STUDYING THE PROMOTING EFFECT OF GLYCINE ON THE KINETICS OF CARBON DIOXIDE REACTION WITH METHYLDIETHANOLAMINE USING STOPPED FLOW TECHNIQUE

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Abstract- The promoting effect of adding Glycine on the kinetics of reaction of carbon dioxide with selected Amines using stopped flow technique is presented in this paper. The selected systems for this work were MDEA+ Glycine (GL), DEA +GL, MEA+GL and AMP+GL for which the overall reaction rate constants were investigated at 303K and total solution concentration of 0.5M. It was found that at each temperature studied, the addition of small amounts of Glycine brings about a considerable increase in the overall rate constant which makes Glycine a potential promoter for the reactions of these amines with CO2.

Keywords- Carbon Dioxide, Methyldiethanolamine, Glycine, Kinetics, Stopped Flow.

I. INTRODUCTION

The removal of acid gas components (such as CO_2 and H_2S) from natural and industrial gas streams is an important industrial chemical process being applied for many decades. Different proprietary amine-based solvents have been proposed by different suppliers over the years. Primary Monoethanolamine (MEA), secondary Diethanolamine (DEA) and tertiary Methyldiethanolamine (MDEA) and Amino-Methyl Propanol (AMP) variants are available through different packages by a number of suppliers. Special proprietary additives are usually added to improve their performances and reduce their drawbacks. Development of more efficient solvents for the removal of CO_2, involves the addition of a promoter to increase the rate of reaction of CO_2 with the amine. Primaray and secondary amines have a maximum theoretical sorption capacity of 1 mole of CO_2 to two moles of amines. However, tertiary amines and amidines have shown a higher theoretical sorption capacity with a ratio of 1:1 molar [1], thereby reducing the required volume of amine, but the reaction rate is much slower which leads to higher amine circulation rate.

Hence, the use of tertiary amines alone is not practical, as it requires a large number of theoretical stages in the absorption column and increased capital cost of acid gases capture plants. As a result, combining the individual absorption characteristics of each amine, blended amines have been suggested for the absorption of acid gases [2]. Tertiary amines are often blended with faster reacting primary and/or secondary amines and/or piperazine to take advantage of their high loading capacity, low degradation rate and low energy for regeneration. Hence, combining tertiary amines possessing high CO2 loading capacity with other promoters for an accelerated, competitive reaction rate are of great interest to the CO_2 capture. The addition of a small amount of promoters to conventional tertiary amines such as MDEA can enhance the rate of absorption of CO_2 to a large extent without appreciably changing the stripping characteristics.

Amino acids salts have several potential benefits over amine systems used in CO_2 separation. With significantly lower vapor pressures than the amines, amino acid systems exhibit less solvent loss to the atmosphere. Furthermore, they tend to be less vulnerable to oxidative degradation and lower toxicity than the alkanolamine based solvents.[3] Due to their excellent characteristics for CO_2 capture, amino acids salts, such as glycine, arginine, taurine, andproline, have been recently proposed as alternatives to the amines [4]-[11]. Amino acids have been commercially employed in acidic gas treating processes, such as the BASF Alkazid solvent and the Giammarco-Vetrocoke(GV) process that uses carbonate solution as absorbing solvent. Despite the importance of amino acids salts, their use as reaction promoters in combination with alkanolamines have been overlooked by researchers as no similar work have been published in the open literature. Since CO_2 is acidic gas, the amino acids are not good candidate for CO_2 absorbent. However, their CO_2 absorption capacity can be enhanced when converted to amino acid salts. In the present work, the stopped flow technique was used. New experimental data on the absorption of CO_2 into aqueous solutions of (MDEA) mixed with Glycine are presented over a temperature range of 293–313 K and amines total concentration of 0.5 molars.

II. REACTION MECHANISM AND RATE MODELS

A. Reaction rate models of CO_2 with MDEA

The overall reaction of CO_2-MDEA interactions can

be written as equation 1 below.

$$CO_2 + R_1R_2R_3N + H_2O \xrightarrow{k_2} R_1R_2R_3NH^+ + HCO_3^- \quad (1)$$

As a result, an increase in the nucleophilic reactivity of the water toward CO_2 is observed. The reaction rate of CO_2-MDEA interactions are given by Eqn(2) :

$$r_{MDEA-CO2} = k_{MDEA}[MDEA]p_{CO2} \quad (2)$$

Besides reaction 1, the bicarbonate formation as given by reaction 3 should be considered to obtain more accurate data. In most cases, this part can be neglected since the concentrations of [OH^-] is much smaller than [MDEA].

$$OH^- + CO2 \rightarrow HCO3^- \quad (3)$$

Its rate of reaction was given by Pinsent et al.[12] as follows:

$$r_{OH-CO2} = k_{OH}[OH^-]p_{CO2} \quad (4)$$

Where,

$$k_{OH^-} = 4.33\times10^{10}\exp(-6666/T) \quad (5)$$

The contribution of OH^- to the overall reaction rate is insignificant because the major ions are MDEA, and [OH-] can be usually neglected. the overall reaction rate can be expressed as:

$$r_{ov} = r_{MDEA-CO2} = k_{MDEA}[MDEA]p_{CO2} \quad (6)$$

If the concentration or partial pressure of CO_2 is fixed, the equation can be simplified to eqn(7):

$$\text{Where, } r'_{ov} = \frac{r_{ov}}{[CO_2]} = k_{MDEA}[MDEA] \quad (7)$$

This treatment is necessary for the current stop-flow process. With such process, the reaction rate r'_{ov} is directly related to the ion concentrations in the liquid solutions. Some important kinetic rate models can be developed with various amine concentrations.

B. Reactions of CO_2 with Amino Acids salts

The molecular structure of amino acid salts [$NHR_1R_2COO^-$] is similar to a secondary amine [R_1R_2NH], the reaction pathway of CO_2-amine interactions is also similar to each other. It is well acknowledged that the carbamate formation processes include 2 steps, Zwitterion generation and proton release in Eqns (8, 9) respectively [13].

$$CO_2 + NHR_1R_2COO^- \rightarrow {}^-OOCNH{+}R_1R_2COO^- \quad (8)$$

$$^-OOCNH{+}R_1R_2COO^- + B: \rightarrow {}^-OOCNR_1R_2COO^- + H^+B: \quad (9)$$

However, sometimes the carbamate formation can also be regarded as a "one-step" process if the rate of second step is instantaneous. The kinetic rate model can be regarded as 1st order reaction for the elementary step of Eqn (8). From Caplow'scarbamate formation mechanism, the CO_2-seondary amine absorption has two sections: non-catalytic and catalytic pathway, which can be written below:

$$r_{CO2-amino\ acid} = k_{amino}[R_2NH]p_{CO2} + k'_{amino}[R_2NH][OH^-]p_{CO2} \quad (10)$$

Where the first term, kamine[R2NH] is a non-catalytic pathway, and the second term, k'amine[R_2NH][OH^-] is a catalytic pathway.[13] Even the amount of [OH-] is very small comparing to the concentrations of amine, but the k' is much bigger than k, these two sections are comparable. If the CO_2 partial pressure is a fixed value, the rate equations can be written as:

$$r'_{ov\,CO2-amino\ acid} = \frac{r_{CO2-amino\ acid}}{[CO_2]} = k_{amino}[GL] + k'_{amino}[GL][OH^-] \quad (11)$$

C. Reactions rate models for MDEA-GL blended amine-amino acid salts

As is known already, the carbamate formation is a base catalysed reaction [13], so that other base than OH- can also catalyse the carbamate formation. There are more than one type of base in the MDEA-GL solution, and the concentration of MDEA is much bigger than OH-. The amine-catalysedcarbamate formation should also be taken into consideration.

Then, the carbamate formation can be written as Eqn(12) below:

$$r_{CO2-GL} = k_{amino}[GL]p_{CO2} + k'_{amino}[GL][OH^-]p_{CO2} + k''_{amino}[GL][MDEA]p_{CO2} \quad (12)$$

Since the CO_2 can be converted to both carbamate and bicarbonate in the solutions, the overall rate equation should be the sum of Eqn (6,12)

$$rov = r_{MDEA-CO2} + r_{amino-CO2} = k_{MDEA}[MDEA]p_{CO2} + k_{amino}[GL]p_{CO2} + k'_{amino}[GL][OH^-]p_{CO2} + k''_{amino}[GL][MDEA]p_{CO2} \quad (13)$$

If CO_2 is fixed in the stopped flow process, the overall reaction rate can be written as below:

$$r'_{ov} = k_{MDEA}[MDEA] + k_{amino}[GL] + k'_{amino}[GL][OH^-] + k''_{amino}[GL][MDEA] \quad (14)$$

III. EXPERIMENTAL MATERIALS AND PROCEDURE

A. Materials

Reagent grade Methyldiethanolamine (MDEA) with a mass purity of 99% obtained from Sigma-Aldrich, Glycine with purity of 99 % purchased from Riedel-de Haen. All chemicals were used without further purification. CO_2 solutions were prepared by bubbling research grade CO_2 for at least half an hour in deionised water. Distilled water was used as the solvent throughout the experiment.

B. Procedure

Stopped-flow technique was used to measure pseudo first-order kinetics of CO_2 reaction with different aqueous mixtures of MDEA with Glycine. For each experiment, a freshly saturated solution of CO_2 was prepared by bubbling the gas through deionized water.

The concentration of CO_2 in water was measured with a gas chromatograph (GC-6890 from Agilent). This solution was then diluted by adding fresh water so that the amine concentration was always more than 15 times greater than CO_2. This is, to make sure that the pseudo first order condition with respect to $[CO_2]$ is always met [14]. The homogeneous reaction rate between dissolved CO_2 in water and amine solution was measured using a standard stopped-flow apparatus (Hi-Tech Scientific Ltd., UK, Model SF-61DX2). The schematic drawing of the stopped flow equipment used is presented in Figure 1.

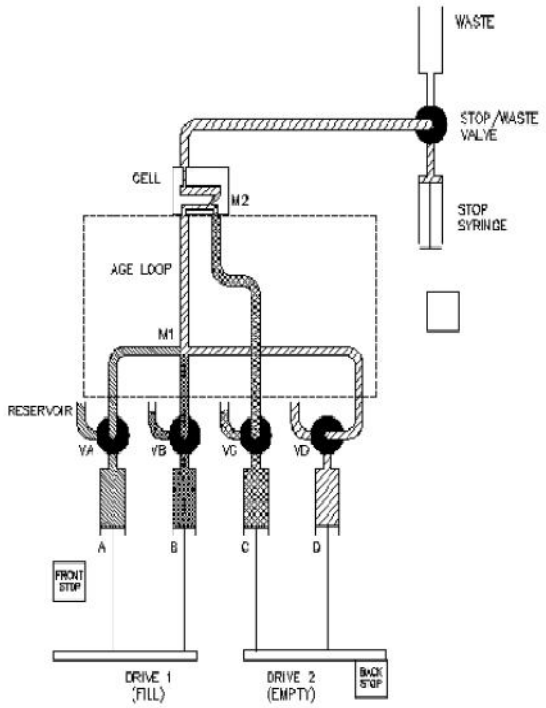


Figure 1: Schematic drawing of the stopped flow apparatus used in this work

In each run, equal volumes of aqueous solutions of amine and CO2 were mixed in the stopped-flow apparatus.

All parts of the flow circuit were tested with thermostat by an external water bath within ± 0.1 K. The reaction was monitored by measuring the conductivity change as function of time in the conductivity cell by an electrical circuit as shown in Figure 2. The change in conductivity with respect to time is fitted according to an exponential equation resembling a first-order kinetic equation:

$$Y=-A.e^{(-k_{ov}.t)}+Y_{\infty} \qquad 15$$

Where$k_{ov}$is the pseudo first-order reaction rate constant, the average of three experimental runs were considered to obtain consistent kov values for the whole ranges concentrations and temperatures. The reproducibility for k_{ov} was less than 3% in all experiments.

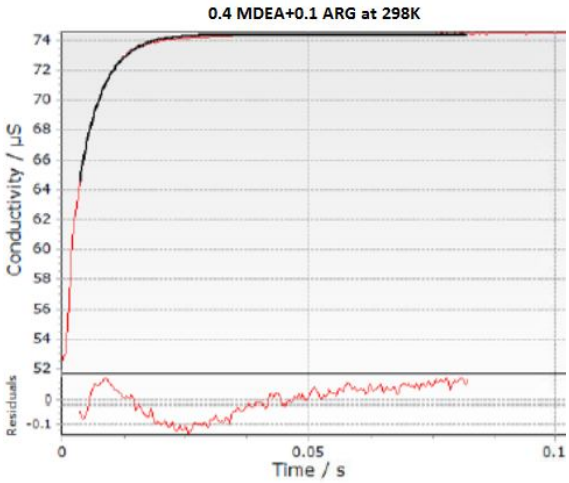


Figure 2. Combined graph of a typical run for aqueous 0.5 kmol/m^3 MDEA+ARG with CO_2 at 298 K..

IV. RESULTS AND DISCUSSION

A. Reaction of CO_2 with MDEA

To assess the effect on the overall reaction rate by adding glycine to MDEA, it was decided to consider first the reaction of CO_2 with aqueous solutions of MDEA. Even though this reaction was extensively studied, most of the kinetics parameters associated to the reactions were derived from chemical absorption experiments at the opposite of this work where stopped flow technique is being applied. During all runs, the concentration of the amine was chosen to be largely in access over CO_2 to ensure a pseudo first order regime, with a rate equation given by Eqns(2, 4). The overall reaction rate constant is given by Eqn(7). As the CO_2 loading in the amine solution is very small, the OH concentration was estimated from the relations given by Astarita[15].

$$[OH^-] = \sqrt{\frac{K_W}{K_P}} \qquad 16$$

The water dissociation constant , K_w, and MDEA protonation constant ,K_p, were expressed as function of temperature according to the following equation:

$$LnK_i = \frac{a_i}{T} + b_i lnT + c_i T + d_i \qquad 17$$

Values of the constants a_i–d_i were taken from the literature and are given in Table 1.

Table 1: Values of different equilibrium constant (all K_i values are in mol/l basis)

Parameter	a_i	b_i	c_i	d_i	validity (°C)	Source
Kp	−8483.95	−13.8328	0	87.3971	20–60	Littel et al. [16]
Kw	−13445.9	−22.4773	0	140.932	0–225	Edwards et al. [17]

The observed equations and k_{MDEA} analysis at 293, 298, 303 and 313 K are presented in Table 2., based on Eqn(18) below.

$$r'_{ov} = k_{MDEA}[MDEA] + k_{OH}[OH^-] \quad 7$$

$$k_{MDEA}[MDEA] = r'_{ov} - k_{OH}[OH^-] \quad 18$$

Table 2: Rate constants at different temperatures and MDEA concentration

Conc	Temp	r'_{ov}	OH□103	$k_{OH}[OH-]$	$k_{MDEA}[MDEA]$
mol/l	K	s-1	mol/l	s-1	s-1
0.5	293	1.52	1.36	0.0777	1.51
0.5	298	2.24	1.46	0.0122	2.23
0.5	303	3.16	1.56	0.0188	3.14
0.5	308	4.49	1.66	0.0286	4.46
0.5	313	6.23	1.76	0.0429	6.19

The constant k was generated from the slope in the equations in Figure 3

Based on Table 2, it is obvious that the rate of k_{OH} $[OH^-]$ is very low comparing to the majority: $k_{MDEA}[MDEA]$. It contributes to less than 2% to the overall rate r_{ov}. The rate contributed from MDEA, $k_{MDEA}[MDEA]$, was listed in Table2.

The rate $k_{MDEA}[MDEA]$ vsTemperature was plotted in Figure 3. The slope (which representing the rate constant k_{MDEA}) increases with the increase of temperature. This is reasonable because higher temperature result in higher reaction rate.

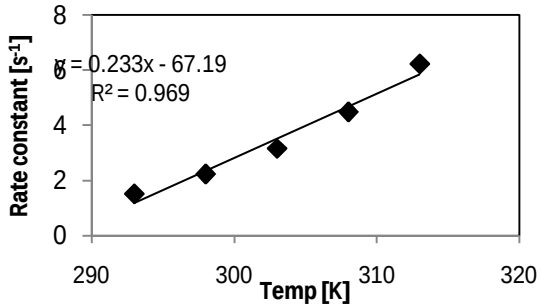


Figure. 3. Plot of k_{MDEA}[MDEA] vs [T] at constant 0.5 molar MDEA concentration

Based on Table 2 and Figure 3, the k_{MDEA} values under different temperatures are plotted versus 1/T as shown in Figure 4. The values of k_{MDEA} experimentally determined in the present work are fitted by Arrhenius equation:

$$k_{MDEA} = 5.61*10^9 \exp(-6452/T) = e^{22.448} e^{\frac{-6452}{T}} \quad 19$$

$$k_{MDEA} = 2.07*10^9 \exp(-5912.7/T) = e^{21.451} e^{\frac{-5912}{T}} \quad 20$$

[18]

The values k_{MDEA} obtained in this work are in good agreement with those derived by Kierzkowska-Pawlak [21] over the whole considered temperature range. The activation energy, estimated from Eqn(19) was found to be 53.73 kJ/mol which is in excellent agreement with the literature value of 49.15 kJ/mol obtained by Eqn(20) from Kierzkowska-Pawlak et al [18]. The $\ln k_0$ is 0.95% deviation (22.448 vs 21.451), and the activation energy is 0.91% deviation (53.73 vs 49.15 kJ/mol).

These very minute discrepancies may mainly result from the inability to determine the exact contact area between gas and liquid in the absorption process as well as the limited number of data points as only one concentration is considered. This result indicated the experimental process of this research is highly accurate, which can generate accurate kinetic results for our MDEA-GL solutions.

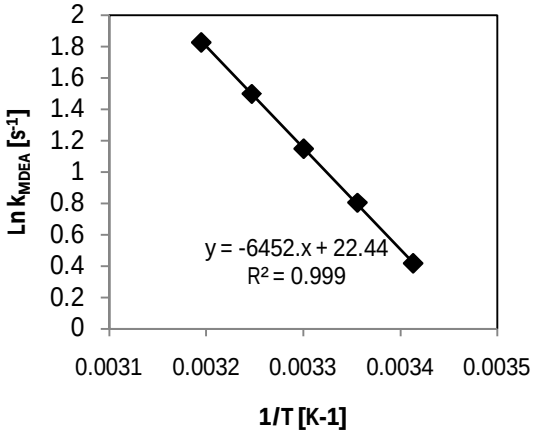


Figure 4. Arrhenius plot for rate constant k_{MDEA} for CO_2-MDEA reaction derived from this work

B. Reaction of CO_2 with MDEA-Glycine

The overall reaction rate r'_{amino} are plotted against Temperature (K) as shown in Figures 5, where rate constants (k_o) increased with increasing Glycine portion in the total solution fixed concentration, as well as temperature (Table 3). For example, in Figure 5, for a total solution concentration of 0.5 molars, we observe that increasing Glycine concentration from 0.0 M to 0.10M with increment of 0.05 in the total amine mixtures leads to a substantial increase in the overall rate constant.

From Figure 5, it is apparent that the overall rate increase with increase of [GL] concentrations, these lines exhibit good linearity of the rate vs[GL] concentration.

It validated our rate model of Eqn(14), that the overall concentration is the linear combination of different terms. On the other hand, some increase does not only result from the increase of the concentration of GL, $k_{amino}[GL]$, but mostly from the other two terms of catalytic pathways: $k'_{amino}[GL][OH^-]$ and $k''_{amino}[GL][MDEA]$. From Caplow's original

researches, the catalytic reaction rate is much faster than the non-catalytic reaction pathway. The $k'_{amino}[GL][OH^-]$ and $k''_{amino}[GL][MDEA]$ are the interest of research.

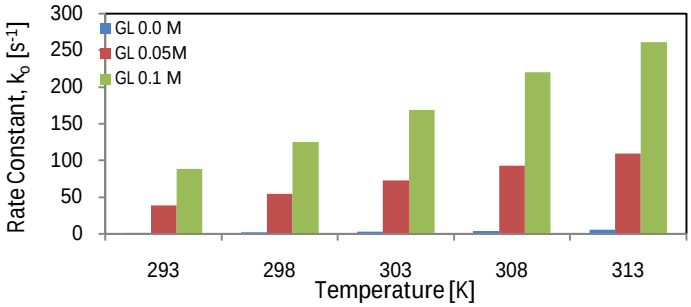


Figure 5. Plot of r'_{ov} versus total 0.5 M [MDEA+GL] at different temperatures and added glycine concentration

Table 3: Rate constants at different temperatures and MDEA+GL concentration

Temp	Concmol/l		r'_{ov}	OH-	r'_{amino}
K	MDEA	GLY	S-1	mol/l	s-1
293	0.45	0.05	39	1.20E-02	38.93
	0.4	0.1	89	1.82E-02	88.90
298	0.45	0.05	55	1.53E-02	54.87
	0.4	0.1	126	2.32E-02	125.81
303	0.45	0.05	73	1.65E-02	72.91
	0.4	0.1	169	2.51E-02	168.86
308	0.45	0.05	93	2.26E-02	92.61
	0.4	0.1	221	3.49E-02	220.40
313	0.45	0.05	110	2.61E-02	109.36
	0.4	0.1	262	4.03E-02	261.02

Table 5: Summerized kinetic rate constants for the CO2-MDEA and CO2-MDEA-GL solutions along 293-313 K

rate	$r'_{ov} = k_{MDEA}[MDEA] + k_{OH}[OH^-] + k_{amino}[GL] + k'_{amino}[GL][OH^-] + k''_{amino}[GL][MDEA]$		
[m^3 mol^{-1} s^{-1}]	Lnk_0	Ea (kJ/mol)	Equation
$k_{MDEA\text{-}b}$exp	22.448	53.71	k = 2.564*109exp(-5922/T)
k_{MDEA} literature [19]	21.451	49.16	k = 2.07*109 exp(5912.7/ T)
k_{OH}	29.491	55.42	$k_{OH} = 4.33\times10^{10}\exp(-6666/T)$

CONCLUSION

The kinetics of the reaction of CO_2 with MDEA + Glycine in aqueous solutions was studied using the stopped-flow apparatus for the first time. The measurements were performed in at 0.5 molar total solution concentration and a temperature range of 293 to 313 K. The rate constant k_{MDEA} was correlated from Arrhenius equation type as follow, which is very close to literature value :

$$k_{MDEA} = 5.61*10^9\exp(-6452/T) = e^{22.448}e^{\frac{-6452}{T}} \quad 19$$

$$k_{MDEA} = 2.07*10^9\exp(-5912.7/T) = e^{21.451}e^{\frac{-5912}{T}} \quad 20 \text{ [18]}$$

The activation energy for the rate constant was determined to be 53.73 kJ/mol, and it is close to the literature value 49.16 kJ/mol. This result confirmed that the experimental equipment and apparatus can generate accurate kinetic results for the blended amine systems.

The overall reaction rate of CO_2-MDEA-GL systems were plotted against temperature for variable Glycine concentration (mol m^{-3}) as shown in Figures 5, where rate constants (k_o) increased with increasing Glycine portion in the total solution fixed concentration, as well as temperature. The obtained results shows that Glycine could be n excellent rate promoter for the reaction between CO2 and Alkanolamines, extensive studies are recommended to better understand the kinetics of these reactions.

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