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The comparative kinetics study of CO₂ absorption into non-aqueous DEEA/MEA and DMEA/MEA blended systems solution by using stopped-flow technique

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HIGHLIGHTS

- The kinetics of the CO₂ absorption has been studied using the stopped-flow technique.
- Establishing the Arrhenius equation of DEEA/MEA, DMEA/MEA.
- The kinetics model based on termolecular mechanism was built.
- There is interaction between the tertiary amine and the primary amine.
- The interaction affects the reaction kinetics and the activation energy.

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ABSTRACT

The kinetics of the absorption of CO₂ into solutions of (monoethanolamine) MEA-Ethanol, (N, N-diethylethanolamine) DEEA-MEA-Ethanol and (N, N-dimethylethanolamine) DMEA-MEA-Ethanol have been studied by applying a stopped-flow apparatus. In this study, the concentration range of both tertiary amine and MEA were chosen to be 0.2–0.4 kmol/m³ with a temperature range of 293–313 K under non-aqueous conditions. The model based on the termolecular reaction mechanism is proposed to interpret the experimental kinetic data of the reaction occurred in the non-aqueous blended amine systems, and the results indicate that the model is well fitted to the experimental data with an AARD of 5.70% for DEEA-MEA-Ethanol system and 6.53% for DMEA-MEA-Ethanol system. Blended amines show many advantages in kinetics because of the existence of the interaction between the tertiary amine and MEA. The kinetics behaviors of CO₂ absorbed in the two non-aqueous blended amine systems are discussed in brief according to the molecular structures of the two tertiary amines. Different from the traditional aqueous systems, this study proved that tertiary amine enhanced the ability of primary amine to absorb CO₂ which is due to tertiary amine didn't react with CO₂ directly in a non-aqueous system. The result in the non-aqueous system also shows that DMEA is more easily participate in the termolecular reaction between MEA and CO₂ compared with DEEA, which indicate the length of alkyl chain on nitrogen atom also plays an important role in the enhancement effect. Additionally, after comparing the kinetic data of the two blended amine systems under aqueous and non-aqueous conditions, it can be found that tertiary amine can participate in the termolecular reaction between MEA and CO₂, and that the protonated MEA can be re-converted to free MEA by the tertiary amine, making it easier for MEA to participate in its own termolecular reactions, so that the overall reaction rate of the blended amine system is accelerated. It can be summarized that there are interactions between the tertiary amine and the primary amine in the non-aqueous blended amine system that positively promote the kinetics.

1. Introduction

In recent years, massive emissions of man-made carbon dioxide

(CO₂) released from the consumption of fossil fuels have led to serious negative climatic effects that also affect societies and economies seriously around the world [1,2]. Carbon Capture, Utilization and Storage

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(CCUS), especially the post combustion capture (PCC) of CO₂, is considered to be the most viable countermeasure all around the world to reduce the emission of CO₂ [3]. Chemical absorption by organic amine solvent is considered to be the most mature technology with higher selectivity and absorption capacity relative to other methods [4–6]. There have been various alkanolamines (primary, secondary and tertiary amines) applied to absorb CO₂ from flue gas due to their high absorptive character and relatively fast reaction rates [7]. Nevertheless, high energy consumption and high corrosiveness are the two major shortcomings which greatly limit further development and adoption of this method.

To alleviate the above shortcomings, non-aqueous conditions which consist of amines with different alcohols such as methanol and ethanol were put forward to be a high feasibility method for CO₂ capture, due to their high solubility and absorption capacity with relatively low corrosiveness and desorption energy consumption [8]. Nowadays, non-aqueous systems have been widely used for capture and hydrogen sulfide adsorption et al, but the recycle loops are indispensable in the course of the operations, which are also more applicable to remove the acid gases [9]. Recently, the reaction kinetics of CO₂ absorbed in amines under non-aqueous conditions has been studied by applying the stopped-flow technique. Various systems have been studied such as the aniline/hexamine/cyclohexamine-ethanol system by Ali et al. [10], the ethylenediamine (EDA)/3-amino-1-propanol (3-AP)- ethanol/methanol system by Kadiwala et al. [11] and the 2-((2-aminoethyl) amino) ethanol (AEEA)- ethanol/methanol system by Rayer et al. [12]. Additionally, some researchers measured the kinetic data of CO₂ absorbed in different amine solutions with various non-aqueous solvents such as methanol, ethanol, ethylene glycol, propylene glycol, 2-propanol and n-butanol by using other experimental techniques which include wetted wall column, stirred cell reactor and laminar jet absorber, and obtained satisfactory results [13–18]. Thus, non-aqueous systems have exhibited significant advantages compared with the corresponding aqueous systems, including high solubility, high absorption capacity, low corrosiveness and low desorption energy consumption [8].

In addition, screening effective amines for the CO₂ absorption process is important. Generally, effective amines need to have many superior properties, such as high absorption capacity, high mass transfer coefficients, fast reaction rates, low regeneration energy consumption and corrosiveness, and must not be degraded [19]. These contradictory properties of single amine solutions limit their further development for CO₂ absorption. In order to improve the effectiveness of existing amines and develop the advantages of low regeneration energy consumption and fast absorption rates, the concept of blended amine solutions was put forward and has become more extensively used. Chakravarty et al. [20] firstly researched CO₂ absorbed in blended amine solutions by mixing a tertiary amine with primary and secondary amines to obtain a solvent system which had the advantages of both of the two type of amines. Xiao et al. [21] researched the kinetics and reaction mechanism of CO₂ absorbed in a blended diethanolamine (DEA)-MEA system which exhibited the faster kinetics compared with the single amine. CO₂ absorption in methyl-diethanolamine (MDEA), piperazine (PZ), MEA and their mixtures was also studied by Dubois et al. [22] and CO₂ absorbed in blended DMEA-MEA, DEEA-MEA and AMP-MEA systems was studied by Conway et al. [23] and also showed the same results. By comparing the characterization of DEEA, DMEA, MEA and their mixtures including DMEA-MEA and DEEA-MEA in the stopped-flow apparatus, Jiang et al. [24] found the kinetics of CO₂ absorption in blended amine systems are more satisfactory. All the above studies have shown the blended amines to be more effective in most respects.

It should be noted that, the intramolecular interaction effect between primary and tertiary amine, which is the main reason why tertiary amine enhanced the CO₂ absorption in the blended amine system, was always investigated in aqueous solution. The water will definitely affect the interaction effects due to the reaction mechanism of both primary and tertiary amine in aqueous solution. Therefore, the study of

reaction kinetics of those kinds of blended amine in non-aqueous solutions becomes very important since there is no effect from solvent side, and this is another object of this work.

DMEA and DEEA are two different tertiary amines with similar molecular structures both of which show positive properties for CO₂ absorption. The reaction kinetics of CO₂ absorbed in aqueous DEEA solution and DMEA solution were studied by Kim et al. [25], and Henni et al. [26], respectively, with relatively high reaction rate compared with other traditional amines. The kinetics equation of DEEA as $k_2 = 9.95 \times 10^7 \exp(-6238.4/T)$ (m³·mol⁻¹·s⁻¹) was derived by Li et al. [27], with the concentration from 0.1965 to 0.9974 kmol/m³ at the temperature range from 298 K to 313 K by using the stopped-flow apparatus. The k_2 of DEEA was calculated as 0.173 (m³·mol⁻¹·s⁻¹) at 303 K with the concentration from 2 to 3 kmol/m³ by Vaidya and Kenig. The kinetics equation of DMEA as $k_2 = 6.82 \times 10^7 \exp(-6450.2/T)$ (m³·mol⁻¹·s⁻¹) was derived by Henni et al. [26] for the concentration range 0.304 to 0.9848 kmol/m³ at the temperature range from 298 K to 313 K by using the stopped-flow apparatus. The k_2 of DMEA was calculated as 0.0066 (m³·mol⁻¹·s⁻¹) at 293 K with the concentration range from 0.324 to 2.388 kmol/m³ by Versteeg and Swaaij [28]. Both amines exhibited good potential for CO₂ capture.

In this study, the kinetics of CO₂ absorbed in MEA-Ethanol solution, in DEEA-MEA-Ethanol solution and in DMEA-MEA-Ethanol solution has been measured by using a stopped-flow apparatus. The model based on the termolecular reaction mechanism is proposed to interpret the experimental kinetic data of the reactions in the non-aqueous blended amine systems. The kinetics behaviors of the two non-aqueous blended amine systems are discussed in brief and related to the molecular structures of the two tertiary amines. Different from the multiple complex reactions in the traditional aqueous systems, this study in a non-aqueous system demonstrate the interaction between the tertiary amine and primary amine clearly.

2. Experiment section

2.1. Chemicals

DMEA (N, N-dimethylethanolamine, purity 99%) was obtained from Kernel Reagent Co., Ltd. (Tianjin, China). DEEA (N, N-diethylethanolamine, purity 99%) was purchased from Xiya Reagent Co., Ltd. (Chengdu, China) and MEA (Monoethanolamine, purity 99%) was provided from Hengxing Chemical Preparation Co., Ltd. (Tianjin, China). High purity gases (CO₂, 99.999%) were purchased from Rizhen gas Co., Ltd. (Shanghai, China). The deionized water used for preparation of amine solutions was obtained by a deionized water unit made by Taoshi Water Equipment Engineering Co., Ltd. (Shenzhen, China). The Chemical molecular structures of all amines are shown in Fig. 1.

2.2. Stopped-flow apparatus

A good understanding of the chemical reaction kinetics is one of the most essential prerequisites to be able to simulate and optimize the process of CO₂ absorption [29]. Several techniques are being used to measure the chemical reaction kinetic data such as wetted wall column, stirred cell reactor, laminar jet absorber and stopped-flow method [30].

The stopped-flow apparatus for studying the reaction in the liquid phase, belongs to the homogeneous reactor category, for which there is no mass transfer between liquid and gas phases and no the gas-liquid contact interface, a big advantage over gas-liquid reactors [21]. In this study, the stopped-flow apparatus facilitates and monitors the reaction between the amine solutions and the CO₂ saturated solutions within the non-aqueous systems being studied so that the kinetic constants of the reaction can be obtained directly without considering gas-liquid phase resistance.

Due to the poor physical solubility of CO₂ in most solvents, the

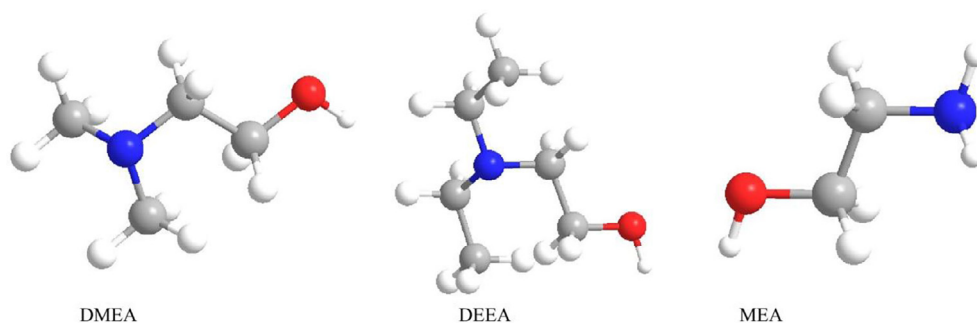


Fig. 1. The chemical molecular structures of DMEA, DEEA and MEA.

stopped-flow technique is only suitable for CO₂ absorption at low CO₂ concentrations. Additionally, the requirements for amine concentrations in such apparatus are relatively strict, and desirable outcomes can only be obtained within a narrow amine concentration range. This is because high concentrations of reactants leads to vigorous reaction in the fast reaction region, resulting in high temperatures from the heat of absorption and extreme conductivity increases, making the experimental conditions unsuitable.

However, the stopped-flow technique has been successfully used to measure the reaction rate of a variety of primary, secondary, tertiary amine and blended amine solutions, the experimental results exhibit good agreement with the predicted outcomes of the data from literature. For example, Saha and Bandyopadhyay [31] measured the reaction rate constants of CO₂ absorbed in AMP by using the wetted wall column, and the experimental data are consistent with Alper's results obtained through the stopped-flow apparatus. Liu et al. [32] measured the activation energy (E_a) of the reaction between DEAB and CO₂ applying the stopped-flow apparatus, and the results are close to the Sema's result obtained through the laminar jet absorber [33], specifically, 62.58 kJ/mol and 62.59 kJ/mol, respectively.

In this study, the stopped-flow apparatus (Model SF-61DX) was made by Hi-Tech Scientific, Ltd. (U.K.). The stopped-flow apparatus consists of four system modules as shown in Fig. 2: a conductivity detection cell, a sample handling unit, a microprocessor and A/D converter, and the thermostatic external circulator to maintain the temperature within ± 0.1 K. The variation of conductivity caused by the formation of ion species in the reaction system was calculated by the conductivity detection cell. A voltage directly proportional to the conductivity change was output by a special circuit [34]. The conductivity changed versus time and was then fitted in a microprocessor by using following equation:

$$G(t) = (G_0 - G_\infty)\exp(-k_0 \times t) + G_\infty \quad (1)$$

where G_0 and G_∞ represent the conductivity at the beginning and the

end of the reaction in the non-aqueous system, k_0 is the pseudo first-order reaction rate constant, which can be automatically generated by "Kinetasyst" software installed on the microcomputer.

2.3. Experimental procedure

Detecting the variation of the conductivity in the non-aqueous system is fundamental to the stopped-flow technique. Solution injected into the stopped-flow apparatus must be relatively low concentration and close to infinite dilution in order for it to be treated as an ideal solution. Under these conditions the interference of ionic strength can be ignored with satisfactory accuracy. Thus, the amine concentration is usually kept less than 1 kmol/m³, and even much lower when blended amines are being studied. In this study, because tertiary amines only participate in the termolecular reaction of MEA in the non-aqueous systems, the concentration range of both tertiary amine and MEA were chosen to be 0.2–0.4 kmol/m³, which has been discovered to be the optimal range to study the effect of the concentration on reaction rate for the non-aqueous systems.

The CO₂ saturated ethanol solutions were obtained by bubbling CO₂ into the absolute ethyl alcohol for at least 30 min. The amine concentration of the amine alcohol solutions should be ten times higher than the CO₂ saturated ethanol solutions to ensure that the homogeneous reaction of amine and CO₂ in the non-aqueous system takes place under the pseudo first-order conditions. The kinetics of blended amine solutions reacting with CO₂ were studied using stopped-flow technique at the temperature range of 293–313 K under non-aqueous conditions.

Further details of this stopped-flow technique have been described and validated in our previous work [32,35] on the kinetics of CO₂ absorption into aqueous 1DEA2P and DEAB solutions at 298 K. The results showed that the kinetics data in terms of pseudo first-order constant (k_0) were in good agreement with the works of Ali et al. [10,36].

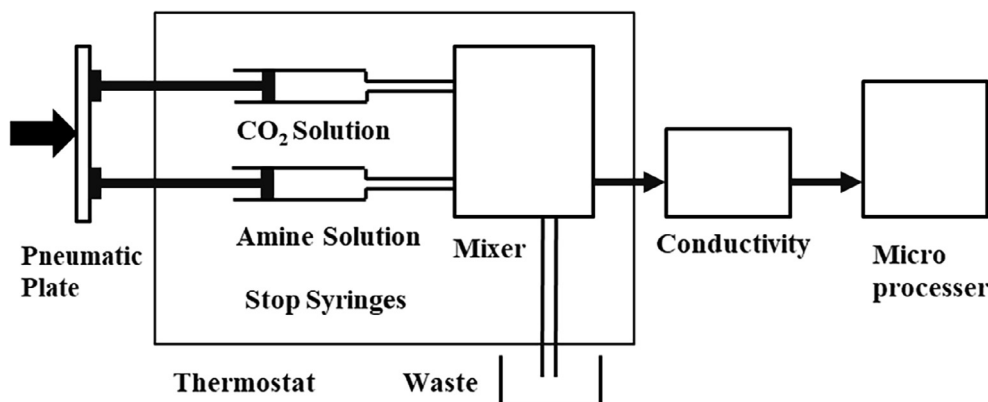


Fig. 2. Schematic drawing of the stopped-flow apparatus.

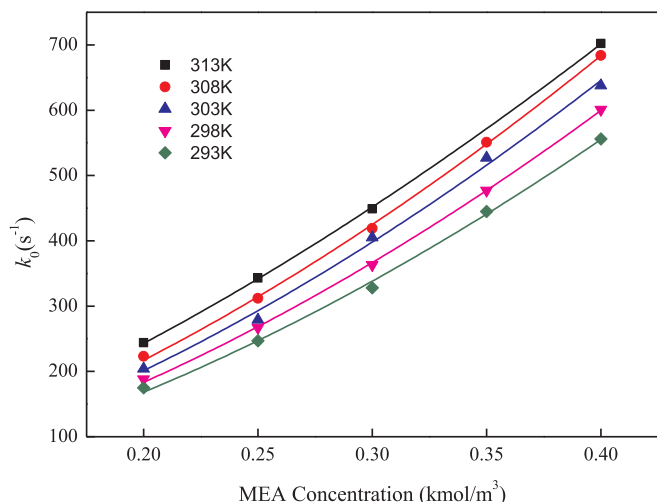
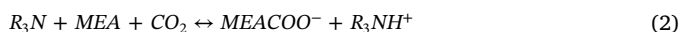


Fig. 3. The reaction rate constant (k_0) versus MEA concentration at different temperatures.

3. Mechanism

3.1. Chemical reactions

The overall chemical reactions for the non-aqueous system between CO_2 and blended DMEA-MEA or DEEA-MEA are as follows:



MEA carbamate produced by the reaction between MEA and CO_2 :



The protons of MEA stripped by R_3N :



where $k_{2,\text{MEA}}$ is the second-order forward rate constant ($\text{m}^3\text{kmol}^{-1}\text{s}^{-1}$) and $k_{-2,\text{MEA}}$ is the second-order reverse rate constant ($\text{m}^3\text{kmol}^{-1}\text{s}^{-1}$) between MEA and CO_2 with MEA as base.

3.2. Kinetics model and reaction mechanism

In this section, the absorption rate of CO_2 with primary amine and R_3N can be assumed to the termolecular reaction mechanism based on the above reactions. The termolecular reaction mechanism, which was presented by Crooks et al. [37] assumes that the amine reacts with both CO_2 and a base molecule and forms a loosely bound encounter complex, like the Eq. (5) shows. Then, the ionic products such as protonated amine, bicarbonate and carbamate are formed. The kinetic model based on the termolecular reaction mechanism was adopted to fit the experimental data and to explain the kinetics for the non-aqueous blended amine system.



3.2.1. Reaction mechanism for MEA-Ethanol- CO_2 system

For the non-aqueous system, the termolecular reaction mechanism was adopted to explain the reaction process of MEA with CO_2 , and the base which started the termolecular reaction is only MEA due to the inability of ethanol to be protonated, as shown in Eq. (6). The total reaction rate of CO_2 absorption using the termolecular reaction mechanism can be depicted as follows:

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

$$k_0^T = k_{\text{MEA}}^T [\text{MEA}][\text{MEA}] \quad (7)$$

where k_0^T is the total reaction rate of MEA (s^{-1}) under non-aqueous conditions, and k_{MEA}^T represents the kinetic rate constant of MEA ($\text{m}^6\text{kmol}^{-2}\text{s}^{-1}$) under non-aqueous conditions.

3.2.2. Reaction mechanism for blended amine-ethanol- CO_2 system

In the non-aqueous system, tertiary amine did not directly react with CO_2 . The main reaction is the termolecular reaction between MEA and CO_2 involving the tertiary amine and MEA itself as alkaline substances. The total reaction rate of CO_2 absorption using the termolecular mechanism can be depicted as follows:

$$r_{\text{CO}_2} = k_0^T [\text{CO}_2] = \{k_{\text{MEA}}^T [\text{MEA}][\text{MEA}] + k_{\text{R}_3\text{N}}^T [\text{R}_3\text{N}][\text{MEA}]\} [\text{CO}_2] \quad (8)$$

$$k_0^T = k_{\text{MEA}}^T [\text{MEA}][\text{MEA}] + k_{\text{R}_3\text{N}}^T [\text{R}_3\text{N}][\text{MEA}] \quad (9)$$

where, k_0^T is the total reaction rate of blended amine (s^{-1}) under non-aqueous conditions, k_0^{T1} represents the total reaction rate of DEEA-MEA and k_0^{T2} represents the total reaction rate of DMEA-MEA, and k_{MEA}^T and $k_{\text{R}_3\text{N}}^T$ represent the reaction rate constants in the termolecular reaction involving MEA and tertiary amine as alkaline substances, respectively ($\text{m}^6\text{kmol}^{-2}\text{s}^{-1}$), where k_{MEA}^{T1} is the reaction rate constant of DEEA-MEA and k_{MEA}^{T2} is the reaction rate constant of DMEA-MEA.

4. Results and discussion

In the non-aqueous blended DMEA-MEA and DEEA-MEA systems there is no hydrolysis reaction occurring so that the effect of H_2O and OH^- can be disregarded in the termolecular reaction between MEA and CO_2 . In this study, comparing the kinetics of the blended non-aqueous amine system with the one under aqueous conditions will definitely help to understand the influence of intramolecular interaction on the kinetics of the CO_2 absorption process, especially in the blended amine system. Additionally, the kinetics data of the reaction between single MEA and CO_2 under non-aqueous conditions were also examined so as to compare with the blended amine.

4.1. Kinetics of CO_2 absorption in MEA-Ethanol solution

The pseudo first-order reaction rate constant (k_0) of CO_2 adsorbed in MEA-Ethanol solution with the concentration range of 0.2 kmol/m^3 to 0.4 kmol/m^3 was measured over the temperature range from 293 K to 313 K. The relationship between the reaction rate constant (k_0) and the concentration of MEA under different temperatures is exhibited in Fig. 3. It can be seen that the pseudo first-order reaction rate constant (k_0) increased with increasing temperature and with increasing MEA concentration.

The reaction order, which is vital for studying the reaction mechanism, was calculated by applying the empirical power law based on the effect of temperatures and concentrations on the pseudo first-order reaction rate constant (k_0). The fitting results showed that all the calculated values of the reaction order under different temperatures and concentrations were in the range of 1.5–1.7, indicating that it is proper to fit the experimental data using the termolecular reaction mechanism, as shown in Eq. (7).

Then the reaction rate constants of MEA (k_{MEA}^T) under non-aqueous conditions can be fitted by Eq. (6) as listed in Table 1.

Table 1
 CO_2 -MEA-Ethanol system reaction rate constants at different temperatures.

Temperature (K)	$k_{\text{MEA}}^T (\text{m}^6 \text{kmol}^{-2} \text{s}^{-1})$
293	3644.44
298	3983.33
303	4303.99
308	4655.55
313	4988.89

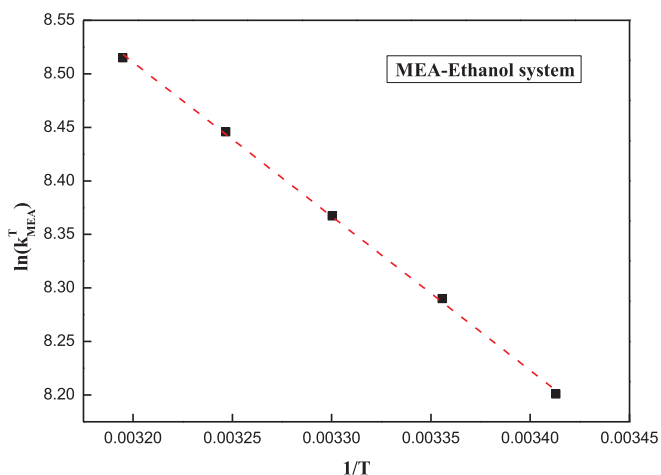


Fig. 4. The Arrhenius plots of $\ln(k_{\text{MEA}}^T)$ versus $1/T$.

In addition, the Arrhenius equation of k_{MEA}^T as a function of temperature in the MEA-Ethanol system is as follows:

$$k_{\text{MEA}}^T = 4.96 \times 10^5 \exp\left(-\frac{1438.8}{T}\right) \quad (10)$$

The activation energy (E_a) of CO_2 absorption into MEA-Ethanol solution was calculated as 11.96 kJ/mol. The Arrhenius plots of $\ln(k_{\text{MEA}}^T)$ against $1/T$ are exhibited in Fig. 4 and show excellent agreement, with the AARD (average absolute relative deviation) of 7.67%, indicating that the termolecular reaction mechanism is correct in this case.

4.2. Kinetics of CO_2 absorption in DEEA-MEA-Ethanol solution

The pseudo first-order reaction rate constants (k_0) of CO_2 adsorbed in DEEA-MEA-Ethanol solution were measured over the temperature range of 293 K to 313 K. Five different concentrations of DEEA and MEA from 0.2 kmol/m^3 to 0.4 kmol/m^3 were tested and 25 experimental data were obtained. It can be seen that the pseudo first-order reaction rate constant (k_0) increased with increasing temperature and with increasing MEA concentration as shown in Fig. 5.

By analyzing the exponential relationship between the pseudo first-order reaction rate constant (k_0) and MEA concentrations, the values of the MEA reaction order in DEEA-MEA-Ethanol solution were found to be between 1.3 and 1.5, indicating that the termolecular reaction

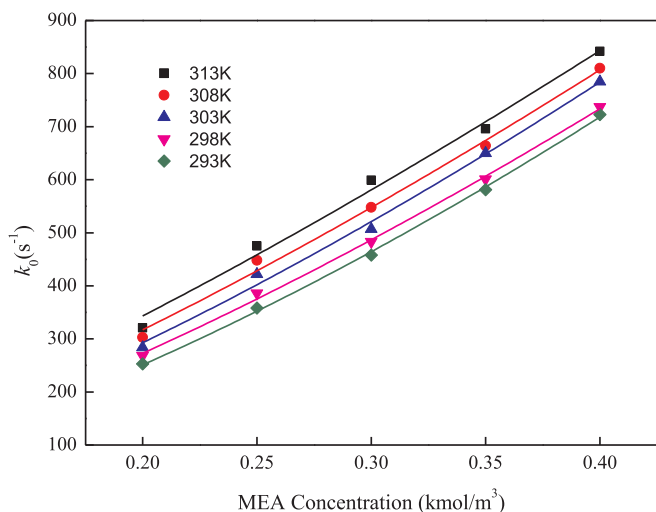


Fig. 5. The reaction rate constant (k_0) versus MEA concentration at different temperatures (DEEA concentration is set at 0.2 kmol/m^3).

Table 2

The k_{MEA}^T and k_{DEEA}^T of DEEA-MEA-Ethanol system at different temperatures.

Temperature (K)	$k_{\text{MEA}}^T (\text{m}^6 \text{kmol}^{-2} \text{s}^{-1})$	$k_{\text{DEEA}}^T (\text{m}^6 \text{kmol}^{-2} \text{s}^{-1})$
293	2870.85	1781.97
298	2981.93	1964.59
303	3096.68	2161.96
308	3190.75	2381.29
313	3309.46	2576.72

mechanism is feasible as shown in Eq. (11):

$$k_0^T = k_{\text{MEA}}^T [\text{MEA}] [\text{MEA}] + k_{\text{DEEA}}^T [\text{DEEA}] [\text{MEA}] \quad (11)$$

The reaction rate constants of MEA (k_{MEA}^T) and DEEA (k_{DEEA}^T) can be fitted by Eq. (11) and are listed in Table 2.

The Arrhenius type of equation for k_{MEA}^T and k_{DEEA}^T in DEEA-MEA-Ethanol system can be fitted against temperature, as shown in Eqs. (12) and (13).

$$k_{\text{MEA}}^T = 2.60 \times 10^4 \exp\left(-\frac{645.89}{T}\right) \quad (12)$$

$$k_{\text{DEEA}}^T = 6.03 \times 10^5 \exp\left(-\frac{1706.4}{T}\right) \quad (13)$$

The Arrhenius plots of $\ln(k_{\text{MEA}}^T)$ and $\ln(k_{\text{DEEA}}^T)$ against $1/T$ also showed good agreement and are exhibited in Fig. 6. The activation energies (E_a) for k_{MEA}^T and k_{DEEA}^T can then be determined to be 5.37 kJ/mol and 14.19 kJ/mol, respectively.

The AARD between the experimental pseudo first-order reaction rate constant (k_0) and those calculated based on the kinetics model was 5.70% and the parity plot is shown in Fig. 7, indicating that the termolecular reaction mechanism was also successfully applied in DEEA-MEA-Ethanol system as in the previous section.

4.3. Kinetics of CO_2 absorption in DMEA-MEA-Ethanol solution

As in the previous section, 25 data sets were obtained when mixing DMEA and MEA at each concentration with the reactions carried out under the same experimental conditions.

It can be found that the values of the pseudo first-order reaction rate constants (k_0) increased with the increasing of temperature and MEA concentration as shown in Fig. 8.

The MEA reaction order in DMEA-MEA-Ethanol solution was calculated to be between 1.3 and 1.5 by analyzing the exponential relationship between pseudo first-order reaction rate constant (k_0) and MEA concentration, indicating that the termolecular reaction mechanism is feasible as shown in Eq. (14).

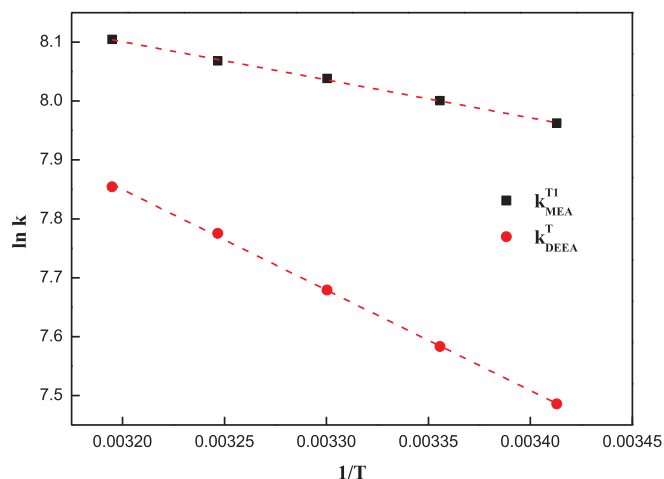


Fig. 6. The Arrhenius plots of $\ln(k_{\text{MEA}}^T)$ and $\ln(k_{\text{DEEA}}^T)$ against $1/T$.

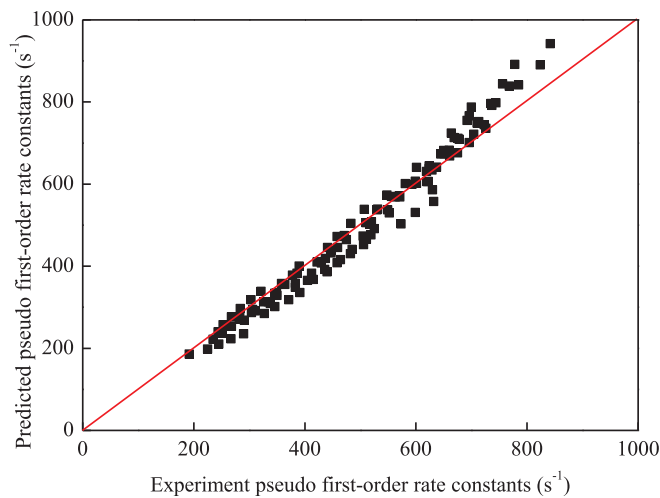


Fig. 7. Parity plot of experimental k_0 and predicted k_0 in DEEA-MEA-Ethanol system.

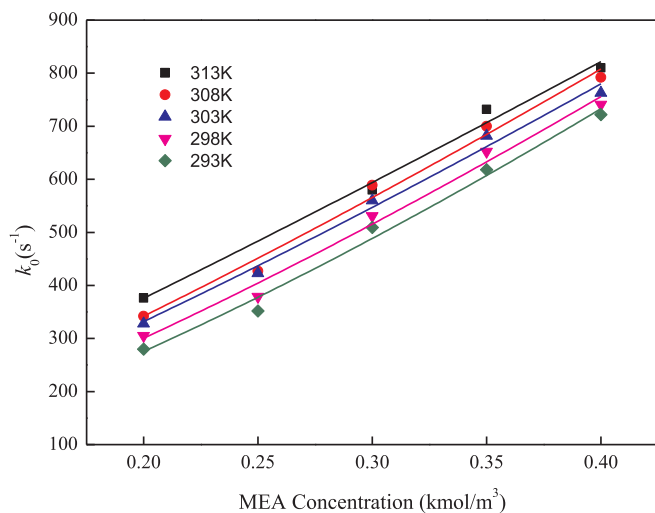


Fig. 8. The reaction rate constant (k_0) versus MEA concentration at different temperatures (DMEA concentration is set at 0.3 kmol/m³).

$$k_0^{T2} = k_{\text{MEA}}^{T2} [\text{MEA}][\text{MEA}] + k_{\text{DMEA}}^T [\text{DMEA}][\text{MEA}] \quad (14)$$

The reaction rate constants of MEA (k_{MEA}^{T2}) and DMEA (k_{DMEA}^T) can be fitted by Eq. (14) and the results are listed in Table 3.

The Arrhenius equation for k_{MEA}^{T2} and k_{DMEA}^T in the DMEA-MEA-Ethanol system can be calculated by correlating temperature with the reaction rate constants, as shown in Eqs 15. and 16.

$$k_{\text{MEA}}^{T2} = 8.22 \times 10^3 \exp\left(-\frac{280.68}{T}\right) \quad (15)$$

$$k_{\text{DMEA}}^T = 3.60 \times 10^5 \exp\left(-\frac{1477.7}{T}\right) \quad (16)$$

Table 3

The k_{MEA}^{T2} and k_{DMEA}^T of DMEA-MEA blended amine system at different temperatures.

Temperature (K)	k_{MEA}^{T2} (m ⁶ kmol ⁻² s ⁻¹)	k_{DMEA}^T (m ⁶ kmol ⁻² s ⁻¹)
293	3154.21	2324.09
298	3205.13	2534.86
303	3254.29	2751.42
308	3305.93	2970.02
313	3352.66	3211.78

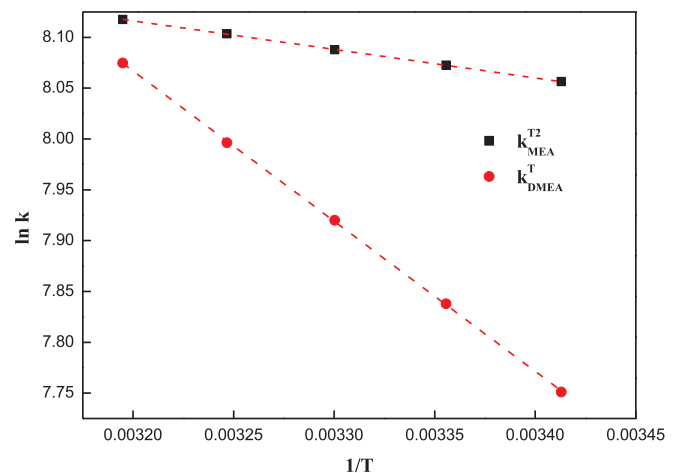


Fig. 9. The Arrhenius plots of $\ln(k_{\text{MEA}}^{T2})$ and $\ln(k_{\text{DMEA}}^T)$ against $1/T$.

The Arrhenius plots of $\ln(k_{\text{MEA}}^{T2})$ and $\ln(k_{\text{DMEA}}^T)$ against $1/T$ are exhibited in Fig. 9. The activation energies (E_a) for k_{MEA}^{T2} and k_{DMEA}^T were calculated as 2.33 kJ/mol and 12.29 kJ/mol, respectively.

The pseudo first-order reaction rate constants (k_0) calculated by the reaction rate constants of MEA (k_{MEA}^{T2}), which were obtained from Eq. (15) are in excellent agreement with the experimental values with an AARD of 6.53% as shown in Fig. 10, indicating that the termolecular reaction mechanism was suitable for non-aqueous blended amine system to describe the kinetic data.

4.4. Comparison of the experimental results in the non-aqueous system

By comparing the pseudo first-order reaction rate constants in the above three systems (MEA-Ethanol, DEEA-MEA-Ethanol and DMEA-MEA-Ethanol), it can be observed that introducing tertiary amine leads to a significant increase in the reaction rate, as shown in Fig. 11. In non-aqueous system, there is no dissociation of amines with absence of water, and the tertiary amine will not react with CO₂ directly. So that the reason of this enhanced phenomenon is the tertiary amine molecular causing MEA molecular deprotonations, which increases the number of free MEA molecules produced and enhances the reaction rate, as shown in Eqs. (3) and (4).

In addition, DMEA can better promote the reaction than DEEA can in the non-aqueous system as shown in Fig. 11, indicating that DEMA more easily participates in the termolecular reaction between MEA and

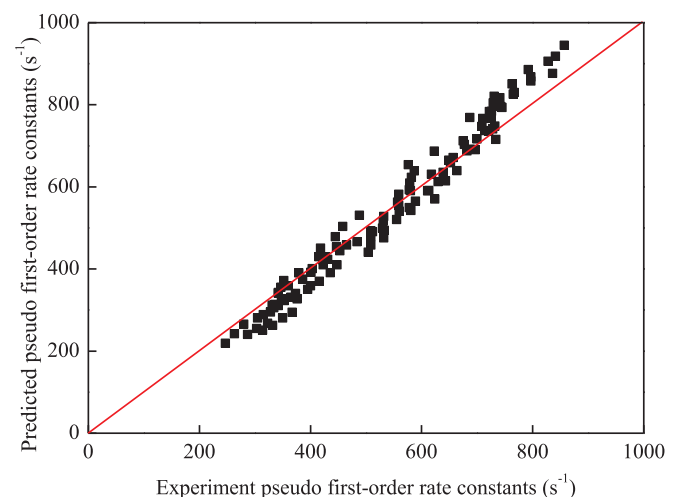


Fig. 10. Parity plot of experimental k_0 and predicted k_0 in DMEA-MEA-Ethanol system.

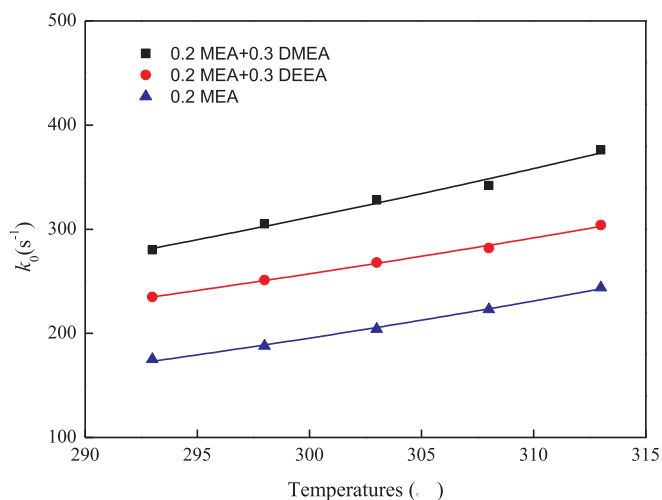


Fig. 11. The reaction rate constant (k_0) in different systems at different temperatures.

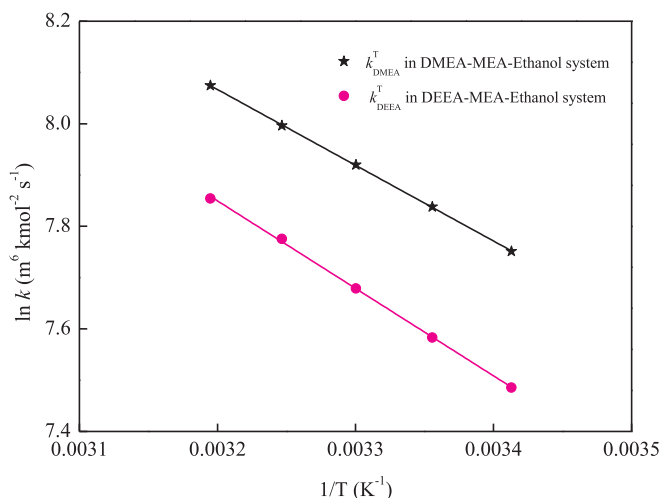


Fig. 12. k_{DEEA} and k_{DMEA} of DEEA and DMEA in respective blended systems as a function of $1/T$.

CO_2 . This is in full agreement with the result of the aqueous system in our previous study [24]. The reaction rate constants of DMEA (k_{DMEA}^T) and DEEA (k_{DEEA}^T) in the non-aqueous conditions also follow the trend $k_{DMEA}^T > k_{DEEA}^T$ as shown in Fig. 12. This is because of the DMEA molecule having a weaker proton binding capacity than DEEA, which resulted in less protonated DMEA occurred in the non-aqueous system with the same amine concentrations of DEEA-Ethanol system, leading to more free DMEA than DEEA as occurred in the non-aqueous systems. Thus the reaction rate of the termolecular reaction mechanism is faster with the DMEA molecule is the base. Furthermore, the activation energy (E_a) for k_{DEEA}^T and k_{DMEA}^T in the DMEA-MEA-Ethanol and DEEA-MEA-Ethanol systems are 12.19 kJ/mol and 14.19 kJ/mol, respectively, which also indicates the same result that DEMA more easily participates in the termolecular reaction between MEA and CO_2 .

By comparing the activation energy (E_a) for k_{DEEA} and k_{DMEA} in both aqueous and non-aqueous systems, as shown in Table 4, it was found that the E_a of the tertiary amines in the aqueous systems are much larger than the activation energy (E_a) in non-aqueous systems. This is because tertiary amines can react directly with CO_2 in aqueous system but cannot in non-aqueous systems, as Eqs. (17) and (18) presented:



Table 4

The activation energy of in blended amine systems.

	DEEA- MEA system (kJ/mol)	DMEA- MEA system (kJ/mol)
Aqueous systems	36.28	30.17
Non-aqueous systems	14.19	12.29

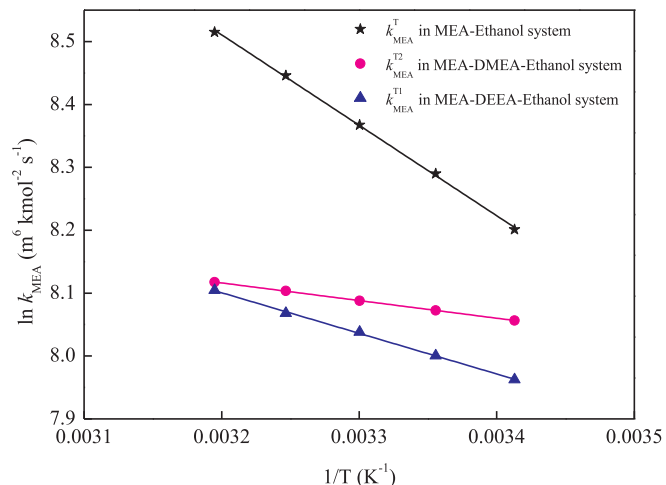


Fig. 13. Comparison of the k_{MEA} in different ethanol systems as a function of $1/T$.

In addition, Eq. (17) is a spontaneous reaction, where higher temperature can promote hydrolysis. Thus the activation energy (E_a) is more sensitive to temperature in aqueous systems, which leads to higher activation energy (E_a).

As shown in Fig. 13, k_{MEA}^T is the kinetic rate constant of MEA in the MEA-Ethanol system, and k_{MEA}^{T1} and k_{MEA}^{T2} represent the kinetic rate constants of MEA in DEEA-MEA-Ethanol system and DMEA-MEA-Ethanol system, respectively. It can be observed that k_{MEA}^T is much larger than k_{MEA}^{T1} and k_{MEA}^{T2} which were obtained after introducing tertiary amine. This is because the termolecular reaction only takes place between MEA and itself in MEA-Ethanol system, but in non-aqueous blended amine systems, part of MEA reacts with tertiary amine causing a decrease in the amount of MEA which can participate in the termolecular reaction.

Considering the activation energies (E_a) of MEA-Ethanol system and non-aqueous blended amine systems, it can be observed that the activation energy (E_a) in MEA-Ethanol system is 11.96 kJ/mol compared to 5.37 kJ/mol and 2.33 kJ/mol in DEEA-MEA-Ethanol system and DMEA-MEA-Ethanol systems, respectively, indicating that the addition of tertiary amine promotes the termolecular reaction rate, but because the decrease of the MEA concentration which participates the termolecular reaction, the kinetic rate constants show a decreasing trend.

In addition, it can be found in Fig. 13 that the kinetic rate constants of MEA in DMEA-MEA-Ethanol system (k_{MEA}^{T2}) are larger than the values in the DEEA-MEA-Ethanol system (k_{MEA}^{T1}). In other words, the reaction rate of the termolecular reaction between MEA and itself is faster in the DMEA-MEA-Ethanol system. Although the kinetic rate constants of MEA are decreasing in non-aqueous blended amine systems, the decrement of k_{MEA}^{T2} is less than k_{MEA}^{T1} due to DMEA being more apt to participate in the termolecular reaction.

In the non-aqueous solutions, where the alkali-catalyzed hydrolysis reaction for the tertiary amine can not occur without H_2O involvement, the termolecular reaction between MEA and CO_2 involving tertiary amine and the reaction between tertiary amine and MEA which is protonated are the only two reactions in the system, as shown in Fig. 14. Blended amines show more advantages in their kinetics because of the existence of the interaction effects between the tertiary amine

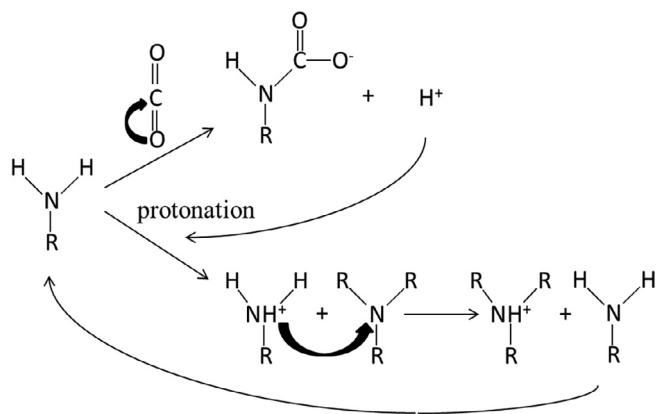


Fig. 14. The interaction between tertiary amine and primary amine under non-aqueous conditions.

and primary amine.

5. Conclusion

In this work, a stopped-flow apparatus was applied to study the kinetics of the absorption of CO₂ in non-aqueous blended DMEA-MEA and DEEA-MEA solutions. The concentration range for both MEA and tertiary amine was 0.2 kmol/m³ to 0.4 kmol/m³, and the temperature range was 293 K–313 K. The termolecular reaction mechanism was applied to describe the experimental data. It is clear that the termolecular reaction mechanism provides a satisfactory prediction.

Different from the multiple complex reactions in the traditional aqueous systems, this study in a non-aqueous system can clearly demonstrate that the interaction between the tertiary amine and primary amine leads to the enhancement of the reaction rate because of there is no reaction occurred between tertiary amine and CO₂ in the non-aqueous system. On the one hand, tertiary amine participate in the termolecular reaction between MEA and CO₂ as alkaline substances. On the other hand, introducing tertiary amine releases protons from the protonated MEA, freeing up MEA molecules and further enhancing the reaction rate.

Additionally, the reaction rate of the termolecular reaction mechanism in the DMEA-MEA-Ethanol system is faster than it in the DEEA-MEA-Ethanol system, this is because DMEA molecules have a weaker proton binding capacity than DEEA, which results in less protonated DMEA formed in this non-aqueous system with the same amine concentrations as in DEEA-Ethanol system, leading to more free DMEA than DEEA being available. This result also indicates that the length of alkyl chain on nitrogen atom also plays an important role in the enhancement of the reaction rate.

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