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The absorption rate of $CO_2/SO_2/NO_2$ into a blended aqueous AMP/ammonia solution

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Abstract−The Inter-governmental Panel on Climate Change (IPCC) reported that human activities result in the production of greenhouse gases (CO_2, CH_4, N_2O and CFCs), which significantly contribute to global warming, one of the most serious environmental problems. Under these circumstances, most nations have shown a willingness to suffer economic burdens by signing the Kyoto Protocol, which took effect from February 2005. Therefore, an innovative technology for the simultaneously removal carbon dioxide (CO_2) and nitrogen dioxide (NO_2), which are discharged in great quantities from fossil fuel-fired power plants and incineration facilities, must be developed to reduce these economical burdens. In this study, a blend of AMP and NH_3 was used to achieve high absorption rates for CO_2, as suggested in several publications. The absorption rates of CO_2, SO_2 and NO_2 into aqueous AMP and blended AMP+NH_3 solutions were measured using a stirred-cell reactor at 293, 303 and 313 K. The reaction rate constants were determined from the measured absorption rates. The effect of adding NH_3 to enhance the absorption characteristics of AMP was also studied. The performance of the reactions was evaluated under various operating conditions. From the results, the reactions with SO_2 and NO_2 into aqueous AMP and AMP+NH_3 solutions were classified as instantaneous reactions. The absorption rates increased with increasing reaction temperature and NH_3 concentration. The reaction rates of 1, 3 and 5 wt% NH_3 blended with 30 wt% AMP solution with respect to $CO_2/SO_2/NO_2$ at 313 K were $6.05\sim8.49\times10^{-6}$, $7.16\text{-}10.41\times10^{-6}$ and $8.02\sim12.0\times10^{-6}$ kmol m^{-2} s^{-1}, respectively. These values were approximately 32.3-38.7% higher than with aqueous AMP solution alone. The rate of the simultaneous absorption of $CO_2/SO_2/NO_2$ into aqueous AMP+NH_3 solution was $3.83\text{-}4.87\times10^{-6}$ kmol m^{-2} s^{-1} at 15 kPa, which was an increase of 15.0-16.9% compared to 30 wt% AMP solution alone. This may have been caused by the NH_3 solution acting as an alternative for $CO_2/SO_2/NO_2$ controls from flue gas due to its high absorption capacity and fast absorption rate.

Key words: Carbon Dioxide, Sulfur Dioxide, Nitrogen Dioxide, Blended Gas, Simultaneous Absorption, 2-Amino-2-methyl-1-propanol, Ammonia

INTRODUCTION

According to the United Nations Framework Convention on Climate Change (UNFCCC) in Kyoto, a commitment to reduce CO_2 emissions by 6% below 1990 levels was made by several countries. Industrialized countries, who should take the lead in combating climate change and its adverse effects [1] because they have been responsible for the majority of historical cumulative emissions, therefore were given quantified obligations to reduce emissions in the Kyoto Protocol [2].

Recently, the State of World Forum (2009.8), held in Brazil Belo Horizonte, decided to reduce 80% of greenhouse gas emissions by 2020 in the Global 2020 Climate Leadership Campaign. There are various technologies being used to separate CO_2 from the flue gas of conventional fossil fuel fired power plants: chemical absorption, physical absorption, cryogenic methods, membrane separation and biological fixation [3]. The chemical absorption process is generally recognized as the most effective technology [4].

Aqueous MEA solution is the most frequently used alkanolamines absorbent, owing to its high reactivity with CO_2, low solvent cost and ease of regeneration [5]. However, the maximum CO_2 absorption capacity in MEA is limited by the stoichiometry to 0.5 mol CO_2/mol amine. A different class of chemical absorbents, sterically hindered amines, such as 2-amino-2-methyl-1-propanol (AMP), have been proposed as commercially attractive new CO_2 absorbent because of their advantages in absorption capacity, absorption rate, degradation resistance and ease of regeneration [6].

Previous investigations have shown that the CO_2 absorption load capacity of ammonia was twice that of AMP, with a much enhanced removal efficiency over that of MEA, the use of an anti-bubbling is also not required and AMP is much cheaper than MEA. It is also expected that AMP will be able to complement the weak point of the excessive energy consumption and the corrosion of reactor during the regeneration process of MEA.

Consequently, this study hopes to show that the addition of ammonia, which has excellent absorption efficiencies for CO_2, SO_2 and NO_2, will improve the AMP absorption ratio. The simultaneous absorption rates of $CO_2/SO_2/NO_2$ on the addition of NH_3 into aqueous AMP solutions were measured using a plane agitation absorption reactor, with the results compared with those for AMP alone. The performances were evaluated under various operating condi-

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tions in order to investigate the absorption characteristics of the absorbents for the removal of $CO_2/SO_2/NO_2$.

THEORETICAL BACKGROUND

The following reactions occur with CO_2 in aqueous solutions of primary alkanolamines [7].

$$CO_2+2RNH_2 \rightleftarrows RNHCOO^- + RNH_3^+ \quad (1)$$

The Zwitterion mechanism originally proposed by Caplow [8], and reintroduced by Danckwerts [7], is generally accepted as the mechanism for reaction (1).

$$CO_2+RNH_2 \rightleftarrows RNH_2+COO^- \quad (2)$$

$$RNH_2^+ + COO^- + B \rightleftarrows RNHCOO^- + B'H^+ \quad (3)$$

This mechanism is comprised of two steps: the reaction for the formation of the CO_2-amine Zwitterion, followed by base-catalyzed deprotonation of this Zwitterion [reaction (3)]. Here B′ is a base, which could be an amine, OH, or H_2O [9]. The equilibrium loading capacities of primary and secondary alkanolamines are limited by the stoichiometry of reaction (1) to 0.5 mol of CO_2/mol of amine. For normal primary amines, such as monoethanolamine (MEA), the carbamate formed from reaction (1) is quite stable. If the carbamate is unstable, as in the case of a hindered amine carbamate, such as AMP, it undergoes carbamate reversible reaction, as follows [10]:

$$RNHCOO^- + H_2O \rightleftarrows RNH_2 + HCO_3^- \quad (4)$$

Reaction (4) indicates that 1 mol of CO_2 is absorbed per 1 mol of hindered amine. However, a certain amount of carbamate hydrolysis [reaction (4)] occurs with all amines; therefore, the CO_2 loading may exceed stoichiometry (0.5), even with MEA, particularly at high pressures. Another alternative mechanism for the bicarbonate formation has been proposed by Chakraborty et al. [11].

$$RNH_2+CO_2+H_2O \rightleftarrows RNH_3^+ + HCO_3^- \quad (5)$$

The chemical reactions between CO_2 and NH_3 can be expressed by the following reactions [12,13]:

$$2NH_3(l)+CO_2(g)+H_2O(l) \rightleftarrows (NH_4)_2CO_3(s) \quad (6)$$

$$NH_3(l)+CO_2(g)+H_2O(l) \rightleftarrows NH_4HCO_3(s) \quad (7)$$

The wet method of ammonia scrubbing into flue gas to capture CO_2 produces ammonium carbonate ($(NH_4)_2CO_3$) and ammonium bicarbonate (NH_4HCO_3) [14].

The chemical reactions between SO_2 and AMP are based on the assumption that the SO_2 combines with water [15] in an aqueous alkali solution [16]. The reaction is as follows:

$$SO_2(g)+H_2O \rightleftarrows 2H^+ + SO_3^{2-} \quad (8)$$

$$H_2SO_3+2RNH_2 \rightleftarrows (RNH_3)_2SO_3 \quad (9)$$

The overall reaction of amine-.SO_2 is as follows:

$$SO_2+2RNH_2+H_2O \rightleftarrows 2RNH_3^+ + SO_3^{2-} \quad (10)$$

In addition, NH_3 absorbs SO_2 according to Eqs. (11) and (12) at room temperature and atmospheric pressure. The ammonium sulfite ($(NH_4)_2SO_3$) and ammonium bisulfite (NH_4HSO_3) are formed by reacting NH_3 with SO_2 [17].

$$2NH_3(g)+SO_2(g)+H_2O(g) \rightleftarrows (NH_4)_2SO_3(s) \quad (11)$$

$$NH_3(g)+SO_2(g)+H_2O(g) \rightleftarrows NH_4HSO_3(s) \quad (12)$$

The reaction between NO_2 and AMP is assumed to be based on the combination with water and aqueous nitric acid solution.

$$2NO_2(g) \rightleftarrows N_2O_4(g) \quad (13)$$

$$N_2O_4(g) \rightarrow N_2O_4(aq) \quad (14)$$

$$N_2O_4(aq)+H_2O \rightarrow HNO_2+HNO_3 \quad (15)$$

$$HNO_2+HNO_3+2RNH_2 \rightarrow 2RNH_3^+ + NO_2^- + NO_3^- \quad (16)$$

Reaction (17) indicates the reaction for the generalization of N_2O_4 from Eqs. (13)-(16)

$$N_2O_4(aq)+H_2O+2RNH_2 \rightarrow 2RNH_3^+ + NO_2^- + NO_3^- \quad (17)$$

In addition, ammonia absorbs NO_2 via reactions (18)-(19) at room temperature and atmospheric pressure.

$$2NH_3(g)+NO_2(g)+H_2O(g) \rightleftarrows (NH_4)_2NO_3(s) \quad (18)$$

$$NH_3(g)+NO_2(g)+H_2O(g) \rightleftarrows NH_4HNO_3(s) \quad (19)$$

For a chemical reaction between a gaseous constituent A and a liquid reactant B in an aqueous solution to yield a product P:

$$A+\upsilon B \xrightarrow{k_{mn}} \text{Products} \quad (20)$$

It is generally accepted that the Zwitterion mechanism governs the formation of a carbamate from primary and secondary amines. The first step in the reaction of CO_2 with AMP is the formation of an intermediate Zwitterion:

$$CO_2+RNH_2 \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} RNH_2^+COO^- \quad (21)$$

On the basis of the Zwitterion mechanism and the assumption of quasi-steady state for the concentration of the Zwitterion, the expression for the CO_2 reaction rate is as follows:

$$r_A = \frac{k_2[CO_2][RNH_2]}{1+k_{-1}/\sum k_b[B]} \quad (22)$$

When the term k−1/Skb[B]«1, the analysis is simplified to second-order kinetics, and the following equation can be used:

$$r_A = k_2[CO_2][RNH_2] \quad (23)$$

The influence on the absorption kinetics of all the chemical reactions between dissolved CO_2 and the reactants in solution is usually expressed by an "enhancement factor", E, over physical absorption [18]:

$$N_A = Bk_L C_A^+ \quad (24)$$

where E is a function of the Hatta number (H_a) and the instantaneous reaction enhancement factor (E_i) is defined as follows:

$$H_a = \left(\frac{2}{m+1} D_A k_{mn} (C_A^+)^{m-1} C_B^n\right)^{1/2} / k_L \quad (25)$$

$$E_i = \left(\frac{D_A}{D_B}\right)^{1/2} + \left(\frac{D_B}{D_A}\right)^{1/2} \frac{C_B}{\nu C_A^+} \quad (26)$$

where C_A^* is the concentration of the gas at the interface given by Henry' law:

$$C_A^+ = p_A/H_A \tag{27}$$

The experimental conditions were selected to ensure the absorption of CO_2 into amine solutions in a region of fast pseudo mn- order reaction was in the range of H_a between 3 and E_i. If the value of H_a is within this range, E becomes equal to H_a, and the following specific absorption rate is obtained [18,19]:

$$N_A = \left(\frac{p_A}{H_A}\right)^{(m+1)/2}\left(\frac{2}{m+1}D_A k_{mn} C_B^n\right)^{1/2} \tag{28}$$

The slope of the straight line fitting the data of ln versus ln will give an order of m with respect to the dissolved gas concentration. The order of n with respect to the amine concentration can also be found in an analogous manner by plotting versus ln. For a fast chemical reaction between the dissolved gas and a reactant, the specific absorption rate is as follows [18-21]:

$$N_A = C_A^+\sqrt{D_A k_{ov}} \tag{29}$$

Similarly, using reaction 30, the overall reaction rate (k_{ov}) can be calculated, as follows:

$$k_{ov} = k_{mn} = (N_A H_A^{(m+1)/2}/p_A^{(m+1)/2}/D_A^{1/2})^2 \tag{30}$$

For fast pseudo-*mn*-order reaction conditions, when the equilibrium pressure of CO_2 contributed by the CO_2 in solutions is small compared to the absorption pressure, and where the gas phase resistance is negligible, the absorption rate is given by reaction 31 [15,16] After integrating reaction 28, a reaction rate constant (k_2) can be achieved from reaction 29.

$$-\frac{V_g}{RT}\left(\frac{dP_A}{dt}\right) = A_s\sqrt{D_A k_{ov}}\left(\frac{P_A}{H_A}\right) \tag{31}$$

$$-\left(\frac{dn}{dt}\right) = A_s\sqrt{D_A k_{ov}}C_A^+ \tag{32}$$

$$\left(\frac{N_A H_A}{\sqrt{D_A}P_A}\right)^2 = k_{ov} \tag{33}$$

$$\left(\frac{N_A H_A}{\sqrt{D_A}P_A}\right)^2 = k_2 C_B \tag{34}$$

EXPERIMENTAL MATERIALS AND METHODS

1. Materials

Analytical grade AMP solution, with a purity of 99%, was supplied by Acros Organics. A 28 wt% ammonia solution was supplied by Junsei Chemical. Aqueous solutions were prepared with distilled water. The CO_2 and N_2 gases were of commercial grade, with purities of 99.99%.

2. 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 adhering to the inner wall of the reactor to act as baffles. The total volume of the reactor was about 1,134 cm^3, with an active interface area (*As*) of 70.88 cm^2. A two-blade impeller (70 mm×20 mm) was installed in the middle of the liquid level. The reactor 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 pressures. The gas flow rates were controlled by using mass flow controllers (5850E, Brooks Instruments). After the reactor had been purged with N_2, 300 mL of an absorbent was injected, and the reactor then agitated. The stirring speed was limited to 50 rpm to keep the gas-liquid interface planar and smooth. To achieve a good gas-liquid contact, the gas was introduced into the top of the reactor. The absorption rates were calculated from the difference in the amounts of gas between the inlet and outlet. A ZRF model CO_2 analyzer (Fuji Electric, 0-20 vol%) was used to measure the CO_2 gas concentration at the reactor outlet.

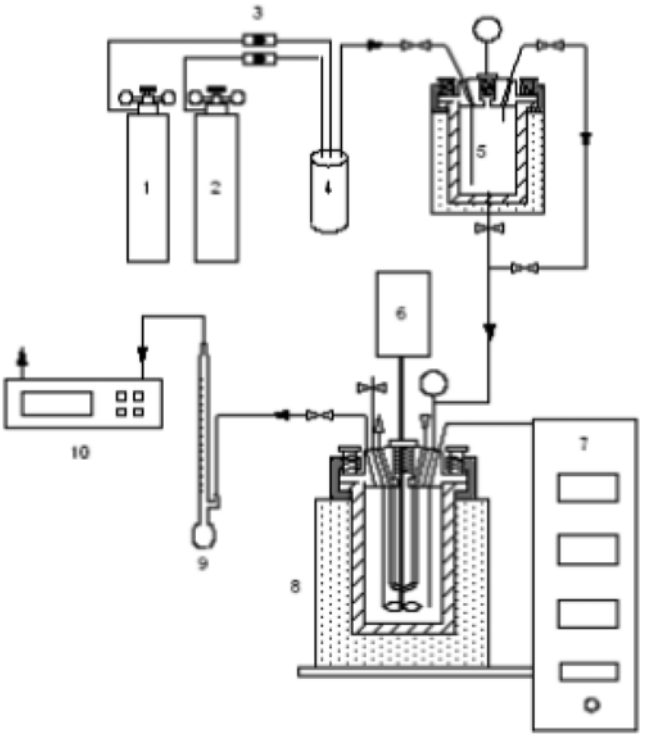

Fig. 1. Schematic diagram of the experimental apparatus for measurement of the absorption rate.

1. N_2 cylinder
2. CO_2, SO_2, and NO_2 cylinder
3. Mass flow controller
4. Mixing chamber
5. Saturator
6. Magnetic drive
7. Controller of temperature and stirrer speed
8. Reactor (Agitated vessel)
9. Soap film flow meter
10. Analyzer

EXPERIMENTAL RESULT

1. Reaction Region Separation

If the reaction rate between AMP and SO_2/NO_2 is fast pseudo-1st-order, like that of AMP/CO_2, the absorption rate of SO_2/NO_2 can be determined by measurement of the gas partial pressure and absorption, according to reaction (28).

To determine m-order and n-order to distinguish the reaction region of SO_2/AMP, the absorption rate is measured with 3, 5, 10 and 15 kPa of SO_2 and 10, 20 and 30 wt% of AMP at 313 K.

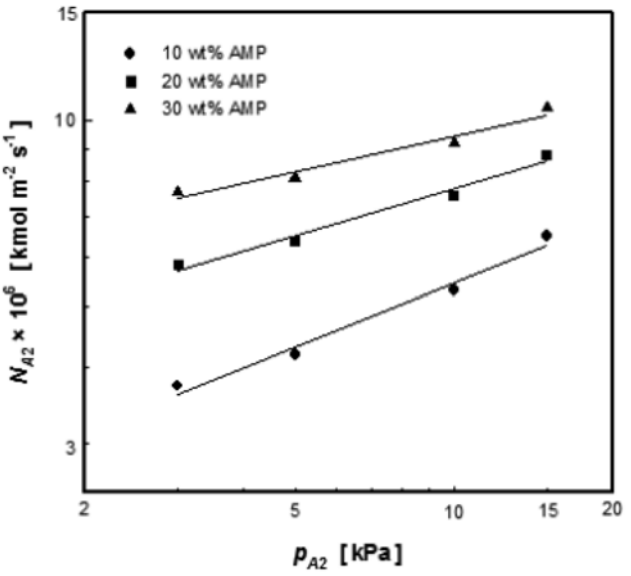

Fig. 2. Determination of m-order with respect to SO_2 partial pressure at different AMP concentrations and 313 K.

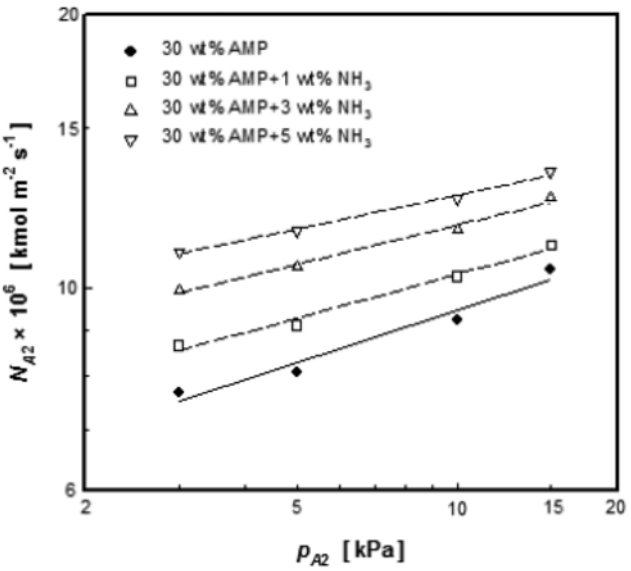

Fig. 3. Determination of m-order with respect to SO_2 partial pressure with different NH_3 concentrations at 313 K.

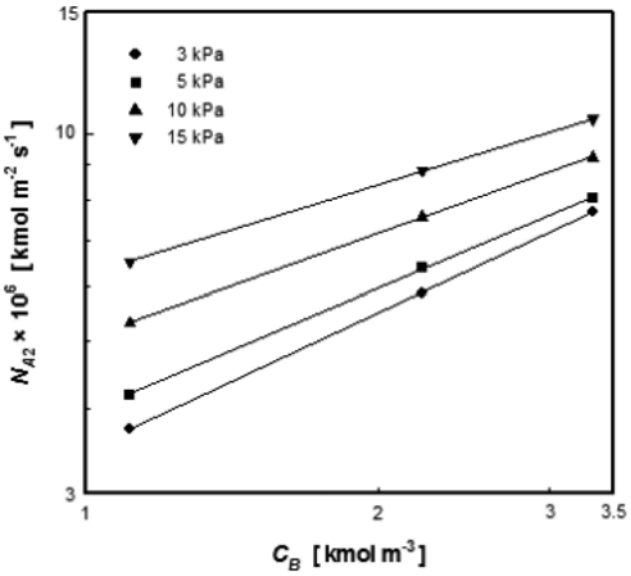

Fig. 4. Determination of m-order with respect to the AMP concentration at 313 K.

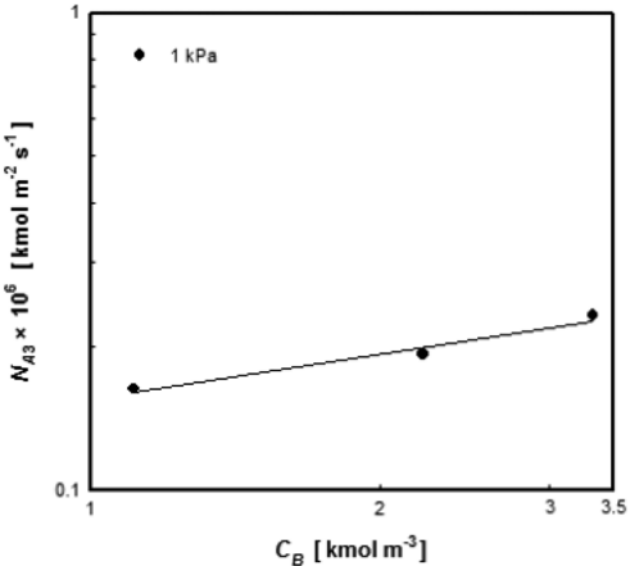

Fig. 5. Determination of n-order with respect to the AMP concentration at 313 K.

Fig. 2 shows a absorption rates between AMP solution and SO_2 as a function of the partial pressure of SO_2; the slopes of these plots were 0.345, 0.251 and 0.192, with reaction orders, m, of –0.31, –0.50 and –0.62 for 10, 20 and 30 wt% AMP, respectively.

Fig. 3, in addition, shows the absorption rates for 30 wt% AMP on the additions of 1, 3 and 5 wt% NH_3 as a function of the partial pressure of SO_2, with slopes of 0.160, 0.143 and 0.124 and reaction orders, m, of –0.68, –0.71 and –0.75, respectively. Therefore, as seen in Figs. 2 and 3, a reaction region between SO_2 and AMP is decided not to fast pseudo-1st-order because m in reaction (28) from chapter 2 is not 1. As SO_2 absorbed in alkali solution also is widely known for very fast reaction with water like hydration, a reaction region between AMP and SO_2 is supposed to be an instantaneous reaction.

Fig. 4 shows an n reaction order for the absorption rate (N_{A_2}) and amine concentration, which involved diffusivity and physical solubility. As seen in Fig. 4, all the plots give straight lines, with slopes of 0.659, 0.600, 0.502 and 0.435 at 3, 5, 10 and 15 kPa, respectively. In the relation between concentration (C_B) and absorption rate (N_{A_2}) for a 1st-order reaction, the slope of the plot by reaction equivalent ratio should be 0.5, but n-order for AMP concentration is not 1 for all pressure variables.

To find the m- and n-orders to distinguish the reaction region of NO_2/AMP, the absorption rate was measured with an NO_2 partial pressure of 1 kPa and AMP concentrations of 10, 20 and 30 wt% at 313 K. An experiment to find the m-order was impossible because

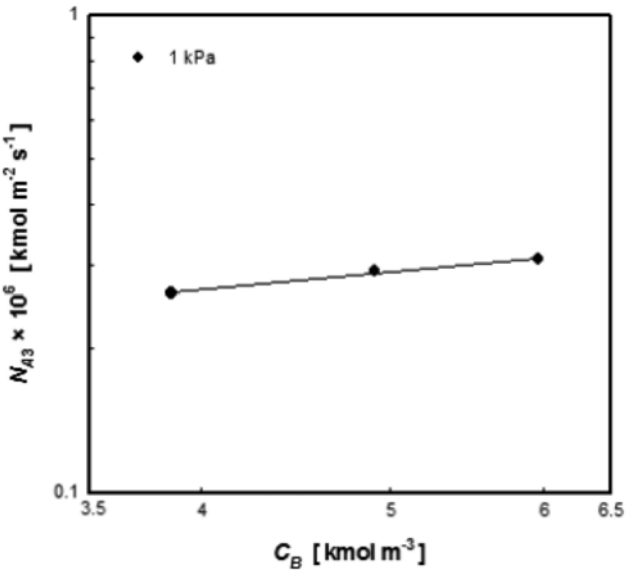

Fig. 6. Determination of n-order with respect to the concentration of NH_3 added with 30 wt% AMP at 313 K.

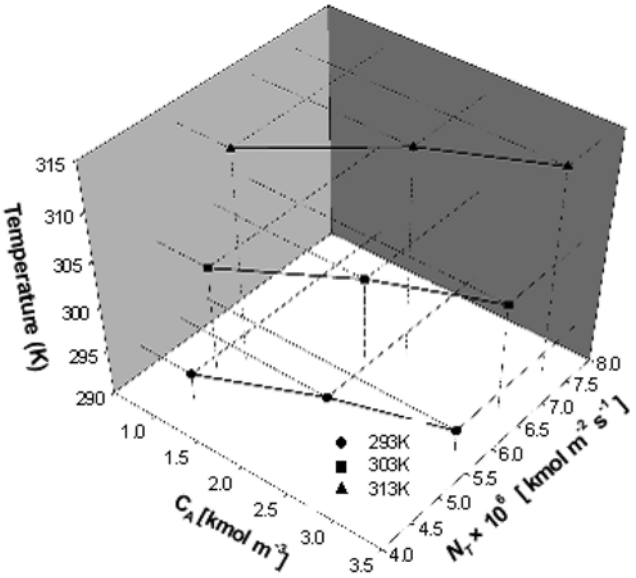

Fig. 7. The absorption rate of $CO_2/SO_2/NO_2$ into aqueous AMP solution as a function of the AMP concentration (10, 20 and 30 wt%) at 303 K.

of the low NO_2 concentration, so the reaction follows an n-order. Therefore, an experimental n-order reaction for the absorption (N_{A_3}) and amine concentration (C_B) was performed for the absorption reaction between the gas and liquid phase.

Figs. 5 and 6 show the absorption rates between 30 wt% AMP solution and NO_2 with the addition of NH_3 to the 30 wt% AMP solution to determine the n-order. As seen in Fig. 5 and Fig. 6, the plots give a straight line, with slopes of 0.3130 and 0.3777, respectively, with 30 wt% AMP on the addition of 1, 3 and 5 wt% NH_3. In the relation between the concentration (C_B) and absorption rate (N_{A_3}) for a 1st-order reaction, the slope of the plot by reaction equivalent ratio should be 0.5, but the n-order is not 0.5 from this result. Therefore, the reaction region between NO_2 and AMP is not fast 1st-order, but an instantaneous reaction.

2. Effect of NH_3 Addition

Absorption rate tests of the complex gas ($CO_2/SO_2/NO_2$) into aqueous AMP containing NH_3 as an additive were conducted under many conditions. The AMP concentrations were 10, 20 and 30 wt%, and those of the NH_3 additive 1, 3 and 5 wt%. The absorption rates of $CO_2/SO_2/NO_2$ were measured at an NO_2 partial pressure of 1 kPa, and because of the low gas pressure in the cylinder, the effect of NO_2 cannot be tested at high partial pressures. However, the experimental error is large and the experiment hard to conduct; therefore, the experiments with low partial pressure of NO_2 were excluded from this study. Similarly to another test using a single gas, the phenomenon of resistance was disregarded at the gas-liquid interface, with the stirring speed limited to 50 rpm to maintain a planar and smooth gas-liquid interface.

To observe the effects of the concentration of the NH_3 added to the AMP solution, the partial pressures of $CO_2(p_{A_1})$, $SO_2(p_{A_2})$ and $NO_2(p_{A_3})$ were fixed at 15, 1 and 1 kPa, respectively. Figs. 7 and 8 show the absorption rates of CO_2 into aqueous AMP solutions as a function of the AMP (10, 20 and 30 wt%) and NH_3 (1, 3 and 5 wt%) concentrations.

Fig. 7 shows the absorption rates as a function of the AMP concentration (10, 20 and 30 wt%). The simultaneous absorption rates of $CO_2/SO_2/NO_2$ were 4.51 to 5.42×10^{-6}, 5.18 to 6.65×10^{-6} and 5.65 to 7.37×10^{-6} kmol m^{-2} s^{-1}, respectively, and generally increased with increasing AMP concentration. As shown in Fig. 7, the increases in the rates of absorption as a function of temperature, presented in the Z axis, were smaller than those due to changes in the solution concentrations. This was a result of the promotion of mass transfer with increasing concentration gradient. Also, the absorption of $CO_2/SO_2/NO_2$ into the absorbent causes increases the temperature, and therefore, increases the reaction rates, which is why the absorption rates increased.

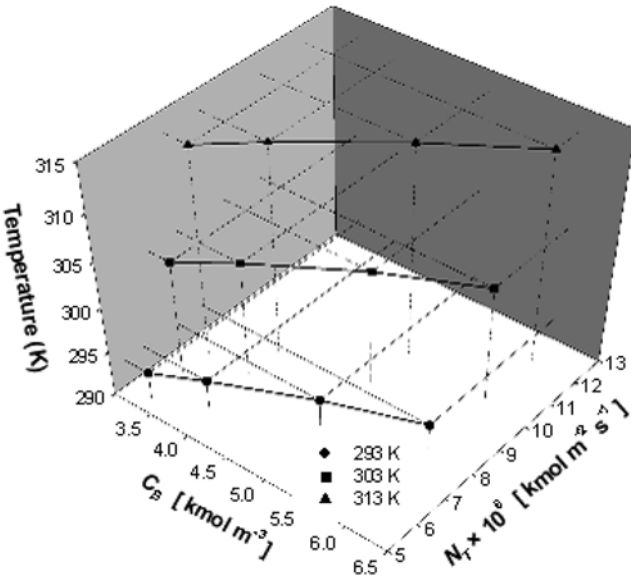

Fig. 8. The absorption rates of $CO_2/SO_2/NO_2$ into aqueous AMP+ NH_3 solution as a function of the NH_3 concentration (1, 3 and 5 wt%) at 303 K.

Fig. 8 compares the absorption rates of CO_2 into 30 wt% AMP on the addition of 1, 3 and 5 wt% NH_3 solution compared to that of 30 wt% AMP solution alone. On the addition of 1, 3 and 5 wt% NH_3, the simultaneous absorption rates of $CO_2/SO_2/NO_2$ were 6.05 to 8.49×10^{-6}, 7.16 to 10.41×10^{-6} and 8.02 to 12.0×10^{-6} kmol m^{-2} s^{-1}, respectively, increases of about 32.3 to 38.7% due to the addition of NH_3. Also, the absorption rates increased with increasing temperature, but these variations were smaller than those with respect to concentration. However, on increasing the temperature, the range of variation also increased because the activation energy (E_{NH_3}) of NH_3 is larger than that of AMP (E_{AMP}); therefore, the contribution of NH_3 increases the absorption rates. The simultaneous absorption rates of $CO_2/SO_2/NO_2$ increased with concentration of solution, and that of CO_2 into the 30 wt% AMP solution with the addition of NH_3 was faster than that with AMP solution alone. Therefore, the addition of NH_3 increases the simultaneous absorption rates of $CO_2/SO_2/NO_2$ into AMP solution.

3. Effect of CO_2 Partial Pressure

Absorption rate tests of complex gas into aqueous AMP containing NH_3 as an additive were conducted under numerous conditions, with the influence of the CO_2 concentration observed. Figs. 9-10 show the absorption rates of CO_2 with respect to the AMP and NH_3 solution concentrations; the variables during these experiments were: NO_2 1 kPa, AMP concentrations of 3, 5 and 10 wt%, 1 wt% NH_3 in 10 wt% AMP solution and CO_2 partial pressures of 5, 10 and 15 kPa.

Fig. 9 shows the absorption rates of the complex gas into solutions as a function of the CO_2 partial pressure. The absorption rates of $CO_2/SO_2/NO_2$ into 3-10 wt% AMP were 1.54 to 1.92×10^{-6} and 3.83 to 4.87×10^{-6} kmol m^{-2} s^{-1} at 5 and 15 kPa, respectively. As the AMP concentration and CO_2 partial pressure were increased, the absorption rates of the complex gas also increased. The absorption rate into 10 wt% AMP with the addition of NH_3 as a function of the CO_2 partial pressure (5-15 kPa) was 2.31 to 5.73×10^{-6} kmol

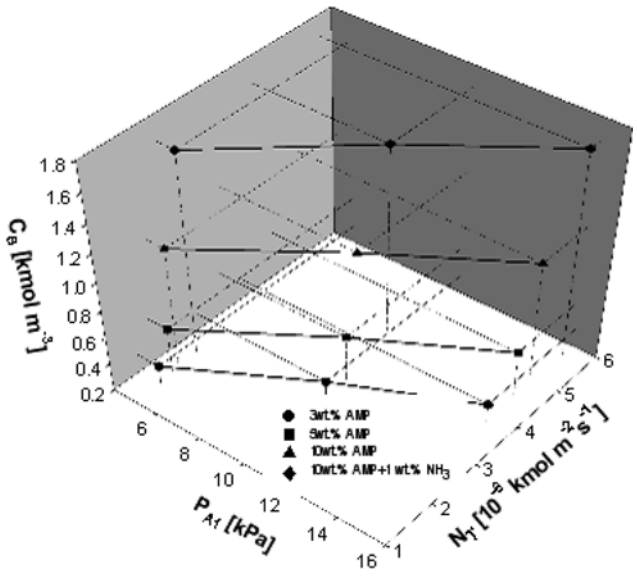

Fig. 9. The absorption rates of $CO_2/SO_2/NO_2$ into aqueous AMP and AMP+NH_3 solutions as a function of the pressure of CO_2 at 303 K.

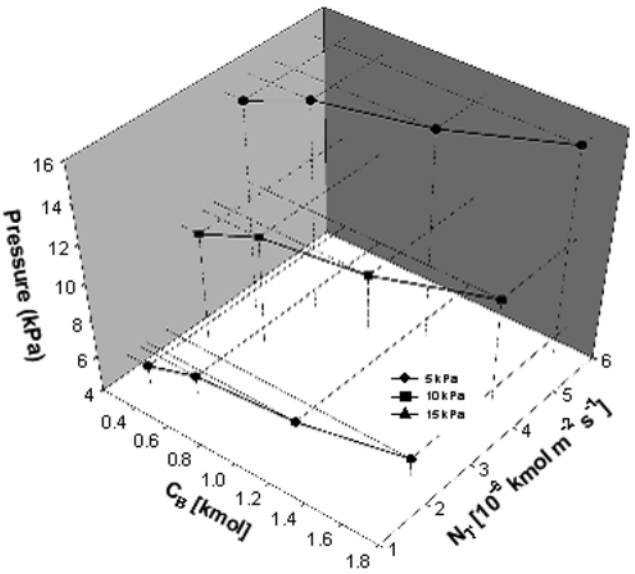

Fig. 10. The absorption rates of $CO_2/SO_2/NO_2$ into aqueous AMP and AMP+NH_3 solution as a function of the concentrations of AMP and NH_3 at 303 K.

m^{-2} s^{-1}. These results show that the increase in the absorption rate was higher than those at the partial pressures for SO_2 and NO_2. In this case, NH_3 dominates the CO_2 in the reaction because the partial pressures of SO_2 and NO_2 were lower than 1 kPa. However, as a function of the partial pressure of SO_2, because the partial pressure of SO_2 was relatively high, the NH_3 has an effect on the absorption of SO_2 into solution. Conversely, the absorption rates of SO_2 and NO_2 were almost uniform, but that of CO_2 was increased. Because the partial pressures of SO_2 and NO_2 were 1 kPa, which was lower than that of CO_2, the absorption of SO_2 was dominated by a hydration reaction; therefore, SO_2 had no effect on the partial pressure of CO_2.

Fig. 10 shows the absorption rate as a function of the partial pressure of CO_2 from the results in Fig. 9, showing increased absorption rates with increasing concentrations of AMP and NH_3. In general, the simultaneous absorption rates of $CO_2/SO_2/NO_2$ were increased by increasing the partial pressure of CO_2, as indicated on the Z axis, and the rate of increased with 10 wt% AMP+1 wt% solution more than with 10 wt% AMP solution alone. Therefore, the addition of NH_3 into AMP solution is an effective means of enhancing the absorption rates of blended gases.

4. Effect of SO_2 Partial Pressure

To estimate the effects of the $SO_2(p_{A_2})$ partial pressures and NH_3 additive concentrations in 30 wt% AMP solution, the partial pressures of $CO_2(p_{A_1})$ and $NO_2(p_{A_3})$ were fixed at 15 and 1 kPa, respectively. Figs. 11-12 show the absorption rates of CO_2 into aqueous AMP solution as a function of the SO_2 partial pressure (1, 3 and 5 kPa) with 10 wt% AMP solution and NH_3 additive concentrations of 1, 3 and 5 wt%.

Fig. 11 shows the absorption rates of the blended gas into the AMP solution as a function of the SO_2 partial pressure. The absorption rates of $CO_2/SO_2/NO_2$ into 3-10 wt% AMP solution were 3.83 to 4.87×10^{-6} and 4.82 to 5.82×10^{-6} kmol m^{-2} s^{-1} at 1 and 5 kPa, respectively, and increased as the AMP concentration and SO_2 partial pres-

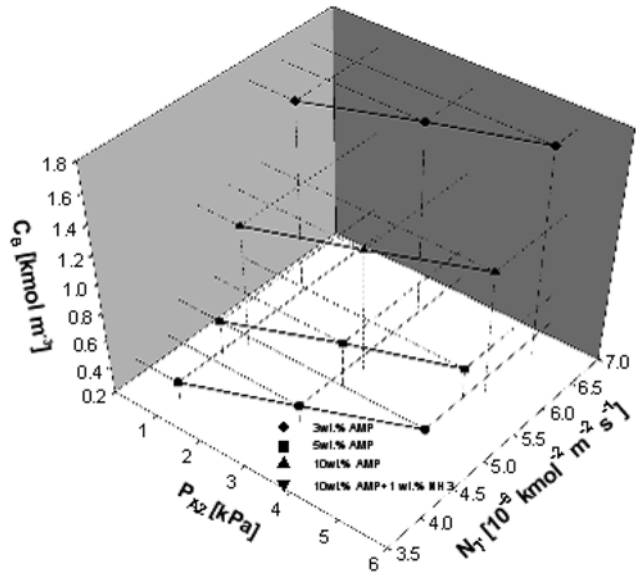

Fig. 11. The absorption rates of $CO_2/SO_2/NO_2$ into aqueous AMP and AMP+NH_3 solutions as a function of the partial pressure of SO_2 at 303 K.

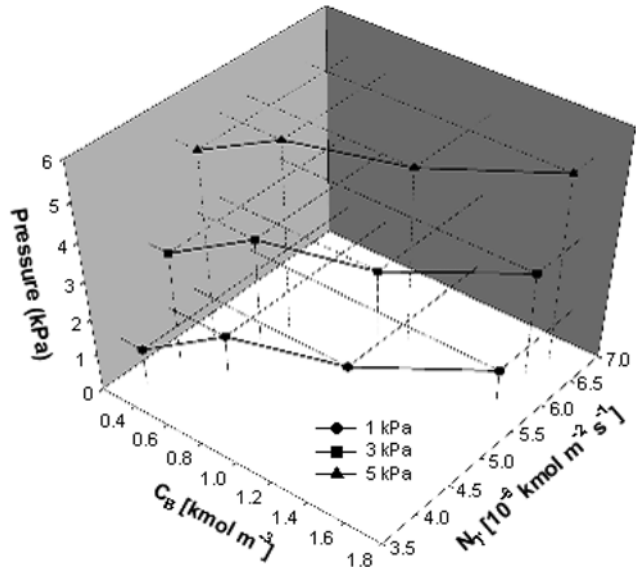

Fig. 12. The absorption rates of $CO_2/SO_2/NO_2$ into aqueous AMP and AMP+NH_3 solutions as a function of the AMP and NH_3 concentrations at 303 K.

sure increased. This resulted from the increased concentration gradient with increasing amount of SO_2 absorbed at the gas-liquid interface. On increasing the concentration of the NH_3 addition (1, 3 and 5 wt%), the simultaneous absorption rates of $CO_2/SO_2/NO_2$ ranged from 5.73 to 6.64×10^{-6} kmol m^{-2} s^{-1}, increases of about 12.4-15.0% for the range of SO_2 partial pressures (1, 3 and 5 kPa).

Fig. 12 shows the absorption rates as a function of the partial pressure of SO_2 from the results in Fig. 9, showing increases with increasing concentrations of AMP and NH_3. Also, the increased rate with 10 wt% AMP solution and the addition of 1 wt% NH_3 was higher than that with 10 wt% AMP solution alone, so the addition of NH_3 into 10 wt% AMP solution was effective in enhancing the absorption rates of blended gases.

CONCLUSION

NH_3 solution was added to aqueous AMP solution for the simultaneous absorption of $CO_2/SO_2/NO_2$. The absorption rate of $CO_2/SO_2/NO_2$ into the aqueous blended amine solutions was investigated by using a stirred cell reactor. The reaction region between SO_2/NO_2 and AMP was not fast 1st-order but an instantaneous reaction. The NH_3 additive concentrations to the 10 wt% AMP solution were 1, 3 and 5 wt%. The absorption rates of $CO_2/SO_2/NO_2$ into a blend of AMP and NH_3 as a function of temperature were 32.3 to 38.7% higher than with of AMP alone. The simultaneous absorption rates of $CO_2/SO_2/NO_2$ into aqueous AMP+NH_3 solution ranged from 3.83 to 4.87×10^{-6} kmol m^{-2} s^{-1} at 15 kPa, which was increased by 15.0 to 16.9% than with 30 wt% AMP solution alone. This means that NH_3 solution could act as an alternative control for $CO_2/SO_2/NO_2$ from a flue gas due to its high absorption capacity and fast absorption rate.

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