

## Transport properties of mixtures composed of iso-propanol, water, and supercritical carbon dioxide by molecular dynamics simulation

N. Sohrevardi<sup>a</sup>, M.R. Bozorgmehr<sup>a\*</sup>, M.M. Heravi<sup>a</sup>, M. Khanpour<sup>b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Mashhad Branch, Islamic Azad University, Mashhad, Iran.

<sup>b</sup> Department of Chemistry, Ayatollah Amoli Branch, Islamic Azad University, Amol, Iran.

Submitted May14, 2017; Received August 21, 2017

Transport properties of various mixtures of supercritical carbon dioxide, isopropanol, and water at different concentrations are evaluated at temperatures 313.15K and pressure 150bar by molecular dynamics simulations. The results show that the self-diffusion (viscosity) coefficient is increased (decreased) for all mixtures studied when the concentration of the isopropanol is increased. In addition, the densities of the mixtures will lower, when the isopropanol concentrations is increased. We have also observed that the first peak heights of the radial distribution functions become higher when the isopropanol and water concentrations are decreasing which mean the self-diffusion coefficients will decrease while its density and viscosity will increase.

**Keywords:** Supercritical carbon dioxide mixtures, water, Transport properties, Molecular dynamics

### 1. INTRODUCTION

In the last two decades molecular dynamics (MD) simulations have been employed successfully for the study of transport properties of fluids, such as diffusion coefficients and viscosities. Quantitative predictions of diffusivity and viscosity are of great importance in designing experiments and improving engineering designs, such as molecular sieve operations. Catalytic processing of heavy liquid petroleum fractions, gel permeation chromatography and membrane separation technologies [1]. 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 in these days [2, 3]. It is known that transport properties of liquid state are mainly determined by the short-range intermolecular repulsive forces, whereas the equilibrium thermodynamic properties are essentially influenced by the long-range attraction forces [4]. Therefore, selection of suitable force field is important for accurate simulation [5].

Carbon dioxide is the most commonly used supercritical fluid because it is non-toxic, non-flammable, has moderate critical temperature and pressure (31°C and 7.4MPa) and more important is considered a green solvent.6 Supercritical CO2 densities and solvation power are intermediate between those of gases and liquids and can be easily modified with small changes in temperature and

pressure; meanwhile the fluid maintains good transport properties. The utilization of CO2 in the Supercritical Anti Solvent (SAS) method is also based on its relatively low solvent power for solutes such as polymers or pharmaceuticals and its good miscibility with many organic solvents. Other advantages are operation at moderate temperatures in an inert atmosphere thus avoiding the drug degradation and the possibility of tuning the fluid properties through changes in temperature and pressure that enables us to control particle size and/or morphology [6,7-10]. An alternative route to obtaining transport properties is to use molecular dynamics methods, which rely only on the knowledge of intermolecular potentials to provide averages of macroscopic thermophysical quantities and molecular structural information [11]. These methods have become particularly interesting with the increasing availability of computational resources and highly parallelized algorithms [12,13]. A major advantage of molecular dynamics over stochastic methods is their ability to generate configurations of the system of interest that are dependent on time, and thus naturally, providing means to estimate time-dependent properties. The basic concept used to perform experimental measurements can be extended to simulation methods, i.e., transport properties can be obtained as a response of the fluid to an imposed perturbation that drives the system away from equilibrium [14]. Recent developments of transient molecular dynamics (TMD) have been shown to provide signal-to-noise ratios comparable to those obtained via non-equilibrium molecular dynamics (NEMD) methods, but require shorter simulations to the estimation of viscosities, since there is no need to

---

To whom all correspondence should be sent:  
E-mail: Mohammadreza bozorgmehr@gmail.com

reach a steady state. On the other hand, an average of multiple simulations are generally required to ensure statistical accuracy [15,16]. In an effort to lower computing times in shear viscosity calculations, the momentum impulse relaxation (MIR) technique can be used to provide similar results to those obtained via conventional equilibrium and non-equilibrium methods, with more than an order of magnitude reduction in computational demand [17,18]. Furthermore, a synthetic field method such as the SLLOD algorithm allows the evaluation of systems under shear [19]. The importance of supercritical carbon dioxide, alcohols in many industrial and biochemical applications can be reflected by the interest in modeling these two compounds. Hawlicka and Swiatla-Wojcik studied the self-diffusion coefficients of water and methanol in NaCl-methanol-water systems using flexible potential models [20,21]. In this work, transport properties of supercritical carbon dioxide, isopropanol, and water in their mixtures are studied as well as the concentration dependence of these properties. In the next section we will present the details of simulations. The obtained results and their meaning are discussed in subsequent sections.

## 2. SIMULATION DETAILS

Isopropanol-water in supercritical carbon dioxide mixtures were prepared and then simulations performed using facilities present in the GROMACS package, version 4.5.4 [13,22]. We evaluated the quality of molecules topologies generated by the automated server PRODRG [23,24] under the GROMOS43a1 force fields [25] MD simulations were carried out at four different concentrations of the isopropanol (0.532–0.832, at 0.1 intervals) and five different concentrations of the carbon dioxide ( $x_c$ ) and pressure 150 bar were taken from ref [26] Each system box was equilibrated initially under an isothermal-isochoric (*NVT*) production runs of 100ps (313.15K) using the Nose-Hoover thermostat [27] with an time step of 2.0fs. Then, isothermal-isobaric (*NPT*) simulations were performed for 1000ps (313.15K, 150bar) in order to establish the equilibrium density. Periodic boundary conditions were imposed. In all simulations the standard Shake algorithm was used to constrain bond lengths [28] The Ewald summation method was employed to evaluate long-range electrostatic interactions [29] All simulation cells contained 1000 molecules with various concentrations of isopropanol, water, and supercritical carbon dioxide. The constructed mixtures were placed in the cubic boxes with dimension of 6.5nm × 6.5nm × 6.5nm. Finally, each system was simulated for 50000ps production run under the same conditions.

## 3. TRANSPORT PROPERTIES

In the last two decades, several simulation methods for the prediction of shear viscosities have been proposed. In equilibrium molecular dynamics (EMD), the shear viscosity is obtained from pressure or momentum fluctuations based on the Einstein and Green-Kubo relations [29,30, 31]. In conventional NEMD, the shear viscosity can be calculated by reproducing the experimental setup; i.e., an appropriate perturbation is applied, the ensemble averages of the resulting flux and the corresponding field are measured, the ratio of flux and field gives the shear viscosity. In addition, the NEMD method needs fewer particle and fewer steps than a Green-Kubo type EMD method, because the system can be kept stationary [32]. For instance, the shear viscosity of a fluid of interest in the canonical ensemble can be defined by the time integral of the autocorrelation function of any off-diagonal component of the pressure tensor:

$$\eta = \frac{V}{k_B T} \int_0^{\infty} \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle dt \quad (1)$$

Where  $V$  and  $T$  represent the volume and the temperature of the mixture, respectively, and  $k_B$  is the Boltzmann constant. The term  $\langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle$  refers to equilibrium ensemble average of the autocorrelation function computed for a component of the mixture's pressure tensor, in which  $\alpha$  and  $\beta$  stand for any pair of distinct Cartesian coordinates  $x$ ,  $y$ , and  $z$  [33] The integral over time converges asymptotically, as the tensor components lose strong correlation after long periods of time. Although formally defined as an infinite integral, the knowledge on how the pressure tensor correlation decays can allow for reasonable estimates of viscosity to acquire through the truncation of the integral after a finite time. For isotropic systems, the autocorrelation function can be averaged over multiple time intervals and over all pairs of coordinates  $xy$ ,  $xz$  and  $yz$  in order to excell the quality of the results. The periodic perturbation method in NEMD are used here to calculate shear viscosity [34]. The details of this method is described at length in the study of Hess [35] According to ref. [35] one can expand the shear viscosity to third order by

$$\eta(k) = \eta(0)(1 - ak^2) + O(k^4) \quad (2)$$

Where  $k$  represents the wave-vector. An extrapolation to  $k = 0$  provides the macroscopic shear viscosity. A Green-Kubo formula is employed for the calculation of self-diffusion coefficients via the time integral of the velocity autocorrelation function (VACF). However, an equivalent approach,

which may be more suitable in some cases for practical reasons, is the Einstein relation:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |r_i(t) - r_i(0)|^2 \rangle \quad (3)$$

Where  $r_i$  is the atom coordinate vector and the term inside the angle brackets is the mean square displacement (MSD). In this method, the self-diffusion coefficient ( $D$ ) is proportional to the slope of the MSD as a function of time in the diffusional regime. Equation (2) already takes into account the self-diffusion coefficient calculated as the average of this property along three dimensions  $x$ ,  $y$ , and  $z$ . Furthermore, the averaging over all atoms at multiple time intervals can be applied for computational efficiency purposes, also providing enhanced statistical results [36].

#### 4. RESULTS AND DISCUSSIONS

We have provided various concentrations of the three components to study their transport properties at constant temperature (313.15K), pressure (150bar), and densities from 818 to 972 kg/m<sup>3</sup> at which carbon dioxide, as the main solvent, is supercritical. Transport properties of the mixtures and their constituents have been obtained by above mentioned methods. In this work, the shear viscosity is calculated by NEMD method. The values should be fitted with Eq. (2) from which one can estimate the shear viscosity at  $k = 0$ . The results are gathered and shown in the **Tables 1-4**. They show that, the viscosities of the mixtures ( $\eta$ ) will decrease; when isopropanol concentrations ( $x_i$ ), increase.

**Table I:** transport coefficients of mixtures obtained from MD simulation at  $x_i = 0.532$  and 313.15K and pressure 150 bar

| $xc$         | $\rho$ (kgm <sub>3</sub> ) | $D \times 10^{-5}$ (cm <sup>2</sup> s <sup>-1</sup> ) | $\eta$ (10-3kgm-1s-1) |
|--------------|----------------------------|---|-----------------------|
| <b>0.052</b> | 847.854                    | 2.1792 ± 0.4305                                       | -0.001661             |
| <b>0.132</b> | 874.588                    | 3.3039 ± 1.1704                                       | 29.03                 |
| <b>0.192</b> | 891.251                    | 2.2179 ± 0.2564                                       | -0.03252              |
| <b>0.332</b> | 942.606                    | 2.4111 ± 0.7528                                       | 6.531                 |
| <b>0.432</b> | 972.494                    | 1.7948 ± 0.4371                                       | 22.03                 |

**Table II:** transport coefficients of mixtures obtained from MD simulation at  $x_i = 0.632$  and 313.15K and pressure 150 bar

| $xc$         | $\rho$ (kgm <sub>3</sub> ) | $D \times 10^{-5}$ (cm <sup>2</sup> s <sup>-1</sup> ) | $\eta$ (10-3kgm-1s-1) |
|--------------|----------------------------|---|-----------------------|
| <b>0.052</b> | 832.723                    | 2.1608 ± 0.3711                                       | 0.9925                |
| <b>0.132</b> | 857.024                    | 2.8818 ± 0.7857                                       | -0.00631              |
| <b>0.232</b> | 889.083                    | 2.447 ± 0.6679  | 7.063                 |
| <b>0.29</b>  | 907.172                    | 2.0373 ± 0.5513                                       | 6.205                 |
| <b>0.352</b> | 927.136                    | 1.4628 ± 0.0157                                       | 0.01814               |

**Table III:** transport coefficients of mixtures obtained from MD simulation at  $x_i = 0.732$  and 313.15K and pressure 150 bar

| $xc$         | $\rho$ (kgm <sub>3</sub> ) | $D \times 10^{-5}$ (cm <sup>2</sup> s <sup>-1</sup> ) | $\eta$ (10-3kgm-1s-1) |
|--------------|----------------------------|---|-----------------------|
| <b>0.052</b> | 824.531                    | 2.09 ± 0.3349   | 0.5441                |
| <b>0.132</b> | 847.153                    | 2.564 ± 0.6601  | 1.013                 |
| <b>0.192</b> | 864.916                    | 2.779 ± 0.9953  | 10.04                 |
| <b>0.232</b> | 877.153                    | 2.4215 ± 0.8662                                       | 1.621                 |
| <b>0.252</b> | 882.992                    | 2.1182 ± 0.4701                                       | 1.054                 |

**Table IV.** Transport coefficients of mixtures obtained from MD simulation at  $x_i = 0.832$  and 313.15K and pressure 150 bar

| $xc$         | $\rho$ (kgm <sub>3</sub> ) | $D \times 10^{-5}$ (cm <sup>2</sup> s <sup>-1</sup> ) | $\eta$ (10-3kgm-1s-1) |
|--------------|----------------------------|---|-----------------------|
| <b>0.052</b> | 818.453                    | 1.8449 ± 0.3362                                       | 0.7141                |
| <b>0.1</b>   | 831.214                    | 2.2446 ± 0.5603                                       | 0.7608                |
| <b>0.115</b> | 835.233                    | 2.4166 ± .05877                                       | 2.386                 |
| <b>0.132</b> | 839.896                    | 2.4215 ± 0.6601                                       | 1.01                  |
| <b>0.136</b> | 840.986                    | 2.273 ± 0.662   | 1.52                  |

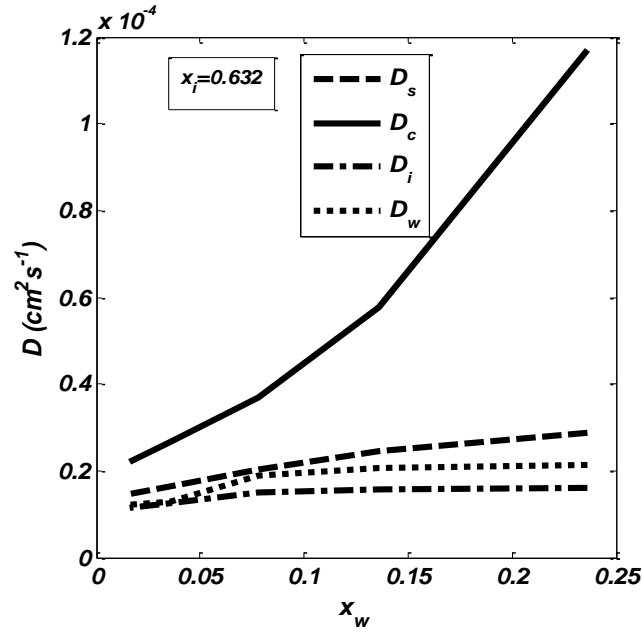


Fig. 1. Self-diffusion coefficients of mixture, isopropanol, water, and carbon dioxide.

Fig. 1 shows that the self-diffusion coefficients for carbon dioxide are maximum for all mixtures, but while water concentration ( $x_w$ ) rises, the self-diffusion coefficient of carbon dioxide is increasing.

Indeed, self-diffusion coefficients for the mixtures ( $D$ ) tend to increase when  $x_i$  rises. However, by increasing of  $x_w$ , the diffusivity of mixtures will initially increase and then decrease, as shown in Fig. 2.

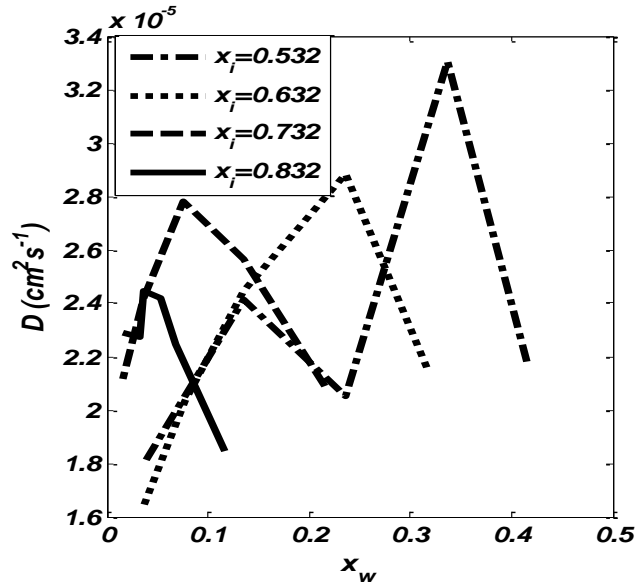


Fig. 2. Self-diffusion coefficients of mixture at 313.15K as a function of mole fraction water.

Also, the density of the mixtures will decrease by increasing the isopropanol and water concentration, as Fig. 3 shows.

The classical Stokes-Einstein relation states that the self-diffusion coefficients and viscosity are inversely proportional [37-39]:

$$D = \frac{k_{\beta} T}{6\pi\eta r_s} \quad (4)$$

Here  $k_{\beta}$  is the Boltzmann constant,  $r_s$  is the effective hydrodynamic radius, and  $T$  is temperature. Based on the MD simulation results, we can affirm that the following equation (from [40]) between the viscosity, self-diffusion, and density holds:

$$\eta = K \frac{\rho T}{D} \quad (5)$$

As Tables 1-4 and Fig. 3 show, the self-diffusion coefficients (density) are inversely (directly)

proportional to the viscosities consistent with the equation.

Radial distribution function (RDF) represents the spherically averaged local order around a center site or atom, giving the probability of finding another particle at a given distance. It is one of the important tools to characterize the local structure of dense fluids, reflecting the effective pairwise interaction, i.e., the potential of mean force between two species.

The RDFs between various atoms in carbon dioxide – isopropanol – water mixtures are obtained to study the local structure in the mixture. The obtained results indicate that the oxygen of water ( $O_w$ ) have a maximum interaction with isopropanol hydrogen ( $H_i$ ). As a result, it can be concluded that probability of existence of  $O_w$  around the  $H_i$  is higher, see Fig.4.

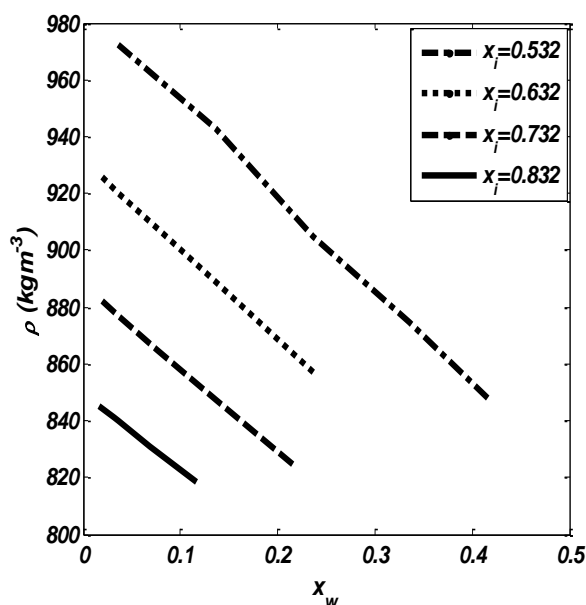


Fig. 3. Density of mixture at 313.15 K as a function of mole fraction water.

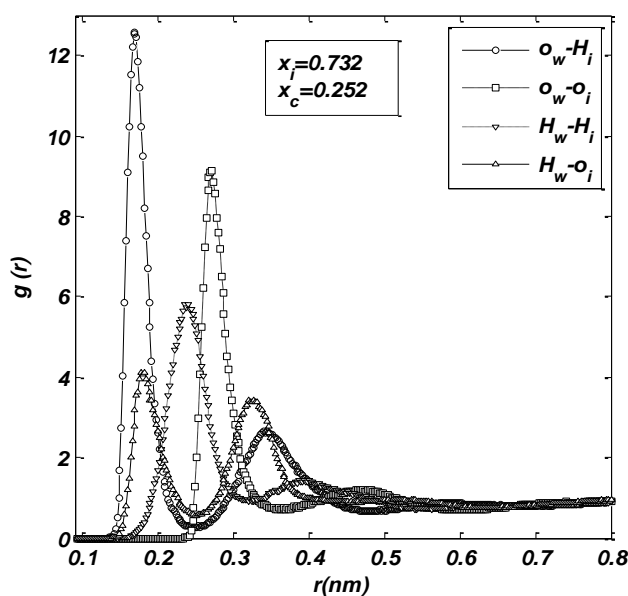
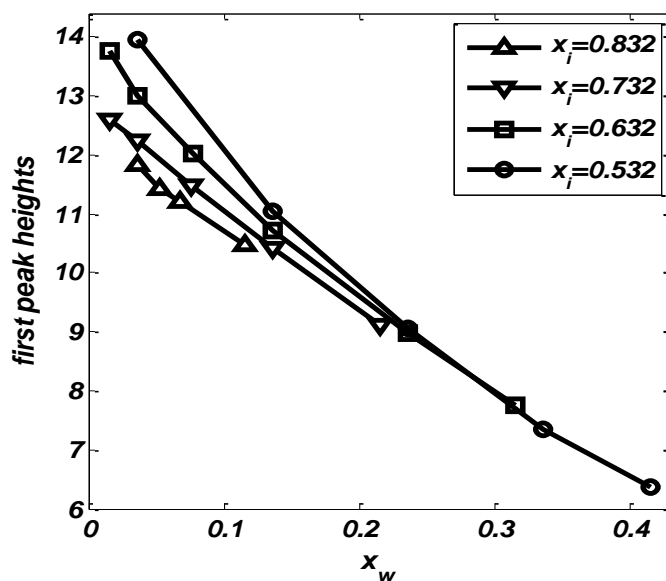


Fig. 4. Various partial radial distribution functions for  $x_i=0.732$ ,  $x_c=0.252$  in carbon dioxide – isopropanol – water mixture.

The figure clearly shows that the correlation between water and carbon dioxide molecules and isopropanol – carbon dioxide molecules is less than that of water – isopropanol.

This explains why mixture diffusivity decreases when  $x_w$  rises (Fig. 2). Upon increasing the water concentrations, the isopropanol molecules are bound to them stronger than carbon dioxide molecules,

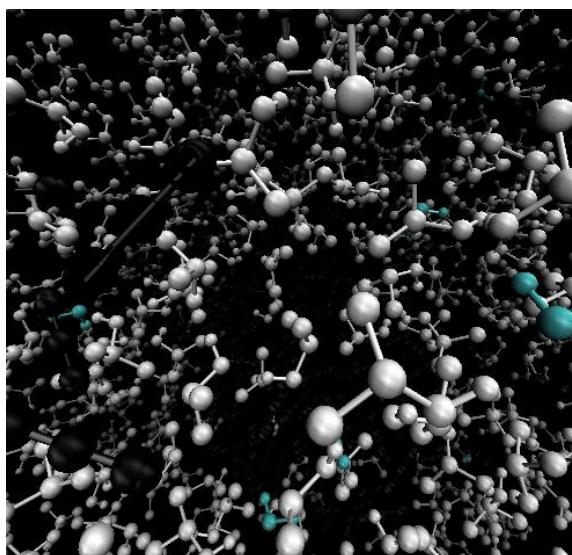
hence the diffusivity of mixture molecules will lower.



**Fig. 5.** First peak heights in the *Ow-Hi* radial distribution functions. The line is aided to eye by ▽ for  $x_i = 0.832$ ; by △ for  $x_i = 0.732$ ; □ for  $x_i = 0.632$ ; and ○ for  $x_i = 0.532$ .

In **Fig. 5** the first peak heights in the *Ow-Hi* RDF's are plotted against the mole fractions of water which shows that the first peak heights will decrease while isopropanol and water concentration is increasing. The first maximum peak indicates the

local structural order of water molecules around the isopropanol molecules. With the enhancement of local structure order, the self-diffusion coefficient of mixtures decreases, but their densities and viscosities will increase.



**Fig. 6.** A typical snapshot of the molecular dynamics simulation for carbon dioxide – iso propanol – water mixture corresponding to the mole fraction of ethanol 0.632, the mole fraction of CO2 0.352. Black color represents the CO2 molecule and white color represents the iso-propanol molecule.

A snapshot of carbon dioxide – isopropanol – water molecules and local cluster molecules is pictorially represented in **Fig. 6**, taken from a simulation trajectory in a simulation box with  $x_i = 0.632$  and  $x_c = 0.352$ . The snapshot shows that carbon dioxide and isopropanol and water molecules

are not randomly distributed and most of the water molecules exist as small clusters in the solution, and rare water molecules are isolated. These results and analyzes confirm again that the water structure can exist in a relatively concentrated carbon dioxide – isopropanol – water solution [41]

The results show that  $O_w-H_i$  RDF's have maximum peaks at around 0.17 nm for different concentrations, so the concentration does not affect the positions of the peaks and the valleys in the RDFs, but only alter their heights and depths.

## 5. CONCLUSION

In this work, molecular dynamics simulations are performed for the carbon dioxide – iso propanol – water mixture in order to study transport properties of the mixtures. Results show that by increasing the concentration of isopropanol, the self-diffusion coefficient is increased for the whole system but, the viscosity the mixtures will decrease. Also the density of the mixtures will decrease by increasing the isopropanol concentration. The obtained results indicate that the oxygen of water have a maximum interaction with iso-propanol hydrogen, which means that probability of existence of oxygen of water around the isopropanol hydrogen is higher. We observe that the first peak heights of the radial distributions functions become higher when the isopropanol concentrations are decreasing, and hence the self-diffusion coefficients will decrease while its density and viscosity will increase.

**Acknowledgment.** We would like to thank the Islamic Azad University, Mashhad Branch for generous financial support of the research project

## REFERENCES

- Satterfield C N, Colton C K, Pitcher W H, *AIChE J.* **19**, 628 (1973).
- S. Singh, P.J. Krueger, *J. Raman Spectr*, **13**, 178 (1982).
- E. Matteoli, L. Lepori, *J. Chem. Phys.*, **80**, 2856 (1984). Doi: 10.1063/1.447034
- W. Liang, H. Li, Y. Lei, S. Han, *J. Mol. Struct.*, **686**, 109 (2004). Doi:10.1016/j.theochem.2004.08.024
- W.L. Jorgensen, D.S. Maxwell, J. Tirado-Rives, *J. Amer. Chem. Soc.*, **118**, 11225 (1996).
- H. Machida, M. Takesue, R.L. Smith, *J. Supercrit. Fluids*, **60**, 2 (2011).
- A. Martín, M.J. Cocero, *Adv. Drug Deliv. Rev.*, **60**, 339 (2008). Doi:10.1016/j.addr.2007.06.019
- M.J. Cocero, A. Martín, F. Mattea, S. Varona, *J. Supercrit. Fluids*, **47**, 546 (2009).
- A.Z. Chen, Y. Li, F.T. Chau, T.Y. Lau, J.Y. Hu, *J. Supercrit. Fluids*, **49** 394 (2009).
- A.Z. Chen, L. Li, S.B. Wang, C. Zhao, Y.G. Liu, G.Y. Wang, *J. Supercrit. Fluids*, **67**, 7 (2012).
- D. Frenkel, B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, 2002.
- S. Plimpton, *J. Comput. Phys.*, **117**, 1 (1995).
- B. Hess, C. Kutzner, D. van der Spoel, E. Lindahl, *J. Chem. Theory Comput.*, **4**, 435 (2008).
- M.P. Allen, D.J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, 1987.
- J.C. Thomas, R.L. Rowley, *J. Chem. Phys.*, **127**, 174510 (2007). Doi: 10.1063/1.2784117
- J.C. Thomas, R.L. Rowley, *J. Chem. Phys.*, **134**, 6 (2011).
- G. Arya, E.J. Maginn, Chang H-C., *J. Chem. Phys.* **113**, 2079 (2000).
- M.S. Kelkar, E.J. Maginn, *J. Chem. Phys.*, **123**, 224904 (2005) . Doi: 10.1063/1.2131060
- D.J. Evans, G.P. Morriss, *Statistical Mechanics of Non-equilibrium Liquids*, (Academic Press, 1990).
- Hawlicka E, Swiatla-Wojcik D, *Phys Chem. Chem. Phys.*, **2**, 3175 (2000).
- W.L. Jorgensen, *J. Phys. Chem.* **90**, 1276 (1986).
- E. Lindahl, B. Hess, D.J. van der Spoel, *J. Mol. Model.*, **7**, 306 (2001).
- D.M.F. van Aalten, R. Bywater, J.B.C. Findlay, M. Hendlich, R.W.W. Hoof, *J. Comput. Aided Mol. Des.*, **10**, 255 (1996).
- A.W. Schuettelkopf, D.M.F. van Aalten, *Acta Crystallogr D*, **60**, 1355 (2004).
- W.F. van Gunsteren, S.R. Billeter, A.A. Eising, P.H. Hu"nenerer, A.E. Mark, W.R.P. Scott, L.G. Tironi, *Biomolecular Simulation: The GROMOS96 Manual and User Guide*; Verlag de Fachvereine: Zu"rich, Switzerland, 1996.
- V. Prosapio, E. Reverchon, I. De Marco, *J. Supercrit. Fluids*, **94**, 189 (2014).
- S. Nose, *J. Chem. Phys.*, **81**, 511 (1984).
- J.P. Ryckaert, G. Ciccotti, H.J.C. Berendsen, *J. Comput. Phys.*, **23**, 327 (1977).
- M.P. Allen, D.T. Tildesley, *Computer Simulation of Liquids*, Oxford, New York, 1987.
- M.S. Green, *J. Chem. Phys.*, **22**, 398 (1954).
- R. Kubo, *J. Phys. Soc. Jpn.*, **12**, 570 (1957).
- W. Lees, S.F. Edwards, *J. Phys. C*, **5**, 1921 (1972).
- S.H. Lee, *Bull. Korean Chem. Soc.*, **28**, 1371 (2007).
- G. Ciccotti, G. Jacucci, I.R. Mc Donald, *J. Stat. Phys.*, **21**, 1 (1979).
- B. Hess, *J. Chem. Phys.*, **116**, 209 (2002). Doi: 10.1063/1.1421362
- D. Dubbeldam, D.C. Ford, D.E. Ellis, R.Q. Snurr, *Mol. Simul.*, **35**, 1084 (2009).
- A. Einstein, R. Furth, A.D. Cowper, *Investigations on the theory of, the Brownian Movement*, Dover Publications, Inc., 1956.
- W. Sutherland, *Phil. Magazine Series*, **6.9**, 781 (1905).
- G.G. Stokes, *Trans Camb. Phil. Soc.*, **9**, 8 106 (1856).
- D. Bedrov, G.D. Smit, T. Sewell, *J. Chem. Phys.*, **112**, 7203 (2000). Doi: 10.1063/1.481285
- S. Dixit, J. Crain, W.C.K. Poon, J.L. Finney, A.K. Soper, *Nature*, **416**, 829 (2002).