Tertiary amine blend for CO2 capture: A kinetic investigation using Monoethanolamine, Triethanolamine and Piperazine

Safa Waleed Shakir1, Ahmed Daham Wiheeb2, Sahar Adnan Ahmed3
1,3Chemical Engineering Department, College of Engineering, Tikrit University, Tikrit, Sallahaddin, Iraq
2Chemical Engineering Department, College of Engineering, University of Diyala, Baqubah, Diyala, Iraq

Email: eng.safawaleed@tu.edu.iq

Abstract. The kinetics reaction of the tertiary amine blend of monoethanolamine (MEA), triethanolamine (TEA), and piperazine (PZ) with carbon dioxide (CO2) considered in a packed bed. The mechanism of reaction and kinetics of this tertiary amine were studied at (298-308) K and 1 atm with total blend concentration varied from (4-6) molar. The current experiments revealed a new good absorbent of (MEA,TEA, PZ) blend to capture CO2, due to it is potential upon CO2. Therefore, the proposed mechanism found to be suitable in determining the kinetics of the involved reactions. The reaction mechanism was defined using a mechanism of zwitterion and termolecular. It’s found that the absorption follows the fast kinetic reaction with first-order kinetics for CO2 and second-order for the blend concentration. The rate constant value $k_2$ (m³/kmol.s) of the tertiary blend of (MEA,TEA, PZ) found to be (8050) that is greater than that of commonly used amine MEA(7500). Also, the activation energy was calculated and found to be 24 kJ/mol.

1. Introduction
Carbon dioxide emissions are a global concern that requires a rapid solution to mitigate climate change risks [1-2]. The interest of many researchers is directed towards capturing carbon dioxide due to it is high amount emitted into the atmosphere compared to other greenhouse gases and it is risks to climate change [3]. Many capturing processes applied to remove CO2 from mixture of gases such: absorption, membranes, adsorption, and cryogenic [3]. Industrially, the chemical absorption of CO2 has been considered the preferred method [1]. The solutions of alkanol amine are usually used for capturing acidic gas for example CO2 capture from mixture of gases in the refineries, natural gas, and synthetic. Many choices are presented for acid gases removing. Nevertheless, the most used technology is the absorption of CO2 using solution of amine such as monoethanolamine (MEA), diethanolamine (DEA), N methyl diethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), and, triethanolamine (TEA), in reversible processes [2-3]. MEA is usually used as a chemical adsorption solvent for carbon dioxide due to it is high absorption capacity, low cost, and easy availability [2-4]. However, MEA has required high energy for regeneration, high rate of degradation in addition to it is corrosive nature [4]. Therefore, it is necessary to find other solvents to capture CO2 and to avert common alkanol amines defects [4]. Researchers revealed that the absorption characteristics of each alkanol amine can be combined. Therefore, the blended of alkanol amine has been suggested to
remove the acid gases by chemical absorption. According to the researches, two types of blend were examined: binary blend (consist of two alkanol amine) and tertiary blend (consist of three alkanol amine). The choice of blend type governed by the kinetic behavior of alkanol amine with CO2 [4]. It’s found that the study of the kinetics of alkanol amine blends with CO2 was appropriate due to it is significant characteristics [1-4]. The addition of a primary or secondary amine to conventional tertiary amines with a small amount of cyclic amine can improve the absorption rate of CO2 to a large amount without significantly changing the desorption characteristics, [4]. In this study, it managed to prove that MEA, TEA, PZ blend is an efficient CO2 absorption solution. The current experiments show that MEA, TEA, PZ blends represent an especially promising absorbent, compared to commonly used solvent 5M MEA. However, by now, there is no data on the chemical kinetics of the (CO2-MEA, TEA, PZ and H2O) system. For that reason, it would be motivating to study the mechanism of the CO2 reaction with MEA, TEA, PZ blend, Kinetic experiments were held in a highly limited range of MEA, TEA, PZ blend concentration (4-6) molar, (298 -308) K and 1 atm.

2. The mechanism of the absorption reaction MEA, TEA, PZ

The CO2 solubility and it is reaction by solutions of blended amine (aqueous solution) include many complex reversible reactions similar to that of an acid-base reaction that occurred in the liquid phase. For this aqueous amine solution of TEA, PZ and MEA, the mechanism of reaction with CO2 explained as following:

\[
\begin{align*}
2\text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{O} + \text{OH}^- & (1) \\
\text{CO}_2 + 2\text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{O}^+ + \text{HCO}_3^- & (2) \\
\text{HCO}_3^- + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{O}^+ + \text{CO}_3^{2-} & (3) \\
\text{TEA} + \text{CO}_2 + \text{H}_2\text{O} & \leftrightarrow \text{TEAH}^+ + \text{HCO}_3^- & (4) \\
\text{CO}_2 + \text{OH}^- & \leftrightarrow \text{HCO}_3^- & (5) \\
\text{PZH}_2^+ + \text{H}_2\text{O} & \leftrightarrow \text{PZH}^+ + \text{H}_3\text{O}^+ & (6) \\
\text{PZH}^+ + \text{H}_2\text{O} & \leftrightarrow \text{PZ} + \text{H}_2\text{O}^+ & (7) \\
\text{MEAH}^+ + \text{H}_2\text{O} & \leftrightarrow \text{MEA} + \text{H}_3\text{O}^+ & (8) \\
\text{CO}_2 + \text{H}_2\text{O} + \text{PZ} & \leftrightarrow \text{PZCOO}^- + \text{H}_2\text{O}^+ & (9) \\
\text{PZCOO}^- + \text{CO}_2 + \text{H}_2\text{O} & \leftrightarrow \text{HPZCOO}^- + \text{HCO}_3^- & (10) \\
\text{HPZCOO}^- + \text{H}_2\text{O} & \leftrightarrow \text{PZCOO}^- + \text{H}_2\text{O}^+ & (11) \\
\text{PZCOO}^- + \text{CO}_2 + \text{H}_2\text{O} & \leftrightarrow \text{PZ(COO)}_2^- + \text{H}_3\text{O}^+ & (12) \\
2\text{MEA} + \text{CO}_2 & \leftrightarrow \text{MEACOO}^- + \text{MEAH}^+ & (13) \\
\text{MEACOO}^- + \text{H}_2\text{O} & \leftrightarrow \text{MEA} + \text{HCO}_3^- & (14)
\end{align*}
\]

Equations (1), (2) and (3) represent the classic ionization for aqueous systems that have CO2. Equations (4) and (5) are the reactions of TEA protonation [5-6]. As said by Sartori and Savage (1983), TEA may rapidly go through hydrolysis, this step forming bicarbonates and free amine molecules [7]. According to (Equation (5)), the amine theoretical loading can be increasing to 1mol CO2/mol due to the easy hydrolysis of TEA [7]. The reaction mechanism of CO2 with PZ can be suggested to form carbamate of PZ and PZ hydrogenated carbamate with existence of a base [8]. Also, each base in the amino aqueous solution can undergo for this reaction. The interaction of any base will be affected by it is concentration and the strength of the base [9-10]. As a result, in an aqueous solution containing TEA, PZ, and MEA, carbamate formation is likely to be generally activated by either a mixture of amines (such as PZ, AMP, and MEA) or PZCOO-, H2O, OH− and PZH. Equations (9) and (12) are the interactions between CO2 and PZ to produce carbamates [11]. The stable carbamate coordinated from the reaction of MEA with CO2 is the main reaction restricting loading to theoretically 0.5 molCO2 / mol MEA, as shown in Equation (13) [9]. The CO2 loading of MEA can be higher than
0.5 (mol\(_{\text{CO}_2}\)/mol\(_{\text{solvem}}\)) at high pressure due to the increasing of the carbamate hydrolysis equation (14). Conversely, this hydrolysis usually occurs in a very small amount. The reaction supports free MEA generation for reaction with additional carbon dioxide, allowing loading to just over 0.5 [9]. The mechanism of the desorption reaction throughout the process can predicted to be the opposite of the mechanism of the absorption reaction due to the reversibility nature of the reaction of \(\text{CO}_2\) with amines. This allows the amount of \(\text{CO}_2\) absorbed, either in the form of carbamate or unrelated such bicarbonate and carbonate to be free from the solution of amine again [7-9].

2.1 The mechanism of zwitterion

The mechanism of the zwitterion reaction had been explained in some comprehensive reviews [12]. This mechanism assumes that carbon dioxide and (an amine mixture) interact to form zwitterion as an intermediate product:

\[
\text{CO}_2 + (\text{AMINE BLEND})\text{H} \quad \overset{k_2}{\underset{k_{-1}}{\rightleftharpoons}} \quad (\text{AMINE BLEND})\text{HCOO}^- \quad (15)
\]

Where \(k_2\) and \(k_{-1}\) are the forward and backward rate constant respectively. This zwitterion undergoes deprotonation by a base (or bases) B, thereby resulting in carbamate formation:

\[
\text{B} + (\text{AMINE BLEND})\text{HCOO}^- \quad \overset{k_B}{\rightleftharpoons} \quad \text{BH}^+ + (\text{AMINE BLEND})\text{COO}^- \quad (16)
\]

Sartori [9] stated that the influence of steric affects the steadiness of the carbamates formed by the reaction of \(\text{CO}_2\) with amine. The carbamates possibly will also freely hydrolysis. Because of the low stability; the hydrolysis results are bicarbonates and amine that will react with \(\text{CO}_2\) again. Consequently, bicarbonate ions amounts will be more than carbamate ions. Danckwerts [13] supposed that the intermediate (zwitterion) is similar to the carbamate in stability. Applying the principle of steady state to the Equation (16) of the intermediate zwitterion, the overall \(\text{CO}_2\) rate-reaction in solutions of aqueous amine can be stated generally as:

\[
R_{\text{CO}_2} = \frac{k_2 (\text{CO}_2)(\text{AMINE BLENDH})}{1 + \frac{k_{-1}}{k_B(B)}} \quad (17)
\]

Where, the kinetic constant \(K_B\) (B) denotes the deprotonation of a zwitterion by every base, such as \(\text{H}_2\text{O}, \text{OH}^-, \text{Amine blend}, \text{or by a blend of bases.} \) The rate of reactions of the \(\text{CO}_2\) with \(\text{OH}^-\) and \(\text{H}_2\text{O}\) according to the overall rate is supposed to be insignificant. The reaction-rate symbolized by Equation (17) displays an order of the reaction between one and two that related to the concentration of Amine blend. Equation (17) becomes:

\[
R_{\text{CO}_2} = K_{\text{obs}}(\text{CO}_2) \quad (18)
\]

Where the observed reaction rate constant, \(K_{\text{obs}}\), is expressed by:

\[
K_{\text{obs}} = \frac{1}{k_2} + \frac{k_{-1}}{k_2 k_B(B)} = \frac{(\text{AMINE BLENDH})}{1 + \frac{1}{k_2} + \frac{1}{k_B(B)}} \quad (19)
\]

Where: \(k_b = k_2 k_B / k_{-1}\).

The deprotonation occurs instantaneously compared to that of the reversible reaction in Equation (16), that means \(k_{-1} \ll k_b\) (B) and the formation of zwitterion is rate determining, Equation (17) written as:

\[
R_{\text{CO}_2} = k_2 (\text{CO}_2)(\text{AMINE BLENDH}) \quad (20)
\]
Therefore, the order of reaction has been suggested to be first order to CO$_2$ and amine blend. Hence, the overall order of the reaction is second order. Indeed, the de protonation of zwitterion is the rate-determining step thereby ($k_1$)$>$ $k_B$ (B)), Equation (17) becomes:

$$ R_{CO_2} = \frac{k_2k_B(B)}{k_{-1}}(CO_2)(AMINE\ BLENDH) $$

(21)

Like Equation (17), the final expression proposes a reaction order of amine blend concentration between one and two. When, the presence of amine blend to the deprotonation of zwitterion is weightier compared to other bases (H$_2$O and OH$^-$), then the overall order of the reaction is second respected to amine blend.

2.2. Mechanism of termolecular

The mechanism of termolecular supposes that the amine, amine blend, reacts with CO$_2$ molecule and base molecule instantaneously. Then, the complex as the intermediate reaction forms by a single step [14]. This symbolized as:

$$ CO_2 + (Amine\ blend)\ HB \leftrightarrow (Amine\ blend)COO + BH^+ $$

(22)

Thereafter, the formed complex suffers a breakdown to give the molecules of the reactants (carbon dioxide and amine) even though a small amount of these substances react with another molecule of amine or water to give ionic products (carbamates). In case, the forward reaction where OH$^-$, H$_2$O and (Amine blendH) are the governing bases the reaction rate can be described by:

$$ R_{CO_2} = \left[k_{H_2O}(H_2O) + k_{OH} (OH) + k_{(Amine\ blendH)(Amine\ blendH)}(Amine\ blendH)(CO_2)\right]$$

(23)

$$ R_{CO_2} = k_{obs}(CO_2) $$

(24)

Equation (23) proposes that OH$^-$, H$_2$O, and (an amine mixture) H and any other bases can affect the reaction in the same way. This formula is identical to that of the specific case of the zwitterion mechanism indicated by equation (21), and it can explain the fractional kinetics and the reaction with higher order also [15]. In aqueous solutions, proton removal is mostly performed with alkanol amine and water [16]. When the water is the solvent (main base), the reaction become first order respected to amine blend, and the rate of reaction represented by:

$$ R_{CO_2} = [k_{H_2O}(H_2O)(CO_2)(Amine\ blendH)] = K (CO_2)(Amine\ blendH) $$

(25)

Where: $K = k_{H_2O} (H_2O).$ While, the amine blend is the main base, the reaction rate is second order respected to amine blend and the rate can be stated as:

$$ R_{CO_2} = k_{(Amine\ blendH)} (CO_2)(Amine\ blendH) $$

(26)

When the amount of water is equivalent to that of the amine (in the intermediate) case, $k_{obs}$ be:

$$ k_{obs} = [k_{H_2O} (H_2O) + k_{(Amine\ blendH)}(Amine\ blendH)](Amine\ blendH) $$

(27)
2.3. Measurement of kinetics

When the CO$_2$ concentration in the liquid is low and the resistance to the entire mass transfer is in the liquid phase, it can be demonstrated, based on the theory of the two-film of mass transfer [34], that expressed by the following relativity:

$$ R_{CO_2} = k_L (CO_2) E $$

(28)

Where: $E$ is the enhancement factor which describes the enhancing influence of chemical reaction on the transport of the mass. $(CO_2)$ is the concentration of CO$_2$ in the interface then the reaction kinetics can be calculated from the measurement of the absorption rate and $k_L$ is the liquid phase resistance which according to the film theory depends on the dissolved gas diffusivity in the liquid and the film thickness [13]. Also, under the conditions of the fast pseudo-first class the $E$ equals the Hatta number [13-18] expressed as:

$$ Ha = \frac{\sqrt{D_{CO_2} k_{obs}}}{k_L} $$

(29)

The conditions for the rapid reaction system are: $10 < Ha << (Ei - 1)$. The improvement factor for the immediate reaction is expressed by:

$$ Ei = 1 + \left[ \frac{(Amine\ blendH) D_{(Amine\ blendH)}}{z(CO_2) D_{CO_2}} \right] $$

(30)

Where: $z$ is the stoichiometric coefficient of amine blend in the balanced reaction equation.

It should be noted that equation (30) is only valid when using the film theory. Via equations (28) and (29), the absorption rate in the aqueous amine mixture described as follows:

$$ R_{CO_2} = (CO_2) \sqrt{D_{CO_2} K_{obs}} $$

(31)

3. Experimental

3.1. Materials

MEA (99%), Hydrochloric acid (HCl) with 37% purity, Phenolphthalein (Ph. Ph.) (99%), Sulfuric acid (95 – 97%), Sodium chloride(99.9%) and Sodium bicarbonate (99%) were acquired from Merck Germany while PZ (99%) and TEA (99%) were supplied from Sigma Aldrich, India, and methyl orange (0.10%) indicator was used to determine the concentration of all amines used in this study. All materials were used without extra purification. N$_2$ (99.99%) and the CO$_2$ (99.99%) cylinders were acquired from SDI samarra, Iraq.

3.2. Experimental setup

Absorption assessment was studied by a packed bed (see Figure 1). It has been defined in previous work by detail [18]. The main benefit of using a packed bed is that absorption rates are easy to measure. Figure 1 shows the schematic diagram of the experimental bed. The packed bed is made of glass with an inner diameter of 4 cm, a column height of 140 cm, the column packed with 0.3 cm glass ring packing diameter chosen due to the corrosive nature of the solvent with 88 cm bed height. The gases of CO$_2$ and N$_2$ were mixed at desired % of CO$_2$ and the rest was N$_2$ (volume %) by fine-tuning the calibrated flow meters (all used flow meters calibrated by bubble soap calibration method). The gas mixture was then passed through the absorption column and in contact with the solvent. To get a good evaluation, the flow rates of gas, the flow rates of liquid, and the temperature were kept constant through the experimental absorption analysis. 1200 mL of the solvent with the required concentration at 9 L/h was fed into the packed bed from the top with the gas mixture from the bottom at 240 L/h and allowed to interact till the equilibrium was reached (constant loading).
Absorption properties are estimated based on time and CO$_2$ output. The CO$_2$ loading capacity of the solution samples recorded at constant interval of time (every 10 minutes) was estimated by the titration with acid using Chittick device (see Figure 2) [18].

**Figure 1.** Schematic diagram of the absorption process

**Figure 2.** Schematic diagram of the Chittick apparatus

### 3.3 Procedure of experiments

A series of tests were conducted with a combination of amine concentrations and partial pressures of carbon dioxide. During all experiments, an aqueous solution of a fresh amine mixture was charged to the packed bed and allowed to circulate till saturated. N$_2$ and CO$_2$ gases were charged from the gas cylinders and mixed at the required CO$_2$ vol. % (10-20%) and the rest was N$_2$. Then, the gas mixture allowed entering the packed bed. The amount of carbon dioxide absorbed by an aqueous solution of an amine mixture was measured for a period of time with a Chittick instrument. When C$_{CO2}$ is plotted against time for the period between t = 0 min and t = 60 min. The absorption rates were calculated from the slope values of dC$_{CO2}$/dt [4]. This measurement method allowed direct estimation of
absorption rates. Additionally, there is no need for further examination whereas, an increase in the CO₂ concentration in the solvent was the only factor required to assess the kinetic parameters. On the way to demonstrate the kinetic measurement technique, the reaction kinetics of the mixture of carbon dioxide and amine, the MEA rate constant was examined in the packed bed absorption system. The rate constant of the CO₂ absorption by MEA was 7531 (m²/kmol s) at the initial concentration of 2.5 M and 298 K agreed with that described by [21]. According to the previous study [12], it is found that the mass transfer rate is independent of the gas side mass transfer coefficient (kg). As a result, the absorption process was set to be controlled by the liquid phase. The mass transfer coefficient was estimated from the liquid side k_L in a packed bed according to Sánchez et al [19] and found to be the value of k_L is 2.4 10⁻⁴ (m/s).

4. Results and discussion
4.1. CO₂-MEA-TEA-PZ-H₂O kinetics

The CO₂ reaction with MEA-TEA-PZ over the ranges of amine concentrations, (4-6) molar was studied. The CO₂ absorption rates against amine blend concentration at 298 K are plotted in Figure 3 to check the reaction regime. By using linear regression, it’s found that the R-squared value is poor (R² = 0.95) and the association is nonlinear. Consequently, the immediate reaction is improbable to occur.

![Figure 3](image-url)

Figure 3. A plot of CO₂ absorption rate versus amine blends concentration at 298 K

A plot of CO₂ absorption rates against CO₂ concentration at 298 K is shown in Figure 4; this figure observes that the reaction undergoes first-order kinetics for concentration of CO₂. From the slope, √(D_{CO₂} k_{obs}) at 298 K was found to be equal to 1×10⁻² (kmol/m²) according to Equation (31). The solubility and diffusivity of CO₂ in water and amine blend at 298 K was calculated by Equation (32 and 33) [7].

\[
D_{CO₂-water} = 2.35 \times 10^{-6} \ exp \left( \frac{-2119}{T} \right)
\]
\[ D_{CO_2-Amine blend} = D_{CO_2-water} \left( \frac{\mu_{water}}{\mu_{Amine blend}} \right)^{0.8} \]  

\( k_{obs} \) was calculated and found to be equal to \( 113 \times 10^3 \) (1/s). moreover, the values of Hatta number (Ha) and enhancement factor (Ei -1) are vital to diagnose the kinetic regime. The values of Ha and (Ei -1) are equal in the reduction regime. Ha and (Ei -1) were calculated using the values of \( H_{CO_2, Amine blend} \) and \( D_{CO_2} \) at 298 K [20-24], it’s found that Ha and (Ei -1) are equivalent to 37 and 75 respectively. These results show that the amine reduction in the liquid film is neglectful and that the reaction is rapid and complete within the liquid film [23]. Accordingly, the order of reaction is second order to the mixture of the amine, and first order to the carbon dioxide, then the total order is third, equation (31) can be represented as follows:

\[ R_{CO_2} = C_{CO_2} \sqrt{D_{CO_2} \cdot k_2 \cdot (Amine blend)^2} \]  

**Figure 4.** A plot of CO\(_2\) absorption rate versus CO\(_2\) concentration (mol/l) at 6M amine blends concentration and 298 K

A plot of CO\(_2\) absorption rates/ CO\(_2\) concentration (\( R_{CO_2}/C_{CO_2} \)) against amine blend concentration at 298 K is shown in Figure 5. The linear plot approves the assumed second order reaction for amine blend. From the relevant slope, \( \sqrt{(k_2 \cdot D_{CO_2})} \) at 298 K was initiated to be equivalent to \( 9 \times 10^4 \) (m\(^3\)/s. kmol).
Knowing the values of $D_{CO_2}$ at 298 K then, the $k_2$ was calculated and found to be equal to $765 \text{ (m}^3/\text{kmol}^2.\text{s)}$. On the other hand, in case of the availability of the zwitterion mechanism (two-step mechanism), Equation (17) becomes:

$$R_{CO_2} = \frac{k_2 (CO_2)(Amine\ blend)}{1 + \frac{k_{Amine\ blend}(Amine\ blend) + k_{H_2O}(H_2O) + k_{OH}(OH)}{k_{-2}}}$$

and $k_{obs}$ can be expressed as:

$$k_{obs} = \frac{k_2 (Amine\ blend)}{1 + \frac{k_{Amine\ blend}(Amine\ blend) + k_{H_2O}(H_2O) + k_{OH}(OH)}{k_{-2}}}$$

Because the rate of the reaction depends on the concentration of the amine with a second degree effect, it is evident that both zwitterion formation and deprotonation are important in the overall reaction. Moreover, the contribution of the amine to deprotonation is large. For this, equation (36) will take the following form:

$$k_{obs} = k_2 (Amine\ blend)^2$$

In contrast, termolecular model is the fitting model, it would be clear that the amine is the governing base (as Eq. (27)). Consequently, $k_{obs}$ can be written as:

$$k_{obs} = k_{amine\ blend} (Amine\ blend)^2$$

Therefore, the reaction of CO$_2$ and amine can be explained similarly fit by the zwitterion and the termolecular mechanism. In addition, the influence of temperature on the absorption rate as well as the constant rate was studied. As shown in Figure 6 ($ln k_2$) against (1/T) was plotted the slope was -2876 which represent $-E_a/R$ according to (Equation (39)) [21].

$$ln k_2 = -\frac{E_a}{R} \left(\frac{1}{T}\right)$$
Where: $E_a$: activation energy (kJ/mol), $R$: gas constant (kJ/mol.K). Then, the activation energy was found to be 24 (kJ/mol).

![Temperature independence plot for MEA, TEA, PZ, H$_2$O system.](image)

**Figure 6.** Temperature independence plot for MEA, TEA, PZ, H$_2$O system.

5. **Solvent comparison**

The kinetics of the CO$_2$ absorption is the critical influence governing the overall removal efficiency if the column is operated under typical situations (no thermodynamics restrictions). So the CO$_2$ absorption performance can be evaluated according to the reaction rate constant ($k$). As shown in Table (1), the rank of single amine is MEA> DEA> AMP> DIPA> MDEA> TEA. Conversely, in the case of blended alkanolamines, the CO$_2$ absorption performance is usually related with the performance of their single alkanolamines. However, the linear association does not essential and differs according to the concentration and the alkanolamine type. The performance of the studied blend MEA-TEA-PZ shows slightly higher than MEA as the effect of the presence of PZ.

| Alkanolamine | Temperature (K) | Concentration (kmol/m$^3$) | $k_2$ (m$^3$/kmol.s) |
|--------------|----------------|-----------------------------|----------------------|
| MEA          | 298            | 1.60-4.80                   | 7500$^{24}$          |
| MEA          | 298            | 0.25-1.90                   | 7140$^{25}$          |
| DEA          | 298            | 0.25-1.92                   | 1340$^{26}$          |
| DEA          | 298            | 0-0.09                      | 1400$^{27}$          |
| DIPA         | 298            | 0.33-2.16                   | 467$^{28}$           |
| DIPA         | 293-298        | 0.23-3.96                   | 443$^{29}$           |
| MDEA         | 298            | 0.50-1.63                   | 4.8$^{28}$           |
| MDEA         | 298            | 0-1.14                      | 7.8$^{30}$           |
| AMP          | 288-318        | 0.25-3.50                   | 681$^{31}$           |
| TEA          | 298            | 2.488                       | 2.77$^{32}$          |
| EMEA         | 298            | 0.028-0.082                 | 8000$^{33}$          |
| PZ           | 303            | 0.23                        | 1365.74$^{34}$       |
| MEA-TEA-PZ   | 298            | 6                           | 8050                 |

**Table 1:** Literature data on the rate constants ($k_2$) for the reaction of CO$_2$ and alkanolamine.
6. Conclusions

In this work, the kinetics of the CO₂ reaction with aqueous alkanolamine blends was explored. The kinetics of the CO₂ reaction with this amine blend was investigated in a packed bed at 298 K and amine concentration (4-6 M). Various reaction mechanisms that described the reaction paths, are explained in detail, for instance zwitterion, termolecular and base catalyzed CO₂ hydration, which. The zwitterion mechanism generally describes the CO₂ reaction with primary, secondary, and sterically hindered amines, while the reaction of tertiary amines with CO₂ governed by the base catalyzed CO₂ hydration mechanism. New kinetic data of amine-based solvents are discussed. The result revealed that the reaction kinetic with the Amine blend of MEA, TEA, and PZ can be described by two mechanisms zwitterion, termolecular. The studied revealed that the reaction is appropriate to the fast pseudo-first order reaction. The observed reaction rate constant at 298 K was estimated. The reaction order with an amine blend was found to be second order. Finally, it’s concluded that the Amine blend of (MEA, TEA, PZ) can be considered as a promising solvent to remove CO₂. In conclusion, the experimental results, shown that the application of an amine blend of (MEA, TEA, PZ) is a promising solvent; nevertheless, additional study in the direction of the examination of beneficial properties of this solvent in regeneration, for example requirement of the regeneration energy and regeneration efficiency, is essential.

References

[1] Wiheeb A D, Shamsudin I K., Ahmad M A, Murat M N, Kim J and Othman M R 2013 Sep Rev Chem Eng. 29 449–470
[2] Ye Q, Lu H, Du Y, Zhang S, Wang X and Lu Y 2017 Energy Procedia. 114 813-822.
[3] Wiheeb, A D, Shakir S W and Othman M R 2018 IOP Conference Series. 454 012107.
[4] Nwaoha C, Saiwan C, Tontiwachwuthikul P, Supap T, Rongwong W, Idem R, Al-Marri M J and Benamor A 2016 Int J Greenh Gas Con. 53 292-304.
[5] Camacho F, Sanchez S, Pacheco R, Sanchez A and La Rubia M D 2005 Ind Eng Chem Res. 44 7451–7457.
[6] Mahajani VV and Joshi 1988 J Gas Sep Purif. 2 50–64.
[7] Olajire A A 2010 Energy. 35 2610-2628.
[8] Tontiwachwuthikul, P., Melsen, A. and Lim, C.J., 1991 J Chem Eng Data. 36 130-133.
[9] Sartori G and Savage D W 1983 Ind Eng Chem Fundam. 22 239-249.
[10] Bishnoi S and Rochelle GT 2000 Chem Eng Sci. 55 5531-5543.
[11] Samanta A and Bandyopadhyay S S 2007 Chem Eng Sci. 62 7312-7319.
[12] Chakravarty T, Phukan U. K., and Weiland R H, Chem. 1985 Eng. Prog. 81 32-36.
[13] Danckwerts P V 1979 Chem Eng Sci. 34 443–446.
[14] Da Silva E F, Svendsen H F, Iniito Ab 2004 Ind Eng Chem Res. 43 3413-3418.
[15] Versteeg G F and van Swaaij W P M 1988 Chem Eng Sci. 43 573-585.
[16] Doraiswamy L K and Sharma M M 1984 Wiley and Sons John New York.
[17] Danckwerts P V 1970 McGraw-Hill, New York.
[18] Wiheeb A D, Shakir S W, Ahmed M A and Rajab E A 2018 1st Int Sci Con of Eng Sci - 3rd Sci Conf of Eng Sci (ISCES) diyala. 152-156.
[19] Sutardja S, Sánchez E P and Silva R S 2016 Nexo Revista Científica. 29 83-104.
[20] Sutar P N, Jha A, Vaidya P D and Kenig E Y 2012 Chem Eng J. 207 718-724.
[21] Hikita H, Asai S, Ishikawa H and Honda M 1977 Chem Eng J. 13 7-12.
[22] Versteeg G F, van Dijck L A J and van Swaaij W P M 1996 Chem. Eng. Commun. 144 113-158.
[23] Clarke J K A 1964 *Ind. Eng Chem Fundam.* 3 239.
[24] Sada E, Kumazawa H, Butt M A and Hayashi D *Chem.* 1976 *Eng. Sci.* 31 839.
[25] Sada E, Kumazawa, H, Butt M A 1976 *Can. J Chem Eng.* 54 421.
[26] Donaldson T L, and Nguyen Y N 1980 *Ind Eng Chem Fundam* 19 260.
[27] Blauwhoff P M M, Versteeg G F and van Swaaij W P M 1984 *Chem Eng Sci.* 39 207.
[28] Versteeg G F and van Swaaij W P M 1988 *Chem Eng Sci.* 43 573.
[29] Benitez-Garcia J, Ruiz-Ibanez G, Al-Ghawas H A and Sandall O C 1991 *Chem Eng Sci.* 46 2927.
[30] Xu S, Wang Y W, Otto F and Mather A E 1996 *Chem Eng Sci.* 51 841.
[31] Rangwala H A, Morrell B R, Mather A E and Otto F D 1992 *Can J of Chem Eng.* 70 482-490.
[32] Li J, Henni A and Tontiwachwuthikul P 2007 *Ind Eng Chem* 46 4426.
[33] Sun W C, Yong C B and Li M H 2005 *Chem Eng Sci.* 60 503-516.
[34] Aroonwilas A and Veawab A 2004 *Ind Eng Chem Res.* 43 2228-2237.