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# Mass Transfer Coefficients for CO<sub>2</sub> Absorption into Aqueous Ammonia Solution Using a Packed Column

Qing Zeng, Yincheng Guo,\* Zhenqi Niu, and Wenyi Lin

Department of Engineering Mechanics, Tsinghua University, Beijing 100084, China

**ABSTRACT:** The absorption of carbon dioxide into aqueous ammonia solution using a packed column was investigated. The volumetric overall mass transfer coefficients ( $K_G a_V$ ) for CO<sub>2</sub> absorption into aqueous ammonia solutions were evaluated over ranges of main operating variables, that is, up to 15 kPa partial pressure of CO<sub>2</sub>, 61–214 m<sup>3</sup>/(m<sup>2</sup>·h) gas flow rate, 0.76–3.06 m<sup>3</sup>/(m<sup>2</sup>·h) liquid flow rate, 2%–16% ammonia mass fraction, and 20–50 °C temperature. An empirical  $K_G a_V$  correlation for this system was proposed. Experimental results show that the mass transfer process in CO<sub>2</sub> absorption into aqueous ammonia solution is mainly controlled by the resistance in the liquid phase and the ammonia concentration has a great effect on the overall mass transfer coefficient.

## 1. INTRODUCTION

The global warming caused by increasing emission of carbon dioxide is one of the most serious environmental problems. Carbon dioxide discharged by the consumption of fossil fuel for power and heat production is said to occupy nearly 35% of the amount of discharged CO<sub>2</sub> all over the world.<sup>1</sup> Therefore, removal of carbon dioxide from flue gases is a key measure to reduce CO<sub>2</sub> emission. Several technologies of CO<sub>2</sub> sequestration include chemical solvent absorption methods, adsorption methods, cryogenic methods, membrane separation and biological fixation, and the O<sub>2</sub>/CO<sub>2</sub> combustion process. The absorption process is one of the most common industrial technologies today. Chemical solvent absorption methods are considered as a reliable method for reducing CO<sub>2</sub> emission from fossil fuel power plants.<sup>2</sup> Among the chemical solvent absorption processes, the monoethanolamine (MEA) scrubbing is widely used in the chemical engineering process of gas purification and carbon dioxide capture. However, the cost to capture CO<sub>2</sub> from flue gas of power plants is very high when using MEA scrubbing. It is estimated that the energy penalty from using this method for CO<sub>2</sub> capture from coal-fired power plants is about 15% to 35%.<sup>3,4</sup> Besides, the MEA process suffers disadvantages,<sup>5–7</sup> such as low CO<sub>2</sub> loading capacity, high equipment corrosion rate, amine degradation by SO<sub>2</sub>, NO<sub>2</sub>, HCl, and O<sub>2</sub> in the flue gas, and high energy consumption during absorption and regeneration. So, the MEA process requires that the flue gas be clean, therefore SO<sub>2</sub> and NO<sub>2</sub> must be removed first.

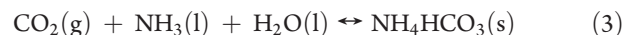
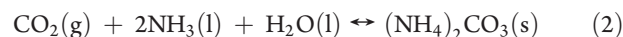
Some researchers found that ammonia seems to be an alternative and promising absorbent for removing CO<sub>2</sub> from flue gas.<sup>6</sup> Aqueous ammonia is not easily degraded, the energy input is much lower than that of the MEA process, and the ammonia solution does not have a corrosion problem. Three major acid gases, SO<sub>2</sub>, NO<sub>2</sub>, and CO<sub>2</sub>, will be captured in the aqueous ammonia process, which is expected to reduce the total cost and complexity of emission control systems.<sup>7</sup> Yeh and Bai<sup>8</sup> carried out experimental investigations of the ammonia and MEA capturing CO<sub>2</sub> in a bubble reactor. The tests showed that the NH<sub>3</sub> absorbent is superior to MEA absorbent in its capacity to absorb and remove CO<sub>2</sub> from flue gas systems. Yeh et al.<sup>9</sup>

performed CO<sub>2</sub> absorption and regeneration with aqueous ammonia in a semicontinuous flow reactor. It is found that the regeneration energy saving for the aqueous ammonia process is approximately 62% compared with the MEA process. Diao et al.<sup>10</sup> studied the mechanism and kinetics of the reaction between CO<sub>2</sub> and NH<sub>3</sub> solvent in a sieve-plate tower. Their experimental results showed that the CO<sub>2</sub> removal efficiency reaches its highest value at 33 °C.

The focus in the above literatures seems to lie on the determination of the removal efficiency and absorption capacity; the mass transfer efficiency of carbon dioxide absorption into aqueous ammonia solution is rarely reported. The motivation of this paper focuses on the mass transfer performance of the CO<sub>2</sub> absorption process using dumped packing and aqueous ammonia solution as the column internal and absorption solvent, respectively. The performance of the packed column was evaluated experimentally under various conditions to reveal the effects of process parameters, including CO<sub>2</sub> partial pressure in gas phase, gas flow rate, liquid flow rate, concentration of ammonia, and temperature.

## 2. ABSORPTION MECHANISM OF CO<sub>2</sub> INTO AQUEOUS AMMONIA SOLUTION

**2.1. Reactions of CO<sub>2</sub> with Ammonia.** The reaction between aqueous ammonia and carbon dioxide mainly occurred in the liquid phase of the gas–liquid interface, the reactions in the liquid phase of the CO<sub>2</sub>–ammonia system are given as follows:<sup>9,11–14</sup>



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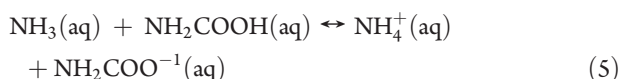
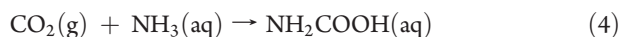
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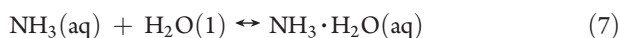
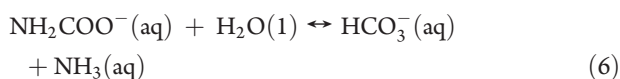
**Table 1. Kinetic Data for the Absorption of CO<sub>2</sub> into Aqueous Ammonia Solution**

<i>T</i> (K)	<i>C</i> <sub>NH<sub>3</sub></sub> (%)	[NH <sub>3</sub> ] (kmol m <sup>-3</sup> )	<i>k</i> <sub>2</sub> (m <sup>3</sup> kmol <sup>-1</sup> s <sup>-1</sup> )	<i>k</i> <sub>2</sub> [NH <sub>3</sub> ] (s <sup>-1</sup> )	<i>k</i> <sub>OH<sup>-</sup></sub> (m <sup>3</sup> kmol <sup>-1</sup> s <sup>-1</sup> )	[OH <sup>-</sup> ] (kmol m <sup>-3</sup> )	<i>k</i> <sub>OH<sup>-</sup></sub> [OH <sup>-</sup> ] (s <sup>-1</sup> )
293.15	2	1.16	300	348	5747.91	0.0045	25.87
293.15	4	2.30	300	690	5747.91	0.0063	36.21
293.15	6	3.43	300	1032	5747.91	0.0077	44.26
293.15	8	4.54	300	1362	5747.91	0.0088	50.58
293.15	12	6.71	300	2013	5747.91	0.0107	61.50
293.15	16	8.81	300	2643	5747.91	0.0123	70.70

Reaction 1 is actually composed of the following two steps:<sup>14,15</sup>



And then, NH<sub>2</sub>COONH<sub>4</sub> hydrolyzes in solution instantaneously and generates free ammonia:<sup>15,16</sup>



Reaction 4 is very fast and irreversible,<sup>14</sup> and reaction 5 is instantaneous. Reaction 6 is too slow to influence the rate of the absorption directly.<sup>11</sup> Therefore, the reaction between aqueous ammonia and carbon dioxide is mainly controlled by reaction 4. It is a second-order reaction with first-order for CO<sub>2</sub> and NH<sub>3</sub>, respectively.

On the other hand, reactions 2 and 3 are reversible, with ammonium carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>) or bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) as the products.<sup>12,13</sup> The forward reactions are dominant at room temperature.<sup>17</sup> The backward reactions occur at temperatures of around 38–60 °C.<sup>6</sup>

**2.2. Hydration of CO<sub>2</sub> in Aqueous Solution.** The ammonia solution is weakly alkaline, thus, the hydration of CO<sub>2</sub> in aqueous solutions would occur in the liquid phase; the reactions are given as follows:



The contribution of reaction 8 to the overall reaction rate is very small as the reaction has a very low rate constant (*k* = 0.026 s<sup>-1</sup> at 298 K) and may usually be neglected.<sup>18</sup>

**2.3. Reaction Rate for CO<sub>2</sub> Absorption into Aqueous Ammonia Solution.** On the basis of all considerations concerning the various reactions with CO<sub>2</sub> in aqueous ammonia, the reaction rate for CO<sub>2</sub> absorption into ammonia solution mainly controlled by the reactions are given in eq 4 and eq 9. The reaction rate for CO<sub>2</sub> absorption into aqueous ammonia solution can be described as follows:

$$r_{\text{CO}_2\text{-NH}_3} = k_2[\text{NH}_3][\text{CO}_2] \quad (10)$$

$$r_{\text{CO}_2\text{-OH}^-} = k_{\text{OH}^-}[\text{OH}^-][\text{CO}_2] \quad (11)$$

The overall reaction rate can be described as

$$\begin{aligned} r_{\text{OV}} &= r_{\text{CO}_2\text{-NH}_3} + r_{\text{CO}_2\text{-OH}^-} \\ &= k_2[\text{NH}_3][\text{CO}_2] + k_{\text{OH}^-}[\text{OH}^-][\text{CO}_2] \end{aligned} \quad (12)$$

where the values for rate constant *k*<sub>2</sub> for reaction between CO<sub>2</sub> and ammonia is about 300 L/(mol·s) in 20 °C.<sup>11</sup> The kinetic rate constant *k*<sub>OH<sup>-</sup></sub> can be described in terms of temperature:<sup>19</sup>

$$\log_{10}(k_{\text{OH}^-}) = 13.635 - 2895/T \quad (13)$$

The value of *k*<sub>OH<sup>-</sup></sub> equals to 5747.91 m<sup>3</sup>/(kmol·s) when the temperature is 20 °C. The hydroxyl ion concentration and the pH value of aqueous ammonia are estimated by the following relations:

$$[\text{OH}^-] = \sqrt{K_b[\text{NH}_3]} \quad (14)$$

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10} \frac{K_w}{[\text{OH}^-]} \quad (15)$$

where *K*<sub>b</sub> represents the ionization equilibrium constant of the aqueous ammonia and the value of *K*<sub>b</sub> is 1.710 × 10<sup>-5</sup> at 20 °C. The *K*<sub>w</sub> is the dissociation constant of water which responds to changes in temperature, and the value of *K*<sub>w</sub> equals to 10<sup>-14</sup> in the room temperature.

The calculated kinetic data for the absorption of CO<sub>2</sub> into aqueous ammonia at 20 °C are given in Table 1. The value of *k*<sub>OH<sup>-</sup></sub> [OH<sup>-</sup>] is much smaller than that of *k*<sub>2</sub>[NH<sub>3</sub>] as the reaction has a very low hydroxyl ion concentration. The contribution of reaction 6 to the overall reaction rate is less than 7%. Thus, the reaction rate between CO<sub>2</sub> and ammonia solution is mainly controlled by reaction 4 and the action of CO<sub>2</sub> with OH<sup>-</sup> ion can be neglected.

Then, the overall reaction rate can be approximately described as

$$r_{\text{OV}} = r_{\text{CO}_2\text{-NH}_3} = k_2[\text{NH}_3][\text{CO}_2] \quad (16)$$

The reaction between NH<sub>3</sub> and CO<sub>2</sub> is very fast,<sup>14</sup> and the CO<sub>2</sub> concentration in the liquid phase can be assumed to be zero in the fast pseudo-first-order reaction regime.

To verify whether the absorption of CO<sub>2</sub> into aqueous ammonia occurs in the fast pseudo-first-order reaction regime (1 ≪ *Ha* ≪ β<sub>i</sub> or 2 < *Ha* < (β<sub>i</sub>)/(2)), some chemical kinetic parameters of the reaction between NH<sub>3</sub> and CO<sub>2</sub> are discussed according to Higbie penetration theory, where

$$\beta_i = \sqrt{\frac{D_{\text{CO}_2\text{L}}}{D_{\text{NH}_3\text{L}}}} + \frac{[\text{NH}_3]}{z[\text{CO}_2^i]} \sqrt{\frac{D_{\text{NH}_3\text{L}}}{D_{\text{CO}_2\text{L}}}} \quad (17)$$

The diffusivities of CO<sub>2</sub> and NH<sub>3</sub> will be taken as equal to simplify the argument, for they are only about 20% different in

fact.<sup>11</sup> As the value of the mole concentration of ammonia is bigger than 1.16 kmol/m<sup>3</sup> and the partial pressure of CO<sub>2</sub> is less than 15 kPa, the value of  $\beta_i$  is satisfied  $\beta_i > 100$ .

The Hatta number  $Ha$  is expressed as

$$Ha = \frac{\sqrt{k_2[\text{NH}_3]D_{\text{CO}_2\text{L}}}}{k_L} \quad (18)$$

The mass transfer coefficient in the liquid phase is expressed as

$$k_L = 2\sqrt{\frac{D_{\text{CO}_2\text{L}}}{\pi t_c}} \quad (19)$$

Thus,

$$Ha = \sqrt{\frac{\pi}{4} t_c k_2 [\text{NH}_3]} \quad (20)$$

where  $t_c$  is the contact time (given in seconds). In this study, the gas–liquid contact time is much bigger than 0.03 s and less than 20 s. Thus, the relationship of  $1 \ll Ha \ll \beta_i$  can be satisfied. Therefore, the absorption of CO<sub>2</sub> into ammonia occurs in the fast pseudo-first-order reaction regime where the enhancement factor  $\beta$  equals  $Ha$  and the carbon dioxide is completely exhausted in the liquid film, so the equilibrium mole fraction of CO<sub>2</sub> in the liquid phase ( $y^*$ ) can be assumed to be zero.

### 3. DETERMINATION OF OVERALL MASS TRANSFER COEFFICIENT

**3.1. Traditional Two-Film Theory.** The absorption of CO<sub>2</sub> into aqueous ammonia is a gas–liquid reaction. According to the two-film model,<sup>11,20,21</sup> a thin gas film exists on one side of the interface and a thin liquid film exists on the other side with the controlling factors being molecular diffusion through each of the films. In case of chemical absorption, the overall mass transfer coefficient is based on the individual gas, liquid-phase mass transfer coefficients, and the enhancement factor  $\beta$ .<sup>22–24</sup>

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{\beta k_L} \quad (21)$$

In a gas-absorption apparatus such as packed column, the effective gas–liquid interfacial area ( $a_V$ ) is considered as another important parameter in mass transfer process in addition to the mass transfer coefficients.<sup>23</sup> Transfer unit theory has been used for a number of years to design absorption columns, and it is in this theory where the  $K_G a_V$  appears in engineering design.<sup>22</sup> Therefore, it is more practical to determine the volumetric overall mass transfer coefficients ( $K_G a_V$ ):

$$\frac{1}{K_G a_V} = \frac{1}{k_G a_V} + \frac{H}{\beta k_L a_V} \quad (22)$$

Apparently, the overall coefficient  $K_G a_V$  can be directly determined from eq 22. However, this approach is not extensively used because experimental determinations of the individual mass transfer coefficients involve the use of extremely difficult techniques. In experiments, it is convenient to measure the mole fraction of CO<sub>2</sub> at the top and the bottom of the packed column, and the overall mass transfer coefficient can be determined based on the measured CO<sub>2</sub> concentration.

**3.2. Determination of Overall Mass Transfer Coefficient According to the Measured CO<sub>2</sub> Concentrations at the Top and Bottom of the Packed Column.** The overall mass transfer

coefficient is affected by three main factors, there is the interfacial area between gas phase and liquid phase, the resistance in the gas phase, and the resistance in the liquid phase. In the derivation of the overall mass transfer coefficient, it is assumed that the liquid flow rate is unchanged. So, the interfacial area between gas phase and liquid phase is unchanged. Then, the overall mass transfer coefficient is unchanged about the interfacial area between gas phase and liquid phase. In the process of absorption, the total gas flow rate is constantly changing due to CO<sub>2</sub> absorption into aqueous ammonia solution. However, the variation of the total gas flow rate along the height of the tower is little as the mole fraction of the inert gas of nitrogen in gas steam is above 85%. Therefore, there is a slight effect of gas flow rate on the total mass transfer resistance. Besides, as the liquid flow rate, the concentration of ammonia solution and the inlet CO<sub>2</sub> loading of the solution are regarded as unchanged, and the amount of the aqueous ammonia solution is very sufficient in the whole absorption process. Thus, it is considered that the overall mass transfer coefficient would not be significantly changed along the height of the tower.

Then, considering an element of column with height  $dh$  due to the inert gas flow rate is constant along the height of the tower, the mass balance can be given as follows:

$$dm_A = \Omega G_B dY = N_A a_V \Omega dh \quad (23)$$

and

$$G_B dY = K_G P a_V (y - y^*) dh \quad (24)$$

Where  $m_A$  represents the amount of carbon dioxide absorbed per unit time in kmol/h,  $Y$  is the mole ratio of component A,  $h$  is column height in m,  $G_B$  is inert gas flow rate in kmol/(m<sup>2</sup>·h),  $y$  is the mole fraction of component A in the gas stream.

From eq 24, the element of column  $dh$  can be determined as

$$dh = \frac{G_B}{K_G P a_V} \frac{dY}{(y - y^*)} \quad (25)$$

When used for the chemical absorption,  $y^*$  in eq 25 is assumed to be zero since the chemical reaction is fast.<sup>25,26</sup> Thus, eq 25 can be expressed as

$$dh = \frac{G_B}{K_G P a_V} \frac{dY}{y} \quad (26)$$

and

$$y = \frac{Y}{1 + Y} \quad (27)$$

Therefore,

$$\int_0^h dh = \frac{G_B}{K_G P a_V} \int_{Y_2}^{Y_1} \frac{dY}{\frac{Y}{1 + Y}} = \frac{G_B}{K_G P a_V} \int_{Y_2}^{Y_1} \frac{1 + Y}{Y} dY \quad (28)$$

and

$$h = \frac{G_B}{K_G P a_V} \left[ \ln \frac{Y_1}{Y_2} + (Y_1 - Y_2) \right] \quad (29)$$

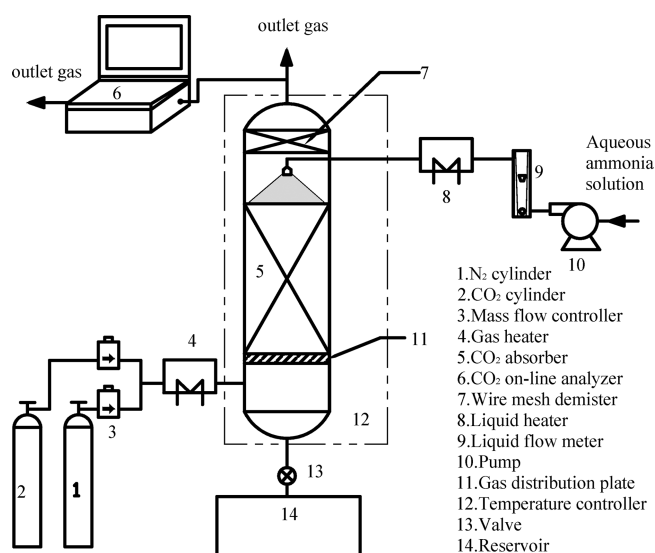


Figure 1. Schematic diagram of CO<sub>2</sub> absorption apparatus.

Then, the expression of  $K_G a_V$  can be obtained as follows

$$K_G a_V = \frac{G_B}{Ph} \left[ \ln \frac{Y_1}{Y_2} + (Y_1 - Y_2) \right] \quad (30)$$

In this paper, the CO<sub>2</sub> concentration at the top and bottom of the column was measured and used for evaluating the  $K_G a_V$  value according to eq 30.

#### 4. EXPERIMENTAL SETUP

The schematic diagram of the experimental setup is shown in Figure 1. The packed column was made of stainless steel with measurements of 0.6 m high and 0.1 m inside diameter. The packing height of the reactor was 400 mm, and the filler of the packed column was a ceramic Raschig ring with 8 mm inner diameter. The void fraction of packing layer is 0.64 (m<sup>3</sup>/m<sup>3</sup>) and the specific surface area is about 570 (m<sup>2</sup>/m<sup>3</sup>).

To control the reaction temperature, experiments were carried out under water bath conditions. The water bath was kept at constant temperature by the temperature controller and an electric heater, and also, the aqueous ammonia solution and inlet artificial flue gas of CO<sub>2</sub> and nitrogen mixture were kept at the same temperature with the heater. The simulated flue gas was mixed using two mass flow controllers with an accuracy of  $\pm 1.0\%$  S.P. which controlled the flow rates of CO<sub>2</sub> and nitrogen, respectively, and the mixture gas passed through the packed column from its bottom to the top. When the mixture gas reached a steady state, the heated aqueous ammonia solution was then pumped at a given flow rate to the column top. So, the mixture gas and the aqueous ammonia solution were in counter-flow pattern; it is beneficial to make CO<sub>2</sub> and aqueous ammonia contact and react thoroughly. The CO<sub>2</sub> concentration at the top of the column was determined by an infrared gas analyzer with an accuracy of  $\pm 2\%$  of the full-scale reading. Each absorption experiment was operated until the concentration of CO<sub>2</sub> in the gas phase reached a steady-state condition. All experiments were carried out under atmospheric pressure. Details of the operating conditions are shown in Table 2.

To validate the repeatability of the experimental system, one test case had been repeated three times, the experimental results

Table 2. Experimental Conditions of the Packed Column

parameter	condition
absorption solvent	aqueous ammonia solution
gas flow rate (m <sup>3</sup> /(m <sup>2</sup> ·h))	76–214
feed CO <sub>2</sub> partial pressure (kPa)	5, 10, 15
liquid flow rate (m <sup>3</sup> /(m <sup>2</sup> ·h))	0.76–3.06
aqueous ammonia concentration (%)	2, 4, 6, 8, 12, 16
temperature (°C)	20, 25, 30, 35, 40, 45, 50, 55

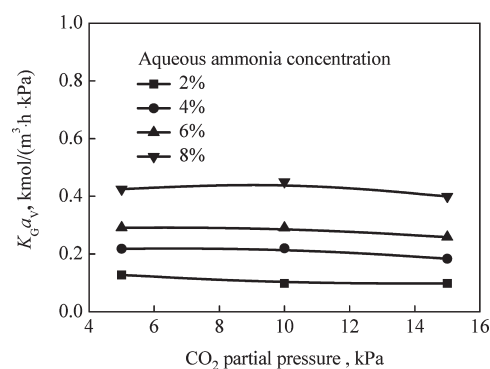


Figure 2. Effect of CO<sub>2</sub> partial pressure on the overall mass transfer coefficient.

show that the standard deviation of the CO<sub>2</sub> concentration at the top of the packed column is 0.14%; this indicates that the experiment system has a good repeatability.

#### 5. RESULTS AND DISCUSSION

Effects of different operating and design parameters on  $K_G a_V$  including CO<sub>2</sub> partial pressure, total gas flow rates, volume flow rate of aqueous ammonia solution, aqueous ammonia concentration, and reaction temperature were investigated.

**5.1. Effect of CO<sub>2</sub> Partial Pressure.** The effect of the CO<sub>2</sub> partial pressure on the overall  $K_G a_V$  value for CO<sub>2</sub> absorption using aqueous ammonia solution was shown in Figure 2. The  $K_G a_V$  value decreases slightly as the CO<sub>2</sub> partial pressure increases. Such behavior was also reported by Aroonwilas et al.<sup>27</sup> using AMP aqueous solution to absorb CO<sub>2</sub> in columns packed with structured packing. According to two-film theory, the mass-transfer resistance of the gas phase will decrease with the increasing CO<sub>2</sub> partial pressure. Logically, an increase in the CO<sub>2</sub> partial pressure allows more CO<sub>2</sub> molecules to travel from gas bulk to the gas–liquid interface, which would result in higher mass transfer performance. However, the rate of gas absorption is not exclusively dependent upon the mass transfer phenomenon in the gas phase. The mass transfer behavior in the liquid phase also plays an important role, and diffusion of solvent molecules in the liquid phase is restricted in comparison with that of CO<sub>2</sub> from the gas phase to the gas–liquid interface. Thus, mass transfer process of CO<sub>2</sub> absorption into aqueous ammonia solution is mainly controlled by the resistance of the liquid phase.

**5.2. Effect of Liquid Flow Rate.** Figure 3 shows the effect of liquid flow rate on the overall mass transfer coefficient. It is found that an increase in the liquid flow rate results in an increase in  $K_G a_V$  value. Previous studies on CO<sub>2</sub> absorption in rotating packed bed,<sup>28</sup> spray tower,<sup>29</sup> and membrane contactor<sup>30,31</sup> have



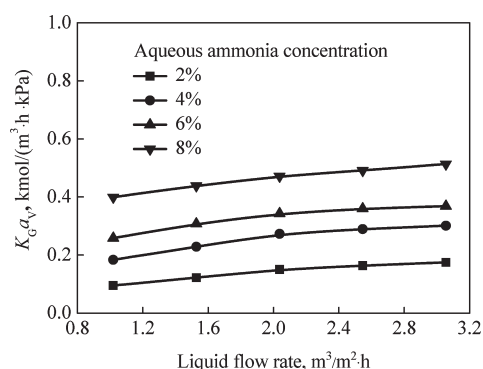


Figure 3. Effect of liquid flow rate on overall mass transfer coefficient.

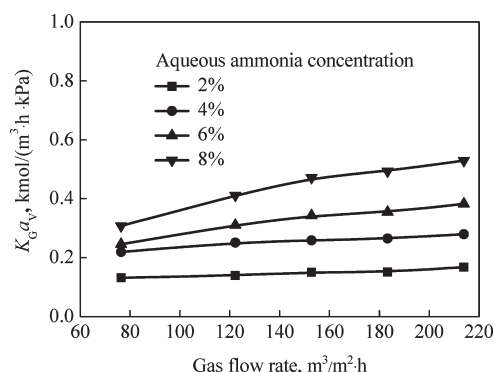


Figure 4. Effect of gas flow rate on overall mass transfer coefficient.

also revealed a similar trend of increasing  $K_G a_v$  with increasing liquid flow rate. With the liquid flow rate increasing, more liquid would be spread on the packing surface, and this leads to an increase in the interfacial area per unit volume ( $a_v$ ). Besides, the higher liquid flow rate leads to a higher liquid-side mass transfer coefficient ( $k_L$ ) in the case of liquid-phase controlled mass transfer. According to eq 22, both of the increases in  $k_L$  and  $a_v$  lead to a higher  $K_G a_v$  value.

**5.3. Effect of Gas Flow Rate.** Gas flow rate has an effect on the absorption performance in the packed column. Increase in the gas flow rate leads to a higher  $K_G a_v$  value especially when the ammonia concentration is high. As shown in the Figure 4, the gas flow rate has little effect on the overall mass transfer coefficient when the ammonia concentration is 2%. When the ammonia concentration increased to the values of 6% and 8%, the effect of gas flow rate on the overall mass transfer coefficient becomes apparent. This phenomenon indicates that the overall  $\text{CO}_2$  absorption rate is not only dependent upon the gas flow rate, it is also dependent upon the availability of reactive in the liquid.<sup>32</sup> When the ammonia concentration is low, the enhancement factor  $\beta$  would be small, which leads to higher value of the resistance in the liquid phase ( $H/(\beta k_L)$ ). Thus, the resistance in the gas phase can be negligible. So, the overall mass transfer coefficient is not dependent upon the gas flow rate when the ammonia concentration is low. Whereas, the resistance in the liquid phase ( $H/(\beta k_L)$ ) decreased with increasing concentration of the ammonia, the impact of the resistance in the gas phase becomes increasingly significant. Previous  $\text{CO}_2$  absorption studies in spray scrubber<sup>29,33</sup> and rotating packed bed<sup>34</sup> have also revealed a similar trend of increasing  $K_G a_v$  with increasing gas flow rate, but generally more rapidly.

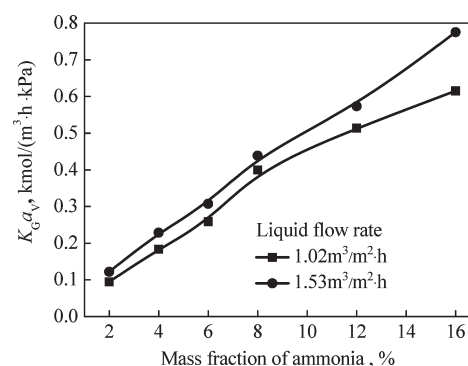


Figure 5. Effect of mass fraction of ammonia on overall mass transfer coefficient.

**5.4. Effect of Aqueous Ammonia Concentration.** Figure 5 shows the effect of the mass fraction of aqueous ammonia on the overall mass transfer coefficient. The aqueous ammonia concentration obviously has an impact on the absorption performance. As shown in Figure 5, an increase in the solvent concentration induces a higher  $K_G a_v$  value. When the mass fraction of ammonia increases from 2% to 16%, the  $K_G a_v$  value increases from nearly  $0.1 \text{ kmol}/(\text{m}^3 \cdot \text{h} \cdot \text{kPa})$  to  $0.6 \text{ kmol}/(\text{m}^3 \cdot \text{h} \cdot \text{kPa})$ . However, the finding that the  $K_G a_v$  increases as the ammonia concentration increases differs from what has been normally observed about  $\text{CO}_2$  absorption into MEA in the packed column and membrane contactor.<sup>22</sup> Previous research shows that the mass transfer coefficient decreases with MEA concentration increasing beyond  $5.0 \text{ mol/L}$  in a packed column. The reduction in the  $K_G a_v$  results from an increase in the viscosity of the liquid solution which causes the rate of molecular diffusion to reduce.<sup>22,35</sup> The increasing viscosity also tends to cause a reduction in the effective interfacial area between gas and liquid in the packed column.<sup>35</sup> However, the increasing  $K_G a_v$  of the packed column due to the increasing ammonia concentration seems to show that the effect of ammonia concentration on the liquid viscosity is less than the effect of MEA concentration.

Viscosity of aqueous ammonia solution was calculated with the correlations given by Frank et al.<sup>36</sup>

$$\mu^{\text{NH}_3\text{-sol}} = (0.67 + 0.78x_{\text{NH}_3}) \times 10^{-6} \exp\left(\frac{17900}{RT}\right) \quad (31)$$

Where  $\mu^{\text{NH}_3\text{-sol}}$  represents the viscosity of aqueous ammonia solution and  $x_{\text{NH}_3}$  represents the molar solute fraction of  $\text{NH}_3$  in aqueous ammonia solution. The viscosity of aqueous ammonia solution increases only 20% when the mass fraction of ammonia increases from 2% to 16%, which has a little effect on the effective interfacial area between gas and liquid in the packed column.

Diffusivity of  $\text{CO}_2$  in aqueous ammonia solution was estimated by applying the modified Stokes–Einstein equation as follows:<sup>37,38</sup>

$$D_{\text{CO}_2}^{\text{NH}_3\text{-sol}} = D_{\text{CO}_2}^{\text{H}_2\text{O}} \left( \frac{\mu^{\text{H}_2\text{O}}}{\mu^{\text{NH}_3\text{-sol}}} \right)^{0.8} \quad (32)$$

Where  $D_{\text{CO}_2}^{\text{NH}_3\text{-sol}}$  and  $D_{\text{CO}_2}^{\text{H}_2\text{O}}$  represent the diffusivity of  $\text{CO}_2$  in aqueous ammonia solution and water, respectively. From this equation, the viscosity of aqueous ammonia solution decreases only 15.7% when the mass fraction of ammonia increasing from

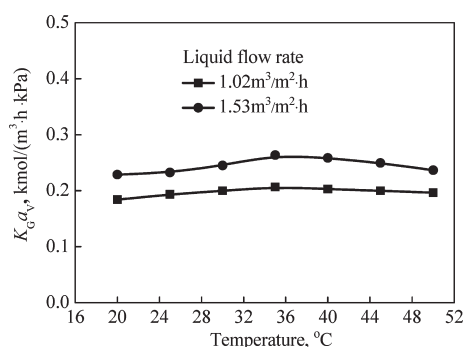


Figure 6. Effect of temperature on overall mass transfer coefficient.

2% to 16%. Thus, the increasing of ammonia concentration has a little effect on the rate of molecular diffusion.

The increasing concentration yields an amount of the active ammonia available to diffuse toward the gas–liquid interface and react with  $\text{CO}_2$ . This will greatly promote the enhancement factor increase, which leads to a higher  $K_G a_V$  value according to eq 22.

**5.5. Effect of Temperature.** Temperature is an important parameter influencing reaction kinetics. The reaction of  $\text{CO}_2$  absorption into aqueous ammonia solution is reversible, the forward reactions are dominant at room temperature, the backward reactions occur at temperatures of around 38–60 °C.<sup>6</sup> As shown in Figure 6, increasing the temperature in the packed column from 20 to 50 °C results in shifting the  $K_G a_V$  value. The  $K_G a_V$  value increases with the temperature when the temperature of the water bath is lower than 40 °C. Such behavior is attributable to the nature of  $\text{CO}_2$  absorption kinetics. The second-order reaction rate constant  $k_2$  of  $\text{CO}_2$ –ammonia system increases with the reaction temperature which is beneficial to enhance the absorption rate, whereas, the  $K_G a_V$  value decreases with the increasing temperature when the temperature of water bath is higher than 40 °C. The chemical reaction between the  $\text{CO}_2$  and ammonia system at this point shifts from the forward reaction to the reverse controlling mechanism. A similar trend was reported by Aroonwilas et al.<sup>39</sup> for the absorption of  $\text{CO}_2$  into MEA solution in columns with structured packing. In general, the change of the  $K_G a_V$  value is small when the temperature in the packed column goes from 20 to 50 °C. From the principle of molecular dynamics, the diffusion coefficient and rate-constant of reaction increase with increasing temperature, which are beneficial to enhance the mass transfer. However, the  $\text{CO}_2$  solubility coefficient decreases with increasing temperature which gives rise to an increase of the resistance in the liquid phase.

**5.6. Proposed Correlation.** The absorption of carbon dioxide into aqueous ammonia is mainly controlled by the resistance in the liquid phase especially when the ammonia concentrations are low. Therefore, the overall mass transfer coefficient  $K_G a_V$  is mainly related to the mass fraction of ammonia and liquid flow rate.

To further research the relationship between  $K_G a_V$  and the liquid flow rate ( $L$ ) as well as the mass fraction of ammonia ( $C_{\text{NH}_3}$ ), variations of  $K_G a_V$  are plotted in a logarithmic scale versus the liquid flow rate ( $L$ ) and the mass fraction of ammonia ( $C_{\text{NH}_3}$ ). Figure 7 shows that the slopes of the straight lines are 0.56 for a given mass fraction of 2% and 0.48 for a given mass fraction of 4%, the averaged value of the

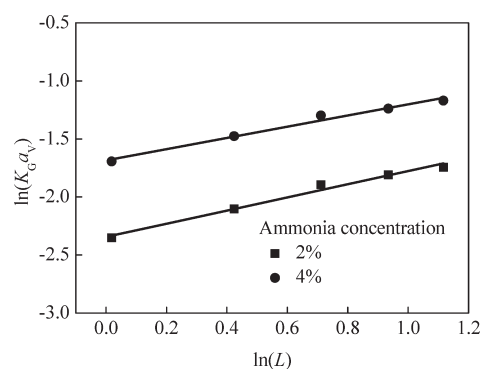


Figure 7. Effect of liquid flow rate on overall mass transfer coefficient in terms of logarithm.

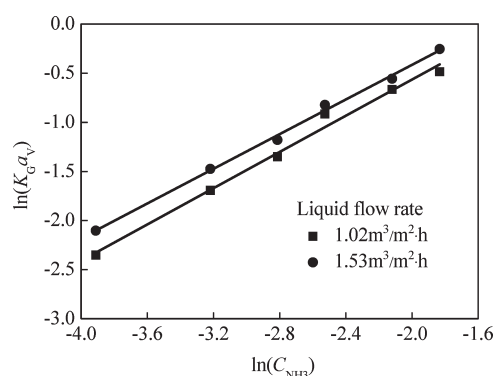


Figure 8. Effect of mass fraction of ammonia on overall mass transfer coefficient in terms of logarithm.

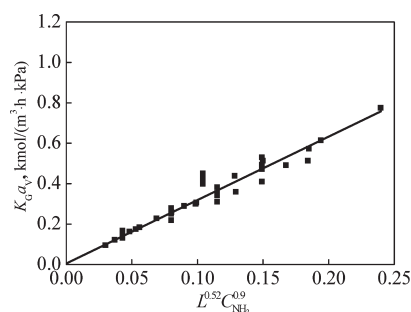
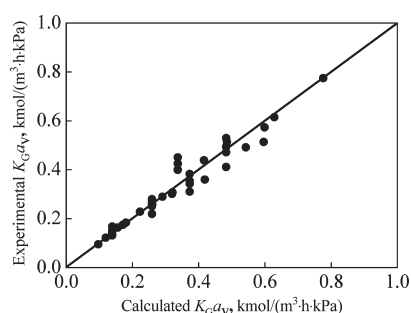


Figure 9. Correlation of liquid flow rate and mass fraction of ammonia to overall mass transfer coefficient.

exponent is 0.52. Thus, the results show that  $K_G a_V$  is approximately proportional to  $L^{0.52}$ . This phenomenon was also found in the  $\text{CO}_2$ -amine system; experimental results by Aroonwilas and Tontiwachwuthikul<sup>23</sup> showed that the  $K_G a_V$  increases approximately as the 0.5 power of the liquid flow rate.

The term of  $\ln(K_G a_V)$  plotted against  $\ln(C_{\text{NH}_3})$  is shown in Figure 8. The slope of the straight lines are 0.88 and 0.92 for the liquid flow rate of 1.53  $\text{m}^3/(\text{m}^2 \cdot \text{h})$  and 1.02  $\text{m}^3/(\text{m}^2 \cdot \text{h})$ , respectively. The averaged value of the exponent is 0.9. Therefore, the  $K_G a_V$  value increases approximately as the 0.9 power of the mass fraction of ammonia  $C_{\text{NH}_3}$ , the correlation between



**Figure 10.** Comparison between  $K_{GaV}$  values from proposed correlation and experiments.

$K_{GaV}$  and  $C_{NH_3}$  can be expressed as follows:

$$K_{GaV} \propto L^{0.52} C_{NH_3}^{0.9} \quad (33)$$

The term  $(K_{GaV})$  plotted against  $L^{0.52} C_{NH_3}^{0.9}$  is shown in Figure 9. A linear relationship consequently leads to the following correlation:

$$K_{GaV} = 3.24 L^{0.52} C_{NH_3}^{0.9} \quad (34)$$

The  $K_{GaV}$  calculated from eq 34 plotted against the  $K_{GaV}$  from the experiments is shown in Figure 10. There is a good agreement between the two data sets. Equation 34 gives the correlation of  $K_{GaV}$  and operating parameters. It should be noted that eq 34 was developed on the basis of  $CO_2$  absorption into aqueous ammonia using laboratory dumped packing of ceramic Raschig rings.

## 6. CONCLUSIONS

The overall mass transfer coefficients for  $CO_2$  absorption into aqueous ammonia in a packed column were investigated. The following major conclusions can be drawn from this work: (1) The overall mass transfer coefficient ( $K_{GaV}$ ) was measured according to the  $CO_2$  concentrations at the top and bottom of the packed column. Experimental results show that the mass transfer process in  $CO_2$  absorption into ammonia aqueous solution is mainly controlled by the resistance in the liquid phase and the aqueous ammonia concentration has a great effect on the overall mass transfer coefficient. (2) An empirical correlation between mass transfer coefficient and operating parameters of liquid flow rate and mass fraction of ammonia was proposed for  $CO_2$  absorption into aqueous ammonia solution.

## AUTHOR INFORMATION

### Corresponding Author

\*Tel.: (8610) 6277 2112. Fax: (8610) 6278 1824. E-mail: guoyoc@tsinghua.edu.cn.

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## NOMENCLATURE

$a_v$  = interfacial area per unit volume,  $m^2 \cdot m^{-3}$   
 $G$  = gas flow rate,  $kmol \cdot m^{-2} \cdot h^{-1}$   
 $G_B$  = inert gas flow rate,  $kmol \cdot m^{-2} \cdot h^{-1}$

$H$  = Henry's constant,  $kPa \cdot m^3 \cdot kmol^{-1}$

$h$  = total height of the reactor, m

$K_G$  = overall mass transfer coefficient,  $kmol \cdot m^{-2} \cdot h^{-1} \cdot kPa^{-1}$

$K_{GaV}$  = the volumetric overall mass transfer coefficient,  $kmol \cdot m^{-3} \cdot h^{-1} \cdot kPa^{-1}$

$k_G$  = gas phase mass transfer coefficient,  $kmol \cdot m^{-2} \cdot h^{-1} \cdot kPa^{-1}$

$k_{GaV}$  = volumetric mass transfer coefficient in the gas phase,  $kmol \cdot m^{-3} \cdot h^{-1} \cdot kPa^{-1}$

$k_L$  = liquid mass transfer coefficient,  $m \cdot h^{-1}$

$k_{LaV}$  = volumetric mass transfer coefficient in the liquid phase,  $h^{-1}$

$L$  = liquid flow rate,  $m^3 \cdot m^{-2} \cdot h^{-1}$

$N_A$  = rate of absorption of A per unit interface area,  $kmol \cdot m^{-2} \cdot h^{-1}$

$P$  = total pressure on the system, kPa

$Y$  = mole rate of  $CO_2$  in gas steam

$Y_1$  = mole ratio of gas phase  $CO_2$  entering the absorption column

$Y_2$  = mole ratio of gas phase  $CO_2$  leaving the absorption column

$y$  = mole fraction of  $CO_2$  in gas steam

$y_i$  = mole fraction of component A on the gas-side of the gas–liquid interface

$y^*$  = equilibrium mole fraction of  $CO_2$

$\Omega$  = cross-sectional area of the column,  $m^2$

$\beta$  = enhancement factor

## Superscripts

\* = gas–liquid equilibrium

## Subscripts

A =  $CO_2$

G = gas phase

I = inert gas

i = at the interface

L = liquid phase

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