Abstract

In the present work the absorption of carbon dioxide into aqueous ammonia solutions has been studied in a stirred cell reactor, at low temperatures and ammonia concentrations ranging from 0.1 to about 7 kmol/m³. The absorption experiments were carried out at conditions where the so-called pseudo first order mass transfer regime was obeyed – and hence the kinetics of the reaction between carbon dioxide and ammonia could be derived. The results were interpreted according to the well-established zwitterion mechanism.

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1. Introduction

Post combustion capture (PCC) with aqueous (alkanol)amine solutions is currently regarded as the most mature and feasible technology to reduce the carbon dioxide emissions from coal and natural gas fired power plants. In this capture process, usually the flue gas is countercurrently contacted in an absorber column, where the carbon dioxide reacts selectively with the solvent. The cleaned gas leaves the absorber top, while the loaded solvent is sent to a desorber, where it is regenerated at higher temperature, after which it is sent back to the absorber. The carbon dioxide leaving the desorber top is to be compressed and stored at a suitable location.

The major part of research within PCC is focused on solvent development, as the current ‘base case solvent’, an aqueous ethanolamine (MEA) solution, suffers from severe drawbacks: Degradation and corrosion issues and the relatively high heat of regeneration required in the stripper section are valid reasons to search for a more attractive solvent to be used in the post combustion capture technology.

The so-called “chilled ammonia” process, which has gained a lot of interest recently, is a post combustion
technology based on a new solvent. In this process, the carbon dioxide is absorbed in an aqueous NH$_3$-CO$_2$-H$_2$O system, at temperatures between 0 and 10 °C [1]. Indispensable for an optimal design and operation of absorber and stripper is detailed knowledge on mass transfer and kinetics on one hand and thermodynamic equilibrium on the other hand. Several studies have been reported in the open literature dealing with the thermodynamic vapor-liquid-solid equilibrium in the NH$_3$-CO$_2$-H$_2$O system [e.g. 2,3,4]. Unfortunately, relatively few studies have actually focused on the elemental kinetics of the individual reactions that occur when carbon dioxide is absorbed in aqueous ammonia based solvents [5,6]. The focus in the literature seems to lie on the determination of the more macroscopic potential of aqueous ammonia based solvents, such as e.g. its cyclic capacity and removal efficiency in bubble columns [e.g. 7,8]. The impact of the reaction kinetics on the process performance seems less important at this stage.

In this work, the kinetics of the reaction between ammonia and carbon dioxide in aqueous solutions are studied at temperatures between 5 and 25 °C; both the kinetic rate and the mechanism of the reaction are reported and discussed.

2. Kinetics

When carbon dioxide is absorbed in aqueous ammonia, its overall reaction rate will be determined by the following two reactions:

$$\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^- \quad (1)$$

$$\text{CO}_2 + 2\text{NH}_3 \rightarrow \text{NH}_2\text{COO}^- + \text{NH}_4^+ \quad (2)$$

The aim of this study is to identify the reaction mechanism and kinetic rate constant of reaction (2). Depending on the order of magnitude of this reaction, a correction for the contribution of reaction (1) might be necessary.

The reaction between ammonia and carbon dioxide is, similarly to the reaction between CO$_2$ and primary and secondary alkanolamines, expected to proceed via the well-known zwitter-ion mechanism [9,10]. In a first reaction step (3), carbon dioxide reacts with ammonia to form a zwitterion, which is deprotonated in the second step (4) by any base present in solution (e.g. NH$_3$ or H$_2$O).

$$\text{CO}_2 + \text{NH}_3 \xrightleftharpoons[\kappa_{-1}]{\kappa_2} \text{NH}_3^+\text{COO}^- \quad (3)$$

$$\text{NH}_3^+\text{COO}^- + B \xrightleftharpoons[\kappa_{k-y}]{\kappa_{k-x}} \text{NH}_2\text{COO}^- + \text{BH}^+ \quad (4)$$

The overall rate equation is then given by equation (5):

$$r_{\text{CO}_2-\text{NH}_3} = \frac{C_{\text{NH}_3}C_{\text{CO}_2}}{1 + \frac{k_{-1}}{k_2} \sum k_B C_B} \quad (5)$$

The theory and the experimental procedures used in the experimental determination of the reaction rate will be described in the following two subsections.
3. Mass Transfer

The absorption rate of CO$_2$ into a lean, freshly prepared, (reactive) solution is generally described using equation 6:

$$J_{CO_2} = k_L E \frac{mP_{CO_2}}{RT}$$  \hspace{1cm} (6)

where $J_{CO_2}$ is the absorption rate (in mol m$^{-2}$ s$^{-1}$), $k_L$ the physical liquid-side mass transfer coefficient (in m s$^{-1}$), E the enhancement factor for chemical reaction, m the distribution coefficient ($m = C_L / C_g$) and P/RT the gas phase CO$_2$ concentration (in mol m$^{-3}$).

In case the absorption occurs in the so-called pseudo-first-order regime, the enhancement factor equals the Hatta number:

$$E = Ha = \sqrt{\frac{k_{OV} D_{CO_2}}{k_L}}$$  \hspace{1cm} (7)

where $D_{CO_2}$ is the diffusion coefficient of CO$_2$ in the solution (in m$^2$ s$^{-1}$). The overall kinetic rate constant $k_{OV}$ is defined by:

$$k_{OV} = k_{OH} C_{OH} + \frac{r_{CO_2-NH_3}}{C_{CO_2}}$$  \hspace{1cm} (8)

The kinetic rate constant of reaction (1), $k_{OH}$, is known in literature, while the hydroxide concentration can be estimated using the pKa of ammonia and the concentration used in the absorption rate experiment.

N.B. The criterion to ensure pseudo-first-order behaviour is:

$$3 < Ha << E_{inf}$$  \hspace{1cm} (9)

where $E_{inf}$ is the infinite enhancement factor:

$$E_{inf} = 1 + \frac{D_{NH_3} C_{NH_3} RT}{D_{CO_2} \nu_{NH_3} mP_{CO_2}}$$  \hspace{1cm} (10)

4. Experimental

All absorption experiments were carried out in a thermostatted stirred-cell type of reactor equipped with both a pressure transducer and a thermocouple. Also, the reactor was connected to two gas supply vessels filled with either carbon dioxide or nitrous oxide. A schematic drawing of the experimental setup is shown in Figure 1.
In a typical experiment, an ammonia solution with desired concentration was prepared from more concentrated ammonia solutions (e.g. 5.0 N and ca. 30 wt.% in water – obtained from Sigma-Aldrich) by dilution with water. Subsequently, 500 mL of the solution was transferred to the reactor, where inerts were removed by applying vacuum for a short while. Next, the solution was allowed to equilibrate at the desired temperature – and its vapor pressure was recorded. Then a predetermined amount of carbon dioxide was added from the gas supply vessel to the reactor, the stirrer was started (at about 100 rpm to ensure a flat gas-liquid contact area), and the pressure decrease was recorded with time. The actual concentration of ammonia in the solution was verified after the experiment using volumetric titration with a standard hydrochloric acid solution.

A carbon dioxide mass balance over the gas phase yields in combination with equations (6) and (7), the following equation:

\[
\frac{d \ln P_{CO2}}{dt} = \sqrt{k_{OV} D_{CO2} A_{Gl,m}} \frac{k_{OV} D_{CO2} A_{Gl,m}}{V_G}
\]

Hence, a plot of the natural logarithm of the CO\textsubscript{2} partial pressure versus the time is to yield a straight slope, from which the overall kinetic rate constant k\textsubscript{OV} can be determined, once the required physico-chemical constants are known. (see also e.g. Blauwhoff et al [11] or Derks et al. [12]) The methods used to estimate the diffusion and distribution coefficient of CO\textsubscript{2} in aqueous ammonia are described below:

The diffusion coefficient of CO\textsubscript{2} is estimated from the solution’s viscosity using a modified Stokes-Einstein equation:

\[
D_{CO2}^{NH3\text{-sol}} = D_{H2O}^{H2O} \left( \frac{\eta_{H2O}}{\eta_{NH3\text{-sol}}} \right)^{0.8}
\]

The diffusion coefficient of CO\textsubscript{2} in water was taken from Versteeg and Van Swaaij [13]:
Viscosities of aqueous ammonia and pure water were calculated with the correlations given by Frank et al. [14]:

\[ \eta^{H_2O} = 1.18 \cdot 10^{-6} \exp\left(\frac{16400}{RT}\right) \]  

(15)

\[ \eta^{NH_3-sol} = \left(0.67 + 0.78 \cdot x_{NH_3}\right) \cdot 10^{-6} \exp\left(\frac{17900}{RT}\right) \]  

(16)

The distribution coefficient of CO2 is estimated using the CO2:N2O analogy:

\[ m^{NH_3-sol}_{CO2} = m^{H_2O}_{CO2} \left(\frac{m^{NH_3-sol}_{N_2O}}{m^{H_2O}_{N_2O}}\right) \]  

(17)

The distribution coefficients of both CO2 and N2O in water were calculated using the correlations given by Jamal [15]. The physical solubility of N2O in aqueous ammonia was experimentally determined for some experimental conditions, relevant for the present study. The experimental procedure for the experimental determination was identical to the ones described in e.g. Versteeg and Van Swaaij [13] or Derks et al. [16].

5. Results

The physical solubility of nitrous oxide in aqueous ammonia solutions was measured at temperatures between 5 and 25 °C and concentrations ranging from 0 to ca. 5 kmol m\(^{-3}\). The experimental results are shown graphically in Figure 2. From the experimental data listed in Figure 2, it can be concluded that the physical solubility of N2O is hardly influenced by the presence of ammonia.

Figure 2. Physical solubility of N2O in aqueous ammonia solutions between 5 and 25 °C.
All results on the absorption rate experiments of carbon dioxide in aqueous ammonia solutions are shown graphically in Figure 3: the apparent kinetic rate constant $k_{\text{app}}$ is given as a function of ammonia concentration for temperatures of 5, 10, 20 and 25 °C. Also the values reported by Pinsent et al. at 10 and 20 °C are included in the graphs. 

![Graph showing experimental data and zwitter-ion fits](image)

**Figure 3.** Experimentally determined apparent kinetic rate constants as a function of ammonia concentration.

The obtained apparent rate constants $k_{\text{app}}$ were subsequently correlated using the previously described zwitter-ion mechanism. The individual rate constants were assumed to have the following temperature dependence:

$$k_X = k_{X-283} \exp\left(\frac{A}{283.15} - \frac{A}{T}\right)$$

The zwitterion parameters as found by fitting them to the present experimental data and the data reported by Pinsent et al. [6], are listed in Table 1. A graphical comparison between the experimental $k_{\text{app}}$ as a function of ammonia concentration, and the curves according to the zwitter-ion mechanism, are given in Table 1:

**Table 1.** Kinetic parameters of the reaction between NH$_2$ and CO$_2$ according to the zwitter-ion mechanism.

|                  | $k$ at 283.15 K | $A$ [K$^{-1}$] |
|------------------|-----------------|----------------|
| $k_1$            | > 7.5 m$^3$ mol$^{-1}$ s$^{-1}$ | 3.0 · 10$^3$ |
| $k_{\text{NH}_3} + k_2 / k_4$ | 3.8 · 10$^4$ m$^2$ mol$^{-2}$ s$^{-1}$ | 8.5 · 10$^3$ |
| $k_{\text{H}_2\text{O}} + k_2 / k_4$ | 2.6 · 10$^4$ m$^2$ mol$^{-2}$ s$^{-1}$ | 5.5 · 10$^3$ |

A comparison between the apparent rates of reaction of carbon dioxide and ammonia, and the conventional alkanolamines monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA) is given in Table 2. The comparison is made at three different concentrations, namely $C_1 = 0.6$ kmol m$^{-3}$; $C_2 = 1.0$ kmol m$^{-3}$ and $C_3 = 4.5$ kmol m$^{-3}$.
Table 2. Comparison of the kinetic rates of aqueous ammonia, MEA, DEA and MDEA with carbon dioxide.

| Source | k_{app} \times 10^3 \text{ s}^{-1} | C = 0.6 \text{ kmol m}^{-3} | C = 1.0 \text{ kmol m}^{-3} | C = 4.5 \text{ kmol m}^{-3} |
|--------|--------------------------------|-----------------------------|-----------------------------|-----------------------------|
| NH_3 @ 5 °C | 0.14 | 0.3 | 8 | this work |
| NH_3 @ 10 °C | 0.21 | 0.7 | 10 | this work |
| NH_3 @ 20 °C | 0.76 | 1.4 | 30 | this work |
| NH_3 @ 25 °C | 1.0 | 2.1 | - | this work |
| MEA @ 25 °C | 3.6 | 6.0 | 27 | Versteeg et al. [17] |
| DEA @ 25 °C | 0.27 | 0.58 | 6.5 | Versteeg & Oyevaar [18] |
| MDEA @ 25 °C | \approx 10^{-7} | \approx 10^{-7} \times 10^{-7} | \approx 10^2 | Versteeg et al. [17] |

\[ k_{app} = k_1 \tilde{C}_{\text{ammonia}} \] in the case of MEA and MDEA.

From the results in Table 2, it can be concluded that the rate of reaction of molecular ammonia with CO_2 is in the same order of magnitude as MEA or DEA (depending on the applied concentration) – and in this respect it could be an attractive solvent for CO_2 capture. However, the major disadvantage of applying such high concentrations of ammonia, is its volatility, which would require one or more washing sections to remove the ammonia from the gas leaving the top of the absorber.

6. Conclusion

The kinetics of the (carbamate formation) reaction between carbon dioxide and ammonia in aqueous solutions were determined in a stirred cell type of contactor at temperatures between 5 and 25 °C and ammonia concentrations ranging from 0.1 to about 7 kmol m^{-3}. The obtained overall kinetic rate results were interpreted using the well-known zwitterion mechanism.

It was observed that the rate of the reaction between ammonia and carbon dioxide in aqueous solution is in the same order of magnitude as the conventional alkanolamines MEA and DEA – and hence substantially faster than the reaction between CO_2 and MDEA.

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8. References

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