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Supercritical Fluid Effect on the Rates of Elementary Bimolecular Reactions

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Abstract—The effect of the supercritical fluid (SCF) present in the reaction system on the rate of a bimolecular reaction has been investigated theoretically. Calculations have been carried out in the framework of the theory of nonideal reaction rates in condensed phases. The intermolecular interactions of the nearest neighbors are described in the quasi-chemical approximation taking into account the short-order correlation effects. The competing effects of raising the reaction temperature (which increases the reaction rate) and raising the pressure by increasing the amount of SCF (which hinders the meeting of the reactants) are discussed. Increasing the proportion of SCF reduces the self-diffusion coefficient and increases the viscosity of the reaction mixture.

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Gas mixtures are brought to the supercritical state by raising the temperature and pressure in the system [1–3]. When surface processes occur in the system, an increase in the gas phase pressure affects both the rates of the elementary reactions involving gaseous components of the reaction system and the equilibria in these reactions. The variation the surface coverage by gaseous components of the system due the changes in the rates of the elementary steps of the exchange of adsorbed molecules between the surface and the gas phase alters the surface coverages by other (intermediate) components. In turn, this exerts an effect on the rates of other steps of the surface processes. Therefore, varying the gas pressure provides a means of controlling the overall process. As a rule, the reaction temperature is also elevated in supercritical processes, and these factors produce different effects on adsorption on open surfaces and in porous materials. The amount adsorbed decreases with increasing temperature and grows with increasing pressure.

The conventional description of the rates of elementary bimolecular reactions is based on the law of mass action: $w_{ij} = k_{ij} n_i n_j$, where k_{ij} is the rate constant of the elementary reaction $i + j \rightarrow$ products and n_i is the molecule concentration as the number of molecules of sort i in a unit volume. If the surface area in a heterogeneous process is invariable during the reaction, the surface concentration of species i can be characterized in terms of the surface coverage θ_i; hence,

$$w_{ij} = k_{ij}\theta_i\theta_j, \quad k_{ij} = k_{ij}^0 \exp\left(-E_{ij}/k_B T\right), \qquad (1)$$

where k_{ij}^0 is the preexponential factor of the rate constant and E_{ij} is the activation energy of the reaction between reactants i and j. Reaction rate constants are most widely calculated using absolute reaction rate theory [4], which relates the rate constant to the statistical sums of the reactants and activated complex.

The equations of the law of mass action assume that the equilibrium distribution of molecules takes place in the reaction system and that the rate-limiting step is the chemical reaction. In other words, it is assumed that there are no diffusion limitations at the macroscopic level, there is no diffusion control at the molecular level, and there is no effect of intermolecular interactions.

In dense phases (as distinct from the gas phase), the reactants are continually in the field of action of the neighbor molecules. This interaction causes deviations from the laws governing ideal reaction systems, so we have nonideal reaction systems. For the first time, the effect of raising the reaction pressure relative to atmospheric pressure on catalytic ammonia synthesis was studied theoretically by Temkin [5] (see also [6, 7]). Temkin [5] demonstrated that the nonideality of the reaction system at elevated pressures changes the rate constants of elementary steps.

Here, we consider the effect of the intermolecular interaction of the reactants with the supercritical component on the rate of bimolecular reactions under supercritical conditions. The purpose of this analysis is to separate the contributions from increasing temperature and pressure—two basic parameters of the supercritical state. The rate of a chemical reaction depends strongly on the activation energy of the reaction, and this dependence manifests itself strictly in the absence of a supercritical fluid (SCF). Expression (1) takes into account the SCF effect through the product of the reactant concentrations when SCF reacts

chemically with other components of the reaction mixture, and it disregards the SCF effect when the SCF is not involved in the reaction. However, as the pressure is raised, the reaction slows down even when the SCF is inert. This is due to the fact that the SCF occupies some space in the system and thereby hinders the meeting of reactant molecules and the lateral interaction of the reactants with the SCF produces an association species of inert molecules around each reactant.

Below, we will focus on the role of the concentration of the supercritical component. By comparing the SCF effects on the concentration dependences of the reaction rate, it is possible to estimate the role of the lateral interactions in the change of the apparent activation energy of the reaction, E_{AB}^{app}, caused by the temperature and pressure variation in the system. In the case of a very high activation energy E_{AB}, the presence of an SCF practically has no effect on the reaction rate if the reaction remains under kinetic control. However, as the pressure in the reaction system is raised via addition of inert SCF molecules, the bimolecular reaction may pass from kinetic control to diffusion control.

Any real chemical process consists of several steps, which depend on the overall reaction mechanism and molecular transport. Knowledge of the concentration dependences of the transport coefficients is also essential for simulation of the overall supercritical process in continuous and batch reactors. Here, we will discuss how intermolecular interactions affect the self-diffusion coefficient and viscosity of homogeneous systems (bulk phase or uniform surface) as the SCF concentration is increased.

In the general case, the discussion of the SCF effect on the overall process should include the following aspects of this problem: (1) raising the pressure (density) makes the lateral interactions more significant; (2) raising the temperature shifts the equilibrium concentrations of the components in the reaction system, and this can initiate chemical reactions that would be unlikely at low temperatures (e.g., the thermal dissociation of water, which causes a marked increase in the ionic product) [8, 9]; (3) passing to supercritical conditions changes the states of materials in the reaction system (e.g., SCFs change the state of coke on catalysts and the properties of polymer matrices in membranes). All of these issues should be considered together, but of greatest importance is the first one: What are the changes in the rates of the separate reactions that constitute the mechanisms of the overall processes specified in items (2) and (3)? The accuracy of description of the overall process depends on the solution for this issue.

Below, we elucidate the role of the lateral interactions by calculating the apparent activation energies E_{ij}^{app}, which differ from the corresponding activation energies E_{ij} calculated within the law of mass action (Eq. (1)). The theory of nonideal reaction systems provides means to separate the contributions from the temperature and pressure in supercritical processes: if the contribution from the temperature is dominant, the differences between E_{ij}^{app} and E_{ij} are small and Eq. (1) can be used. In the opposite case, the contribution from the change in pressure is significant and the differences between E_{ij}^{app} and E_{ij} determine the SCF density region in which the properties of an ideal system are retained. This approach distinguishes the chemical aspects of reaction systems from the cooperative properties of multicomponent mixtures at high pressures (densities). It is quite natural that, for water, raising the temperature by ~10 deg over its critical temperature causes a sharp decrease in its density, and the resulting SCF is a dense vapor up to very high pressures (one order of magnitude higher than the critical pressure P_c), which are not considered in practical applications [10].

We will divide SCFs into two types according to whether or not the SCF molecules react with the main reactants of the system. In the latter case, the SCF will be referred to as inert. The third issue for inert SCFs was elucidated in part in our earlier study [11]. An analysis of the effect of CO_2-type molecules on the adsorption isotherms and separation curves demonstrated that these molecules change surface coverages both in the case of physical adsorption and in the case of chemisorption. They also can loosen solid particles if the energies of the bonds between the components of the solid are not higher than the ~15-fold energy of the bond between SCF molecules.

If SCF reacts with the main components of the system, then passing to supercritical conditions can increase the density of the supercritical reactant to an extent at which the bimolecular reaction is pseudo-first-order. In this case the reaction will be kinetically controlled and will depend mainly on temperature.

Model

In theoretical analysis, we will use absolute reaction rate theory for nonideal reaction systems in the framework of the lattice gas model, which operates with intermolecular interaction parameters [12–15]. Limiting our consideration to qualitative estimates, we will take into account the lateral interactions between all nearest-neighbor (reactant and SCF) molecules in the quasi-chemical approximation describing the short-order correlation effects. This theory makes it possible to consider the entire fluid density range from a rarefied gas to a liquid. It covers the wide temperature range between the triple point of the system and temperatures many times exceeding the critical temperature. This approach ensures obtaining a self-consistent description for the equilibrium state of the reaction mixture and for the rates of elementary reactions. This makes it possible to consider complicated,

multistep physicochemical processes using atomic–molecular level models.

The reaction system will be described in terms of the lattice gas model in which each component occupies one cell (or one lattice site) [14, 16–20]. Any cell can be occupied by a species of sort i, where $1 \le i \le s-1$ (s is the number of components in the system), or be vacant. In the latter case, $i = s$. With the surface coverage by sort i species designated θ_i, we have $\sum_{j=1}^{s} \theta_i = 1$. The total surface coverage by all adsorbed species i ($1 \le i \le s-1$) is $\theta = \sum_{j=1}^{s-1} \theta_i$. The fraction of vacant sites is $\theta_s = 1 - \theta$. The $x_i = \theta_i/\theta$ ratio is the mole fraction of the ith component among all molecules of the mixture.

Each cell has z nearest neighbors, among which lateral interaction takes place. The parameter of the lateral interaction in a pair of neighbor species ij will be designated ε_{ij}. The parameter of the interaction between any species and a vacancy is zero. The interactions between species lead to a correlated (not chaotic) spatial distribution of the reactants. To account for this fact, it is necessary to use pair distribution functions θ_{ij} characterizing the probability of two reactants meeting one another. This is necessary for a chemical reaction to occur, because chemical reactions take place when the distance between the reactants is short. It is due to this fact that, in chemical kinetic problems, it is sufficient to consider the spatial distribution of only the nearest neighbors.

According to nonideal reaction system theory [12–15], the expression for the rate of Langmuir–Hinshelwood type bimolecular reaction between the components A and B occurring at the neighbor sites f and g of a uniform system (w_{fg}^{AB}) is written as follows:

$$w_{fg}^{AB} = k_{fg}^{AB} \exp\left(-\beta \varepsilon_{fg}^{AB}\right) \theta_{fg}^{AB} \Lambda_{fg}^{AB}, \qquad (2)$$

where $\beta = (k_B T)^{-1}$, $k_B T$ is the product of the Boltzmann constant and absolute temperature, and Λ_{fg}^{AB} is the nonideality function expressed as

$$\Lambda_{fg}^{AB} = \prod_{h \in (z(f)-1)} S_{fh}^{A} \prod_{h \in (z(g)-1)} S_{gh}^{B},$$
$$S_{fh}^{A} = \sum_{j=1}^{s} t_{fh}^{Aj} \exp\left(\beta\left(\varepsilon_{Aj}^{*} - \varepsilon_{Aj}\right)\right). \qquad (3)$$

Here, the subscript h pertains to the nearest neighbors of the site f or g, excluding g and f, respectively; for S_{gh}^{B}, the superscript A and subscript f in (3) are replaced with B and g, respectively; ε_{ij}^{*} is the interaction parameter for the activated complex formed from a sort i species and a nearest-neighbor sort j species.

In expressions (2) and (3), the θ_{fh}^{ij} functions have the meaning of the probability of two species i and j being close together and the $t_{fh}^{ij} = \theta_{fh}^{ij}/\theta_f^i$ functions are the conditional probabilities of species j being close to species i. Since the system is uniform, the subscripts designating the adjacent site numbers are used only to indicate that the reactants occupy different positions: $\theta_{fh}^{ij} = \theta_{ij}$ and $t_{fh}^{ij} = t_{ij}$. In the approximation discussed here, the rate constant of the reaction, k_{AB}, is assumed to be constant and equal to the rate constant in Eq. (1). In the general case, $\theta_{ij} \ne \theta_i \theta_j$. When there is no intermolecular interaction, the above equations turn into the well-known equations for ideal reaction systems, for which $\theta_{ij} = \theta_i \theta_j$ [21–23].

The lateral interactions exert a dual effect on the rates of the elementary steps. They change the probability of the reactants meeting one another (formula (2) contains the factor θ_{AB} rather than the product $\theta_A \theta_B$) and the height of the activation barrier relative to the barrier in the ideal system (e.g., a gas phase). The latter contribution is represented by the nonideality function Λ_{fg}^{AB}. Summation in the functions S_A and S_B is performed over all of the s sorts of nearest-neighbor species, designated by the subscript j. The function S_i represents the components of the nonideality function of the reaction system that account for the effect of the nearest-neighbor species on the height of the activation barrier of the reaction. The difference $\delta\varepsilon_{ij} = \varepsilon_{ij}^{*} - \varepsilon_{ij}$, which appears in formula (3), determines the change in the activation energy of the reaction $A + B$ due to the effect of species j adjacent to reactant i relative to the activation energy E_{AB} in formula (1) for low coverages (or an ideal system).

In the gas-phase chemical kinetics, the greatest attention is paid to the temperature dependence of the reaction rate [22, 23], which obeys an exponential law, and the concentration dependence of the reaction rate for a bimolecular reaction obeys a quadratic law. For nonideal systems, for which the nonideality function is the product of the functions $\exp(\beta\delta\varepsilon_{ij})$ and t_{ij}, as is clear from expressions (2) and (3), the temperature and concentration factors are interrelated, so the concentration dependence of the reaction rate is as important as its temperature dependence.

The equilibrium distribution of molecules in a uniform system is given by the θ_{ij} functions determined in the quasi-chemical approximation from the following set of equilibrium equations with the following normalization condition:

$$\theta_{ij}\theta_{ss} = \theta_{is}\theta_{sj} \exp(-\beta\varepsilon_{ij}), \quad \sum_{j=1}^{s} \theta_{ij} = \theta_i. \qquad (4)$$

It follows from Eq. (4) that $\theta_{ij} > \theta_i \theta_j$, if species i and j are attracted at $\varepsilon_{ij} > 0$; likewise, $\theta_{ij} < \theta_i \theta_j$, if species i and j are repulsed at $\varepsilon_{ij} < 0$.

When performing calculations for a bimolecular reaction on a uniform surface, it should be taken into account that the surface concentrations of molecules involved in the reaction rate equations are determine

from the equations of adsorption of the main reactants A and B in the presence of the supercritical component C. The equations describing the adsorption of a mixture on a uniform surface in the quasi-chemical approximation with the interspecies interaction taken into account are written as follows:

$$a_i P_i = \left(\frac{\theta_i}{\theta_s}\right) S_i^z, \quad S_i = 1 + \sum_{j=1}^{s-1} x_{ij} t_{ij}. \tag{5}$$

Here, the partial isotherms relate the pressures P_i in the gas phase ($1 \le i \le s-1$) to the surface coverage θ_i; $a_i = a_{i0} \exp(\beta Q_i)$, where a_{i0} is the preexponential factor of the Henry constant and Q_i is the species i –surface bond energy; and $x_{ij} = \exp(-\beta\varepsilon_{ij}) - 1$.

The apparent activation energy of the bimolecular reaction, E_{AB}^{app}, is determined via Eq. (1) as

$$W_{12} = w_{AB} \Big/ \left(k_{AB}^0 \theta_A \theta_B\right) = \exp\left[-\beta E_{AB}^{app}\right], \tag{6}$$

or

$$E_{AB}^{app} = E_{AB} + \varepsilon_{AB} - \beta^{-1} \ln\left(\theta_{AB}/\theta_A\theta_B\right) - (z-1)\ln\left(S_A S_B\right). \tag{7}$$

For low coverages, $E_{AB}^{app} = E_{AB}$ for high, SCF-dominated coverages with small contributions from the reactants A and B ($\theta_C \gg \theta_A + \theta_B$), formula (7) can approximately be rewritten as

$$E_{AB}^{app} \approx E_{AB} - (z-1)\left(\delta\varepsilon_{AC} + \delta\varepsilon_{BC}\right) = E_{AB} + (z-1)(1-\alpha)\left(\varepsilon_{AC} + \varepsilon_{BC}\right),$$

where the same ratio $\alpha_{ij} = \alpha$ is used for both reactants in the second equality. This expression demonstrates the effect of the interaction of the reactants with SCF molecules on the apparent activation energy. When $\alpha < 1$, the formation of SCF association species around the reactants increases the apparent activation energy of the reaction. When $\alpha > 1$, the formation of SCF association species reduces the E_{AB}^{app} value. The difference $\Delta E_{AB}(\theta) = E_{AB}^{app} - E_{AB}$ characterizes the role of the concentration factor associated with the increase in the SCF pressure and with the SCF effect on the activation energy through lateral interactions.

Calculation

Supercritical processes are usually conducted at temperatures exceeding the critical temperature T_c by a factor not larger than 3. For this reason, most of the calculated data presented here refer to reduced temperatures of $\tau = T/T_c = 1.10$–2.5, where the unit of temperature ($\tau = 1$) is the critical temperature of the SCF ($T_c = 304$ K for CO_2). The energy of the lateral interaction between CO_2 molecules, equal to the energy parameter of the Lennard-Jones potential, is $\varepsilon_0 = 0.4$ kcal/mol. This energy was used as the unit of measure for the lateral interaction between other (sort i) reactants; that is, $\varepsilon_{ii} = \gamma_i \varepsilon_0$. As usual, cross interaction parameters were expressed according to the following rule: $\varepsilon_{ij} = \left(\varepsilon_{ii}\varepsilon_{jj}\right)^{1/2} = \varepsilon_0\left(\gamma_i\gamma_j\right)^{1/2}$. It was accepted in all calculations that $\alpha_{ij} = \varepsilon_{ij}^* \big/ \varepsilon_{ij} = 0.5$; that is, the interaction between the activated complex in the transition state with the nearest neighbor j is weaker than the interaction between the initial species i in the ground state and the same neighbor. For surface processes, this condition reflects the decrease in the energy of interaction between the activated complex and its nearest neighbors due to the activated complex receding from the surface plane.

The effect of the density of the supercritical component was studied as a function of the density θ_C varying between zero and $(1 - \theta_A - \theta_B)$, where $\theta_B = \theta_A$, for two values of the main component coverage, $\theta_A = 0.01$ and 0.1. These reactant concentrations allow the role of the commensurability of the amounts of the reactants and SCF to be assessed. An increase in the SCF density is equivalent to a pressure rise. In the first case, the fraction of the reactants can practically be neglected; in the second case, their fraction is comparable with the SCF fraction.

The reaction rate was calculated for the following two situations: (a) the amount of the components A and B is fixed (as in a batch reactor), and the amount of SCF is varied from zero up to the complete surface coverage; (b) the mole fractions of the reactants are fixed (as in a continuous reactor).

In order to display the entire W_{12} range for the situation in which the amounts of the reactants are fixed, we plot, in Fig. 1a, $\log W_{12}$ for the A–B–C three-component system at different amounts of the supercritical component C. Figure 1b plots the $E_{AB}^{app} \big/ E_{AB}$ ratio, which characterizes the change in the apparent activation energy relative to the activation energy of the reaction in the ideal system. The calculation was carried out for $\gamma_A = 3.16$ for the first reactant and for $\gamma_B \approx 4.0$ and 2.4 for the second reactant. These values represent the typical variation range of the lateral interactions between reactants. The activation energy was taken to be $E_{AB} \equiv E_{12} = 3$, 10, and 20 kcal/mol. These values are typical of the activation energy of the interaction between chemisorbed species in catalysis.

The abscissa axis in Fig. 1 shows the total amount of matter in the system, $\theta = \theta_A + \theta_B + \theta_C$. The curves begin at fixed values of the total density θ in the absence of the supercritical component C. Raising the reactant concentration changes the initial θ value (Fig. 1c). As the amount of SCF is increased, the curves plotted in Figs. 1a and 1c behave in a similar way because of the dominant effect of the SCF, but they do not coincide because of

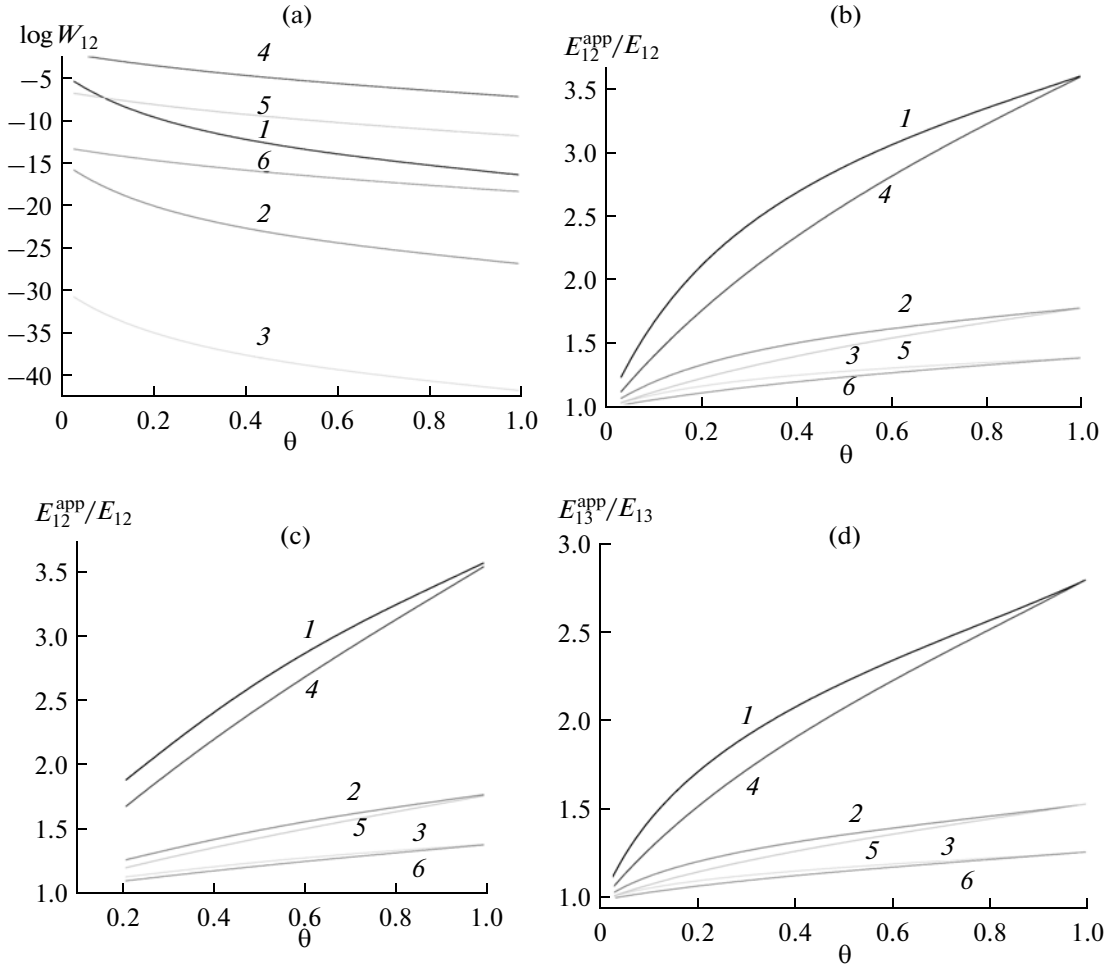

Fig. 1. Characteristics of the reaction rate as a function of the surface coverage θ at $\varepsilon_{CC} = 0.380$ kcal/mol, $\varepsilon_{AA} = 4\varepsilon_{CC}$, and $\varepsilon_{BB} = 2.4\varepsilon_{CC}$ for $T = (1–3)\ 1.1T_c$ and $(4–6)\ 2.5T_c$ and $E_{12} = (1, 4)$ 3000, $(2, 5)$ 10000, and $(3, 6)$ 20000. (a–c) Fixed amounts of the reactants: (a, b) $\theta_A = \theta_B = 0.01$ and (c) $\theta_A = \theta_B = 0.1$. (d) Fixed mole fractions of the reactants: $x_A = x_B = 0.01$.

the difference between the amounts of the reactants (in Fig. 1c, the *A* and *B* coverages are one order of magnitude higher).

For a fixed E_{AB} value, an increase in temperature reduces the E_{AB}^{app}/E_{AB} ratio. The larger E_{AB}, the weaker the effect of the lateral interactions; that is, with an increasing E_{AB}, the temperature factor begins to dominate over the concentration factor if the bimolecular reaction remains kinetically controlled. Calculations demonstrated that, for $E_{AB} > 20$ kcal/mol, the role of the nonideality of the environment in the case of supercritical CO_2 is insignificant.

Curves *1* and *4* in Fig. 1 illustrate the case of a comparatively low activation energy of $E_{AB} = 3$ kcal/mol. Clearly, the effect of the nonideality of the system in this case is the strongest. In the general case, low activation energies of $E_{AB} \sim 0$ mean that practically any encounter of the reactants *A* and *B* will lead to their reaction, making formula (1) invalid, because the reaction will be diffusion-controlled. Such reactions are described by kinetic equations taking into account diffusion [15].

Although the $\ln W_{12}$ and E_{AB}^{app}/E_{AB} curves deviate only slightly from linearity with respect to θ, particularly at large E_{AB} values, a rougher, mean-field approximation cannot be used, because it does not ensure self-consistent calculation of the reaction rate and equilibrium state of the system [12–15].

As was mentioned above, the calculated data presented in Fig. 1 refer to the case of a single rate-limiting step. If the SCF is involved as a reactant in intermediate steps of the overall process (see, e.g., [24]), then this process will include, for example, the $A + C$ step. The dependence of E_{AB}^{app}/E_{AC} on θ for this case is shown in Fig. 1d ($E_{AC} \equiv E_{13}$). In this case, the contribution from the lateral interactions is smaller than in the case of the $A + B$ type bimolecular reaction, but the SCF concentration appears as a factor in Eq. (1) and, as a consequence, the role of the supercritical component is greater. In order to analyze this role, it is neces-

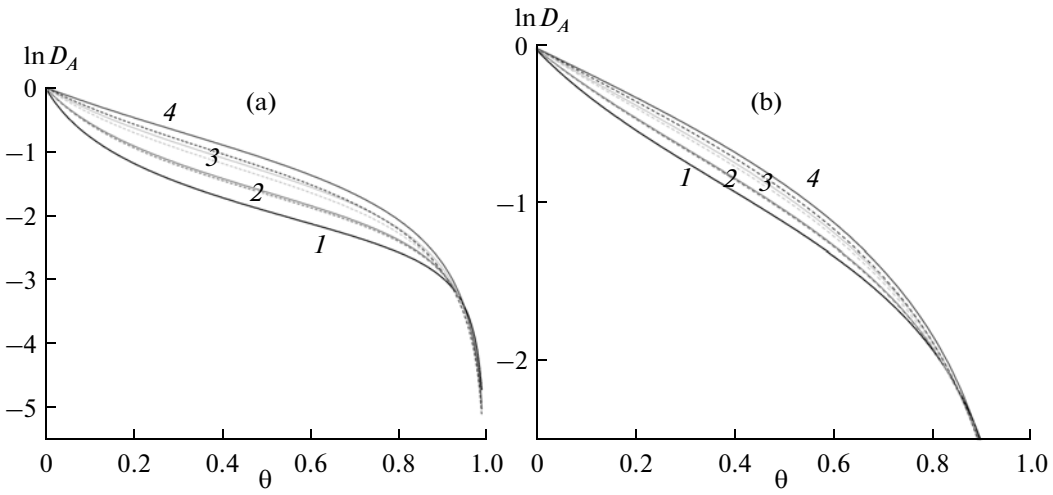

Fig. 2. Self-diffusion coefficient of the component A (D_A) as a function of θ at γ_A = (*1*) 1, (*2*) 1.6, (*3*) 3.2, and (*4*) 6.4 for τ = (a) 1.15 and (b) 2.5. Solid lines: $\theta_A = 0.01$; dotted lines: $\theta_A = 0.1$.

sary to calculate all steps of the reaction mechanism, taking into account the nonideality of the reaction system.

Self-Diffusion Coefficient

The theory of nonideal reaction systems provides means to consider transport characteristics. The simplest characteristic of molecular transport in mixtures is the self diffusion coefficient of component i ($1 \le i \le (s-1)$), which characterizes the thermal motion of the sort i molecules under equilibrium conditions. In practice, the self-diffusion coefficient is usually associated with the motion of an isotopic label locally introduced into some region of the system, and the temporal distribution of the label over the rest of the solution is monitored. For labeled sort i molecules, we have the following expression for the local partial self-diffusion coefficient [25]:

$$D_i^* = z_{fg}^* w_{iV} \big/ \theta_f^i, \tag{8}$$

where z_{fg}^* is the number of possible hops to nearest-neighbor sites g for the fth cell along the direction in which the label moves. The expression for w_{iV} is given by formula (2). It refers to the bimolecular hop of molecule i, $i + V \to V + i$, in which the first "reactant" is a moving sort i molecule and the second "reactant" is the vacancy into which the molecule i is transferred. The activation energy of this process is $E_{iV} = 0$ for a bulk phase and $E_{iV} > 0$ for the surface migration step.

The structure of this expression indicates that the self-diffusion coefficient of all components depends on the local distributions of the components of the mixture: it is expressed in terms of the conditional probabilities $t_{ij} = \theta_{ij}/\theta_i$ via formula (3), in which $S_{gh}^{V} = \sum_{j=1}^{s} t_{gh}^{Vj} \exp\left(\beta\varepsilon_{Vj}^*\right)$, because $\varepsilon_{Vj} = 0$ and $\varepsilon_{Vj}^* = \varepsilon_{Aj}^*$. Therefore, the self-diffusion coefficient also depends on the total local density of the system, because the density of vacancies (free volume) and intermolecular interactions is important. As the total density of the system increases, the free volume fraction decreases and so does the self-diffusion coefficient of any species.

The apparent activation energy of the self-diffusion of component i is written in the form of formula (7):

$$E_{iV}^{app} = E_{iV} - \beta^{-1} \ln\left(\theta_{iV}/\theta_i\theta_V\right) - (z-1)\ln\left(S_i S_V\right). \tag{9}$$

For high SCF coverages, it follows from formula (9) that $\Delta E_{iV} = E_{iV}^{app} - E_{iV} = (z-1)(1-2\alpha)\varepsilon_{AC}$. For $\alpha = 0.5$, $\Delta E_{iV} = 0$ and the decrease in the self-diffusion coefficient is only due to the decrease in the free volume fraction.

Figure 2 plots the concentration dependences of the self-diffusion coefficient of the main component A (D_A) in the SCF bulk ($E_{iV} = 0$). The effect of the density of the supercritical component was studied as a function of the density θ_C varying between zero and $1 - \theta_A$ for two main-component coverages, $\theta_A = 0.01$ and 0.1.

In these calculations, we fixed the mole fraction of the main component A relative to the supercritical component C; accordingly, all curves begin at $\theta = 0$. The curves descend as the total density increases. This is due to the decrease in the free volume, which is necessary for molecular transport. The self-diffusion coefficients of SCF in the bulk are plotted in Fig. 3. The run of the D_C curves is similar to the run of the curves shown in Fig. 2. The concentration dependence of the self-diffusion coefficients depends strongly on the nature of the supercritical component. The stronger the interaction between SCF molecules, the greater the extent to which diffusion slows down

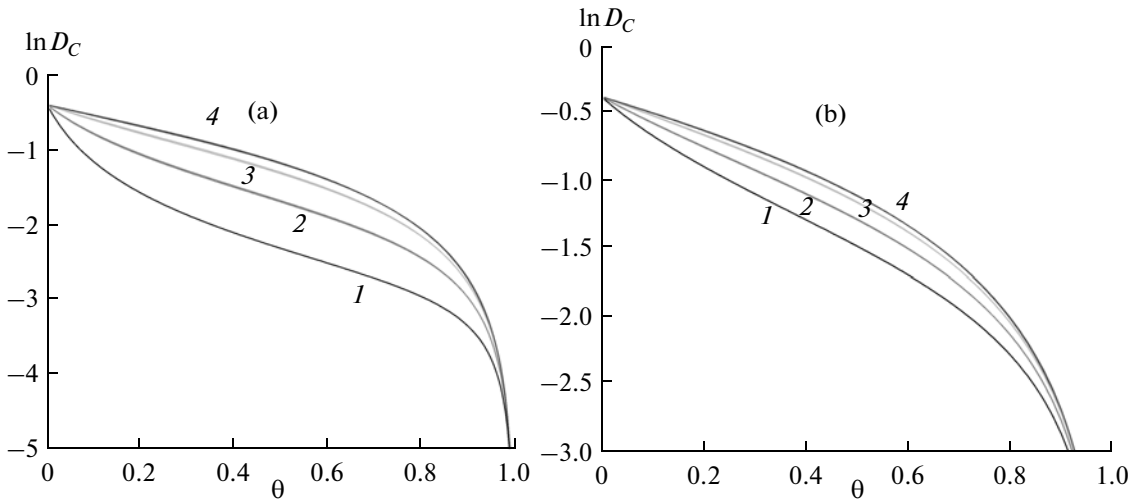

Fig. 3. SCF self-diffusion coefficient (D_C) as a function of θ for τ = (a) 1.15 and (b) 2.5. All designations are the same as in Fig. 2.

with an increasing SCF concentration. The self-diffusion coefficient decreases as the temperature is raised.

The concentration dependences of the self-diffusion coefficients of the components *A* and *C* in Figs. 2 and 3 are normalized to the self-diffusion coefficient of the component *A* in a rarefied gas at 1 atm.

Viscosity

Another important transport characteristic is viscosity. Knowledge of this characteristic is necessary for calculating flow velocities in various reactors. Like the self-diffusion coefficient, viscosity is expressed in terms of the thermal velocities of molecules.

The local shear viscosity η_{fg} for spherical molecules of comparable sizes is expressed as follows [25]:

$$\eta = \left[\sum_{j=1}^{s-1} x_j (\eta_j)^{-1}\right]^{-1}, \quad \eta_j = \theta_j / w_{iV}, \qquad x_i = \theta_i/\theta, \quad \theta = \sum_{j=1}^{s-1} \theta_i, \tag{10}$$

where x_i is the mole fraction of component *j* and θ is the total coverage of the system.

For pure components, it follows from this expression that η depends on temperature as $T^{1/2}$ and depends linearly on the density. For high densities, we have an exponential temperature dependence, as in Eyring's conventional model [4]. Expression (10) allows viscosity to be calculated for any composition of a multicomponent mixture.

Figure 4 plots viscosity versus the total mixture density θ. In these calculations, we fixed the mole faction of the main component *A* relative to the supercritical component *C*; accordingly, all curves begin at θ = 0. With this way of expressing the amount of the main component *A*, the difference between the θ_A values for mole fractions of 0.01 and 0.1 is smaller than in the case of the fixed amounts of the component *A*. The concentration dependences of viscosity are normalized to the viscosity of the component *A* in a rarefied gas.

The calculations were carried out at a fixed ε_{AA} value for the component *A* and a decreasing ε_0 value or an increasing $\gamma_A = \varepsilon_{AA}/\varepsilon_0$ ratio. An increase in γ_A leads to an increase in the energy of the lateral interactions between the main component *A* and SCF. As a result, the viscosity of the system decreases. Therefore, by changing the SCF, it is possible to vary the viscosity of the system in a fairly wide range. This range is temperature-dependent: it widens with increasing temperature.

DISCUSSION

The theory of reaction rates in condensed phases [12–15] demonstrates that, under supercritical conditions, intermolecular interactions cannot be ignored even for an inert supercritical component, which may exert a significant effect on the rates of elementary processes.

The curves shown in Fig. 1 indicate the characteristic interval of possible deviations from the law of mass action in the temperature and activation energy ranges typical of supercritical processes in the gas phase, as distinct from a process in an ordinary gas atmosphere at 1 atm. An increase in the density of the supercritical component decreases the probability of the reactants meeting one another, and the SCF–reactant lateral interactions, though comparatively weak, stabilize the initial states of the reactants and reduce the rates of the reactions. The latter circumstance is significant for the most reactive reactants, such as ozone [8, 24]. The calculations were carried out for the entire SCF density range, so it can readily be seen from the calculated curves whether it is possible to neglect the interactions between the SCF mole-

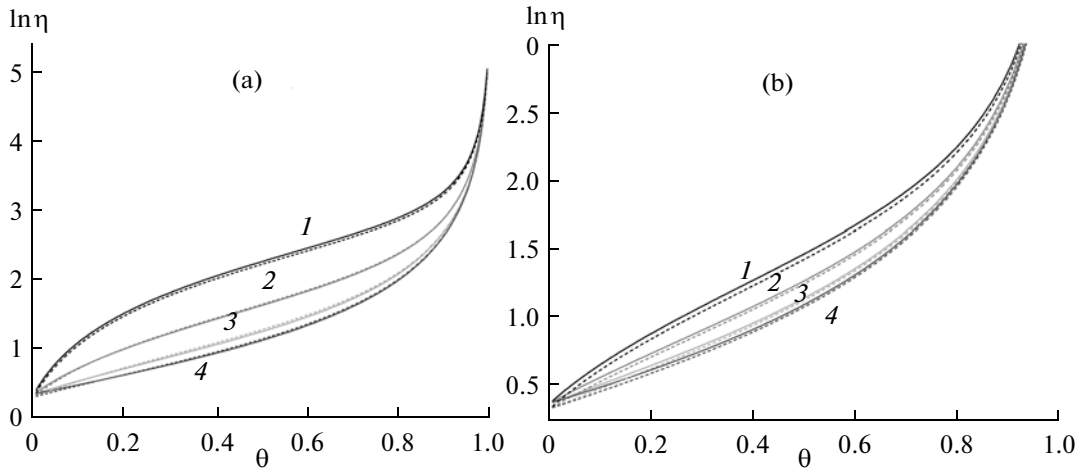

Fig. 4. Viscosity as a function of θ at $\gamma_A = (1)$ 1, (2) 1.6, (3) 3.2, and (4) 6.4 for $\tau =$ (a) 1.15 and (b) 2.5. Solid lines: $\theta_A = 0.01$; dotted lines: $\theta_A = 0.1$.

cules under given conditions. (If the lateral interactions can be neglected, then $E_{AB}^{app} = E_{AB}$ at any θ_C.)

The same is true for the transport coefficients plotted in Figs. 2–4. The calculated data indicate that the self-diffusion coefficients and viscosity characterizing the transport properties of the entire supercritical system depend on the density of the supercritical component to a lesser extent than the reaction rates. This is due to the fact that the thermal velocities of molecular migration, which determine both of the transport coefficients, depend on temperature much less strongly than chemical reactions.

The above results correlate well with the known similar relationships for the same steps occurring at atmospheric pressure. At the same time, they were obtained by an analysis of the processes in a very wide SCF density range. The validity of the above inferences throughout the pressure and temperature ranges typical of supercritical processes suggests that this good correlation is a more general point than a simple corollary of the law of mass action.

Along with the problem of taking into account the nonideality of the system, another problem in the calculation of reaction rates is to determine the validity limits for the assumption that the reaction is kinetically controlled. By raising the SCF density ($\theta \to 1$), it is always possible to attain the state in which the reaction can pass from kinetic control to reactant transport control, particularly at low reactant concentrations. There is no such problem when a bimolecular reaction turns into a quasi-monomolecular reaction (in excess SCF) if the SCF is one of the reactants in the given step.

In an analysis of the role of supercritical conditions, it is necessary to take into consideration not only the fact that the reaction rate increases with increasing temperature and that the reaction rate and self-diffusion coefficient decrease (and viscosity increases) with increasing pressure, but also the abovementioned fact that the mechanism of the process and the states of other materials change with temperature and pressure. For implementation of supercritical processes, it is essential to find optimum conditions for reaction rates and reactant mobility. Simply raising one of the state parameters (temperature or pressure) may make the conditions less favorable for the realization of elementary steps. On passing to particular mechanisms of overall processes, the theory of nonideal reaction systems provides means to correlate the kinetic parameters observed under normal conditions at atmospheric pressure with the same parameters for supercritical conditions.

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