Reactive Absorption of CO$_2$ 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$_2$ 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 ($k_o$) that are greater than the sum of the $k_o$ 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-1-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 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 CO$_2$ 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:

\[
\text{DEAH}^+ \rightleftharpoons \text{DEA} + \text{H}^+ \quad (1)
\]

\[
\text{MDEAH}^+ \rightleftharpoons \text{MDEA} + \text{H}^+ \quad (1a)
\]

Formation of carbamate:

\[
\text{DEACOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{DEA} + \text{HCO}_3^- \quad (2)
\]

Dissociation of carbon dioxide:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad (3)
\]

Dissociation of bicarbonate ion:

\[
\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad (4)
\]

Ionization of water:

\[
\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+ \quad (5)
\]

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

Amine balance:

\[ [\text{DEA}] + [\text{MDEA}] = [\text{DEA}] + [\text{MDEA}] + [\text{DEAH}^+] + [\text{MDEAH}^+] + [\text{RR'}\text{NCOO}] \]

CO₂ balance:

\[ \alpha ([\text{DEA}] + [\text{MDEA}]) = [\text{HCO}_3^-] + [\text{RR'}\text{NCOO}] + [\text{CO}_2] \]

Charge balance:

\[ [\text{DEAH}^+] + [\text{MDEAH}^+] = [\text{HCO}_3^-] + [\text{RR'}\text{NCOO}] + 2[\text{CO}_2] \]

\[ \ln K_i \left( H_{\text{CO}_3^-} \right) = \frac{\alpha}{T} + b \ln T + c T + d_i \]

where \( \alpha \) and \( d_i \) are constants whose values for reactions (1) – (5) and for the Henry’s constant are taken from the literature as given in Table I.

### Table I. Thermodynamic Parameters Used in this Work

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( a_i )</th>
<th>( b_i )</th>
<th>( c_i )</th>
<th>( d_i )</th>
<th>Source</th>
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<td>( K_1,\text{DEA} )</td>
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<td>6.776904</td>
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<td>-48.7594</td>
<td>[16]</td>
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<tr>
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<td>87.39717</td>
<td>[17]</td>
</tr>
<tr>
<td>( K_1 )</td>
<td>-17067.2</td>
<td>-66.3007</td>
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<td>439.709</td>
<td>[18]</td>
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<tr>
<td>( K_a )</td>
<td>-12431.7</td>
<td>-35.4819</td>
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<td>220.067</td>
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<tr>
<td>( K_{-1} )</td>
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<td>( K_{-2} )</td>
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<td>( H_{\text{CO}_3^-} )</td>
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<td>-11.4519</td>
<td>-0.010454</td>
<td>94.4914</td>
<td>[19]</td>
</tr>
</tbody>
</table>

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

### III. Reaction Pathways

In aqueous mixtures of DEA + MDEA, the absorption of CO₂ can be considered as a combination of several reactions involving CO₂-DEA, CO₂-MDEA and CO₂-H₂O. In case of DEA, it reacts with CO₂ according to the zwitterion mechanism [20]:

\[ \text{CO}_2 + \text{DEA} \xrightarrow{k_1} \text{DEAH}^+ + \text{COO}^- \]

\[ \text{DEAH}^+ + \text{COO}^- + \text{H}^+ \xrightarrow{k_2} \text{DEACOO}^- + \text{BH}^+ \]

CO₂-MDEA reaction can be described as a base catalyzed hydration of CO₂ according to the reaction [21]:

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

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

\[ \text{CO}_2 + \text{OH}^- \xrightarrow{\text{hydration}} \text{HCO}_3^- \]
The overall reaction rate would be:

\[
R_a = \frac{k_{2,\text{REA}} [\text{CO}_2] [\text{DEA}]}{k_1 + k_{\text{H,O}} [\text{H}_2\text{O}] + k_{\text{OH}} [\text{OH}]} \cdot [\text{DEA}] \cdot [\text{DEA}] k_{2,\text{REA}} [\text{CO}_2] [\text{MDEA}] + k_{\text{in}} [\text{CO}_2] [\text{OH}]
\]

(23)

Therefore, the apparent reaction rate would be:

\[
k_{\text{app}} = \frac{1}{k_{2,\text{REA}} + \frac{k_{2,\text{REA}} k_{\text{H,O}} [\text{H}_2\text{O}]}{k_1} + \frac{k_{2,\text{REA}} k_{\text{OH}} [\text{OH}]}{k_1} + \frac{k_{2,\text{REA}} k_{2,\text{REA}} [\text{DEA}]}{k_1} + \frac{k_{2,\text{REA}} k_{\text{MDEA}} [\text{MDEA}]}{k_1}}\]

(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

\[
J = \frac{(C_{\text{CO}_2,L} - C_{\text{CO}_2,G})/m_{\text{CO}_2}}{1/k_i + 1/m_{\text{CO}_2} k_i E_{\text{CO}_2}}
\]

(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 \((C_{\text{CO}_2,L} = 0)\). Assuming an ideal gas behaviour for CO\(_2\), its concentration in the gas phase can be represented by \(C_{\text{CO}_2,L} = \rho \text{CO}_2 / RT\) and \(m_{\text{CO}_2} = RT / H_{\text{CO}_2}\). Furthermore, assuming there is no resistance to mass transfer in the gas phase \((1 / k_i = 0)\), the absorption of pure CO\(_2\) is then given by:

\[
J = k_i E_{\text{CO}_2} \frac{m_{\text{CO}_2} \rho_{\text{CO}_2}}{RT} = k_i E_{\text{CO}_2} \left( \frac{\rho_{\text{CO}_2}}{RT} \right)
\]

(26)

The enhancement factor, \(E_{\text{CO}_2}\), is a function of the Hatta number \(Ha\) and the infinite enhancement factor \(E_{\text{inf}}\). The Hatta number is defined as:

\[
Ha = \sqrt{\frac{D_{\text{CO}_2}}{k_i}}
\]

(27)

According to the penetration model [23], the infinite enhancement factor, \(E_{\text{inf}}\), is given by

\[
E_{\text{inf}} = \sqrt{\frac{D_{\text{CO}_2}}{D_{\text{CO}_2} + \frac{[\text{Am}]}{[\text{CO}_2]} \frac{D_{\text{CO}_2}}{D_{\text{CO}_2}}}}
\]

(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 \(E_{\text{inf}}\), 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\(_2\) 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:

\[
2 < Ha \ll E_{\text{inf}}
\]

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 \(E_{\text{CO}_2} = Ha\). Consequently, Eq. (19) becomes

\[
J_{\text{CO}_2} = \frac{\rho_{\text{CO}_2} \rho_{\text{CO}_2}}{RT} \left( \frac{\rho_{\text{CO}_2}}{RT} \right)
\]

(30)

It is obvious from Eq. (23) that the kinetic rate constant \(k_{\text{in}}\) 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 \(E_{\text{inf}}\) was derived by DeCoursey [24]:

\[
E_{\text{CO}_2} = \frac{Ha^3}{2(E_{\text{inf}} - 1)} + \frac{Ha^3}{4(E_{\text{inf}} - 1)^2} + \frac{E_{\text{inf}} Ha^3}{(E_{\text{inf}} - 1)^2} + 1
\]

(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 \(E_{\text{inf}}\), 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:

\[
2 < E_{\text{inf}} \ll Ha
\]

(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

\[
E_{\text{inf}} = k_i \left( \frac{D_{\text{CO}_2}}{D_{\text{CO}_2} + \frac{[\text{Am}]}{[\text{CO}_2]} \frac{D_{\text{CO}_2}}{D_{\text{CO}_2}} + \frac{m_{\text{CO}_2} \rho_{\text{CO}_2}}{RT}} \right)
\]

(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 CO$_2$ partial pressures (and hence constant $Ha$ number), until a linear relationship is found between the experimental CO$_2$ 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$_2$ in amine solutions were estimated using Laddha et al. [25] relationships. The diffusion coefficient 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$_2$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$_2$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 Haën 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 cm$^2$. The internal diameter of the reactor was 10 cm with a volume of about 1800 cm$^3$. 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 CO$_2$ 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$_2$ concentration were continuously recorded using a 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.

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$_2$ 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$_2$ 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:

$$k_L = \frac{R_{CO_2}}{(C_{CO_2} - C_{CO_2}^b)}.$$  (34)

where $C_{CO_2}^b$ and $C_{CO_2}$ are the concentrations of CO$_2$ at the
interface and in the liquid bulk, respectively.

**B. Liquid Side Mass Transfer Coefficient**

The experimental results are correlated by the equation type \( Sh = \alpha \cdot Re^{0.5} \cdot Sc^{0.5} \) as shown in Fig. 3. The following relationship is obtained: \( Sh = 0.1217 \cdot Re^{0.4} \cdot Sc^{0.5} \) where, Sherwood, Schmidt and Reynolds numbers are given by the respective equations:

\[
Sh = k_{app} \cdot D_{CO2} \cdot Sc = \mu / \rho \cdot D_{CO2}, \quad Re = D_{app} \cdot (rpm/60) / \mu.
\]

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

\[
\begin{align*}
Sh & = k_{app} \cdot D_{CO2}, \quad Sc = \mu / \rho \cdot D_{CO2} \\
Re & = D_{app} \cdot (rpm/60) / \mu.
\end{align*}
\]

![Fig. 2. Negligible gas phase resistance.](image2)

![Fig. 3. Liquid side mass transfer coefficient.](image3)

**C. Absorption of CO₂ in Amine Blends**

The absorption data of CO₂ 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 \( 2 < Ha \ll E_a \). 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 CO₂.

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).

![Fig. 4. Mixture composition effect on the absorption flux for total 1 M at 293K.](image4)

![Fig. 5. Mixture composition effect on the absorption flux for total 1 M at 313K.](image5)

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$_2$ in the mixture is clearly between those of CO$_2$ in single amines as shown in Fig. 7. At lower CO$_2$ partial pressure, the mixture absorption curves lie approximately in the middle of single amines absorption curves. However, at increased CO$_2$ 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$_2$-DEA reaction is much faster than that of CO$_2$-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 CO$_2$ with DEA

![Fig. 6. Rate constant as function of DEA concentration in total 1M mixture.](image)

![Fig. 7. Performances of single and mixed amines for total 1 M mixture at 313K.](image)

**D. Rate Constants**

To obtain the kinetic constants of the reaction, we fitted the apparent reaction rate, $k_{\text{app}}$, to Eq. (24). In this approach, the individual rate constants for the CO$_2$-DEA and CO$_2$-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.

The regressed values of $k_{2,\text{DEA}}$, $(k_{2,\text{DEA}} k_{\text{H}_2\text{O}})/k_{1}$, $(k_{2,\text{DEA}} k_{\text{DEA}})/k_{1}$ and $(k_{2,\text{DEA}} k_{\text{MDEA}})/k_{1}$ 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 CO$_2$**

<table>
<thead>
<tr>
<th>Temp K</th>
<th>$k_{2,\text{DEA}}$ $\text{m}^2\text{mol}^{-1}\text{s}^{-1}$</th>
<th>$k_{2,\text{DEA}} k_{\text{H}<em>2\text{O}}/k</em>{1}$</th>
<th>$k_{2,\text{DEA}} k_{\text{DEA}}/k_{1}$</th>
<th>$k_{2,\text{DEA}} k_{\text{MDEA}}/k_{1}$</th>
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<td>298°</td>
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<td>298°*</td>
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<td>1.68</td>
<td>7.23</td>
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<td>303°</td>
<td>7.37</td>
<td>6.57</td>
<td>6.76</td>
<td>4.42</td>
</tr>
</tbody>
</table>

(°): Glasscock et al. [1991], (*): Littel et al. [1992], (*°): This work

**VII. CONCLUSIONS**

Kinetics of the absorption of CO$_2$ into MDEA + DEA + H$_2$O was investigated at 20, 30, and 40 °C using a laboratory
stirred cell. The total amine concentrations studied were 1 and 2 kmol/m³ 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 CO₂ absorption rates. The N₂O analogy was applied to estimate the solubilities and diffusivities of CO₂ in the amine systems considered in this work. Based on the pseudo first-order regime for the CO₂ 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, H₂O and OH⁻, MDEA also acts as a base for the removal of a proton H⁺ 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 CO₂ absorption rate into MDEA + DEA + H₂O systems.

REFERENCES