Kinetics and mass transfer of carbon dioxide absorption into aqueous ammonia

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Abstract

Aqueous ammonia can be used to capture CO$_2$ from flue gas of coal-fired power plant with acceptable CO$_2$ removal efficiency, high loading capacity of CO$_2$, low corrosion, low cost, and less degradation, and it could remove other acid gas pollutants at the same time. However, the CO$_2$ absorption rate and mass transfer in aqueous ammonia still need to study more deeply. The mass transfer characteristics of CO$_2$ in aqueous ammonia were investigated in this paper.

A small wetted wall column (WWC) was used to study the kinetics of CO$_2$ absorbed in aqueous ammonia. The correlation of gas-side mass transfer coefficient $k_g$ was fitted as $Sh = 3.79(ReSc \times d / h)^{0.466}$ based on the experimental data of CO$_2$ absorption in 30%wt MEA solution for this WWC reactor. The reaction rates of CO$_2$ in 1 wt%, 2.5 wt%, 5 wt% to 7.5 wt% aqueous ammonia were measured at the temperatures of 10°C, 20°C, 30°C to 40°C, and the second-order reaction rate constant $k_2$ was calculated. The termolecular mechanism model was used and discussed according to the experimental results. The kinetics constants of $k_{H,0}$ and $k_{H,0}$ in termolecular mechanism were also fitted in this paper.

Keywords: Carbon dioxide, Aqueous ammonia, Absorption, Mass transfer, Kinetics, Separations

1. Introduction

Alkanolamines, such as monoethanolamine (MEA), are common absorbents in CO$_2$ capture process. The drawbacks of normal alkanolamines include easily degradation, high corrosion rate, and a high energy requirement for regeneration. Different from organic amines, aqueous ammonia has recently been considered to have potential as an effective and economic solvent for CO$_2$ capture since its high loading capacity of CO$_2$, low corrosion, low cost, and less degradation, and it could remove other acid gas pollutants at the same time, and has also an acceptable CO$_2$ removal efficiency.[1,9]

Detailed kinetic data are required for the optimal design and operation of an absorber. Studies have reported kinetic reaction rate constants for different temperatures. A rapid method of measuring the absorption rate was developed and applied to CO$_2$ absorption in partially carbonated ammonia solution at 0–40°C by Andrew[10], and the reaction was considered to be first order for both CO$_2$ and ammonia. The reaction rate was determined by Pinsent et al[11]. in a bubble reactor for the same temperature range as Andrew[10]. Gibson et al[12] presented the relationship between mass transfer and the solution flow rate/concentration in a packed column. Hsu[13] studied the rate of reaction between CO$_2$ and ammonia in a semi-batch reactor from 25°C to 65°C. The rate of reaction in a spray tower was given by Diao et al[14]. for
temperatures from 28°C to 43°C. The important parameters for the gas-liquid reaction such as the gas-liquid contact time and area cannot be accurately measured in these studies.

Wetted-wall column studies on the kinetics of CO₂ absorption in unloaded and partially carbonated ammonia solution were conducted by Qin et al. [14] and Zheng et al. [15]. At temperatures from 20°C and 50°C, and the reaction was considered to be first order for both CO₂ and ammonia. The zwitterion mechanism was applied to CO₂ absorption in ammonia solution in a well-stirred cell reactor from 5°C to 25°C by Derks and Versteeg [16]. In addition, Puxty et al. [17] presented their latest kinetics results for a reaction in a wetted-wall column reactor at temperatures from 5°C to 20°C. Though these studies use the reactors with fixed gas-liquid contact area such as wetted-wall column to measure the kinetic parameters of CO₂ absorption into ammonia, the data do not agree well, as shown later in this paper, and the experimental ranges of the concentration and temperature of ammonia solution were not wide enough.

In this work, more data will be contributed to the study of the kinetics of CO₂ absorption in aqueous ammonia. The gas-side mass transfer coefficient kₜ was fitted based on the experimental data of CO₂ absorption in 30 wt% MEA solution. The termolecular mechanisms were applied to characterize the kinetics and mechanisms of the reaction. The kinetic experiments, using a wetted-wall column with a contact area of about 41.45 cm², cover the concentration of aqueous ammonia from 1wt% to 7.5wt% and temperature from 10°C to 40°C, which expanded the range of temperature and concentration of aqueous ammonia, and also laid an experimental basis for a more comprehensive and systematic description of the absorption process of CO₂ into aqueous ammonia.

2. Chemical reaction

2.1 Reaction description

The total reaction of CO₂ absorption into aqueous ammonia can be described as the eq. (1):

$$CO_2 + NH_3 + H_2O \rightarrow NH_4HCO_3$$

(1)

The actual process of the reaction is more complicated, which can be described as step-by-step reactions.

First of all, the eq. (2) occurs, that is, CO₂ and NH₃ react to generate NH₂COONH₄, and then NH₂COONH₄ hydrolyzes in solution instantaneously.

$$CO_2 + 2NH_3 + H_2O \rightarrow NH_2COO^- + NH_4^+$$

(2)

Secondly, NH₄⁺ and NH₂COO⁻ have an irreversible reaction (3) in solution:

$$NH_2COO^- + NH_4^+ + 2H_2O \rightarrow NH_4HCO_3 + NH_3 + H_2O$$

(3)

2.2 Reaction mechanism

The zwitterion mechanism was proposed to describe the reaction between CO₂ and amines firstly by Caplow [17] and further discussed by Danckwerts [18]. Based on the mechanism, amine and CO₂ form zwitterions firstly, and then zwitterion is further deprotonated by a base (B). Eq. (4) and eq. (5) show the reaction between ammonia and CO₂ when the zwitterion mechanism is applied to this non-amine system.

$$CO_2 + NH_3 \rightarrow NH_4^+COO^-$$

(4)

$$NH_4^+COO^- + B \rightarrow NH_3 + COO^- + BH^+$$

(5)

The termolecular mechanism was proposed by Crooks and Donnellan [19], which concluded that the reaction between amine and CO₂ is single-step and termolecular. The initial product is not zwitterion, but a loosely bound encounter complex. Most of the complexes break up to give reagent molecules again. The reagent molecules do not react with a second molecule of amine or a water molecule to give ionic products. Bond formation and charge separation occur only in the second step.

This mechanism was reviewed by da Silva and Svendsen [20] in their ab initio study of carbamate formation from CO₂ and alkanolamines, and the termolecular mechanism was further developed. A single-step third-order reaction mechanism is most likely for the formation of carbamate from CO₂ and alkanolamines in solution. The observed broken-order and higher-order kinetics can be explained by this mechanism.

The mechanism applied to the ammonia system is written as

$$CO_2 + NH_3 + B \rightarrow NH_3 + COO^- + BH^+$$

(6)

If ammonia and water are the dominating bases, the reaction rate for the termolecular mechanism can be given as follows:

$$r_{CO_2-NH_3} = (k_{NH_3}^T[NH_3] + k_{H_2O}^T[H_2O])[CO_2][NH_3]$$

(7)

The termolecular mechanism was used to describe the reaction of aqueous ammonia and CO₂ in this work, and the correlation of $k_2$, $k_{NH_3}^T$ and $k_{H_2O}^T$ with temperature were fitted by the experimental data in this paper.
2.3 Correction of the reaction rate for hydroxyl ions

Aqueous ammonia is a weak alkali solution. CO₂ reacts with both of ammonia and hydroxyl when carbon dioxide dissolves into aqueous ammonia solution. The reaction rate is determined by both reactions as shown in eq. (9). Pinsent et al. [11] suggested that the effect of reaction (8) should be taken into account.

\[ \text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^- \]  \hspace{1cm} (8)

\[ r_{\text{abs}} = r_{\text{CO}_2 - \text{NH}_3} + k_{\text{OH}^-} [\text{OH}^-][\text{CO}_2] \]  \hspace{1cm} (9)

\[ k_{\text{OH}^-} = \frac{r_{\text{CO}_2 - \text{NH}_3}}{[\text{CO}_2]} + k_{\text{OH}^-}[\text{OH}^-] \]  \hspace{1cm} (10)

\( k_{\text{OH}^-} \) could be calculated by the following eq. (11).

\[ \lg(k_{\text{OH}^-}) = 13.635 - 2895/T \]  \hspace{1cm} (11)

[OH⁻] could be calculated by eq.(12), and the correlation of \( K_{\text{NH}_3} \) is shown as eq. (13) [21-24].

\[ K_{\text{NH}_3} = \frac{[\text{OH}^-][\text{NH}_3^+]}{[\text{NH}_3][\text{H}_2\text{O}]} \]  \hspace{1cm} (12)

\[ \ln K_{\text{NH}_3} = A + B/T + C \ln T + DT \]  \hspace{1cm} (13)

And the value of the parameters \( A, B, C \) and \( D \) in eq.(13) could be -1.256563, -3335.7, 1.4971 and -3.7056, according to Aspen Plus. So the apparent kinetic rate constant for the formation of carbamate in the \( \text{NH}_3 - \text{CO}_2 - \text{H}_2\text{O} \) system can be written as:

\[ k_{\text{app}} = k_{\text{abs}} - k_{\text{OH}^-}[\text{OH}^-] = k_2[N\text{H}_3] \]  \hspace{1cm} (14)

\[ k_2 = k_{\text{NH}_3}^0[N\text{H}_3] + k_{\text{NH}_3}^0[H_2\text{O}] \]  \hspace{1cm} (15)

3. Experimental apparatus and methods

3.1 The wetted-wall column

A wetted wall column with a contact area of about 41.45 cm² has been built [25]. The gas-liquid contactor was constructed from a stainless steel tube, measuring 11.0 cm in height and 1.2 cm in diameter. The gas-liquid contact region is enclosed by a 31.0 cm thick-walled glass tube, separated from a water-bath. The chemical solution is pumped through the inside of the tube, overflows on the top, and is evenly distributed across the outer surface of the tube. After collection at the base of the column, the liquid is pumped to a liquid reservoir. Gas enters near the base of the column, counter-currently contacting with the liquid as it flows up into the gas outlet.

![Fig.1. Overall experimental flowsheet of WWC.](image)

The water/oil-bath, with circulation of the water/oil inside, is used to control the temperature of the inlet gas, liquid and the reactor. Two reservoirs are used in this system, one of which is used for the amine solution storage, and the other is used to hold the waste solution out of the reactor. A micro-pump pushes the solution from the reservoir through a coil submerged in the water/oil-bath, flowing through a rotameter for flowrate determination. The liquid flow rate was 2-3 cm³/s. After heated, the solution flows into the wetted-wall column, contact with the gas stream, and then returns to the reservoir.

3.2 Aqueous Ammonia and CO₂ Reactions

The mass flux with chemical absorption can be described as follows based on two-film model, where the total resistance to mass transfer was divided as the sum of resistances from gas side and liquid side as eq.(16).

\[ \frac{1}{k_g} + \frac{1}{k_g} = \frac{1}{K_g} \]  \hspace{1cm} (16)
The overall gas transfer coefficient $K_G$ can be calculated by the Flux and $P_{CO_2, in}$ and $P_{CO_2, out}$. At the same temperature and concentration of ammonia, the value of $K_G$ is fixed and can be calculated by the Flux- CO$_2$ partial pressure curve.

$$K_G = \frac{Flux}{P_{CO_2, in} - P_{CO_2}}$$ (17)

Where, $P_{CO_2, in}$ is the operational partial pressure of CO$_2$ in the wetted wall column, which was the log mean average, as eq. (18):

$$P_{CO_2, in} = \frac{P_{CO_2, in} - P_{CO_2, out}}{\ln(P_{CO_2, in} / P_{CO_2, out})}$$ (18)

The gas–liquid mass transfer process is enhanced by chemical absorption when the acid gas is treated with amines/ammonia. The mass flux with chemical absorption is as eq.(19):

$$Flux = \frac{1}{E_A k_L} + \frac{RT}{H_k} (C_A^* - C_{A,b})$$ (19)

Where $E_A = \sqrt{1 + H_k}$ and $H_k = \sqrt{\frac{k_{obs} D_A}{k_L}}$.

The reaction is considered to be a pseudo-first-order irreversible reaction. If the Hatta number $Ha>3$, the expression for the enhancement factor ($E_A$) based on the two-film model, penetration model and surface renewal model can be simplified as eq. (20) [26-27].

$$E_A = Ha = \sqrt{\frac{k_{obs} D_A}{k_L}}$$ (20)

Physicochemical properties of the aqueous ammonia solution required in determination of mass transfer, such as density, viscosity, solubility and diffusivity, were measured or taken from the literature before the experiment.

The viscosities of ammonia solutions of different concentrations and water were calculated using eq. (21) and (22) [28].

$$\eta_{NH_3} = (0.67 + 0.78x_{NH_3}) \exp\left(\frac{17900}{RT}\right)$$ (21)

$$\eta_{H_2O} = 1.18 \times 10^{-6} \exp\left(-\frac{16400}{RT}\right)$$ (22)

The methods used to estimate the diffusion coefficient of CO$_2$ in aqueous ammonia are described below. The diffusion coefficient of CO$_2$ is estimated from the solution’s viscosity using a modified Stokes-Einstein equation [29].

$$D_{CO_2}^{NH_3-H_2O} = D_{CO_2}^{H_2O} \left(\frac{\eta_{H_2O}}{\eta_{NH_3-H_2O}}\right)^{0.8}$$ (23)

$$D_{CO_2}^{H_2O} = 2.35 \times 10^{-6} \exp\left(-\frac{2119}{T}\right)$$ (24)

In this paper, the concentration of ammonia is very low, so we can use Henry’s law constant of CO$_2$ in water to estimate the Henry’s law constant $H_{CO_2}$ in aqueous ammonia. Pacheco [30] recalibrate the Henry’s Law constant using the following correlation.

$$H_{CO_2} (atm \times cm^3 / mol) = 1.7107 \times 10^7 \times \exp\left(-\frac{1886.1}{T(K)}\right)$$ (25)

If we can calculate the gas-side mass transfer coefficient $k_g$, therefore, the value of $k_G$ can be got by eq. (16), and we can get the value of the observed reaction rate constant $k_{obs}$ by eq. (26).

$$k_g = \frac{k_g^0 E_A}{H_{CO_2}}$$ (26)

The correlation of gas film mass transfer coefficient $k_g$ for this WWC is very important and need to be fitted by the experiment.

3.3 The correlation of gas film mass transfer coefficient $k_g$ for this WWC is very important and need to be fitted by the experiment.

The characterization of gas-side mass transfer coefficient $k_g$ was given by eq. (27).

$$Sh = \alpha(Re \times Sc \times d_h / h)^{\beta}$$ (27)

Where $Sh = RT k_g d_h / D_{CO_2}$, $Re = \rho_g V d_h / \mu_g$, $Sc = \nu / D_{CO_2}$, $d_h$ is the hydraulic diameter of the annulus and $h$ is the length of the column. The parameters of $\alpha$ and $\beta$ were fitted based on the experimental data of CO$_2$ absorption into MEA solution. The reaction rate between CO$_2$ and MEA solution is supposed to be high enough that the resistance from film side can be dominated [30].
This work determined the gas–phase mass transfer coefficient of the apparatus by absorption of carbon dioxide into 30 wt% MEA solution. The experimental temperature was from 20°C to 60°C, and the gas flow rate range chosen as 3-40 cm³/s.

The gas-side mass transfer coefficient \( k_g \) is fitted by Fig. 2 and the correlation is given by the eq. (28) for this WWC.

\[
Sh = 3.79 (Re \times Sc \times d / h)^{0.446}
\]

(28)

4. Results and discussions

4.1 Experimental data of \( CO_2 \) absorption rate in aqueous ammonia

According to the results of this work, the reaction is considered to be a pseudo-first-order irreversible reaction. With Hatta number \( Ha >> 3 \), the expression for the enhancement factor \( (E_A) \) based on the two-film model, penetration model and surface renewal model can be simplified as eq. (17), and therefore, \( k_{obs} \) can be calculated using the eq. (29)

\[
k_{ij} = \sqrt{\frac{k_{obs} D_{CO_2}}{H_{CO_2}}}
\]

(29)

The apparent kinetic rate constant \( k_{app} \) and the second-order reaction rate constant \( k_2 \) discussed in section 2 can be calculated by eq. (14).

4.2 Determination of the kinetics constants and comparison

The second-order reaction rate constant \( k_2 \) of 5 wt% aqueous ammonia in this work was also compared with the prior researchers’ results at the same temperature. Fig. 4 shows that \( k_2 \) in this paper was in good agreement with Hsu, Pinsent and Qin, and significantly lower than Versteeg and Ptux [11,13,14,16,31]. Moreover, this work expanded the range of
temperature and concentration of aqueous ammonia, which has laid an experimental basis for a more comprehensive and systematic description of the absorption process of CO₂ into aqueous ammonia.

The termolecular mechanism, discussed deeply in section 2, was used to describe the reaction of aqueous ammonia and CO₂ in this work, and the correlation of \( k_2 \), \( k_{NH_3}^T \), and \( k_{H_2O}^T \) with temperature were fitted by the experimental data in this paper.

\[
k_2 = k_{NH_3}^T \left[ NH_3 \right] + k_{H_2O}^T \left[ H_2O \right]
\] (15)

The kinetics constants \( k_{NH_3}^T \) and \( k_{H_2O}^T \) in termolecular mechanism were fitted and expressed as a function of temperature according to the \( k_2 \) and the concentrations of aqueous ammonia.

\[
k_{NH_3}^T = 4.69 \times 10^4 \exp(-3793/T)
\] (30)

\[
k_{H_2O}^T = 4.36 \times 10^6 \exp(-3847/T)
\] (31)

\( k_{NH_3}^T \) and \( k_{H_2O}^T \) were important constants to describe the reaction process of CO₂ absorption into aqueous ammonia.

The correlation of \( k_{NH_3}^T \) and \( k_{H_2O}^T \) with temperature were given as eq. (30) and eq. (31) according to fig. 6.
These correlations provide an effective method for the calculations of $k_2$ and gas-liquid reaction liquid phase mass transfer coefficient $k_l$ at different ammonia concentration and temperature.

The kinetics constants $k_{T,NH_3}^T$ and $k_{H,O}^T$ were also compared with some amines solution. The reaction rate of aqueous ammonia was much lower than MEA and some other amines according to the results shown in Table 3.

Table 3 Comparison of kinetics constants between aqueous ammonia and amines at 25°C

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>$10^{-3}k_{NH_3}^T$ $(\text{m}^3 \text{kmol}^{-2} \text{s}^{-1})$</th>
<th>$k_{H,O}^T$ $(\text{m}^6 \text{kmol}^{-2} \text{s}^{-1})$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>0.139</td>
<td>10.79</td>
<td>This work</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>0.13</td>
<td>17.10</td>
<td>Qin, 2010$^{[32]}$</td>
</tr>
<tr>
<td>MEA</td>
<td>1.7</td>
<td>73.7</td>
<td>Aboudheir, 2003$^{[33]}$</td>
</tr>
<tr>
<td>AEEA</td>
<td>2.35</td>
<td>161</td>
<td>Ma'mun, 2007$^{[34]}$</td>
</tr>
<tr>
<td>EDA$^a$</td>
<td>2.79</td>
<td>17.72</td>
<td>Li, 2007$^{[35]}$</td>
</tr>
<tr>
<td>DETA</td>
<td>17.5</td>
<td>179.7</td>
<td>Hartono, 2009$^{[36]}$</td>
</tr>
<tr>
<td>PZ</td>
<td>70.1</td>
<td>550</td>
<td>Cullinane, 2007$^{[37]}$</td>
</tr>
</tbody>
</table>

5. Conclusions

The reaction rates of CO$_2$ in 1 to 7.5 wt% aqueous ammonia were determined at the temperatures of 10 to 40°C. The second-order reaction rate constant $k_2$ of CO$_2$ with aqueous ammonia was calculated and also compared with the prior researchers’ results. The second-order reaction rate constant $k_2$ of aqueous ammonia was much lower than MEA and some other active amines.

The kinetics constants $k_{T,NH_3}^T$ and $k_{H,O}^T$ in termolecular mechanism were fitted and expressed as a function of temperature. The correlations of $k_{T,NH_3}^T$ and $k_{H,O}^T$ with temperature provide an effective method for the calculations of second-order reaction rate constant $k_2$ and liquid phase mass transfer coefficient $k_l$. Moreover, this work expanded the range of temperature and concentration of aqueous ammonia and laid an experimental basis for future research.

Notation

$B$ base species  
$D$ diffusivity, m$^2$ s$^{-1}$  
$E$ enhancement factor  
$H$ Henry constant, kPa m$^3$ kmol$^{-1}$  
$Ha$ Hatta number  
$K_G$ overall mass transfer coefficient, mol·pa$^{-1}$·cm$^{-2}$·s$^{-1}$  
$k_G$ mass transfer coefficient based on gas phase, mol·pa$^{-1}$·cm$^{-2}$·s$^{-1}$  
$k_2$ forward reaction constant, m$^3$ kmol$^{-1}$ s$^{-1}$  
$k_{app}$ apparent reaction rate constant, s$^{-1}$  
$k_k$ gas-side mass transfer coefficient, mol·pa$^{-1}$·cm$^{-2}$·s$^{-1}$  
$k_{H_2O}^T$ termolecular reaction rate constant contributed by water, m$^6$ kmol$^{-2}$·s$^{-1}$  
$k_l$ liquid-side mass transfer coefficient, m s$^{-1}$  
$k_{NH_3}^T$ termolecular reaction rate constant contributed by ammonia, m$^6$ kmol$^{-2}$·s$^{-1}$  
$k_{obs}$ observed reaction rate constant, s$^{-1}$  
$k_{OH}$ reaction rate constant for CO$_2$ hydration, s$^{-1}$  
$N$ absorption flux, kmol m$^{-2}$·s$^{-1}$  
$r$ reaction rate, kmol m$^{-3}$·s$^{-1}$  
$R$ universal gas constant, 8.314 J mol$^{-1}$·K$^{-1}$  
$Re$ Reynolds number  
$Sc$ Schmidt number  
$Sh$ Sherwood number  
$T$ Temperature, K  
$v$ velocity, m s$^{-1}$  
$\eta$ viscosity, Pa s  
$\rho$ density, kg m$^{-3}$
References

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