

Structure properties of mixtures composed of ethanol and water by molecular dynamics simulation

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Abstract: Transport properties of various mixtures of ethanol and water at different concentrations evaluated at temperatures 298.15K and pressure 1bar by MD method (molecular dynamics) simulation. Obtained results from study showed that the self-diffusion coefficients of ethanol and water in mixtures are in nearly qualitative agreement with the experimental data. The self-diffusion coefficients are increasing when the concentration of the water is increased. We have also observed that the first peak of the radial distribution functions ascended when the water concentrations decreased. The results indicated that the oxygen in ethanol (O_e) has a maximum interaction with ethanol hydrogen (H_e) at low mole fraction of ethanol. Therefore, it can be concluded that probability of existence of O_e around the H_e of ethanol molecule is higher than the water atoms at low mole fraction of ethanol. The higher the first peak heights is, the stronger the interactions of two water molecules can be. Therefore, the self-diffusion coefficients will decrease while the water concentrations are decreasing. Coordination numbers of water–water structure are more than the ethanol–ethanol structure coordination numbers. With the enhancement of coordination numbers, more molecules participated in the reaction, hence stronger bounds formed between molecules.

Keywords: Structure properties mixtures, Water, Ethanol, Molecular dynamics.

Introduction

Major changes have been recently developed in the perspective to molecular dynamics of hydrogen bonded liquids. Formation of hydrogen bonds between alcohol and water makes a more complex binary mixture and results in alcohol solubility [1, 2]. Mixture of alcohol and water shows different properties from the individual components such as different diffusion and structure properties [3]. Available information on solutions' structural behavior is too fundamental to help us understand the mixture diffusion properties, therefore simulation of molecular dynamics can be used as a powerful tool to investigate these properties of solutions at molecular level [4,5].

Information on density and viscosity the different liquid mixtures and the relation between the composition and temperature is very important in chemical industry for pipeline systems, mass transfer operations and etc. [6-8]. The detailed knowledge of the liquid structure and of the microdynamics of water, therefore, is one of the outstanding problems in condensed-matter physics and in biophysics as well. Many investigations toward a better understanding of the unusual characteristics of water as liquid and solvent have been performed using selected organic solutes as probes [9,10]. Because understanding the aqueous solvation is essential for understanding the biochemical process as they occur in vivo, small molecule-water system become an active topic of research these days. Mixtures' properties measurement is very expensive and finding a way to predict these properties would be

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very beneficial and cost effective. Chemical industry conducted a competition to get the best computer based predictions [11], with the objective of predicting fluid properties of a mixture like density and viscosity. Simulations of Molecular dynamics (MD) can be a valuable tool in this aspect, as they allow prediction of equilibrium and non-equilibrium properties [12–14]. Series of studies on alcohol and water mixtures are published, with the aim of studying details of atomic interactions such as mixture density of methanol and water [15, 16] and their structural properties [17–24]. In the present study, structure properties of ethanol and water in the mixture and the concentration dependency of these properties are investigated.

Various concentrations of the two components were used to study the structure properties at constant temperature of 298.15K and 1bar pressure. Above mentioned method was used to obtain self-diffusion coefficient of the mixtures and their constituents. Results for the mixtures and their constituents were compared to the experimental data. Equilibration of the simulations was checked by monitoring the density and self-diffusion coefficients. In all cases values had equilibrated within 50000 ps. Self-diffusion coefficients for ethanol (D_e) in mixture are given in (Figure 1) with MD values and the experimental data [31]. As shown in (Figure 1), our results were lower than the experimental data.

Result and Discussion

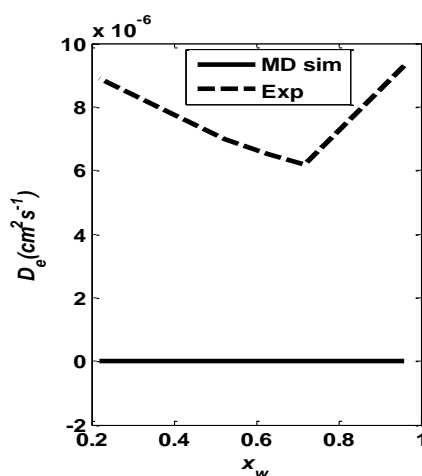


Figure 1: enthalpy change of the mixture, pure isopropyl alcohol as a function of temperature in pressure 1 bar.

In Figure 2, we plotted the self-diffusion coefficients of water (D_w) for mixtures.

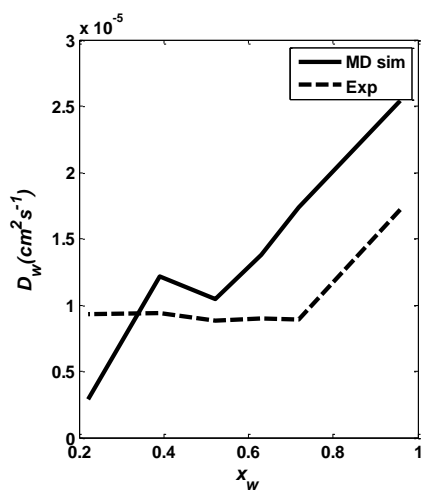


Figure 2: Simulated and experimental Self-diffusion coefficients of water at 298.15K as a function of mole fraction water.

The results showed simulation values are higher than the experimental data. Figure 3(a) and 3(b) are showing

lower self-diffusion coefficient of ethanol comparing to water.

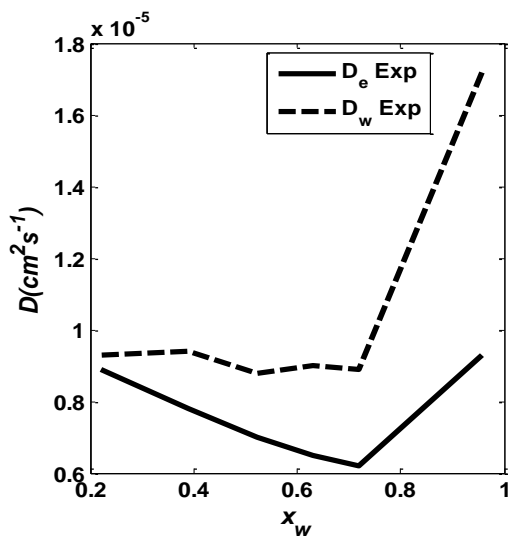


Figure 3(a): experimental Self-diffusion coefficients of water and ethanol at 298.15K as a function of mole fraction water

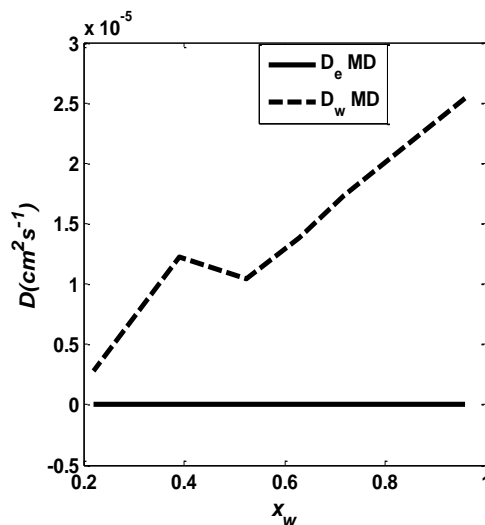


Figure 3(b): Simulated Self-diffusion coefficients of water and ethanol at 298.15K as a function of mole fraction water

Self-diffusion coefficients of the mixtures (D) increase when x_w rises (Figure 4).

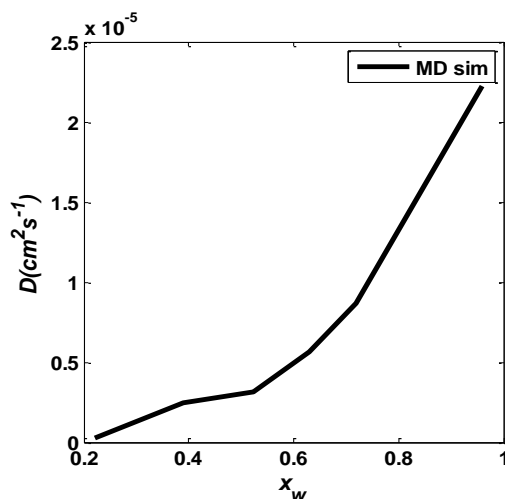


Figure 4: Simulated Self-diffusion coefficients of mixture for MD data at 298.15K as a function of mole fraction water.

Among different tools used for characterization of the structure of dense fluids is RFD or Radial Distribution Function. It reflects the effective pairwise interaction and the potential of mean force between two species. MD simulation was used to attain the radial distribution functions of ethanol and water mixtures at different concentrations.

The RDFs of different atoms in ethanol and water mixtures were obtained to study the mixture's local structure. Corresponding coordination numbers ($N_c(r)$) which is the number of molecules in the first shell around a central molecule, was determined by integration of the pair radial distribution functions. The results indicated that the oxygen in ethanol (O_e) has a

maximum interaction with ethanol hydrogen (H_e) at low mole fraction of ethanol. Therefore, it can be concluded that probability of existence of O_e around the H_e of another molecule is higher than the water atoms at low mole fraction of ethanol, see Figures 5(a), 5(b). Figure 6 shows ethanol/water molecules, taken from a simulation box with $x_e = 0.281$. It showed that at low mole fraction

of ethanol in the mixture, more water molecules lie around the ethanol molecules and therefore, the distance between ethanol molecules in mixture will decrease.

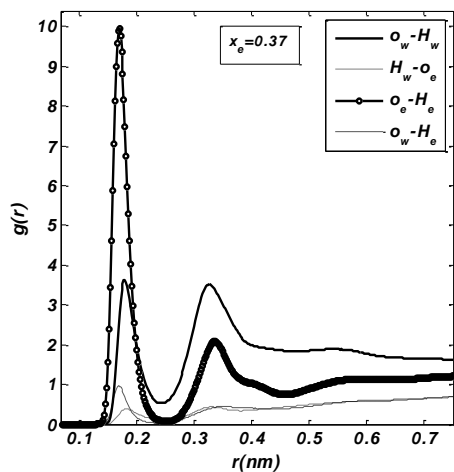


Figure 5(a): Various partial radial distribution functions for $x_e = 0.37$ in ethanol/water mixture.

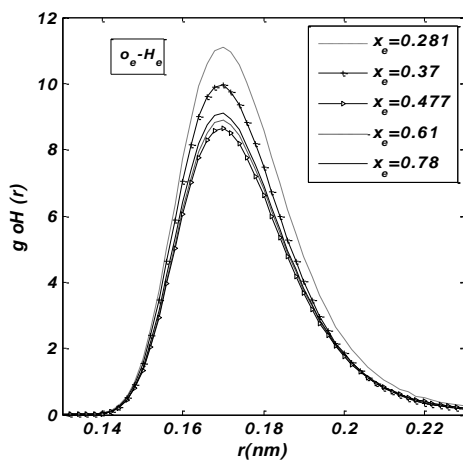


Figure 5(b): O_e-H_e partial radial distribution functions for different mole fractions in ethanol/water mixture.

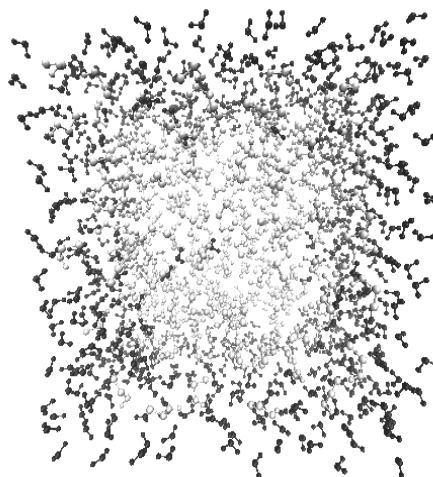


Figure 6: A typical snapshot of the molecular dynamics simulation for ethanol/water mixture corresponding to the mole fraction of ethanol 0.281. Black color represents the water molecule and white color represents the ethanol molecules.

The bond between ethanol's oxygen and hydrogen atoms will be stronger bond between water molecules, as seen in Figure 5(a). In Figure 7 high ethanol concentration, $x_e=0.78$ was studied,

according to the obtained results the water's oxygen (O_w) has a maximum peak with water's hydrogen (H_w).

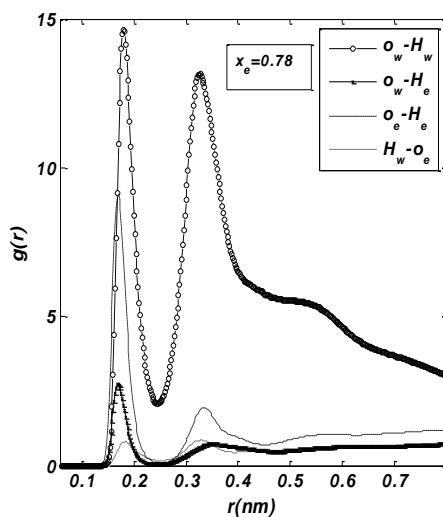


Figure 7: Various partial radial distribution functions for $x_e=0.78$ in ethanol/water mixture.

Results indicated that probability of existence of O_w around the H_w is higher than the ethanol atoms. (Figure 8) taken from a simulation trajectory in a simulation box with $x_e = 0.78$, shows increasing ethanol concentration, will cause clusters formation of water molecules in the mixture. Hence the probability of existence of water

molecules around the other molecules increases (see Figure 7). The higher the first peak heights are, the stronger the interactions of two water molecules can be. (Figure 9) shows that by increasing ethanol concentration, the first peak heights of O_w-H_w RDF's will increase. In (Figure 10) the first peak heights in the

Ow-Hw RDF's were plotted against the mole fractions of water. It shows that increasing water concentration decreases the first peak heights.

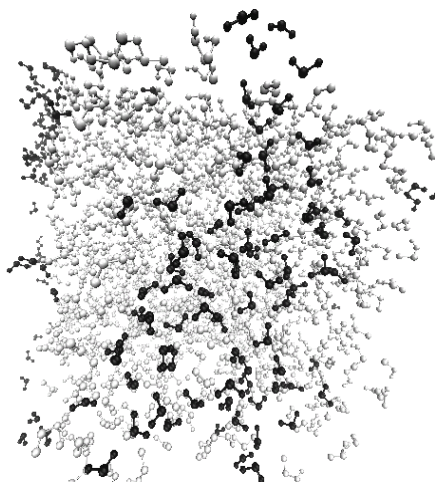


Figure 8: Same as Figure 6 but the mole fraction of ethanol 0.78.

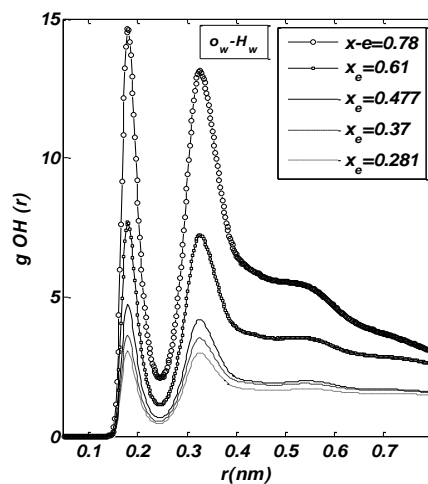


Figure 9: O_w-H_w partial radial distribution functions for different mole fractions in ethanol/water mixture.

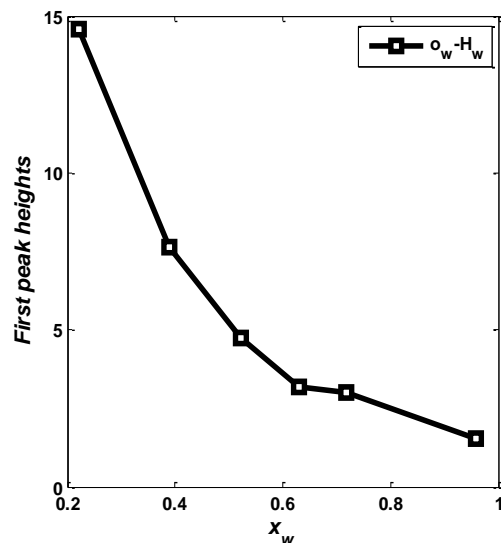


Figure 10: First peak heights in the O_w-H_w radial distribution functions.

The first maximum peak indicates the local structural order of water molecules around the water other molecules. When the water concentrations are increasing, local structure order will decrease, but self-diffusion coefficients of mixtures increase.

The O_w-H_w RDFs have maximum peaks at around 0.15–0.25 nm in different concentrations, the second peak is around 0.25–0.45 nm, so it was concluded that, the concentration does not affect the peaks positions and the valleys in the RDFs, but alters their heights and

depths (Figure 9). By decreasing ethanol concentration the coordination numbers of the O_w-H_w RDFs decrease (Figure 11(a)). The coordination numbers of the O_e-H_e RDFs, increases as the ethanol concentration decreases (Figure 11(b)). The O-H coordination numbers of water–water correlation are more than the ethanol–ethanol correlation. With enhancement of coordination numbers, more molecules participate in the reaction, hence stronger bounds are formed between molecules.

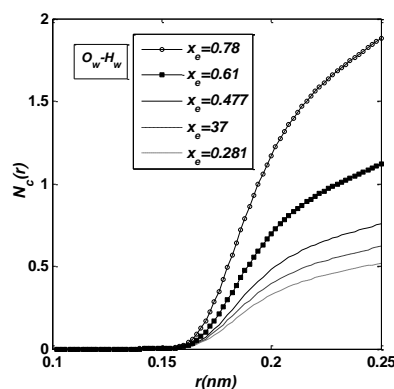


Figure 11(a): O_w-H_w coordination numbers for different mole fractions in ethanol/water mixture.

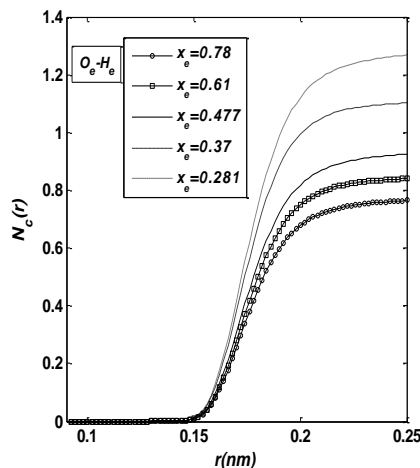


Figure 11(b): O_e-H_e coordination numbers for different mole fractions in ethanol/water mixture.

The expression used for calculating average absolute deviation (AAD) is as follow:

$$AAD = \frac{1}{N} \sum_{i=1}^N \left| \frac{A_{i,exp} - A_{i,calc}}{A_{i,exp}} \right| 100\%$$

N is the number of experimental data points and $A_{i,exp}$ and $A_{i,calc}$ are the experimental value and value obtained by molecular dynamics simulation, respectively. The obtained value of AAD (%) for the self-diffusion coefficients of water (D_w) in mixtures is 5.65%.

Conclusion

In this study, molecular dynamics simulations of ethanol/water mixture were performed in order to evaluate transport properties of the mixtures. Results showed that self-diffusion coefficients for the mixtures (D) increased when x_w rised. RDF figures showed that at high mole fraction of water, the first peaks of O_w-H_w RDF's become larger when the water concentrations are decreasing, which means the self-diffusion coefficients will decrease by decreasing water concentration. The coordination numbers for water–water structure, is more than the ethanol–ethanol structure. Enhancement of coordination numbers, resulted in participation of more molecules in the reaction. Hence stronger molecular bounds were formed.

Experimental

Fluid modeling

We considered N_1 system as particles or atoms of m_1 mass, and N_2 system as particles of m_2 mass in a volume V , mediated through a Lennard-Jones (LJ) 12-6 potential. The intermolecular interaction between site i and site j is given by Lennard–Jones potential and the Coulomb contribution.

$$u_{ij}(r_{ij}) = 4\varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) + \frac{q_i q_j}{r_{ij}} \quad (1)$$

Lennard-Jones parameters for interactions between different atom types were derived from combination rules:

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j}, \quad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$

where σ is the van der Waals radius and ε is the depth of the potential well [25,26,27].

Simulation method

Molecular dynamics of ethanol and water mixture with various concentrations were simulated in systems consist of 1000 molecules in a cubic cell. The prepared mixtures were placed in the boxes with dimension of $6.5nm \times 6.5nm \times 6.5nm$. We evaluated the quality of molecules topologies generated by the automated server PRODRG [28, 29] under the GROMOS43a1 force fields [30]. Temperature and pressure were fixed at 298.15K and 1 bar respectively [31]. The particle-mesh Ewald (PME) algorithm [12] was used for long-range electrostatics interactions. In all simulations the standard LINCS algorithm was used to constrain bond

lengths [32]. In all simulations a time step of 2 fs was employed with the leap-frog integrator [33]. A steepest-descent algorithm was used to minimize the energy of each system. Finally, each system was simulated for 50000ps production run under the same conditions.

Self-diffusivities from simulation

The self-diffusion coefficient D_i for particle i can be obtained using the Green-Kubo method (velocity autocorrelation function, VACF) $C_{v_i}(t)$ in the GK integrand,

$$C_{v_i}(t) = \langle v_i(0)v_i(t) \rangle,$$

where v_i is the particle i velocity and $\langle \dots \rangle$ is an average over time origins. Time-dependent self-diffusion coefficient of particle i is given by:

$$D_i = \frac{1}{3} \int_0^{\infty} \langle v_i(0)v_i(t) \rangle dt$$

The self-diffusion coefficient of particle i can also be obtained directly by MD from the linear region of the mean-square displacement as [34-39]:

$$D_i = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |r_i(t) - r_i(0)|^2 \rangle$$

Where r_i is the absolute position of particle i at a time t after an arbitrarily defined time origin, and the term inside the angle brackets is the mean square displacement (MSD). In this method, self-diffusion coefficient (D) is proportional to the slope of the MSD as a function of time in the diffusional regime [14].

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