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Carbon dioxide in monoethanolamine: Interaction and its effect on structural and dynamic properties by molecular dynamics simulation



Fatemeh Moosavi*, Farkhondeh Abdollahi, Mohammad Razmkhah

Department of Chemistry, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran

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ABSTRACT

Molecular dynamics simulation study of carbon dioxide-monoethanolamine, CO_2 –MEA, was performed at constant pressure and temperature in a spanning range of CO_2 mole fraction. Since alkanolamine is an industrial solvent to capture gas impurity, investigating the structural analysis and interaction with gas seems substantial. Force field validation was carried out regarding the thermophysical and transport properties of pure MEA at 313 and 333 K. Structural analyses revealed that gas molecules locate among solvent particles by compacting some parts of MEA in order to achieve a position through free spaces of solvent confirmed by atomic Z-density and trajectory. Diffusion coefficient and energy contribution introduced x = 0.036 as dissolving point. The orientation of gas molecules among solvent, hydrogen bond interaction, and coordination number calculations demonstrated a stronger interaction of solute and solvent and its involvement with N–H(N) head of MEA.

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1. Introduction

The growing trend of greenhouse gas emission has stimulated the study of carbon dioxide capture technologies. Natural gas purification, steel production, fossil fuel power plants, and cement production are the multiple potential sources of carbon dioxide production. Carbon dioxide is an acidic gas; as a result, presence of this gas more than the standard limit can undertake serious problems such as pipeline corrosion, gas heating value reduction, and catalyst poisoning. In a gas purification unit, natural gas transition pipelines may tolerate CO_2 up to 5 mass percent (Buckingham, 1964).

One solution for these problems is process of gas sweetening, which eliminates carbon dioxide and hydrogen sulfide from natural gas. The procedure needs a solvent to absorb the impurity. It is suggested the absorber possesses some characteristics like high stability, low corrosiveness, high absorption rate for carbon dioxide, and being executable with low cost (Ma'mun et al., 2007). Some candidates to be used in gas sweetening process are alkanolamine solvents with different amine structures such as monoethanolamine (MEA) as primary amine, diethanolamine (DEA) as secondary amine, and methyl diethanolamine (MDEA)

http://dx.doi.org/10.1016/j.ijggc.2015.03.015 1750-5836/© 2015 Elsevier Ltd. All rights reserved. as tertiary amine. Besides, ionic liquids (Shi and Maginn, 2008), amino-acid based solvents (Aronu et al., 2011), and sodium and potassium carbonate solutions (Knuutila et al., 2010) are other choices with desired specifications. Since solvent selection in a pilot industrial process involves a direct relationship with its economic advantage and easy access, alkanolamines may remain of first priority. Among the mentioned specifications, these solvents contain some advantages such as high reactivity and reasonable thermal degradation rate (Ma'mun et al., 2007). In addition, low molecular weight and high absorbing capacity on a mass basis makes MEA in this family the best choice for CO₂ capture (Martin et al., 2012).

To investigate different aspects of this selection, a powerful tool is required. Molecular dynamics (MD) simulation seems an efficient method since it leads to a deep insight into the properties of solute and solvent in terms of structural and molecular interactions (Allen, 2004).

MEA was first modeled in liquid phase (Button et al., 1996) by applying optimized potential for liquid simulation (OPLS). It was shown that temperature increase limits hydrogen bond interactions and fewer molecules are able to be at short distances of interaction.

From the other side of view, studying radial distribution function, energy, and atomic Z-density profile with help of ab initio calculations demonstrated ethanolamine molecules have intermolecular hydrogen bonding stronger than water, both as pure and aqueous solutions (López-Rendón et al., 2006).

^{*} Corresponding author. Tel.: +98 513 880 5553. *E-mail address*: moosavibaigi@um.ac.ir (F. Moosavi).

Knowing the mechanism of reaction between carbon dioxide and alkanolamine is additionally a crucial factor to gather comprehensive information on the behavior of these substances. The kinetics of reaction between carbon dioxide and aqueous solution of alkanolamines was studied (Vaidya and Kenig, 2007) in order to explore reaction mechanisms such as zwitterions and basecatalyzed CO_2 hydration. They indicated primary and secondary amines obey the zwitterions mechanism while tertiary amines are governed by the base-catalyzed hydration of CO_2 .

Da Silva et al. (Da Silva et al., 2007) compared pure MEA in liquid phase with aqueous solution by means of MD simulation. Investigating structural properties showed stable conformer in both conditions is gauche with respect to O–C–C–N dihedral angle.

Han et al. (Han et al., 2013) carried out ab initio MD calculations to focus on CO_2 capture by pure besides aqueous solution of MEA from energy consumption aspect. The results showed that CO_2 sorption with pure MEA was less exothermic than aqueous solution, which permitted CO_2 desorption at lower temperature than the later resulting in a significant decrease in energy consumption to regenerate MEA.

Masy et al. (Masy et al., 2013) investigated self-diffusion of a system containing carbon dioxide, water, and alkanolamine finding amine mobility is the slowest in the system due to more complex structure from the motion point of view.

Yu et al. (Yu et al., 2013) used a multiamine solution in order to find an optimized composition for carbon dioxide capture by applying synergy molecular dynamics. They demonstrated that ternary system containing triethanolamine (TEA), MDEA, and DEA had better operation than quaternary and quintuple amine systems.

Regarding this opening area of research, the aim of the present work will be performing MD simulation with the approach of structural analysis of systems containing pure MEA and mixture of alkanolamine and carbon dioxide in a variety of CO₂ mole fraction values. The more we know about the structure, sound judgment can be made; therefore, likely hydrogen bond between CO₂ and MEA will be investigated by going into details. The effect of carbon dioxide insertion on the structural organization of alkanolamine is also an effective factor which will be discussed in the current study; besides, research about the orientation of molecules after entering CO₂ is of interest. At this point, it is noticeable to mention that though there has been provided (Da Silva et al., 2007; Han et al., 2013) information on various aspects of structure as well as transport properties of CO₂ capture by the above solvent, the lack of information on the solubility of CO₂ in MEA solvent and special type of intermolecular interaction, hydrogen bond, is obvious. In addition, the focus is to propose the dissolving point of CO₂ in the target alkanolamine by considering structural and physicochemical properties. Force field parameters play a significant role on thermophysical and transport properties like density and diffusion, respectively. Consequently, this investigation compares MD results literature to achieve a right attitude about the nature of interactions.

2. Theory

2.1. Force field

Accuracy of a force field for a liquid may be proved by the agreement of properties, e.g. density and self-diffusivity, obtained from MD with experimental results. This is the case for MEA at two different temperatures, 313 and 333 K, by using standard interaction parameters, assisted model building with energy refinement (AMBER) (Cornell et al., 1995) that is the force field applied in this study. Due to the flexibility of alkanolamine in question, both intramolecular and intermolecular interactions play a significant role on properties. With respect to all-atom force field, all bond lengths and angles are flexible and a simple harmonic expression represents them.

$$U_r = K_r \left(r - r_{\rm eq} \right)^2 \tag{1}$$

$$U_{\theta} = K_{\theta} \left(\theta - \theta_{\text{eq}} \right)^2 \tag{2}$$

where r and θ are bond length and bond angle, r_{eq} and θ_{eq} also refer to equilibrium values of r and θ , respectively; K_r represents bond constant and K_{θ} is defined as spring constant.

The dihedral energies are handled by a Fourier expansion of dihedral angle as;

$$U_{\text{dihedral}} = A \left[1 + \cos\left(n\varphi - y\right) \right] \tag{3}$$

where *A* represents the magnitude of torsion, *n* shows the periodicity of the torsion, φ represents the dihedral angle, and *y* is the equilibrium torsion angle.

The intermolecular part of potential for alkanolamine is given by combination of (12–6) potential (Cornell et al., 1995) and Coulomb potential.

$$U_{ij} = \sum_{i < j} \left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{r_{ij}} \right]$$
(4)

where *q* represents the charge of any i and j atoms, $A_{ij} = \epsilon_{ij} (r_{ij}^*)^{12}$ and $B_{ij} = 2\epsilon_{ij} (r_{ij}^*)^6$, which r_{ij}^* is the place where potential has minimum value, and ϵ_{ij} represents potential well depth. Carbon dioxide short-range interaction is modeled by Lennard-Jones (LJ) potential (Panhuis et al., 1998);

$$U_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$
(5)

where σ_{ij} is the distance at which the interparticle potential is zero. The intermolecular parameters between carbon dioxide and MEA atoms were calculated by using the arithmetic mean for σ_{ij} and geometric mean for ϵ_{ij} .

To have more accurate bonds and angles among system atoms, geometry of molecules were optimized by Gaussian03 package (Frisch et al., 2004). Computations were carried out at B3LYP/6-311G (d,p) level of theory and atomic charges were also derived by fitting the electrostatic potential (ESP) at the same level of theory. In order to be sure the structures are in their stable form, the vibrational analysis was as well conducted. The equilibrium parameters containing equilibrium bond lengths, angles, and dihedral angles as well as atomic charges computed as mentioned above are reported in Tables 1A to 3A of Appendix; additionally, the atomic labels are illustrated in Fig. 1A. All bonded and non-bonded constants including K_r , K_θ , A, n, A_{ij} , B_{ij} , ϵ_{ij} , and σ_{ij} were taken from literature (Cornell et al., 1995; Panhuis et al., 1998).

2.2. Simulation details

To explore the properties of MEA, NPT ensemble based on a cubic simulation box containing 216 target molecules, with molecular dynamics package DL_POLY 2.17 (Smith and Forester, 1996), was constructed; the simulation box obeyed periodic boundary conditions. Nose–Hoover thermostat (Evans and Holian, 1985) and barostat kept temperature and pressure constant with relaxation time of 0.1 and 0.1 ps, respectively, at temperature 313 K and constant pressure of 1.01 kPa. The same simulation at just different temperature, 333 K, was carried out for MEA to compare some features of results with temperature variation.

For the mixed system, CO₂-alkanolamine, the same number of MEA molecules as preceding MD, with a various number of carbon

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