

Kinetics of Carbon Dioxide (CO₂) with 3-(Dimethylamino)-1-propylamine in Water and Methanol Systems Using the Stopped-Flow Technique

Devjyoti Nath and Amr Henni*

Cite This: <https://dx.doi.org/10.1021/acs.iecr.0c01157>

Read Online

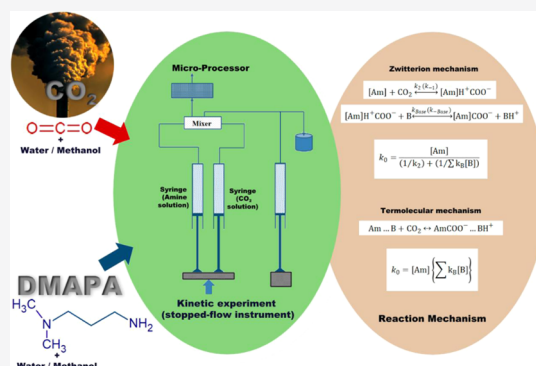
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: The kinetics for the reaction of carbon dioxide with primary 3-(dimethylamino)-1-propylamine (DMAPA) in water and methanol systems were investigated using the stopped-flow technique over a temperature range of 298.15–313.15 K. Pseudo-first-order rate constants for the reaction of (CO₂ + DMAPA) in aqueous and methanol systems at 298.15–313.15 K were estimated at concentrations ranging from 40 to 150 mol·m⁻³ and 100 to 300 mol·m⁻³, respectively. Both the Zwitterion and termolecular mechanisms successfully correlated the experimentally observed pseudo-first-order rate constants. The estimated second-order rate constants were in the range of 9.70–19.30 m³·mol⁻¹·s⁻¹. Aqueous solutions of DMAPA (primary and tertiary amino groups, 1/3°) exhibited faster kinetics than primary amines such as monoethanolamine (MEA), 1-amino-2-propanol (1AP), 3-amino-1-propanol (3AP), or a hindered amine such as 2-amino-2-methyl-1-propanol (AMP). DMAPA kinetic rate was lower than in diamines such as 2-(2-aminoethyl) amino ethanol (AEEA, 1/2°) and ethylenediamine (EDA, 1/1°). The estimated reaction orders varied from 1.15 to 1.37 and 1.04 to 1.22 in aqueous and methanol systems, respectively. The activation energies in aqueous and methanol systems were estimated using an Arrhenius expression. The estimated value of the activation energy in aqueous DMAPA was 39.47 kJ·mol⁻¹, which was lower than that of MEA (46.6 kJ·mol⁻¹). As expected, the reaction of CO₂ with DMAPA was faster in water than in methanol.



1. INTRODUCTION

Global warming due to emissions of carbon dioxide (CO₂) engendered by human activities is a major concern for modern societies.¹ Large amounts of CO₂ emissions are generated by power and cement plants and also the transportation industry. CO₂ capture from point sources and subsequent sequestration is one of the most technologically advanced methods presently used to mitigate CO₂ emissions.² Mixtures of aqueous amine solutions are the main type of solvents used in this technology. However, this technology is still not economically viable without funding from governments. A good number of amine-based solvents have been proposed in different research studies, but all solvents have pros and cons. Potential amine-based solvents for CO₂ capture should have certain characteristics such as high CO₂ absorption capacity, high selectivity for CO₂, high kinetic rate, low heat of reaction, low corrosion rate, and high stability in terms of degradation.^{3–5}

Fast kinetics for the reaction of CO₂ is a requirement for any new potential solvent. Reaction kinetics also play a significant role in process simulation and the design of CO₂ capture plants. These characteristics have often been used as key factors for evaluating or screening new solvents.⁶ Several kinetic studies of CO₂ reacting with primary, secondary, and tertiary amines have been performed since 1960.⁷ Several

instruments such as stirred cell reactor, wetted wall column, laminar jet absorber, wetted sphere absorber, and stopped-flow apparatus have been used for performing these kinetic studies in aqueous and nonaqueous amine solutions.⁸ The stopped-flow technique has several advantages including easy and fast operation, less requirement of solvent, etc.; therefore, it is one of the most commonly used techniques for performing kinetic studies of homogenous reactions.⁹ Since amine directly reacts with the CO₂ dissolved in the liquid phase, this technique is known as a direct technique.⁸

A number of kinetic studies for CO₂ reactions in several amine-based solvents including primary, secondary, tertiary, hindered primary, and cyclic amines have been performed using the stopped-flow technique.^{1,6,10,11} In addition, Ali used this technique to investigate the kinetics of CO₂ in amine blends and amine in mixed solvents.^{1,11} Stopped-flow has also been used for nonaqueous systems such as methanol, ethanol,

Received: March 6, 2020

Revised: July 26, 2020

Accepted: July 27, 2020

Published: July 27, 2020

Table 1. Structure, Abbreviation, Supplier, and Purity of the Chemicals Used in This Study

| Compound | Structure | IUPAC names (Abbreviation) | Source and Purity |
|---------------------------------|-----------|---|--|
| 3-(Dimethylamino)-1-propylamine | | N',N'-dimethylpropane-1,3-diamine (DMAPA) | Sigma-Aldrich (99 wt.%) ^a |
| Monoethanolamine | | 2-aminoethanol (MEA) | Sigma-Aldrich (≥ 98 wt.%) ^a |
| Diethanolamine | | 2-(2-hydroxyethylamino) ethanol (DEA) | Sigma-Aldrich (≥ 98.0%) ^a |
| Carbon dioxide | $O=C=O$ | Carbon dioxide (CO ₂) | Praxair (99.995 vol.%) ^a |
| Distilled Water | | Water (H ₂ O) | Prepared in the lab |

^a Provided by the supplier

glycol, and others.^{7,11} Nonaqueous systems of amine solvents have several advantages such as (i) less energy requirement for regeneration due to low heat capacity and low heat of vaporization of the solvent, (ii) less corrosiveness, (iii) high CO₂ capacity, and (iv) reduction in solvent decomposition;^{12–15} hence, nonaqueous systems are considered potential alternatives to aqueous systems.

Since diamines demonstrate higher CO₂ absorption capacity and kinetics compared to monoamines due to the presence of the two amino groups,¹⁶ they have received great emphasis in recent carbon capture research. Six different combinations of amino groups can be present in diamines: primary–primary (1/1°), primary–secondary (1/2°), primary–tertiary (1/3°), secondary–secondary (2/2°), secondary–tertiary (2/2°), and tertiary–tertiary (3/3°).¹⁷ Diamines with two primary amino groups exhibit high kinetics, but high energy is required for regeneration; on the other hand, diamines with two tertiary amino groups exhibit high CO₂ absorption capacity but slow kinetics.^{17,18} Finally, amines with a secondary amino group are less stable against oxidation and may lead to the production of undesirable nitrosol amines.^{17,19}

Chen and co-workers^{16,17,20} investigated a series of diamines as potential solvents for postcombustion CO₂ capture. Yu et al.¹⁶ investigated the effect of the diamine's molecular structure by studying the kinetics of six linear diamines using a bubble column. The investigation demonstrated that the methyl group and longer chain lengths increased the kinetics and capacity for CO₂ absorption, while the presence of the hydroxyl group decreased CO₂ absorption. Among the investigated amines, N-methylpropane-1,3-diamine (MAPA) exhibited the highest absorption rates for CO₂. In a different study, Yu et al.¹⁷ also used a bubble column to perform a detailed kinetic study of four diamines (1/3°). Results showed that a long alkyl chain between the primary amino group and tertiary amino group increases the reaction kinetics, while a significant decrease occurs in reaction kinetics when a tertiary amino group was present in the cyclic structure.¹⁷ Among the diamines studied, 3-(dimethylamino)-1-propylamine (DMAPA) exhibited the

highest kinetic rate. The kinetics for a group of cyclic and linear diamines in aqueous and nonaqueous systems were investigated by Henni and co-worker using the stopped-flow technique.^{12,21–23} A kinetic study for six cyclic diamines in aqueous systems was performed in the temperature range of 298.15–313.15 K. Results show that the estimated rates of the cyclic amines were higher than those for linear primary and secondary amines.²¹ A different kinetic study was performed by Henni and his co-workers in aqueous and nonaqueous systems for two diamines. Results show that 2-((2-aminoethyl) amino) ethanol (AEEA) and ethylenediamine (EDA) exhibited very high kinetic rates.^{12,22,23} DMAPA is compared to these two diamines later in the article. The kinetic studies for diethylenetriamine (DETA), a linear triamine, were performed by Salvi et al.²⁴ and Zhong et al.¹³ in aqueous and nonaqueous systems, respectively. DETA exhibited very high reaction rates, which made it a potential candidate for CO₂ capture operations.

3-(Dimethylamino)-1-propylamine (DMAPA) is a diamine with one primary and one tertiary amino group (1/3°). This combination makes it a good candidate as a solvent for CO₂ capture. In a recent solubility study, we showed that DMAPA exhibited very high capacity for CO₂ absorption compared to other benchmark amines such as monoethanolamine (MEA), piperazine (PZ), etc.²⁵ In the present study, the kinetic rates for the reaction of carbon dioxide with the same diamine, DMAPA, were measured in aqueous and methanol systems using the stopped-flow technique. Pseudo-first-order rate constants for the reaction of carbon dioxide (CO₂) with DMAPA in aqueous and methanol systems were measured within the temperature range of 298.15–313.15 K over concentration ranges of 40–150 mol·m⁻³ and 100–3000 mol·m⁻³, respectively. The second-order rate constants were estimated using the Zwitterion and termolecular mechanisms by correlating the experimentally measured pseudo-first-order rate constants.

2. EXPERIMENTAL METHODOLOGY

2.1. Materials. 3-(Dimethylamino)-1-propylamine (DMAPA), monoethanolamine (MEA), and diethanolamine (DEA) were purchased from Sigma-Aldrich and used without further purification. Carbon dioxide was acquired from Praxair. IUPAC names, structures, suppliers, and purities of all of the chemicals used in the present study are listed in Table 1.

2.2. Experiment. Details about the experimental procedure are provided in a previous study published by our research group.⁷ The schematic diagram of the experimental setup that was used in this study is shown in Figure 1. A standard SF-51

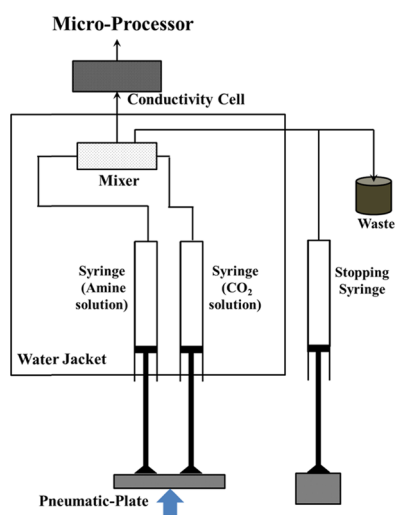


Figure 1. Schematic diagram of the experimental setup.

stopped-flow unit (Hi-Tech Scientific Ltd., U.K.) was used in this study. It consists of four major units: (i) a sample-handling unit, (ii) a conductivity-detection cell, (iii) an A/D converter, and (iv) a microprocessor. Sample-handling is performed by a stainless steel frame that supports a pneumatic-plate drive and the entire sample flow unit. Sample syringes and the flow circuit are immersed in a thermostatic water jacket placed around the sample-handling unit to maintain the system at a preset temperature. The jacket's temperature was controlled with an external water bath within 0.1 K of the desired temperature. Fixed amounts of amine and CO₂ solutions are transferred to the mixing unit with a pneumatically controlled drive-plate located at the bottom of the syringe (Figure 1).

At the beginning of each experiment, a fresh CO₂ solution was prepared by bubbling and mixing CO₂ for half an hour into double distilled water for the aqueous system and into methanol for the nonaqueous system. A pH meter was used to make sure the solvent was saturated with CO₂. The prepared solution was then diluted with the respective medium to maintain the pseudo-first-order conditions with respect to CO₂. Approximate concentrations of CO₂ in water and methanol at 298.15 K and 100 kPa partial pressure of CO₂ were estimated using Henry's law constant, which is provided in the Supporting Information. The measured ranges of the ratios of amine/methanol to CO₂ concentration were maintained within 7.5–12 and 10–20 in aqueous and methanol systems, respectively.

During each experiment, freshly prepared CO₂ and amine solutions were first loaded into two sample syringes. Then, the pneumatic drive-plate was actuated by the "Kinetasyst"

software so that it can push equal volumes of solutions and accurately transfers them to the mixing unit. Changes of the conductivity were measured as a function of time, as described by Knipe et al.,^{7,26} and the output signal was the voltage, which was proportional to the mixture's conductivity. Conductivity-detection range was set for 0–0.0005 Siemens for both systems (water and methanol), while the range factor (S per volt) was set at 0.00005. Conductivity changes with respect to time were fitted to an exponential equation to resemble the behavior of the first-order kinetic equation, as shown in eq 1. In this equation, k_0 is the pseudo-first-order reaction rate constant. A sample data run for the reaction between DMAPA and CO₂ water system is shown in Figure 2.

$$Y = -A e^{-k_0 t} + Y_{\infty} \quad (1)$$

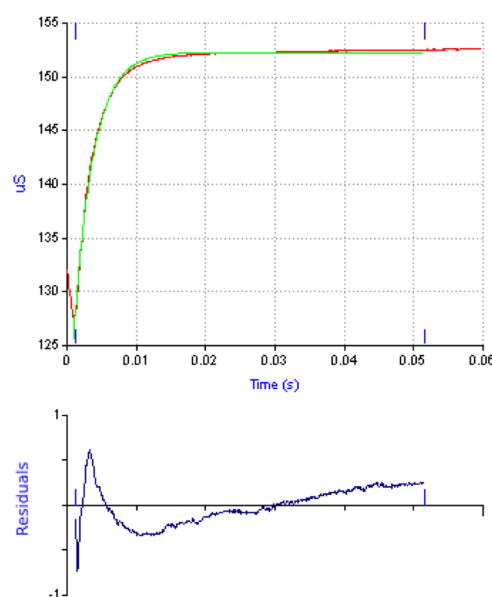


Figure 2. Sample data run for the reaction between DMAPA and CO₂ in the water system ($T = 298.15$ K, $[\text{DMAPA}] = 60 \text{ mol} \cdot \text{m}^{-3}$).

The estimated pseudo-first-order rate constants were fitted with power-law equation (eq 2) to determine the order of the reaction (n) with respect to amine concentration.

$$k_0 = k_n [\text{Amine}]^n \quad (2)$$

2.3. Experimental Uncertainty and Reproducibility.

Pseudo-first-order rate constants (k_0) for the reaction of carbon dioxide (CO₂) and amine solution in aqueous and nonaqueous systems were estimated as a function of amine concentration and temperature. Rate constants for all concentrations of amine at each temperature were estimated at least eight times to estimate the reproducibility. The experimental reproducibilities were estimated by taking the absolute average deviation of k_0 values from their mean values. The average estimated reproducibility in the present study was 8.6%. Experimental uncertainty was estimated with statistical analysis by taking into account the overall standard deviation. Estimation of the uncertainty of the estimated pseudo-first-order rate constant (k_0) is provided in the Supporting Information. The maximum estimated uncertainties for the pseudo-first-order rate constant (k_0) were 4.8 and 3.4% in water and methanol systems, respectively. The temperature uncertainty measurement was 0.4 K.

2.4. Verification of Rate Constant Measurement.

Pseudo-first-order rate constant for (CO₂ + MEA) in an aqueous system was estimated at 298.15 K, and pseudo-first-order rate constants for (CO₂ + DEA) in aqueous system were estimated at the temperature range varying from 298.15 to 313.15 K. The estimated pseudo-first-order rate constants were compared to those published in the literature,^{1,27} and the results are shown in Figures 3 and 4. Pseudo-first-order rate

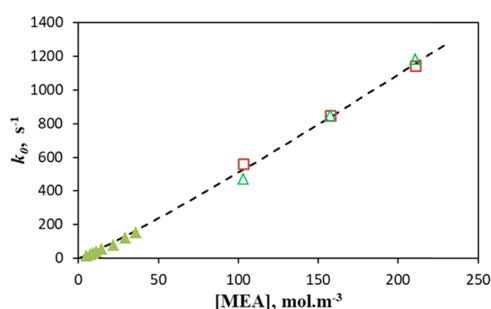


Figure 3. Pseudo-first-order rate constants for the reaction of carbon dioxide (CO₂) and MEA in an aqueous system were compared with those in the literature at 298.15 K [open green triangle: this study, open red box: Alper,²⁷ solid green triangle: Ali,¹ and dashed line: fitted with power-law equation (eq 2)].

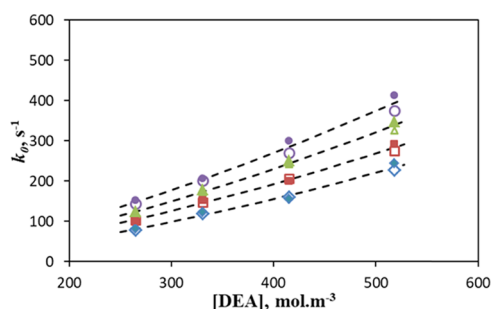


Figure 4. Pseudo-first-order rate constants for (CO₂ + DEA) in an aqueous system were compared with those in the literature at 298.15 K (diamond), 303.15 K (square), 308.15 K (triangle), and 313.15 K (circle). [Solid symbol: present study, open symbols: Ali,¹ and dashed line: fitted with power-law equation (eq 2)].

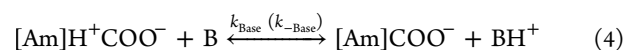
constant data are reported in Tables S1 and S2 (Supporting Information). In the present study, the estimated pseudo-first-order rate constants for the reaction of CO₂ with MEA and DEA were found to be in good agreement with those published in the literature.

3. REACTION MECHANISM AND KINETICS

In general, the Zwitterion mechanism is used to explain the reaction of CO₂ with primary and secondary amines, and the base-catalyzed mechanism is used to explain the reaction between CO₂ and tertiary amines. The termolecular mechanism is also used to explain the reaction of CO₂ with primary and secondary amines.

3.1. Zwitterion Mechanism. The Zwitterion mechanism can successfully explain the reaction between CO₂ and primary/secondary amines. Caplow²⁸ first proposed this mechanism that suggests that a carbamate is formed upon reaction between CO₂ and primary/secondary amine (R₂NH) via Zwitterion formation, and later Danckwerts²⁹ reintroduced this model to explain reaction in amine systems.³⁰ The Zwitterion mechanism occurs in two steps. According to this

mechanism, a Zwitterion is first formed as an intermediate species after reaction between CO₂ and amine (eq 3), and then the Zwitterion deprotonates in the second step by any base (B) present in solution such as an amine, water, a hydroxyl ion, etc., as shown in eq 4.³⁰ Methanol or ethanol can also carry out the deprotonation in nonaqueous systems.³¹



According to this mechanism, the overall forward rate of reaction of CO₂ can be derived using the quasi-steady-state condition for the intermediate zwitterion concentration, as shown in eq 3.^{7,11,30} k_{B} in eq 5 denotes the deprotonation of Zwitterion by any base present in the system or a combination of bases.⁷

$$\begin{aligned} r_{\text{CO}_2} &= \frac{[\text{CO}_2][\text{Am}]}{(1/k_2) + (k_{-1}/k_2 \sum k_{\text{Base}}[\text{B}])} \\ &= \frac{[\text{CO}_2][\text{Am}]}{(1/k_2) + (1/\sum k_{\text{B}}[\text{B}])} \end{aligned} \quad (5)$$

where $k_{\text{B}} = k_2 k_{\text{Base}}/k_{-1}$ [$\sum k_{\text{B}}[\text{B}] = k_{\text{A}}[\text{A}_{\text{min}}] + k_{\text{W}}[\text{H}_2\text{O}] + k_{\text{OH}^-}[\text{OH}^-]$ for an aqueous system and $\sum k_{\text{B}}[\text{B}] = k_{\text{A}}[\text{A}_{\text{min}}] + k_{\text{M}}[\text{methanol}]$ for a methanol system].

At the pseudo-first-order condition, the overall rate constant can be derived with respect to CO₂ concentration using eq 6.¹¹

$$r_{\text{CO}_2} = k_0[\text{CO}_2] \quad (6)$$

A new expression for the pseudo-first-order rate constants can be derived by combining eqs 5 and 6 leading to eq 7.

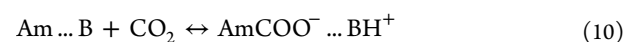
$$k_0 = \frac{[\text{Am}]}{(1/k_2) + (1/\sum k_{\text{B}}[\text{B}])} \quad (7)$$

There are two possible limiting cases for eq 7: (i) when the Zwitterion deprotonates relatively fast in comparison to the reversion reaction rate of amine and CO₂, term $(1/k_2)$ becomes much bigger than the term $(1/\sum k_{\text{B}}[\text{B}])$ ^{10,13} and (ii) when the Zwitterion deprotonation reaction is relatively slower in comparison with the reverse reaction rate, then it is considered as the rate-determining step and the term $(1/k_2)$ becomes much smaller than the term $(1/\sum k_{\text{B}}[\text{B}])$.^{10,13} When $(1/k_2)$ is much bigger than the term $(1/\sum k_{\text{B}}[\text{B}])$, the pseudo-first-order rate constant expression can be shown as eq 8;^{10,13} on the other hand, when the term $(1/k_2)$ becomes much smaller than the term $(1/\sum k_{\text{B}}[\text{B}])$, the pseudo-first-order rate constant expression can be reduced to eq 9.^{10,13}

$$k_0 = k_2[\text{Am}] \quad (8)$$

$$k_0 = \left(\sum k_{\text{B}}[\text{B}] \right) [\text{Am}] \quad (9)$$

3.2. Termolecular Mechanism. Crooks and Donnellan first proposed the termolecular mechanism,^{7,32} and later da Silva and Svendsen reinvestigated this mechanism.^{7,33} According to this mechanism, carbamate formation is a single-step process where bond formation between CO₂ and amine molecules and proton transfer to base occur simultaneously (eq 10).



The termolecular mechanism is quite similar to a limiting case of the Zwitterion mechanism. When the deprotonation of the Zwitterion is slower compared to the reverse reaction, the Zwitterion deprotonation becomes the rate-determining step. The derivation of the pseudo-first-order rate constant is shown in eqs 11 and 12.

$$r_{\text{CO}_2} = k_0[\text{CO}_2] = [\text{CO}_2][\text{Am}]\left\{\sum k_{\text{B}}[\text{B}]\right\} \quad (11)$$

$$k_0 = [\text{Am}]\left\{\sum k_{\text{B}}[\text{B}]\right\} \quad (12)$$

where $k_{\text{B}} = k_2k_{\text{Base}}/k_{-1}$ [$k_{\text{A}} = k_2k_{\text{Amine}}/k_{-1}$, $k_{\text{W}} = k_2k_{\text{Water}}/k_{-1}$, and $k_{\text{OH}^-} = k_2k_{\text{OH}^-}/k_{-1}$ for an aqueous system and $k_{\text{A}} = k_2k_{\text{Amine}}/k_{-1}$ and $k_{\text{M}} = k_2k_{\text{Methanol}}/k_{-1}$ for the methanol system].

3.3. OH⁻ Contribution. Several studies considered that OH⁻ had an insignificant contribution to the overall reaction rates considering different rationales such as possibilities that OH⁻ ion concentration is low, the chance of overestimation of the influence of the reaction between OH⁻ and CO₂ due to the presence of other negative charges (e.g., HCO₃⁻, CO₃²⁻), etc.^{7,34} On the other hand, several studies considered the influence of OH⁻ on the overall reaction rates since the reaction between amine and H₂O is instantaneous as it involves only a proton transfer (eq 13).³⁵



Although OH⁻ may have an influence on the overall rate constant, the contribution to the overall pseudo-first-order rate constant is very low. Therefore, the contribution of OH⁻ was not considered for correlating the experimental data in this study.

4. RESULTS AND DISCUSSION

4.1. (DMPA + CO₂) in an Aqueous System. The kinetics of the reaction between carbon dioxide and DMPA in aqueous systems were studied at the temperature range of 298.15–313.15 K and over a concentration range of 40–150 mol·m⁻³ using the stopped-flow technique. Estimated pseudo-first-order reaction rate constants for (DMPA + CO₂) in aqueous systems are plotted against the concentration of DMPA in Figure 5, and the experimental results are provided in Table 2. Figure 5 infers that the pseudo-first-order reaction rate constants increased with concentration almost linearly and also increased with temperature. The reaction order with

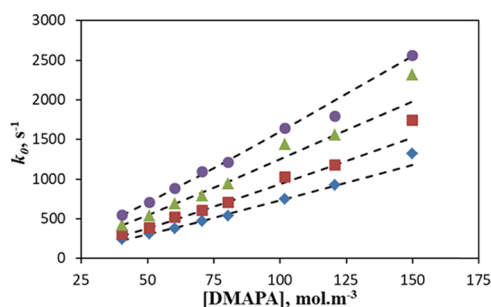


Figure 5. Pseudo-first-order rate constants (DMPA + CO₂) in an aqueous system in the temperature range of 298.15–313.15 K [solid blue diamond: 298.15 K, solid red box: 303.15 K, solid green triangle: 308.15 K, solid purple circle: 313.15 K, and dashed line: fitted with eq 7].

respect to the concentration of DMPA was always slightly higher than unity.

Pseudo-first-order rate constants for (CO₂ + DMPA) in the aqueous system were compared to various primary amines at 298.15 K, as shown in Figure 6. This figure shows that pseudo-first-order rate constants of DMPA were higher than those of primary amines such as MEA, 1-amino-2-propanol (1AP), and 3-amino-1-propanol (3AP). However, diamines such as ethylenediamine (EDA) and 2-((2-aminoethyl) amino) ethanol (AEEA) exhibited higher kinetics than DMPA. EDA has two primary amino groups in its structure (1/1°), and AEEA has one primary and one secondary amino group (1/2°). 2-Amino-2-methyl-1-propanol (AMP), a hindered amine, showed as expected the lowest kinetic rates. Note that diamines with two primary amino groups (1/1°) are known to require high energy of regeneration and those with a secondary amine are prone to oxidative degradation and may lead to the production of nitrosamines, a major environmental concern.¹⁷ DMPA has one primary and one tertiary amino group in its structure (1/3°) and it seems that this combination is very advantageous. Again, in most cases, diamines demonstrated higher CO₂ absorption capacity and kinetics compared to monoamines due to the presence of the two amino groups.¹⁶ Yu et al.¹⁶ concluded that the presence of hydroxyl group decreases the electron density of the amino group and forms a hydrogen bond between OH⁻ and NH₂. The presence of hydroxyl group therefore decreases the rate of CO₂ absorption, and, on the other hand, the presence of the methyl group and longer carbon chain increases CO₂ absorption capacity and reaction kinetics.¹⁶ Replacement of a hydroxyl group of an amine by a tertiary amino group improves the reactivity with CO₂,^{17,17} and the addition of an alkyl spacer between the primary and tertiary amino groups of the diamines promotes the absorption kinetics.¹⁷ The molecular structure provides a special advantage to DMPA to become a potential CO₂ capture solvent.

The reaction order with respect to amine concentration was estimated using the power-law equation (eq 14), and the second-order rate constants for (CO₂ + DMPA) in the aqueous phase at different temperatures were estimated from the pseudo-first-order rate constant data using different kinetic mechanisms. Since DMPA is a diamine, the reaction between CO₂ and both amino groups may have a combined effect on the rate constant. Published studies showed that primary amines are much faster than tertiary amines. For example, the second-order rate constant of MEA at the temperature ranges from 298.15 to 313.15 K is in the range of 5.51–13.60 m³·mol⁻¹·s⁻¹,¹ and the second-order rate constants of MDEA from 298.15 to 313.15 K are in the range of 0.012–0.028 m³·mol⁻¹·s⁻¹.⁷ Furthermore, the basicity of primary amines is higher than that of tertiary amines,^{36,37} therefore, the primary amino group of a diamine should react first with the CO₂, and then the reaction between the tertiary amino group and CO₂ would take place. However, the tertiary amino group does not react with CO₂ directly, as it catalyzes the slow hydration of CO₂ as a base.⁸ In a reaction with an acid, the primary amino group in a diamine dissociates first (pK_{a1}) and then the tertiary amino group dissociates second (pK_{a2}).³⁶ Moreover, all reactions in this study are of pseudo-first-orders, where the concentration of amine is much higher than that of CO₂. Hence, the chance of the reaction between the tertiary amino group and CO₂ is quite low taking into account the fast

Table 2. Pseudo-First-Order Reaction Rate Constants for (DMAPA + CO₂) in an Aqueous System

| DMAPA concentration (mol·m ⁻³) | Pseudo-first-order reaction rate constants (k_0^b) | | | |
|--|--|------------------|------------------|------------------|
| | $T^a = 298.15$ K | $T^a = 303.15$ K | $T^a = 308.15$ K | $T^a = 313.15$ K |
| 40.5 | 239 | 298 | 416 | 549 |
| 50.8 | 311 | 385 | 538 | 705 |
| 60.3 | 380 | 519 | 690 | 883 |
| 70.6 | 467 | 602 | 793 | 1090 |
| 80.4 | 540 | 703 | 946 | 1208 |
| 101.7 | 745 | 1028 | 1435 | 1641 |
| 120.8 | 924 | 1177 | 1554 | 1793 |
| 149.9 | 1317 | 1742 | 2315 | 2558 |

^a $u(T) = 0.4$ K. ^b $u(k_0) = 4.8\%$.

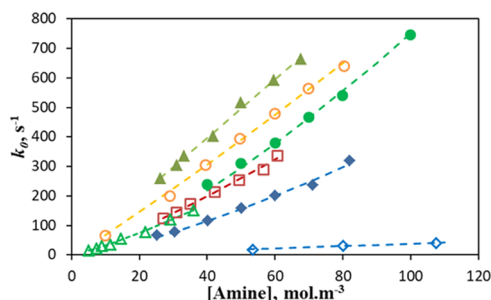


Figure 6. Pseudo-first-order rate constants for (CO₂ + DMAPA) in an aqueous phase compared with those of various primary amines at 298.15 K [solid green triangle: EDA,²³ open orange circle: AEEA,¹² solid green circle: DMAPA (this study), open red box: 3AP,¹⁰ open green triangle: MEA,¹ blue tilted square solid: IAP,¹⁰ open blue diamond: AMP,¹ and dashed line: fitted with power-law equation (eq 2)].

measurement in the stopped-flow technique. Therefore, the contribution of the reaction between CO₂ and the tertiary amino group of diamine to the overall rate constant is deemed to be small, as confirmed by the analysis reported by Yu et al.¹⁷ Hence, only the reaction between CO₂ and the primary amino group was considered for the estimation of the second-order rate constant using the Zwitterion and termolecular mechanisms. Yu et al.¹⁷ recently published the results of the kinetics study of DMAPA performed only at 298 K. The protonation effects in DMAPA were investigated using a comprehensive study of the mechanism of reaction using ¹H/¹³C NMR and

FTIR and experimentally using a wetted wall. They concluded that the primary amino group had a greater protonation constant than the tertiary group, and carbamate species were dominant in the reaction. The formation of bicarbonates was only present at high loadings of 0.9 mol CO₂/mol amine. At equilibrium, the tertiary group contribution to CO₂ absorption (solubility) was noticeable, as expected, allowing the tertiary amine to produce loadings as high as 1 mole CO₂/mol amine. Yu et al. used the Zwitterion mechanism to model the data and under pseudo-first-order conditions, the model was therefore equivalent to eq 8. The second-order rate constants were estimated by correlating the experimental pseudo-first-order rate constant data by minimizing the %AAD defined in eq 14.

$$\%AAD = \frac{1}{n} \sum_n \text{abs} \left(\frac{\text{experimental } (k_0) - \text{correlated } (k_0)}{\text{experimental } (k_0)} \right) \times 100 \quad (14)$$

The estimated reaction orders with respect to the concentration of DMAPA using the power-law equation and the second-order rate constants for the Zwitterion and termolecular mechanisms in a water system are provided in Table 3. The estimated reaction orders with respect to the concentration of DMAPA varied from 1.15 to 1.37 for the temperature range of 298.15–313.15 K. The reaction orders with respect to amine concentration for DMAPA were very close to those of MEA. Sada et al.³⁸ reported the reaction order for the MEA in an aqueous system to be one, while Aboudheir et al.³⁹ reported the reaction order for MEA for the

Table 3. Second-Order Rate Constants for (DMAPA + CO₂) in an Aqueous System

| equation | parameters | T (K) | | | |
|----------|---|---|---|---|---|
| | | 298.15 | 303.15 | 308.15 | 313.15 |
| eq 7 | k_2 (m ³ ·mol ⁻¹ ·s ⁻¹) | 9.32 | 12.28 | 14.82 | 20.44 |
| | k_A (m ⁶ ·mol ⁻² ·s ⁻¹) | 3.28×10^{-1} | 3.87×10^{-1} | 7.95×10^{-1} | 5.72×10^{-1} |
| | k_W (m ⁶ ·mol ⁻² ·s ⁻¹) | 1.76×10^{-5} | 1.06×10^{-5} | 2.32×10^{-5} | 3.08×10^{-4} |
| | R^2 | 0.978 | 0.966 | 0.951 | 0.969 |
| | %AAD | 3.00 | 4.06 | 4.65 | 2.34 |
| eq 8 | k_2 (m ³ ·mol ⁻¹ ·s ⁻¹) | 7.69 ± 0.34 | 10.11 ± 0.48 | 13.56 ± 0.63 | 15.87 ± 0.39 |
| | R^2 | 0.941 | 0.934 | 0.935 | 0.977 |
| | %AAD | 14.8 | 16.7 | 16.4 | 7.4 |
| eq 12 | k_A (m ⁶ ·mol ⁻² ·s ⁻¹) | $2.78 \times 10^{-2} \pm 1.65 \times 10^{-3}$ | $3.76 \times 10^{-2} \pm 4.47 \times 10^{-3}$ | $4.69 \times 10^{-2} \pm 8.00 \times 10^{-3}$ | $2.65 \times 10^{-2} \pm 7.80 \times 10^{-3}$ |
| | k_W (m ⁶ ·mol ⁻² ·s ⁻¹) | $8.28 \times 10^{-5} \pm 3.53 \times 10^{-6}$ | $1.07 \times 10^{-4} \pm 9.56 \times 10^{-6}$ | $1.50 \times 10^{-4} \pm 1.71 \times 10^{-5}$ | $2.34 \times 10^{-4} \pm 1.67 \times 10^{-5}$ |
| | R^2 | 0.999 | 0.994 | 0.989 | 0.991 |
| | %AAD | 1.79 | 2.82 | 3.35 | 3.16 |
| eq 2 | order (n) ^a | 1.36 ± 0.04 | 1.37 ± 0.06 | 1.35 ± 0.07 | 1.15 ± 0.05 |

^aReaction order was estimated with respect to amine concentration using the power-law model.

temperature range of 293–333 K within the range of 1.04–1.31 and 1.29–1.45 for concentrations from 193 to 3879 mol·m⁻³ and from 1405 to 5498 mol·m⁻³, respectively. The reaction order for DMAPA is also slightly higher than those of two other common diamines with primary amino groups present in their structures, namely, EDA²³ (1/1°) and AEEA (1/2°).¹² The reaction orders with respect to amine concentration for EDA and AEEA in the aqueous system varied within the range of 1.01–1.18 and 1.03–1.10 for the temperature range of 298.15 to 313.15 K, respectively.^{12,23}

Table 3 shows that k_2 for the Zwitterion mechanism increased with the increase in temperature. The estimated second-order rate constants for (CO₂ + DMAPA) in the aqueous phase at the temperature range of 298.15–313.15 K are in the range of 9.70–19.30 m³·mol⁻¹·s⁻¹. These values are higher than those obtained in the reaction between CO₂ and MEA in an aqueous phase [(5.51–13.60) m³·mol⁻¹·s⁻¹]¹ over the same temperature range. The expression for second-order rate constant for the termolecular mechanism is similar to the second limiting case of the Zwitterion mechanism when the deprotonation reaction is relatively slow in comparison to the reverse reaction rate and is considered the rate-determining step. Therefore, the second-order rate constant expressions shown in eqs 9 and 12 are similar. Equations 7 and 12 successfully correlated the first-order rate constants, and %AAD for the model's correlations were less than 4%. The percentages of AAD for the model correlation using eq 8 were a little high. Based on their study of the mechanism of the reaction and the analytical results of the NMR and FTIR studies, Yu et al.¹⁷ also neglected CO₂ hydration and assumed the deprotonation of the Zwitterion to be instantaneous (equivalent to model in eq 8). The value of k_2 was found to be 6.997 m³·mol⁻¹·s⁻¹ at 298 K, which is in very good agreement with our own measurement if we take into account the difference in concentrations and technique used.

The relative significance of the terms (1/ k_2) and (1/((k_A [Amine]) + (k_W [Water])))) of the rate constant expression shown in eq 7 on the overall pseudo-first-order rate constant was investigated and is shown in Table 4. The estimated term (1/ k_2) is bigger than the term (1/Σ k_B [B]); however, the influence of the term (1/Σ k_B [B]) is non-negligible.

The second-order rate constant increased with increasing temperature. The second-order rate constants were fitted to the Arrhenius expression shown in eq 15 to estimate the

activation energy, leading to a value of 39.47 kJ·mol⁻¹. Arrhenius plot of the second-order rate constant for the reaction of CO₂ in aqueous DMAPA is shown in Figure 7, and

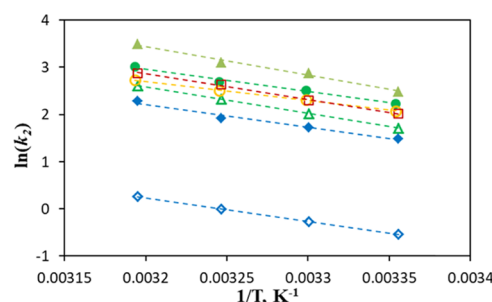


Figure 7. Arrhenius plots for (amine + CO₂) in the aqueous system [solid green circle: DMAPA (this study), solid green triangle: EDA,²³ open orange circle: AEEA,¹² open red box: 3AP,¹⁰ open green triangle: MEA,¹ solid blue diamond: 1AP,¹⁰ open blue diamond: AMP,¹ and dashed line: linear fit].

the Arrhenius expression for the aqueous (DMAPA + CO₂) system is presented in eq 16. Arrhenius plot for DMAPA is compared to other amine systems published in the literature in Figure 7.^{1,10,12,23} The rank of the amine in ascending order based on the activation energy is as follows: AEEA (34.19 kJ·mol⁻¹)¹² < DMAPA < 1AP (40.14 kJ·mol⁻¹)¹⁰ < 3AP (45.35 kJ·mol⁻¹)¹⁰ < MEA (46.6 kJ·mol⁻¹)¹ < EDA (50.56 kJ·mol⁻¹).²³

$$k_2 = A e^{-E_a/RT} \quad (15)$$

where A , E_a , and R are the Arrhenius constant (m³·mol⁻¹·s⁻¹), activation energy (kJ·mol⁻¹), and the universal gas constant, respectively.

$$k_2 = (7.621 \times 10^7) e^{-39.47/RT} [R^2 = 0.990] \quad (16)$$

Penny and Ritter⁴⁰ plotted the logarithms of the second-order rate constants against the dissociation constant of various primary amines at 293.15 K and observed a Brønsted relationship between the second-order rate constants and the dissociation constants at 293.15 K. As the Zwitterion formation of an amine is an acid–base reaction, a Brønsted relationship between the rate constants and dissociation constants should exist.³⁴ The Brønsted relationship between the second-order rate constants and the acid dissociation constant for DMAPA over the temperature range of 298.15–313.15 K is shown in Figure 8. The dissociation constants for DMAPA at 298.15, 303.15, and 308.15 K were directly taken

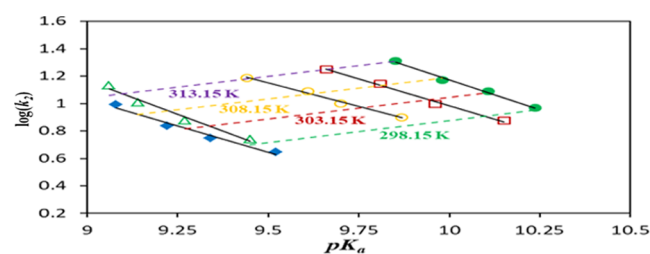


Figure 8. Brønsted plot for (amine + CO₂) in the aqueous system [solid green circle: DMAPA (this study), open orange circle: AEEA,^{12,41} open red box: 3AP,^{10,42} open green triangle: MEA,^{1,43} solid blue diamond: 1AP,^{10,42} and lines (continuous and dashed lines): linear fit].

Table 4. Relative Significance of the Terms (1/ k_2) and (1/((k_A [Amine]) + (k_W [Water])))) on the Overall Pseudo-First-Order Rate Constant

| DMAPA concentration (mol·m ⁻³) | T (K) | | | |
|--|---|--------|--------|--------|
| | 298.15 | 303.15 | 308.15 | 313.15 |
| 40.5–149.9 | 1/ k_2 | | | |
| | 0.107 | 0.081 | 0.067 | 0.049 |
| 40.5 | 1/((k_A [Amine]) + (k_W [Water])) | | | |
| | 0.070 | 0.061 | 0.030 | 0.025 |
| 50.8 | 0.057 | 0.049 | 0.024 | 0.022 |
| 60.3 | 0.048 | 0.042 | 0.020 | 0.019 |
| 70.6 | 0.042 | 0.036 | 0.017 | 0.017 |
| 80.4 | 0.037 | 0.032 | 0.015 | 0.016 |
| 101.7 | 0.029 | 0.025 | 0.012 | 0.013 |
| 120.8 | 0.025 | 0.021 | 0.010 | 0.012 |
| 149.9 | 0.020 | 0.017 | 0.008 | 0.010 |

from Tissier and Barillier.³⁶ However, the dissociation constant at 313.15 K was predicted with linear fitting of the dissociation constant data provided by Tissier and Barillier against temperature.³⁶ The Brønsted relationship for DMAPA is shown in eq 17. The Brønsted relationships for other common amines are also shown in Figure 8 for comparison using the second-order rate constants and the acid dissociation constants from the literature.^{1,10,12,23,41–43} The dissociation constants for AEEA at 303.1 and 313.15 K were directly taken from the study by Ma'mun et al.,⁴¹ and the dissociation constants at 298.15 and 308.15 K were predicted from the linear fitting of the data. Figure 8 infers that primary amines including diamines with the primary amino group exhibit a Brønsted relationship. Dissociation constants of all amines increase with the decrease in temperature, and the second-order rate constants for all amine decrease linearly with the increase in the dissociation constants. This figure also infers that the higher the dissociation constant of an amine at a given temperature, the higher is the rate constant compared to the amine with a lower dissociation constant at the same temperature, as suggested by Versteeg et al.³⁴

$$\log_{10}(k_2) = -0.8598 \text{ p}K_a + 9.7707 [R^2 = 0.999] \quad (17)$$

4.2. (DMAPA + CO₂) in a Methanol System. The kinetics of the reaction between carbon dioxide and DMAPA in the methanol system was studied in the temperature range of 298.15–313.15 K over a concentration range of 100–300 mol·m⁻³ using stopped-flow technique. The estimated pseudo-first-order reaction rate constants for (DMAPA + CO₂) in the methanol system were plotted against the concentration of DMAPA in Figure 9, and the experimental results are provided

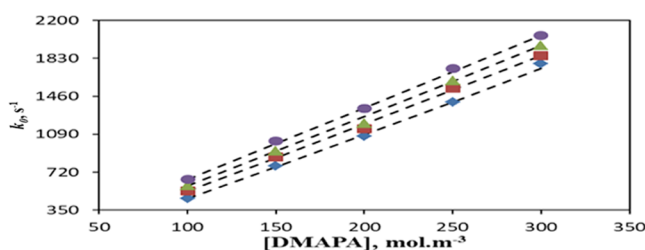


Figure 9. Pseudo-first-order rate constants for (DMAPA + CO₂) in the methanol system in the temperature range of 298.15–313.15 K [solid blue diamond: 298.15 K, solid red box: 303.15 K, solid green triangle: 308.15 K, solid purple circle: 313.15 K, and dashed line: fitted with eq 7].

in Table 5. Figure 9 suggests that the pseudo-first-order reaction rate constants increased with concentration almost linearly and with temperature.

Second-order rate constants for the reaction of CO₂ in DMAPA for the methanol system were estimated from the pseudo-first-order rate constant data using a different kinetic mechanism. As previously discussed, primary amines are much faster than tertiary amines, and the contribution of the reaction between CO₂ and tertiary amino group of diamine to the overall rate constant should be very small. Therefore, only the reaction between CO₂ and the primary amino group present in DMAPA was considered for the estimation of the second-order rate constant by taking into account the Zwitterion and termolecular mechanisms. Second-order rate constants were estimated by correlating the experimental pseudo-first-order rate constant data by minimizing the %AAD defined in eq 14.

The estimated reaction order with respect to amine concentration using the power-law equation and the second-order rate constants based on the Zwitterion and termolecular mechanisms are provided in Table 6. Since the expression for second-order rate constant for the termolecular mechanism is similar to the limiting case of Zwitterion mechanism where the deprotonation reaction is relatively slower in comparison to the reverse reaction rate, it was therefore considered the rate-determining step. The second-order rate constant expressions shown in eqs 9 and 12 are similar. Table 6 shows that k_2 for the Zwitterion mechanism increases with temperature.

The second-order rate constants increased with an increase in temperature. The second-order rate constants were fitted to an Arrhenius expression, shown in eq 15, to estimate the activation energy, leading to a value of 39.74 kJ·mol⁻¹. The Arrhenius plot of the second-order rate constants for the reaction of CO₂ in aqueous DMAPA is shown in Figure 10, and the Arrhenius expression for (DMAPA + CO₂) in the methanol system is represented by eq 18. The Arrhenius plot for DMAPA in methanol is compared in Figure 10 to those of two other diamines, AEEA¹² and EDA,⁷ having a primary amino group present in their structure.

The rank of the amine in ascending order based on the activation energy is as follows: EDA (11.42 kJ·mol⁻¹)⁷ < AEEA (17.28 kJ·mol⁻¹)¹² < DMAPA.

$$k_2 = (29.90)e^{-39.74/RT} [R^2 = 0.999] \quad (18)$$

5. CONCLUSIONS

Pseudo-first-order rate constants of the reaction of carbon dioxide (CO₂) with a (1/3°) diamine, 3-(dimethylamino)-1-propylamine (DMAPA), in water and methanol systems were measured using a stopped-flow apparatus at a temperature range of 298.15–313.15 K and over concentration ranges of 40–150 mol·m⁻³ and 100–300 mol·m⁻³, respectively. Pseudo-first-order rate constants of DMAPA were higher than most other commonly used amines such as MEA, 1AP, and 3AP.

Table 5. Pseudo-First-Order Reaction Rate Constants for (DMAPA + CO₂) in the Methanol System

| DMAPA concentration (mol·m ⁻³) | Pseudo-first-order reaction rate constants (k_0^b) | | | |
|--|--|------------------|------------------|------------------|
| | $T^a = 298.15$ K | $T^a = 303.15$ K | $T^a = 308.15$ K | $T^a = 313.15$ K |
| 100.8 | 463 | 537 | 588 | 650 |
| 150.6 | 781 | 871 | 924 | 1027 |
| 200.4 | 1070 | 1144 | 1196 | 1341 |
| 250.5 | 1405 | 1539 | 1611 | 1732 |
| 300.8 | 1777 | 1857 | 1953 | 2055 |

^a_u(T) = 0.4 K. ^b_u(k_0) = 3.4%.

Table 6. Second-Order Rate Constants for (DMAPA + CO₂) in the Methanol System

| equation | parameters | T (K) | | | |
|----------|---|---|---|---|---|
| | | 298.15 | 303.15 | 308.15 | 313.15 |
| eq 7 | k_2 (m ³ ·mol ⁻¹ ·s ⁻¹) | 6.65 | 6.77 | 6.97 | 7.13 |
| | k_A (m ⁶ ·mol ⁻² ·s ⁻¹) | 1.40×10^{-1} | 2.20×10^{-1} | 2.93×10^{-1} | 4.89×10^{-1} |
| | k_W (m ⁶ ·mol ⁻² ·s ⁻¹) | 2.83×10^{-5} | 1.46×10^{-4} | 2.58×10^{-4} | 7.53×10^{-4} |
| | R^2 | 0.998 | 0.998 | 0.996 | 0.998 |
| | %AAD | 1.09 | 1.37 | 1.20 | 1.05 |
| eq 8 | k_2 (m ³ ·mol ⁻¹ ·s ⁻¹) | 5.59 ± 0.17 | 6.01 ± 0.12 | 6.32 ± 0.11 | 6.81 ± 0.05 |
| | R^2 | 0.976 | 0.988 | 0.990 | 0.998 |
| | %AAD | 8.00 | 5.35 | 4.29 | 1.86 |
| eq 12 | k_A (m ⁶ ·mol ⁻² ·s ⁻¹) | $6.18 \times 10^{-3} \pm 5.43 \times 10^{-4}$ | $4.37 \times 10^{-3} \pm 9.59 \times 10^{-4}$ | $4.08 \times 10^{-3} \pm 1.02 \times 10^{-3}$ | $1.93 \times 10^{-3} \pm 8.12 \times 10^{-4}$ |
| | k_W (m ⁶ ·mol ⁻² ·s ⁻¹) | $1.71 \times 10^{-4} \pm 5.72 \times 10^{-6}$ | $2.06 \times 10^{-4} \pm 1.01 \times 10^{-5}$ | $2.22 \times 10^{-4} \pm 1.07 \times 10^{-5}$ | $2.65 \times 10^{-4} \pm 8.55 \times 10^{-6}$ |
| | R^2 | 0.999 | 0.998 | 0.998 | 0.999 |
| | %AAD | 1.36 | 1.95 | 1.48 | 1.57 |
| eq 2 | order (n) ^a | 1.22 ± 0.02 | 1.13 ± 0.03 | 1.11 ± 0.04 | 1.04 ± 0.02 |

^aReaction order was estimated with respect to amine concentration using power-law model.

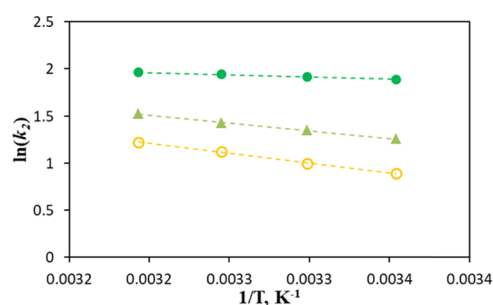


Figure 10. Arrhenius plots for (amine + CO₂) in the methanol system [solid green circle: DMAPA (this study), solid green triangle: EDA,⁷ open orange circle: AEEA,¹² and dashed line: linear fit].

However, as expected, two other diamines EDA (1/1°) and AEEA (1/2°) exhibited higher kinetics than DMAPA. But, as reported in the literature, the presence of a tertiary amine in DMAPA leads to a higher capacity for CO₂ absorption.

The second-order rate constants were estimated using the Zwitterion and termolecular mechanisms by successfully correlating the experimentally estimated pseudo-first-order rate constants. The estimated reaction orders with respect to DMAPA using a power-law model varied within the range of 1.15–1.37 in the temperature range of 298.15–313.15 K. The range of the reaction orders with respect to amine concentration for DMAPA was very close to that of MEA. The activation energy for the formation of Zwitterion in water and methanol systems was estimated using an Arrhenius expression. The estimated activation energy of DMAPA in the aqueous system (39.47 kJ·mol⁻¹) was lower than the activation energy of MEA (46.6 kJ·mol⁻¹). The second-order rate constant of DMAPA decreases linearly with the increase in dissociation constant (pK_a). The amine with a higher dissociation constant demonstrated a higher rate constant.

Pseudo-first-order rate constants and second-order rate constants for the reaction of CO₂ with DMAPA in methanol systems were, as expected, lower than those in the aqueous system.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.0c01157>.

Concentration of CO₂ in water and methanol; uncertainty of estimated pseudo-first-order rate constant (k_0); measured pseudo-first-order reaction rate constants for (CO₂ + MEA) and (CO₂ + DEA) in an aqueous system (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Amr Henni — Acid Gas Removal Laboratory, Process Systems Engineering, Clean Energy Technologies Research Institute (CETRI), University of Regina, Regina, Saskatchewan S4S 0A2, Canada; orcid.org/0000-0002-8016-1693; Phone: +1 306 585 6236; Email: amr.henni@uregina.ca

Author

Devjyoti Nath — Acid Gas Removal Laboratory, Process Systems Engineering, Clean Energy Technologies Research Institute (CETRI), University of Regina, Regina, Saskatchewan S4S 0A2, Canada

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.iecr.0c01157>

Notes

The authors declare no competing financial interest.

■ NOMENCLATURE

| | |
|-----------------------------|--|
| A | Arrhenius constant (m ³ ·mol ⁻¹ ·s ⁻¹) |
| E _a | activation energy (kJ·mol ⁻¹) |
| k ₀ | Pseudo-first-order reaction rate constants (s ⁻¹) |
| k ₋₁ | backward-first-order reaction rate constants (s ⁻¹) |
| k ₂ | forward second-order reaction rate constant for Zwitterion and termolecular mechanisms (m ³ ·mol ⁻¹ ·s ⁻¹) |
| k _B | $k_2 k_{\text{Base}} / k_{-1}$ (m ⁶ ·mol ⁻² ·s ⁻¹) |
| k _A | $k_2 k_{\text{Amine}} / k_{-1}$ (m ⁶ ·mol ⁻² ·s ⁻¹) |
| k _W | $k_2 k_{\text{Water}} / k_{-1}$ (m ⁶ ·mol ⁻² ·s ⁻¹) |
| k _{OH⁻} | $k_2 k_{\text{OH}^-} / k_{-1}$ (m ⁶ ·mol ⁻² ·s ⁻¹) |
| k _M | $k_2 k_{\text{Methanol}} / k_{-1}$ (m ⁶ ·mol ⁻² ·s ⁻¹) |
| r _{CO₂} | reaction rate with respect to CO ₂ (m ³ ·mol ⁻¹ ·s ⁻¹) |

t time (s)
Y measured signal (μS)
%AAD percentage of average absolute deviation

REFERENCES

- (1) Ali, S. H. Kinetics of the Reaction of Carbon Dioxide with Blends of Amines in Aqueous Media Using the Stopped-Flow Technique. *Int. J. Chem. Kinet.* **2005**, *37*, 391–405.
- (2) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T. H.; Long, J. R. Carbon Dioxide Capture in Metal-Organic Frameworks. *Chem. Rev.* **2012**, *112*, 724–781.
- (3) Rayer, A. V.; Mobley, P. D.; Soukri, M.; Gohndrone, T. R.; Tanthana, J.; Zhou, J.; Lail, M. Absorption Rates of Carbon Dioxide in Amines in Hydrophilic and Hydrophobic Solvents. *Chem. Eng. J.* **2018**, *348*, 514–525.
- (4) Wu, X.; Yu, Y.; Qin, Z.; Zhang, Z. The Advances of Post-Combustion CO₂ Capture with Chemical Solvents: Review and Guidelines. *Energy Procedia* **2014**, *63*, 1339–1346.
- (5) Liang, Z.; Rongwong, W.; Liu, H.; Fu, K.; Gao, H.; Cao, F.; Zhang, R.; Sema, T.; Henni, A.; Sumon, K.; et al. Recent Progress and New Developments in Post-Combustion Carbon-Capture Technology with Amine Based Solvents. *Int. J. Greenhouse Gas Control* **2015**, *40*, 26–54.
- (6) Liu, H.; Sema, T.; Liang, Z.; Fu, K.; Idem, R.; Na, Y.; Tontiwachwuthikul, P. CO₂ Absorption Kinetics of 4-Diethylamine-2-Butanol Solvent Using Stopped-Flow Technique. *Sep. Purif. Technol.* **2014**, *136*, 81–87.
- (7) Kadiwala, S.; Rayer, A. V.; Henni, A. Kinetics of Carbon Dioxide (CO₂) with Ethylenediamine, 3-Amino-1-Propanol in Methanol and Ethanol, and with 1-Dimethylamino-2-Propanol and 3-Dimethylamino-1-Propanol in Water Using Stopped-Flow Technique. *Chem. Eng. J.* **2012**, *179*, 262–271.
- (8) Liu, H.; Liang, Z.; Sema, T.; Rongwong, W.; Li, C.; Na, Y.; Idem, R.; Tontiwachwuthikul, P.; Idem, R. Kinetics of CO₂ Absorption into a Novel 1-Diethylamino-2-Propanol Solvent Using Stopped-Flow Technique. *AIChE J.* **2014**, *60*, 3502–3510.
- (9) Liu, H.; Xiao, M.; Liang, Z.; Rongwong, W.; Li, J.; Tontiwachwuthikul, P. Analysis of Reaction Kinetics of CO₂ Absorption into a Novel 1-(2-Hydroxyethyl)-Piperidine Solvent Using Stopped-Flow Technique. *Ind. Eng. Chem. Res.* **2015**, *54*, 12525–12533.
- (10) Henni, A.; Li, J.; Tontiwachwuthikul, P. Reaction Kinetics of CO₂ in Aqueous 1-Amino-2-Propanol, 3-Amino-1-Propanol, and Dimethylmonoethanolamine Solutions in the Temperature Range of 298–313 K Using the Stopped-Flow Technique. *Ind. Eng. Chem. Res.* **2008**, *47*, 2213–2220.
- (11) Ali, S. H. Kinetic Study of the Reaction of Diethanolamine with Carbon Dioxide in Aqueous and Mixed Solvent Systems-Application to Acid Gas Cleaning. *Sep. Purif. Technol.* **2004**, *38*, 281–296.
- (12) Rayer, A. V.; Henni, A.; Li, J. Reaction Kinetics of 2-((2-Aminoethyl) Amino) Ethanol in Aqueous and Non-Aqueous Solutions Using the Stopped-Flow Technique. *Can. J. Chem. Eng.* **2013**, *91*, 490–498.
- (13) Zhong, N.; Liu, H.; Luo, X.; Al-Marri, M. J.; Benamor, A.; Idem, R.; Tontiwachwuthikul, P.; Liang, Z. Reaction Kinetics of Carbon Dioxide (CO₂) with Diethylenetriamine and 1-Amino-2-Propanol in Nonaqueous Solvents Using Stopped-Flow Technique. *Ind. Eng. Chem. Res.* **2016**, *55*, 7307–7317.
- (14) Mobley, P. D.; Rayer, A. V.; Tanthana, J.; Gohndrone, T. R.; Soukri, M.; Coleman, L. J. I.; Lail, M. CO₂ Capture Using Fluorinated Hydrophobic Solvents. *Ind. Eng. Chem. Res.* **2017**, *56*, 11958–11966.
- (15) Barzagli, F.; Mani, F.; Peruzzini, M. Efficient CO₂ Absorption and Low Temperature Desorption with Non-Aqueous Solvents Based on 2-Amino-2-Methyl-1-Propanol (AMP). *Int. J. Greenhouse Gas Control* **2013**, *16*, 217–223.
- (16) Yu, B.; Yu, H.; Li, K.; Yang, Q.; Zhang, R.; Li, L.; Chen, Z. Characterisation and Kinetic Study of Carbon Dioxide Absorption by an Aqueous Diamine Solution. *Appl. Energy* **2017**, *208*, 1308–1317.
- (17) Yu, B.; Yu, H.; Yang, Q.; Li, K.; Ji, L.; Zhang, R.; Megharaj, M.; Chen, Z. Postcombustion Capture of CO₂ by Diamines Containing One Primary and One Tertiary Amino Group: Reaction Rate and Mechanism. *Energy Fuels* **2019**, *33*, 7500–7508.
- (18) Tong, C.; Perez, C. C.; Chen, J.; Marcos, J.-C. V.; Neveux, T.; Le Moullec, Y. Measurement and Calculation for CO₂ Solubility and Kinetic Rate in Aqueous Solutions of Two Tertiary Amines. *Energy Procedia* **2013**, *37*, 2084–2093.
- (19) Pang, S. H.; Lee, L.-C.; Sakwa-Novak, M. A.; Lively, R. P.; Jones, C. W. Design of Aminopolymer Structure to Enhance Performance and Stability of CO₂ Sorbents: Poly(Propylenimine) vs Poly(Ethylenimine). *J. Am. Chem. Soc.* **2017**, *139*, 3627–3630.
- (20) Yu, B.; Li, L.; Yu, H.; Maeder, M.; Puxty, G.; Yang, Q.; Feron, P.; Conway, W.; Chen, Z. Insights into the Chemical Mechanism for CO₂(Aq) and H⁺ in Aqueous Diamine Solutions - An Experimental Stopped-Flow Kinetic and 1H/13C NMR Study of Aqueous Solutions of N,N-Dimethylethylenediamine for Postcombustion CO₂ Capture. *Environ. Sci. Technol.* **2018**, *52*, 916–926.
- (21) Khalili, F.; Rayer, A. V.; Henni, A.; East, A. L. L.; Tontiwachwuthikul, P. Kinetics and Dissociation Constants (pK_a) of Polyamines of Importance in Post-Combustion Carbon Dioxide (CO₂) Capture Studies. In *Recent Advances in Post-Combustion CO₂ Capture Chemistry*; ACS Symposium Series; American Chemical Society, 2012; pp 3–43.
- (22) Kadiwala, S.; Rayer, A. V.; Henni, A. Kinetics of Carbon Dioxide (CO₂) with Ethylenediamine, 3-Amino-1-Propanol in Methanol and Ethanol, and with 1-Dimethylamino-2-Propanol and 3-Dimethylamino-1-Propanol in Water Using Stopped-Flow Technique. *Chem. Eng. J.* **2012**, *179*, 262–271.
- (23) Li, J.; Henni, A.; Tontiwachwuthikul, P. Reaction Kinetics of CO₂ in Aqueous Ethylenediamine, Ethyl Ethanolamine, and Diethyl Monoethanolamine Solutions in the Temperature Range of 298–313 K, Using the Stopped-Flow Technique. *Ind. Eng. Chem. Res.* **2007**, *46*, 4426–4434.
- (24) Salvi, A. P.; Vaidya, P. D.; Kenig, E. Y. Kinetics of Carbon Dioxide Removal by Ethylenediamine and Diethylenetriamine in Aqueous Solutions. *Can. J. Chem. Eng.* **2014**, *92*, 2021–2028.
- (25) Nath, D.; Henni, A. Solubility of Carbon Dioxide (CO₂) in Aqueous Solution of 3-(Dimethylamino)-1-Propylamine (DMPA). *Fluid Phase Equilib.* **2020**, *511*, No. 112506.
- (26) Knipe, A. C.; McLean, D.; Tranter, R. L. A Fast Response Conductivity Amplifier for Chemical Kinetics. *J. Phys. E* **1974**, *7*, 586–590.
- (27) Alper, E. Reaction Mechanism and Kinetics of Aqueous Solutions of 2-Amino-2-Methyl-1-Propanol and Carbon Dioxide. *Ind. Eng. Chem. Res.* **1990**, *29*, 1725–1728.
- (28) Caplow, M. Kinetics of Carbamate Formation and Breakdown. *J. Am. Chem. Soc.* **1968**, *90*, 6795–6803.
- (29) Danckwerts, P. V. The Reaction of CO₂ with Ethanolamines. *Chem. Eng. Sci.* **1979**, *34*, 443–446.
- (30) Ali, S. H.; Merchant, S. Q.; Fahim, M. A. Reaction Kinetics of Some Secondary Alkanolamines with Carbon Dioxide in Aqueous Solutions by Stopped Flow Technique. *Sep. Purif. Technol.* **2002**, *27*, 121–136.
- (31) Ali, S. H.; Merchant, S. Q.; Fahim, M. A. Kinetic Study of Reactive Absorption of Some Primary Amines with Carbon Dioxide in Ethanol Solution. *Sep. Purif. Technol.* **2000**, *18*, 163–175.
- (32) Crooks, J. E.; Donnellan, J. P. Kinetics and Mechanism of the Reaction between Carbon Dioxide and Amines in Aqueous Solution. *J. Chem. Soc., Perkin Trans. 2* **1989**, 331–333.
- (33) Da Silva, E. F.; Svendsen, H. F. Ab Initio Study of the Reaction of Carbamate Formation from CO₂ and Alkanolamines. *Ind. Eng. Chem. Res.* **2004**, *43*, 3413–3418.
- (34) Versteeg, G. F.; Van Dijk, L. A. J.; Van Swaaij, W. P. M. On the Kinetics between CO₂ and Alkanolamines Both in Aqueous and

Non-Aqueous Solutions. An Overview. *Chem. Eng. Commun.* **1996**, *144*, 133–158.

(35) Littel, R. J.; Van Swaaij, W. P. M.; Versteeg, G. F. Kinetics of Carbon Dioxide with Tertiary Amines in Aqueous Solution. *AIChE J.* **1990**, *36*, 1633–1640.

(36) Tissier, C.; Barillie, P. Acidity Constants and Thermodynamic Functions of Acids Conjugated With Some Propanediamines. *C. R. Seances Acad. Sci., Ser. C* **1969**, *268*, 1953.

(37) Perrin, D. D. *pKa Prediction for Organic Acids and Bases*; Dempsey, B.; Serjeant, E. P., Eds.; Chapman and Hall: London, New York, 1981; Vol. 152.

(38) Sada, E.; Kumazawa, H.; Osawa, Y.; Matsuura, M.; Han, Z. Q. Reaction Kinetics of Carbon Dioxide with Amines in Non-Aqueous Solvents. *Chem. Eng. J.* **1986**, *33*, 87–95.

(39) Aboudheir, A.; Tontiwachwuthikul, P.; Chakma, A.; Idem, R. Kinetics of the Reactive Absorption of Carbon Dioxide in High CO₂-Loaded, Concentrated Aqueous Monoethanolamine Solutions. *Chem. Eng. Sci.* **2003**, *58*, 5195–5210.

(40) Penny, D. E.; Ritter, T. J. Kinetic Study of the Reaction between Carbon Dioxide and Primary Amines. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 2103–2109.

(41) Ma'mun, S.; Jakobsen, J. P.; Svendsen, H. F.; Juliussen, O. Experimental and Modeling Study of the Solubility of Carbon Dioxide in Aqueous 30 Mass % 2-((2-Aminoethyl)Amino)Ethanol Solution. *Ind. Eng. Chem. Res.* **2005**, *45*, 2505–2512.

(42) Liu, S.; Ling, H.; Gao, H.; Tontiwachwuthikul, P.; Liang, Z.; Zhang, H. Kinetics and New Brønsted Correlations Study of CO₂ Absorption into Primary and Secondary Alkanolamine with and without Steric-Hindrance. *Sep. Purif. Technol.* **2020**, *233*, No. 115998.

(43) Rayer, A. V.; Sumon, K. Z.; Jaffari, L.; Henni, A. Dissociation Constants (pK_a) of Tertiary and Cyclic Amines: Structural and Temperature Dependences. *J. Chem. Eng. Data* **2014**, *59*, 3805–3813.