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**REVIEW PAPER**

# Improvement in $CO_2$ absorption and reduction of absorbent loss in aqueous $NH_3$/triethanolamine/2-amino-2-methyl-1-propanol blends

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**Abstract**−Changes in the $CO_2$ absorption rates and capacities of the absorbent 2-amino-2-methyl-1-propanol (AMP), blended with $NH_3$ and other additives, were investigated toward performance improvement. The $NH_3$-blended absorbent removed $CO_2$ more efficiently than the AMP absorbent alone. However, absorbent loss through $NH_3$ evaporation was observed under these conditions. A second absorbent, the tertiary amine triethanolamine (TEA), which has a low vapor pressure, was selected and blended with the $NH_3$/AMP system to reduce $NH_3$ evaporation. Its effects on $NH_3$ loss and the absorption rate and capacity of the $NH_3$/AMP system were investigated, and the optimum blending ratios were determined. In addition, the absorbent blend at the optimum blending ratio was compared to AMP alone and the commercially available absorbent monoethanolamine at the same weight ratio. The thermal stabilities of the absorbents, under conditions used in the $CO_2$ absorption process, were compared by thermogravimetric analysis.

Key words: $CO_2$ Capture, $CO_2$ Absorption, Absorbent Loss, Blending Absorbent Ratio, Thermogravimetric Analysis

## INTRODUCTION

The development of modern industry has driven a continuous increase in energy use. The accompanying environmental problems are of global scale, and solutions are urgently needed, particularly to combat the emission of greenhouse gases. These have contributed to global warming ever since the start of the Industrial Revolution, and are mainly attributed to the drastically increased use of fossil-based energy sources. This anthropogenic climate change is recognized as one of the major problems facing society today [1].

Thermoelectric power plants as incinerating facilities are the main energy providers for the steel, petrochemical, and cement industries, emitting considerable quantities of $CO_2$ into the air. The development of technology to eliminate $CO_2$ emissions is desperately needed. In general, exhaust mixtures are separated by processes such as absorption, adsorption, and membrane separation. A currently commercialized technology, which appears to hold the most promise in the short term, is the absorption separation of combustible waste gases [2]. In comparison to other technological developments, however, absorption separation technology is relatively costly. The enhancement of absorbent performance is therefore necessary.

Two examples are AMP (2-amino-2-methyl-1-propanol) and MEA (monoethanolamine), which have an absorbent that is widely used for $CO_2$ absorption. At high pressure, AMP was proposed as better solvent than MEA because its $CO_2$ load capacity is higher than that of a single absorbent for acid gas removal. However, there is characteristic corrosion of the single absorbent as well as a degradation reaction, and there are problems regarding highly renewable energy. Therefore, an absorbent that promotes the absorption capacity of the existing single absorbent and reduces production time energy is considered. In this regard, the amine absorbent was being used for a long time. But because the $CO_2$ absorption capacity is small and there is a great deal of corrosion due to the acidic gas it is necessary to use the new absorbent.

On the other hand, with regard to the ammonia solution absorbent, the $CO_2$ removal efficiency and absorption capacity are bigger than those of the amine absorbent. In addition, the exhaust gas processing technology required for the renewable energy of the absorption liquid is manageable, and there is no corrosion problem with this absorbent. In comparison with the existing amine absorbent, the ammonia solution is cheap and effective, and its $CO_2$ absorption is adequate for $CO_2$ control. However, the high vapor pressure of the ammonia solution reduces the absorbent loss and carbon dioxide absorption rate and decreases the processing efficiency. Therefore, with regard to the amine and ammonia solution absorbent, the main focus is on the pros and cons of a method that uses a mixture of these absorption liquids. Research has to be done on such a solution to improve the absorption capacity for the absorption of carbon dioxide and to reduce the loss that occurs due to evaporation [3].

Usually, the absorbents in the $CO_2$ absorption process are not used independently but rather are mixed; the admixtures improve the absorbent performance and mitigate problems such as corrosion, energy use, and wear and tear. Recently, research has focused on the exact mixing ratios of absorption liquids, the improvement of the absorption liquid properties, and the use of additives. Here, the combination of physical and chemical absorption through the use of alkanolamines is a recurrent research theme [4,5]. In this study, we sought to increase control over the adsorption kinetics and the gas absorption capacity of the selected absorbent, and to reduce the time and energy costs of the process, which result primarily from the increased density of the alkanolamines.

The process performance for $CO_2$ collection by absorption is critically related to the choice of absorbent. Indeed, research on the effec-

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tiveness of new absorbent mixtures or entirely new absorbents, and related studies of absorbent corrosion or other degradation reactions and the generation of renewable energy, are continuously ongoing [6,7].

We studied the addition of $NH_3$ to the single absorbent, 2-amino-2-methyl-1-propanol (AMP), to improve both its absorption rate and capacity, as well as to enhance its reactivity and absorption capacity. The $CO_2$ removal efficiency was excellent and the performance was approximately twice that of AMP alone. Furthermore, we tried to optimize the $NH_3$/AMP mixing ratio to improve the absorbent performance beyond that of AMP alone. An additional performance increase was attempted by suppressing the evaporation of $NH_3$ by blending with the tertiary amine, triethanolamine (TEA), which displays low vapor pressure. Its contribution to solvent loss, as well as $CO_2$ absorption characteristics such as absorption rate and absorption capacity, is presented, and an optimum mixing ratio is suggested. The absorption characteristics of the blends at an optimum ratio of the mixed absorbents were compared to both AMP and the commercially available monoethanolamine (MEA) absorbents at the same weight ratio. The thermal stability of the absorbents in the $CO_2$ absorption process at the optimum mixing ratio, in the presence of $CO_2$, was investigated by thermogravimetric analysis. In our study, we pursued an absorbent that improves both the performance of a single absorbent and the $CO_2$ absorption characteristics.

## THEORETICAL BACKGROUND

### 1. Mechanism of the Absorption Reaction

The interaction of $CO_2$ with a primary amino group gives rise to three possible reactions: the formation of bicarbonate from carbamate, the reverse reaction, and the formation of carbonate [8].

Carbamate formation:

$$CO_2\ (g)+2RNH_2\ (l) \rightleftharpoons RNH_3^+\ (aq)+RNHCOO^-\ (aq) \tag{1}$$

Bicarbonate formation:

$$RNHCOO^-\ (aq)+H_2O\ (l) \Leftrightarrow RNH_2\ (l)+HCO_3^-\ (aq) \tag{2}$$

The equilibrium loading capacity of primary and secondary amines is limited by the stoichiometry of the reaction (0.5 mol $CO_2$/mol amine; Eq. (1)). The zwitterion mechanism, originally proposed by Caplow [9] and reintroduced by Danckwerts [10], is the generally accepted reaction mechanism:

$$CO_2\ (g)+RNH_2\ (l) \Leftrightarrow RNH_2^+COO^-\ (aq) \tag{3}$$

$$RNH_2^+COO^-\ (aq)+B'\ (aq) \rightarrow RNHCOO^-\ (aq)+B'\ H^+\ (aq) \tag{4}$$

Where B' is amine. If the carbamate ion is unstable, as occurs with hindered amines, it decomposes to the bicarbonate ion (Eq. (2)). The reaction mechanism thus implies that one mole of hindered amine allows the loading of up to one mole of $CO_2$. However, a certain amount of carbamate hydrolysis occurs, regardless of the amine, so that even in the case of MEA, $CO_2$ loading may exceed the stoichiometry, particularly at high pressures.

The interaction of $CO_2$ with $NH_3$ may give rise to the following reactions [11,12]:

$$CO_2\ (g)+2NH_3\ (aq) \rightarrow NH_4^+\ (aq)+NH_2COO^-\ (aq) \tag{5}$$

$$CO_2\ (g)+2NH_3\ (l)+H_2O\ (l) \Leftrightarrow (NH_4)_2CO_3\ (s) \tag{6}$$

$$CO_2\ (g)+NH_3\ (l)+H_2O\ (l) \Leftrightarrow NH_4HCO_3\ (s) \tag{7}$$

The method of scrubbing $CO_2$ from flue gas using liquid $NH_3$ (i.e., the wet method) produces ammonium carbonate ($(NH_4)_2CO_3$) and ammonium bicarbonate ($NH_4HCO_3$) [8,13]. In contrast to primary amines and ammonia, tertiary alkanolamines do not directly produce carbamates from $CO_2$, but rather, they produce $OH^-$ in the presence of water, as they have no nitrogen-bound hydrogen. The $OH^-$ produced then reacts with $CO_2$ to give bicarbonate as the major product [14,15]. The chemical absorption of $CO_2$ by tertiary amines occurs through the following mechanism:

$$CO_2\ (g) \Leftrightarrow CO_2\ (aq) \tag{8}$$

$$CO_2\ (aq)+2H_2O \Leftrightarrow HCO_3^-+H_3O^+\ (aq) \tag{9}$$

$$HCO_3^-+H_2O \Leftrightarrow CO_3^{2-}+H_3O^+ \tag{10}$$

$$\text{Amine}+H_2O \Leftrightarrow \text{AmineH}^++OH^- \tag{11}$$

$$\text{AmineH}^++H_2O \Leftrightarrow \text{Amine}+H_3O^+ \tag{12}$$

Kinetics studies have shown that TEA acts as a base catalyst. The absorption capacity of tertiary amines is higher than that of primary and secondary amines: ca. 0.9 mol of tertiary amine will absorb 1 mol of $CO_2$ [16]. However, this advantage is offset by a lower rate of absorption.

### 2. Determination of $CO_2$ Absorption

The absorption capacities of the absorbents were determined experimentally by first measuring pressure changes between initial and equilibrium states of the system. Then, the partial pressure of $CO_2$ ($P_{CO_2}$, in atm) was calculated from the difference between the initial pressure ($P_{N_2}$) and the equilibrium pressure ($P_{eq}$) at equilibrium absorption.

$$P_{CO_2}=(P_{eq}-P_{N_2}) \tag{13}$$

This value was used with the ideal gas equation of state to determine the extent of $CO_2$ absorption (Eq. (14)). The carbon dioxide absorption (in mol) was calculated by multiplying its volume V by the carbon dioxide injection pressure ($P_{N_2+CO_2}$), and subtracting the equilibrium pressure ($P_{eq}$), followed by dividing by RT.

$$n_{CO_2}=\frac{(P_{N_2+CO_2}-P_{eq})V}{RT} \tag{14}$$

The absorption capacity ($\alpha$) could then be obtained by dividing the number of moles of carbon dioxide ($n_{CO_2}$) by the absorbed moles of amine:

$$\alpha=n_{CO_2}/(\text{mole of amine}) \tag{15}$$

We calculated the rate of absorption ($N_A$), and the amount of gas absorption from the difference between the absorption and the flow of gas from the reactor into the reactor's initial flow. When converted into moles, the absorption per unit area of the reactor in the gas-liquid interfacial was obtained. The absorption rate was calculated using the following equation, with the initial volumetric absorption rates, $V(t_1)/t_1$, obtained from the cumulative volume of gas which has flowed through the $CO_2$ analyzer:

$$N_A=\frac{P_T-P_W}{SRT}\frac{V(t_1)}{t_1} \tag{16}$$

where $P_T$ is the atmospheric pressure, $P_w$ is the vapor pressure of water, S is the surface area of liquid phase, and $V(t_1)$ is the cumulative volume of gas during the absorption time, $t_1$.

### 3. Thermogravimetric Analysis and Loss of Absorbent

Additives can be employed to control the evaporation of $NH_3$ absorbent and increase $CO_2$ absorption performance through modulation of the vapor pressure. Even though the vapor pressure of the mixed solutions is lower than the pure solute, the intermolecular binding force between ammonia and the additive increases solvation; as a result, the absorbent performance does not degrade, especially if the additive contains an amino group. Furthermore, the presence of a hydroxyl group (-OH) in the solvent (or additive) increases the solvation by hydrogen bonding, thus preventing the fast vaporization of ammonia. In this experiment, the weight change of the absorbent resulting from $NH_3$ evaporation was measured as a function of time by measuring the weight of the aqueous absorbent solution over time, as in [17]:

$$\text{Weight Loss }\% = \frac{\begin{array}{c}(\text{weight of absorbent at } t=0\text{ s})\\ -(\text{weight of absorbent at } t=n\text{ s})\end{array}}{(\text{weight of absorbent at } t=0\text{ s})}\times 100 \qquad (17)$$

## MATERIALS AND METHODS

### 1. Materials

Analytical grade AMP (2-amino-2-methyl-1-propanol, 95%), $NH_3$ (28%), and TEA (99%) were supplied by Sigma Aldrich (USA), Junsei Chemical Co. (Tokyo, Japan), and Samchun Pure Chemicals (Korea), respectively. Aqueous solutions were prepared using distilled water. $CO_2$ and $N_2$ gases were commercial grade with purities of 99.99%.

### 2. Instrumental Procedures

2-1. Absorption Rate

A schematic diagram of the experimental setup is presented in Fig. 1. Absorption experiments were carried out in an agitated vessel. The absorption vessel was constructed of glass, with an internal diameter of 0.073 m and a height of 0.151 m. The surface area, calculated as the ratio between the volume of water added and the measured height of the water in the reactor, was 40.947 $cm^2$. All tests were conducted at a reaction volume of 200 mL. The stirring speed was limited to 50 rpm to maintain a planar and smooth gas-liquid interface. Gas flow rates were controlled using mass flow controllers (5850E, Brooks Instruments, USA) with an accuracy of 1% (of the full scale). A gas chromatograph (GC, model 7890A, Agilent) $CO_2$ analyzer was used to measure $CO_2$ gas concentration at the reactor outlet.

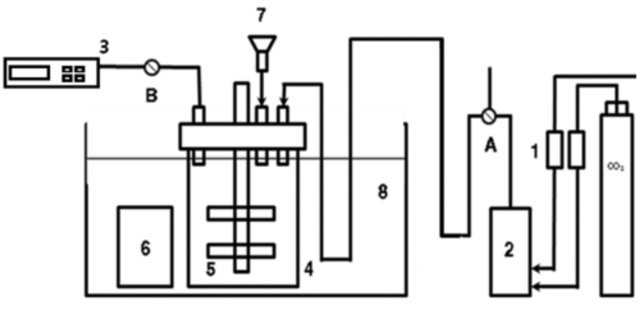

**Fig. 1. Experimental setup for measuring absorption rate.**

| | |
|---|---|
| 1. Mass-flow controller | 5. Impeller |
| 2. Mixing chamber | 6. Liquid bottle |
| 3. $CO_2$ analyzer | 7. Funnel |
| 4. Reactor | 8. Water bath |

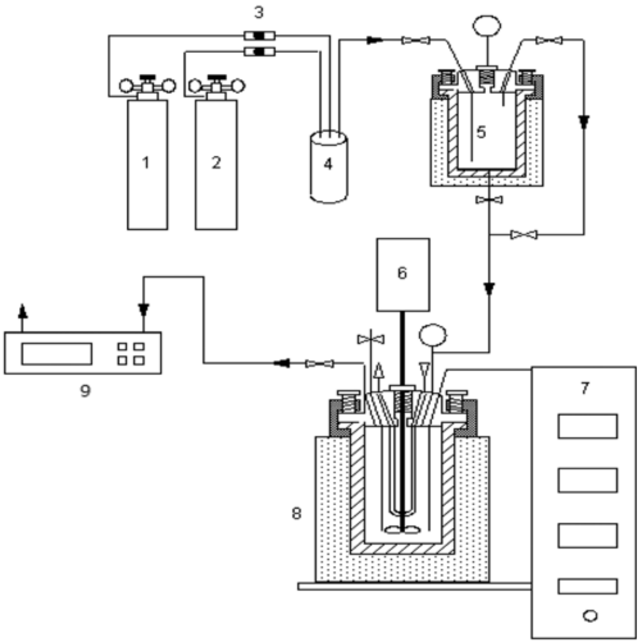

**Fig. 2. Schematic representation of the experimental setup for measuring $CO_2$ absorption capacity.**

| | |
|---|---|
| 1. $N_2$ cylinder | 6. Magnetic drive |
| 2. $CO_2$ cylinder | 7. Temperature and agitation speed controller |
| 3. Mass-flow controller | 8. Reactor (agitated vessel) |
| 4. Mixing chamber | 9. Computer |
| 5. Saturator | |

Absorption rates ($N_A$) were calculated from the gas-liquid absorption per interfacial unit per mole, and obtained from the difference in the gas volume between inlet and outlet. Each experiment was repeated once.

2-2. Absorption Capacity

The instrument constructed to explore the absorption capacity of $CO_2$ in amine-containing solutions is shown in Fig. 2. Absorption experiments were performed in an agitated reactor. The reactor, with a height of 160 mm, was located inside a temperature-controlled vessel, with four glass plates (5 mm in width) adhering to the inner wall of the reactor, functioning as baffles. A two-blade impeller (70 mm×20 mm) was installed at the mid-height of the liquid level. The temperature of the reactor was measured with a K-type thermocouple, with an accuracy of ±0.1 K. The stirring speed was limited to 50 rpm to maintain a planar and smooth gas-liquid interface. All tests were conducted at a volume of 300 mL. Partial gas pressures were measured by using a pressure data logger (PR2000, MadgeTech, USA) with an accuracy of 0.25% at 298 K. Absorption capacities were measured at 313 K and 383 K, at partial $CO_2$ pressures ranging from 0 to 600 kPa. The $CO_2$ absorption capacities of the amine solutions were calculated according to Eqs. (13)-(15).

2-3. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to measure heat flow and the weight change of the sample [18]. The absorbent mass was approximately 10 mg, and TGA was measured in a platinum pan by using a PerkinElmer TGA 7 Pyris 1 (USA) over the temperature range 35-200 °C. The heating rate was 10 °C min$^{-1}$. Each data point was an average of multiple readings.

## RESULTS AND DISCUSSION

### 1. Effect of $CO_2$ Absorption Rate in $NH_3$-blended AMP Aqueous Solution

Because the absorption rate of AMP as a single absorbent is low, $NH_3$ absorbent, which exhibits an excellent $CO_2$ absorption rate, was blended with AMP to enhance uptake. AMP was fixed at 20 wt%, an appropriate initial concentration expected to prevent the occurrence of degradation reactions [21]. In industrial applications, an anticorrosive agent is generally not necessary when 20-30 wt% amine is used. The absorption rate as a function of the temperature (293, 303, 313, and 323 K) was measured for $NH_3$ blends at 1, 3, 5, and 7 wt%.

As shown in Fig. 3, the absorption rate of AMP alone increased linearly from 1.72 to $4.77\times10^{-6}$ kmol m$^{-2}$ s$^{-1}$ as the temperature increased. This was due to the higher collision rate resulting from increased diffusion at the gas-liquid interface with every temperature increment. The absorption rates of 20 wt% AMP in the presence of 1, 3, 5, and 7 wt% $NH_3$ increased with $NH_3$ content, as well as reaction temperature, from 2.72 to $12.32\times10^{-6}$ kmol m$^{-2}$ s$^{-1}$. Because the activation energy of ammonia ($E_{NH_3}$; 41.2 kJ mol$^{-1}$) is higher than the activation energy of AMP ($E_{AMP}$: 25.1 kJ mol$^{-1}$), the contribution of $NH_3$ to the absorption rate should increase as the reaction temperature increases.

As to this, the activation energy of the piperazine is big as 53.4 kJ mol$^{-1}$ than the activation energy 33.1 kJ mol$^{-1}$ of MDEA. Therefore, the absorption rate resembles the thing which the contribution of the piperazine increases as the temperature increases [22].

Overall, the absorption rate was highest for the 7 wt% $NH_3$ blend, yet the absorption rate increase was highest for 5 wt% blends. The bicarbonate (i.e., dissolved $CO_2$), carbonate, and carbamate ions, which are generated as the $NH_3$ concentration increases, should, in theory, balance with the generated ammonium ions, and $NH_4^+$ should increase as free ammonia increases. However, the $CO_2$ removal rate is high at high $NH_3$ concentrations, and this may lead to eutectic phase formation as a result of the generated salts (see Eqs. (6) and (7)). When the ammonia absorbent concentration is 7 wt% or greater, as in references [23,26], as time goes by, disorder is caused by the scaling in the absorption process and the precipitate is generated. So, when these problems occur, approximately 7-8 wt% or more is considered to be a high concentration of ammonia solution. Therefore, an optimal ratio of 5 wt% was selected.

### 2. Effect of Absorption Capacity in $NH_3$-blended AMP Aqueous Solutions

The absorption and desorption areas were measured for $CO_2$ absorption capacity at 313 and 373 K to assess the impact on the absorption capacity of the 20 wt% AMP single absorbent and 1, 3, 5, and 7 wt% $NH_3$ blends. A partial $CO_2$ pressure of 100 kPa was used to estimate the loading ratio defined as the number of moles of carbon dioxide absorbed by moles of absorbent (Eq. (15)) [29]. At 313 K, AMP alone absorbed 0.6 mol $CO_2$ per mol AMP, which increased from 0.7 to 1.05 mol with 1, 3, 5, and 7 wt% $NH_3$ blends (Fig. 4). Thus, the absorption capacity increased when $NH_3$ was added in comparison to AMP by itself.

In addition, the amine regeneration process at temperatures over 373 K was examined; the absorption capacities at 373 K are shown in Fig. 5. By itself, AMP showed an absorbance of 0.4 mol $CO_2$ per mol amine, and absorption capacities of ca. 1 mol per 0.3 mol AMP were observed for 1, 3, 5, and 7% $NH_3$ blends. The eutectic phase separation of $CO_2$ and its collection are facilitated by absorption at low temperature, whereas regeneration is conducted at high temperature. Therefore, for each area, the higher the absorption capacity, the larger the loading ratio, thus presenting an excellent absorbent. As can be seen by comparing the loading ratio between the low temperature absorption region in Fig. 4 and the high temperature regeneration region in Fig. 5, the loading ratio was larger for the $NH_3$/AMP blends than for the AMP single absorbent, as were the regeneration capacities. The results of the absorption capacity were the highest as in the section 1 on the $NH_3$ absorbent 7 wt%

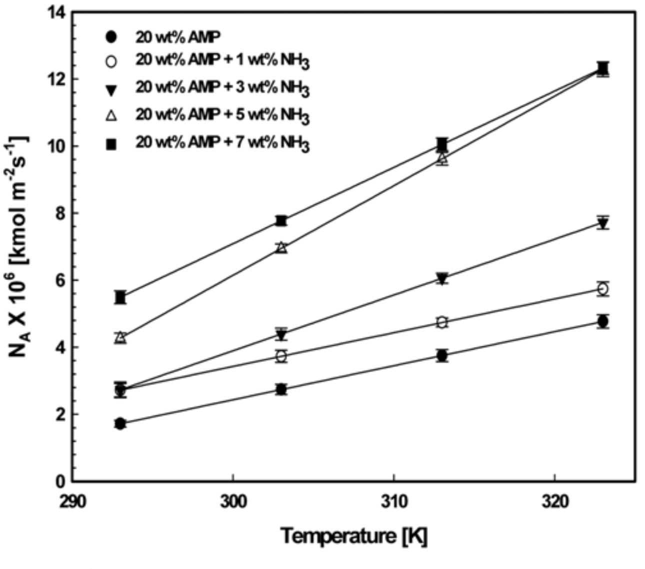

**Fig. 3. $CO_2$ absorption rates ($N_A$) of $NH_3$-blended AMP aqueous solutions as a function of temperature.**

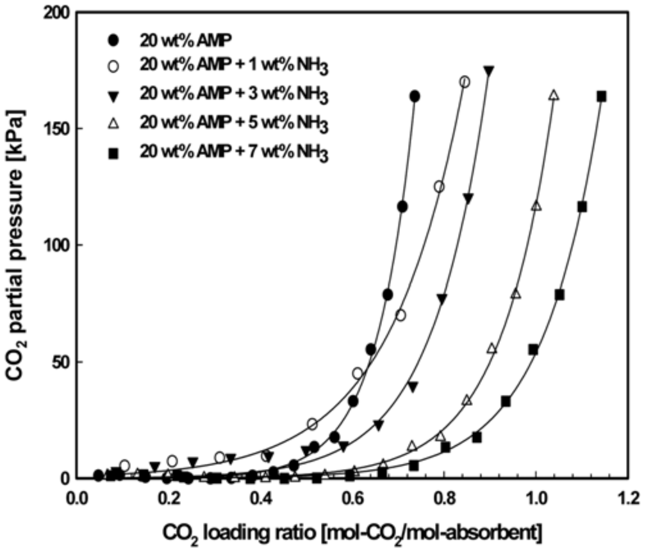

**Fig. 4. Absorption capacity of $CO_2$ into AMP/$NH_3$ blends in aqueous solution at 313 K.**

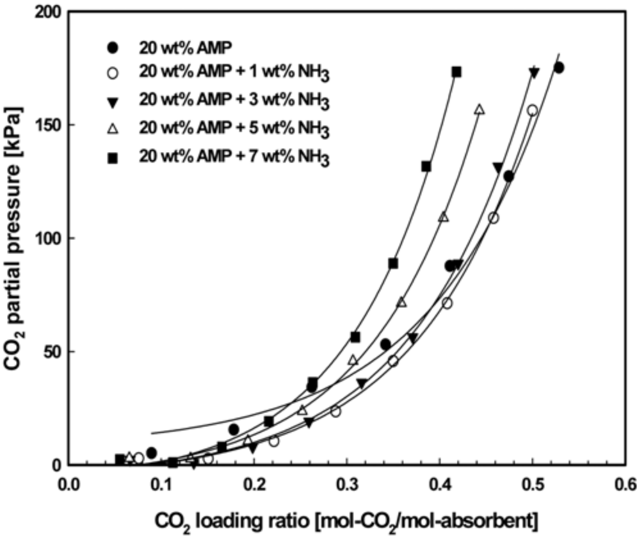

**Fig. 5. Absorption capacity of $CO_2$ in AMP/$NH_3$ blends in aqueous solution at 373 K.**

blending. The amount of improvement in the absorption showed the absorption/regeneration area in 5 wt% blending. This was the highest when the absorbent 1 kg $CO_2$ absorption volume was 5 wt% rather than 7 wt%. This result was due to the improved $CO_2$ reactivity and $CO_2$ absorption capacity. The reason for this result is that the 7 wt% $NH_3$ caused the $CO_2$ removal efficiency to decrease faster than it did at 5 wt% due to the scale formation problem [22]. Therefore, the $NH_3$ absorbent for the absorption capacity improvement of the AMP absorbent was selected as the optimal ratio in 5 wt% blending.

### 3. Selection of Additives for Absorbent Loss Reduction in Aqueous AMP/$NH_3$ Blends

Evaporation from the solution state, which is a problem in $CO_2$ absorption processes using $NH_3$, can be suppressed by absorbents. Ideally, the solvent should bind intermolecularly with $NH_3$ in such a way to ensure that a decrease in absorption capacity does not occur. We measured the mass change through absorbent loss over time at 313 K using 10 wt% $NH_3$ and 3 wt% of an additive (piperazine (PZ), ethylene glycol (EG), glycerol (Gly), methyldiethanolamine (MDEA), diethanolamine (DEA), or TEA) (Fig. 6). The simple 10 wt% $NH_3$ absorbent blend showed high absorbent loss after one hour, along with a vapor pressure loss of $NH_3$. In which $CO_2$ is dissolved and which is created as the concentration of the $NH_3$ increases ammonium ion comprised the bicarbonate and carbonate or the carbamate ion, theoretically, the balance, and $NH_4^+$ are due to increase and this result is due to increase the free ammonia. When the ratio of free ammonia is high, the interactions between the compounds are weak, and free ammonia is expected to be a factor in $NH_3$ absorbent loss.

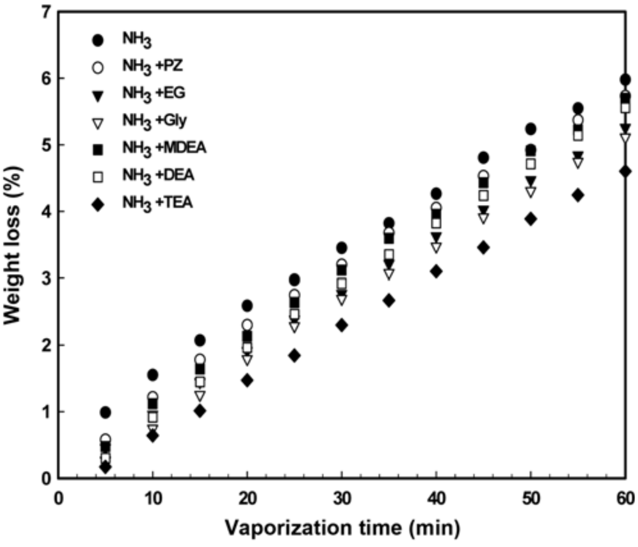

**Fig. 6. Weight loss from additive/$NH_3$/AMP aqueous solutions at 313 K, as a function of vaporization time (piperazine (PZ), ethylene glycol (EG), glycerol (Gly), methyldiethanolamine (MDEA), diethanolamine (DEA), or triethanolamine (TEA)).**

Piperazine as a reaction catalyst did not have an effect on the loss of $NH_3$ because in both structures the amino functional groups exist in the molecular structure. This is because the hydroxyl functional group lowers the absorbent loss to a greater extent than piperazine. The amount of $NH_3$ loss decreased, however, when the tertiary amine TEA was added. The presence of an amino functional groups in the molecular structure, allows the absorption of $CO_2$ while the hydroxyl functional groups suppresses evaporation of the absorbent. In case of TEA, the number of molecular structures with hydroxyl functional groups is high in comparison with the other absorbents. Therefore, to decrease the loss of $NH_3$ absorbent, TEA was selected.

### 4. Reduction of Absorbent Loss in $NH_3$/TEA Blends in AMP Aqueous Solutions

$NH_3$ single absorbent mass with an increase in the concentration of the absorbing solution based on the absolute absorption of carbon dioxide will increase the capacity. In addition to the absorption with increasing temperature, the reactivity and the rate of absorption increased [12]. However, the absorbent loss became more apparent due to the evaporation of $NH_3$. Therefore, to reduce this loss, the blending of TEA absorbent was analyzed. As described above,

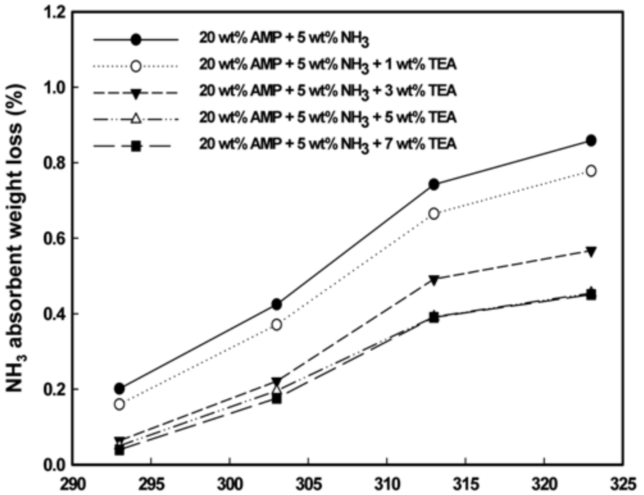

**Fig. 7. $NH_3$ absorbent weight loss in the presence of TEA in AMP aqueous solution, as a function of temperature.**

an AMP concentration of 20 wt% and an $NH_3$ concentration of 5 wt% were selected to improve the absorption rate of AMP absorbent. TEA absorbent was blended at 1, 3, 5, and 7 wt% and the loss in $NH_3$ absorbent was measured as a function of temperature at 293, 303, 313, and 323 K.

Fig. 7 shows the results of the TEA concentration and temperature change. The $NH_3$ absorbent blending with AMP resulted in an ammonia absorbent loss of about 0.2-0.8% according to the temperature increase. On the other hand, TEA absorbent blending showed a loss of 0.02-0.4% according to when the temperature increases in the absorbent. There was a difference of about 0.4% depending on the temperature change. The reason for this was determined to be that as the temperature increases, the reactivity is enhanced and the evaporation of the ammonia absorbent is easily caused and the absorbent loss occurs. Absorbent losses occur with increasing temperature. This process reduces the $CO_2$ absorption rate, decreasing efficiency. Therefore, the appropriate concentration selection of TEA absorbent suppressing the ammonia solution absorbent loss is important.

Fig. 8 shows the $NH_3$ absorbent loss as a function of reaction time at 313 K, in the presence of 1, 3, 5, and 7 wt% TEA absorbent, 20 wt% AMP, and 5 wt% $NH_3$. The loss of $NH_3$ was reduced as the TEA absorbent concentration increased. Because the vapor pressure in the presence of the TEA absorbent was low, the loss of absorbent was also low, mainly because of the presence of the hydroxyl functional groups, which prevents rapid evaporation of $NH_3$. In addition, the coupling of TEA and the free ammonia molecule that carries the hydroxyl functional groups plays a role.

The reduction in $NH_3$ weight was highest for 7 wt% TEA blends. Significant improvement was also observed at 5 wt% blending, however, and the difference between 7 and 5 wt% blends was negligible. Therefore, the optimal value for decreasing $NH_3$ loss was 5 wt% TEA absorbent.

**5. Absorbent TGA**

Based on the foregoing results, we investigated the thermal stability of the amines used as carbon dioxide absorption process absorbents at a blending ratio of 30% (20 wt% AMP/5 wt% $NH_3$/5 wt% TEA). The values obtained were compared with AMP and MEA absorbents at the same weight ratios.

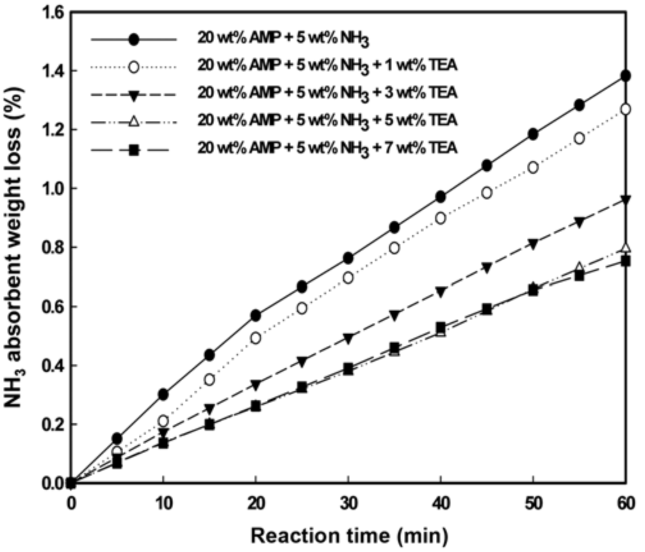

**Fig. 8. $NH_3$ absorbent weight loss in the presence of TEA in AMP aqueous solution, as a function of reaction time.**

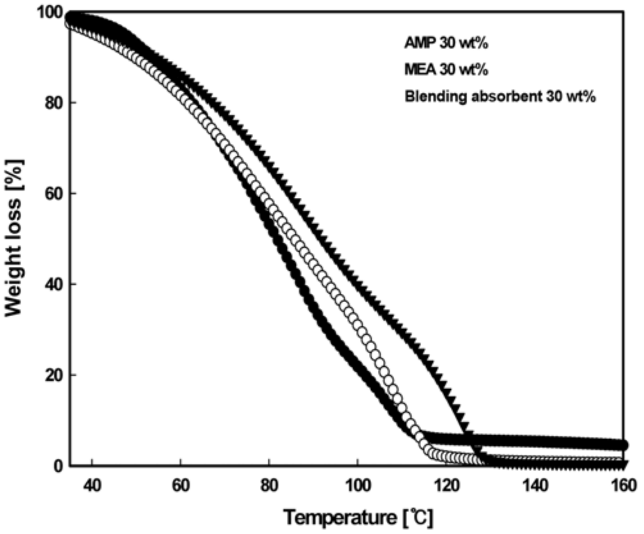

**Fig. 9. TGA of amine absorbents (in wt% loss) as a function of temperature.**

Fig. 9 shows TGA characteristic of the single absorbent (MEA, AMP) and the blending absorbent. The difference was shown in the analyzed result on TGA, blending, MEA, and AMP absorbent order. As to this tendency, there seems to be a relationship with the boiling point according to the absorbent [17]. The boiling point according to the absorbent is approximately 165 °C AMP, MEA 170 °C, $NH_3$ 239 °C, and TEA 335 °C. As shown in Fig. 9, the higher the boiling point of the absorbent, the stability to the degradation during which the absorbent itself is disassembled. That is, after stripping low MEA and AMP absorbent, the boiling point has to be reached. Otherwise, the absorbent will seriously degrade or alter the concentration by evaporation. Therefore, the risk of the single absor-

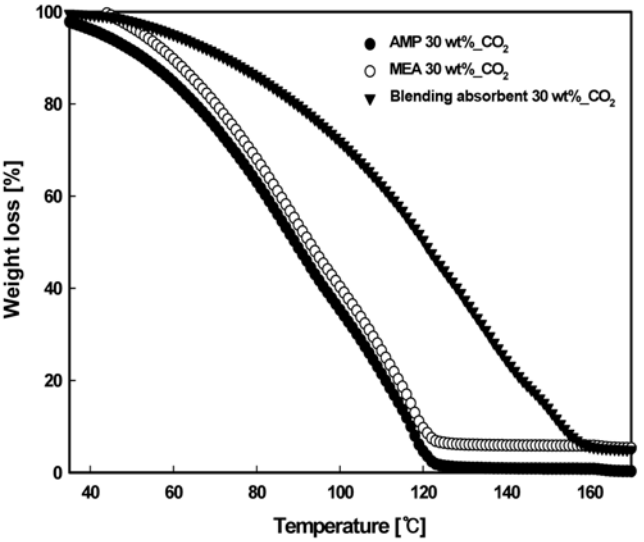

**Fig. 10. TGA of amine absorbents (in wt% loss) as a function of temperature and in the presence of $CO_2$.**

bent MEA and AMP is bigger than that of the blending absorbent.

Fig. 10 shows the analyzed result of TGA on the absorbent saturating the carbon dioxide. Weight loss occurs at a higher temperature than the absorbed carbon dioxide absorbent, and the TGA curves did not saturate the absorbent. It is expected that the absorbent for carbon dioxide formed by the reaction of the carbamate is thermally stable. Thischanges steadily into the carbamate formation due to the heat. Therefore, the boiling point is relatively high and the blending absorbent can be determined for the heat in comparison with the stability of the existing single absorbent.

Based on these results, we can predict the degradation associated with the thermal stability of the absorbent. These results are associated with the degradation of the absorbent can be predicted.

First, the degradation process of absorbent damage results in the loss of the possible reaction with carbon dioxide absorbent, which results in corrosion and causes many problems in the operation of the process. This degradation reaction mechanism is very complex, and it is difficult to determine the exact degradation products. According to the literature, MEA absorbent, which is widely used as a $CO_2$ absorbent, is the primary amine, but AMP, which is combined with the third carbon and has a hindrance is to degradation, is the best absorbent. The degradation of the secondary amine DEA absorbent is the most generated by far. As to the secondary amine, the OH group is 2 within the molecule. And at the same time, the degradation by the OH group and amine radical is due to occur. On the other hand, because the tertiary amine had 2 OH groups of the molecule I but did not form the carbamate in the case of the tertiary amine, it was shown to be relatively stable in the deterioration [19].

Generally, the corrosion rate of the deterioration specificity according to the chemical structure of the absorbent result and MEA absorbent was shown to be high [20]. If the absorbent concentration does not add the anticorrosive agent in the industry, generally 20-30 wt% as to amine concentration is known to be suitable. It is appropriate to maintain the initial concentration less than 20 wt%. However, if the concentration is low, the liquid-vapor ratio has to be increased in order to maintain the absorption efficiency at the optimal level. In this case, there is a problem in that according to the increase in the absorbent circulation amount, the energy requirement for the production time is increased. The absorption liquid has to be frequently exchanged. Because of that, the appropriate concentration of the amine absorbent is 30 wt%. Therefore, in this research, it corresponded to the weight ratio condition that 30 wt% of the amine concentration range is identical. We concluded that the same weight ratio (30 wt%) was present in the overall absorption characteristics and thermal stability analysis of MEA and AMP compared to the blending absorbent. Modified terms were obtained from the literature.

For the proposed blending absorbent, the highest AMP degradation of stability and TEA as a mixture of AMP and $NH_3$, TEA absorbents were mixed. In the case of the $NH_3$ absorbent, generally the corrosive is known to be less than the amine absorbent. In addition, the TGA analysis (section 5) through the MEA, AMP, and blending of the absorbent (30 wt%) in the same weight ratio and thermal stability were analyzed in this study. As a result, the blending absorbent exhibited the most thermally stable results. Therefore, because the chemical characteristic does not change even if the absorbent is mixed, it is determined in comparison with MEA absorbent that the corrosiveness of the blending absorbent is low.

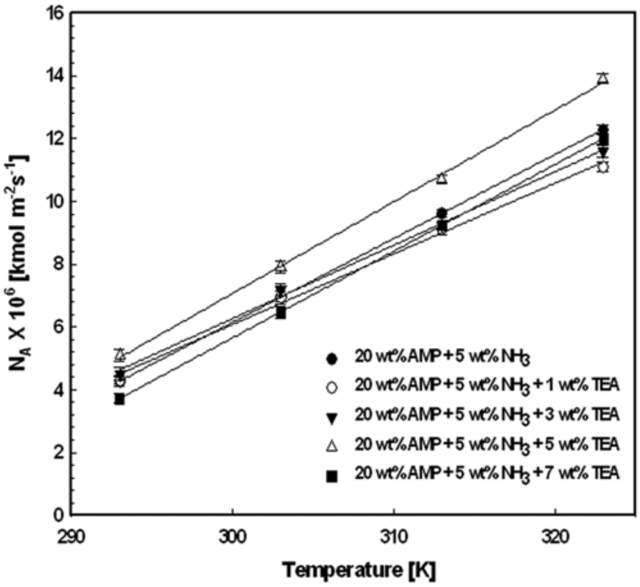

**Fig. 11. Absorption rates ($N_A$) of $CO_2$ in $NH_3$/TEA blends in AMP aqueous solution, as a function of temperature.**

### 6. $CO_2$ Absorption Rates in $NH_3$/TEA Blends in AMP Aqueous Solution

In the foregoing experiments, ammonia was blended with AMP to improve absorption performance, and TEA was then added to suppress $NH_3$ evaporation. We next investigated the effect of the combined additives on the absorption rate and absorption capacity. At fixed AMP (20 wt%) and $NH_3$ (5 wt%) contents, TEA was blended at 1, 3, 5, and 7 wt%, and the absorption rate as a function of concentration and temperature (293, 303, 313, and 323 K) was measured. Fig. 11 shows a 61-79% increase in the absorption rate in the presence of TEA with increasing temperature. The absorption rate increased linearly with temperature and was largely similar for all TEA loadings, due to the low reactivity of the tertiary amine. Considering its effect on the absorption rate and lowered loss of $NH_3$ absorbent, an optimal ratio of 5 wt% TEA absorbent was selected.

### 7. Absorption Capacity of $NH_3$/TEA Blends in AMP Aqueous Solution

The effect of the presence of $NH_3$ and TEA in aqueous AMP on the absorption capacity was studied. The $CO_2$ absorption capacity at 313 K and 373 K was measured at 20 wt% AMP, 5 wt% $NH_3$, and 1, 3, 5, and 7 wt% TEA. As shown in Fig. 12, the absorption capacity load of the 5 wt% $NH_3$ blend was 1 mol $CO_2$ per 0.9 mol of blended absorbent under a partial $CO_2$ pressure of 100 kPa. In addition, an absorption capacity of ca. 1.1 mol was found when $NH_3$ and TEA were blended. In the presence of the tertiary amine, the absorption capacity improved because of its 1 : 1 absorption capacity. Furthermore, after reaction with $CO_2$, the tertiary amine and the sterically hindered amine rapidly hydrolyzed so that the absorption rate of carbon dioxide increased.

At a partial pressure of 100 kPa at 373 K (Fig. 13), the absorption capacity of $CO_2$ was ca. 0.4 mol per mol AMP in the 5 wt% $NH_3$ blend. In the presence of TEA, this number increased to 0.2-0.32 mol $CO_2$, depending on the additive concentration.

The optimal conditions for the blending of the absorbent at 30

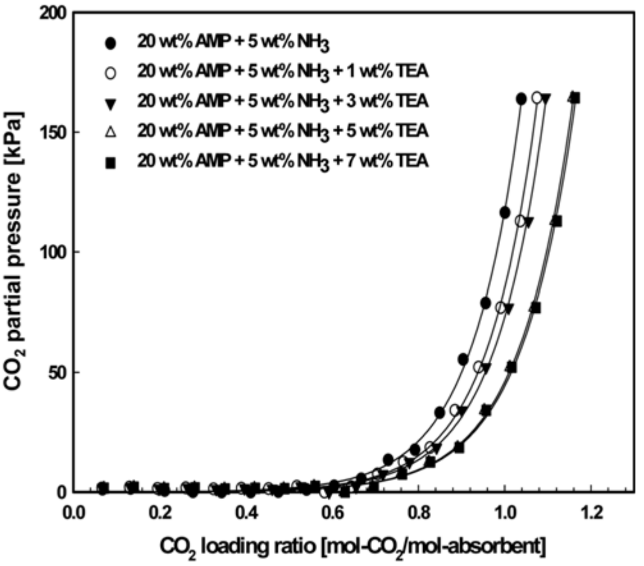

**Fig. 12.** $CO_2$ absorption capacity of $NH_3$/TEA blends in AMP aqueous solution at 313 K.

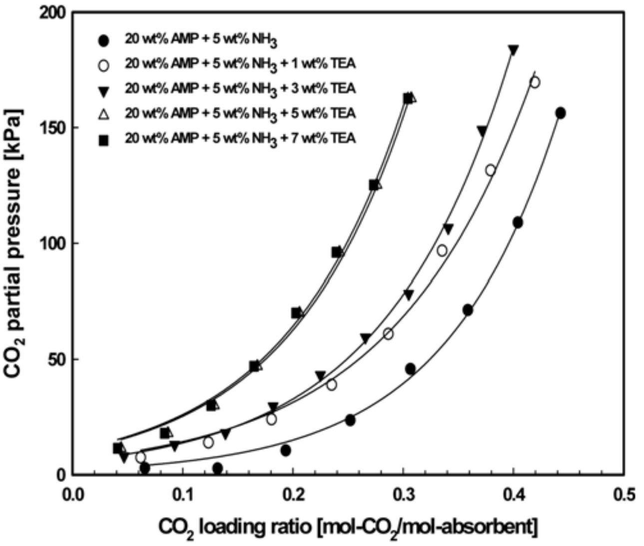

**Fig. 13.** $CO_2$ absorption capacity of $NH_3$/TEA blends in AMP aqueous solution at 373 K.

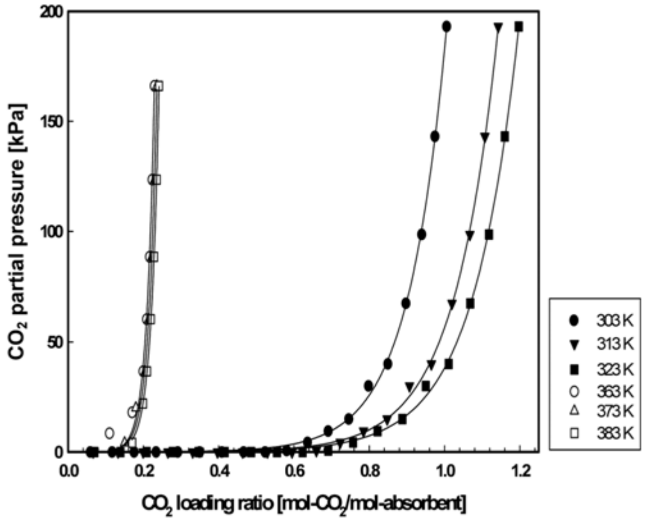

**Fig. 14.** $CO_2$ absorption capacity of $NH_3$/TEA blends in AMP aqueous solution with respect to the temperature.

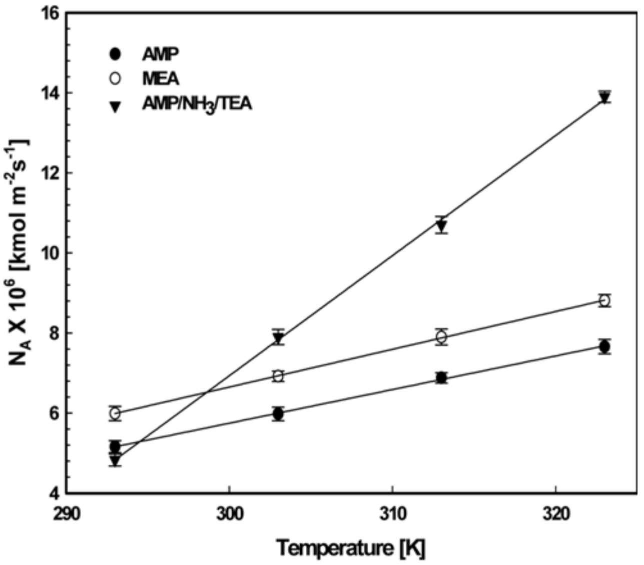

**Fig. 15.** Absorption rate of $CO_2$ in aqueous AMP or MEA single absorbent solutions, and the blended absorbent, as a function of temperature.

wt% (20 wt% AMP/5 wt% $NH_3$/5 wt% TEA) when the influence of the temperature changes according to the absorption capacity of 30, 40, 50 and 90, 100, 110 °C of the results are shown in Fig. 14. A change of 30-50 °C in the absorption area, and one can see that the increase of temperature and the equilibrium partial pressure of $CO_2$ according to the $CO_2$ loading increased the absorption of carbon dioxide, which can amount to a slight reduction. Approximately 0.9, 1.1, 50, and 40 °C, showing similar results to 1.15 at 30 °C, was confirmed. The area of 90-110 °C in the absorption capacity of the difference is almost invisible.

In summary, Fig. 12 shows the loading ratio at low temperature (i.e., absorption region), while Fig. 13 shows the loading ratio result in the regeneration area (high temperature). The difference in loading ratio was higher in the presence of $NH_3$ and TEA than for AMP alone, or in the presence of $NH_3$ only.

## 8. Comparison of the Absorption Characteristics of MEA and AMP, with and without Blended Absorbents

We studied the optimum mixing ratio of $NH_3$ and TEA absorbents for the enhancement of $CO_2$ absorption by AMP. As a result, a blending ratio of 5 wt% $NH_3$ and 5 wt% TEA in 20 wt% AMP (total absorbent concentration: 30 wt%) was found to be optimal. Fig. 15 compares the $CO_2$ absorption rates as a function of temperature of the blended absorbent with the commercial sorbents AMP and MEA, at the same weight ratios (30 wt%). The absorbents showed increased $CO_2$ absorption rates with increasing temperature, in the ranges 7.90-13.90 kmol $m^{-2}$ $s^{-1}$ (blended absorbents), 6.92-8.81 kmol $m^{-2}$ $s^{-1}$ (MEA), and 5.98-7.66 kmol $m^{-2}$ $s^{-1}$ (AMP). Thus, the reactivity and absorption rate of the blended absorbent clearly improved

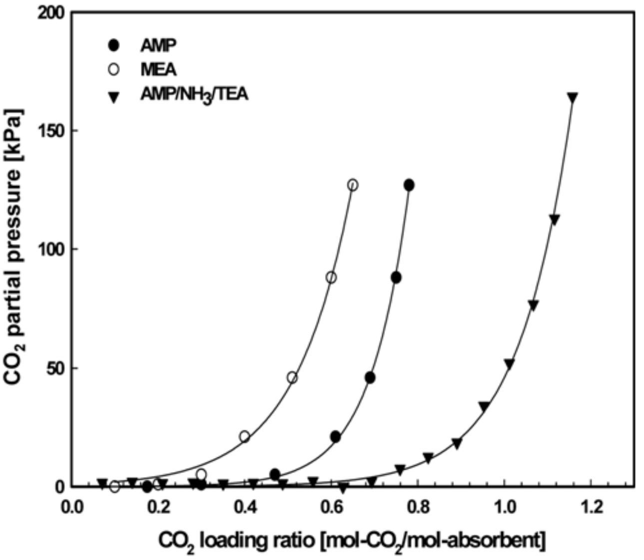

**Fig. 16. $CO_2$ absorption capacity in aqueous AMP or MEA single absorbent solutions, as well as the blended absorbent, at 313 K.**

compared to the single absorbents. This is because of the accessibility of the amino groups of the blended absorbent with $CO_2$.

A comparison of the absorption capacities of the blended absorbent with the single absorbents is shown in Fig. 16. AMP and MEA displayed absorption capacities of ca. 0.7 and 0.6 mol, respectively, while the blended absorbent had a value of 1.1 mol. The main reaction is the steric hindrance of the amine and $CO_2$ carbamate formation reaction by stoichiometric mol per 0.5 mol of $CO_2$ absorption. Generally, as to the tertiary amine, the absorption capacity was improved in the TEA mixture due to the absorption capacity of the amine, which is 1 mol per 1 mol. Tertiary amines and steric hindrance in the reaction of $CO_2$ with amine should be hydrolyzed easily and generated by the high $CO_2$ absorption rate compared to other absorbents.

We performed studies to evaluate $CO_2$ separation technology with the goal of making it simpler. Absorption technology can improve the performance of an absorbent by combining its characteristics. The blending absorbent discussed in this paper was a mixture of the $NH_3$ absorbent, for which the absorption rate for $CO_2$ and the reactivity were low and it could be used to promote the absorption capacity of a widely used AMP absorbent. With regard to the ammonia solution absorbent, the $CO_2$ removal efficiency is high, the $CO_2$ absorption capacity is large, and the cost is lower than that of the existing amine absorbent. However, the tertiary amine TEA was mixed in order to reduce the high volatility and ammonia solution absorbent loss. Thus, it can likely be used as an absorbent for the large amounts of $CO_2$ emissions from coal-fire and incineration plants and steel mills. Recently, research on the absorbent mixture has been done in an attempt to improve its functionality. The blending absorbent studied in this paper exhibited an improved absorbent performance and reduced absorbent loss in comparison with the existing single absorbent due to the problems involving AMP and $NH_3$. To apply these results, the loss of the absorbent in the absorption process must be controlled, and use of a blending absorbent rather than another $CO_2$ removal method should be considered.

## CONCLUSION

The absorption rates and absorption capacities of $NH_3$ absorbent blends as functions of temperature and concentration were studied to improve the absorption performance of the AMP absorbent. However, the high $NH_3$ concentration required to improve the performance of the AMP single absorbent was accompanied by absorbent loss resulting from the generation of salts and a high vapor pressure. Therefore, an optimum blending ratio of 5 wt% $NH_3$ absorbent was selected. To further improve the absorbent loss profile resulting from the volatility of the AMP/$NH_3$ blend, the tertiary amine TEA was selected as an additive, as it was reasoned that the presence of hydroxyl groups would decrease $NH_3$ absorbent loss by strong intermolecular interactions.

The $NH_3$ loss was investigated with respect to reaction temperature and TEA concentration in the AMP/$NH_3$ blend; losses were lowered as the TEA concentration increased. Because the reactivity of TEA was low, its effect was to increase the absorption efficiency. A TEA absorbent concentration of 5 wt% was found to promote the absorption rate and increase the absorption capacity, without affecting absorption efficiency.

## ACKNOWLEDGEMENT

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## REFERENCES

1. A. Henni, J. Li and P. Tontiwachwuthikul, *Ind. Eng. Chem. Res.*, **47**, 2213 (2008).
2. S. Morimoto, K. Taki and T. Maruyama, Oct. 5, RITE (2002).
3. A. Bandyopadhyay, *Clean Technologies & Environmental Policy*, **13**, 269 (2011).
4. P. V. Danckwerts, *Gas-liquid reactions*, McGraw-Hill (1970).
5. J. H. Kim, J. H. Lee, K. R. Jang and J. G. Shim, *J. Korean Soc. Environ. Eng.*, **31**, 883 (2009).
6. B. P. Mandal and S.S. Bandyopadhyay, *Chem. Eng. Sci.*, **61**, 5440 (2006).
7. W.-J. Choi, B.-M. Min, J.-B. Seo, S.-W. Park and K.-J. Oh, *Ind. Eng. Chem. Res.*, **48**, 4022 (2009).
8. S.-M. Yih and K.-P. Shen, *Ind. Eng. Chem. Res.*, **27**, 2237 (1998).
9. M. Caplow, *J. American Chem. Soc.*, **90**, 6795 (1968).
10. P. V. Danckwerts, *Chem. Eng. Sci.*, **34**, 443 (1979).
11. H. L. Bai and A. C. Yeh, *Ind. Eng. Chem. Res.*, **36**, 2490 (1997).
12. Y. F. Diao, X. Y. Zheng, B. S. He, C. H. Chen and X. C. Xu, *Energy Convers. Manage.*, **45**, 2283 (2004).
13. A. C. Yeh and H. Bai, *Sci. Total En Viron.*, **228**, 121 (1999).
14. T. L. Donaldson and T. N. Nguyen, *Ind. Eng. Chem. Fundam.*, **19**, 260 (1980).
15. P. Singh and G. F. Versteeg, *Process Saf. Environ. Prot.*, **86**, 347 (2008).
16. D. Bonenfant, M. Mimeault and R. Hausler, *Ind. Eng. Chem. Res.*, **42**, 3179 (2003).
17. B. G. Choi, G. H. Kim, K. B. Yi and J.-N. Kim, *Korean J. Chem. Eng.*, **29**, 478 (2012).

18. S.-T. Kim, J.-W. Kang, J.-s. Lee and B.-M. Min, *Korean J. Chem. Eng*., **28**, 2275 (2011).
19. K.-J. Oh, W.-J. Choi, S.-S. Lee, J.-J. Lee and B.-H. Shon, *J. Korean Soc. Environ. Eng.*, **24**, 985 (2002).
20. J.-H. Kim, J.-H. Lee, K.-R. Jang and J.-G. Shim, *J. Korean Soc. Environ. Eng.*, **31**, 883 (2009).
21. W.-J. Choi, J.-S. Lee, K.-H. and B.-M. Min, *Korean Chem. Eng. Res*., **49**, 256 (2011).
22. G. W. Xu, C. F. Zhang, S. J. Qin and Y. W. Wang, *Ind. Eng. Chem. Res*., **31**, 921 (1992).
23. D.-H. Lee, W.-J. Choi, S.-J. Moon, S.-H. Ha, I.-G. Kim and K.-J. Oh, *Korean J. Chem. Eng*., **25**, 279 (2008).
24. K.-H. Han, J.-S. Lee and B.-M. Min., *Korean Chem. Eng. Res*., **45**, 197 (2007).
25. O. F. Dawodu and A. Meisen, *J. Chem. Eng. Date*, **39**, 548 (1994).
26. J.-K. You, H.-S. Park, W.-H. Hong, J.-K. Park and J.-N. Kim, *Korean Chem. Eng. Res*., **45**, 258 (2007).
27. A. Muhammad, M. I. Abdul Mutalib, C. D. Wilfred, T. Murugesan and A. Shafeeq, *J. Chem. Eng. Data*, **54**, 2317 (2009).
28. H. Kierzkowska-Pawlak and A. Chacuk, *Chem. Eng*., **168**, 367 (2011).
29. J. H. Choi, S. G. Oh, M. Jo, Y. I. Yoon, S. K. Jeong and S. C. Nam, *Chem. Eng. Sci*., **72**, 87 (2012).