

Effect of Temperature on Diffusivity of Monoethanolamine (MEA) on Absorption Process for CO₂ Capture

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Abstract- Diffusion coefficient study gains an interest to know the mass transfer properties of molecules especially in study of the absorption process. The main objective of this study is to investigate the effect of temperature on diffusivity of MEA absorption process for CO₂ capture. Three different values of process temperature were chosen for simulation in this study, 298 K, 313 K and 318 K. The MD simulation was carried out at NVE (200ps) and NPT (1ns) ensemble in Material Studio 7.0 software. Mean Square Displacement (MSD) analysis was done to compute the self-diffusion coefficient of molecules in tertiary system (MEA+H₂O+CO₂). The results show that the rate of the diffusion coefficient is increased as temperature increased. Diffusion coefficient at 318 K is the highest compared to others temperature. MD simulation is used to study details about absorption process and capture CO₂ acid gases. The simulation diffusivity result obtained from this work shows higher compared with theoretical results.

Index Terms- Molecular Dynamic, Simulation, Amine Absorption Process, Monoethanolamine, Carbon Dioxide, Mean Square Displacement.

I. INTRODUCTION

Recently, the increment of CO₂ composition in air will be contributing the increment of the global temperature. IPCC (Intergovernmental Panel on Climate Change) is an international agency, whose plays a role in preparing a report about the global climate change [1]. IPCC is one of agencies in this world which extensively conduct the research to overcome the global climate change problem. At present, there are many CO₂ capturing chemical materials are known such as amine-solvent, organic molecular cages, ionic liquids, metal-organic framework, zeolite and carbon-materials [2]. In this study, amine-solvent is used to determine the diffusivity of CO₂ in amine-based absorption process. Absorption process is a process in the scope of post-combustion capture process. This technology has been established over the year since 1930's [3]. MEA, monoethanolamine (C₂H₇NO) is a primary amine. Which has been used as solvent in CO₂ capture due to higher performance in the absorption process [4].

Molecular Dynamic (MD) simulation was run on molecules species to calculate the diffusion coefficient. This computational method has become an effective tool to explore more deeply about absorption process and also CO₂ capture. MD simulation used to study the molecular properties such as the diffusion coefficient [5]. This computation technique can also study others thermodynamic condition at atomic level that cannot be study by doing experimental. Moreover, this technique has many advantages compare to chemical experimental study such as environmental friendly and money saving [6]. In CO₂ capture cost process, more than half is distributed to the absorbent regeneration part [7]. Study on the thermodynamic properties is essential before operating the absorption process in pilot plant. In addition, cost for experimental research to study the diffusion coefficient is high particularly at operating condition of higher pressure and temperature [8]. Besides that, the equipment used for study diffusion coefficient of solute in liquid solvent in low concentration is expensive. MD simulation also is an option to study the diffusion coefficient of solute in supercritical fluid because it's difficult to run by experimental [9]. Therefore, the computation measurement study offers better approach to do the research on diffusivity.

Factors that affected the diffusion are concentration gradient, pressure gradient and temperature gradient [10]. Diffusion coefficient, density and viscosity are used to calculate the mass transport

properties of molecule in a system [11]. Diffusion coefficient is usually seen as D_{AB} in equation which represent as the flux of a diffusing component A and B with unit m^2/s . In MD simulation, mean square displacement (MSD) analysis or the mean square of the distance molecule move is used calculate the rate of diffusion coefficient. The theories which can be used to study MSD analysis are the Fick's laws, Einstein-Smoluchowski theory [5], [12] and the Maxwell-Stefan theory [13]. In MD simulation, the Maxwell-Stefan theory will be used in MSD analysis. This theoretical can be used to calculate the diffusion of mixture system [14]. Besides MSD analysis, velocity auto-correlation function analysis also used to study transport diffusion system [12].

The literature study on diffusion coefficient by using MD simulation is very limited in open literature. Result diffusion coefficients of MEA, CO_2 and H_2O in various systems were reported in the literature such as study diffusion coefficient of H_2 , H_2O and CO in various *n*-alkanes by using MD simulation [15], calculate diffusion coefficient of pure water by MD simulation [16], calculate diffusion coefficient of MEA, DEA, MDEA and DIPA [17] by experimental, calculate diffusion coefficient of PZ and MDEA by Tylor dispersion method experiment [18].

The temperature and pressure as operating conditions in actual absorption process in pilot plant are in ranges 311 K-333 K and 1 bar, respectively [19]. The aim of this paper is to discuss the effect of temperature on diffusivity of CO_2 and MEA in MEA solution during absorption process.

II. SIMULATION METHODOLOGY

MD simulation was done by using software of Material Studio (version 7.0) which installed on HP Z420 workstation. This software is licensed software manufacture by Acceryls (San Diego, USA) [20]. The MD simulation was started with replicate the structure of single molecule. The structure of molecules was obtained from Royal Society of Chemistry database [21]. There are three phases in running MD simulation which are the relaxing phase, the equilibrium phase and the sampling phase [5]. Geometry optimization step were carried out on each of the molecules to ensure the stable molecular geometry to be used in further simulation steps. The default algorithm used is the Smart Algorithm and Fine convergence level. The simulation boxes are developed using the amorphous cell calculation model in Material Studio software. Type of forcefield used is COMPASS and summation method used is Ewald to calculate electrostatic energy or electrical interaction [22]. Once the simulation box is developed, this model is simulated for box energy minimization. The simulation is started with equilibration of the system under constant number moles, volume and energy (NVE) ensemble for 200 ps with random initial velocities. The simulation process is continued in dynamic mode under constant number of moles, pressure and temperature (NPT), isothermal-isobaric ensemble for 1ns. Within this time step, the integration of equation algorithm is going through. The time step choose to be used is 1 fs. 1 fs time step is reported to enough for ensure the molecules in amorphous cell box does not overlapping [22]. Pressure is kept constant at 1 atm to achieve an equilibrium density. The simulation box consists of 300 molecules of MEA, 300 molecules of CO_2 and 1000 molecules of H_2O . Figure 1 shows the molecular structure of molecules CO_2 , H_2O and MEA. Table 1 shows the simulation parameters to represent MEA absorption process. This study is an the extension of previous study [23]. This model is simulated at three different temperatures, 298 K, 313 K and 318 K.

Table 1 Simulation parameters to represent MEA absorption process at tertiary system

System	Number of Molecules	Density (g/ml)			Box size A x B x C
		298K	313K	318K	
MEA	300	0.989	0.972	0.967	43Å x 43Å x 43Å
CO_2	300				
H_2O	1000				

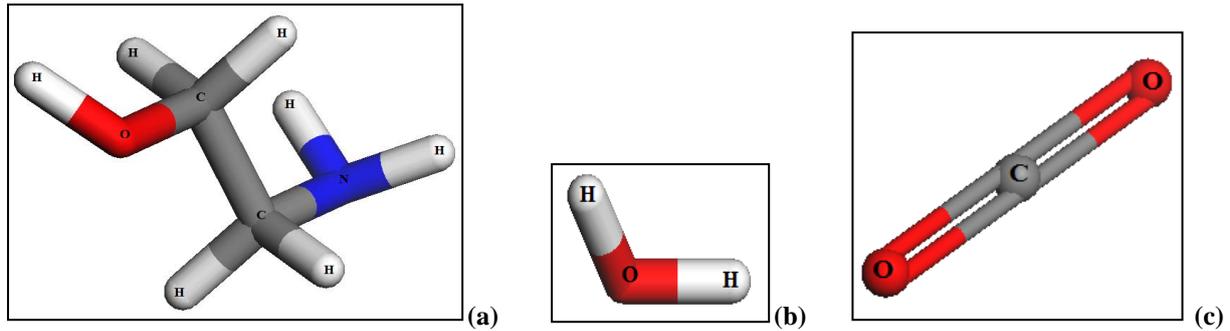


Figure 1 Schematic labeling of molecules (a), Monoethanolamine (b) Water (c) Carbon Dioxide

The Einstein relation is used to calculate MSD in MD simulation. Equation 1 shows equation to determine coefficient of molecular diffusion, D in MD simulation [13]. The slope of MSD graph is diffusion coefficient value, D . The value have divide with 6 as the system is in 3-dimensional system and do conversional unit ($\text{\AA}^2/\text{ps}$ to m^2/s) as shown in equation 1.

$$D_{i,\text{self}} = \frac{1}{6N_i} \lim_{m \rightarrow \infty} \frac{1}{m \cdot \delta t} \sum_{l=1}^{N_i} [(r_{l,i}(t + m \cdot \delta t) - r_{l,i}(t))^2] \quad (1)$$

N_i = the number of the molecules of component i

δt = the time step used in the simulation

m = the total number of the time steps

$r_{l,i}(t)$ = the position of the l th molecule of component I at time t

The Stokes-Einstein relation also can be used in calculation of MSD. Equation 2 shows the Einstein equation over the time interval [24]:

$$6Dt = \langle |r(t) - r(0)|^2 \rangle = MSD(t) \quad (2)$$

Where $r(t) = [x(t), y(t), z(t)]$ show the coordinates atoms at time t . Equation 3 is used to calculate the diffusion coefficient as a function of MSD results [25].

$$D = \frac{1}{6} \frac{d}{dt} MSD(t) = \text{constant} \quad (3)$$

III. RESULT AND DISCUSSION

MD simulation is used to calculate CO_2 and MEA diffusivity in MEA solution [13]. MEA is classified as bases with the presence of nitrogen atom which has unshared electron pair. It consists of hydroxyl group which help for the solubility in water and amino group is used to assist the alkalinity in water to absorb the acid gas [26].

Table 2 shows the diffusion result in simulation. As shown in Table 2, as temperature increased, the value of diffusion coefficient also increased. Molecule is colliding with each other in periodic boundary, result the repeat motion which called as diffusion. When give a heat, the atom will be vibrational motion and collide with other neighbour atom [27]. Moreover, increasing in temperature condition will be affect the rate constant of reaction [28]

The diffusion coefficient of CO_2 is higher than MEA and H_2O as depicted in Table 2. The molecular mass of MEA, CO_2 and H_2O are 61, 44 and 18, respectively. As the molecular mass (size of the molecule) increase, the diffusion rate will be slower.

In this simulation, MEA solution is selected as chemical solvent were used to absorb CO₂ gas. CO₂ gas will diffuse from gas to liquid phase then dissolve in liquid phase to do interaction and reaction [29].

Table 2 Diffusion result for simulation

Simulation			
Components/ Temperature	45°C	40°C	25°C
CO ₂ (m ² /s)	9.0897E-09	8.6780E-09	7.2200E-09
H ₂ O (m ² /s)	6.6975E-09	6.6600E-09	5.8200E-09
MEA (m ² /s)	5.2770E-09	5.3830E-09	4.6400E-09

Figures 2 to 4 shows the plot of the MSD versus time at temperature 318 K, 313 K and 298 K, respectively. These graph used to calculate diffusion coefficient have a straight line with a constant slope. The slope was the MSD value increase linearly with time. From these graphs, can be seen that the slope were increased with the increased of temperature. The results obtain from this work show some different with the theoretical calculation.

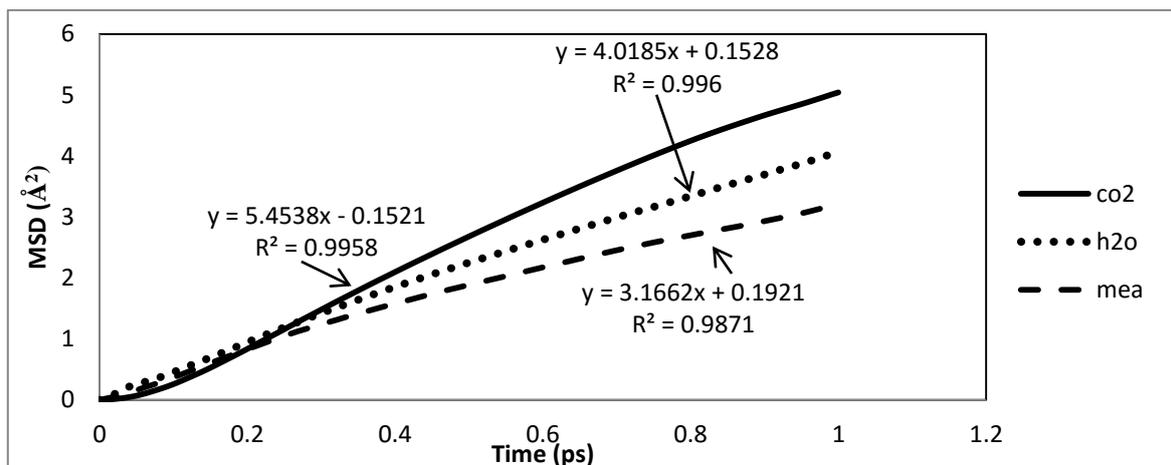


Figure 2 Prediction of diffusion coefficient graph for MEA, H₂O and CO₂ at 318 K

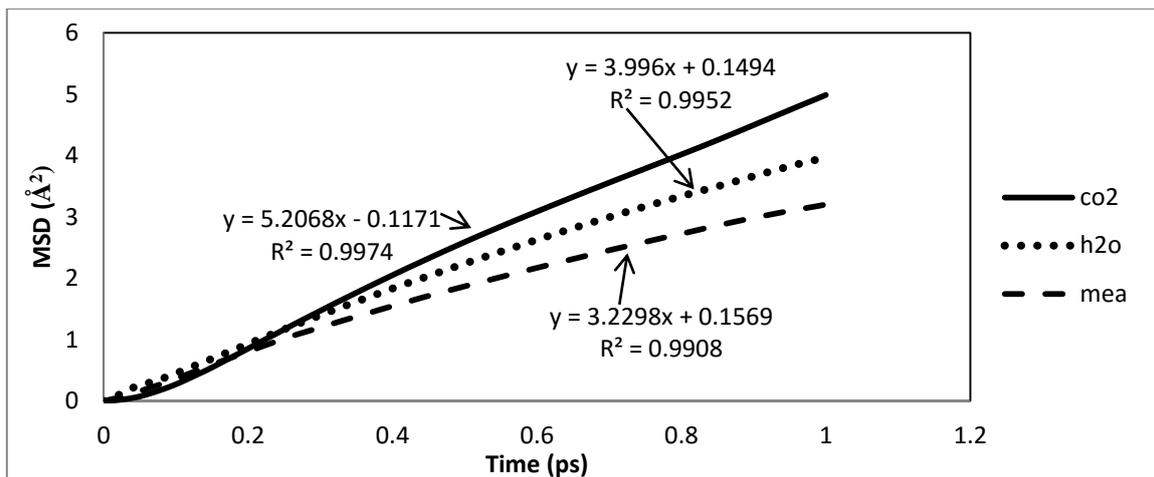


Figure 3 Prediction of diffusion coefficient graph for MEA, H₂O and CO₂ at 313 K

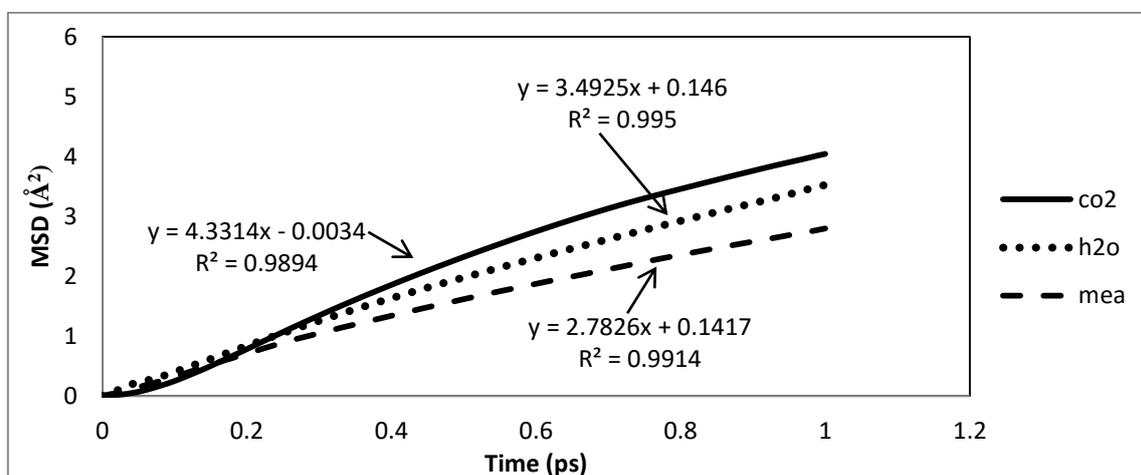


Figure 4 Prediction of diffusion coefficient graph for MEA, H₂O and CO₂ at 298 K

Compare with mathematical equation

In order to validate the accuracy of simulation result, theoretical calculation is done. Two type of theoretical calculation is used which are Wilke-Chang equation [30] and based on Versteeg and van Swaaij (1988) study [17]. Versteeg and van Swaaij (1988) study is used because related to CO₂ diffusion in amine solution.

Theoretical calculation of diffusivities in liquids (Wilke-Chang equation)

The Wilke-Chang equation is used to calculate the diffusivity of MEA and H₂O [30]. Equation 4 shows the Wilke-Chang equation.

$$D_{AB} = 1.173 \times 10^{-16} (\phi M_A)^{1/2} \frac{T}{\mu_B V_A^{0.6}} \quad (4)$$

M_A = the molecular weight of solvent B

μ_B = the viscosity of B

V_A = the solute molar volume at the boiling point

\emptyset = the association parameter for solvent, 2.6 for water

T = the temperature of system

Theoretical calculation of diffusion CO_2 in MEA aqueous from Versteeg and van Swaaij (1988)

The diffusion of CO_2 in MEA aqueous can be calculate by using the N_2O analogy in literature [17] [31]. Equations 5 to 9 are shows the way how CO_2 diffusivity calculated on aqueous MEA amine.

$$D_{CO_2} = D_{N_2O} \left(\frac{D_{CO_2}}{D_{N_2O}} \right) \text{ in water} \quad (5)$$

$$D_{CO_2} (m^2 \cdot s^{-1}) = 2.35 \times 10^{-6} \exp \left\{ -\frac{2119}{T(K)} \right\} \quad (6)$$

$$D_{N_2O} (m^2 \cdot s^{-1}) = 5.07 \times 10^{-6} \exp \left\{ -\frac{2371}{T(K)} \right\} \quad (7)$$

$$D_{N_2O} = (5.07 + 0.865C_{MEA} + 0.278C_{MEA}^2) \times 10^{-6} \exp \left(\frac{-2371 - 93.4C_{MEA}}{T(K)} \right) \quad (8)$$

$$C_{MEA} = \frac{10C_{\%w/w}d}{M_w} \quad (9)$$

D = the diffusivity

C = the concentration

$\%w$ = the percent of weight

Table 3 shows the comparison of simulation results with theoretical results. Based on this Table 3, the value of exponent (E-09) is same for all results. But when compared to diffusivity value, the simulation result is quite larger compared to theoretical results.

The simulation result obtained from this work shows bigger than theoretical result. The reasons are these two systems were different in number of molecules, operating conditions and simulation approximation (force field, summation method, ensemble, algorithm etc.) as previous simulation work. In this simulation work, it applied the molecular mechanics principle. Its means, MD simulation consider the physical interaction and without chemical interaction such in quantum mechanics and experimental study. Furthermore, a reliable result of diffusion coefficient of solutes in solution can be obtained if longer MD simulation need to run expect up to 3 ns of NPT ensemble [5], 2 ns of NVT ensemble [22] and 30 ns of NVT ensemble [15]. [25] Also literature shows the calculation of diffusion coefficient by using numerical computation need to run over a long time periods and/or used large ensemble size for statistical reasons. However, this present simulation work only can be done NPT ensemble part until 1 ns due to limited time and lower performance of computer processor used. Different type of ensemble for production phase contribute to different result of diffusion coefficient. [12], [22], [9] proposed the simulation procedure by using the canonical equilibrium ensemble (NVT) and [25] used PVT ensemble (the temperature-pressure-volume) in order to compute the diffusion coefficient.

Table 3 Comparison simulation results with theoretical results

Simulation			
Components/ Temperature	45°C	40°C	25°C
CO ₂ (m ² /s)	9.0897E-09	8.6780E-09	7.2200E-09
H ₂ O (m ² /s)	6.6975E-09	6.6600E-09	5.8200E-09
MEA (m ² /s)	5.2770E-09	5.3830E-09	4.6400E-09
Theoretical (used Wilke-Chang equation)			
CO ₂ (m ² /s) in water	3.3893E-09	3.1661E-09	1.1034E-09
H ₂ O (m ² /s) in water	5.1372E-09	4.7989E-09	3.3537E-09
MEA (m ² /s) in water	1.9655E-09	1.8360E-09	1.2831E-09
Theoretical (used Versteeg and van Swaaij (1988))			
CO ₂ (m ² /s) in water	3.0001E-09	2.6972E-09	1.9183E-09
H ₂ O (m ² /s) in water	2.9303E-09	2.6013E-09	1.7766E-09
MEA (m ² /s) in aqueous MEA	2.2954E-09	2.0577E-09	1.4467E-09
CO ₂ (m ² /s) in aqueous MEA	2.4002E-09	2.1181E-09	1.4214E-09

IV. CONCLUSIONS

Mean square displacement calculation is used to calculate the diffusivity of molecules in MEA solution. The rate of the diffusion coefficient is increased as temperature increased. Rate of diffusion coefficient at 318 K is the highest compared to 313 K and 298 K. The diffusion coefficient of CO₂ is larger than H₂O and MEA in liquid state due to small molecular weight. Even though the values of diffusion coefficient of this simulation work are higher than experimental and theoretical data, the trend follows the theoretical with CO₂ has the highest diffusion coefficient. While, it is good effort to study the diffusion coefficient by MD simulation. The main reason of different diffusivity value is probably due to MD simulation used molecular mechanic principle that may ignore some factors for cheaper calculation. MD simulation basically involved the physical interaction and based on molecular mechanic principle. Besides that, this simulation is run in condition of 1 ns NPT ensemble and on lower performance of computer processor. Further study need to carry out in order to study deeply about CO₂ absorption in MEA solution.

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Nomenclature:

ps	Picoseconds
ns	Nanoseconds
fs	Femtoseconds
g/ml	Grams to milliliters
Å	Angstrom
m	Meter
s	Second
E	Exponential
T	Temperature
K	Kelvin
Q	Heat transfer

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