Iranian Journal of Organic Chemistry Vol. 12, No. 3 (2020) 2899-2904

Molecular dynamics simulation of carbon dioxide in ethanol and water

Nahid Sohrevardi[a]* and Masoumeh Hosseinzadeh[b]

[a]*Department of Chemistry, Ayatollah Amoli Branch, Islamic Azad University, Amol, Iran*
[b]*Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran*

Received: May 2020; Revised: June 2020; Accepted: June 2020

Abstract: In this study solvation, density of carbon dioxide in ethanol and water in different temperatures at atmospheric and 150 bar pressures were studied by molecular dynamics simulations. The radial distribution functions show that the bound between carbon dioxide molecules in carbon dioxide -ethanol mixture are stronger than carbon dioxide -water mixture. It shows interaction among atoms of ethanol and $CO_2$are lower than water and CO_2, then bound carbon dioxide with water atoms are stronger than bound carbon dioxide –ethanol molecules. We have observed that the first peak heights of the radial distribution functions and density become lower but the mutual diffusion coefficient is increased when the temperature is increasing. Also, the mutual diffusion coefficients show solvation carbon dioxide in ethanol at atmospheric pressure is maximum. The results show, with the enhancement of local structure orders, the mutual-diffusion coefficient of mixtures decrease, but their densities will increase.

Keywords: Carbon dioxide, Ethanol, Water, Diffusion coefficients, Molecular dynamics.

Introduction

Research and applications in the field of supercritical fluids (SCFs) have increased due to their unique properties like high diffusivity, low viscosity, and adjustable solvency power [1]. Recent research is focused on the prediction of fundamental property values need for design and understanding of the molecular interactions for physicochemical process such as SCFs system that have been widely used as solvents in chemical reactions, extraction and adsorption processes [2-4]. Diffusion coefficients of highboiling compounds in supercritical fluids need for the design of supercritical extractors, separators and reactors. So it is necessary the values of the mass transfer parameters of the system in the modeling and subsequent design of industrial processes.

Recent research is expanding the database for binary diffusion coefficients and exploring the influence on solute diffusivities the addition of a second component to the process fluid [5-8]. To compare transport properties, experimental data on diffusion coefficients are scarce because of the technical difficulties of these measurements [9]. In the traditional sense, predictive equations for diffusion in liquids or gases are not applicable in the supercritical region, and high-pressure experiments are time intensive and difficult to perform; thus molecular dynamic (MD)simulation can prove a useful tool to obtain thermodynamic properties [10].Usually, computer simulation methods have been used to investigate structural, transport properties thermodynamic properties, and other useful information that is hardly obtained by experiment [11]. In this work, salvation of the carbon dioxide in ethanol and water are studied. In the next section we present the details of simulations. The obtained results and their meaning are discussed in subsequent sections.

---

*Corresponding author: Tel: +98 3442335743, E-mail: nahid_sohrevardi@yahoo.com

Result and Discussion

We have provided various simulation for CO_2-water and ethanol -CO_2mixtures with the same concentrations at temperature range of T = 283.15 K to T= 320.15 K and at atmospheric and 150 bar pressures. Carbon dioxide is at temperature range of (305.13, 312.15,320.15*K*), pressure (150 bar)as supercritical state. In this work, density and solvation of carbon dioxide and also the supercritical carbon dioxide in ethanol and water were studied by radial distribution functions (RDF).RDFs ofCO_2-water, CO_2-ethanol mixtures at pressure 1 and 150 bar and at various temperatures have obtained through the MD simulations. Detail descriptions of the nearest environment of CO_2- water, CO_2- ethanol are provided by distinct RDFs for the solvent components. Thus six RDFs have been computed, three of them for the sites of water (O_w and H_w) and three for the sites of CO_2 (O_c and C_c).The RDFs between various atoms in CO_2-water and CO_2-ethanol mixtures are obtained to study the local structures in the mixture.

Table 1: The coordination numbers ($N_c(r)$) and the first peak heights of the radial distributions functions for mixture supercritical carbon dioxide- water at 283.15K and pressure 150 bar

Interaction	first peak heights in RDF (nm)	N_C(r)
$H_W - H_W$	**2.215**	**1.2343**
$C_C - O_C$	280.1	0.9549
$O_W - H_W$	2.549	0.4320
$O_W - O_W$	5.123	2.1385
$C_C - C_C$	4.806	10.1826
$O_C - O_C$	3.247	5.2288

Table 2: The coordination numbers ($N_c(r)$) and the first peak heights of the radial distributions functions for mixture supercritical carbon dioxide- water at 320.15K and pressure 150 bar

Interaction	first peak heights in RDF (nm)	N_C(r)
$H_W - H_W$	**2.125**	**1.2686**
$C_C - O_C$	290.7	0.9548
$O_W - H_W$	2.294	0.4227
$O_W - O_W$	4.63	2.4733
$C_C - C_C$	4.549	10.0218
$O_C - O_C$	3.056	5.0007

Table 3: The coordination numbers ($N_c(r)$) and the first peak heights of the radial distributions functions for mixture carbon dioxide- water at 283.15K and pressure 1 bar

Interaction	first peak heights in RDF (nm)	N_C(r)
$H_W - H_W$	**2.221**	**1.226**
$C_C - O_C$	281.7	0.9548
$O_W - H_W$	2.592	0.4261
$O_W - O_W$	5.129	2.1236
$C_C - C_C$	4.819	9.9690
$O_C - O_C$	3.267	5.2068

Table 4: The coordination numbers ($N_c(r)$) and the first peak heights of the radial distributions functions for mixture carbon dioxide- water at 320.15K and pressure 1 bar

Interaction	first peak heights in RDF (nm)	$N_C(r)$
$H_W - H_W$	**2.133**	**1.2332**
$C_C - O_C$	293	0.9548
$O_W - H_W$	2.305	0.415
$O_W - O_W$	4.691	2.2567
$C_C - C_C$	4.521	10.1045
$O_C - O_C$	3.059	5.0257

Table 5: The coordination numbers ($N_c(r)$) and the first peak heights of the radial distributions functions for mixture supercritical carbon dioxide- ethanol at 283.15K and pressure 150 bar

Interaction	first peak heights in RDF (nm)	$N_C(r)$
$O_e - O_e$	**7.057**	**0.9167**
$C_C - O_C$	620.4	0.9549
$O_C - O_C$	5.518	3.8126
$H_e - H_e$	5.478	0.9397
$C_C - C_C$	8.152	7.6796
$O_e - H_e$	7.915	0.4495

Table 6: The coordination numbers ($N_c(r)$) and the first peak heights of the radial distributions functions for mixture supercritical carbon dioxide- ethanol at 320.15K and pressure 150 bar

Interaction	first peak heights in RDF (nm)	$N_C(r)$
$O_e - O_e$	5.99	0.8866
$C_C - O_C$	646.5	0.9548
$O_C - O_C$	4.29	3.1147
$H_e - H_e$	4.79	0.916
$C_C - C_C$	6.316	6.4794
$O_e - H_e$	6.515	0.4304

Table7: The coordination numbers ($N_c(r)$) and the first peak heights of the radial distributions functions for mixture carbon dioxide- ethanol at 283.15K and pressure 1 bar

Interaction	first peak heights in RDF (nm)	$N_C(r)$
$O_e - O_e$	**7.069**	**0.9217**
$C_C - O_C$	628.4	0.9549
$O_C - O_C$	5.55	4.0738
$H_e - H_e$	5.523	0.9556
$C_C - C_C$	8.228	7.8202
$O_e - H_e$	7.962	0.4499

Table 8: The coordination numbers ($N_c(r)$) and the first peak heights of the radial distributions functions for mixture carbon dioxide- ethanolat 320.15K and pressure 1 bar

Interaction	first peak heights in RDF (nm)	N_C(r)
$O_e - O_e$	**6.01**	**0.8877**
$C_C - O_C$	657.1	0.9548
$O_C - O_C$	4.296	3.0805
$H_e - H_e$	4.866	0.9575
$C_C - C_C$	6.304	6.3036
$O_e - H_e$	6.594	0.4209

Figure **1** shows the mutual diffusion coefficients (D_M) for CO_2-water mixture andCO_2-ethanol mixture at various temperaturesand at atmospheric and 150 bar pressures. Fig.1 shows that by increasing temperature, the mutual diffusion coefficients increases. With increasing temperature, the first peak heights of the radial distributions functions lower, local structure order lower, then mutual diffusion coefficient of mixtures increase. Also, it shows solvation substance in each other tend to increase when temperature increase. Figure **1,** shows solvation carbon dioxide in ethanol at atmospheric pressure is maximum for all mixtures. The lowest salvation related to CO_2 in water at 150 bar pressure. Also, the density of the mixtures will decrease by increasing temperature, the results are presented in

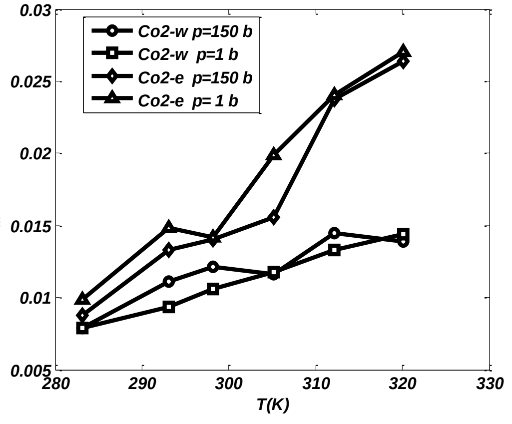

Figure 1: mutual diffusion coefficients (DM) for CO_2-water and ethanol - CO_2mixtures as a function of temperatureat atmospheric and 150 bar pressures.

As Figure **1** and **2** show, the mutual- diffusion coefficients are inversely proportional to the density, Based on the MD simulation results, we can affirm that the following equation (from [26, 27]) between the, mutual- diffusion, and density holds:

$$\eta = K\frac{\rho T}{D} \qquad (4)$$

With the enhancement of local structure order, the mutual-diffusion coefficient of mixtures decrease, but their densities will increase.

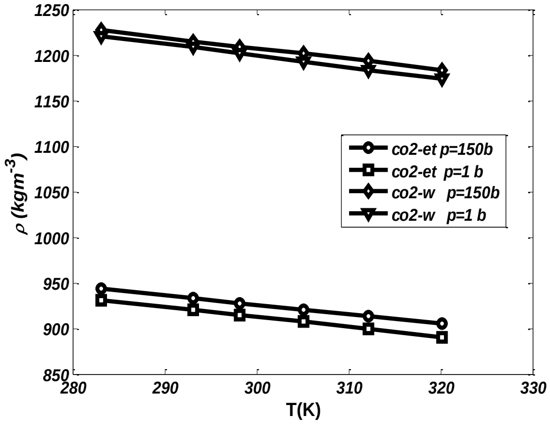

Figure 2: Density for Co_2-water and ethanol - CO_2 mixtures as a function of temperature at atmospheric and 150 bar pressures

The first peak heights between various atoms CO_2-water and CO_2-ethanol mixtures are obtained and shown at temperatures T = 283.15 K and T= 320.15 K at pressure 1 and 150 bar Tables **1-8.** The first peak heights of the radial distributions functions show that with increasing the temperatures, the first peak heights of the radial distributions functions become lower as shown in Tables **1-8**.Also, the first peak heights of RDF in pressure 150bar in mixtures is lower than of the atmospheric pressure. The higher the first peak heights, the stronger are the interactions between atoms. Also showing that the bound between atoms decreases with temperature increasing .The results show that the bound between CO_2-CO_2molecules in CO_2-ethanol mixture is stronger than bound between CO_2-CO_2molecules in CO_2-water mixture (Tables **1-8**).). It shows interaction among atoms of ethanol and $CO_2$is lower than water and CO_2, then bound between CO_2 atoms with water atoms is stronger than boundCO_2-ethanole molecules, as seen in (Tables **1-8**). The corresponding coordination numbers ($N_c(r)$) i.e., the number of molecules contained in the first shell around a central molecule, is determined by integration of the pair radial distribution functions. The coordination numbers ($N_c(r)$) is presented in Tables **1-8**. With the enhancement of coordination numbers ($N_C(r)$) of the RDFs, more molecules participated in the reaction, hence stronger bounds are formed between molecules. The coordination numbers ($N_C(r)$) of the RDFs decrease as temperatures increases (Tables **1- 8**).

Simulation method

Mixtures of water-carbon dioxide and carbon dioxide -ethanol were prepared in the same concentrations at temperature range of T = 283.15 K to T= 320.15 K and at atmospheric and 150 bar pressures. We have prepared different boxes at various temperatures to do these calculations. The binary system prepared with the carbon dioxide mole fractions (x_c) x_c =0.33. In the mdp runs the Temperature (v-rescale) and pressure (Parrinello-Rahman), in NPT runs the Temperature (v-rescale) and pressure (Berendsenbarostat) were controlled in the simulation boxes [12,13,14].We evaluated the quality of molecules topologies were generated by the automated server PRODRG [15,16] under the GROMOS43a1 force fields [17]. A cut-off distance for the short-range neighbor list (1 nm) for all interactions and Particle Mesh Ewald (PME) method is used only for the electrostatic interactions [18]. In all simulations the standard LINCS algorithm was used to fix bond lengths [19]. Each system was simulated with a time step of 2*fs* for the total time 50*ns* [20]. A steepest-descent algorithm was invoked to minimize the energy of each system. The obtained results were finally shown in graphs and tables.

Self-diffusivities and mutual diffusivities from simulation

A Green–Kubo formula is used to calculate of the self-diffusion coefficients through the time integral of the velocity autocorrelation function (VACF).

Although, the Einstein relation is an equivalent method, which may be more appropriate in several cases for practical reasons:

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}\langle \left| r_i\left(t\right) - r_i\left(0\right)\right|^2 \rangle \qquad (1)$$

Where r_i refers to the vector of atom coordinate and the term in the brackets of angle presents the mean square displacement (MSD). In this technique, the self-diffusion coefficient (D) refers to proportionate of the of the MSD slope as a time function in the diffusional system [21]. In Equation (1), the coefficient of self-diffusion is already considered as the mean of this feature over three dimensions of x, y, and z. Moreover, the averaging at multiple time intervals for all atoms can be used for computational recovery goals, also presenting increased statistical outcomes [22]. A Darken formula is used to calculate of the mutual self-diffusion. The Darken relation show that the composition dependence of the binary Maxwell–Stefan diffusivity is given by [23-25]

$$D_{ij} = x_i D_{j,self} + x_j D_{i,self} \qquad (2)$$

Where $D_{i,self}$ and $D_{j,self}$ representthe self-diffusion coefficient of speciesiandthe self-diffusion coefficient of species j in the mixture.

Conclusion

In this study the mutual-diffusion coefficients mixtures of carbon dioxide - ethanol and carbon dioxide -water at different temperatures and at atmospheric and 150 bar pressures were calculated by molecular dynamics simulation. The results show that mutual diffusion coefficient is increased for all various mixtures were studied when the temperature is increased. Also, it showed that solvation carbon dioxide in ethanol at atmospheric pressure is maximum for all mixtures. In addition, the densities of the mixtures will lower, when the temperature is increased. We have observed that the first peak heights of the radial distribution functions become lower when the temperature is increasing, and hence the mutual diffusion coefficients will increase while its density will decrease.

Acknowledgements

Authors sincerely thank the Islamic Azad University of Ayatollah Amoli University for providing financial support of this work.

References

[1] Higashi, H.; Tamura, K. Calculation *of* diffusion coefficient *for* supercritical carbon dioxide *and* carbon dioxide+naphthalene system *by* molecular dynamics.**2010**,*3*6, 772-777.

[2] Tsekhanskaya, Y. V.; Iomtev, M. B.; Mushkina, E. V. *J. Phys. Chem.* **1996**, 38, *1173*–1176.

[3] Yoo, J. H.; Breitholz, A.; Iwai, Y.; Yoo, K. P. *Kor. J. Chem. Eng.* **2012**, *29*, 935–940

[4] Ago, K.; Nishiumi, H.; *Ind. Eng. Chem. Res.* **1998**, *3*7, *1692*-1695.

[5] Higashi, H.; Iwai, Y.; Nakamura, Y.; Yamamoto, S.; Arai, Y. *Fluid Phase Equilib.,* **1999**, *166*, *101*–110.

[6] Fermeglia, M.; Pricl, S. *Fluid Phase Equilib*., **1999**, *166*, *21*–37

[7] Kiran, E.; Brennecke, J. F. Supercritical fluid engineering science, *American Chemical Society* Symposium Series, Los Angeles., **1991**, *95*,4540.

[8] Bueno, J. L.; Suarez, J. J.; Dizy, J.; Medina, I., *J. Chem. Eng.*, **1998**, *38*, *344*–347.

[9] Nasrabad, A. E. *J. Chem. Phys.*, **2009**,*130*, 024503.

[10] Eaton, A. P.; Akgerman, A. *Ind. Eng. Chem. Res.*, **1997**, *36*, *923*-931.

[11] Xu, W. H.; Yang, J. C.; Hu, Y. Y. *J. Phys. Chem. B.*, **2009**, *113*, 4781–4787.

[12] Nosé. S., *J. Chem. Phys.* **1984**, *81*,511–519.

[13] Hoover. W. G. Phys. Rev. A. **1985**, 31, 1695–1697.

[14] Berendsen, H. J. C.; Postma, J. P. M.; Vangunsteren, W. F. *J. Chem. Phys.* **1984**, *81*, 3684–3690.

[15] Van Aalten, D. M. F. ; Bywater, R.; Findlay, J. B. C.; Hendlich, M.; Hooft. R. W. W. *J. Comput. Aided Mol. Des.* **1996**, *10*, 255–265.

[16] Schuettelkopf, A. W.; Van Aalten, D. M. F., *Acta Crystallogr D.* **2004**, *60,* 1355–1363.

[17] Van Gunsteren, W. F. ; Billeter, S. R.; Eising, A.; Hu¨nenberer, P. H.; Mark, A. E.; Scott, W. R. P.; Tironi, I. G. Biomolecular Simulation*: The GROMOS96 Manual and User Guide;* Verlag de Fachvereine: Zu¨rich, Switzerland **1996**.

[18] Allen, M. P.; Tildesley, D. J. *Computer Simulations of Liquids* (Oxford Science, Oxford, **1987**).

[19] Ryckaert, J.-P.; Ciccotti, G.; Berendsen,H. J. C. *J. Comput. Phys.* **1997**, *23* , 327-341.

[20] Berendsen, H. J. C.; Van Gunsteren, W. F., in Molecular-Dynamics Simulation of Statistical-Mechanical Systems, edited by G. Ciccotti and W. G. Hoover (North-Holland, Amsterdam), **1986**, 43–65.

[21] Frenkel, D.; Smit, B., Understanding Molecular Simulation: From Algorithms to Applications (Academic Press), **2002**.

[22] Dubbeldam, D.; Ford, D. C.; Ellis, D.E.; Snurr, R.Q. *J. Mol. Simul.* **2009**, *35*, 1084-1097.

[23] Krishna, R.; VanBaten, J. M., *Ind. Eng. Chem. Res*. **2005**, *44*, *6939*-6947.

[24] Bardow, A.; Kriesten, E.; Voda, M. A.; Casanova, F.; Blümich, B.; Marquardt, W., *Fluid Phase Equilib.* **2009**, *278*, *27*-35.

[25] Krishna, R.; Van Baten, J. M., *Chem. Eng. Technol.* **2006**, *29*, *761*-765.

[26] Bedrov, D.; Smit, G. D.; Sewell, T. *J. Chem. Phys.* **2000**, *112*, 7203-7208.

[27] Sohrevardi, N.; Bozorgmehr, M. R.; Khanpour, M., J. S*uper. Fluids*, **2017**, 130, 321-326.