**Effect of carbon nanotubes and activated carbon addition to the blends of monoethanolamine and triethanolamine on CO₂ absorption at low partial pressures**

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**ABSTRACT**

Carbon dioxide is a major greenhouse gas that contributes to the global warming by more than %60. Absorption has been widely used to treat high concentrations of CO₂ in synthesis gas production, hydrogen manufacturing, and natural gas processing. The most well established method to capture CO₂ is its removal by absorption into amine solutions in the presence of activators. In this research, CO₂ absorption was measured in aqueous solutions of triethanolamine+monoethanolamine with different concentrations in the presence and absence of carbon nanotubes and activated carbon at temperatures ranging from 30 to 70 °C and low partial pressures in an absorption cell. Partial pressures were changed in the range of 10-70 kPa. The results revealed that the CO₂ absorption rate and capacity increases by adding small amounts of MEA to TEA. Moreover, CO₂ absorption rate and capacity increased with addition of carbon nanotubes and activated carbon to amine mixtures and the enhancement is higher for carbon nanotubes than activated carbon. Lowering the temperature increases CO₂ loading in solution.

**KEYWORDS:**
Carbon Dioxide, Absorption, Blended Amines, Carbon Nanotubes, Partial Pressures, Activated Carbon

1. **INTRODUCTION**

There are various technologies to separate CO₂ from flue gas of conventional fossil-fuel-fired power plants, e.g. chemical absorption, physical absorption, membrane separation and biological fixation. Chemical absorption is generally recognized as the most effective technology among all the technologies at present [1]. The most well-established method to capture CO₂ is its removal by absorption into amine solutions in conventional equipments. Amines are weak basic compounds that react with CO₂ to form weak chemical bonds. These chemical bonds are broken upon heating, leading to the regeneration of amine solution. Although chemical absorption technology has important commercial significance, judicious selection of a competitive absorbent that is capable of high CO₂ loading, rapid absorption rate and low cost for regeneration remains as a challenge [2]. The absorption of acidic gases such as CO₂ in alkali solutions is a common and important industrial process especially in sweetening the natural gas, and has been used for many years. Examples of alkali solutions are alkanolamines, such as monoethanolamine(MEA), methyl diethanolamine (MDEA) and triethanolamine (TEA).

In 1968, Caplow [3] presented a hypothesized mechanism for carbamate (R₂NCOO⁻) formation,
in the absorption of CO$_2$ by a secondary alkanolamine solution, involving the formation of an intermediate called zwitterion. This mechanism has two steps: formation of CO$_2$-amine zwitterion (reaction 1), followed by base-catalyzed deprotonation of zwitterion (reaction 2) [4].

\[
CO_2 + R_2NH \overset{k_1}{\underset{k_{-1}}{\Leftrightarrow}} R_2NH^+CO_2^- (1)
\]

\[
R_2NH^+CO_2^- + B \overset{k_2}{\underset{k_{-2}}{\Leftrightarrow}} R_2NCO_2^- + B^+H^+ (2)
\]

Where B$_i$ designates any species in solution that can act as a base to abstract proton from the zwitterion ($R_2NH^+CO_2^-$) in the second reaction step. B$_i$ can be diethanolamine, hydroxide ion, water and tertiary alkanolamines.

Reaction rates between CO$_2$ and primary, secondary and tertiary amines are different; it is slow in tertiary amines. The overall reaction for tertiary amines can be written as:

\[
CO_2 + H_2O + R_3N \rightarrow R_3NH^+ + HCO_3^- (3)
\]

The following reactions can also occur in aqueous solutions of tertiary amines, which have role in total reaction rate [5, 6]:

Bicarbonate formation:

\[
CO_2 + OH^- \rightarrow HCO_3^- (4)
\]

Carbonic acid formation:

\[
CO_2 + H_2O \rightarrow HCO_3^- + H^+ (5)
\]

Alkyl carbonate formation:

\[
CO_2 + OH^- + R,NCH$_2$CH$_3$OH \rightarrow
R,NCH$_2$CH$_3$OOCO^- + H$_2$O (6)
\]

Primary alkanolamines react with CO$_2$ to produce stable carbamate compounds, so they need more energy in regeneration step, while tertiary sterically hindered alkanolamines can not react with CO$_2$ directly and so, carbamate production is zero or minimum. So, they absorb CO$_2$ by acid–base reaction mechanism and as a result they have lower heat of reaction and will be regenerated with lower energy consumption to reverse the direction of reaction with CO$_2$ [7].

The absorption of acid gases in mixed amines has specific advantages over the use of single amines. The addition of small amounts of primary amines to conventional tertiary amine solutions can enhance the rate of CO$_2$ absorption to a large extent without appreciably affecting the stripping characteristics. By varying the relative concentrations of primary and tertiary amines in solution, an optimum solvent can be designed for a specific absorption application [8]. Carbon nanotube (CNT) and activated carbon (AC) have large surface area and therefore may interact with CO$_2$ and solvent or act as a medium between them; this establishes a potential to enhance carbon dioxide absorption by alkanolamine solutions. So in this research, CO$_2$ absorption experiments were carried out at various amine blends in the presence and absence of CNT and AC at low CO$_2$ partial pressures in an absorption cell.

2. Experimental

2.1. Chemicals

The solutions were prepared using distilled water. MEA was from Merck with %99 purity. AC and TEA with %99 purity were from Merck, too. CNTs were with minimum purity of %95. CO$_2$ was from Ehterami Co. with minimum purity of %98 and argon was from Roham Gas Co. with certified purity of %99.999.

2.2. Apparatus and procedures

The solubility data were obtained using an atmospheric pressure apparatus (Fig. 1) similar to the one used by Xu et al [9]. The temperature in the reactor was fixed by a temperature controller (Jumo iTron 04, Germany) within ±0.1°C, adjusting the temperature in a thermostated water bath. A 270-cm$^3$ glass cell containing 75 cm$^3$ of alkanolamine solution and known amounts of AC or CNT, as suspension, was used. The proper flows of CO$_2$ and Argon were adjusted (Flow Controller, Supelco, VCD 1000, ±%0.3) and then mixed in a mixing tube to produce a proper CO$_2$ partial pressures in the range of 10-70 kPa. The total gas flow in all experiments was about 150 cm$^3$/min. The resulting gas stream passed through a water saturator at room temperature then, the saturated gas stream was bubbled into the alkanolamine solution. The outlet gas passed through a room temperature condenser to return evaporated water into the cell. The CO$_2$ content in the liquid phase was determined by the addition of excess amounts of phosphoric acid into the solutions and then by measuring the evolved volume of CO$_2$ by a graduated burette (Fig. 2) [7].
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Fig. 1: Simplified flow diagram of the atmospheric pressure system for the measurement of CO$_2$ equilibrium solubility.

Fig. 2: Simplified flow diagram of the atmospheric pressure system for measurement of CO$_2$ absorption.

2.3. Typical calculations

We consider that CO$_2$ and Ar are mixed with each other with flow rates of $F_{CO2}$ (ml/min) and $F_{Ar}$ (ml/min) respectively, and the mixture enters into amine solution with concentration of $M$ (mol/L) at temperature of $T$(K). A known volume of solution ($V_{sam}$: ml) is selected as sample at equilibrium conditions and the volume of CO$_2$ gas released from the sample in room temperature ($T_{Room}$: K) is $V_{1,CO2}$(ml). The ambient pressure ($P$: kPa) is obtained (±0.1 kPa) from the meteorological office. CO$_2$ can be considered as an ideal gas and so, the calculation of released CO$_2$ volume in standard temperature and pressure ($0^o$C and 1 atm) can be done as the followings:

$$\frac{pV_{1,CO2}}{T_{Room}} = \frac{101.325}{273.15} V_{2,CO2} = \frac{F_{CO2}}{T_{Room}(101.325)}$$  \hspace{1cm} (7)

The moles of CO$_2$ released ($m_1$) is obtained by Eq. 8:

$$m_1 = \frac{V_{2,CO2}}{22400}$$  \hspace{1cm} (8)

The moles of CO$_2$ released from 1ml of solution ($m_2$) is calculated by $m_2 = m_1 \div V_{sam}$. There are $M/1000$ moles of amine in 1ml of solution, so CO$_2$ loading in solution ($\alpha_{CO2}$) is found by:

$$\alpha_{CO2} = \frac{m_2}{(M/1000)}$$  \hspace{1cm} (9)

$\alpha_{CO2}$ is moles of absorbed CO$_2$ per mole of amine in the solution. The equilibrium partial pressure of CO$_2$ above solution ($P_{CO2}$: kPa) is obtained from Eq. 10:

$$P_{CO2} = P_{Ar} + P_{H2O} + P_{ip} = P$$  \hspace{1cm} (10)

$P_{Ar}$, $P_{H2O}$ and $P_{ip}$ are the partial pressures (kPa) of Argon, H$_2$O and impurities above solution, respectively. $P_{H2O}$ can be obtained from:

$$P_{H2O} = X_{H2O} P_{sat}$$  \hspace{1cm} (11)

$X_{H2O}$ is mole fraction of H$_2$O in absorbent solution and $P_{sat}$(kPa) is saturated H$_2$O vapor pressure in equilibrium temperature. Now we have:

$$F_{1,CO2} = F_{CO2} \cdot \left(\frac{W_{1,CO2}}{100}\right)$$  \hspace{1cm} (12)

$F_{1,CO2}$ is the flow rate of pure CO$_2$ (ml/min) and $W_{1,CO2}$ is the volume percentage of CO$_2$ in its capsule. The pure CO$_2$ percent in total mixture of CO$_2$, Ar and impurities ($W_{2,CO2}$) is calculated from:

$$W_{2,CO2} = \left[\frac{F_{1,CO2}}{(F_{CO2} + F_{Ar})}\right] \times 100$$  \hspace{1cm} (13)

So we can calculate the partial pressure of CO$_2$ ($P_{CO2}$: kPa) above amine solution in absorbance cell using Eq. 14:

$$P_{CO2} = (P_{CO2} + P_{Ar} + P_{ip}) \times \left(\frac{W_{2,CO2}}{100}\right)$$  \hspace{1cm} (14)

3. Results and Discussion

Fig. 3 compares our data with those reported previously by other researchers [7] for CO$_2$ absorption on a 15.3 %wt MEA aqueous solution at 40°C. It is obvious that our data are in good agreement with the literature and so, our system is calibrated.
3.1. The effect of MEA addition to TEA aqueous solution at 40°C

Increasing the MEA/TEA ratio, increases the CO₂ loading (Fig. 4) so that, 6% MEA + 18.75% TEA aqueous solution has the highest absorption capacity. This is because primary alkanolamines such as MEA react with CO₂ in alkaline solutions to produce stable carbamate as reaction (15). It is also possible the protonation of MEA according to reaction (16), but because of its low equilibrium constants (the mol fraction ratio of right hand reagents to left hand ones) compared to reaction (15) (Table 1), we can disregard it.

Tertiary alkanolamines such as TEA, contrary to primary and secondary ones (secondary alkanolamines produce unstable carbamates), are unable to produce carbamates and so, only react with CO₂ via acid–base reaction mechanism (reaction 16) and have lower absorption capacity [7].

\[
RNH_2 + CO_2 + OH^- \leftrightarrow RNHCOO^- + H_2O \quad (15)
\]

\[
R_3N + CO_2 + H_2O \leftrightarrow R_3NH^+ + HCO_3^- \quad (16)
\]

Table 1. Equilibrium constants of MEA in reactions (15) and (16) at various temperatures [7]

<table>
<thead>
<tr>
<th></th>
<th>303 K</th>
<th>318 K</th>
<th>333 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction 15</td>
<td>1.61×10^{13}</td>
<td>3.71×10^{12}</td>
<td>9.46×10^{11}</td>
</tr>
<tr>
<td>Reaction 16</td>
<td>5.27×10^{3}</td>
<td>1.83×10^{3}</td>
<td>6.55×10^{2}</td>
</tr>
</tbody>
</table>

The equilibrium constants are calculated using mole fractions and so, are dimensionless.

3.2. The effect of CNTs addition on the absorption behavior of different solutions of TEA+MEA at 40°C

Results showed that addition of 1 g/L CNTs to the solutions, increased the loading of CO₂ and absorption rate, and decreased the time necessary to reach equilibrium (Fig. 5). The increase in the absorption rate in the presence of CNTs may be explained by the shuttle mechanism [10], wherein it is proposed that the CNTs adsorb the dissolved gas in the gas-rich layer adjacent to the interface. CNTs then move to the bulk where desorption of the adsorbed gas takes place. This increases CO₂ uptake and enhances the rate of absorption.
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### 3.3. The effect of AC and CNTs on CO₂ absorption

In this study, AC and CNTs were used as additives in TEA %18.75 + MEA %6 solution at 40°C. The results showed that the addition of 1 g/l of CNTs into the solution increases CO₂ loading higher than the equal dosage of AC. This is perhaps related to small sizes and regular shapes of CNTs which provide more surface area to take part in interactions which are effective in the absorption of CO₂ (Fig. 6).

### 3.4. The effect of CNT amount on CO₂ loading in different solutions of TEA+MEA

Experiments were done with the addition of 0.2, 0.5, 1 and 1.5 g/L CNT to different solutions of TEA+MEA. Results showed that increasing the amount of CNT is effective on CO₂ loading (Fig. 7).

### 3.5. The effect of AC amount on CO₂ loading in TEA+MEA solution

Experiments were done with the addition of 0.5, 1, 1.5 and 2 g/L AC to TEA+MEA solution. Results showed that increasing AC amount has no measurable influence on CO₂ loading (Fig. 8).

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Fig. 5: The effect of CNTs on CO₂ absorption at 40°C

Fig. 6: The effect of AC and CNTs on CO₂ absorption in TEA %18.75 + MEA %6 solution at 40°C

Fig. 7: The effect of AC and CNTs on CO₂ absorption in different solutions of TEA+MEA

Fig. 8: The effect of AC amount on CO₂ loading
3.6. The effect of temperature on the behavior of CO$_2$ absorption into TEA+MEA mixture

Fig. 9 shows the loading of CO$_2$ in aqueous solutions of TEA %18.75 + MEA %6 at 30, 40, 50, 60 and 70 °C. It can be seen that increasing the temperature, decreases the CO$_2$ loading due to a decrease in physical solubility of gases. It should be noted that, CO$_2$ absorption in aqueous alkanolamine solutions has two steps. First, CO$_2$ molecules physically dissolve in water and then, they chemically react with alkanolamine species in the solution. Increasing the temperature, limits the first step and so, total absorption of CO$_2$ decreases.

Fig.9: CO$_2$ loading vs. time at various temperatures in an aqueous solution of TEA % 18.75 + MEA%6.

4. Conclusion

In this work, aqueous solutions of TEA + MEA with different concentrations in the presence and absence of CNTs and AC at temperatures ranging from 30 to 70 °C and low partial pressures were used for CO$_2$ absorption from gas stream. The results showed that replacing some of TEA with MEA in the solution or addition of some CNTs or AC to the solution increases the CO$_2$ loading but CNTs have more influence on absorption process. CNTs addition increased CO$_2$ absorption rate and capacity but raising the absorption capacity was less noticeable. Lowering the temperature increased CO$_2$ loading in the solution.

5. Acknowledgements

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6. Nomenclature

- $F_{CO_2}$: Flow rates of CO$_2$ [ml/min]
- $F_{Ar}$: Flow rate of Ar [ml/min]
- $F_{Ar_{CO_2}}$: Flow rate of pure CO$_2$ [ml/min]
- $P$: Ambient pressure [kPa]
- $P_{CO_2}$: Equilibrium partial pressure of CO$_2$ above solution [kPa]
- $P_{Ar}$: Argon partial pressure above solution [kPa]
- $P_{H2O}$: H$_2$O partial pressures above solution [kPa]
- $P_{p}$: Partial pressure of gas impurities above solution [kPa]
- $P_{sat}$: Saturated vapor pressure of H$_2$O in equilibrium temperature [kPa]
- $T$: Temperature [K]
- $T_{room}$: Room temperature [K]
- $V_{sam}$: Volume of sample solution [ml]
- $W_{1,CO_2}$: Volume percentage of CO$_2$ in its capsule
- $\alpha_{CO_2}$: Moles of absorbed CO$_2$ per mole of amine in solution
- $X_{H_2O}$: Mole fraction of H$_2$O in solution

7. References


