



Kinetics of CO₂ absorption into ethanolamine + water + ethanol system—mechanism, role of water, and kinetic model



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HIGHLIGHTS

- CO₂ absorption in MEA + H₂O + Ethanol is explained by zwitterion mechanism with rate-limiting of deprotonation.
- Water accelerates reactions by participating in the deprotonation of MEA-zwitterion and changing the solvation environment.
- An improved kinetic model based on zwitterion mechanism was proposed with an average absolute relative difference of 6.73%.

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ABSTRACT

The kinetics of CO₂ absorption in ethanolamine (MEA) + H₂O + ethanol systems was investigated using stopped-flow apparatus. The first-order reaction rate constant (k_0) values were tested with varying H₂O and MEA concentrations. Transiting from the aqueous to non-aqueous solvents, the k_0 decreases and the reaction order for MEA shifts from 1.05 to 1.88. The zwitterion mechanism with the rate-limiting step of deprotonation was used to explore the role of water and its effect. Results showed that water could impact reactions through direct involvement and changing solvation environment. An improved kinetic model based on the zwitterion mechanism was obtained to indicate the quantitative influence of H₂O concentration on the reaction kinetics of MEA + H₂O + ethanol systems. The predicted values from the model well agreed to the experimental data with the average absolute relative difference of 6.73%. This study highlights the important effects of water on the reaction kinetics of CO₂ absorption into water-lean amine solutions.

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1. Introduction

The deployment of large-scale carbon capture and storage (CCS) technology plays a key role to reduce anthropogenic carbon emission and mitigate climate change (Luo et al., 2019; Tobin et al., 2018). The amine scrubbing method for post-combustion CO₂ capture is one of the most promising technologies to control the CO₂ emission of thermal power plants (Rochelle, 2009). The technology takes advantage of high removal rate, less retrofit cost and good capability to handle large gas flux (Liu et al., 2019). However, regenerating aqueous amine-based solvents requires large energy consumption, hampering its industrialization (Leung et al., 2014).

Many researchers have been focusing on the development of new absorbents to decrease overall energy consumption (Wang et al., 2015). Among those new absorbents, water-lean amine solvents, the mixture of organic diluents and aqueous amines, have gained momentum owing to their unique properties for CO₂ capture (Heldebrant et al., 2017; Zheng et al., 2020). The low latent heat and sensible heat of water-lean solvent could potentially benefit the solvent regeneration (Tan et al., 2011; Wanderley et al., 2020). It is also possible to bypass energy intensive carbamate formation and alter CO₂ absorption product to alkyl carbonate, which can be reversed more easily (Wanderley et al., 2021). With the increasing interest towards water-lean solvent, other critical properties in carbon capture including CO₂ capacity (Leites, 1998; Wang et al., 2010), mass transfer (Sema et al., 2013; Yuan and Rochelle, 2018) and solvent stability (Zoghi et al., 2020) were widely studied.

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Reducing water content with additional organic diluent will not change CO₂ absorption mechanism in most commercial conditions for most benchmark amines (Wanderley et al., 2021). However, there are some discrepancies among reported kinetic datasets, especially when they are obtained from different methods, which might cause troubles in understanding the reaction details between CO₂ and water-lean solvent. When the kinetics data were obtained using stopped-flow apparatus, the reaction was found to be faster at high water concentration. The kinetics of CO₂ absorption into the water, methanol, and ethanol 2-((2-aminoethyl) amino) ethanol (AEEA) solutions have been conducted by Rayer et al. (2013), the reaction rate in the aqueous-AEEA system was found to be much faster than that in methanol or ethanol. Zhong et al. (2016) studied the kinetics of CO₂ with 1-Amino-2-Propanol (1-AP) in methanol and ethanol, while Henni et al. (2008) and Liu et al. (2020) investigated the kinetics of CO₂ absorption into aqueous 1-AP solutions, the results also revealed that the reaction rate in water was much faster than that in methanol or ethanol. When the kinetic data were acquired through other methods including stirred cell reactor and wetted-wall column, the reaction rate was enhanced by organic diluents (Garcia et al., 2018; Kang et al., 2017; Zheng et al., 2015).

Bian et al. (2019) studied the kinetics of CO₂ reacting with potassium prolinatate (ProK) in water, ethanol, and ethylene glycol (EG), the results showed that the first-order reaction rate constant (k_0 , s⁻¹) in ethanol or EG was unexpectedly larger than that in water. Li and Shen (2019) studied the kinetics of CO₂ reacting with ProK in EG water-lean solution, the k_0 in water-lean solution was, dramatically, five times larger than that in aqueous solution. The inconsistency could be partially caused by many assumptions to separate mass transfer influence. Some of them may not be negligible for the measured kinetic rates (Jiru and Eimer, 2013), especially for water-lean solvent with high viscosity.

Overall, these results suggest that the role of H₂O molecules or organic diluents in the CO₂ absorption with water-lean solvent is not fully understood. The reduction of H₂O molecules and additional organic diluents may not only affect the gas-liquid mass transfer but also show impact on the reaction in the solvent. The impact could be through both direct participating the reaction and changing solvation environment. And the kinetics data that cover a wide variety of H₂O concentration, especially from stopped-flow technique is scarce, making it more difficult to investigate the impact.

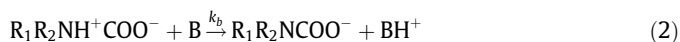
Therefore, this work aimed to study the role of H₂O and organic diluents in CO₂ absorption using water-lean solvent, especially the quantitative influence of H₂O concentration on reaction kinetics, hoping to provide more insights to the underlying reaction mechanism. Considering the complexity of solvents makeup and the multiple intermolecular interactions with multi-component systems, the single-component water-lean amine solvents (ethanolamine + H₂O + ethanol systems) were selected as our focus for the current research. Stopped-flow technique was used because it eliminates the mass transfer limitation by measuring the homogeneous reaction through rapid liquid samples mixing (Luo et al., 2022). The first-order reaction rate constant (k_0) values for CO₂ absorption in water-lean ethanolamine (MEA) solutions were measured. The role of H₂O in the CO₂ absorption process was studied and the influences of solvation, enthalpy, and temperatures on kinetics were evaluated. Finally, an improved kinetic model based on the zwitterion mechanism was proposed to take the quantitative influence of H₂O concentration into account, and the apparent activation energy (E_a) was discussed.

2. Mechanisms

For the past decades, a lot of works focused on the kinetics and mechanisms of primary and secondary amine reacting with CO₂. Caplow (1968) studied the Brønsted relationship between the reaction rate constant and acid dissociation constant (pKa) values of a series of primary and secondary amine, and proposed the zwitterion mechanism as a two-step reaction. The mechanism was reintroduced by Danckwerts (1979). The zwitterion mechanism is widely used to interpret kinetic data for both primary and secondary amines (Vaidya and Kenig, 2007). However, there are a few limitations where Da Silva and Svendsen suggested that zwitterion intermediate has short lifetime in the system (da Silva and Svendsen, 2004). Termolecular mechanism proposed by Crooks and Donnellan (1989) is another way to interpreting kinetics data. The mechanism involved three molecules with a single step. It was supported by da Silva and Svendsen (2004) as the ab initial calculations showed that a single-step reaction with third-order, instead of the zwitterion mechanism, is more likely in MEA and DEA solutions. The mechanism was also satisfactorily used to analyze kinetics data in several solvent examples (Vaidya and Kenig, 2010). Luo et al. (2012) further summarized the kinetic research for MEA reacting with CO₂, found the broken behavior of reaction order, and developed a direct mechanism model. Above all, this work focuses more on the role of water in water-lean solvent during CO₂ absorption, rather than the debate between these approaches.

2.1. Zwitterion mechanism

The mechanism was described as a two-step reaction for primary and secondary amine reacting with CO₂, which can be presented as Eqs. (1)–(2). The R₁R₂NH represents primary or secondary amines, R₁R₂NH⁺COO⁻ (zwitterion) is the intermediate product, R₁R₂NCOO⁻ is the carbamate, and BH⁺ is the protonated base. B is the base for proton extraction, it can be the amine, H₂O, and hydroxide ion (OH⁻) in solutions. The k_1^Z and k_{-1}^Z are the reaction rate constants for the forward reaction and reverse reaction of the zwitterion formation (Eq. (1)), respectively, k_b is the forward reaction rate constant for the deprotonation of the zwitterion (Eq. (2)).



Based on the pseudo-steady state hypothesis, the overall reaction rate can be derived as Eq. (3), the $[\text{R}_1\text{R}_2\text{NH}]/[\text{CO}_2]/[\text{B}]$ represents the molar concentration of species in brackets.

$$r_{\text{CO}_2} = \frac{k_1^Z[\text{R}_1\text{R}_2\text{NH}][\text{CO}_2]}{1 + \frac{k_{-1}^Z}{k_b[\text{B}]}} \quad (3)$$

In the case of $k_{-1}^Z \ll \sum k_b[\text{B}]$, the expression of overall reaction rate can be simplified as Eq. (4), and the overall reaction order is 2, and step one (Eq. (1)) is the rate-limiting step.

$$r_{\text{CO}_2} = k_1^Z[\text{R}_1\text{R}_2\text{NH}][\text{CO}_2] \quad (4)$$

In the case of $k_{-1}^Z \gg \sum k_b[\text{B}]$, Eq. (3) can be expressed as Eq. (5), and the overall reaction order is 3, and step two (as in Eq. (2)) is the rate-limiting step. It should be noted that the B only refers to the amines in non-aqueous solutions, while the B can be amines and

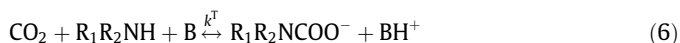
H₂O in blended H₂O/ethanol or aqueous solutions, the contribution of OH[−] was too small to be ignored in this work (Versteeg et al., 1996).

$$r_{\text{CO}_2} = \frac{k_1^Z \sum k_b [B]}{k_{-1}^Z} [R_1 R_2 \text{NH}] [\text{CO}_2] \quad (5)$$

When k_{-1}^Z is close to $\sum k_b [B]$, then the overall reaction order is between 2 and 3, the reaction rate can be simultaneously limited by two steps.

2.2. Termolecular mechanism (Direct reaction mechanism)

The mechanism stated a one-step reaction involving three molecules (amine, CO₂, and base), as shown in Eq. (6). The k^T represents the third-order reaction rate constant.



The overall reaction rate is displayed as shown in Eq. (7), and the overall reaction order is 3. It is like the case of the zwitterion mechanism with the condition of $k_{-1}^Z \gg \sum k_b [B]$, as shown in Eq. (5).

$$r_{\text{CO}_2} = \sum k^T [B] [R_1 R_2 \text{NH}] [\text{CO}_2] \quad (7)$$

Many studies (Ali et al., 2002; Patil and Vaidya, 2020) indicated that the reaction rate between amine solutions and CO₂ is the good pseudo-first-order fit over CO₂ concentration, which can be given by:

$$r_{\text{CO}_2} = k_0 [\text{CO}_2] \quad (8)$$

$$k_0 = \sum k^T [B] [R_1 R_2 \text{NH}] \quad (9)$$

where, k_0 is the first-order reaction rate constant and can be measured using the stopped-flow apparatus in our work.

3. Chemicals and experiments

3.1. Chemicals

MEA (99 wt%), Aniline (99.5% wt%), and p-Anisidine (99 wt%) were purchased from Aladdin Reagent (Aladdin Industrial Corporation, Shanghai, China), the 3APD with the purity of 98% was obtained from Meryer Reagent (Meryer Co. Ltd., Shanghai, China), the ethanol with the purity of 99.7 wt% were purchased from Fuyu chemical reagent (Tian Jin Fuyu Fine Chemical Co. Ltd., Tianjin, China). The CO₂ gas (99.9 vol%) and nitrogen (N₂) gas (99.99 vol %), were supplied by Changsha Rizhen Gas Co. Ltd., China. The deionized water was prepared by reverse osmosis ultra-pure water equipment (Model TS-RO-10L/H, $\leq 0.1 \mu\text{S}/\text{cm}$, Taoshi Water Equipment Engineering Co. Ltd.), and the deionized water was degassed by distillation and ultrasonic treatment before being used for aqueous solution preparation.

3.2. Preparation of amine and CO₂ solutions

The MEA or blended MEA + H₂O ethanol solutions, as well as the amines + ethanol solutions were prepared at room temperature by using a volumetric flask (25 ml \pm 0.03 ml). The CO₂ solutions were prepared by pure CO₂ gas saturation at 303 K and volumetric dilution with blank solution, the ratio of MEA concentration to CO₂ concentration was about 20. The saturated CO₂ molar concentration in H₂O, ethanol, and their blended solutions can be known and calculated with reference data (Carroll et al., 1991; Dalmolin et al., 2006).

3.3. Kinetics with Stopped-flow apparatus

The first-order reaction rate constant k_0 (s^{−1}) was measured using a stopped-flow apparatus (SF-61DX, Hi-Tech Scientific, Ltd. (U.K.)). It can determine kinetic constant ranged between about 0.01 and 1000 S^{−1} (Herri et al., 2014). As mentioned before, this direct homogeneous method is free from mass transfer between gas and liquid phase. However, the apparatus is not suitable to obtain kinetics data under industrial conditions where solvent has high amine concentration and fast reaction rate. In Fig. 1 (a), two seal syringes were filled with amine solution and CO₂ solution, and preheated to a constant temperature by circulating water (with the accuracy of ± 0.1 K). The solutions were then injected into the reaction cell by a pneumatic actuator to achieve rapid mixing. The electrical conductivity of the mixed solution was recorded with the time. The k_0 data under corresponding temperature and solvent composition was obtained by fitting the time-conductivity curve, as displayed in Fig. 1 (b). The k_0 was used for regressions based on the Eq. (10) and other equations, depending on the mechanism used to interpret these kinetics data. To confirm the data reliability in this work, repeated experiments of CO₂ absorption into MEA aqueous and ethanol solutions were performed at 313 K and with the MEA concentration of 0.06–0.5 M. As shown in Fig. 1 (c), it can be observed that the tested plots can be in good agreement with the reference data (Ali, 2005; Chen et al., 2020; Liu et al., 2020), proving that the experiments can be reliable, and the original data with error can be found in Table S1.

4. Results and discussion

4.1. Role of water

4.1.1. Demonstration of the mechanism

To understand how water participates in the reaction of MEA with CO₂, the k_0 values with the MEA concentration of 0.1, 0.2, and 0.3 mol/L were investigated at 303 K and with the H₂O concentration of 0–55 mol/L in ethanol solutions, as presented in Fig. 2 and Table S2. It can be observed that: (i) the k_0 value increased with the increasing concentration of MEA. (ii) the k_0 value increased rapidly when the H₂O concentration was less than about 30 mol/L, and then grew gently as the H₂O concentration was beyond 30 mol/L.

Wanderley et al., (2021) indicated that both the zwitterion mechanism and termolecular mechanism expressions satisfactorily cover the same range of experimental kinetic data in aqueous amine solutions through compare different studies. Meanwhile, the zwitterion framework can be readily converted to that of the termolecular mechanism, suggesting that these two frameworks work equally. Therefore, we want to choose one mechanism as the framework for kinetics, which may be more appropriate to explain the role of H₂O in CO₂ absorption, instead of delving into a debate for these two mechanisms.

When we tried to adopt termolecular mechanism for MEA + H₂O + Ethanol systems with different H₂O concentration from Fig. 2, the effect of H₂O concentration in k_0 can be expressed by the following equation according to Eq. (10).

$$k_0 = k_{\text{Am}}^T [R_1 R_2 \text{NH}]^2 + k_{\text{H}_2\text{O}}^T [R_1 R_2 \text{NH}] [\text{H}_2\text{O}] \quad (10)$$

Therefore, the k_0 can be plotted by the linear fitting of H₂O concentration. The fitting parameters (k_{Am}^T , $k_{\text{H}_2\text{O}}^T$), the values of $k_{\text{Am}}^T [R_1 R_2 \text{NH}]^2$, $k_{\text{H}_2\text{O}}^T [R_1 R_2 \text{NH}] [\text{H}_2\text{O}]$ and their contributions on k_0 were shown in Table S3 (a)–(c). It can be found out that when the H₂O concentration was higher than 25 mol/L, the

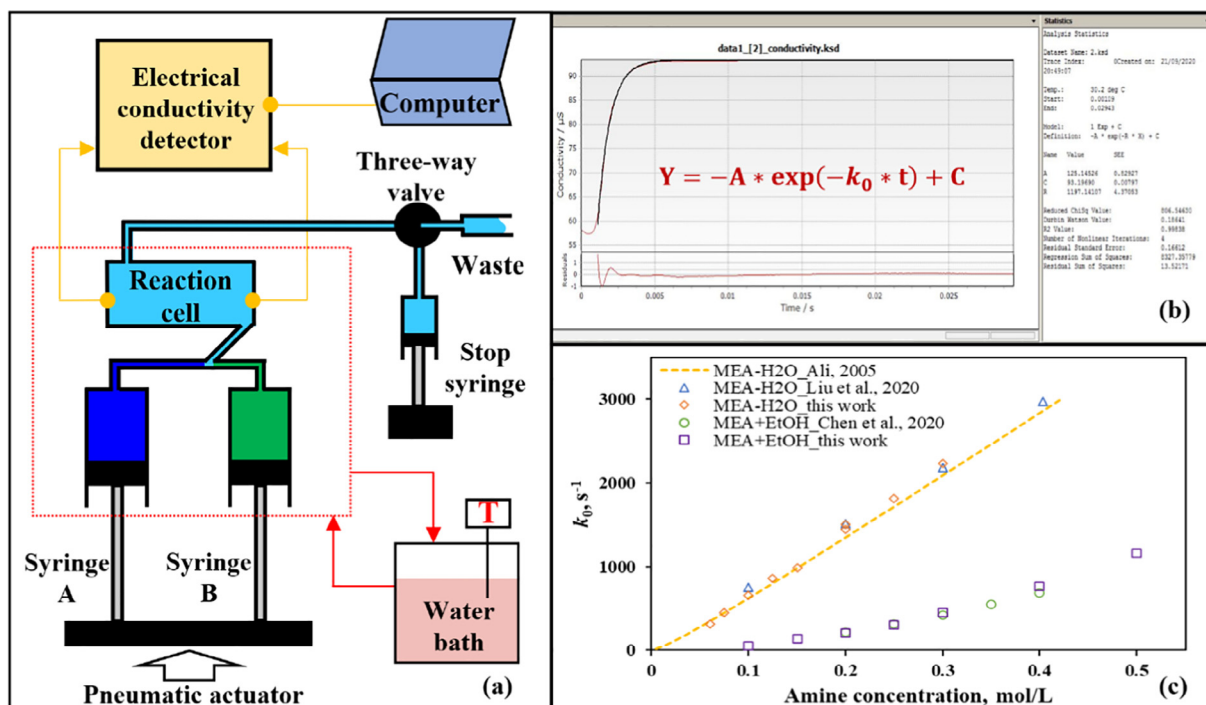


Fig. 1. Apparatus and validation of the kinetic experiments: (a) Schematic diagram for kinetic apparatus; (b) Fitting method and curves for k_0 data; (c) Comparison of experimental and reference k_0 data for CO_2 absorption into MEA aqueous and ethanol solutions at 303 K.

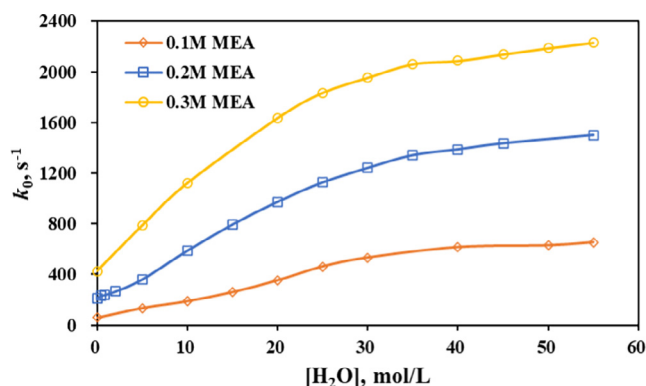


Fig. 2. k_0 plots with H_2O concentration for CO_2 absorption into MEA + H_2O + ethanol system at 303 K.

$k_{\text{H}_2\text{O}}^{\text{T}}[\text{R}_1\text{R}_2\text{NH}][\text{H}_2\text{O}]$ played the primary role in the reaction kinetics (>50%). Combining the termolecular mechanism, which suggests that the rate determining step is the three-molecular complexation, the MEA- H_2O - CO_2 complexation seems to be the primary reaction pathway. While, considering the basicity of MEA and H_2O and the thermodynamic stability of products (MEA-carbamate and H_3O^+), the direct reaction through MEA- H_2O - CO_2 complexation should be less favorable. Therefore, we try to use zwitterion mechanism for better describing the effect of H_2O concentration in k_0 .

Furthermore, when we adopt the zwitterion mechanism (Crooks and Donnellan, 1989) with the rate-limiting step of deprotonation to describe the change of k_0 with the increase of H_2O concentration, we may get the similar expression compared to that of termolecular mechanism.

$$k_0 = k_{\text{MEA-MEA}}^{\text{Z}}[\text{MEA}][\text{MEA}] + k_{\text{MEA-H}_2\text{O}}^{\text{Z}}[\text{MEA}][\text{H}_2\text{O}] \quad (11)$$

Here, $k_{\text{MEA-H}_2\text{O}}^{\text{Z}}[\text{MEA}][\text{H}_2\text{O}]$ also plays the primary role in the reaction kinetics, suggesting that the deprotonation of MEA-zwitterion through H_2O is more favorable than that through another MEA. But this can be understood as our previous molecular simulations (Zheng et al., 2022) indicated that the proton transfer from amine-zwitterion to H_2O is the main pathway for the deprotonation of amine-zwitterion, followed by the barrierless proton transfer from H_3O^+ to amine.

Therefore, in this study, we choose the zwitterion mechanism as the theoretical framework for reaction kinetics of MEA + H_2O + ethanol systems based on our molecular understanding, which doesn't mean that the termolecular mechanism is not suitable for the reaction kinetics of amine aqueous systems or water-lean systems.

Adopting the zwitterion mechanism as a framework, the increasing of k_0 under different MEA concentration with the increase in H_2O concentration (as shown in Fig. 2) can be related to the increase in k_1^{Z} and a simultaneous increase in $\sum k_b[\text{B}]$. As the zwitterion ion is particularly unstable in the ethanol solvent, the zwitterion formation reaction speeds up (k_1^{Z} increases) and the reverse reaction slows down (k_1^{Z} decreases) with the increase of H_2O concentration. Moreover, the rapid increase of k_0 value could also be caused by the participation of the H_2O molecules in the reaction of rate-limiting step, which may accelerate the reaction rate. The H_2O molecules could be a base to extract the proton as shown in Eq. (2), while the deprotonation of amine-zwitterion may be the rate-limiting step in the formation of carbamate through the zwitterion mechanism (Caplow, 1968). Due to the high basicity of MEA, the proton captured by H_2O will eventually transfer to MEA to form the protonated MEA (MEA^+H), while the H_2O molecules remain unchanged after participating in those reactions. Above all, the results suggested that the H_2O molecules take significant role in the reactions between MEA with CO_2 , but further research is required to determine the exact kinetic function of H_2O molecules.

4.1.2. Determination of the reaction order

The reaction order was obtained by fitting the k_0 with varying MEA and H₂O concentration using the exponential function at 303 K, as presented in Fig. 3. It can be observed that the k_0 increased with the increasing MEA and H₂O concentration. The reaction order of MEA obtained from the fitted curves in non-aqueous solutions (MEA + ethanol + CO₂ systems) is 1.87, which is close to that obtained by Sada et al. (1985) (1.72) and by Alvarez-Fuster et al. (1980) (2); the reaction order in aqueous solutions (MEA + H₂O + CO₂ systems) is 0.97, which is consistent with 1 found by Sada et al. (1985) and 1.09 estimated by Couchaux et al. (2013). Meanwhile, the reaction orders in water-lean solutions (MEA + H₂O + ethanol + CO₂ systems) decreased with the increase of H₂O concentration. The difference of reaction orders can be explained by the participation of H₂O, and the reaction order of the H₂O cannot be taken into account here.

To be specific, based on the zwitterion mechanism (Eq. (1)–(5)), in the non-aqueous solutions, MEA was almost the only base as the acceptor of proton in the deprotonation of the zwitterion process (Eq. (2)). And the reaction order of MEA was 1.87 (close to 2), suggesting that the deprotonation of zwitterion by MEA is the rate-limiting step in nonaqueous MEA solution, where $k_{-1}^Z \gg k_{\text{MEA}}[\text{MEA}]$. In the aqueous MEA solution, the estimated reaction order of MEA was 0.98 (very close to 1). Two hypotheses can support this phenomenon: (a) the zwitterion formation is the rate-limiting step; (b) the deprotonation of zwitterion is the rate-limiting step, and water plays the primary role in the deprotonation, where $k_{-1}^Z \gg k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]$.

According to the work of Caplow (1968), the second-order rate constant for hydrogen ion catalyzed decarboxylation of carbamates was plotted as the pK_a values (−1.05 to 11.27) for 14 amines, the slope of the solid fitted line is 0.77 and 0, it suggests that the weakly basic amines (pK_a < 6) reacting with CO₂ was limited by the step of zwitterion formation and breakdown, while the deprotonation of amine-zwitterion may be rate limiting when the basic amines (pK_a > 6) react with CO₂. Therefore, the overall reaction order of the amine varies from 2 to 3 with the increase of basicity. We also explored the k_0 of four primary amines (two weakly basic amines (Aniline and p-Anisidine) and two basic amines (MEA and 3APD)) to further confirm the inference above, more details can be found in the “S2 Reaction Order of Different Amines” in Supporting Information. In addition, Kumar et al. (2003) also suggested that deprotonation by water is the limiting step at low concentration of amine. Therefore, the latter hypothesis that in aqueous MEA

solution the deprotonation of the zwitterion by water is the rate limiting step, seems to be more suitable to describe our experimental results.

Therefore, the rate-limiting step of CO₂ absorption in the non-aqueous and aqueous MEA solutions is the deprotonation of zwitterion by MEA and the deprotonation of zwitterion by water, respectively. Meanwhile, we can infer that in water-lean MEA solutions the deprotonation of zwitterion is still the rate-limiting step, with a competition between deprotonation by MEA and deprotonation by water, leading to the apparent MEA order between 1 and 2.

4.1.3. Influences of solvation

The effect of water in reaction kinetics can be divided into two parts, one part is the direct involvement in reactions as aforementioned, and the other part is the effect of the solvation environment. To understand the influence of solvation, the k_0 values with different solvation ways were studied for CO₂ absorption into MEA solutions, also the solvation enthalpies were estimated.

The k_0 values of different solvation ways were tested at 303 K, with the MEA concentration range of 0.06–0.25 mol/L for the MEA + H₂O + CO₂ + ethanol system, as presented in Fig. 4 and Table S5. Here, we mixed different MEA solutions (MEA/H₂O, MEA/ethanol, and MEA/H₂O/ethanol) with the same volume of different CO₂ saturated solutions (CO₂/H₂O, CO₂/ethanol, and CO₂/H₂O/ethanol) to get different solvation way, and the volume ratio of H₂O to ethanol was 1:1 in both MEA/H₂O/ethanol and CO₂/H₂O/ethanol. It should be noted that, due to the different saturation concentrations of CO₂ in H₂O and ethanol, the CO₂ capacity of those CO₂ saturated solutions follows the order that CO₂/H₂O > CO₂/H₂O/ethanol > CO₂/ethanol. In addition, the MEA/H₂O + CO₂/ethanol, MEA/ethanol + CO₂/H₂O, and MEA/H₂O/ethanol + CO₂/H₂O/ethanol has the same ethanol and H₂O concentration, the difference among them is the dissolved CO₂ concentration.

It can be observed that k_0 values give an order of MEA/ethanol + CO₂/H₂O > MEA/H₂O + CO₂/H₂O > MEA/H₂O/ethanol + CO₂/H₂O/ethanol > MEA/H₂O + CO₂/ethanol > MEA/ethanol + CO₂/ethanol. This result stated that: (i) the reaction between MEA and CO₂ in nonaqueous solvent (MEA/ethanol + CO₂/ethanol) was much slower than in other solvation ways; (ii) the H₂O played multiple roles in the reaction rate (MEA/H₂O + CO₂/H₂O < MEA/ethanol + CO₂/H₂O, while MEA/H₂O + CO₂/ethanol > MEA/ethanol + CO₂/ethanol); (iii) the solvation of CO₂ in H₂O has a little enhancement on the reaction rate (MEA/ethanol + CO₂/H₂O > MEA/H₂O/ethanol + CO₂/H₂O/ethanol > MEA/H₂O + CO₂/ethanol). The water could affect the reaction between MEA and CO₂

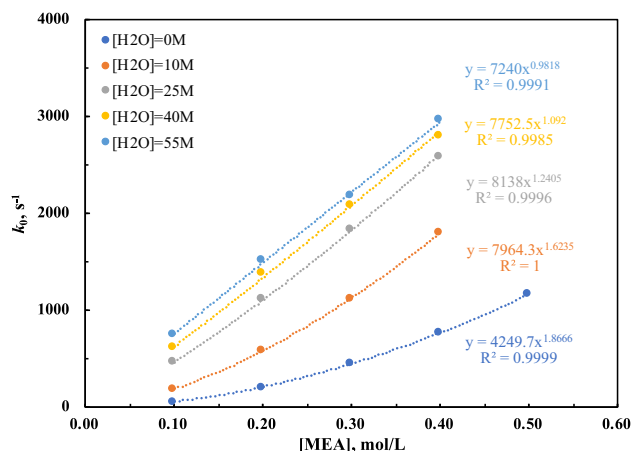


Fig. 3. k_0 plots with simultaneously various MEA and H₂O concentrations at 303 K. The dotted lines are the fitting curves.

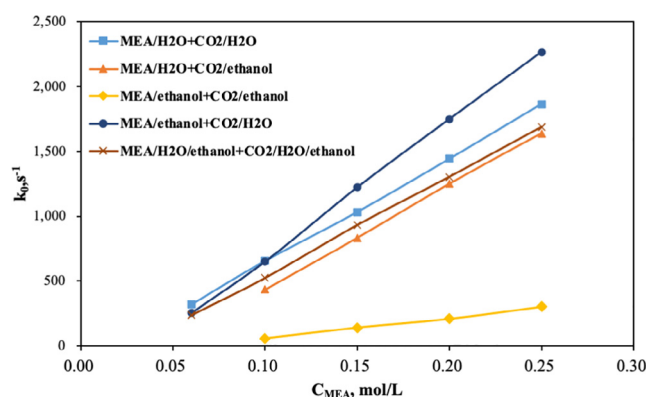


Fig. 4. k_0 plots with various MEA concentrations at 303 K for different solvation ways in the stopped-flow apparatus.

Table 1

Solvation enthalpies of blended MEA/H₂O, MEA/ethanol, and ethanol /H₂O systems at room temperatures.

Solute	Solvent	Concentration of solute (mol/L)	Solvation enthalpy (kJ/mol)
MEA	H ₂ O	5	9.2
MEA	ethanol	5	0.6
ethanol	H ₂ O	5	5.1

in many ways: (a), as discussed before, the H₂O can participate in the reaction between MEA and CO₂, which will help the deprotonation process of zwitterion and accelerate the reaction rate; (b), the addition of H₂O could generate more intermolecular hydrogen bonding between the -NH₂ of MEA and H₂O, which can weaken the electronegativity of the N atom and basicity of amines (da Silva et al., 2007), leading to relatively slower reaction rate; (c), with the further addition of H₂O, the strong hydrogen bonds around the MEA will form the first and second hydration shells, which can prevent the approach of CO₂ to the N atom and led a decrease in the reaction rate.

To further understand the MEA solvation effect on the reaction rate, the solvation enthalpies of three systems (i.e., MEA/H₂O, MEA/ethanol, and ethanol/H₂O) were roughly determined in this work, as displayed in Table 1. The temperatures of the solutions were tested before and after the solute was injected into the solvent in a Dewar flask, with the known mass and specific heat capacity (Miyazawa et al., 2012; Mundhwa et al., 2009). Then, the solvation enthalpies can be calculated, and more details of the experimental apparatus and procedures can be seen in Supporting Information (S1 Enthalpies of Solvation). The tested solvation enthalpy values gave out an order of MEA/H₂O > ethanol/H₂O > MEA/ethanol. As the structural difference between MEA molecule and ethanol molecule is only an (additional) amino group, the comparison results suggested that more intermolecular hydrogen bonding between -NH₂ and H₂O could be generated when MEA dissolved by H₂O, although the amount of intermolecular hydrogen bonding between -OH (MEA or ethanol) and H₂O is also significant with the solvation enthalpy of 5.1 kJ/mol, this results is in good agreement with the conclusions of molecular dynamics study in the reference (da Silva et al., 2007). Therefore, the solvation of MEA in H₂O can reach a stable state with lower energy (with significant intermolecular hydrogen bonding between -NH₂ and H₂O), which as mentioned above will weaken the basicity of MEA and be bad for CO₂ absorption.

4.2. Reaction kinetics of CO₂ absorption

4.2.1. Influences of reaction temperature

To understand the effect of temperature on the kinetics, the k_0 values of CO₂ absorption into the MEA + H₂O + ethanol systems were tested with 0.1 mol/L MEA, at the temperature range of 288–308 K and with the H₂O concentration range of 0–55 mol/L, as displayed in Fig. 5. Under all the H₂O concentrations, the k_0 value increased with the increasing temperature, because that the higher temperature endowed more activated molecules in the solution. It can be seen that the curves of k_0 plot varied as the temperature can have larger curvature with the increasing H₂O concentration (details of exponential fitting of k_0 are shown in Table S6 in Supporting Information), which will be further discussed by taking the effect of H₂O concentration on reaction kinetics into account in the following sections.

4.2.2. Effect of H₂O concentration

Based on the experimental results above, the addition of water can bring significant influences on the reaction rate and apparent

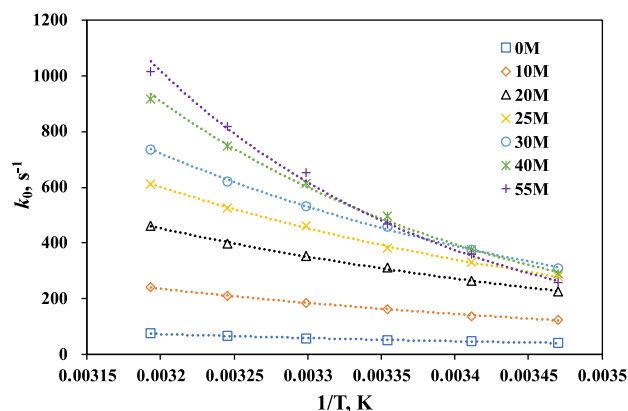


Fig. 5. k_0 plots with temperatures for CO₂ reacting with MEA + H₂O + ethanol solutions with different H₂O concentrations and the MEA concentration of 0.1 mol/L. The dotted lines are the fitting curves.

activation energy for MEA reacting with CO₂. Therefore, the k_0 data were further measured at the MEA concentration range of 0–0.5 mol/L, the temperature range of 283–308 K, and the water concentration of 0–40 mol/L, as shown in Fig. 6 and Table S7. The k_0 plots were fitted by a power function with MEA concentration as a base, the index can be the reaction order getting rid of the contribution of CO₂. It can be observed that the average apparent reaction order was about 1.88, 1.64, 1.23, and 1.05 when the H₂O concentration was 0, 10, 25, 40 mol/L. The zwitterion mechanism with rate-limiting step of deprotonation can be used to explain this phenomenon, that the H₂O participates in the deprotonation of MEA⁺COO⁻ (Eq. (2)) in reactions, while the order of H₂O concentration cannot be taken into account in those plots. Based on the different base molecules involved in the deprotonation of MEA⁺COO⁻, the reaction between MEA aqueous/water-lean solutions and CO₂ can be divided into the deprotonation by MEA and the deprotonation by water. With the increasing H₂O concentration, the deprotonation by water could contribute more to the k_0 values, then it will lead to a relatively smaller apparent reaction order. It can be easily found out that the overall reaction order of MEA with CO₂ in ethanol was about 3. Consistent with that, in the aqueous solutions, the deprotonation by water could dominate the deprotonation process, leading to the overall reaction order to be about 3 if the H₂O concentration was taken into consideration.

4.2.3. Improved kinetic model

Based on the previous discussions, the zwitterion mechanism with the rate-limiting step of deprotonation can be adopt to the reaction between nonaqueous/water-lean/aqueous MEA solutions and CO₂, and both the H₂O and MEA take part in the deprotonation process of MEA-zwitterion. Therefore, to further understand the role of water and its quantitative influence on the kinetics, the experimental k_0 data in this work as well as the k_0 data in water obtained from our previous work were fitted by an improved deprotonation-controlled zwitterion model to obtain the apparent second-order rate constants ($k_{\text{MEA-MEA}}^2$ and $k_{\text{MEA-H}_2\text{O}}^2$), as shown in the following equation.

$$k_0 = \left(k_{\text{MEA-MEA}}^2 + A \right) [\text{MEA}] [\text{MEA}] + \left(k_{\text{MEA-H}_2\text{O}}^2 + B \right) [\text{MEA}] [\text{H}_2\text{O}] \quad (12)$$

where A and B is the impact factor, indicating the effect of the solvation environment, and is related to the concentration of H₂O. The specific values and equations of A and B were shown in Table S8.

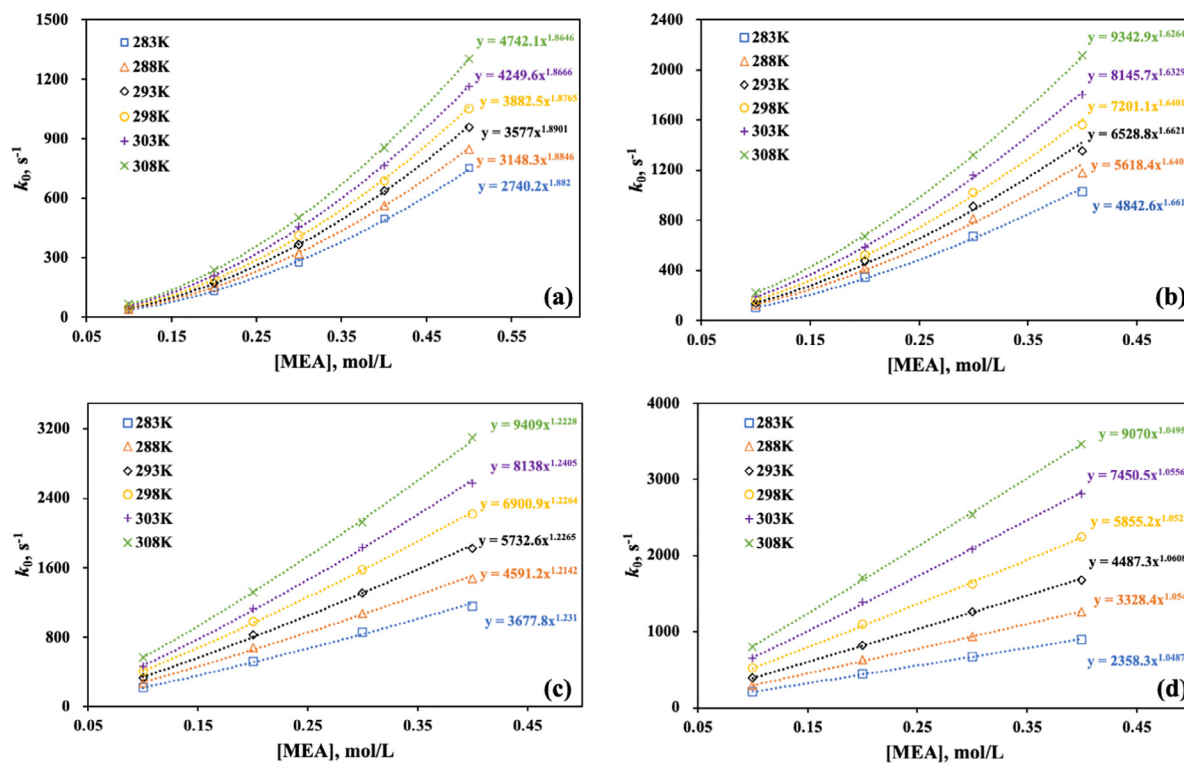


Fig. 6. k_0 plots versus MEA concentration at 283–308 K and with various H_2O concentrations of: (a) 0 mol/L; (b) 10 mol/L; (c) 25 mol/L and (d) 40 mol/L. The dotted lines are the fitting curves.

The values of $k_{\text{MEA-MEA}}^2$ and $k_{\text{MEA-H}_2\text{O}}^2$ at various temperatures were presented in Table 2. Here, the $k_{\text{MEA-MEA}}^2$ and $k_{\text{MEA-H}_2\text{O}}^2$ refer

Table 2

Correlated $k_{\text{MEA-MEA}}^2$ and $k_{\text{MEA-H}_2\text{O}}^2$ for MEA + H_2O + CO_2 + ethanol systems at the MEA concentration of 0.1–0.5 mol/L and H_2O concentration of 0–55 mol/L.

T, K	$k_{\text{MEA-MEA}}^2, \text{L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$	$k_{\text{MEA-H}_2\text{O}}^2, \text{L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$
283.15	3386.3	145.3
288.15	3916.9	165.92
293.15	4878.7	179.74
298.15	5187.9	196.66
303.15	5906.2	233.14
308.15	6562.9	277.49

the apparent second-order rate constant of the reaction in MEA/MEA/ CO_2 and MEA/ H_2O / CO_2 systems, as MEA and H_2O take participate in the deprotonation of MEA^+COO^- , respectively. Meanwhile, the average absolute relative difference (AARD) between the predicted and experimental k_0 was calculated, as displayed in Fig. S3 (Supporting Information). It can be observed that the plots of experimental k_0 versus predicted k_0 almost distribute on the diagonal line, and the absolute average relative difference (AARD) between the experimental and predicted k_0 values is 6.73%, it proved that the fitting model and its result can be reliable.

Then, the Arrhenius relationship between $k_{\text{MEA-MEA}}^2$ or $k_{\text{MEA-H}_2\text{O}}^2$ with the temperature was presented in Fig. 7. The activation energy (E_a) based on the Arrhenius equation was calculated to be 4.57 kcal/mol and 4.29 kcal/mol for the reaction among MEA/

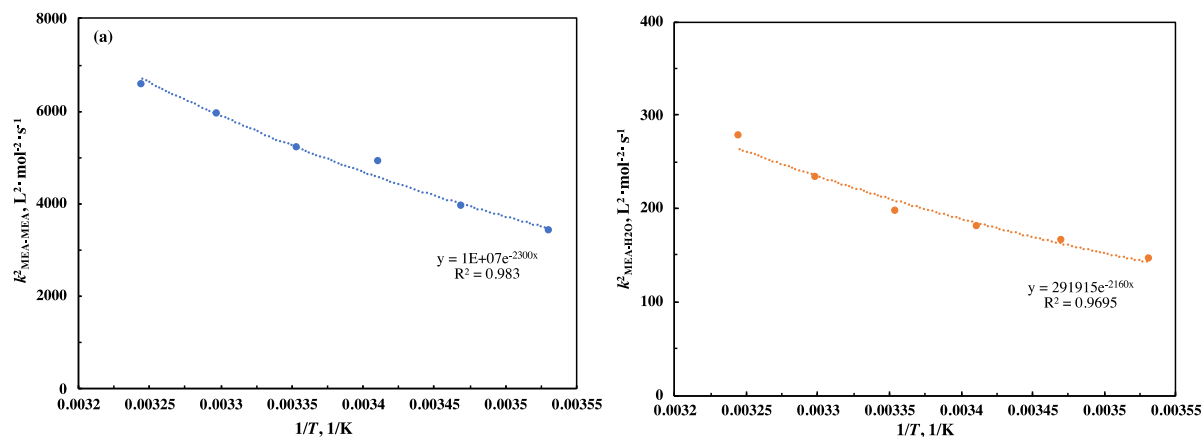


Fig. 7. Arrhenius relationship between (a) $k_{\text{MEA-MEA}}^2$ and (b) $k_{\text{MEA-H}_2\text{O}}^2$ with the temperature.

MEA/CO₂ system and MEA/H₂O/CO₂ system, respectively. It can be observed that the E_a of the MEA/H₂O/CO₂ reaction was a bit lower than that of MEA/MEA/CO₂, indicating that the deprotonation of MEA⁺COO⁻ through the H₂O was more kinetically favorable.

Therefore, for the nonaqueous MEA solution, the deprotonation of MEA⁺COO⁻ is totally through the MEA. When the concentration of MEA and H₂O in water-lean solutions is comparable, both MEA and H₂O play the role of proton acceptor for the deprotonation of MEA⁺COO⁻. With the further increment of H₂O concentration, the deprotonation of MEA⁺COO⁻ is almost through the H₂O molecule. Thus, with the increase of H₂O concentration in solutions, the reaction order of MEA decreased from 2 to 1, as the main proton acceptor in the deprotonation process of MEA⁺COO⁻ changes from MEA to H₂O molecule.

5. Conclusions

In this work, the kinetics of CO₂ reacting with MEA was comprehensively investigated in water, ethanol, and their blended solutions using stopped-flow apparatus, the results can be concluded as:

- (I) The zwitterion mechanism with the rate-limiting step of deprotonation can be used to explain the change tendency of k_0 with H₂O concentration and the different reaction orders of MEA in nonaqueous/water-lean/aqueous solutions.
- (II) The water can accelerate the CO₂ absorption by participating in the deprotonation of MEA⁺COO⁻ and changing the solvation environment. With the increasing of H₂O concentration, the contribution of water in deprotonation increases.
- (III) An improved kinetic model based on the zwitterion mechanism was proposed, which can predict the k_0 very well with the AARD of 6.73%. Meanwhile, the E_a of the reaction among MEA/MEA/CO₂ system and MEA/H₂O/CO₂ system was estimated based on the Arrhenius relationship between the second-order reaction constants $k_{\text{MEA-MEA}}^2$ and $k_{\text{MEA-H}_2\text{O}}^2$ and the temperature, in which MEA and H₂O participate in the deprotonation of MEA⁺COO⁻, respectively.

CRediT authorship contribution statement

Qinlan Luo: Writing – original draft, Conceptualization, Data curation. **Qiang Sun:** Methodology, Investigation. **Qi Liu:** Software. **Sen Liu:** Visualization. **Min Xiao:** Writing – review & editing, Formal analysis. **Mengjie Chen:** Investigation. **Yuanyuan Li:** Software. **Hongxia Gao:** Resources, Validation. **Zhiwu Liang:** Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ces.2022.117732>.

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