

## Absorption kinetics of carbon dioxide into aqueous ammonia solution: Addition of hydroxyl groups for suppression of vaporization

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**Abstract**—Aqueous ammonia can act as an alternative absorbent for CO<sub>2</sub> removal, but it has high volatility and reduces the ammonia concentration. We analyzed the hydroxyl additives 2-amino-2-methyl-1-propanol (AMP), ethylene glycol, and glycerol to reduce the vapor pressure of ammonia solutions. In addition, absorption efficiency groups of aqueous ammonia solutions containing hydroxyl additives were investigated. The results show that the addition of AMP, ethylene glycol, or glycerol to NH<sub>3</sub> reduced the vapor pressure of the absorbent by 14.0%, 22.7%, and 75.2%, respectively. The reaction rate constants of aqueous NH<sub>3</sub> containing AMP, ethylene glycol, and glycerol additives at 293, 303, 313 and 323 K are given by  $k_{2, \text{NH}_3/\text{AMP}} = 4.565 \times 10^5 \exp(-1396.5/T)$ ,  $k_{2, \text{NH}_3/\text{ethylene glycol}} = 1.499 \times 10^6 \exp(-1978.7/T)$  and  $k_{2, \text{NH}_3/\text{glycerol}} = 7.078 \times 10^6 \exp(-2413.3/T)$ , respectively.

Key words: Aqueous Ammonia, CO<sub>2</sub>, AMP, Ethylene Glycol, Glycerol

### INTRODUCTION

Diverse methods have been applied to capture CO<sub>2</sub> from the flue gas of general steam power plants and petroleum chemical plants. These methods include chemical absorption, physical adsorption, membrane separation, and biological fixation [1]. Widely used chemical absorbents include monoethanolamine (MEA), diethanolamine (DEA), and *N*-methyldiethanolamine. Additionally, amine solutions have been generally used in the economical production of CO<sub>2</sub>, and have been tested for the removal of CO<sub>2</sub> on a demonstration level.

However, the abovementioned technologies require a large amount of energy, especially in the regeneration process. In addition, the use of amines entails some problems related to amine degradation and corrosion of equipment [2]. An aqueous ammonia (NH<sub>3</sub>) solution can serve as an alternative for controlling the CO<sub>2</sub> emitted from flue gas, because it has a high absorption capacity and high absorption rate, and it does not cause significant corrosion [3].

Aqueous ammonia is an effective absorbent with suitable characteristics that has been used for a long time for capture of CO<sub>2</sub> and sulfur compounds from blast furnace gas and coke oven gas. Research on the use of aqueous ammonia for the absorption of CO<sub>2</sub> has made progress since the work of Yeh and Bai [4] and Yeh et al. [5]. Moreover, Resnik et al. [6] and Diao et al. [7] reported an aqueous ammonia process and ammonia scrubbing for CO<sub>2</sub> removal. Therefore, aqueous ammonia, which has low regeneration energy, is suggested for use in the process of CO<sub>2</sub> absorption at iron and steel factories that create large amounts of low- and medium-temperature waste heat [8].

Although a solution with a high ammonia concentration facili-

tates high CO<sub>2</sub> absorption efficiency, it causes ammonium ions to be lost as ammonia vapor, which in return results in a lower ammonia concentration in the solution and, therefore, a reduction in the CO<sub>2</sub> absorption. In previous studies, several materials that have glycol, glycerol, and ethylene glycol have been added to ammonia solutions to reduce its vaporization [2,9]. These materials have hydroxyl functional groups in the molecule.

Such solutions are expected to exhibit good performance in CO<sub>2</sub> absorption because of the interactions between the hydroxyl groups of the additives and ammonia via hydrogen bonding [9]. Ethylene glycol and glycerol are alcohols that have potential for use in the control of vapor pressure of ammonia and for the improvement of its CO<sub>2</sub> absorption characteristics. AMP (2-amino-2-methyl-1-propanol) has been chosen for comparing the absorption performance of amines with hydroxyl additives [2]. In these studies, various materials containing hydroxyl groups were used to control the vapor pressure of ammonia and improve the CO<sub>2</sub> absorption characteristics.

In various studies [10,11], small amounts of additives have been shown to enhance the rate of absorption of CO<sub>2</sub>. However, the absorbent mixtures have more complicated reaction mechanism than do single absorbents such as MEA, AMP, and NH<sub>3</sub>. The absorbent mixtures produce different results in terms of absorption kinetics.

To design appropriate acid gas treatment equipment such as for CO<sub>2</sub> absorption/regeneration processes, it is important to understand the CO<sub>2</sub> absorption kinetics in the absorbent mixture system.

Thus, in the present study, vaporization of aqueous ammonia solutions blended with AMP, ethylene glycol, and glycerol was characterized to confirm the suppression of the vaporization by means of additives. In addition, the rates of absorption of CO<sub>2</sub> in the aqueous ammonia solutions and blended absorbents (NH<sub>3</sub>/AMP, NH<sub>3</sub>/ethylene glycol, and NH<sub>3</sub>/glycerol) at 293, 303, 313, and 323 K were measured using a stirred-cell reactor. The kinetics and rate constants were

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determined by measuring their rate of CO<sub>2</sub> absorption.

## THEORETICAL BACKGROUND

### 1. Reaction Mechanism

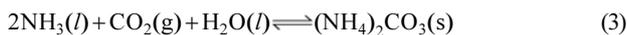
The reaction of CO<sub>2</sub> with AMP follows the formation of carbonate ion or the formation of carbamate and bicarbonate, and the reversion of carbamate to bicarbonate [18].

Caplow [13] and Dankwerts [17] proposed the zwitterion mechanism, which is the generally accepted mechanism for primary and secondary amines. Thus, the first step in the reaction of CO<sub>2</sub> with AMP is the formation of an intermediate zwitterion:



The zwitterion reaction is followed by base-catalyzed deprotonation by any base B', which could be amine, OH<sup>-</sup>, or H<sub>2</sub>O existing in the solution, to produce a carbamate ion and protonated base, because the carbamate of a sterically hindered amine is very unstable.

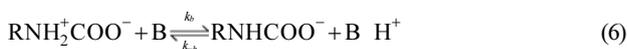
In the reaction of CO<sub>2</sub> with ammonia solution, ammonium carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>) and ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) can be produced as follows [4,7]:



In CO<sub>2</sub> scrubbing technology, ammonium carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>) and ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) may occur, depending on the operating conditions [4,15].

### 2. Determination of the Reaction Rate Constant

It is generally accepted that the zwitterion mechanism governs the formation of carbamate from primary and secondary amines. The first step in the reaction of CO<sub>2</sub> with amine is the formation of an intermediate zwitterion [15]:



The following deprotonation reactions occur in aqueous AMP solutions:



Based on the zwitterion mechanism and the assumption of a quasi-steady state, the expression for the CO<sub>2</sub> reaction rate is as follows:

$$r_A = \frac{k_2[\text{CO}_2][\text{RNH}_2]}{1 + k_{-1}/\sum k_b[\text{B}]} \quad (10)$$

When  $k_{-1}/k_b[\text{B}] \ll 1$ , the analysis is simplified to second-order kinetics, and the following equation can be used:

$$r_A = k_2[\text{CO}_2][\text{RNH}_2] \quad (11)$$

The reaction order and reaction rate constant can be found by

using the following specific absorption equation [16]:

$$N_A = \left(\frac{P_A}{H_A}\right)^{(m+1)/2} \left(\frac{2}{m+1} D_A k_{mn} C_B^n\right)^{1/2} \quad (12)$$

where  $n$  and  $m$  are reaction orders that are functions of amine concentration and partial pressure of CO<sub>2</sub> ( $P_A$ ), respectively. For a fast chemical reaction between the dissolved gas and a reactant, the specific absorption rate is as follows:

$$N_A = C_A^* \sqrt{D_A k_{ov}} \quad (13)$$

Similarly, by using Eq. (14), the overall reaction rate constant ( $k_{ov}$ ) can be calculated as follows:

$$k_{ov} = k_{mn} = (N_A H_A^{(m+1)/2} / P_A^{(m+1)/2} / D_A^{1/2})^2 \quad (14)$$

For fast pseudo- $mn$ -order reaction conditions, when the equilibrium pressure of CO<sub>2</sub> in solution is small compared with the absorption pressure, and when the gas-phase resistance is negligible, the absorption rate is given by Eq. (15). After integrating Eq. (16), a reaction rate constant ( $k_2$ ) can be obtained using Eq. (18).

$$-\frac{V_g}{RT} \left(\frac{dP_A}{dt}\right) = A_s \sqrt{D_A k_{ov}} \left(\frac{P_A}{H_A}\right) \quad (15)$$

$$-\left(\frac{dn}{dt}\right) = A_s \sqrt{D_A k_{ov}} C_A^* \quad (16)$$

$$\left(\frac{N_A H_A}{\sqrt{D_A P_A}}\right)^2 = k_{ov} \quad (17)$$

$$\left(\frac{N_A H_A}{\sqrt{D_A P_A}}\right)^2 = k_2 C_B \quad (18)$$

## EXPERIMENTAL

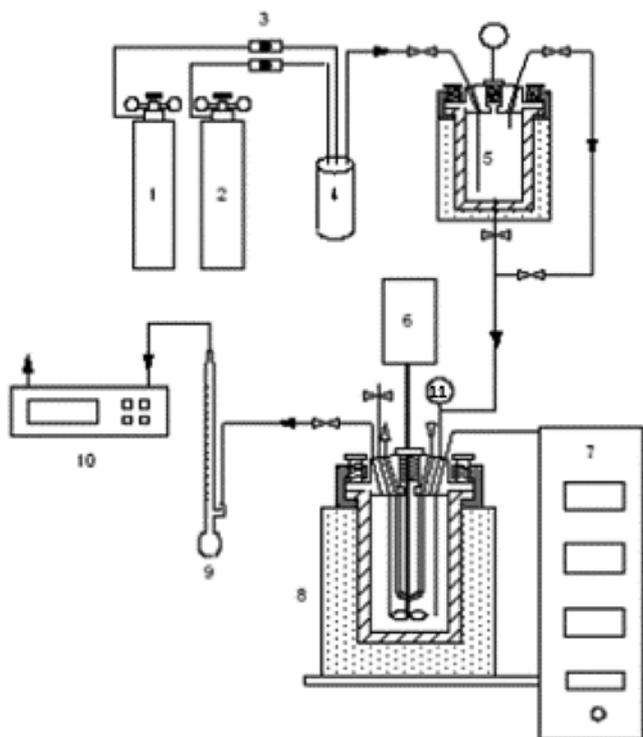
### 1. Materials

Analytical-grade AMP solution with a purity of 95 wt% was supplied by Acros Organics. Ammonia solution (28 wt%), glycerol (99 wt%), and ethylene glycol (99.5 wt%) were supplied by Junsei Chemical Co., Ltd. All chemicals were used without further purification. Aqueous solutions were prepared by using distilled water. Double-distilled water degassed by boiling was used to prepare the ammonia solutions. The CO<sub>2</sub> and N<sub>2</sub> gases were of commercial grade (purities of 99.9%). High-purity N<sub>2</sub>O (99.9%) gas was also used.

### 2. Selection of Additives

As mentioned earlier, the operation of the aqueous ammonia process requires special consideration with respect to the vaporization of NH<sub>3</sub> because of its high volatility. Although a solution with a high ammonia concentration enables high CO<sub>2</sub> absorption efficiency, ammonium ions are lost as ammonia vapor, resulting in reduced CO<sub>2</sub> absorption because of the lower concentration of the ammonia absorbent.

Alcoholic materials and hydroxides have strong polarities and form hydrogen bonds with the ammonia molecule. These effects after adding various materials containing hydroxyl groups are expected. They could reduce the vapor pressure of the ammonia solutions. Therefore, in this study, ethylene glycol, glycerol, and AMP were chosen as additives to reduce the vaporization of NH<sub>3</sub> in the continuous CO<sub>2</sub> absorption system. Each quantity of additive was



**Fig. 1. Schematic diagram of experimental apparatus for measurement of absorption rate.**

- |                             |  |
|-----------------------------|--|
| 1. N <sub>2</sub> cylinder  | 7. Controller of temperature and stirrer speed |
| 2. CO <sub>2</sub> cylinder | 8. Reactor (agitated vessel)                   |
| 3. Mass flow controller     | 9. Soap film flow meter                        |
| 4. Mixing chamber           | 10. Analyzer                                   |
| 5. Saturator                | 11. Pressure sensor                            |
| 6. Magnetic drive           |  |

based on the weight concentration.

The vaporization and CO<sub>2</sub> absorption test were conducted with blended solutions to confirm the effect on absorbent loss and CO<sub>2</sub> absorption rate.

### 3. Absorption Rate Measurement

The experimental apparatus for measuring the absorption rate is shown in Fig. 1. The reactor, with a height of 160 mm and i.d. of 95 mm, was located inside a temperature-controlled vessel, with four 5 mm wide glass plates attached to the inner wall of the reactor as baffles. The total volume of the reactor was about 1,134 cm<sup>3</sup> with an active interfacial area of 70.88 cm<sup>2</sup>. A two-blade impeller (70 mm × 20 mm) was installed at a location in the middle of the liquid level. The temperature was measured by a K-type thermocouple with an accuracy of 0.1 K. Pressure transducers (MGI/MGAMP series) with an accuracy of 0.1 kPa were installed in the reactor and the feeder to measure their pressure. The gas flow rates were controlled with

mass flow controllers (5850E, Brooks Instruments). CO<sub>2</sub> and N<sub>2</sub> gases were mixed in the mixing chamber and were allowed to flow into the saturator, which compensated for the gas temperature. After the reactor was purged with N<sub>2</sub>, 300 mL of an absorbent was injected, and then agitation was started by using the magnetic drive. The stirring speed was limited to 50 rpm to keep the gas-liquid interface planar and smooth. The temperature and stirring speed were controlled by an auto-control system. To achieve a good gas-liquid contact, the gas was introduced from the top of the reactor. The absorption rates were calculated from the difference in the amount of gas between the inlet and outlet. The flow rate of gas was measured with a soap film flow meter for the outlet gas. A ZRF model CO<sub>2</sub> analyzer (Fuji Electric, 0–20 vol%) was used to measure the CO<sub>2</sub> gas concentration at the reactor outlet.

### 4. Ammonia Vaporization Measurement

The experimental apparatus and the procedure that were employed in a previous study were used [2]. Vaporization of the NH<sub>3</sub>-water solution was measured by using a pressure data logger (PR2000, Madgetech, USA) with an accuracy of ±0.25% at 313 K. The measured data from the pressure transducer were stored automatically in a computer. The NH<sub>3</sub> gas concentration was measured with an NH<sub>3</sub> analyzer (accuracy of ±0.1%).

The vaporization experiments proceeded via three stages. The first stage was the measurement of the vaporization of the aqueous ammonia solutions and blended alcohol solutions with no CO<sub>2</sub> reaction. These vaporizations were observed through a pressure indicator and the results were then saved to a computer. The second stage was the measurement of the initial gaseous ammonia concentration when the absorbent reacted with CO<sub>2</sub>, which was measured for 30 min using an NH<sub>3</sub> analyzer. Lastly, the vaporizations of the aqueous ammonia solutions and blended alcohol solutions loaded with 1 mol L<sup>-1</sup> CO<sub>2</sub> were measured for 120 min.

## RESULTS AND DISCUSSION

### 1. Suppression of Ammonia Vaporization

Table 1 shows the effect of the vapor emitted from the aqueous ammonia solutions and blended alcohol solutions by continuing the CO<sub>2</sub> absorption process. Glycerol, ethylene glycol, and AMP played a role in reducing the vaporization at 313 K.

Table 1(a) presents the measurements at stable vaporization after 1 h, taken from the plotted data represented as the average and percentiles. The average of the measurement values for 9 wt% aqueous ammonia was 5.20 kPa and that of the blended solutions with ethylene glycol, AMP, and glycerol was 4.02, 4.47, and 1.29 kPa, respectively. The reduction in the vaporization added glycerol exhibited the most effective result compared with 9 wt% aqueous ammonia with the additions of 0.161 mol L<sup>-1</sup> ethylene glycol or 0.111 mol

**Table 1. Average of vaporization in continuous CO<sub>2</sub> absorption at 313 K**

	9 wt% NH <sub>3</sub>	9 wt% NH <sub>3</sub> + 0.161 M ethylene glycol	9 wt% NH <sub>3</sub> + 0.111 M AMP	9 wt% NH <sub>3</sub> + 0.109 M glycerol
(a) Non-reacted with CO <sub>2</sub> (%)	5.2015	4.0161	4.4680	1.2890
(b) Initial absorption with CO <sub>2</sub> (ppm)	37390	21380	27276	13418
(c) Loaded with 1 M CO <sub>2</sub> (%)	2.6189	1.1202	2.2240	0.1215

L<sup>-1</sup> AMP, which were decreased by 22.7% and 14.0%, respectively.

Table 1(b) shows the concentrations of ammonia gas discharged from the absorbents that reacted with CO<sub>2</sub> in the batch reactor. The ammonia gas was measured with an ammonia analyzer. The concentration of CO<sub>2</sub> gas that reacted with the aqueous ammonia solutions and blended alcohol solutions was 20.0 vol%, which was the same as that for coke oven gas. The experiments generally lasted for 30 min. When the average ammonia gas concentrations for the 9 wt% aqueous ammonia solution were calculated, those with the additions of either 0.161 mol L<sup>-1</sup> ethylene glycol, 0.109 mol L<sup>-1</sup> glycerol, or 0.111 mol L<sup>-1</sup> AMP were found to be 21 380, 13 418, and 27 276 ppm, respectively. Compared with the 9 wt% aqueous ammonia, the average ammonia gas concentrations with the additions of 0.161 mol L<sup>-1</sup> ethylene glycol and 0.111 mol L<sup>-1</sup> AMP decreased by 43% and 50%, respectively. Reduction of vaporization induced by 0.109 mol L<sup>-1</sup> glycerol was 64%, which was higher than that for the other additives. The absorbent with 0.109 mol L<sup>-1</sup> glycerol added was the most effective in reducing the ammonia vaporization, which was similar to the experiments that had no reaction with CO<sub>2</sub>.

Table 1(c) presents the stable vaporization of solutions loaded with 1 mol CO<sub>2</sub> after 1 h. The average for the 9 wt% aqueous ammonia solution was 2.62 kPa, and those of the solutions blended with 0.161 mol L<sup>-1</sup> ethylene glycol, 0.109 mol L<sup>-1</sup> glycerol, and 0.111 mol L<sup>-1</sup> AMP were 1.12, 0.12, and 2.23 kPa, respectively. Compared with the experiments with no CO<sub>2</sub> reaction, the average ammonia gas concentrations in the cases with addition of 0.161 mol L<sup>-1</sup> ethylene glycol and 0.111 mol L<sup>-1</sup> AMP decreased by 57% and 15%, respectively. The rate of decrease induced by 0.109 mol L<sup>-1</sup> glycerol was 93%, which exhibited the most effective reduction of vaporization.

As in the results, the vaporization of aqueous ammonia solution could be depressed by loading CO<sub>2</sub> and adding hydroxyl groups. The formation of ammonium carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>), ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>), and ammonium carbamate (NH<sub>2</sub>COONH<sub>4</sub>) could reduce the vapor pressure, depending on the decrease in free ammonia in the solution. In addition, the vapor pressure could be reduced by each of the hydroxyl functional groups that bonded with water molecules. In the process of CO<sub>2</sub> capture using aqueous ammonia solution, adding hydroxyl functional groups to the CO<sub>2</sub>-loaded aqueous ammonia solution was expected to reduce the absorbent loss and high efficiency of CO<sub>2</sub> absorption.

## 2. Kinetics of CO<sub>2</sub> Absorption by NH<sub>3</sub> Absorbents

To investigate the characteristic of CO<sub>2</sub> absorption by ammonia solutions with added AMP, ethylene glycol, and glycerol, absorption rate tests were conducted by varying the temperature and the additive concentration.

Andrew [20] and Derks et al. [16] observed the first-order reaction of ammonia with CO<sub>2</sub>. These studies observed that the aqueous ammonia solution reacts with CO<sub>2</sub> in the same order as MEA or DEA.

The CO<sub>2</sub>-NH<sub>3</sub> reaction has been studied [16,20] to check the validity of the method. It has been found to be first order with respect to CO<sub>2</sub> and NH<sub>3</sub>. Literature information confirms this reaction order.

The value of 1,956 m<sup>3</sup> kmol<sup>-1</sup> s<sup>-1</sup> for k<sub>2</sub> of the CO<sub>2</sub>-NH<sub>3</sub> reaction obtained at 313 K in the present work is in good agreement with the results of Derks et al. [16]. Specific absorption rates (N<sub>A</sub>, kmol m<sup>-2</sup> s<sup>-1</sup>) were obtained for the concentrations of each additive (1, 3, and 5 wt%) blended with 9 wt% NH<sub>3</sub> at several temperatures (293, 303, 313, and 323 K). Table 2 shows the unit conversion of each absorbent, and the results for the absorption rates are summarized in Table 3. The specific rate of CO<sub>2</sub> absorption into NH<sub>3</sub> was increased by all the additives. AMP showed the best performance in increasing the specific absorption rate of CO<sub>2</sub>. AMP added into ammonia solution reacts with CO<sub>2</sub> and it undergoes a zwitterion mechanism such as the CO<sub>2</sub>-ammonia reaction.

Using the results, the order with respect to the concentration of additives in the NH<sub>3</sub> solution was determined from Eq. (20) by plotting (N<sub>A</sub>H<sub>A</sub>/D<sub>A</sub><sup>0.5</sup>/P<sub>A</sub>)<sup>2</sup> against the concentration of each additive in 9 wt% NH<sub>3</sub> solution. The values of the diffusion coefficients of gas in liquid (D<sub>A</sub>) and Henry's law constants (H<sub>A</sub>) were obtained from the literature [16]. These plots, marked in Figs. 2, 3, and 4, show straight lines (correlation coefficient of 0.98). A plot of (N<sub>A</sub>H<sub>A</sub>/D<sub>A</sub><sup>0.5</sup>/

**Table 2. Unit conversion of each absorbent**

Absorbents (wt%)	Conversion/kmol m <sup>-3</sup>			
	NH <sub>3</sub>	AMP	Ethylene glycol	Glycerol
1		0.111	0.161	0.109
3		0.333	0.483	0.327
5		0.555	0.805	0.545
9	4.73			

**Table 3. Specific rates of CO<sub>2</sub> absorption into aqueous solutions with additives and temperatures**

Absorbent	N <sub>A</sub> of CO <sub>2</sub> /kmol m <sup>-2</sup> s <sup>-1</sup> × 10 <sup>5</sup>			
	293 K	303 K	313 K	323 K
NH <sub>3</sub> 9 wt%	0.76	0.82	0.86	0.95
+AMP (0.111 M)	0.88	0.96	0.99	0.99
+AMP (0.333 M)	1.07	1.14	1.19	1.22
+AMP (0.555 M)	1.27	1.36	1.41	1.42
+Ethylene glycol (0.161 M)	0.88	0.90	0.94	0.92
+Ethylene glycol (0.483 M)	1.02	1.06	1.10	1.11
+Ethylene glycol (0.805 M)	1.19	1.27	1.32	1.32
+Glycerol (0.109 M)	0.89	0.91	0.96	0.98
+Glycerol (0.327 M)	0.99	1.02	1.11	1.15
+Glycerol (0.545 M)	1.11	1.16	1.24	1.24

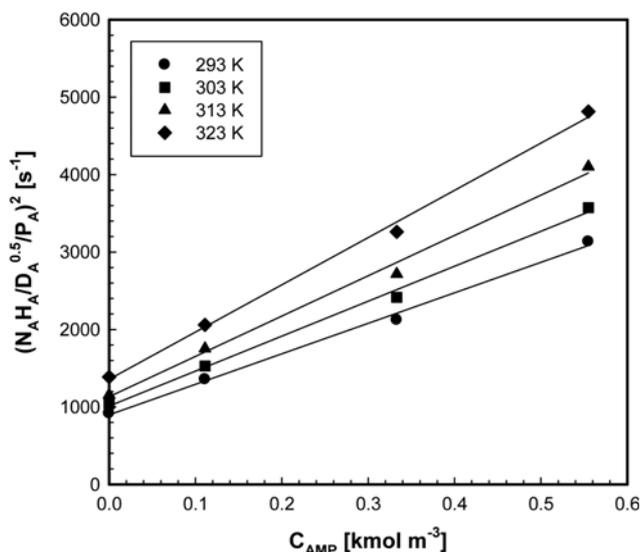


Fig. 2. Determination of reaction order with respect to the concentration of AMP in 9 wt% aqueous ammonia at various temperatures.

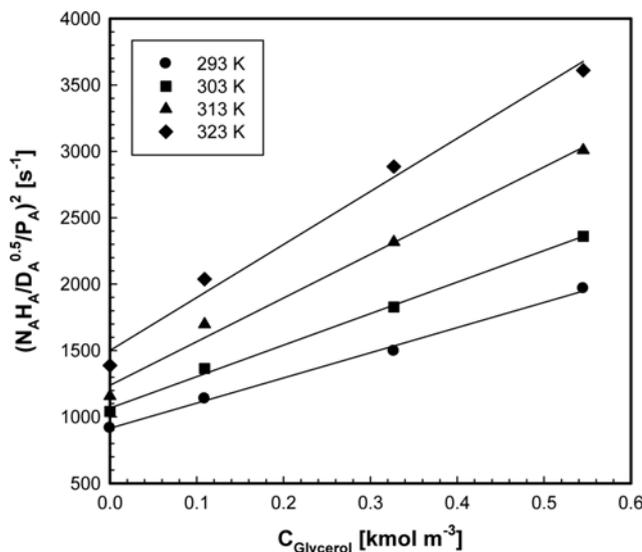


Fig. 4. Determination of reaction order with respect to the concentration of glycerol in 9 wt% aqueous ammonia at various temperatures.

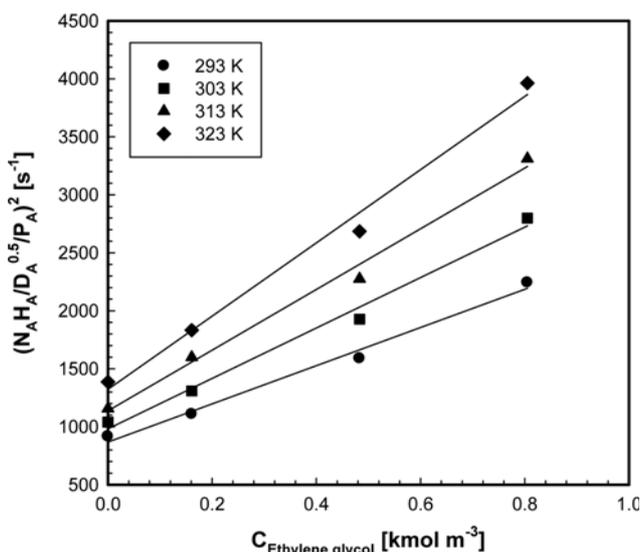


Fig. 3. Determination of reaction order with respect to the concentration of ethylene glycol in 9 wt% aqueous ammonia at various temperatures.

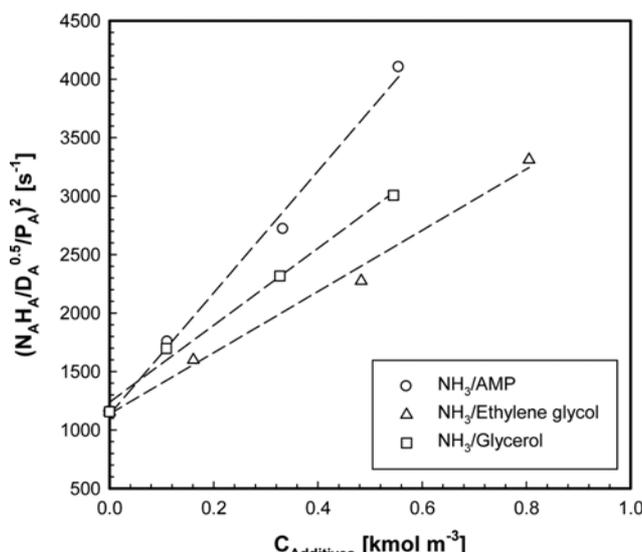


Fig. 5. Effect of additive concentration on  $(N_A H_A / D_A^{0.5} / P_A)^2$  at 313 K.

$P_A)^2$  versus the concentration of additive for  $\text{CO}_2$  absorption into blended solutions shows a linear trend (correlation coefficient  $>0.98$ ). The values of  $(N_A H_A / D_A^{0.5} / P_A)^2$  increase as the temperature or additive concentration increases.

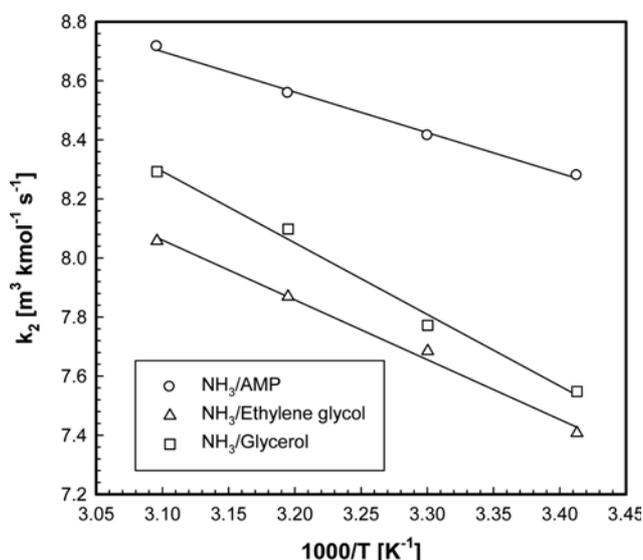
The  $k_2$  value for each additive was obtained by plotting  $(N_A H_A / D_A^{0.5} / P_A)^2$  versus the concentration of each additive at fixed temperature (293, 303, 313, and 323 K), as shown in Fig. 5. The calculated  $k_2$  values are 5,207, 2,616, and 3,288  $\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$  at 313 K for the additives of AMP, ethylene glycol, and glycerol blended with 9 wt%  $\text{NH}_3$ , respectively. These values are, respectively, about 160%, 33%, and 68% higher than that of aqueous ammonia solution without an additive. This indicates that each additive acts as an effective activator in the  $\text{NH}_3$  solution for its own absorption mechanism, as shown

by Eqs. (2) to (5). In addition, the solvation of  $\text{RNHCOO}$  formed between the polar solvent and the alkanolamine activates the  $\text{CO}_2$  absorption reaction given by Eq. (2) [18]. In the  $\text{NH}_3$  solution with added AMP, the  $\text{CO}_2$  absorption rate shows higher values than those with other added additives. This phenomenon could be partially explained by the shuttle mechanism by Astarita et al. [21]. The kinetics of the reaction between  $\text{CO}_2$  and ammonia/AMP might be quite complicated.  $\text{CO}_2$  first reacts with  $\text{NH}_3$ , which is more reactive than AMP, in the film close to the surface, and then transferred to the bulk liquid. In the bulk liquid,  $\text{CO}_2$  is released from  $\text{NH}_3$  and reacts with AMP, so that the  $\text{NH}_3$  can be shuttled back to the liquid film. As explained by this phenomenon, the reaction rate constants increased on addition of AMP, ethylene glycol, and glycerol.

Clearly, the rate of  $\text{CO}_2$  absorption into  $\text{NH}_3$  is increased by the use of additives such as AMP, ethylene glycol, and glycerol. The

**Table 4. Reaction rate constants for each additive at different temperatures**

Temperature/ K	$k_2/\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$		
	NH <sub>3</sub> /AMP	NH <sub>3</sub> /Ethylene glycol	NH <sub>3</sub> /Glycerol
293	3941	1648	1897
303	4511	2175	2373
313	5207	2616	3288
323	6098	3158	3995

**Fig. 6. Arrhenius plots for determining reaction rate constants.**

use of AMP as an additive is the most effective way to increase the absorption rate among the three additives used in these tests.

Table 4 shows the reaction rate constants for each additive at different temperatures. In addition, a linear regression analysis for Arrhenius plots, shown in Fig. 6, leads to the following expressions for the reaction-rate-constant equations of addition of hydroxyl groups to 9 wt% NH<sub>3</sub> solution:

$$k_{2, \text{NH}_3/\text{AMP}} = 4.565 \times 10^5 \exp(-1396.5/T) \quad (19)$$

$$k_{2, \text{NH}_3/\text{ethylene glycol}} = 1.499 \times 10^6 \exp(-1978.7/T) \quad (20)$$

$$k_{2, \text{NH}_3/\text{glycerol}} = 7.078 \times 10^6 \exp(-2413.3/T) \quad (21)$$

The values of activation energies obtained from the Arrhenius plots and reaction rate constant equations were 11.5, 19.8, and 16.2 kJ mol<sup>-1</sup>, respectively, for AMP, ethylene glycol, and glycerol blended with 9 wt% NH<sub>3</sub>.

## CONCLUSION

To reduce the vaporization of the absorbent, various compounds with hydroxyl groups were added to aqueous ammonia solution. The characteristics of CO<sub>2</sub> absorption into the blended absorbents and vaporization were investigated using a stirred-cell reactor. The reduction in the vaporization of 9 wt% aqueous ammonia solution with glycerol was higher than that with ethylene glycol and AMP. In addition, the absorption rate of aqueous ammonia solution with

AMP was higher than that with ethylene glycol or glycerol. In the results of these experiments, considering the vapor loss and absorption rate, glycerol was suitable for reduction of vapor pressure while maintaining an appropriate absorption rate. The addition of AMP, ethylene glycol, and glycerol to NH<sub>3</sub> increases the reaction rate constant by 160%, 33%, and 68% compared with NH<sub>3</sub> without an additive. Of the three aqueous ammonia solutions blended with AMP, ethylene glycol and glycerol, a blend of AMP and NH<sub>3</sub> shows the highest reaction rate for CO<sub>2</sub> removal. The reaction rate constants are given by  $k_{2, \text{NH}_3/\text{AMP}} = 4.565 \times 10^5 \exp(-1396.5/T)$ ,  $k_{2, \text{NH}_3/\text{ethylene glycol}} = 1.499 \times 10^6 \exp(-1978.7/T)$ , and  $k_{2, \text{NH}_3/\text{glycerol}} = 7.078 \times 10^6 \exp(-2413.3/T)$ .

## ABBREVIATIONS

- $A_S$  : interfacial area of gas in contact with liquid [m<sup>2</sup>]
- $C_A^*$  : dissolved gas concentration in equilibrium at the gas-liquid interface ( $C_A^* = P_A/H_A$ ) [kmol m<sup>-3</sup>]
- $C_B$  : total amine concentration [kmol m<sup>-3</sup>]
- $D_A$  : diffusion coefficient of gas in liquid [m<sup>2</sup> s<sup>-1</sup>]
- $H_A$  : Henry's law constant [kPa m<sup>3</sup> kmol<sup>-1</sup>]
- $k_{-1}$  : reverse first-order reaction rate constant [s<sup>-1</sup>]
- $k_2$  : second-order reaction rate constant [m<sup>3</sup> kmol<sup>-1</sup> s<sup>-1</sup>]
- $k_b$  : second-order reaction rate constant for base B [m<sup>3</sup> kmol<sup>-1</sup> s<sup>-1</sup>]
- $k_{ov}$  : overall pseudo-first-order reaction rate constant [s<sup>-1</sup>]
- $N_A$  : specific absorption rate [kmol m<sup>-2</sup> s<sup>-1</sup>]
- $P_A$  : CO<sub>2</sub> partial pressure kPa]
- $R$  : gas constant [J mol<sup>-1</sup> K<sup>-1</sup>]
- $T$  : temperature [K]
- $V_g$  : gas volume [m<sup>3</sup>]

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