

# Reaction kinetics of carbon dioxide with 2-amino-2-hydroxymethyl-1,3-propanediol in aqueous solution obtained from the stopped flow method

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Carbon dioxide (CO<sub>2</sub>) capture has attracted great interest these days due to the role of CO<sub>2</sub> in global warming and its effects in industrial processes. Thus, higher energy efficient and affordable technologies are required for its removal so as to address these problems.

In this work, the reaction kinetics of CO<sub>2</sub> with 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), a sterically hindered amine (SHA), was studied by direct stopped flow method. The aim was to research CO<sub>2</sub> absorbent with better CO<sub>2</sub> absorption capacity and reaction kinetics than the commonly applied amine solvents. The study was carried out at 288, 298, and 303 K in a concentration range of 0.5-2.0 kmol/m<sup>3</sup> of AHPD. Based on the pseudo-first-order for the reaction of CO<sub>2</sub>, it was found that the reaction can be modeled by a single termolecular reaction mechanism. The reaction rate between CO<sub>2</sub> and aqueous solution of AHPD was 9.99, 12.03, and 16.05 m<sup>3</sup>/kmol.s at 288, 298, and 303 K, respectively, while its activation energy was 31.59 kJ/mol. The results obtained were compared with published reaction rate data of other amines. The present study shows that AHPD is a potential SHA as CO<sub>2</sub> absorbent if the reaction rate is enhanced by an additional amine.

**Key Words:** AHPD, CO<sub>2</sub> capture, sterically hindered amine, stopped flow method

## Introduction

Policy makers, industrialists, scientists, and environmentalists are generally interested in acid gas capture and storage as a vital means to mitigate greenhouse gas (GHG) emissions as well as maintain a cleaner atmospheric

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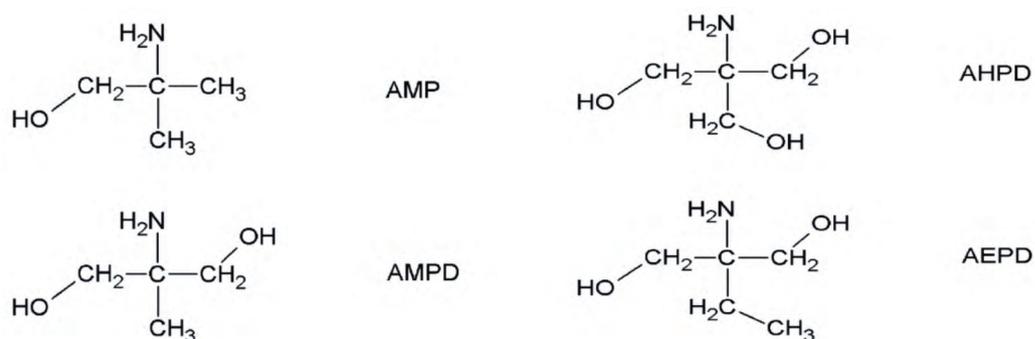
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environment. "Energy demand has been projected to rise by 60% in 2030".<sup>1</sup> This implies rising demand for fossil fuels and higher release of CO<sub>2</sub> to the environment; thus, minimizing CO<sub>2</sub> emissions by capturing it becomes a necessity.

To date, the most mature and commercial CO<sub>2</sub> capture technology is the chemical absorption–desorption process, where aqueous alkanolamines are used as solvents.<sup>2</sup> The amines basically in use are monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). Although there has been improvement in the absorption technique and its availability for acid gas removal, the process still demands high energy input and is thus costly. There are also issues of corrosion, solvent degradation, and high heat duty associated with the process. To resolve these problems and boost CO<sub>2</sub> capture technology application in many industries so as to achieve GHG emission mitigation targets and control CO<sub>2</sub> effects in industrial processes, the need to develop a higher efficient and economically affordable CO<sub>2</sub> capture technology cannot be overemphasized.

Currently, the vigor in seeking for alternative CO<sub>2</sub>/acid gas capture technology has led to considerable interest in sterically hindered amines (SHAs) due to their peculiar properties, especially their unstable carbamates formation. Primary and secondary alkanolamines such as MEA and DEA have fast reactivity as a result of their stable carbamates formation but with high solvent regeneration cost. Moreover, they have relatively low CO<sub>2</sub> loading, a maximum of 0.5 mol CO<sub>2</sub>/mol amine. Tertiary alkanolamines, such as MDEA, have high CO<sub>2</sub> theoretical loading capacity (1 mol CO<sub>2</sub>/mol amine) and low solvent regeneration cost but low chemical reactivity with CO<sub>2</sub> because they cannot form carbamate. However, the application of SHAs in gas-treating technology offers a higher absorption capacity, absorption rate, selectivity, and degradation resistance advantages over conventional amines for CO<sub>2</sub> capture; hence SHAs offer important industrial advantages.<sup>3</sup> A sterically hindered amine can simply be defined as an amine with one or more side groups attached to the central carbon atoms linked to the nitrogen atom. They form carbamate ions that are unstable and this leads to bicarbonate. Typical sterically hindered amines include 2-amino-2-methyl-1-propanol (AMP), 1,8-p-menthane diamine (MDA), and 2-piperidine ethanol (PE).

Among the SHAs 2-amino-2-methylpropanol (AMP) is the most frequently used.<sup>4</sup> AMP is a simple hindered form of MEA, and others derived from it are as follows: 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), and 2-amino-2-ethyl-1,3-propanediol (AEPD); their structures are illustrated in Figure 1.<sup>4</sup>



**Figure 1.** Structure of AMP, AMPD, AHPD, and AEPD.

Apart from AMP, data concerning the other potential SHAs are quite scarce. In view of AHPD, which is

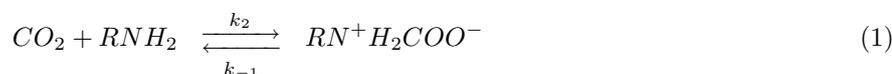
the SHA of interest in this study, the previous work done on it is very scarce and was carried out using indirect gas absorption. For instance, Park et al.<sup>4</sup> examined AHPD as a potential CO<sub>2</sub> absorbent and compared their result with the most commonly used absorbent MEA through equilibrium solubility measurements and <sup>13</sup>C-NMR spectroscopic analyses. In that study, the reaction rate constants were not evaluated as done in the present work. They observed only the solubility range, noting that “the solubility of CO<sub>2</sub> in aqueous 10 mass % AHPD solutions were higher than its corresponding solubility in aqueous 10 mass % MEA solutions above 4 kPa at 298.15 K, but below 4 kPa, the solubility behavior appeared to be the opposite”.<sup>4</sup> Based on <sup>13</sup>C-NMR spectroscopy analysis they noted that, in the CO<sub>2</sub>-amine-H<sub>2</sub>O solutions, amine reacted with CO<sub>2</sub> to form mainly the protonated amine (AMH<sup>+</sup>), bicarbonate ion (HCO<sub>3</sub><sup>-</sup>), and carbamate anion (AMCO<sub>2</sub><sup>-</sup>), where the quantitative ratio of bicarbonate ion to carbamate anion strongly influenced the CO<sub>2</sub> loading in the amine solutions. Bougie and Iliuta<sup>5</sup> determined the kinetics of the reaction of CO<sub>2</sub> with AHPD at a temperature range of 303.15-323.15 K and concentrations of 0.5-2.4 kmol/m<sup>3</sup> for AHPD by wetted wall column contactor, while Paul et al.<sup>6</sup> studied at 303-323 K and concentrations of 0.179-1.789 kmol/m<sup>3</sup>. Both researchers applied indirect methods in their studies, while the present work used the direct method. Their works first required the calculation of the diffusivity and solubility of CO<sub>2</sub> from N<sub>2</sub>O measurement through the N<sub>2</sub>O analogy. Thus, in view of the projected relevance of AHPD to CO<sub>2</sub> absorption as well as to expand information on SHAs, the present direct kinetics study on AHPD using the stopped flow method was deemed relevant.

## Experimental

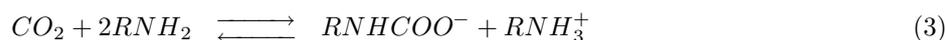
### Reaction analysis

There are 2 established mechanisms to describe the reaction between carbon dioxide and amines. They are the zwitterions mechanism, originally proposed by Caplow<sup>7</sup> and then Danckwerts,<sup>8</sup> and the single-step termolecular mechanism proposed by Crooks and Donnellan,<sup>9</sup> and also supported by Alper.<sup>10</sup>

According to the zwitterions mechanism, a 2-step process is involved in the reaction where zwitterions intermediate exist in solution. The 2 steps are represented as in Eqs. (1) and (2). As shown in Eq. (2), the proton from the zwitterion is transferred to a base (B), where B represents a water molecule, an amine, or any base.

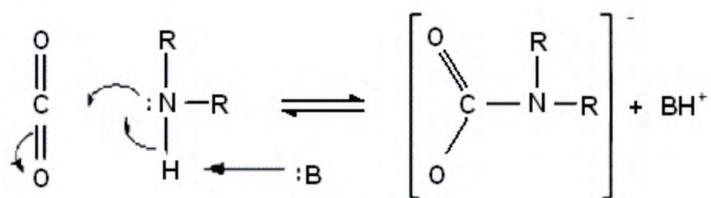


When the base is an amine and the carbamate ion is stable, the overall reaction follows:



In a single-step termolecular mechanism as represented by Eq. (4) and illustrated in Figure 2, only one step is involved in the reaction process.



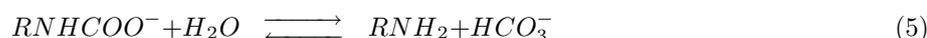


**Figure 2.** Schematic drawing of single-step termolecular reaction mechanism.<sup>10</sup>

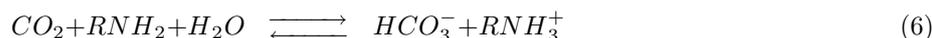
However, regardless of the mechanism, a carbamate and a protonated base are the generally accepted products of the  $\text{CO}_2$ -amine reaction. In addition, a recent review of amine with  $\text{CO}_2$  reaction mechanisms by Vaidya and Kenig<sup>11</sup> emphasized that many reaction systems with fractional- and higher-order kinetics can be satisfactorily described with both the zwitterion and termolecular mechanism.

Thus, this present work applied a single-step termolecular mechanism and the obtained kinetic data were fitted to the mechanism as proposed by Crooks and Donnellan.<sup>9</sup> It is worth noting that, with common amines such as MEA and DEA, Reaction (1) prevails to form a stable carbamate, requiring 2 moles of amine per mole of  $\text{CO}_2$ . This limits solution capacity to 0.5 mole amine/mole  $\text{CO}_2$  as in Eq. (3). However, when the base is a SHA, the carbamate ion is unstable and hence has a preferential reaction with amine compared to water, so that 1 mole of amine can capture 1 mole of  $\text{CO}_2$ .

Unstable carbamate:



Overall reaction:



Tertiary amines like MDEA that cannot form carbamates tend to achieve equivalent  $\text{CO}_2$  absorption mole ratios but the reaction rates are relatively slow. The SHA, on the other hand, may reduce carbamate stability without significantly compromising reactivity. Therefore, sterically hindered amines stand as a potential leading technology for  $\text{CO}_2$  capture.

The termolecular observed rate equation is given by:

$$r_{obs} = k_o[\text{CO}_2] \quad (7)$$

where:

$$k_o = k_{\text{H}_2\text{O}}[\text{H}_2\text{O}][\text{RNH}_2] + k_{\text{RNH}_2}[\text{RNH}_2]^2 \quad (8)$$

At low amine concentrations, the concentration of water remains constant

$$k_o = k_{\text{RNH}_2}[\text{RNH}_2]^2 + k_2[\text{RNH}_2] + k \quad (9)$$

Here, taking  $\text{RNH}_2$  as AHPD, which is a sterically hindered amine, Eq. (9) gives:

$$k_o = k_{\text{AHPD}}[\text{AHPD}]^2 + k_2[\text{AHPD}] + k \quad (10)$$

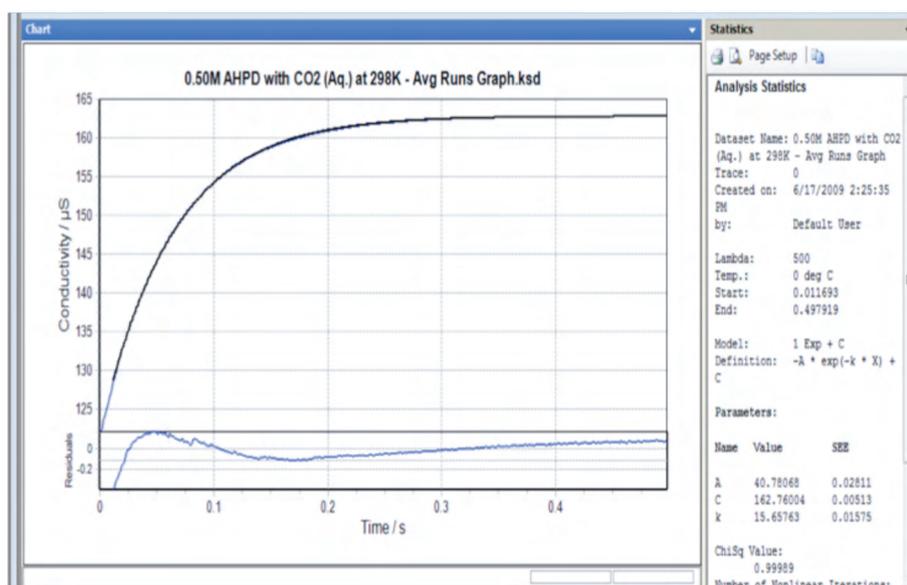
## Materials and methods

AHPD: 2-amino-2-hydroxymethyl-1,3-propanediol, also called tris(hydroxymethyl) amino methane, of reagent grade 99.8% was supplied by MERCK, Germany. The experiments were carried out at concentration range of 0.5-2.0 kmol/m<sup>3</sup> of AHPD at 288, 298, and 303 K, respectively.

The experimental technique applied in this study is a direct method using a standard stopped-flow apparatus (Hi-Tech Scientific, UK, Model SF-61SX2). It is made up of 4 main units: a sample handling unit, a conductivity detection cell, an A/D converter, and a micro-processor unit, other pertinent details of which can be found elsewhere.<sup>10</sup>

The rates of reactions of aqueous AHPD with CO<sub>2</sub> were measured using the standard stopped-flow equipment. In the sample handling unit, the AHPD and CO<sub>2</sub> solutions were placed in respective sealed drive syringes. For each experimental run, equal volumes of the solutions were pushed into and mixed in the stopped-flow mixer cell for the reaction to occur. The conductivity detection unit measures directly the intrinsic rate of a rapid homogeneous reaction between aqueous solutions of CO<sub>2</sub> and AHPD. It monitors the ion formation as a function of time as the ion formation initiates a voltage change within the cell. The reaction software (Kinetic Studio) automatically calculates the observed pseudo-first-order rate constant ( $k_o$ ) based on least square regression. All parts of the flow circuit were thermostated and the temperature control was within  $\pm 0.1$  K. Under pseudo-first-order conditions, the concentration of amine is always much in excess of that of CO<sub>2</sub>. Thus, the concentration of AHPD was always much in excess of that of CO<sub>2</sub>; the molar ratio was about 20:1 for all the experiment.

In this work, a set of experimental run involved repeating the experiment for an average of 10 times to obtain consistent  $k_o$  values for all the concentrations at the respective temperatures. Figures 3 and 4 show the combined average graph output from our standard stopped-flow equipment. Similar results were obtained for the other temperatures and concentration ranges studied.



**Figure 3.** Combined avg. graphs of 0.5 kmol/m<sup>3</sup> AHPD-CO<sub>2</sub> system at 298 K.

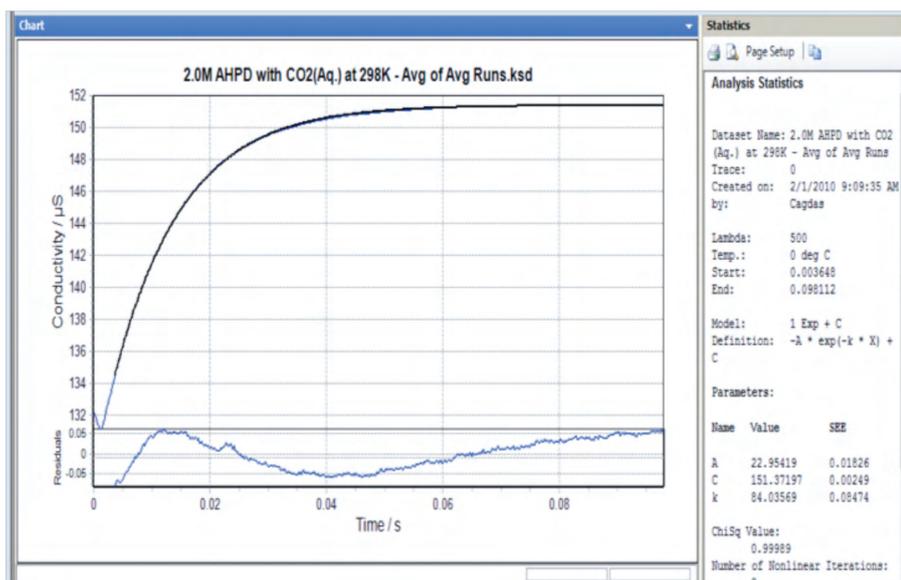


Figure 4. Combined avg. graphs of 2.0 kmol/m<sup>3</sup> AHPD-CO<sub>2</sub> system at 298 K.

## Results and discussion

The experimental observed pseudo-first-order rate constant ( $k_o$ ) values obtained were plotted as a function of AHPD concentration at the various temperatures (Figure 5). The stopped-flow data gave very satisfactory pseudo-first-order plots according to Eq. (7). The  $k_o$  values show a progressive increase as the temperature increases as well as with increases in the AHPD concentration. Noting that the reaction between OH<sup>-</sup> and CO<sub>2</sub> was not measured by the conductivity unit, the fitted rate constant corresponded directly to  $k_o$  in Eq. (7).

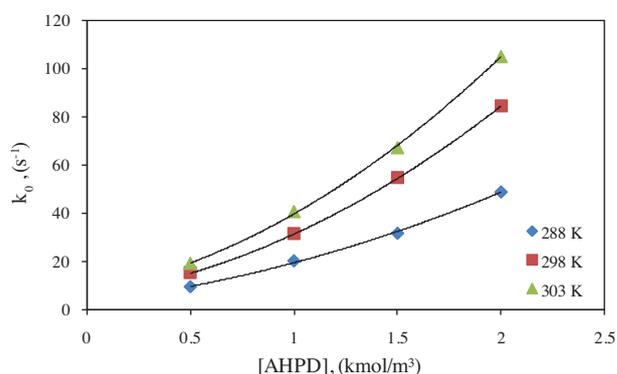
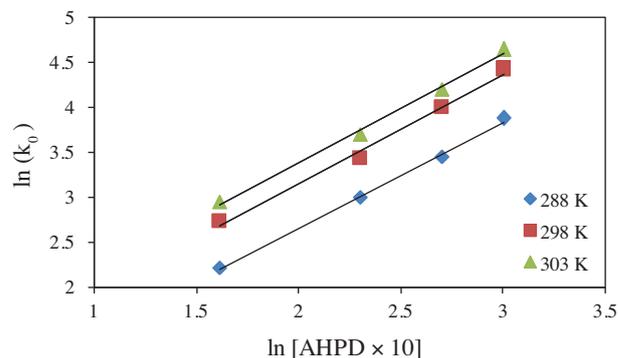


Figure 5. Effect of [AHPD] on  $k_o$  values at 288, 298, and 303 K.

By least-square-method, empirical power law kinetics was plotted with the data as in Figure 6, which gave good straight line graphs at temperatures of 288, 298, and 303 K. Accordingly, its slopes correspond to the reaction orders of 1.18, 1.22, and 1.21 with regression values of  $R^2 = 0.997, 0.992,$  and  $0.995,$  respectively. This

order for the concentrations studied implies that the termolecular reaction mechanism might be appropriate for this chemical reaction. The reaction rate data for AHPD with CO<sub>2</sub> (Eq. (10)) as obtained in this work are presented in Table 1.

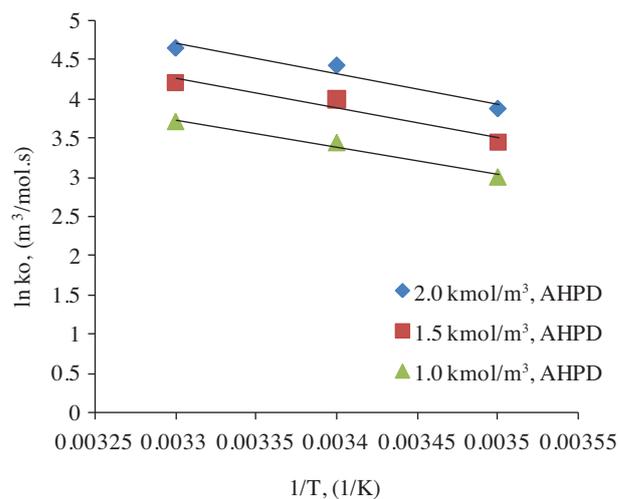


**Figure 6.** Empirical power law kinetics plots for reaction of aq. CO<sub>2</sub>-AHPD system.

**Table 1.** Fitted reaction rate data for reaction of CO<sub>2</sub>-AHPD in aqueous media.

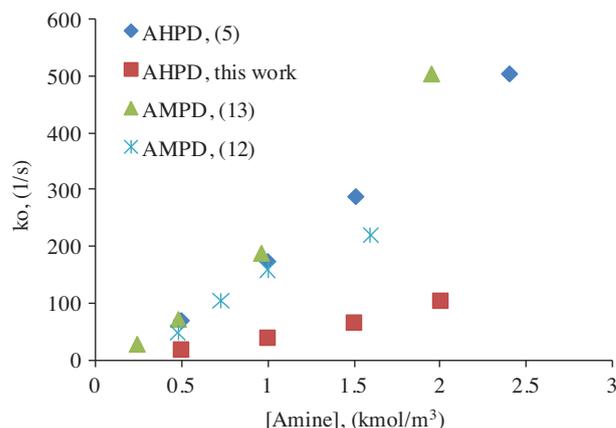
Temp., (K)	Order, (n)	$k$ , (m <sup>6</sup> /kmol <sup>2</sup> .s)	$k$ , (m <sup>3</sup> /kmol.s)	$k_2$ , (s <sup>-1</sup> )
288	1.18	6.38	9.99	2.91
298	1.22	13.56	12.03	5.82
303	1.21	16.29	16.05	7.41

Furthermore, the Arrhenius diagram was plotted as shown in Figure 7 and the activation energy of the reaction was found to be 29.51, 31.59, and 32.01 kJ/mol at 1.0, 1.5, and 2.0 M of AHPD concentrations, respectively.



**Figure 7.** Arrhenius diagram for reaction of aqueous CO<sub>2</sub>-AHPD system.

The results of this work were compared with the published data of SHAs like AHPD and AMPD as shown in Figure 8.



**Figure 8.** Comparison of AHPD obtained data with other SHAs published data.

The observed rate constants obtained in this work were lower than the AMPD values as expected. This can be attributed to the higher hydroxyl group in the AHPD than in the AMPD, which increases the hindrance effect on the AHPD. Moreover, the variation can be said to be in conformity with increasing reactivity order—AHPD, AMPD, and AMP—as noted by Bougie and Iliuta.<sup>5</sup> However, the AHPD reaction rate constants obtained by both Bougie and Iliuta, and Paul et al.<sup>6</sup> are higher than those in the present work. The activation energy of this work was found to be 31.56 kJ/mol at 1.5 kmol/m<sup>3</sup> AHPD, which was in close resemblance to that of AMPD as reported by Bouhamra et al. (33.7 kJ/mol)<sup>12</sup> and Yoon et al (38.3 kJ/mol).<sup>13</sup> This, however, is in variance with the values from Bougie et al. (53.7 kJ/mol)<sup>5</sup> and Paul et al. (65.2 kJ/mol)<sup>6</sup> for AHPD; although both researchers used the same method and applied the same model in analyzing their experimental gas absorption data, their results were very different. It should be noted that the activation energy values obtained for AMP were 41.7 kJ/mol<sup>14</sup> and 41.9 kJ/mol.<sup>15</sup> Hence, it can be inferred that the trend for the activation energy for these SHAs should be in decreasing order—AMP, AMPD, and AHPD—which this work shows.

The results obtained in this study indicate that the sterically hindered amine AHPD has advantages in terms of CO<sub>2</sub> capacity but the reaction rate is significantly lower than those of conventional amines.

## Conclusion

The reaction between aqueous AHPD with CO<sub>2</sub> was investigated using the direct-stopped flow method and was found that it can be modeled with a single termolecular reaction mechanism. The reaction rate of the AHPD is lower than that of MEA, which is the established solvent for commercial CO<sub>2</sub> capture. However, AHPD is a sterically hindered amine, its carbamate is unstable, leading to a theoretical CO<sub>2</sub> capture that is significantly higher than 0.5 mol CO<sub>2</sub>/mol amine, and it has lower activation energy.

Our result therefore shows that aqueous solution of AHPD is a potential sterically hindered amine for CO<sub>2</sub> capture to be considered in amine mixture formulation as an alternative solvent to regular amines. It offers a higher absorption capacity, as well as lower regeneration heat over conventional amines for CO<sub>2</sub> capture. On the other hand, the reaction rate should be enhanced by adding more reactive amines such as piperazine, which is currently being pursued in our laboratory.

## Acknowledgement

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