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New AMP/polyamine blends for improved CO₂ capture: Study of kinetic and equilibrium features

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Abstract

2-Amino-2-methyl-1-propanol (AMP), which is the sterically hindered form of monoethanolamine (MEA), is a credible substitute to conventional CO₂-capturing solvents. Its performance can be improved by blending with a highly reactive polyamine promoter. Two such aqueous blends of AMP/TETA and AMP/TEPA were chosen here (TETA = triethylenetetramine and TEPA = tetraethylenepentamine). The kinetics of CO₂ absorption in the proposed blends was investigated at 308, 313, and 318 K using the stirred cell technique. The concentrations of AMP and polyamine were varied between 2 to 3 kmol/m³ and 0.1 to 0.5 kmol/m³, respectively. From the measured values of the fast pseudo-first order constants, the second-order rate constants for the reactions of CO₂ with TETA (14 695 m³/(kmol s)) and TEPA (19 250 m³/(kmol s)) were determined at T = 313 K. Both TETA and TEPA react faster with CO₂ than MEA. Further, the respective activation energy values were found (40 and 37 kJ/mol). Finally, the equilibrium solubility of CO_2 for both blends was measured at T = 303 K. The loading capacity was higher than that for the aqueous blends of AMP/MEA, AMP/DEA, and AMP/MDEA (here, DEA and MDEA denote diethanolamine and N-methyldiethanolamine). The highest value of loading capacity (1.12 mol CO₂/mol amine at 2.01 kPa equilibrium partial pressure of CO₂) was noted in AMP/TEPA mixtures. The new findings on our proposed blends will strengthen the AMP/polyamine application in CO₂ separation.

KEYWORDS

absorption, carbon dioxide, hindered amine, polyamine

1 | INTRODUCTION

Reactive absorption is a renowned method for reducing the CO₂ content of many industrial gaseous streams. In this process, alkanolamines are often employed as solvents, eg, monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA).^[1] However, MEA and DEA load less CO₂ and desorb CO₂ at high temperatures. Also, MDEA reacts slowly with CO₂. Thus, much effort is focused on other options, such as sterically hindered amines (SHA). In particular, the performance of the sterically hindered form of MEA, viz. 2-amino-2-methyl-1-propanol

(or AMP) is widely reported. AMP is high-loading and easily regenerable, and it avoids the usual problems in amine-based plants, such as solvent degradation and corrosion in equipment and piping.^[2,3] It has moderate reactivity with CO_2 ,^[2,4] and the addition of absorption activators to AMP is beneficial.^[2,5] Recently, the kinetic and equilibrium features of AMP-based solvents promoted with polyamines such as ethylenediamine, (methylamino)propylamine, diethylenetriamine, and hexamethylenediamine were reported.^[5–8]

Two more polyamines, triethylenetetramine (or TETA) and tetraethylenepentamine (or TEPA), are promising because they load more CO_2 and boil at higher temperatures than the





Tetraethylenepentamine (TEPA)

FIGURE 1 Structure of the promoters TETA and TEPA used in this study

traditional amines; besides, the heat of absorption is lower.^[9–13] As shown in Figure 1, both comprise multiple amine groups (two primary and two secondary amines in TETA, and two primary and three secondary amines in TEPA). According to Singh et al,^[8] TETA and TEPA load up to as high as 2.5 mol CO_2 /mol and 3 mol CO_2 /mol amine due to multiple amine functionalities. In past works,^[12,14–16] these polyamines improved the performance of MDEA and AMP solutions.

Today, much effort is focused to explore superior amine-based solvents.^[17–20] In particular, the characterization of individual amines and amine/promoter mixtures is performed to determine their reaction kinetic, thermodynamic, and regeneration features.^[21–27] Here, we chose to work with AMP/promoter mixtures. The performance of non-conventional solvents, such as polyamines^[28] and ionic liquids,^[29,30] is encouraging. We anticipated that a thorough investigation on AMP/polyamine mixtures, not reported hitherto, would be very interesting.

This work reports the kinetic and equilibrium characteristics of AMP/TETA/H₂O and AMP/TEPA/H₂O blends. Using the stirred cell technique, reaction kinetics was investigated in the 308 to 318 K range. The total amine concentration was varied between 2.1 and 3.5 kmol/m³. The rate constants for the CO₂ reaction with the chosen polyamines were determined. The dependence of the equilibrium partial pressure of CO₂ on loading capacity was measured in an ambient-pressure vapour-liquid equilibrium setup at 303 K. A comparison with the loading capacity of other AMP-based solvents was provided. Thus far, there is no such information available on the aforesaid chosen solvents, and our work has filled this gap. This will stimulate further research and strengthen the case for employing AMP/polyamine mixtures for improved CO₂ capture.

2 | THEORY

The two-step zwitterion pathway describes the reaction between CO_2 and AMP (or Am_1H) in aqueous solutions.^[31,32]

The formation of unstable carbamate of AMP is represented by the overall reaction:

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$$CO_2 + 2Am_1H \leftrightarrow Am_1COO^- + Am_1H_2^+$$
(1)

The carbamate undergoes further hydrolysis. This results in the formation of bicarbonate ions and a free amine molecule:

$$Am_1COO^- + H_2O \leftrightarrow Am_1H + HCO_3^-$$
(2)

Typically, the steric hindrance of AMP resists carbamate formation. Instead, the following reaction is significant:

$$CO_2 + Am_1H + H_2O \leftrightarrow Am_1H_2^+ + HCO_3^-$$
 (3)

Both polyamines TETA and TEPA (denoted here as Am_2H) form polycarbamates upon reaction with CO_2 .^[13,14] The reactions with polyamines in aqueous solutions can be represented by the following:

$$\operatorname{CO}_2 + \operatorname{Am}_2 \operatorname{H} \stackrel{k_2, k_{-1}}{\leftrightarrow} \operatorname{Am}_2 \operatorname{H}^+ \operatorname{COO}^-$$
 (4)

$$Am_2H^+COO^- + B \xrightarrow{k_B} Am_2COO^- + BH^+$$
 (5)

Besides, the reactions of CO₂ with hydroxyl ions and water are inevitable:

$$CO_2 + OH^- \stackrel{k_{OH^-}}{\leftrightarrow} HCO_3^-$$
 (6)

$$\operatorname{CO}_2 + \operatorname{H}_2\operatorname{O} \stackrel{\operatorname{K}_{\operatorname{H}_2\operatorname{O}}}{\leftrightarrow} \operatorname{HCO}_3^- + \operatorname{H}^+$$
 (7)

where k_{OH^-} and k_{H_2O} denote rate constants for the reactions represented by Equations (6) and (7). The kinetics of the CO₂ reaction with water is slow and hence its contribution to the overall rate is overlooked.^[33]

The general form of the rate of reaction in aqueous amine is given by the following:

$$R_{CO_2} = \frac{k_2(CO_2)(amine)}{1 + \frac{k_{-1}}{k_B(B)}}$$
(8)

where $\hat{k}_B(B)$ represents the deprotonation constant for several bases B (viz., amine, OH⁻ or H₂O). Using Equation (8), the overall rate in promoted AMP/polyamine mixtures is given by the following:

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$$R_{CO_{2}} = \frac{k_{2,AMP}(CO_{2})(AMP)}{1 + \frac{k_{-1,AMP}}{\hat{k}_{AMP}(AMP) + \hat{k}_{Promoter}(Promoter) + \hat{k}_{H_{2}O}(H_{2}O) + \hat{k}_{OH^{-}}(OH^{-})}} + \frac{k_{2,Promoter}(CO_{2})(Promoter)}{1 + \frac{k_{-1,Promoter}}{\hat{k}_{AMP}(AMP) + \hat{k}_{Promoter}(Promoter) + \hat{k}_{H_{2}O}(H_{2}O) + \hat{k}_{OH^{-}}(OH^{-})}} + k_{H_{2}O}(CO_{2})(H_{2}O) + k_{OH^{-}}(CO_{2})(OH^{-})}$$
(9)

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The observed reaction rate constant k_{obs} (= $R_{CO_2}/(CO_2)$) is given by the following:

T = 308 K. Our value of the rate constant $(k_{2,MEA} = 9760 \text{ m}^3/(\text{kmol s}))$ was close to that reported by

$$k_{obs} = \frac{k_{2,AMP}(AMP)}{1 + \frac{k_{-1,AMP}}{\hat{k}_{AMP}(AMP) + \hat{k}_{Promoter}(Promoter) + \hat{k}_{H_2O}(H_2O) + \hat{k}_{OH^-}(OH^-)}} + \frac{k_{2,Promoter}(Promoter)}{1 + \frac{k_{-1,Promoter}}{\hat{k}_{AMP}(AMP) + \hat{k}_{Promoter}(Promoter) + \hat{k}_{H_2O}(H_2O) + \hat{k}_{OH^-}(OH^-)}} + k_{H_2O}(H_2O) + k_{OH^-}(OH^-)}$$
(10)

When the contribution of Equation (6) to the rate is neglected and zwitterion deprotonation is instantaneous, ie, $k_{-1,AMP} \ll [\hat{k}_{AMP}(AMP) + \hat{k}_{Promoter}(Promoter) + \hat{k}_{H_2O}(H_2O) + \hat{k}_{OH^-}(OH^-)]$ and $k_{-1,Promoter} \ll [\hat{k}_{AMP}(AMP) + \hat{k}_{Promoter}(Promoter) + \hat{k}_{H_2O}(H_2O) + \hat{k}_{OH^-}(OH^-)]$, Equation (10) can be rewritten as follows:

$$k_{obs} = k_{2,AMP}(AMP) + k_{2,Promoter}(Promoter)$$
(11)

3 | EXPERIMENTAL SECTION

3.1 | Materials

AMP (CAS No. 124-68-5), TETA (CAS No. 112-24-3), and TEPA (CAS No. 112-57-2) (purity 98%) were obtained from Spectrochem Pvt. Ltd. (Mumbai, India). Compressed gas cylinders containing CO₂, nitrogen (N₂), and nitrous oxide (N₂O) (purity 99.5%) were procured from Inox Air Products Ltd. (Mumbai, India). CO₂ standard and buffer solutions for anion-selective electrode were purchased from Thermo-Fisher Scientific (USA).

3.2 | Experimental methodology

The experimental technique was described in our past works.^[5,34] A batch stirred cell reactor (volume 1260 cm³, inner diameter 7.6 cm, interfacial surface area 45 cm²) with a flat, horizontal gas-liquid interface was used for studying kinetics (see apparatus in Figure 2). To ensure the precision of the experimental technique, the reaction between CO_2 and aqueous MEA solution was studied at

Hikita et al^[35] ($k_{2,MEA} = 10\ 069\ m^3/(kmol\ s)$). Thus, the experimental methodology was corroborated.

At first, N₂ was fed inside the reactor to flush off the air. Then, a vacuum pump was used for evacuation and the reactor was charged with the proposed solvent (400 mL). The temperature was set to a desired value (accuracy ± 0.1 K) and monitored. After the reaction temperature was reached, CO₂ was fed into the reactor. Its partial pressure was ~ 5 to 6 kPa. The gas and liquid phases were stirred at 1000 rpm and 600 rpm. The reactor pressure decreased due to the reactive absorption process. This drop in pressure was continuously recorded by a data acquisition system with a precision of ± 0.1 kPa. The CO₂ absorption rate was evaluated by using the fall-inpressure method. It was expressed as follows:

$$R_{CO_2}\hat{a} = -\left[\frac{V_G}{V_L RT}\frac{dP_{CO_2}}{dt}\right]$$
(12)

This method enabled a study on reaction kinetics even without an analysis of the liquid samples. The uncertainty in the absorption rate measurements was <3%. When the partial pressure of the inert gas is low and the gas phase is intensely mixed, there is no gas-side diffusion resistance.^[36] For these reasons, this resistance was neglected in this work. The importance of liquid-side diffusion resistance was ascertained by studying the dependence of the rate on the speed of stirring in the liquid phase. At T = 308 K, the rate did not vary in the 40 rpm-100 rpm range. Thus, it was evident that the rate was independent of k_L (liquid-side mass transfer coefficient) and the reaction type was fast pseudo**FIGURE 2** Stirred cell reactor used in this study



first order. Henceforth, the liquid phase was stirred at 60 rpm in all runs.

3.3 | Measurement of vapour-liquid equilibrium (VLE)

It is essential to know thermodynamic features of the solvent systems for effective design and operation of the absorber. The experimental technique used for such measurements was outlined in our recent work.^[37] We measured equilibrium CO₂ solubility in AMP/TEPA/H₂O and AMP/TETA/H₂O blends in a static, low-pressure VLE setup at T = 303 K. The CO₂ concentration of gas and liquid samples was analyzed in CO₂-anion selective meter.

3.4 | Study of reaction kinetics

The procedure for kinetics measurement was discussed in our previous work.^[5] The rate of absorption of CO_2 in the aforesaid blends can be expressed as follows:

$$\mathbf{R}_{\mathrm{CO}_2} = \mathbf{k}_{\mathrm{L}} \left(\mathrm{CO}_2 \right) \mathbf{E} \tag{13}$$

where (CO_2) denotes the interfacial concentration of CO_2 and the enhancement factor (E) denotes the effect of chemical reactions on the mass transfer process. Equation (13) holds when two conditions are met: first, the gas-film mass transfer resistance is absent, and second, CO_2 concentration in the bulk liquid is insignificant.^[38,39]

If the reaction system belongs to the fast pseudo-first order regime, E and the dimensionless Hatta number (or Ha) are identical (E = Ha). The value of Ha explains whether the reaction occurs in the liquid film or bulk. The mathematical expression for Ha is given by the following:

$$Ha = \frac{\sqrt{D_{CO_2} k_{obs}}}{k_L}$$
(14)

In the fast reaction regime, the disparity $10 < \text{Ha} \ll (\text{E}_{i} - 1)$ should be fulfilled. Here, E_{i} defines the enhancement factor for an instantaneous reaction and is expressed by Equation (15), according to Doraiswamy and Sharma^[38] and Danckwerts^[39]:

$$E_{i} = 1 + \left[\frac{(AmH)}{z (CO_{2})} \frac{D_{AmH}}{D_{CO_{2}}}\right]$$
(15)

where z and D_{AmH} highlight the stoichiometric coefficient and the diffusivity of amine in liquid.

Equation (15) is valid when the two-film theory is applied.

From Equations (13) and (14), the following can be shown:

$$R_{CO_2} = P_{CO_2} H_{CO_2} \sqrt{D_{CO_2} k_{obs}}$$
 (16)

where k_{obs} is given by Equation (11). Putting the value of k_{obs} in Equation (16), it follows that the rate is given by:

$$R_{CO_2} = P_{CO_2} H_{CO_2} \sqrt{D_{CO_2} [k_{2,AMP}(AMP) + k_{2,promoter}(Promoter)]}$$
(17)

Littel et $al^{[40]}$ proposed the following mathematical expression to estimate the value of k_L in a stirred cell reactor:

$$ln \left[\frac{P(t) - P_{final}}{P_{initial} - P_{final}} \right] = - \left[\frac{(\hat{m}V_L + V_G}{V_L V_G} \right] k_L t A$$
(18)

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To obtain k_L , we studied the physical absorption of N_2O in water at T = 308 K. By knowing the appropriate parameters ($\hat{m} = 0.28 \frac{mol}{mol}$, $V_G = 860 \text{ cm}^3$, $V_L = 400 \text{ cm}^3$, $A = 45 \text{ cm}^2$), the value of k_L was found to be 0.005 cm/s at T = 308 K, which agrees with the values typical of this gas-liquid contactor.^[2]

4 | RESULTS AND DISCUSSION

4.1 | Physico-chemical properties of the chosen blends

The measurement of physical properties (solution density, viscosity, CO₂ diffusivity, and physical CO₂ solubility) is essential to establish reaction kinetics. The procedure and methodology for such measurements were adopted from our previous work.^[2] The density and viscosity of the chosen blends were measured with a densitometer and capillary viscometer, respectively. The reproducibility of measurements was checked and the error was <2%. The N₂O diffusivity in blends was estimated by Stokes-Einstein relationship by knowing viscosity. The N₂O solubility in blends was found using the aforesaid stirred cell. The diffusivity and solubility of CO₂ in the amine blends were determined by N₂O analogy.^[41] The values of physical properties for the chosen blends are shown in Table 1. From the results, it is evident that AMP/TETA mixtures were more viscous than AMP/TEPA.

TABLE 1 Physicochemical properties of the chosen blends

As the molarity of TETA increased from 0.1 to 0.5 kmol/m³ in aqueous AMP solutions (2.5 kmol/m³), the value of H_{CO_2} in the blend decreased at T = 308 K. For the 2.5/0.5 kmol/m³ blend, the value of D_{CO_2} increased and H_{CO_2} decreased with the rise in temperature in the 308 to 318 K range. A similar trend was also seen for AMP/TEPA/H₂O blend. In general, CO₂ solubility in AMP/TEPA was always higher.

4.2 | Role of polyamines in aqueous AMP solution

At first, the CO₂ absorption rate in the individual amines AMP (2.5 kmol/m³), TETA (0.5 kmol/m³), and TEPA (0.5 kmol/m^3) was measured at T = 308 K. The partial pressure of CO_2 was ~ 5 to 7 kPa. The results are shown in Table 2. It is evident that the CO_2 reactivity of AMP is modest. Among the polyamines, TEPA reacts faster with CO₂ than TETA. When these promoters were added to aqueous AMP solution, the CO₂ absorption rates improved. At T = 308 K, the rate in aqueous AMP (2.5 kmol/m^3) was $2.96 \times 10^{-6} \text{ kmol/(m}^2 \text{ s})$ and it increased to 6.34×10^{-6} kmol/(m² s) in the AMP/TETA blend (2.5/0.5 kmol/m³). A similar behaviour was also observed for the AMP/TEPA blend at the same temperature. Next, the role of promoter concentration was investigated in the 0.1 to 0.5 kmol/m³ range. The CO₂ absorption rate significantly improved even when TETA and TEPA were added at lower concentrations (0.1 and 0.3 kmol/m^3) to aqueous AMP (2.5 kmol/m³) at T = 308 K. The best results were obtained at the highest promoter concentration (0.5 kmol/m^3) . The value of k_{obs} in 2.5/0.5 kmol/m³ mixtures of AMP/TETA and AMP/TEPA were 8108 1/s and 9909 1/s, respectively. Clearly, the chosen blends are high-performing and deserve further attention.

Aqueous amine mixture	Temp. (K)	Concentration (kmol/m ³)	ρ (kg/m ³)	μ (mPa · s)	$D_{\rm CO_2} \times 10^9$ (m ² /s)	$H_{CO_2} \times 10^4 \text{ (kmol/} (m^3 \text{ kPa}))$
	308	2.5/0.1	988.8	0.926	1.98	2.92
	308	2.5/0.3	991.7	0.909	2.01	2.89
AMP/TETA	308	2.5/0.5	994.2	0.887	2.05	2.85
	313	2.5/0.5	992.7	0.817	2.26	2.81
	318	2.5/0.5	990.7	0.719	2.59	2.78
	308	2.5/0.1	977.5	0.736	2.38	3.16
	308	2.5/0.3	980.4	0.748	2.35	3.14
AMP/TEPA	308	2.5/0.5	983.2	0.76	2.32	3.12
	313	2.5/0.5	982.1	0.754	2.41	3.08
	318	2.5/0.5	981.1	0.751	2.5	3.02

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in aq	ueous	AMP	solution	n at T	= 30	8 K

Aqueous amine	Concentration	$P_{\rm CO_2}$	$\rm R_{\rm CO_2} \times 10^6$	k _{obs}	E = Ha	$\mathbf{E}_{\mathbf{i}}$
mixture	(kmol/m ³)	(kPa)	(kmol/(m ² s))	(1/s)		
AMP	2.5	5.59	2.96	2390	46	1928
TETA	0.5	5.11	4.40	5755	76	432
TEPA	0.5	5.81	5.65	6560	86	367
	2.5/0.1	5.66	3.15	1834	42	1574
AMP/TETA	2.5/0.3	6.08	4.89	3853	61	1594
	2.5/0.5	5.46	6.34	8108	82	1929
	2.5/0.1	5.56	3.64	1803	42	1480
AMP/TEPA	2.5/0.3	5.22	5.83	5383	72	1709
	2.5/0.5	5.00	7.48	9909	96	1924

TABLE 3	Role of AMP in aqueous
solutions of TE	TA and TEPA at 308 K,
313 K, and 318	K

Aqueous amine	Temp.	Concentration		
mixture	(K)	(kmol/m ³)	P _{CO2} (kPa)	$R_{\mathrm{CO}_2} \times 10^6 \; (kmol/(m^2 \; s))$
	308	2/0.5	6.26	5.50
		2.5/0.5	5.46	6.34
		3/0.5	5.80	7.54
AMP/TETA	313	2/0.5	5.81	6.67
		2.5/0.5	6.21	8.55
		3/0.5	6.13	9.12
	318	2/0.5	5.98	8.16
		2.5/0.5	6.52	11.0
		3/0.5	6.39	11.92
		2/0.5	5.38	6.22
	308	2.5/0.5	5.00	7.48
		3/0.5	5.41	8.56
		2/0.5	5.7	8.83
AMP/TEPA	313	2.5/0.5	5.59	9.6
		3/0.5	6.36	11.57
		2/0.5	5.58	10.27
	318	2.5/0.5	6.56	12.7
		3/0.5	5.87	15.24

4.3 | Role of AMP in aqueous solutions of polyamine

Next, the influence of varying AMP concentration was studied in the 2 to 3 kmol/m³ range in blends containing 0.5 kmol/m³ polyamine. The partial pressure of CO₂ was ~ 5 to 7 kPa. The results at 308, 313, and 318 K are shown in Table 3. As expected, high AMP concentration facilitated the reactive absorption process. At T = 318 K, the rate of absorption in AMP/TEPA (3/0.5 kmol/m³) blend was 15.2×10^{-6} kmol/(m² s). This was much higher than that in AMP/TETA (3/0.5 kmol/m³) blend (11.9 × 10⁻⁶ kmol/(m² s)).

Hence, it can be confirmed that AMP/TEPA is more reactive among the two chosen blends.

4.4 | Kinetics study of the formulated blends

The dependency of the rate of absorption in AMP/TETA and AMP/TEPA blends (2.5/0.5 kmol/m³) on the partial pressure of CO₂ was investigated in the 5 to 25 kPa range at 308, 313, and 318 K. The respective results are shown in Figures 3 and 4. The absorption rate increased linearly with CO₂ partial pressure. Such behaviour is in good agreement with past works on alkanolamine blends.^[2,34] The higher the

number of amine groups in the solvent, the higher the rate. Thus, rates in AMP/TEPA were higher than those in AMP/TETA.

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Furthermore, the influence of temperature on the performance of the chosen blends was studied. The results are shown in Table 4. The absorption rate in both mixtures and the rate constant k_{obs} increased significantly, due to the rise in temperature from 308 to 318 K. The dependency of k_{obs} on the molarity of AMP at T = 308 K was investigated (see Figure 5). The value of k_{obs} for both blends increased with the rise in AMP concentration. For instance, the highest values of k_{obs} (12 938 1/s for AMP/TEPA and 11 044 1/s for AMP/TETA) at 308 K were observed for the 3/0.5 kmol/m³ mixtures.

The second order rate constants ($k_{2,TETA}$ and $k_{2,TEPA}$) were easily calculated from Equation (11) using the values of k_{obs} and $k_{2,AMP}$ at T = 313 K.^[2] The values of $k_{2, TETA}$ and $k_{2, TEPA}$ were found to be 14 695 m³/(kmol s) and 19 250 m³/(kmol s) at T = 313 K, respectively. The k_2 values for polyamines were markedly higher than the value of $k_{2,AMP}$ reported by Vaidya and Jadhav.^[2] Next, our k_2 , TETA and $k_{2, TEPA}$ values were compared to those reported previously for other AMP/promoter blends, ie, AMP/ MDEA,^[42] AMP/DEA,^[43] and AMP/MEA^[44] at T = 313 K. The comparative results are shown in Table 5. Clearly, the estimated values of $k_{2, TETA}$ and $k_{2, TEPA}$ were much higher than those for other AMP/promoter mixtures. It is evident that the chosen blends AMP/TETA and AMP/TEPA are very attractive for bulk CO₂ removal.

The temperature dependency of the second-order rate constant for the two investigated blends is shown in



FIGURE 3 A plot of R_{CO_2} vs P_{CO_2} at 308, 313, and 318 K (AMP/TETA = 2.5/0.5 kmol/m³)



FIGURE 4 A plot of R_{CO_2} vs P_{CO_2} at 308, 313, and 318 K (AMP/TEPA = 2.5/0.5 kmol/m³)

Figure 6. The temperature dependency of $k_{2, TETA}$ and $k_{2, TETA}$ and $k_{2, TETA}$ can be written as follows:

$$k_{2,\text{TETA}} = 6.78 \times 10^{10} \exp\left(\frac{-4804}{\text{T}}\right)$$
 (19)

$$k_{2,\text{TEPA}} = 2.65 \times 10^{10} \exp\left(\frac{-4428}{\text{T}}\right)$$
 (20)

The values of activation energy for the reactions with TETA and TEPA were found to be 40 and 37 kJ/mol, respectively.

4.5 | Equilibrium CO₂ solubility of blends

The equilibrium CO_2 solubility in the two investigated blends was measured. A plot of equilibrium partial pressure of CO_2 (\hat{P}_{CO_2}) vs loading (α) was made at T = 303 K (see Figure 7). The loading capacity (α) reported in this work was higher than that reported in the past for other AMP/promoter blends, viz. AMP/DEA at T = 313 K,^[45] AMP/MEA at T = 313 K,^[46] and AMP/MDEA at T = 303 K.^[47] In other words, both TETA and TEPA outperformed MEA, DEA, and MDEA as promoters in aqueous AMP solutions. As shown in Figure 7, the equilibrium partial pressure of CO₂ was higher at high values of the loading capacity. For instance, as the equilibrium partial pressure of CO₂ rose from 0.51 to 1.51 kPa, the loading capacity of AMP/TETA at 303 K increased from 0.16 mol CO₂/mol amine to 0.81 mol CO₂/mol amine. A similar behaviour was THE CANADIAN JOURNAL OF CHEMICAL ENGINEERING ① ♦ ♣ ⑩ ♥ Canadian Society for Chemical Engineering | For Our Future (Chemical Engineering | For Our Future)

TABLE 4 Kinetic characterization of chosen blends (AMP = 2.5 M, TETA = 0.5 M, TEPA = 0.5 M)

Aqueous amine	Temperature	$P_{\rm CO_2}$	$R_{\rm CO_2} \times 10^6$	k _{obs}	E = Ha	$\mathbf{E}_{\mathbf{i}}$	k _{2,Promoter}
mixture	(K)	(kPa)	(kmol/(m ² s))	(1/s)			(m ³ /(kmol s))
	308	5.46	6.34	8108	82	1929	11 440
AMP/TETA (2.5/0.5 kmol/m ³)	313	6.21	8.55	10 622	97	1720	14 695
	318	6.52	11.0	14 220	118	1656	18 685
	308	5.0	7.48	9909	96	1924	15 044
AMP/TEPA (2.5/0.5 kmol/m ³)	313	5.59	9.60	12 900	111	1743	19 250
	318	6.56	12.7	16 438	125	1515	23 120



FIGURE 5 Dependency of k_{obs} on (AMP) at T = 308 K

TABLE 5	Comparison	of kinetic	works on	aqueous
AMP/promoter	blends at T =	313 K		

Promoter in	$\frac{k_{2,Promoter}}{(m^{3}/$	
aqueous AMP	(kmol s))	References
MDEA	30.7	Huang et al ^[42]
DEA	3100	Mandal et al ^[43]
MEA	9500	Mandal and Bandyopadhyay ^[44]
TETA	14 695	This work
TEPA	19 250	This work

also observed for the other blend (AMP/TEPA). The highest value of loading capacity (1.12 mol CO₂/mol amine at 2.01 kPa) was noted in AMP/TEPA mixtures. A simple polynomial relation between \hat{P}_{CO_2} and α was established for both of the blends:



FIGURE 6 Arrhenius plots for the CO₂-TETA and CO₂-TEPA in aqueous AMP solution

$$\log(P_{CO_2-(AMP/TETA/H_2O)}) = 0.064 + 3.504 \propto -4.782 \propto^2 - 3.292 \propto^3$$
 (21)

$$\log(\hat{P}_{CO_2-(AMP/TEPA/H_2O)}) = -1.122 - 5.615$$

\$\approx + 5.612\approx^2 + 2.767\approx^3\$ (22)

4.6 | Some general remarks

It is noteworthy that our solvent propositions exhibit two encouraging features worthy of commercial CO₂-separation solvents, viz. high reactivity and loading capacity. This, in turn, will result in smaller absorption towers and lower solvent circulation rates, and hence, lower the capital and operating costs. Besides, AMP, TETA, and TEPA are available at an acceptable industrial cost and avoid the usual operational problems associated with conventional gas-treating solvents. It is now necessary to further investigate the regeneration features of aqueous AMP/TETA and AMP/TEPA mixtures and this is part of our impending investigation.

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FIGURE 7 Equilibrium CO₂ partial pressure vs loading capacity (**a**, AMP/DEA/H₂O (2.7/0.6 kmol/m³) at T = 313 K^[45]; •, AMP/MEA/H₂O (2/3 kmol/m³) at T = 313 K^[46]; *, AMP/MDEA/H₂O (1/1 kmol/m³) at T = 303 K^[47]; •, AMP/TETA/H₂O (2.5/0.5 kmol/m³) at T = 303 K in this work; and Δ , AMP/TEPA/H₂O (2.5/0.5 kmol/m³) at T = 303 K in this work)

5 | CONCLUSIONS

AMP/TETA/H₂O and AMP/TEPA/H₂O are new encouraging blends for the removal of CO₂ from industrial gaseous streams. In this study, kinetics of the reaction of CO₂ with the two aforesaid blends was studied in a stirred cell reactor. Among the two chosen polyamines, TEPA is more reactive than TETA. Using the two-step zwitterion mechanism, the kinetics of the chosen blends was described. At T = 313 K, the values of the second-order reaction rate constant in aqueous solutions of TETA and TEPA were found to be 14 695 $m^3/(kmol s)$ and 19 250 $m^3/(kmol s)$, respectively. The activation energy values for the reactions with TETA and TEPA were found to be 40 and 37 kJ/mol, respectively. The equilibrium CO₂ solubility was measured at T = 303 K. The loading capacity and equilibrium CO₂ partial pressure values were as follows: 0.81 mol CO₂/mol amine at 1.51 kPa for AMP/TETA/H₂O, and 1.12 mol CO₂/mol amine at 2.01 kPa for AMP/TEPA/ H₂O. The loading capacities of the chosen blends were superior to those for AMP/DEA/H2O, AMP/MEA/H2O, and AMP/MDEA/H₂O blends.

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NOMENCLATURE

AmH	amine (denoted by AMP, TETA, or TEPA)
(AMP)	initial concentration of AMP in liquid $(kmol/m^3)$
(CO ₂)	interfacial concentration of CO_2 (kmol/m ³)
Domino	diffusivity of amine in liquid (m^2/s)
D _{CO} .	diffusivity of CO ₂ in liquid (m^2/s)
E 2002	enhancement factor due to chemical
	reaction
E _i	enhancement factor for an instantaneous reaction
H_{CO_2}	solubility of CO_2 in liquid (kmol/ $(m^3 kPa)$)
На	Hatta number
(promoter)	initial concentration of promoter (TETA
u	or TEPA) in liquid (kmol/m ³)
(H ₂ O)	concentration of water (kmol/m ³)
k _{2,AmH}	reaction rate constant between CO ₂ and
	AMP, TETA, or TEPA (m ³ /(kmol s))
k-1,AmH	reverse reaction rate constant between $\ensuremath{\text{CO}}_2$
	and AMP, TETA, or TEPA) (m ³ /(kmol s))
\hat{k}_{AmH}	deprotonation constant for AMP, TETA, or TEPA
\hat{k}_{H_2O}	deprotonation constant for water
k _L	liquid-side mass transfer coefficient (m/s)
k _{obs}	observed pseudo-first order reaction rate constant (1/s)
k̂ _{OH} −	deprotonation constant for OH ⁻
(OH ⁻)	hydroxyl ion concentration (kmol/m ³)
P _{CO2}	partial pressure of CO ₂ in bulk gas
	phase (kPa)
R _{CO2}	specific absorption rate of CO_2 (kmol/(m ² s))
R	universal gas constant (J/(mol K))
t	time (s)
Т	temperature (K)
V _G	volume of gas inside reactor (m ³)
V _L	volume of liquid inside reactor (m ³)

Abbreviations

AMP	2-amino-2-methyl-1-propanol
DEA	diethanolamine
MDEA	methyldiethanolamine
TETA	triethylenetetramine
TEPA	tetraethylenepentamine
MEA	monoethanolamine
H_2O	water

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