Amine-based carbon dioxide absorption: evaluation of kinetic and mass transfer parameters

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ABSTRACT

Global emission of carbon dioxide (CO₂), a major contributor to the climate change, has increased annually and it reached over 37 Gt in 2017. An effort to reduce the emission, therefore, needs to be conducted, e.g. post-combustion capture by use of amine-based absorption. The objective of this study is to evaluate the kinetic and mass transfer parameters in a CO₂ absorption process using monoethanolamine (MEA), 2-(methylamino)ethanol (MMEA), and 2-(ethylamino)ethanol (EMEA) as absorbents. The experiments were conducted in a bubble reactor at atmospheric pressure and 40 °C with 10-vol% CO₂ flowrate of 5 NL/men. The CO₂ concentration leaving the reactor was measured by an IR CO₂ analyzer. The results obtained from this experiment were the overall absorption rates consisting of both chemical reaction and mass transfer. Analysis result shows that the reaction between CO₂ and amines takes place fast, therefore the mass transfer of CO₂ from the gas into the liquid through the gas film would control the overall absorption rate.

Keywords: Kinetics; mass transfer; absorption; carbon dioxide; alkanolamine; bubble reactor

INTRODUCTION

Global warming phenomenon is mainly caused by greenhouse gas (GHG) emissions, e.g. carbon dioxide (CO₂), in the atmosphere. The CO₂ emission tends to rise annually. In 2010, CO₂ emission reached 30 Gt and increased to over 37 Gt in 2017 [1]. Some attempts have been taken to reduce the CO₂ emission, such as implementation of CO₂ Capture and Storage (CCS) technology. In addition, utilization of natural gas and biomass-based energy may also reduce the CO₂ emission [2-6]. Post-combustion capture is one of the CO₂ capture technologies in which it can either be built separately or it can also be retrofitted to an existing plant. In this technology, CO₂ will be absorbed from a CO₂ source such as flue gas stream from a coal-fired power plant. Carbon dioxide absorbed may then be transported into underground geological storage or is utilized for other purposes, e.g.
Enhanced Oil Recovery (EOR), enhanced coal bed methane, polymer processing, synthetic fuels, mineralization, urea production, dry ice, food and beverage carbonation, and soda ash industry. Recently, CO$_2$ is also utilized for essential oil production using supercritical CO$_2$ extraction process [7-16].

Absorption is the most common process used in the acidic gas removal today. For economic reasons, a low cost and energy-saving absorbent is a must. In addition, a commercial absorbent must offer high absorption rate, high cyclic capacity, low corrosive, good chemical stability, etc. Amine-based CO$_2$ absorption is one of the processes that can be applied to post-combustion capture. This technology has been proven and mature and is still competitive to be developed in the future [17].

This study aims to evaluate kinetic and mass transfer parameters in the amine-based CO$_2$ absorption process. The results obtained from the experiment are the overall absorption rate over time at which the overall absorption rate comprises chemical reactions and mass transfer that took place simultaneously. Furthermore, some approaches were taken so that regimes that control the process could be evaluated. The kinetics of CO$_2$ absorption can, therefore, be predicted which is subsequently used in designing absorber and desorber columns.

Research on the kinetic and mass transfer parameters determination for the amine-based CO$_2$ absorption process was conducted by many researchers using string of discs contactor, wetted wall column, stopped flow technique, stirred cell, square bubble column, etc. [18-27]. The current investigation is important to determine which regimes that control the overall process in a bubble reactor.

### Short Review on Kinetic and Mass Transfer Theory

The amine-based CO$_2$ absorption is considered as a chemical absorption in which a series of mass transfer and chemical reaction equilibria for the CO$_2$ absorption into an aqueous solution of primary alkanolamine are as follows [28, 29]:

**Dissolution of CO$_2$:**

\[ \text{CO}_2(g) \leftrightarrow \text{CO}_2(l) \]  
(1)

**Dissociation of water:**

\[ 2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \]  
(2)

**Dissociation of CO$_2$:**

\[ \text{CO}_2(l) + 2\text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+ \]  
(3)

**Dissociation of bicarbonate ion:**

\[ \text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{CO}_3^{\text{II}} + \text{H}_3\text{O}^+ \]  
(4)

**Dissociation of protonated amine:**

\[ \text{AmH}^+ + \text{H}_2\text{O} \leftrightarrow \text{Am} + \text{H}_3\text{O}^+ \]  
(5)

**Carbamate formation:**

\[ \text{Am} + \text{CO}_2(l) + \text{H}_2\text{O} \leftrightarrow \text{AmCOO}^- + \text{H}_3\text{O}^+ \]  
(6)

**Dissociation of protonated carbamate:**

\[ ^+\text{HAmCOO}^- + \text{H}_2\text{O} \leftrightarrow \text{AmCOO}^- + \text{H}_3\text{O}^+ \]  
(7)

where Am refers to alkanolamine.

The amine-based CO$_2$ absorption can be approximated by the two-film theory [30] as shown in Figure 1. Based on this theory, the overall reaction rate for the absorption process by chemical reaction in alkanolamine solution can be written as follows:
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\[ -r_{CO_2} = \frac{1}{k_{CO_2,G} a} + \frac{H_{CO_2}}{k_{CO_2,G} aE} + \frac{H_{CO_2}}{k_{Am} f_L} \]  \hspace{1cm} (8)

where \( k_L \) and \( k_G \) are the liquid and gas mass transfer coefficients, while \( a, k, C, p, H, E, \) and \( f_L \) are interfacial area, reaction rate constant, concentration, partial pressure, Henry’s constant, enhancement factor, and liquid holdup, respectively.

Figure 1. The two-film theory for gas-liquid reaction

In general, for the absorption process carried out by bubbling gas into batch absorbent, the overall reaction rate can be expressed as follows [30]:

\[ -r_A = \frac{P_V}{F_G} + \frac{1}{k_{A,G} a} + \frac{H_A}{k_{A,L} aE} + \frac{H_A}{k_{Cf_L}} \]  \hspace{1cm} (9)

where \( P, V \), and \( F_G \) are total pressure (Pa), reactor volume (m\(^3\)), and inert gas flowrate (mol/s), respectively.

MATERIALS AND METHOD

The purities of \( CO_2 \) and \( N_2 \) obtained from AGA Gas GmbH were 99.99 and 99.6 mol%, respectively. MEA \([H_2N(CH_2)_2OH]\), MMEA \([CH_3NH(CH_2)_2OH]\) and EMEA \([CH_3CH_2NH(CH_2)_2OH]\) were obtained from Acros Organics with the reported purities of more than 99, 98, and 99 wt%, respectively.

The absorption rate measurement was carried out in a bubble reactor as shown in Figure 2. Similar apparatus was used by [31] and was then modified by [32] to be capable of desorption measurement. The apparatus equipped with six thermocouples, a water bath, an IR \( CO_2 \) analyzer, and a mass flow controller is designed to operate at a temperature up to 80 °C and at atmospheric pressure. Before starting the experiment, the analyzer was first calibrated by a gas mixture of \( CO_2-N_2 \) with 10 vol% of \( CO_2 \) through a by-pass valve. The absorption process begins after the calibration is completed by automatically closing the by-pass valve. At the same time, the \( CO_2-N_2 \) gas mixture flows through a saturator and to the reactor containing 750 mL of the absorbent. The gas coming out of the reactor is cooled before entering the IR \( CO_2 \) analyzer to condense water. The
absorption process that operates at 40 °C is terminated after the CO\textsubscript{2} concentration coming out of the reactor has reached 9.5 vol\% of CO\textsubscript{2} (i.e. p\textsubscript{CO\textsubscript{2}} = 9.5 kPa). Furthermore, a certain amount of liquid was taken for analysis of CO\textsubscript{2} content in the liquid phase.

**RESULTS AND DISCUSSION**

The CO\textsubscript{2} absorption into aqueous solutions of primary amine (MEA) and secondary amines (MMEA and EMEA) was carried out at 40 °C. The concentration of three absorbents used was similar, i.e. 30 wt\%. The data obtained in this experiment were the CO\textsubscript{2} partial pressures from a stream coming out of the reactor at various times. The absorption rate of CO\textsubscript{2} can then be calculated by the following equation:

$$r_{\text{CO}_2} = \frac{1}{V_l} \left[ n_{\text{CO}_2,\text{in}} - \frac{y_{\text{CO}_2,\text{out}}}{(1 - y_{\text{CO}_2,\text{out}})} n_{\text{N}_2} \right]$$

(10)

where $V_l$, $n$, and $\gamma$ are the liquid volume (L), gas flowrates (mol/s), and the mole fraction. It should be noted that the determination of Rate Determining Step (RDS) is semi-quantitative, in the sense that during all experiments there is no guarantee that the gas-liquid interfacial area (i.e. the bubble structure) was exactly the same. However, the superficial gas velocity was the same, so any differences would, according to [31], arise mainly due to variations in bubble coalescence properties, interfacial tension, density, and viscosity.

Figure 3 shows the absorption rate of CO\textsubscript{2} into aqueous solutions of MEA, MMEA, and EMEA with concentration of 30 wt\% each at various times. It is seen that at the beginning of the process, the absorption rate is still high, such that a significant amount of CO\textsubscript{2} is absorbed into the solution resulting in the CO\textsubscript{2} partial pressure coming out of the reactor still low. The absorption rate decreases as the time increases. This is followed by the increase of CO\textsubscript{2} concentrations both in the gas and liquid phases. It can also be seen from the figure that the absorption rate of CO\textsubscript{2} into aqueous solution of MEA is higher than into MMEA and EMEA. In other words, the overall absorption rate of CO\textsubscript{2} into the primary amine is higher than into the secondary amine.
It was observed during the experiment that the absorbent was sufficiently mixed in the reactor due to the bubbling of the CO$_2$-N$_2$ gas mixture. In addition, the circulation of the solution from the bottom up occurs inside the glass sleeve inside the reactor. These conditions make the liquid phase completely mixed, so that it is expected to accelerate the mass transfer of CO$_2$ from gas phase to liquid phase, i.e. the gas and liquid film resistances could be neglected. It can thus be assumed that the reaction in the liquid bulk controls the overall absorption rates. Based on this assumption, Equation (9) can then be simplified into a pseudo-first order reaction:

$$-r_A = \frac{p_{CO_2, in}}{\frac{H_{CO_2}}{kC_{Am}f_L}} = k_{obs}C_{CO_2}$$

where $k_{obs}$ refers to an observed pseudo-first order reaction rate constant. Equation (11) shows a linear relationship between the overall absorption rate and the CO$_2$ concentration in the liquid phase. As seen in Figure 4 that the absorption rate of CO$_2$ into MEA aqueous solution might fall into a pseudo-first order reaction up to an accumulated CO$_2$ concentration of about 1.43 mol/L, while for MMEA and EMEA up to 0.75 and 0.71 mol/L, respectively. The observed pseudo-first order reaction rate constant, $k_{obs}$, can be determined from the graph of the CO$_2$ absorption rate vs. the CO$_2$ concentration in the liquid phase, where $k_{obs}$ is the slope of the graph as shown in Figure 5. A similar procedure is then applied to calculate $k_{obs}$ for the absorption of CO$_2$ into aqueous solutions of MMEA and EMEA, and the results are presented in Table 1.

As seen in Figures 4 and 5 that the pseudo-first order reaction approximation occurs at low CO$_2$ concentrations (i.e. low CO$_2$ loadings). At higher CO$_2$ concentrations, the reaction order in the CO$_2$ might be larger than one. In MEA case, this approach is not in agreement with the zwitterion mechanism as well as the single step – termolecular mechanism. The zwitterion mechanism was first proposed by [33] and reintroduced later.
by [34]. For this mechanism, the reaction between CO₂ and amines results a formation of zwitterion intermediate followed by the removal of a proton by a base B. The overall reaction rate can then be expressed as written in Equation (12) by using the pseudo-steady-state assumption for the zwitterion concentration.

\[
-r_{\text{CO}_2} = \frac{k^Z_2[R_1R_2\text{NH}][\text{CO}_2]}{1 + \frac{k_{-1}}{\sum k_b}[B]}
\]  

(12)

If \((k_{-1}/\sum k_b[B]) \ll 1\), a simple second-order reaction is obtained and the zwitterion formation is being the RDS, such as MEA in aqueous solutions:

\[
-r_{\text{CO}_2} = k^Z_2[R_1R_2\text{NH}][\text{CO}_2]
\]  

(13)

where \(k^Z_2\) is the second-order reaction rate constant for the zwitterion mechanism.

Figure 4. Relationship between the overall absorption rates of CO₂ and accumulated CO₂ in the liquid phase at 40 °C: ○, MEA; □: MMEA; Δ: EMEA

Based on the zwitterion mechanism, the overall reaction order according to Equation (13) has a value of two and the partial order in the CO₂ is equal to one, see [35]. Moreover, based on the single step – termolecular mechanism that was first proposed by [36], the partial order in the CO₂ is also equal to one. By applying the zwitterion mechanism, this mechanism proposed that the zwitterion intermediate is formed by assuming that the reaction proceeds through a loosely-bound encounter complex as the initial product, see [37]. The overall reaction rate for this mechanism is defined as follows:

\[
-r_{\text{CO}_2} = k^T_2[R_1R_2\text{NH}][\text{CO}_2]
\]  

(14)
where $k_2^T$ is the second-order reaction rate constant for the single step – termolecular mechanism and is defined as the following:

$$k_2^T = \{k_{Am}[R_1R_2NH] + k_{H_2O}[H_2O] + k_{OH^-}[OH^-]\} \tag{15}$$

According to those two mechanisms, it is obvious that the pseudo-first order reaction approximation in this study might be accepted only at low CO$_2$ loadings, while at high CO$_2$ loadings, the partial order in the CO$_2$ might be larger than one. However, as seen in Table 1, the $k_2$ value for aqueous MEA system is much smaller (i.e., $1.17 \times 10^{-5}$ L/mol/s) compared to the $k_2$ values from [22] which is ranging from about 12 to 50 L/mol/s at the CO$_2$ loadings up to 0.4 and at 41.0 °C. Therefore, it can be concluded that the gas and liquid film resistances cannot be neglected for the bubble reactor. In the present work, bubbling the gas mixture and gas-liquid circulation inside the glass sleeve inside the reactor is not sufficient to get the system well mixed. To reduce the gas and liquid film resistances, one may use multiple stirrers both for liquid and gas phases [18].

![Figure 5. Pseudo-first order reaction approximation of the CO$_2$ absorption into aqueous solution of alkanolamines at 40 °C: ○, MEA; □: MMEA; Δ: EMEA](image)

<table>
<thead>
<tr>
<th></th>
<th>$k_{obs} \times 10^5$, 1/s</th>
<th>$k_2 \times 10^5$, L/(mol.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>5.84</td>
<td>1.17</td>
</tr>
<tr>
<td>MMEA</td>
<td>5.03</td>
<td>1.17</td>
</tr>
<tr>
<td>EMEA</td>
<td>6.97</td>
<td>1.94</td>
</tr>
</tbody>
</table>

From the $k_2$ value of MEA obtained in this study and that obtained from [22], it is clearly seen that the reaction between CO$_2$ and MEA took place fast, therefore the CO$_2$ mass transfer from the gas bulk to the liquid through the gas film might control the overall absorption rate. Since $1/(k_{AG}a) \gg \left[P_V/F_G + H_A/(k_{A,L}aE) + H_A/(k_{CB}f_L)\right]$, Equation (9) can then be simplified into:

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\[ -r_{\text{CO}_2} = k_{\text{CO}_2,g} a p_{\text{CO}_2,\text{in}} \]  

(16)

where \( k_{\text{CO}_2,g} a \) refers to the volumetric mass transfer coefficient of \( \text{CO}_2 \) in the gas phase.

**CONCLUSION**

The \( \text{CO}_2 \) absorption rate into aqueous solutions of MEA, MMEA, and EMEA with concentration of 30 wt% each were measured in a bubble reactor at 40 °C. The results show that the absorption rate of \( \text{CO}_2 \) into aqueous solution of MEA is relatively higher than into MMEA and EMEA. Moreover, the \( k_2 \) value for the \( \text{CO}_2-\text{MEA}-\text{H}_2\text{O} \) system obtained in the present study is much smaller {i.e., \( 1.17 \times 10^{-5} \) L/(mol.s)} in comparison to the \( k_2 \) value for similar system obtained from the literature {i.e., 12 to 50 L/(mol.s)}. Based on this condition, the reaction between \( \text{CO}_2 \) and those aqueous solutions took place fast. The \( \text{CO}_2 \) mass transfer from the gas bulk to the liquid through the gas film might, therefore, control the overall absorption rate.

**REFERENCES**


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