

PERPUSTAKAAN UMP



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**MOLECULAR SIMULATION STUDIES OF AMP/MDEA ABSORPTION PROCESS  
FOR CO<sub>2</sub> CAPTURE**

**NUR ALIA ADNIN BINTI ZAINOL ABIDIN**

PERPUSTAKAAN UNIVERSITI MALAYSIA PAHANG	
No. Perolehan <b>107880</b>	No. Panggilan PICLSA
Tarikh <b>07 MAR 2016</b>	.ALY 2015 r BC.

**BACHELOR OF CHEMICAL ENGINEERING**

**UNIVERSITI MALAYSIA PAHANG**

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**MOLECULAR SIMULATION STUDIES OF AMP/MDEA ABSORPTION PROCESS  
FOR CO<sub>2</sub> CAPTURE**

**NUR ALIA ADNIN BINTI ZAINOL ABIDIN**

Thesis submitted in partial fulfillment of the requirements  
for the award of the degree of  
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering  
UNIVERSITI MALAYSIA PAHANG**

JUNE 2015

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### **Supervisor's Declaration**

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature :

Name of main supervisor : Dr. Noorlisa Binti Harun

Position : Senior Lecturer

Date :

## **Student's Declaration**

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :

Name : Nur Alia Adnin Binti Zainol Abidin

ID Number : KA11093

Date :

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## **Acknowledgement**

I owe my deepest gratitude to my supervisor Dr. Noorlisa Binti Harun. Her extensive knowledge over the issue in addition to her inspiring character was always a great help in every single step of the work. I learnt many things under her supervision during this project.

I am greatly indebted to master student Emyra Ezzaty Binti Masiren who generously helped me during entire semester. We had many useful discussions around different parts of the work which was undeniably instructive for me. She reviewed my entire proposal and gave me several useful comments with her pinpoint accuracy. It was close to impossible for me to cope with the programming issue without her extensive programming knowledge.

## **Abstract**

Carbon capture using post-combustion technology is the most mature technology nowadays. Post-combustion process is based on the absorption process with a solution of *N*-methyldiethanolamine (MDEA) 30wt. % in water. However, despite the advantages of MDEA which have highly efficient energy utilization, there have been some drawbacks especially the low reactivity with CO<sub>2</sub> during the absorption process. For this reason, there is a need to innovate and optimize solvents for CO<sub>2</sub> capture in order to improve the solvent capture efficiency. This work focuses on the blended amine using 2-amino-2-methyl-1-propanol (AMP) and MDEA. The aim of this study is to perform molecular dynamic simulation using Material Studio software to give insight on this process at molecular level. Process operating conditions (obtained from previous research) is used to set the process condition i.e. pressure, temperature and concentration in Material Studio software. The intermolecular interaction is analyzed in terms of radial distribution function which would determine the intermolecular interactions in the solution. It is expected that this study will give more insight and understanding on CO<sub>2</sub> absorption process for further improvement and suggestion for development of new solvent.

## **Abstrak**

Pengumpulan karbon menggunakan teknologi pasca-pembakaran adalah teknologi yang paling sesuai pada masa kini. Proses pasca-pembakaran ini adalah berdasarkan kepada proses penyerapan menggunakan campuran N-methyldiethanolamine (MDEA) 30wt. % di dalam air. Walau bagaimanapun, dengan pelbagai kelebihan yang dimiliki oleh MDEA iaitu memanfaatkan penggunaan tenaga yang sangat berkesan, terdapat juga beberapa kelemahan terutamanya kereaktifan yang rendah semasa proses penyerapan CO<sub>2</sub>. Atas hal ini menunjukkan betapa perlunya bagi kita membuat inovasi dan mengoptimumkan pelarut untuk menangkap CO<sub>2</sub> bagi meningkatkan kecekapan penyerapan CO<sub>2</sub>. Kajian ini memberi tumpuan kepada campuran pelarut antara 2-amino-2-metyl-1-propanol (AMP) dengan MDEA. Tujuan kajian ini adalah untuk melaksanakan simulasi dinamik molekul menggunakan perisian Material Studio untuk menunjukkan proses penyerapan ini pada peringkat molekul. Keadaan operasi proses (yang diperolehi daripada penyelidikan terdahulu) digunakan untuk menetapkan keadaan proses iaitu tekanan, suhu dan kepekatan dalam perisian Material Studio. Interaksi antara molekul dianalisis dari segi fungsi taburan jejarian yang akan menentukan interaksi antara molekul dalam larutan. Ia dijangka bahawa kajian ini akan memberikan gambaran yang lebih dan pemahaman mengenai proses penyerapan CO<sub>2</sub> untuk peningkatan dan cadangan untuk pembangunan pelarut baru.



## Contents

Supervisor's Declaration.....	i
Student's Declaration.....	ii
Acknowledgement .....	iii
Abstract .....	iv
Abstrak .....	v
Chapter 1 .....	2
Introduction.....	2
1.1. Background of study .....	2
1.2. Objective .....	4
1.3. Scope of research .....	4
1.4. Main contribution of this work.....	5
1.5. Organization of this thesis .....	5
Chapter 2.....	6
Literature review.....	6
2.1. Overview .....	6
2.2. CO <sub>2</sub> process capture .....	6
2.3. CO <sub>2</sub> separation technologies .....	8
2.3.1 Physical and chemical absorption.....	8
2.3.2 Adsorption.....	9
2.3.3 Membrane separation.....	9
2.3.4 Cryogenic separation.....	9
2.4. Amine-based absorption process.....	10
2.5. Categorization of Alkanoamines .....	11
2.6. Reaction mechanism .....	12
2.7. Improvement of the System .....	14
2.8. Molecular Dynamic simulations .....	15
2.8.1 Boundary condition.....	16
2.8.2 Initial condition.....	17
2.8.3 Force calculation.....	18
2.8.4 Thermodynamic ensemble .....	18

2.8.5 Analysis parameter.....	19
Chapter 3.....	21
Methodology.....	21
3.1. Molecular Dynamic simulation.....	21
3.2. Speciation of the System.....	21
3.3. Molecular structure.....	22
3.3.1 Geometry optimization.....	22
3.3.2 Simulation box.....	22
3.3.3 Equilibrium phase under NVE and NVT ensemble.....	23
3.3.4 Data analysis.....	24
Chapter 4.....	26
Results and Discussion.....	26
4.1. Binary system.....	26
4.2. Tertiary System.....	29
4.3. Mean square displacement.....	33
Conclusion.....	36
References.....	37

## List of Figures

Figure 1.1: Global Greenhouse Gas Emissions

Figure 1.2: Plot of CO<sub>2</sub> emission over the years of 2000-2010 in Malaysia

Figure 2.1: Classification of CO<sub>2</sub> Capture System

Figure 2.2: Technical options for CO<sub>2</sub> capture technologies

Figure 2.3: Amine solvent based post-combustion capture process

Figure 2.4: Molecular structure of Monoethanolamine (MEA)

Figure 2.5: Molecular structure of Diethanolamine (DEA)

Figure 2.6: Molecular structure of Monodiethanolamine (MDEA)

Figure 2.7: Molecular structure of 2-Amino-2-Methyl-1-Propanol (AMP)

Figure 2.8: Illustration of MD simulation system

Figure 2.9: Illustration of periodic boundary condition (PBC)

Figure 2.10: Schematic explanation of  $g(r)$  of a monoatomic fluid

Figure 3.1: 2-Dimension and 3-Dimension view of simulation box at 35°C

Figure 3.2: 2-Dimension and 3-Dimension view of simulation box at 40°C

Figure 3.3: Summarization of MD simulation procedure

Figure 4.1: Molecular interactions of hydroxyl group in binary system at 35°C

Figure 4.2: Molecular interactions of amino group in binary system at 35°C

Figure 4.3: Molecular interactions of hydroxyl group in binary system at 40°C

Figure 4.4: Molecular interactions of amino group in binary system at 40°C

Figure 4.5: Molecular interaction between amino group of AMP and MDEA with CO<sub>2</sub> at 35°C

Figure 4.6: Molecular interaction between hydroxyl group of AMP and MDEA with CO<sub>2</sub> at 35°C

Figure 4.7: Molecular interaction between amino group of AMP and MDEA with CO<sub>2</sub> at 40°C

Figure 4.8: Molecular interaction between hydroxyl group of AMP and MDEA with CO<sub>2</sub> at 40°C

Figure 4.9: N-O and N-C branches in MDEA structure

Figure 4.10: MSD graph at 35°C

Figure 4.11: MSD graph at 40°C

# Chapter 1

## Introduction

### 1.1. Background of study

One of the greatest challenges nowadays is the preservation of nature with a growing demand of energy driven by the increasing population of people and the expectation of higher standard of living. Although energy is one of the main sources of country's economic and development as well as social progress, energy also gives catastrophic impact to environment through the direct and indirect energy consumption. Judging from recent conditions, it is necessary to re-evaluate and improving the way of dealing with energy. Reducing energy waste as well as promoting renewable energy is the best solutions towards sustainable energy system. Another solution is to reduce the energy consumption effect on the environment by lowering the emission of greenhouse gases, especially CO<sub>2</sub> which is the most widely produced greenhouse gas, as evident in Figure 1.1. The impacts of CO<sub>2</sub> emissions to the environment in Malaysia are not the new issue to discuss but this issue has been growing for the last two decades.

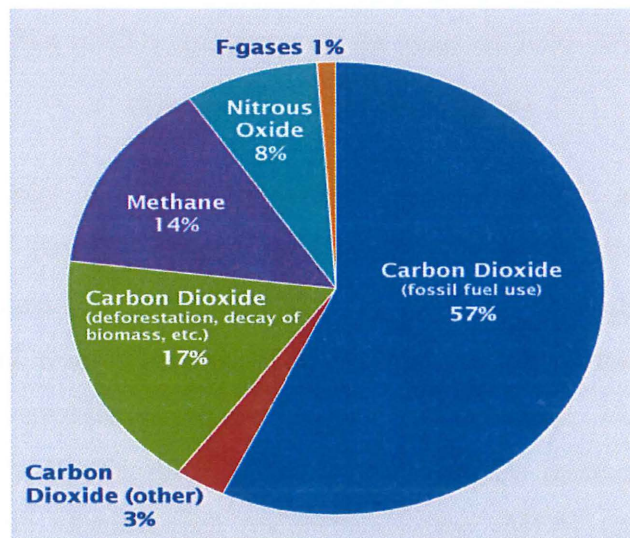


Figure 1.1: Global Greenhouse Gas Emissions

(Intergovernmental Panel On Climate Change, 2007)

The high level of CO<sub>2</sub> in the atmosphere are mainly caused by the burning of fossil fuels (coal oil, petroleum, natural gas) for the purpose of electrical power generation, transportation and

solvent regeneration in the desorber, formation of degradation products, solvent losses due to high vapor pressure, relatively high corrosiveness and the limit of loading capacity of up to 0.5 mol CO<sub>2</sub>/ mol amine (Kim & Svendsen, 2007). In the past few years, mixed alkanolamines have received increasing attention. In most cases, the mixtures contain N-methyldiethanolamine (MDEA) as the base amine with the addition of one or two more reactive amines, such as monoethanolamine (MEA) or diethanolamine (DEA) has been widely proposed. (Rebolledo-Librerosa & Trejo, 2004)

## 1.2. Objective

The objectives of the proposed research are stated as follows:

- i. To investigate the intermolecular interaction of the amine-based solvent using Molecular Dynamic (MD) simulation.
- ii. To study the effect of temperature on the intermolecular interaction of system.

## 1.3. Scope of research

This study focused on several scopes in order to achieve the research objectives and stated as follows:

- i. Molecular Dynamic (MD) simulation was used to study and give insight on the intermolecular interaction between the blended solvents and CO<sub>2</sub> during the absorption process. The simulation is conducted at NVE ensemble and NVT ensemble as to observe the effect of varies parameters on the interaction of the molecules.
- ii. There are two different systems at various operating conditions are considered in this study; binary system (MDEA+AMP+H<sub>2</sub>O) and tertiary system (MDEA+AMP+CO<sub>2</sub>+H<sub>2</sub>O).
- iii. The temperature of 308K and 313K were selected as referring to the application of amine-based absorption process in industry and were analyzed in terms of radial distribution function (RDF).
- iv. Mean square displacement (MSD) was used to determine the diffusion coefficient of the molecules.

#### **1.4. Main contribution of this work**

This study gives insight on the molecular interaction between carbon dioxide with blended 2-amino-2-methyl-1-propanol (AMP) and methyldiethanolamine (MDEA) during the absorption process. The maximum interaction during the absorption process will be determined at various process operating conditions. All the data in this simulation process can be used to contribute to the development of technologies for CO<sub>2</sub> removal.

#### **1.5. Organization of this thesis**

The structure of the thesis is outlined as follow:

Chapter 2 describes on the open literature of published researches relating to this study. Brief explanation on amine based absorption process for carbon dioxide and reactivity of different types of alkanolamines are included in this chapter. The intermolecular interactions involved during the simulations and the thermodynamic properties used in this study also clearly explained in this chapter.

Chapter 3 describes the methodology applied in this study and force fields involve in the simulation process. This chapter also explains the method to interpret radical distribution function into graphical form to analyze the intermolecular interaction between atoms.

Chapter 4 discussing on the results obtained from the simulation. The results are interpreted to give an insight on how the intermolecular interaction between the solvents and determining the optimum temperature of the absorption process.

## Chapter 2

### Literature review

#### 2.1. Overview

This chapter discussing the molecular simulation studies of blended amines solution of AMP/MDEA absorption process for CO<sub>2</sub> capture. Material Studio software was used as simulation tool to complete this study. The aim of this chapter is to review the fundamental science of the absorption process and the simulation technique.

#### 2.2. CO<sub>2</sub> process capture

There are basically three processes for carbon dioxide capture and they are classified as shown in Figure 2.1.

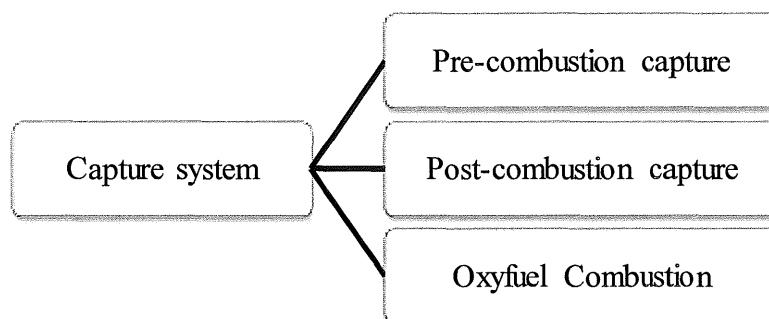


Figure 2.1: Classification of CO<sub>2</sub> Capture System

(Kothandaraman, 2010)

Pre-combustion system process the primary fuel in a reactor with steam and air or oxygen under high temperature and pressure to produce a mixture of carbon monoxide and hydrogen where the carbon monoxide is let to react with steam in the second reactor to produce carbon dioxide and hydrogen which is then separated (Office of Fossil Energy, 2014). Pre-combustion would be used at power plants that employ integrated gasification combined cycle (IGCC) technology (IPCC, 2005) and will cost around \$60/tonne to capture CO<sub>2</sub> (Office of Fossil Energy, 2014) which is nearly RM100 per tonne in Malaysia.

In oxy-fuel combustion, air is replaced by oxygen in the combustion process producing concentrated CO<sub>2</sub> (Harun, 2012). The flue gas stream is therefore mainly composed of water

## **2.3. CO<sub>2</sub> separation technologies**

Post-combustion capture offers some advantages as existing combustion technologies can still be used without radical changes on them. This makes post-combustion capture easier to implement as a retrofit option to existing plants. A number of separation technologies could be employed with post-combustion capture such as adsorption, membrane separation and cryogenic separation, physical and chemical absorption (Harun, 2012).

### **2.3.1 Physical and chemical absorption**

#### ***2.3.1.1 Physical absorption***

This involves the physical absorption of CO<sub>2</sub> into a solvent based on Henry's law which means that they are temperature and pressure dependent with absorption occurring at high partial pressures of CO<sub>2</sub> and low temperatures. The solvents are then regenerated by either heating or pressure reduction. The advantage of this method is that it requires relatively little energy; but the CO<sub>2</sub> must be at high partial pressure. Typical solvents such as DEPG (Selexol), N-Methyl-2-Pyrrolidone (Purisol), Methanol (Rectisol), and Propylene Carbonate (Fluor Solvent) are becoming increasingly popular as gas treating solvents (Burr & Lyddon). Physical solvents tend to be favored over chemical solvents when the concentration of acid gases or other impurities is very high.

#### ***2.3.1.2 Chemical absorption***

Chemical absorption involves the reaction of CO<sub>2</sub> with a chemical solvent to form a weakly bonded intermediate compound which may be regenerated with the application of heat producing the original solvent and a CO<sub>2</sub> stream. Alkanolamines remove CO<sub>2</sub> from the gas stream by the exothermic reaction of CO<sub>2</sub> with the amine functionality of the alkanolamine. Different amines have different reaction rates with respect to the various acid gases. The selectivity of this form of separation is relatively high. In addition, a relatively pure CO<sub>2</sub> stream could be produced. These factors make chemical absorption well suited for CO<sub>2</sub> capture for industrial flue gases. However, in order to employ it on the scale required for CO<sub>2</sub> capture, there needs to be development and identification of optimal solvents for absorption. To minimize the energy penalty of capture, the capture system needs to be well integrated with the power plant.



### **2.3.2 Adsorption**

Gas separation based on adsorption using various kind of adsorbent has been well developed. However, there is still plenty of room to optimize the performance of these materials and investigate a wider range of new sorbents. Conventional solid adsorbents include activated carbons (Plaza, et al., 2010, Guo, et al., 2006), silica gel, ion-exchange resins, zeolites (Wang, et al., 2011), and meso-porous silicates, activated alumina, metal oxides, and other surface-modified porous media (Li et al., 2011). In some review on CO<sub>2</sub> capture by adsorption (Choi, et al., 2009, Sayari & Belmabkhout, 2010), to develop an excellent and appropriate adsorbent, one should satisfy a low-cost materials, low heat capacity, fast kinetics reaction, high CO<sub>2</sub> adsorption capacity, high selectivity and lastly thermal, chemical and mechanical stabilities under extensive recycling. Depending on the regeneration methods, several adsorption processes can be adopted to achieve CO<sub>2</sub> separation, including vacuum and pressure swing adsorption (VSA and PSA), temperature swing adsorption (TSA), electric swing adsorption (ESA), simulated moving bed (SMB), and purge displacement.

### **2.3.3 Membrane separation**

Membranes have great potential in CO<sub>2</sub>/H<sub>2</sub> separation in pre-combustion capture and post-combustion CO<sub>2</sub>/N<sub>2</sub> separation. A wide variety of different membrane materials and processes are available, some of which already on an industrial scale, and potentially applicable in CO<sub>2</sub> separation. The performance and associated cost of these membrane-based technologies in large scale CO<sub>2</sub> capture mainly relies on the membrane materials themselves. Inorganic ceramic membranes and organic polymeric membranes have been used in CO<sub>2</sub> separation from flue gas in post-combustion. However, reaching a high degree of CO<sub>2</sub> separation by using single-stage ceramic or polymeric membrane is difficult as of yet (although it is feasible in terms of cost). New materials are still required to achieve the desired effectiveness in CO<sub>2</sub> separation by membranes (Li et al., 2011).

### **2.3.4 Cryogenic separation**

Cryogenic distillation uses a principle of separation based on cooling and condensation, and has been used in liquid separations for a long time. This technique is theoretically sound for CO<sub>2</sub> separation; however, the considerable energy demand deems it unreasonable for practical

application. This method is more effective when the gas stream contains high CO<sub>2</sub> concentration and it can be adopted in oxygen production for oxyfuel combustion. It is presently the most widely used system for the large-scale production of O<sub>2</sub> from the separation of air. Hart & Gnanendran, 2009, have proposed The CryoCell process technology uses a cryogenic process to remove CO<sub>2</sub> from the natural gas, while avoiding the short comings of the conventional acid gas treatment processes. The CryoCell technology eliminates water consumption, usage of chemicals, and corrosion related issues. This new cryogenic CO<sub>2</sub> removal method has been researched and tested in a demonstration plant and is soon to be implemented in commercial field applications

#### 2.4. Amine-based absorption process

The current predominant technology is based on chemical absorption involving ammonia or amine solvent. Figure 2.3 shows the post-combustion process using amine solvent.

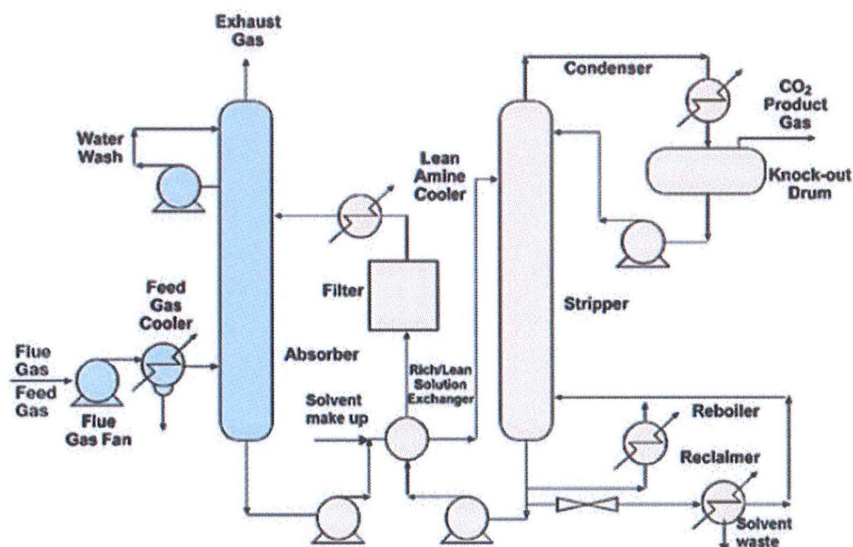


Figure 2.3: Amine solvent based post-combustion capture process

During the absorption process, the flue gas is contacted with a selected liquid amine solvent. The process takes place in tall columns known as absorber; in which turbulent flow promotes rapid CO<sub>2</sub> transfer from gas to liquid. Differences in density make it easy to separate the emerging gas and liquid. To recover the captured CO<sub>2</sub>, the loaded solvent is pumped to a stripper in which it is exposed to hotter CO<sub>2</sub>-free gas, typically steam. Heating of the solvent causes desorption of the

CO<sub>2</sub>. The stripped liquid is pumped back to the scrubber, while the steam/CO<sub>2</sub> mixture is cooled to condense the steam, leaving high-purity CO<sub>2</sub> suitable for compression (Herzog et al., 2009).

## 2.5. Categorization of Alkanoamines

Alkanolamines are a group of ammonia derivatives consisting at least one hydroxyl group, -OH, and one amine group, -NH<sub>2</sub>. Aqueous solutions of alkanolamine have been used extensively as solvents for the capture of CO<sub>2</sub> from effluent streams (Masy, 2013). The amine group can be divided into different subcategories based on the number of substituents on the nitrogen atom (Farmahini, 2010).

- i. Primary alkanolamine: Where nitrogen atom carries one substituent group (ethanol group) and two hydrogen atoms which are directly bonded to the nitrogen (Farmahini, 2010). The best-known example is MEA as shown in Figure 2.4.

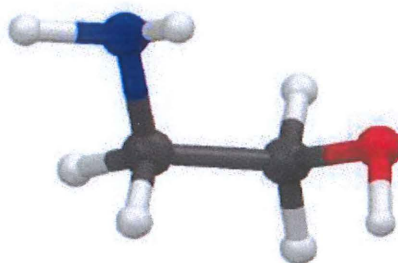


Figure 2.4: Molecular structure of Monoethanolamine (MEA)

- ii. Secondary alkanolamine: Where two hydrogens of the amine group have been replaced by two ethanol groups (Farmahini, 2010) as shown in Figure 2.5.

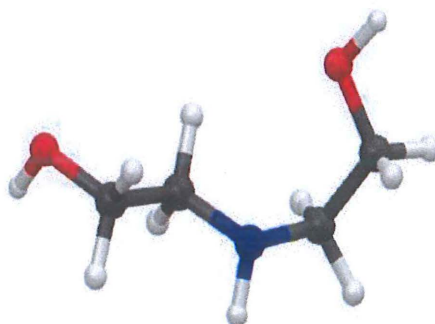


Figure 2.5: Molecular structure of Diethanolamine (DEA)

- iii. Tertiary alkanolamine: These alkanolamines possess no hydrogen atom directly bonded to the nitrogen, meaning all the hydrogen atoms have been replaced by the substituent groups (alkyl or alkanol groups) (Farmahini, 2010). The most popular example is MDEA as depicted in Figure 2.6.



Figure 2.6: Molecular structure of Monodiethanolamine (MDEA)

- iv. Sterically hindered (alkanol)amine: Where the reactive center (the nitrogen) is partially shielded by neighboring group so that larger molecules cannot easily approach and react with the nitrogen (Mohd Zulkifli, 2009) as shown in Figure 2.7.

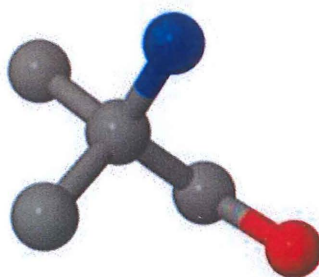
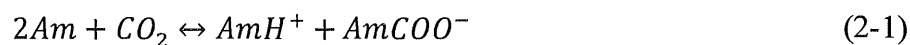


Figure 2.7: Molecular structure of 2-Amino-2-Methyl-1-Propanol (AMP)

## 2.6. Reaction mechanism

In aqueous solutions, primary, secondary and tertiary alkanolamines exhibit a different behavior towards  $\text{CO}_2$  due to their molecular structure in order to form either bicarbonate or carbamate. Bicarbonate is produced by the reaction of a  $\text{CO}_2$  molecule with a water molecule, while carbamate is formed by the reaction of a  $\text{CO}_2$  molecule with an amine molecule.  $\text{CO}_2$  in the liquid is bound almost entirely in one of these two forms, and only a small fraction is found as free  $\text{CO}_2$ .

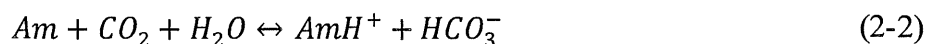
Primary and secondary alkanolamines react with CO<sub>2</sub> under the formation of a carbamate species according to the following overall reaction ( Derks, 2006)



Where *Am* is the amine molecule and *AmCOO*<sup>-</sup> is the amine carbamate.

However, due to the additional heat of absorption associated with the formation of carbamate ions, the regeneration energy requirement for primary and secondary amines is higher compared to tertiary or other amines which do not form carbamates ions.

A different behavior is shown by tertiary amines which are unable to form carbamates due to their lack of N–H bond required and therefore do not react directly with CO<sub>2</sub>. However, in aqueous solutions, tertiary amines promote the hydrolysis of CO<sub>2</sub> to form bicarbonate and a protonated amine, but with much slower kinetics than those of primary and secondary amines. Other than that, the advantage of using tertiary amines is that one mole of amine is needed to react with one mole of CO<sub>2</sub>, which indicates higher equilibrium CO<sub>2</sub> loading than primary and secondary amines due to very low carbamate stability.



Where *HCO*<sub>3</sub><sup>-</sup> is the bicarbonate.

Meanwhile for sterically hindered amines, the initial reaction rate is lowered due to steric hindrance and producing less stable carbamates, which then undergo hydrolysis and form bicarbonates while releasing the free amine. This free amine then reacts with CO<sub>2</sub> leading to an overall higher loading. These amines are considered as a breakthrough in the solvent development field due to the combined advantages of primary, secondary and tertiary amines that they offer, including a high CO<sub>2</sub> absorption capacity and low heat regeneration requirements. Moreover, when compared to other amine solvents, they have lower degradation rate, lower solvent circulation rate, low corrosivity, less solvent losses and thus, lower costs. A disadvantage of sterically hindered amines is the lower reaction kinetics as compared to primary and secondary amines

Two major criteria must be considered to choose the adequate amine solution: the absorption performances (higher with primary and secondary amine) and the energy requirement for the

solvent regeneration (lower with tertiary and sterically hindered amine). The different types of amine can also be mixed in order to combine the specific advantage of each type of amine (Dubois & Thomas, 2011).

## 2.7. Improvement of the System

The most widely studied alkanolamines are primary amines like monoethanolamine (MEA) and tertiary amines like methyl-diethanolamine (MDEA). However, the use of alkanolamine presents several concerns (Feng et al, 2010):

- i. Corrosion of amines system limits the concentration of amine in the solution and causes extra cost.
- ii. Amines are prone to degrade under high temperature especially in the regeneration process.
- iii. Oxidative degradation of amines occurs in the presence of oxygen.
- iv. Amines are volatile and lost into the gas stream. The loss of absorbents not only produces extra waste streams but also leads to additional absorbent cost there have been some concerns regarding the use of alkanolamine exhibit lower affinity towards CO<sub>2</sub>.

Due to low reactivity with CO<sub>2</sub>, MDEA is often combining with other classes of amines in order to take advantage of the desirable properties. In the past years, Sartori et al, (1983) proposed the use of sterically hindered amines, because of their high absorption capacity and high absorption rate. A sterically hindered amine presents a type of structure that could be a primary or secondary amine in which an amine group is attached to the ternary carbon or a secondary carbon, respectively. The principle of such an aqueous blend with a tertiary amine is based on the relatively high rate of reaction of CO<sub>2</sub> with the hindered alkanolamine combined with the low heat of reaction of CO<sub>2</sub> with the tertiary alkanolamine, which leads to higher rates of absorption in the absorber column ( Derks, 2006). Previous studies (da Silva, 2005; Freeman et al, 2010; Pei et al, 2008) have been suggested 2-amino-2-methyl-1-propanol (AMP) as the greatest use in the CO<sub>2</sub> absorption process due to its relatively low regeneration energy and high thermal stability. Some authors (Samanta & Bandyopadhyay, 2009; Dash et al, 2014) recommended adding an activator such as piperazine (PZ) to the AMP solution or mixing it with primary or secondary amines in order to increase the reaction rate of this solution. Blended MDEA-MEA solutions

have been widely investigated also for several years (Sema, et al., 2012; Naami et al, 2013; Mandal et al, 2001; Setameteekul, Aroonwilas, & Veawab, 2008).

Studies on absorption of CO<sub>2</sub> into aqueous blends of AMP with MDEA have not been much studied so far as the AMP is a new solvent that is commercially available. According to experimental work done by Aroua et al, (2002) it shows that higher CO<sub>2</sub> uptake in AMP solvent as compared to that of MDEA. Hence, the addition of AMP to MDEA will enhance the CO<sub>2</sub> loading of the latter. The way in which CO<sub>2</sub> capture could be describe via the so-called shuttle mechanism theory where the fast reacting property of AMP is utilize to quickly absorb CO<sub>2</sub> and the products formed will then react with MDEA and the free AMP will continue reacting with CO<sub>2</sub> and the process goes on, thus allowing more CO<sub>2</sub> molecules to be captured (Huang et al, 2011).

## **2.8. Molecular Dynamic simulations**

Molecular dynamics (MD) has also been employed to investigate physical properties of selected solutions used for CO<sub>2</sub> capture. The MD method has been successfully used to compute reaction kinetics of solutions. The MD method is also used to calculate the diffusivity of gaseous molecules. In this study, we used a general purpose molecular dynamics simulation package which is called MDynaMix package Ver. 5.1 (Lyubartsev & Laaksonen, 2000) to perform parallel MPI-based NVT simulations for the two systems.

Molecular Dynamic (MD) simulation depends on time evolution of the system. A microscopic replication of a macroscopic system constructed in a manageable box of molecules to study the configurations of the molecules and properties of the system in future. A working definition of molecular dynamics (MD) simulation is technique by which one generates the atomic trajectories of a system of N particles by numerical integration of Newton's equation of motion, for a specific interatomic potential, with certain initial condition (IC) and boundary condition (BC).

Considering a system with  $N$  atoms in a volume  $\Omega$  (see Figure 2.8). Its internal energy can be defined by,  $E = K+U$  where  $K$  is the kinetic energy as shown in Equation (2-3)

$$K = \sum_{i=1}^N \frac{1}{2} m_i |\dot{x}_i(t)|^2 \quad (2-3)$$

And  $U$  is the potential energy,

$$U = U(x^{3N}(t)) \quad (2-4)$$

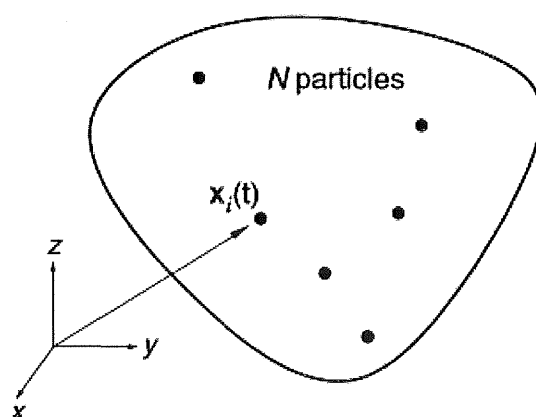


Figure 2.8: Illustration of MD simulation system

There are five key ingredients to a MD simulation, which are boundary condition, initial condition, force calculation, integrator/ensemble, and property calculation.

### 2.8.1 Boundary condition

There are two major types of boundary conditions which are isolated boundary condition (IBC) and periodic boundary condition (PBC). IBC is ideally suited for studying clusters and molecules, while PBC is suited for studying bulk liquids and solids. There could also be mixed boundary conditions such as slab or wire configurations for which the system is assumed to be periodic in some directions but not in the others. In IBC, the  $N$  particle system is surrounded by vacuum; these particles interact among themselves, but are presumed to be so far away from everything else in the universe that no interactions with the outside occur except perhaps responding to some well-defined “external forcing.” In PBC, one explicitly keeps track of the



motion of  $N$  particles in the so-called supercell, but the supercell is surrounded by infinitely replicated, periodic images of itself. Therefore a particle may interact not only with particles in the same supercell but also with particles in adjacent image supercells.

### 2.8.2 Initial condition

Since Newton's equations of motion are second-order ordinary differential equations (ODE), IC basically means  $x^{3N}(t=0)$  and  $\dot{x}^{3N}(t=0)$  the initial particle positions and velocities. Generating the IC for crystalline solids is usually quite easy, but IC for liquids needs some work, and even more so for amorphous solids. A common strategy to create a proper liquid configuration is to melt a crystalline solid. And if one wants to obtain an amorphous configuration, a strategy is to quench the liquid during a MD run.

Referring to Figure 2.9, we explicitly keep track of trajectories of only the atoms in the center cell called the supercell (defined by edge vectors  $h_1$ ,  $h_2$  and  $h_3$ ), which is infinitely replicated in all three directions (image supercells). An atom in the supercell may interact with other atoms in the supercell as well as atoms in the surrounding image supercells.  $r_c$  is a cut-off distance of the interatomic potential, beyond which interaction may be safely ignored.

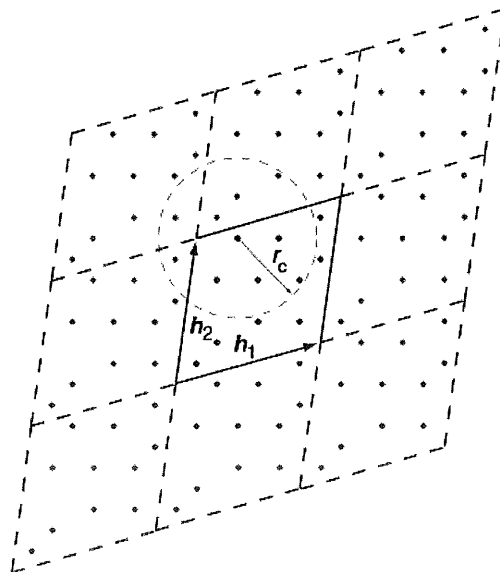


Figure 2.9: Illustration of periodic boundary condition (PBC)

### 2.8.3 Force calculation

The most time-consuming part of the molecular dynamics simulations is the calculation of the forces due to non-bonded interactions which in principle, requires a double sum over all the atom pairs. For long-range Coulomb interactions, special algorithms exist to break them up into two contributions: a short-ranged interaction, plus a smooth, field-like interaction, both of which can be computed efficiently in separate ways. In this study the focus is on issues concerning short-range interactions only.

There are varieties of short range interactions. Those included dipole-dipole, induced dipole and dispersion interactions in combination with the repulsive contribution. Short range interaction is more complex than long range interaction. Electron clouds overlap causes a strong short range repulsive force when electron density and nuclear shielding are reduced. This means the increase in the columbic repulsion between the positively charged nuclei. This is also the force that prevents a crystal lattice from collapsing itself. However, before nuclear repulsion becomes significant there is also quantum mechanical effect because the electrons are forced to occupy a smaller portion of space. So, there is a weaker and contrasted longer range attractive interaction at larger interatomic distances arising from the formation of instantaneous dipoles between adjacent electron clouds. This effect is known as the Van der Waals interaction which is also quantum mechanical in origin (Adam, et al., 2014).

### 2.8.4 Thermodynamic ensemble

Ensembles such as the micro-canonical, canonical, and grand-canonical are concepts in statistical physics that refer to the distribution of initial conditions. There are three types of ensembles normally being employed in MD simulation. The first type is NVE ensemble or microcanonical ensemble which fixed the number of particles (N), volume (V) and energy (E). The second type is the NPT or Isobaric-isothermal ensemble where the number of particles (N), pressure (P) and temperature (T) are fixed during the dynamic process through the usage of pressure and temperature controller. The third type is the canonical ensemble (NVT) which allows energy and pressure to be fluctuated. Amongst these ensembles, NVE and NVT are the ensembles chosen to be applied in this study.

### 2.8.5 Analysis parameter

Radial distribution function (RDF) is an important structural property that basically used to characterize compound in general. In particularly, RDF measures the probability of finding the neighboring molecules at particular distance  $r$  from a reference molecule. RDFs can be calculated for all pairs or for a selected set of different atom pairs (Lyubartsev & Laaksonen, 2000). The RDF has the ability to be expressed in thermodynamic function such as in the internal energy  $E$  which is the sum of kinetic and potential energy,  $U$  as in Equation (2-5).

$$E = \frac{3}{2}NkT + U \quad (2-5)$$

Where  $T$  is temperature and  $k$  is the Boltzmann constant.

Integrating the equation will producing the potential energy,  $U$  and the equation can be rewritten as Equation (2-6).

$$\frac{E}{NkT} = \frac{3}{2} + \frac{\rho}{2kT} \int_0^{\infty} u(r)g(r,\rho,T)4\pi r^2 dr \quad (2-6)$$

The radial distribution function can be defined by the Equation (2-7).

$$g(r, \delta r) = \frac{V \langle N(r, \delta r) \rangle_M}{N^2 4\pi r^2 \delta r} \quad (2-7)$$

Where  $g(r, \delta r)$  is dimensionless pair distribution function,  $N(r, \delta r)$  is the number of particles in spherical shell, subscript M signifies the average (mean) value,  $V$  is volume of the system,  $N$  is number of particles in the system and  $4\pi r^2 \delta r$  is volume of the spherical shell with thickness  $\delta r$ .

As can be seen from Figure 2.10, the atom at the origin is highlighted by a black sphere. The dashed regions between the concentric circles indicate which atoms contribute to the first and second coordination number shells, respectively (Ziman, 1979).

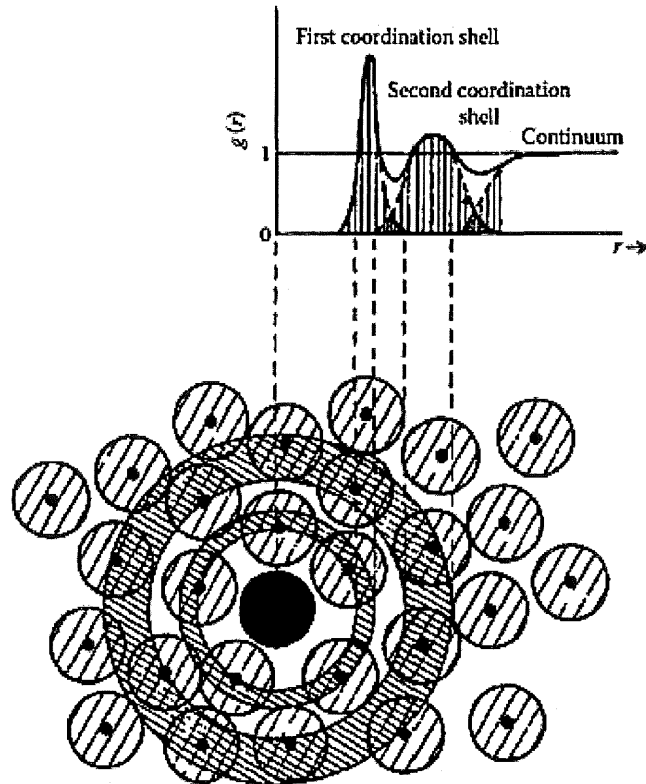


Figure 2.10: Schematic explanation of  $g(r)$  of a monoatomic fluid

## Chapter 3

### Methodology

#### 3.1. Molecular Dynamic simulation

Molecular dynamics simulation is a computer simulation in which atoms and molecules are allowed to interact for a period of time. The material behavior and its deformation are described in atomistic modeling. The purpose of molecular simulation is to understand the properties of molecules in terms of their structure and the microscopic interactions between them.

#### 3.2. Speciation of the System

System composition is an important issue for any studies involving simulation of the alkanolamine systems. In order to replicate true behavior of the system in actual life, speciation of the system needs to be determined accurately. On the other hand, modeling of the molecular entities in first place requires information about composition of the system because major molecules and species which have the higher concentrations in the system have to be modeled.

This includes both liquid and gas phases. For the gas phase, it is carbon dioxide and the concentration of impurities was disregarded and for the liquid phase or - in other words - the amine solution.

In this work, the speciation of MDEA and AMP solution are taken from literature which is based on experimental measurements. Due to lack of enough experimental data for temperature and molarities, it was very problematic to find the exact speciation of the system of interest. Considering this, approximation of liquid composition around the available experimental data, which are close to the condition of interest, had to be made. Speciation of the liquid phase in this thesis has been determined mainly based on reactions and experimental data given by Huang et al. (2011).

Huang et al. (2011) have reported seven different concentration of the solvent system in which MDEA concentration was varied as 1.0 and 1.5  $\text{kmol.m}^{-3}$ , and that of AMP, as 0.1, 0.2, 0.3, 0.4 and 0.5  $\text{kmol.m}^{-3}$  at 30, 35, and 40°C. The concentration of 1.0  $\text{kmol.m}^{-3}$  aqueous MDEA and 0.5

kmol.m<sup>-3</sup> AMP at 35 and 40°C was chosen for the system of our interest. Pressure is kept constant at 1 atm to achieve an equilibrium density.

### **3.3. Molecular structure**

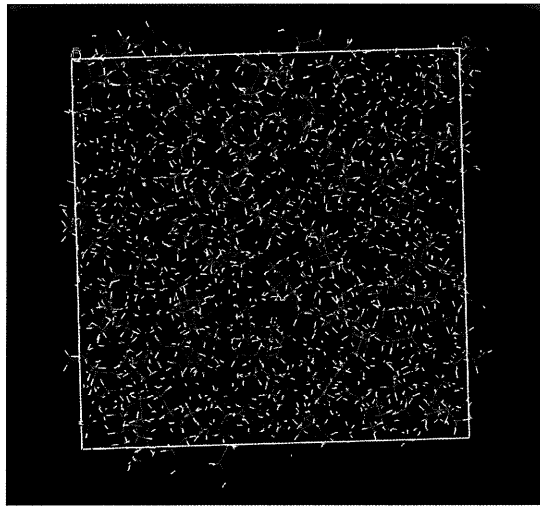
Once molecule speciation of the system is determined, modelling of the decided species can be started. For this research four different species had to be modelled. They were AMP, MDEA, water and carbon dioxide molecules. The molecular structures are downloading from ChemSpider database.

#### **3.3.1 Geometry optimization**

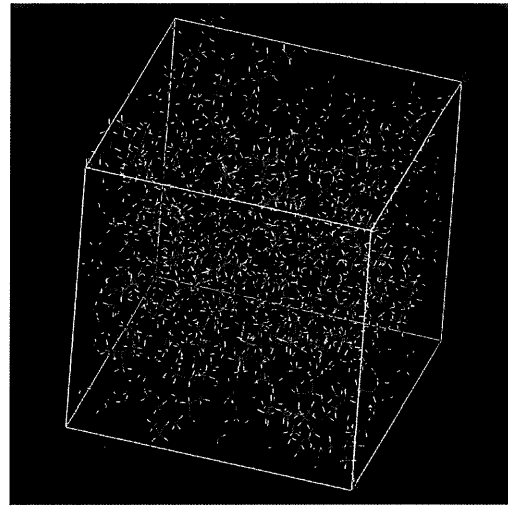
The geometry optimization step was done prior to the creation of Amorphous Cell box in Materials Studio software. Type of forcefield used is COMPASS and summation method used is Ewald. Continuously adjust dihedral angles of bond orbit until interaction minimum, the optimum molecular structure is achieved.

#### **3.3.2 Simulation box**

In order to perform the MD simulation, the amorphous cell simulation box was constructed consisting of 30 molecules of AMP, 45 molecules of MDEA and 543 molecules of water for binary system, and 20 molecules of AMP, 30 molecules of MDEA, 28 molecules of carbon dioxide and 296 molecules of water for tertiary system. The size of simulation box was referring to the amount of molecule in amorphous box. In principle, size of the simulation box should be appropriately chosen so that the box can contain dimensions of the fluctuations or interactions which are supposed to be observed during the simulation (Farmahini, 2010).

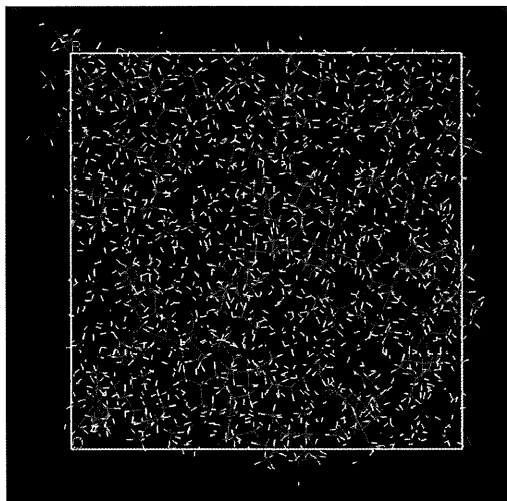


(2-dimension)

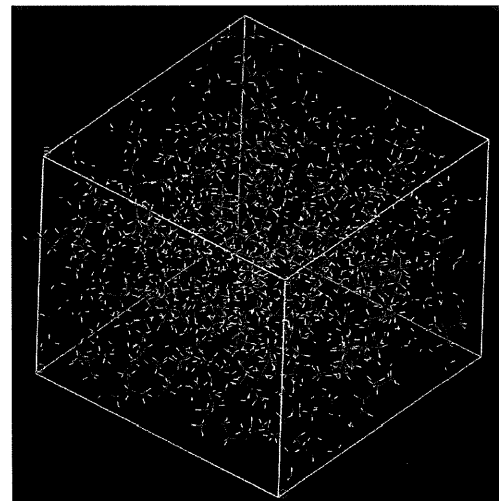


(3-dimension)

Figure 3.1: 2-Dimension and 3-Dimension view of simulation box at 35°C



(2-dimension)



(3-dimension)

Figure 3.2: 2-Dimension and 3-Dimension view of simulation box at 40°C

### 3.3.3 Equilibrium phase under NVE and NVT ensemble

*Micro canonical* ensemble (NVE) and *canonical ensemble* (NVT) keeps the energy (E) and temperature (T) constant (Farmahini, 2010). Even in a constant NVE simulation it is common

practice to adjust the temperature to the desired value during this phase. It may be required to determine the behaviour of the system changes with temperature (Leach, 2001). Ewald summation for calculation of electrostatic interactions is employed. NVT was employed where temperature was kept constant at approximately 303 and 313 K in each system by scaling the velocities during the equilibration phase. This also contains some tools to facilitate some calculation such as calculation of pair distribution function.

### **3.3.4 Data analysis**

Radial distribution functions (RDF) play an important role in the theory of simple fluids considering many thermodynamic properties in addition to the structure of the system can be identified from them (Leach, 2001).



The MD simulation procedure applied in this study is summarized in Figure 3.3.

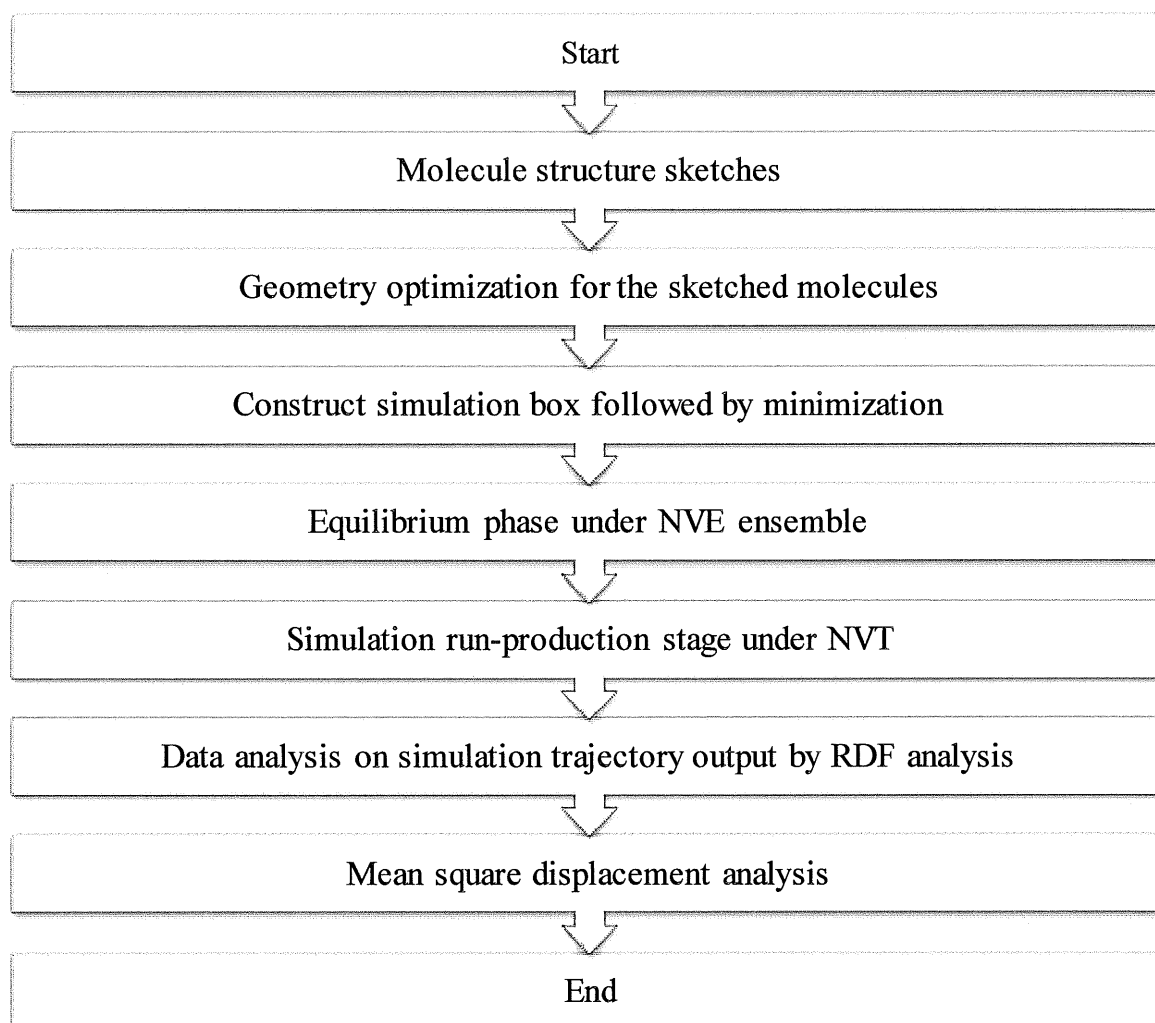


Figure 3.3: Summarization of MD simulation procedure

## Chapter 4

### Results and Discussion

#### 4.1. Binary system

Binary system which consists of amine solvent and water is simulated to study the interaction between these molecules at concentration 15 wt. % of AMP, 30 wt. % of MDEA and 55 wt. % of H<sub>2</sub>O. In this system, the MD simulation was performed for 30 AMP atoms, 45 MDEA atoms and 543 water atoms inside a cubic box at temperature of 35°C and 40°C for 1000 ps. As one can observe, there are some maximum and minimum value in the Figure 4.1. It shows the interaction between hydroxyl group, -OH of MDEA (blue line) and AMP (red line) with water at 35°C. As can be seen from the figure, the intermolecular interaction between -OH of MDEA is higher than AMP at 1.75 Å. It shows that hydroxyl group of MDEA have higher chances of finding any pair of atoms at the mentioned separation than AMP. This interaction presenting the hydrogen bonding formed between these molecules. It is also important to notice that the probability of finding of any atom pair within the distances shorter than the atomic diameter is zero due to highly repulsive forces. In contrary, the probability of intermolecular interaction tends towards one as the distance increases, signifying the liquid is representing the bulk fluid.

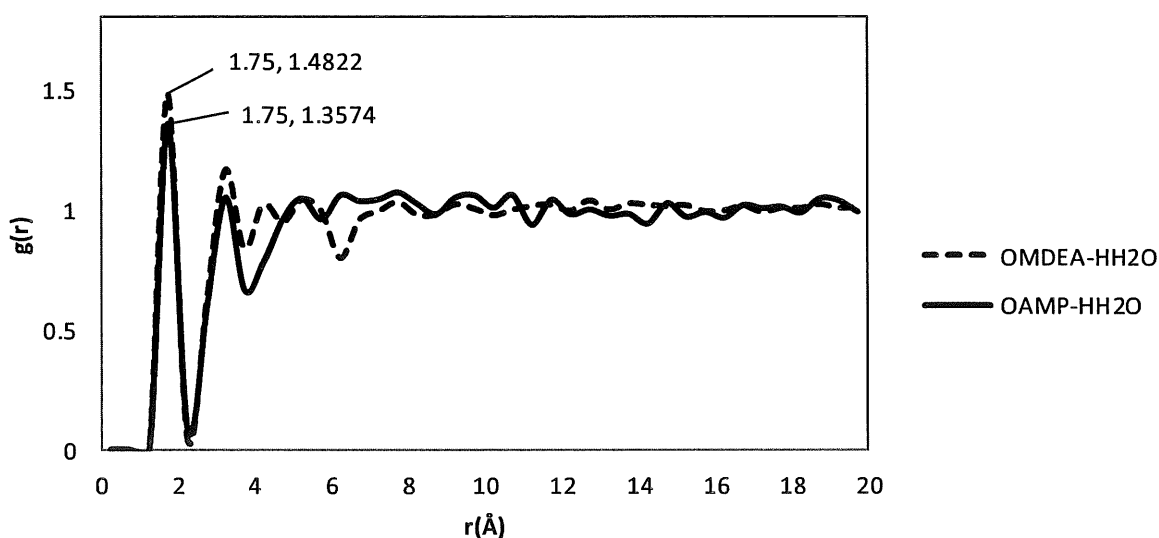


Figure 4.1: Molecular interactions of hydroxyl group in binary system at 35°C

Meanwhile, the interaction of amino group,  $-N$  of MDEA and AMP at  $35^{\circ}\text{C}$  is represented in Figure 4.2. As can be seen from this figure, the intermolecular interaction of  $-N$  group of AMP shows the first peak at  $1.75 \text{ \AA}$  with value of  $1.4042$  implying that it is  $1.4042$  times a higher probability of finding any atom pair within this distance. Whereas, the intermolecular interaction of  $-N$  group of MDEA have its first peak at  $1.75 \text{ \AA}$  with value of  $1.0610$  and followed by its second peak which have the highest intermolecular interaction at  $4.75 \text{ \AA}$  possessing value of  $1.3548$ . This is also due to the hydrogen bonding. In comparison between the intermolecular interaction of hydroxyl group and amino group of AMP and MDEA, it can be concluded that  $\text{H}_2\text{O}$  has stronger intermolecular force of polar bond with the  $-\text{OH}$  group of MDEA compared with its  $-N$  group since the electronegativity for oxygen atom is bigger than nitrogen atom.

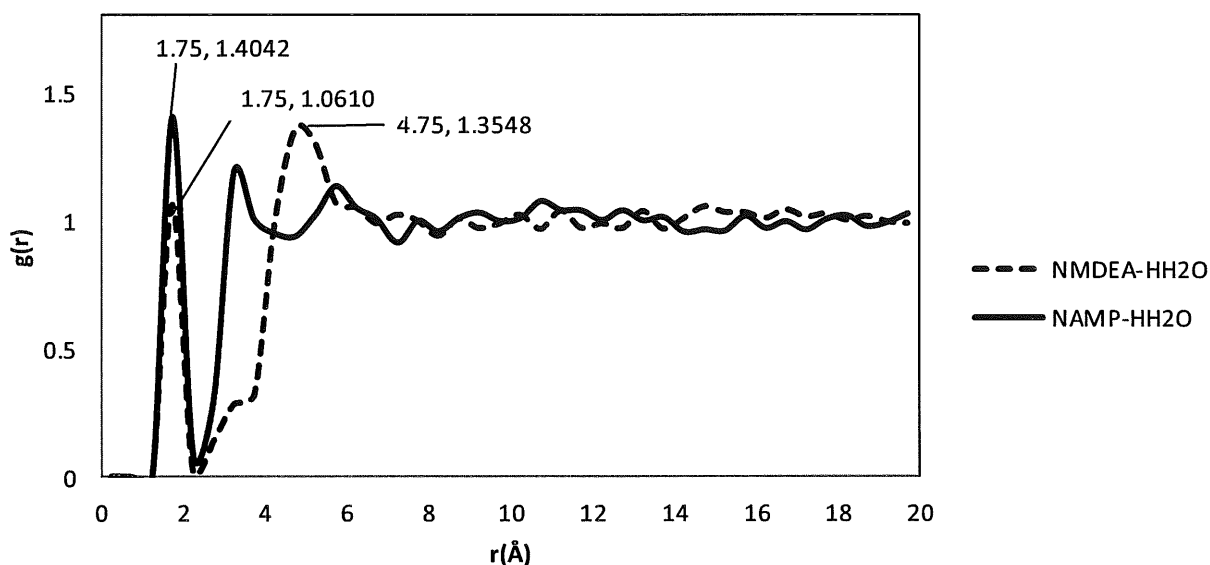


Figure 4.2: Molecular interactions of amino group in binary system at  $35^{\circ}\text{C}$

Meanwhile, Figure 4.3 and Figure 4.4 represented the intermolecular interaction of  $-\text{OH}$  and  $-N$  of MDEA and AMP at  $40^{\circ}\text{C}$  respectively. As can be seen from the figure, the intermolecular interaction between  $-\text{OH}$  of MDEA with water is the highest at  $3.25 \text{ \AA}$  with value of  $1.0686$ , slightly higher than AMP at the same distance. However, their first peak for both MDEA and AMP do not represent their highest intermolecular interaction. As well as for the intermolecular interaction between  $-N$  of MDEA and AMP with water at  $40^{\circ}\text{C}$ , the first peak of  $-N$  of MDEA

occur at 2.25 Å by the value of 1.6151 and for -N of AMP, the highest probability of finding pair of atoms is at the distance of 5.75 Å with the value of 1.2269.

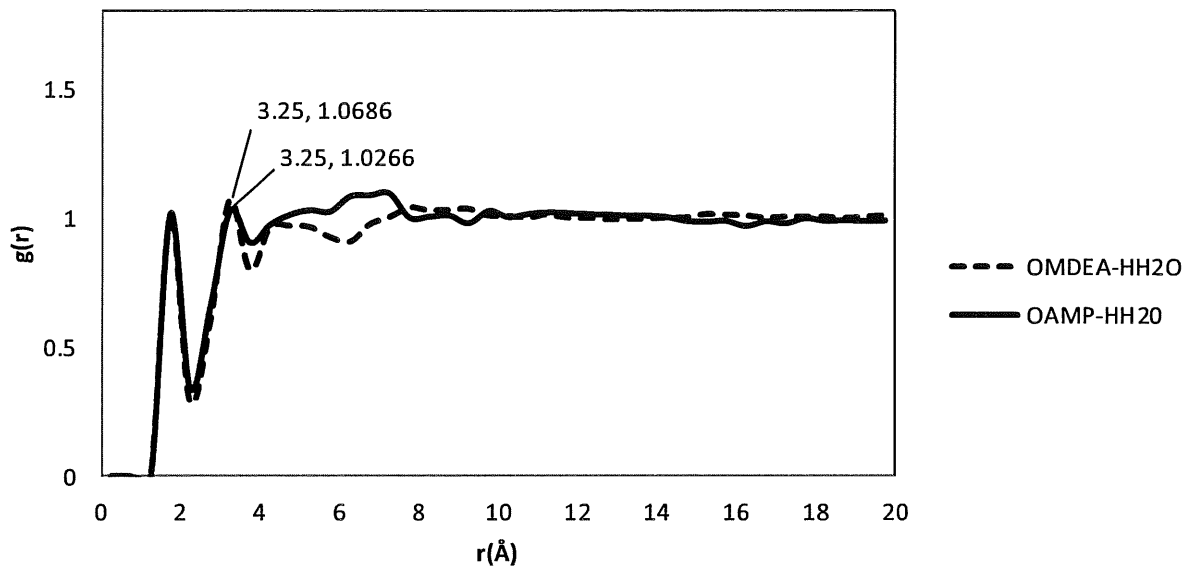


Figure 4.3: Molecular interactions of hydroxyl group in binary system at 40°C

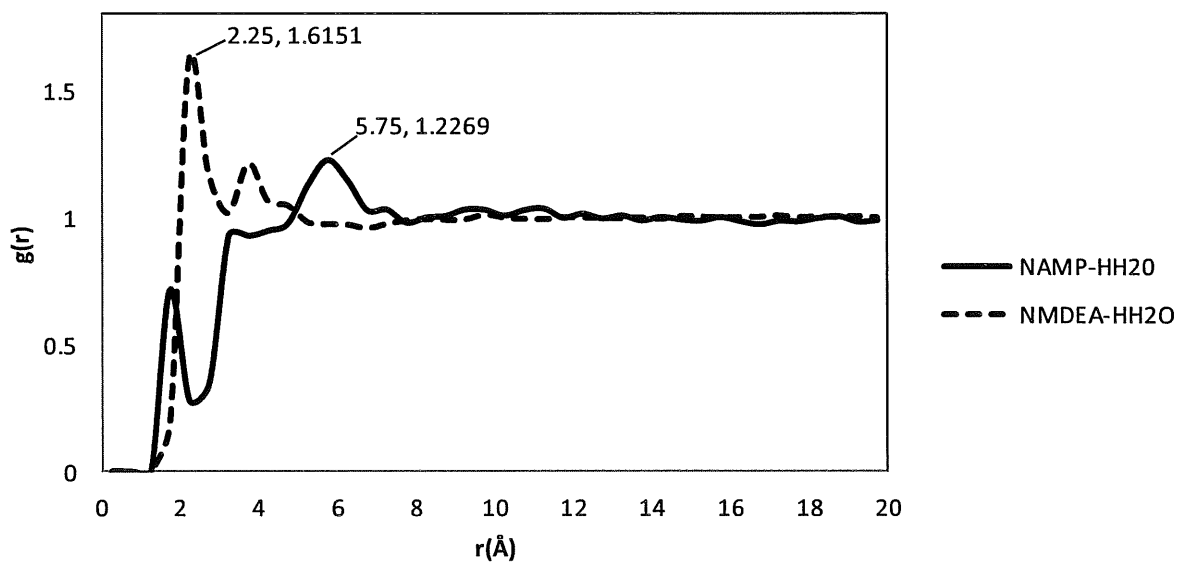


Figure 4.1: Molecular interactions of amino group in binary system at 40°C

For binary system, the study is focusing on the hydrogen bonding of water with -OH and -N group of MDEA and AMP. Based on the analysis, at temperature of 35°C it is proven that the -

OH group of MDEA has the higher hydrogen bonding with water and the –N group for both AMP and MDEA have weaker interaction of hydrogen bonding. However, at temperature of 40°C it shows that the highest interaction would be from the –N group of MDEA. As the temperature increase, the kinetic energy of the molecules will increase as well thus lead to the weakening of intermolecular hydrogen bonds. The binary system's data acts as a reference and interpretation for tertiary system. As summary, the data collected is tabulated into Table 4.1.

Table 4.1: Summary data of RDF analysis for binary system at 35°C and 40°C

	35°C		40°C	
	r(Å)	g(r)	r(Å)	g(r)
OMDEA - HH <sub>2</sub> O	1.75	1.4822	3.25	1.0686
OAMP - HH <sub>2</sub> O	1.75	1.3574	3.25	1.0266
NMDEA - HH <sub>2</sub> O	4.75	1.3548	2.25	1.6151
NAMP – HH <sub>2</sub> O	1.75	1.4042	5.75	1.2269

\* According to each first peak at both temperature

#### 4.2. Tertiary System

Tertiary system which consists of amine solvent, carbon dioxide and water was simulated to study the interaction between these molecules at concentration 15 wt. % of AMP, 30 wt. % of MDEA, 45 wt. % of H<sub>2</sub>O and 10 wt. % of CO<sub>2</sub>. In this system, the MD simulation was performed for 20 AMP atoms, 30 MDEA atoms, 296 water atoms and 28 carbon dioxide atoms inside a cubic box at temperature of 35°C and 40°C for 1000 ps. Referring from Figure 4.5, it shows the intermolecular interaction between the –N of AMP and MDEA with carbon atom of CO<sub>2</sub>. The first peak for both AMP and MDEA do not represent their highest interaction with CO<sub>2</sub>. For MDEA, the highest interaction would be at 5.25 Å with value of 1.7842 whereas for AMP, the highest interaction is at 5.75 Å possessing value of 1.2874. The amino group of MDEA shows the highest intensity of interaction with CO<sub>2</sub> at this temperature.

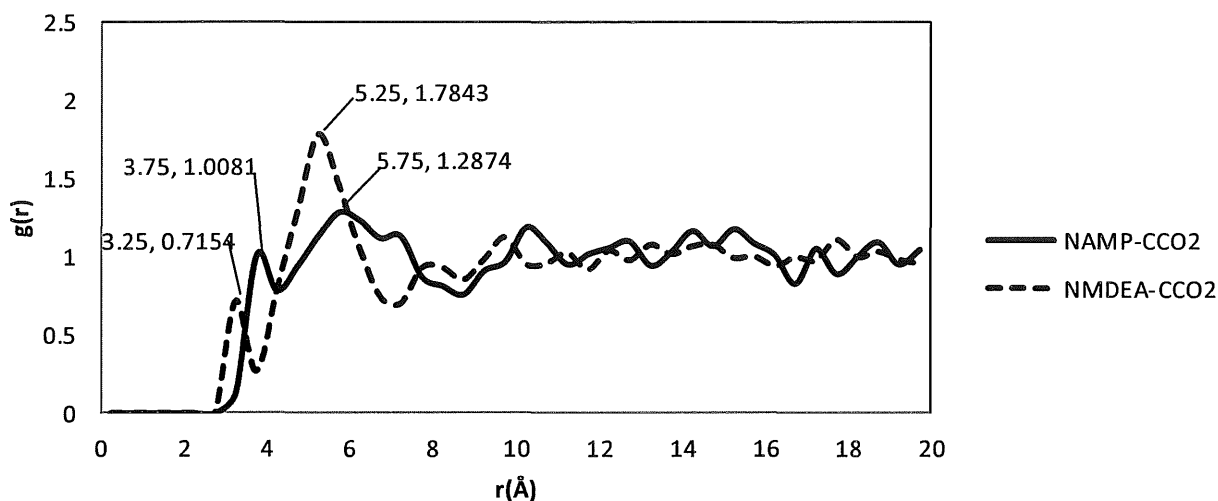


Figure 4.5: Molecular interaction between amino group of AMP and MDEA with  $\text{CO}_2$  at  $35^\circ\text{C}$

Meanwhile, referring to Figure 4.6 shows the intermolecular interaction between the  $-\text{OH}$  group of AMP and MDEA with  $\text{CO}_2$  at  $35^\circ\text{C}$ . At the distance of  $3.25 \text{ \AA}$  the intermolecular interaction between  $-\text{O}$  of AMP with  $\text{CO}_2$  has the peak of  $1.0731$  whereas the intermolecular interaction between  $-\text{O}$  of MDEA with  $\text{CO}_2$  at the distance of  $3.75 \text{ \AA}$  has the peak of  $0.9744$ . The highest probability of finding an adjacent atom for MDEA is at  $5.25 \text{ \AA}$  with the value of  $1.2695$  while AMP has the highest intermolecular interaction at a longer distance of  $7.25 \text{ \AA}$  with a value of  $1.3499$ .

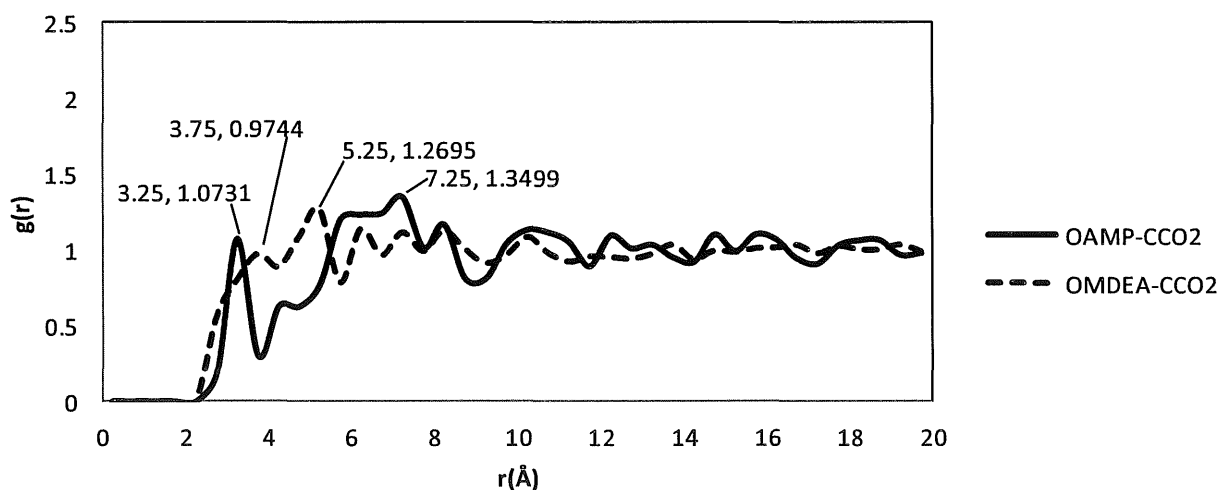


Figure 4.6: Molecular interaction between hydroxyl group of AMP and MDEA with  $\text{CO}_2$  at  $35^\circ\text{C}$

As depicted from Figure 4.7, it shows the intermolecular interaction between -N of AMP and MDEA with CO<sub>2</sub> at 40°C. The highest intermolecular interaction is from AMP at the distance of 3.75 Å with value of 2.2690 whereas MDEA is having the highest intermolecular interaction at a longer distance of 5.25 with a value of 1.7929. Since AMP has the highest first peak than MDEA, it shows that the probability of AMP having the interaction with the first neighboring atom is higher than MDEA at this temperature. Therefore, the interaction between -N of AMP is stronger than the interaction between -N of MDEA.

During the absorption process, CO<sub>2</sub> reacts with AMP to form carbamate ions through zwitterion reaction mechanism. The following reaction may occur in the system:

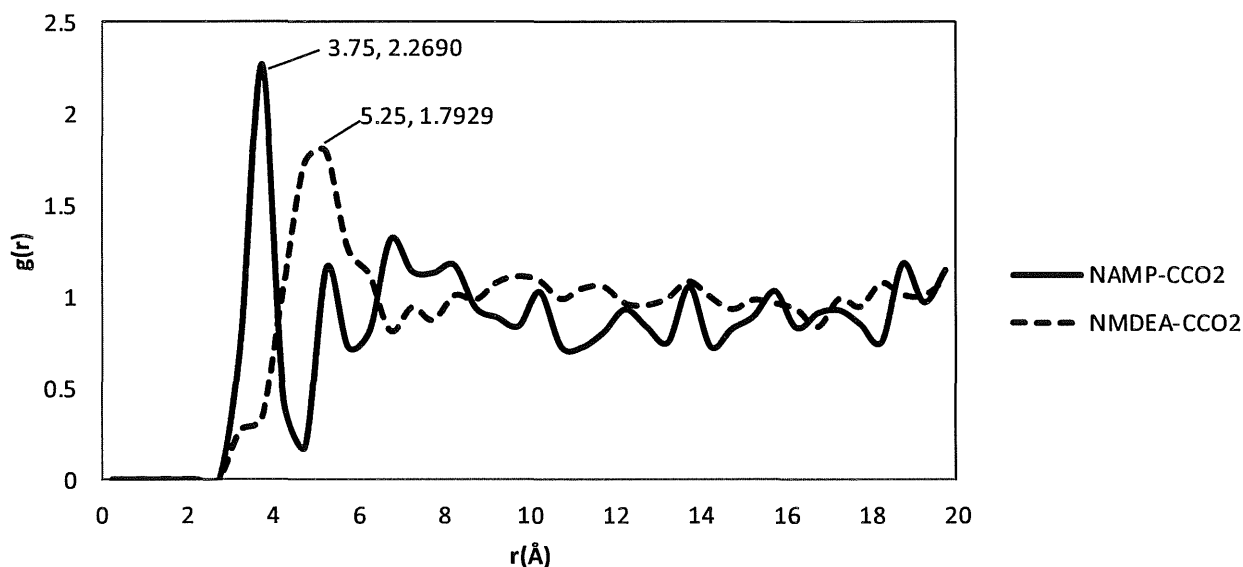
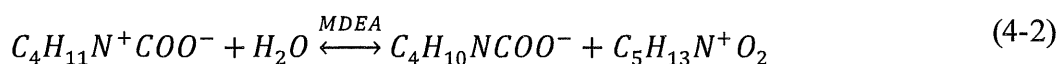
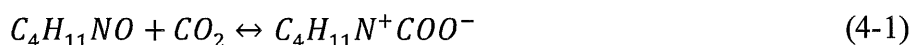


Figure 4.7: Molecular interaction between amino group of AMP and MDEA with CO<sub>2</sub> at 40°C

Figure 4.8 show the interaction between -O of AMP and MDEA with CO<sub>2</sub> at 40°C. As can be seen, the first intermolecular interaction for AMP is at the distance of 3.25 Å with vale of 1.0783 whereas for MDEA, the first intermolecular interaction which is also represents the highest

probability of having interaction with the neighboring atom is at 4.25 with value of 1.4726. The highest peak for the intermolecular interaction for AMP is at a longer distance of 7.25 Å possessing value of 1.2480. Therefore the interaction between -O of AMP with CO<sub>2</sub> is stronger than the interaction from -O of MDEA at this temperature.

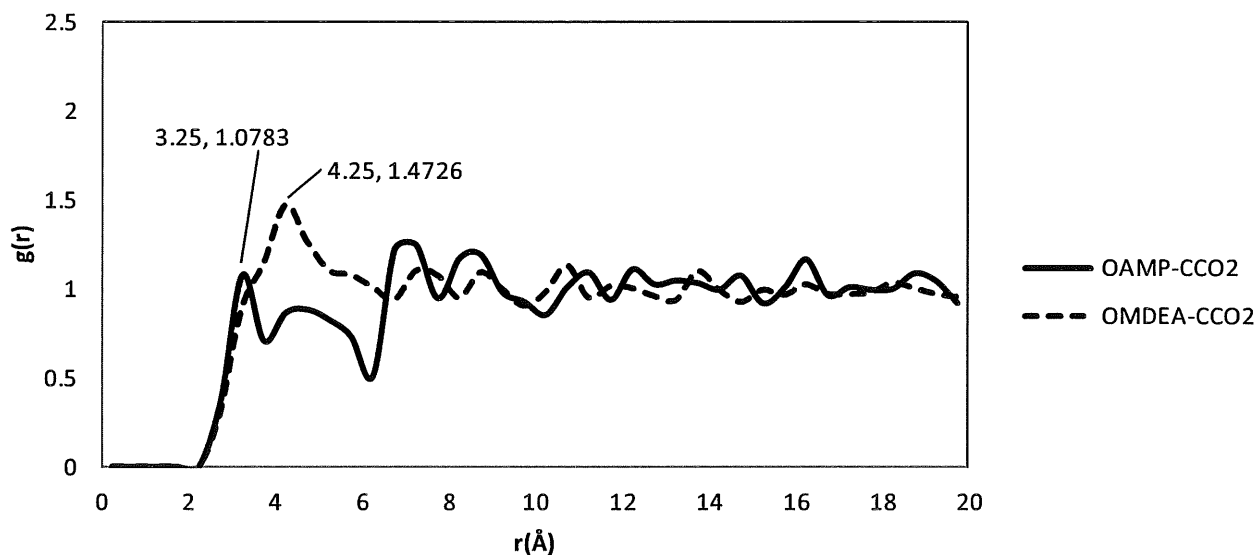


Figure 4.8: Molecular interaction between hydroxyl group of AMP and MDEA with CO<sub>2</sub> at 40°C

By referring to the Figure 4.5 and Figure 4.7, the  $g(r)$  value for the intermolecular interaction between -N of AMP and CO<sub>2</sub> are 1.2874 and 2.2690 at 35°C and 40°C respectively. From equation (4-1), it is proven that CO<sub>2</sub> is more favorable to react with AMP and the highest CO<sub>2</sub> absorption rate would be at 40°C. Figure 4.9 shows the molecular structure of MDEA where the nitrogen is connected to three branches of carbon and at least two of them are quite long. These branches are CH<sub>3</sub> and -(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>. Thus it can be concluded that it is impossible for carbon dioxide to form the first intermolecular interaction around nitrogen within very short distance. That is why the position of the first peak is fairly far (3.25 Å).



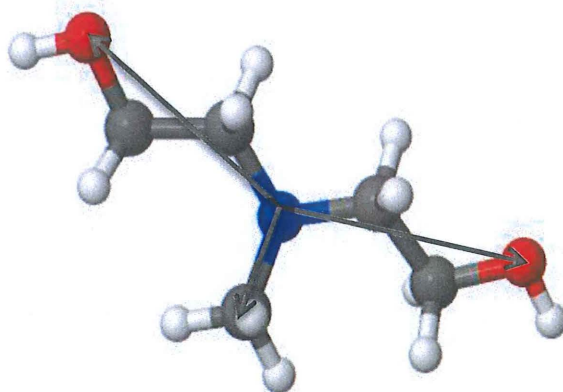


Figure 4.9: N-O and N-C branches in MDEA structure

In contrary, such limitation does not exist for  $\text{CO}_2$  to surround the oxygen in alcohol group. Oxygen atoms are located at the end of two long tails of MDEA and it is quite feasible for  $\text{CO}_2$  molecules to approach them. Observing from Figure 4.6 and Figure 4.8, the first intermolecular interaction of oxygen with  $\text{CO}_2$  is closer ( $2.75 \text{ \AA}$ ) compared to nitrogen atom of MDEA.

### 4.3. Mean square displacement

The motion of an individual molecule in a dense fluid does not follow a simple path. As it travels, the molecule is jostled by collisions with other molecules which prevent it from following a straight line. This relationship can be written as  $\langle r^2 \rangle = 6Dt$ .

Referring to figure and figure, the plots are not linear with respect to time. This is because the path of molecule takes will be an approximately straight until it collides with its neighbor. Only when it starts that first collision will its path start to resemble a random walk. Until it makes that first collision, it moves with approximately constant velocity, meaning that the distance it travels is proportional with time, and its MSD is therefore proportional to the time squared. This is of course a simplification - the collision between molecules is not like the collision between two pebbles, it is not instantaneous in space or time, but is 'spread out' a little in both. This means that the behavior of the MSD at short time is sometimes more complicated than this MSD plot shows.

From Figure 4.10 and Figure 4.11, gradient of each line represent the diffusion coefficient of each molecule. Hence, the diffusion coefficient and of each molecule at different temperature is

Table 4-1: MSD/t and diffusion coefficient of each molecule at different temperature

Molecule	MSD/t ( $\text{\AA}^2/\text{ps}$ )		D( $\text{m}^2/\text{s}$ )	
	35°C	40°C	35°C	40°C
H <sub>2</sub> O	4.8493	4.5606	8.08E-09	7.60E-09
CO <sub>2</sub>	5.0773	5.2081	8.46E-09	8.68E-09
MDEA	3.8272	2.5338	6.38E-09	4.22E-09
AMP	4.96	3.0793	8.27E-09	5.13E-09

It shows that the diffusion coefficient for CO<sub>2</sub> is the largest followed by AMP, H<sub>2</sub>O and MDEA. CO<sub>2</sub> can diffuse faster due to its smaller size compared to other molecules.

## Conclusion

The study of intermolecular interaction in blended N-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) absorption process for carbon dioxide capture via molecular dynamic simulation technique is performed at temperature of 35°C and 40°C. The blend under investigation has proven itself effective for absorption of carbon dioxide from the natural gas.

It was found out that the physical interaction between CO<sub>2</sub>, MDEA, AMP and water molecule is increased as temperature is increased. CO<sub>2</sub> has stronger interaction with –N group of AMP compared to –N group of MDEA as this is the initial step for the chemical reaction to occur during the absorption process to produce carbamate ions. H<sub>2</sub>O is more attractive to –OH group of MDEA to form hydrogen bonding which will increase the solubility of MDEA in water.

In the aspect of molecular diffusion, a study on mean square displacement (MSD) is carried out. It is found that the size of molecule can influence the diffusion coefficient of each molecule. The smaller size of the molecule results to the larger value of diffusion coefficient. Moreover, the phase of the molecule while occurring diffusion brings effect to the diffusion coefficient too.

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