The Effect of MDEA/AMP and Span-80 in Water-in-Oil (W/O) Emulsion for Carbon Dioxide Absorption

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ABSTRACT

Emulsion liquid membrane (ELM) has been widely studied as an alternative method for amine absorption technology in the removal of acid gases such as carbon dioxide (CO\textsubscript{2}) and hydrogen sulphide (H\textsubscript{2}S). However, searching for stable ELM formulation with an enhanced CO\textsubscript{2} absorption remains as challenge. Therefore, in this study, the aqueous solution containing a mixture of methyl diethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) in sodium hydroxide (NaOH) solution was introduced as a dispersed phase, kerosene as continuous phase and Span-80 acts as a surfactant for the formation of water-in-oil (W/O) emulsion. In this study, the dispersed phase consists of 8% v/v MDEA and 4% v/v AMP and the continuous phase which contains 6% v/v Span-80 produced a stable emulsion and exhibited 65.2% of CO\textsubscript{2} removal. This study indicates that the introduction of blended amine able to produce stable emulsion with an enhanced CO\textsubscript{2} removal.

Keywords: Absorption, amine, carbon dioxide, liquid emulsion, stability

1.0 INTRODUCTION

In the sweetening process of the natural gas, the amines are usually used as a reactant to absorb the carbon dioxide (CO\textsubscript{2}) and hydrogen sulphide (H\textsubscript{2}S). Alkanoloamines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropylamine (DIPA), methyldiethanolamine (MDEA), and diglycolamine (DGA) are commonly amines used for acid gas removal [1, 2, 3]. The effectiveness of alkanolamines is depending on the rate of reaction between CO\textsubscript{2} and the amine, as well as the absorption capacity. A primary amine like aqueous MEA has been used widely because of its high reactivity and low solvent cost. However, this amine has a low loading capacity of CO\textsubscript{2} [2]. It is proved that CO\textsubscript{2} loading in MEA is only 0.5 mol of CO\textsubscript{2} per mol of amine. This value is relatively lower as compared to MDEA which has higher loading capacity of CO\textsubscript{2} (1 mol of CO\textsubscript{2}/1 mol of amine). However, this tertiary amine has low performance in CO\textsubscript{2} absorption rate [2]. Thus, blended amine has been introduced to further improve the performance of CO\textsubscript{2} absorption, by combining MDEA with...
MEA, DEA and piperazine, and AMP with MEA and DEA [2]. A study also showed that sterically hindered amines offer better results in term of absorption capacity, selectivity and degradation resistance in the CO₂ separation processes as compared to the conventional amines [4]. It was reported that AMP gave high CO₂ absorption rate and high CO₂ loading [3]. The CO₂ loading in AMP is high (1mol of CO₂ /mol of amine), thus the blend of AMP with MDEA would give high results of CO₂ absorption.

Furthermore, there are some disadvantages if direct amine was used, where the CO₂ loading capacity is low, corrosion may occur, and amine is degraded after several treatments [5]. Thus, to overcome low loading capacity of CO₂, a mixture of primary or secondary alkanolamine with tertiary alkanolamine is suggested in order to enhance the absorption ability of amine. This blended technology combines the higher equilibrium capacity of the tertiary amine for CO₂ with the higher CO₂ reaction rate of the primary or secondary amine [6].

Using water-in-oil (W/O) emulsion, amines in aqueous solution formed a globule and dispersed in a continuous organic phase. Thus, the removal process depends on the transfer of solute (CO₂) through the emulsion. Recently, W/O emulsion has been introduced as an alternative way of CO₂ separation as compared to the conventional separation that gives high simultaneous purification and concentration of the solute. The separation occurs when the solute permeates through the liquid phase from a feed phase to the receiving phase [7]. The effectiveness of emulsion depends on the stability of the emulsion, diffusivity of the adsorbate, which depends on the surface area and the thickness of emulsion.

In the W/O emulsion technique, aqueous amine is sealed inside the non-corrosive, organic phase membrane of emulsion. However, the use of emulsion has been limited because of physical instability of emulsion globules caused by fluid shear [8]. The extraction process is also hindered due to the emulsion breakup and the unwanted release of internal receiving phase to the external contributing phase. A surfactant that stabilizes the emulsion also affects the stability and CO₂ absorption. A good surfactant should be soluble in the membrane phase only and not react with the extractant in the membrane phase to prevent the decomposition of the extractant and enhance the efficiency of the emulsion process [9]. Span-80 gives high relatively stable and easily demulsified emulsions and shows less resistance to mass transfer than other surfactant [10]. It also has a low HLB value (4.3) that gives high solubility in oil than water [11, 12].

This study was not rare, but it has been challenging to find good formulation for specific applications, especially for CO₂ removal. Therefore, it is crucial to find the suitable formulation of W/O emulsion which exhibited stable emulsion with enhanced CO₂ absorption. In this study, blended amine (MDEA/AMP) and role of surfactant in stabilizing the emulsion and as resistance in the diffusion were identified. Therefore, this research investigates the effect of W/O formulation on CO₂ absorption performance. The parameters that affect the stability of emulsion and CO₂ absorption were to be determined.

2.0 METHODS

2.1 Emulsion Preparation

An emulsion was prepared according to a method described by Bhatti et al.
[13] using different types of amines. The aqueous phase consists of amines in NaOH solution as extractant, while the organic phase consists of kerosene as continuous phase and Span 80 as surfactant. The liquid emulsion membrane was prepared by homogenizing the aqueous and the organic solution. 100 mL of the aqueous phase was prepared by adding amine into 0.1 M 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 solutions 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 dropwise into the beaker containing the organic phase to produce water-in-oil emulsion. Table 1 presents the emulsion formulation and parameter used to determine the percentage removal of CO₂ using different types of single amine, methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP). Table 2 shows the emulsion formulation of blended amine using different ratios of MDEA and AMP where the amount of MDEA is fixed at 8% v/v and Table 3 consists of emulsion formulation using different amounts of Span-80.

2.2 Emulsion Stability

The stability of emulsion was measured based on visual observation. Sedimentation is an early process that leads to the emulsion breakdown after a certain period of time [14]. It is a process in which droplets move downwards since the droplet density is greater than the density of the continuous phase. Sedimentation was demonstrated by the presence of a layer in the top of the test tube (2 layers) while emulsion breakdown shows another layer in the top and bottom of the test tube (3 layers) [15]. The emulsion condition becomes less homogenous as it starts to settle. The stability test of the emulsion was conducted prior to CO₂ absorption process for different amines, different MDEA/AMP ratio, and different amounts of Span-80. The measurement proceeds by filled in emulsion in the graduated test tubes and left in the room for 24 hours. The determination of emulsion stability was based on the percentage of emulsion sedimentation where the volume of the top layer was measured. The percentage of separation is determined by Eqn. 1.

\[
\text{\% stability} = \frac{V_t - V_s}{V_t} \times 100
\]

where \(V_t\) is the total volume (ml) and \(V_s\) is the top layer volume (ml).

The emulsion’s viscosity was measured by using Programmable Rheometer Brookfield Model DV-III.

2.3 CO₂ Absorption

In this study, the rotating disc contactor (RDC) column was used for CO₂ absorption in the emulsion. Figure 1 illustrates the schematic diagram of CO₂ absorption system used in this study. The function of RDC is to maintain the stability and homogeneity of the emulsion in the column. The column was filled with 200 mL of emulsion and the flow rate of gas entering the column was fixed at 20 LPM (Litre per minute). Longer contact time was achieved as the CO₂ enters the column from the bottom of the column.
Table 1  Emulsion formulation using different types of amines

<table>
<thead>
<tr>
<th>Formulation / Condition</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous phase (100 mL)</td>
<td>Amine used: MDEA, AMP, 8 % v/v: 92 % v/v</td>
</tr>
<tr>
<td>Ratio Amine to NaOH</td>
<td>92 % v/v: 8 % v/v</td>
</tr>
<tr>
<td>Organic phase (100 mL)</td>
<td>92 % v/v: 8 % v/v</td>
</tr>
<tr>
<td>Ratio Kerosene to Span-80</td>
<td>5 minutes</td>
</tr>
<tr>
<td>Emulsification Speed</td>
<td>10 000 rpm</td>
</tr>
<tr>
<td>Absorption Time</td>
<td>1 minute</td>
</tr>
</tbody>
</table>

Table 2  Emulsion formulation using various amine composition

<table>
<thead>
<tr>
<th>MDEA: AMP</th>
<th>Aqueous Phase</th>
<th>Organic Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MDEA: AMP: NaOH (100 mL)</td>
<td>Kerosene: Span-80 (100 mL)</td>
</tr>
<tr>
<td>8:0</td>
<td>8% v/v: 0% v/v: 92% v/v</td>
<td>92% v/v: 8% v/v</td>
</tr>
<tr>
<td>8:2</td>
<td>8% v/v: 2% v/v: 90% v/v</td>
<td>92% v/v: 8% v/v</td>
</tr>
<tr>
<td>8:4</td>
<td>8% v/v: 4% v/v: 88% v/v</td>
<td>92% v/v: 8% v/v</td>
</tr>
<tr>
<td>8:6</td>
<td>8% v/v: 6% v/v: 86% v/v</td>
<td>92% v/v: 8% v/v</td>
</tr>
<tr>
<td>8:8</td>
<td>8% v/v: 8% v/v: 84% v/v</td>
<td>92% v/v: 8% v/v</td>
</tr>
</tbody>
</table>

| Emulsification time | 5 min |
| Emulsification speed | 10 000 rpm |
| Absorption time     | 1 min |

Table 3  Emulsion formulation using different amount of Span-80

<table>
<thead>
<tr>
<th>Span-80</th>
<th>Aqueous Phase</th>
<th>Organic Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MDEA: AMP: NaOH (100 mL)</td>
<td>Kerosene: Span-80 (100 mL)</td>
</tr>
<tr>
<td>8</td>
<td>8% v/v: 4% v/v: 88% v/v</td>
<td>92% v/v: 8% v/v</td>
</tr>
<tr>
<td>6</td>
<td>8% v/v: 4% v/v: 88% v/v</td>
<td>98% v/v: 6% v/v</td>
</tr>
<tr>
<td>4</td>
<td>8% v/v: 4% v/v: 88% v/v</td>
<td>96% v/v: 4% v/v</td>
</tr>
<tr>
<td>2</td>
<td>8% v/v: 4% v/v: 88% v/v</td>
<td>94% v/v: 2% v/v</td>
</tr>
</tbody>
</table>

| Emulsification time | 5 min |
| Emulsification speed | 10 000 rpm |
| Absorption time     | 1 min |

Figure 1  The schematic diagram for CO₂ absorption system [13]
The speed of the rotating disc was kept at 450-500 rpm range. Gas chromatography (GC) was used to determine the amount of CO$_2$ entering and leaving the RDC. The percentage of CO$_2$ absorption was calculated based on the amount of CO$_2$ leaving the column by using Eqn. 2.

Percentage of CO$_2$ absorption:

$$\frac{A_r - A_e}{A_r} \times 100\%$$  (2)

where,

$A_r$: Area of Reference ($\mu$V/s)

$A_e$: Area of Emulsion ($\mu$V/s)

3.0 RESULTS AND DISCUSSION

3.1 Effect of Emulsion Formulation on Stability and Viscosity

In the preparation of W/O emulsion for CO$_2$ removal, the two immiscible liquids were emulsified, which gives the energy to form a stable emulsion through the fragmentation of one phase into another. Emulsion breakdown was indicated by the presence of three layers as shown in Figure 2 (a), while the sedimentation was indicated by the presence of another layer on the top of the test tube (2 layers) as shown in Figure 2 (b). The stability of emulsion was measured after 24 hours.

![Figure 2 Emulsion stability (a) emulsion breakdown and (b) sedimentation](image)

Interfacial shear between the continuous phase and dispersed phase caused the interfacial layer to thin and in some cases, breakdown. Moreover, it was reported that stable emulsion resulted in high CO$_2$ removal [16] thus, it is crucial to get stable emulsion in this study. In this study, Span-80 has been chosen as a surfactant in emulsion because it has low hydrophile-lipophile balance (HLB) value of 4.3, which gives higher solubility in oil, as compared to water [11, 12]. The emulsion can be stabilized by the absorption of surfactant molecule at the interface between oil and water, thus giving low free energy to the phase boundary. However, the solute diffusivity from external phase into internal phase is reduced when the interface layer becomes thicker, thus decreasing the efficiency of extraction process.
Two types of amines were used in the preparation of emulsion. Each formulation consists of 8 % of MDEA and varied ratio of AMP in NaOH solution, and the organic phase that consists of 92 % kerosene and 8 % Span-80. Span-80 acts as a surfactant to stabilize the emulsion. Emulsion stability refers to the ability of emulsion droplets to homogenously disperse in a continuous phase. As mentioned earlier, coalescence, creaming or sedimentation is one-step occurrence before emulsion breakdown. As reported by Aroua et al. [3], AMP gave a higher CO$_2$ absorption rate and high CO$_2$ loading when combined with MDEA. The CO$_2$ loading in AMP is high (1 mol of CO$_2$ /mol of amine), thus the blend of AMP with MDEA would give higher results of CO$_2$ absorption. However, the stability of the emulsion containing blended amine should also be observed. A study by Dolmat [17] on single amine also found that 8 % v/v of MDEA in dispersed phase was the best formulation for CO$_2$ removal. Therefore, in this study, several samples were prepared with the amount of MDEA which was fixed at 8 % v/v, with varied amount of AMP. Table 4 shows the stability of emulsion containing different ratios of MDEA and AMP.

**Table 4: Emulsion stability and viscosity with different MDEA-AMP ratio**

<table>
<thead>
<tr>
<th>MDEA:AMP</th>
<th>Stability (%)</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:0</td>
<td>66</td>
<td>225</td>
</tr>
<tr>
<td>8:2</td>
<td>70</td>
<td>645</td>
</tr>
<tr>
<td>8:4</td>
<td>78</td>
<td>864</td>
</tr>
<tr>
<td>8:6</td>
<td>80</td>
<td>908</td>
</tr>
<tr>
<td>8:8</td>
<td>92</td>
<td>1112</td>
</tr>
</tbody>
</table>

Table 4 shows the percentage stability of emulsion increases as the amount of AMP increases. The presence of amine (AMP/MDEA) in aqueous solution also affects the viscosity of the emulsion. The viscosity of emulsions containing blended amines (MDEA/AMP) increases as the quantity of AMP increases. If the emulsion is viscous, it forms a more stable emulsion. As reported by Mohamed et al. [18], viscosity affected emulsion stability. In addition, as reported by Shi et al. [19], water content has a strong influence on viscosity of crude oil, and the viscosity of water-in-oil emulsion increases gradually as water content increases. However, too viscous emulsion may reduce the diffusion of solute. It is also important to note that viscosity of emulsion is far different from the individual liquids. The viscosity of kerosene (1.64 cP) is relatively low as compared to NaOH solution (87 cP), AMP (147 cP) and MDEA (101 cP).

The stability of emulsion was determined after 24 hours by visual observation. In each sample, two layers were formed in which the bottom layer is thicker than the top layer, which indicates sedimentation has occurred. As shown in Table 4, a sample with 8 % MDEA and 8% AMP shows the highest viscosity (1112 cP) and stability (92 %). The results also indicated that combination of MDEA/AMP in dispersed phase produced higher emulsion stability than single amine as stated by Chakravarti [6]. The effect of Span-80 amount on viscosity and stability of emulsion was also observed using 8 % MDEA and 4 % AMP in 100 mL NaOH as aqueous solution on next section.

### 3.2 CO$_2$ Removal

CO$_2$ was removed by means of absorption. The absorption in the emulsion can be described as a transfer
of CO₂ from the continuous phase into the dispersed phase through oil-water interphase. Then, CO₂ reacted with MDEA and AMP in the dispersed phase to produce bicarbonates (HCO₃⁻). MDEA has a higher loading capacity (1 mol of amine/1 mol of CO₂) than conventionally used amine like MEA. Theoretically, MDEA does not react directly with CO₂ since MDEA is a tertiary amine, but it acts as a base that catalysed the hydration of CO₂.

According to Sema et al. [20], the reaction is essentially base-catalysed CO₂ hydrolysis, and MDEA does not combine with CO₂, thus leading to low absorption. As reported by Ali Khan et al. [21], MDEA has the lowest reaction rate compared to MEA and AMP. Due to the low reaction between MDEA and CO₂, MDEA is commonly combined with activator such as piperazine (PZ) or sterically hindered amine of AMP to improve the reaction with CO₂. The hindered amine carbamates undergo hydrolysis forming bicarbonate and releasing free amine since AMP has low stability constants. The fast reaction of AMP will quickly absorb the CO₂. Then, the free amine molecule will react faster with CO₂. The reaction of CO₂ with AMP could result in three reactions: the formation of carbamate, the formation of bicarbonate, and the reversion of carbamate to bicarbonate or formation of the carbonate ion [22].

Rotating Disc Contactor (RDC) column was used to conduct the CO₂ absorption study. The emulsion was placed in the column and a mixture of CO₂ gases was allowed to get into contact for absorption to occur. The amount of CO₂ absorbed was determined from the Gas Chromatography (GC) results. The initial result showed that CO₂ removal using single amine is almost the same (52.3 % and 51.8 % for MDEA and AMP respectively) as shown in Figure 3. Based on 1-minute absorption time, the result shows that the absorption rate of MDEA-CO₂ is slightly higher than that of AMP-CO₂. The result is consistent with a study conducted by Rodriguez et al. [23] where they also reported that AMP in individual systems gave low absorption rates.

![Figure 3 Emulsion stability and percentage of CO₂ removal](image)

However, AMP offers an additional advantage over MDEA, particularly for CO₂ removal, due to the fact that the CO₂-AMP reaction rate is much faster than the CO₂-MDEA reaction rate [24]. Figure 4 shows that the blended MDEA/AMP mixture in emulsion improved the percentage of CO₂ removal. As stated by Mandal et al. [2], MDEA has an advantage of removing more CO₂ where it has a high equilibrium loading of 1.0 mol of CO₂ per mol of amine. However, the reaction rate of MDEA is low, hence the MDEA needs to blend with AMP which possess high CO₂ absorption rate and high CO₂ loading capacity [16].
In the emulsion formulation, it is expected that CO$_2$ removal increases as more amines (MDEA and AMP) in the dispersed phase react with CO$_2$. However, the results show that CO$_2$ removal initially increased but began to decrease when the amount of AMP reached 6% v/v. The percentage of CO$_2$ removal is the lowest when the emulsion consisted of single amine (AMP) in the dispersed phase (Figure 3). This condition is due to the viscosity of the emulsion; as more MDEA/AMP are present in the dispersed phase, the viscosity of the solution also increases and the emulsification procedure, highly viscous solution requires more energy to form a good dispersion in a continuous phase. Thus, as the fixed emulsification parameters are fixed, the size of droplet size in the emulsion would be larger for more viscous solution. Consequently, the total surface area would be less, hence reducing the percentage of CO$_2$ removal. In addition, as the droplet size increases, emulsion homogeneity also decreased, which also leads to low CO$_2$ removal. In case of blended amines, emulsion containing 8% v/v MDEA with 4% v/v AMP showed the highest CO$_2$ removal (61.6%) while emulsion containing 8% v/v MDEA with 8% v/v exhibited the lowest CO$_2$ removal (54.6%). On the other hand, for single amine emulsion, the percentage of CO$_2$ removal for emulsion containing MDEA-only is 52.3%. These results show that blended amine in W/O emulsion improved the percentage of CO$_2$ removal where blended AMP with tertiary amine will give high absorption capacity as stated by Aroua et al. [3] and Xiao et al. [4]. However, viscosity plays significant influence on the formation of emulsion droplets, emulsion stability and directly affects the overall performance of CO$_2$ removal.

In order to produce consistent and stable emulsion, a suitable amount of emulsifier should be included in the emulsion formulation. As mixture of 8% v/v MDEA with 4% v/v AMP shows highest percentage of CO$_2$ removal, it has been selected for further investigation for their stability in a varying amount of emulsifier, as shown in Table 3. The selection of an appropriate emulsifier is one of the important decisions when formulating the emulsion [25]. Span-80 was chosen as a surfactant in the formulation because it has low hydrophilic-lipophilic balance (HLB) value (4.3) that gives higher solubility in oil than water. The emulsion was stabilized by the absorption of surfactant molecule at the interface between oil and water, thus giving low free energy to the phase boundary. Figure 5 shows the effect of Span-80 on the viscosity, emulsion stability and percentage of CO$_2$ removal. The stability of emulsion increases steadily as the amount of Span-80 increased. According to Li et al. [26], the stability of the emulsion and the viscosity increases by the proportion of surfactant in the organic phase, which explains why the emulsion stability increases as the amount of Span-80 increased.
Emulsion containing 6% v/v Span-80 shows the highest CO₂ absorption (65.2%). As stated by Skelland and Meng [27], the increased viscosity significantly decreases the diffusivity for Newtonian fluids. Thus, the addition of more Span-80 reduces the solute diffusivity and decreases the extraction rate, thus reducing the efficiency of CO₂ separation process as shown at 8% v/v Span-80. Ansel et al. [28] also proposed that the size of emulsion droplets is directly proportional to the velocity of sedimentation process where large emulsion droplets decreased the total surface area, therefore reducing the absorption of carbon dioxide.

4.0 CONCLUSION

The use of blended amines such as MDEA and AMP in W/O emulsion may enhance the removal of CO₂. In this study, the stability of the emulsion increases as the amount of amine increased. The CO₂ removal of 61% can be achieved by using 12% of amines (8% MDEA/ 4 % AMP). Furthermore, the CO₂ absorption of resulting W/O emulsion has been further improved by varying the amount of Span-80, reached 65.2% of CO₂ removal using 6% v/v Span-80.

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