



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

2-amino-2-methyl-1-propanol as Additive to Enhance Carbon Dioxide Removal by Monoethanolamine Emulsion Liquid Membrane

S.N. Suahadah and K.S.N. Kamarudin

Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi Malaysia,
81310 UTM Skudai, Johor Bahru, Johor, Malaysia

Abstract: Aqueous Monoethanolamine (MEA) is widely used as the Carbon dioxide (CO₂) absorbent in process industries. Recent technology has shown that a mixture of MEA with other amines can enhance its capability as CO₂ absorbent. The addition of 2-amino-2-methyl-1-propanol (AMP) into aqueous phase containing MEA was reported in this study. The aqueous solution was homogenized with the organic solution containing kerosene and Span-80 to produce Emulsion Liquid Membrane (ELM). Rotating disc contactor was used in the CO₂ absorption process to maintain the stability of the emulsion. 55.17% of CO₂ was removed when 8 mL of MEA was used in the aqueous phase whereas when 8 mL AMP was used, only 41.72% of CO₂ was removed. On the other hand, CO₂ percentage removal increased to 60.72% when 2 mL of AMP was added into the ELM that containing 6 mL of MEA. Stability of the MEA/AMP mixture ELM after 24 h was 89%. The results indicate that a mixture of MEA/AMP is stable and can enhance the CO₂ removal.

Key words: Emulsion liquid membrane, CO₂ absorption, amines mixture, rotating disc contactor, span-80

INTRODUCTION

Due to the increasing awareness of carbon dioxide (CO₂) capability to cause global warming, technologies of CO₂ capture are rapidly grow as well. The best way to prevent excesses build-up of CO₂ in the air is by capturing the CO₂ gas from industries that produced enormous amount of CO₂ such as fossil-fuel-fired power plants, steel works and cement works before the flue gases were released into the air (Park *et al.*, 2002). Beside the need of removing CO₂ for a better environment, industries such as gas refinery plant, ammonia synthesis plant and hydrogen manufacturer require the removal of CO₂ either to avoid corrosion of pipeline and equipment, to prevent clogging due to dry-ice formation, to prevent catalyst poisoning, to meet fuel gas specifications or for business purposes (Aroonwilas and Tontiwachwuthikul, 1997).

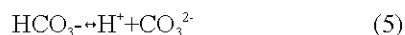
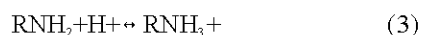
For last few decades, absorption by using aqueous solution of alkanolamines such as Monoethanolamine (MEA), diethanolamine (DEA) and N-Methyldiethanolamine (MDEA) are well known method to remove the CO₂. MEA was found to be the best amine used for the CO₂ absorption process due to its high reactivity, low cost, ease of reclamation and low absorption of hydrocarbons (Mandal and Bandyopadhyay, 2006a). However, recent

study shows that sterically hindered amines offer better results in term of absorption capacity, selectivity and degradation resistance in the CO₂ separation processes compare to the conventional primary and secondary amines (Xiao *et al.*, 2000).

The 2-amino-2-methyl-1-propanol (AMP) is one of the sterically hindered amines. AMP requires 1 mol of amine to react with 1 mol of CO₂ compare to primary and secondary amines that require 2 mol of amine to react with 1 mol of CO₂. This is due to the unstable carbamate ions produced during reaction of AMP with the CO₂ as stated in Eq. 1 (Mandal and Bandyopadhyay, 2006b). The unstable carbamate ions will undergo hydrolysis to form bicarbonate ions and release free amine. Eq. 2 shows the reformation of amine from the carbamate as given by Veawab and Aroonwilas (2002). The free amine then can react again with the CO₂ (Sartori and Savage, 1983). Equation 4 shows the overall chemical Equation of the reaction between CO₂ with AMP (Mandal *et al.*, 2003). Bicarbonate ion (HCO₃⁻) produced in the reaction will be further reduced into hydrogen ion (H⁺) and carbonate ion (CO₃²⁻). Equation (5) shows the reaction of bicarbonate to form carbonate.



Corresponding Author: Syahidatul Nazirah Suahadah, Department of Gas Engineering, Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi, Malaysia (UTM), 81310 UTM Skudai, Johor Bahru, Johor, Malaysia



where, R = C(CH₃)₂CH₂OH).

Reaction 2 does not occur in primary and secondary amines since the carbamate ions produced is stable thus free amine can not be produced (Mandal and Bandyopadhyay, 2006b). On the other hand, tertiary amine solution such as aqueous MDEA solution has the same CO₂ absorption capacity (1 mol of amine to 1 mol of CO₂) as sterically hindered amine. However, as compared to MDEA, AMP has higher rate of reaction with CO₂ (Mandal *et al.*, 2001). AMP also causes less corrosion, the major problem in the industrial CO₂ separation process, as compared to other type of amines (Aroonwilas and Tontiwachwuthikul, 1997).

With the rapid growth of knowledge and technology, the solution with mixture of amines was found to have better ability to remove CO₂ (Aroua *et al.*, 2002). A mixture solution of highly reactive amine from the group of primary amine and the sterically hindered amine with higher CO₂ loading capacity has higher CO₂ uptake as compared to the solution of single amine. Due to the less usage of corrosive primary amine, the corrosion problem also can be reduced.

In addition to traditional gas absorption process by using aqueous alkanolamines, liquid membranes such as Supported Liquid Membrane (SLM) and Emulsion Liquid Membrane (ELM) that also contained the amines emerged as an alternative for CO₂ absorption process. They offer several advantages such as capability to provide extremely large membrane surface areas and are applicable in situations where the desired solute in the feed stream is in low concentrations (Fouad and Bart, 2008).

Separation of CO₂ from other gasses mixture by using SLM had been one of the most favourable studies in the liquid membrane field since the last 17 years (Neves *et al.*, 2010). ELM on the other hand was more popular as liquid-liquid extractant to remove impurities or desired solute from liquid stream as compared to the liquid-gas absorber.

ELM is an emulsion that formed by organic solvent and water, which can be stabilized by the addition of surfactant. This emulsion is then contacted with a continuous phase containing the desired solute, stirred to yield globules and transported across the extremely thin membrane layer that separates internal phase droplets inside the emulsion globule from the external phase (Othman *et al.*, 2006).

Some of the attractive features of ELM systems include simple operation, high efficiency, large interfacial area and scope for continuous operation. In addition, ELM also offers other advantages of low cost factors and a single stage operation of both extraction and stripping (Naim and Monir, 2003). In ELM, the amine will not directly in contact with the equipment since the amine will be trapped inside the uncorrosive organic solvent. Thus, the use of ELM can further decreases the corrosive problem in the plant. Generally, there are two types of ELM configuration can be made which are water in oil emulsion (w/o) and oil in water emulsion (o/w). In this study, the membrane produced was water in oil (w/o) type, where water phase was dispersed into the organic phase.

However, the use of ELM can be limited due to poor stability of emulsion globules against fluid shear (Fouad and Bart, 2008). Poor stability means membrane rupture and leakage. Leakage of the internal phase into the external continuous phase will failed the purpose of the liquid membrane process and it will also cause the advantage of ELM as the method for decreasing the corrosion problem in the plant gone. Factors that recognized to influence the stability of ELM are speed of agitation, emulsion droplets size per unit specific interfacial area, surfactant concentration, pH and the presence of different tracers.

Yang *et al.* (2007) reported that excess negative charges on the interface of w/o emulsion, caused by OH⁻ ions from the aqueous phase will decreases the stability of emulsion however Bhowal and Datta (2001) in his study reported that if the anion (OH⁻) is predominant at internal phase while the feed gas is acidic, the faster absorption will take place. These statements show that the optimum formulation is needed in order to produce the best ELM for CO₂ removal process.

Therefore, the objective of this study is to formulate ELM containing MEA and AMP or their mixture for CO₂ removal and to determine the effect of AMP in CO₂ removal. The effect of pH on ELM stability and CO₂ absorption was also investigated.

MATERIALS AND METHODS

Aqueous phase preparation: Aqueous phase is prepared by dissolving the amines or their mixture in 0.1 M of sodium hydroxide (NaOH) solution. 92 mL of NaOH solution was taken in the 150 mL glass beaker and 8 mL of the amines or the mixture was poured into it. Then the mixture was stirred and heated for 15 min to produce the amine's aqueous solution. The stirring speed and temperature of the heating plate was fixed at 700 rpm and 30°C, respectively. The compositions of amine tested in this study are as shown in the Table 1.

Table 1: Composition of aqueous phase

| MEA (mL) | AMP (mL) | 0.1 M NaOH (mL) |
|----------|----------|-----------------|
| 8 | 0 | 92 |
| 6 | 2 | 92 |
| 0 | 8 | 92 |

Table 2: Composition of emulsion liquid membrane

| Aqueous phase | | | Organic phase | |
|---------------|----------|----------------|---------------|--------------|
| MEA (mL) | AMP (mL) | NaOH 0.1M (mL) | Kerosene (mL) | Span-80 (mL) |
| 8 | 0 | 92 | 92 | 8 |
| 6 | 2 | 92 | 92 | 8 |
| 0 | 8 | 92 | 92 | 8 |



Fig. 1(a-b): (a) Rotating disc contactor (RDC) column and (b) Rotating disc

Organic phase preparation: Organic phase is composed of organic diluents and the surfactant. 92 mL of kerosene as the diluent and 8 mL of span-80 were poured into the beaker. The beaker was then covered with aluminum foil and was stirred and heated for 15 min. The stirring speed and temperature of the heating plate was fixed 700 rpm and 30°C, respectively.

Water in oil emulsion liquid membrane (ELM) preparation:

Emulsion was prepared by homogenizing the organic phase using high performance Ultra Turrax 18G shaft at 8000 rpm. The aqueous phase was poured drop wise into the organic phase. After completely adding the aqueous phase into the organic phase, the speed of the homogenizer was increased to 10,000 rpm for 7 min. Table 2 shows the prepared ELM composition.

Emulsion liquid membrane performance test: The performance of ELM as CO₂ absorbent was measured by contacting CO₂ with the ELM in rotating disc contactor (RDC). Figure 1 shows the RDC column that has been used in this experiment.

To determine the actual amount of CO₂ supplied to the ELM, the CO₂ gas was directly injected into the Gas Chromatograph (GC). The CO₂ gas flow rate was fixed at 20 L min⁻¹ (LPM) and the pressure was fixed at 20 psig. The result given by GC was kept as the reference for initial amount of CO₂ supplied to the ELM. To exactly know the amount of CO₂ supplied, ideal gas Eq. 6 was used to calculate the mole per min of CO₂:

$$n = \frac{PV}{RT} \tag{6}$$

Where:

- n = Mol
- P = Pressure inside the RDC
- V = Volumetric flow rate of supplied CO₂
- R = Gas constant
- T = Temperature

The RDC was filled with prepared ELM and stirred in a range of 480-500 rpm. The known amount of CO₂ was supplied to the RDC. This step was achieved by feeding the CO₂ gas with the same flow rate and pressure into the RDC that contain the ELM for 1 min. The experiments were carried out at temperature (27±2°C).

After 1 min, the valve from the CO₂ gas cylinder was turned off meanwhile the valve from the RDC to the GC was opened. The GC was run at the same time.

The peak area produced from GC analysis is proportional to the actual amount of substances detected. With the known amount of initial CO₂, the area of the CO₂ peak was taken as the basis for the calculation of CO₂ absorption. The Eq. used to calculate the amount of remaining CO₂, C_f was as the following Eq. 7:

$$\frac{A_i}{A_f} = \frac{C_i}{C_f} \tag{7}$$

Where:

- A_i = Basis CO₂ peak's area
- A_f = Remaining CO₂ peak's area
- C_i = Basis CO₂ amount
- C_f = Remaining CO₂ amount

The amount of CO₂ being removed, (C_a) then was calculated by using Eq. 8:

$$C_a = C_i - C_f \tag{8}$$

Table 3: pH of emulsion liquid membrane before and after absorption

| MEA (mL) | AMP (mL) | pH before | pH after | pH difference |
|----------|----------|-----------|----------|---------------|
| 8 | 0 | 10.67 | 9.83 | 0.84 |
| 6 | 2 | 10.33 | 9.27 | 1.06 |
| 0 | 8 | 10.08 | 9.81 | 0.27 |

The percentage of CO₂ removed then was calculated by using Eq. 9:

$$\frac{C_a}{C_i} \times 100\% \quad (9)$$

pH and stability studies: pH of the ELM was measured before and after CO₂ absorbing in the rotating disc contactor. After the absorption, the emulsion was filled in the scaled test tubes and was left at the room condition (27±2°C) for 24 h. After 24 h, the separation ratio of the water and oil was measured. Equation 10 was used to calculate the percentage stability:

$$\frac{L_f}{L_i} \times 100\% \quad (10)$$

Where:

L_f = Level of unseparated portion after 24 h

L_i = Level of initial ELM

RESULTS AND DISCUSSION

pH analysis: Since the desired gas to be absorbed is an acidic gas, the ELM to be used should be in the alkali form. In this study, factors that determined the alkalinity of ELM are the concentration and amount of NaOH, MEA and AMP. Since the molarity of NaOH and its volume are constant in this study, only the amount of MEA and AMP influence the pH of the aqueous phase. MEA used in this study has the pH value of 12.41 meanwhile AMP has slightly lower pH at 11.75.

The difference between initial and final pH of the ELM indicates the absorption of CO₂ in the ELM. Table 3 shows the pH of ELM prepared before and after the absorption take place.

From the result we can see that ELM containing MEA only has the highest initial pH meanwhile ELM containing AMP only is less alkali. As expected, the addition of AMP into MEA's emulsion reduces the initial pH of the emulsion.

The introduction of AMP into the ELM also widens the difference of initial and final pH of the ELM. Based on the pH differences, it is expected that ELM containing mixture of MEA and AMP has higher absorption of CO₂. The relation of pH with the stability and absorption ability of the ELM will be further discussed in this study.

Table 4: Result for CO₂ absorption

| MEA (mL) | AMP (mL) | Area remaining A _r | CO ₂ removed (mol min ⁻¹) | Removal percentage(%) |
|----------|----------|-------------------------------|--|-----------------------|
| 8 | 0 | 86415 | 0.993 | 55.17 |
| 6 | 2 | 75707 | 1.093 | 60.72 |
| 0 | 8 | 112329 | 0.751 | 41.72 |

Table 5: Stability after 24 h

| MEA (mL) | AMP (mL) | Stability(%) |
|----------|----------|--------------|
| 8 | 0 | 91 |
| 6 | 2 | 89 |
| 0 | 8 | 87 |

Emulsion liquid membrane performance test: The actual amount of CO₂ supplied for the absorption process was calculated by using simple ideal gas Equation. This Equation was used because the sorption process took place at the pressure of 20 psi close to the atmospheric pressure. Since the pressure and volume of the supplied CO₂ are the same throughout the experiments and taken that the room temperature is constant at 27°C, the amount of CO₂ used was calculated as 1.8 mol min⁻¹ with the peak area of 192,748. Table 4 shows area produce from the GC as well as calculated amount of CO₂ absorbed by the ELM.

From the pH analysis, the amine mixture of 6 mL MEA and 2 mL AMP has the highest CO₂ removal as compared to the usage of same amount of MEA and AMP only. This result proved that the addition of AMP into MEA improved the ability of CO₂ absorption. AMP that has higher CO₂ absorption capacity but less reactivity rate than MEA slightly enhances the absorption rate compare to MEA alone because the time allowed for the reaction to take place was only 1 min. If longer time of reaction applied, the removal of CO₂ by the mixture may be greater.

There is quite a big different of the removal percentage of MEA and AMP alone. For 1 min of reaction, MEA can absorb more than AMP eventhough AMP has higher CO₂ loading capacity. This result agreed with the theory that eventhough AMP has higher CO₂ loading capacity than MEA due to the unstable carbamate form during the reaction of AMP with CO₂ but the reaction was slower than MEA.

Beside that, MEA with higher pH than AMP shows significant role in CO₂ absorption. Acidic gas like CO₂ will be absorbed faster by more alkaline liquid.

Stability study: After 24 h left in the test tube, the separation of the ELM was measured. Table 5 shows the stability of the ELMs after 24 h.

The stability of the ELM does not significantly differ from each other. MEA and its mixture still have greater stability as compared to AMP alone.

CONCLUSION

The addition of AMP into the aqueous solution enhanced the CO₂ absorption capability of the ELM. The high efficiency and high rate of reaction of MEA towards CO₂ combined with the large capacity of CO₂ absorption by AMP produced a better ELM formulation. However, further study on the effect of AMP should be carried out. It is intended to increase the reaction time so that the actual capability of AMP for CO₂ absorption can be clearly seen. The stability of the ELM that consists of MEA and AMP is above 85%. The pH of the ELM prepared showed a great influence on the CO₂ absorption amount as more alkaline ELM can absorb more CO₂. Therefore, the best emulsion of ELM formulation should be both high CO₂ absorption and high ELM stability.

ACKNOWLEDGMENT

The authors are grateful to the Ministry of Higher Education and Universiti Teknologi Malaysia (00H42) for the opportunity to conduct this research of carbon dioxide separation using emulsion liquid membrane.

REFERENCES

- Aroonwilas, A. and P. Tontiwachwuthikul, 1997. High-efficiency structured packing for CO₂ separation using 2-amino-2-methyl-1-propanol (AMP). *Separ. Purific. Technol.*, 12: 67-79.
- Aroua, M.K., M.Z. Sulaiman and K. Ramasamy, 2002. Modelling of carbon dioxide absorption in aqueous solutions of AMP and MDEA and their blends using Aspenplus. *Separ. Purific. Technol.*, 29: 153-162.
- Bhowal, A. and S. Datta, 2001. Studies on transport mechanism of Cr (VI) extraction from an acidic solution using liquid surfactant membranes. *J. Memb. Sci.*, 188: 1-8.
- Fouad, E.A. and H. J. Bart, 2008. Emulsion liquid membrane extraction of zinc by a hollow-fiber contactor. *J. Memb. Sci.*, 307: 156-168.
- Mandal, B.P. and S.S. Bandyopadhyay, 2006. Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and monoethanolamine. *Chem. Eng. Sci.*, 61: 5440-5447.
- Mandal, B.P. and S.S. Bandyopadhyay, 2006. Simultaneous Absorption of CO₂ and H₂ S into aqueous blends of N-methyldiethanolamine and diethanolamine. *Environ. Sci. Technol.*, 40: 6076-6084.
- Mandal, B.P., A.K. Biswas and S.S. Bandyopadhyay, 2003. Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and diethanolamine. *Chem. Engin. Sci.*, 58: 4137-4144.
- Mandal, B.P., M. Guha, A.K. Biswas and S.S. Bandyopadhyay, 2001. Removal of carbon dioxide by absorption in mixed amines: Modelling of absorption in aqueous MDEA/MEA and AMP/MEA solutions. *Chem. Engin. Sci.*, 56: 6217-6224.
- Naim, M.M. and A.A. Monir, 2003. Desalination using supported liquid membranes. *Desalination*, 153: 361-369.
- Neves, L.A., J.G. Crespo and I.M. Coelho, 2010. Gas permeation studies in supported ionic liquid membranes. *J. Memb. Sci.*, 357: 160-170.
- Othman, N., H. Mat and M. Goto, 2006. Separation of silver from photographic wastes by emulsion liquid membrane system. *J. Membr. Sci.*, 282: 171-177.
- Park, S.W., H.B. Cho, I.J. Sohn and H. Kumazawa, 2002. CO₂ absorption into w/o emulsion with aqueous amine liquid droplets. *Separ. Sci. Technol.*, 37: 639-661.
- Sartori, G. and D.W. Savage, 1983. Sterically hindered amines for CO₂ removal from gases. *Indus. Engin. Chem. Fundamen.*, 22: 239-249.
- Veawab, A. and A. Aroonwilas, 2002. Identification of oxidizing agents in aqueous Amine-CO₂ systems using a mechanistic corrosion model. *Corrosion Sci.*, 44: 967-987.
- Xiao, J., C.W. Li and M.H. Li, 2000. Kinetics of absorption of carbon dioxide into aqueous solutions of 2-amino-2-methyl-1-propanol+monoethanolamine. *Chem. Engin. Sci.*, 55: 161-175.
- Yang, F., Q. Niu, Q. Lan and D. Sun, 2007. Effect of dispersion pH on the formation and stability of Pickering emulsions stabilized by layered double hydroxides particles. *J. Colloid. Interface Sci.*, 306: 285-295.