Abstract

Objectives: Modelling and simulation of amine absorption process for CO$_2$ removal at macro-scale is well established. This study used to investigate the amine-CO$_2$ absorption process at molecular level using Molecular Dynamic (MD) simulation. Methods/Statistical Analysis: Analysis on different types of amine and blended amines for absorption process was conducted in this study. COMPASS and Ewald models used for force field and summation method calculation, respectively. Findings: The results shows MEA solvent was the highest tendency (39.70%) to interact with CO$_2$ compared to DEA and MDEA because can directly react with CO$_2$ and easily form carbamate ions. Due to the lack of –HN bond in MDEA, it was determined to be less reactive and suggested to be blended with other reactive amines. Blended MDEA/AMP (33.50%) and MDEA/PZ (23.80%) improved the efficiency of MDEA in CO$_2$ absorption process. The addition of AMP and PZ assisted MDEA to have intermolecular interaction with CO$_2$. Application/Improvements: Research on molecular modelling of amine absorption process for CO$_2$ capture was proposed in this study to give insight about this process at molecular level and to analyse the intermolecular interaction between CO$_2$ and amine solution.

Keywords: Alkanolamines, Absorption Process, Carbon Dioxide, Molecular Dynamic Simulation, Radial Distribution Function Analysis

1. Introduction

Anthropogenic Carbon Dioxide (CO$_2$) emissions occur when it is produced from burning activities and enters the atmosphere. The concentration of CO$_2$ in atmosphere is increasing to 43% in 2015. There are many technologies nowadays to capture and store CO$_2$ in order to prevent its emission to the atmosphere. At present, the most promising technology for CO$_2$ removal from coal-fired power stations is aqueous amine-based post combustion capture. Simulation works for amine absorption process for CO$_2$ capture at macro scale that emphasizes on process simulation, optimization and control is well established. One of the challenges of amine-based absorption process for CO$_2$ removal is the stability of the carbamate ion which requires high heat demand for the solvent regeneration process. Thus suggested that the future research should focus on the absorbent formulation so that the chemical absorption process efficiency can be improved. Considering the amine-based solvent characteristics, it is important to develop a clear understanding on the solvent molecular structure and its intermolecular interactions that influence the CO$_2$ absorption process. The understanding of fundamental in chemistry and the molecular level actually give benefit in study the process of removal CO$_2$. Strength of attraction or repulsion interaction based on distance and coordinate calculated in the Radial Distribution Function analysis (RDF). The application of MD simulation in amine absorption process is capable to improve the understanding and give insight about this process at molecular level. Several studies such as proposed the use of blended amine to increase efficiency of single amine for CO$_2$ absorption process. MDEA is a tertiary amine that is known as a less reactive compared to other amines. Two amine activators,
Molecular Dynamic Simulation of Amine-CO$_2$ Absorption Process

In this research, focus on study effect different type of amines and effect when blend two (2) amines toward CO$_2$ absorption process. Alkanolamine is an amine/ammonia compound that contain Hydroxyl (-OH) and amino (-NH) functional groups on an alkane chain. The hydrogen atom in ammonia compound (NH$_3$) is replaced first by alkyl or aryl group to form amine compound. Different amines have different reaction rate for CO$_2$ absorption process. The reaction of amine with CO$_2$ and water will produce carbamate, bicarbonate, and carbonic ions.

This manuscript was divided into two case studies. First, aim to determine the best amine that has strong intermolecular interaction with CO$_2$ and water, and to discover causes for it to happen. Second, analyse how the addition of other amine will affect the intermolecular interaction between amine and CO$_2$.

### 2. Simulation Methodology

The simulation was performed using Material Studio (7.0) software on HP Z400 workstation. The software was supplied by Accelrys. The methodology involved, determined type of speciation based on actual CO$_2$ absorption process. The structure of speciation was sketched by download from established database (http://www.chemspider.com/). The structure was optimized to ensure stability of molecular geometry. Amorphous cell box was constructed to represent the bulk system. Size of box was depending on amount of molecule inserted. The energy within box have to minimize before proceed to equilibrium and production step. 200 ps NVE (Moles, Volume And Enthalpy) and 1 ns NVT (Moles, Volume, Temperature) used respectively to each steps. Final structure on production step was used for analysis purpose. Algorithm model used were COMPASS (condensed-phase optimized molecular potentials for atomic simulation studies) and Ewald summation method. Radial Distribution Function (RDF) calculation was carried out to analyse the intermolecular interaction between molecules in simulation box. In this study, types of amine used were Monoethanolamine (MEA), Diethanolamine (DEA), Methy Diethanolamine (MDEA), Piperazine (PZ) and 2-Amino-2-Methyl-1-Propanol (AMP) which has different physical and chemical characteristic thus will influence to their reaction mechanism as representing in Figure 1. All amines are analyzed with conditions of 30 wt. %, 313 K and 1 atm.

![Molecular structure of amines](image)

**Figure 1.** Molecular structure of amines.

\[
g_{xy}(r) = \frac{N_y(r, r + dr)}{\rho_y 4\pi r^2 dr} \tag{1}
\]

where $N_y(r, r + dr)$ is the number of $y$ atom in shell of width $\Delta r$ at distance $r$, $r$ is the spherical radius, $\rho_y$ is the density of $y$ atom and $x$ is the reference atom.

### 3. Results and Discussion

#### 3.1 Effect Different Types of Amines

The aim of this part is to identify amine solvent that has higher tendency to interact with CO$_2$. Table 1 shows the RDF results of MEA, DEA, MDEA, AMP, and PZ solutions. For amino group (N$_{amine}$-C$_{co2}$), the trends of the highest interaction to the lowest are MEA> PZ> AMP> MDEA> DEA.

At same distance of $r = 4.25$ Å, MEA showed the highest tendency for intermolecular interaction to occur about 39.70% compared to AMP. The results obtained have good agreement with CO$_2$ absorption efficiencies was MEA> PZ> AMP> MDEA. MEA was supposed to have the strongest intermolecular interaction with CO$_2$ because it easily absorbed CO$_2$ compared to other amines. AMP and PZ also showed high value of $g(r)$ same as MEA. AMP has sterically hindered amine properties. The reaction mechanism of AMP was proposed by. The reaction of AMP with water produces low stable carbamate ion. Then, carbamate ion reacts with water again through hydrolysis to produce bicarbonate ion and free amine molecule. This free amine molecule will react with CO$_2$, representing the overall absorption process. However, due to the molecular structure of AMP, the reactivity with CO$_2$ is lower than MEA. When there were more substituent's such as methyl and alcohol groups were added, the reactivity of amine towards CO$_2$ would be decreased. In AMP structure, it has two methyl groups at $\alpha$-carbon to the nitrogen atom. The presence of substituent methyl group to the
Table 1. Summary data of RDF result for intermolecular interaction of amine solutions with CO$_2$

<table>
<thead>
<tr>
<th>Amine</th>
<th>O$<em>{amine}$–C$</em>{carbon dioxide}$</th>
<th>N$<em>{amine}$–C$</em>{carbon dioxide}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>3.75, 1.0612</td>
<td>4.25, 1.4058</td>
</tr>
<tr>
<td>DEA</td>
<td>3.75, 1.1399</td>
<td>5.25, 1.4259</td>
</tr>
<tr>
<td>MDEA</td>
<td>3.75, 1.1488</td>
<td>4.75, 1.5158</td>
</tr>
<tr>
<td>AMP</td>
<td>4.25, 1.0416</td>
<td>4.25, 1.0063</td>
</tr>
<tr>
<td>PZ</td>
<td>–</td>
<td>4.25, 1.0705</td>
</tr>
</tbody>
</table>

Amino functional group caused the reaction of AMP with CO$_2$ to form unstable carbamate ion. Then, the reaction with CO$_2$ was faster than MDEA. AMP size is much bigger than MEA and consequently the intermolecular interaction strength of AMP with CO$_2$ is lower than MEA even both of amines are categorised as primary amines. Furthermore, the attraction of base (amine) to positively charge CO$_2$ for zwitterions reaction became slower when the sterically hindered properties were present. PZ contains two nitrogen atoms in its molecular structure which will result to double CO$_2$ absorption compared to nitrogen at shorter time interaction. In$^2$ also stated that activator amine showed good efficiencies for CO$_2$ absorption. AMP and PZ amines are always chosen to blend with MEA and DEA, because these amines are difficult to separate from amine-CO$_2$ bond in the stripper. MDEA amine has low tendency to create the intermolecular interaction with CO$_2$ about 89.47%. This is because MDEA has lack of hydrogen atom attached in amino group there will be neoformation of carbamate ion. MDEA cannot directly absorb CO$_2$. Therefore, it is recommended to blend MDEA with activator amine such as AMP and PZ. DEA amine also shows low tendency to make intermolecular interaction with CO$_2$ compared to MEA, AMP, and PZ about 80.95%. DEA is a secondary amine and it is recognised as medium amine in CO$_2$ absorption efficiency. It was proved that DEA was neither the fastest nor the slowest to dissolve in water and to absorb CO$_2$. Also DEA poses medium energy requirement for regeneration. In addition, DEA amine gives moderate difficulty to break amine-CO$_2$ bond.

3.2 Effect blended MDEA/AMP and MDEA/PZ

The intermolecular interaction between O$_{mdea}$–C$_{co2}$ in single MDEA system was (3.75, 1.1488) as in Figure 2(a) and at the same distance (3.75 Å), the RDF result in blended MDEA/AMP was increased to 1.5336 (33.50%) as in Figure 2(b). The similar trend was observed on the intermolecular interaction between N$_{mdea}$–C$_{co2}$. At a distance of 5.25 Å, the tendencies for the interaction to happen were 1.5158 and 1.8256 for single MDEA and blended MDEA/AMP, respectively. Blended MDEA/AMP also showed strong intermolecular interaction with CO$_2$ compared to single AMP system. At a distance of 4.25 Å, the tendencies for intermolecular interaction to happen on O$_{amp}$–C$_{co2}$ were 1.0416 and 1.3185, for single AMP and blended MDEA/AMP systems, respectively. For N$_{amp}$–C$_{co2}$, the tendencies for intermolecular interaction to happen were 1.0063 and 1.1560 for single
AMP and blended MDEA/AMP systems, respectively. RDF results clearly showed that the blended MDEA/AMP gave strong intermolecular interaction with CO$_2$ compared to single MDEA and AMP. The molecular structure of AMP has the addition of two branches chain of methyl group to carbon atom caused steric hindrance properties with two hydrogen atom attach to nitrogen atom. On the other hand, the molecular structure of MDEA where the nitrogen is connected to three branches of carbon and at least two of them are quite long. That is why the position of the first peak $N_{mdea}$-$C_{co2}$ was fairly far for single MDEA system (5.25 Å, 1.5158) and (5.25 Å, 1.8256) for blended MDEA/AMP system compared to (4.25 Å, 1.0063) for single AMP system and (4.25 Å, 1.1560) for blended MDEA/AMP system. Higher intermolecular interaction of nitrogen atom in blended amine with CO$_2$ than single amine was fit with the expectation. The structural property of AMP can cover the limitation of MDEA, which is cannot directly react with CO$_2$ by forming carbamate and bicarbonate formation. The properties of sterically hindered made blended amine to be more reactive and easily formed carbamate ion when reacted with CO$_2$. The reaction of AMP with CO$_2$ formed less stable carbamate ion. Reducing the carbamate stability will affect the electron-withdrawing of the molecule. On a positive note, AMP will help MDEA to react with CO$_2$. The reaction of CO$_2$ with AMP formed an unstable carbamate ion due to the structure of AMP induces the steric hindrance character which unfavourable for carbamate formation.

It was reported that CO$_2$ loading in 2.0 M AMP solution was higher than 2.0 M MDEA solution due to higher basicity of AMP compared to MDEA.

Therefore, blended of MDEA with AMP was essential to improve the CO$_2$ absorption efficiency and capacity. The mechanism of the chemical reaction of blended MDEA and AMP amines solution with CO$_2$ is shown\(^{15}\). Sterically hindered amine, AMP will directly react with CO$_2$ first (to form carbamate ion) and then faster transfer of CO$_2$ to MDEA. The reaction of MDEA with CO$_2$ was slow due to the lack of hydrogen atom in amino group. Therefore, the presence of AMP will accelerate the reaction of MDEA with CO$_2$. In blended amine, the presence of more nitrogen atom can double CO$_2$ capture compared to single amine\(^{16}\). Nitrogen atom in the molecule influences the attraction of CO$_2$ towards amine solvent. Intermolecular interaction of amino group with CO$_2$ reflects the reaction rates with CO$_2$.

Figure 2(c) also shows RDF result for reaction between amine with CO$_2$ on MDEA and blended MDEA/PZ system. The values of $r$ and $g(r)$ for blended MDEA/PZ system were (3.75, 1.1883) and (5.25, 1.8766) for $O_{mdea}$-$C_{co2}$ and $N_{mdea}$-$C_{co2}$ respectively. The results show 3.44% and 23.82% for $O_{mdea}$-$C_{co2}$ and $N_{mdea}$-$C_{co2}$ respectively the increment after a small quantity of PZ was added into MDEA. Again, the addition of PZ in MDEA solution could increase the strength of intermolecular interaction between MDEA and CO$_2$ (see Figure 2(c)). The absorption of CO$_2$ by MDEA solution was more efficient by the additional chemical reaction of PZ\(^{15}\). PZ as an activator was added to MDEA solution in order to accelerate the intermolecular interaction of MDEA with CO$_2$. Based on Figure 2(c), the distance for intermolecular interaction of $N_{pz}$-$C_{co2}$ (4.25, 1.4911) was shorter than $N_{mdea}$-$C_{co2}$ (5.25, 1.8766) because PZ was reacted first with CO$_2$. MDEA cannot react directly with CO$_2$ due to the lack of hydrogen atom at amino group. PZ was attracted and combined with CO$_2$ then transferred to MDEA rapidly\(^{22}\). The reaction of PZ with CO$_2$ produced carbamate that subsequently reacted with MDEA to form bicarbonate. PZ was acted as a promoter to activate the MDEA to absorb CO$_2$. The reaction of CO$_2$ and PZ was in parallel with the reaction of CO$_2$ with MDEA in the condition of rapid pseudo-first-order reaction\(^{12}\). The properties of activator caused PZ to coalesce with CO$_2$ and rapidly transferred to MDEA. Due to rapid transfer of CO$_2$ to MDEA, the concentration of PZ did not depleted. The reaction is also known as instantaneous zwitterions mechanism. Membrane gas absorption (MGA) process using hollow fibre contactor study shows the average overall mass-transfer coefficient of blended MDEA/PZ was 2.25 times higher than single MDEA\(^{15}\). PZ plays an important role for accelerating the absorption process of CO$_2$ in MDEA solution. Because PZ is a cyclic secondary diamine, its efficiency is attributed to its cyclic diamine structure that may favour rapid formation of carbamate with CO$_2$. As a mild base, it may serve to catalyse proton extractions in the reaction mechanism. Due to this, interest in using hybrid solvents has increased to date.

### 4. Conclusion

The conclusions from this research was Five amines were compared, i.e., MEA, DEA, MDEA, AMP, and PZ. MEA showed the strongest intermolecular interaction with CO$_2$. Due to this, it was expected that MEA easily absorb
CO₂ compared to secondary and tertiary amines. It was also observed that MDEA had low tendency to create the intermolecular interaction with CO₂. Moreover, the good interaction of steric hinder amine, AMP and cyclic amine, PZ, with CO₂ was expected to activate the reactivity of MDEA absorption process. Blended MDEA/AMP and MDEA/PZ showed strong intermolecular interactions with CO₂ compared to single MDEA system. The presence of activator amine, AMP and PZ, improved the intermolecular interaction of MDEA with CO₂.

5. Acknowledgement

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6. References