the case of capillary condensation. Closed equations and expressions for the transport coefficient were constructed using the quasichemical approximation with account for the intermolecular interactions and short-range effects.

The processes occurring in mixtures of gases and liquids are very complex, which makes the study of the concentration dependences of the transfer coefficients in narrow pores of dense gas and liquid mixtures difficult. In the present work, we attempted to investigate the concentration dependences of the shear-viscosity coefficients of a binary mixture in narrow pores filled to a different degree (from dense gases to liquids) with the use of the lattice-gas model [12]. Investigations on generalization of the equations for a one-component fluid to multicomponent mixtures were begun in [14].

A new approach takes a much shorter time for its realization and provides a good agreement with molecular-dynamic calculations of the self-diffusion in one-component fluids [15–17]. The phase diagrams constructed for one-

---

L. Ya. Karpov Physicochemical Scientific-Research Institute, 10 Vorontsovo Pole Str., Moscow, 105064, Russia; email: tovbin@cc.nifhi.ac.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 79, No. 1, pp. 121–132, January–February, 2006. Original article submitted October 13, 2004.

component, narrow-pore fluids with the use of the indicated model agree well with the diagrams obtained in [18, 19] when the viscosity coefficients of these fluids [20] are determined by the Monte Carlo method and the method of molecular dynamics. To calculate the shear viscosity of a mixture in a pore, it is necessary to know the equilibrium local distributions of mixture components in the cross section of the pore, which depends substantially on the adsorbent–adsorbate interaction potential and the width of the pore.

Qualitative analysis of the dependence of the viscosity of a binary mixture on its concentration was performed, as in [14], on the assumption that the molecules of the mixture components have a spherical form and approximately equal sizes. Strictly speaking, this assumption limits the application of the results obtained only to isotopic mixtures because different molecules have different sizes. However, this approximation allows one to obtain valid results for mixtures of molecules with close sizes and, therefore, can be used for solid solutions [21, 22] (even though the lattice-gas model is suitable for mixtures of different-size molecules).

In the present work, we theoretically investigated the concentration dependences of the shear-viscosity coefficients of molecules of different binary mixtures with pores filled to a different degree (from a rarefied gas to a liquid) and considered the role of the interaction potential between a molecule and the wall of a slot-like pore and the molecular nature of the sliding friction of a fluid near the wall of this pore.

Model. In the lattice-gas model [14, 23], the volume of a slot-like pore V_{p} is divided into monoatomic layers of linear size (width) λ parallel to the wall of the pore. Each layer is divided into cells (adsorption centers or sites) with a volume equal to the volume of a particle $v_0 = \lambda^3$, which excludes their double filling with different molecules. In this case, $V_{\text{p}} = Nv_0$. The number of nearest lattice sites will be denoted by z. Only one particle can be located at each site: an i-type (ith) molecule (with a center of mass located inside a cell) or a vacancy v. The index i denotes the number of a mixture component. The number of different occupation states of any site of a system will be denoted by the index s, i.e., the number of components will be equal to $s - 1$.

It is usually assumed that the concentration of molecules is equal to the number of these molecules N_i in a unit volume: $C_i = N_i/V_{\text{p}}$. In the lattice-gas model, the concentration of a component of a fluid is characterized by the quantity $\theta_i = N_i/N$, equal to the ratio between the number of actual particles in any volume and the maximum possible number of close-packed particles in the same volume. Then $\theta_i = C_i v_0$. The local density of ith particles in a cell itemized under No. f (fth cell) will be denoted by θ_f^i and it will be assumed that $\sum_{i=1}^{s-1} \theta_f^i + \theta_f^{\text{v}} = 1$. The average partial concentration of the fluid θ_i is determined through the local concentrations as $\theta_i = \sum_{f=1}^{N} F_f \theta_f^i / N$ and the average complete filling of a pore is determined as $\theta = \sum_{i=1}^{s-1} \theta_f^i$. By the symbol $\{P\} \equiv P_1, \ldots, P_{s-1}$, we will denote the total set of partial pressures of mixture components P_i, $1 \le i \le s - 1$.

Each fth cell is characterized by the energy of interaction Q_f^i of ith molecules with its walls and by the Henry constant a_f^i, by which the lattice sites can be divided into groups with equal properties. The number of such groups will be denoted by t. If the walls of a chink-like pore are uniform, all sites of one layer are equivalent; therefore, the number of an fth layer is identical to the number of the site found in it. For an even number of monolayers, $t = H/2$, and $t = (H + 1)/2$ for an odd number of monolayers. The local Henry constant $a_f^i = a_f^{i0} \exp(\beta Q_f^i)$, where $a_f^{i0} = \beta F_i/F_i^0$; $Q_f^i = u_i(f) + u_i(H - f + 1)$, $1 \le f \le t$; $u_i(f) = \varepsilon_i/f^3$ for the part of the Mie potential (3–9) accounting for attraction [24]. The fraction of sites F_f in an fth layer is equal to $2/H$ for an even H and an odd H at $1 \le f \le t - 1$, and $F_f = 1/H$ at $f = t$. The normalizing condition for sites of different types has the form $\sum_{f=1}^{t} F_f = 1$.

To calculate the average partial adsorption isotherms $\theta_i(\{P\})$ and local fillings $\theta_f^i(\{P\})$ of different adsorption centers, we used the system of equations derived in [14, 23], in which the energy inhomogeneity of lattice sites and the interaction between molecules are taken into account:

$$\theta_i(\{P\}) = \sum_{f=1}^{t} F_f \theta_f^i(\{P\}), \quad a_f^i P_i = \theta_f^i \Lambda_f^i / \theta_f^{\mathrm{v}}, \tag{1}$$

$$\Lambda_f^i = \prod_r \prod_g \left(1 + \sum_{j=1}^{s-1} x_{fg}^{ij}(r)\, t_{fg}^{ij}(r) \right)^{z_{fg}(r)}, \quad x_{fg}^{ij}(r) = \exp(-\beta\varepsilon_{fg}^{ij}(r)) - 1,$$

where the function Λ_f^i is calculated in the quasichemical approximation. In formulas (1), allowance is made for the layer distribution of different sites in slot-like pores. It is assumed that the parameter $\varepsilon_{fg}^{ij}(r)$ of lateral interaction between the ith and jth neighboring molecules separated by a distance equal to the radius r of a coordination sphere is a function of the temperature and the local composition of the substance around the fth and gth sites and that the interactions with vacancies (i, $j = s$) are equal to zero. The index g takes values corresponding to all neighbors $z_f(r)$ located at a distance $r \leq R_{\mathrm{m}}$ from the fth site inside a pore.

The function $t_{fg}^{ij} = \theta_{fg}^{ij}(r)/\theta_f^i$ defines the conditional probability that the central ith particle from an fth site is separated from the neighboring jth particle from a gth site by a distance r; the function $\theta_{fg}^{ij}(r)$ defines the analogous total probability. For them, the equations $\theta_{fg}^{ij}(r)\theta_{fg}^{ss}(r) = \theta_{fg}^{is}(r)\theta_{fg}^{sj}(r) \exp[-\beta\varepsilon_{fg}^{ij}(r)]$ are true. These equations are solved with regard for the following normalizing relations: $\sum_{j=1}^{s} \theta_{fg}^{ij}(r) = \theta_f^i$, $\sum_{i=1}^{s} \theta_{fg}^{ij}(r) = \theta_g^j$, and $\sum_{i=1}^{s} \theta_f^i = 1$. The equilibrium distribution of particles over different sites θ_f^i was determined from the system of equations (1) by the Newton iteration method at a given set of $\{\theta\}$ or $\{P\}$ values. The accuracy of solving system (1) is not less than 0.1%.

Calculations were carried out for slot-like pores with walls consisting of graphite atoms. One of the components of the mixture was argon with constant parameters ($Q_1^1 = 9.24\varepsilon_{\mathrm{ArAr}}$ at $\varepsilon_{\mathrm{ArAr}}/k = 119$ K), and the properties of the other component were varied; to the krypton atoms corresponds $Q_1^2 = 12.17\varepsilon_{\mathrm{ArKr}}$ [24, 25]. The lateral interactions were determined using the Lennard-Jones potential: $\varepsilon_{ij} = 4\varepsilon_{ij}^0[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6]$ at $r/\sigma_{ij} = 2^{1/6}$, which corresponds to the minimum of this potential. The parameter of interaction between particles of different types was assumed to be equal to $\varepsilon_{12} = (\varepsilon_{11}^0\varepsilon_{22}^0)^{1/2}$. The width of a pore changed from 3 to 25 monolayers. It was assumed that the radius of the adsorbate–adsorbent interaction potential is equal to three and, therefore, sites are occupied equivalently, beginning with the fourth monolayer. The structure of a fluid was simulated by a lattice, in which the number of nearest neighbors was equal to 12.

The equilibrium characteristics of a binary mixture are presented in Fig. 1. Figure 1a and b presents local degrees of filling, with argon and krypton atoms, of different monolayers for five vapor compositions at a constant gross density of a mixture ($\theta = \theta_1 + \theta_2 = 0.25$ and 0.75). The calculations were performed for different molar fractions of the second component $\gamma = P_2/P$ (here, $P = P_1 + P_2$); the numbers of monolayers are plotted on the abscissa. Figure 1c and d presents the average partial isotherms for different molar compositions γ of the mixture and different values of the pore width H.

Since the walls of a slot-like pore are identical, the curves of distribution of the mixture components over the cross section of the pore, shown in Fig. 1a and b, are symmetric relative to its center. Figure 1a corresponds to the case where the total occupation is relatively small ($\theta = 0.25$): both components are concentrated near the walls and the central part of the pore is occupied to a much smaller degree. Krypton atoms are attracted more strongly; therefore, in the absence of argon, their concentration in the surface layer is higher (curve 5) than the concentration of the pure argon (curve 1). As the fraction of the second component γ increases, the concentration of the first component near the wall decreases and the concentration of the second component increases. The potential of the wall influences three

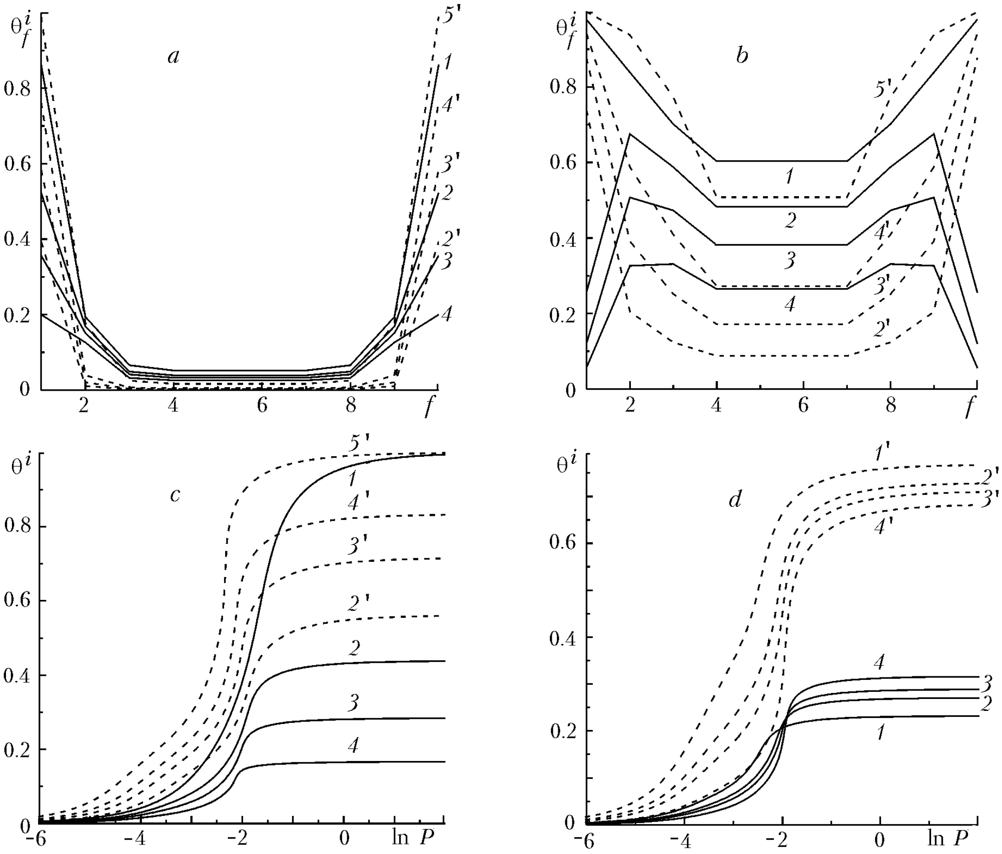

Fig. 1. Equilibrium characteristics of adsorption $\theta_f^i(P)$ of argon atoms (i = 1) and krypton atoms (i = 2) in a symmetric slot-like graphite pore of width ten monolayers ($1 \leq f \leq 10$) obtained for five vapor compositions: γ = 0 (1), 0.333 (2), 0.5 (3), 0.666 (4), and 1.0 (5); 1–4) argon; 1′–5′ krypton; a) distribution of mixture components over the cross section of a pore at θ = 0.25 (curve number corresponds to variant γ); b) distribution of mixture components at θ = 0.75; c) average partial isotherms $\theta^i(P)$ of argon and krypton as functions of the total vapor pressure P for vapor mixtures of different composition γ; d) average partial isotherms of argon and krypton as functions of the total vapor pressure P for pores of different width (H = 5. 8, 11, and 25 monolayers).

monolayers, and the contribution of this potential to the filling of the fourth and fifth monolayers is small. All curves have a similar shape with a minimum concentration at the center of the pore.

In the case where a larger volume of a pore is filled (θ = 0.75), the distribution of the mixture components is more complex. The concentration of the pure components (curves 1 and 5′) is minimum at the center of the pore. However, in this case, the concentration of the components at the center of the pore differs from their surface concentration by a much smaller value. As in the previous case, the potential of the wall influences three monolayers on each side of the pore. Krypton, introduced into mixtures, accumulates predominantly near the wall. It displaces argon from the surface layer; therefore, the distribution of argon over the cross section of the pore has maxima in the region of the second or third monolayers, while the krypton distribution in layers decreases monotonically from the wall to the center of the pore (as in Fig. 1a).

The degree of filling of each monolayer increases with increase in the total pressure (Fig. 1c). The surface monolayers are filled first, and then the second, third, and other layers are filled (the counting is done from the wall of the pore). Since the attraction of krypton is stronger, all of its partial isotherms are shifted toward smaller values of the total pressure as compared to the partial isotherms of argon. The influence of the width of a slot-like pore on the average partial isotherms of the mixture components is demonstrated in Fig. 1d. The partial degrees of filling are plotted against the total gas pressure P at $\gamma = 0.5$. The smaller the value of H, the larger the rate of filling of the pore because of the influence of the attractive potential of the wall. A further increase in the width of the pore weakly influences the conditions of filling of its central part, on which the potential of the lattice does not have any influence. In all cases, the degree of filling with krypton is larger than the degree of filling with argon.

Knowledge of the equilibrium distributions of the components of a molecular mixture is of great importance in investigating the dynamics of various processes, in particular for analysis of its shear viscosity.

Thermal Rate of Molecular Motion. Since the local densities of molecules are distributed very inhomogeneously over the cross section of a slot in the case where the molecules are strongly attracted to its walls, it is necessary that the representation of the molecular motion in the rarefied vapor regions in the central part of the pore agree with the representation of the molecular motion in the dense liquid regions near the walls of the pore. Under these conditions, it is difficult to use the mean free path of molecules, because this quantity for the liquid and vapor phases can differ by four orders of magnitude. In the lattice model, instead of the mean free path, the probability of jump $W_i(\rho)$ of an ith molecule for a distance ρ is used: $W_i(\rho) = U^i_{fg}(\rho)/\theta^i_f$. The mean thermal velocity of travel of molecules is determined as $w^i_{fg} = \rho U^i_{fg}(\rho)/\theta^i_f$.

To calculate the rate of jump of a particle, we used the Eyring transient-state model [26], in which molecules shift as a result of the activation process of overcoming a potential barrier. Such a model for nonideal reaction systems, where a barrier is formed by the potentials of neighboring particles and the surface of a solid body, is described in [12, 27–29]. At the state of equilibrium, the quantity U^i_{fg} is equal to

$$U^i_{fg}(\rho) = K^{i\nu}_{fg}(\rho)\, V^{i\nu}_{fg}(\rho)\,, \quad V^{i\nu}_{fg}(\rho) = \theta^{i\nu}_{fg}(\rho)\, \Lambda^i_{fg}(\rho)\,, \quad \theta^{i\nu}_{fg}(\rho) = \theta^{i\nu}_{fg(1)}(1) \prod_{\xi} t^{\nu\nu}_{\xi\xi+1}(1)\,, \tag{2}$$

where $K^{i\nu}_{fg}(\rho) = (8/(\pi m_i \beta))^{1/2} \exp\,[-\beta E^{i\nu}_{fg}(\rho)]/4\rho$. The quantity $E^{i\nu}_{fg}(\rho)$ differs from zero (for the cells located at a large distance from the wall of the pore, $E^{i\nu}_{fg}(\rho) = 0$).

The concentration dependence of the rate of molecule migration is determined by the cofactor $V^{i\nu}_{fg}(\rho)$, which accounts for (1) the probability of realization of a free path $\theta^{i\nu}_{fg}(\rho)$ from an fth cell to a gth cell of length ρ (to avoid its blocking by other molecules) and (2) the influence of the lateral interactions of the neighboring molecules located around this path on the probability of a jump along it (these interactions are determined by the nonideality function of the system $\Lambda^i_{fg}(\rho)$). The function $\theta^{i\nu}_{fg}(\rho)$ is expressed in terms of the probabilities of realization of the sequence of free cells $g(1)$, $g(2)$, ... , $g \equiv g(\rho)$ forming a given path. The number of cofactors for ξ is equal to $(\rho - 1)$. (For $\rho = 1$, the cell $g(1)$ is finite.) The function $\Lambda^i_{fg}(\rho)$ has the form [12, 27–29]

$$\Lambda^{i\nu}_{fg}(\rho) = \prod_{r=1}^{R} \prod_{\omega_r=1}^{\pi_r} \prod_{h \in m(\omega_r)} \sum_{j=1}^{\nu} \frac{\theta^{ij}_{fh}(r_1)\, \theta^{\nu j}_{gh}(r_2)}{\theta^i_f\, \theta^\nu_g\, \theta^j_h}\, E^{i\nu j}_{fgh}(\omega_r)\,, \tag{3}$$

$$E^{i\nu j}_{fgh}(\omega_r) = \exp\left\{\beta\left[\delta\varepsilon^{ij}_{fh}(r_1) + \delta\varepsilon^{\nu j}_{gh}(r_2)\right]\right\}, \quad \delta\varepsilon^{ij}_{fh}(r) = \varepsilon^{*ij}_{fh}(r) - \varepsilon^{ij}_{fh}(r)\,.$$

The dimensionless parameter $\alpha = \varepsilon^{*ij}_{fg}(r)/\varepsilon^{ij}_{fg}(r)$ was used in the calculations. The distance from an hth site to an fth site is equal to r_1 and the distance from an hth site to a gth site is equal to r_2. The symbol ω_r characterizes the position of an hth site through the angle formed by the line connecting a pair of "central" fth and gth sites and the line connecting the hth site with the center of the portion of the fg line positioned at a distance r from one of the two central fth and gth sites; $m(\omega_r)$ is a set of neighboring sites with fixed values of r and ω_r.

In the absence of lateral interactions, formula (2) has the form $U^i_{fg}(\rho) = K^{i\nu}_{fg}\theta^i_f(1 - \theta_g)^\rho$. Away from the walls of pores, the constant $K^{i\nu}_{fg}(\rho) = (8/\pi m_i \beta)^{1/2}$, i.e., it is the average thermal velocity of travel of molecules in the gas phase [30].

Shear-Viscosity Coefficient. The shear viscosity of a fluid was calculated using a modified model [10] constructed by extending the Eyring model [26] to the whole range of fluid densities. In the model obtained, formulas (2)

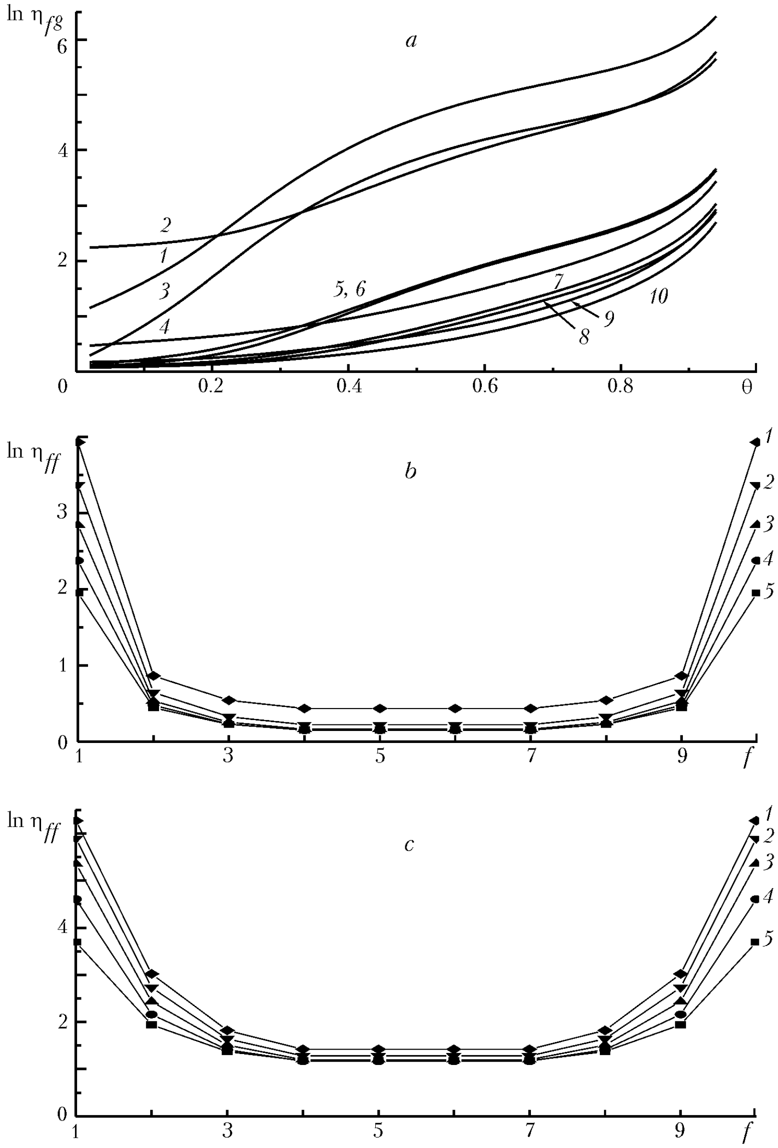

Fig. 2. Local coefficients of shear viscosity η_{fg} in a slot-like carbon pore of width ten monolayers: a) normalized concentration dependences of the coefficients η_{fg} of an equimolar mixture of argon and krypton ($X_{\mathrm{Ar}} = 0.5$) as functions of the total density of the mixture at $\alpha_{11} = 0.1$: the curves correspond to the following pairs of neighboring cells in layers: fg = 11 (1), 12 (2), 21 (3), 22 (4), 23 (5), 32 (6), 33 (7), 34 (8), 43 (9), and 55 (10); the profiles of the coefficients η_{ff} along the cross section of a pore at $\theta = 0.25$ (b) and 0.75 (c): X_{Ar} = 0 (1), 0.333 (2), 0.5 (3), 0.666 (4), and 1.0 (5).

and (3) are used. (Recall that the initial Eyring model, in which it is assumed that a liquid has a cellular structure free of vacancies, correctly defines the exponential dependence of the shear viscosity of a liquid on the temperature; however, this model cannot be used for rarefied fluids.) The shear viscosity coefficient of a mixture of spherical molecules η_{fg}, corresponding to a shift of the fluid in a gth cell relative to the fluid in an fth cell, is defined as

$$\eta_{fg} = \left[\sum_{j=1}^{s-1} x_j \left(\eta_{fg}^{j}\right)^{-1} \right]^{-1}, \quad \eta_{fg}^{j} = \theta_f^{j} / U_{fg}^{j}, \quad x_f^{i} = \theta_f^{j} / \theta_f, \quad \theta_f = \sum_{i=1}^{s-1} \theta_f^{i}. \qquad (4)$$

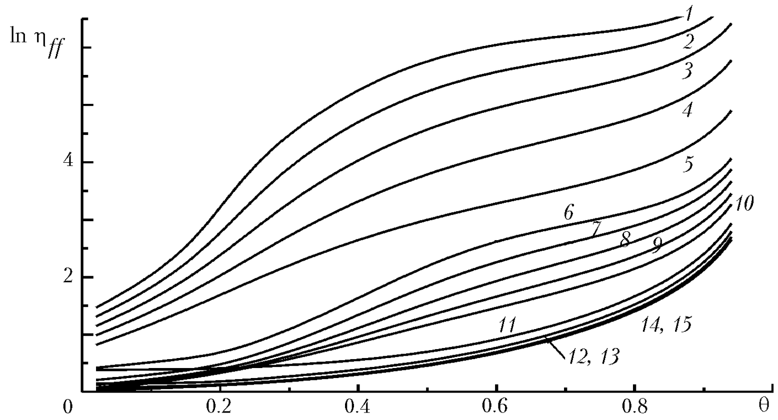

Fig. 3. Concentration dependences of the local viscosity coefficients of an argon–krypton mixture with a varying composition for the pairs of neighboring sites 11 (1–5), 22 (6–10), and 55 (11–55) in different monolayers of a graphite pore of width ten monolayers: $X_{\mathrm{Ar}} = 0$ (1, 6, 11), 0.25 (2, 7, 12), 0.50 (3, 8, 13), 0.75 (4, 9, 14), and 1.0 (5, 10, 15).

At small densities, this expression is transformed into the Wilke and Brokaw approximations [31] for locally inhomogeneous gas mixtures. For pure components, it shows that the quantity η depends on $T^{1/2}$ and linearly depends on the density; in the case of large densities, this quantity exponentially depends on the temperature as in the traditional Eyring model [26]. The indicated formula for pure components was tested in calculating the volume viscosities of the gases Ar, He, H_2, N_2, NH_3, and CO_2 [32, 33]; the data obtained were in good agreement with the experimental ones [34, 35].

It is seen from (4) that the viscosity of a fluid depends substantially on the local distributions of its components over the cross section of a pore and on the direction of its motion. The viscosity of flow-density fluids depends linearly on the degree of filling of the pores, as in the case of an ideal gas, and, when θ increases, the ratio between the quantities ε and ε^* begins to influence the dependence $\eta(\theta)$.

Calculations were performed for the simplest case of jumps of molecules for a distance $\rho = 1$ to the nearest neighboring cells. Below are given the concentration dependences of the shear-viscosity coefficient for the following molecular parameters: $H = 10\lambda$, $R = 1$, $\alpha = 0.6$, and $\alpha_{11} = E_{11}^{iv}(1)/Q_1^i = 0.1$ (this value corresponds to a small height of the activation barrier for surface jumps). The temperature of the system is equal to $T = 1.38T_{\mathrm{Ar}}^{\mathrm{c}}$, where $T_{\mathrm{Ar}}^{\mathrm{c}}$ is the critical temperature of the argon in a slot-like, argon–graphite pore of width H, which provides a one-phase state of the mixture in the pore in the case where argon is completely displaced by krypton (for which $T = 1.06T_{\mathrm{Kr}}^{\mathrm{c}}$). The value of the parameter α used corresponds to the experimental data [34, 35] on the shear-viscosity coefficient of argon, obtained for a wide range of its densities from a rarefied gas to a liquid. All the curves were normalized to the shear-viscosity coefficient of argon in the gas phase.

The concentration dependences of local shear-viscosity coefficients are shown in Fig. 2a for a slot-like pore of width 10 monolayers. They characterize the stagnation of a flow (dissipation of its momentum) passing through a pore; their values are substantially dependent on the direction of a local flow and the distance to the wall of the pore. The argon–carbon system is characterized by a fairly strong attraction of molecules to the walls of the pore. The position and shape of curves 1–3 in the near-wall region are determined by the quantities Q_1^1 and $E_{11}^{1\mathrm{v}}$ (through the ratio $\alpha_{11} = E_{11}^{1\mathrm{v}}/Q_1^1$). Curve 4 corresponds to the viscosity in the second layer. In the central region of the pore (curves 5–10), the viscosity increases as the pore is filled. It changes from the value corresponding to the gas phase to the value corresponding to the liquid phase (the concentration dependences were normalized to the corresponding value of η_0 for the bulk phase of argon at $\theta = 0$ and $Q_1^1 = 0$). The distributions of components over the layers were calculated for a definite fraction ($X_{\mathrm{Ar}} = 0.5$) of components in the pore (unlike the dependences in Fig. 1, obtained for definite fractions of components in the vapor phase γ). The calculations have shown that the viscosity of a fluid depends substantially on the local distributions of its components over the cross section of a pore and the direction of the fluid motion. The attractive potential of the wall of a pore influences the near-wall regions and, in doing so, increases the viscosity coefficient.

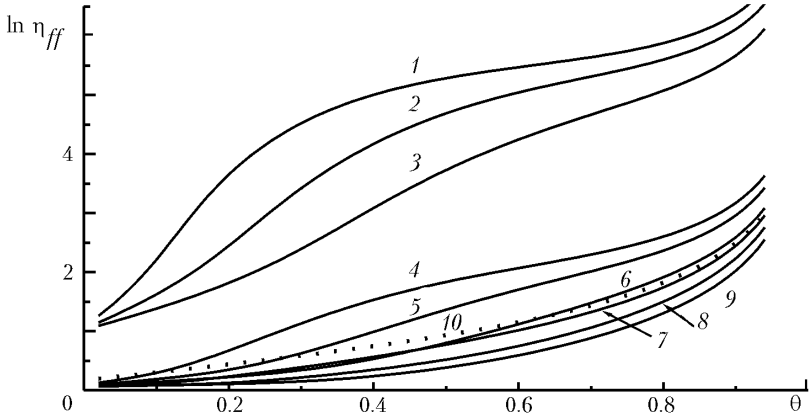

Fig. 4. Concentration dependences of the viscosity coefficients of an argon–krypton mixture at $X_{\mathrm{Ar}} = 0.5$ in the surface layer (η_{11}, curves 1–3), in the second near-surface layer (4–6), and at the center of a pore (η_{55}, curves 7–9) for pores of different width $H/\lambda = 20$ (1, 4, 7), 10 (2, 5, 8), and 6 (3, 6, 9); 10) bulk phase.

Figure 2b and c presents the profiles of the shear-viscosity coefficients of argon–krypton mixtures of different molar compositions in a pore of width $H = 10$ monolayers (corresponding to the profiles of the partial degrees of filling in Fig. 1). The coefficient η_{ff} decreases as the distance between a layer and the wall increases and increases monotonically with increase in the total degree of filling.

Figure 3 presents dependences of the local coefficients of viscosity of argon–krypton mixtures of different compositions in the first surface layer (curves 1–5), in the second near-surface layer (curves 6–10), and at the center of a carbon pore of width 10 monolayers (curves 11–15). When the fraction of argon decreases and the fraction of krypton increases, the viscosity of a mixture increases because the fractions of its components in the surface monolayer and at the center of the pore change. Of significant importance is the fact, demonstrated by the distributions of the concentrations of components in Fig. 1, that krypton displaces argon to the central part of the pore because it is adsorbed more strongly by the surface.

The influence of the width of a pore on the local viscosities in the first surface layer (curves 1–3), in the second near-surface layer (curves 4–6), and at the center of the pore (7–9) is shown in Fig. 4. For comparison, curve 10, corresponding to the volume viscosity of a mixture with an equimolecular composition $X_{\mathrm{Ar}} = 0.5$, is dotted. The general regularities obtained for a mixture of constant composition are close to the regularities obtained earlier for one-component fluids [36]. The shear viscosity of the adsorbate in the central layer depends relatively weakly on the width of a pore, even though the influence of this quantity cannot be completely ignored. The viscosity in the surface layer increases with increase in the pore width H. This is explained by the fact that the degree of filling of the surface layer θ_1 increases with increase in H at a constant total density of the mixture θ in a pore. (Recall that the results of calculations performed within the framework of the lattice-gas model considered are in good agreement with the analogous data on the concentrations distributions and the shear viscosity of one-component fluids in slot-like pores of width 4 and 18 monolayers [37], obtained using the method of nonequilibrium molecular dynamics and on the basis of the continual kinetic theory.)

The molecular approach [10, 11, 14] for calculating the shear viscosity of mixtures allows one to make a molecular interpretation of their sliding friction. The coefficient of sliding friction β_1 of mixtures is involved in hydrodynamical equations used for calculating the velocities of their flows near surfaces [38, 39]. Recall that the coefficient β_1 is determined from the ratio between the tangential force acting on a unit surface and the relative velocity of a flow near a solid wall: $\beta_1 u = -\eta \partial u/\partial r\big|_{r=R}$. The ratio $\eta/\beta_1 = \lambda$ has the dimensions of length.

It was noted in [36] that the coefficient of sliding friction can be determined on the basis of the experimentally verified molecular notions on the surface mobility of molecules and surface flows [2, 5]. The results of calculation of the contributions of the "surface" and "volume" transport of molecules to the common flow of labeled molecules along the axis of a pore (in the absence of a hydrodynamic flow) presented in [20] point to the fact that

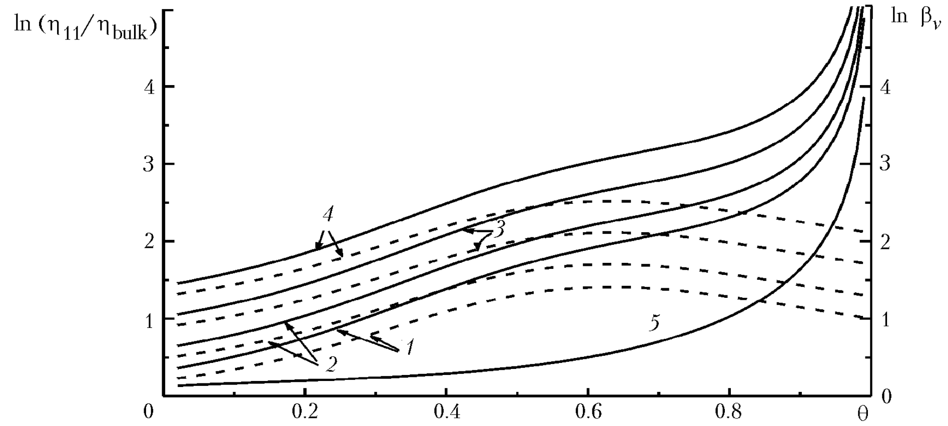

Fig. 5. Influence of the activation energy of the surface molecule migration on the viscosity of the surface layer η_{11} at $X_{\text{Ar}} = 0.5$ and $\alpha = 0.60$: $\alpha_{11} = E_{11}^{iv}/Q_1^i = 0.1$ (1), 0.333 (2), 0.666 (3), and 1.0 (4) (solid lines); curve 5 corresponds to the shear-viscosity coefficient η_{55} at the center of a pore; curves 1–4 (dashed) represent the corresponding ratios η_{11}/η_{55} (right-hand axis).

the surface mobility of molecules plays an important role in their thermal motion characterized by the self-diffusion coefficient. The surface flow of molecules is predominant in the case where molecules are strongly attracted to the walls of a pore and the density of the fluid filling the pore is low; this flow remains commensurable with the volume transport of molecules as long as the surface monolayer is filled. When the walls of a pore possess a repulsive potential, the role of the surface transport of molecules increases with increase in the degree of filling of the pore. The effects of sliding were considered earlier only for rarefied gases. Unlike the rarefied gases, where the specular reflection of molecules from the walls of a pore plays a decisive role, the sliding effect in dense fluids is determined by the surface mobility of molecules.

According to [36], $\beta_1 = \eta_{11}/\lambda$, where indices 11 correspond to the near-surface monolayer. Therefore, the above-indicated normalized values of η_{11} characterize the coefficient of sliding friction accurate to a constant size of a monolayer λ. As a result, the velocity of a flow in the near-surface layer $u = -(\lambda\beta_{\text{v}})\, \partial u/\partial r|_{r=R}$, where $\beta_{\text{v}} = \eta_{tt}/\eta_{11}$ (the indices tt denote the central region of a narrow pore or the volume viscosity in wide channels). In the case of a strong adsorbate–adsorbent attraction or a decrease in temperature, the ratio η_{11}/η_{tt} sharply increases, which leads to an increase in the coefficient β_1 and a decrease in the velocity of a flow near the wall of a pore.

For a mixture, of importance is the activation energy of the surface migration E_{11}^{iv} of both components. Figure 5 shows local viscosities of an equimolar mixture in the surface layer for different activation energies of the surface migration of the mixture components (in this case, the values of α_{11} for argon and krypton are assumed to be equal). For comparison, the viscosity of the mixture at the center of a pore is given. The difference between the logarithms of the local viscosities on the surface and at the center of the pore (the logarithm of the ratio $\beta_v = \eta_{11}/\eta_{55}$), i.e., the difference between the corresponding dashed lines, behaves nonmonotonically when the total density of the mixture increases. However, the main feature of the dependence $\beta_v(\theta)$ is that it does not change with increase in the degree of filling of a pore with the liquid phase when $\theta \to 1$ (in this case, the densities corresponding to the solid state of the mixture are not considered), and its value characterizes the intensity of sliding of the liquid near the solid wall. The smaller the value of E_{11}^{iv}, the larger the contribution of the surface flow of molecules of each component to the common "sliding" flow of molecules. The case where $\alpha_{11} = 0.1$ corresponds to small migration activation energies (characteristic of the migration of metal atoms on their own ideal faces of single crystals), while the value of $\alpha_{11} = 1$ corresponds to high activation energies, at which molecules break the bond with a substrate and jump to the neighboring sites. Accordingly, the curves $\beta_v(\theta)$ shift toward larger values with increase in α_{11}.

The appearance of maxima on the curves $\beta_v(\theta)$ is explained by the difference between the rates of increase in the coefficients of shear viscosity of a fluid near the wall of a pore and in the bulk phase. At a fairly high density of the bulk phase, the rates of increase in the viscosity of the fluid with increase in θ become equal in both systems. However, at one and the same value of θ, the central part of the pore is more rarefied (because of the increased density on the walls) than the bulk phase; this being so, the viscosity of the fluid in the bulk increases at a larger rate than its viscosity in the pore. (Note that not only the possibility of such nonmonotone behavior of $\beta_v(\theta)$, but also the sliding effect in the liquid phase were practically not considered earlier because there was no unified approach to the study of the gas and liquid phases.)

CONCLUSIONS

1. Calculations perfumed for slot-like pores have shown that the shear-viscosity coefficients of the components of a binary mixture subjected to strong adsorption fields are anisotropic in character and depend substantially on the distance between the fluid region considered and the wall of a pore and on the direction of the momentum transfer. They change especially strongly near the walls of the pore. At the center of the pore, the quantity η_{tt} depends on the potential of the wall and on the total concentration of the mixture.

2. It has been shown that the traditional notions of the constancy of the dynamic characteristics of molecules in narrow pores [2–4] are wrong. Experimental data should be analyzed with allowance for the fact that the dynamic characteristics of an adsorbate in narrow pores depend fairly strongly on its concentration because of the influence of both the potential of the walls of the pores and the intermolecular interaction.

3. The molecular approach [10, 11, 14] allows one to represent various fluid flows containing liquid and/or gas phases in complex porous systems and to make molecular interpretation of their sliding friction. The effect of sliding of a dense-fluid flow is due to the surface migration of molecules. The energies of binding of components of a mixture to the surface determine the surface composition of the mixture, and the energies of activation of the surface migration of the mixture components determine the probabilities of elementary jumps of components in the process of their surface migration.

This work was carried out with financial support from the Russian Basic Research Foundation (grant 03-03-32072).

NOTATION

a_f^i, local Henry constant of an ith molecule located at an fth site; a_f^{i0}, preexponent of the Henry constant of an ith molecule located at an fth site; C_i, concentration of ith molecules; $E_{fg}^{iv}(\rho)$, activation energy of jump of an ith molecule from an fth site to a free gth site positioned at a distance ρ, kJ/mole; $E_{fgh}^{ivj}(\omega_r)$, energy contribution of a jth molecule located at an hth site positioned at a distance equal to the radius r of the coordination sphere of a pair of "central" fth and gth sites with a coordination ω_r to the nonideality function of jump of an ith molecule from an fth site to a gth site; f, number of a monolayer in a slot-like pore and the type of the site located in this monolayer; F_f, normalized fraction of fth sites, $1 \le f \le t$; F_i and F_i^0, statistical sums of the states of ith molecules in the lattice system and in the gas; H, number of monolayers (width of a slot-like pore); i, type of a molecule; k, Boltzmann constant; $K_{fg}^{iv}(\rho)$, rate constant of jump of an ith molecule from an fth cell to a free gth cell positioned at a distance ρ in an unfilled lattice; m_i, mass of an ith molecule; $m(\omega_r)$, set of neighboring sites with definite values of r and ω_r; N, number of cells in a system; N_i, number of ith molecules; P_i and P, partial pressure of ith molecules and the total pressure in the system; Q_f^i, energy of binding of an ith molecule located at an fth site of a layer to the walls of the pore, kJ/mole; R, radius of the channel of a pore (for a slot with $R = H/2$), m; $R_{\rm m}$, radius of the intermolecular interaction potential related to λ; r, distance related to λ; s, number of components of a mixture; t, number of different-type sites in the system; T, temperature; $T_i^{\rm c}$, critical temperature of an ith component; $t_{fg}^{ij}(r)$, conditional probability of location of a jth molecule at a gth site positioned at a distance r from an ith molecule located at an fth site; u, velocity of a flow, m/sec; $u_i(f)$, potential of interaction of an ith molecule with the wall of a pore, kJ/mole; $U_{fg}^i(\rho)$, average rate of jump of ith molecules from an fth cell to a free gth cell positioned at a distance ρ; V_{fg}^{iv}, concentration component of the rate of jump of an ith molecule from an fth cell to a free gth cell; $V_{\rm p}$, volume of a pore; v_0, volume of a cell; $W_i(\rho)$, probability of jump of an ith molecule to a distance ρ; w_{fg}^i, average thermal velocity of travel of ith molecules between the fth and gth sites; x_f^i, mole fraction of the jth component at an fth site; $X_{\rm Ar}$, mole fraction of Ar in a pore; z, number of nearest neighbors; $z_{fg}(r)$, number of neighboring sites in a gth layer positioned at a distance r from the site located in an fth layer; α, dimensionless parameter equal to $\varepsilon/\varepsilon^*$; α_{11}, dimensionless parameter equal to $E_{11}^{i\mathrm{v}}(1)/Q_1^i$, characterizing the height of the activation barrier for surface jumps of the ith component between the nearest sites; β, reciprocal of the thermal energy kT^{-1}, mole/kJ; β_1, coefficient of sliding friction, kg/(m^2·sec); β_v, dimensionless ratio between the shear-viscosity coefficients of the surface and central layers of a pore; $\delta\varepsilon_{fh}^{ij}(r)$, difference between the quantities $\varepsilon_{fh}^{*ij}(r)$ and $\varepsilon_{fh}^{ij}(r)$; ε_i, interaction potential between the ith adsorbate and the adsorbent, kJ/mole; ε_{ij}, Lennard-Jones interaction potential between the ith and jth components of a mixture, kJ/mole; ε_{ij}^0, energy parameter of the function ε_{ij}, kJ/mole; $\varepsilon_{fg}^{ij}(r)$, parameter of interaction of an ith molecule located at an fth site with the neighboring jth molecule located at a gth site positioned at a distance r, kJ/mole; $\varepsilon_{fh}^{*ij}(r)$, parameter of interaction of the activated complex of migration of an ith molecule from an fth site to a free gth site positioned at a distance r with the neighboring jth molecule in the ground state located at an hth site, kJ/mole; γ, mole fraction of the second component of a binary mixture in the gas phase; λ, size of a cell and width of a monolayer ($\sim 1.12\sigma$), m; Λ_f^i, nonideality function of an adsorption system for ith molecules at an fth site; $\Lambda_{fg}^i(\rho)$, nonideality function of an adsorption system for jump of an jth molecule from an fth site to a free gth site; η, viscosity of liquid, N·sec/m^2; η_{fg}, local coefficient of shear viscosity of the mixture located between the fth and gth sites, kg/(m·sec); η_{bulk}, viscosity of argon atoms in the volume of the gas phase at a temperature considered, kg/(m·sec); η_{fg}^i, partial contribution of a jth molecule to the shear viscosity; ρ, length of a molecule jump related to λ; σ_{ij}, shortest distance between the ith and jth components of the mixture, m; σ, average value of the quantities σ_{ij}; θ, degree of full filling of a pore ($0 \le \theta \le 1$); θ_i, degree of partial filling of the volume of a pore with ith molecules; θ_f, local full filling of an fth site; θ_f^i, degree of partial filling of an fth monolayer with ith molecules; $\theta_{fg}^{ij}(r)$, total probability that the neighboring ith particles located at an fth site and jth particles located at a gth are separated by a distance r; ω_r, orientation of a site positioned in the rth coordination sphere of the "central" pair of sites. Subscripts: i, j, types of molecules; v, vacancy; c, critical; f, g, h, types of sites; m, molecular; p, pore; v, velocity.

REFERENCES

1. B. V. Deryagin, N. V. Churaev, and V. M. Muller, *Surface Forces* [in Russian], Nauka, Moscow (1985).
2. D. P. Timofeev, *Adsorption Kinetics* [in Russian], Izd. AN SSSR, Moscow (1962).
3. L. I. Kheifets and A. V. Neimark, *Multiphase Processes in Porous Media* [in Russian], Khimiya, Moscow (1982).
4. V. V. Rachinskii, *Introduction to the General Theory of Sorption Kinetics and Chromatography* [in Russian], Khimiya, Moscow (1964).
5. C. N. Satterfield, *Mass Transfer in Heterogeneous Catalysis* [Russian translation], Khimiya, Moscow (1976).
6. A. Mason and A. Malinauskas, *Gas Transport in Porous Media: The Dusty Gas Model* [Russian translation], Mir, Moscow (1986).
7. Yu. K. Tovbin and E. V. Votyakov, Adsorption in pores with heterogeneous surfaces, *Langmuir*, **9**, No. 10, 2652–2660 (1993).
8. Yu. K. Tovbin, Volumetric filling of pores and classification of porous systems, in: *Proc. Conf. "State-of-the-Art and Perspectives of the Development of Adsorption Theory" devoted to the 100th Anniversary of M. M. Dubinin* [in Russian], IFKh PAN, Moscow (2001), pp. 11–15.
9. Yu. K. Tovbin and E. V. Votyakov, Special features of diagrams of adsorbate stratification in narrow pores, *Izv. Ross. Akad. Nauk*, *Ser. Khimicheskaya*, No. 1, 48–56 (2001).
10. Yu. K. Tovbin, Molecular principles of microdynamics: Transport of molecules in narrow pores, *Zh. Fiz. Khim.*, **76**, No. 1, 76–83 (2002).
11. Yu. K. Tovbin, Transport of gas and liquid in narrow pores, *Teor. Osnovy Khim. Tekhnol.*, **36**, No. 3, 240–251 (2002).
12. Yu. K. Tovbin, *Theory of Physico-Chemical Processes on the Gas–Solid Body Interface* [in Russian], Nauka, Moscow (1990).
13. T. L. Hill, *Statistical Mechanics. Principles and Selected Applications* [Russian translation], IL, Moscow (1960).
14. Yu. K. Tovbin, Transport of dense mixtures of fluids in nanosize channels, *Khim. Fiz.*, **23**, No. 2, 82–97 (2004).

15. M. A. Mazo, A. B. Rabinovich, and Yu. K. Tovbin, Mobility of fluid in a slot-like micropore: model of a lattice gas and molecular-dynamic modeling, *Zh. Fiz. Khim.*, **77**, No. 11, 2053–2059 (2003).
16. M. A. Mazo, A. B. Rabinovich, and Yu. K. Tovbin, Local mobility of argon atoms in a microslot: comparison of molecular-dynamic and theoretical calculations, *Khim. Fiz.*, **23**, No. 5, 243–250 (2004).
17. Yu. K. Tovbin, E. E. Gvozdeva, D. V. Eremich, Dynamic characteristics of adsorbate in narrow cylindrical pores, *Zh. Fiz. Khim.*, **77**, No. 5, 878–883 (2003).
18. E. V. Votyakov, Yu. K. Tovbin, J. M. D. MacElroy, and A. Roche, A theoretical study of the phase diagrams of simple fluids confined within narrow pores, *Langmuir*, **15**, No. 18, 5713–5721 (1999).
19. A. M. Vishnyakov, E. M. Piotrovskaya, E. N. Brodskaya, E. V. Votyakov, and Yu. K. Tovbin, Critical properties of a Lennard—Jones fluid in narrow slot-like pores, *Zh. Fiz. Khim.*, **24**, No. 2, 221–226 (2000).
20. Yu. K. Tovbin and N. F. Vasyutkin, Concentration dependences of the dynamic characteristics of adsorbate in narrow slot-like pores, *Zh. Fiz. Khim.*, **76**, No. 2, 349–354 (2002).
21. I. R. Prigozhin, *Molecular Theories of Solutions* [in Russian], Metallurgiya, Moscow (1990).
22. N. A. Smirnova, *Molecular Theory of Solutions* [in Russian], Khimiya, Leningrad (1987).
23. Yu. K. Tovbin, Application of lattice-gas model to describe mixed gas adsorption equilibria on heterogeneous solid surfaces, in: W. Rudzinski, W. A. Steele, and G. Zgrablich (Eds.), *Dynamics of Gas Adsorption on Heterogeneous Solid Surfaces*, Elsevier, Amsterdam (1996), pp. 105–152.
24. W. A. Steele, *The Interactions of Gases with Solid Surfaces*, Pergamon, New York (1974).
25. S. Sokolowski and J. Fischer, Lennard-Jones mixtures in slit-like pores: A comparison of simulation and density-functional theory, *Molec. Phys.*, **71**, 393–412 (1990).
26. G. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* [Russian translation], IL, Moscow (1948).
27. Yu. K. Tovbin, Kinetics and equilibrium in ordered systems, *Dokl. Akad. Nauk SSSR*, **277**, No. 4, 917–921 (1984).
28. Yu. K. Tovbin, Local characteristics of particle transfer in inhomogeneous systems, *Dokl. Akad. Nauk SSSR*, **312**, No. 6, 1423–1427 (1990).
29. Yu. K. Tovbin, Lattice-gas model in kinetic theory of gas–solid interface processes, *Progr. Surf. Sci.*, **34**, 1–236 (1990).
30. J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* [Russian translation], IL, Moscow (1961).
31. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids* [Russian translation], Khimiya, Leningrad (1982).
32. B. V. Egorov, V. N. Komarov, Yu. E. Markachev, and Yu. K. Tovbin, Concentration dependence of viscosity under the conditions of its clusterization, *Zh. Fiz. Khim.*, **74**, No. 4, 882–888 (2000).
33. Yu. K. Tovbin, Calculation of compressibility and viscosity of real gases with the use of the lattice model, *Zh. Fiz. Khim.*, **75**, No. 3, 579–584 (2001).
34. B. A. Rabinovich, A. A. Vasserman, V. I. Nedostup, and L. S. Veksler, *Thermophysical Properties of Neon, Argon, Krypton, and Xenon* [in Russian], Standartgiz, Moscow (1976).
35. M. A. Anisimov, V. A. Rabinovich, and V. V. Sychev, *Thermodynamics of the Critical State* [in Russian], Energoatomizdat, Moscow (1990).
36. Yu. K. Tovbin, L. K. Zhidkova, and E. E. Gvozdeva, Rheological properties of dense-gas and liquid flows in narrow slot-like pores, *Inzh.-Fiz. Zh.*, **76**, No. 3, 124–130 (2003).
37. E. Akhmatskaya, B. D. Todd, P. J. Davis, D. J. Evans, K. E. Gubbins, and L. A. Pozhar, A study of viscosity inhomogeneity in porous media, *J. Chem. Phys.*, **106**, 4684–4691 (1997).
38. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena* [Russian translation], Khimiya, Moscow (1974).
39. G. Lamb, *Hydrodynamics* [Russian translation], OGIZ, Moscow–Leningrad (1947).