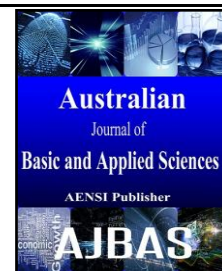




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Reactive Absorption of Carbon Dioxide into Piperazine Activated Diethanolamine Solutions

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ABSTRACT

The use of alkanolamines for the removal of acid gases from natural and flue gases is widely used in the industry. The most commonly used amines are Monoethanolamine (MEA), Diethanolamine (DEA), and Methyldiethanolamine (MDEA). Blending these amines with rate promoters such as Piperazine to enhance their absorption rates has become a common practice in the industry. In this work, Kinetics of CO₂ reaction with blends of diethanolamine (DEA) and Piperazine (PZ) was investigated using a stirred cell reactor. The reaction temperature ranged from 303K to 323K and the total amine concentration was varied from 0.5 to 2 molar. The increase in promoter concentration resulted in the expected increase in the absorption rates. The overall reaction can be regarded as a reaction between CO₂ and DEA in parallel with the reaction of CO₂ with PZ. The rate constant for the blended amine (DEA/PZ) was determined and the effect of temperature was assessed using Arrhenius plot.

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INTRODUCTION

There is a broad consensus that climate change is occurring due to the accumulation of greenhouse gases (GHGs) in the atmosphere. Carbon dioxide (CO₂) is the most significant of these GHGs (IPCC 2005). CO₂ capture from natural and flue gases can be accomplished through various means such as: low-temperature distillation, membranes, adsorption and absorption. Low temperature distillation has considerable use in the purification and liquefaction of carbon dioxide. However, carbon dioxide cannot be efficiently condensed from atmospheric pressure flue gases. Producing a carbon dioxide-rich stream with high purity from flue gases using membrane or pressure swing adsorption (PSA) processes generally requires either a high degree of compression or deep vacuum or multiple separation steps; the associated costs are very high.

Physical absorption processes are temperature and pressure dependent, with absorption occurring at high pressures and low temperatures. Such processes are typically used for carbon dioxide separation when partial pressures of carbon dioxide are high. For low CO₂ partial pressure a significant amount of

compression is needed. Thus, a significant energy penalty will be incurred making the process uneconomical.

Chemical absorption is well suited for carbon dioxide recovery from flue gases. Low temperature amine scrubbing is the most likely technology deployed of such systems. Such scrubbing technology has been widely used in the oil/gas sector for the separation of CO₂ from natural gas; the chemical reaction between carbon dioxide and amines greatly enhances the driving force for the separation, even at low carbon dioxide partial pressures. The cost of this technology is relatively insensitive to the feed of carbon dioxide content. Consequently, chemical absorption with amines provides the most cost-effective means of removing carbon dioxide from flue gases in a single step.

An amine scrubber as depicted by Fig.1.comprises two separate units, the absorber where the CO₂-lean solvent reacts with the flue gas CO₂ at temperatures typically between 40 and 60°C and the stripper where the CO₂-rich solvent is heated to 100 - 140°C with steam as the strip gas near to atmospheric pressure

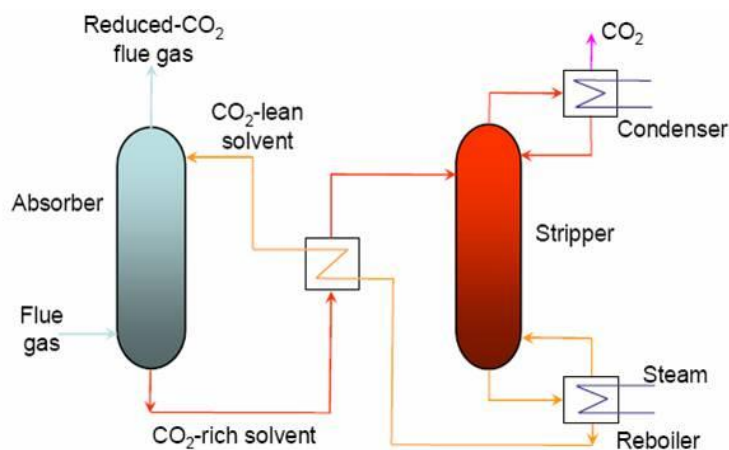


Fig. 1: Simplified Schematic Diagram of an Amine Scrubber.

Industry standard approaches to the design of amine absorption systems involve considerable uncertainty regarding the calculation of the required packing height in the absorber and stripper. This uncertainty is resolved in the gas processing industry and the chemical engineering design companies by the use of empirical methods supported by substantial experience in the design of many hundreds if not thousands of commercial operating units which treat gaseous hydrocarbon, hydrogen, CO, H₂S and CO₂ streams usually, however, without the presence of large concentrations of oxygen such as would be found with power plant flue gas.

In recent years with the development of flow sheet simulation packages, the design of amine units is becoming more certain. However, the majority of these packages still require the concept of the equilibrium stage and a corresponding height equivalent to an equilibrium stage (HETP) to deduce a required height of packed column. In the case of absorption with chemical reaction (such as amines/CO₂), these approaches are not theoretically valid. Their use has persisted however because of their simplicity and the large amount of operational data available to correlate performance with calculation. With the advent of high speed personal computers new methods have been developed which are based on reaction kinetic approaches coupled with fundamental mass transfer theories. These methods treat the absorber as a chemical reactor with complex hydrodynamic considerations to deal with the mass transfer issues. The notion of equilibrium stages and an HETP is no longer necessary.

Amine-based solvents have been enhanced over the years (Rojey and Torp, 2005), such that primary (Monoethanolamine (MEA) & Diglycolamine (DGA)), secondary (Diethanolamine (DEA) & Diisopropanolamine (DIPA)) and tertiary (Methyldiethanolamine (MDEA) & Triethanolamine (TEA)) variants are available through different suppliers, many of which include special proprietary additives to improve performance and other characteristics. The choice of a particular

alkanolamine is primarily dictated by the requirements of the specific application. With the exception of a few, these amines have a maximum sorption capacity of 1 mole of CO₂ to two moles of amines. Liquid tertiary amines and amidines have shown a higher sorption capacity with a ratio of 1:1 molar (Benamor *et al.* 2008), thereby reducing the volume of amine, but the reaction rate is much slower. Amine blends have been used to compensate for this difference in order to reduce regeneration and recirculation costs and increase CO₂ loading capacity.

The use of Piperazine as an activator in conventional amine systems for acidic gases removal has increasingly been reported in the literature. This is, because of its high absorption capacity, high selectivity, and low regeneration energy. Bisnhoi and Rochelle [2000] used a wetted wall contactor to measure the kinetics of the reaction within a temperature range from 298 K to 333 K and 0.2 M aqueous solution. They reported that Piperazine (PZ) could directly react with CO₂ to form piperazinecarbamate following a second-order reaction. Zhang *et al.* (2001) investigated the rate of absorption using a disc column within 303 to 343 K in a 3 molar concentration PZ-MDEA aqueous solution and varying MDEA/PZ ratios. Derks *et al.* (2010) reported new experimental equilibrium data on the solubility of carbon dioxide into aqueous solutions of N-methyldiethanolamine (MDEA) and piperazine (PZ). His data as well as those reported in the literature were fairly well correlated using Fürst and Renon equation of state. Rochelle *et al.* (2011) studied a new process that uses piperazine (40 wt% PZ) with regeneration at 150 °C by a two-stage flash as a substitute to the conventional 30wt % MEA scrubbing process. He claimed that Piperazine can be used up to 150 °C without significant thermal degradation, it is resistant to oxidative degradation and has less volatility than MEA, and is not corrosive to stainless steel.

The removal of acid gases such as CO₂ and H₂S from natural and refinery gases is an important

industrial process. The use of alkanolamine-based solvents such as MEA, DEA, and MDEA is still the choice in gas treating technology. The design and analysis of separation processes involving aqueous solutions of such species require accurate knowledge on the kinetics of the reactions involved.

Although the reaction of carbon dioxide with diethanolamine is among one of the most extensively studied reactions in CO₂-alkanolamine systems, significant differences exist between the results obtained by different investigators either in terms of the overall reaction order or in the kinetic rate constant. The only agreement is that the reaction order is unity with respect to CO₂. The order of the reaction with respect to DEA concentration is still under speculations with reported values varying from one to two.

These discrepancies may be related to the different reaction mechanisms being proposed for the interpretation of the experimental data. In addition, the experimental techniques used to generate the kinetic data may also have contributed to the observed differences. Furthermore, studies concerning the variation of the reaction rate constant with temperature are still insufficient. The available data in the open literature are very limited, Blanc and Demarais (1984) measured the kinetics of the reaction at a temperature range 293-333 K for amine concentration varying from 0.005 to 4 mol/L. However, he used a non-zwitterion based mechanism to interpret his data. Rinker *et al.* (1996) studied a wider temperature range from 293-343 K and amine concentration from 0.25 to 2.8 mol/L. Blauwhoff *et al.* [1984], by applying the Zwitterion mechanism originally proposed by Caplow (1968) and reintroduced to chemical engineering literature by Dankwerts (1970), showed that most of the previous

work could be understood according to this mechanism. Versteeg *et al.* (1988) critically reviewed all previous work and concluded that at 298 K the kinetics of DEA are well established and in line with the Zwitterion mechanism. However, the influence of temperature is scarcely correctly studied which makes additional contributions still needed for a better understanding of the reaction kinetics especially that most of the published work in the open literature does not include raw absorption data, which makes the analysis of the available kinetic data using different mechanisms a tedious task if not impossible. Furthermore, the contribution of the carbamate formation reaction, which is the most important step in systems involving primary and secondary amines, is still scarce in the literature.

In this work, additional data on kinetics of the reaction between CO₂ and DEA in aqueous solutions are presented. We measured the absorption rate of CO₂ into aqueous DEA at different pressures and a wide range of amine concentration using a laboratory stirred cell reactor. The temperature was chosen in such a way to cover a range of typical industrial absorption columns that is 293 to 323 K.

Reaction mechanism:

Different reaction mechanisms were proposed to analyze the absorption data of CO₂ in aqueous DEA solutions. The generally accepted mechanism is the one originally proposed by Caplow (1968). This mechanism involves the formation of an intermediate zwitterion followed by the removal of a proton by a base B. As a result; carbamate ion is formed from the reaction between CO₂ and primary or secondary alkanolamines. For the secondary amine DEA, its reaction with CO₂ can be described as follows:



The formation of carbamate proceeds as follows:
Formation of zwitterion



Removal of the proton by a base B



Where the base B, could be the amine itself water molecules, or hydroxyl ions. In aqueous solutions, the corresponding reactions are as follows:



Assuming quasi-steady state condition for the zwitterion concentration, the overall forward reaction rate is given by the following relationship:

$$R_{\text{CO}_2\text{-DEA}} = \frac{k_2 [\text{CO}_2] [\text{DEA}]}{1 + \frac{k_{-1}}{k_{\text{H}_2\text{O}} [\text{H}_2\text{O}] + k_{\text{OH}^-} [\text{OH}^-] + k_{\text{RRNH}} [\text{DEA}]}} \quad (7)$$

Or in a general form

$$R_{CO_2, RR, NH} = -k_1 [CO_2] [DEA] / \left(1 + \frac{k_1}{\sum k_b [B]} \right) \quad (8)$$

Beside the reaction between CO₂ and DEA to form carbamate, other parallel reactions take place in the aqueous medium. The first reaction to be considered is the CO₂ hydration according to the following scheme:



This reaction obeys a first order law with respect to CO₂ with a rate constant of $k_{H_2O} = 0.026 s^{-1}$ at 298 K Pinsent *et al.* (1956). Due to its smaller rate, the contribution of this reaction to the overall reaction rate is insignificant and is usually neglected in the overall rate expression. The other reaction, which is considered important, is the bicarbonate formation as shown by the following equation:



This reaction can enhance mass transfer even at lower concentrations of hydroxyl ion as indicated by Blauwhoff *et al.* (1984). The forward rate of reaction firstly given by Pinsent *et al.* (1956) is described as follows:

$$R_{CO_2, OH^-} = -k_{OH}^* [CO_2] [OH^-] \quad (11)$$

Where,

$$\log_{10} k_{OH}^* = 13.635 - 2895/T \quad m^3 \cdot kmol^{-1} \cdot s^{-1} \quad (12)$$

Taking into account Equations 7 and 11, the net effect of reactions involved in CO₂ absorption by an aqueous solution of DEA becomes

$$R_{CO_2} = R_{CO_2, DEA} + R_{CO_2, OH^-} \quad (13)$$

Thus,

$$R_{CO_2} = \left(\frac{k_1 [CO_2] [DEA]}{1 + \frac{k_1}{(k_{H_2O} [H_2O] + k_{OH}^- [OH^-] + k_{RR, NH} [DEA])}} + k_{OH}^* [CO_2] [OH^-] \right) \quad (14)$$

In this case, the overall reaction rate is presented by the followings:

$$k_{ov} = k_{app} + k_{OH}^- [OH^-] \quad (15)$$

Where k_{app} is the apparent rate of the reaction calculated as follows:

$$k_{app} = \frac{[DEA]}{\frac{1}{k_2} + \frac{1}{k_2 \frac{k_2 k_{H_2O}}{k_{-1}} [H_2O] + \frac{k_2 k_{OH}^-}{k_{-1}} [OH^-] + \frac{k_2 k_{DEA}}{k_{-1}} [DEA]}} \quad (16)$$

Mass transfer with chemical reaction:

The experimental results of this work were analysed using the theory of mass transfer with chemical reaction. The data presented in this work have been obtained at conditions where the mathematical treatment of the problem was simplified assuming a pseudo-first-order assumption for kinetics. In this case, the concentration of the amine across the cross section of the liquid boundary layer was assumed to be uniform. Thus, transforming the second-order reaction expression of carbon dioxide with amine into an approximated first-order expression. Hence, For piperazine:

$$\begin{aligned} R_{CO_2} &= k_2 ([AM]) \{CO_2 - CO_2^*\} \\ R_{CO_2} &= k_1 \{CO_2 - CO_2^*\} \end{aligned} \quad (17)$$

where [CO₂*] is the equilibrium concentration of carbon dioxide. Danckwerts (1970) presents a pseudo-first-order expression for the flux using surface renewal theory:

$$R_{CO_2} = k_1^0 \sqrt{1 + \frac{k_1 [AM] D_{CO_2}}{k_1^0} \left(\frac{P_{CO_2}^l - P_{CO_2}^*}{H_{CO_2}} \right)} \quad (18)$$

At high enhancement factor values, the value of 1 under the square root will have no effect. Thus, Eq. 18 can be even further simplified. Furthermore, in most conducted experiments, the equilibrium partial pressure will approach zero since the solution loading is low. With these simplifications, Eq.18 becomes

$$R_{CO_2} = \sqrt{k_1 [AM] D_{CO_2}} \frac{(P_{CO_2}^l)}{H_{CO_2}} \quad (19)$$

The diffusion coefficient of carbon dioxide in water was calculated using Versteeg and van Swaaij (1988) correlation:

$$D_{\text{CO}_2-\text{H}_2\text{O}} = 2.35 \times 10^{-6} \exp(-2119/T) \text{ m}^2 \text{ s}^{-1} \quad (20)$$

Henry's Law constant for carbon dioxide in pure water correlated by Versteeg and Swaaij (1988) was also used in this work:

$$H_{\text{CO}_2-\text{H}_2\text{O}} = 2.82 \times 10^6 \exp(-2044/T) \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1} \quad (21)$$

The reaction of carbon dioxide with piperazine is a much faster reaction than those of CO₂ with conventional carbamate-forming amines such as MEA or DEA. For this reason, experiments had to be conducted at different conditions than those of the work of Benamor *et al.* (2007). Analysis of the data was simplified significantly by running experiments at three conditions: high gas rates, very low partial pressure and very low solution loading.

To avoid depletion of reactants at the interface, experiments were run at very low partial pressure. This lowered the fluxes and mass transfer in the liquid film. Hence limiting the absorption to almost purely by reaction kinetics. All of the rate experiments in this work were conducted at very low loading and fresh solutions were used during each run so that the equilibrium partial pressure was essentially zero. The rate of absorption was determined from a gas-phase material balance and this was combined with the gas/liquid contact area to determine flux. Eqs.18 and 19 were used to determine the kinetic parameters associated to the reaction of amine-piperazine with carbon dioxide.

Material:

The chemicals used in the investigation were 99% assay Methyldiethanolamine and 98.5% Purity Piperazine obtained from Riedel-de Haën, commercially available carbon dioxide and nitrogen with purity of 99.99% and 99.999%, respectively. Reagecon standard 1M aqueous NaOH and 0.1M HCl solutions were also used. All of these chemicals were used as received. Distilled water was used as the solvent throughout the experiment

Apparatus and methods:

The experiments were carried out in a stirred cell reactor. The operation was batch-wise with respect to the liquid phase. The stirred cell reactor constructed from resistant glass with interfacial area for mass transfer of 76.93 cm². The internal diameter of the reactor was 10 cm with a total volume of about 1800 cm³. The gas and liquid phases were stirred separately using two stirrers. To prevent the formation of vortex, four equidistant baffles were placed inside the reactor. An infrared Rosemount® model 880A CO₂ analyzer was used to measure the amount of carbon dioxide at the exit of the reactor.

For a typical run, the amine solutions was charged into the reactor, stirred and maintained at preset temperature. Then the gas stream of nitrogen

was fed through the reactor continuously to purge out any possible contaminant gas before starting the experiment. Calibrated 5080E Series Brooks mass flow controller measured the flow rate in of the gases. The reaction gas, a mixture of CO₂ and N₂, was mixed in different proportions and pre-saturated with water at the same temperature of the experiment. The outlet CO₂ gas concentration was continuously determined by Rosemount infrared CO₂ analyser and recorded using a computerized data acquisition system. Experiments were repeated for different amine concentrations and temperatures.

RESULTS AND DISCUSSIONS

Experimental data on the absorption of CO₂ in blends of Diethanolamine (DEA) and Piperazine (PZ) reported in the literature are very little. The finding of additional kinetics is very much valuable. In this work, the CO₂ absorption rate into aqueous solutions of mixture DEA and PZ was measured and the experimental results are presented in Fig.1-4. The absorption flux, R_{CO₂}, was analysed using the Eq.18 and Eq.19.

The pseudo-first order reaction regime assumption was verified by calculating Hatta number; $Ha = \sqrt{(k_1 D_{\text{CO}_2} [\text{AM}]) / k_L^2}$. In all cases, $Ha \gg 1$ indicating that the reaction occurred within the liquid film and surface area is the controlling factor. The liquid-side mass transfer coefficient is related to Sherwood equations: $Sh = K_L D_{\text{imp}} / D_{\text{CO}_2}$, and $Sh = a Re^b Sc^c$,

Where a, b, and c are parameters experimentally determined. Schmidt and Reynolds numbers are given by $Sc = \mu / \rho D_{\text{CO}_2}$ and $Re = D_{\text{imp}}^2 (\text{rpm}/60) \rho / \mu$.

where, K_L : Liquid phase mass transfer coefficient, [m².s]

D_{imp} : Diameter of the impeller [m]

μ : Viscosity of the solution [cP]

ρ : Density of the solution [kg/liter]

Using Eq.19, a plot of the flux versus interfacial partial pressure will yield a straight line. Fig.1 shows the results of several temperatures, partial pressures and amine-piperazine concentration (0.9M - 0.1M). The data fit a straight line which passes through the origin as predicted by Eq.19. Fig.2. also represents a comparison of rates of absorption data obtained in this work for DEA 2M solution and mixture of DEA0.5M-PZ 0.5M solution. Fig.3. represents a comparison of rates of absorption data obtained in this work for a solution of total 2M and varying mixture composition, the effect of substituting DEA by PZ is well noticed. Temperature dependence on the rate constant is represented by an Arrhenius plot as shown in Fig.4. An Arrhenius expression obtained from these data can be expressed as $k_1 = k_0 \exp(-E_a / RT)$ where, $k_0 = 4.15 \times 10^3 \text{ m}^3 / \text{kmol s}$, $E_a = 4.22 \text{ kJ/kmol}$, and $R = 8.314 \text{ kJ/kmol K}$.

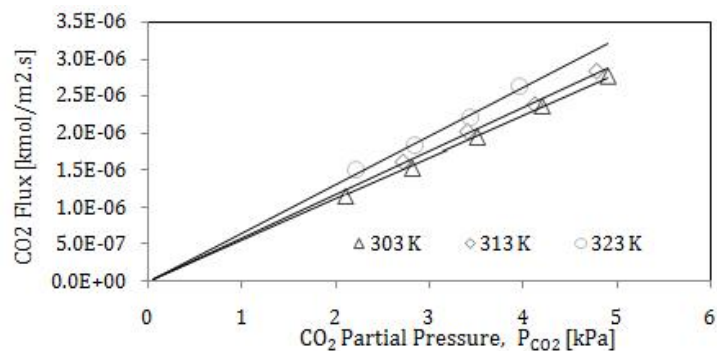


Fig. 1: CO₂ absorption rate into (DEA0.9-PZ0.1M) aqueous solutions.

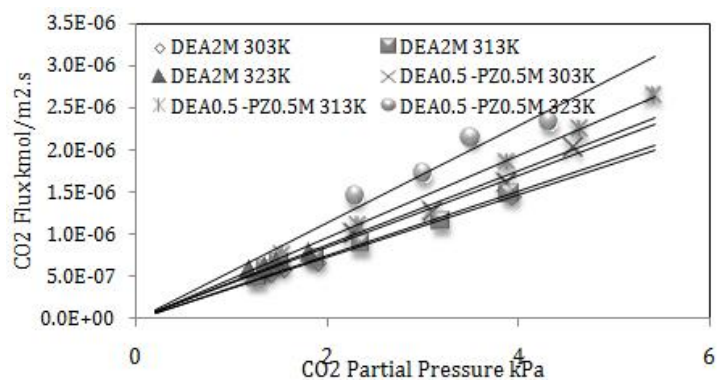


Fig. 2: CO₂ absorption rate into (DEA0.9-PZ0.1M) aqueous solutions.

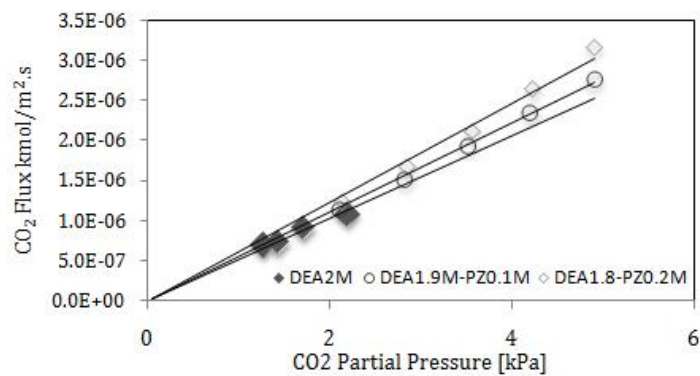


Fig. 3: CO₂ absorption rate into total 2M (DEA-PZ) aqueous solutions at 303K.

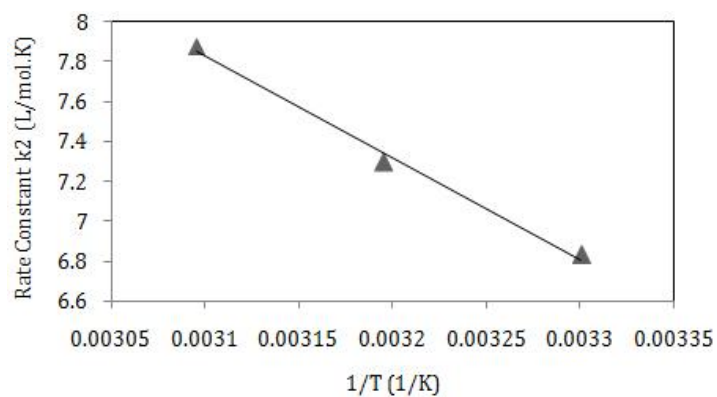


Fig. 4: Second-order rate constant of DEA-PZ and carbon dioxide reaction.

Conclusions:

Additional kinetic data on the CO₂ absorption rate by aqueous blends of diethanolamine (DEA) and piperazine (PZ) were obtained at 303, 313 and 323 K. The total amine concentration was varied from 0.5 to 2 M. From overall kinetics results, it is confirmed that the reaction between CO₂-DEA+PZ is much faster compared to that of CO₂-DEA. It was also shown that overall rate constant, k_{ov} of PZ is higher than that of DEA due to high reactivity of PZ, which is due to its cyclic and diamine characteristics. The temperature effect on the overall rate constant was assessed and expressed using Arrhenius plot as $k_{ov} = k_0 \exp(-E_a/RT)$ where, $k_0 = 4.15 \times 10^3 \text{ m}^3/\text{kmol s}$, $E_a = 4.22 \text{ kcal}$. The kinetics demonstrate that PZ can be an effective promoter for carbon dioxide removal from gas streams.

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