



Dynamic properties of methanol–water mixtures at the temperatures up to 476.2 K and at high pressures via molecular dynamics simulation



Takumi Ono^{*}, Kyouhei Horikawa, Yuki Maeda, Masaki Ota, Yoshiyuki Sato, Hiroshi Inomata

Research Center of Supercritical Fluid Technology, Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, 6-6-11-403, Aoba, Aramaki, Sendai 980-8579, Japan

ARTICLE INFO

Article history:

Received 30 September 2015

Received in revised form

6 December 2015

Accepted 7 December 2015

Available online 12 December 2015

Keywords:

Non-equilibrium molecular dynamics

Methanol–water mixture

Viscosity

Diffusion coefficient

ABSTRACT

Viscosities and self-diffusion coefficients of methanol–water mixtures were calculated via molecular dynamics simulation from 298.2 to 476.2 K and at pressures up to 40 MPa. The periodic perturbation method (non-equilibrium molecular dynamics) and the Green-Kubo method with three-site flexible potential models were adopted for evaluating the viscosities and the diffusion coefficients, respectively. The calculated viscosities and diffusion coefficients of methanol–water mixtures agreed qualitatively with literature experimental values. The three-site flexible potential models used in this study provided similar performance to the previous studies that used rigid models. Results correlated with the Stokes–Einstein relation show the possibility that the effective hydrodynamic radii were approximately constant for the studied condition and might be little affected by the clathrate-type structure at lower methanol compositions.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Many anomalistic physical properties observed in aqueous solutions are related to inhomogeneities that exist on the microscopic level. Short chain alcohol–water mixtures are typical examples [1–9] for which clathrate-type structures of water molecules are formed through three-dimensional hydrogen bonding network around an alcohol molecule at low alcohol concentrations. The clathrate-type structure is also known as the “ice-berg” model [10]. An increase in alcohol concentration in aqueous solution leads to a decay of the number of the clathrate-type structures because of an insufficient number of water molecules and a two-dimensional hydrogen bonding network gradually becoming dominant [4,11]. The clathrate model is now widely accepted as a description of the hydrophobic hydration effect observed in alcohol–water mixtures and is one of the dominant factors of macroscopic physical properties [11]. A large decrease in the self-diffusion coefficients of alcohol and water is observed by the addition of a small amount of alcohol to water [11] and this behavior is attributed to the existence of clathrate-type structures, although a number of possible

explanations of nonlinear behavior of diffusional characteristics have been proposed [12,13]. The viscosity increases with a small amount of added alcohol for which the clathrate-type structure is considered to be also one of the reasons for observed changes in viscosity as well as those for the self-diffusion coefficient [14].

The inhomogeneous structure caused by clathrate formation in alcohol–water mixtures is strongly influenced by temperature and pressure. Experimental and theoretical approaches have revealed that hydrogen bonding still exists in sub- and supercritical water and for short chain alcohols [15,16]. Therefore, unique features in the physical properties of alcohol–water mixtures should be expected at high temperatures and pressures. There have been a number of reports on density and viscosity measurements of alcohol–water mixtures at high temperatures and high pressures to discuss specific physical properties in terms of hydrogen bonding [17,18]. The correlation of their properties has been also attempted using Eyring-theory-based model coupled with the equation of state in the temperature range from 350.7 to 476.2 K at pressures up to 40 MPa [19]. The importance of considering the inhomogeneity for describing the density and viscosity behavior was shown in that report although it was not clear how the clathrate-type structures contribute to inhomogeneity [19].

Although the formation of clathrate-type structure should have a strong effect on the behavior of viscosity and diffusion coefficient,

^{*} Corresponding author.

E-mail address: onot@scf.che.tohoku.ac.jp (T. Ono).

alcohol concentrations that correspond to the maximum in viscosity and minimum in diffusion coefficient are different from each other [20], indicating that the viscosity and diffusion coefficient have different contributions to the solution properties. In general, the viscosity is known to describe the macroscopic transport of momentum by the collective motion of the particles, while the diffusion coefficient tends to describe single-particle diffusive transport [21]. These properties are fundamentally influenced by hydrogen bonding, and a change in the relation between viscosity and diffusion coefficient is predicted at high temperature. The information of this relation is important for establishing a theory for describing the dynamic properties of aqueous solution in which clathrate-type structures exist.

In this work, we focused on the dynamic properties and calculated the viscosities and the diffusion coefficients of methanol–water mixtures by molecular dynamic simulation at temperatures up to 476.2 K and at pressures up to 40 MPa. The relationship between the viscosity and the diffusion coefficient was studied.

2. Computational details

Methods for determining viscosity from molecular dynamics (MD) simulation can be roughly divided into two types: (i) equilibrium simulation and (ii) non-equilibrium simulation. Pressure fluctuation methods [22], using either Green-Kubo integration or Einstein relation, are the basis of equilibrium simulations [23]. The momentum fluctuation methods, which measure the intrinsic fluctuation of momentum, are also equilibrium simulations. While the simple equilibrium MD simulation codes are available for viscosity calculation, these methods need long convergence times because of the large fluctuations in pressures and low signal-to-noise ratios for the intrinsic momentums [24,25]. One of the non-equilibrium MD simulations is the SLLOD algorithm [26] in which the viscosity is estimated by imposing a linear velocity profile on the simulation box. The periodic perturbation (PP) method is based on the same theoretical foundation as a momentum fluctuation method. In these methods, an artificial force profile is applied to the simulation box and the viscosities are calculated from the fluctuation of induced momentum instead of measuring the intrinsic fluctuations of the momentum. Therefore, the signal-to-noise ratio is improved, leading to better statistics of the calculation results than those of equilibrium MD simulation methods.

In the PP method, the viscosity can be calculated by applying an external force in the form of acceleration to the system. At each time step during the simulation, a periodic external force in the x -direction, which is a function of the y component only, can be imposed on each molecule (Eqs. (1–3)):

$$u_x(y, t) = v \left(1 - e^{-t/\tau_r} \right) A \cos(ky) \quad (1)$$

$$v = A \frac{\rho}{\eta k^2} \quad (2)$$

$$\tau_r = \frac{\rho}{\eta k^2} \quad (3)$$

where, u_x is the velocity of molecule in the y -direction, ρ is the density and k is the wave-index number. A detailed description of the PP method used in this study is given elsewhere [23].

In this study, we developed a method to calculate viscosity of methanol–water mixtures by imposing an external acceleration profile to a equilibrium molecular dynamics simulation code developed by our group [7,17]. The water and methanol potential models used in this study were the three-site flexible models

proposed by Honma et al. [27,28]. These molecular models can provide quantitative representation of the PVT and saturated properties of methanol and water in their gas, liquid and supercritical states. The three-site for methanol are oxygen (O), hydrogen (H) and methyl group ($-\text{CH}_3$). Potential of both flexible models were formulated as a sum of intra- and intermolecular potentials. The intramolecular potential is given by the angular form of the Toukan–Rahman (TR) potential. The details of the potentials are given in the supplementary material. In the simulations of this work, a cut-off radius of $0.997 L_{\text{box}}$ (L_{box} is the simulation box) was applied for all Lennard-Jones (LJ) interactions. The reaction field method was used to account for long-range electrostatic interactions. Unlike interactions were computed using the Lorentz–Berthelot combination rules:

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \quad (4)$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (5)$$

All simulations were performed with NVT -ensembles with external acceleration profile for several methanol mole fractions. The simulations began from initial configurations with random distributions of molecular positions. The temperature and pressure conditions in the simulation were set nominally as ambient (298.2 K - 0.1 MPa), 350.7–476.2 K and 10–40 MPa. Hence, the number densities (N/V) in the simulation were set to the experimentally determined densities [19] to follow the isobaric behavior at the given temperature. The total number of molecules was 2048. The temperature was initially (~ 60 ps) controlled by momentum scaling and afterwards (~ 60 ps) by the Nosè–Hoover thermostat for computational stability. The equation of motion was integrated using the velocity Verlet technique. Time steps were 1 fs for the intermolecular motion and 0.2 fs for the intramolecular motion. Statistical sampling in the simulation was done for 500 ps after 100 ps equilibration.

3. Result and discussion

3.1. Optimization of acceleration and validation of viscosity calculation

In the PP method, acceleration A is adopted to generate shear rate for viscosity calculation and the calculated viscosity depends on the acceleration values [20,29]. Firstly, the acceleration amplitude value dependence of the viscosity was evaluated via the PP method. Fig. 1 shows simulated viscosities of pure methanol and pure water for several acceleration amplitudes. The small acceleration amplitude causes large dispersion in the simulated viscosity leading to large error bars, although the size of the errors tends to decrease with increasing acceleration amplitude values. A decrease in calculated viscosities in the large acceleration amplitude region can be caused by disturbing the equilibrium of the system by strong perturbation [30]. A value of $A = 4 \times 10^{13} \text{ m/s}^2$ was adopted that allowed reliable convergence of the simulated viscosity values.

Simulated viscosities with $A = 4 \times 10^{13} \text{ m/s}^2$ for pure methanol and for pure water at different densities and temperatures are plotted in Figs. 2 and 3, and compared with literature simulation values [20,31]. In addition, simulated viscosities with molecular models, in which the internal degrees of freedom were eliminated from above three-site flexible models, are shown in Figs. 2 and 3 to confirm the effect of the internal degrees of freedom in a molecular model for viscosity calculation via PP method. Calculated values by Wensink et al. [20] via PP method with the OPLS potential for methanol molecule [32] and TIP4P for water [33] and those by Guevara-Carrion et al. [31] via equilibrium molecular dynamics and

Download English Version:

<https://daneshyari.com/en/article/201171>

Download Persian Version:

<https://daneshyari.com/article/201171>

[Daneshyari.com](https://daneshyari.com)