Journal of Molecular Liquids 167 (2012) 34–39

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Molecular dynamics study of diffusion of heavy water in normal water at different temperatures

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ARTICLE INFO

Article history:
Received 6 July 2011
Received in revised form 20 November 2011
Accepted 21 December 2011
Available online 2 January 2012

Keywords:
Water
Heavy water
Diffusion coefficient
Molecular dynamics

ABSTRACT

In the present work we study the diffusion of heavy water in the ordinary water and their mutual diffusion coefficient. Molecular dynamics studies of a binary mixture of heavy water (SPC/HW) and ordinary water (SPC/E), at heavy water mole fraction of 0.024 have been done at different temperatures ranging from 295 K to 318 K. Oxygen–oxygen radial distribution functions (RDF) have been evaluated. Self-diffusion coefficients of both solvent and solute have been determined by means of mean-squared displacement (MSD) versus time curves using Einstein's diffusion relation. Darken's relation has been used for determining the mutual diffusion coefficients at the respective temperatures. The variation of the diffusion coefficients along with temperature has been analyzed. Our results agree very well with the available previously reported experimental data.

1. Introduction

Computational techniques for the molecular modeling to predict the accurate physical properties of realistic systems to design new stable materials with desired properties are nowadays frequent [1–5]. The computational techniques like Monte Carlo and Molecular Dynamics have successfully described the properties of liquids in molecular levels. Grigera studied the effective potential of heavy water using computational methods [6]. Use of these techniques to study the dynamic properties especially the diffusion coefficient was suggested long time ago [7,8]. The study of heavy water has attracted a great deal of attention because of its intriguing physical properties as well as technological applications [9]. The molecular simulation of such a substance, particularly in comparison with ordinary water has a great importance not only in physical sciences but also in biological sciences. Heavy water is a poison for most organisms and only the most primitive forms can survive in it. Even the survival of simple life forms involves such an extreme adaptation that the organism undergoes a virtual species change.

Recently, it has been reported that the deuterium oxide can be used for stabilizing the oral polio vaccine (OPV) [9]. Poliomyelitis better known in common term as 'Polio' is a malignant disease which stops the growth of the skeleton of the legs and thereby causing disability and deformity. The OPV is highly heat sensitive and hence is always stored under refrigerated conditions, loses its potency the moment it is exposed to ambient temperatures (above 30 °C).

The dynamical property of heavy water especially in the presence of normal water is also important in nuclear reactors. Heavy water is one of the two principal moderators which allow a nuclear reactor to operate with natural uranium as its fuel. The hydration of macromolecules is expected to be altered by the substitution of H_2O by D_2O, which will alter the stabilizing effect of water, directly or through hydrophobic interaction [10]. The present work is focused to study the diffusion of heavy water in normal water using the molecular dynamics simulation technique. In fact, in a mixture of normal water and heavy water there exists semi-heavy water also as hydrogen atoms (^1H and ^2H) are rapidly exchanged between water molecules. In the present communication, we have studied the diffusion of heavy water in water. The study of more realistic system i.e., mixture of normal water (H_2O), semi-heavy water (DOH) and heavy water (D_2O) will be our future work. The present study also clearly gives the idea of the diffusion of heavy water in water. Malenkov et al. have studied the dynamics of both the isotope varieties H_2O and D_2O by computer simulation [11] and by neutron scattering [12] also. Further, Malenkov has studied the structure and physical properties including dynamics of liquid water and ices [13,14]. They used a huge system of water molecules (3456 molecules of water) [14] to study the correlation coefficient. Their findings show that the correlation coefficient decreases with time but does not reach zero.

We have carried out the molecular simulations of water and heavy water by using GROMACS (GROningen MAchine for Chemical Simulations) version 3.3 [15]. In the present work, we have used the modification of SPC/E (Simple Point Charge Extended) model for modeling the heavy water and named the model SPC/HW (Simple Point Charge Heavy Water) model [6]. Molecular dynamics simulation performed using the SPC/HW (Simple Point Charge/Heavy

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doi:10.1016/j.molliq.2011.12.008

Water) model [6], shows good agreement with the experimental data. The success and simplicity of SPC/E model [16] makes SPC/HW a good starting model.

In Section 2, we describe the modeling and simulation techniques. Section 3 focuses on the results and discussion of the present work and finally we close it with conclusions and future outlook.

2. Model and simulation technique

2.1. Diffusion

Diffusion is a transport phenomenon which arises due to the presence of concentration gradient. Diffusion coefficient is defined by the Fick's law [17] which states that the rate of transfer of diffusing substance through unit area of a section that is the particle flux **J**, is proportional to the concentration gradient measured normal to the section i.e.;

$$\mathbf{J} = -D\nabla C(r,t) \tag{1}$$

where C(r,t) is the concentration gradient and the proportionality constant *D* is known as diffusion coefficient. Einstein extended the Fick's law and has given the relation of diffusion coefficient as a function of mean-squared displacement and time. The Einstein's relation [13] for diffusion is given by,

$$D = \lim_{t\to\infty} \frac{<r^2(t)>}{6t} \tag{2}$$

where $<r^2(t)>$ is the mean-squared displacement and t is time.

2.2. Model of heavy water and water

The model of water used in the present work is the SPC/E (Simple Point Charge Extended) model. This model is quite successful to describe the dynamical properties of water. For the heavy water we have modified the SPC/E water model and extended it to define a heavy water by replacing the hydrogen by deuterium [6]. The modeling parameters for intermolecular interactions include the dispersion and repulsion coefficient of the Lennard–Jones form of potential (C_6, C_{12}) and partial charges on the oxygen, hydrogen and deuterium atoms. In the present model, a water molecule is characterized by three point masses corresponding to the oxygen and the two deuterium atoms. The O–D distance is set to 0.1 nm and the DOD angle to 109.47°. The charges on the oxygen and deuterium are equal to $-0.870\mathbf{e}$ and $+0.435\mathbf{e}$, where $\mathbf{e}$ is the electronic charge, respectively. The molecules interact through a Lennard–Jones dispersion and repulsion terms located on the oxygen center and Coulomb terms due to charges on oxygen and deuterium [6]. The intermolecular interaction can be written as,

$$U_{\mathrm{i,j}} = \frac{C_{12}}{[r_{\mathrm{oo}}(i,j)]^{12}} - \frac{C_6}{[r_{\mathrm{oo}}(i,j)]^6} + \sum_{\alpha=1}^{3}\sum_{\beta=1}^{3} \frac{q_\alpha(i)q_\beta(j)}{4\pi\epsilon_o r_{\alpha\beta}(i,j)} \tag{3}$$

where $U_{i,j}$ is potential energy, $r_{oo}(i, j)$ is the oxygen–oxygen distance between molecule i and molecule j, q_α and q_β the charges on atoms α and β of molecules i and j, and $r_{\alpha\beta}(i, j)$ is the distance between atom α of molecule i and atom β of molecule j. Table 1 summarizes the parameters used for modeling of heavy water [6,16].

In Table 1, σ and ε are Lennard–Jones parameters, K_{OD} and K_{OH} are spring constants for bond stretching, b_{OD} and b_{OH} are the equilibrium bond lengths, K_{DOD} and K_{HOH} are the spring constants for the bond-angle vibration for heavy water and water respectively, θ_0 is the equilibrium angle. Parameters for the SPC/E water are inherent in the GROMACS topology file. Only the difference arises in the parameters C_6 and C_{12} of Table 1 for normal water which are $2.617345*10^{-3}$ KJ/mol^{-1} nm^6 and $2.634129*10^{-6}$ KJ/mol^{-1} nm^{12} respectively.

Table 1
Model of heavy water.

D_2O parameters	Values
K_{OD}	3.45×10^5 kJ mol^{-1} nm^{-2}
b_{OD}	0.1 nm
K_{DOD}	3.83×10^2 kJ mol^{-1} rad^{-2}
θ_o	109.47°
$C_6=4\,\varepsilon\sigma^6$	2.61690E−03 kJ mol^{-1} nm^6
$C_{12}=4\,\varepsilon\sigma^{12}$	2.63323E−06 kJ mol^{-1} nm^{12}

2.3. Simulation details

After choosing the model of both heavy water and water, 5 molecules of the heavy water are mixed in 203 water molecules. The simulation of the mixture was carried out using the GROMACS 3.3 package at temperatures 295 K, 300 K, 305 K, 310 K and 318 K. The processes used for the simulation include the preparation of the system, energy minimization using steepest descent algorithm, equilibration of the system for all temperatures under NPT ensemble using berendsen barostat at one Barr and berendsen thermostat at respective temperatures [15,18–20]. The equilibration (NPT) process was carried out for 50 ns with the time step of 2 fs. We have performed simulation at fixed pressure (NPT ensemble) just to check the intra- and intermolecular interaction parameters of the H_2O and D_2O implemented in the present work. Table 2 presents the equilibrated densities of the systems with water and heavy water. The density of the system in each temperature is close to the density of normal water at the respective temperatures.

After checking the simulation parameters by estimating the density of the system we performed production runs in a system fixing number of particles, volume and temperature (NVT ensemble). We used berendsen thermostat for this case. The simulation was run for 200 ns with time step 2 fs.

2.4. Radial distribution function

For the structural analysis, the radial distribution functions [21,22] have been studied. They are $g_{DO\text{-}DO}$ (r), oxygen–oxygen radial distribution function of heavy water; $g_{OW\text{-}OW}$ (r), oxygen–oxygen radial distribution function of water and $g_{DO\text{-}OW}$ (r), oxygen–oxygen radial distribution function of heavy water and water molecules respectively. Fig. 1 represents the radial distribution function of oxygen of heavy water for temperatures 295 K, 300 K, 305 K, 310 K and 318 K. Table 3 presents the data related to the graph shown in Fig. 1.

In Table 3 the acronyms represent as follows:

- FPP—first peak position,
- FPV—first peak value,
- SPP—second peak position,
- SPV—second peak value,
- TPP—third peak position and
- TPV—third peak value.

Table 2
Equilibrium densities at different temperatures.

S.N.	Temperature (K)	Density (kg m^{-3})
1	295	1008.88 ± 0.04
2	300	1005.81 ± 0.04
3	305	1002.82 ± 0.04
4	310	999.53 ± 0.04
5	318	954.53 ± 0.04