

# Kinetic effect and absorption performance of piperazine activator into aqueous solutions of 2-amino-2-methyl-1-propanol through post-combustion CO<sub>2</sub> capture

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(Received 16 February 2019 • accepted 9 May 2019)

**Abstract**—The current study investigates the absorption kinetics of carbon dioxide (CO<sub>2</sub>) released from power plant exhaust using activated mixture of 2-amino-2-methyl-1-propanol (AMP) upgraded by piperazine (PZ). An absorption experiment of (AMP+PZ+H<sub>2</sub>O) was conducted in a wetted wall column absorber with a temperature variation of 298–313 K and CO<sub>2</sub> partial pressure of 5–15 kPa. PZ is considered to be a rate promoter by adjustable mass proportion varying from 2 to 10 wt%, while the concentration of entire amine solution remained constant at 30 wt%. Based on the Zwitterions mechanism, an overall reaction pattern of (AMP+PZ+H<sub>2</sub>O) with CO<sub>2</sub> was designed. Considering pseudo-first order reaction criteria, the kinetic rate factors and the overall second order rate constants were calculated. The overall rate constant ( $k_{ov}$ ) experienced a significant enhancement with a small addition of PZ into aqueous AMP solution. The observed second-order rate constants ( $k_{2,PZ}$ ) in this experimental study were 60,403, 81,925, 98,591 and 116,521 m<sup>3</sup>·kmol<sup>−1</sup>·s<sup>−1</sup> at 298, 303, 308 and 313 K correspondingly. The experimental specific rate of absorption into (AMP+PZ+H<sub>2</sub>O) in connection with the model anticipated rate was determined with deviation of around 4.86% average absolute deviation (AAD).

Keywords: CO<sub>2</sub> Capture, Absorption, Kinetics, (AMP+PZ+H<sub>2</sub>O), Flue Gas

## INTRODUCTION

Gradual escalation of anthropogenic CO<sub>2</sub> emissions around the world from different point sources is having the largest impact towards global warming. The present situation demands dedicated efforts of researchers and scientists throughout the world to combat the hostile effects of global warming. The most recent report of CO<sub>2</sub> intensity worldwide substantiates a continuous rise of 408.50 ppm as of November 23, 2018, which is highly associated with 316 ppm on the year 1958 [1]. Based on the assessment of the Intergovernmental Panel on Climate Change report, the worldwide average surface temperature has increased progressively from 1.4 to 5.8 °C from 1990 to 2100 [2]. The reduction of CO<sub>2</sub> emissions has received significant attention and one of the most obvious pathways for CO<sub>2</sub> capture, utilization and storage (CCUS) from coal-fired power plant exhaust gases along with the improvement of global climate in view of stabilizing the concentration of atmospheric CO<sub>2</sub> towards improvement of global climate [3]. The most efficient and economical technique for CO<sub>2</sub> capture is the well-established chemical sorption using aqueous amine solutions, since it has superiority in selective capture performance of CO<sub>2</sub> coming out from industrial exhaust comprising relatively higher volume and low CO<sub>2</sub> partial pressure [4,5] Monoethanolamine (MEA), diethanolamine (DEA),

di-isopropanolamine (DIPA), N-methyldiethanolamine (MDEA), tri-ethanolamine (TEA), 2-amino-2-methyl-1-propanol (AMP) are the widest range of industrially accepted chemical absorbents for arresting the CO<sub>2</sub> from industrial flue gas [6–9]. Remarkably, there is no distinct solvent available which possesses entire excellent features for CO<sub>2</sub> capture through absorption method. Consequently, significant investigations are headed for advancement of suitable solvent owing to the features of elevated rate kinetics and higher CO<sub>2</sub> loading capacity with advantage of reduced energy demand for solvent regeneration and lesser operational expenses. The main objective of this study was the selection of an optimum solvent blend with good physico-chemical properties: high CO<sub>2</sub> loading capacities, low vapor pressure, reasonable viscosity, thermal and chemical stability and higher rate kinetics of absorption. The basics of solvent blend are the combination of appreciative qualities of different single amines, for instance, the advantage of superior CO<sub>2</sub> loading capacity of tertiary amines as well as benefit of moderately reduced energy needed for solvent regeneration along with faster reaction rate kinetics of primary or/and secondary amines [10–18]. In recent days, there has been attention towards reaction rate promoted amine solution through a reaction rate accelerator, e.g., PZ (piperazine). PZ promoted aqueous AMP solution for CO<sub>2</sub> absorption acquires advantages of higher rate of reaction of CO<sub>2</sub> with PZ and also with the superior CO<sub>2</sub> loading capacity [19–22]. Nowadays, accomplishing higher overall reaction rate kinetics for CO<sub>2</sub> capture and considerably lesser regeneration energy requirement employing activated solvent blend such as piperazine (PZ) activated

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AMP or MDEA for CO<sub>2</sub> removal by absorption technique has been a subject of paramount interest. Gordesli et al. investigated the mixing effect of activating agent PZ into sterically-hindered amines AMP and tertiary amines MDEA [23]. They experienced that addition of PZ enhances the rate of reaction prominently in case of AMP and a higher equilibrium CO<sub>2</sub> loading capacity achieved for activated MDEA. The improved performance related to solvent blend is due to a sterically hindered structure where unstable carbamate formation leads to free amine generation, which enhances the CO<sub>2</sub> absorption performance along with a drawback of relatively slower reaction rate. In addition of a reaction rate promoter, i.e., piperazine (PZ) possessing very fast reaction kinetics within the aqueous solution of AMP could compensate this shortcoming of AMP alone [24]. Gordesli et al. informed that the pseudo-first-order rate constant of CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O) is relatively very high as compared to each individual amine and considerably higher than that of conventional monoethanolamine (MEA) for CO<sub>2</sub> capture [23]. In the activated MDEA process of BASF, PZ is treated as a rate accelerator during absorption of CO<sub>2</sub> as described by [25], and it is conveyed that PZ acts as an impressive rate accelerator than the conventional one [19]. Dash et al. found that addition of small quantities of PZ into aqueous solution of AMP, e.g., (28 wt% AMP+2 wt% PZ), considerably enhances the rate of CO<sub>2</sub> absorption and also the enhancement factor during the absorption process [26]. Although the activated solutions like (AMP+PZ+H<sub>2</sub>O) and (MDEA+PZ+H<sub>2</sub>O) offer very efficient CO<sub>2</sub> removal characteristics through absorption process, yet literature on CO<sub>2</sub> capture using such solutions is very scant. Hence, the present research work was performed to contribute some knowledge to this area.

In the current study, the absorption characteristics of CO<sub>2</sub> into aqueous amine blend were performed considering a temperature range of 298–313 K and CO<sub>2</sub> partial pressure of 5–15 kPa. The rate of specific absorption over (AMP+PZ+H<sub>2</sub>O) along with different solvent characteristics—density, viscosity, physical solubility and diffusivity of CO<sub>2</sub> of this blended solvent—was determined. Four dif-

ferent mass percentage combination of. 28/2, 25/5, 22/8 and 20/10 of (AMP+PZ) was considered as activated absorbent possessing an overall concentration of 30 wt% in blended solution, and absorption study was carried out in a wetted wall column. Physical solubility and diffusivity of all individual (AMP+PZ) blends were evaluated using N<sub>2</sub>O analogy. Here, kinetics of CO<sub>2</sub> absorption into (AMP+PZ+H<sub>2</sub>O) are described and the various kinetic parameters determined on the basis of pseudo-first-order reaction specification from observed experimental rate at each parametric situation.

## THEORETICAL BACKGROUND

### 1. Reaction Scheme

When CO<sub>2</sub> gas is dissolved into the aqueous mixture of (AMP+PZ), many reversible reaction stages are observed to proceed through the absorption method. The reactions of CO<sub>2</sub>- (AMP+PZ+H<sub>2</sub>O) schemes are described in our previous work [27] as suggested by [26].

### 2. Reaction Procedure

In case of AMP, which is sterically hindered in nature, the important reaction with CO<sub>2</sub> is proposed to be hydration of CO<sub>2</sub> which is catalyzed by AMP and the CO<sub>2</sub> molecule is transformed into bicarbonate ion. In this case, stability of carbamate formation is very less and the formation of carbamate is insignificant. Therefore, it can be ignored as well.

The probable reaction procedure associated with CO<sub>2</sub> and PZ consists of two steps: the construction of a complex chemical termed as zwitterion (CO<sub>2</sub>, PZ and PZCOO<sup>-</sup>); after that, the base catalyzed deprotonation of this zwitterion through a base (AMP, PZ and PZCOO<sup>-</sup>) to generate PZ-monocarbamate, PZ-dicarbamate and protonated base [28–30]. The Zwitterion mechanism was initially suggested by Caplow [31] and re-established by Danckwerts [32]. It states that the deprotonation of zwitterions can take place through some base existing in the solution. The reaction between CO<sub>2</sub> and PZ is enhanced catalytically due to the existence of noticeably more AMP concentration in (AMP+PZ+H<sub>2</sub>O) solution. The

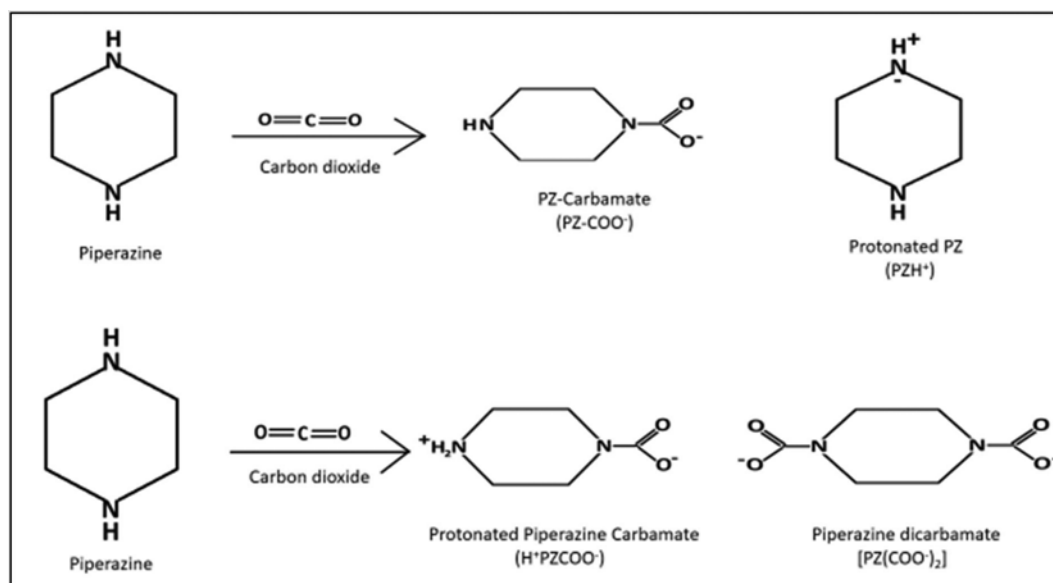


Fig. 1. Schematic representation of mechanism between CO<sub>2</sub> and PZ.

probable reaction mechanism between CO<sub>2</sub> and PZ is schematically represented in Fig. 1.

Presuming a quasi-steady-state circumstance during zwitterion formation and an irreversible deprotonation stage, the kinetic rate expression is represented as follows:

$$r_{\text{CO}_2\text{-PZ}} = \frac{k_{2,\text{PZ}}[\text{PZ}][\text{CO}_2]}{1 + \frac{k_{-1}}{\Sigma k_b[\text{B}]}} \quad (1)$$

where,  $\Sigma k_b[\text{B}]$  denotes the involvement of entire bases existing in the aqueous solution (PZ, PZCOO<sup>-</sup>, PZH<sup>+</sup>, H<sub>2</sub>O and OH<sup>-</sup>) for the proton elimination.

The two asymptotic circumstances may be arrived against the preceding kinetic expression:

$$\text{Case I. When, } \frac{k_{-1}}{\Sigma k_b[\text{B}]} \ll 1$$

At this condition, zwitterion construction is the rate controlling step and zwitterion deprotonation step is very fast as compared to reverse reaction. Hence, the kinetic rate illustration, i.e., Eq. (1) follows a simple second-order rate kinetics, represented as follows:

$$r_{\text{CO}_2\text{-PZ}} = k_{2,\text{PZ}}[\text{PZ}][\text{CO}_2] \quad (2)$$

$$\text{Case II. When, } k_{-1} \gg \Sigma k_b[\text{B}]$$

In this situation, zwitterion deprotonation step is the rate determining one, then the overall rate kinetics results as:

$$r_{\text{CO}_2\text{-PZ}} = \frac{k_{2,\text{PZ}}\Sigma k_b[\text{B}]}{k_{-1}}[\text{CO}_2][\text{PZ}] \quad (3)$$

This kinetic rate expression is recommended to verify the changes in reaction order between first and second considering amine intensity, and the assessment is done on the basis of involvement of distinct bases to deprotonate the zwitterions. The absorption of CO<sub>2</sub> into aqueous PZ solution and the kinetics rate equation is expected to obey the condition performing to Case I, i.e., the zwitterion formation step essentially be the rate controlling one; however, deprotonation steps involve merely the proton removal only and these are relatively very fast. In addition to carbamate formation reaction during the absorption of CO<sub>2</sub> with aqueous amine blend, other reactions take place in parallel, i.e., the hydration of CO<sub>2</sub> and it has been ignored in this study due to very slow reaction rate ( $k=0.026\text{ s}^{-1}$  at 25 °C) [33] and considered to be insignificant towards determination of overall reaction rate. Again, the direct reaction with hydroxyl ions and its influence can be overlooked because the amount of hydroxyl ion contribution to the overall kinetics is much less (<2%) [34,35].

### 3. Reaction Rate Kinetics for CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O)

The reaction between CO<sub>2</sub> and AMP is well recognized as a second-order reaction that has been already established by several researchers [36,37]. The reaction rate kinetics of CO<sub>2</sub> with aqueous AMP solution can be represented as

$$r_{\text{CO}_2\text{-AMP}} = k_{2,\text{AMP}}[\text{CO}_2][\text{AMP}] = k_{\text{OV-AMP}}[\text{CO}_2] \quad (4)$$

where,  $k_{\text{OV-AMP}}$  represents the overall pseudo-first-order reaction rate constant for CO<sub>2</sub>-AMP reaction.

The reaction of CO<sub>2</sub> through aqueous PZ solution can be represented with the help of zwitterion mechanism, and the development of zwitterion might be the rate controlling step. The prevailing equation for CO<sub>2</sub> absorption into aqueous PZ solution can be expressed as

$$r_{\text{CO}_2\text{-PZ}} = k_{2,\text{PZ}}[\text{PZ}][\text{CO}_2] \quad (5)$$

Accordingly, the overall reaction rate of CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O) is articulated as

$$\begin{aligned} r_{\text{CO}_2} &= r_{\text{CO}_2\text{-PZ}} + r_{\text{CO}_2\text{-AMP}} \\ &= k_{2,\text{PZ}}[\text{PZ}][\text{CO}_2] + k_{2,\text{AMP}}[\text{CO}_2][\text{AMP}] \\ &= k_{\text{OV}}[\text{CO}_2] \end{aligned} \quad (6)$$

where,  $k_{\text{OV}}$  signifies an overall rate constant of CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O) blend and is represented as

$$k_{\text{OV}} = k_{2,\text{PZ}}[\text{PZ}] + k_{2,\text{AMP}}[\text{AMP}] \quad (7)$$

### 4. Mass Transfer

The reaction criteria for CO<sub>2</sub> absorption into amine solutions were chosen carefully to make sure that absorption takes place in fast pseudo-first-order reaction regime, which entails the criteria as follows:

$$3 < \text{Ha} < E_{\infty} \quad (8)$$

where Ha denotes the Hatta number and can be articulated as follows:

$$\text{Ha} = \frac{\sqrt{k_{\text{OV}} D_{\text{CO}_2}}}{k_L} \quad (9)$$

where  $k_{\text{OV}}$  symbolizes the overall reaction kinetics rate constant.  $D_{\text{CO}_2}$  and  $k_L$  are the diffusivity of CO<sub>2</sub> and liquid phase mass transfer coefficient, respectively. Based on the penetration theory, the instantaneous enhancement factor ( $E_{\infty}$ ) is:

$$E_{\infty, \text{CO}_2} = \sqrt{\frac{D_{\text{CO}_2}}{D_{\text{amine}}}} + \frac{[\text{amine}]}{Z[\text{CO}_2]} \sqrt{\frac{D_{\text{amine}}}{D_{\text{CO}_2}}} \quad (10)$$

where  $D_{\text{amine}}$  and  $Z$  are the diffusivity of amine blend and stoichiometric coefficient, respectively. When the gas phase mass transfer is unimportant and liquid phase CO<sub>2</sub> content is zero, the specific rate of mass transfer of CO<sub>2</sub> in the fast pseudo-first-order (PFO) regime is as follows as proposed by [47]:

$$N_A = [\text{CO}_2]_i \sqrt{D_{\text{CO}_2} k_{\text{OV}}} = \frac{P_{\text{CO}_2}}{H_{\text{CO}_2}} \sqrt{D_{\text{CO}_2} k_{\text{OV}}} \quad (11)$$

Here,  $N_A$  denotes the absorption flux and  $[\text{CO}_2]_i$  signifies the CO<sub>2</sub> interfacial concentration.

The specific rate of CO<sub>2</sub> absorption i.e.,  $N_A$  into various (AMP+PZ+H<sub>2</sub>O) was measured through various CO<sub>2</sub> partial pressures and temperatures. The  $k_{\text{OV}}$  value was determined from Eq. (13), substituting the CO<sub>2</sub> solubility ( $H_{\text{CO}_2}$ ) in solution, CO<sub>2</sub> partial pressure ( $P_{\text{CO}_2}$ ), and CO<sub>2</sub> diffusivity in solution ( $D_{\text{CO}_2}$ ).

## MATERIAL AND METHODS

### 1. Materials

In the experimental study, piperazine (PZ) accelerated aqueous

**Table 1. Physicochemical properties of aqueous solution of (AMP+PZ+H<sub>2</sub>O)**

Mass % AMP	Mass % PZ	[AMP] (kmol m <sup>-3</sup> )	[PZ] (kmol m <sup>-3</sup> )	T (K)	Density, $\rho$ (kg m <sup>-3</sup> )	Viscosity, $\mu \times 10^3$ (kg m <sup>-1</sup> s <sup>-1</sup> )	Solubility, H <sub>1</sub> (kPa m <sup>3</sup> kmol <sup>-1</sup> )	Diffusivity, D <sub>1</sub> $\times 10^9$ (m <sup>2</sup> s <sup>-1</sup> )
28	2	3.12	0.24	298	998.76	3.740	3893	0.67
28	2	3.12	0.24	303	995.98	3.006	4247	0.77
28	2	3.12	0.24	308	993.10	2.526	4698	0.94
28	2	3.12	0.24	313	990.37	2.056	4973	1.22
25	5	2.80	0.58	298	1001.04	3.881	3777	0.63
25	5	2.80	0.58	303	998.48	3.126	4110	0.75
25	5	2.80	0.58	308	995.64	2.593	4645	0.85
25	5	2.80	0.58	313	992.71	2.186	4915	1.10
22	8	2.47	0.93	298	1003.76	4.065	3736	0.58
22	8	2.47	0.93	303	1001.07	3.314	4068	0.72
22	8	2.47	0.93	308	998.24	2.710	4534	0.81
22	8	2.47	0.93	313	995.08	2.303	4858	0.99
20	10	2.25	1.16	298	1004.76	4.115	3702	0.52
20	10	2.25	1.16	303	1002.12	3.624	4042	0.68
20	10	2.25	1.16	308	999.23	3.176	4424	0.75
20	10	2.25	1.16	313	996.86	2.446	4806	0.93

2-amino-2-methyl-1-propanol (AMP) solution was utilized during CO<sub>2</sub> capture escaping from the stack of self-modified coal-fired boiler. Reagent grade piperazine (PZ) with mass concentration (>99%) was procured from Sigma-Aldrich, Germany and the reagent grade 2-amino-2-methyl-1-propanol (AMP) having the pureness of more than 99% was from Acros Organics, U.S.A. Both of these chemicals were utilized with no added purification for making the aqueous amine blends. The entire amine blends were made with consequent mass fraction of each amine and measured via a Mettler Toledo balance, model ML204/A01 with an accuracy of  $\pm 0.01\%$ . For the preparation of particular blend with exact mass percentage ratio, bidistilled water was used. Reagent grade hydrochloric acid (HCl, 37%) supplied by Merck, India and methyl orange indicator were used to analyze the blended amine concentration as well as equilibrium CO<sub>2</sub> loading capacity. A combination of four different mass fractions of AMP and PZ, such as 28:2, 25:5, 22:8 and 20:10, was selected for removal of CO<sub>2</sub> gas retaining total solvent concentration of 30 wt% in the blend. Flue gas containing concentrated CO<sub>2</sub> with partial pressure of 5-15 kPa was used as the source of CO<sub>2</sub> gas originating from a modified mini coal-fired boiler.

The nitrous oxide (N<sub>2</sub>O) cylinder was purchased from British Oxygen Company (BOC), India with purity >99.99%. A pure carbon dioxide (CO<sub>2</sub>) cylinder was bought from Hydrogas, India with purity >99.9%. These two gases were considered for the determination of physical solubility and diffusivity of water and (AMP+PZ+H<sub>2</sub>O).

## 2. Physicochemical Properties of Aqueous Amine Blend

### 2-1. Density and Viscosity Measurement

The physicochemical properties, specifically density and viscosity of aqueous amine blends, are measured to know the thermodynamics, hydrodynamics and best possible functioning conditions of CO<sub>2</sub> absorption process. These properties also play vital roles in column fabrication, rate estimation and reaction rate constants calculation. Density measurement was performed for each individual

blend prepared from (AMP+PZ+H<sub>2</sub>O) with the help of a 25 ml Gay-Lussac bottle. The density of each blend was calculated over the temperature variation of 298-313 K in a thermostatic water bath with a precision of  $\pm 0.2$  K. The specified density data was the mean of three measured values. The uncertainty of temperature measurement was about  $\pm 0.1$  K. Water was chosen as a reference solvent for the density measurement of amine blend, and the value was predicted to be comparable with the data available in the internationally recognized book [38].

An Ostwald viscometer was used to determine the viscosity of each amine blend at a temperature ranging from 298-313 K. The viscometer was dipped in a thermostat connected bath having an accuracy of  $\pm 0.2$  K. Laboratory grade double refined water was considered as a reference liquid for measuring viscosity of the blended solution encompassing with a measurement uncertainty of  $\pm 0.1$  K. Each indicated viscosity value in Table 1 was the average of three measured values. The viscosity values of water as a reference standard were taken from [38]. The measurement accuracy was projected to be  $\pm 1.0\%$ . Subsequently, a collection of investigational values of density and viscosity of selected four (AMP+PZ+H<sub>2</sub>O) blend over different temperature and mass combination ratio are represented in Table 1.

### 2-2. Solubility and Diffusivity Measurement

Since CO<sub>2</sub> reacts with amine solution, it is not usually possible to find the physical solubility and diffusivity of CO<sub>2</sub> in aqueous amine solution directly. Clarke [39] suggested that nitrous oxide (N<sub>2</sub>O), which has a similar molecular assembly, molecular mass, and parallel electronic arrangement as CO<sub>2</sub>, might be considered to characterize the CO<sub>2</sub> performance in reactive systems. Therefore, nitrous oxide (N<sub>2</sub>O) is commonly considered as a non-reacting gas for the assessment of the physical solubility and diffusivity of CO<sub>2</sub> in aqueous blend [40-42]. The solubility of CO<sub>2</sub> in each individual amine blend with different mass ratio was determined over the temperature range of 298-313 K using N<sub>2</sub>O-analogy method.

**Table 2. Measured solubility and diffusivity of CO<sub>2</sub> and N<sub>2</sub>O in water**

Temperature (K)	Solubility, H (kPa m <sup>3</sup> kmol <sup>-1</sup> )		Diffusivity, D×10 <sup>9</sup> (m <sup>2</sup> s <sup>-1</sup> )	
	N <sub>2</sub> O in water	CO <sub>2</sub> in water	N <sub>2</sub> O in water	CO <sub>2</sub> in water
298	4035	3030	1.76	1.93
303	4506	3332	1.98	2.18
308	5086	3810	2.27	2.50
313	5654	4184	2.54	2.85

The solubility of N<sub>2</sub>O in aqueous amine blends was estimated through a solubility apparatus with the same experimental technique as proposed by [41,43]. The detailed investigational procedure of solubility and diffusivity measurement adopted was identical with that described by [44]. The standard technique is to take a pre-set amount of liquid sample interacting with an identified extent of gas sample at fixed temperature and pressure. One agitator is used for equilibrium enrichment and then the residual quantity of gas is determined. The observed variation of gas volume provides the extent of dispersed quantity in liquid sample. A glass absorption bottle was used having a capacity of 0.25×10<sup>-3</sup> m<sup>3</sup>. The arrangement was first expunged with saturated N<sub>2</sub>O gas at uniform temperature for each run after the attainment of thermal equilibrium. A quantified volume of 10 ml aqueous solutions of all the experimented blended amines was then introduced into the container and the solvent was mixed by means of a magnetic stirrer till the solution experienced any further variation in gas volume within a completely sealed environment. The observed change in volume is represented as amount of gas absorbed. The solubility of CO<sub>2</sub> in water and N<sub>2</sub>O in water and different amine blends were estimated over the temperature range of 298–313 K in a thermostat water bath having a precision of ±0.1 K. Besides, the experimental arrangement was stored in an enclosure where the environmental temperature was retained constant within ±0.2 K. The entire procedure of solubility measurements was performed at atmospheric pressure and it was maintained all through the process with the help of a manometric device. The experimental uncertainty in the calculated physical solubility was assessed within a range of ±3%.

A 0.0281 m o.d. glass wetted wall absorber was fabricated for the measurement of diffusivities of CO<sub>2</sub> in water and N<sub>2</sub>O in water and different amine blends of (AMP+PZ+H<sub>2</sub>O). The apparatus and the measurement technique are similar to those referred by [44]. The gas-liquid interaction time might be regulated from 0.35 to 0.85 s by maintaining a constant liquid flow rate with changing the absorption length. Volume uptake technique equipped with a soap film meter was introduced for the determination of rate of gas absorption. A rotameter was used for monitoring the liquid flow rate at several experimental temperatures and various amine concentrations. The diffusivity of each aqueous amine blend was estimated across the temperature variation of 298–313 K in an invariable temperature water bath with a precise accuracy of ±0.1 K. The experimental uncertainty in the estimated diffusivity was assessed within a range of ±5%.

At first the solubilities and diffusivities of CO<sub>2</sub> and N<sub>2</sub>O in water were quantified at 298, 303, 308 and 313 K for the validation of experimental method and apparatus. The observed results presented in

Table 2 are corroborated with the previous reported data with minimal deviation.

The physical solubility and diffusivity of CO<sub>2</sub> in different (AMP+PZ) blended amine solvents are assessed from the measured solubility and diffusivities of CO<sub>2</sub> and N<sub>2</sub>O by means of N<sub>2</sub>O analogy as represented by Eqs. (12)–(13) [40,45,46].

$$H_1 = H_{N_2O-amine} \left( \frac{H_{CO_2-water}}{H_{N_2O-water}} \right) \quad (12)$$

$$D_1 = D_{N_2O-amine} \left( \frac{D_{CO_2-water}}{D_{N_2O-water}} \right) \quad (13)$$

where  $H_{N_2O-amine}$  and  $H_{N_2O-water}$  signifies the calculated solubility of N<sub>2</sub>O in amine solution and water correspondingly.  $D_{N_2O-amine}$  and  $D_{N_2O-water}$  indicates the calculated diffusivity of N<sub>2</sub>O in amine solution and water, respectively.  $H_{CO_2-water}$  and  $D_{CO_2-water}$  denote the measured solubility and diffusivity of CO<sub>2</sub> in water, respectively.  $H_1$  and  $D_1$  are the estimated solubility and diffusivity values respectively which are presented in Table 1.

### 2-3. Experimental Absorption Apparatus and Procedure

A 0.0281 m o.d. glass made wetted wall column was considered for the CO<sub>2</sub> absorption performance using (AMP+PZ+H<sub>2</sub>O) as an absorbent. The experimental apparatus and process was identical with one described by [37]. Absorption experiments were executed with (28 wt% AMP+2 wt% PZ), (25 wt% AMP+5 wt% PZ), (22 wt% AMP+8 wt% PZ), (20 wt% AMP+10 wt% PZ) and 30 wt% AMP across the temperature deviation of 298–313 K and CO<sub>2</sub> partial pressure variant of 5–15 kPa. The solvent blend was brought into the top of the wetted wall column from the solvent drum. The absorption study was accomplished in a controlled atmosphere where the absorption temperature was regulated within ±0.2 K through a temperature controller. A gas flow rate of 180×10<sup>-6</sup> m<sup>3</sup>s<sup>-1</sup> and solvent stream of 2×10<sup>-6</sup> m<sup>3</sup>s<sup>-1</sup> were maintained throughout all runs. An online flue gas analyzer (TESTO 350-S, Germany) was employed for determination of inlet and outlet CO<sub>2</sub> concentration during the absorption through wetted wall column. After achieving the steady state of absorption, the absorbed aqueous blends were collected at a fixed interval from the lower end of the column. The amount of total CO<sub>2</sub> content in each loaded blended solvent was determined from the equilibrium cell performance study in a desorption chamber. Desorption investigation was accomplished in a temperature-regulated water bath with a precision of ±0.1 K and the apparatus and procedure previously illustrated in author's work published earlier [27]. The resultant rate of CO<sub>2</sub> absorption in the amine blend of (AMP+PZ) was calculated from liquid phase CO<sub>2</sub> concentration. A schematic representation of the wetted wall column is depicted in Fig. 2.

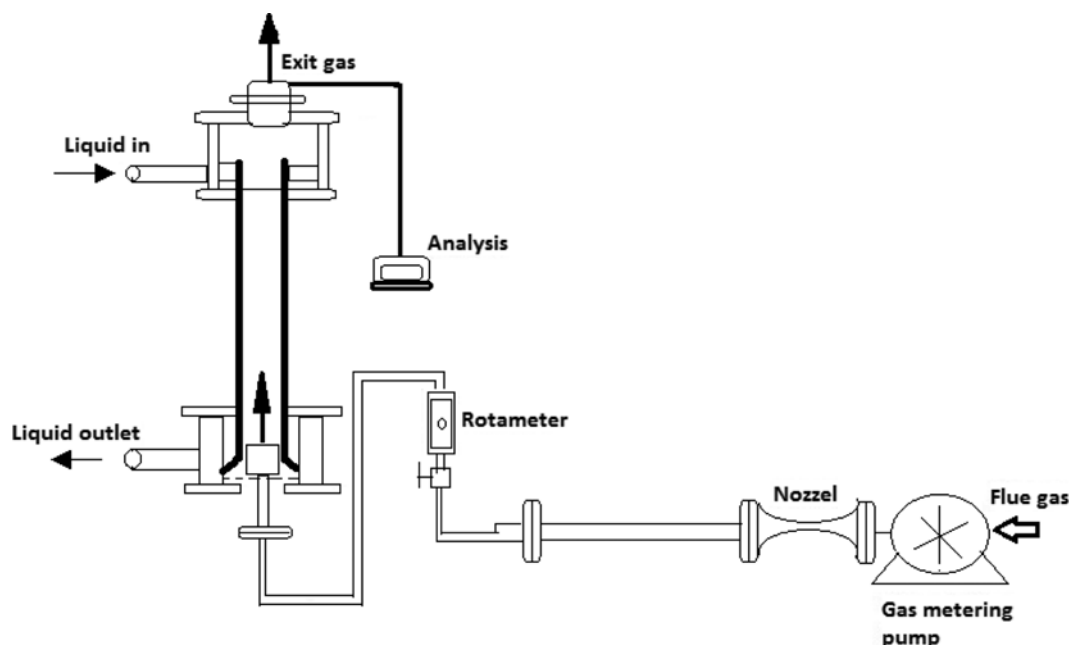


Fig. 2. Schematic of wetted wall column.

## RESULTS AND DISCUSSION

### 1. Physicochemical Properties

#### 1-1. Density and Viscosity

The experimentally measured physical properties, i.e., density and viscosity values of aqueous amine blends of (AMP+PZ) are pro-

vided in Table 1. The density and viscosity values of (AMP+PZ+H<sub>2</sub>O) were observed to increase with rise in percentage of PZ concentration in aqueous blend and decreased with increase in temperature. The density value differs marginally as the PZ concentration increases, but the variation in viscosity is more significant with rise in PZ mass ratio in the blend. The effect of temperature

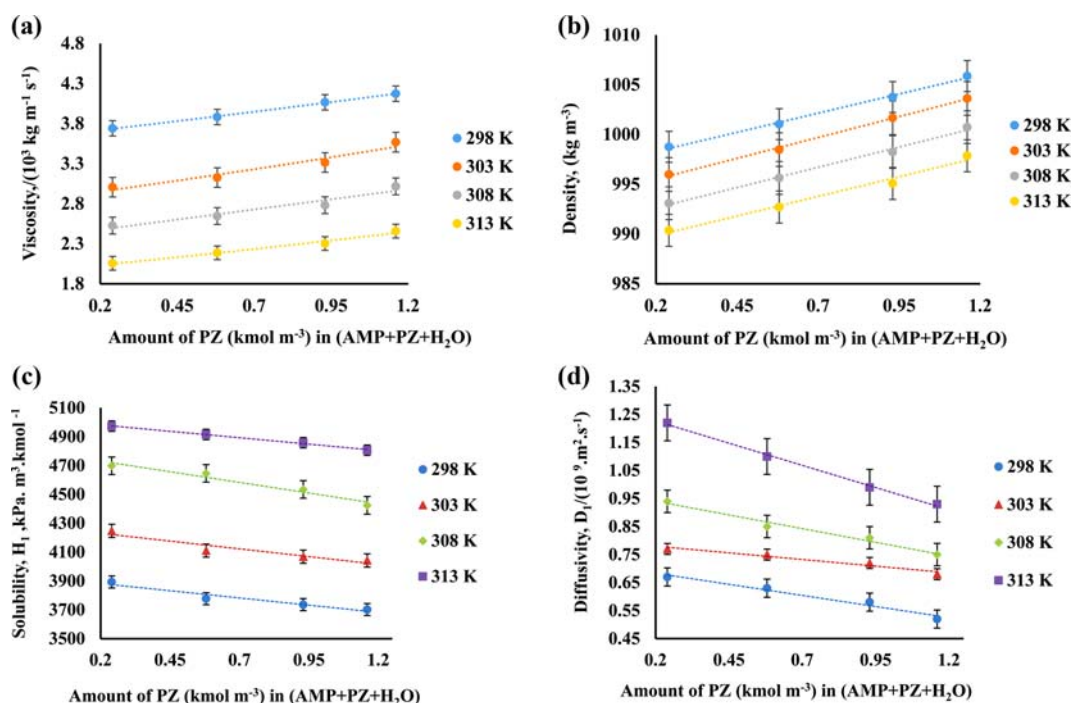


Fig. 3(a) Effect of temperature and PZ concentration on viscosity of aqueous blend of (AMP+PZ+H<sub>2</sub>O). (b) Effect of temperature and PZ concentration on density of aqueous blend of (AMP+PZ+H<sub>2</sub>O). (c) Estimated solubility of CO<sub>2</sub> in aqueous blend of (AMP+PZ+H<sub>2</sub>O) using N<sub>2</sub>O analogy. (d) Estimated diffusivity of CO<sub>2</sub> in aqueous blend of (AMP+PZ+H<sub>2</sub>O) using N<sub>2</sub>O analogy.

and concentration of PZ on viscosity and density of amine blend of (AMP+PZ+H<sub>2</sub>O) is illustrated in Figs. 3(a) and 3(b), respectively.

#### 1-2. Solubility and Diffusivity

The measured solubility of N<sub>2</sub>O in amine blend of (AMP+PZ+H<sub>2</sub>O) is estimated in terms of Henry's constant ( $H_1$ ). The estimated solubility values of aqueous blended solution upsurgs with rise in temperature from 298 to 313 K and reduces with growing mass fraction of PZ in the blend, though the effect of PZ quantity in solution is less pronounced. The measured diffusivities of CO<sub>2</sub> in (AMP+

PZ+H<sub>2</sub>O) are shown in Table 1. At fixed temperature, the diffusivity of CO<sub>2</sub> in (AMP+PZ+H<sub>2</sub>O) decreased as the PZ percentage increased, and increased as the temperature rose at the same amine combination. The effect of temperature and solvent concentration with respect to PZ mass fraction on solubility and diffusivity measurement is presented in Figs. 3(c), 3(d) respectively.

#### 2. Determination of the Overall Rate Kinetics of Aqueous Blend of (AMP+PZ)

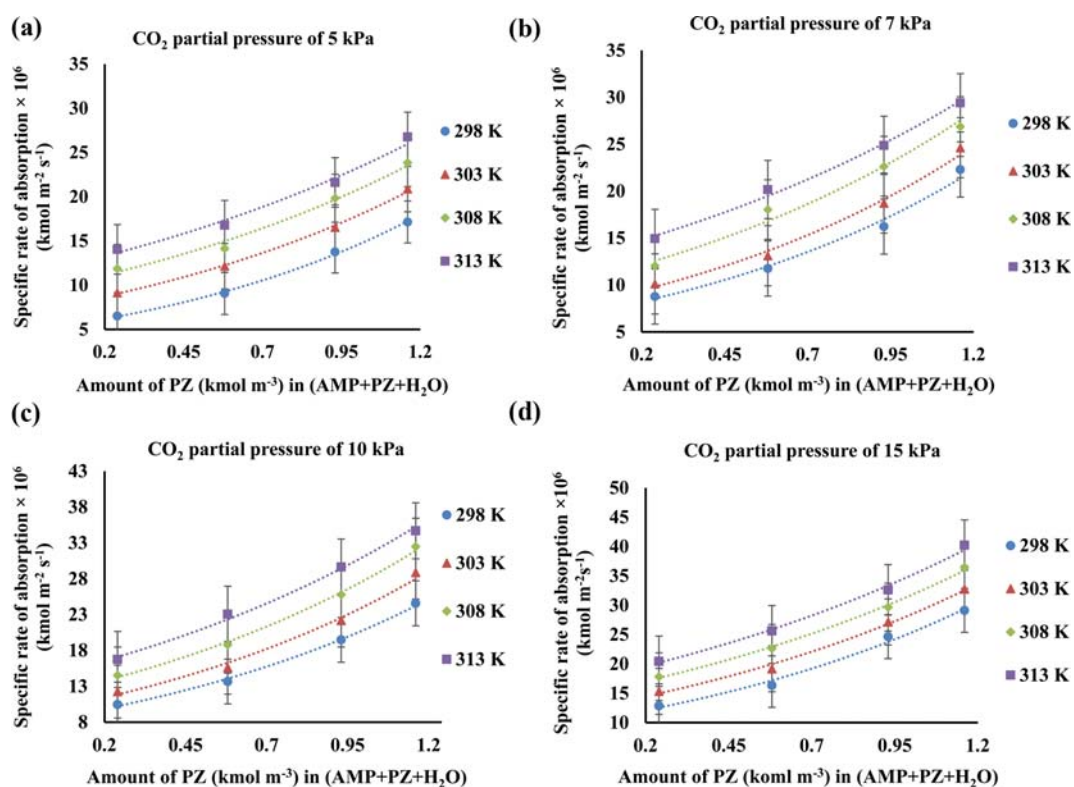
The absorption rate of CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O) blend is ob-

**Table 3. Experimental results for the absorption of CO<sub>2</sub> into aqueous (AMP+PZ) blend in the wetted wall column**

[AMP] (kmol m <sup>-3</sup> )	[PZ] (kmol m <sup>-3</sup> )	P <sub>1</sub> (kPa)	T (K)	t <sub>c</sub> (s)	k <sub>L</sub> ×10 <sup>5</sup> (m s <sup>-1</sup> )	N <sub>A</sub> ×10 <sup>6</sup> (kmolm <sup>-2</sup> s <sup>-1</sup> )	Model projected N <sub>A</sub> ×10 <sup>6</sup> (kmolm <sup>-2</sup> s <sup>-1</sup> )
3.12	0.24	5	298	0.72	3.44	6.52	6.418
3.12	0.24	7	298	0.71	3.47	8.78	8.247
3.12	0.24	10	298	0.71	3.47	10.45	10.329
3.12	0.24	15	298	0.70	3.5	12.85	12.006
3.12	0.24	5	303	0.68	3.82	9.14	8.846
3.12	0.24	7	303	0.68	3.83	10.12	10.743
3.12	0.24	10	303	0.67	3.84	12.25	12.917
3.12	0.24	15	303	0.66	3.85	15.32	14.750
3.12	0.24	5	308	0.64	4.32	11.88	11.144
3.12	0.24	7	308	0.62	4.37	12.06	13.103
3.12	0.24	10	308	0.62	4.40	14.52	15.370
3.12	0.24	15	308	0.60	4.47	17.82	17.356
3.12	0.24	5	313	0.57	5.22	14.05	13.306
3.12	0.24	7	313	0.57	5.22	14.96	15.326
3.12	0.24	10	313	0.56	5.27	16.74	17.685
3.12	0.24	15	313	0.55	5.32	20.45	19.826
2.80	0.58	5	298	0.77	3.17	9.07	9.056
2.80	0.58	7	298	0.77	3.23	11.76	11.365
2.80	0.58	10	298	0.76	3.26	13.66	14.153
2.80	0.58	15	298	0.74	3.29	16.34	17.007
2.80	0.58	5	303	0.72	3.63	12.15	11.750
2.80	0.58	7	303	0.72	3.66	13.12	14.118
2.80	0.58	10	303	0.70	3.69	15.58	16.998
2.80	0.58	15	303	0.69	3.72	19.18	20.006
2.80	0.58	5	308	0.68	3.97	14.18	14.304
2.80	0.58	7	308	0.68	3.99	18.04	16.733
2.80	0.58	10	308	0.67	4.00	18.78	19.706
2.80	0.58	15	308	0.66	4.02	22.66	22.869
2.80	0.58	5	313	0.60	4.83	16.78	16.721
2.80	0.58	7	313	0.60	4.83	20.18	19.213
2.80	0.58	10	313	0.58	4.91	23.05	22.278
2.80	0.58	15	313	0.57	4.96	25.65	25.595
2.80	0.93	5	298	0.84	2.95	13.76	13.766
2.80	0.93	7	298	0.84	2.97	16.23	16.556
2.47	0.93	10	298	0.82	3.0	19.48	20.070
2.47	0.93	15	298	0.80	3.04	24.65	24.136
2.47	0.93	5	303	0.79	3.41	16.54	16.720
2.47	0.93	7	303	0.78	3.43	18.73	19.572
2.47	0.93	10	303	0.77	3.45	27.15	27.399
2.47	0.93	15	303	0.76	3.47	28.85	27.399

Table 3. Continued

[AMP] (kmol m <sup>-3</sup> )	[PZ] (kmol m <sup>-3</sup> )	P <sub>1</sub> (kPa)	T (K)	t <sub>c</sub> (s)	k <sub>L</sub> ×10 <sup>5</sup> (m s <sup>-1</sup> )	N <sub>A</sub> ×10 <sup>6</sup> (kmolm <sup>-2</sup> s <sup>-1</sup> )	Model projected N <sub>A</sub> ×10 <sup>6</sup> (kmolm <sup>-2</sup> s <sup>-1</sup> )
2.47	0.93	5	308	0.76	3.79	19.84	19.534
2.47	0.93	7	308	0.76	3.75	22.65	22.452
2.47	0.93	10	308	0.75	3.71	25.78	26.151
2.47	0.93	15	308	0.73	3.76	29.67	30.525
2.47	0.93	5	313	0.70	4.24	21.62	22.219
2.47	0.93	7	313	0.69	4.27	24.88	25.195
2.47	0.93	10	313	0.69	4.27	29.63	28.987
2.47	0.93	15	313	0.68	4.31	32.63	33.515
2.25	1.16	5	298	0.85	2.79	17.15	17.953
2.25	1.16	7	298	0.85	2.8	22.31	21.062
2.25	1.16	10	298	0.84	2.81	24.56	25.054
2.25	1.16	15	298	0.83	2.82	29.12	29.916
2.25	1.16	5	303	0.82	3.22	20.87	21.081
2.25	1.16	7	303	0.82	3.23	24.63	24.251
2.25	1.16	10	303	0.80	3.25	28.85	28.336
2.25	1.16	15	303	0.79	3.27	32.75	33.352
2.25	1.16	5	308	0.79	3.41	23.85	24.072
2.25	1.16	7	308	0.79	3.46	26.88	27.304
2.25	1.16	10	308	0.77	3.5	32.48	31.481
2.25	1.16	15	308	0.76	3.52	36.46	36.651
2.25	1.16	5	313	0.73	4.03	26.76	26.926
2.25	1.16	7	313	0.72	4.06	29.42	30.220
2.25	1.16	10	313	0.72	4.06	34.68	34.490
2.25	1.16	15	313	0.70	4.11	40.24	39.814

Fig. 4. (a)-(d) Specific rate of absorption of CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O) at different temperatures.

**Table 4. Kinetic data for the absorption of CO<sub>2</sub> into aqueous solution of (AMP+PZ)**

T (K)	[AMP] (kmol m <sup>-3</sup> )	[PZ] (kmol m <sup>-3</sup> )	$\alpha$ , CO <sub>2</sub> loading (kmol/kmol)	$k_{ov}$ (s <sup>-1</sup> )	Ha (Hatta number)	E
298	3.12	0.24	0.0825	16215	96	96
303	3.12	0.24	0.0855	22008	108	108
308	3.12	0.24	0.0878	26790	116.2	116.2
313	3.12	0.24	0.0882	32028	120	120
298	2.80	0.58	0.0855	36522	152.4	152.4
303	2.80	0.58	0.0879	49626	168.1	168.1
308	2.80	0.58	0.0884	60031	180	180
313	2.80	0.58	0.090	71232	183.3	183.3
298	2.47	0.93	0.0875	57420	195.6	195.6
303	2.47	0.93	0.091	78032	219.8	219.8
308	2.47	0.93	0.0933	94215	230.5	230.5
313	2.47	0.93	0.0945	111557	247.9	247.9
298	2.25	1.16	0.092	71801	219	219
303	2.25	1.16	0.0942	96688	237.8	237.8
308	2.25	1.16	0.0972	116672	274.3	274.3
313	2.25	1.16	0.0982	138057	281.2	281.2

served and presented in Table 3. Here PZ acts as a rate accelerator towards absorption of CO<sub>2</sub> using the amine blend. Table 3 represents the calculated rates of absorption of CO<sub>2</sub> into four (AMP+PZ+H<sub>2</sub>O) blends holding the mass proportion of (28/2, 25/5, 22/8 and 20/10) at 298, 303, 308 and 313 K by the wetted wall column absorber. Table 3 shows that the specific rate of absorption escalates steadily through a gradual increase in reaction temperature together with an increase in amount of activator PZ into (AMP+PZ+H<sub>2</sub>O).

The influence of temperature and blending mass combination over specific rate of absorption of CO<sub>2</sub> is presented in Figs. 4(a)-4(d) at different CO<sub>2</sub> partial pressure of 5, 7, 10 and 15 kPa. It can be concluded that the rate of absorption rises steadily with rise in temperature at constant PZ mass concentration and CO<sub>2</sub> partial pressure. The reason behind this behavior is that due to increasing temperature, the reaction rate constant and diffusivity of CO<sub>2</sub> also increase. Similarly, with growing mass concentration of PZ into the blend at fixed temperature, the flux is increased, and this enhancement is resulting from the reaction of more free and active amine in the aqueous blend with CO<sub>2</sub>.

The Hatta number (Ha) is higher than 3 in all the cases, and the

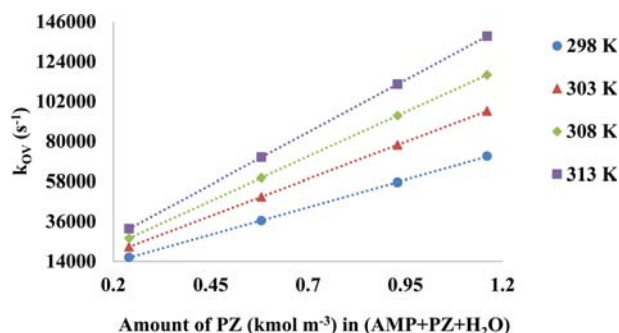
enhancement factor in the instantaneous reaction region ( $E_{in}$ ) is considerably higher than Ha, i.e., the condition of ( $3 < Ha < E_{in}$ ) is fulfilled and both the values are presented in Table 4. The enhancement factor (E) is equal to (Ha) and the corresponding values are illustrated in Table 4.

The overall reaction rate constant,  $k_{ov}$  is determined using Eq. (7) and the obtained values are presented in Table 4. A plot of  $k_{ov}$  vs. mass fraction of PZ into (AMP+PZ+H<sub>2</sub>O) is displayed in Fig. 5.

Clearly, from Fig. 4, with an increasing temperature and/or PZ concentration in aqueous blend the  $k_{ov}$  value increases gradually. The obtained  $k_{ov}$  values of the present study have been equated with the previously reported values of Sun et al. [20] with the same blending composition but different mass ratio combination, and the values are too large as compared to their result within the temperature variation of (303-313) K. The kinetics parameters,  $k_{2,PZ}$  and  $k_{2,AMP}$  have been determined from Eq. (7) using the  $k_{ov}$  values and these set of data have been solved via simultaneous linear algebraic equation for two variables and are incorporated in Table 5.

The second-order rate constant  $k_{2,PZ}$  value was determined and the Arrhenius plot for the rate constant over temperature effect is offered in Fig. 6(a); the resulting values ( $k_{2,PZ}$ =60403, 81925, 98591 and 116521) are marginally larger than that of Bishnoi and Rochelle [28] and these are too large as compared with values found by Xu et al. [48] at the temperature of 298-313 K.

The second-order reaction rate constant  $k_{2,AMP}$  on behalf of the reaction of CO<sub>2</sub> with aqueous AMP solution was also determined

**Fig. 5. Overall reaction rate constants ( $k_{ov}$ ) for the reaction of CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O).****Table 5. Kinetic constants of aqueous mixture of (AMP+PZ)**

Temperature (K)	$k_{2,AMP}$ (m <sup>3</sup> kmol <sup>-1</sup> s <sup>-1</sup> )	$k_{2,PZ}$ (m <sup>3</sup> kmol <sup>-1</sup> s <sup>-1</sup> )
298	560	60403
303	750	81925
308	1010	98591
313	1300	116521

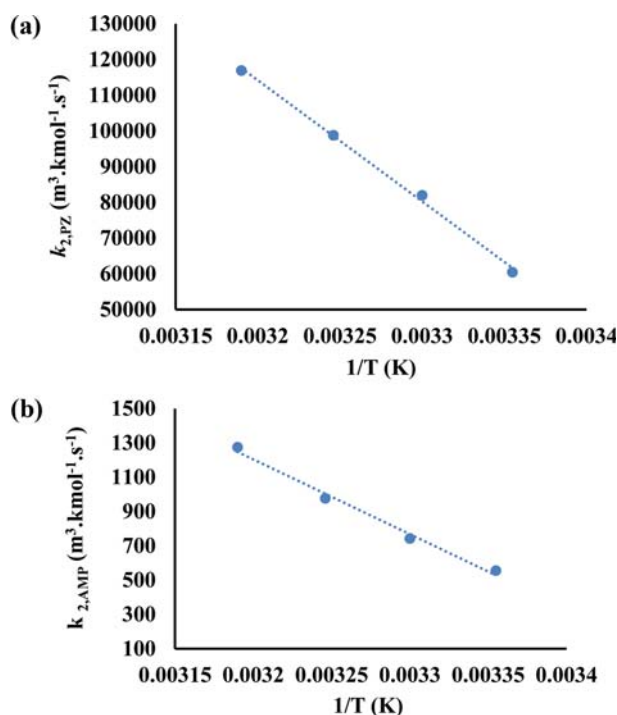


Fig. 6. (a) The Arrhenius plot of the second-order rate constant  $k_{2,PZ}$  for the reaction of CO<sub>2</sub> with PZ as a function of temperature. (b) The Arrhenius plot of the second-order rate constant  $k_{2,AMP}$  for the reaction of CO<sub>2</sub> with AMP as a function of temperature.

and are expressed through Arrhenius equation around the temperature variation of 298–313 K (Fig. 6(b)).

The temperature dependency of the second-order rate constants values,  $k_{2,PZ}$  and  $k_{2,AMP}$  are represented by the following expression:

$$\ln(k_{2,PZ}/(\text{m}^3\text{kmol}^{-1}\text{s}^{-1})) = 32.52 - \frac{6433.73}{(T/K)} \quad (14)$$

$$\ln(k_{2,AMP}/(\text{m}^3\text{kmol}^{-1}\text{s}^{-1})) = 23.69 - \frac{5172.2}{(T/K)} \quad (15)$$

The activation energy for these  $k_{2,PZ}$  and  $k_{2,AMP}$  was estimated to be 53.49 and 43.0 kJ mol<sup>-1</sup>, respectively. These values can highly be compared with the value reported by Bishnoi and Rochelle [28] with the activation energy of 53.4 kJ mol<sup>-1</sup> for  $k_{2,PZ}$  and Saha et al. [37] holding the value of 43.0 kJ mol<sup>-1</sup> for  $k_{2,AMP}$ . The condition stated in Eq. (8) during CO<sub>2</sub> absorption into amine blend (PZ+AMP+H<sub>2</sub>O) was found satisfactory; hence it falls into the fast pseudo-first-order reaction regime. Fig. 7(a) represents a comparative assessment of the Arrhenius plot of  $k_{2,PZ}$  for aqueous PZ solution attained in this experimental investigation along with the value reported in some previous literatures [20,28,48–50]. The observed values of  $k_{2,PZ}$  in the present experimental study show good agreement with the reported values by Bishnoi and Rochelle [28] and Zhang et al. [50]. The experimental and model projected (Matlab-rstool) specific rates of absorption matched and the parity plot is presented in Fig. 7(b). The model projected values of specific rate of absorption of CO<sub>2</sub> into amine blend of (AMP+PZ+H<sub>2</sub>O) are presented in Table 3.

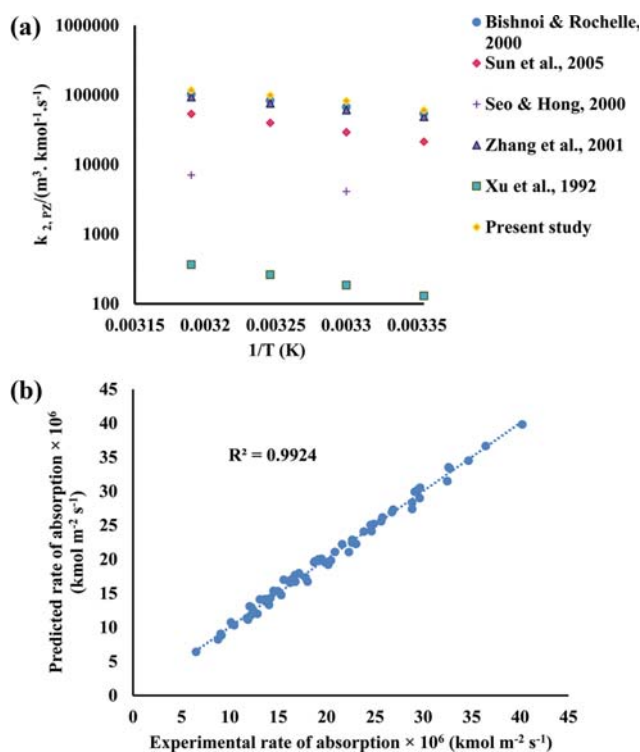


Fig. 7. (a) The Arrhenius plot of the second-order rate constant  $k_{2,PZ}$  for the reaction of CO<sub>2</sub> with PZ as a function of temperature (some previous studies). (b) Parity plot of model predicted rates and experimental rates of absorption of CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O).

### 3. Enhancement of CO<sub>2</sub> Absorption Using (AMP+PZ+H<sub>2</sub>O)

Table 3 represents the experimental and model estimated specific rate of absorption of CO<sub>2</sub> into four different mass proportions such as 28/2, 25/5, 20/10 and 20/10 via the temperature variant of 298–313 K and 30 wt% AMP at 313 K. Table 6 demonstrates that the specific rate of absorption was significantly enhanced by adding up of a small quantity of PZ into the aqueous AMP solution. The specific rate of absorption data was compared with the previous published data of Samanta and Bandyopadhyay [21]. They performed the absorption of CO<sub>2</sub> into (28 mass% AMP+2 mass% PZ), (25 mass% AMP+5 mass% PZ), (22 mass% AMP+8 mass% PZ), and 30 wt% AMP across the temperature deviation of 298–313 K and CO<sub>2</sub> partial pressure variation of 5–15 kPa in a wetted wall column. Their reported value of specific rate of absorption data was within the range of 6.33–31.60 kmol m<sup>-2</sup> s<sup>-1</sup>, which is highly comparable with the present study with the value ranging from 6.52–40.24 kmol m<sup>-2</sup> s<sup>-1</sup>. It is noticed from Table 6 that the enhancement factors for absorption of CO<sub>2</sub> into aqueous solution of 30 wt% AMP (28 wt% AMP+2 wt% PZ), (25 wt% AMP+5 wt% PZ), (22 wt% AMP+8 wt% PZ) and (20 wt% AMP+10 wt% PZ) at CO<sub>2</sub> partial pressure of 5 kPa and temperature of 313 K are around 43.67, 120, 183.3, 247.9 and 281.2, respectively. Hence, by substituting 2 wt% of AMP with 2 wt% PZ, the enhancement factor was found to be increased by around 175%. The resultant enhancement factor augmented further to the tune of 52.7% when an additional 3 wt% of AMP was substituted by an exact quantity of PZ. Again,

**Table 6.** Enhancement factor for the absorption of CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O) as a function of CO<sub>2</sub> interfacial concentration

T (K)	[AMP] (kmol m <sup>-3</sup> )	[PZ] (kmol m <sup>-3</sup> )	[CO <sub>2</sub> ] <sub>i</sub> × 10 <sup>3</sup> kmol m <sup>-3</sup> at 5 kPa	E at 5 kPa	E <sub>∞</sub> at 5 kPa	[CO <sub>2</sub> ] <sub>i</sub> × 10 <sup>3</sup> kmol m <sup>-3</sup> at 15 kPa	E at 15 kPa	E <sub>∞</sub> at 15 kPa
298	3.12	0.24	1.284	96	2499	3.85	94.2	833
303	3.12	0.24	1.18	108	2756	3.53	106.9	909
308	3.12	0.24	1.06	116.2	3023	3.193	112.3	1005
313	3.12	0.24	1.0	120	3177	3.02	117.5	1053
298	2.80	0.58	1.323	152.4	2442	3.97	145.8	814
303	2.80	0.58	1.216	168.1	2651	3.65	164	884
308	2.80	0.58	1.08	180	2984	3.23	177.7	998
313	2.80	0.58	1.02	183.3	3129	3.05	178.5	1047
298	2.47	0.93	1.34	195.6	2426	4.01	190	811
303	2.47	0.93	1.13	219.8	2635	3.69	216	879
308	2.47	0.93	1.103	230.5	2937	3.308	232.3	980
313	2.47	0.93	1.03	247.9	3116	3.09	243.8	1040
298	2.25	1.16	1.35	219	2412	4.65	216.7	701
303	2.25	1.16	1.24	237.8	2627	3.711	248	878
308	2.25	1.16	1.13	274.3	2876	3.39	265.7	959
313	2.25	1.16	1.04	281.2	3099	3.12	275.7	1033

substituting an extra 3 wt% of AMP with PZ improved the enhancement factor by an additional 35.2%. A further substitution of 2 wt% AMP with same quantity of PZ results in the enhancement factor by added 13.4%. So the replacement of a small magnitude of PZ with AMP into (AMP+PZ+H<sub>2</sub>O), a considerable upsurge of enhancement factor was witnessed. This result is experienced because of the higher concentration of AMP appearing in the blend, which promoted the formation of PZ-carbamate and PZ-dicarbamate ions. It is also perceived that the initial enhancement factor is very high and these values are gradually decreasing. The reason might be due to the decrease in diffusivity with increase in amount of PZ and decrease in AMP concentration in the aqueous amine blend. Table 6 also illustrates the influence of CO<sub>2</sub> interfacial concentration [CO<sub>2</sub>]<sub>i</sub> on the enhancement factor and clearly obtains that lower CO<sub>2</sub> interfacial concentration (lower partial pressure) has a greater value than the higher one (higher partial pressure). The justification behind this result, as the CO<sub>2</sub> interfacial concentration decreases, the influence of physical absorption on overall CO<sub>2</sub> absorption reduces and the impact of chemical reactions among CO<sub>2</sub> and (AMP+PZ+H<sub>2</sub>O) increases.

## CONCLUSION

The rate of absorption and reaction rate kinetics of CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O) were inspected using a wetted wall column along with temperature variation of 298–313 K and CO<sub>2</sub> partial pressure range of 5–15 kPa. Densities, viscosities, solubilities and diffusivities of the aqueous blended system of (AMP+PZ) were determined. The N<sub>2</sub>O analogy was employed to assess the physical solubility and diffusivity of CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O) blended system. Significant enhancement of the specific rate of CO<sub>2</sub> absorption and enhancement factor was achieved by means of adding up of little measure of PZ mass fraction into aqueous solution of AMP. Addition of small quantities of PZ into aqueous solution of AMP, e.g.,

(28 wt% AMP+2 wt% PZ), considerably enhanced the rate of CO<sub>2</sub> absorption. Among the four mass percentage combinations of (AMP+PZ) blend, (20 wt% AMP+10 wt% PZ) showed the highest specific rate of absorption and enhancement factor. The kinetics of CO<sub>2</sub> into (AMP+PZ+H<sub>2</sub>O) was obtained considering the reaction of CO<sub>2</sub> with AMP in parallel with a reaction between CO<sub>2</sub> and PZ followed by Zwitterion mechanism. Based on the fast pseudo-first-order reaction regime for the CO<sub>2</sub> absorption, the overall pseudo first-order reaction rate constants were calculated from the kinetic parameters. The second-order reaction rate constants estimated through the reaction of CO<sub>2</sub> with PZ were in an excellent agreement with the results reported by other researchers. The experimental and model projected specific rate of absorption were compared and the parity diagram shows the model calculated rate of absorption values are in excellent agreement with experimentally obtained value with AAD of about 4.86%. The present study of the rate of absorption performance and kinetics measurement of (AMP+PZ+H<sub>2</sub>O) concludes that PZ activated aqueous AMP might be a prospective alternative towards enhancement of absorption of CO<sub>2</sub> as compared to a single aqueous AMP solution.

## ACKNOWLEDGEMENT

The authors acknowledge the financial support from Ministry of Science and Technology, West Bengal Government vide project reference no: 827(Sanc.)/ST/P/S&T/5G-2/2010 to perform the current piece of genuine research assignment successfully.

## NOMENCLATURE

- o.d. : external diameter of wetted wall absorber [m]
- D : diffusivity of CO<sub>2</sub> in solution [m<sup>2</sup> s<sup>-1</sup>]
- E<sub>∞</sub> : enhancement factor in instantaneous reaction section
- H : Henry law constant [kPa m<sup>3</sup> kmol<sup>-1</sup>]

Ha : Hatta number  
 $k_L$  : liquid phase mass transfer coefficient  
 $k_{OV}$  : overall reaction rate constant [ $s^{-1}$ ]  
 $L$  : solvent flow rate [ $m^3 s^{-1}$ ]  
 $N_A$  : specific absorption rate [ $kmol m^{-2} s^{-1}$ ]  
 $P_1$  : CO<sub>2</sub> partial pressure [kPa]  
 $t_c$  : contact time [s]  
 $T$  : temperature [K]

### Greek Letters

$\alpha$  : CO<sub>2</sub> loading in amine blend, kmol of CO<sub>2</sub>/kmol of amine  
 $\mu$  : viscosity [ $kg m^{-1} s^{-1}$ ]  
 $\rho$  : density [ $kg m^{-3}$ ]

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