



## Removal characteristics of CO<sub>2</sub> using aqueous MEA/AMP solutions in the absorption and regeneration process

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### Abstract

The carbon dioxide (CO<sub>2</sub>) removal efficiency, reaction rate, and CO<sub>2</sub> loading into aqueous blended monoethanolamine (MEA) + 2-amino-2-methyl-1-propanol (AMP) solutions to enhance absorption characteristics of MEA and AMP were carried out by the absorption/regeneration process. As a result, compared to aqueous MEA and AMP solutions, aqueous blended MEA + AMP solutions have a higher CO<sub>2</sub> loading than MEA and a higher reaction rate than AMP. The CO<sub>2</sub> loading of rich amine of aqueous 18 wt.% MEA + 12 wt.% AMP solution was 0.62 mol CO<sub>2</sub>/mol amine, which is 51.2% more than 30 wt.% MEA (0.41 mol CO<sub>2</sub>/mol amine). Consequently, blending MEA and AMP could be an effective way to design considering economical efficiency and used to operate absorber for a long time.

**Key words:** carbon dioxide; monoethanolamine; 2-amino-2-methyl-1-propanol; absorption; regeneration

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### Introduction

The atmospheric concentration of green-house gases (CO<sub>2</sub>, CH<sub>4</sub>, CFCs, and N<sub>2</sub>O) have increased strongly since the industrial revolution. The Inter-governmental Panel on Climate Change (IPCC) has reported that human activities result in the production of greenhouse gases which contribute significantly to global warming. Among these gases, CO<sub>2</sub> has the greatest adverse impact and causes approximately 55% of the observed global warming (IPCC, 1990).

According to the United Nations Framework Convention on Climate Change (UNFCCC) in Kyoto, a commitment to reduce CO<sub>2</sub> emissions by 6% below 1990 levels was made by several countries. Industrialized countries should take the lead in combating climate change and its adverse effects (UNFCCC, 1997). They were responsible for the majority of the historical cumulative emissions, thereby they were given quantified commitments to reduce emissions in the Kyoto Protocol (Harald *et al.*, 2002).

As we have known, there are various technologies being used to separate CO<sub>2</sub> from the flue gas of conventional fossil fuel fired power plants, e.g., chemical absorption, physical absorption, cryogenic methods, membrane separation, and biological fixation (Um *et al.*, 2003). Chemical absorption process is generally recognized as the most effective technology (Rao and Rubin, 2002). The major

industrially chemical absorbents are monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), and di-2-propanolamine (DIPA). Aqueous MEA solution is the most frequently used alkanolamines absorbent owing to its high reactivity with CO<sub>2</sub>, low solvent cost, and can be regenerated easily (Mandal *et al.*, 2003). However, the maximum CO<sub>2</sub> absorption capacity in MEA is limited by stoichiometry to 0.5 mol CO<sub>2</sub>/mol amine. A different class of chemical absorbents, the sterically hindered amine such as 2-amino-2-methyl-1-propanol (AMP) has been proposed as commercially attractive new CO<sub>2</sub> absorbent because of their advantages in absorption capacity, absorption rate, degradation resistance, and regeneration energy (Mandal and Bandyopadhyay, 2006).

Recently, the use of blends of alkanolamines, a solution of two or more amines in varying concentrations, has been shown to produce absorbents with excellent absorption characteristics as well as savings in energy requirements. A number of research articles related to the absorption of CO<sub>2</sub> into aqueous AMP solutions and blended amine solutions containing AMP have been reported (Xiao *et al.*, 2000; Oh *et al.*, 2001; Mandal *et al.*, 2003; Aroonwilas and Veawab, 2004; Mandal and Bandyopadhyay, 2006; Park *et al.*, 2006; Choi *et al.*, 2007; Lee *et al.*, 2008). These blended amines enhance the absorption capacity and absorption rate of CO<sub>2</sub> even though they maintain the stripping characteristics of sterically hindered amines (Li and Chang, 1995). The kinetics of CO<sub>2</sub> into aqueous blends

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of MEA and AMP was studied by Xiao *et al.* (2000).

Unlike the studies for the CO<sub>2</sub> solubilities and kinetics of aqueous amine solutions as mentioned above, in this study, MEA and AMP were mixed to enhance each absorption characteristic of single absorbent. The absorption rate of CO<sub>2</sub> and CO<sub>2</sub> removal efficiency, absorption amount, and CO<sub>2</sub> loading for blended aqueous MEA + AMP solutions were measured using a stirred-cell reactor and absorption/regeneration process, respectively. The performances were evaluated under various operating conditions to investigate the absorption characteristic of absorbents. The optimum blending ratio of MEA and AMP considering reactivity and efficiency were evaluated.

## 1 Theoretical background

### 1.1 Reaction mechanism

The following reactions occur with CO<sub>2</sub> in the aqueous solutions of primary alkanolamines (Danckwerts, 1979). The zwitterion mechanism originally proposed by Caplow (1968) and reintroduced by Danckwerts (1979) is generally accepted as the reaction mechanism for Reaction (1).



This mechanism comprises two steps, namely, formation of the CO<sub>2</sub>-amine zwitterions (Reaction (2)), followed by base catalyzed deprotonation of this zwitterions (Reaction (3)).



where, B' is a base which could be amine, OH<sup>-</sup>, or H<sub>2</sub>O (Blauwhoff *et al.*, 1983). The equilibrium loading capacities of primary and secondary alkanolamines are limited by stoichiometry of Reaction (1) to 0.5 mol CO<sub>2</sub>/mol amine. For normal primary amines such as MEA, the carbamates formed (Reaction (1)) are quite stable.

If the carbamate is unstable, as in the case of a hindered amine carbamate, it undergoes carbamate reversion reaction as follows (Mandal *et al.*, 2003).



According to Reaction (4), for the hindered amines one mole of CO<sub>2</sub> is absorbed per mole of amine. However, a certain amount of carbamate hydrolysis produced with all amines so that even with MEA the CO<sub>2</sub> loading may exceed 0.5, particularly at high pressure.

### 1.2 Reaction rate

The influence on absorption kinetics of all chemical reactions between dissolved gas and reactants in solution are expressed by enhancement factor,  $E$ , over physical absorption (Yih and Shen, 1988):

$$N_A = Ek_L C_A^* = EN_{A0} \quad (5)$$

where, A is gaseous species that is being absorbed into the liquid species B;  $N_A$  (kmol/(m<sup>2</sup>·s)) is specific absorption

rate;  $k_L$  (m/s) is liquid-phase mass transfer coefficient of CO<sub>2</sub> in amine;  $C_A^*$  (kmol/m<sup>3</sup>), equals  $p_A/H_A$ , is dissolved gas concentration in equilibrium at the gas-liquid interface.  $H_A$  ((kPa·m<sup>3</sup>)/kmol) is Henry's law constant;  $p_A$  (kPa) is CO<sub>2</sub> partial pressure.  $E$  is a function of the Hatta number ( $H_a$ ) and the instantaneous reaction enhancement factor ( $E_i$ ) is defined as follows.

$$H_a = \frac{(\frac{2}{m+1} D_A k_{mn} (C_A^*)^{m-1} C_B^n)^{1/2}}{k_L} \quad (6)$$

$$E_i = (\frac{D_A}{D_B})^{1/2} + (\frac{D_B}{D_A})^{1/2} \frac{C_B}{\nu C_A^*} \quad (7)$$

where,  $m$  is the order of reaction with respect to species A;  $n$  is order of reaction with respect to species B;  $D_A$  (m<sup>2</sup>/s) is diffusion coefficient of gas in liquid;  $D_B$  (m<sup>2</sup>/s) is diffusion coefficient of reactants in liquid;  $k_{mn}$  ((m<sup>3</sup>/kmol) <sup>$m+n-1$</sup> /s) is rate-constant for reaction,  $m$ th order in A and  $n$ th order in B;  $C_B$  (kmol/m<sup>3</sup>) is total amine concentration;  $E_i$  is value of  $E$  in instantaneous reaction regime;  $\nu$  is stoichiometric coefficient.

The experimental conditions were selected to ensure that the absorption of gas into amine solutions in a region of fast pseudo- $mn$ -order reaction in  $H_a$  range 3– $E_i$ . If the value of  $H_a$  is in this range,  $E$  equals  $H_a$ , and the following specific absorption rate is obtained (Yih and Shen, 1988; Saha *et al.*, 1995).

$$N_A = (\frac{p_A}{H_A})^{(m+1)/2} (\frac{2}{m+1} D_A k_{mn} C_B^n)^{1/2} \quad (8)$$

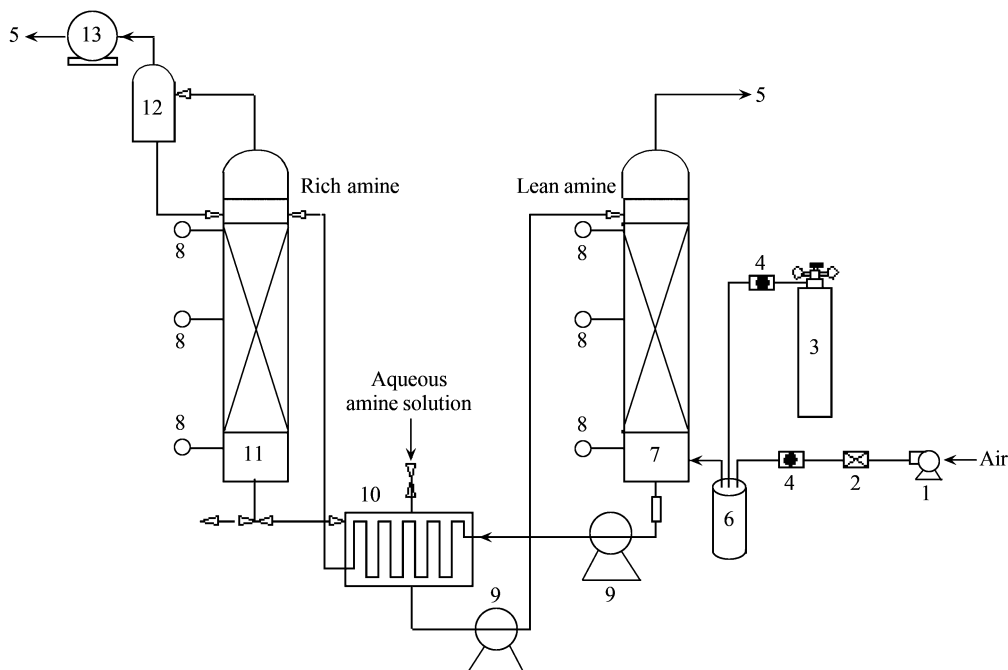
A second-order reaction rate constant,  $k_2$  (m<sup>3</sup>/(kmol·s)) can be achieved by Eq. (9) (Choi *et al.*, 2007).

$$(\frac{N_A H_A}{\sqrt{D_A p_A}})^2 = k_2 C_B \quad (9)$$

## 2 Experimental

### 2.1 Apparatus

The CO<sub>2</sub> absorption rates were measured with the apparatus described by Choi *et al.* (2007). The schematic diagram of the experimental system for studying CO<sub>2</sub> absorption/regeneration is shown in Fig. 1. The experimental apparatus consisted of a gas injection, absorber, regenerator, and CO<sub>2</sub> analyzer. The absorber and regenerator, which were made of 316 stainless steel with an internal diameter of 50.8 mm, have a height of 900 mm and 800 mm, respectively. Packing material (1/4 inch ceramic raschig ring) was packed inside to enhance the reaction of liquid and gas. The temperature of the absorber and regenerator were measured by a K-type thermocouple with an accuracy of ± 0.1 K. Compressed air was sent to a HEPA filter (YSHF-332, Yusing Filter Co., Ltd., Korea) to remove particulate and then dehumidified by passing it through a silica gel air dryer. The clean air was served as diluting gas and mixed with pure CO<sub>2</sub> gas. Flow rates of gases were controlled by mass flow controllers (5850E, Brooks Instruments, USA). The CO<sub>2</sub> gas analyzers of the ZRF model (0–20 vol.%, Fuji Electric, Japan) and the GIR



**Fig. 1** Schematic diagram of the absorption and regeneration experimental system. (1) air compressor; (2) filter; (3) CO<sub>2</sub> cylinder; (4) mass flow controller; (5) analyzer; (6) mixing chamber; (7) absorber; (8) thermocouple; (9) liquid pump; (10) heat exchanger and storage tank; (11) regenerator; (12) condenser; (13) gas meter.

5000 model (0–100 vol.%, Hitec Instruments, USA) were used for measuring CO<sub>2</sub> outlet gas concentrations in the absorber and regenerator, respectively. The condenser was connected to the top of the regenerator to prevent the loss of absorbent.

## 2.2 Procedure

Analytical grade MEA and AMP with purities of 99% were supplied by Kanto Chemical Co., Inc. (Japan) and Acros Organics (USA), respectively. Aqueous amine solutions (MEA:AMP, wt.%/wt.%, 30/0, 24/6, 18/12, 12/18, 6/24, 0/30) were prepared with distilled water. CO<sub>2</sub> gas was commercial grade with a purity of 99.9%. The absorption rates of CO<sub>2</sub> were measured along the procedure similar to those reported elsewhere (Choi *et al.*, 2007). For absorption and regenerator experiment, the absorber and regenerator were heated to the desired temperature, and then aqueous amine solution was injected into a storage tank. A pump (AX1-12-PEC-Z, Cheonsei Co., Ltd., Korea) was used for circulating aqueous amine solution which reacts with CO<sub>2</sub> gas. The outlet CO<sub>2</sub> concentration was measured continuously by analyzer. The CO<sub>2</sub> removal efficiency and absorption amount in this study were calculated via the breakthrough curves and the CO<sub>2</sub> absorption amount expressed in mol CO<sub>2</sub>/mol amine was determined.

## 2.3 Absorption process

The experiments to study the absorption characteristics were carried out by operating only one absorber. Aqueous amine solution of 1 L was injected into a storage tank. Aqueous amine solution which reacts with CO<sub>2</sub> in the absorber was circulated through the regenerator. The temperatures in the absorber and regenerator were remained constant to prevent the effect of regeneration. The outlet CO<sub>2</sub> concentration from the absorber was measured con-

tinuously by a ZRF model CO<sub>2</sub> gas analyzer.

## 2.4 Absorption and regeneration continuous process

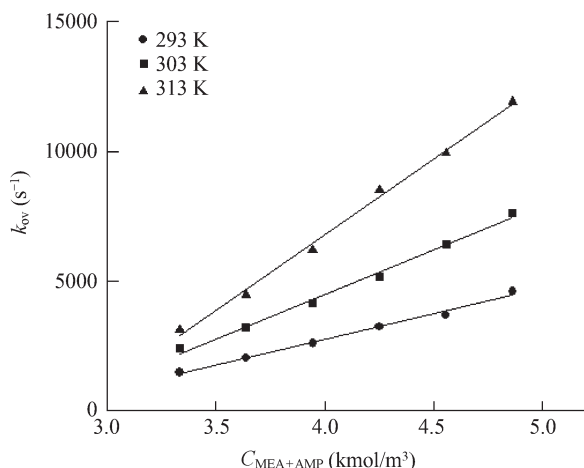
To investigate the effects of regeneration the experiments were carried out by operating absorber and regenerator. Aqueous amine solution of 1 L was injected into the storage tank. The outlet CO<sub>2</sub> concentration from the absorber was measured continuously by a ZRF model CO<sub>2</sub> gas analyzer. The amount of CO<sub>2</sub> stripped from the regenerator was calculated by gas meter (W-NK-0.5, Shinagawa, Japan) and it was confirmed by a GIR 5000 model CO<sub>2</sub> gas analyzer.

Rich amine and lean amine were extracted from the absorber and regenerator, respectively. To determine the characteristics of CO<sub>2</sub> absorption and regeneration, they were analyzed according to the titrimetric method. First, 100 mL distilled water was injected into a 250-mL beaker. The beaker was stirred with magnetic stirrer. The pH of the distilled water was raised to 11.4–11.6 by adding a 0.5 mol/L NaOH solution. Either a rich or lean amine solution was added to the beaker by a 10-mL pipette for the rich amine solution or a 25-mL pipette for the lean. Then, 0.5 mol/L NaOH was added to the amine solution by the titrimetric method until its pH reached 11.5.

## 3 Results and discussion

### 3.1 CO<sub>2</sub> reaction rate of MEA and AMP

Specific absorption rates ( $N_A$ ) for aqueous MEA/AMP solutions (4.86, 4.56, 4.25, 3.94, 3.64, 3.33 kmol/m<sup>3</sup>) were measured by a stirred cell reactor. Reaction rate constants ( $k_2$ ) for each amine solution were obtained by plotting overall reaction rate constant ( $(N_A H_A / D_A^{0.5} / p_A)^2$ ,  $k_{ov}$ ) with the concentration at 20, 30, and 40°C (Fig. 2).



**Fig. 2** The pseudo-first order overall reaction rate constant ( $k_{ov}$ ) for the reaction of  $\text{CO}_2$  into aqueous monoethanolamine (MEA) + 2-amino-2-methyl-1-propanol (AMP) solution as a function of concentration at different temperatures.

The values of diffusivity ( $D_A$ ) and Henry's constant ( $H_A$ ) were obtained from literature (Messaoudi and Sada, 1996; Xu *et al.*, 1996).

It was observed that the  $k_{ov}$  of aqueous MEA + AMP solutions increased with temperature and concentration. Compared with  $k_2$  obtained from slopes of the  $k_{ov}$  versus the concentration at 20, 30, and 40°C, the  $k_2$  of AMP was  $1000.1 \text{ m}^3/(\text{kmol}\cdot\text{s})$ , which was sharply different from the values by Xu *et al.* (1996) ( $1245.3 \text{ m}^3/(\text{kmol}\cdot\text{s})$ ) and Alper (1990) ( $1165 \text{ m}^3/(\text{kmol}\cdot\text{s})$ ) at 40°C. However, the value suggested by Yih and Shen (1988) ( $1048 \text{ m}^3/(\text{kmol}\cdot\text{s})$ ) was similar. These differences of  $k_2$  could be due to the reactor configuration, reaction conditions and factors such as  $D_A$  and  $H_A$ .  $k_{ov}$  of MEA solution ( $11909.6 \text{ s}^{-1}$ ) was higher than that of AMP solution ( $3143.6 \text{ s}^{-1}$ ), reaction rate increased with an increase of MEA contents.

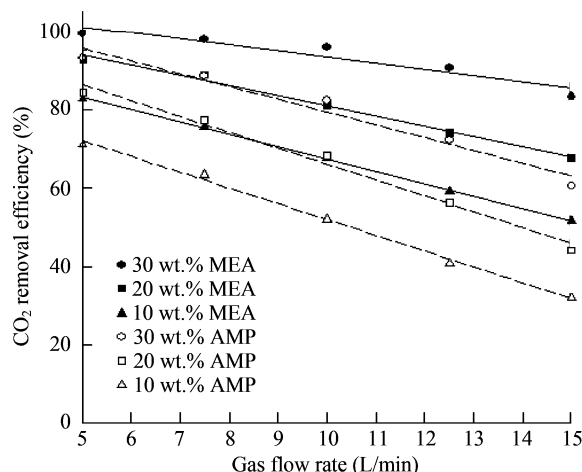
### 3.2 Effect of gas flow rate and absorbent concentration

The removal efficiency ( $\eta$ ) was simply determined from the difference between the amounts of  $\text{CO}_2$  absorbed onto ( $y_{\text{CO}_2,\text{in}}$ , mol) and released from ( $y_{\text{CO}_2,\text{out}}$ , mol) the absorber, which can be expressed by Eq. (10) (Aroonwilas and Veawab, 2004)

$$\eta = \left(1 - \left(\frac{y_{\text{CO}_2,\text{out}}}{1 - y_{\text{CO}_2,\text{out}}}\right) \left(\frac{1 - y_{\text{CO}_2,\text{in}}}{y_{\text{CO}_2,\text{in}}}\right)\right) \times 100\% \quad (10)$$

Figure 3 shows  $\text{CO}_2$  removal efficiency as a function of gas flow rate and absorbent concentration. It was observed that the  $\text{CO}_2$  removal efficiencies of aqueous 30 wt.% MEA and 30 wt.% AMP solutions decreased from 99.3% to 83.2% and from 93.1% to 60.5%, respectively, with an increase in the gas flow rates from 5 to 15 L/min. Therefore, the  $\text{CO}_2$  removal efficiency was found to decrease in the decrease of liquid-gas flow rate. The  $\text{CO}_2$  removal efficiencies of aqueous 10 wt.%, 20 wt.% and 30 wt.% MEA solutions were 12%–20%, 9%–23%, and 6%–23% higher than that of AMP, respectively. This was caused by that the reaction rate of MEA was higher than that of AMP as mentioned in Section 3.1.

Typically, to compare the performance with various

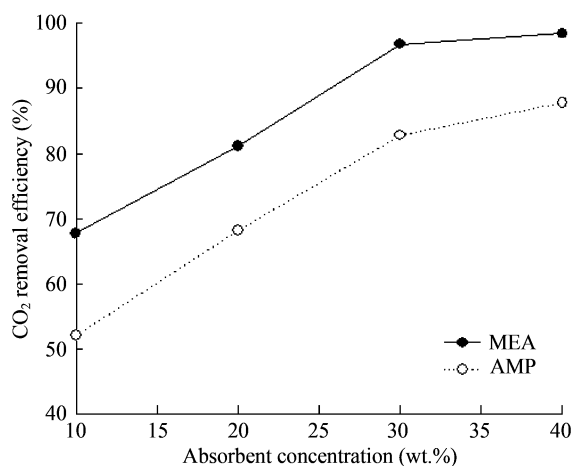


**Fig. 3** Effect of gas flow rates and absorbent concentrations on  $\text{CO}_2$  removal efficiencies using aqueous MEA and AMP solutions.

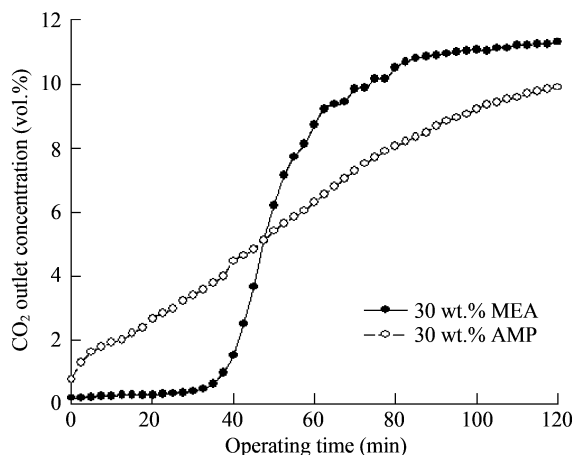
absorbent concentrations at the gas flow rate of 10 L/min, the  $\text{CO}_2$  removal efficiencies of aqueous MEA and AMP solutions are shown in Fig. 4. It was observed that with an increase of absorbent concentrations from 10 wt.% to 40 wt.%, the  $\text{CO}_2$  removal efficiencies of aqueous MEA and AMP solutions increased from 67.8% to 98.4% and from 52.1% to 87.8%, respectively. The increasing rate of  $\text{CO}_2$  removal efficiency decreased when MEA and AMP concentrations were greater than 30 wt.%. When alkanolamines concentration was 40 wt.%, a degradation rate constant was the highest (Kennard and Melsen, 1985). Therefore, 30 wt.% is optimum concentration for  $\text{CO}_2$  removal. These tendencies were similar to results obtained by Yeh and Bai (1999). However, Yeh and Bai (1999) reported that the effect of absorbent concentration on  $\text{CO}_2$  absorption of MEA solution was almost negligible.

### 3.3 $\text{CO}_2$ removal efficiency of MEA and AMP

Figure 5 shows the changes of  $\text{CO}_2$  outlet concentration as a function of operating time (both MEA and AMP solutions are 30 wt.%). The absorption was operated at the gas flow rate of 10 L/min and the liquid flow rate of 110 mL/min. It was observed that the  $\text{CO}_2$  outlet concentration was 0.31 vol.%, which corresponds to 97.7%  $\text{CO}_2$  removal



**Fig. 4** Effect of MEA and AMP concentrations on  $\text{CO}_2$  removal efficiencies at gas flow rate of 10 L/min.



**Fig. 5** Effect of operating time on CO<sub>2</sub> removal efficiencies of aqueous MEA and AMP solutions.

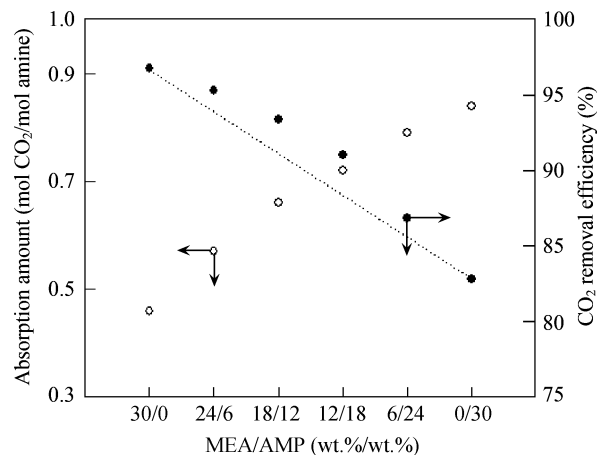
efficiency at the beginning of absorption for the aqueous MEA solution. In addition, the high CO<sub>2</sub> removal efficiency could be maintained for 27.5 min. However, the CO<sub>2</sub> outlet concentration of the aqueous AMP solution was 1.95 vol.% and increased continuously when the solution was second cycling. At that time, the CO<sub>2</sub> removal efficiency was 85.4%. This indicates that the reaction rate of MEA was faster than that of AMP.

Furthermore, the capacity of MEA as the absorbent was fallen significantly after 35 min because MEA was limited by stoichiometry to 0.5 mol CO<sub>2</sub>/mol amine as indicated in Reaction (1) and the carbamate formed from Reaction (1) is quite stable (Danckwerts, 1979). However, the capacity of AMP decreased more slightly than that of MEA due to the influence of the alkyl group attached to the amine. The carbamate is very unstable, thereby having a fast hydrolysis reaction and releasing free amine as shown Reaction (4). Next, the free amine molecule again reacts with CO<sub>2</sub> (Xu *et al.*, 1996). The CO<sub>2</sub> removal efficiency of AMP was maintained highly for a long time due to the additional reaction by zwitterions mechanism as mentioned above. Therefore, the use of blended solution of the MEA and AMP for CO<sub>2</sub> removal could be more useful to enhance absorption characteristics than a single absorbent. Meanwhile, CO<sub>2</sub> absorption amount of aqueous 30 wt.% MEA and 30 wt.% AMP solutions were 0.46 and 0.84 mol CO<sub>2</sub>/mol amine, respectively.

### 3.4 Effect of blending with MEA and AMP

Aqueous MEA solution have a high removal efficiency and a fast reaction rate for CO<sub>2</sub>, as shown in Figs. 2–5. This was similar to the results of Blauwhoff *et al.* (1983). The CO<sub>2</sub> removal efficiency of AMP was lower than that of MEA but the CO<sub>2</sub> absorption amount was higher than that of MEA. The effect of blending with MEA and AMP was investigated.

Figure 6 shows CO<sub>2</sub> removal efficiencies and CO<sub>2</sub> absorption amount with regard to the blending ratio of MEA and AMP. The experimental conditions were mentioned in Section 2.2. The CO<sub>2</sub> removal efficiency of 30/0 of MEA/AMP ratio (wt.%/wt.%) was higher than that of 0/30 for a single aqueous amine solution. The CO<sub>2</sub> removal



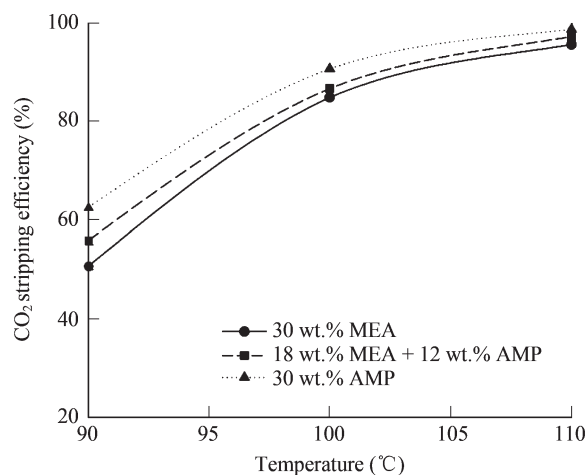
**Fig. 6** Effect of MEA/AMP ratio on CO<sub>2</sub> removal efficiencies and CO<sub>2</sub> absorption amount.

efficiencies of blended MEA+AMP solution (24/6, 18/12, 12/18, 6/24) decreased with increasing AMP concentration. The removal efficiencies of blended MEA+AMP solutions were higher than that of 30/0 and 0/30. In cases of 24/6 and 18/12, the CO<sub>2</sub> removal efficiencies remained high levels over 90%. As the blended ratios of AMP were increased from 30/0 to 24/6 and from 24/6 to 18/12, the increasing rate of CO<sub>2</sub> absorption amount were 23.9% and 15.8%, respectively, which were much better than that of 12/18 and 6/24.

### 3.5 Effect of regenerator temperature

Absorption and regeneration continuous experiments were carried out to study the effect of regeneration on the CO<sub>2</sub> absorption amount.

First, the effect of the regenerator temperature on stripping efficiency were investigated at 90, 100, and 110°C. The experimental conditions were as follows: the absorber temperature of 40°C, the gas flow rate of 7.5 L/min, the CO<sub>2</sub> inlet concentration of 12 vol.%, and the liquid flow rate of 90 mL/min. Figure 7 shows stripping efficiencies with respect to the regenerator temperature. The stripping efficiencies were expressed as a ratio of the amount of CO<sub>2</sub> stripped from the regenerator to the amount of CO<sub>2</sub>



**Fig. 7** Effect of regenerator temperatures on CO<sub>2</sub> stripping efficiencies of MEA and AMP solutions.

**Table 1** Amount of CO<sub>2</sub> absorbed and stripped with different regenerator temperatures of MEA and AMP solutions

Regenerator Temp. (°C)	Absorbed CO <sub>2</sub> (g/min)			Stripped CO <sub>2</sub> (g/min)			Stripping efficiency (%)		
	30/0 <sup>a</sup>	18/12	0/30	30/0	18/12	0/30	30/0	18/12	0/30
90	1.60	1.58	1.52	0.81	0.88	0.95	50.6	55.7	62.5
100	1.58	1.55	1.49	1.34	1.34	1.35	84.8	86.5	90.6
110	1.56	1.52	1.47	1.49	1.47	1.45	95.5	96.8	98.6

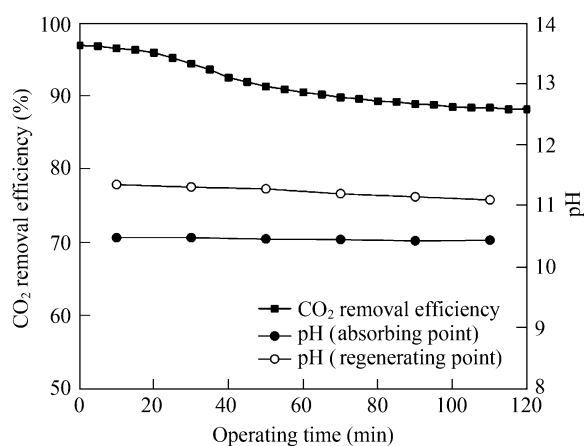
<sup>a</sup> MEA/AMP: wt.%/wt.%.

absorbed in the absorber during the steady-state. The results are summarized in Table 1. AMP solution have a better stripping efficiency than MEA solution. In blended amine solution, the stripping efficiency is determined by content of AMP or MEA, that is, chemical stability of carbamate. The regenerator temperature of 110°C was used in following experiments because the stripping efficiency at 110°C was the highest.

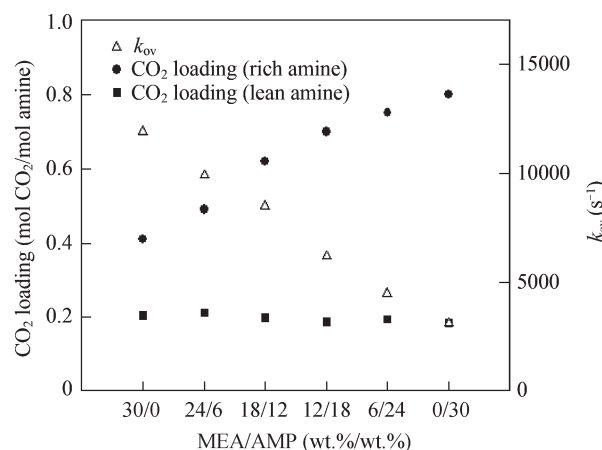
### 3.6 Removal of CO<sub>2</sub> from aqueous MEA+AMP solution

Figure 8 shows the effect of operating time on the CO<sub>2</sub> removal efficiency and pH of aqueous 18 wt.% MEA + 12 wt.% AMP solution. The experimental conditions were mentioned in Section 3.5 and carried out at the regenerator temperature of 110°C. The temperature of absorber and regenerator was reported with the optimum condition according to above-mentioned and literature (Mofarahi *et al.*, 2008; Zhang *et al.*, 2008). It was found that the CO<sub>2</sub> removal efficiencies with time decreased but a slight breakthrough curve appeared due to continuous regeneration, unlike Fig. 5. The pH value after regenerating with operating time decreased approximately 2.2% and that is similar to the CO<sub>2</sub> removal efficiency with operating time tendency. Zhang *et al.* (2008) reported that the pH affects the formation of the carbamate. Therefore, the variety of pH with time determines the removal efficiency and stripping efficiency of CO<sub>2</sub>.

Figure 9 presents reaction rate constant obtained from the result in Fig. 2 and CO<sub>2</sub> loading of amine obtained by the titrimetric method, which shows the optimum blending ratio of MEA and AMP considering reaction rate and CO<sub>2</sub> loading of absorbent. The CO<sub>2</sub> loading of lean amine



**Fig. 8** Effect of operating time on CO<sub>2</sub> removal efficiencies and pH of aqueous 18 wt.% MEA + 12 wt.% AMP solution in absorption/regeneration continuous process.



**Fig. 9** Effect of aqueous blended MEA+AMP solutions on CO<sub>2</sub> loading and overall pseudo-first order reaction rate constant  $k_{ov}$ .

with respect to blending conditions were very similar. This could be caused by a higher CO<sub>2</sub> absorption amount of 0/30 relative to 30/0 and continuous use for a long time due to the excellent CO<sub>2</sub> regeneration of 0/30. In particular, the increasing rate of CO<sub>2</sub> loading of rich amine from 30/0 to 24/6 and from 24/6 to 18/12 were 19.5% and 26.5%, respectively. On the other hand, the reaction rate of 30/0 was higher than that of 0/30, the reaction rate of blended amine solutions decreased with an increase of AMP contents according to blending conditions. Consequently, blending MEA and AMP could be an effective way to design considering economical efficiency and to use absorbent for a long time as shown in Figs. 6 and 9. It was considered that the optimum blending rate of AMP and MEA according to reactivity and efficiency is 18/12.

## 4 Conclusions

This study performed comparative tests on the aqueous MEA, AMP and blended MEA+AMP solutions. In absorption process, the tests showed that MEA was superior to AMP in the CO<sub>2</sub> removal efficiency but AMP was better than MEA in CO<sub>2</sub> absorption amount. In absorption/regeneration process, reaction rate constant of blended MEA+AMP solutions increased and CO<sub>2</sub> loading of rich amine decreased with an increase of MEA contents. On the other hand, with the increase of AMP contents, the reverse results were obtained comparing to the previous results. This was caused by that the reaction rate of MEA (11909.6 s<sup>-1</sup>) by the fast carbamate reaction was higher than that of AMP (3143.6 s<sup>-1</sup>) at 40°C. However, due to the carbamate formed from Reaction (1) is quite stable, its CO<sub>2</sub> loading limited by stoichiometry to 0.5 mol CO<sub>2</sub>/mol amine. In case of AMP, the carbamate is very unstable,

thereby having a fast hydrolysis reaction and releasing free amine as shown in Reaction (4). The CO<sub>2</sub> loading was highly maintained to 1.0 mol CO<sub>2</sub>/mol amine due to the additional reaction by zwitterion mechanism.

In cases of aqueous blended solutions such as 24/6 and 18/12, the CO<sub>2</sub> removal efficiencies are similar with AMP, but the reaction rate increased by the mixing of MEA. The CO<sub>2</sub> loading of rich amine of 24/6 and 18/12 were 0.49 and 0.62 mol CO<sub>2</sub>/mol amine, respectively, which were 19.5%, 51.2% more than 30 wt.% MEA (0.41 mol CO<sub>2</sub>/mol amine). Consequently, blending MEA and AMP could be an effective way to design economical efficiency and used to operate absorber for a long time.

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