# Reactive Absorption of CO<sub>2</sub> into Aqueous Mixtures of Methyldiethanolamine and Diethanolamine

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Abstract—The effect of mixing a tertiary amine. N,N-Methyldiethanolamine (MDEA), with a secondary amine, diethanolamine (DEA), on the kinetics of the reaction with carbon dioxide in aqueous media has been studied in a stirred cell reactor with a plane, horizontal gas-liquid interface. Temperature was varied from 293 to 313K over a range of blend composition and total mixture concentration ranging from one to two molars. The proposed model representing the reaction of CO<sub>2</sub> with the blends studied is found to be satisfactory in determining the kinetics of the involved reactions. This model is based on the zwitterion mechanism for the DEA and water hydration catalysis for MDEA. Blending MDEA with DEA results in observed pseudo-first-order reaction rate constant values  $(k_0)$  that are greater than the sum of the  $k_0$  values of the respective single amines. This is due to the role played by MDEA in the deprotonation of the zwitterion of the other amine (DEA). Species concentration profile needed to fit the experimental data to the model to extract the kinetic parameters associated with the reactions was calculated using the modified Deshmukh-Mather model.

*Index Terms*—Methyldiethanolamine, diethanolamine, absorption, carbon dioxide, kinetics.

# I. INTRODUCTION

Aqueous alkanolamine solutions are frequently used for removal of acidic gases such as carbon dioxide and hydrogen sulfide from gas streams in the natural gas, synthetic, and refinery industries. Several options are available for removing acid gases, but by far the most popular is the absorption by amine based solvents such as monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), di-isopropanolamine (DIPA), triethanolamine (TEA), N-methyldiethanolamine (MDEA), 2-amino-2-methyl-l-propanol (AMP), and 2-piperidineethanol (2-PE) in reversible absorption-regeneration processes [1].

Combining the absorption characteristics of each amine, blended amines have been suggested for the absorption of acid gases [2]. The addition of a small amount of primary or secondary amine to conventional tertiary amines can enhance the rate of absorption of  $CO_2$  to a large extent without appreciably changing the stripping characteristics. Due to their importance in acid gas treating, it is appropriate to have a better understanding on the kinetics of the reaction involving different types of alkanolamine blends with  $CO_2$ . Experimental and simulation studies on these systems have

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been proposed among others by by Bosch *et al.* [3]. Glasscock *et al.* [4] presented experimental data for  $CO_2$  absorption into mixed amine systems of MEA/MDEA using a batch liquid, continuous gas-stirred cell reactor. Blends of DEA/ AMP had been studied by Mandal *et al.* [5] to absorb carbon dioxide. Absorption rates for  $CO_2$  into aqueous blends of MEA/MDEA and MEA/TEA were reported by Rangwala et al. [6] using a stirred cell.

Available data concerning the absorption rates of  $CO_2$  into aqueous blends of DEA/MDEA in the literature are very little. Among others, Glasscock *et al.* [4] and Zhang *et al.* [7] reported some absorption data of  $CO_2$  into aqueous solutions of DEA/MDEA using a laboratory disk column. Mandal and Bandyopadhyay [8] studied similar systems (aqueous solutions of DEA/MDEA) theoretically and experimentally using wetted wall column experiment. However, still some discrepancies exist in the results obtained by the different investigators that may be attributed to the different reaction mechanisms used in the interpretation of the kinetics data or to the different experimental apparatus employed in collecting the data. Hence, additional data on the kinetics of  $CO_2$  absorption into blends of DEA and MDEA seem to be still welcomed.

# II. EQUILIBRIUM REACTIONS OF CO2 WITH DEA AND MDEA

An equilibrium solution of  $CO_2$  in aqueous solution of alkanolamine is governed by the following set of equations:

Dissociation of protonated amine:

$$\mathsf{DEAH}^{+} \Leftrightarrow \mathsf{DEA} + \mathsf{H}^{+} \tag{1}$$

$$MDEAH^{+} \Leftrightarrow MDEA + H^{+}$$
(1a)

Formation of carbamate:

$$DEACOO^{-} + H_2O \Leftrightarrow DEA + HCO_3^{-}$$
(2)

Dissociation of carbon dioxide:

$$CO_2 + H_2O \Leftrightarrow HCO_3^{-} + H^+$$
 (3)

Dissociation of bicarbonate ion:

$$HCO_{3}^{-} \Leftrightarrow CO_{3}^{2-} + H^{+}$$
(4)

Ionization of water:

$$H_2O \Leftrightarrow OH^- + H^+$$
 (5)

The equilibrium constants for the above equations are expressed as follows:

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$$K_{1} = \frac{[RR'NH]_{e}[H^{+}]_{e}}{[RR'NH_{2}^{+}]_{e}} \frac{\gamma_{RR'NH} \gamma_{H^{+}}}{\gamma_{RNH_{1}^{+}}}$$
(6)

$$K_{1a} = \frac{[MDEA]_{e} [H^{+}]_{e}}{[MDEAH^{+}]_{e}} \frac{\gamma_{MDEA} \gamma_{H^{+}}}{\gamma_{MDEAH^{+}}}$$
(6a)

$$K_{2} = \frac{[RR'NCOO']_{e}[H^{+}]_{e}}{[RR'NH]_{e}[CO_{2}]_{e}} \frac{\gamma_{_{RE'NCOO'}} - \gamma_{H^{+}}}{\gamma_{_{RE'NH}}\gamma_{CO_{2}}}$$
(7)

$$K_{3} = \frac{[HCO_{3}^{-}]_{e} [H^{+}]_{e}}{[CO_{2}]_{e}} \frac{\gamma_{HCO_{3}^{-}} \gamma_{H^{+}}}{\gamma_{CO_{2}}}$$
(8)

Amine balance:

$$[DEA]_{t} + [MDEA]_{t} = [DEA]_{t} + [MDEA]_{t} + [DEAH^{\dagger}]_{t} + [MDEAH^{\dagger}]_{t} + [RR'NCOO^{\dagger}]_{t}$$
(11)

CO<sub>2</sub> balance:

$$\alpha \left( [DEA]_{t} + [MDEA]_{t} \right) = [HCO_{3}]_{t} + [RR'NCOO]_{t} + [CO_{3}]_{t} + [CO_{2}]$$
(12)

conditions must also be satisfied.

Charge balance:

$$[DEAH^{+}]_{e} + [MDEAH^{+}]_{e} = [HCO_{3}^{-}]_{e} + [RR'NCOO^{+}]_{e} + 2[CO_{3}^{2-}]_{e}$$
(13)

The concentrations of H<sup>+</sup> and OH<sup>-</sup> were discarded in the charge balance due to their negligible amounts.  $\alpha$  is the CO<sub>2</sub> loading, and the concentration of carbon dioxide in the liquid phase was estimated from Henry's law, i.e.

$$P_{CO_{2}} = H_{CO_{2}}[CO_{2}] \tag{14}$$

# A. Solubility Model

A modified Deshmukh-Mather model [9] was used to estimate the species concentrations in the liquid bulk. This model is based on an activity coefficient approach according to Debye-Hückel theory [10] where the activity coefficients are calculated by the equation of Guggenheim and Stokes [11] and Scatchard [12]:

$$\ln \gamma_i = -\frac{AZ_i^2 \sqrt{I}}{1 + B\sqrt{I}} + 2\sum \beta_{i,j} m_j$$
(15)

where  $Z_i$  and  $m_j$  are respectively the electrical charges and concentrations of the corresponding species and *I* is the ionic strength of the solution. The value of *A* is taken as a function of temperature as proposed by Lewis *et al.* [13] and *B* equals to 1.2, a value suggested by Pitzer [14], [15].  $\beta_{ij}$  are the interaction parameters between the different ionic and molecular species in the system excluding interactions between solutes and solvent and are represented in the following form

$$\beta_{ij} = a_{ij} + b_{ij}T \tag{16}$$

where  $a_{ij}$ ,  $b_{ij}$  are parameters to be estimated by regression of solubility data.

The ionic strength, I, of the solution is calculated by the following equation:

$$I = \frac{1}{2} \sum m_j Z_j^2 \tag{17}$$

### B. Thermodynamic Parameters

The dependency of the equilibrium constant,  $K_i$ , as well as

the Henry's constant,  $H_{CO_2}$ , with temperature is expressed as

 $K_{4} = \frac{[CO_{3}^{2-}]_{e} [H^{+}]_{e}}{[HCO_{3}^{-}]_{e}} \frac{\gamma_{CO_{3}^{2-}} \gamma_{H^{+}}}{\gamma_{HCO_{3}^{-}}}$ 

 $K_{5} = \frac{[OH^{-}]_{e}[H^{+}]}{a_{H_{2}O}} \gamma_{OH^{-}} \gamma_{H^{+}}$ 

coefficients of the different species respectively.

where [J] and  $\gamma_i$  are the concentrations and activity

In addition to the above equations, the following set of

(9)

(10)

$$\ln K_{i} \left( H_{CO_{2}} \right) = \frac{a_{i}}{T} + b_{i} \ln T + c_{i} T + d_{i}$$
(18)

where  $a_i - d_i$  are constants whose values for reactions (1) – (5) and that for the Henry's constant are taken from the literature as given in Table I.

TABLE I: THERMODYNAMIC PARAMETERS USED IN THIS WORK

Parameter	$a_i$	$b_i$	$c_i$	$d_i$	Source
$K_{1,\text{DEA}}$	-3071.15	6.776904	0	-48.7594	[16]
$K_{1,\text{MDEA}}$	-8483.95	-13.8328	0	87.39717	[17]
$K_2$	-17067.2	-66.8007	0	439.709	[18]
$K_4$	-12431.7	-35.4819	0	220.067	[19]
<i>K</i> <sub>3</sub>	-12092.1	-36.7816	0	235.482	[19]
$K_5$	-13445.9	-22.4773	0	140.932	[19]
H <sub>CO2</sub>	-6789.04	-11.4519	-0.010454	94.4914	[19]

(\*): Values of  $K_2$  taken from [18] are being regressed according to equation (18).

# **III. REACTION PATHWAYS**

In aqueous mixtures of DEA + MDEA, the absorption of  $CO_2$  can be considered as a combination of several reactions involving  $CO_2$ -DEA,  $CO_2$ -MDEA and  $CO_2$ -H<sub>2</sub>O. In case of DEA, it reacts with  $CO_2$  according to the zwitterion mechanism [20]:

$$\operatorname{CO}_2 + \operatorname{DEA}_{\underset{k_1}{\underbrace{k_2}}} \operatorname{DEAH^+COO^-}$$
 (19)

$$DEAH^{+}COO^{-} + B \xrightarrow{k_{b}} DEACOO^{-} + BH^{+}$$
(20)

 $CO_2$ -MDEA reaction can be described as a base catalyzed hydration of  $CO_2$  according to the reaction [21]:

$$CO_2 + MDEA + H_2O \xrightarrow{k_{2:MDEA}} MDEAH^+ + HCO_3^-$$
 (21)

Other reactions that may take place in an aqueous medium include bicarbonate formation according to the following reaction:

$$CO_2 + OH^- \Longrightarrow HCO_3^-$$
 (22)

The overall reaction rate would be:

$$R_{\rm ov} = \frac{k_{2:\rm DEA} [\rm CO_2\ ][\rm DEA]}{1 + \frac{k_{.1}}{k_{\rm H_2O}[\rm H_2O] + k_{\rm OH}[\rm OH^-] + k_{\rm DEA}[\rm DEA] + k_{\rm MDEA}[\rm MDEA]}} + k_{2:\rm MDEA} [\rm CO_2\ ][\rm MDEA] + k_{\rm OH^-}^* [\rm CO_2\ ][\rm OH^-]$$
(23)

Therefore, the apparent reaction rate would be:

$$k_{app} = \frac{[DEA]}{\frac{1}{k_{2-DEA}} + \frac{1}{\frac{k_{2-DEA}k_{H_2O}}{k_{.1}}} [H_2O] + \frac{k_{2-DEA}k_{OH}}{k_{.1}} [OH^-] + \frac{k_{2-DEA}k_{DEA}}{k_{.1}} [DEA] + \frac{k_{2-DEA}k_{MDEA}}{k_{.1}} [MDEA]}$$
(24)

#### IV. MASS TRANSFER WITH CHEMICAL REACTION

Theory of gas-liquid reactions is well established [22]. The absorption flux of  $CO_2$  into a reactive liquid solution is generally described by the following equation

$$J = \frac{(C_{\rm CO_2,G} - C_{\rm CO_2,L}/m_{\rm CO_2})}{1/k_{\rm G} + 1/m_{\rm CO_2}k_{\rm L}E_{\rm CO_2}}$$
(25)

Equation (18) can be simplified using a fresh liquid free from any dissolved gas. Hence, the concentration of the gas in the liquid phase is equal to zero ( $C_{\text{CO}_2,\text{L}}=0$ ). Assuming an ideal gas behaviour for CO<sub>2</sub>, its concentration in the gas phase can be represented by  $C_{\text{CO}_2,G} = P_{\text{CO}_2}/RT$  and  $m_{\text{CO}_2} = RT/H_{\text{CO}_2}$ . Furthermore, assuming there is no resistance to mass transfer in the gas phase  $(1/k_G \simeq 0)$ , the absorption of pure CO<sub>2</sub> is then given by:

$$J = k_{L} E_{CO_{2}} \frac{m_{CO_{2}} P_{CO_{2}}}{RT} = k_{L} E_{CO_{2}} \left( P_{CO_{2}} / H_{CO_{2}} \right)$$
(26)

The enhancement factor,  $E_{CO_2}$ , is a function of the Hatta number Ha and the infinite enhancement factor  $E_{inf}$ . The Hatta number is defined as:

$$Ha = \sqrt{k_{\rm ov} D_{\rm CO_2}} / k_L \tag{27}$$

According to the penetration model [23], the infinite enhancement factor,  $E_{inf}$ , is given by

$$E_{\rm inf} = \sqrt{\frac{D_{CO_2}}{D_{Am}}} + \frac{[Am]}{z[CO_2]_i} \sqrt{\frac{D_{Am}}{D_{CO_2}}}$$
(28)

It must be noted, however, that Eq. (21) is only valid for irreversible reactions:. However, the reversible reaction does not play a significant role during the absorption of  $CO_2$  into aqueous amine solutions, so the use of Eq. (21) is justified.

Depending on the absolute value of Ha and the ratio between Ha and  $E_{inf}$ , three absorption regimes can be distinguished. For a constant value for the Hatta number (Ha>2) and with decreasing infinite enhancement factor (for the experiments carried out at constant amine concentration this is related to an increasing CO<sub>2</sub> partial pressure), they are:

# A. The Pseudo-First-Order Regime

If the ratio between the *Ha* number and the infinite enhancement factor is sufficiently large, the following criterion is to be obeyed:  $2 < Ha \ll E_{\rm inf} \tag{29}$ 

Upon satisfaction of Eq. (22), the reaction of  $CO_2$  with the amine can be considered to take place in the pseudo first-order regime and in that case the enhancement factor equals the *Ha* number  $E_{CO_2} = Ha$ . Consequently, Eq. (19) becomes

$$J_{\rm CO_2} = \sqrt{k_{\rm ov} D_{\rm CO_2}} \frac{m_{\rm CO_2} P_{\rm CO_2}}{RT} = \left(\frac{P_{\rm CO_2}}{H_{\rm CO_2}}\right) \sqrt{D_{\rm CO_2} k_{\rm ov}}$$
(30)

It is obvious from Eq. (23) that the kinetic rate constant  $k_{ov}$  can be experimentally determined from the absorption flux.

# B. The Intermediate Regime

In this regime, it is not possible to derive the kinetic data directly from the  $CO_2$  fluxes and the corresponding enhancement factors. The amine concentration at the interface start to deplete as a consequence of increased  $CO_2$  partial pressure (and hence decreased infinite enhancement factor). An approximate solution for the enhancement factor as a function of both *Ha* and *E*<sub>inf</sub> was derived by DeCoursey [24]:

$$E_{\rm CO_2} = -\frac{Ha^2}{2(E_{\rm inf} - 1)} + \sqrt{\frac{Ha^4}{4(E_{\rm inf} - 1)^2} + \frac{E_{\rm inf}Ha^2}{(E_{\rm inf} - 1)} + 1}$$
(31)

Eq. (24) is valid only for irreversible second order chemical reaction based on Danckwerts' surface renewal theory. Deriving the kinetics of reversible reactions in this regime requires knowledge about the equilibrium constant of the involved reaction as this constant influences  $E_{inf}$ , which makes this region not reliable to derive the kinetic rate data.

#### C. The Instantaneous Regime

The instantaneous regime is defined by an infinite enhancement factor significantly smaller than *Ha* according to the following relationship:

$$2 < E_{\rm inf} \ll Ha \tag{32}$$

In this regime, the reaction is instantaneous with respect to mass transfer. The determination of the kinetics of the reaction from experimental absorption rate data is not possible as the absorption is completely limited by diffusion of the reactants. The instantaneous enhancement factor is described as

$$E_{\rm inf} = k_L \left( \sqrt{\frac{D_{CO_2}}{D_{Am}}} + \sqrt{\frac{D_{Am}}{D_{CO_2}}} \frac{[Am]RT}{v_{Am}m_{CO_2}P_{CO_2}} \right) \frac{m_{CO_2}P_{CO_2}}{RT}$$
(33)

It is not possible to determine beforehand in which regime the absorption experiments are carried out. Therefore, it is necessary to conduct series of absorption experiments at constant temperature, liquid stirrer speed and amine concentration and decreasing CO2 partial pressures (and hence constant Ha number), until a linear relationship is found between the experimental CO<sub>2</sub> absorption flux and its partial pressure. In this case, the assumption of pseudo first-order regime is indeed correct according to Eq. (23) and kinetic data can be extracted from the slope.

Solubility and diffusivity of CO<sub>2</sub> in amine solutions were estimated using Laddha et al. [25] relationships. The difusion coeficient of carbon dioxide in water as well as Henry's Law constant for carbon dioxide in pure used in this work were calculated using Versteeg and van Swaaij correlations [26]. The diffusion coefficients of N<sub>2</sub>O in amine blends as well as the solubilities in aqueous DEA and MDEA were estimated from the work of Li and Lee [27]. The diffusivity of N<sub>2</sub>O in alkanolamine solutions was estimated using the modified Stokes-Einstein equation [28]. Diffusion coefficients of DEA and MDEA in their respective solutions were estimated using the correlations established by Snijder et al. [29]. The viscosity of the amine solution was estimated using the correlation of Glasscock et al. [4]. The viscosity of water was taken from Handbook of Chemistry and Physics [30].

# V. EXPERIMENTAL

# A. Material

The employed alkanolamines were DEA and MDEA obtained from Riedel de Ha ën with 99% and 98.5% assay respectively. The reaction gases were carbon dioxide (99.99%) and oxygen-free nitrogen. Other chemicals used include standard aqueous sodium hydroxide (1N) and hydrochloric acid (1N) obtained from Merck. All chemicals were used as received and distilled water was used to prepare solutions.

# B. Apparatus and Methods

The experiments were carried out in a stirred cell reactor constructed from resistant glass with interfacial area for mass transfer of 77  $\text{cm}^2$ . The internal diameter of the reactor was 10 cm with a volume of about 1800 cm<sup>3</sup>. The gas and liquid phases are stirred separately. To prevent the formation of vortex, four equidistant baffles were placed inside the reactor. An infrared Rosemount® model 880A CO2 analyzer was employed to measure the Carbon dioxide concentration at the exit of the reactor. The amine solutions was charged into the reactor, stirred and maintained at a preset temperature. A calibrated 5080E Series Brooks mass flow controller used to control the gases flow rates. The changes in CO<sub>2</sub> concentration were continuously recorded using а computerized data acquisition system. To avoid depletion of reactants at the interface, experiments were run at very low partial pressure. This lowered the absorption fluxes and consequently, the mass transfer in the liquid film was controlled essentially by reaction kinetics. All of the rate experiments were conducted at very low loading and fresh solutions were used during each run, which makes the equilibrium partial pressure essentially zero. The rate of absorption was determined from a material balance around the reactor. Equation (30) was used to determine the overall reaction rate constant. A schematic diagram of the experimental setup is shown in Fig. 1.



Fig. 1. Schematic diagram of the experimental setup.

# VI. RESULTS AND DISCUSSION

### A. Gas Phase Resistance

Verification of negligible gas phase resistance is obtained using (25). The obtained straight line shown in Fig. 2 clearly indicates, as assumed, a negligible gas phase resistance.

Mass transfer coefficient  $(k_L)$  was determined from the absorption of pure CO<sub>2</sub> in water at 20°C using the same stirred cell. Mixing speed of the liquid is varied from 25 to 127 rpm while keeping a smooth gas-liquid interface. The absorption rate of CO<sub>2</sub> in water is calculated from the difference between the inlet and the outlet of the reactor using soap film meter. The values of  $(k_L)$  are calculated using the following expression:

$$k_{L} = R_{\rm CO_{2}} / \left( C_{\rm CO_{2}}^{*} - C_{\rm CO_{2}}^{b} \right), \tag{34}$$

where  $C_{CO_1}^*$  and  $C_{CO_2}^b$  are the concentrations of CO<sub>2</sub> at the

interface and in the liquid bulk, respectively.

# B. Liquid Side Mass Transfer Coefficient

The experimental results are correlated by the equation type  $Sh = a \cdot Re^b \cdot Sc^c$  as shown in Fig. 3. The following relationship is obtained:  $Sh = 0.1217 Re^{0.69} Sc^{0.5}$  where, Sherwood, Schmidt and Reynolds numbers are given by the respective equations:

$$Sh = k_L D_{imp} / D_{CO_2}$$
,  $Sc = \mu / \rho D_{CO_2}$  and  $Re = D_{imp}^2 (rpm/60) \rho / \mu$ .

The exponent on *Sc* was assumed 0.5 as the range of Sherwood number in the experiment is not too large. The exponent on  $R_e(0.69)$  is in accordance with the value obtained by Rangwala *et al.* [6] for the same type of experimental apparatus



Fig. 3. Liquid side mass transfer coefficient.

# C. Absorption of CO<sub>2</sub> in Amine Blends

The absorption data of CO<sub>2</sub> into aqueous blends of MDEA and DEA are given in Tables II-III. The experiments were carried out in the so-called pseudo first-order regime characterized by  $2 < Ha \ll E_{inf}$ . The ratio of DEA to MDEA was selected in a way that the overall reaction rate would not be dominated by the reaction between DEA and CO<sub>2</sub>.

The effect of amine mixture composition on the absorption flux at different total amine concentration and varying temperature is presented here. For a total amine concentration equals to one mole and T = 293 K, we observe that an increase in DEA/MDEA ratio, as shown in Fig. 4, brings about a significant increase in the absorption flux. The same trend is observed in Fig. 5 for the same composition but at higher temperature (T = 313 K).

TABLE II: ABSORPTION DATA OF CO2 IN TOTAL 1 M (DEA+MDEA) AT

DIFFERENT TEMPERATURES						
DEA	MDEA	P <sub>CO2</sub>	R <sub>CO2</sub> .10 <sup>7</sup>	k <sub>ov</sub>		
(mol/l)	(mol/l)	(kPa)	(mol/m <sup>2</sup> .s)	$(s^{-1})$		
	293K					
0.05	0.95	9.66	4.34	10.24		
0.1	0.9	9.56	5.57	18.79		
0.15	0.85	9.21	7.67	39.14		
303 K						
0.05	0.95	9.41	6.85	40.24		
0.1	0.9	9.28	8.10	62.56		
0.15	0.85	9.19	8.97	86.77		
313 K						
0.1	0.9	9.12	9.60	111.23		
0.08	0.892	17.60	14.05	60.17		
0.062	0.881	26.08	17.97	39.88		

TABLE III: KINETICS DATA FOR CO<sub>2</sub> Absorption in Total 2 M (DEA+MDEA) at 313 K

DEA	MDEA	P <sub>CO2</sub>	R <sub>CO2</sub> .10 <sup>7</sup>	k <sub>ov</sub>
(mol/l)	(mol/l)	(kPa)	(mol/m <sup>2</sup> .s)	$(s^{-1})$
0.4	1.6	8.78	12.94	349.44
0.3	1.7	8.97	11.08	223.72
0.2	1.8	9.07	10.09	163.89
0.1	1.9	9.34	7.48	76.85



Fig. 4. Mixture composition effect on the absorption flux for total 1 M at 293K.



Fig. 5. Mixture composition effect on the absorption flux for total 1 M at 313K.

The effect of DEA concentration and temperature on the apparent rate constant is further illustrated in Fig. 6, where we observe that the apparent rate constant  $(k_{app})$  increases with increasing DEA and temperature.

A comparison between the absorption rate of  $CO_2$  in single and mixed amines is shown in Fig. 7 and Fig. 8 it is observed that the absorption flux curve for blended solutions of DEA +MDEA lie above that of single MDEA and below that of Single DEA. Using fresh amines, the absorption flux of CO<sub>2</sub> in the mixture is clearly between those of  $CO_2$  in single amines as shown in Fig. 7. At lower CO<sub>2</sub> partial pressure, the mixture absorption curves lie approximately in the middle of single amines absorption curves. However, at increased CO<sub>2</sub> partial pressure, the performance of amine blends approaches that of MDEA as shown in Fig. 8. This can be explained by the fast depletion of DEA in the mixture at high pressures since the CO<sub>2</sub>-DEA reaction is much faster than that of CO<sub>2</sub>-MDEA. Thus, reaching a situation where the quasi totality of DEA in the mixture is consumed which makes solution not anymore a mixture of DEA and MDEA, but a solution of MDEA heavily loaded with the products of the reaction of CO2 with DEA





Fig. 6. Rate constant as function of DEA concentration in total 1M mixture.

Fig. 7. Performances of single and mixed amines for total 1 M mixture at 313K.

# D. Rate Constants

To obtain the kinetic constants of the reaction, we fitted the apparent reaction rate,  $k_{app}$ , to Eq. (24). In this approach, the individual rate constants for the CO<sub>2</sub>-DEA and CO<sub>2</sub>-MDEA reaction systems were taken from previous works [31], [32]. Species concentrations needed to fit Eq. (24) were estimated using the modified Deshmukh-Mather model described earlier, interaction parameter needed to estimate activity coefficients were taken from a previous work [9]. An example of species concentration profile using this model is shown in Fig. 9.



Fig. 8. Performances of single and mixed amines for total 1 M mixture at 303K.



Fig. 9. Concentration profile in carbonated solution of 0.5 M DEA + 1.5 M MDEA at T = 303 K.

The regressed values of  $k_{2\text{-DEA}}$ ,  $\left(k_{2\text{-DEA}} k_{H_2O}/k_{-1}\right)$ ,  $\left(k_{2\text{-DEA}} k_{DEA}/k_{-1}\right)$  and  $\left(k_{2\text{-DEA}} k_{MDEA}/k_{-1}\right)$  as well as  $k_{2\text{-MDEA}}$  at 303 K presented in Table IV seem to be very close to those available in the open literature. The obtained values compare favorably in order of magnitude with the values of Glasscock *et al.* [4] and those of Littel *et al.* [33] as shown in Table IV. These results confirm the conclusion that the zwitterions deprotonation rate constants increase with the increasing basicity of the deprotonating base as pointed out by Little *et al.* [33].

TABLE IV: KINETIC PARAMETERS FOR THE REACTION BETWEEN (DEA + MDEA) AND  $\mathrm{CO}_2$ 

Temp K	k <sub>2-DEA</sub> m <sup>3</sup> /mol.s	$\frac{\frac{k_{2\text{-DEA}}}{k_{H_2O}}}{k_{.1}}_{10^6\text{.m}^6\text{/mol}^2\text{s}}}$	$\frac{\frac{k_{2\text{-DEA}}}{k_{-1}}}{10^{4}\text{.m}^{6}\text{/mol}^{2}\text{.}}$	$\frac{\frac{k_{2\text{-DEA}}}{k_{\text{-1}}}}{10^4.\text{m}^6/\text{mol}^2.}$	
298*	-	4.1	6.37	4.57	
298**	3.13	1.68	7.23	3.54	
303#	7.37	6.57	6.76	4.42	
( <sup>*</sup> ): Glasscock <i>et al.</i> [1991], ( <sup>**</sup> ): Littel <i>et al.</i> [1992], ( <sup>#</sup> ): This work					

## VII. CONCLUSIONS

Kinetics of the absorption of  $CO_2$  into MDEA + DEA + H<sub>2</sub>O was investigated at 20, 30, and 40 °C using a laboratory

stirred cell. The total amine concentrations studied were 1 and 2 kmol/m<sup>3</sup> of (DEA+MDEA) while the DEA/MDEA ratio was varied in a way not to allow any single amine to dominate the other one. The addition of small amounts of DEA to MDEA results in a significant enhancement of CO<sub>2</sub> absorption rates. The N2O analogy was applied to estimate the solubilities and diffusivities of CO<sub>2</sub> in the amine systems considered in this work. Based on the pseudo first-order regime for the CO<sub>2</sub> absorption, the overall pseudo first-order reaction rate constants were determined from the kinetic measurements. A reaction model consisting of a first-order reaction mechanism for MDEA and a zwitterions mechanism for DEA was used to represent the kinetic data. Beside DEA, H<sub>2</sub>O and OH<sup>-</sup>, MDEA also acts as a base for the removal of a proton H<sup>+</sup> from the zwitterion intermediate. The overall absolute percentage deviation of the calculation of the overall pseudo first order rate constant by this reaction model was less than 7%. This result upholds the validity of the chosen reaction rate model in representing the CO<sub>2</sub> absorption rate into  $MDEA + DEA + H_2O$  systems.

#### REFERENCES

- L. Kohl and R. B. Nielsen, *Gas Purification*, 5<sup>th</sup> ed., Gulf, Houston, U.S.A., 1997.
- [2] T. Chakravarty, U. K. Phukan, and R. H. Weiland, "Reaction of acid gases with mixtures of amines," *Chem. Eng. Prog*, vol. 81, pp. 32-36, 1985.
- [3] H. Bosch, G. F. Versteeg, and. W. P. M. van Swaaij, "Gas-liquid mass transfer with parallel reversible reactions-III. absorption of CO<sub>2</sub> into solutions of blends of amines," *Chem. Eng. Sci*, vol. 44, pp. 2745-2750, 1989.
- [4] D. A. Glasscock, J. E. Critchfield, and G. T. Rochelle, "CO<sub>2</sub> absorption-desorption in mixtures of methyldiethanolamine with monoethanolamine or diethanolamine," *Chem. Eng. Sci*, vol. 46, pp. 2829-2845, 1991.
- [5] P. Mandal, A. K. Biswas, and S. S. Bandyopadhyay, "Absorption of carbon dioxide into aqueous blends of 2-Aamino-2-methyl-1-propanol and Diethanolamine," *Chem. Eng. Sci*, vol. 58, pp. 4137-4144, 2003.
- [6] H. A. Rangwala, B. R. Morrell, A. E. Mather, and F. D. Otto, "Absorption of CO<sub>2</sub> into Aqueous Tertiary Amine/MEA solutions," *Can. J. Chem. Eng.*, vol. 70, pp. 482–490, 1992.
- [7] X. Zhang, C. F. Zhang, and Y. Liu, "Kinetics of Absorption of CO<sub>2</sub> into aqueous solution of MDEA blended with DEA," *Ind. Eng. Chem. Res*, vol. 41, pp. 1135–1141, 2002.
- [8] P. Mandal and S. S. Bandyopadhyay, "Simultaneous absorption of CO<sub>2</sub> and H<sub>2</sub>S into aqueous blends of n-methyldiethanolamine and diethanolamine," *Environ. Sci. Technol*, vol. 40, pp. 6076-6084, 2006.
- [9] A. Benamor and M. K. Aroua, "Modeling of CO<sub>2</sub> solubility and carbamate concentration in DEA, MDEA and their mixtures using the deshmukh-mather model," *Fluid Phase Equilibria Journal*, vol. 231, pp. 150–162, 2005.
- [10] M. Z. Haji-Sulaiman and M. K. Aroua, "Equilibrium of CO<sub>2</sub> in aqueous diethanolamine (DEA) and Amino Methyl Propanol (AMP) solutions," *Chem Eng. Comm*, vol. 140, pp. 157-171, 1996.
- [11] E. A. Guggenheim and R. H. Stokes, "Activity coefficients of 2: 1 and 1 : 2 electolytes in aqueous solution from isopiestic data," *Trans. Faraday Soc.*, vol. 54, pp. 1646-1649, 1958.
- [12] Scatchard, "Concentrated solutions of strong electrolytes," *Chem. Rev.*, vol. 19, pp. 309-327, 1936.
- [13] G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, *Thermodynamics*, 2<sup>nd</sup> ed., McGraw Hill, 1961.
- [14] K. S. Pitzer, "Thermodynamics of electrolytes. (1) Theoretical basis and general equations," J. Phys. Chem., vol. 77, pp. 268-277, 1973.

- [15] K. S. Pitzer and J. J. Kim, "Thermodynamics of electrolytes. (4) Activity and osmotic coefficients for mixed electrolytes," J. Am. Chem. Soc., vol. 96, pp. 5701-5707, 1974.
- [16] D. D. Perrin, *Dissociation Constants of Organic Bases in Aqueous Solutions*, Butterworths, London, 1965.
- [17] J. I. Littel, M. Bos, and G. J. Knoop, "Dissociation constants of some alkanolamines at 293, 303,318 and 333 K," *J. Chem. Eng. Data.*, vol. 35, pp. 276-277, 1990.
- [18] M. K. Aroua, A. Benamor, and M. Z. Haji Sulaiman, "Temperature dependency of the equilibrium constant for the formation of carbamate from diethanolamine," *J. Chem. Eng. Data*, pp. 692-696, 1997.
- [19] T. J. Edwards, G. Maurer, J. Newman, and J. M. Prausnitz, "Vapor-liquid equilibria in multicomponent... aqueous solutions of volatile weak electrolytes," *AIChEJ.*, vol. 24, pp. 966-976, 1978.
- [20] M. Caplow, "Kinetics of carbamate formation and breakdown," J. Am. Chem. Soc, vol. 90, pp. 6795-6803, 1968.
- [21] T. L. Donaldson and Y. N. Nguyen, "Carbon dioxide reaction kinetics and transport in aqueous amine membrane," *Ind. Eng. Chem. Fundam*, vol. 19, pp. 260-266, 1980.
- [22] P. V. Danckwerts, Gas Liquid Reactions, McGraw Hill, USA, 1970.
- [23] R. Higbie, "The rate of absorption of a pure gas into a still liquid during short periods of exposure," *Trans. Am. Inst. Chem. Engrs*, vol. 31, pp. 365, 1935.
- [24] W. DeCoursey, "Absorption with chemical reaction: development of a new relation for the Danckwerts model," *Chem. Eng. Sci.* vol. 29, pp. 1867–1872, 1974.
- [25] S. S. Laddha, J. M. Diaz, and P. V. Danckwerts, "The N<sub>2</sub>O analogy: The solubilities of CO<sub>2</sub> and N<sub>2</sub>O in aqueous solutions of organic compounds," *Chem. Eng. Sci*, vol. 36, pp. 229-230, 1981.
- [26] G. F. Versteeg and W. P. M. Van Swaaij, "Solubility and diffusivity of acid gases (CO<sub>2</sub>, N<sub>2</sub>O) in aqueous alkanolamine solutions," *J. Chem. Eng. Data*, vol. 33, pp. 29-34, 1988.
- [27] M. H. Li and W. C. Lee, "Solubility and diffusivity of N<sub>2</sub>O and CO<sub>2</sub> in (diethanolamine + N-methyldiethanolamine + water) and in (diethanolamine + 2-amino-2-methyl-1-propanol + water)," *J. Chem. Eng. Data*, vol. 41, no. 3, pp. 551-556, 1996.
- [28] G. F. Versteeg, L. A. J. Van Dijck, and W. P. M. Van Swaaij, "On The kinetics between CO<sub>2</sub> and alkanolamines both on aqueous and non-aqueous solutions," *Chem. Eng. Sci*, vol. 144, pp. 113-158, 1996.
- [29] D. Snijder, M. J. M. Riele, G. F. Versteeg, and W. P. M. Van Swaaij, "The diffusion coefficient of several aqueous alkanolamine solutions," *J. Chem. Eng. Data*, vol. 38, pp. 475-480, 1993.
- [30] Handbook of Chemistry and physics, 83rd Ed, CRC press, 2002.
- [31] A. Benamor and M. K. Aroua, "An experimental investigation on the rate of CO<sub>2</sub> absorption into aqueous methyldiethanolamine solutions," *The Korean J. Chem. Eng.*, vol. 24, no. 1, pp. 16-23, 2007.
- [32] A. Benamor, B. Si-Ali, and M. K. Aroua, "Kinetic of CO<sub>2</sub> absorption and carbamate formation in aqueous solutions of diethanolamine," *The Korean J. of Chem. Eng.*, vol. 25, no. 3, pp. 451-460, 2008.
- [33] R. J. Little, G. F. Versteeg, and W. P. M. Van Swaaij, "Kinetics of CO<sub>2</sub> with primary and secondary amines in Aqueous Solutions-II. Influence of temperature on Zwiterion formation and deprotonation rates," *Chem. Eng. Sci.*, vol. 47, pp. 2037-2045, 1992.



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