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# Mixture of MEA/2-MAE for Effective CO<sub>2</sub> Capture from Flue Gas Stream

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The climate change and global warming are the main environmental concerns because of  $CO_2$  emission into the atmosphere. The main sources of  $CO_2$  is from power plants in the form of flue gas. Recently, the effective technology to capture  $CO_2$  is chemical absorption by using aqueous amine solutions. The commonly used amine solution is monoethanolamine (MEA). It has disadvantages like low capacity and high energy consumption. 2-methylaminoethanol (2-MAE) as a new solvent has been formulated to improve the performance of  $CO_2$  mitigation but the cost of this chemical is higher. The two amines are mixed together to obtain higher performance and to compensate the drawbacks of each solvents. The objective of this research is to measure the solubility of  $CO_2$  in a mixed solvent with 20 : 10 wt% of MEA and 2-MAE for  $CO_2$  capture from the flue gas stream at the temperature of 313.15 K and 353.15 K and  $CO_2$  partial pressures ranging from 5 to 100 kPa. The experimental results are compared with that of single solution of MEA and 2-MAE at the same conditions. From the results, it is reported that in term of cyclic capacity, the amine mixture provides a better performance, which is higher than that of MEA ranging from 2.35 % to 61.90 % but lower than that of 2-MAE from 8.76 % to 43.45 %. The rate of  $CO_2$  loading of mixed solution is relatively close to that of MEA but lower than that of 2-MAE. Therefore, in the future, the mixed solvent may be used as an alternative solution for  $CO_2$  capture instead of using single amine.

# 1. Introduction

Nowadays, climate change and global warming are the main concern due to the huge amount of CO<sub>2</sub> in the atmosphere (Chauhan et al., 2003). The sources of this gas come from fossil-fuel combustion such as flue gas stream from power generation (Kohl and Nielsen, 1997). Now, the effective technology to remove CO2 is chemical absorption such as amine solutions. The commercially used amines solutions are monoethanolamine (MEA) and methyldiethanolamine (MDEA) as a primary and tertiary amine. They have some disadvantages such as low capacity, high energy requirement for regeneration and high corrosion (Chakma, 1999). To compensate these drawbacks, new amine solvents have been developed to improve the performance for CO<sub>2</sub> capture (Singh et al., 2011). For this study, 2-(methylamino)ethanol or 2-MAE, which is investigated by some researchers as a potential absorbent (Haider et al., 2011) and 2-MAE with other chemicals (Chowdhury et al., 2013), are selected for further study in the form of a mixed solvent of MEA and 2-MAE. It is very interesting to mix solvents with high potential of CO<sub>2</sub> absorption to get the essential data for the solubility of CO2. Many research works have been done on mixed amines such as MEA and MDEA (Idem et al., 2006) and MEA mixed with new formulated solvent (Chakma, 1995). This data plays a significant role in the design of absorption column. The objective of this work is to measure the solubility of CO<sub>2</sub> in a mixed aqueous solvent of MEA and 2-MAE as a formulated solution at CO<sub>2</sub> partial pressures ranging from 5 to 100 kPa, temperature from 313.15 K to 353.15 K and 20 : 10 wt% of MEA and 2-MAE concentration. The solubility results of CO2 in 20 : 10 wt% of MEA and 2-MAE solution will be compared with those of aqueous solution of MEA at the same conditions. The simplified rates of reaction for both two single amines and a mixed amine solution are measured and compared.

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# 1.1 CO<sub>2</sub> reaction mechanism

The principal reactions of CO<sub>2</sub> with amines occurring when solutions of an amine, such as MEA and 2-MAE, are used to absorb CO<sub>2</sub> may be represented as follows (Kohl and Nielsen, 1997):

Dissociation of water H <sub>2</sub> O $\leftrightarrow$ H <sup>+</sup> + OH <sup>-</sup>	(1)
Hydrolysis of CO <sub>2</sub> H <sub>2</sub> O + CO <sub>2</sub> $\leftrightarrow$ H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup>	(2)
Dissociation of bicarbonate ion $HCO_3^- \leftrightarrow H^+ + CO_3^{2^-}$	(3)
Protonation of amine RNH <sub>2</sub> + H <sup>+</sup> $\leftrightarrow$ RNH <sub>3</sub> <sup>+</sup>	(4)
Carbamate formation $2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+$	(5)
Bicarbonate formation R <sub>1</sub> R <sub>2</sub> NH + CO <sub>2</sub> + H <sub>2</sub> O $\leftrightarrow$ HCO <sub>3</sub> <sup>-</sup> + R <sub>1</sub> R <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	(6)

 $R_1R_2NH + CO_2 + H_2O \leftrightarrow HCO_3^- + R_1R_2NH_2^+$ 

# Where R<sub>1</sub>, R<sub>2</sub> are alkyl group.

Through these reactions, reaction (5) is the main absorption reaction. For MEA and 2-MAE, reaction (5) is predominant. CO<sub>2</sub> can form carbamate. Theoretically the absorption capacity of the solution is approximately 0.5 mole of CO<sub>2</sub> per mole of amine.

# 2. Experiment

#### 2.1 Materials

MEA is purchased from the Sigma Aldrich with 99 % purity and 2-MAE is obtained from Merck with 99.9+ % purity. Hydrochloric acid (HCI) is purchased from Fisher Scientific with 99 % purity. They are used without further purification. Distilled water is used to prepare aqueous solution to a desired concentration of 20 : 10 wt% of MEA and 2-MAE concentration. Nitrogen (N2) (99.5 %) and CO2 (99.5 %) are obtained from Praxair Inc., Thailand.

#### 2.2 Equipment and Procedure

For this study, MEA and 2-MAE are weighed and mixed together at 20 : 10 wt% with distilled water to prepare an aqueous solution of mixed amines. It is fed into a reactor which is placed into the constant temperature water bath to control the temperature. N2 and CO2 are introduced and mixed into the system. The flow rates are adjusted to meet the required partial pressure of CO<sub>2</sub> and N<sub>2</sub> which can be controlled by using the digital mass flow meters. This gas mixture is fed to the reactor through the saturation cell and reactor until it reaches the equilibrium taking approximately 13 - 20 hours. The samples are taken for 3 times to analyse the equilibrium solubility data by using titration with 1M HCI.

Finally, the solubility of CO<sub>2</sub> is presented in term of CO<sub>2</sub> loading, the amount in mole of CO<sub>2</sub> per number of mole of amine in the solution. The solubility is calculated from the average of the three equilibrium data of samples. The rate of loading change has been measured by taking samples at different times to investigate the CO<sub>2</sub> transferred rate from gas to liquid and equilibrium of this solution.

# 3. Results and discussion

# 3.1 Verification of equipment and procedure

A verification of the equipment and procedure of this study is performed by comparing the solubility results of MEA at 5 M with the results from literature over the entire pressure and temperature ranging from 5 to 100 kPa for pressure and 303.15 K to 353.15 K as shown in Figure 1. The average and maximum percent average absolute deviations between this study and previous work obtained by Shen and Li (1992) are 2.75 and 11.05 %. It can be concluded that the equipment and procedures for this study can be applied for further solubility studv.

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Figure 1: Verification of equipment and procedure by comparing the solubility in 5 M MEA at 313.15 K

#### 3.2 Effect of types of solvents

The solubility results of  $CO_2$  in MEA, 2-MAE and mixed solvents are illustrated in Figures 2 to 6. Figure 2 and 3 demonstrate the effects of types of chemicals and their mixtures on the solubility of  $CO_2$  at the same weight percent in the solution at 313.15 K and 353.15 K. From Figure 2, in term of  $CO_2$  loading, 2-MAE provides the highest absorption capacity, higher than that of the mixed solvent and MEA at 15 kPa and 313.15 K for 11.51 % and 14.31 %. At the concentration of 20 : 10 wt% of mixed amines, mixed solvent offers slightly higher absorption capacity than that of MEA for 2.52 %. Figure 3 presents the results at higher temperature. It is obvious that the mixed amine provides the lower absorption capacity compared to 2-MAE and relatively lower than that of MEA. It can be explained that this mixture contains more portion of MEA in the solution than 2-MAE. The property of mixture can be shifted close to MEA property than that to 2-MAE. Other formulated amines such as 15 : 15 wt% and 10 : 20 wt% will be studied and compared in the future.



Figure 2: Solubility of CO₂ in 30 wt% MEA, 30 wt% 2-MAE and 20 : 10 wt% MEA:2-MAE at 313.15 K

#### 3.3 Effect of temperature and partial pressure

As shown in Figure 4, the temperature of this study ranges from 303.15 K to 353.15 K and partial pressure of  $CO_2$  varies from 5 - 100 kPa on the solubility of  $CO_2$  in each solution. These temperatures and partial pressures are considered as the working temperature and pressure for absorption and regeneration conditions for flue gas from coal-fired power plant. It is obvious that the solubility decreases with an increase in

temperature and solubility increases as partial pressure increases because gas has higher absorption at a lower temperature and higher partial pressure.



Figure 3: Solubility of CO₂ in 30 wt% MEA, 30 wt% 2-MAE and 20 : 10 wt% MEA:2-MAE at 353.15 K



Figure 4: Solubility of CO₂ in 20 : 10 wt% MEA:2-MAE from 303.15 K to 353.15 K and 5 to 100 kPa

# 3.4 Cyclic capacity of the solution

Figure 5 shows the results of solubility of CO<sub>2</sub> in aqueous solutions of MEA, a mixed solution and 2-MAE at 15 % CO<sub>2</sub> and temperature from 313.15 K to 353.15 K. From this data, one new parameter, the cyclic capacity can be calculated. The cyclic capacity is defined as the value of difference of CO<sub>2</sub> loading at absorption and regeneration conditions, for this study, which are the CO<sub>2</sub> loading at 313.15 K and 353.15 K.

According to Figure 4, the cyclic capacity can be explained graphically, which is the gap between the loadings at two temperatures. The results clearly reveal that the wider the gap is, the higher the cyclic capacity can be obtained.

The result shows that from 313.15 K to 353.15 K and 15 kPa CO<sub>2</sub>, the mixed solution provides higher cyclic capacity than that of 2-MAE and MEA for 52.70 % and 102.70 %, even though 2-MAE offers higher absorption capacity for both high and low temperatures as discussed in the previous section.

It means that practically, the cyclic capacity is more important than the absorption capacity because this leads to the decrease of the liquid circulation rate in the absorption process. The size of equipment can be reduced as well. Therefore, capital and operating costs for CO<sub>2</sub> absorption can be reduced and carbon capture can be viable.



Figure 5: Cyclic capacity of all solutions at 30 wt% MEA, 20 : 10 wt% MEA and 2-MAE and 30 wt% 2-MAE at 15 % CO<sub>2</sub> partial pressure

#### 3.5 Rate of CO<sub>2</sub> loading change

Figure 6 presents the rate of  $CO_2$  loading change for three amine solutions or the apparent  $CO_2$  transfer rate from the gas to liquid phase at 15 kPa and temperature from 313.15 K for 9 h. As shown in the figure, the  $CO_2$  loading increases with time, especially at the first hour of the experiment and becomes constant at a certain level.

The rate of CO<sub>2</sub> loading change for 2-MAE increases at a higher rate compared to that of MEA and mixed amine because gas can be reacted and absorbed better and faster compared to MEA and mixed solvent at the same conditions. This rate of loading change can be used or explained approximately the design of the absorption column for acid gas removal with various operating conditions.



Figure 6: Rate of CO<sub>2</sub> loading change of three amine solutions at 15 kPa and 313.15 K

# 4. Conclusions

The mixed solvent of MEA and 2-MAE is performed experimentally to measure the solubility of CO<sub>2</sub>. The results are compared with that of single solution of MEA and 2-MAE at the same conditions. From the results, it is reported that in term of absorption capacity and rate of loading change, 2-MAE offer better results because it provides higher capacity and higher rate. However, for cyclic capacity, the amine mixture provides a better performance higher than that of 2-MAE and MEA for 52.70 % and 102.70.

This leads to the lower liquid circulation rate and less energy requirement for solution regeneration. Therefore, capital and operating costs for  $CO_2$  absorption can be reduced and carbon capture can be viable. The rate of  $CO_2$  loading of mixed solution is relatively close to that of MEA but comparatively lower than that of 2-MAE. In the future, the mixed solvent with various percent content of 2-MAE may be used as an alternative solution for  $CO_2$  capture.

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