Kinetic Study of Carbon Dioxide Reaction with Binding Organic Liquids

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A B S T R A C T

Binding organic liquids are strong base of amidine have been used for CO$_2$ capture. Up to now, there is no known datum on the reaction kinetics of CO$_2$ with 1,5-Diazabicyclo [4.3.0] non-5-ene (DBN). In this paper, Kinetics of reaction between CO$_2$ and DBN/MDEA in 1-Pentanol was performed utilizing the stirred cell reactor with DBN concentration (2 – 2.9 M) and at room temperature. The reaction path was qualified using zwitterion and the termolecular mechanism. From the kinetic datum with DBN concentrations (2 - 2.9 M), it was found that the capturing process happened in a fast reaction system with a second-order reaction kinetics of DBN/MDEA and first order with CO$_2$. In addition, CO$_2$ absorption was achieved using gas-liquid contact system. CO$_2$ absorption rate was $(2 \times 10^{-5} – 2.8 \times 10^{-5} \text{kmol/m}^2\cdot\text{sec})$ at DBN concentration (2 – 2.9 M). Finally, it is known that DBN/MDEA/1-Pentanol/CO$_2$ system is easily switchable and can be used both CO$_2$ capture and for other applications that require rapid change of medium from nonionic to ionic liquid.

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1. INTRODUCTION

There was a great importance for the increased capture of CO$_2$ and storage studies over the past decades as a result of the global warming problem. At the present time, all the components of the CO$_2$ capture industry are available and stored, so far these components have not yet been used in the concept of CO$_2$ capture and storage. The direct reason behind this, is the operational cost of the absorption/adsorption processes and thus the inability to expand absorption capacities [1-4]. Generally, the process of CO$_2$ capture requires high power consumption due to the need to re-boil conventional processing. The researchers are focusing their attention on the development of the solvent and finding a new solvent that is less energy intensive when the solvent is regeneration. They proposed several solvents, the most important of which was the binding organic liquids (CO$_2$BOLS).

CO$_2$BOLS are a liquid solution consisting of a linear alcohol and strong base of amidine or guanidine that captures CO$_2$ [5, 6]. When the CO$_2$ is captured by the CO$_2$BOLS the output of the CO$_2$ interaction with CO$_2$BOLS an amidinium or guanidinium alkylcarbonate depending on the base. Furthermore, CO$_2$BOLS has a significant advantage compared with the traditional alkanolamine in terms of CO$_2$-binding enthalpy, Carbonate and bicarbonate salts that produced from CO$_2$ reaction with alkanolamine have a lower hydrogen bonds compared with the alkylcarbonate salts that produced by the CO$_2$ reaction with CO$_2$BOLS [7, 8]. This means that the renewing process of CO$_2$BOLS requires less energy compared with the traditional amine system. In fact, CO$_2$BOLS has many advantages compared with the alkanolamine, such as the widely used monoethanolamine (MEA) for CO$_2$ capture. Specifically, CO$_2$BOLS has a high boiling point, low vapor pressure, perfect physical and chemical properties, low thermal capacity compared with water and no corrosion problems [8].

Before proposing CO$_2$ BOLS was to capture CO$_2$, these solvents were labeled as "reverse ionic liquids" and were also bringing to light to be able to replace their polarity using CO$_2$ [8]. CO$_2$ is able to switch the polarity of non-ionic solvents to ionic solvents by passing CO$_2$ to the solvent and returning it to a polarizer by stripping of the solvent at a temperature much below the solvent boiling point [6, 9]. Therefore, CO$_2$BOLS has many applications that have emerged in recent years, while there are a limited number of studies including the study of the kinetics reaction of CO$_2$BOLS with CO$_2$ such as: the combination of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) amidine base in 1-Hexanol or 1-Propanol [10] and 1,1,3,3-Tetramethylguanidine (TMG) guanidine base in 1-hexanol and 1-propanol with CO$_2$ [11, 12]. In the light of all these advantages for CO$_2$BOLS, this paper aimed to study the kinetics and the reaction mechanism of CO$_2$ reaction with DBU/MDEA in 1-Pentanol.

2. THEORY

2.1. Reaction Pathways

The base of CO$_2$BOLS does not immediately react with CO$_2$ as the amine is formed carbamate. The alcohol group was found in CO$_2$BOLS first it react to be alkylcarboxylic acid, which then protonates the base to form a liquid alkylcarbamate [5, 13]. Where CO$_2$BOLS interacts with CO$_2$ and forming alklylecarbonate salts, as shown in the following interaction:

\[
\text{DBU} + \text{ROH} + \text{CO}_2 \rightarrow [\text{DBU}^\text{+}][\text{ROCO}_2^\text{−}] \quad (1)
\]

2.2. Zwitterion Mechanism

This mechanism was suggested by Caplow and Danckwert [14, 15]. Zwitterions mechanism assumes that CO$_2$ interact with amine and form zwitterions as an intermediary:

\[
\text{CO}_2 + \text{R}^\text{`RNH} \rightleftharpoons \text{R}^\text{`RNH} + \text{COO}^\text{−} \quad (2)
\]

The zwitterion passed through deprotonation by base (or bases) BM, forming carbamate as shown in the reaction below:

\[
\text{R}^\text{`RNH}^\text{+COO}^\text{−} + \text{BM} \rightarrow \text{R}^\text{`RNCOO}^\text{−} + \text{BM}^\text{+} \quad (3)
\]

The reaction rate could be express as folow:

<table>
<thead>
<tr>
<th>List of symbols</th>
<th>Molar Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>DBN</td>
<td>1,5-Diazabicyclo[4,3,0]non-5-ene</td>
</tr>
<tr>
<td>MDEA</td>
<td>Methylidethanolamine</td>
</tr>
<tr>
<td>CO$_2$BOLS</td>
<td>Binding organic liquids</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
</tr>
<tr>
<td>TMG</td>
<td>Tetramethylguanidine</td>
</tr>
<tr>
<td>$K_{\text{obs}}$</td>
<td>Observe reaction rate constant</td>
</tr>
<tr>
<td>$K_1$</td>
<td>Forward reaction rate in Eq. (10)</td>
</tr>
<tr>
<td>$K_2$</td>
<td>Forward reaction rate in Eq. (2)</td>
</tr>
<tr>
<td>$K_3$</td>
<td>Reverse reaction rate constant in Eq. (2)</td>
</tr>
<tr>
<td>$K_{\text{BM}}$</td>
<td>Deprotonation reaction rate constant of the zwitterion by a base</td>
</tr>
<tr>
<td>BM</td>
<td>Base</td>
</tr>
<tr>
<td>R$_{\text{CO}_2}$</td>
<td>Absorption rate</td>
</tr>
<tr>
<td>V$_G$</td>
<td>The volume of gas inside the cell reaction</td>
</tr>
<tr>
<td>V$_L$</td>
<td>The volume of liquid inside the cell reaction</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>D$_{\text{CO}_2}$</td>
<td>Diffusivity of CO$_2$ in solvent</td>
</tr>
<tr>
<td>H$_{\text{CO}_2}$</td>
<td>Solubility of CO$_2$ in solvent</td>
</tr>
</tbody>
</table>

\[
\text{CO}_2 + \text{R}^\text{`RNH} \rightleftharpoons \text{R}^\text{`RNH} + \text{COO}^\text{−} \quad (2)
\]

The reaction rate could be express as folow:
\[ R_{\text{CO}_2} = \frac{\text{CO}_2 \cdot [\text{CO}_2][R' \text{RNH}]}{1 + \frac{k_3}{k_B[BM]}} \]  

(4)

where: \( k_B \) [BM]: kinetic constant represents deprotonation of the zwitterions by base such as (H$_2$O, OH$^-$, or DBN, or by combination of bases). Eq. (4) displays a fractions order between one and two with respect to DBN concentration. Eq. (4) becomes:

\[ R_{\text{CO}_2} = K_{\text{obs}}[\text{CO}_2] \]  

(5)

\( K_{\text{obs}} \) is the observed reaction rate constant and represent via:

\[ K_{\text{obs}} = \frac{[R' \text{RNH}]}{k_2 + k_3k_B[BM]} \]  

(6)

where:

\[ k_B[BM] = \frac{k_2k_B[BM]}{k_3} \]  

(7)

When deprotonation is near quick contrast to reverberate interaction in its Eq. (1) (\( k_3 << k_B[BM] \)) and zwitterion formation is rate-determining. Eq. (5) pick the compose:

\[ R_{\text{CO}_2} = k_2[\text{CO}_2][R' \text{RNH}] \]  

(8)

Indicating that the reaction is the first order of both the \( \text{CO}_2 \) and the amine, and hence, overall of the second order.

When zwitterion deprotonation is rate-determining (\( k_3 >> k_B[BM] \)) Eq. (5) become:

\[ R_{\text{CO}_2} = \frac{k_2k_B[BM][\text{CO}_2]}{K_3}[R' \text{RNH}] \]  

(9)

Similar to Eq. (4), suggested the final expression reaction order between one and two for concentration amines. In the specific state where the concentration of the amine is the most important contribution in zwitterion deprotonation of those base such as H$_2$O and OH$^-$, the overall reaction is a second order with the amine [16]. However, the zwitterions is not sufficient to explain the laboratory results when the solvent is composed of two more reactants [17, 18]. So the researchers adjusted termolecular mechanism for blends and found it satisfactory since then [19-21].

2.3. Termolecular Mechanism

This mechanism is offer via Crooks and Donnellan [22]. It is assumed that reaction of \( \text{CO}_2 \) molecule with amine molecule (DBN) and the base molecule (BM) to form loosely bound encounter complex in a single step as shown in Fig. 1

![Fig. 1. Single step reaction.](image)

The net reaction of this mechanism is:

\[ \text{R}_2 \ + \ \text{R}_3 \ \overset{k_5, k_3}{\rightarrow} \ \text{R}_4 \ + \ \text{R}_5 \]  

(10)

(BM) is represents either one of two reactants (such as, two various amine for a dual blend) and solvent molecule. BM stands for base and \( \text{RNH}_2 \) is the amine. Regardless of the amine. The controlling base may be water or ion hydroxyl in aqueous systems or a liner alcohol in non-aqueous solution. This mechanism assumes the correlation between the amine molecule and \( \text{CO}_2 \) molecule and transfer the proton as shown in Fig. 1, whereas the binding middle part weak and transformed into reactors. The remaining part interacts with one other amine and forms ionic productions. As in reactions below:

\[ \text{RNHCOO}^- \ ... BM^+ + \text{RNH}_2 \rightarrow \text{RNHCOO}^- + \text{RNH}_3^+ + \text{BM} \]  

(11)

\[ \text{RNHCOO}^- \ ... BM^+ + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{RNH}_3^+ + \text{BM} \]  

(12)

Utilize the pseudo first – steady state on the ionic intermediated created in Eq. (10) [21, 23]. The reaction rate in Eq. (11) and (12) could be written:

\[ r_2 = \frac{k_1k_3[R\text{NH}_2][\text{R}_2 \ ... BM][\text{H}_2\text{O}]}{k_2 + k_3[R\text{NH}_2] + k_4[\text{H}_2\text{O}]} \]  

(13)

\[ r_3 = \frac{k_1k_4[R\text{NH}_2][\text{R}_2 \ ... BM][\text{H}_2\text{O}]}{k_2 + k_3[R\text{NH}_2] + k_4[\text{H}_2\text{O}]} \]  

(14)

Assuming that \( [\text{R}_2 \ ... BM] = K[\text{RNH}_2] \), where \( K \) is a fixed and the overall reaction rate is:

\[ R_{\text{CO}_2} = r_2 + r_3 \]  

(15)

Thus the \( R_{\text{CO}_2} \) is:

\[ R_{\text{CO}_2} = \left( \frac{K_1k_3[R\text{NH}_2] + Kk_4[\text{H}_2\text{O}]}{k_2 + k_3[R\text{NH}_2] + k_4[\text{H}_2\text{O}]} \right)[\text{RNH}_2][\text{CO}_2] \]  

(16)

The interaction in Eq. (10) is a quick, two-way interaction where the result is intermediary and short. So that \( k_1 \) and \( k_2 \) much larger than \( k_3 \) and \( k_4 \) in Eqs. (11) and (12). So it can be assumed that \( k_2 \) is dominate on \( k_3[R\text{NH}_2] \) and \( k_4[\text{H}_2\text{O}] \) to simplify the Eq. (16) by \( K = k_1, k_3 = k_{\text{RNH}_2} \) and \( K_k_1, k_4 = k_{\text{H}_2\text{O}} \) to obtain reaction rate:

\[ R_{\text{CO}_2} = (k_{\text{RNH}_2}[\text{RNH}_2] + k_{\text{H}_2\text{O}}[\text{H}_2\text{O}])[\text{RNH}_2][\text{CO}_2] \]  

(17)

replacing water with a linear alcohol, Eq. (12) becomes as follows [24, 25]:

\[ \text{RNHCOO}^- \ ... BM^+ + \text{ROH} \Rightarrow \text{RCO}_3^- + \text{RNH}_3^+ + \text{BM} \]  

(18)

And reaction rate could be expressed:

\[ R_{\text{CO}_2} = (k_{\text{RNH}_2}[\text{RNH}_2] + k_{\text{ROH}}[\text{ROH}])[\text{RNH}_2][\text{CO}_2] \]  

(19)
For pseudo first order condition wherever the solvent (i.e amine or amine blend and liner alcohol) would be in overabundance, the reaction rate could be represented as in Eq. (20):

\[ R_{CO_2} = K_{obs} [CO_2] \]  

(20)

Where:

\[ K_{obs} \] is the observed reaction rate constant and could be expressed as:

\[ K_{obs} = (k_{RNH2}[RNH2] + k_{ROH}[ROH])[RNH2] \]  

(21)

Whether the amine (DBN blend in this research) is the controlling base, the interaction was ranked second with the amine and Eq. (21) becomes:

\[ K_{obs} = k_{DBN}[DBN]^2 \]  

(22)

And the overall reaction rate is:

\[ R_{CO_2} = K_{DBN} [DBN]^2 [CO_2] \]  

(23)

If alcohol is the controlling base, reaction rate constant becomes:

\[ K_{obs} = k_{ROH}[ROH][DBN] \]  

(24)

And the interaction was ranked second with respect to [DBN] and the overall reaction rate is:

\[ R_{CO_2} = K_{ROH} [ROH][DBN][CO_2] = K [CO_2][DBN] \]  

(25)

where: \( K = k_{ROH}[ROH] \).

3. EXPERIMENTAL WORK

3.1. Materials

1,5-Diazabicyclo [4.3.0] non-5-ene (DBN) (purity ≥ 98%), Methyldiethanolamine (MDEA) (purity 99%) and 1-Pentanol (purity 99%) used in experiments which were purchased from TCL. Carbon dioxide and nitrogen gases with a pureness of 99.95% from SDI Samarra.

3.2. Experimental Procedure

The metering device is consisting of a glass stirred cell 100 ml, and a pressure transducer (0 – 1) bar. Fig. 2 illustrates schematically the diagram of the stirred cell set up. The CO₂ reaction kinetics are measured for the DBN/MDEA/1-Pentanol where 40 ml of solvent was placed at the designed concentration in the reactor-cell and the solution was mixed by stirring vigorously. Pure CO₂ gas was controlled by a flow meter and then pumped into the reactor after ensuring closing all outlets reactor-cell. This is starting point the experiment and the pressure starts to decrease. The pressure was measured by the pressure transducer during each half minute. The recorded partial pressure of CO₂ (P₉) was drawn with time and inclination represented \( -\frac{dP_{CO_2}}{dt} \) by using the relationship:

\[ R_{CO_2} \hat{a} = -\left[ \frac{V_G}{V_LRT} \frac{dP_{CO_2}}{dt} \right] \]  

(26)

Where: \( R_{CO_2} \hat{a} \) is the reaction rate of CO₂ (kmol/m². s), \( V_G \): is the volume of gas inside reactor (m³), \( V_L \): is the liquid volume inside the reactor (m³), \( R \): is gas constant (m³ kPa/kmol. K), \( T \): is temperature (K), \( t \): is time (sec), \( P_{CO_2} \): is partial pressure of CO₂ in bulk gas phase (kPa) and \(-\frac{dP_{CO_2}}{dt}\): represent the slope which represents the absorption rate.

![Fig. 2. The schematic of the stirred-cell apparatus.](image)

The calculated \( R_{CO_2} \) was used to evaluate the observed reaction rate constant (\( k_{obs} \)) using the following relationship:

\[ R_{CO_2} = [CO_2] \sqrt{D_{CO_2} k_{abs}} = P_{CO_2} H_{CO_2} \sqrt{D_{CO_2} k_{obs}} \]  

(27)

where: \([CO_2]: \) is the interfacial concentration of CO₂ (kmol/m²), \( D_{CO_2}: \) is diffusivity of CO₂ in solvent (m²/sec) and \( H_{CO_2}: \) is solubility of CO₂ in solvent (kmol/m³. kPa).

4. RESULTS AND DISCUSSION

The CO₂ interaction with DBN/MDEA/1-Pentanol is studied at room temperature with DBN concentrations of (2 - 2.9) M by calculating the CO₂ reaction rate with DBN/MDEA/1-Pentanol mixture. As shown in fig. 3, the reduction of the CO₂ partial pressure was gradually over time indicates the CO₂ interaction with DBN/MDEA/1-Pentanol. The interaction rate of CO₂ \( R_{CO_2} \hat{a} \) were illustrated in Table 1. \( R_{CO_2} \) was plotted against \([DBN]_0 \) at room temperature as shown in Fig. 4. Using linear regression, it found that the R-squared value is poor (\( R^2 = 0.9 \)) and the relationship is not-linear. Therefore, the system is not the first order [16].

**Table 1**

Reaction rate of CO₂ \( R_{CO_2} \hat{a} \) in \([DBN]_0 \) at room temperature.
A comparison with other previous studies was revealed in Table 2. It could be noticed that this work value of $k_{obs}$ is higher than that reported in the literature because DBN concentration was 2.9 M higher than the other studies.

Table 2
Values of $k_{obs}$ for CO$_2$-binding organic liquids at 308 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Wt%</th>
<th>$k_{obs}$ sec</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBN/1-Hexanol</td>
<td>20</td>
<td>891</td>
<td>[27]</td>
</tr>
<tr>
<td>DBN/1-Propanol</td>
<td>15</td>
<td>763.1</td>
<td>[28]</td>
</tr>
<tr>
<td>DBN/MDEA/1-Pentanol</td>
<td>38</td>
<td>1025</td>
<td>this work</td>
</tr>
</tbody>
</table>

Impose second-rank kinetics for DBN, and later, overall third-rank kinetics, Eq. (27) could be appeared as:

$$R_{CO_2} \hat{a} = H_{CO_2} P_{CO_2} \sqrt{D_{CO_2} K_2 [DBN]_0^2} \quad (28)$$

Fig. 5 shows a plot of $(R_{CO_2} \hat{a})$ against the partial pressure of CO$_2$ $(R_{CO_2} \hat{a})$ at room temperature. If it is assumed that the reaction is the first-order and is the slope for the plot of Fig. 4 which is equal to $2.64 \times 10^{-6} \text{ kmol/m}^2\cdot\text{s.kPa}$. This slope represents $H_{CO_2} \sqrt{D_{CO_2} K_2}$ at room temperature. Using the solubility and the diffusivity values of CO$_2$ according to Versteeg and Van Swaaij [26], (i.e $H_{CO_2}$-solvent = 0.019 kmol/kPa.m$^2$ and $D_{CO_2}$-solvent = $1.87 \times 10^{-11} \text{ m}^2/\text{sec}$, $k_{obs}$ was found to be equal 1025 sec$^{-1}$.

Table 3
Kinetic comparison of different CO$_2$ capture.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Reaction order</th>
<th>$k_2$, m$^2$/kmol.sec</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBN/MDEA/1-Pentanol</td>
<td>2</td>
<td>6532</td>
<td>This work</td>
</tr>
<tr>
<td>DBU/1-Hexanol</td>
<td>1.21</td>
<td>627</td>
<td>[10]</td>
</tr>
<tr>
<td>AMP</td>
<td>1.15</td>
<td>502</td>
<td>[29]</td>
</tr>
<tr>
<td>MEA</td>
<td>1.04</td>
<td>5545</td>
<td>[29]</td>
</tr>
</tbody>
</table>

It is important to note that in the event the two-step zwitterions are suitable, $k_{obs}$ can be written as follows:
The observed reaction rate constant was observed to be significant in the overall reaction. On the top of all, the DBN contribution to deprotonation is a critical factor. It is clear that DBN is the controlling base. Thus, $k_{obs}$ is equal to $k_{DBN}[DBN]^{-2}$. Therefore, the CO$_2$/DBN reaction system could be appear evenly well by both zwitterion and termolecular mechanism.

5. CONCLUSIONS

In this paper, the kinetic reaction of the CO$_2$ reaction with CO$_2$BOLs system (DBN/MDEA/1-Pentanol) at concentrations (2.0 – 2.9 M) and room temperature was performed in a stirred-cell reactor. It was found that the initial concentration values of DBN give increase in the capturing rates of CO$_2$. The two-steps zwitterion and the single-step termolecular mechanism were used to describe the carbonate formation. The CO$_2$ reaction with DBN/MDEA/1-Pentanol system was found to be of the second order. The observed reaction rate constant was evaluated at 308 K and its value 1025 sec$^{-1}$ which is within the range of the previous studies.

REFERENCES


