INTERNATIONAL JOURNAL OF
ENERGY RESEARCH WILEY

Chemical kinetics of carbon dioxide in the blends of different amino acid salts and methyldiethanolamine

Nafis Mahmud[1] | Abdelbaki Benamor[1] | Mustafa S. Nasser[1] |
Muneer M. Ba-Abbad[1] | Muftah H. El-Naas[1] | Hazim Qiblawey[2]

[1]Gas Processing Centre, College of Engineering, Qatar University, Doha, Qatar

[2]Department of Chemical Engineering, College of Engineering, Qatar University, Doha, Qatar

Correspondence
Nafis Mahmud, Gas Processing Centre, College of Engineering, Qatar University, 2713 Doha, Qatar.
Email: n.mahmud@qu.edu.qa

Funding information
Qatar National Research Fund, Grant/Award Number: NPRP-7 - 1154 - 2 - 433

Summary

In the present study, the reaction kinetics of carbon dioxide (CO_2) with two blends of N-methyldiethanolamine; potassium salts of taurine and potassium salts of glycine were investigated. The experiments were performed using a stopped flow apparatus over a range of temperature varying from 293 to 313 K. The concentration of solution was varied from 0.2 to 0.8M in different proportions of potassium salts of taurine and glycine. For both cases, the overall reaction rate constant (k_{ov}) increased with increased temperature and amino acid salts proportions in the blends. Results also indicated that addition amino acid salts (AAS) could improve the overall reaction rate of methyldiethanolamine (MDEA) with CO_2 by more than 100 times. The kinetics data were interpreted using the widely accepted mechanisms namely; zwitterion and termolecular mechanisms. An average absolute deviation of 8.8% was observed for both mechanisms applied to MDEA-KTau blend, while an AAD% of 7.4 and 7.2 were observed for the case of MDEA-KGly system when applying the zwitterion and termolecular mechanisms, respectively. The results showed that blends of MDEA and potassium salts amino acids react faster with CO_2 compared to conventional amine systems. Hence, the use of both potassium salts of taurine and glycine as rate promotors can significantly enhance the reactivity of MDEA toward CO_2.

KEYWORDS

blends, carbon dioxide, methyldiethanolamine, potassium glycinate, potassium taurinate, reaction kinetics

1 | INTRODUCTION

Carbon dioxide (CO_2) released mainly from anthropogenic sources is considered to be one of the major contributors to climate change and global warming. CO_2 absorption using reactive amine-based solvents is the most commonly deployed technology for capture industrial CO_2.[1,2] However, these solvents are associated with a number of drawbacks such as, high cost of regeneration due to high energy requirement, solvent losses due to evaporation, low CO_2 loading, formation of degradation products, and slower reaction kinetics.[3,4] Tertiary amines like methyldiethanolamine (MDEA) are known to have high loading capacity, less vulnerable to degradation and require lower regeneration energy but their reaction rate is quite slow.[5] To enhance their kinetics properties, these tertiary amines are usually blended with small amounts of fast reacting primary, secondary amines or piperazine

to improve their CO_2 absorption rate while maintaining their characteristics.[6] Thus, developing new blends of MDEA with fast reacting chemicals to overcome the drawbacks of the conventional amines is a good option.

Aqueous amino acid salts or amino acid salts (AAS) have recently emerged as potential alternative solvent to the conventional amines for CO_2 capture.[7-10] The structure of AAS contains an amino group (NH_2) similar to alkanolamines, allowing them to be used as individual solvents or as rate promoters. Carboxylic acid group (COOH) is also present with a counter ion (Na^+ or K^+) within their structure. The AAS are known to be environment friendly as they are less volatile compared to the amines; and less susceptible to oxidative degradation, making them more suitable for CO_2 absorption.[11-13] To design a CO_2 absorption plant that can accommodate the CO_2-AAS systems, knowledge of their reaction kinetics is imperative. A number of researchers have studied the reactions kinetics of CO_2 with different AAS and found their kinetics to be comparable to that of the conventional amines.[14-19]

Potassium salts of Glycine (KGly), a typical amino acid salt has generated significant interest as an alternative solvent for CO_2 capture. Structurally, it consists of a potassium ion connected to an amino carboxylic group (Figure 1B). The reaction kinetics of potassium salts of glycine with CO_2 was investigated by Kumar et al.[12] They found out that the reactivity of potassium salts of glycine toward CO_2 was higher than that of potassium salts of taurine, due to their higher pKa values compared to latter. The reaction of KGly was further investigated by Portugal et al[20] over concentrations of 0.1M to 3M and temperatures from 293 to 313 K. They reported that the reaction rate for KGly was higher than that of MEA. Potassium salts of taurine (KTau) are other potential amino acid salts for CO_2 absorption. Their structure is a typical to the common AAS; however, instead of having carboxylic group, a sulfonic group is present in their structure as shown in Figure 1C. This sulfonic group was found to add some useful attributes to their characteristics compared to other amino acid salts by making them less susceptible to degradation and more resistive to corrosion.[13] The reaction kinetics of potassium salts of Taurine was studied by Kumar et al[11] using a stirred cell reactor at different concentrations (0.1-4.0M) and at a temperature range of 285 to 305 K. They reported that the reaction showed an order of 1.0 to 1.5 with respect to Taurine, and the order increased with increasing temperatures. They observed that this reaction was faster than the reaction CO_2 with MEA. Contrary to their findings, Sodiq et al[16] found the CO_2-KTau reaction to be slower than the CO_2-MEA reaction using stopped-flow apparatus. Moioli et al[21] carried out a techno-economic evaluation for the postcombustion CO_2 removal by potassium taurate using Aspen plus and concluded a significant decrease in the capital and operational costs of the process compared to that of MEA.

From these works, it is perceived that, salts of amino acids are highly reactive with CO_2 and can possibly improve CO_2 absorption if used as solvents or as rate promoters with conventional amines. With this growing interest among scientific community to shed more lights on different CO_2-AAS systems, some drawbacks associated with use of amino acid salts for CO_2 capture were reported as well. The use of AAS at high concentrations, causes a formation of a precipitate which was also observed at high CO_2 loading. The formation of precipitate will not only cause a reduction in mass transfer rate; but it may eventually increase the chances of causing damage to the process equipment.[12] Therefore, these drawbacks may prevent their use as individual solvents for CO_2 absorption. However, their fast reacting property is indicative of the possibility of AAS being used as rate promoters to potentially improve the reaction rate of CO_2 with slow reacting tertiary amines.

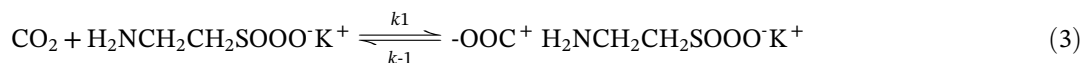The objective of this study is to present completely new experimental data on the reaction kinetics of CO_2 in aqueous solutions of two MDEA-AAS blends; one with

(A) Methyldiethanolamine   (B) Potassium Salts of Glycine   (C) Potassium Salts of Taurine
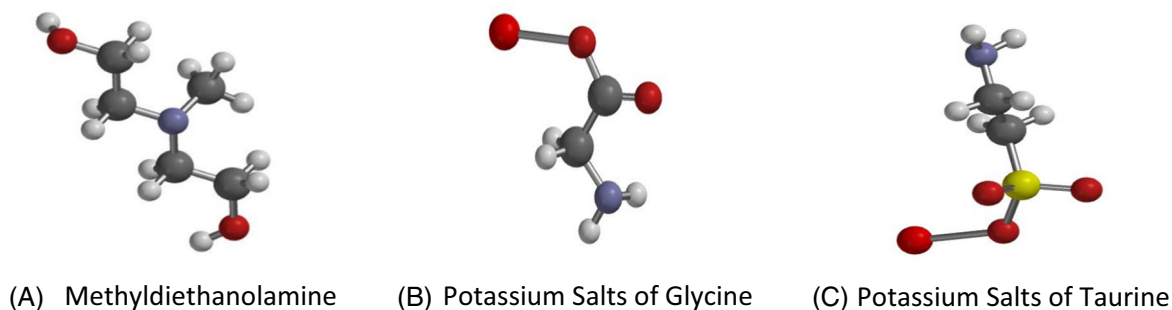
FIGURE 1   Molecular Structure of methyldiethanolamine and potassium salt of Glycine and Taurine [Colour figure can be viewed at wileyonlinelibrary.com]

potassium salts of Glycine and the other with potassium salts of Taurine. The experiments were conducted using stopped flow technique and the total concentration was varied from 0.2 to 0.8M at different amino acid salts proportions in the blend and a temperature range of 293 to 313 K. Zwitterion and termolecular mechanisms were used

synonymous to that of amines, it is expected that their reaction with CO_2 will also follow a similar pathway.[12] Hence, the CO_2-AAS reaction will also form an intermediate zwitterion (Equation 3) followed by exchange of protons (Equation 4) as shown in the case of CO_2-KTau reactions.

$$CO_2 + H_2NCH_2CH_2SOOO^-K^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^-OOC^+ H_2NCH_2CH_2SOOO^-K^+ \qquad (3)$$

$$^-OOC^+ H_2NCH_2CH_2SOOO^-K^+ + B \overset{K_b}{\rightleftharpoons} {}^-OOC^+ HNCH_2CH_2SOOO^-K^+ + BH^+ \qquad (4)$$

to analyze the obtained data and the generated rate constants along with their activation energies were evaluated. Overall, this work aims to provide new understandings of the fundamental kinetics and mechanisms of MDEA blended with potassium salts of Glycine and MDEA blended with potassium salts of Taurine, which can lead to development of new and improved blended solvent systems that can be utilized in CO_2 absorption processes.

2 | REACTION MECHANISM

2.1 | Zwitterion mechanism

The reaction of CO_2 with mixtures of MDEA and potassium salts of amino acids can be taken as the sum of CO_2-MDEA and CO_2-AAS reactions. The reaction of CO_2 with MDEA can be written as follows[22]:

$$CO_2 + H_3CN(C_2H_4OH)_2 + H_2O$$
$$\overset{k_{MDEA}}{\rightleftharpoons} H_3CNH^+ (C_2H_4OH)_2 + HCO_3- \qquad (1)$$
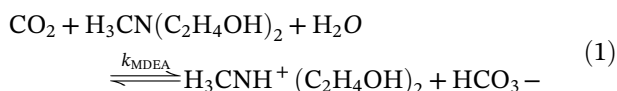
The rate of this reaction assuming the reaction to be under pseudo first-order condition is given as;

$$r_{CO_2-MDEA} = -k_{MDEA}[CO_2][MDEA] \qquad (2)$$

Caplow et al[23] proposed that CO_2 reacts with primary and/or secondary amines via the zwitterion mechanism. According to this mechanism, CO_2 molecules will form a zwitterion by binding with the NH_2 group commonly present within the structure of the primary or secondary amines. This zwitterion will subsequently get deprotonated by water and with other bases present within the solution to form Carbamates. Since the amino acids are structurally

It is to be noted that, CO_2-KGly reaction is also expected to proceed via the same reaction pathway as the CO_2-KTau reactions. Applying steady-state principle to the intermediate zwitterion, the rate of the reaction can be expressed as follows;

$$r_{CO_2-AAS} = -k_{app}[CO_2] = -\frac{k_2[CO_2][AAS]}{1 + (k_{-1}/(\sum k_{b_i}[B_i]))} \qquad (5)$$

Here, the terms within '[ ]' indicates the concentrations in mole/l; while, the term 'B' stands for all the bases present within the solution. The term 'k_{bi}' represents the zwitterion deprotonation rate by the bases in solution, while the overall contribution of the bases is accounted by the term '$k_i[B_i]$'. The contribution gives rise to two main asymptotic cases, which further simplifies the Equation (5). When the formation of zwitterion is the rate limiting step, then $\frac{k_{-1}}{\sum k_{b_i}[B_i]} \ll 1$, then Equation (5) reduces to a simple second-order reaction as follows[24]:

$$r_{CO_2-AAS} = -k_2[CO_2][AAS] \qquad (6)$$

However, if the proton removal from the zwitterion is the rate-limiting step (Equation 4), then $\frac{k_{-1}}{\sum k_{b_i}[B_i]} \gg 1$, thus Equation (5) becomes:

$$r_{CO_2-AAS} = -\frac{k_2[CO_2][AAS](\sum k_{b_i}[B_i])}{k_{-1}} \qquad (7)$$

This complex rate equation can explain reaction of any order depending on bases contributing in proton exchange with the zwitterion. This equation can also explain the shift in reaction order with the variations in amine concentrations. This phenomenon is commonly

observed in the kinetics of CO_2 with primary and secondary amines.[25,26]

In addition to these reactions, it is also necessary to consider the formation of bicarbonates in aqueous systems,

$$CO_2 + OH^- \overset{k_{OH}}{\rightarrow} HCO_3\text{-} \tag{8}$$
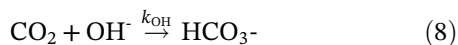
Its rate of reaction was given as follows[27]:

$$r_{CO_2-OH^-} = -k_{OH}[CO_2][OH^-] \tag{9}$$

From Equations 2, 5, and 9, the overall reaction rate of CO_2 with mixtures of MDEA and AAS in water can be expressed as:

$$r_{CO_2} = r_{CO_2-AAS} + r_{CO_2-MDEA} + r_{CO_2-OH^-} \tag{10}$$

Which can be written as:

$$-r_{CO_2} = k_{ov}[CO_2] = \left(\frac{k_2[AAS]}{1 + \frac{k}{\Sigma k_{b_i}[B_i]}} + k_{MDEA}[MDEA] + k_{OH}[OH^-] \right)[CO_2] \tag{11}$$

$$\text{With,} \ k_{ov} = k_{app} + k_{MDEA}[MDEA] + k_{OH}[OH^-] \tag{12}$$

This equation can be rewritten to find the apparent rate constant, 'k_{app}', as follows;

$$\text{With,} \ k_{app} = k_{ov} - k_{MDEA}[MDEA] - k_{OH}[OH^-] \tag{13}$$

The works of Pinsent et al[27] and Benamor et al[28] were used to obtain the values of k_{OH} and k_{MDEA}, respectively. They were determined to be as follows:

$$k_{OH} = 4.33 \times 10^{10} \exp^{-\frac{66666}{T}} \tag{14}$$

$$k_{MDEA} = 2.56 \times 10^{09} \exp^{-\frac{5922}{T}} \tag{15}$$

In this case,

$$k_{app} = \frac{k_2[AAS]}{1 + \left(\frac{k}{k_{AAS}[AAS] + k_{OH^-}[OH^-] + k_{MDEA}[MDEA] + k_{H_2O}[H_2O]} \right)} \tag{16}$$

Now by defining new constants as $k_\alpha = \frac{k_2 k_{MDEA}}{k_{-1}}$, $k_{\beta,AAS} = \frac{k_2 k_{AAS}}{k_{-1}}$, $k_{hyd} = \frac{k_2 k_{OH^-}}{k_{-1}}$ and $k_w = \frac{k_2 k_{H_2O}}{k_{-1}}$, Equation (16) then can be rewritten as:

$$k_{app} = \frac{[AAS]}{\frac{1}{k_2} + \frac{1}{k_\alpha[MDEA] + k_{\beta,AAS}[AAS] + k_{hyd}[OH^-] + k_w[H_2O]}} \tag{17}$$

2.2 | Termolecular mechanism

In addition to zwitterion mechanism, an alternative single-step termolecular mechanism was proposed by Crooks and Donnellan[29] to explain the CO_2-amine reactions. This mechanism can be applied to explain the CO_2-AAS reactions. Based on the termolecular mechanism, the CO_2-KTau reactions are expected to proceed as shown in Equation (18).
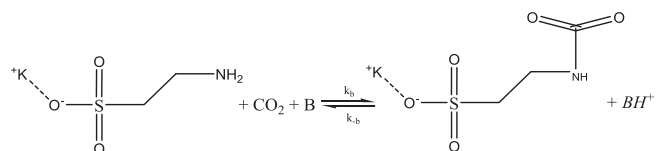
It is to be noted that, the CO_2-KGly reactions are also expected to follow a similar pathway as shown in Equation (18). Silva and Svendsen[30] investigated this mechanism and proposed that the reaction proceeds through the formation of a bond between CO_2 molecule and the amine. The hydrogen bonds of the solvent molecules aids in stabilizing the CO_2-amine bond eventually leading toward the formation of loosely bounded complex. They further claimed that the carbamate forms only if the amine molecule is in close proximity of the zwitterion. Based on termolecular mechanism, the reaction of CO_2 with amine is second order with respect to amine and accordingly, Equation (5) becomes,

$$\begin{aligned} -r_{CO_2-AAS} &= k_{app}[co_2] = [CO_2][AAS]\left\{\sum k_{b_i}[B_i]\right\} \\ &= [CO_2][AAS]\{k_\alpha[MDEA] + k_{\beta,AAS}[AAS] \\ &\quad + k_w[H_2O] + k_{hyd}[OH^-]\} \end{aligned} \tag{19}$$

It is to be noted that the resulting equation for termolecular mechanism is similar to the second rate limiting case as observed for the zwitterion kinetics model (Equation 7) when the proton removal from the zwitterion acts as the rate limiting step.

3 | EXPERIMENTAL MATERIALS AND PROCEDURE

3.1 | Materials

Reagent grade MDEA and Taurine both with a mass purity of 99%, potassium hydroxide (KOH) of purity 85% and standard HCl acid solutions were all obtained
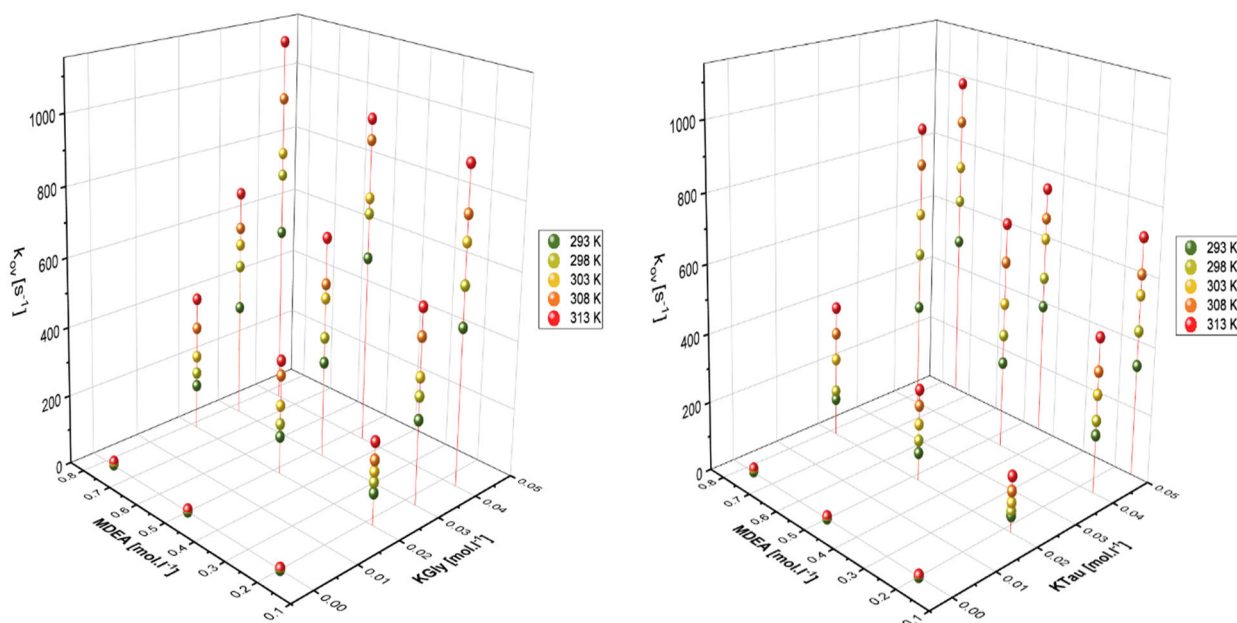
FIGURE 2 Overall reaction constants for MDEA-KGly-CO$_2$ (left) and MDEA-KTau-CO$_2$ (right) reactions at different temperatures [Colour figure can be viewed at wileyonlinelibrary.com]

from Sigma-Aldrich. Glycine of mass purity 99% was obtained from Riedel de Haen. All chemicals were used without further purification. Reagent grade CO$_2$ (99.99 %) was bubbled into deionized water to prepare CO$_2$ solutions. Deionized water was used throughout the experiment as solvent.

3.2 | Procedure

The homogeneous reaction rate between MDEA-AAS solutions and the dissolved CO$_2$ in water was measured using stopped-flow apparatus (Hi-Tech Scientific, Ltd, UK, Model SF-61DX2) with a dead time of 1 ms. The stopped flow apparatus mainly consists of a sample-handling unit, a conductivity-detecting cell, an A/D converter, a microprocessor and a PC equipped with 'Kinetasyst' software. An external water bath (Lauda model Alpha RA8) was used to control the temperature of the flow circuits. Freshly CO$_2$ saturated water solution was prepared for each experiment by bubbling CO$_2$ in deionized water. The concentration of CO$_2$ in deionized water was determined via gas chromatography (GC-6890 from Agilent) according to Shell method-SMS 2239-04. The CO$_2$ solution was diluted afterward to keep the amine solution concentration at least 15 times higher than that of CO$_2$ concentration in water. This is to ensure that pseudo-first-order condition with respect to CO$_2$ prevails.[31,32] Potassium salts of amino acids were prepared from an equimolar neutralization reaction of

potassium hydroxide and the respective amino acid in a volumetric flask at 298 K. The mixed solutions of MDEA-AAS were prepared by mixing equal volumes of MDEA and amino acid salt solution. The concentrations of all prepared solutions were checked by titration with standard hydrochloric acid solution. In two separate syringes, the solution containing MDEA-AAS blend and CO$_2$-water were loaded. Equal volumes of both aqueous solutions were pumped into the conductivity cell. The total concentrations of MDEA-AAS solutions were varied from 0.2 to 0.8 molar. For each experimental run, different concentrations of MDEA-AAS solutions were mixed with CO$_2$ at different temperatures within the stopped-flow unit. Depending on the working temperature, the experimental run time was varied between 0.5 and 5 s. Then the reaction was observed by measuring the change of conductivity, 'Y', against time as described by Knipe et al.[33] A typical experimental run is provided in the supplementary document (Figure S1). The acquired curve was then fitted according to an exponential equation resembling a first-order kinetic equation:

$$Y = -\mathrm{A}.\exp(-k_{ov}.t) + Y_{\infty} \qquad (20)$$

The term 'k_{ov}' denotes the overall pseudo first-order reaction rate constant. The average value of three experimental values was taken into consideration and the error in reproducibility was less than 3 % under all experimental conditions.

TABLE 1 Rate constant for the reaction of MDEA-KTau-CO_2 system based on Zwitterion mechanism

KTau mol dm^{-3}	MDEA mol dm^{-3}	OH × 10^4 mol dm^{-3}	H$_2$O mol dm^{-3}	k_{app} s^{-1}	$k_{app-pred}$ s^{-1}	k_2 × 10^{-13} m^3 kmol^1 s	k_α × 10^{-4} m^6/kmol^2 s	$k_{\beta,Ktau}$ × 10^{-3} m^6/ kmol^2 s	k_{hyd} × 10^{-1} m^6/kmol^2 s
293 K									
0.02	0.18	1.16	54.3	46.7	55.7	4.1	10.0	4.4	8.5
0.02	0.48	1.89	52.4	79.5	82.1				
0.02	0.78	2.41	50.4	105.3	108.6				
0.04	0.16	1.54	54.2	170.2	187.7				
0.04	0.46	2.62	52.3	253.6	240.5				
0.04	0.76	3.36	50.4	306.9	293.4				
0.05	0.15	1.67	54.2	326.4	282.3		AAD%	9.1	
0.05	0.45	2.89	52.3	384.7	348.3				
0.05	0.75	3.73	50.4	479.8	414.4				
298 K									
0.02	0.18	1.24	54.3	59.4	72.3	5.3	12.6	6.1	10.7
0.02	0.48	2.02	52.3	115.8	109.1				
0.02	0.78	2.58	50.4	129.1	145.9				
0.04	0.16	1.65	54.2	213.2	240.2				
0.04	0.46	2.80	52.3	339.8	313.8				
0.04	0.76	3.60	50.4	477.8	387.4				
0.05	0.15	1.79	54.2	428.6	360.0		AAD%	12.4	
0.05	0.45	3.10	52.3	473.6	452.0				
0.05	0.75	4.00	50.4	611.9	544.0				
303 K									
0.02	0.18	1.41	54.3	82.9	95.9	7.4	14.7	10.3	13.7
0.02	0.48	2.30	52.3	161.0	157.4				
0.02	0.78	2.93	50.4	223.1	218.9				
0.04	0.16	1.88	54.2	289.5	301.3				
0.04	0.46	3.18	52.3	435.1	424.5				
0.04	0.76	4.09	50.4	603.0	547.6				
0.05	0.15	2.03	54.2	533.3	445.5		AAD%	6.4	
0.05	0.45	3.52	52.3	592.9	599.3				
0.05	0.75	4.54	50.4	718.5	753.0				
308 K									
0.02	0.18	1.41	54.3	115.7	118.4	9.8	16.6	14.4	16.0
0.02	0.48	2.30	52.3	216.5	204.8				
0.02	0.78	2.93	50.4	302.4	291.2				
0.04	0.16	1.88	54.2	356.3	358.4				
0.04	0.46	3.18	52.3	559.1	531.2				
0.04	0.76	4.09	50.4	756.0	704.0				
0.05	0.15	2.03	54.2	593.7	524.0		AAD%	6.7	
0.05	0.45	3.52	52.3	654.6	741.0				
0.05	0.75	4.54	50.4	859.7	956.0				

TABLE 1 (Continued)

KTau mol dm^{-3}	MDEA mol dm^{-3}	OH × 10^4 mol dm^{-3}	H$_2$O mol dm^{-3}	k_{app} s^{-1}	$k_{app-pred}$ s^{-1}	k_2 × 10^{-13} m^3 kmol^1 s	k_α × 10^{-4} m^6/kmol^2 s	$k_{\beta,Ktau}$ × 10^{-3} m^6/kmol^2 s	k_{hyd} × 10^{-1} m^6/kmol^2 s
313 K									
0.02	0.18	1.49	54.2	157.6	142.4	12.7	20.5	16.8	18.0
0.02	0.48	2.44	52.3	261.2	243.4				
0.02	0.78	3.11	50.4	378.1	344.4				
0.04	0.16	1.99	54.2	455.0	435.1				
0.04	0.46	3.38	52.3	672.8	637.1				
0.04	0.76	4.34	50.4	864.9	839.0				
0.05	0.15	2.16	54.2	700.0	637.7		AAD%	9.3	
0.05	0.45	3.73	52.3	743.3	890.2				
0.05	0.75	4.82	50.4	977.8	1148.0				
Overall AAD%								8.8	

TABLE 2 Equilibrium constants of water and MDEA

Parameter	a	b	C	d	Temperature range	References
k_w	13445.9	22.4773	0	140.932	0°C-225°C	Edwards et al[36]
K_p (MDEA)	−8483.95	−13.8328	0	87.397	5°C-125°C	Littel et al[37]

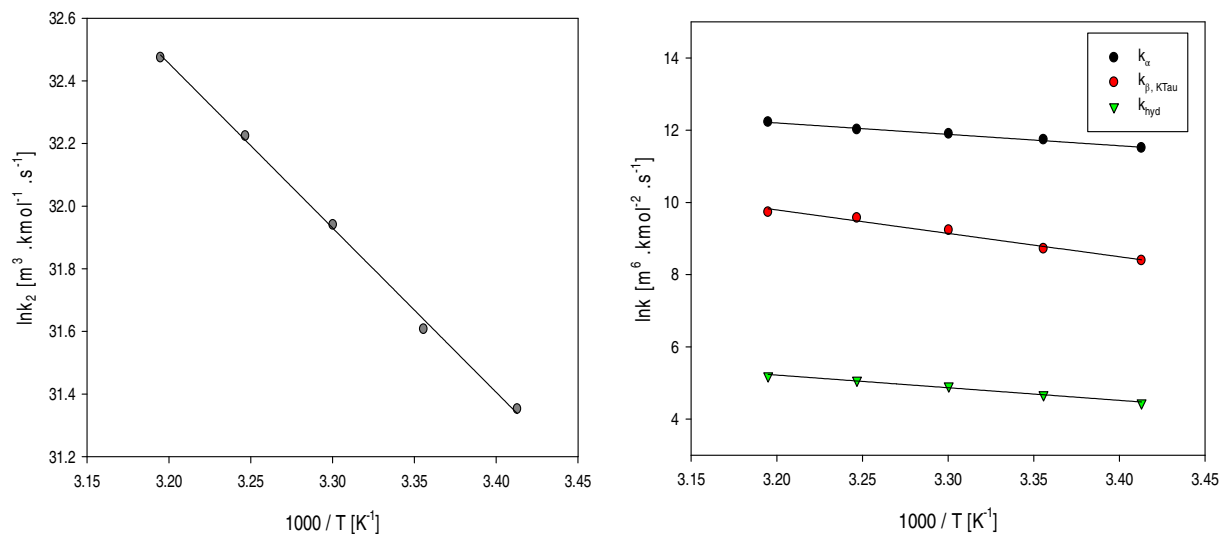Abbreviation: MDEA, methyldiethanolamine.

FIGURE 3 Arrhenius plots of rate constants of individual rate constants for CO$_2$-MDEA-Ktau reaction fitted according zwitterion mechanism [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Rate constants for MDEA-KTau-CO$_2$ over 293 to 313 K

Rate	$\ln k_0$	E_a/R (K)	E_a (kJ mol^{-1})	Equation
k_2 (m^3 kmole^{-1} s^{-1})	49.27	5252.9	43.67	$k_2 = 2.49 \times 10^{21} e^{-\frac{5252.9}{T}}$
k_α (m^6 kmole^{-2} s^{-1})	22.30	3154.6	26.22	$k_\alpha = 4.89 \times 10^9 e^{-\frac{3154.6}{T}}$
$k_{\beta,KTau}$ (m^6.kmole^{-2} s^{-1})	30.59	6499.3	54.04	$k_{\beta,KTau} = 1.93 \times 10^{13} e^{-\frac{6499.3}{T}}$
k_{hyd} (m^6 kmole^{-2} s^{-1})	16.42	3500.7	29.10	$k_{hyd} = 1.35 \times 10^{07} e^{-\frac{3500.7}{T}}$
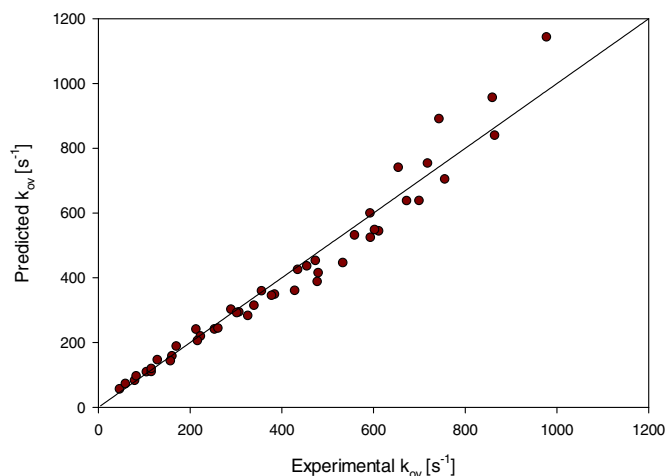
FIGURE 4 Parity plot of CO_2-MDEA-KTau system-based zwitterion mechanism [Colour figure can be viewed at wileyonlinelibrary.com]

4 | RESULTS AND DISCUSSION

4.1 | Reaction of CO_2 with MDEA-KTau and MDEA-KGly blends

The kinetics of CO_2 with MDEA-AAS blends were studied using stopped flow apparatus at different temperatures within 293 to 313 K with an increment of 5 K. The concentrations of amino acids were varied from 0.02 to 0.04M for potassium glycinate, and from 0.02 to 0.05M for potassium taurate; while the MDEA concentration were varied from 0.15 to 0.78M in order to maintain a total blend concentration of 0.2, 0.5, and 0.8M. The overall rate constant (k_{ov}) of MDEA and CO_2 reactions without the AAS were also determined for concentrations equal to the maximum concentrations of blended solutions to elucidate the effect of adding AAS promoters on overall rate constants. The obtained pseudo-first-order rate constants (k_{ov}) were plotted against the different blend concentrations for the two blends as shown in Figure 2. In both cases, an increase in the overall rate constants, 'k_{ov}' was observed with the increase in potassium taurate and potassium glycinate concentrations. It is evident from Figure 2, that the rise in temperature caused an increase in the pseudo-first-order rate constants (k_{ov}) for the two blends. Using the power law kinetics, the average reaction order was found to be around 1.56 and 1.93 with respect to the KTau and KGly concentrations, respectively. Contrary to the observed reaction order, Kumar et al[12] reported the reaction order for potassium salts to be in the range of 1 to 1.5 at 285 to 305 K. This high reaction order observed for both KTau and KGly in blended solutions indicates the effect of multiple bases in the deprotonation of the zwitterion.[34] Hence, the observed experimental pseudo-first-order rate constants were then

analyzed using both the zwitterion and termolecular mechanisms.

4.2 | Zwitterion mechanism

The obtained 'k_{ov}' values for the reaction of MDEA-KTau-CO_2 systems at different concentrations and temperatures were used to obtain 'k_{app}' values according to Equation (13), which was then used in Equation (15) to obtain the rate expressions for all reactions involved using excel solver through nonlinear regression analysis. The generated rate constants for MDEA-KTau-CO_2 system were further used to predict the overall rate constant ($k_{app-pred}$). The regressed and the predicted overall rate constants for MDEA-KTAU-CO_2 are summarized in Table 1. To account for the concentration of the hydroxyl ion, the expression reported by Astaria et al[35] was used.

$$[OH^-] = \sqrt{\frac{K_w}{K_p}[AA]} \qquad (21)$$

Here, the term 'K_w' represents the dissociation constants of water; while, the dissociation constants of amine is represented by the term 'K_p'. Both of these terms are functions of temperature and were expressed by the following equation:

$$\ln K = \frac{a}{T} + b \ln T + cT + d \qquad (22)$$

The value of the constant a, b, c, and d are given in the Table 2.

To generate the Arrhenius equation for the individual blocks of rate constants (k_2, k_α, $k_{\beta,KTau}$, and k_{hyd}) given in Table 1, their natural logarithm were plotted against T^{-1} as shown in Figure 3. The Arrhenius equations were used to calculate the activation energy for each equation. Based on Arrhenius plots of CO_2-MDEA-Ktau system, k_α showed the most sensitivity with the increase in temperature followed by k_{hyd}, k_2, and k_β. This, means that the catalytic contribution of MDEA toward the formation of carbamate has a significant effect on the k_{ov}. Initially, the influence of water molecule was taken into account to perform the regression analysis. But its influence on k_{ov} was found to be negligible and hence, it was discarded from the final rate model. The rate expressions along with the activation energies obtained for the MDEA-KTau-CO_2 reaction are shown in Table 3. A parity plot (Figure 4) between the experimental and predicted k_{ov} values was used to verify the validity of the adopted
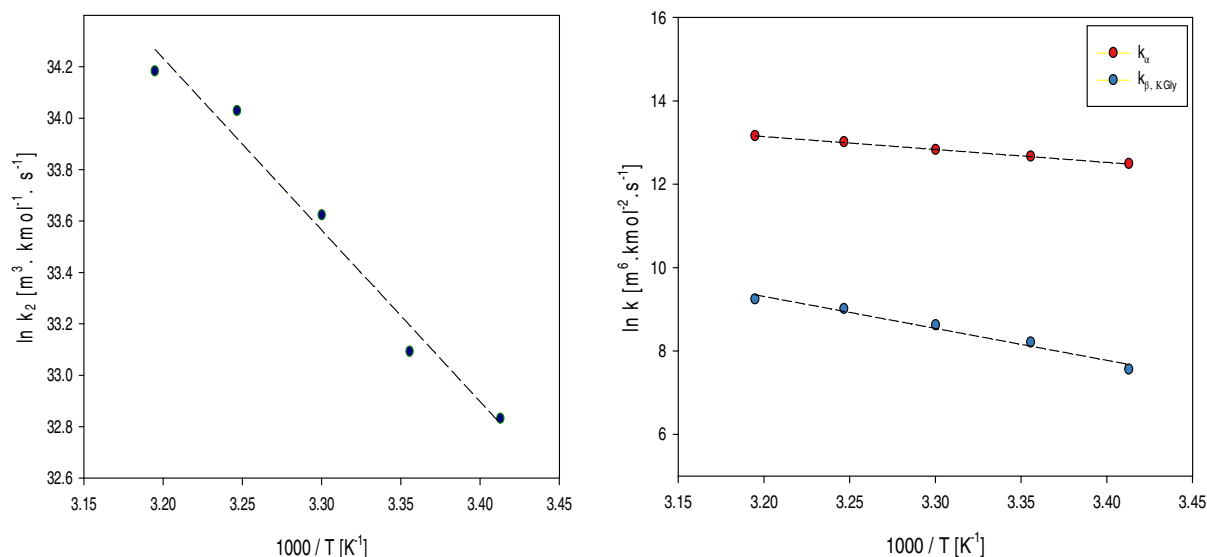
TABLE 4 Rate constant for the reaction of MDEA-KGly-CO_2

KGly mol. dm^{-3}	MDEA mol dm^{-3}	OH $\times 10^4$ mol dm^{-3}	H_2O mol dm^{-3}	k_{app} s^{-1}	$k_{app-pred}$ s^{-1}	$k_2 \times 10^{-14}$ m^3 $kmol^{-1}$ s^{-1}	$k_\alpha \times 10^{-5}$ m^6 $kmol^{-2}$ s^{-1}	$k_{\beta,KGly} \times 10^{-3}$ m^6 $kmol^{-2}$ s^{-1}
293 K								
0.02	0.18	1.16	54.3	92.7	112.8	1.81	2.65	1.91
0.02	0.48	1.89	52.4	109.9	124.3			
0.02	0.78	2.41	50.4	130.5	135.7			
0.03	0.17	1.54	54.2	246.5	247.6			
0.03	0.47	2.62	52.3	282.6	265.3			
0.03	0.77	3.36	50.4	330.5	282.5			
0.04	0.16	1.67	54.2	463.4	436.1		AAD%	10.2
0.04	0.46	2.89	52.3	553.0	459.0			
0.04	0.76	3.73	50.4	528.3	481.9			
298 K								
0.02	0.18	1.24	54.3	123.9	139.5	2.35	3.16	3.66
0.02	0.48	2.02	52.3	147.5	168.0			
0.02	0.78	2.58	50.4	169.7	189.8			
0.03	0.17	1.65	54.2	314.0	312.0			
0.03	0.47	2.80	52.3	356.8	345.7			
0.03	0.77	3.60	50.4	458.2	378.2			
0.04	0.16	1.79	54.2	582.9	542.2		AAD%	10.2
0.04	0.46	3.10	52.3	684.3	585.7			
0.04	0.76	4.00	50.4	706.2	629.1			
303 K								
0.02	0.18	1.41	54.3	153.5	168.5	4.00	3.16	3.66
0.02	0.48	2.30	52.3	202.1	201.5			
0.02	0.78	2.93	50.4	220.7	234.6			
0.03	0.17	1.88	54.2	368.3	360.9			
0.03	0.47	3.18	52.3	473.0	412.1			
0.03	0.77	4.09	50.4	524.7	461.7			
0.04	0.16	2.03	54.2	704.3	629.8		AAD%	6.6
0.04	0.46	3.52	52.3	729.9	695.9			
0.04	0.76	4.54	50.4	772.8	762.1			
308 K								
0.02	0.18	1.41	54.3	186.0	207.8	6.00	4.46	8.15
0.02	0.48	2.30	52.3	291.4	265.9			
0.02	0.78	2.93	50.4	308.6	314.5			
0.03	0.17	1.88	54.2	482.3	455.0			
0.03	0.47	3.18	52.3	514.7	530.3			
0.03	0.77	4.09	50.4	575.8	603.1			
0.04	0.16	2.03	54.2	782.2	785.1		AAD%	4.7
0.04	0.46	3.52	52.3	898.0	882.2			
0.04	0.76	4.54	50.4	938.3	979.4			
313 K								
0.02	0.18	1.49	54.2	237.8	254.7	7.00	5.17	10.25
0.02	0.48	2.44	52.3	334.5	315.8			

TABLE 4 (Continued)

| KGly mol. dm^{-3}	MDEA mol dm^{-3}	OH ×10^4 mol dm^{-3}	H$_2$O mol dm^{-3}	k_{app} s^{-1}	$k_{app\text{-}pred}$ s^{-1}	k_2 ×10^{-14} m^3 kmol^{-1} s^{-1}	k_α ×10^{-5} m^6 kmol^{-2} s^{-1}	$k_{\beta,KGly}$ × 10^{-3} m^6 kmol^{-2} s^{-1}
0.02	0.78	3.11	50.4	397.6	377.0			
0.03	0.17	1.99	54.2	564.4	531.2			
0.03	0.47	3.38	52.3	649.3	625.9			
0.03	0.77	4.34	50.4	681.2	717.6			
0.04	0.16	2.16	54.2	921.5	915.2		AAD%	5.1
0.04	0.46	3.73	52.3	958.8	1037.4			
0.04	0.76	4.82	50.4	1108.4	1159.7			
Overall AAD%					7.4			

FIGURE 5 Arrhenius plots of rate constants for CO$_2$-MDEA-Ktau reaction using zwitterion mechanism [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 5 Rate constants for MDEA-KGly-CO$_2$ over 293 to 313 K

Rate	lnk_0	E_a/R (K)	E_a (kJ mol^{-1})	Equation
k_2 (m^3 kmole^{-1} s^{-1})	55.62	6683.4	55.57	$k_2 = 1.43 \times 10^{24} e^{-\frac{6683.4}{T}}$
k_α (m^6.kmole^{-2} s^{-1})	23.03	3090.5	25.69	$k_\alpha = 1.00 \times 10^{10} e^{-\frac{3090.5}{T}}$
$k_{\beta,kGly}$ (m^6 kmole^{-2} s^{-1})	33.81	7658.8	63.68	$k_{\beta,KGly} = 4.82 \times 10^{14} e^{-\frac{6499.3}{T}}$

zwitterion mechanism to interpret the experimental data shows that the rate model adopted to interpret the experimentally obtained data was very successful with an overall AAD of 8.7% between experimental and predicted values. Similarly, the obtained 'k_{ov}' data for the MDEA-KGly and CO$_2$ reactions from stopped flow experiments were used to obtain 'k_{app}' values using Equation (13) and then fitted to Equation (16) using nonlinear regression Excel solver. The generated rate constants for MDEA-KGly-CO$_2$ reaction system along with the predicted apparent rate constant ($k_{app\text{-}pred}$) are summarized in Table 4.

Furthermore, the individual blocks of rate constants (k_2, $k_{\beta,KGly}$, and k_α) for MDEA-KGly-CO$_2$ system presented in Table 4 were plotted in term of their natural logarithm against T^{-1} to obtain Arrhenius equation as shown in Figure 5, from which the corresponding activation energies were estimated. The results obtained are summarized in the Table 5. Similar to the analysis done for the CO$_2$-MDEA-KTau system, the Arrhenius plots of the obtained rate expressions for CO$_2$-MDEA-KGly showed that k_α (ie, the catalytic contribution of MDEA) showed the largest effect with temperature increase followed by
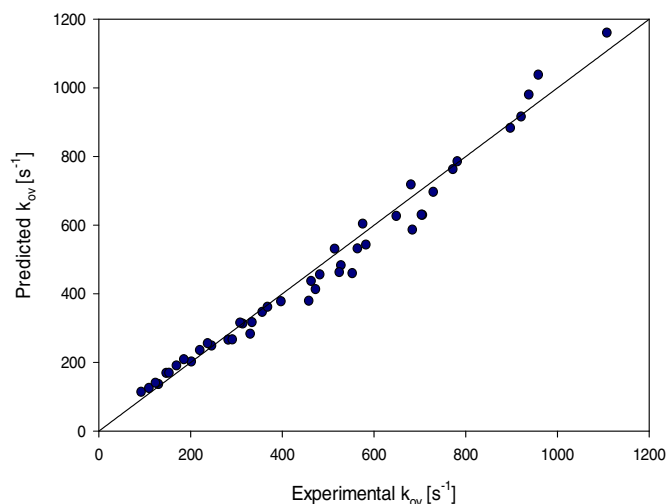
FIGURE 6 Parity plot of rate constants for CO_2-MDEA-KGly system based on zwitterion mechanism [Colour figure can be viewed at wileyonlinelibrary.com]

k_2 and $k_{\beta,KGly}$. This behavior was similar to that observed in the work of Gou et al[38] for the case of CO_2-Gly^- system, where they concluded that in the presence of an additional base a significant increase in the 'k_{ov}' is obtained. The influence of all the bases present was taken into consideration in regression analysis. However, based on sensitivity analysis, the influence of both the water molecule and hydroxyl ion were discarded from the final rate model. The validity of adopted zwitterion mechanism was then verified using a parity plot between the experimental and predicted k_{ov} values. Figure 6 clearly shows that the rate model chosen to interpret the experimental data along with associated blocks of rate was very successful in representing the experimental results with an overall AAD of 7.4%.

4.3 | Termolecular mechanism

A further investigation of the acquired kinetics data for CO_2-MDEA-KTau data were done using termolecular mechanism by regressing obtained k_{app} data to Equation (20) using excel solver. The predicted $k_{app-pred}$ along with the generated rate constants for the termolecular mechanism are shown in Table 6. The obtained results showed remarkable similarities with the ones obtained using the zwitterion mechanism. The contribution of the k_α was the most significant similar to the case of the zwitterion mechanism. Likewise, the contribution of k_{H2O} was found to be negligible. Surprisingly, the contribution of k_{hyd} was also found to be negligible similarly to the case of zwitterion mechanism. Rate expressions of k_α and k_β were then correlated according to Arrhenius equation

by plotting their natural logarithm against the T^{-1} as shown in Figure S2. The generated rate expressions along with the activation energies are provided in Table 7. The predicted $k_{app-pred}$ using the generated individual rate constants and the experimental k_{app} values were compared in a parity plot as shown in Figure 7. An AAD of 8.8% was obtained between predicted and experimental values of both rate constant blocks, indicating excellent agreement between the experimental and predicted k_{app}. It is to be noted that the AAD using the termolecular mechanism was identical to that obtained from zwitterion mechanism (8.8%). Moreover, an evaluation of the activation energies of the k_α and k_β also reveals that their values are almost identical in both mechanisms. Therefore, it can be concluded that the mechanism of the reaction between CO_2 and MDEA-KTau can be explained using both the zwitterion and termolecular mechanisms. The obtained 'k_{ov}' data for the MDEA-KGly and CO_2 reactions were also interpreted using the termolecular mechanism. The generated rate constants for MDEA-KGly-CO_2 system for the specific reactions along with the predicted apparent rate constant ($k_{app-pred}$) are summarized in Table 8.

Similar to the MDEA-KTau-CO_2 system, the obtained results showed that only the contributions of k_α and k_β were important, with k_α being the most significant. However, contrary to the case of MDEA-KTau-CO_2 system, the application of termolecular mechanism to MDEA-KGly-CO_2 system has generated new rate expressions. The Arrhenius plots of the k_α and k_β against the T^{-1} and the generated rate expressions of are shown in Figure S3 and Table 9, respectively. A parity plot was used to compare the predicted $k_{app-pred}$ against the experimental k_{app} as shown in Figure 8. Similar to that of the MDEA-KTau-CO_2 system, an almost identical AAD was obtained for the MDEA-KGly-CO_2 system using termolecular mechanism compared to that obtained via zwitterion mechanism (7.2 against 7.4%). This indicates that an excellent agreement exist between the experimental and predicted k_{app} values and that both zwitterion and termolecular mechanisms can be used to explain the reactions between MDEA-KGly-CO_2 and MDEA-KTau-CO_2 systems.

5 | COMPARISON

5.1 | Comparison of rate constant of salts of Taurine and Glycine

The k_2 values of the second-order reaction rate constants of CO_2 with blends of MDEA-KGly and MDEA-KTau obtained using zwitterion mechanism were compared to

TABLE 6 Rate constant for the reaction of MDEA-KTau-CO$_2$ based on termolecular mechanism
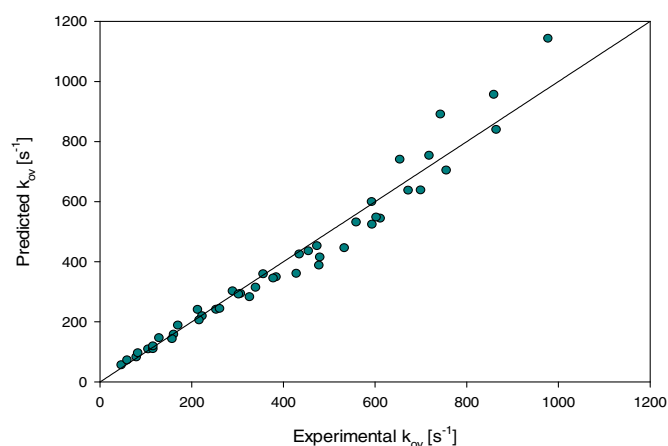
KTau mol dm^{-3}	MDEA mol dm^{-3}	OH ×10^4 mol dm^{-3}	H$_2$O mol dm^{-3}	k_{app} s^{-1}	$k_{app\text{-}pred}$ s^{-1}	k_α ×10^{-5} m^6 kmol^{-2} s	k_β ×10^{-4} m^6 kmol^{-2} s
293 K							
0.02	0.18	1.16	54.26	46.7	55.73	3.99	1.76
0.02	0.48	1.89	52.35	79.5	82.14		
0.02	0.78	2.41	50.44	105.3	108.55		
0.04	0.16	1.54	54.24	170.2	187.71		
0.04	0.46	2.62	52.33	253.6	240.54	AAD%	9.10
0.04	0.76	3.36	50.42	306.9	293.36		
0.05	0.15	1.67	54.23	326.4	282.30		
0.05	0.45	2.89	52.32	384.7	348.33		
0.05	0.75	3.73	50.41	479.8	414.36		
298 K							
0.02	0.18	1.24	54.26	59.4	72.32	5.02	2.45
0.02	0.48	2.02	52.34	115.8	109.12		
0.02	0.78	2.58	50.42	129.1	145.92		
0.04	0.16	1.65	54.23	213.2	240.22		
0.04	0.46	2.80	52.32	339.8	313.83	AAD%	12.40
0.04	0.76	3.60	50.40	477.8	387.43		
0.05	0.15	1.79	54.22	428.6	360.02		
0.05	0.45	3.10	52.31	473.6	452.02		
0.05	0.75	4.00	50.39	611.9	544.02		
303 K							
0.02	0.18	1.41	54.25	82.9	95.88	5.90	4.10
0.02	0.48	2.30	52.32	161.0	157.40		
0.02	0.78	2.93	50.40	223.1	218.91		
0.04	0.16	1.88	54.23	289.5	301.50		
0.04	0.46	3.18	52.30	435.1	424.54	AAD%	6.40
0.04	0.76	4.09	50.38	603.0	547.57		
0.05	0.15	2.03	54.22	533.3	445.46		
0.05	0.45	3.52	52.29	592.9	599.26		
0.05	0.75	4.54	50.37	718.5	753.05		
308 K							
0.02	0.18	1.41	54.25	115.7	118.40	6.66	5.76
0.02	0.48	2.30	52.32	216.5	204.80		
0.02	0.78	2.93	50.40	302.4	291.19		
0.04	0.16	1.88	54.23	356.3	358.41		
0.04	0.46	3.18	52.30	559.1	531.20	AAD%	6.70
0.04	0.76	4.09	50.38	756.0	703.99		
0.05	0.15	2.03	54.22	593.7	524.02		
0.05	0.45	3.52	52.29	654.6	740.00		
0.05	0.75	4.54	50.37	859.7	955.99		
313 K							
0.02	0.18	1.49	54.25	157.6	142.43	8.18	6.73
0.02	0.48	2.44	52.32	261.2	243.42		

TABLE 6 (Continued)

KTau mol dm^{-3}	MDEA mol dm^{-3}	OH ×10^4 mol dm^{-3}	H$_2$O mol dm^{-3}	k_{app} s^{-1}	$k_{app\text{-}pred}$ s^{-1}	k_α ×10^{-5} m^6 kmol^{-2} s	k_β ×10^{-4} m^6 kmol^{-2} s
0.02	0.78	3.11	50.38	378.1	344.41		
0.04	0.16	1.99	54.23	455.0	435.09		
0.04	0.46	3.38	52.30	672.8	637.06	AAD%	9.30
0.04	0.76	4.34	50.36	864.9	839.03		
0.05	0.15	2.16	54.22	700.0	637.74		
0.05	0.45	3.73	52.29	743.3	890.21		
0.05	0.75	4.82	50.35	977.8	1142.67		
AAD%							8.80

TABLE 7 Rate constants for MDEA-KTau-CO$_2$ over 293 to 313 K based on termolecular mechanism

Rate	lnk_0	E_a/R (K)	E_a (kJ mol^{-1})	Equation
k_α (m^6 kmole^{-2} s^{-1})	22.30	3154.6	26.23	$k_\alpha = 4.82 \times 10^9 e^{-\frac{3154.6}{T}}$
$k_{\beta,KTau}$ (m^6 kmole^{-2} s^{-1})	30.59	6499.3	54.04	$k_\beta = 1.93 \times 10^{13} e^{-\frac{6499.3}{T}}$

FIGURE 7 Parity plot of rate constants for CO$_2$-MDEA-KTau based on termolecular mechanism [Colour figure can be viewed at wileyonlinelibrary.com]

each other as shown in Figure 9. We clearly observe that CO$_2$ reaction with blends of MDEA-KGly is faster compared to the CO$_2$ reaction with blends of MDEA-KTau. The obtained second-order rate constants (k_2) were further compared with available data in the literature summarized in Table 10. The k_2 values obtained from this work and derived from blends of MDEA-KGly and MDEA-KTau data were compared to k_2 values derived from single KGly and single Ktau as shown in Figure 10. A significant increase in rate constant k_2 for CO$_2$ reactions with both blends was observed compared to those derived solely from CO$_2$ reactions with single amino acids (potassium salts of Taurine or Glycine) due to the presence of MDEA in the mixture. In this case, MDEA

acts as an additional base in the deprotonation of the zwitterion intermediate formed by potassium salts of amino acids and CO$_2$, resulting in an increase in second-order rate constant k_2 for both potassium salts of Taurine and Glycine. Upon comparing the activation energies, it is observed that the activation energy obtained from this work is lower than the ones available in the literature for the cases of single amino acids salts, which means that deprotonation of zwitterion intermediate seemed to occur faster in the amine blends compared to single amino acids salts. For the reaction of potassium salts of taurine, Kumar et al[12] and Wei et al[17] reported activation energy of 47.40 and 50.50 kJ mol^{-1}, respectively. While Sodiq et al[16] obtained an activation energy of 48.10 kJ mol^{-1} in their investigation of sodium salts of taurine reaction with CO$_2$, which is higher than the one obtained from this work. On the other hand, in case of potassium salts of glycine, the activation energy for the deprotonation of zwitterion seemed to be higher than that of 48.22 and 45.79 kJ mol^{-1} reported by Portugal et al[20] and Penny and Ritter,[39] respectively. A comparison with CO$_2$-sodium salts of glycine reaction, the activation energy was found to be lower than the ones reported by Lee et al[40] and Park et al[41] as shown in Table 10. It is to be noted, that in both cases potassium salts of Taurine and Glycine, the activation energies were higher than the ones reported for their respective sodium salts. This finding is similar to what was obtained from the works of Kumar et al,[12] Holst et al,[42,43] and Lim et al,[44] where faster kinetics of CO$_2$ reaction was observed with potassium salts of amino acids compared to that of sodium salts of amino acids.

TABLE 8 Rate constant for the reaction of MDEA-KGly-CO_2 based on termolecular mechanism

KGly mol dm^{-3}	MDEA mol dm^{-3}	OH × 10^4 mol dm^{-3}	H$_2$O mol dm^{-3}	k_{app} s^{-1}	$k_{app\text{-}pred}$ s^{-1}	k_α× 10^{-5} m^6 kmol^{-2} s^{-1}	$k_{\beta,KGly}$ × 10^{-3} m^6 kmol^{-2} s^{-1}
293 K							
0.02	0.18	1.16	54.3	92.7	112.8	2.65	1.91
0.02	0.48	1.89	52.4	109.9	124.3		
0.02	0.78	2.41	50.4	130.5	135.7		
0.03	0.17	1.54	54.2	246.5	247.6		
0.03	0.47	2.62	52.3	282.6	265.3		
0.03	0.77	3.36	50.4	330.5	282.5		
0.04	0.16	1.67	54.2	463.4	436.1	AAD%	10.2
0.04	0.46	2.89	52.3	553.0	459.0		
0.04	0.76	3.73	50.4	528.3	481.9		
298 K							
0.02	0.18	1.24	54.3	123.9	146.1	3.39	2.95
0.02	0.48	2.02	52.3	147.5	163.8		
0.02	0.78	2.58	50.4	169.7	181.5		
0.03	0.17	1.65	54.2	314.0	319.0		
0.03	0.47	2.80	52.3	356.8	346.4		
0.03	0.77	3.60	50.4	458.2	372.9		
0.04	0.16	1.79	54.2	582.9	560.7	AAD%	9.6
0.04	0.46	3.10	52.3	684.3	596.1		
0.04	0.76	4.00	50.4	706.2	631.5		
303 K							
0.02	0.18	1.41	54.3	153.5	174.6	3.91	5.01
0.02	0.48	2.30	52.3	202.1	204.7		
0.02	0.78	2.93	50.4	220.7	234.7		
0.03	0.17	1.88	54.2	368.3	376.4		
0.03	0.47	3.18	52.3	473.0	422.9		
0.03	0.77	4.09	50.4	524.7	468.0		
0.04	0.16	2.03	54.2	704.3	658.4	AAD%	6.0
0.04	0.46	3.52	52.3	729.9	718.5		
0.04	0.76	4.54	50.4	772.8	778.6		
308 K							
0.02	0.18	1.41	54.3	186.0	208.9	4.47	8.36
0.02	0.48	2.30	52.3	291.4	259.1		
0.02	0.78	2.93	50.4	308.6	309.3		
0.03	0.17	1.88	54.2	482.3	442.5		
0.03	0.47	3.18	52.3	514.7	520.3		
0.03	0.77	4.09	50.4	575.8	595.6		
0.04	0.16	2.03	54.2	782.2	768.8	AAD%	5.0
0.04	0.46	3.52	52.3	898.0	869.2		
0.04	0.76	4.54	50.4	938.3	969.6		
313 K							
0.02	0.18	1.49	54.2	237.8	247.3	5.20	10.95
0.02	0.48	2.44	52.3	334.5	313.0		
0.02	0.78	3.11	50.4	397.6	378.7		

TABLE 8 (Continued)

KGly mol dm^{-3}	MDEA mol dm^{-3}	OH $\times 10^4$ mol dm^{-3}	H$_2$O mol dm^{-3}	k_{app} s^{-1}	$k_{app-pred}$ s^{-1}	$k_\alpha \times 10^{-5}$ m^6 kmol^{-2} s^{-1}	$k_{\beta,KGly} \times 10^{-3}$ m^6 kmol^{-2} s^{-1}
0.03	0.17	1.99	54.2	564.4	520.2		
0.03	0.47	3.38	52.3	649.3	622.1		
0.03	0.77	4.34	50.4	681.2	720.7		
0.04	0.16	2.16	54.2	921.5	901.5	AAD%	5.3
0.04	0.46	3.73	52.3	958.8	1032.9		
0.04	0.76	4.82	50.4	1108.4	1164.0		
Overall AAD%					7.2		

TABLE 9 Rate constants for MDEA-KGly-CO$_2$ over 293 to 313 K based on termolecular mechanism

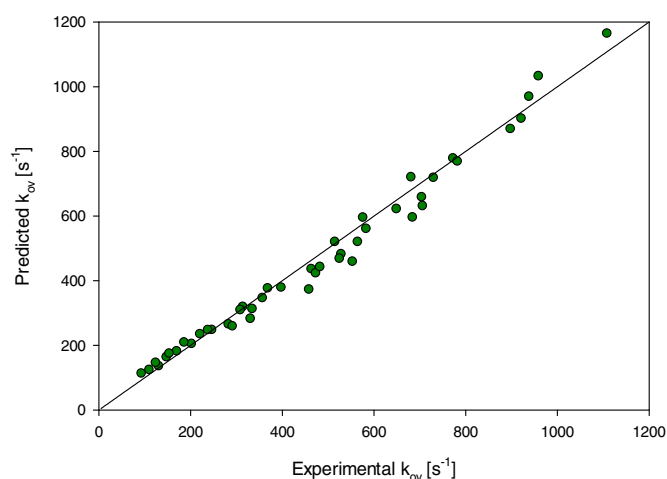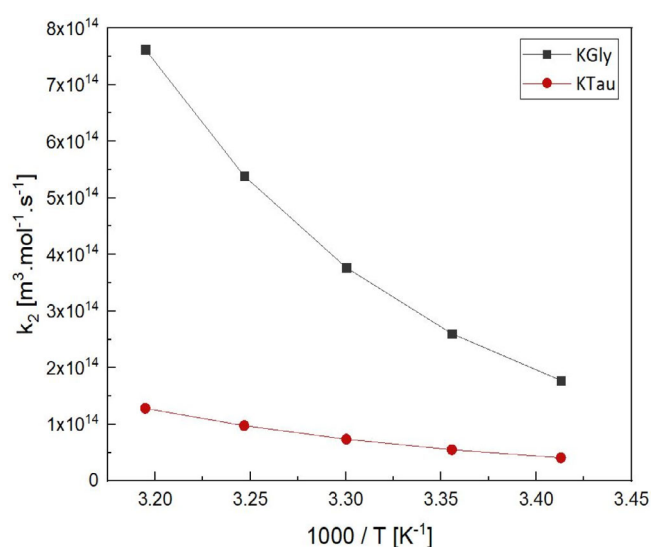| Rate	$\ln k_0$	E_a/R (K)	E_a(kJ mol^{-1})	Equation
k_α (m^6 kmole^{-2} s^{-1})	22.72	2986.3	24.83	$k_\alpha = 7.33 \times 10^9 e^{-\frac{2986.3}{T}}$
$k_{\beta,KGly}$ (m^6 kmole^{-2} s^{-1})	35.99	8330.1	69.26	$k_{\beta,KGly} = 4.25 \times 10^{15} e^{-\frac{8330.1}{T}}$

FIGURE 8 Parity plot of the rate constants for CO$_2$-MDEA-KGly based on termolecular mechanism [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 9 Comparison of the second-order rate constants for the amino acids via zwitterion [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 10 Summary of second-order rate expressions for salts of Taurine and Glycine

Amino acid	Counter ion	Reaction order	Temperature range (K)	E_a (kJ mol^{-1})	Equation	References
Taurine	K$^+$	1.0-1.5	285-305	47.40	$k_2 = 3.23 \times 10^{12} e^{-\frac{5700.0}{T}}$	Kumar et al[12]
		1.0	323-353	50.50	$k_2 = 2.70 \times 10^{12} e^{-\frac{6074.0}{T}}$	Wei et al[17]
		1.56*	293-313	43.67	$k_2 = 2.49 \times 10^{21} e^{-\frac{5252.9}{T}}$	This Work
	Na$^+$	1.0	298-313	48.10	$k_2 = 5.44 \times 10^{11} e^{-\frac{5780.0}{T}}$	Sodiq et al[16]
Glycine	K$^+$	-	293-303	48.22	$k_2 = 2.81 \times 10^{10} e^{-\frac{5800.0}{T}}$	Potugal et al[20]
		-	278-303	45.79	$k_2 = 8.51 \times 10^8 e^{-\frac{5508.0}{T}}$	Penny and Ritter[39]
		1.93*	293-313	55.57	$k_2 = 1.43 \times 10^{24} e^{-\frac{6683.4}{T}}$	This Work
	Na$^+$	-	303-323	63.77	$k_2 = 1.95 \times 10^{13} e^{-\frac{7670.0}{T}}$	Lee et al[40]
		1.0	298-318	59.76	$k_2 = 3.82 \times 10^{12} e^{-\frac{7188.0}{T}}$	Park et al[41]

*Average.
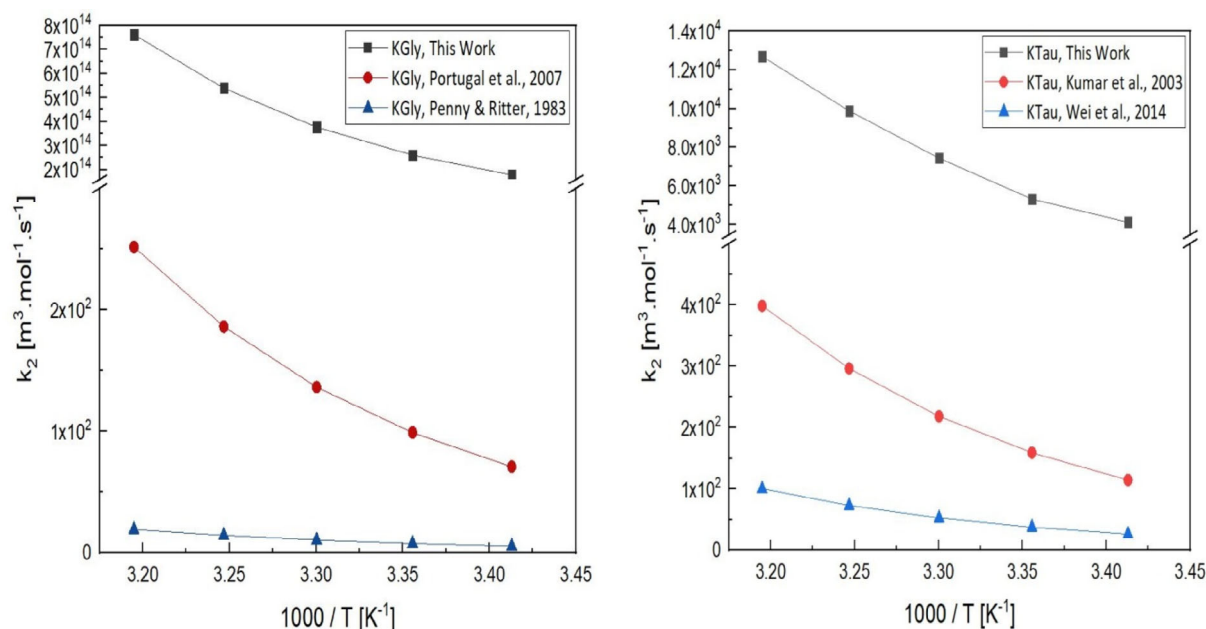
FIGURE 10 Comparison of the second-order rate constants for obtained KGly (left) and KTau (right) via zwitterion with available literature [Colour figure can be viewed at wileyonlinelibrary.com]
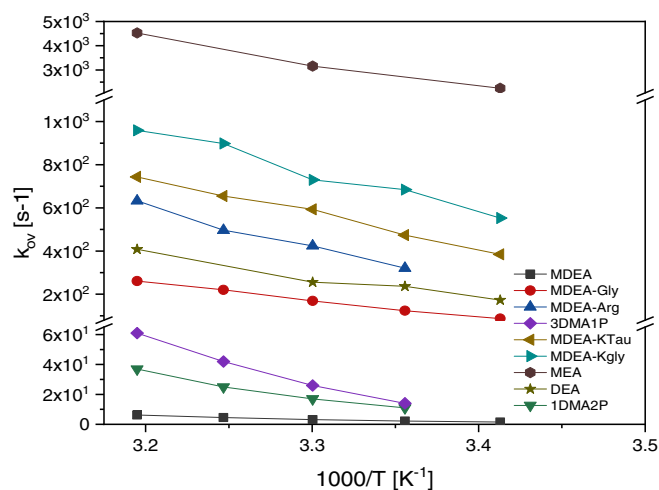
FIGURE 11 Comparison between the overall reaction kinetics of different amine-CO_2 systems [Colour figure can be viewed at wileyonlinelibrary.com]

5.2 | Comparison with other amine systems

The obtained kinetics data for the CO_2-MDEA-KTau and CO_2-MDEA-KGly reactions were compared to the available kinetics data for CO_2-MDEA-Gly,[28] CO_2-MDEA-Arg,[45] CO_2-MDEA,[28] CO_2-DEA,[46] CO_2-MEA,[47] CO_2-3DMA1P,[48] and CO_2-1DMA2P[48] as shown in Figure 11. An overall concentration of 0.5M was used as a basis of comparison for all amine/amino acids systems at different temperatures. Even though, three different concentrations for promotors were

investigated for the CO_2-MDEA-KTau and CO_2-MDEA-KGly reactions, in this work, only the highest promoter concentrations were selected for comparison, that is, 0.05M potassium salt of taurine and 0.04M potassium salt of Glycine. Of all the amine systems compared, CO_2-MEA reaction had the fastest reaction kinetics. Among the rest, Itis evident that CO_2 reaction with MDEA-KGly showed the fastest reaction rate followed by that of MDEA-KTau with CO_2. The obtained order for MDEA blends reactions with CO_2 was as follows: MDEA-KGly> MDEA-KTau> MDEA-Arg> MDEA-Gly. Of all the amine systems, the rate constant of the tertiary amine (MDEA) was found to be the lowest. This further indicates that the addition of AAS as promotor to a tertiary amine can certainly enhance the overall kinetics. Overall, it can be said that MDEA promoted by amino acid salts reacts faster than secondary, hindered and tertiary amines. Based the analysis of the overall reaction rate constants (Figure 11), the order of the CO_2-amine systems was found to be as follows: MEA >MDEA-KGly> MDEA-KTau>MDEA-Arg>DEA > MDEA-Gly> 3DMA1P > 1DMA2P > MDEA.

6 | CONCLUSIONS

The reaction kinetics of CO_2 with aqueous solutions of MDEA-AAS blends in concentrations varying from 0.2 to 0.8 molars and temperatures from 298 to 313 K was performed using stopped flow apparatus. Promoting effect of both Potassium salts of taurine and potassium salts of

glycine was evident from the obtained experimental data, as the addition of small amounts of AAS lead to the overall reaction rate of MDEA in blends to increase by more than 100 times. Two different mechanisms namely; Zwitterion and Termolecular mechanism were adopted to represent the experimental results for both MDEA-AAS systems over the entire range of operating conditions (different temperatures and concentrations) and were found to fit pretty well the experimental kinetics data. Overall, an AAD of 8.8 and 7.4% was observed using zwitterion mechanism and 8.8 and 7.2% using termolecular mechanism for MDEA-KTau and MDEA-KGly, respectively. In both CO_2-MDEA-AAS systems, significant contribution of MDEA concentration to the overall reaction rate was observed using both mechanisms. In case of CO_2-MDEA-KTau system, the analysis of the rate constant using zwitterion mechanism showed that the contribution of MDEA, KTau, and OH^- were found to be the most important. However, the contribution of hydroxyl ions to the overall reaction was found to be negligible using termolecular mechanism. As for the case of CO_2-MDEA-KGly system, both zwitterion and termolecular mechanisms showed that the contribution of MDEA and KGly was significant. However, the contribution of hydroxyl ion was found to be negligible.

Arrhenius equation was used to correlate the individual blocks of rate constants for the reactions involved. A comparison of the obtained second-order rate expression showed that the activation energy of the KTau obtained from this work was lower than that available in the literature, while the opposite was observed for the case of KGly. A comparison based on the overall reaction constants of the two MDEA-AAS blends showed that MDEA-KGly exhibits faster kinetics than MDEA-KTau. Finally, an expansion of the comparison with other MDEA blends and other recently studied amine systems revealed that the both MDEA-KGly and MDEA-KTau systems exhibited faster reaction kinetics with CO_2 compared to the other MDEA blends and amine systems.

NOMENCLATURE

MDEA	*N*-methyldiethanolamine
KTau	potassium salts of Taurine
KGly	potassium salts of Glycine
Gly	Glycine
Arg	L-arginine
MEA	monoethanolamine
DEA	diethanolamine
AMP	2-amino-2-methyl-1-propanol
DEAB	4-diethylamine-2-butanol
3DMA1P	3-dimethylamino-1-propanol
1DMA2P	1-dimethylamino-2-propanol
DEA-1,2-PD	3-diethylamino-1, 2-propanediol

$r_{CO2\text{-}MDEA}$ [dm^3 mol^{-1} s^{-1}]	reaction rate of CO_2 with MDEA
$r_{CO2\text{-}OH\text{-}}$ [dm^3 mol^{-1} s^{-1}]	reaction rate of CO_2 with hydroxyl ions
$r_{CO2\text{-}AAS}$ [dm^3 mol^{-1} s^{-1}]	reaction rate of CO_2 with amino acid salts
r_{CO2} [dm^3 mol^{-1} s^{-1}]	reaction rate of CO_2 with MDEA-KTau
k_{MDEA} [s^{-1}]	overall reaction rate of CO_2 and MDEA
k_{OH} [s^{-1}]	overall reaction rate of CO_2 and OH^- ion.
k_{AAS} [s^{-1}]	overall reaction rate of CO_2 and amino acid salts.
k_{ov} [s^{-1}]	overall reaction rate with CO_2 with MDEA and KTau
k_2 [m^3 kmol^{-1} s^{-1}]	rate constant for the formation reaction of the Zwitterion intermediate
k_{-1} [s^{-1}]	rate constant for the consumption reaction of the Zwitterion intermediate
$k_{b,i}$ [s^{-1}]	reaction rate constants of individual species based on Zwitterion mechanism
T [K]	temperature
t [s]	time
K_w [mol dm^{-3}]	water dissociation constant
k_{Pi} [mol dm^{-3}]	protonation constant for MDEA and KTau
k_{app} [s^{-1}]	apparent rate constant
$k_{app\text{-}pred}$ [s^{-1}]	predicted rate constant
Ea [kJ mol^{-1}]	activation energy
k_{α} [m^6 kmol^{-2} s^{-1}]	catalytic influence of MDEA on the overall reaction
k_{β} [m^6 kmol^{-2} s^{-1}]	catalytic influence of AAS on the overall reaction
k_{hyd} [m^6 kmol^{-2} s^{-1}]	catalytic influence of OH^- ions on the overall reaction

ORCID

Nafis Mahmud https://orcid.org/0000-0002-2443-7974
Abdelbaki Benamor https://orcid.org/0000-0003-0150-8431
Mustafa S. Nasser https://orcid.org/0000-0002-7646-558X

REFERENCES

1. Wang M, Joel AS, Ramshaw C, Eimer D, Musa NM. Process intensification for post-combustion CO_2 capture with chemical absorption: a critical review. *Appl Energy*. 2015;158:275-291.

2. Liang ZH, Rongwong W, Liu H, et al. Recent progress and new developments in post-combustion carbon-capture technology with amine based solvents. *Int J Greenhouse Gas Control*. 2015; 40:26-54.

3. Mumford KA, Wu Y, Smith KH, Stevens GW. Engineering. Review of solvent based carbon-dioxide capture technologies. *Front Chem Sci Eng*. 2015;9(2):125-141.

4. Rochelle GT. Amine scrubbing for CO_2 capture. *Science*. 2009; 325(5948):1652-1654.

5. Benamor A, Ali BS, Aroua MK. Kinetic of CO_2 absorption and carbamate formation in aqueous solutions of diethanolamine. *Korean J Chem Eng*. 2008;25(3):451-460.

6. Chakravarty T, Phukan U, Weilund R. Reaction of acid gases with mixtures of amines. *Chem Eng Prog*. 1985;81(4):32-36.

7. Hu G, Smith KH, Wu Y, Kentish SE, Stevens GW. Screening amino acid salts as rate promoters in potassium carbonate solvent for carbon dioxide absorption. *Energy Fuels*. 2017;31(4): 4280-4286.

8. Suleman H, Maulud AS, Syalsabila A. Thermodynamic modelling of carbon dioxide solubility in aqueous amino acid salt solutions and their blends with alkanolamines. *J CO2 Util*. 2018;26:336-349.

9. Zhang Z, Li Y, Zhang W, et al. Effectiveness of amino acid salt solutions in capturing CO_2: a review. *Renew Sustain Energy Rev*. 2018;98:179-188.

10. Sang Sefidi V, Luis P. Advanced amino acid-based technologies for CO_2 capture: a review. *Ind Eng Chem Res*. 2019;58(44): 20181-20194.

11. Kumar P, Hogendoorn J, Feron P, Versteeg G. Equilibrium solubility of CO_2 in aqueous potassium taurate solutions: part 1. Crystallization in carbon dioxide loaded aqueous salt solutions of amino acids. *Ind Eng Chem Res*. 2003;42(12):2832-2840.

12. Kumar P, Hogendoorn J, Versteeg G, Feron P. Kinetics of the reaction of CO_2 with aqueous potassium salt of taurine and glycine. *AIChE J*. 2003;49(1):203-213.

13. Vaidya PD, Konduru P, Vaidyanathan M, Kenig EY. Kinetics of carbon dioxide removal by aqueous alkaline amino acid salts. *Ind Eng Chem Res*. 2010;49(21):11067-72.

14. Thee H, Nicholas NJ, Smith KH, da Silva G, Kentish SE, Stevens G. A kinetic study of CO_2 capture with potassium carbonate solutions promoted with various amino acids: glycine, sarcosine and proline. *Int J Greenhouse Gas Control*. 2014;20: 212-222.

15. Majchrowicz ME, Kersten S, Brilman WJ. Reactive absorption of carbon dioxide in L-prolinate salt solutions. *Ind Eng Chem Res*. 2014;53(28):11460-11467.

16. Sodiq A, Rayer AV, Olanrewaju AA, Abu Zahra MR. Reaction kinetics of carbon dioxide (CO_2) absorption in sodium salts of taurine and proline using a stopped-flow technique. *Int J Chem Kinet*. 2014;46(12):730-745.

17. Wei C-C, Puxty G, Feron P. Amino acid salts for CO_2 capture at flue gas temperatures. *Energy Proc*. 2014;107:218-226.

18. Shen S, Yang Y-N, Bian Y, Zhao Y. Kinetics of CO_2 absorption into aqueous basic amino acid salt: potassium salt of lysine solution. *Environ Sci Technol*. 2016;50(4):2054-2063.

19. Shen S, Yang Y-N, Zhao Y, Bian Y. Reaction kinetics of carbon dioxide absorption into aqueous potassium salt of histidine. *Chem Eng Sci*. 2016;146:76-87.

20. Portugal AF, Derks PWJ, Versteeg GF, Magalhães FD, Mendes A. Characterization of potassium glycinate for carbon dioxide absorption purposes. *Chem Eng Sci*. 2007;62(23):6534-6547.

21. Moioli S, Pellegrini LA, Ho MT, Wiley DE. A comparison between amino acid based solvent and traditional amine solvent processes for CO_2 removal. *Chem Eng Res Des*. 2019;146: 509-517.

22. Donaldson TL, Nguyen YN. Carbon dioxide reaction kinetics and transport in aqueous amine membranes. *Ind Eng Chem Fundamen*. 1980;19(3):260-266.

23. Caplow M. Kinetics of carbamate formation and breakdown. *J Am Chem Soc*. 1968;90(24):6795-6803.

24. Blauwhoff P, Versteeg G, Van Swaaij WPM. A study on the reaction between CO_2 and alkanolamines in aqueous solutions. *Chem Eng Sci*. 1983;38(9):1411-1429.

25. Danckwerts PJ. The reaction of CO_2 with ethanolamines. *Chem Eng Sci*. 1979;34(4):443-446.

26. Versteeg G, Oyevaar MJ. The reaction between CO_2 and diethanolamine at 298 K. *Chem Eng Sci*. 1989;44(5):1264-1268.

27. Pinsent B, Pearson L, Roughton F. The kinetics of combination of carbon dioxide with hydroxide ions. *Trans. Faraday Soc*. 1956;52:1512-1520.

28. Benamor A, Al-Marri MJ, Khraisheh M, Nasser MS, Tontiwachwuthikul PJ. Reaction kinetics of carbon dioxide in aqueous blends of N-methyldiethanolamine and glycine using the stopped flow technique. *J Nat Gas Sci Eng*. 2016;33: 186-195.

29. Crooks JE, Donnellan JP. Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution. *J Chem Soc, Perkin Trans 2*. 1989;4:331-333.

30. Da Silva EF, Svendsen HF. Computational chemistry study of reactions, equilibrium and kinetics of chemical CO_2 absorption. *Int J Greenhouse Gas Control*. 2007;1(2):151-157.

31. Ali SH, Merchant SQ, Fahim MA. Kinetic study of reactive absorption of some primary amines with carbon dioxide in ethanol solution. *Sep Sci Technol*. 2000;18(3):163-175.

32. Mahmud N, Benamor A, Nasser MS, Al-Marri MJ, Qiblawey H, Tontiwachwuthikul PJ. Reaction kinetics of carbon dioxide with aqueous solutions of l-Arginine, Glycine & Sarcosine using the stopped flow technique. *Int J Greenhouse Gas Control*. 2017;63:47-58.

33. Knipe A, McLean D, Tranter R. A fast response conductivity amplifier for chemical kinetics. *J Phys E Sci Instrum*. 1974;7 (7):586.

34. Benamor A, Al-Marri MJ. Reactive absorption of CO_2 into aqueous mixtures of methyldiethanolamine and diethanolamine. *Int J Chem Eng Appl*. 2014;5(4):291.

35. Astaria G, Savage DW, Bisio A. *Gas treating with chemical solvents*. New York, NY: John Wiley & Sons; 1983.

36. Edwards T, Maurer G, Newman J, Prausnitz J. Vapor-liquid equilibria in multicomponent aqueous solutions of volatile weak electrolytes. *AIChE J*. 1978;24(6):966-976.

37. Littel RJ, Bos M, Knoop GJ. Dissociation constants of some alkanolamines at 293, 303, 318, and 333 K. *J Chem Eng Dat*. 1990;35(3):276-277.

38. Guo D, Thee H, Tan CY, et al. Amino acids as carbon capture solvents: chemical kinetics and mechanism of the glycine + CO2 reaction. *Energy Fuels.* 2013;27(7):3898-3904.

39. Penny DE, Ritter TJ. Kinetic study of the reaction between carbon dioxide and primary amines. *J Chem Soc, Faraday Trans 1.* 1983;79(9):2103-2109.

40. Lee S, Song H-J, Maken S, Park J-W. Kinetics of CO2 absorption in aqueous sodium glycinate solutions. *Ind Eng Chem Res.* 2007;46(5):1578-1583.

41. Park S-W, Son Y-S, Park D-W, Oh K-J. Absorption of carbon dioxide into aqueous solution of sodium glycinate. *Sep Sci Technol.* 2008;43(11-12):3003-3019.

42. van Holst J, Versteeg G, Brilman DWF, Hogendoorn J. Kinetic study of CO2 with various amino acid salts in aqueous solution. *Chem Eng Sci.* 2009;64(1):59-68.

43. Holst JV, Kersten SRA, Hogendoorn KJA. Physiochemical properties of several aqueous potassium amino acid salts. *J Chem Eng Data.* 2008;53(6):1286-1291.

44. J-A L, Kim DH, Yoon Y, et al. Absorption of CO2 into aqueous potassium salt solutions of L-alanine and L-proline. *Energy Fuels.* 2012;26(6):3910-3918.

45. Mahmud N, Benamor A, Nasser M, El-Naas MH, Tontiwachwuthikul PJP. Reaction kinetics of carbon dioxide in aqueous blends of N-methyldiethanolamine and L-arginine using the stopped-flow technique. *Processes.* 2019;7(2):81.

46. Siemieniec M, Kierzkowska-Pawlak H, Chacuk ASE. Reaction kinetics of carbon dioxide in aqueous diethanolamine solutions using the stopped-flow technique. *Ecol Chem Eng.* 2012;19(1):55-66.

47. Aboudheir A, Tontiwachwuthikul P, Chakma A, Idem R. Kinetics of the reactive absorption of carbon dioxide in high CO2-loaded, concentrated aqueous monoethanolamine solutions. *Chem Eng Sci.* 2003;58(23):5195-5210.

48. Kadiwala S, Rayer AV, Henni A. Kinetics of carbon dioxide (CO2) with ethylenediamine, 3-amino-1-propanol in methanol and ethanol, and with 1-dimethylamino-2-propanol and 3-dimethylamino-1-propanol in water using stopped-flow technique. *Chem Eng J.* 2012;179:262-271.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.