Kinetics of CO_2 Absorption into a Novel 1-Diethylamino-2-propanol Solvent Using Stopped-Flow Technique

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A stopped-flow apparatus was used to measure the kinetics of carbon dioxide (CO_2) absorption into aqueous solution of 1-diethylamino-2-propanol (1DEA2P) in terms of observed pseudo-first-order rate constant (k_o) and second-order reaction rate constant (k_2), in this work. The experiments were conducted over a 1DEA2P concentration range of 120–751 mol/m^3, and a temperature range of 298–313 K. As 1DEA2P is a tertiary amine, the base-catalyzed hydration mechanism was, then, applied to correlate the experimental CO_2 absorption rate constants obtained from stopped-flow apparatus. In addition, the pK_a of 1DEA2P was experimentally measured over a temperature range of 278–333 K. The Brønsted relationship between reaction rate constant (obtained from stopped-flow apparatus) and pK_a was, then, studied. The results showed that the correlation based on the Brønsted relationship performed very well for predicting the absorption rate constant with an absolute average deviation of 5.2%, which is in an acceptable range of less than 10%.
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Introduction

Carbon dioxide (CO_2), which is considered to be the major culprit of worldwide climate change and greenhouse effect because of its abundance, has been recommended to be reduced by 50% by 2050 to limit the increase of the earth surface temperature to less than 2°C.[1,2] Thus, research into an effective method to remove CO_2 from industrial exhaust gas streams before they are released into the atmosphere, has become vital importance for the sustainable development of society. Currently, absorption using a chemical solvent is considered as one of the most promising technologies for capturing CO_2 due to its maturity, cost effectiveness, and capability of handling lager amount of exhaust streams.[2] However, one of the most pivotal points of this technology is to use a highly effective solvent, which can satisfy several essential requirements, such as fast reaction kinetics, high absorption capacity, high solvent stability, low corrosiveness, and low energy requirement for regeneration.[3–5]

Recently, 4-diethylamine-2-butanol (DEAB), which is a new tertiary amine developed by Tontiwachwuthikul et al.,[6] has been drawing growing attention for its performance on capturing CO_2. According to the work of Sema et al.,[7] DEAB has a higher CO_2 absorption capacity than the conventional amines (i.e., monoethanolamine [MEA], diethanolamine [DEA], methyldiethanolamine [MDEA], 2-amino-2-methyl-1-propanol [AMP]). It was also found that the solvent regeneration energy of DEAB is lower than those of MDEA, DEA, and MEA.[8] Also, the results from Sema et al.[4] showed that the reaction kinetics of CO_2 absorption into DEAB is (1) faster than those into diethylmonoethanolamine (DEMEA), dimethylmonoethanolamine (DMMEA), and MDEA; (2) comparable with those of AMP and DEA, and (3) slower than those of piperazine (PZ) and MEA. With respect to the mass transfer performance in packed column in terms of overall volumetric mass-transfer coefficient ($K_G a_v$), DEAB was found to have higher $K_G a_v$ than that of MDEA, but less than that of MEA.[9]

A new tertiary amine, 1-diethylamino-2-propanol (1DEA2P), whose structure is extremely similar to that of DEAB (which shows excellent performance in terms of absorption capacity, energy requirement for solvent regeneration, reaction kinetics,

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and mass transfer[4,6,9]) should also provide a good performance for CO_2 absorption. However, the performance of 1DEA2P for capturing CO_2 has not yet been studied. Therefore, several investigations (on thermophysical properties, reaction kinetics, mass transfer, corrosion, and degradation behaviors) need to be performed before 1DEA2P can be effectively used.

Reaction kinetics is one of the key factors for evaluating the potential of a new solvent that can be used for removing CO_2. In addition, the reaction kinetics is of vital significant for process simulation and effective designing of a CO_2 treating plant.[10] For the kinetics studies of CO_2 absorption, several devices (e.g., a stirred cell reactor, a wetted wall column, a laminar jet absorber and a wetted sphere absorber and a stopped-flow apparatus) can be used to obtain the experimental CO_2 absorption rate.[11] The stopped-flow apparatus is considered to be a direct method because CO_2 is saturated in the liquid phase which is, then, directly reacted with the amine solvent. The stopped-flow technique that has frequently been used for kinetics study exhibits several intrinsic advantages, such as no involvement of a gas phase (i.e., no effect of gas phase resistance), no effect of the reversibility of reaction, small amount in terms of consumption of solvent ($\sim$0.1 mL for every experiment), easy operation, and quick experimental run.[12] Based on its good performance for the kinetics study, the stopped-flow apparatus has been used for the kinetics studies of a primary amine (e.g., MEA), secondary amine (e.g., DEA), tertiary amine (e.g., DEMEA), and sterically hindered amine (e.g., AMP).[13–16] It was found that the experimental kinetics values obtained from the stopped-flow technique compared favorably with those obtained from the indirect techniques (i.e., rapid mixing, competitive reaction, stirred cell, laminar jet absorber).[13–16] In addition, the kinetics of a mixed amine system of AMP-MEA was also investigated using the stopped-flow technique as reported in the work of Ali et al.[17] Rayer et al.[18] successfully used the stopped-flow technique to examine the kinetic performance of 2-((2-aminoethyl) amino) ethanol (AEEA) in nonaqueous solutions (i.e., methanol and ethanol).

According to the work of Brønsted and Guggenheim,[19] there is a linear relationship between the pK_a and the rate constant of CO_2-amine reaction. This relationship was verified by several researchers and found to contribute to comprehending the CO_2 absorption kinetics.[20–24] Additionally, the pK_a of its conjugate acid, which can be used to quantify the basicity of the solvent, is considered to play an important factor on reaction rate in the CO_2 absorption process in that the higher the pK_a, the faster the absorption kinetics.[25] Thus, it can be concluded that the accurate determination of the pK_a value is vital not only for analytical scientists but also for separation engineers on the absorption kinetics study.[26,27]

For a new system of 1DEA2P-H_2O-CO_2, the study of reaction kinetics is extremely essential to effectively use 1DEA2P as a solvent; and to properly design the absorption column. In this work, the stopped-flow apparatus was used to measure the reaction kinetics of 1DEA2P over a 1DEA2P concentration range of 120–751 mol/m^3 and at temperatures of 298, 303, 308, and 313 K. The obtained kinetics data were, then, presented and evaluated in terms of observed pseudo-first-order rate constant (k_o) and second-order reaction rate constant (k_2). Meanwhile, the temperature dependency of pK_a and the thermodynamic properties (Gibbs energy of molar reaction; $\Delta_r G_m$and molar reaction enthalpy; $\Delta_r H_m$) of 1DEA2P were also determined. In addition, the Brønsted-based relationship between the pK_a values and the second-order reaction rate constants k_2 for 1DEA2P was, then, established. The chemical structures of amines used in this work are shown in Figure 1.

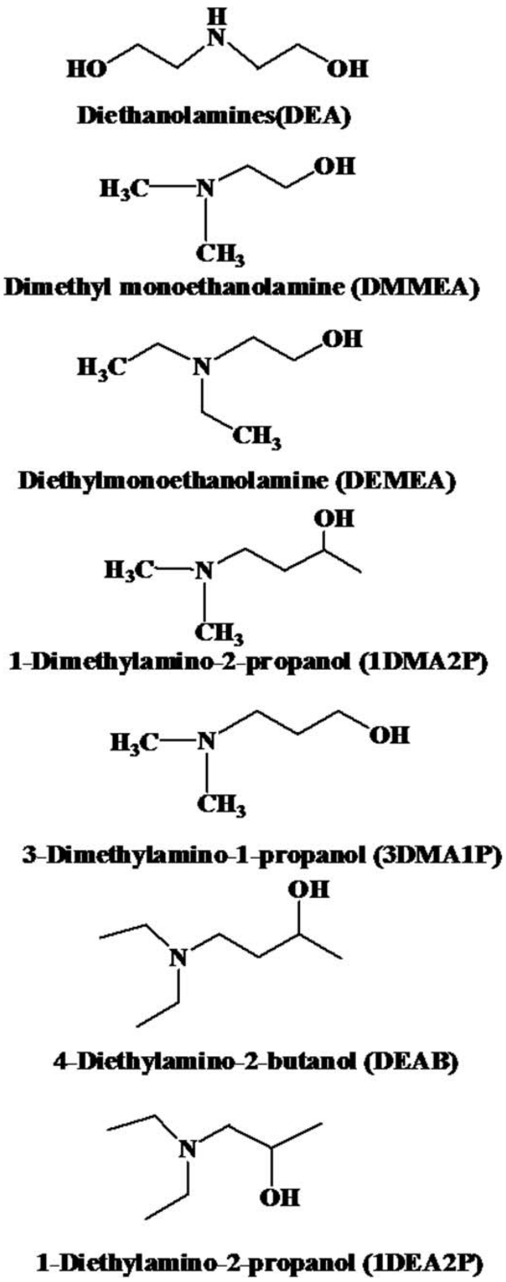

Figure 1. Chemical structures of amine solvents used in this work.

Theory

Reaction kinetics

Donaldson and Nguyen[28] originally proposed the base-catalyzed hydration mechanism that the tertiary amine does not react directly with CO_2, but acts as a base that catalyzes the hydration of CO_2. As 1DEA2P is a tertiary amine, the absorption mechanism of 1DEA2P, then, follows the base-catalyzed hydration mechanism as can be expressed as

$$\text{1DEA2P}+CO_2+H_2O \overset{k_2}{\longleftrightarrow} \text{1DEA2PH}^+ + HCO_3^- \qquad (1)$$

In the aqueous solution, the following reactions can be occurred

$$CO_2 + OH^- \overset{k_{OH^-}}{\longleftrightarrow} HCO_3^- \tag{2}$$

$$CO_2 + H_2O \overset{k_{H_2O}}{\longleftrightarrow} H_2CO_3 \tag{3}$$

Based on the reactions 1–3, the overall reaction rate of CO_2 absorption (r_{CO_2}; kmol/m^3 s) can be expressed as

$$r_{CO_2} = k_o[CO_2] = \{k_2[1DEA2P] + k_{OH^-}[OH^-] + k_{H_2O}[H_2O]\}[CO_2] \tag{4}$$

where k_o is overall reaction rate constant or observed pseudo-first-order reaction rate constant (s^{-1}), k_2 is second-order reaction rate constant of reaction 1 (m^3/kmol s), k_{OH^-} is reaction rate constant of reaction 2 (m^3/kmol s), k_{H_2O} is reaction rate constant of reaction 3 (m^3/kmol s), and [] is concentration (kmol/m^3).

Due to its slow reaction rate with respect to mass transfer compared to reactions 1 and 2, reaction 3 can be neglected.[29] Therefore, the rate expression based on reactions 1 and 2 can be expressed as

$$r_{CO_2} = k_o[CO_2] = \{k_2[1DEA2P] + k_{OH^-}[OH^-]\}[CO_2] \tag{5}$$

In aqueous amine solution, the contribution of OH^- to overall reaction could be neglected.[22,30–33] Thus, the main contributor is amine itself, which in this case is 1DEA2P. The overall reaction rate expression of CO_2 absorption into aqueous of 1DEA2P based on base-catalyzed hydration mechanism can be written as

$$r_{CO_2} = k_o[CO_2] = k_2[1DEA2P][CO_2] \tag{6}$$

Therefore

$$k_o = k_2[1DEA2P] \tag{7}$$

Dissociation constant and thermodynamics properties

For aqueous solution of 1DEA2P, the deprotonation reaction of conjugate acid of 1DEA2P ($1DEA2PH^+$) can be expressed as follows

$$1DEA2PH^+ \overset{K_{a,1DEA2P}}{\longleftrightarrow} 1DEA2P \ + \ H^+ \tag{8}$$

Based on the assumption that the solution is ideal (when the concentration is very low, activity coefficient can be considered to be 1), the pK_a of the aqueous 1DEA2P solution can be calculated as follows

$$pK_a = -\log\left(K_{a,1DEA2P}\right) = -\log\left(\frac{[1DEA2P][H^+]}{[1DEA2PH^+]}\right) \tag{9}$$

or

$$K_{a,1DEA2P} = \frac{[1DEA2P][H^+]}{[1DEA2PH^+]} = 10^{-pK_a} \tag{10}$$

Meanwhile, the well-known thermodynamic relations for Gibbs energy of molar reaction ($\Delta_r G_m$; kJ/mol) and molar reaction enthalpy ($\Delta_r H_m$; kJ/mol) can be obtained from the dissociation constant of its conjugate acid as (Hamborg et al.[25])

$$\Delta_r G_m = -RT\ln K_a \tag{11}$$

$$\Delta_r H_m = -R\frac{d\ln K_a}{d(1/T)} \tag{12}$$

where R is gas constant 0.008315 (kJ/mol K) and T is temperature (K)

Experimental Section

Chemicals

Reagent grade 1DEA2P with a mass purity of ≥97% was obtained from Acros Organics, Belgium. The amine solutions were prepared to the desired concentration using deionized water. Commercial-grade CO_2 cylinder (with a purity of ≥99%) was supplied by Changsha Jingxiang Gas Co., China. In addition, DEA (with a purity of ≥99%) was purchased from Chengdu Ai Keda Chemical Technology Co., China; and MDEA (with a purity of ≥99%) was purchased from Tianjin Hengxing Chemical Preparation Co., China (which was used to validate the stopped-flow apparatus and the experimental procedure for calculating dissociation constant, respectively).

Measurement of kinetics data from stopped-flow apparatus

For the amine-CO_2-H_2O system, the technology of stopped-flow was used to represent the kinetics data in this work. The experimental equipment used in this work was the standard model SF-61DX manufactured by Hi-Tech Scientific, (U.K.). It is made up of four main sections: a sample handing unit, a conductivity-detection cell, A/D converter, and a microprocessor. Figure 2 shows a schematic drawing of the experimental stopped-flow apparatus. The sample-flow circuits are immersed in a constant temperature water bath to make sure that the temperature can be controlled within ±0.1 K. A pneumatically air supply pushes two internal syringes which contain the saturated CO_2 solution and amine solution to mix in the stopped-flow apparatus. "Kinetasyst" software is used to actuate the pneumatically controlled drive plate which pushes accurate equal doses of solution into the conductivity-detection cell of the equipment. The voltage change caused by ion formation as a function of time is monitored by the conductivity cell. The conductivity change as a function of time is measured by a circuit as described by Knipe et al.,[34] which gives an output voltage directly proportional to the solution conductivity. The observation pseudo-first-order constant (k_o) can be automatically generated based on the typical graph of vs. time using "Kinetasyst" software. Experiments are repeated at least nine times at each temperature for all of the concentrations.

In this work, the stopped-flow apparatus was validated using aqueous solutions of DEA over a concentration range of 100–500 mol/m^3 and a temperature range of 298–313 K. The results obtained from this work were, then, compared with those of Ali et al.[35,36] as presented in Figure 3. It can be clearly seen that the kinetics data in terms of pseudo-first-order constant (k_o) obtained from this work were found to be in good agreement with those obtained from the literature with an absolute average deviation (AAD) of 5%, which is in an acceptable range of less than 10%. Therefore, it can be inferred from this verification that the kinetics data obtained using the stopped-flow apparatus in this work were accurate and reliable. For the new system of 1DEA2P-CO_2-H_2O, the kinetics experiments were conducted using the stopped-flow apparatus in mild conditions to eliminate other influence parameters (e.g., CO_2 loading, viscosity, density, diffusivity).

Measurement of dissociation constant

In this work, the dissociation constant of conjugate acid of 1DEA2P ($K_{a,1DEA2P}$), which is presented in Eq. 12, was

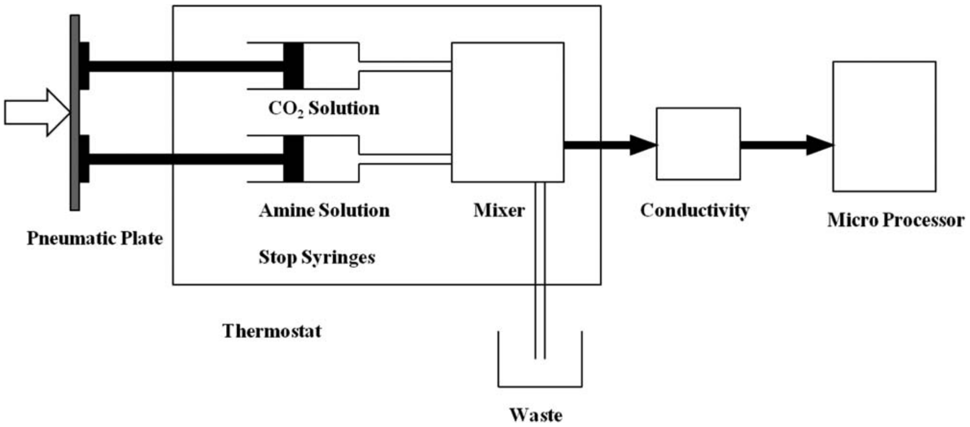

Figure 2. Schematic drawing of the experimental stopped-flow equipment (Li et al.[12]).

experimentally determined according to the procedure described in the literature.[37–39] Briefly, the $K_{a,1DEA2P}$ can be calculated based on Eq. 12, in which 1.0 M hydrochloric acid (HCl) was added into the aqueous amine solution. The concentration of H^+ was, then, measured by the pH meter using electrode model E-201-C (model Rex PHS-3C, INESA Scientific Instruments Co., China., the pH value varies from 0 to 14 with a ±0.01 accuracy). The reliability of the pH meter was checked by calibrating with standard buffer solutions (Potassium hydrogen phthalate with pH 4.00, and Sodium tetraborate decahydrate with pH 9.18). The compensation for temperature was achieved by adjusting the temperature of pH meter to be the same temperature with as the measured aqueous solvent. The concentration of free amine and protonated amine can be calculated by total proton mass balance and amine mass balance, respectively. Apparently, the values of $K_{a,1DEA2P}$ at different temperature can be obtained.

Additionally, the experimental and calculation procedures used for determining the dissociation constant of 1DEA2P was validated using MDEA over a temperature range of 280–333 K. As shown in Figure 4, the dissociation constants of MDEA in terms of pK_a obtained from this work was found to be in excellent accordance with those from the work of Kamps and Mourer[37] with an AAD of 0.12%. Therefore, it can be said that the experimental equipments and methods for determining the value of pK_a used in this work is deemed to be valid.

Results and Discussion

pK_a *of the aqueous 1DEA2P solutions*

The pK_a is considered to be very important parameter for an effective selection of the amine solution used for acid gas removal; and a good interpretation of the kinetic of the acid gas absorption.[21] Therefore, the reliable pK_a values and the accurate predictive correlation of aqueous 1DEA2P solution are vitally necessary for further investigation and commercialization of 1DEA2P. In this work, the pK_a values of 1DEA2P were measured over a temperature range of 278–333 K and plotted against temperature as shown in Figure 5. As expected, it can be obviously seen from this figure that the pK_a values of aqueous 1DEA2P solutions decreased as temperature increased. Based on a non-linear regression analysis, the predictive correlation for pK_a for aqueous 1DEA2P solution can be presented as

$$pK_{a,1DEA2P} = \frac{2131}{T} + 2.76 \quad \rightarrow (R^2 = 0.999) \tag{13}$$

As can be found in Figure 5, the predicted pK_a values calculated from Eq. 13 were found to be in a very good

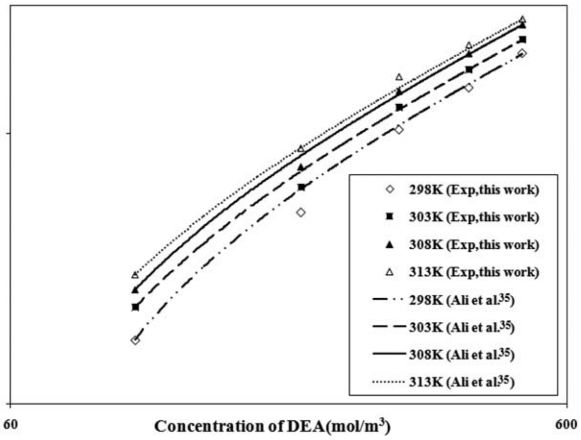

Figure 3. Validation of stopped-flow apparatus for the kinetics data (k_o) using DEA (dots are experimental results obtained in this work, and lines are those obtained from the work of Ali et al.[35]).

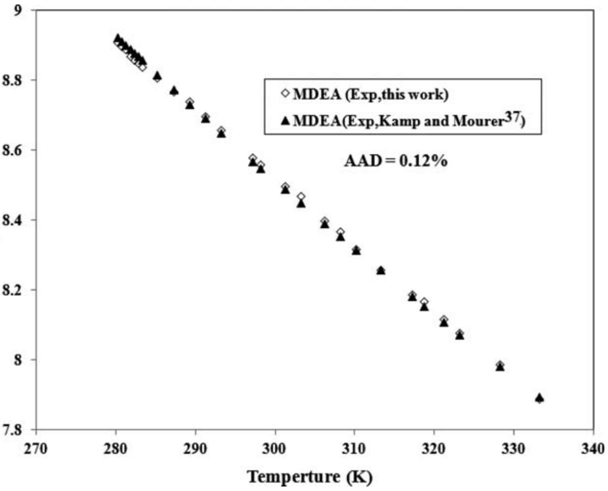

Figure 4. Validation of experimental and calculation procedures for determining dissociation constant (in terms of pK_a) using MDEA.

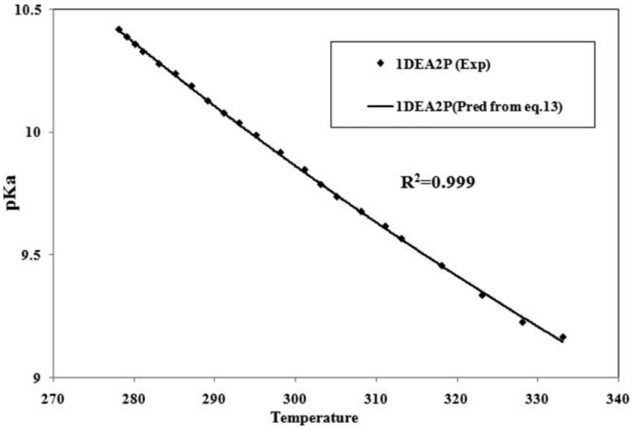

Figure 5. The pK_a values of 1DEA2P over a temperature range of 278–333 K (dots are experimental results measured from this work, and solid line are the predicted results obtained from Eq. 13).

agreement with the experimental results with an AAD of 0.08%. Apparently, the predictive correlation presented in this work (Eq. 13) is adequately reliable for estimating pK_a values of 1DEA2P. In addition, the changes of standard state properties ($\Delta_r G_m^{\circ}$ and $\Delta_r H_m^{\circ}$) of aqueous 1DEA2P solution were obtained by applying Eqs. 11 and 12, respectively. It was found that the values of $\Delta_r G_m^{\circ}$ and $\Delta_r H_m^{\circ}$ of 1DEA2P are 56.61 and 40.1 kJ/mol, respectively. These two thermodynamics properties can be used to interpret the performance of amine that may be used as a solvent for CO_2 capture process.[40] The $\Delta_r G_m^{\circ}$ can be used to represent the basic strength of amine in that the higher value of $\Delta_r G_m^{\circ}$, the stronger the basic strength of amine. Sema et al.[11] and Brønsted and Guggenheim[19] mentioned that the higher the basic strength of amine, the faster the CO_2 absorption kinetics of that amine. Additionally, $\Delta_r H_m^{\circ}$ indicates the change of basic strength of amine from a lower temperature to a higher temperature. The higher value of $\Delta_r H_m^{\circ}$ results in a favorable shift of basic strength of amine during cooling/heating cycle of the absorber/desorber sections.[23,26]

CO_2 absorption kinetics of 1DEA2P

To examine the CO_2 absorption kinetics of 1DEA2P, the absorption experiment was done using the stopped-flow apparatus over a 1DEA2P concentration range of 120–751 mol/m^3, and a temperature range of 298–313 K. By applying pseudo-first-order reaction respected to the concentration of CO_2, the overall absorption rate of CO_2 can, then, be expressed as presented in Eq. 7. The pseudo-first-order reaction rate constant (k_o) extracted from the stopped-flow apparatus are presented in Table 1 and plotted in Figure 6. It can be seen from Figure 6 and Table 1 that the CO_2 absorption kinetics of 1DEA2P increased as the concentration of 1DEA2P and/or the temperature increased over ranges of concentration and temperature of 120–751 mol/m^3 and 298–313 K, respectively.

Table 1. Experimental Kinetics Data (in terms of k_o) of 1DEA2P Extracted from Stopped-Flow Apparatus over a 1DEA2P Concentration Range of 120–751 mol/m^3, and a Temperature Range of 298–313 K

Concentration (mol/m^3)	Pseudo-first-order rate constant, k_o (s^{-1})			
	298 K	303 K	308 K	313 K
120	8.12	12.16	18.42	26.52
207	14.43	20.33	27.58	37.48
304	17.02	25.12	35.16	49.64
389	21.11	30.82	45.98	61.77
495	31.91	45.34	57.47	80.58
640	38.31	53.06	78.04	98.00
751	46.39	63.35	92.09	104.40

The pseudo-first-order rate constants (k_o) were fitted with the power law equation (Eq. 14), which gave the reaction order of 0.93, 0.89, 0.88, and 0.78, with respect to [1DEA2P] for 298, 303, 308, and 313 K, respectively. To obtain k_2, the values of k_o at various concentrations and temperatures of 1DEA2P (from Table 1) were, then, fitted with Eq. 7. All the fitted results can be found in Table 2

$$k_o = k_n[1DEA2P]^n \tag{14}$$

where n is reaction order.

As, it has been generally accepted that k_2 is a function of temperature through Arrhenius relationship (Eq. 15),[11,29] the values of k_2 obtained from the stopped-flow apparatus were, then, plotted as a function of reciprocal temperature as presented in Figure 7. As expected, the k_2 was found to be increased as the temperature increased

$$k_2 = A\exp\left(\frac{-E_a}{RT}\right) \tag{15}$$

where A is Arrhenius constant (m^3/mol s), and E_a is activation energy (kJ/mol)

The temperature dependency of k_2 through Arrhenius relationship of 1DEA2P can be expressed as

$$k_2 = (2.80\times10^{18})\exp\left(-\frac{11326}{T}\right) \tag{16}$$

As can be seen in Figure 7, the predicted values of k_2 calculated from Eq. 16 were found to be in a good agreement with those experimentally obtained from stopped-flow apparatus with an acceptable AAD of 8.0%. From the slope of

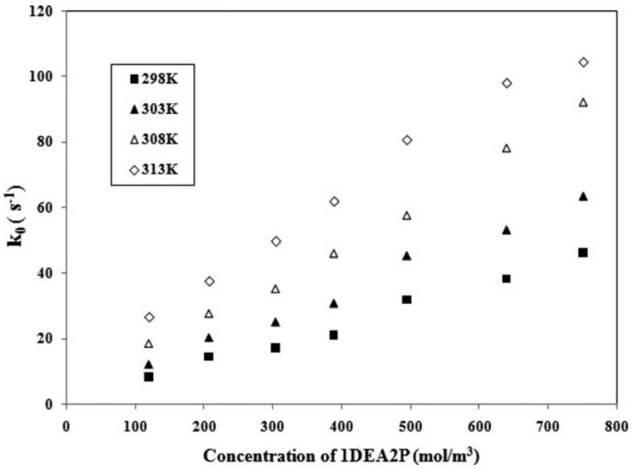

Figure 6. The reaction kinetics (in terms of pseudo-first-order reaction rate constant, k_o) of 1DEA2P over a concentration range of 120–751 mol/m^3 and a temperature range of 298–313 K.

Table 2. Second-Order Reaction Rate Constant (k_2) of CO_2 Absorption into Aqueous Solution of 1DEA2P

T (K)	k_2 (m^3/kmol s)
298	91.5
303	165.3
308	256.6
313	599.8

the plot, the activation energy (E_a) was found to be 94.18 kJ/mol.

Prediction of k_2 of 1DEA2P through the Brønsted relationship

The Brønsted relationship involving the relation of the second-order rate constant (k_2) and pK_a proposed by Versteeg and van Swaaij[41] was normally used to represent the relationship of the second-order rate constant (k_2) of different tertiary amines and their respective pK_a values at the same temperature.[4] Chen and Rochelle,[42] and Silva and Svendsen[43] also reported the isothermal Brønsted relationships of some amine solvents. In this work, the data of 1DEA2P and other tertiary amines were collected to develop the isothermal correlation,[4,12,22,30,37,38,44] which is given in the Figure 8.

In addition, a linear regression of the Brønsted relationship at different temperatures of some amines have been reported.[23] Little et al.[30] presented the regression of Brønsted relationship for some tertiary amines (e.g., MDEA and TEA) at temperatures ranging from 293 to 333 K. In addition, the linear Brønsted plots between k_2 and pK_a at different temperatures have also been reported by Rabindran.[45] In this work, the Brønsted plot of 1DEA2P, which is shown in Figure 9, was generated using the experimental pK_a experimentally measured in this work and the k_2 obtained from the stopped-flow reactor over a temperature range of 298–313 K. The developed Brønsted relationship of 1DEA2P can be expressed as

$$\ln(k_{2,1DEA2P}) = (-5.42pK_a) + 58.23 \qquad (17)$$

As can be seen in Figure 9, it was found that Brønsted relationship of Eq. 17 can be effectively used to predict the k_2 of 1DEA2P with an AAD of 5.2%, which is in an acceptable range of less than 10%. In addition of 1DEA2P, the Brønsted plots of DEAB, 1-dimethylamino-2-propanol (1DMA2P), and 3-dimethylamino-1-propanol (3DMA2P) were also established (values of pK_a and k_2 were collected from the works of Sema et al.,[4] Shi et al.,[38] Kadiwala and Henni[44] over the temperature range of 298–313 K) as follows

$$\ln(k_{2,DEAB}) = (-4.91pK_a) + 57.35 \qquad (18)$$

$$\ln(k_{2,1DMA2P}) = (-3.22pK_a) + 33.72 \qquad (19)$$

$$\ln(k_{2,3DMA2P}) = (-3.08pK_a) + 32.94 \qquad (20)$$

The predicted k_2 (calculated from Eqs. 18–20) were found to be in a very good accordance with the experimental k_2 obtained from the literature[4,44] with AADs of 3.5% for DEAB, 2.6% for 1DMA2P, and 2.3% for 3DMA2P. Therefore, it can be summarized that the Brønsted relationship can provide accurate reaction kinetics (in terms of k_2) results for tertiary amines. Even though the Brønsted relationship could predicate accurate reaction kinetics (in terms of k_2) results for tertiary amines, the reaction kinetics must be confirmed using experimental investigations.

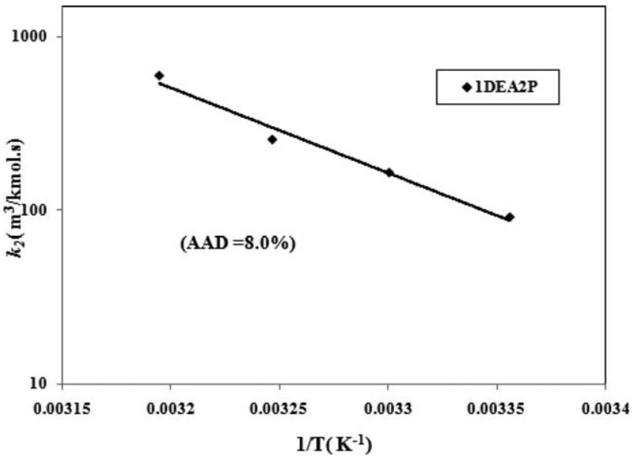

Figure 7. Arrhenius plot for the kinetics constant of CO_2 absorption into aqueous 1DEA2P solutions over a temperature range of 298–313 K.

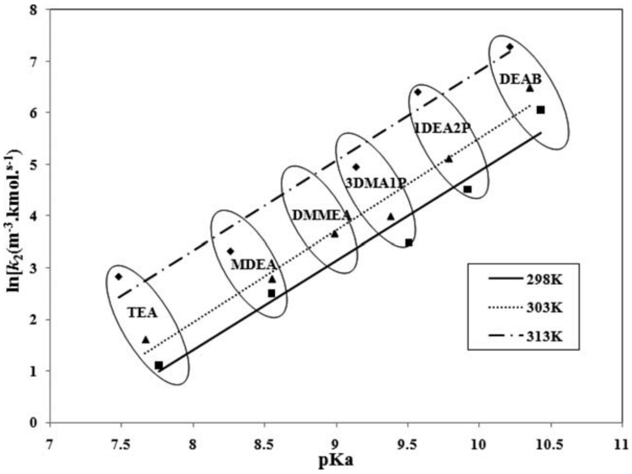

Figure 8. The isothermal Brønsted plot between lnk_2 and pK_a of six tertiary amines at 298 K, 303 K, and 313 K.

Comparative performance of 1DEA2P with conventional tertiary amines

As 1DEA2P is a tertiary amine, it, therefore, would be reasonable to compare the performance of 1DEA2P with the conventional amines (i.e., MDEA, DEMEA, and DMMEA). This comparison will provide very useful information about 1DEA2P as a possible alternative absorbent for CO_2 removal. As presented in Figure 10, the pK_a of 1DEA2P is compared with those of MDEA, DEMEA, and DMMEA over a temperature range of 293–333K. It can be seen from this figure that the pK_a of 1DEA2P is higher than those of DEMEA, DMMEA, and MDEA, respectively.

As previously discussed that the reaction kinetics of CO_2 absorption of tertiary amine can be related to its pK_a value in that the higher the pK_a, the faster the reaction kinetics, it, therefore, can be simply interpreted from the pK_a results presented in Figure 10 that the reaction kinetics tertiary amines can be ranked as: 1DEA2P > DEMEA > DMMEA > MDEA. This ranking of reaction kinetics can be confirmed by the second order of reaction rate constants (k_2) at 298 K of

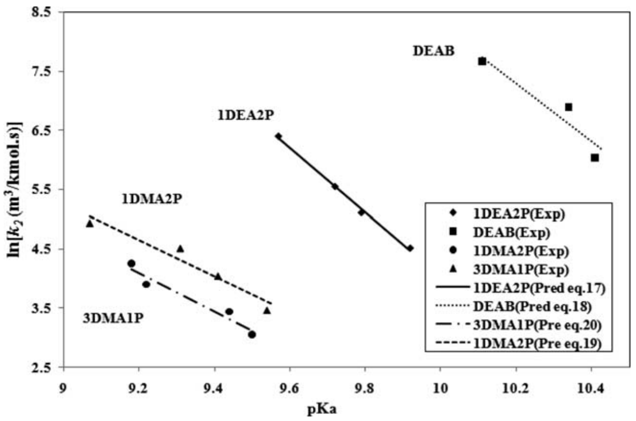

Figure 9. Brønsted plot between lnk_2 and pK_a for 1DEA2P, DEAB, DMMEA, DEMEA, and MDEA.

1DEA2P, DEMEA, DMMEA, and MDEA (which are shown in Table 3). According to the general acceptance that the higher value of k_2, the faster reaction kinetics; it can be found from Table 3 that 1DEA2P can react with CO_2 faster than DEMEA, DMMEA, and MDEA, respectively. After comparing the value of pK_a and the absorption kinetics of 1DEA2P and DEAB (in which they have similar structure as presented in Figure 1), it can be seen that (1) the pK_a of 1DEA2P was found to be lower than that of DEAB as shown in Figure 10 and (2) the absorption kinetics of 1DEA2P (in terms of k_2) was found to be lower than that of DEAB as presented in Figure 10 and Table 3. In addition, two thermodynamics properties of $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ of 1DEA2P are reported together with those of DEMEA, DMMEA, and MDEA in Table 4. It can be seen from Table 4 that the $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ values of 1DEA2P are higher than those of DEMEA, DMMEA, and MDEA.

In addition of the reaction kinetics, the CO_2 equilibrium solubility is considered to be one of the very most important parameters for amine-based CO_2 capture process. Generally, these two parameters should be considered together in that the promising solvent should have fast reaction kinetics and high equilibrium solubility.[3,5,7,8,27] In this work, the CO_2 equilibrium solubility of 1DEA2P was experimentally measured (in comparison with those of MEA, AMP, MDEA, DEAB) using the absorption cell at temperature of 313 K and atmospheric pressure. The experimental setup and procedure are similar to our previous work.[7,8] Briefly, the main features of this experiment are a saturation cell, an absorption reactor, a mass flow meter, and a water bath with a temperature controller. For each experiment, the saturated cell and the absorption reactor were immersed in a water bath with the temperature controller. The gaseous stream with a CO_2 concentration of $\geq$99.9% was, then, passed through the saturated cell and bubbled into the liquid amine sample. The liquid sample was, then, taken for measuring a CO_2 loading using acidification technique.

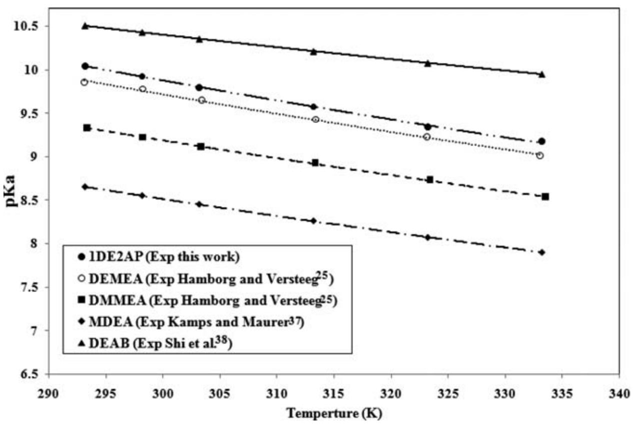

Figure 10. The values of pK_a of 1DEA2P, DEAB, DEMEA, DMMEA, and MDEA over a temperature range of 293–333 K.

Table 3. Second-Order Reaction Rate Constant (k_2) at 298 K and Activation Energy of MDEA, DMMEA, DEMEA, 1DEA2P, and DEAB

Tertiary Amines	k_2 (m^3/kmol s)	Activation Energy (kJ/mol)
MDEA	12.0	41.93
DMMEA	27.2	53.63
DEMEA	79.8	51.87
1DEA2P	91.5	94.18
DEAB	416.5	62.59

The results showed that the CO_2 equilibrium solubility of 1DEA2P was found to be the highest and higher than those of DEAB, MDEA, AMP, and MEA, respectively.[7,8,46,47] The results shown in Figure 11 also revealed that the equilibrium CO_2 solubility of 1DEA2P is slightly higher than that of DEAB, which was not correlated with the pK_a. This might be due to the experimental conditions used in this study. As 1DEA2P is tertiary amine, it would be reasonable to compare its performance with DEAB and MDEA. Even though the absorption kinetics of 1DEA2P is slower than that of DEAB as presented in Table 3, the main advantage of 1DEA2P is that it has a higher equilibrium solubility than DEAB as shown in Figure 11. More importantly, it can be clearly seen that both reaction kinetics and equilibrium solubility of 1DEA2P are higher than those of MDEA, which is the mostly used tertiary amine,[1,11] as presented in Figure 11 and Table 3. Therefore, in terms of reaction kinetics and equilibrium solubility, it can be said that 1DEA2P has a great potential to be the next generation tertiary amine that can be alternately used for capturing CO_2.

The volatility of amine in the amine-water is of key industrial interest that is required in the selection of a suitable solvent for CO_2 absorption and in the design of water wash unit.[48,49] The amine Henry's constants (the primary amine indicator of amine volatility) could be estimated using an empirical correlation given the contribution of the molecular groups and structural shape according to the work of Nguyen et al.[50] In this work, the estimated $H_{\text{amine},313\text{K}}$ for 1DEA2P-H_2O system was found to be much higher than that of the conventional amines (e.g., MEA, MDEA, and PZ), which may be a limitation for the commercial use of 1DEA2P for CO_2 capture. However, the good performance of 1DEA2P in

Table 4. Standard State Thermodynamic Properties ($\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$) of MDEA, DMMEA, DEMEA, and 1DEA2P

Tertiary Amines	$\Delta_r G_m$ (kJ/mol)	$\Delta_r H_m$ (kJ/mol)
MDEA	48.81	34.0
DMMEA	52.63	34. 4
DEMEA	55.64	36.2
1DEA2P	56.61	40.1

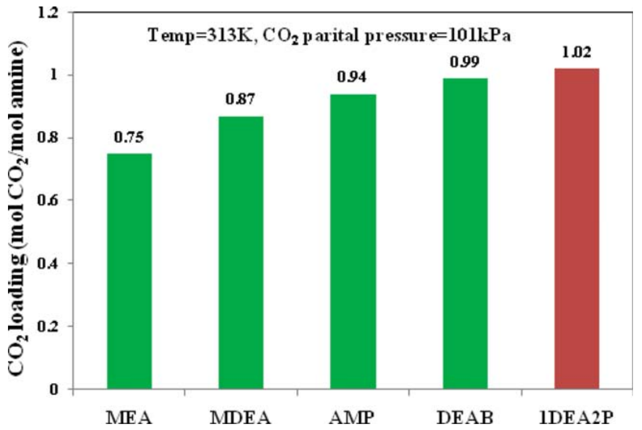

Figure 11. Equilibrium solubility of CO$_2$ absorption into aqueous solutions of 2M MEA, 2M MDEA, 2M AMP, 2M DEAB, and 2M 1DEA2P.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

terms of reaction kinetics and equilibrium solubility could provide useful elements to formulate good solvents for CO$_2$ removal applications. This new solvent will most likely be used as an additive ingredient in formulated solvents (e.g., PZ+1DEA2P and MEA+1DEA2P), but not as a single-component solvent.

Conclusions

The CO$_2$ absorption kinetics of novel 1DEA2P was experimentally determined using stopped-flow apparatus over a 1DEA2P concentration range of 120–751 mol/m^3 and a temperature range of 298–313 K. In addition, the pK_a of aqueous solution of 1DEA2P were experimentally determined over a temperature range of 278–333 K. The results showed that the CO$_2$ absorption kinetics increased as the concentration of 1DEA2P and/or the temperature increased. It was also found that the second-order reaction rate constant (k_2) of 1DEA2P can be correlated using an Arrhenius equation with an AAD of 8.0%. The k_2 of 1DEA2P can be simply predicted through the Brønsted relationship with an acceptable AAD of 5.2%. By comparing with the conventional tertiary amines, the novel tertiary amine, 1DEA2P, was found to have faster reaction kinetics than those of DEMEA, DMMEA, and MDEA, respectively. Based on the outstanding performance of 1DEA2P for high equilibrium solubility and fast reaction kinetics, 1DEA2P could be considered to be one of candidate solvents for CO$_2$ removal applications. However, several additional investigations of 1DEA2P (e.g., mass transfer, corrosion, volatility and degradation behaviors) need to be further investigated before 1DEA2P can be widely used for CO$_2$ capture applications. According to the calculation model for the volatility proposed by Nguyen et al.,[48–50] the calculated volatility of 1DEA2P is higher than those of other conventional amines. However, 1DEA2P provides useful elements to formulate good solvents for CO$_2$ removal applications based on the outstanding performance of 1DEA2P of high equilibrium solubility and fast reaction kinetics.

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Notation

1DEA2P = 1-diethylamino-2-propanol
1DMA2P = 1-dimethylamino-2-propanol
3DMA1P = 3-dimethylamino-1-propanol
A = Arrhenius constant (m^3/mol.s)
AEEA = 2-((2-aminoethyl) amino) ethanol
AMP = 2-amino-2-methyl-1-propanol
DEA = diethanolamine
DEAB = 4-diethylamino-2-butanol
DEMEA = diethylmonoethanolamine
DMMEA = dimethylmonoethanolamine
E_a = activation energy (kJ/mol)
k_o = observed pseudo-first-order reaction rate constant, s^{-1}
k_2 = forward second-order reaction rate constant, m^3/kmol s
k_{H_2O} = reaction rate constant of reaction 3, m^3/kmol s
k_{OH^-} = reaction rate constant of reaction 2, m^3/kmol s
$K_{a,1DEA2P}$ = dissociation constant of conjugate acid of 1DEA2P, mol/m^3
K_W = dissociation constant for water, mol^2/m^6
MEA = monoethanolamine
MDEA = methyldiethanolamine
PZ = piperazine
r_{CO_2} = overall CO$_2$ absorption rate, kmol/m^3 s
R = universal gas constant, 0.008315 kJ/mol K
T = temperature, K

Greek letters

α = solution CO$_2$ loading, mol CO$_2$/mol amine
$\Delta_r G_m$ = Gibbs energy change, kJ/mol
$\Delta_r H_m$ = reaction enthalpy change, kJ/mol

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