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Effect of hydrogen bonding on self-diffusion in methanol/water liquid mixtures: A molecular dynamics simulation study

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ABSTRACT

Self-diffusion motion is strongly dependent on hydrogen bonding and temperature. In this work, the methanol/water mixtures of molalities from 1 to 5 m have been studied by molecular dynamics simulation. A definition of hydrogen bonding state is proposed to detailedly analyze the effects of the type and number of hydrogen bonds on the water self-diffusion. It is shown that most water molecules are in the hydrogen bonding state f_k^k, which means that one water molecule simultaneously hydrogen bonded to k water molecules with one hydrogen bond, respectively. Methanol prefers to produce isolated water molecules by the insertion of its hydrophobic group into the hydration shell of water. Besides, calculation of mean square displacements of water in different hydrogen bonding states shows that one water molecule with more hydrogen bonds diffuses more slowly. Pair energy of the hydrogen bonded molecules is also calculated to compare the attractive interactions of different types of hydrogen bonds. The hydrogen bonds between methanol and water present stronger attraction than that between water molecules. It indicates that increasing the concentration of methanol is conductive to restricting the water self-diffusion. Cluster analysis reveals that methanol cluster is more stable than water cluster in the binary mixtures. Thus high concentration of methanol enhances the blockage of the methanol cluster to water movement. These findings will lead us to further understand the mechanisms of water self-diffusion in the methanol/water mixture.

1. Introduction

In aqueous solutions, amphiphiles exhibit attractive and powerful ability of organizing the local structure where the amphiphilic molecules tend to be pushed together by the low affinity of water to the hydrophobic groups, and hydrogen bond (H-bond) to the surrounding water molecules by hydrophilic groups [1]. The H-bonds between amphiphilic molecules and water are a substitution of the H-bonds between water molecules, resulting in the rearrangement of the local hydrogen bonding (H-bonding) structure. Methanol is one of the simplest amphiphiles with both hydrophobic and hydrophilic groups. It is widely used in the fields of organic synthesis, biochemistry and biotechnology. Moreover, the development of direct methanol fuel cell leads to a growing interest in the studies of the microscopic properties of methanol [2–4]. Therefore, it is important to acquire a deep comprehension of the methanol/water mixture properties. The hydroxyl group of each methanol molecule can simultaneously act as H-bond donor and acceptor, and the methyl group has a negative effect on the formation of H-bonds [5]. The structure arrangement of the methanol/water mixtures has close correlation with the local hydration structure and dynamics of the amphiphilic solutes in the polar solvent [1,6]. Thus the tetrahedral-like H-bonding network formed by water molecules is apt to be interrupted by the presence of methanol [7]. Although methanol is soluble in water, their binary mixtures are incompletely mixed at the microscopic scale resulted from the formations of water and methanol clusters [6]. Some interesting non-ideal properties of methanol/water mixtures are considered to be correlated to intermolecular interaction such as H-bonding [8].

Investigations of the effect of methanol on the structure and dynamics of its aqueous solutions have been carried out in various fields by experiments and simulations. Dougan et al. [9] employed both neutron diffraction experiment and molecular dynamics simulation to investigate the structural properties of methanol/water mixtures with various proportions. The results show that the H-bonding and hydrophobic interactions lead to a bi-percolating network near the molar fraction of 0.27, where many properties such as transport coefficients and thermodynamic functions present abnormal values. The bi-percolating network in methanol/water mixtures was also found by Zhong and coworkers [8].

H-bonds play a determining role in understanding the microscopic structural and dynamical properties of the aqueous solutions, thus numerous studies [10–13] provide the information of the H-bonding effect on several properties including self-diffusivity. Molecular dynamics

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(MD) simulation has become a widely used tool for calculating self-diffusion coefficients [14,15], and efforts have been devoted to the application of molecular-level techniques to macroscopic evolution equations [16,17]. The mechanisms of the dependences of water self-diffusion motion on concentration and temperature are still open to question. In our previous study [6], the diffusion motion of methanol and water molecules was found to be germane to the intermolecular interaction of H-bonding in their binary mixtures. The mean square displacements of water molecules in different H-bonding states were calculated to quantitatively evaluate the H-bonding effect on the self-diffusion motion. The results revealed that one water molecule with high content of H-bonds has low self-diffusion coefficient, resulting in high viscosity in the macroscopic view. However, different types of H-bonds were not specifically considered in the statistical and dynamical analysis for each H-bonding state. There are two probable types of H-bonds (i.e., water–water (W–W) and methanol–water (W–M) H-bonds) presenting in the methanol/water mixtures. For example, one water molecule in the H-bonding state f_1 denotes that one water molecule initially with one H-bond, where f_1 is the collection of one water molecule hydrogen bonded (H-bonded) to another water or methanol molecule; and three probable combinations (i.e., 2W–W, 2W–M and 1W–W + 1W–M H-bonds) may exist in the H-bonding state f_2, etc. [6]. The previous paper [6] only presented a mean effect of different types of H-bonds on the water self-diffusion, thus each H-bonding state should be subdivided to analyze the effects of different H-bonding types.

In this work, we will propose a definition, by which the contribution of two types of H-bonds (i.e., W–W and W–M H-bonds) to the water molecules of different H-bonding states could be distinguished. By means of the definition, the effects of temperature and concentration on the water molecules of different H-bonding states are investigated by calculating the distributions of the corresponding H-bonding states. The paper also studies the self-diffusion motion of the water molecules in different H-bonding states. An in-depth analysis is made to elucidate the relation between self-diffusion and H-bonding state, and explore which hydrogen bonding state is the dominant role in retarding the water self-diffusion. Then the pair energies of the W–W and W–M H-bonded pairs are calculated to interpret the effect of H-bonding interaction on the water self-diffusion.

2. Computational details

Classical MD simulations using the package NAMD 2.7 were performed in the isothermal-isobaric (NpT) ensemble for the methanol/water mixtures of different compositions. The compositions of the mixtures are denoted by molality ranging from 1 to 5 m, which are summarized in Table 1. The methanol/water mixtures were simulated under the conditions of the pressure 1 atm and the three different temperatures (273, 288 and 298 K). TIP3P potential [18] was used as the model of water. Force fields described by MacKerell et al. [19] was adopted to model methanol. Table 2 provides the results of the densities of the simulation systems at 288 K.

All simulations were performed under periodic boundary conditions in three dimensions to minimize the edge effect. The temperatures and pressure were controlled using Langevin dynamics and Langevin piston Nosé–Hoover methods to fluctuate around the abovementioned values, respectively. The particle mesh Ewald (PME) method was used to solve the full electrostatic interactions, in which the grid spacing was set to 1.0 Å. The cut-off distances of the switching and shifting functions were both set to 12 Å, which specified the distances where van der Waals interaction was truncated and the long and short range forces were separated for electrostatic interactions. The SHAKE algorithm was employed to constrain the covalent bond between hydrogen atom and its bonded atom around the nominal length.

Table 1
Compositions of the water and methanol molecules in different systems.

m (m)	*x* (%)	N_m	N_w
1	1.8	50	2803
2	3.4	75	2102
3	5.1	80	1496
4	6.7	90	1150
5	8.2	100	1121

m denotes molality of methanol in aqueous solution; *x* is the percentage of mass fraction of methanol; N_m and N_w are the numbers of methanol and water molecules, respectively.

Table 2
Comparison between the simulation and experimental results of the density for different systems at 288 K.

m (m)	ρ_{sim} (g/ml)	ρ_{exp} (g/ml)	$(\rho_{sim} - \rho_{exp})/\rho_{exp}$ (×100%)
1	1.0101	0.9958	1.4
2	1.0013	0.9930	0.8
3	0.9940	0.9901	0.4
4	0.9170	0.9875	−7.1
5	0.9809	0.9852	−0.4

The experimental data for density of the methanol/water mixtures are given by the reference.

For each simulation, the methanol/water system was first optimized with energy minimization, and the time step was set to 2.0 fs. The equilibration phase of each system was continued to run until the total energy of the system appeared to plateau. Equilibration took about 2.0 ns to reach. After equilibration of the system was reached, a production run was carried out for 3.0 ns to analyze the microscopic properties, during which the sampling frequency was set to once per 1000 time steps. For the calculation of mean square displacement (MSD), a subsequent production run for 200 ps was performed with sampling frequency of once per 10 time steps.

3. Results and discussion

3.1. Statistical analysis of H-bonding

3.1.1. Definition of H-bonds

Definition of H-bonds should be determined prior to the H-bonding analysis of the methanol/water systems. Following the previous studies [6,20], two H-bonded molecules should fulfill the geometric criterion involving the three conditions below:

(1) The distance R_{OO} between the donor and acceptor should be shorter than the threshold value R^C_{OO};
(2) The distance R_{OH} between the acceptor and donor hydrogen should be shorter than the threshold value R^C_{OH};
(3) The angle O–H…O should be smaller than the threshold value φ^C.

The threshold values R^C_{OO} and R^C_{OH} are determined from the positions of the first minima of the corresponding radial distribution functions (RDFs). The threshold values R^C_{OO} and R^C_{OH} are determined as at 3.5 and 2.45 Å [21] (not presented for brevity). The threshold value φ^C is defined as the widely accepted value 30 [1,6]. We also checked the variations of the threshold value φ^C up to 70, and observed negligible changes of the average number of H-bonds and their probability distribution with φ^C larger than 30.

3.1.2. Definition of H-bonding state

In the methanol/water mixtures, there are six H-bonding states for water molecules as reported in the previous study [6]. Except for the H-bonding state f_0, each H-bonding state could be composed of different combinations. Herein, a quantity f^n_k is defined to detailedly describe the constituents of each H-bonding state of water, where *k* denotes the total number of H-bonds one water molecule has, and *n* denotes the number of water molecules H-bonded to the same water. In other words, one