Kinetics of CO$_2$ reaction with N-methyldiethanolamine and aminobutanol using stopped flow technique

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Abstract. Removal of carbon dioxide (CO$_2$) from natural gas streams is mandatory to avoid pipeline corrosion, increase the heating value of the gas and reduce the gas volume in case of liquefied natural gas (LNG). The use of N-Methyl-diethanolamine (MDEA) solution combined with other rate promoters such as Piperazine (PZ) is a common practice in Gas treatment technology. In this work, the use of Aminobutanol (AB) mixed with MDEA for the removal of (CO$_2$) from natural gas streams is presented. The reaction kinetics of (CO$_2$) with mixtures of MDEA and AB was investigated using stopped flow technique. The experiments were performed over a temperature range of 293 to 313 K and solution concentration of 0.5 and 1 moles/l in different MDEA/AB proportions. Obtained kinetics data were interpreted using zwitterion mechanisms for the primary amine AB. The individual rate constants of the participating reactions were regressed and their corresponding activation energies were estimated.

1. Introduction
Natural gas is a vital source of energy. It consists of methane with other hydrocarbons and non-hydrocarbon components. Compositions of natural gas varies in accordance to its formation process and it may contain diluents like CO$_2$ and N$_2$ [1]. The presence of carbon dioxide within natural gas stream causes an increase in the gas volume, reduces its heat value and may enhance corrosion within the pipelines and treatment plants. Therefore, CO$_2$ need to be removed to meet the required pipeline or LNG specifications [2]. Amine based absorption technology is a recognized and industrially implemented technology to remove CO$_2$ [3]. Many variants of chemical solvents based on primary, secondary and tertiary amines are available in the market with distinguished performances. However, several drawbacks such as low absorption rate, solvent degradation, high regeneration energy and severe equipment corrosion are encountered with their use.

Blended amines have been suggested for the absorption of acid gases [4]. As a common practice in the industry, tertiary amines are mixed with faster reacting primary, secondary amines or Piperazine that act as rate promoters. The addition of small amounts of promoters to slow reacting tertiary amines can enhance the rate of absorption of CO$_2$ to a large extent without appreciably changing the stripping characteristics [5].

Amino butanol, a primary amine, have recently been investigated by Idris et al [6] as a possible solvent for CO$_2$ capture. The equilibrium solubility of carbon dioxide in aqueous solutions of 4-amino-1-butanol at low partial pressures and two different concentrations (5 molar and 30 wt. %) and a temperature of 40 °C was presented [6]. It was found that CO$_2$ solubility in amino butanol is higher than its solubility in MEA. Benamor et al [7] recently presented kinetics data involving the reaction of amino
butanol with CO₂ over a temperature range varying from 293 to 313 K. The kinetics data were interpreted using two different reaction mechanisms and compared to several primary and secondary amines. It was found that aminobutanol, has a rate constant lower than that of MEA but still higher than those of secondary amine, DEA, and sterically hindered amine, AMP.

In this work, the reaction kinetics of carbon dioxide with aqueous mixtures of MDEA and AB using stopped flow technique is presented for the first time. The temperature was varied from 298 to 313 K while the amine total concentration was varied from 0.5 to 1 mole/l in different proportions of AB/MDEA.

2. Reaction Mechanism and Rate Models

2.1. Reaction of CO₂ with MDEA

The overall reaction of CO₂ and MDEA in aqueous solution is well documented and can be written as [8]:

\[ \text{CO}_2 + \text{MDEA} + \text{H}_2\text{O} \xrightarrow{k_{\text{MDEA}}} \text{MDEAH}^+ + \text{HCO}_3^- \]  

(1)

Its pseudo-first-order reaction rate is given as:

\[ R_{\text{CO}_2, \text{MDEA}} = k_{\text{MDEA}} [\text{CO}_2][\text{MDEA}] \]  

(2)

Beside reaction 1, the reaction of bicarbonate formation in water is given by

\[ \text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^- \]  

(3)

However, the contribution of this reaction is minimal and is usually neglected and is not considered here.

2.2. Reaction of CO₂ with Aminobutanol

The reaction of CO₂ with primary amine aminobutanol is well explained [7]. According to the zwitterion mechanism, this proceeds first by the formation of an intermediate zwitterion, which then undergoes a deprotonation by all bases present in the solution resulting in carbamate formation according to the following Eqs (4, 5):

\[ \text{CO}_2 + \text{RR'NH} \xrightarrow{k_1} \text{RR'NH}^+ \text{COO}^- \]  

(4)

\[ \text{RR'NH}^+ \text{COO}^- + \text{B} \xrightarrow{k_b} \text{RR'NCOO}^- + \text{BH}^+ \]  

(5)

The rate of reaction of CO₂ in aqueous solutions of 2-amino-1-butanol can be described as:

\[ R_{\text{CO}_2} = -k_{\text{ov}} [\text{CO}_2] = -\frac{k_1 [\text{CO}_2][\text{AB}]}{1 + (k_{-1} / \left( \sum k_{b_i} [B_i] \right))} \]  

(6)

\(k_{\text{bi}}\) denote the deprotonation rate constants of the zwitterion by any base, such as [H₂O], [OH⁻] or [AB]. Eq. (6) can be re-arranged in the following form:

\[ k_{\text{ov}} = -\frac{[\text{AB}]}{1/k_2 + \left( 1 / \left( k_{\text{w}} [\text{AB}] + k_{\text{w}yd} [\text{OH}^-] + k_{\text{w}} [\text{H}_2\text{O}] \right) \right)} \]  

(7)
where, the new constants are defined as $k_a = k_2 k_{AM}/k_{1}$, $k_{hyd} = k_2 k_{OH}/k_{1}$, $k_w = k_2 k_{H_2O}/k_{1}$

In a single-step termolecular mechanism [9] as represented by Eq. (8) and illustrated in figure 1, only one step is involved in the reaction.

$$\text{CO}_2 + \text{RR'NH}...\text{B} \rightleftharpoons \text{RR'NHCOO}...\text{BH}^+$$

Figure 1. Schematic drawing of single-step termolecular reaction mechanism [8]

According to this mechanism, the CO$_2$ reaction rate expression is a second order with respect to amine, it is very similar to the one derived by Crooks and Donnellan [8]:

$$\text{Am}...\text{B} + \text{CO}_2 \leftrightarrow \text{AmCOO}^−...\text{BH}^+$$

(9)

Analysis of the rate expression above shows that termolecular mechanism is equivalent to the asymptotic limit of the zwitterion mechanism when deprotonation is the rate-determining step:

$$1 \ll (k_{-1}/\sum k_{hi}[B_i])$$

In this case Eq (6) becomes:

\[
R_{CO_2} = k_{ov} \left[ CO_2 \right] = \left[ CO_2 \right] [AB] \left\{ \sum k_n \left[ B_i \right] \right\} = \left[ CO_2 \right] [AB] \left\{ k_a [AB] + k_w [H_2O] + k_{hyd} \right\}
\]

(10)

In general and regardless of the employed mechanism, a carbamate and a protonated base are the accepted products of the CO$_2$-amine reaction. In this present work, only zwitterion mechanisms is applied to interpret the obtained kinetics data.

2.3. Reaction of CO$_2$ with Mixtures of MDEA and Aminobutanol

For blends of MDEA and AB, the overall reaction rate with CO$_2$ is considered as the sum of reaction rates of CO$_2$-MDEA and CO$_2$-AB; hence:

$$R_{CO_2} = R_{CO_2,AB} + R_{CO_2,MDEA}$$

(11)

Using zwitterion mechanism, Equation 11 can be written as:

\[
R_{CO_2} \equiv \left( k_{AB} [AB] \right) / \left( 1 + \left( k_{-1}/\sum k_n \left[ B_i \right] \right) \right) + k_{MDEA} \left[ \text{MDEA} \right] \left[ CO_2 \right]
\]

(12)

Or $R_{CO_2} = \left( k_{AB} + k_{MDEA} \right) \left[ \text{MDEA} \right] \left[ CO_2 \right] = k_{ov} \left[ \text{CO}_2 \right]$

(13)

where $k_{AB} = \frac{k_2 [AB]}{1 + \left( k_{-1}/\left( k_{AB} + k_{OH} \right) \left[ OH^- \right] + k_{MDEA} \left[ \text{MDEA} \right] + k_{H_2O} \right) [H_2O]})$

(14)

which can be written as:
\[ k_{AB} = \frac{[AB]}{1 + \left(1 + \frac{k_{k2,AB}[AB]}{k_{k1} + \frac{k_{k2,OH}}{k_{k1} - \frac{k_{k1} - \frac{k_{k2,MDEA}}{k_{k1} + \frac{k_{k2,H2O}}{k_{k1}}}}}ight)} \]  

For simplicity, new constants, \( k_a, k_{hyd}, k_b \), and \( k_w \) are defined as:

\[ a = k_{k2,AB}/k_{k1}, \quad k_{hyd} = k_{k2,OH}/k_{k1}, \quad k_b = k_{k2,MDEA}/k_{k1}, \quad k_w = k_{k2,H2O}/k_{k1}. \]

Then, Eq 15 becomes:

\[ k_{AB} = \frac{[AB]}{\left(1/k_2\right) + \left(1/k_a[AB] + k_{hyd}[OH^-] + k_b[MDEA] + k_w[H_2O]\right)} \]  

3. Materials and Methods

Reagent grade N-methyldiethanolamine (MDEA) with a mass purity of 99% and 2-amino-1-butanol (AB) with a mass purity of 99% purchased from Sigma-Aldrich were used in this work. CO\(_2\) solutions were prepared by bubbling CO\(_2\) (> 99.99% pure) in deionized water (DI) that was previously degassed using pure N\(_2\). The concentration of CO\(_2\) in the water was measured with a gas chromatograph (GC-6890, Agilent). This solution was then diluted by adding fresh water until the amine concentration used was at least 20 times higher than that of CO\(_2\) to ensure that the pseudo first order condition with respect to CO\(_2\) is always met [10]. The concentrations of amine mixture were checked by titration using standard 0.1M hydrochloric acid solution. The homogeneous reaction rate between CO\(_2\) dissolved in water and amine solution was measured using stopped-flow apparatus (Hi-Tech Scientific Ltd., UK, Model SF-61DX2). Temperature was controlled by Lauda water bath model Alpha RA8 within ± 0.1 K. In all cases, the change of the amine concentration within the run time was very small and can be considered negligible for very low CO\(_2\) loading (such as our case) as was demonstrated by Kierzkowska-Pawlak et al [11].

4. Results and discussion

The experimental data of the observed rate (\( k_{ov} \)) of the CO\(_2\) reaction with methyldiethanolamine (MDEA) and aminobutanol (AB) were obtained by fitting the conductivity-time curves to Eq (13). The rate constant \( k_{AB} \) was calculated by taking into account Eqs (13) and (14), Values of \( k_{MDEA} \) were taken from a previous work [13]. The obtained overall reaction rate constants, \( k_{ov} \), were plotted against temperatures for different total concentrations (Figures 2 and 3). As observed in all runs, the overall rate constants (\( k_{ov} \)) increased with increased temperature and increased proportion of aminobutanol in the blend.

Upon applying the power law kinetics by plotting the CO\(_2\)-AB rate constant against the concentrations of aminobutanol (figure 4), an average exponent of 1.08 was obtained, which affirms that the pseudo first order regime prevails. Therefore, within the experimental concentration range, the reaction can be analyzed via the zwitterion mechanism [14].
Experimental rate constants, $k_{AB}$, data were fitted to Eq (16) to extract the individual blocks of rate constants described in this equation. The concentrations of water molecules (H$_2$O) were calculated by mass balance while hydroxyl ions (OH$^-$) were estimated from the relation given by Astarita et al [10].

$$[\text{OH}^-] = \sqrt{\frac{K_w}{K_{pi}}} \text{[AM]}$$

(18)

In this equation, amine concentration [AM] was considered to be the concentrations of MDEA and Arg independently. In this case, the total [OH$^-$] was taken to be the sum of [OH$^-$] ions produced by both MDEA and AB. The water dissociation constant, $K_w$, and protonation constant, $K_{pi}$, for MDEA and AB were taken from the literature [15-17]. Using Excel solver® nonlinear regression technique, experimental $k_{AB}$ values were fitted to Eq (17) taking into account the species concentrations, H$_2$O, AB, OH$^-$ and MDEA previously calculated. The generated rates constants are summarized in table 1. values of $k_2$ were taken from a previous work [7].

Using these generated rate constants, the $k_{AB}$ reaction rate constant values were predicted using Eq (16) and were plotted against the experimental ones as shown in figure 5. It is very clear that the adopted rate model along with extracted individual rate constants represent very well the experimental results.
Table 1. Reaction rate constants at different temperatures

| Rate constant | 293 K  | 298 K  | 303 K  | 308 K  | 313 K  |
|---------------|--------|--------|--------|--------|--------|
| \( k_a \) (m\(^6\) mol\(^{-2}\) s\(^{-1}\)) | 2045.0 | 2580.9 | 3270.3 | 5544.0 | 6192.9 |
| \( k_{hyd} \) (m\(^6\) mol\(^{-2}\) s\(^{-1}\)) | 891.6  | 4144.7 | 5537.5 | 9134.8 | 12552.0|
| \( k_b \) (m\(^6\) mol\(^{-2}\) s\(^{-1}\))  | 8.0    | 7.6    | 9.9    | 17.5   | 22.0   |
| \( k_w \) (m\(^6\) mol\(^{-2}\) s\(^{-1}\))  | 23.4   | 24.4   | 33.8   | 37.7   | 45.7   |

with an average absolute deviation, AAD, of 6.8%, which validated the choice of the kinetics model used to interpret the data represented by Eq (12). Furthermore, these results confirm the contribution of AB, OH- and MDEA, AB species in the base-catalytic formation of carbamate.

![Figure 5. Calculated versus experimental rate constants](image)

The individual rate constants in table 1 were plotted as function of temperature as shown in figure 6 and the results are summarized in table 2. The activation energy \( (E_a) \) of each reaction derived from the Arrhenius plots along with the pre-exponential coefficient of each rate constant are given in table 2.

Table 2. Summarized kinetics rate constants for CO\(_2\)-MDEA-AB reaction

| Rate   | \( k_{AB} = \frac{[AB]}{(1/k_a + 1/(k_a[AB] + k_{hyd}[OH] + k_b[MDEA] + k_w[H_2O])} \) |
|--------|---------------------------------------------------------------------------------|
|        | Ln\( k_a \) | \( E_a \) (kJ/mol) | Equation |
| \( k_a \) (m\(^6\) mol\(^{-2}\) s\(^{-1}\)) | 26.23 | 4423.0 | \( k_a = 2.46 \times 10^{11} \exp(-5464/T) \) |
| \( k_{hyd} \) (m\(^6\) mol\(^{-2}\) s\(^{-1}\)) | 19.68 | 5211.1 | \( k_{hyd} = 3.52 \times 10^9 \exp(-5211.1/T) \) |
| \( k_b \) (m\(^6\) mol\(^{-2}\) s\(^{-1}\)) | 45.49 | 11217.0 | \( k_b = 5.75 \times 10^9 \exp(-11217/T) \) |
| \( k_w \) (m\(^6\) mol\(^{-2}\) s\(^{-1}\)) | 14.22 | 3256.9 | \( k_w = 1.50 \times 10^9 \exp(-3256.9/T) \) |

The \( E_a \) for AB, OH-, MDEA and H\(_2\)O catalytic carbamate formation showed that the contribution of water molecules to the overall formation of carbamate (14.22 kJ/mole) is the most important followed by that of Hydroxyl ions (19.68 kJ/mole) and aminobutanol molecules (26.23 kJ/mole). While the contribution of MDEA molecules to this reaction (45.49 kJ/mole) were found to be the least influential.
5. Conclusion

The reaction kinetics of CO$_2$ with AB in aqueous solutions was studied for the first time using stopped-flow apparatus. The kinetics measurements were performed for concentrations ranging from 0.1 to 0.3 M of AB and a temperature range of 293 to 313 K. Using nonlinear regression technique, the overall rate constants of CO$_2$-AB were fitted to two different kinetic models derived from zwitterion termolecular mechanisms respectively. Among the two rate models adopted to interpret the kinetics data, the zwitterion mechanism was found to be very successful in accurately representing the experimental data with an AAD of 6.1 %. Subsequent rate constants and their temperature dependency along with their respective activation energies were derived. Analysis on the contribution of OH$^-$, AB and H$_2$O to the catalytic carbamate formation pathway showed that the contribution of H$_2$O to the overall formation of carbamate ($E_a = 91.96$ kJ/mole) is more important, followed by the contribution of OH$^-$ ($E_a = 104.41$ kJ/mole). The contribution of AB was found to be the smallest ($E_a = 201.57$ kJ/mole). Comparison between the Kinetics of CO$_2$-AB reaction and those of CO$_2$ with MEA, MDEA, DEA and AMP showed that the CO$_2$-AB reaction is slower that of CO$_2$ with MEA but faster than those of CO$_2$ with MDEA, DEA and AMP, respectively.

Acknowledgement

This paper was made possible by an NPRP Grant #7-1154-2-433 from the Qatar National Research Fund (a member of Qatar Foundation). The statements made herein are solely the responsibility of the authors.

References

[1] Faramawy S, Zaki T and Sakr A A E 2016 Natural gas origin, composition, and processing: A review Journal of Natural Gas Science and Engineering 34 pp 34–54
[2] Peters L, Hussain A, Follmann M, Melin T and Hägg M B 2011 CO2 removal from natural gas by employing amine absorption and membrane technology—A technical and economical analysis Chemical Engineering Journal 172 pp 952–60

[3] Qi R and Henson M A 1998 Optimization-based design of spiral-wound membrane systems for CO2/CH4 separations Separation and purification technology 13 pp 209–25

[4] Chakravarty T, Phukan U K and Weiland R H 1985 REACTION OF ACID GASES WITH MIXTURES OF AMINES Chemical Engineering Progress 81 pp 32–6

[5] Liang Z, Rongwong W, Liu H, Fu K, Gao H, Cao F, Zhang R, Sema T, Henri A, Sumon K, Nath D, Gelowitz D, Srisang W, Saiwan C, Benamor A, Al-Marri M, Shi H, Supap T, Chan C, Zhou Q, Abu-Zahra M, Wilson M, Olson W, Idem R and Tontiwachwuthikul P 2015 Recent progress and new developments in post-combustion carbon-capture technology with amine based solvents International Journal of Greenhouse Gas Control

[6] Idris Z, Peresunko N, Jens K J and Eimer D A 2015 Equilibrium solubility of carbon dioxide in aqueous solutions of 3-amino-1-propanol, 4-amino-1-butanol and 5-amino-1-pentanol at low partial pressures Fluid Phase Equilibria 387 pp 81–7

[7] Benamor A, Mahmud N, Nasser M S and Tontiwachwuthikul P 2018 Reaction Kinetics of Carbon Dioxide with 2-Amino-1-butanol in Aqueous Solutions Using a Stopped-Flow Technique Industrial & Engineering Chemistry Research 57 pp 2797–804

[8] Crooks J E and Donnellan J P 1988 Kinetics of the formation of N, N-dialkylcarbamate from diethanolamine and carbon dioxide in anhydrous ethanol Journal of the Chemical Society, Perkin Transactions 2 pp 191–4

[9] da Silva E F and Svendsen H F 2004 Ab initio study of the reaction of carbamate formation from CO2 and alkanolamines Industrial & engineering chemistry research 43 pp 3413–8

[10] Astaria G, Savage D W and Bisio A 1983 Gas treating with chemical solvents (John Wiley)

[11] Kierzkowska-Pawlak H, Siemieniec M and Chacuk A 2013 Investigation of CO2 and ethylenolamine reaction kinetics in aqueous solutions using the stopped-flow technique Chemical Papers 67 pp 1123–9

[12] Knipe A C, McLean D and Tranter R L 1974 A fast response conductivity amplifier for chemical kinetics Journal of Physics E: Scientific Instruments 7 p 586

[13] Benamor A, Al-Marri M J, Khraisheh M, Nasser M S and Tontiwachwuthikul P 2016 Reaction kinetics of carbon dioxide in aqueous blends of N-methyldiethanolamine and glycine using the stopped flow technique Journal of Natural Gas Science and Engineering 33 pp 186–95

[14] Alper E and Bouhamra W 1994 Kinetics and mechanisms of reaction between carbon disulphide and morpholine in aqueous solutions Chemical Engineering & Technology 17 pp 138–40

[15] Littel R J, Bos M and Knoop G J 1990 Dissociation constants of some alkanolamines at 293, 303, 318, and 333 K Journal of Chemical and Engineering Data 35 pp 276–7

[16] Mahmud N, Benamor A, Nasser M S and Tontiwachwuthikul P 2018 Carbamate Formation and Amine Protonation Constants in 2-Amino-1-Butanol–CO2–H2O System and Their Temperature Dependences Journal of Solution Chemistry 47 pp 262–77

[17] Edwards T, Maurer G, Newman J and Prausnitz J 1978 Vapor-liquid equilibria in multicomponent aqueous solutions of volatile weak electrolytes AIChE Journal 24 pp 966–76