Methyldiethanolamine and Piperazine as Extractant in Emulsion Liquid Membrane for Carbon Dioxide Removal

Kamarudin K. S. N., Dolmat N., and Najib S. B. M.

Abstract—Emulsion liquid membrane was formulated using MDEA and piperazine as extractant in sodium hydroxide solution. Span-80 in the organic solution acts as surfactant to stabilize the formation emulsion. The effects of MDEA/PZ ratio on emulsion stability and CO$_2$ absorption were investigated. CO$_2$ absorption was carried out in rotating disc contactor (RDC) column and gas chromatography (GC) was used to determine the amount of CO$_2$ leaving the column. This study showed that 8% v/v Span-80 has produced a stable emulsion. The emulsion was able to remove 60.3% of CO$_2$. In the presence of methane (CH$_4$), 54.1% of CO$_2$ and 13.2% of CH$_4$ were removed from CH$_4$/CO$_2$ mixtures. The finding demonstrates the promising technique of ELM for CO$_2$ removal.

Index Terms—Emulsion liquid membrane, carbon dioxide removal, stability.

I. INTRODUCTION

CO$_2$ that emitted to the environment can be reduced by the separation process such as chemical and physical absorption, adsorption, cryogenic separation and membrane separation [1]-[3]. Absorption is a process in which soluble components of gas mixture are dissolved in a liquid phase. CO$_2$ absorption by using alkanolamines has been widely used in plants such as ammonia plant [4]. Aqueous solutions of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), di-isopropanolamine (DIPA), and N-methyldiethanolamine (MDEA) are the possible solvent that mostly used in the industry for CO$_2$ absorption.

For several decades, MEA was exclusively used as extractant for CO$_2$ absorption. However the used of MDEA as a solvent for CO$_2$ absorption becomes more effective than MEA due to the low operating costs, less corrosive and high CO2 capacity (1 mol CO$_2$/1 mol amine) [5]. The slower rate of reaction between CO$_2$ and MDEA was overcome by the addition of activator such as piperazine (PZ) [6]. PZ is a cyclic diamine structure which each mole of PZ can theoretically react with two moles of CO$_2$ [7]. It was also reported that the reaction rate of PZ with CO$_2$ was higher than MEA [8].

MDEA activated by PZ was proven as a promising solvent for CO$_2$ absorption and has been investigated by many researchers [9]-[13]. However, the presence of acid gases (CO$_2$ and H$_2$S) in any alkanolamine solutions during absorption process leads to the corrosion problem. Corrosion becomes one of the serious problems in CO$_2$ absorption that always occurred in some plant locations such as regenerator, boiler and absorber [14], [15]. It was reported that stated that about 9 million of dollars are annually spent to mitigate the corrosion from the plant systems [16]. Besides, about 25% of maintenance cost was spent in the corrosion problems in the removal of acid gases plants [17]. Zhoa et al. [18] mentioned that the corrosion rate was increased with the increasing of PZ in MDEA solution. The blended of MDEA-PZ was more corrosive than AMP-PZ blended but less corrosive compare to MEA-PZ, MEA-AMP and MEA-MDEA blended [19].

Recently, liquid membrane separation becomes one of the alternative technologies for CO$_2$ absorption. The separation occurs when the solute permeate through the liquid phase from a feed phase to receiving phase. There are three types of liquid membranes including bulk liquid membrane (BLM), supported liquid membrane (SLM) and emulsion liquid membrane (ELM). ELM separation technique was proven as a potential way to remove any pollutants such as metal from wastewater or effluents [20], [21]. However, CO$_2$ absorption by using ELM is still a new technology and need further investigation. The application of ELM is limited because of the emulsion stability problem. Unstable emulsion leads to breakage of emulsion particle that leads to the loss of internal phase [22]. Emulsion stability was influenced by some factors including the concentration of surfactant and the condition of emulsification process.

Typically, ELM is prepared by homogenizing two immiscible liquids. The particles formed are dispersed in the continuous phase. Very large surface area to volume ratios is one of the advantage of ELM [23]. The fast separation process can be achieved by ELM due to the small thickness of the membrane (organic film) and large surface area [24]. In addition, other advantages of ELM are simple operation, high efficiency and scope for continuous operation [25]. ELM provides high mass transfer area than the other two membranes because thickness of the membrane is very small while the surface area is high that resulting in very fast separations [26]. However, there are some issues regarding emulsion stability that can cause a membrane leakage that limited their commercial potential. Thin membranes tend to leak or rupture and the inner phase can swell cause an unstable membrane. Separation process by using ELM also has a low...
operating cost compare to the conventional separation method [27]. This paper presents stability of emulsion and the percentage of CO₂ absorbed by the ELM method using MDEA and piperazine as extractants.

II. EXPERIMENTAL PROCEDURE

A. Emulsion Preparation

Emulsion liquid membrane (ELM) was formed by homogenizing the aqueous and the organic solution. Aqueous solution consists of monodiethanolamine (MDEA), piperazine (PZ) and sodium hydroxide (NaOH) solution while organic phase consists of Span-80 as surfactant and kerosene. 100 mL of aqueous phase was prepared by mixing MDEA and PZ into 0.1M NaOH solution. The solution was stirred for 15 minutes. For organic solution, 100 mL of organic phase was prepared by adding Span-80 into the kerosene oil and stirred for 15 minutes. The stirring speed and temperature of the heating plate for aqueous and organic phase solution were fixed at 700 rpm and 27°C respectively. For the preparation of emulsion, the high performance disperser Ultra Turrax® T25 with 18G mixing shaft was used. 100 mL organic phase mixture was placed in the beaker and the aqueous phase mixture was poured drop wise in the beaker containing the organic phase and homogenized to produce water-in-oil emulsion.

B. Stability of Emulsion

The stability of emulsion was measured based on sedimentation of particles. Sedimentation is an early process that leads to the emulsion breakdown after a certain time [28]. The emulsion becomes less homogenous as it starts to settle. Stability test of the emulsion was conducted before CO₂ absorption process for different concentration of Span-80 and different MDEA/PZ concentration. The stability of emulsion was also measured after CO₂ absorption. To do the measurement, the emulsion was filled in the graduated test tubes and left in the room for 24 hours. The sedimentation process was demonstrated by the presence of another layer on the top of emulsion while emulsion breakdown was indicated by the presence of layers on the top and bottom of the emulsion [29]. The determination of emulsion stability was based on the percentage of emulsion sedimentation where the volume of top layer was measured.

\[
\% \text{ stability} = \frac{V_T - V_S}{V_T} \times 100\% \tag{1}
\]

where

\[V_T = \text{Total volume (ml)}\]
\[V_S = \text{Top layer volume (ml)}\]

In addition, the viscosity of the organic phases and aqueous phases were measured using Programmable Rheometer Brookfield Model DV-III at room temperature. The viscosity of the organic phases was measured to estimate the diffusivities of the emulsion. A spindle type 00 was used to test the viscosity and motor speed at 60 rpm.

C. Carbon Dioxide Removal

Rotating disc contactor (RDC) column (Fig. 1) that connected to the gas chromatography (GC) was used for CO₂ absorption study. The column was filled with 200 mL of the prepared emulsion. The flow rate of carbon dioxide to the column was fixed at 20 LPM (Liter per minute). The speed of the rotating disc was in a range of 450-500 rpm. The pressure of the RDC was also recorded. Gas chromatography (GC) was used to determine the amount of CO₂ in the inlet and outlet streams of the RDC.

Fig. 1. Rotating disc contactor (RDC) system for CO₂ adsorption study.

III. RESULTS AND DISCUSSION

Fig. 2 shows stability of emulsion and the percentage of CO₂ absorption at different concentration of Span-80. Emulsion containing 8% v/v of Span-80 shows the highest percentage of CO₂ absorption (54.8%) followed by 10% v/v Span-80 (42%), 6% v/v Span-80 (37.8%), 12% v/v Span-80 (35.4%). The emulsion contained 0.5% v/v Span-80 and 1% v/v Span-80 were not tested for CO₂ absorption since it formed 3 layers immediately after emulsification. This phenomenon indicates the occurrence of emulsion breakage. For 2 – 12 % v/v Span-80, the emulsions formed 2 layers due to sedimentation. Sedimentation occurs as the emulsion droplets collides and merges to form the larger droplets and started to settle at the bottom of graduated test tube. Size of emulsion droplets is directly proportional to the velocity of sedimentation process [30], [31].

Further addition of Span-80 from 8% v/v to 12% v/v decrease the percentage of CO₂ absorption from 54.8% to 35.4%. This is probably due to the high viscosity of the emulsion. Several investigations also have demonstrated that by increasing the surfactant concentration, the viscosity of emulsion increased. High emulsion viscosity would decrease the diffusion and mass transfer coefficient [32]-[34].

Gas diffusion coefficient in liquid media was estimated the Based on Wilke – Chang correlation [35]. As shown in Eq. (1), the diffusion coefficient decrease when the viscosity increases.

\[
D = \left[7.48 \times 10^{-8}\right] \frac{T \sqrt{\alpha M_g}}{\mu^2 V_1^{3/2}} \tag{2}
\]

where

\[\alpha - \text{association constant}\]
\[V_1 - \text{molar volume of gas solute (cm}^3/\text{mol})\]
\[\mu - \text{viscosity (mPa/s)}\]
\[T - \text{temperature (K)}\]
\[M - \text{molecular weight of the solvent (g/mol)}\]

The viscosity and diffusion coefficient are shown in Table I. As the viscosity of the organic phase increase, the diffusion
coefficient decreases. The decrease explains the reduction of CO$_2$ absorption.

![Graph showing CO$_2$ absorption and stability of emulsion at different amount of Span-80.]

**Fig. 2.** Percentage of CO$_2$ absorption and stability of emulsion at different amount of Span-80.

<table>
<thead>
<tr>
<th>[Span-80], % v/v</th>
<th>Viscosity, cP</th>
<th>Diffusion Coefficient, $D$ ($x 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.90</td>
<td>4.79</td>
</tr>
<tr>
<td>1</td>
<td>1.12</td>
<td>3.85</td>
</tr>
<tr>
<td>2</td>
<td>1.16</td>
<td>3.72</td>
</tr>
<tr>
<td>4</td>
<td>1.20</td>
<td>3.60</td>
</tr>
<tr>
<td>6</td>
<td>1.29</td>
<td>3.34</td>
</tr>
<tr>
<td>8</td>
<td>1.36</td>
<td>3.17</td>
</tr>
<tr>
<td>10</td>
<td>1.44</td>
<td>3.00</td>
</tr>
<tr>
<td>12</td>
<td>1.66</td>
<td>2.60</td>
</tr>
</tbody>
</table>

The effect of MDEA/PZ on emulsion stability and CO$_2$ absorption was illustrated in Fig. 3. The addition of PZ to MDEA in the aqueous solution increased the percentage of CO$_2$ absorption as compared to use MDEA only. The percentage of CO$_2$ absorption increased as the concentration of PZ increased in 8% MDEA solution. 8% v/v MDEA with 6% v/v PZ showed the highest CO$_2$ absorption (54.8%).

According to Mandal *et al.* (2001), MDEA has equilibrium loading of 1.0 mol of CO$_2$ per mole of amine. However, the reaction rate of MDEA is low [36]. The reaction between CO$_2$ and tertiary amines such as MDEA is slower than reaction between CO$_2$ and primary or secondary amines [37]. Therefore, to improve the CO$_2$ absorption, PZ was added that acts as an activator in the MDEA solution due to its ability to react faster than MDEA.

This approach is in agreement with Bishnoi *et al.*, [38], Dang and Rochelle [39], Cullinane *et al.*, [40] and Khalili *et al.*, [41] that also proposed the used of piperazine as an activator to other slower alkanolamines such as MDEA. It was also reported that piperazine has a rapid reaction rate with CO$_2$ than MEA [42], [43]. By increasing the quantity of PZ (additional of 1% v/v for each sample) the emulsion stability remains high.

It is expected that by increasing the quantity of MDEA and PZ in the emulsion formulation, CO$_2$ absorption would increase since more MDEA and PZ are available to react with CO$_2$. However, Fig. 4 shows that emulsion stability and CO$_2$ absorption decreased as the concentration of MDEA and PZ increased. This is possibly due to the presence of MDEA and PZ that increased the viscosity of aqueous solution. Highly viscous solution requires more energy to disperse the particles in a continuous phase (organic phase). The size of particles formed would be larger for highly viscous solution. It also reduced the mass transfer of the solute in ELM system.

![Graph showing CO$_2$ removal from CO$_2$/CH$_4$ mixtures using different extractants.]

**Fig. 4.** The percentage of CO$_2$ absorption and stability of emulsion at different concentration of MDEA and PZ based on ratio of 4:3.

<table>
<thead>
<tr>
<th>[MDEA], % v/v</th>
<th>[PZ], % v/v</th>
<th>Viscosity, cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>6</td>
<td>1.07</td>
</tr>
<tr>
<td>12</td>
<td>9</td>
<td>1.12</td>
</tr>
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<td>16</td>
<td>12</td>
<td>1.45</td>
</tr>
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<td>20</td>
<td>15</td>
<td>1.66</td>
</tr>
<tr>
<td>24</td>
<td>18</td>
<td>2.14</td>
</tr>
</tbody>
</table>

The emulsion containing only 8% v/v MDEA, 6% v/v PZ and a combination of both extractants were prepared to investigate the effect of MDEA and PZ to the CH$_4$ absorption
from CH₂/CO₂ mixture. Fig. 5 shows the percentage of CO₂ and CH₂ for 8% v/v MDEA and 6% v/v PZ. The 8% v/v MDEA had removed about 34.2% of CO₂ and only 5.1% of CH₂ while 6% v/v PZ had absorbed 24% of CO₂ and 17.9% of CH₂.

IV. CONCLUSION

This study has successfully investigated the favorable composition of ELM for CO₂ absorption. The stability of the selected ELM remains high even after the absorption of CO₂. At 8 v/v % Span 80, emulsion break up is negligible and only sedimentation occurred. With the ELM composition of 8% v/v Span 80, 8% v/v MDEA and 6% v/v PZ, 54.1% of CO₂ has been removed from CO₂/CH₂ mixture. A small amount of CH₂ was also absorbed by the ELM.

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REFERENCES


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