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Molecular-dynamics study of anomalous volumetric behavior of water-benzene mixtures in the vicinity of the critical region

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Molecular-dynamics simulations of water-benzene mixtures at 573 K and pressures in the 85–140 bars range have been performed to examine local structure and dynamics of the mixtures, which exhibit anomalously large volume expansion on mixing as recently found by *in situ* near-infrared measurements. Fractional charges for a simple-point-charge-type potential of water were adjusted so as to reproduce liquid densities and the gas-to-liquid transition pressure of neat water at 573 K. A Lennard-Jones-type potential for benzene was used and the Lorentz-Berthelot combination rule was applied to the water-benzene interaction. Simulations with a *N-P-T* ensemble of 800-molecule system have been performed and the results reproduce well the anomalous volumetric behavior of the mixtures with the mole fraction of benzene in the 0.3–0.8 range. Pair distribution functions, coordination numbers, and self-diffusion coefficients for the mixtures are calculated, and it is suggested that the local structure around water molecules undergoes drastic change by dissolution of benzene in the vicinity of the critical region, but that around benzene molecules seems to be understood as that of ordinary liquid mixtures. © 2005 American Institute of Physics. [DOI: 10.1063/1.2145749]

I. INTRODUCTION

Recently, we have found an intriguing volumetric behavior of binary mixtures of water and hydrocarbons at high temperatures and pressures by *in situ* infrared and near-infrared measurements.^{1–3} For example, mixing of water and benzene with a molar ratio of 0.82/0.18 at 573 K and 100 bars induced seven times expansion of the total volume. Similar volumetric behavior on mixing has been found for aqueous toluene, ethylbenzene, hexane, and decane, and is considered to be a characteristic property of the aqueous hydrocarbons in the vicinity of the critical region. Moreover, the region where the anomalous volume expansion occurs proved to be a narrow region enclosed by an extended line of the three-phase equilibrium curve, the one-phase critical curve, and the vapor pressure curve of neat water as illustrated in Fig. 1. These phenomena could be found for the first time by *in situ* spectroscopic measurements, which can provide volumetric concentrations in each of the two coexisting phases, the water-rich and hydrocarbon-rich phases, of the mixtures.

Very recently, we have performed densimeter measurements⁴ of water-methanol mixtures in the same temperature-pressure range as for the water-hydrocarbon mixtures mentioned above. We have found remarkably large volume contraction on mixing at low methanol mole fraction at 573 K and at pressures in the 100–137 bars range, where water is in the liquid state and methanol is in the supercritical state. This volume contraction is a marked contrast to the volume expansion of the water-hydrocarbon mixtures and may be characteristic of aqueous mixtures of a hydrophilic

substance in the vicinity of the critical region. At higher methanol mole fractions, the relative volume change on mixing exhibits a negative-to-positive sigmoidal variation and then takes a positively large value similar to that for the water-hydrocarbon mixtures. In addition, we have found that the volume contraction of the water-methanol mixtures can be reproduced by molecular-dynamics simulations with rather simple model potentials, which is then useful for discussion of a local structure of the mixtures.

The aim of this paper is to perform computer simulations of molecular dynamics in the water-benzene mixtures at 573 K and investigate the molecular-level structures which could not be obtained from spectroscopic measurements. A suggestion about how the anomalous volumetric behavior of the mixtures is related to their molecular-level properties will be provided by the simulations and will be useful for further studies of the mixtures. Experimental measurements, in general, provide limited aspects of the real matter, and sometimes scientists wish to obtain further insight into the molecular-level structure and dynamics of the matter beyond the experimental limit. The computer simulation techniques meet those requirements and have been widely used through the years to support or supplement experimental results, predict properties of matter at extreme conditions, and find new phenomena.

The water-benzene system is typical of water-hydrocarbon systems and has often been studied by computer simulation. The studies were devoted to two main subjects. One is the molecular-level structure of the liquid-liquid benzene-water interface and molecular transfer across the interface,^{5–7} and the other is the structure and dynamics of hydrophobic hydration.^{8–11} The present paper deals with molecular-dynamics simulation of the volumetric behavior of

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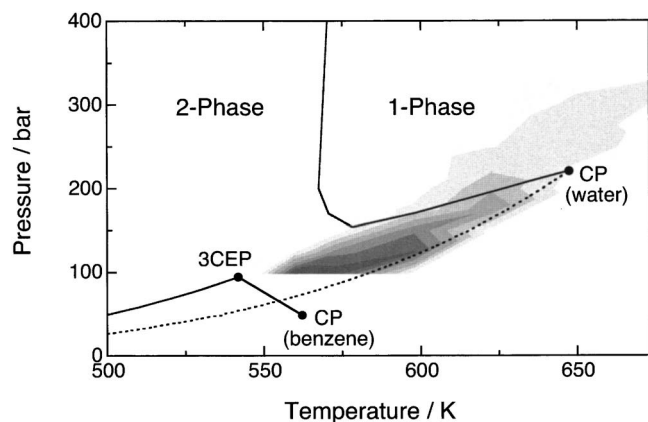


FIG. 1. Experimental contour map of the relative volume change on the pressure-temperature phase diagram of the water-benzene mixtures. The darker region indicates higher degree of the volume expansion. [Reproduced from Ref. 2 with permission. Copyright (2004) American Institute of Physics].

water-benzene mixtures at high temperatures and pressures. Such a study on the volumetric behavior has never been reported so far to our knowledge.

II. MOLECULAR-DYNAMICS SIMULATIONS

Molecular-dynamics simulations of water, benzene, and water-benzene mixtures with various mixing ratios have been performed on the isothermal-isobaric ensemble (N - P - T) at temperatures around 573 K and pressures around 100 bars. The model systems for neat water and water-benzene mixtures are composed of 800 rigid molecules in a cubic unit cell with the periodic boundary condition, while for neat benzene a 200-molecule system was used. The intermolecular interaction is given by pairwise potentials of the Lennard-Jones 12-6 potential plus electrostatic interaction between fractional charges on each atom:

$$U_{mn} = \sum_{i \in n} \sum_{j \in m} \left[4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + \frac{q_i q_j}{r_{ij}} \right]. \quad (1)$$

The Lennard-Jones parameters for water-water interaction are taken to be a simple point charge (SPC) type,¹² while the fractional charges on atoms are adjusted so as to reproduce experimental densities of water at 573 K as shown later. For benzene-benzene interaction, a six-site Lennard-Jones-type model by Friedlich and Lustig¹³ is used. The Lorentz-Berthelot combination rule was applied to the water-benzene interaction. The values of the potential parameters are listed in Table I. The cutoff radius for the Lennard-Jones-type interaction was taken to be 10 Å, which is not less than three times the atomic radii concerned in the present systems. The long-range electrostatic interactions were calculated by the Ewald sum method with appropriately chosen convergent parameters:¹⁴ the width of the virtual charge distribution, $\kappa = 0.5$, and the maximum absolute value of the integer vector to be included in the sum over the reciprocal space, $|\mathbf{n}_{\max}| = 15$. The choice of these parameters is significantly important for proper calculations of densities of the model system on the N - P - T ensemble. The equations of motion were integrated by the fifth-order Gear algorithm with a time step of

TABLE I. Model potential parameters.

	Potential	Geometry
Water-water	$\sigma_{\text{OO}} = 3.17 \text{ \AA}^a$	$r_{\text{OH}} = 1.00 \text{ \AA}^a$
	$\epsilon_{\text{OO}} = 0.155 \text{ kcal mol}^{-1a}$	$\angle_{\text{HOH}} = 109.47^\circ{}^a$
	$q_{\text{H}} = 0.3877$	
	$q_{\text{O}} = -0.7754$	
Benzene-benzene	$\sigma_{\text{RR}} = 3.347 \text{ \AA}^b$	$r_{\text{RR}} = 1.70 \text{ \AA}^b$
	$\epsilon_{\text{RR}} = 0.153 \text{ kcal mol}^{-1b}$	$\angle_{\text{RRR}} = 120^\circ{}^b$
Water-benzene	$\sigma_{\text{OR}} = (\sigma_{\text{OO}} + \sigma_{\text{RR}})/2$	
	$\epsilon_{\text{OR}} = \sqrt{\epsilon_{\text{OO}} \epsilon_{\text{RR}}}$	

^aConverted from parameters in Ref. 12.

^bTaken from Ref. 13.

0.5 fs. The pressure and temperature were regulated by Andersen's algorithm and the velocity-scaling method, respectively. The length of each run was in the 50–200 ps range, depending on conditions. A longer run was required for a mixing system. After equilibration was accomplished, which was confirmed by monitoring the unit-cell volume, temperature, and pressure of the system, statistical averages were taken over the succeeding production run of 25–100 ps duration. Standard deviations of the volumes thus obtained were less than a few percent for neat water, 2%–10% for neat benzene, and 5%–10% for mixtures. In general, it was larger at lower pressures. Fluctuations of pressure and temperature were within 10 bars and 0.3 K, respectively. All the molecular-dynamics calculations were performed by using the program WINMASPHYC 2.0 PRO (Fujitsu Ltd.). First, we show how these model systems reproduce the experimental properties of real systems. Next we discuss dynamical and structural properties of the mixtures on the basis of the simulations.

A. Neat liquids

In view of the fact that the anomalous volumetric behavior has been found at pressures a little above the vapor pressure of pure water at high temperatures, first we intend to find a water model which reproduces densities around the gas-to-liquid transition pressure, 85 bars, at 573 K. It proves that an 800-water molecule system with a SPC-type potential¹² with a readjusted fractional charge, $q_{\text{H}} = 0.3877$, which corresponds to a dipole moment of 2.15 D, reproduces well the experimental densities¹⁵ in the temperature-pressure range of interest, as shown in Fig. 2(a). This figure also shows that the calculations with the original extended simple point charge (SPC/E) model, $q_{\text{H}} = 0.4238$,¹² which corresponds to 2.35 D, provide about 15% higher densities and lower transition pressures. It should be noted that the present potential is useful only at around 573 K, since it failed to reproduce experimental densities at higher temperatures, e.g., 623 K, where calculations provided about 10% higher densities and significantly lower transition pressures. The effectiveness of using different fractional charges for water at different densities and temperatures has been shown previously by Matubayashi *et al.*¹⁶ It should also be mentioned here that the position of the vapor-to-liquid transition shifted to higher pressures when the system size increased, while we could not produce the gas phase when a smaller

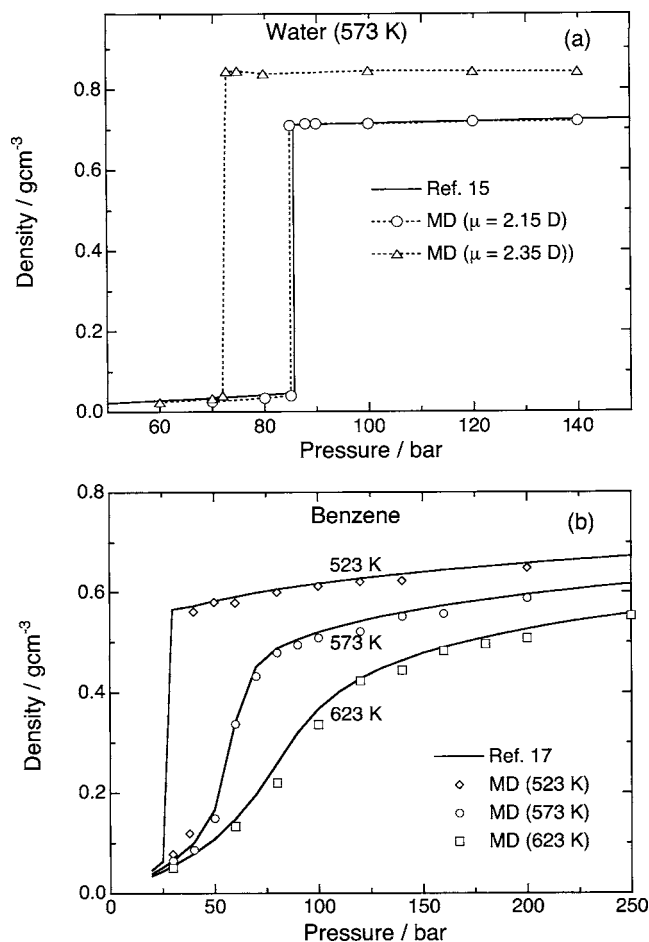


FIG. 2. Calculated and experimental densities plotted against pressure (a) for water at 573 K, where the experimental values were taken from Ref. 15, and (b) for benzene at 523, 573, and 623 K, where the experimental values were taken from Ref. 17.

400-molecule system was used. Therefore, the present calculations are not free from size dependency and further extensive calculations with much more larger systems would be required to reproduce the phase transition in a true sense. However, the present 800-molecule system will be practically useful for a study of the local structure and molecular dynamics of water at pressures around the transition pressure at 573 K.

Calculations of the model benzene system are quite satisfactory for reproducing experimental densities¹⁷ as shown in Fig. 2(b). The six-site Lennard-Jones potential is found to be useful in the wide temperature-pressure range including the supercritical state, as claimed in the original paper.¹³

To assess the model potentials from the viewpoint of dynamical properties, self-diffusion coefficients of the model systems have been calculated by the Einstein relation,

$$D = \frac{1}{6T} \langle |r_i(T) - r_i(0)|^2 \rangle, \quad (2)$$

and compared with experimental results in Fig. 3. So far, only a few high-temperature-pressure measurements¹⁸⁻²¹ have been reported, and those in the temperature-pressure range concerned are plotted in Fig. 3. The calculated values agree fairly well with the experimental results, and the

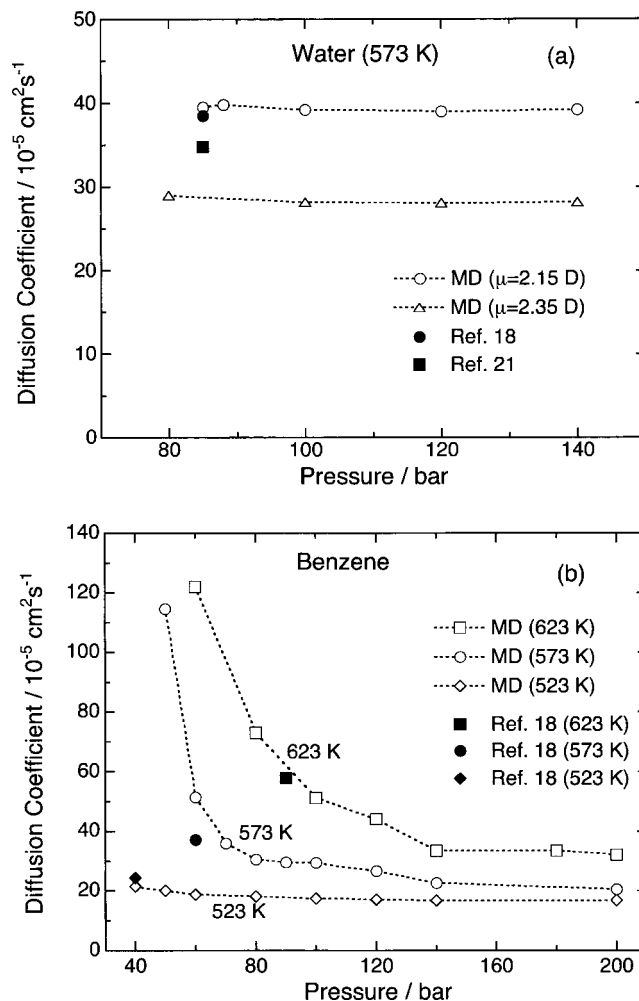


FIG. 3. Calculated and experimental self-diffusion coefficients plotted against pressure (a) for water at 573 K and (b) for benzene at 523, 573, and 623 K, where the experimental values were taken from Refs. 18 and 21.

present model potentials may be appropriate in discussing the molecular translational dynamics in the neat liquids. For comparison, calculations with the original SPC/E fractional charges ($\mu=2.35$ D) are plotted in Fig. 3(a), which are distinctly smaller than those provided by the present model, being consistent with the density deviation shown in Fig. 2(a).

B. Volumetric behavior of the water-benzene mixtures

The relative volume change on mixing is given by

$$\frac{\Delta_{\text{mix}} V}{V_0} = \frac{V - V_0}{V_0} = \frac{\rho_0}{\rho_{\text{mix}}} - 1, \quad (3)$$

where ρ_{mix} and ρ_0 denote the density of mixture and the average density before mixing, respectively. In the previous experimental papers,^{1,2} these were given by the following relationships:

$$\rho_{\text{mix}} = (C_W M_W + C_B M_B) / 1000 \quad (4)$$

and

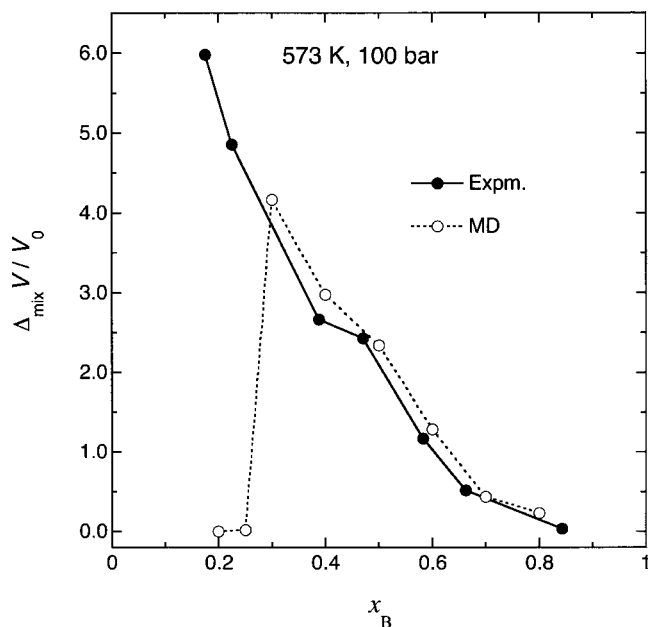


FIG. 4. Calculated and experimental values of relative volume change on mixing of water and benzene at 573 K and 100 bars plotted against mole fraction of benzene.

$$\rho_0 = \frac{C_W M_W + C_B M_B}{(C_W M_W / \rho_W) + (C_B M_B / \rho_B)}, \quad (5)$$

where C_W and C_B are the molarities of water and benzene, respectively, which were determined from the near-infrared absorption intensities, M_W and M_B are the molar weights, and ρ_W and ρ_B denote densities of neat water¹⁵ and neat benzene,¹⁷ respectively.

The molecular-dynamics simulations with the N - P - T ensemble provide directly the mixture volume V . The volume before mixing, V_0 , is given by the sum of the molar volumes of water and benzene, v_W and v_B , respectively, by

$$V_0 = 800[(1 - x_B)v_W + x_B v_B], \quad (6)$$

where x_B denotes the mole fraction of benzene and the v_W and v_B values are given by simulations of neat fluids at the same temperature and pressure. As shown in Fig. 4, the calculated values of the relative volume change are in good agreement with the experimental values^{2,22} in the 0.3–0.8 range of x_B . However, in the range of x_B smaller than 0.25, the calculations cannot reproduce the large volume expansion. The calculated densities of the mixtures in this range are liquidlike against the experimental gaslike densities. This deviation may indicate insufficiencies of the present model potentials for simulations of dilute gaslike fluid mixtures and/or may be due to the sizedependency of the simulations as mentioned before for neat water. Phase separation of the mixtures was not observed in the present calculations. This is consistent with the experimental observations by Rebert and Kay²³ that the water-benzene mixtures of $x_B > 0.11$ form a homogeneous fluid phase at 573 K and 100 bars. Then the present model will be practically useful in discussing structural properties of the mixtures in the 0.3–0.8 range of x_B .

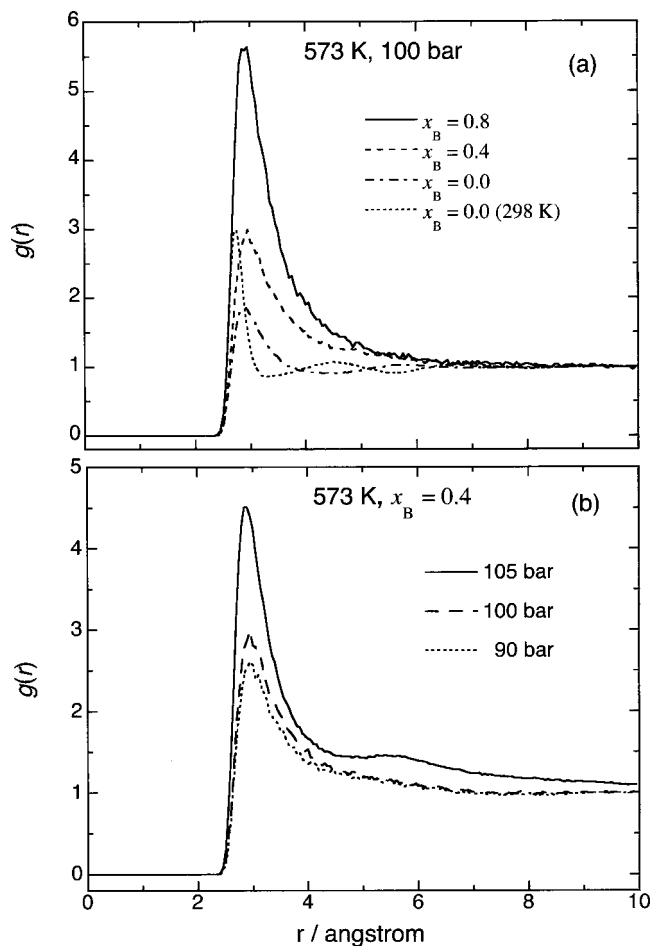


FIG. 5. Pair distribution functions for the center of mass of water: (a) Dependence on the mole fraction of benzene x_B at 573 K and 100 bars and (b) pressure effect at 573 K and $x_B = 0.4$.

C. Pair distribution functions and coordination numbers for the water-benzene mixtures

Pair distribution functions for the center of mass are calculated by

$$g_{nm}(r) = \frac{1}{4\pi r^2 \Delta r} \cdot \frac{V}{N_n N_m} \left\langle \sum_{k=1}^{N_m} \Delta N_{km}(r - \Delta r/2, r + \Delta r/2) \right\rangle, \quad (7)$$

where N_n and N_m denote the numbers of water or benzene molecules contained in the volume V of the model system. Figure 5(a) shows the calculated water-water distribution functions for a few different mixtures at 573 K and 100 bars and for water at 298 K calculated with the original charges of SPC/E potential for comparison. Profiles of the distribution functions for neat water at 298 and 573 K are in good agreement with previous calculations.^{16,24–26} As the temperature rises to 573 K, the second peak around 4.5 Å, which indicates the tetrahedral ordering of the hydrogen-bonded neighbors, completely disappears and the first peak moves from 2.75 to 2.90 Å, broadens, and reduces its height. In addition, a small bulge appears at around 5.8 Å. These facts indicate that water almost loses the characteristic structure of a hydrogen-bonded liquid and becomes like an ordinary liquid at 573 K. It should also be noted here that the profile for the

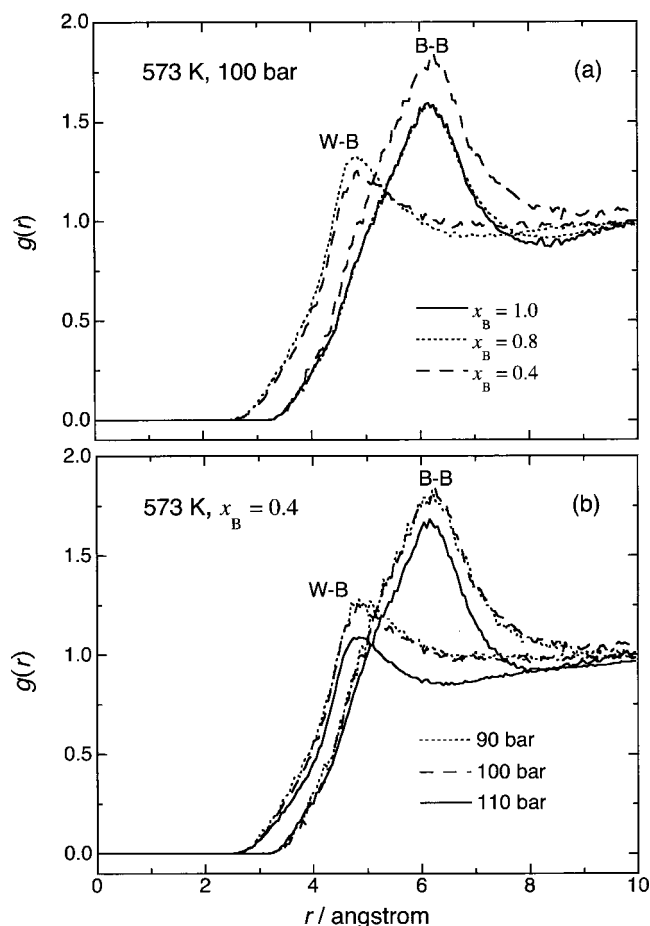


FIG. 6. Pair distribution functions for the center of mass for water-benzene (W-B) and benzene-benzene (B-B): (a) Dependence on the mole fraction of benzene x_B at 573 K and 100 bars and (b) pressure effect at 573 K and $x_B=0.4$.

neat water at 573 K was found to be almost independent of pressure in the 100–160 bars range, being consistent with the fact that the water density varies little with pressure as seen in Fig. 2(a).

In the water-benzene mixtures, the first peak of the water-water distribution grows remarkably with increasing benzene fraction x_B as seen in Fig. 5(a). This fact indicates a tendency of water molecules toward self-association in the hydrophobic circumstance. This first peak sensitively depends on pressure as shown in Fig. 5(b), which suggests significantly large compressibility of the mixture at around 100 bars. It should be noted here that the profile of the distribution function at higher pressures in the 105–160 bars range was found to be approximately independent of pressure, suggesting a liquidlike condition of the mixture with $x_B=0.4$ at higher pressures.

Figure 6 displays benzene-benzene and water-benzene distribution functions. The first peak of the benzene-benzene distribution increases a little by dilution with water as seen in Fig. 6(a). This fact suggests a tendency of benzene molecules toward self-association in the aqueous mixtures and seems to be consistent with the above-mentioned tendency of water molecules. The pressure-dependent change of the benzene-benzene first peak shown in Fig. 6(b) is opposite to that of the water-water distribution mentioned above. Nevertheless,

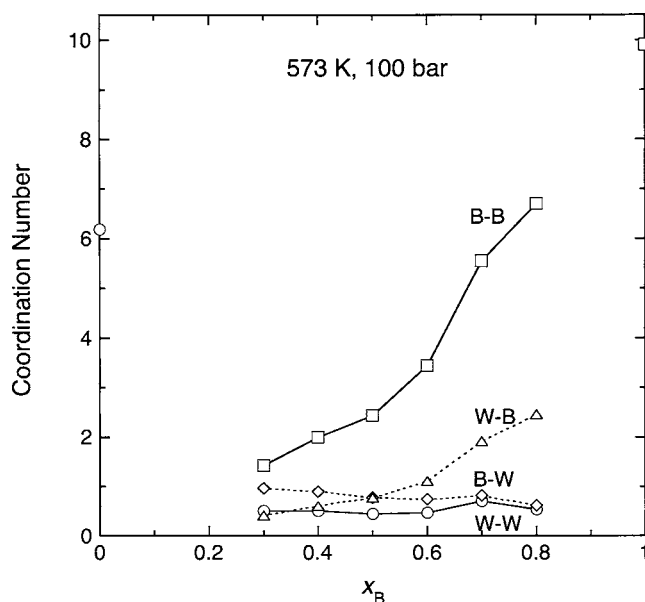


FIG. 7. Calculated coordination numbers around a water molecule (W-W and W-B) and a benzene molecule (B-B and B-W) in the water-benzene mixtures at 573 K and 100 bars.

the benzene-benzene and water-benzene distribution functions show relatively small dependence on x_B and pressure as compared with that of the water-water distribution.

Although the pair distribution functions mentioned above would be useful for a study of structural properties of the mixtures, we need to take account of the considerable variation of the fluid density with benzene mole fraction. More direct measure of the local structure will be obtained from the coordination number that is estimated by integrating the pair-correlation function over an appropriate range,

$$N_{nm}(r) = \frac{N_m}{V} \int_0^r 4\pi r'^2 g_{nm}(r') dr'. \quad (8)$$

The integration limits are taken to be 4 Å for water-water, 6 Å for benzene-water and water-benzene, and 8 Å for benzene-benzene correlations, respectively, and the resulting values are plotted in Fig. 7, where those for neat liquids are plotted on both ends, $x_B=0$ and 1. The coordination number of water molecules around a water molecule (W-W) is about 0.5 in the x_B range of 0.3–0.8, which is an order of magnitude smaller than the value of 6.2 at $x_B=0$. This fact suggests that the local structure of the water molecules undergoes drastic change by dissolution of benzene, and, roughly speaking, half of the water molecules in the mixtures exist as monomers and the other half as dimers. On the other hand, the benzene molecules in the mixtures have a relatively large tendency to aggregate themselves and the B-B coordination number increases monotonously toward the value of 9.9 at $x_B=1.0$. Concerning B-W and W-B, in addition to B-B coordination numbers, their variations against x_B look like those of ordinary liquid mixtures. These facts indicate that the structural feature of the water-benzene mixtures is mainly exhibited by the local structure around the water molecules.

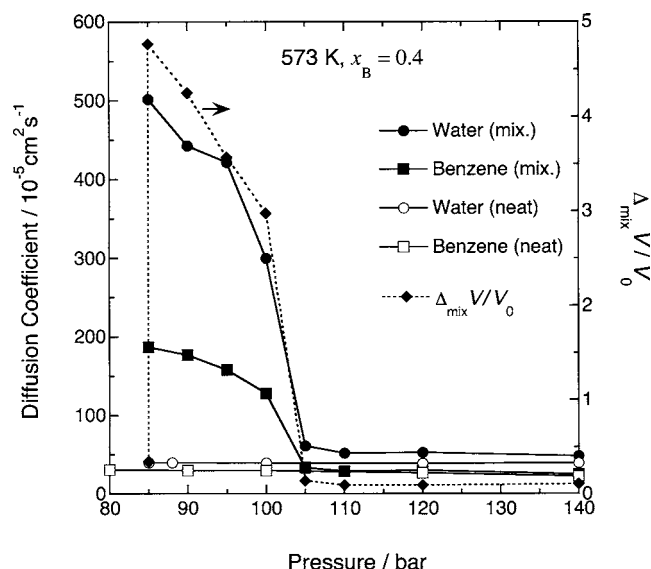


FIG. 8. Self-diffusion coefficients of water and benzene molecules in the mixture of $x_B=0.4$ and neat liquids, and relative volume change on mixing at 573 K plotted against pressure.

D. Self-diffusion coefficients in the water-benzene mixtures

Figure 8 shows the calculated diffusion coefficients of a mixture with $x_B=0.4$ and neat liquids as a function of pressure at 573 K. It is found that those of the mixture increase remarkably with decreasing pressure below 105 bars, while those of neat liquids exhibit a relatively small change in the pressure range of 80–140 bars. The large pressure dependence of the diffusion coefficients of the mixture is consistent with the pressure dependence of the relative volume change on mixing, whose calculated values are also plotted in Fig. 8 for comparison.

Figure 9 shows the dependence of the diffusion coefficients on benzene mole fraction x_B at 573 K and 100 bars, where those of neat liquids are plotted on both ends and the experimental values of the relative volume change are also

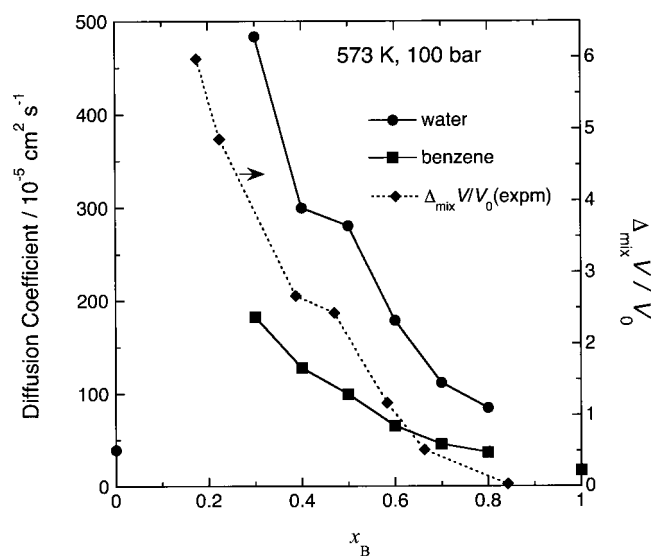


FIG. 9. Dependence of the self-diffusion coefficients and the relative volume change on mole fraction of benzene x_B at 573 K and 100 bars.

plotted for comparison. It proves that the diffusion coefficients increase remarkably with decreasing mole fraction of benzene, being consistent with the volumetric behavior of the mixture. It is intriguing to notice that the water molecules must exhibit a great jump in the self-diffusion coefficient on mixing with benzene somewhere in the 0–0.18 range of x_B . On the other hand, diffusion coefficients of benzene monotonously decrease toward that of neat benzene as x_B increases.

III. CONCLUSION

Structural properties of water-benzene mixtures at 573 K and pressures in the 85–140 bars range, which exhibit anomalously large volume expansion on mixing, were studied by molecular-dynamics simulations. The suitability of the model potentials used was confirmed by reproduction of the experimental densities, the gas-to-liquid transition pressure, and the self-diffusion coefficients for neat water and neat benzene, and the experimental volumetric properties of the mixtures. Structural features of the mixtures were discussed by calculating pair distribution functions, coordination numbers, and self-diffusion coefficients in the mixtures. It has been suggested that the local structure and dynamics of the water molecules undergo drastic change by dissolution of benzene in the vicinity of the critical region where the mixtures exhibit anomalously large volume expansion on mixing. On the other hand, variation of the local structure of the benzene molecules with mixing ratio seems to be understood as that of ordinary liquid mixtures.

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