

Study of Equilibrium Solubility, NMR Analysis, and Reaction Kinetics of CO₂ Absorption into Aqueous *N*¹,*N*²-Dimethylethane-1,2-diamine Solutions

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ABSTRACT: The equilibrium solubility and kinetics of *N*¹,*N*²-dimethylethane-1,2-diamine (DMEDA), a new and potential diamine absorbent for CO₂ capture, have been investigated in this work. The equilibrium solubility of 2 M DMEDA solution was measured at 298.15–333.15 K and with CO₂ partial pressures of 5–100 kPa. The heat (−56.47 kJ/mol) of CO₂ absorption was obtained by the Clausius–Clapeyron equation. In addition, the NMR analysis further confirmed the formation of dicarbamate and that the reaction rate contribution by dicarbamate can be ignored, and showed the CO₂ absorption in the liquid phase can be divided into three regions as the CO₂ loadings increased. The pseudo-first-order rate constant (*k*₀) of CO₂ absorption into aqueous DMEDA solution was then investigated at different amine concentrations (0.025–0.075 mol/L) and temperatures (293.15–313.15 K) with stopped-flow technology. The results show that the *k*₀ value in the DMEDA solution increases with the increase of temperature and amine concentration. The pseudo-first-order assumption, zwitterion mechanism, and termolecular mechanism were respectively applied to the DMEDA–CO₂–H₂O system. The results show that the predicted CO₂ absorption rate exhibits good agreement with the experimental data with absolute average deviations (AADs) of 3.66, 3.77, and 4.51% with respect to the pseudo-first-order assumption, zwitterion, and termolecular models, respectively.

1. INTRODUCTION

Recently, the extreme weather caused by global warming is drawing more and more attention. The chief contributor to the global warming effect is emissions of greenhouse gases (mainly CO₂).^{1–3} Industrial and coal-fired power plant emissions are the main sources of CO₂ in the atmosphere. The reduction of CO₂ emissions by CO₂ capture, utilization, and storage (CCUS) technologies from exhaust gases of industrial and coal-fired power plants is considered a promising method to mitigate global warming.⁴ Among all the CCUS technologies, chemical absorption using aqueous amine solutions is more mature, cost-effective, and of high treatment capacity.

Over the past few decades, many conventional alkanolamines, including primary amines, secondary amines, and tertiary amines, have been extensively investigated for the postcombustion CO₂ capture process.^{5–8} Tertiary amines have a slow reaction rate and low regeneration energy requirement. Primary (and secondary) amines show a fast reaction rate but high regeneration energy requirement.^{7,9,10}

Early in the search for better solvents for CO₂ absorption processes, Chakravarty et al.¹¹ studied blended amine systems. In these systems, a small amount of primary or secondary amine is added into a tertiary amine solution, providing the combination of the high reaction rate of the primary or secondary amines and the low regeneration energy requirement of the tertiary amine. Compared with primary/secondary amines, diamines, such as piperazine (PZ),^{12,13} 2-(2-aminoethylamino)ethanol (AEEA),¹⁴ and ethylenediamine (EDA),¹⁵ become more and more attractive due to their fast

reaction rates. Therefore, it is conjecturable that diamines are better alternatives as a blended amine reaction rate accelerator.

There is much current research of CO₂ absorption into different diamine solutions. Sadiq et al.¹⁶ studied the kinetics model of PZ/methyldiethanolamine (MDEA) at 298–313 K by stopped-flow apparatus and found that the blended amine system had a faster reaction rate than a single MDEA system. Bonenfant et al.¹⁷ studied two blended amine systems of 1.427 mol/L AEEA + 0.418 mol/L MDEA and 1.427 mol/L AEEA + 0.836 mol/L MDEA at 296.15 K and found that AEEA can significantly increase the rate of CO₂ absorbed by MDEA.

*N*¹,*N*²-Dimethylethane-1,2-diamine (DMEDA) is a diamine that adds one methyl to each of the two nitrogen atoms of EDA, as shown in Figure 1, and thus has potential for CO₂ capture. However, an understanding of the chemical properties of CO₂ absorption into DMEDA solution is still lacking. In the present work, the equilibrium solubility of CO₂ absorption into aqueous DMEDA solution was studied with an equilibrium solubility measuring device at the concentration of 2 mol/L,

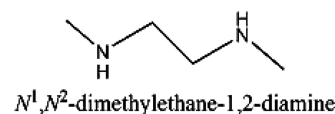


Figure 1. Chemical structure of DMEDA.

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over the temperature range from 298.15 to 333.15 K and the CO₂ partial pressure range from 5 to 100 kPa. ¹³C NMR technology was used to study the speciation of CO₂ loaded DMEDA solution with various CO₂ loadings at 298.15 K. Stopped-flow apparatus was used to investigate the reaction kinetics with DMEDA concentration ranging from 0.025 to 0.075 mol/L, over the temperature range from 293.15 to 313.15 K. The second-order reaction rate constant is obtained by fitting the experimental pseudo-first-order reaction rate constant into the corresponding reaction mechanism equation. As well, the heat of absorption is estimated with the Clausius–Clapeyron equation in this work.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Deionized water was used to prepare aqueous solutions of different DMEDA concentrations. The deionized water was prepared in the iCCS laboratory using a water treater obtained from Taoshi Water Equipment Engineering Co., Ltd. Flow meters (D08-2F) were obtained from Beijing Sevenstar Electronics Co., Ltd. (Beijing). The thermostatic water bath (DC-S010) was obtained from Fandilang Info Technology Co., Ltd. (Nanjing).

DMEDA (purity 99%) was purchased from Kermel Reagent Co., Ltd., and used with no further purification in this work. CO₂ (purity 99%) was provided by Changsha Jingxiang Gas Co., Ltd.

2.2. Equilibrium Solubility and Recyclability Performance. The experiments of equilibrium solubility were performed using a laboratory setup (Figure 2) which has been used widely to measure

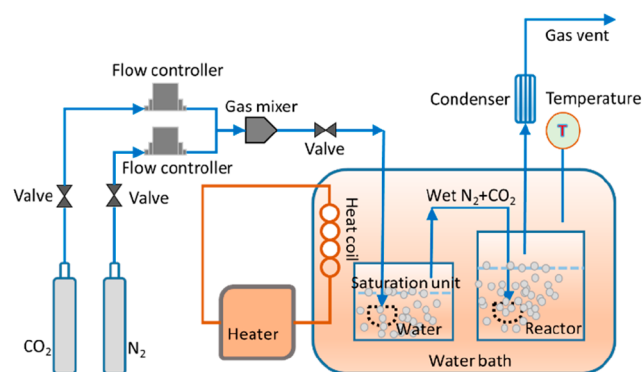


Figure 2. Schematic diagram of the experimental setup for CO₂ loading measurement.

the CO₂ equilibrium solubility in different amine systems as published in our previous work.¹⁸ The experimental procedure for measuring

the equilibrium solubility of DMEDA in this work is the same as in our previous work.^{18,19}

The recyclability experiments were finished using a rapid screening apparatus.²⁰ Absorption and desorption tests were finished at the temperature of 313.15 K, 15 kPa CO₂ partial pressure, and the temperature of 353.15 K and nitrogen protection, respectively.

2.3. Ion Speciation. In order to ascertain the concentration of each species in the loaded amine solution, a Bruker Avance III 400 NMR spectrometer was operated at a frequency of 100.62 MHz (¹³C) to get the quantitative carbon (¹³C) spectra at 298.15 K. 1,4-Dioxane and deuterium oxide (D₂O) with a ratio of 1 (v/v) was used as an external standard for determining the chemical shift in ¹³C NMR spectra and signal lock. Inverse-gated ¹H-decoupled ¹³C NMR spectra were obtained at a pulse angle of 30° (zgig30 pulse program, Bruker) as the sum of 32 scans with a minimum pulse delay time (D1) of 70–90 s which corresponded to a value of (AQ + D1) ≥ 5T_{1max} of the slowest relaxing carbon for each sample. The obtained data were processed with the Bruker TopSpin 3.5 software.

2.4. Reaction Kinetics. In this work, the kinetics data were measured by a stopped-flow apparatus (model SF-61DX) which was manufactured by Hi-Tech Scientific, Ltd. (U.K.), as shown in Figure 3. The stopped-flow apparatus includes four main sections: a sample handling unit, a conductivity-detection cell, an A/D converter, and a microprocessor. Relevant detailed introduction for these components can be found in our previous work.^{5,21} In addition, the temperature of the stopped-flow reaction chamber is controlled within ±0.1 K by circulating water from an external thermostat. When the amine solution is reacted with CO₂ saturated aqueous solution, the ion concentration in the solution will change, leading to the change of the conductivity of the solution. By measuring the change in conductivity versus time with the KinetAsyst software, the apparent reaction constant can be obtained by the fitting equation

$$Y = -A \exp(-k_0 t) + C \quad (1)$$

where k_0 represents the observed pseudo-first-order reaction rate constant.

In order to obtain a saturated CO₂ solution, the CO₂ gas needs to be bubbled into deionized water for 1/2 h. It should be noted that the concentration of amines needs to be more than 10 times greater than the concentration of CO₂, thus ensuring that the reaction in the mixer is pseudo-first-order (k_0 is only related to the concentration of amines).

3. REACTION MECHANISM

When CO₂ is absorbed into aqueous diamine solutions, the CO₂ molecule simultaneously reacts with the amino group, with OH[−], and with H₂O. The reaction kinetics can be described either by the two-step zwitterion mechanism (originally proposed by Caplow²² and later reintroduced by

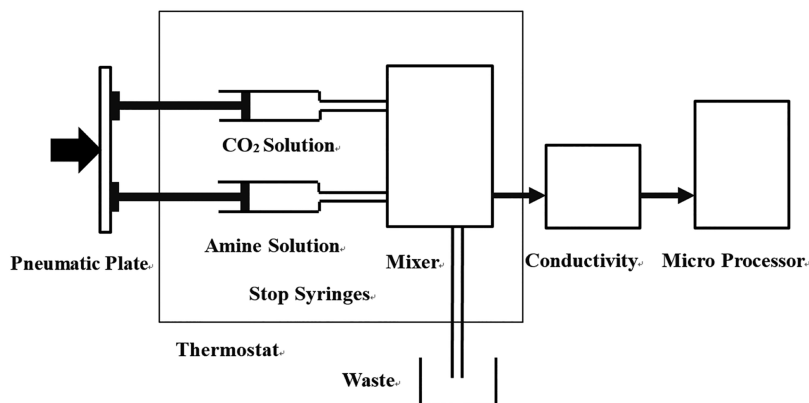
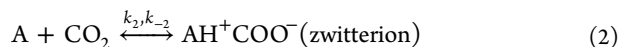


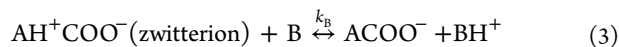
Figure 3. Diagram of stopped-flow apparatus.

Danckwerts²³) or by the single-step termolecular mechanism (originally proposed by Crooks and Donnellan²⁴ and recently revisited by da Silva and Svendsen²⁵).

The zwitterion mechanism is a theory to explain the chemical reaction course between the primary/secondary amine and CO₂. Assuming this mechanism, the reaction between CO₂ and the amine proceeds through the formation of a zwitterion as an intermediate (eq 2).



where “A” represents amine. Then the zwitterion undergoes a deprotonation process in the presence of a base to form a carbamate (eq 3).



where “B” represents base (H₂O, OH[−], amine). In order to simplify the rate equations in complex consecutive reaction pathways, the steady-state principle is applied to the intermediate zwitterion in eqs 2 and 3. The overall reaction rate between the CO₂ and aqueous primary/secondary amine solution can be described as eq 4.

$$r = \frac{d[ACOO^-]}{dt} = \frac{k_2[CO_2][A]}{1 + k_{-2}/k_B[B]} \quad (4)$$

where the kinetic constant k_B represents deprotonation of the zwitterion by any base, such as H₂O, OH[−], or amine. In eq 4, a fractional reaction order between 1 and 2 with respect to the amine concentration was demonstrated. Littel et al.²⁶ found that the concentration of OH[−] ions in amine solution is very low due to the very fast reaction rate of CO₂ with OH[−] leading to the hydroxyl ions being quickly consumed, and the effect of hydroxide ions on the overall reaction rate can be neglected. The concentration of amine is much lower than CO₂ due to a great excess of CO₂ in the absorption process. The overall reaction rate also can be rewritten as follows:

$$r = k_0[CO_2] \quad (5)$$

where k_0 is the observed pseudo-first-order reaction rate constant, which can be measured and is given by

$$k_0 = \frac{[A]}{1/k_2 + k_{-2}/k_B[B]} = \frac{[A]}{1/k_2 + 1/k_B[B]} \\ = \frac{[A]}{1/k_2 + 1/\{k_A[A] + k_{H_2O}[H_2O]\}} \quad (6)$$

when $k_2 \gg k_B$, which means eq 3 is the control step in the zwitterion mechanism. Under this circumstance, k_0 can be simplified into the following equation, which is the same as the termolecular mechanism:

$$k_0 = [A]\{k_{H_2O}[H_2O] + k_A[A]\} \quad (7)$$

when $k_2 \ll k_B$, which means eq 2 is the control step in the zwitterion mechanism. Under this circumstance, the reaction between amine and CO₂ can be regarded as a simple second-order reaction:

$$k_0 = k_2[A] \quad (8)$$

4. RESULTS AND DISCUSSION

4.1. Equilibrium Solubility of CO₂ Absorption in Aqueous DMEDA Solution. Equilibrium solubility (CO₂

loading, defined as mol of CO₂·mol of amine^{−1}) represents the maximum capability of an amine for CO₂ capture and is of crucial importance in the testing and development of theoretical models and correlations. The experimental determinations of the equilibrium solubility of CO₂ in 2.0 mol/L aqueous DMEDA solutions were carried out under various temperatures and CO₂ partial pressures. The experimental results are shown in Figure 4 and Table 1. It is

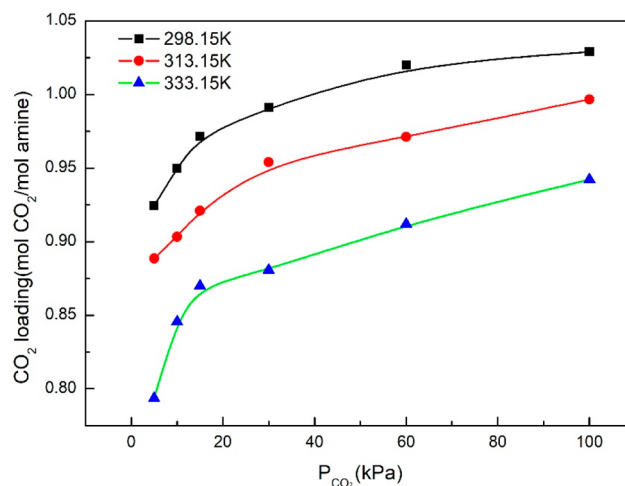


Figure 4. Equilibrium loading of CO₂ in 2.0 mol/L aqueous DMEDA solution.

Table 1. Equilibrium Loading of CO₂ in 2.0 mol/L Aqueous DMEDA Solutions

temp (K)	CO ₂ partial pressure (kPa)					
	5	10	15	30	60	100
298.15	0.92	0.95	0.97	0.99	1.02	1.03
313.15	0.89	0.90	0.92	0.95	0.97	1.00
333.15	0.79	0.85	0.87	0.88	0.91	0.94

obvious that the equilibrium loading of CO₂ in DMEDA is pretty high. At higher temperatures, the equilibrium solubility of CO₂ decreased. This is because the physical solubility of CO₂ is reduced with increasing temperature and the CO₂ absorption in amine solution is an exothermic process. In contrast, the loading of amine increased with CO₂ partial pressure. This is mainly due to higher CO₂ physical solubility in the solution which drives the reaction equilibria of eqs 2 and 3 toward the right side. Therefore, CO₂ absorption with the amine solution is promoted.

In addition, to evaluate the CO₂ absorption performance of DMEDA for CO₂ capture in terms of the CO₂ equilibrium solubility, a comparison between DMEDA and other widely used conventional amines (2-methylpiperazine (2MPZ), 1-diethylamino-2-propanol (1DMA2P),²⁷ EDA,²⁸ and N-(2-hydroxyethyl)pyrrolidine (1-(2HE)PRLD)¹⁸) is made as shown in Figure 5. It shows clearly that DMEDA has the highest CO₂ equilibrium solubility compared to tertiary amines at the same CO₂ partial pressure.

The recyclability performance of DMEDA was qualitatively analyzed by the comparison of the three times absorption (desorption) curve. The blue, red, and green dots are represent first, second, and third absorption (desorption), respectively. As we can observe from the absorption curves in Figure 6, the second absorption curve almost coincides with the first one,

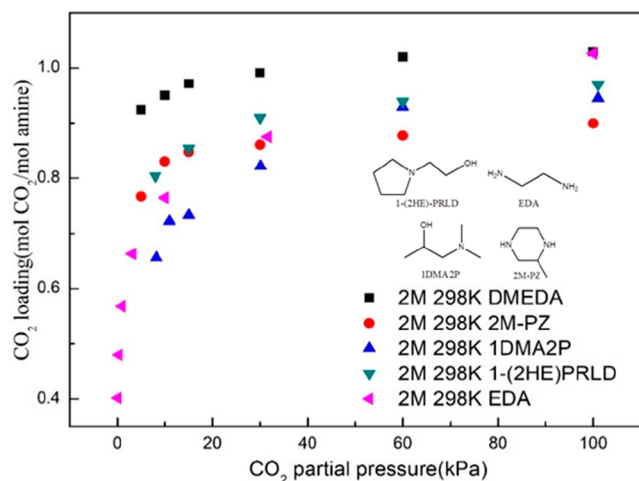


Figure 5. Comparison of the CO_2 equilibrium solubility between DMEDA and 2MPZ, 1DMA2P, EDA, and 1-(2HE)PRLD under various CO_2 partial pressures.

and the third one is slightly shifted to the left, which means the absorption capacity of DMEDA showed no dramatic decline during three times.

4.2. Ion Speciation Plot of the DMEDA– CO_2 – H_2O System. Both the zwitterion and termolecular mechanisms suggest that carbamate is one of the reaction products and is produced in CO_2 loaded DMEDA solution. Because of the two secondary amino groups in the DMEDA structure, monocarbamate and dicarbamate are expected to be generated in the DMEDA– CO_2 – H_2O system. In order to confirm the ion speciation in this system and establish the kinetic model of this system, ^{13}C NMR is used in this work. The ^{13}C NMR technique has been widely used to determine the products of the CO_2 –amine– H_2O systems.^{29–31}

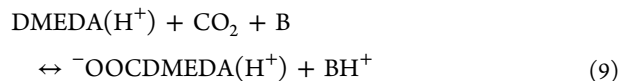
The possible species in CO_2 –DMEDA– H_2O systems are plotted in Figure 7a, including free DMEDA, protonated DMEDA (DMEDAH^+), monocarbamate of DMEDA (DMEDACOO^-), dicarbamate of DMEDA ($\text{DMEDA}(\text{COO}^-)_2$), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). There are two peaks (marked as a_1 and a_2) that appear in the ^{13}C NMR spectra when the CO_2 loading is 0 mol of CO_2 /mol of amine, but four or nine new peaks appeared after the CO_2 was introduced into the solution, which means new species are generated in the CO_2 loaded DMEDA solution. The electron of the carbon (DMEDACOO^-) is hardly affected by the H^+ due to the conjugated effect of carboxyl. The chemical shift

(around 164.2 ppm) marked as b_5 is expected to be the signal of the carboxyl in DMEDACOO^- . This is similar to that of the monoethanolamine (MEA) carbamate. Compared with DMEDACOO^- , $\text{DMEDA}(\text{COO}^-)_2$ can be regarded as DMEDACOO^- connected with an extra $-\text{COO}^-$ group. The chemical shift moves to a lower field while it is connected to an electronegative group, which indicates that the chemical shift marked as c_1 should be the signal of the carboxyl in $\text{DMEDA}(\text{COO}^-)_2$. It also can be seen that, from Figure 7b, the chemical shift of the ^{13}C signal d changed significantly as the CO_2 loading increased. This signal is expected to be the characteristic peak of carbonate and bicarbonate, because their electrons are easily affected by the H^+ and it leads to remarkable changes in the chemical shift.

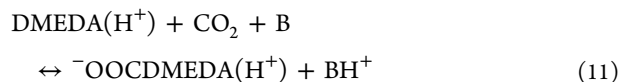
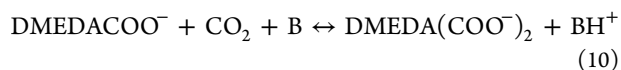
As well, the concentrations of each species in the CO_2 –DMEDA– H_2O system at 298.15 K were calculated by using the method composed by Holmes et al.³² and plotted in Figure 7c. As observed in Figure 7c, the concentration of DMEDA/ DMEDAH^+ decreased and the concentration of monocarbamate increased with the increasing CO_2 loading. The concentration of dicarbamate maintained a very low level. This is because the $-\text{COO}^-$ group in DMEDACOO^- will lead to lower electron density on the other N atom, which means lower reactivity of the N atom to react with one more CO_2 molecule and higher sensitivity of dicarbamate to H^+ . However, lower electron density of the other N atom will lead to easier protonation of DMEDACOO^- , which is similar to the effect of tertiary amine in blended amine which releases more free DMEDA molecules.

According to Figure 7c, the CO_2 absorption in the liquid phase can be divided into three regions as the CO_2 loadings increase.

Reaction in region I. Formation of monocarbamate:



Reaction in region II. Formation of monocarbamate and dicarbamate:



Reaction in region III. Formation of HCO_3^- and decomposition of monocarbamate and dicarbamate:

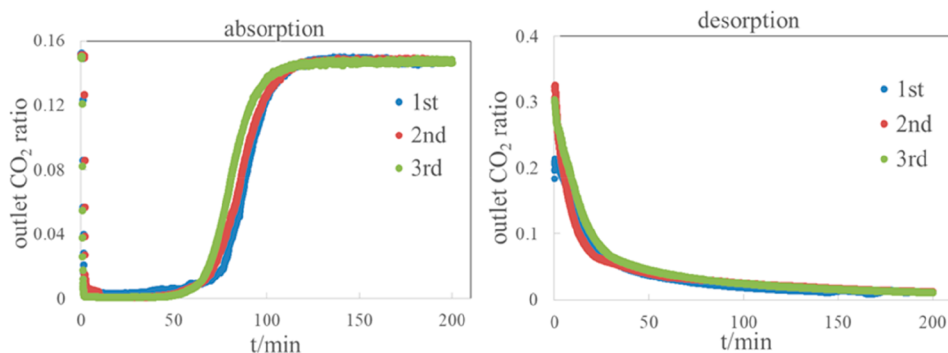


Figure 6. Absorption and desorption curves of DMEDA.

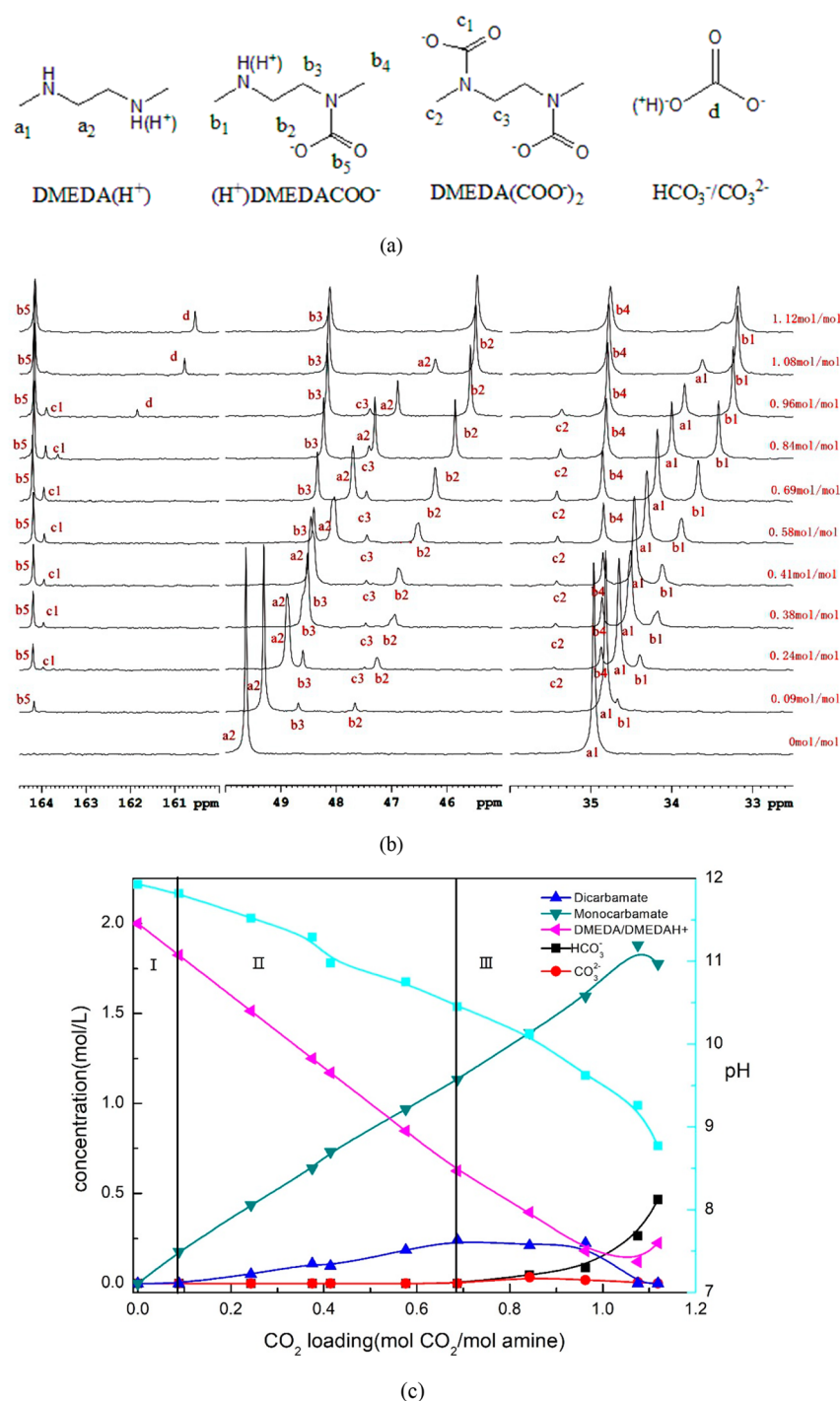
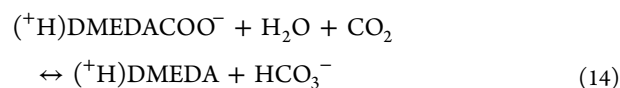
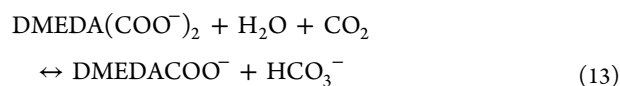
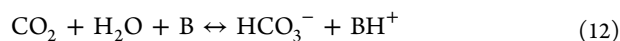


Figure 7. (a) Molecular structures of possible species in CO₂–DMEDA–H₂O system. (b) Stacked ¹³C NMR spectra of CO₂–DMEDA–H₂O system with CO₂ loading from 0 to 1.12 mol of CO₂/mol of amine. (c) Speciation plots of the concentration of each species formed in the CO₂–DMEDA–H₂O system at 298.15 K.



The reaction in region III and Figure 7c indicated that monocarbamate is more stable than dicarbamate and that pH is a chief impact factor. When the pH value decreased to almost 9.6 and 9.2, dicarbamate and monocarbamate begin to decompose, respectively.

4.3. Kinetics of CO₂ Absorption in Aqueous DMEDA Solution. The kinetics experiments of the reactions of DMEDA with equilibrated aqueous CO₂ solutions was investigated in the concentration range from 0.025 to 0.075

kmol/m³ and temperature range from 293.15 to 313.15 K using the stopped-flow apparatus. The first-hand value of k_0 was obtained by the KinetAsyst software which connected to the apparatus. As shown in Table 2 and Figure 8, the pseudo-first-order rate constant (k_0) values increase with the increase in DMEDA concentration and temperature.

Table 2. Experimental k_0 Values of DMEDA

amine concn (mol/L)	pseudo-first-order rate constant (k_0 , s ⁻¹)				
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.025	173.96	696.95	885.58	1000.96	1236.96
0.0375	205.77	1124.01	1379.55	1544.73	1731.24
0.05	278.67	1363.20	1623.69	2006.89	2647.43
0.0625	339.00	1634.03	1937.72	2396.63	2987.89
0.075	387.07	2105.12	2401.64	2872.76	3724.77

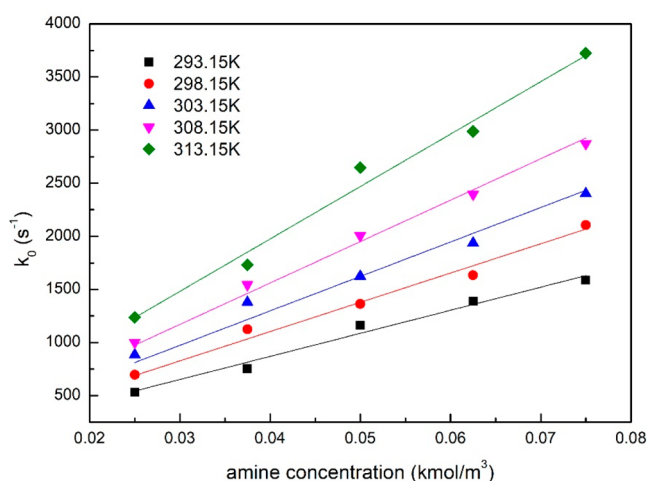


Figure 8. Effects of DMEDA concentration and temperature on k_0 .

The DMEDA kinetics results observed in this work compared with those for other amines (DEA,³³ MEA,³³ 2-amino-2-methyl-1-propanol (AMP),³³ EDA,³⁴ PZ,³⁵ 2MPZ³⁶), in terms of k_0 , is shown in Figure 9. DMEDA shows a faster reaction rate than EDA, which is in accordance with the work

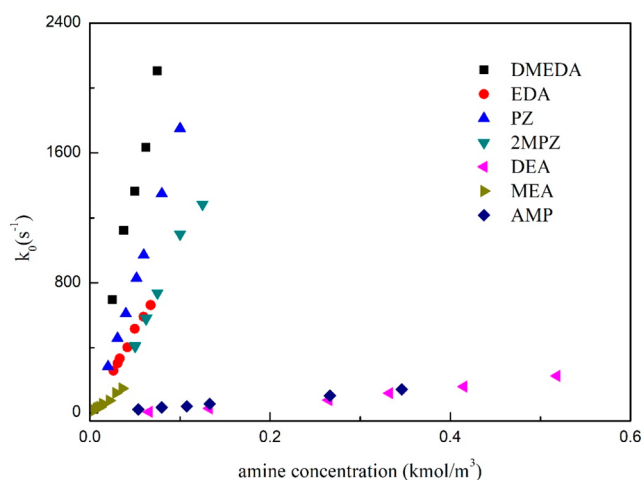


Figure 9. Comparison of k_0 values for DMEDA, EDA, PZ, 2MPZ, DEA, AMP, and MEA, at 298 K.

of Jiang et al.³⁷ which showed that branching can increase the reaction rate of an amine. It is also obvious that DMEDA exhibits the highest k_0 among four diamines (DMEDA, EDA, PZ, 2MPZ) let alone compared with traditional amines (MEA, DEA, and AMP).

4.3.1. Zwitterion Mechanism. For the sake of concise kinetics equation, the kinetics contribution of DMEDACOO⁻ is ignored in this work. Thus, based on the previous derivation in section 3, $k_{0,cal}$, k_2^Z , k_A^Z , and $k_{H_2O}^Z$ were calculated by substituting the obtained “ k_0 ” data set into eq 6 using nonlinear regression. The average absolute deviation (AAD) of $k_{0,exp}$ and $k_{0,cal}$ are calculated by eq 15. The reaction rate constant is generally regarded as a function of temperature, so the obtained data of k_2^Z , k_A^Z , and $k_{H_2O}^Z$ were fitted with the Arrhenius equation (eq 16)^{5,38} and the results are listed in Table 3. The activation energies (E_a 's) of k_2^Z , k_A^Z , and $k_{H_2O}^Z$ can be derived from the corresponding Arrhenius equations and are also presented in Table 3. The $\ln k_2^Z$, $\ln k_A^Z$, and $\ln k_{H_2O}^Z$ are plotted against $1/T$ according to eq 16 as shown in Figure 10. Figure 10 shows that the predicted Arrhenius results fit very well with the obtained data in terms of each reaction rate constant.

$$AAD = \frac{1}{N} \sum \left| \frac{k_{0,exp} - k_{0,cal}}{k_{0,exp}} \right| \times 100\% \quad (15)$$

where N is the number of experimental data points.

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (16)$$

where k represents the k_2^Z , k_A^Z , and $k_{H_2O}^Z$. A , E_a , and R represent the Arrhenius constant (m³/kmol·s⁻¹), activation energy (kJ/mol), and universal gas constant (8.314 J/mol·K⁻¹), respectively.

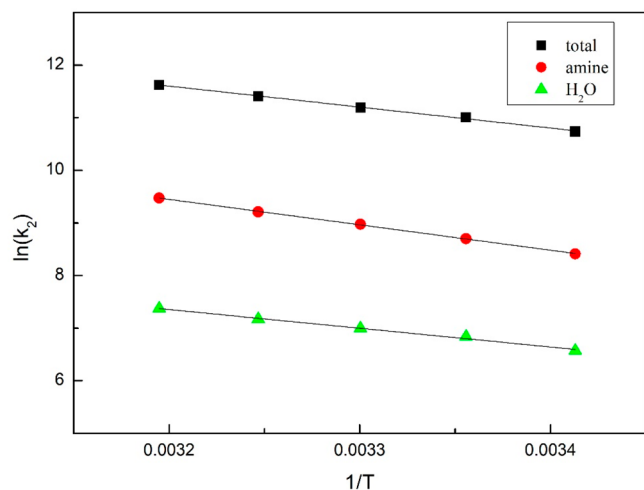
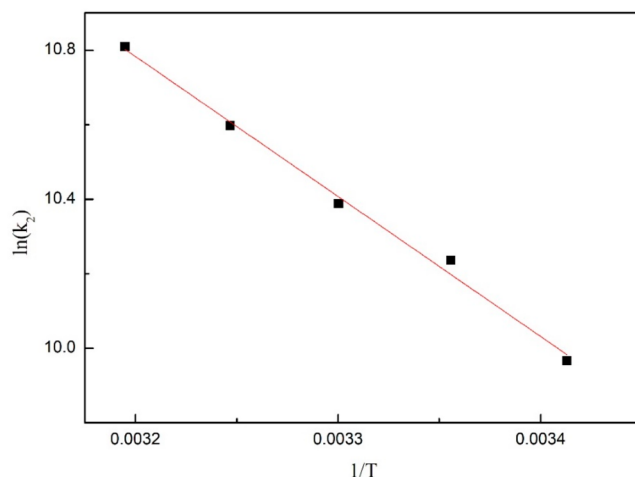
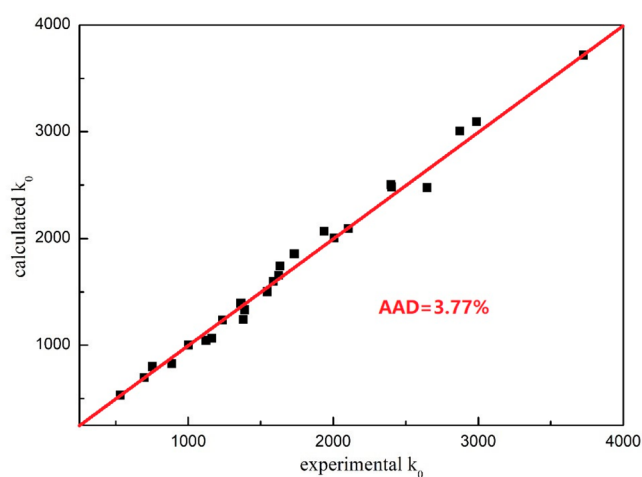
The predicted k_0 values obtained by eq 6 against the experimental $k_{0,exp}$ values are plotted in Figure 11. The acceptable AAD of 3.77% means that the kinetics contribution of DMEDACOO⁻ can be ignored and the zwitterion mechanism can be applied to the DMEDA–CO₂–H₂O system.

Besides, we try to ignore the impact of amine, water, amine, and water as a base in the zwitterion mechanism, respectively. Three AADs of 3.63, 3.72, and 3.66% were obtained. This indicates that the impacts of amine and water as bases can be ignored in the zwitterion mechanism, which means a first-order assumption is advisable. Then $k_{0,cal}$ and k_2 were calculated by substituting the obtained “ k_0 ” data set into eq 8 using nonlinear regression. The results are displayed in Table 4 and Figures 12 and 13.

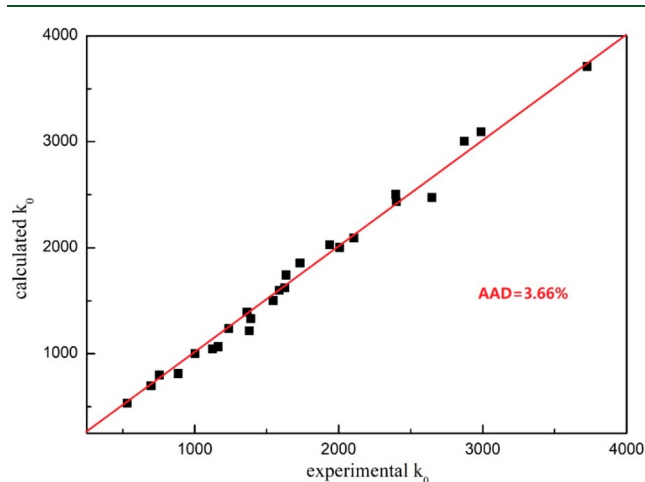
4.3.2. Termolecular Mechanism. Based on the discussion in section 3, k_A^T and $k_{H_2O}^T$ were calculated by substituting the obtained “ k_0 ” data set into eq 7 using nonlinear regression. The obtained values of k_A^T and $k_{H_2O}^T$ were fitted with the Arrhenius equation (eq 16) over the temperature range 293.15–313.15 K, and the obtained equations and the corresponding E_a values are given in Table 5. The Arrhenius results fit very well with the obtained results as shown in Figure 14. A comparison of k_0 values between the predicted results and the experimental results based on the termolecular mechanism is made in Figure 14. The AAD of 3.90% shown in Figure 15 is higher than that obtained by the zwitterion mechanism, indicating that the

Table 3. Summarized Parameters for the Reaction Rate Constants for DMEDA over 293–313.15 K based on the Zwitterion Mechanism

rate const	E_a/R	E_a (kJ/mol)	Arrhenius equation $k = A \exp\left(-\frac{E_a}{RT}\right)$
k_2^Z ($\text{m}^3/\text{kmol}\cdot\text{s}^{-1}$)	3994.1	33.21	$k_2^Z = 3.89 \times 10^{10} \exp\left(-\frac{3994.1}{T}\right)$
k_A^Z ($\text{m}^6/\text{kmol}^2\cdot\text{s}^{-1}$)	4830.1	40.16	$k_A^Z = 6.54 \times 10^{10} \exp\left(-\frac{4830.1}{T}\right)$
$k_{\text{H}_2\text{O}}^Z$ ($\text{m}^6/\text{kmol}^2\cdot\text{s}^{-1}$)	3560.4	29.60	$k_{\text{H}_2\text{O}}^Z = 1.38 \times 10^9 \exp\left(-\frac{3560.4}{T}\right)$

**Figure 10.** Plot of $\ln k_2$ against $1/T$ by using zwitterion mechanism.**Figure 12.** Plot of $\ln k_2$ against $1/T$ by using zwitterion mechanism (without amine and H_2O).**Figure 11.** Relationship between experimental k_0 and calculated k_0 in DMEDA blended system by zwitterion mechanism.**Table 4. Summarized Parameters for the Reaction Rate Constants for DMEDA over 293–313 K Based on the Zwitterion Mechanism (without Amine and H_2O)**

rate const ($\text{m}^3/\text{kmol}\cdot\text{s}^{-1}$)	E_a/R	E_a (kJ/mol)	Arrhenius equation
k_2	3758.8	31.25	$k_2 = 8.04 \times 10^9 \exp\left(-\frac{3758.8}{T}\right)$

**Figure 13.** Relationship between experimental k_0 and calculated k_0 in DMEDA blended system by zwitterion mechanism (without amine and H_2O).

zwitterion mechanism is better than the termolecular mechanism for interpreting the reaction kinetics of DMEDA and CO_2 .

Besides, we try to ignore the impact of amine or water as a base in the termolecular mechanism, and we obtain AADs of 3.61 and 29.40%, respectively. This indicates that the impact of amine as a base can be ignored in the termolecular mechanism.

4.4. Heat of CO_2 Absorption into Aqueous DMEDA Solution. Information on the heat of CO_2 absorption in

Table 5. Summarized Parameters for the Reaction Rate Constants for DMEDA over 293.15–313.15 K Based on the Termolecular Mechanism

rate const	E_a/R	E_a (kJ/mol)	Arrhenius equation
			$k = A \exp\left(-\frac{E_a}{RT}\right)$
k_A^T ($\text{m}^6/\text{kmol}^2\cdot\text{s}^{-1}$)	4783.7	39.77	$k_A^T = 5.63 \times 10^{10} \exp\left(-\frac{4793.7}{T}\right)$
$k_{\text{H}_2\text{O}}^T$ ($\text{m}^6/\text{kmol}^2\cdot\text{s}^{-1}$)	3817.1	31.74	$k_{\text{H}_2\text{O}}^T = 1.74 \times 10^9 \exp\left(-\frac{3817.1}{T}\right)$

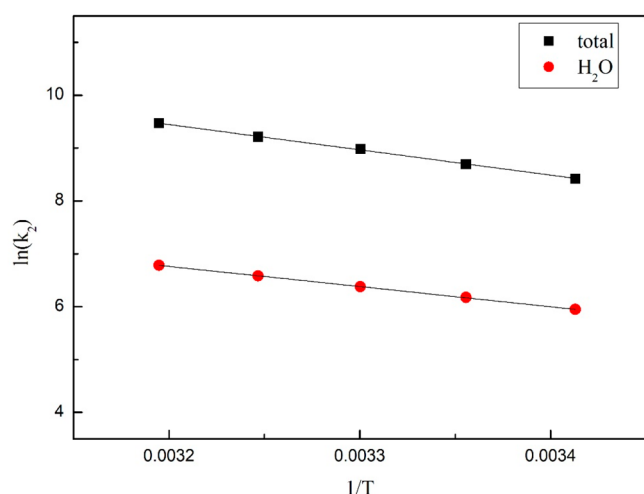


Figure 14. Plot of $\ln k_2$ against $1/T$ by using termolecular mechanism.

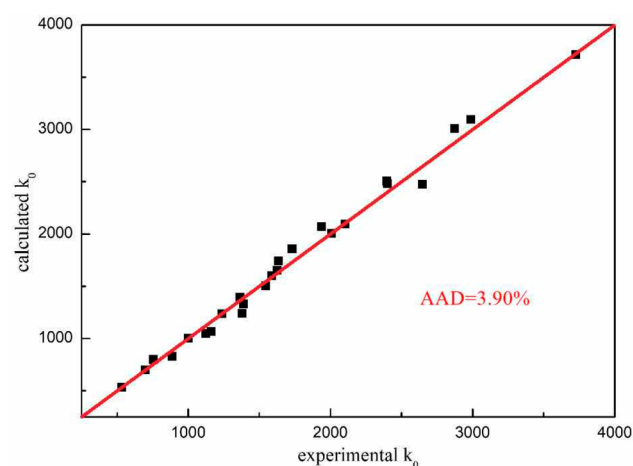


Figure 15. Relationship between experimental k_0 and calculated k_0 in DMEDA blended system by termolecular mechanism.

aqueous solutions of amines is of critical importance for designing the unit operations of CO_2 removal from flue gas because it is directly related to the steam requirements during amine regeneration, although this is only one of the many components of the overall energy consumption.³⁹ The Clausius–Clapeyron equation was considered to be a very reliable method for calculation of the heat of CO_2 absorption. Carson et al.,⁴⁰ Kim et al.,⁴¹ Lee et al.,²⁸ and Rho et al.⁴² have employed it to estimate the absorption heat. In the current work, the Clausius–Clapeyron equation (eq 17) was also applied to estimate the heat of CO_2 absorption (ΔH_{abs}) in DMEDA solution. ΔH_{abs} can be calculated from the slope of \ln

P_{CO_2} versus $1/T$ (Figure 16) at CO_2 loadings of 0.919 and 0.949 mol of CO_2 /mol of amine. The average value (-56.47 kJ/mol) is taken as the final value for ΔH_{abs} of DMEDA.

$$\frac{d(\ln p_{\text{CO}_2})}{d(1/T)} = \frac{\Delta H_{\text{abs}}}{R} \quad (17)$$

where p_{CO_2} , T , and R are the CO_2 partial pressure (kPa), temperature (K), and universal gas constant (8.314 J/(mol·K)), respectively.

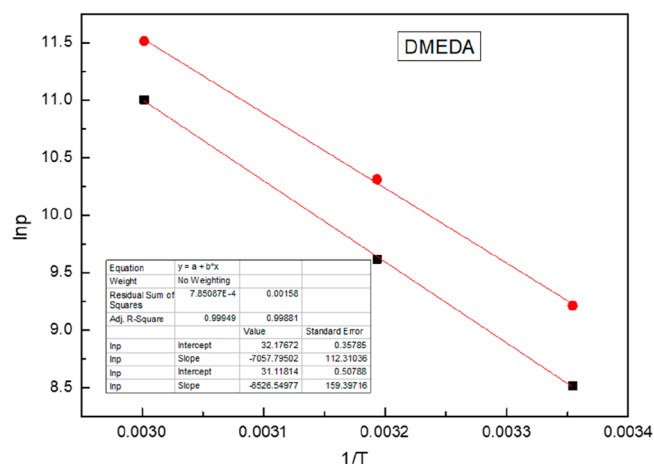


Figure 16. Plot of $\ln P_{\text{CO}_2}$ versus $1/T$.

4.5. Comparison of DMEDA with Other Amines. An efficient amine for CO_2 capture should exhibit fast reaction kinetics with CO_2 and a low energy consumption for regeneration. Faster reaction kinetics of an amine with CO_2 , in terms of k_2 helps to reduce the size of the CO_2 absorber, which is favorable to decreasing the investment cost. For the CO_2 desorption process, the high energy consumption is the current serious challenge for CO_2 capture because it makes up the majority of operating costs. The heat of absorption (ΔH_{abs}) is a critical component for total energy consumption in solvent regeneration process as it directly affects the operation cost for steam consumption in industrial applications. Thus, a lower ΔH_{abs} is favorable for reducing the energy consumption and lowering the operation cost.

However, to select an efficient alternative solvent for CO_2 capture, faster reaction kinetics and a lower heat of absorption should be considered together. Figure 17 plots $\ln k_2$ versus $-\Delta H_{\text{abs}}$ for DMEDA and commonly used conventional amines. It clearly shows that MEA, DEA, and AMP exhibit better kinetics performance but come with a higher heat of absorption. This means that these three amines can help to

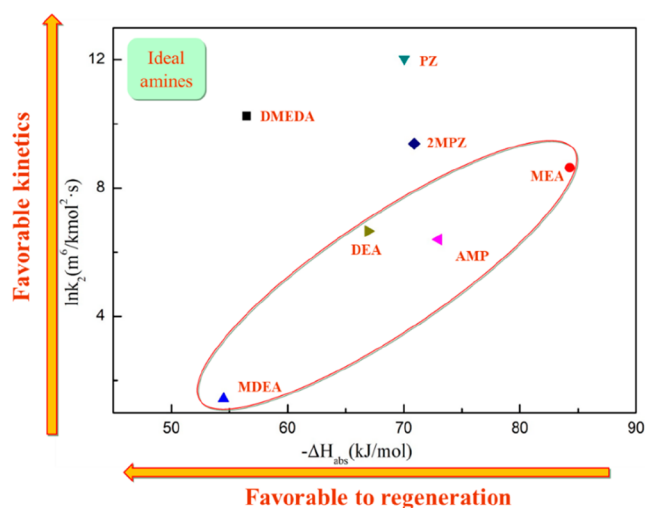


Figure 17. Comparison of CO₂ absorption performance in terms of absorption heat and kinetics (k_2 measured at 298 K).

decrease the investment cost due to the relatively small size of absorber required but cost more for operation in terms of the energy cost.

In contrast, MDEA as a tertiary amine exhibits a lower heat of absorption but has slow kinetics. This indicates that MDEA could benefit the operation cost in terms of the energy cost but needs more capital investment for the CO₂ absorption vessels. PZ shows the best kinetics performance which could lead to a lower investment cost and lower operation cost compared to conventional amines.

Compared to PZ and 2MPZ, DMEDA shows both good kinetics performance and lower absorption heat which could lead to a relatively lower investment cost and lower operation cost compared to conventional amines. Thus, DMEDA could be a better alternative as a blended amine reaction rate accelerator compared to MEA.

5. CONCLUSION

Compared with conventional amines, DMEDA, as a dissecondary amine, shows advantages in terms of equilibrium solubility, absorption kinetics, and energy requirements for CO₂ capture. The equilibrium solubility of CO₂ in 2 M DMEDA was measured for the first time in this work. It was found that aqueous DMEDA exhibits very good CO₂ absorption capacity compared with other amines. The NMR analysis was then done and confirmed the ion species, the formation of DMEDA dicarbamate, and the rationality of the application of pseudo-first-order assumption, zwitterion mechanism, and termolecular mechanism, respectively. The results showed that the predicted absorption rate exhibits good agreement with experimental data with absolute average deviations (AADs) of 3.66, 3.77, and 4.15% with respect to the pseudo-first-order, zwitterion, and termolecular models. It can be concluded, then, that the reaction kinetics between DMEDA and CO₂ can be interpreted correctly using either of the zwitterion and termolecular mechanisms. Moreover, the results of the current work also demonstrate that DMEDA has a lower heat of CO₂ absorption (ΔH_{abs}) than PZ, 2MPZ, MEA, DEA, and AMP and a higher second-order reaction kinetics constant than PZ, MEA, DEA, AMP, and MDEA. Therefore, DMEDA is a potential solvent for the CO₂ chemical absorption process.

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The authors declare no competing financial interest.

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ABBREVIATIONS

- A = Arrhenius constant ($\text{m}^3/\text{kmol}\cdot\text{s}^{-1}$)
- AAD = absolute average deviation
- NMR = nuclear magnetic resonance
- R = universal gas constant ($8.314 \text{ J}/\text{mol}\cdot\text{K}^{-1}$)
- T = temperature (K)
- E_a = activation energy (kJ/mol)
- ΔH_{abs} = heat of CO₂ absorption (kJ/mol)
- P_{CO_2} = CO₂ partial pressure (kPa)
- Y_∞ = constant value of the signal at equilibrium (V)
- k_0 = observed pseudo-first-order reaction rate constant (s^{-1})
- k_A^T = reaction constant of DMEDA based on termolecular mechanism
- $k_{\text{H}_2\text{O}}^T$ = reaction constant of water based on termolecular mechanism
- $k_{0,\text{cal}}$ = observed pseudo-first-order reaction rate constant (s^{-1})
- $k_{0,\text{exp}}$ = predicted pseudo-first-order reaction rate constant (s^{-1})
- k = reaction rate constant
- k_2^Z = second-order reaction rate constant based on zwitterion mechanism
- k_A^Z = reaction rate constant of DMEDA based on zwitterion mechanism
- $k_{\text{H}_2\text{O}}^Z$ = reaction rate constant of water based on zwitterion mechanism
- t = time (s)

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