## Chapter 3

# Kinetics and Dissociation Constants (*pK*$_a$) of Polyamines of Importance in Post-Combustion Carbon Dioxide ($CO_2$) Capture Studies

**F. Khalili,[†] A. V. Rayer,[†] A. Henni,[*,†] A. L. L. East,[‡] and P. Tontiwachwuthikul[†]**

**[†]Industrial Systems Engineering and Applied Science, (International Test Centre for Carbon Capture), University of Regina, Regina, SK S4S 0A2, Canada**
**[‡]Department of Chemistry and Biochemistry, University of Regina, Regina, SK S4S 0A2, Canada**
**[*]E-mail: amr.henni@uregina.ca**

Pseudo-first-order overall rate constants for the loss of $CO_2$ via reaction with different types of amines were measured using a stopped-flow technique at 298.15 K. Polyamines and cyclic amines were found to have higher reaction rates than linear primary and secondary amines. Therefore, six aqueous cyclic polyamine solutions were studied at (298.15 to 313.15) K over a concentration range of (20 to 120) mol·m$^{-3}$ using. The overall reaction orders were calculated using the empirical power law kinetics and were found to be fractional in order, for practically all studied cyclic polyamines. The overall rate constants were fitted with the Crooks-Donnellan termolecular rate expression to determine elementary rate constants. In addition, the dissociation constants (*pK*$_a$) were determined using the potentiometric titration method at (298, 303, 313 and 323) K, and predicted using quantum chemistry techniques (IEFPCM continuum solvation model). A trend was found for the variation of the *pK*$_a$ with the addition of different radical groups to the cyclic base molecules. Computational techniques tested for the prediction of *pK*$_a$ involved *B3LYP* and MP2 levels of electronic structure theory, the addition of an explicit water molecule inside the continuum cavity, and a special scaling of

In Recent Advances in Post-Combustion CO2 Capture Chemistry; Attalla, M.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2012.

the cavity radii for the ions. The procedure developed in this study reduced the error found in a previous technique for cyclic amines by 62%.

## 1. Introduction

In order to satisfy environmental combustion standards, acid gases such as $CO_2$ and $H_2S$ must be removed from gaseous streams in refining, and in chemical and gas associated production plants. Natural gas and synthetic fuels such as coal gasification and shale oil cover broad ranges of both acid gas composition and pressure (*1*). The most common solvents used to capture $CO_2$ are the alkanolamines such as the monoethanolamine (MEA), diethanolamine (DEA) and n-methyldiethanol amine (MDEA). These amines are used commercially in post-combustion $CO_2$ capture as aqueous solution or in aqueous organic medium or in combination with aqueous potassium carbonate solutions (*2*).

$CO_2$ capture by chemical absorption using aqueous solution of amine uses absorper abd stripper units. This technology needs to overcome the challenge of reducing the energy, the environmental impact and the capture cost. Finding a better solvent is the path to solve these issues. High cyclic capacity, fast absorption rate, high equilibrium temperature sensitivity and low enthalpy of absorption are some of the factors to be considered in the selection of the best solvent. Both capital and capture costs of $CO_2$ removal depend on the $CO_2$ absorption and desorption rates. Solvents with fast reaction rates can reduce the height of the packing required in both the absorber and stripper. Energy in the stripper can be saved by faster solvents and by achieving a closer equilibrium in the absorber (*3*). Since 1960, various primary, secondary and tertiary amines were studied for their reaction rate with $CO_2$ to find out faster solvents and many studies were published in the literature, and reviewed by Blauwhoff et al. (*4*), Versteeg et al. (*5*), and more recently by Vaidya et al. (*6*) In this work, a screening study was performed on different types of amines (primary, secondary, tertiary, cyclic and polyamines) using a well established stopped-flow procedure in order to find the best solvents based on their kinetics rates at 298.15 K. Six cyclic aqueous polyamines were studied at (298.15 to 313.15) K over a concentration range of (20 to 120) $mol \cdot m^{-3}$.

The bascity of the solvent, quantified by the $pK_a$ of its conjugate acid, is an important fundamental property which affects the kinetics and possibly the mechanism of the capture process (*3–6*). A linear relationship between the $pK_a$ of an acid or base with its catalytic effect on the reaction rate was reported by Brønsted et al. (*4*) Many literature studies reported on a Brønsted relationship between the rate constant of the reaction of amines with $CO_2$ and the basicity of such amines (*4–8*). The following Brønsted relationship was reported by Versteeg et al. (*5*)for aqueous primary and secondary alkanolamines:

$$\ln k_2 = pK_a + 17.60 - \left(\frac{7188}{T}\right) m^3 \cdot mol^{-1} \tag{1}$$

and for tertiary amines (*5*):

$$\ln k_2 = 1.3pK_a + 11.48 - \left(\frac{8270}{T}\right) m^3 \cdot mol^{-1} \tag{2}$$

Because of the essential need for $pK_a$ values, it would be useful to predict the aqueous $pK_a$ of new amines by a prior means. One direct way is the calculation of such values using a widely popular quantum chemistry program (Gaussian 03) with a continum solvation model, in which the solvent is approximated as a dielectric continuum. A study of this kind was reported by da Silva and Svendsen (*9*), and improved by our previous work to predict the aqueous $pK_a$ values within ± 1 (*10*). The procedure and the choice of conformers for the studied alkanolamines were recently published.

## 2. Experimental Setup

### 2.1. Determination of Chemical Kinetics

A stopped flow technique was used for the direct measurement of pseudo first-order kinetics, $k_0$, for different aqueous and non-aqueous diamines, as well as primary, secondary and tertiary alkanolamines. The experimental setup is a standard SF-51 stopped flow unit from Hi-Tech Scientific Ltd., UK. It is an assembly of four major units; a sample-handling unit, a conductivity-detection cell, an A/D converter and a microprocessor. The sample-handling unit is comprised of a stainless steel case which provides support and an enclosure for the sample flow circuit. Schematics of the sample handling unit is shown in Figure 1. The entire flow circuit, with the exception of the stop/waste syringe, is enclosed in a thermostat and maintained at a constant temperature by an external water bath within ± 0.1 K. The front panel of the sample handling unit displays a temperature indicator with a resolution of 0.1 K and an air pressure indicator. A pneumatic air supply is used to control the movement of drive plate located at the bottom of the internal syringes that contains the $CO_2$ solution and amine solution. During an experimental run, a fresh solution of $CO_2$ is loaded into one syringe and a fresh solution of amine is loaded into the other.

$CO_2$ solutions were prepared by bubbling research grade $CO_2$ for at least half an hour through the desired medium with water for an aqueous solution and methanol or ethanol for a non-aqueous solution. The concentration of $CO_2$ in the liquid medium was measured in a gas chromatograph (GC-6890 from Agilent). It was then diluted with the chosen media to keep the $CO_2$ solution at least 10 times lower than the amine solution in order to achieve pseudo first-order conditions. The pseudo first-order rate constants of the aqueous solution of EDA obtained for different concentrations are compared with previously published data (*11*) in Figure 2. A reproducibility of 4% (absolute average deviation of 15 sets of $k_0$ values from their mean value) and an estimated uncertainty of 5% (absolute average deviation of the obtained value from the literature value) were observed when compared to published data. By fitting the empirical power-law kinetics to the data of the experimentally found pseudo first order constants for $CO_2$ as shown in Figure 2, the reaction order of the amine was determined.

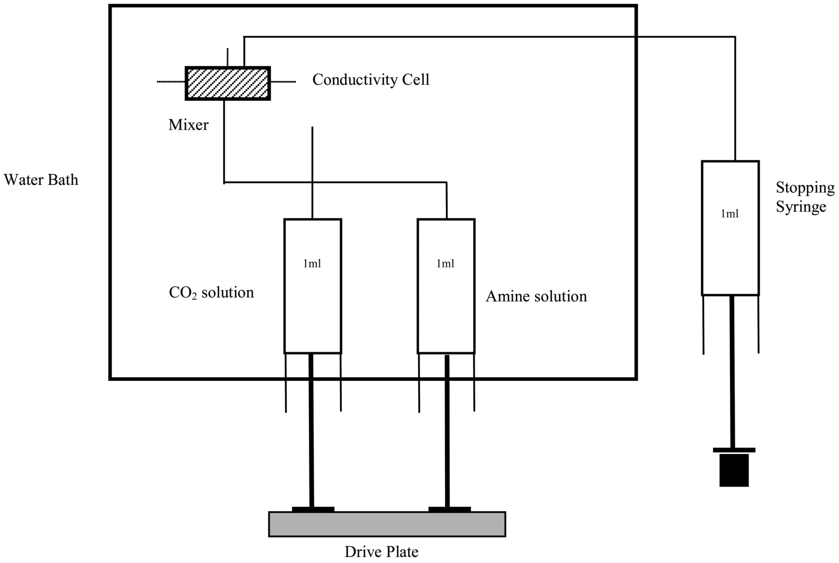


*Figure 1. Schematic diagram of stopped flow instrument*

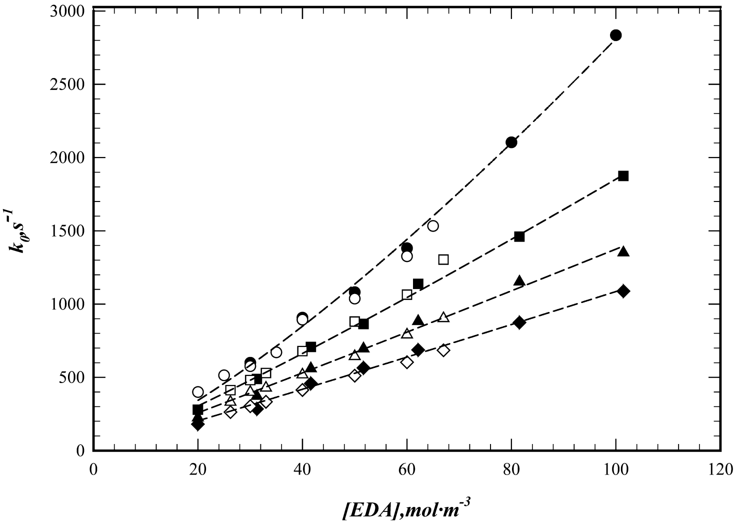


*Figure 2. Pseudo first order reaction for (EDA + $H_2O$) solution. ♦, 298.15 K; ◊, 298.15 K[11]; ▴, 303.15 K; ▵, 303.15 K[11]; ▪, 308.15 K; □, 308.15 K[11]; ●, 313.15 K; ○, 313.15 K[11]; --- Power law kinetics.*

### 2.2. Determination of the Dissociation Constant ($pK_a$)

0.01 M aqueous solutions of amines were prepared using deionized double distilled water. The solution was maintained at the experimental temperature and blanketed with a slow stream of nitrogen. The amine solutions (50 mL) were titrated with 0.1M HCl. Twenty equal portions (0.5 mL) of the titrant were added to the solution and the $pH$ value was read when the equilibrium was reached. The $pK_a$ values were determined using the Albert and Serjeant procedure (*12*). $pK_a$ values of piperazine (PZ), from the experimental work are discussed and the same procedure was used to calculate the $pK_a$ values of other cyclic amines.

PZ is a diacidic base and it ionizes in aqueous solution as follows:

$$PZ + H_3O^+ \underset{K_{a(1)}}{\longleftrightarrow} PZH^+ + H_2O \tag{3}$$

$$PZH^+ + H_3O^+ \underset{K_{a(2)}}{\longleftrightarrow} PZH_2^{2+} + H_2O \tag{4}$$

where $PZH^+$ represents the monoprotonated piperazine, and $PZH_2^{2+}$ denotes the piperazinium ion. Considering the mole fraction of water as unity and expressing the concentration of hydronium ion, $[H_3O^+]$, as $[H^+]$, the $pK_a$ values of $PZ$ can be written as:

$$pK_{a(1)} = pH + \log\frac{[PZH^+]}{[PZ]} - \frac{Az^2 I^{1/2}}{1+Bk_i I^{1/2}} \tag{5}$$

$$pK_{a(2)} = pH + \log\frac{[PZH_2^+]}{[PZH^+]} - \frac{1.5276 I^{1/2}}{1+1.5 I^{1/2}} \tag{6}$$

The last terms in equations (5) and (6) are the thermodynamic corrections. The calculation procedures were explained in Albert and Serjeant (*12*). 0.5 ml of the titrant HCl was added to 50 mL solution of 0.01 M $PZ$ in 10 parts (5ml) to calculate the ratios of $[PZH^+]/[PZ]$ and the next 10 parts of 0.5 ml were added to find the ratios of $[PZH_2{}^{2+}]/[PZH^+]$. The corresponding $pH$ values after each addition of titrant were recorded. These ratios were used in equations 5 and 6 to find $pK_{a(1)}$ and $pK_{a(2)}$ values. Thermal corrections were subtracted from the $pK_{a(1)}$ values and the average values were calculated as the first $pK_a$ of $PZ$. Correspondingly thermal corrections for the second dissociation constants ($pK_{a(2)}$) were deducted to find the average value as the second $pK_a$. The Debye-Hückel equation was used to calculate the activity coefficients:

$$-\log(\gamma_i) = \frac{Az_i^2 I^{1/2}}{1+Bk_i I^{1/2}} \tag{7}$$

where the terms *A* and *B* are called the Debye-Hückel equation constants and vary with the dielectric constant and the temperature of the solvent. $z_i$ is the ion valance and the term $k_i$ is the ionic size parameter, i.e. the mean distance of approach of the ions. *I* represents the ionic strength and depends on the concentration of the solution. The values of *A* and *B* for different temperatures were taken from Manov et al. (*13*) The ionic size parameters ($k_i$) values were also obtained from the literature (*14*). The calculation of the ionic strength follows different procedures for the first and second $pK_as$ as shown in the work of Albert and Serjeant (*13*).

## 3. Reaction Kinetics and Mechanism

The reaction kinetics of $CO_2$ with primary, secondary and sterically hindered amines HXYN (H, X, and Y bonded to N) can be explained with either the zwitterion mechanism or the so-called "termolecular" mechanism, whereas the reaction with tertiary amines is interpreted using a mechanism described by the base-catalyzed hydration of $CO_2$.

### 3.1. Zwitterion Mechanism

The zwitterion mechanism was proposed by Danckwerts (*15*) for alkanolamines, drawing upon an earlier idea for pure amines. This two-step mechanism assumes a formation of an intermediate zwitterion which then undergoes a deprotonation by basic molecules resulting in carbamate formation:

$$HXYN + CO_2 \underset{k_b}{\overset{k_2^Z}{\rightleftarrows}} H^+XYNCOO^- \qquad (8)$$

$$H^+XYNCOO^- + B \xrightarrow{k_B} XYNCOO^- + BH^+ \qquad (9)$$

Applying the steady-state principle to the intermediate zwitterion, the rate of reaction of $CO_2$ ($r_{CO2}$) in aqueous solutions can be described as:

$$r_{CO_2} = k_{ov}[CO_2] = \frac{[HXYN]}{\frac{1}{k_2^Z} + \frac{1}{\sum K_B[B]}}[CO_2] \qquad (10)$$

where $k_{ov}$ is the overall reaction rate constant for $CO_2$ loss, $K_B = k_2^Z k_B / k_b$, and $k_2^Z$, $k_b$ (b = backwards) and $k_B$ (*B* = base) are the elementary rate constants in steps (8) and (9). *B* denotes any proton-accepting species present; if one considers $\{H_2O, OH^-, HXYN\}$, then one has elementary rate constants $k_B = \{k_W, k_{OH-}, k_{HXYN}\}$ and the corresponding composites $K_B$ in equation (10).

Equation (10) is very general and should cover most cases. Fitting this equation to experimental data would give values for the three $K_B$'s as well as $k_2^Z$, but this 4-parameter function often has indeterminacy problems. Danckwerts (*15*) pointed out two limiting cases, arising if $k_b << \sum_B k_B[B]$ [equation (11)] or $k_b >> \sum_B k_B[B]$ [equation (12)]:

$$r_{CO_2} = k_2^Z [CO_2][HXYN] \tag{11}$$

$$r_{CO_2} = \sum_B K_B [B][CO_2][HXYN] \tag{12}$$

Equation (12), like (10), allows for fractional orders of the amine between 1 and 2.

### 3.2. "Termolecular" Mechanism

It turns out that the limiting rate law in equation (12) is identical to the Crooks-Donnellan expression, which arose from assuming that the mechanism consists of one elementary termolecular step (*16*):

$$B + HXYN + CO_2 \rightarrow BH^+ + XYNCOO^- \tag{13}$$

There are theoretical objections to termolecular elementary steps, as any step which requires simultaneous collision of 3 entities is very rare. It is more likely that the single step starts with two of the three reactants initially complexed, either as $B.HXYN$, $HXYN.CO_2$ (Crooks-Donnellan (*16*)), or the zwitterion $H^+XYNCOO^-$ (Danckwerts (*15*)). Hence, the use of equation (12) does *not* confirm or deny the existence of any one of these supposed initial complexes. The label "termolecular" for the rate law in [equation (12)] should be taken to mean that this rate law arises in the limit that the intermediate, regardless of its nature, is in a sufficiently rapid equilibrium with reactants as to make the two-step reaction appear to be one step. Note that it would be incorrect practice to equate equation (12) with equation (11).

Some workers (e.g. Blauwhoff et al. (*4*)) have assumed the zwitterion mechanism and derived values for its elementary rate constants. Values for the $k_W$ and $k_{OH-}$ rate constants, for the uncatalyzed reaction between $CO_2$ and either water or the hydroxide ions, can be determined by the correlations proposed by Pinsent et al. many years ago (*17*). In the current work, results published in ref. (*4*) for primary and secondary amines were used in determining the intial guesses for $K_W$ and $K_{OH-}$ in fits of equations (10) and (12). Calculations without proper intial guesses can lead to erroneous results in estimating the rate constants ($K_a$, $K_W$ and $K_{OH-}$).

### 3.3. Base Catalysis Mechanism

This mechanism seems important only for tertiary amines, which were not studied in this work, but the theory is presented here for completeness. Donaldson and Nguyen (*18*) proposed a different termolecular mechanism for the reaction of $CO_2$ with tertiary amine:

$$Am + CO_2 + H_2O \rightarrow AmH^+ + HCO_3^- \tag{14}$$

Again, a true termoleculecular elementary step is unlikely, and the mechanism is more likely to have an initial rapid equilibrium inconsequential to rate:

$$Am + CO_2 + H_2O \rightleftharpoons intermediate\ complex \quad (15)$$

$$intermediate\ complex \rightarrow AmH^+ + HCO_3^- \quad (16)$$

An additional possibility for the $CO_2$ loss rate could be the uncatalyzed reaction:

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \quad (17)$$

but this was deemed unimportant by Littel, Versteeg, and van Swaaij (*19*). They went on to straightforwardly derive the rate expression from the termolecular mechanism (14):

$$r_{CO_2} = k_{ov}\left[CO_2\right] = k_3[H_2O][CO_2][Am] = k_2^B[CO_2][Am] \quad (18)$$

where $k_2^B = k_3[H_2O]$ should be independent of amine concentration.

Blauwhoff et al. (*4*) studied the kinetics of several amines and concluded that an increase in amine $pK_a$ increases the rate of $CO_2$ loss for primary,secondary, and tertiary amines. In this work, $[OH^-]$ ions contributions are calculated using the relations given by Astarita et al. (*20*):

$$[OH^-] = \sqrt{\frac{K_W}{K_p}[Am]} \quad , \quad \alpha < 10^{-3} \quad (19)$$

$$[OH^-] = \frac{K_W}{K_p}\left[\frac{1-\alpha}{\alpha}\right] \quad , \quad \alpha \geq 10^{-3} \quad (20)$$

where $\alpha$ is the $CO_2$ loading in amine solution (always low in stopped-flow experiments), and $K_p$ is the equilibrium constant for:

$$Am + H_2O \rightleftharpoons AmH^+ + OH^- \quad (21)$$

The value of $K_W$ was estimated based on the correlation of Barth et al. (*21*) and the values of $K_p$ for each amine were estimated using the experimental $pK_a$ values. $pK_a$ values were measured using the experimental set-up described in our previous work (*22*). Depending upon the order of the reactions, all experimental data for the studied aqueous cyclic amines were tested with equations (10), (11), or (12). The equation with the better AAD % (Percentile Absolute Average Deviation) and $R^2$ was chosen to interpret the mechanism of reactions.

## 4. Results and Discussion

### 4.1. Screening of Different Types of Amines

Using the stopped-flow technique, kinetic (pseudo-first order) rate constants ($k_0$) were determined for different types of amines (Primary amines: 1-amino-propanol (1-AP), 3-amino-propanol(3-AP), ethyl aminoethanol (EAE); Secondary amines: ethylene diamine (EDA), 1, 3-diaminopropane (DAP), 2-(amino ethyl) ethanol amine (AEEA);Cyclic amine:piperazine; Polyamine: n-(2-aminoethyl)-1,3-propane diamine (NAEDP)) at 298.15 K over a concentration range of (20 to 120) $mol\cdot m^{-3}$. It was observed (Fig. 3) that polyamines and cyclic amines have higher reaction rates than linear primary and secondary amines: the trend of the rates of reaction followed by the amines was polyamines > cyclic amines > secondary amines > primary amines. The $CO_2$ absorption rate increased with the increase in -NH groups in the amines. Increase in –OH groups in amines decreased the rate of the reaction due to their electron withdrawing effect and a tendency to form intramolecular hydrogen bonding (*21*). Increase in the number of $–CH_3$ and $–CH_2$ groups increases the rate of the reaction due to their electron donor effect to the nitrogen atom.

The order of the reaction in amine (*n*) was found by fitting the data with a power law expression. To mimic Rochelle et al. (*23*), the second-order reaction constants $k_2$ from equation (11) were determined at 298.15 K and $E_a$ value was calculated using the Arrhenius plot (ln $k_2$ vs. $1/T$) for the temperature range (298.15-313.15) K. The screening results are similar to the results of Rochelle et al. (*23*) obtained from Brønsted plot (Figure 4) by comparing the second order reaction rate constant ($k_2$) of various amines with respect to their $pK_a$ (*23*). From Figures 3 and 4, it is notable that there was a considerable reduction in the reaction rates when the primary –OH group was exchanged with a secondary –OH group (example 3-AP to 1-AP).

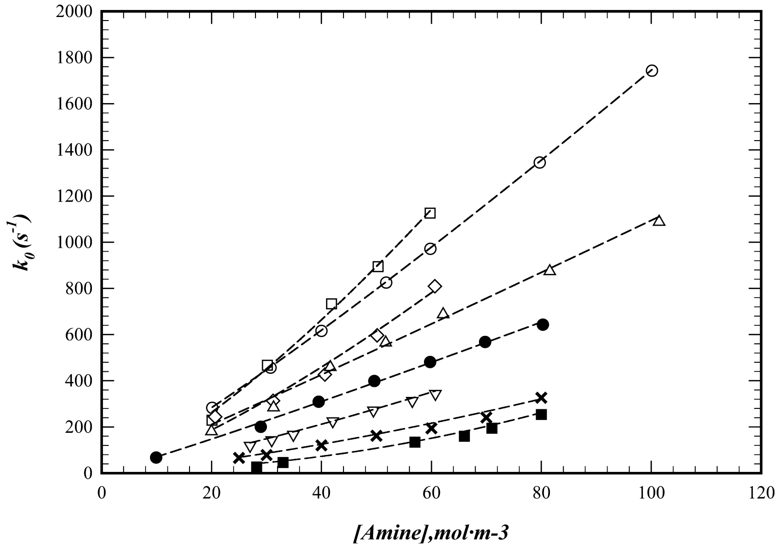


*Figure 3. Comparison of pseudo-first order rate constants ($k_0$) for $CO_2$ absorptionreaction of various amines at 298.15 K: □, NAEDP; ○, PZ; ◊, DAP; ▵, EDA; ▿, 3-AP; ×, 1-AP; ▪, EAE; --- Eq. 11.*

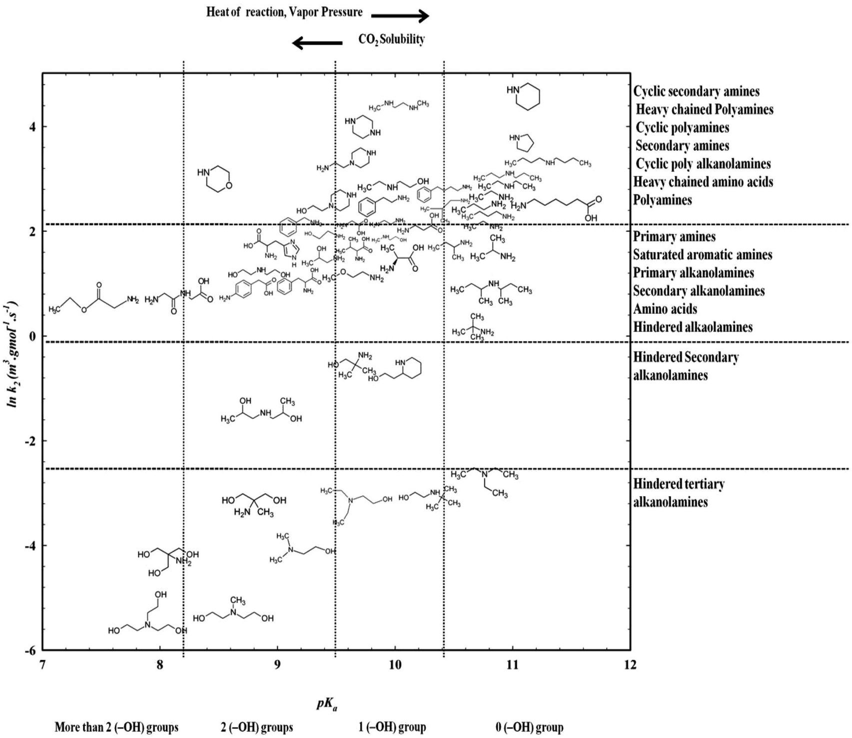


*Figure 4. Brønsted correlation of $CO_2$ reaction rates with amines. (data in this figure was adapted from Rochelle et al. (23))*

Both stopped-flow experiment and $pK_a$ studies concluded that cyclic amines are more suitable for $CO_2$ capture than other amines due to their high absorption rates. Higher second order rate constants for polyamines and cyclic amines mean that the deprotonation reaction of carbamates was very fast in these amines. By comparing EDA, AEEA and EEA, it can be observed that the steric hindrance effect for the reaction kinetics offered by the –OH group is greater than the effect caused by the $–CH_3$ group. The order of the reaction increased in the case of EEA and decreased in the case of AEEA. The temperature sensitivity of the amine can be noted from the activation energies derived from the rate constants. Among the amines studied, PZ has the lowest activation energy and EEA has the highest activation energy. This implies that the highest hindrance effect in EEA for –NH group is the reason for its high activation energy and it decreases as the hindrance effect is reduced. Two –NH groups in PZ contribute to its low activation energy, indicating that the reaction proceeds very fast by forming zwitterion ions. Similar conclusion was made by Bishnoi and Rochelle (*24*) for the increase in the zwitterion formation rate by a reduction in steric hindrance around the amine group.

## 4.2. Screening of Cyclic Amines

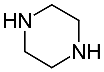
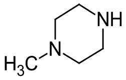
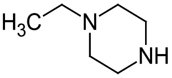
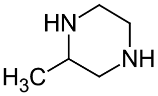
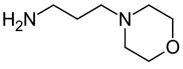
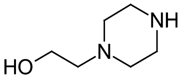
The second order reaction rate constants ($k_2$) of the cyclic amines are higher than those of other types of amines, which was confirmed by both the stopped-flow experiment with the same concentrations, and the Brønsted plot of the amines with similar $pK_a$ (Figure 4). Rochelle et al. (*23*) reviewed the kinetic studies for the cyclic amines studied by other researchers using different equipments for different concentrations and temperatures. Graeme et al. (*25*) and Singh et al. (*26*) conducted screening studies for several cyclic amines from their capacity for $CO_2$ solubility and their absorption rate with $CO_2$. Singh et al. (*26*) investigated the effect of different substituted saturated and unsaturated cyclic amines using an absorbent vessel. The conclusion derived from that work was, an amine group substitution in a saturated cyclic ring increases the protonation reaction, thus increasing the absorption rate and increases the absorption capacity. A substitution of one methyl group increased the absorption rate by increasing the basicity of the compounds to provide faster protonation reaction. But the absorption capacity varied depending on the position of the substitution of methyl group. All unsaturated cyclic amines showed poor absorption rate and capacity.

Graeme et al. (*25*) concluded in their screening experiment that amines that exhibited the fastest initial absorption rate were all polyamines with well separated amine functionality in structurally similar environments. The distance of the hydroxyl functionality (–OH) from the amine and the structural features around it had a significant effect on the solubility of $CO_2$ capacity by formation of intramolecular hydrogen bond between amine and hydroxyl groups. There are four cyclic amines among the top six solvents screened by Graeme et al. (*25*) They were ranked as follows: homopiperazine > piperazine > 1,4,7-triazacyclohexnae > tans-N-hydroxyethyl-1 and 4-diaminocyclohexane. Piperidine and piperazine which are heterocycles have faster reaction rate toward carbamate formation (*27*).

Among the cyclic amines, PZ is considered to be the best solvent and an accelerator in many $CO_2$ capture studies, because of its high loading capacity ($mol_{CO2}/mol_{PZ}$) and fast absorption rate (*24*, *28*). MDEA activated with PZ is being used as a solvent for high capacity $CO_2$ removal and found major application in ammonia and synthesis gas production (*29*). PZ has an ability to be effective at very low activator concentration with MDEA and provides a fast rate and high capacity to remove $CO_2$from industrial gases. Therefore, the kinetics of the reaction of $CO_2$ with six cyclic amines (derivatives of PZ) in aqueous solutions have been studied at (298.15-313.15) K over a concentration range of (20-120) $mol{\cdot}m^{-3}$ using the stopped-flow technique. (piperazine (PZ), 1-methyl piperazine (1-MPZ), 2-methyl piperazine (2-MPZ), 1-ethyl piperazine (1-EPZ), N-(2-hydroxyethyl) piperazine (1-HEPZ) and 3-morpholino propyl amine (3-MOPA). Their molecular structures and other details are given in Table 1.

The measured pseudo first-order rate constants ($k_0$) are plotted against the concentration ($mol{\cdot}m^{-3}$) in Figure 5 showing an expected increase in pseudo first-order rate constant ($k_0$) with concentration as well as temperature i.e. the reaction is favored by a rise in temperature and concentration. Figure 5 represents the pseudo-first order rate constants ($k_0$) for the six studied cyclic amines at 298.15 K. All cyclic amines were found to have fractional reaction order with respect to amine varying from 1 to 2 (Except PZ). PZ has the highest reaction rate and 1-MPZ the lowest. The trend of reaction rates are given as (PZ > 2-MPZ > 1-EPZ > 3-MOPA > HEPZ > 1-MPZ). Aqueous 2-MPZ has an absorption rate similar to aqueous piperazine, but both PZ and 2-MPZ are solid in nature at room temperature.

**Table 1. Details of the studied cyclic amines**

| Structure | Symbols | Purity (mass) | CAS. No |
|---|---|---|---|
|  | PZ | 99% | 110-85-0 |
|  | 1-MPZ | 99% | 109-01-3 |
|  | 1-EPZ | 98% | 5308-25-8 |
|  | 2-MPZ | ≥ 98% | 109-07-9 |
|  | 3-MOPA | 99% | 123-00-2 |
|  | HEPZ | 98% | 103-76-4 |

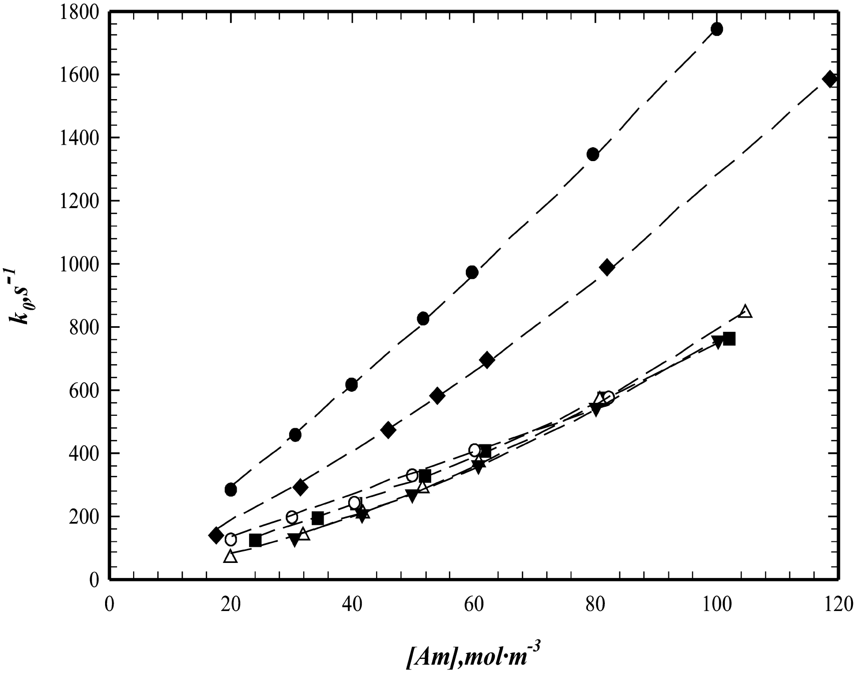


*Figure 5. Comparison of pseudo-first order rate constants for $CO_2$ absorption in aqueous cyclic amines at 298.15 K: ●, PZ ; ▪, 1-MPZ; ♦, 2-MPZ; ▵, HEPZ; ▾, 3-MOPA; ○, 1-EPZ; --- Eq. 12.*

All experimental data for the aqueous six cyclic amines were fitted with a power law kinetics to determine the order of the reaction (*n*) and fitted with equations (10), (11) or (12) to determine the second order rate and the mechanism of the reaction with $CO_2$. An Arrhenius rate equation was used to obtain the value of the activation energy for the reactions. The calculated second order reaction constants for all the six amines are listed in Tables (2-7) with their statistical anaylsis. $pK_a$ values were taken from Khalili et al. (*22*) in order to calculate the [$OH^-$] contribution ($pK_a$ value of 3-MOPA was measured in this work and the values listed in Table 8). The temperature dependent correlations for these dissociation constants were also derived. Equation (12) corresponding to the termolecular mechanism fitted the data better than equations (10) and (11). This confirms that the zwitterion deprotonation is the rate-determining step and it is slow compared to the reverse reaction. According to Blauwhoff et al. (*4*), this indicates that the larger part of the zwitterion is reverted to $CO_2$ and amine and that only a small part is converted to carbamate. Second-order reaction constant ($k_2$) was calculated from equation (11) to estimate $E_a$ using the Arrhenius plot (ln $k_2$ vs. $1/T$) for the temperature range (298.15-313.15) K. But it should be noted that the order of the reaction was taken as unity. Cyclic amines 2-MPZ, 3-MOPA and HEPZ showed poor fitting with equation (11), because the reaction orders for these amines were far greater than unity.

**Table 2. Second order reaction constants for (PZ + $H_2O$) solution**

| ***Parameters*** *(Eq. 12)* | ***T /K*** | | | |
|---|---|---|---|---|
| | ***298.15*** | ***303.15*** | ***308.15*** | ***313.15*** |
| **$K_a$ ($m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 0.0353 | 0.0234 | 0.011 | 1.296E-14 |
| **$K_w$ ($m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 2.53E-04 | 3.05E-04 | 3.47E-04 | 4.11E-04 |
| **$K_{OH^-}$($m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 1.89E-02 | 9.20E-03 | 4.66E-03 | 4.18E-01 |
| **Order (*n*) {Actual}** | 0.961 | 1.076 | 1.134 | 1.028 |
| **$R^2$** | 0.9997 | 0.9999 | 1.0000 | 0.9456 |
| **AAD%** | 1.4 | 0.8 | 0.3 | 1.6 |
| **$k_2^Z$ ( $m^3 \cdot mol^{-1} \cdot s^{-1}$)** (Eq. 11) | 16.7 ± 0.33 | 18.61 ± 0.21 | 19.95 ± 0.09 | 22.65 ± 0.93 |
| **Order (*n*) {Assumed}** | 1 | 1 | 1 | 1 |
| **$R^2$** | 0.9896 | 0.9962 | 0.9994 | 0.9447 |
| **AAD%** | 7.5 | 4.2 | 1.5 | 1.7 |

**Table 3. Second order reaction constants for (1-MPZ + $H_2O$) solution**

| ***Parameters*** *(Eq. 12)* | ***T /K*** | | | |
|---|---|---|---|---|
| | ***298.15*** | ***303.15*** | ***308.15*** | ***313.15*** |
| **$K_a$ ($m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 0.0259 | 0.0269 | 0.026 | 3.310E-02 |
| **$K_w$ ($m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 8.87E-05 | 1.01E-04 | 1.19E-04 | 1.27E-04 |
| **$K_{OH^-}$( $m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 4.64E-02 | 3.33E-05 | 3.32E-02 | 2.83E-01 |
| **Order (*n*) {Actual}** | 1.231 | 1.197 | 1.236 | 1.252 |
| **$R^2$** | 0.9994 | 0.9995 | 0.9995 | 0.9995 |
| **AAD%** | 1.9 | 1.8 | 1.6 | 1.8 |
| **$k_2^Z$ ( $m^3 \cdot mol^{-1} \cdot s^{-1}$)** (Eq. 11) | 6.90± 0.25 | 7.65± 0.26 | 8.56 ± 0.24 | 9.55 ± 0.32 |
| **Order (*n*) {Assumed}** | 1 | 1 | 1 | 1 |
| **$R^2$** | 0.9675 | 0.9708 | 0.9782 | 0.9717 |
| **AAD%** | 14 | 13 | 10 | 12 |

**Table 4. Second order reaction constants for (1-EPZ + $H_2O$) solution**

| ***Parameters*** *(Eq. 12)* | ***T /K*** | | | |
|---|---|---|---|---|
| | ***298.15*** | ***303.15*** | ***308.15*** | ***313.15*** |
| **$K_a$ ($m^6\cdot mol^{-2}\cdot s^{-1}$)** | 1.50E-10 | 2.05E-10 | 2.13E-10 | 1.23E-10 |
| **$K_w$ ($m^6\cdot mol^{-2}\cdot s^{-1}$)** | 1.22E-04 | 1.40E-04 | 1.59E-04 | 1.77E-04 |
| **$K_{OH^-}$( $m^6\cdot mol^{-2}\cdot s^{-1}$)** | 4.21E-02 | 1.92E-02 | 1.00E-02 | 1.65E-02 |
| **Order (*n*) {Actual}** | 1.066 | 1.036 | 1.069 | 1.084 |
| **$R^2$** | 0.9860 | 0.9778 | 0.9821 | 0.9959 |
| **AAD%** | 5.9 | 7.4 | 6.7 | 7.9 |
| **$k_2^Z$ ( $m^3\cdot mol^{-1}\cdot s^{-1}$)** (Eq. 11) | 6.74 ± 0.13 | 7.73 ± 0 .19 | 8.77 ± 0.19 | 9.74 ± 0.11 |
| **Order (*n*) {Assumed}** | 1 | 1 | 1 | 1 |
| **$R^2$** | 0.9846 | 0.9760 | 0.9805 | 0.9717 |
| **AAD%** | 5.6 | 7.1 | 6.5 | 7.8 |

**Table 5. Second order reaction constants for (2-MPZ + $H_2O$) solution**

| ***Parameters*** *(Eq. 12)* | ***T /K*** | | | |
|---|---|---|---|---|
| | ***298.15*** | ***303.15*** | ***308.15*** | ***313.15*** |
| **$K_a$ ($m^6\cdot mol^{-2}\cdot s^{-1}$)** | 4.43E-02 | 6.13E-02 | 1.36E-01 | 2.09E-01 |
| **$K_w$ ($m^6\cdot mol^{-2}\cdot s^{-1}$)** | 5.78E-05 | 5.95E-05 | 9.02E-06 | 1.38E-11 |
| **$K_{OH^-}$( $m^6\cdot mol^{-2}\cdot s^{-1}$)** | 1.12E-02 | 3.69E-03 | 1.07E-02 | 4.89E-01 |
| **Order (*n*) {Actual}** | 1.522 | 1.389 | 1.288 | 1.273 |
| **$R^2$** | 0.9995 | 0.9995 | 0.9998 | 0.9821 |
| **AAD%** | 1.8 | 1.8 | 2.2 | 2.7 |
| **$k_2^Z$ ( $m^3\cdot mol^{-1}\cdot s^{-1}$)** (Eq. 11) | 12.18 ± 0.52 | 14.71 ± 0.79 | 18.23 ± 1.56 | 23.63 ± 3.09 |
| **Order (n) {Assumed}** | 1 | 1 | 1 | 1 |
| **$R^2$** | 0.9846 | 0.9760 | 0.8906 | 0.7994 |
| **AAD%** | 19 | 23 | 38 | 59 |

**Table 6. Second order reaction constants for (3-MOPA + $H_2O$) solution**

| ***Parameters** (Eq. 12)* | ***T /K*** | | | |
|---|---|---|---|---|
| | ***298.15*** | ***303.15*** | ***308.15*** | ***313.15*** |
| **$K_a$ ($m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 4.29E-02 | 6.49E-02 | 1.28E-01 | 0.240 |
| **$K_w$ ($m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 1.52E-04 | 1.63E-04 | 1.25E-04 | 4.45E-05 |
| **$K_{OH^-}$( $m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 6.45E-03 | 1.10E-02 | 4.29E-03 | 3.21E-02 |
| **Order (*n*) {Actual}** | 2.257 | 1.880 | 1.551 | 1.477 |
| **$R^2$** | 0.9992 | 0.9995 | 0.9996 | 0.9983 |
| **AAD%** | 3.6 | 2.2 | 3.7 | 10.3 |
| **$k_2^Z$ ( $m^3 \cdot mol^{-1} \cdot s^{-1}$)** (Eq.11) | 6.62 ± 0.44 | 8.03 ± 0.60 | 11.08 ± 1.35 | 15.88 ± 2.68 |
| **Order (n) {Assumed}** | 1 | 1 | 1 | 1 |
| **$R^2$** | 0.9121 | 0.8936 | 0.7993 | 0.7097 |
| **AAD%** | 23 | 27 | 51 | 87 |

**Table 7. Second order reaction constants for (HEPZ + $H_2O$) solution**

| ***Parameters** (Eq. 12)* | ***T /K*** | | | |
|---|---|---|---|---|
| | ***298.15*** | ***303.15*** | ***308.15*** | ***313.15*** |
| **$K_a$ ($m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 4.91E-02 | 4.56E-02 | 4.88E-02 | 5.28E-02 |
| **$K_w$ ($m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 5.44E-05 | 7.51E-05 | 8.44E-05 | 9.68E-05 |
| **$K_{OH^-}$( $m^6 \cdot mol^{-2} \cdot s^{-1}$)** | 1.00E-02 | 4.74E-02 | 7.29E-04 | 5.96E-04 |
| **Order (*n*) {Actual}** | 1.392 | 1.406 | 1.418 | 1.517 |
| **$R^2$** | 0.9993 | 0.9992 | 0.9992 | 0.9992 |
| **AAD%** | 3.9 | 3.6 | 3.5 | 3.4 |
| **$k_2^Z$ ( $m^3 \cdot mol^{-1} \cdot s^{-1}$)** (Eq.11) | 6.89 ± 0.49 | 7.76 ± 0.46 | 11.08 ± 1.35 | 15.88 ± 2.68 |
| **Order (n) {Assumed}** | 1 | 1 | 1 | 1 |
| **$R^2$** | 0.9121 | 0.933 | 0.9357 | 0.9390 |
| **AAD%** | 36 | 27 | 26 | 25 |

**Table 8. Dissociation constants for aqueous 3-MOPA**

| | ***$pK_a$*** | | | | ***$lnK_p=A+B/T$*** | | ***$K_p$ (298.15 K)*** |
|---|---|---|---|---|---|---|---|
| ***T/K*** | ***298.15*** | ***303.15*** | ***308.15*** | ***313.15*** | ***A*** | ***B*** | |
| **3-MOPA** | 9.98 | 9.73 | 9.58 | 9.51 | -0.307 | -6730 | 1.16E-10 |

Table 9 lists the order of the reactions, the second order reaction rate constants and the activation energies of the studied cyclic amines derived by assuming the rate to be unity. Activation energies and the temperature dependence of the second order reaction rate constants were calculated using an Arrhenius- relation.

Figure 6 represents the Brønsted-plot for the studied amines at different temperatures. For all cyclic amines, a linear relationship exists between ln $k_2$ and $pK_a$. As the $pK_a$ increases the second order rate constants for the cyclic amines decreases. This indicates that the alkalinity of the solution influences the rate of the reaction between $CO_2$ and the amine. From this plot, the effect of methyl group ($-CH_3$) can also be observed. The basicity of the piperazine molecule decreases when it is hindered by the position of methyl group, thereby reducing the reaction rate with $CO_2$.

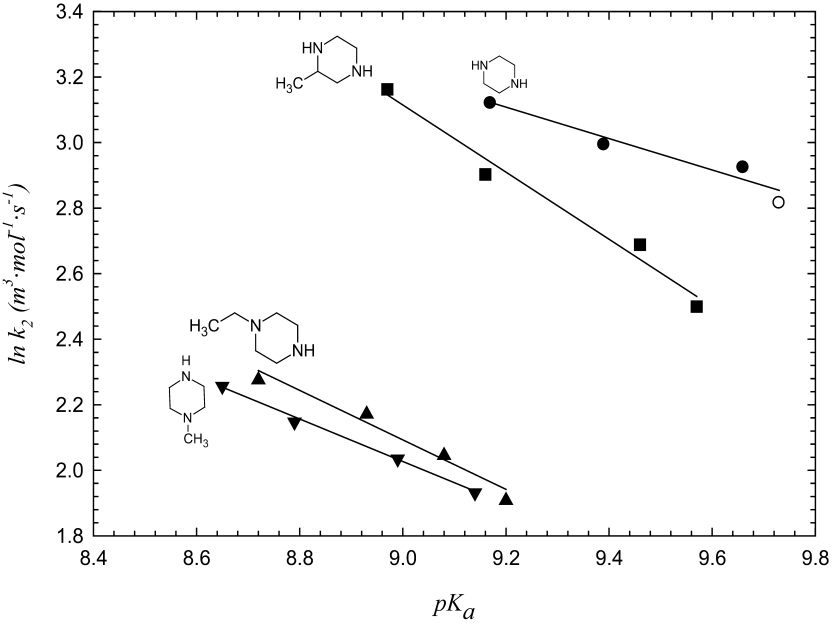


*Figure 6. Brønsted plot for the studied cyclic amines.*

**Table 9. Second order reaction constants and order of the reaction with $CO_2$ for aqueous cyclic amine solutions**

| *Amine* | *Order (n)* | ***$k_2^Z$ ($m^3 \cdot mol^{-1} \cdot s^{-1}$)*** *(Eq. 11)* | ***$E_a$ ($kJ \cdot mol^{-1}$)*** |
|---|---|---|---|
| PZ | 0.96 - 1.1 | $k_2 = 7.84 \times 10^4 * \exp\left[\frac{-1833}{T}\right]$ | 15.24 |
| 1-MPZ | 1.19 - 1.25 | $k_2 = 6.20 \times 10^3 * \exp\left[\frac{-2027}{T}\right]$ | 16.85 |
| 1-EPZ | 1.20 - 1.25 | $k_2 = 1.51 \times 10^4 * \exp\left[\frac{-2297}{T}\right]$ | 19.10 |
| 2-MPZ | 1.27 - 1.93 | $k_2 = 1.14 \times 10^7 * \exp\left[\frac{-4104}{T}\right]$ | 34.13 |
| 3-MOPA | 1.0 - 2 | $k_2 = 6.23 \times 10^8 * \exp\left[\frac{-5486}{T}\right]$ | 45.61 |
| HEPZ | 1.27 - 1.37 | $k_2 = 3.63 \times 10^8 * \exp\left[\frac{-5321}{T}\right]$ | 44.24 |

## 5. Dissociation Constants ($pK_a$) of Cyclic Amines

The dissociation constant is one of the main factors in the choice of a chemical solution for acid gas removal or in the interpretation of the kinetic mechanism for the absorption of the acid gas in the solution (*30*). Information available from the dissociation constants are mainly a measure of the basic strength of the chemical solution (amine) at a specific temperature. Information about a temperature dependent dissociation constant provides the change in the reaction enthalpy by indicating the change of the basic strength of the absorbent within a given temperature range in the absorption/desorption and cooling/ heating cycle for a conventional acid gas removal plant (*31*). $pK_a$ is defined as the negative of the logarithm of the equilibrium constant ($K_a$) for the reaction:

$$HA \underset{K_a}{\longleftrightarrow} H^+ + A^- \tag{22}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{23}$$

where $[H^+]$,$[A^-]$ and $[HA]$ represent the concentrations of the solution species in $mol \cdot L^{-1}$. Then, $pK_a$ will be derived as:

$$pK_a = pH + \log[HA] - \log[A^-] \tag{24}$$

It implies that a solution with 50% dissociation has a $pH$ equal to the $pK_a$ of the acid. For bases, the dissociation constants are reported as $pK_a$ values for the conjugate acid (*32*):

$$BH^+ \underset{K_a}{\longleftrightarrow} H^+ + B \tag{25}$$

An ionization constant $K_b$ was used for the reaction:

$$B + H_2O \underset{K_b}{\longleftrightarrow} BH^+ + OH^- \tag{26}$$

and $pK_b$ is related to $pK_a$ by:

$$pK_a + pK_b = pK_{water} = 14 \text{ at } (\mathrm{T} = 298.15\ \mathrm{K}) \tag{27}$$

The basicity of the solvent, quantified by the $pK_a$ of its conjugate acid, is a key factor for the reaction rate and absorption capacity of the solvent in the process (*22*). A linear relationship between the $pK_a$ of an acid or a base and its reaction rate was derived by Brønsted et al. (*7*) In a previous section, a Brønsted relationship between the rate constant of the reaction of amines with $CO_2$ and the basicity of such amines was discussed. $pK_a$ values of alkanolamines are available in the open literature at different temperatures (*22*, *32–35*). The experimental determination of the $pK_a$ values for five cyclic diamines have been reported in our work at different temperatures. The experimental set-up and its details were reported in our previous work (*20*).

### 5.1. Results and Discussion

Table 10 shows the first and second $pK_a$ values of cyclic amines. As observed in these tables, the $pK_a$ values of PZ calculated in our work, are in good agreement (± 0.05) with the data reported by Hetzer et al. (*36*) Among the cyclic amines studied in this work PZ and 2-MPZ have the highest $pK_a$ values and DMPZ has the lowest value. Secondary amines are stronger bases than tertiary amines. Therefore, DMPZ, with two tertiary amine groups, is the weakest base, and PZ and 2-MPZ, with two secondary amine groups, are the most basic amines. Due to the steric effect, 2-MPZ is a weaker base than PZ. The methyl ($-CH_3$) group on $\alpha$ carbon in this amine causes steric hindrance to the solvation on cation formation which lowers the basicity. Intramolecular hydrogen bonding also lowers the basicity. HEPZ, an alkanolamine with an intramolecular hydrogen bonding tendency has as a lower $pK_a$ value than 1-EPZ (*37*).

**Table 10. First and second $pK_a$ values of amines at different temperatures**

| *Amine* | $pK_{a(1)}$ | | | |
|---|---|---|---|---|
| | *T/K* | | | |
| | *298* | *303* | *313* | *323* |
| **PZ** | 9.78 | 9.66 | 9.39 | 9.17 |
| **2-MPZ** | 9.57 | 9.46 | 9.16 | 8.97 |
| **1-MPZ** | 9.14 | 8.99 | 8.79 | 8.65 |
| **1-EPZ** | 9.20 | 9.08 | 8.93 | 8.72 |
| **HEPZ** | 9.09 | 8.95 | 8.75 | 8.63 |
| **DMPZ** | 8.38 | 8.27 | 8.06 | 7.84 |
| *Amine* | $pK_{a(2)}$ | | | |
| | *T/K* | | | |
| | *298* | *303* | *313* | *323* |
| **PZ** | 5.35 | 5.27 | 5.02 | 4.93 |
| **2-MPZ** | 5.24 | 5.19 | 4.92 | 4.84 |
| **1-MPZ** | 4.63 | 4.40 | 4.31 | 4.18 |
| **1-EPZ** | 4.76 | 4.58 | 4.48 | 4.31 |
| **HEPZ** | 3.92 | 3.89 | 3.74 | 3.60 |
| **DMPZ** | 3.81 | 3.70 | 3.64 | 3.45 |

To sum up and present a clear picture for the change of $pK_a$ with the addition of different radicals to PZ, we suggest the following rules. Starting with the PZ molecule with two secondary amines, the addition of a methyl group ($-CH_3$) on any carbon of the ring introduces a hindrance effect and lowers the $pK_a$. The addition of an ethyl group ($CH_3$-$CH_2$) to PZ further lowers the $pK_a$. The addition of a methyl group lowers the pKa more than in the case of an ethyl group. The addition of a hydroxyl group (-OH) to 1-EPZ or a hydroxyl group to PZ reduces the $pK_a$ further than any previous addition (hydrogen bonding). Finally, the addition of a methyl radical ($-CH_3$) to each secondary amine of PZ to form tertiary amines (DMPZ) leads to the lowest $pK_a$. These conclusions are valid for the first and second $pK_a$ of the studied amines. In the present study, the calculated $\Delta S°$ values from the Van'f Hoff equation were almost negiligible compared to the contribution of the $(-\Delta H°/T)$ term. The higher the value of $-\Delta H°$, the larger is the shift in basicity from low temperature (high basicity leading to better absorption of $CO_2$) to the higher temperature (low basicity leading to better regeneration of $CO_2$). Accordingly, 2-MPZ and PZ should be the most attractive amines for gas swettening in terms of cyclic capacity.

### 5.2. *pK$_a$* Prediction Using Computational Chemistry

Aqueous *pK$_a$* of amines can be predicted by direct calculation using a popular quantum chemistry program (Gaussian 03) with a continuum solvation model, in which the solvent is approximated as a dielectric continuum. A computational study of some alkanolamines was reported by da Silva and Svendsen in 2003 (*9*), but they deemed their results too inaccurate and it was improved by Khalili et al. (*10*) in 2009. In this work, we are reporting that technique to calculate aqueous *pK$_a$* values to ± 1 *pK$_a$* accuracy for the substituted PZs which were used in the kinetic screening experiment. The amines studied are listed in Table 11 with their experimental *pK$_a$* values. The improvents provided in our work are (i) reduction of cavities around cations (an electrostriction technique) and the use of explicit solvent molecules inside the cavities (a semicontinuum technique); (ii) the equations to calculate *pK$_a$* were developed through the continuum salvation methods; (iii) to formalize an approximation for the entropy of multiple conformers; (iv) historical problems involved in ab initio *pK$_a$* calculations to improve the predictions in future.

**Table 11. Experimental *pK$_a$* values of the bases investigated in our work**

| *Base* | *Name or Abbreviation* | *pK$_a$ (298.15 K)* | *Ref* |
|---|---|---|---|
| $C_4H_9N_2(CH_3)$ | 2-methylpiperazine | 9.57 | (*10*) |
| $C_4H_9N_2(C_2H_5)$ | 1-ethylpiperazine | 9.20 | (*10*) |
| $C_4H_9N_2(CH_3)$ | 1-methylpiperazine | 9.14 | (*10*) |
| $C_4H_9N_2(C_2H_4OH)$ | 1-(2-hydroxyethyl)piperazine | 9.09 | (*10*) |
| $C_4H_8N_2(CH_3)_2$ | 1,4-dimethylpiperazine | 8.38 | (*10*) |
| $O(CH_2CH_2)_2NH$ | morpholine | 8.50 | (*37*) |
| $HN(CH_2CH_2)_2NH$ | piperazine | 9.73 | (*37*) |

### 5.3. Theory of *pK$_a$* Calculation

The *pK$_a$* of a base *B* is a scaled version of $\Delta_r G_{(aq)}$, the free energy change of the acid-dissociation reaction:

$$BH^+(aq) \rightarrow B_{(aq)} + H^+_{(aq)} \tag{28}$$

$$pK_a = \frac{\Delta_r G_{(aq)}}{RT \ln 10} \tag{29}$$

where *R* is the gas constant and *T* is temperature. Basicity increases with $\Delta_r G_{(aq)}$ and hence with *pK$_a$*. $\Delta_r G_{(aq)}$ can be expressed as:

$$\Delta_r G_{(aq)} \rightarrow \Delta_h G_{(aq)}(BH^+ \rightarrow B) + G_{(aq)}(H^+) \tag{30}$$

The half-reaction energy $\Delta_h G_{(aq)}(BH^+ \rightarrow B)$ is the quantity of interest in this work. It is computed as the difference of two free energies of compounds in solution:

$$\Delta_h G_{(aq)} = G_{(aq)}(B) - G_{(aq)}(BH^+) \tag{31}$$

$G_{(aq)}(H+)$, is independent of base and is difficult to determine, aqueous $H^+$ exists in several forms, like $H_3O^+$, $H_5O^{2+}$, and $H_9O^{4+}$ (*38*). The best value for $G_{(aq)}(H^+)$ is -270.3 kcal·mol$^{-1}$ ($G_{(g)}(H^+)$ = -6.3 kcal·mol$^{-1}$(1 atm) (*39*) + $\Delta_{solv}G(H^+)$ = -264.0 kcal·mol$^{-1}$ (1 atm gas → 1 mol·L$^{-1}$ aqueous solution) (*40*)). Semicontinuum technique was used to determine the free energies of the compounds in the solution. In order to reduce $pK_a$-proportional error with a semicontinuum technique an explicit water molecule was added inside the solute cavity (*40*). An empirical approach was used to eliminate the known systematic error for predictive uses by different researchers (*41–43*).

$$pK_{a(\exp t)} = m \times pK_{a(theo)} + b \tag{32}$$

Adam (*44*) and Tao (*45*), have found phenomenal accuracy (± 0.2) for a single class of compounds by taking this approach further, replacing $pK_{a(theo)}$ in equation (32) with some other computable property of the solute molecule. Of the direct $pK_a$ computation studies (i.e. not based on linear regressions like equation (32), the few that have reported computed $pK_a$ accuracy of better than ±1 were studies of a handful of compounds within a single class and small $pK_a$ ranges (*46–49*), where the slope errors were hard to observe and constant-shift errors might have cancelled them. A good example would be the work of da Silva et al. (*50*), whose results for carboxylic acids looked very good, but whose ensuing results for three other classes of compounds showed large class-dependent errors (*51*). Similar results can be achieved for PZ of *pH* range 8-11.

## 5.4. Computational Procedures

All calculations were done using the Gaussian 03 software program and the *6-311++G*** basis set. Solvent effects were computed using the continuum solvation method IEFPCM (*52*) with *UA0* radii for spherical cavities. Theelectronic structure levels of theory tested for IEFPCM calculations (including geometry optimization) were *B3LYP* and *MP2*. Geometry optimizations with IEFPCM minimize $E_{elec} + \Delta G_{el}$. All $E_{nuc}(0)^{g@g}$ terms were computed only with *B3LYP* at *B3LYP* gas-phase-optimized geometries. For neutral amine, a hydrogen atom of the explicit water molecule was hydrogen-bonded to the nitrogen atom in amine, while for protonated amine the new proton attached to nitrogen atom was hydrogen-bonded to the oxygen of water molecule. The use of one explicit water molecule was named as *Model II*, to distinguish from *Model I*, where no explicit water is used. The utility of a constant scale factor to contract the radii of charged “united atoms” was tested to accommodate electrostriction. Instead of the default factor of 1.0 for the $NH_x$ groups of protonated amines, 0.9 was used. This was referred to as "special scaling". Conformer choices and entropy calculations are explained in our previous work (*10*). The conformers used were the ones with lowest in energy from IEFPCM/*B3LYP* calculations.

### 5.5. $pK_a$ Results

In order to calculate the $pK_a$ values using equation (29), we must convert $\Delta G_{(aq)}$ to $\Delta_r G_{(aq)}$ via equation (30), by adding the contribution $G_{(aq)}(H^+)$. In this work, empirical choices for $G_{(aq)}(H^+)$ was taken. This parameter was fitted by minimizing the root mean square (rms) of calculated $pK_a$ values versus experimental values. Fitting was done for each model and level of theory. It was also done to convert the results of da Silva and Svendsen (*9*) from relative $\Delta G_{(aq)}$ values into best possible $pK_a$ values. The results are shown in Table 12. The rms errors reveal that the best results are obtained from Model II with default radii scaling. The best two techniques of Table 12 were used to compute the $pK_a$ values in Table 11. This included refitting of $G_{(aq)}(H^+)$ to minimize rms error. This resulted in two fitting parameters for each modelling technique, and improved the rms errors by 42-45% compared to single-parameter results (Table 13). Our most accurate procedure for the calculation of the $pK_a$ of bases studied in this work is *Model II* with the explicit water technique employing IEFPCM/MP2/6-311++G** for the optimized geometries and ensuing energies, with $E_{nuc}(0)^{g@g}$ terms computed with *B3LYP*/6-311++G** at a $C_1$-symmetry gas-phase conformer geometry, statistical entropy corrections and $G_{(aq)}(H^+)$ values of -266.96 kcal/mol for acyclic bases and -269.63 kcal/mol for cyclic bases. It produced an rms error of 0.68 for the $pK_a$ of the 17 compounds studied here. The best experimental value for $G_{(aq)}(H^+)$ is -270.3 kcal/mol. Interestingly, the fitted values in our computational work are close to this value for the cyclic molecules with no electrostriction scaling, and a chemically meaningful *ab initio* procedure in which the empirical fitting of $G_{(aq)}(H^+)$ is replaced by properly fixing its experimental value will be pursued in future work.

**Table 12. Comparison of Theoretical and Experimental $pK_a$ Results**

| *Base* | *B3LYP Model I* *Ref (9)* | *B3LYP Model I* *Def. sc.*[a] | *B3LYP Model II* *Sp. sc.*[a] | *MP2 Model II* *Sp. sc.*[a] | *B3LYP Model II* *Def. sc.*[a] | *MP2 Model II* *Def. sc.*[a] | *expt*[b] |
|---|---|---|---|---|---|---|---|
| morpholine | 10.97 | 9.61 | 9.21 | 8.97 | 9.81 | 9.56 | 8.50 |
| piperazine[c] | 12.49 | 12.21 | 11.26 | 10.87 | 12.02 | 11.61 | 9.73 |
| rms error | 1.79 | 1.85 | 1.47 | 1.30 | 1.22 | 1.00 | |

[a] "Def. sc." means default radii scaling, "Sp. sc." means special scaling; [b] For references see Table 11; [c] $pK_{a(1)}$

**Table 13. Comparison of theoreticaland experimental $pK_a$ results, including extra piperazines**

| | *one fitting parameter* | | *two fitting parameters* | | |
|---|---|---|---|---|---|
| *Base* | *B3LYP* | *MP2* | *B3LYP* | *MP2* | *Expt*[a] |
| Morpholine | 9.13 | 9.04 | 7.65 | 7.89 | 8.50 |
| Piperazine[b] | 11.34 | 11.10 | 9.86 | 9.95 | 9.73 |
| 2-methylpiperazine[b] | 11.01 | 10.46 | 9.53 | 9.31 | 9.57 |
| 1-ethylpiperazine[b] | 10.95 | 10.60 | 9.47 | 9.45 | 9.20 |
| 1-methylpiperazine[b] | 10.40 | 10.02 | 8.92 | 8.87 | 9.14 |
| 1-(2-hydroxyethyl)piperazine[b] | 10.49 | 10.08 | 9.01 | 8.93 | 9.09 |
| 1,4-dimethylpiperazine[b] | 10.65 | 10.37 | 9.17 | 9.21 | 8.38 |
| rms error | 1.48 | 1.18 | 0.81 | 0.68 | |

[a] For references see Table 11; [b] $pK_{a(1)}$

## 6. Conclusion

Screening of primary, secondary, poly and cyclic amines was performed using a stopped-flow technique at 298.15 K over a concentration range of (20 to 120) $mol{\cdot}m^{-3}$. Polyamines and cyclic amines have higher pseudo first order reaction rates compared to linear secondary and primary amines. Consequently, six cyclic amines were studied between (298.15 and 313.15) K over a concentration range of (20 to 120) $mol{\cdot}m^{-3}$. PZ had the highest reaction rate and 1-MPZ the lowest. At the same temperature, the trend of reaction rates is given as (PZ > 2-MPZ > 1-EPZ > 3-MOPA > HEPZ > 1-MPZ). The termolecular mechanism was used for calculating the rate parameters by fitting the experimental data. Higher second order rate constants for polyamines and cyclic amines mean that the deprotonation reactions of carbamates were very fast for these amines. The dissociation constants of the conjuagate acids of six cyclic diamines (PZ, 1-MPZ, 2-MPZ, 1-EPZ, HEPZ and DMPZ) were meaured using a potentiometric titration method at (298, 303, 313 and 323) K. A trend is proposed relating the variation of $pK_a$ with the addition of different radical groups to the base PZ molecule. $pK_a$ values of piperazines were computed using quantum chemistry techniques and the IEFPCM continuum solvation model. Of several techniques tested, the best one involved the incorporation of an explicit water molecule inside the continuum cavity (Model II). Proper entropy corrections, often neglected in $pK_a$ studies, were also included. The use of a second fitting parameter for these compounds dramatically lowered the overall rms error by 42-45%. Our best technique reduced the errors found in a previous technique (*9*) for similar compounds by 62% (*10*).

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