Effect of Side Chain Structure and Number of Hydroxyl Groups of Primary, Secondary and Tertiary Amines on their Post-Combustion CO₂ Capture Performance

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Abstract

The effect of the side chain structure and the number of hydroxyl groups in primary, secondary and tertiary amines on kinetics of CO₂ absorption (40°C, 15% CO₂ feed gas) and desorption (at 90°C), equilibrium loading, heat duty, cyclic capacity, heat of absorption and pKa were investigated. The results showed that, compared with their straight-chain analogues, steric hindrance in branched-chain alkanolamines resulted in much higher solubilities and lower initial absorption rates. Steric hindrance in tertiary amines increased the desorption rate but lowered the heat duty. More hydroxyl groups attached to nitrogen group resulted in a lower absorption rate and amine basicity.

Keywords: CO₂ capture; sterically hindered alkanolamines; heat duty; absorption, desorption; number of hydroxyl groups.

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1. Introduction

Post combustion CO₂ capture using a reactive solvent is one the most mature CO₂ capture technologies. However, no individual solvent has the best of the activity criteria required of a CO₂ capture solvent. There is therefore the need to develop or formulate novel solvent blend systems. Several attempts have been made to improve the solvent blend technology. These mostly involve mass transfer and reaction kinetics studies. However, scanty work has been done in establishing amine-based structure–activity relationships for CO₂ capture for use in designing and synthesizing an optimum amine-based solvent blend. It is essential to have a fundamental understanding of these relationships. Structural differences such as side chain, chain length, number of functional groups, alkyl group position in cyclic amine, etc., have been shown to have significant effect on the amine activity performance. Singh et al. [1] investigated the effect of side chain position of different amines. From their work, it was seen that an introduction of a substituent at the α-carbon position decreased the initial absorption rate for primary amines but increased the absorption capacity when compared to a substituent at the β-carbon position. This behavior was attributed to steric hindrance created by the α-carbon substitution.

According to Satori et al. [2], steric hindrance reduces the stability of the carbamate. Consequently, the carbamate ion can easily undergo hydrolysis to form the bicarbonate ion. A typical example of sterically hindered amines, 2-amino-2-methyl-1-propanol (AMP) has been found to show attractive solvent properties in terms of its very low heat duty and high CO₂ absorption capacity. NMR studies performed by Hook [3] to determine the carbamate, bicarbonate and carbonate concentration in solution showed the level of steric hindrance of different amines. It was found that a higher number of methyl groups present at the α-carbon position resulted in lower carbamate stability, but the effect of one methyl group present at the α-carbon was not strong to induce full conversion of carbamate to bicarbonate. Chowdhury et al. [4] investigated synthetic and commercial amine based absorbents by modifying their chemical structures. The results showed that the placement of functional groups within the amino group affects CO₂ absorption-regeneration performances.

Thus, based on the works done in literature in showing the impact of the various structural differences on the CO₂ capture activities, the objective of the present work is to evaluate the side chain structure–activity relationships for primary, secondary and tertiary amines for the purpose of identifying specific structure traits that are beneficial in formulated and blended solvent for use in a post combustion amine-based CO₂ capture.

2. Experiments

2.1. Chemicals

The amines studied in this work are butylethanolamine (BEA), monoethanolamine (MEA), tertbutyldiethanolamine (tBDEA), butyldiethanolamine (BDEA), tertbutylethanolamine (tBEA), butylamine (BUTYL), sec-butylamine (SEC) and iso-butylamine (ISO). Their chemical structures are as shown below.

2.1.1. Materials and Equipment

Butylethanolamine (> 98%), Monoethanolamine, Butylamine, sec Butylamine, iso Butylamine (≥ 99%), and 1N hydrochloric acid (HCl), were purchased form Sigma-Aldrich Co., Canada. N-Butyldiethanolamine (98%) was purchased from Acros Organics, and N-tertButylethanolamine (96%) was purchased from Oakwood Chemical. The premixed gases used for the solubility experiment, (3, 8, 15, 30 and 100% CO₂ (N₂ balance) were supplied by Praxair Inc., Regina, Canada. The water bath used in the solubility experiment with model number: 12112-12, SN: G29972, which was equipped with a temperature controller (-20 to 200 ºC capacity with ±0.01 ºC accuracy) was obtained from Cole-Palmer, Canada. A mass flow meter (Electronic AALBORG GFM171 with a range of 0-500 ml/min with accuracy ±1%, and a hot plate from Fischer Scientific Company were used.
2.2. Experimental Procedure

2.2.1 Absorption Experiment

The absorption experiment was done using the method described by Singto et al. [5]. A concentration of 2M was selected and used for all amines in order to screen as many amines as possible, including tertiary amines. The experiment was done at 40±1°C, using 15% CO₂ (N₂ balance. A stirring speed of 600 rpm was maintained for all the test runs. All amines used were soluble in water. An average absorption time of 6 hours was allowed. The volume of amine sample used was maintained at 100 ml for all experiments. The apparatus comprised a three-necked round bottomed flask, a thermometer was installed through one neck to measure the amine solution temperature, a condenser to the middle neck to recover amine and water carry over and a gas dispersion tube in the last neck for feeding the gas. The experimental data obtained is then used to generate a plot of loading versus time and the initial absorption rate was determined by finding the slope of the linear part of the absorption profile.

Fig. 1. Simplified diagram of absorption and desorption set up
2.2.2 Desorption Experiment

A measured volume (76 ml) of the equilibrium loaded solution from the absorption tests was used for the desorption experiment. The same setup in Fig 1a was used for this experiment. However, in this test the gas dispersion tube was removed and the neck sealed off. Briefly, at the start of the experiment, the three-necked round bottomed flask was totally immersed in the preheated oil bath and allowed to reach the desorption temperature of 90°C. The heating time was approximately 5 minutes. Samples were taken from the flask at specific times until equilibrium was reached at 90°C. Since the rate of desorption slowed down after 5 min, and gradually reaching equilibrium, the initial desorption rate was calculated by determining the slope of the points from time 0 min to time = 5 min. as most of the removable CO₂ had been removed within this heating time. The initial time of zero min was used also to reflect the practical situation in the regeneration unit where desorption begins all the way from the cross heat exchanger as the rich amine solution is preheated even before it finally enters the desorber.

2.2.3 Equilibrium Solubility

The equilibrium CO₂ solubility tests were done using the procedure described by Maneeintr et al. [6] at the temperature range of 40-90°C for high boiling point amines and 20-40°C for low boiling point amines, for CO₂ partial pressures in the range of 3-100 kPa. The experimental setup, which comprised of a water bath installed with a temperature controller with an accuracy of ± 0.01°C, as shown in Fig. 1, was used. Briefly, prior to the experiment the water bath was set at the desired temperature and a known volume of amine solution (20 ml) was loaded into the absorption reactor, and placed in the bath. A condenser was installed at the outlet of the reactors to recover amine and water carry over. The desired premixed gas at flow rate of 350 ml/min was bubbled first though a water saturation cell and then finally into the reactor through gas dispersion tubes after the solution had attained the desired temperature. To ensure that equilibrium was attained, the process was kept in operation for an average time of 18-20 hours. To confirm that equilibrium was reached, samples were taken and analyzed for loading at a time interval of two hours in order to have two consecutive readings that showed just a slight difference of not greater than 5%. Samples were analyzed using the Chittick apparatus [7]. The CO₂ loading measurements were repeated twice and the average taken. The error of the measurements was typically within ± 0.01. The solubility data obtained for the current work were validated by comparing the solubility data for 5 M MEA obtained from this work with those in the literature [8]. The results, which are shown in Fig. 3, show good reproducibility of our data with the literature.
2.2.4) Heat Duty Determination

The heat duty was calculated by determining the ratio of the steady state heat transfer to the amount of CO₂ removed during desorption over a 5 min period (the linear portion of the desorption kinetics profile). Fourier’s equation of thermal conduction was used to calculate the heat supplied from the oil bath as shown in equation (1):

\[ q = \frac{kA}{dx} \frac{dT}{dx} \tag{1} \]

where \( q \) is the rate of heat transfer at steady state in J/s, \( k \) is the thermal conductivity of the Pyrex glass used for the flask material in W/mK, \( A \) is the cross sectional area normal to the direction of heat flow in m², \( dT/dx \) is the temperature gradient (K.m⁻¹). The temperature difference, \( dT \) was taken as the difference between the oil temperature and the inner wall temperature of the flask, while \( dx \) was the glass wall thickness. The heat duty was then calculated using equation (2):

\[ Q_{reg} = \frac{\text{rate of heat transfer} (J/s)}{\text{CO₂ removed} (\text{mol/s})} \tag{2} \]

The amount of CO₂ removed was obtained by determining the cyclic capacity of the amine in 5 min at 90°C using the linear portion of the desorption profile.

2.2.5 Acid Dissociation Constant (pKa)

The dissociation constant was determined using the titration technique described by Shi et al. [9]. 100 ml of 0.05M of amine solution was prepared and titrated stepwise with 1.0 N HCl until methyl orange endpoint was achieved. After every 0.5 ml addition of HCl, the pH was measured. After obtaining the concentration of H⁺ from the
pH meter, the pKa was then calculated using equations 4-7. The protonation reaction of the amine in aqueous solution is given as:

\[ \text{Amine} + \text{H}^+ \rightleftharpoons \text{AmineH}^+ \]  

(3)

By assuming that the solution is ideal (activity coefficient is equal to 1) [7, 10] the Amine H⁺ dissociation constant \( K \) can be calculated by:

\[
K_{\text{amine}} = \frac{[\text{Amine}][H^+]}{[\text{AmineH}^+]}
\]

hence; pKa = -log(Ka) = -log \left( \frac{[\text{Amine}][H^+]}{[\text{AmineH}^+]} \right)  

(5)

Since there is a reduction in the concentration of H⁺ during the titration as a result of its reaction with the amine to form AmineH⁺ as shown in equation (3), the concentration of AmineH⁺ can be calculated using the mass balance of protons in the equation:

\[ n_{\text{HCl}} - [H^+]V_{\text{total}} = [\text{AmineH}^+]V_{\text{total}} \]  

(6)

The concentration of free amine can be calculated using:

\[ ([\text{Amine}] + [\text{AmineH}^+])V_{\text{total}} = n_{0,\text{amine}} \]  

(7)

where, \( n_{\text{HCl}} \) is the number of moles of HCl added during the titration, \( V_{\text{total}} \) is the total liquid volume after titration, and \( n_{0,\text{amine}} \) is the initial number of moles of Amine, which can be determined by titration with 1.0 N HCl until the methyl orange end point.

2.2.5 Heat of Absorption

The heat of absorption was determined using the Gibbs-Helmholtz equation:

\[
\frac{d(\ln P_{CO_2})}{d(1/T)} = \frac{\Delta H_{\text{abs}}}{R}
\]

(8)

Typically, experimental data used to calculate the heat of absorption involves trial and error experiments to attain the same coinciding loading in at least three different temperatures and partial pressures. Also loadings that is attained may be higher than the actual equilibrium loadings under practical conditions. A new procedure addressing these limitations, which was validated with 5M MEA was described in details in our earlier work [11]. This method was used to calculate the heat of absorption. Equilibrium solubility data at 5 different partial pressures ranging from 3-100 kPa and at least four temperatures was obtained. An exponential type line of best fit equation was then used to describe each curve at each temperature. With this implemented, we can substitute any desired practical loading in the equation of the line of best fit, and calculate the corresponding \( P_{CO_2} \). The \( P_{CO_2} \) and temperature values are then used in equation (8) to determine the heat of absorption.
3. Results and discussion

3.1. Absorption rate

Fig. 4 shows the initial absorption rates of primary (1°), secondary (2°) and tertiary (3°) amine-based solvents. For 1°: ISO > SEC > BUTYL > MEA. A decrease in the initial absorption rate is observed in SEC (α-carbon) when compared to ISO (β-carbon position). This may be due to steric hindrance at the amine group, which decreased the initial rate. Steric hindrance had no significant effect in the β-carbon position as clearly seen in ISO, because the methyl group substituent is further away from the amine group than in SEC, and hence, suffers no strong influence from steric hindrance around the amino group. This trend is consistent with the results of Singh et al. [1] who studied the effect of the alkyl position on the initial absorption rate of SEC, ISO and BUTYL amines using pure CO₂ at an operating temperature of 30°C. It is important to note that all the alkylamines had higher rates than MEA which can be attributed to the presence of alkyl groups which tend to increase the electron density around the amino group thereby increasing their reactivity as compared with MEA (Fig. 4).

For 2° and 3° alkanolamines, BEA > tBEA and BDEA > tBDEA. These results illustrate the impact of steric hindrance on the initial CO₂ absorption rate of primary alkanolamines created by a higher number of methyl groups present at the α-carbon to the amine group. The higher the number of methyl groups attached to the α-carbon the stronger the impact of sterical hindrance. Thus, the rates of absorption of 2° and 3° sterically hindered amines are relatively lower than primary sterically hindered alkylamines as shown in Fig. 5.

The effect of the number of hydroxyl group is seen in the amines with respect to Butylamine (no–OH), Butylethanolamine (1–OH) and Butyldiethanolamine (2–OH). The decrease in the initial absorption rate followed the order: BUTYL > BEA > BDEA (Table 1). This is attributed to the electron withdrawing effect of the –OH group which increases with increasing number of –OH groups. This is illustrated in Fig. 6.

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**Fig. 4. Effect of side chain position on initial CO₂ absorption rates of primary alkyl amines**
Fig. 5. *Initial CO₂ absorption rate of primary, secondary and tertiary amines*

Fig. 6. *Effect of number of hydroxyl group substituents on the initial CO₂ absorption rate of 1°, 2° and 3° unhindered amines*

3.2. pKa

The pKa values for alkyl amines studied was in the order: BUTYL > ISO > SEC (Fig. 9). It shows that the substitution of a methyl group at the α-carbon atom next to the nitrogen group weakens the N-H bond thereby making it a weaker base as reported by Chakarborty et al. [12]. As such, we can see a significant reduction in the pKa value of SEC (α-position) than ISO (β-position) when compared to that of BUTYL. The same effect is also seen in sterically hindered tertiary alkanolamines (BDEA > tBDEA) where the substitution of three methyl groups at the α-position to the amine group impacts the basicity as shown in Fig. 10. For 2° amines on the other hand, the opposite trend is seen where tBEA > BEA.
The alkyl group typically has an electron donating effect which increases their basicity. Consequently, the alkyl amines have higher pKa values than alkanolamines which suffer an electron withdrawing effect from their –OH groups (see Fig. 10).

Also, the number of –OH groups as in BUTYL (no –OH group), BEA (1 –OH group) and BDEA (2 –OH) increases the electron withdrawing effect of the –OH group which lowers the basicity (and pKa) in that order (Fig. 11). BEA and MEA each have one –OH group. However, for BEA, the contribution of the electron donating effect from the alkyl group is higher, and hence, effectively counters the effect of the –OH group (Fig. 10).

![CO₂ absorption Profile for Alkanolamines](image1)

Fig. 7. CO₂ absorption Profile for Alkanolamines

![CO₂ absorption Profile for Alkylamines](image2) and MEA

Fig. 8. CO₂ absorption Profile for Alkylamines and MEA
3.3. Solubility

For 1°, absorption capacity increased in the order: MEA < BUTYL < ISO < SEC. The steric hindrance created by substitution at the α-carbon position in SEC reduces carbamate stability, enhancing its hydrolysis to bicarbonate and thus allowing for higher loadings. However, the level of sterical hindrance at the β-position leads to only marginal increase in the loading. For secondary and tertiary alkanolamines, tBEA > BEA and tBDEA > BDEA, respectively.
(Fig. 11). The same explanation for SEC applies to this trend since all the substituents are located at the α-carbon position.

![Equilibrium Solubility of primary, secondary and tertiary amines](image)

Fig. 11. *Equilibrium Solubility of primary, secondary and tertiary amines*

### 3.4. Heat of Absorption

The reaction between amine and CO₂ is exothermic. The heat released gradually drops as the reaction proceeds. At equilibrium and after, the heat drops drastically as the driving force approaches zero at this point. In order to make a fair comparison, a loading at approximately halfway the equilibrium at 15% CO₂ and absorption temperature of 40°C was selected in order to have this at practical conditions used in industry. From the results (Fig. 12), it can be observed that all the side chain (hindered) amines had higher heat of CO₂ absorption values than the straight chain (unhindered) amines. For secondary amines tBEA > BEA and tertiary amines tBDEA > BDEA. This might be attributed to the higher amount of CO₂ absorbed in hindered amines with a corresponding larger amount of heat produced as compared to their straight chain analogues.

![Heat of CO₂ absorption values for 1°, 2° and 3° alkanolamines](image)

Fig. 12. *Heat of CO₂ absorption values for 1°, 2° and 3° alkanolamines*
3.5. Initial CO₂ Desorption Rate

Sterical hindrance affects the initial absorption rate negatively, however as suggested by literature it appears to enhance desorption. Carbamate instability is created by steric hindrance and thus the breakdown of the intermediate species is accelerated leading to a higher concentration of bicarbonate in the system and consequently resulting in higher and faster release of CO₂ during desorption. This is confirmed from the results obtained for tertiary amines, that is tBDEA > BDEA. (Fig. 13). The alkylamines studied in this work had boiling points in the range of 77-79 °C (for BUTYL), 67-69 °C (for ISO) and 63 °C (for SEC). As such, these amines were not tested for this activity since regenerating low boiling point amines at temperatures higher than their boiling points will result in highly significant amine vapor losses. For secondary amines on the other hand the reverse is seen, that is BEA > tBEA. Desorption is a complex reaction involving so many factors. As such not only sterical hindrance but other factors like amine basicity contribute to the overall desorption performance. In desorption, the following reaction mechanisms take place:  

AmineH⁺ deprotonation:  
\[ BEAH⁺ + H₂O \leftrightarrow BEA + H₃O⁺ \]  

Carbamate breakdown involves:

1. Proton transfer:  
\[ BEA - COO⁻ + H₂O \leftrightarrow BEA - H⁺ - COO⁻(zwitierion) + H₂O \]  

2. N-C bond breaking:  
\[ MEA - H⁺ - COO⁻(zwitierion) \leftrightarrow MEA + CO₂ \]

Reaction one is a critical reaction whose speed depends on the energy involved in transferring the proton to water. The stronger the base the more the energy needed for the proton transfer. Conversely, the weaker the base the easier it is for deprotonation to occur. This explain why BEA being a relatively weaker base than tBEA (Fig. 10) provides faster desorption for CO₂. Another factor that may be considered in the desorption of CO₂ from an amine is its propensity and quantity of bicarbonate formation. In the case of the secondary amines studied, it is expected that tBEA, a sterically hindered amine will produce more bicarbonate than BEA. However, the experimental results on the initial rate of CO₂ desorption of BEA as compared with tBEA show that the contribution from lower basicity of BEA may be stronger than the contribution from sterical hindrance OF tBEA.

3.6. Heat Duty for Solvent Regeneration

The heat duty (Qreg) for the primary, secondary and tertiary alkanolamines studied are given in Fig. 14. The figure shows that heat duty followed the order: tBEA > BEA (for secondary) and tBDEA < BDEA (for tertiary) as shown in Table 1. This can be explained on the basis that for the same amount of energy input, the amines with the faster desorption rates release more CO₂ within the same period of time thereby consuming less energy per unit of CO₂ desorbed.
Fig. 13. Comparison of the initial CO₂ desorption rates of primary, secondary and tertiary alkanolamines

Fig. 14. Heat Duties of primary, secondary and tertiary alkanolamines
Fig. 15. Desorption Profiles for Primary, Secondary and Tertiary Alkanolamines

Table 1. Summary of results for all CO2 Performance Activities investigated

<table>
<thead>
<tr>
<th>AMINE</th>
<th>Heat duty, kJ/mol CO2</th>
<th>Heat of absorption, kJ/mol</th>
<th>Initial CO2 Absorption rate, $\times 10^{-2}$ mol/l.min</th>
<th>pKa</th>
<th>Initial CO2 Desorption rate $\times 10^{-2}$ mol/l.min</th>
<th>Cyclic Capacity, mol CO2</th>
<th>Equilibrium loading, mol CO2/mol amine</th>
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<tbody>
<tr>
<td>MEA</td>
<td>427.6</td>
<td>90.28</td>
<td>1.12</td>
<td>9.33</td>
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<td>0.55</td>
</tr>
<tr>
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<td>1.24</td>
<td>10.66</td>
<td>NA</td>
<td>NA</td>
<td>0.61</td>
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<tr>
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<td>NA</td>
<td>NA</td>
<td>1.3</td>
<td>10.53</td>
<td>NA</td>
<td>NA</td>
<td>0.72</td>
</tr>
<tr>
<td>ISO</td>
<td>NA</td>
<td>NA</td>
<td>1.52</td>
<td>10.6</td>
<td>NA</td>
<td>NA</td>
<td>0.65</td>
</tr>
<tr>
<td>BEA</td>
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<td>9.18</td>
<td>0.64</td>
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<tr>
<td>tBEA</td>
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<tr>
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<tr>
<td>tBDEA</td>
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<td>0.38</td>
<td>8.84</td>
<td>6.7</td>
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</table>
Fig. 16. Equilibrium solubility of butylamines at different partial pressures and temperatures (A: secButylamine (SEC); B: Butylamine (BUTYL); C: isoButylamine(ISO)).
4. Conclusions

- The steric hindrance present in branched alkanolamines resulted in much higher solubility, but only slightly decreased the absorption rate when compared with their straight chain analogues.
- Sterical hindrance present in branched tertiary alkanol amines resulted in a much faster desorption rate and a lower heat duty than the straight chain analogue amines.
- The number of hydroxyl groups attached to the amine group resulted in a lower absorption rate and lower basicity.
- From this work, the specific structure traits that are beneficial in solvent formulation has been identified for use in CO₂ post combustion capture.
Acknowledgements

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