CO$_2$ absorption in blended amine solvent: Speciation, equilibrium solubility and excessive property

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A B S T R A C T

Mixing different amines is a common method to develop better solvents for CO$_2$ capture. As the mixing provides more adjustability on the solvent properties, it introduces complex interaction between dissimilar amine molecules who may perform diverse role in the reactions. Here we studied CO$_2$ absorption in monoethanolamine (MEA), methyldiethanolamine (MDEA) and their mixtures thereof. The speciation profiles along with CO$_2$ loading were provided via NMR to reveal the competition/coordination of MEA and MDEA in participating the key reactions that drove CO$_2$ absorption (i.e. carbamate formation and amine protonation). Furthermore, the CO$_2$ loading of the solvents were measured under equilibrium for various temperature, CO$_2$ partial pressure. The excessive CO$_2$ loading was firstly introduced to analyze the loading data regarding the solvent composition. Accordingly, an excessive property model was applied for data correlation. The calculated CO$_2$ loading agreed well with experimental data with average absolution relative deviation of 1.7%.

1. Introduction

Net-zero carbon dioxide emission requires joint efforts on developing renewable energy and utilizing traditional energy in a better way. Although trend shows that energy structure is shifting with more contribution from the renewable energy, the process will not be smooth and quick as it could face many challenges. Considering the urgency of the global warming issue, CO$_2$ capture from flue gases of fossil fuel power station still plays key role in carbon neutrality [1]. Post-combustion carbon capture (PCC) using amine-based solvents is the most suitable technology for flue gas decarbonization due to large gas flux and low CO$_2$ concentration [2].

Amine-based solvents have been widely studied for CO$_2$ absorption in terms of physical properties and chemical properties [3–5]. These data are necessary for the equipment design, the process optimization and the scale-up in CO$_2$ capture [6–9]. However, it was found that one single amine can hardly exhibit optimal properties that meet multiple requirements in an absorption–desorption integrated system [5,10]. Primary amines, e.g. monoethanolamine (MEA), show fast reaction kinetics with CO$_2$ but consume high amount of energy for their regeneration [11–13]. CO$_2$ capture using secondary amines more readily form

carcinogenic nitrosamines that cause additional environmental and health issues [14]. Tertiary amines typically show higher capacity for CO$_2$ absorption but their practical application is hindered by the slow reaction kinetics [15]. Mixing different amines is a good method to take advantage of each amine and modify the overall solvent performance [16–18]. The addition of the tertiary amine methyldiethanolamine (MDEA) in MEA solvent could facilitate the bicarbonate/carbonate formation and reduce the reboiler heat duty for the solvent regeneration [19–21]. The use of MEA and MDEA blended solvent instead of a single MEA solvent potentially makes the CO$_2$ capture unit less energy intensive [22]. On the other hand, studies have shown that the CO$_2$ absorption rate is significantly affected by MEA and MDEA ratio [23]. Lower MEA concentration has resulted in a decrease of reaction kinetics and mass transfer [24]. The physical properties, e.g. viscosity and density, of the solvents also changed with MEA and MDEA ratio [25]. Vapor-liquid equilibrium (VLE) describes the maximum CO$_2$ capacity in the amine solvent. It is normally referred as equilibrium solubility of CO$_2$ or CO$_2$ loading under equilibrium state, which could also be altered after mixing. This information is used in calculating the solvent circulation rate based on the CO$_2$ removal target. The equilibrium solubility of CO$_2$ in single amine solvent is a function of amine concentration, temperature

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and CO_2 partial pressure [26,27]. Such parameter for blended amine solvents will further influenced by VLE of each single parent amine and their interactions. Many studies have reported VLE data of MEA, MDEA and their blends [28,29]. Evidence shows that the equilibrium solubility of CO_2 in the blended solvent is not a simple add up according to the parent amines [30,31].

In addition to the common MEA and MDEA, different amines have also been explored to form the mixture. Mun et al., worked on the blend of MEA and diisopropanolamine (DIPA) to measure equilibrium solubility of CO_2 [32]. Several models including non-activity coefficient model, activity coefficient model and e-NRTL model were used to correlate the equilibrium solubility of CO_2. Gao et al., studied the kinetic of the blend of secondary amine ethylethanolamine (EAE) and tertiary amine 1-dimethylamino-2-propanol (1DMA2P) using stopped-flow apparatus [33]. Pandey and Mondal obtained equilibrium solubility of CO_2 in the blend of EAE and aminoethylethanolamine (AEEA) [34]. Kent-Eisenberg model was used for data correlation and prediction. Adak and Kundu measured equilibrium solubility of CO_2 in the blend of 1-(2-Hydroxyethyl)piperidine (HEP) and piperazine (PZ) [35]. Luo et al., applied computational methods to further evaluate the thermodynamic stability of absorption products in PZ blends [36]. It can be noted from these previous studies that the CO_2 absorption in the amine mixtures share the similar mechanism as carbamate formation and amine protonation. However, the equilibrium constants for these reactions are necessary for each amine and need to be pre-determined before data correlation under the present thermodynamic model framework. Considering the similarity of the reaction mechanism, a universal model for the amine mixtures that excludes the requirement on the equilibrium constants to make accurate data prediction would be helpful in the preliminary absorbent evaluation.

It can be noted from these previous studies that mixing different amines could lead to changes in several solvent properties. Understanding the mixing rules is important in developing the blended amine solvents as well as in making reasonable predictions about them.

Excessive property analysis quantifies the deviation between ideal and non-ideal behaviors of the mixtures. The model allocates the contribution of each component based on its concentration ratio and the relevant data obtained from the pure form. The difference between the add-up number and the actual value is referred as excessive quantity. The method is frequently used to correlate the properties excess volume, excessive viscosity, excessive enthalpy, etc [37,38]. For an ideal solution, these excessive properties are deemed as zero. We applied the model to correlate the physical solubility of N_2O in binary amine-water system [39]. Based on the concept, it is also possible to further apply this model for correlating CO_2 loading under equilibrium in the blended amine solvent.

Most of the modeling work requires the pre-determined equilibrium constant of each amine for data correlation and prediction. This work aims to develop a universal model to accurately predict equilibrium solubility of CO_2 in amine mixtures without the necessity of constant measurement. Solutions of single MEA, MDEA and their blends were tested for CO_2 absorption. The liquid samples were analyzed at the temperature of 313 K using NMR (nuclear magnetic resonance) technique to obtain liquid phase equilibrium information [40]. The role and contribution of parent amines to the CO_2 absorption of their blends were evaluated as a function of their mixing ratio. The equilibrium solubility of CO_2 in these solvents was measured under different conditions e.g. system temperature, CO_2 partial pressure and solvent composition. An excessive property model was firstly introduced to correlate the CO_2 loading under equilibrium for the amine solvents, which only requires the loading data of parent amines.

2. Experimental methods

2.1. Materials

CO_2 (99.999%) and N_2 (99.9%) were purchased from Hunan Zhongtai Hongyuan Gas Co.Ltd. Hydrochloric acid (HC1, 36–38%) was obtained from Hunan Huihong Reagent Co. Ltd. Monoethanolamine (MEA, 98%) was purchased from Macklin and *N*-methyldiethanolamine (MDEA, 98%) was purchased from Aladdin. All chemicals were used as received without further purification, and the desired concentration of the mixed amine solvent was prepared with ultrapure water. Thermostatic water circulators were purchased from HANNUO, HX20 Shanghai Huanuo Instruments Co. Ltd., and mass flow controllers (Beijing Sevenstar Electronics Co., Ltd., China) with 1.5% of full-scale accuracy were utilized to control the gas flow rates, and the total flow rate was kept at 500 mL/min. ^{13}C NMR analysis was performed using a Bruker Avance III 400 spectrometer.

2.2. CO_2 absorption

Six solvents were prepared for the experiments. Two of them were single MEA solvent and single MDEA solvent with concentration of 5 mol/L. The rest of the solvents consist of MEA and MDEA mixtures in a molar ratio of 4:1, 3:2, 2:3 and 1:4, where the total amine concentration was kept at 5 mol/L. Two sets of experiments were performed to measure the CO_2 absorption. The first set of experiments was carried out by bubbling pure CO_2 into 80 mL of amine solvent. The absorption temperature was maintained at 298 K. Each experiment lasted for 120 min and samples were taken for NMR analysis at 5, 10, 20, 40, 60, 90 and 120 min, by following a well-established procedure [41]. In the second set of experiments, the CO_2 loading was measured at equilibrium by continuously bubbling the water saturated gas mixture ($N_2 + CO_2$) into 25 mL of amine solvent (Fig. 1). A condenser was also used to balance water content in the reactor. The system temperature was controlled at 298, 303, 313 and 323 K and the CO_2 partial pressure varied at 5, 14, 30 and 60 kPa. After CO_2 absorption more than 8 h, a liquid sample (1 mL) was taken every one hour for CO_2 loading measurement by HCl titration (Fig. S1). When the CO_2 loading barely changed for 2 h ($\pm 0.002 C \cdot N^{-1}$), the system was considered as equilibrium and the value was deemed as CO_2 loading under equilibrium. For each specific operating condition (T and P_{CO_2}), the determination of the CO_2 loading of each solution was repeated twice. The maximum deviation from the mean value was <1%. More details on NMR set-up and HCl titration procedure were directed to our previous work [41–44]. For NMR analysis, the spectrometer worked with a pulse sequence with proton decoupling and NOE suppression [43]. Acetonitrile was chosen as an internal reference and tetramethylsilane was selected as an external standard. Deuterium water was sealed in a glass capillary to provide the signal for the deuterium lock. Signal integration of the $-CH_2-$ structure of MEA allows determination of the ratio between the fast equilibrating (MEA)/(MEAH$^+$) and MEA carbamate (estimated error < 2%). Carbon atoms of free amines (MEA and MDEA) and protonated amines (MEAH$^+$ and MDEAH$^+$, respectively) give a single signal due to the fast proton scrambling: their relative amounts can be estimated from the chemical shift of their signals, after constructing appropriate calibration straight lines [21]. Finally, the accurate integration of the peaks in the range 165–160 ppm allows a good estimation of the relative percentages of carbonyl species, i.e. MEA carbamate, bicarbonate and carbonate ions and alkyl carbonates (estimated error < 5%) [18].

3. Theory

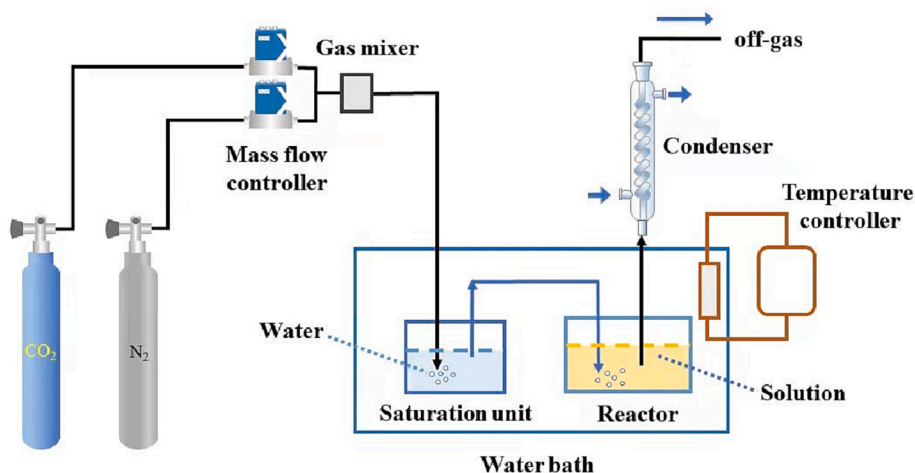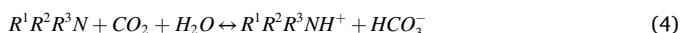CO_2 absorption in MEA and MDEA blends mainly involves following reactions:

$$RNH_2 + CO_2 \leftrightarrow RN^+H_2COO^- \tag{1}$$

Fig. 1. The diagram of the experimental set-up for measuring the equilibrium CO_2 loading.

$$RN^+H_2COO^- + B \leftrightarrow RNHCOO^- + BH^+ \qquad (2)$$

$$RNHCOO^- + H_2O \leftrightarrow RNH_2 + HCO_3^- \qquad (3)$$

$$R^1R^2R^3N + CO_2 + H_2O \leftrightarrow R^1R^2R^3NH^+ + HCO_3^- \qquad (4)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \qquad (5)$$

where RNH_2 is MEA and $R^1R^2R^3N$ is MDEA in this particular blended solvent; B refers to base such as MEA, MDEA, OH^- or water. Alkylcarbonates are normally identified in nonaqoueous system [45] while they could also present in aqueous system, especially for MDEA at high concentration and high CO_2 loading.

$$B + CO_2 + ROH \leftrightarrow BH^+ + ROCOO^- \qquad (6)$$

where ROH represents amine with hydroxyl group.

The excessive property model is firstly introduced to correlate equilibrium solubility of CO_2 in the amine mixture, i.e. MEA and MDEA in this work. Applying excessive property requires the property change of mixing is zero for an ideal solution. It is assumed that in the ideal case, the CO_2 loading of MEA and MDEA blended solvent under equilibrium equals to their individual contribution as in the single solvent. The deviation of actual CO_2 loading from the value for ideal situation is described as the excessive CO_2 loading. The excessive property analysis normally includes all components in the correlation. However, there is large amount of water molecules in amine solvent and majority of them has little contribution in CO_2 loading under given conditions. Hence a specific amine ratio (a_i) is used in the model to calculate excessive CO_2 loading for blended amine solvent.

$$a_i = [MEA]/([MEA] + [MDEA]) \qquad (7)$$

$$R = \alpha_S - a_{MEA} \times \alpha_{MEA} - a_{MDEA} \times \alpha_{MDEA} \qquad (8)$$

where [MEA] and [MDEA] is the initial concentration of MEA and MDEA; R is the excessive quantity; α_S, α_{MEA} and α_{MDEA} is the CO_2 loading of single MEA solvent and single MDEA solvent at equilibrium.

The excessive quantity R is corrected using Redlich-Kister equation [46]:

$$R = a_{MEA}a_{MDEA}\sum_{i=1}^{3} B_i(2a_{MEA} - 1)^{i-1} \qquad (9)$$

where B_i is the constant to be regressed. B_i is considered a function of CO_2 partial pressure (P_{CO2}, kPa) and following regressed parameters b_i is the temperature dependent coefficient (T, K).

$$B_i = \sum_{i=1}^{3} b_i P_{CO_2}{}^{i-1} \qquad (10)$$

$$b_i = \sum_{i=1}^{3} k_i T^{i-1} \qquad (11)$$

4. Results and discussion

4.1. Liquid speciation profiles of CO_2 absorption in amine solvents

The amine-based CO_2 absorption is mainly governed by the chemical reactions in the solvent (reactions (1) to (6)). Amine molecule either participates protonation or carbamate formation upon CO_2 absorption. Using NMR technique, it is feasible to distinguish the role of MEA and MDEA and identify their contributions in the mixture. The increase of CO_2 loading during absorption is summarized in Fig. 2a. Depending on the solvent composition, the specific amine ratio a_{MEA} ranges from 0.0 (single MDEA solvent) to 1.0 (single MEA solvent). Single MEA solvent shows much faster CO_2 absorption rate than single MDEA solvent due to the carbamate formation, whose reaction kinetics could be 3 orders of magnitude faster than CO_2 hydrolysis reaction (the only reaction the single MDEA solution can participate in) [47]. In case of the blended amines, the CO_2 absorption rate decreased with a decrease in the amount of MEA (or the value of a_{MEA}) in the starting solution.

The solution speciation at 120 min of CO_2 absorption is plotted in Fig. 2b. As seen from the figure, mixing MDEA with MEA boosts the formation of bicarbonate, which is considered beneficial for solvent regeneration. The bicarbonate starts to form around $0.515C·N^{-1}$ in single MEA solvent and the value drops to $\sim 0.155C·N^{-1}$ in blended solvent with a_{MEA} of 0.2. For the single MDEA solvent, bicarbonate formation begins at zero loading without carbamate formation. In Fig. 2b, the total CO_2 loading of the solutions at 120 mins is also shown and a decreasing trend in the final CO_2 loading is observed with smaller a_{MEA}. The carbamate contributed to over 60% of absorbed CO_2 in single MEA solvent while $\sim$ 30% absorbed CO_2 exists as bicarbonate. There is a minor contribution from carbonate and alkylcarbonates as well. On the other hand, bicarbonate and alkylcarbonates are the main CO_2 absorption product in single MDEA solvent. Although smaller a_{MEA} means less MEA, the MEA carbamate still forms very fast in the blended amine solvents (Fig. 2a) and continues as a key product in the final solution after 120 min of CO_2 absorption (Fig. 2b). The detailed speciation information for all solvents are tabulated in the Supporting Information (Tables S1–S6).

Both carbamate formation and amine protonation demand MEA molecule when single MEA solvent is used for CO_2 absorption. But the role may shift after mixing other amine into MEA solvent. The
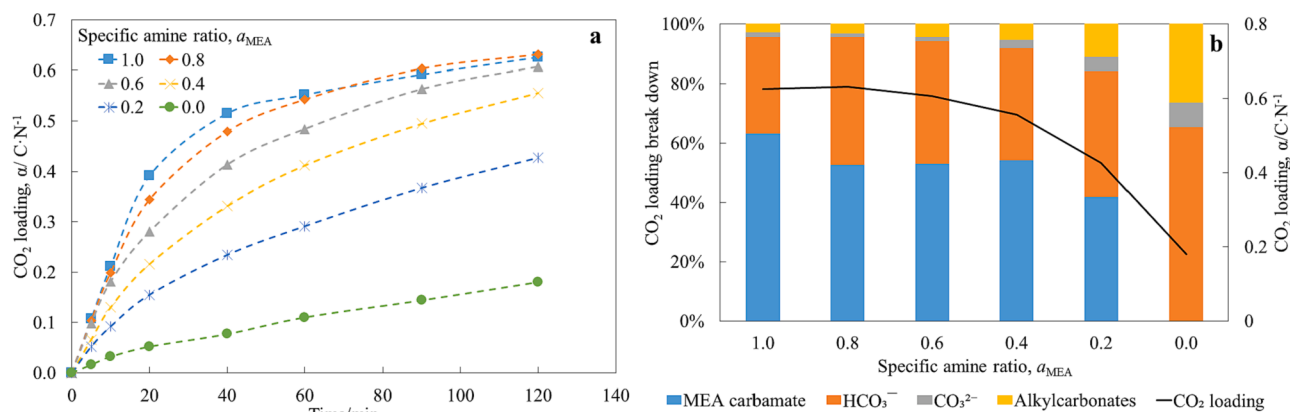
Fig. 2. CO_2 absorption using MEA and MDEA blended solvents. a: CO_2 loading changes with time; b: CO_2 loading breakdown and total CO_2 loading for the samples at 120 min.

proportions of MEA, MEAH$^+$ and MEA carbamate for all solvents are summarized in Fig. 3. During CO_2 absorption in single MEA solvent, only MEA consumption is responsible for the increase of CO_2 loading. The MEA consumption is faster at low a_{MEA} for blended amine solvents, indicating the increase of MDEA contribution on the CO_2 loading. It is interesting to find that with the decrease of a_{MEA} and faster MEA consumption, a greater portion of MEA participate amine protonation initially. Then MEAH$^+$ starts to deprotonate and form carbamate at increased CO_2 loading. Generally, with the decrease of a_{MEA}, MEA is more prone to participate carbamate formation instead of the amine protonation. In the most extreme situation for the blended amine solvent at a_{MEA} of 0.2 and CO_2 loading around $0.3C \cdot N^{-1}$, 94% of MEA is converted to carbamate while MDEA is the dominant compound to accept the proton in the solvent.

NMR results show that changing a_{MEA} has little impact on the protonation of MDEA where the curves follow a similar trend (Fig. 4). The CO_2 absorption in single MDEA solvent only involves MDEA protonation. On the contrary, the CO_2 absorption in single MEA solvent can be divided into two stages (Fig. 3). The first stage is the MEA carbamate formation accompanied by the MEA protonation. The second stage is the conversion of MEA carbamate to other species and further protonation of MEA. The CO_2 absorption in blended amine solvent is more complicated as it could be separated into three stages based on the role of MEA at corresponding CO_2 loading. In the first stage, i.e., at low CO_2 loading, the concentration of MDEAH$^+$ increases too slowly compared to MEA: thus, MEA is more favorable in amine protonation. Here, MEA governs CO_2 absorption by participating both carbamate formation and amine protonation. In the second stage of absorption, with further increase in CO_2 loading, MDEA becomes more important in amine protonation and the concentration of MDEAH$^+$ increases more rapidly. Most of unreacted MEA or even protonated MEA tends to form MEA carbamate with CO_2 absorption until MEA carbamate reaches a maximum value. In the last stage, a portion of MEA carbamate decomposes to generate MEAH$^+$ again for the further increase of CO_2 loading. There are two critical CO_2 loadings for the absorption stage transition, i.e. from first stage to second stage and from second stage to last stage. Both of them depends on the a_{MEA} of the solvent. When a_{MEA} is as low as 0.2, the transition of CO_2 absorption from first stage to second stage occurs at $0.1C \cdot N^{-1}$ and from second to last stage happens at $0.3C \cdot N^{-1}$. With the increase of a_{MEA}, the critical CO_2 loadings for both transitions increase and their difference reduces. For the blended amine solvent with a_{MEA} of 0.8, the stage transitions are vague and become closer to sing MEA solvent.

4.2. CO_2 loading of amine solvent under equilibrium

The equilibrium solubility of CO_2 in amine solvent includes physically dissolved CO_2 and chemically bonded CO_2. Under relatively low

CO_2 partial pressure, as used in this work, the physically dissolved CO_2 is trivial and can be ignored compared to the chemically bonded CO_2 while calculating CO_2 loading [48]. The CO_2 loadings in single MEA solvent and single MDEA solvent are plotted in Fig. 5 as a function of temperature and CO_2 partial pressure. Although CO_2 absorption in form of carbamate formation is limited by $0.5C \cdot N^{-1}$ (reactions (1) and (2)) while bicarbonate formation has higher stoichiometry (reaction (4), the single MEA solvent has generally larger CO_2 loading than single MDEA solvent under same equilibrium conditions. This is due to the CO_2 hydrolysis reaction greatly depends on the pKa and MDEA has relatively low pKa (8.54 at 298 K) among the tertiary amine [49]. It also shows that the CO_2 loading in single MDEA solvent is more sensitive to the change of temperature and CO_2 partial pressure. This is likely because carbamate is more stable than bicarbonate and equilibrium constant of carbamate formation will be less affected by the temperature change.

CO_2 capture using single amine solvent has less adjustment in terms of the CO_2 absorption and desorption performance. Mixing different types of amine provides an additional way to regulate solvent properties, offering more opportunities in the process optimization. The molecular interaction is altered by additional amine molecule, which enables the solvent properties to be tuned accordingly. However, this also means a more complicated non-ideal behaviour of the mixture. As shown in the previous section, the CO_2 absorption in the blended amine solvents involve both parent amines who have different reaction mechanism. The chemistries in CO_2 absorption become more complicated. The actual CO_2 loading in blended amine solvent under equilibrium deviates from the ideal situation that the CO_2 loading is only an addition based on the contribution of each parent amine. Herein, excessive property is introduced to analyse the CO_2 loading in MEA and MDEA blended solvents under equilibrium.

The CO_2 loading of blended amine solvents under equilibrium at 298 K are summarized in Fig. 6a as a function of a_{MEA}. The symbols are referred as experimental value and the curves are calculated based on the excessive property model which will be discussed in the next section. With the decrease of a_{MEA}, there is a shift of CO_2 loading from the single MEA solvent to MDEA solvent. Because the CO_2 loading in single MDEA solvent is more sensitive to the change of CO_2 partial pressure, blended amine solvent with smaller a_{MEA} i.e. more MDEA also shows greater difference in CO_2 loading regarding to the pressure change. It is noted that the CO_2 loading changes with a_{MEA} while the trend varies for the different CO_2 partial pressure. The CO_2 loading continuously decreases for 5 and 14 kPa CO_2 partial pressure since single MDEA solvent has less absorption capacity than single MEA solvent at these conditions. But in the case of CO_2 partial pressure at 30 kPa, CO_2 loading of single MDEA solvent is slightly lower than that of single MEA solvent. There is a relatively steeper decrease of CO_2 loading when a_{MEA} decreases from 1.0 to 0.8. With the further decrease in a_{MEA}, the CO_2 loading barely
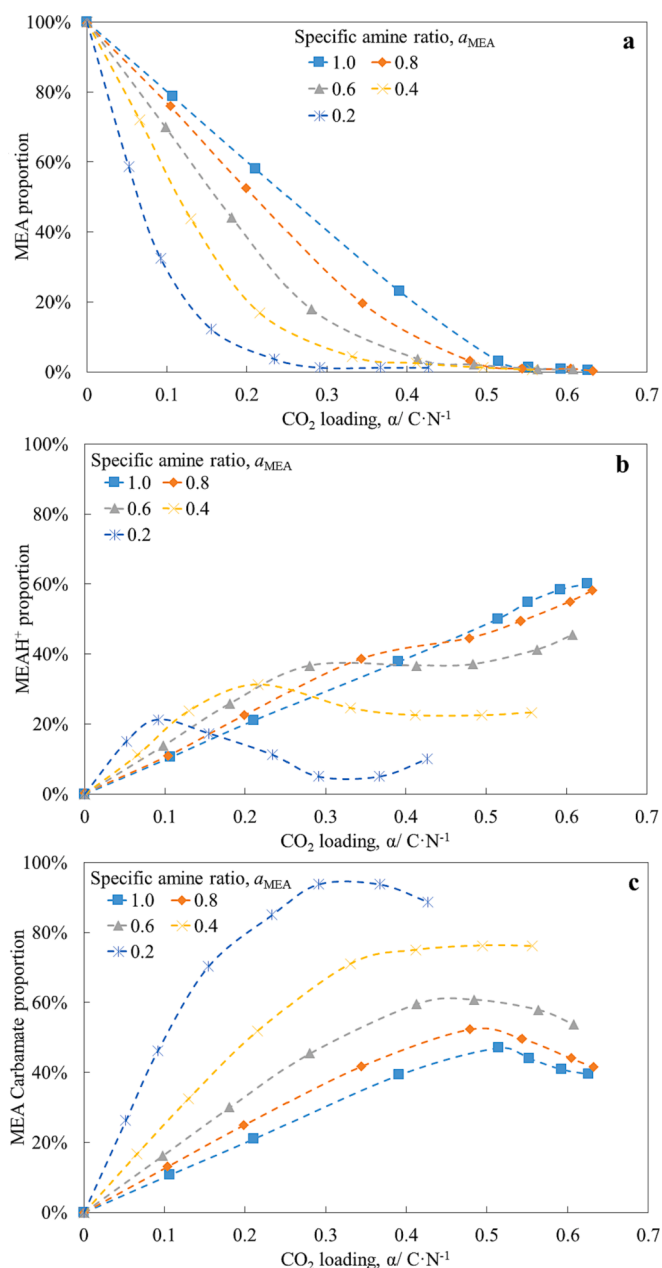
Fig. 3. Proportion of MEA, MEAH$^+$ and MEA carbamate in the blended amine solvents for CO_2 absorption.

changes. When the single MDEA solvent and the single MEA solution have comparable CO_2 loadings, as in the case for CO_2 partial pressure of t60 kPa, there is a decrease of CO_2 loading from 1.0 to 0.8 a_{MEA}. With the continuing decrease of a_{MEA}, the CO_2 loading starts to increase and approach the value for single MDEA solvent. This could be explained based on the NMR results as shown in Section 4.1. When CO_2 loading approaches the equilibrium, the CO_2 absorption in single MEA solvent would be in the stage where MEA carbamate starts to decompose and the generation of MEAH$^+$ governs the further CO_2 absorption (see Fig. 3b and c). The addition of MDEA molecule is supposed to facilitate MEA carbamate formation and suppress MEAH$^+$ formation by taking the role of amine protonation. However, the CO_2 absorption via amine protonation strongly depends on the pKa. Since the pKa of MDEA (8.54 at 298 K) is lower than that of MEA (9.45 at 298 K), a small amount of MEA (20%) substituted by MDEA shows weaker capability in amine protonation, leading to a negative impact on CO_2 loading under equilibrium. With the continuing decrease of a_{MEA} and large amount of MDEA presents in the solvent, the protonation of MDEA governs the CO_2 absorption especially when it is approaching the equilibrium. There will be less competition between MEA and MDEA in amine protonation. This CO_2 loading shift highlights an underlying swing of CO_2 absorption mechanism from carbamate formation to bicarbonate formation (via amine protonation). Similar phenomenon can be found at other temperatures as shown in Fig. 7a to 9a.

The excessive CO_2 loadings under equilibrium conditions at 298 K are summarized in Fig. 6b. It shows that the excessive CO_2 loading depends on the CO_2 partial pressure. Overall, higher CO_2 partial pressure leads to lower excessive CO_2 loading. Most of the excessive CO_2 loading are positive at 5 and 14 kPa. The excessive property increases with the decrease of a_{MEA} before reaching a maximum value. Then it starts to decrease to zero for the single MDEA solvent. On the other hand, most of the excessive CO_2 loadings are below zero at 30 and 60 kPa CO_2 partial pressure. It follows an opposite trend that the excessive CO_2 loading decreases initially and then increases at smaller a_{MEA}. If the CO_2 loading under equilibrium in blended solvent equals to the contribution of MEA and MDEA in their single solvent, the excessive CO_2 loading is zero. Positive values of the excessive CO_2 loadings correspond to a CO_2 capacity higher than that of the ideal situation and suggest a coordination between MEA and MDEA in the CO_2 absorption process. Similarly, negative excessive property, corresponding to CO_2 capacity lower than the ideal situation, reveals a competition between MEA and MDEA in CO_2 absorption. Fig. 7b to 9b show excessive CO_2 loading at 303, 313 and 323 K. With an increase in temperature, excessive CO_2 loadings at 30 and 60 kPa CO_2 partial pressure change from negative to positive. Meanwhile, the excessive CO_2 loadings at CO_2 partial pressures of 5 and 14 kPa remain positive despite the temperature change. As a result, CO_2 partial pressure has a lower impact on the excessive CO_2 loading at higher temperature. The concentration of physically dissolved CO_2,
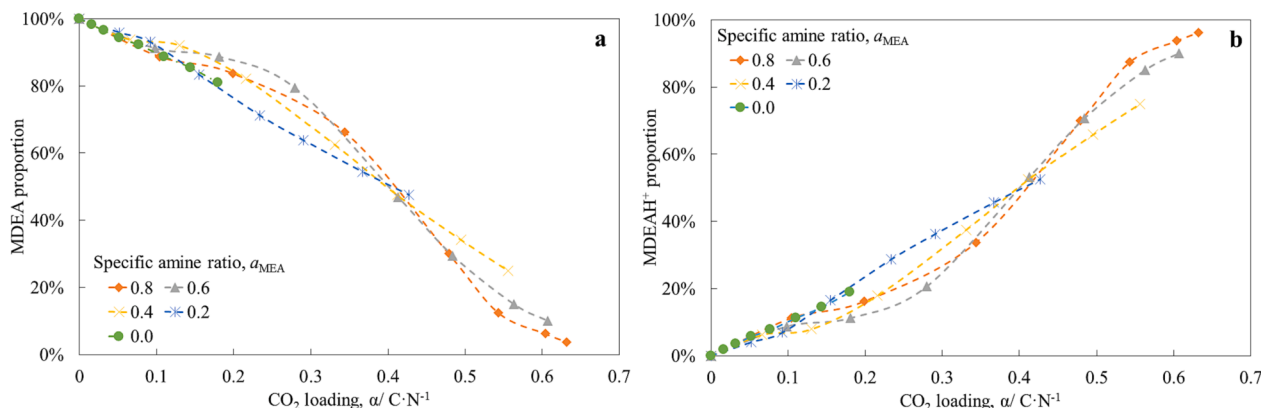

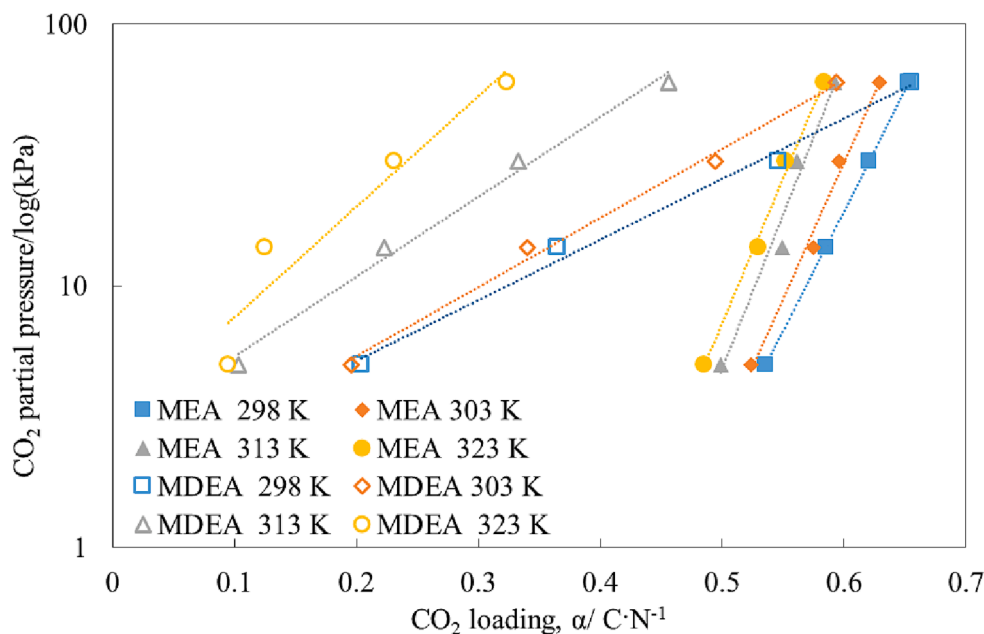**Fig. 4.** NMR analysis of MEA and MDEA blended solvent after 120 min CO_2 absorption.

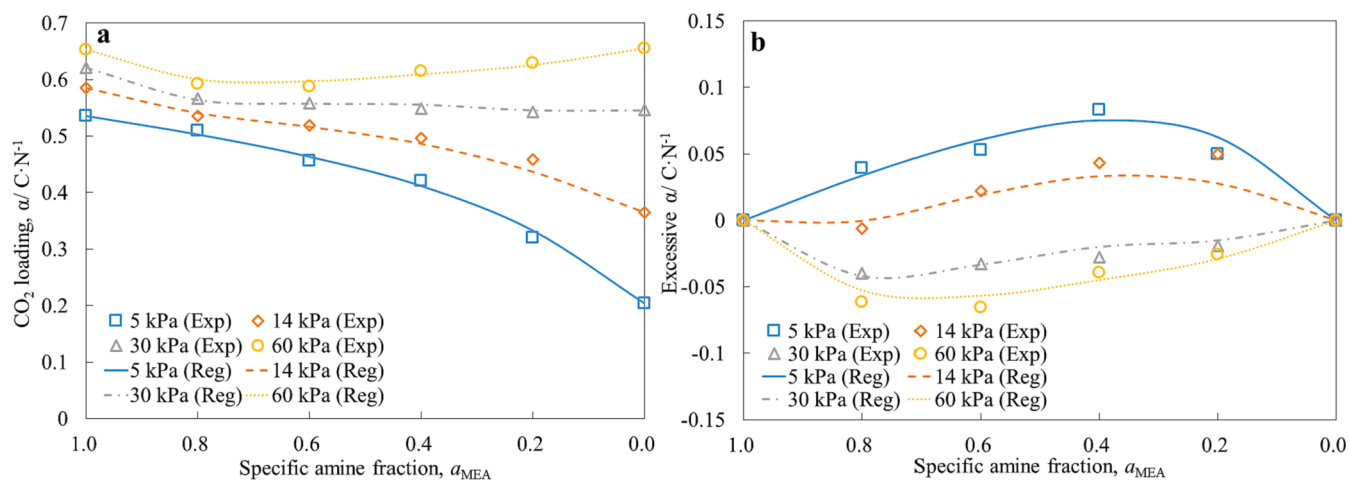**Fig. 5.** CO_2 loading of single MEA and MDEA solvents under vapor–liquid equilibrium.

Fig. 6. CO_2 loading of vapor–liquid equilibrium system at 298 K. a: Experimental and regressed data of single MEA, MDEA and their blend solvents; b: Excessive CO_2 loading.

which tents to increase with the CO_2 partial pressure decrease with the temperature (based on Henry's law), could be the key factor that governs the behavior of the excessive CO_2 loading. The excessive CO_2 loading is negative under the high CO_2 partial pressure or low temperature, corresponding to the relative high concentration of physically dissolved CO_2. At this circumstance MEA and MDEA shows a competition in the chemical reaction for CO_2 absorption. With the increase of temperature and/or decrease in CO_2 partial pressure, the concentration of physically dissolved CO_2 decreases and there appears a coordination of MEA and MDEA in CO_2 absorption.

4.3. Excessive property model for CO_2 loading under equilibrium

Many mathematical models have been developed to correlate the VLE data of CO_2 absorption in amine solvent. They involve different method to represent the non-idealities of the gas–liquid system. Kent-Eisenberg model and its modifications correlate experimental data with the reaction equilibrium constants to describe the non-ideal behaviour [50,51]. To avoid modifying the true values of these

equilibrium constants, an additional correction factor could be used for the correlation [26]. Other type of models are based on activity coefficients, e.g. e-NRTL model, extended-UNIQUAC and UNIFAC model [52,53]. In these models, interaction parameters are regressed to the experimental data. Most of the models require to determine the carbamate formation and/or amine protonation equilibrium constants. However, these data are not always available which highlights the necessity to develop a simple model to make accurate prediction in the amine mixtures without the equilibrium constants. Since the reaction mechanism has certain degree of similarity despite the change of parent amines, it is possible to apply the excessive property model for correlating the equilibrium solubility of CO_2. Herein, the excessive CO_2 loading is obtained for the MEA and MDEA blended solvent. Similar like other excessive properties, it is also possible to correlate the excessive CO_2 loading with the influential factors i.e. solvent composition, temperature and CO_2 partial pressure.

A mathematical correlation is established accordingly to calculate the CO_2 loading under equilibrium. There are no specific descriptions on CO_2-H_2O chemistry, amine protonation and carbamate formation in this
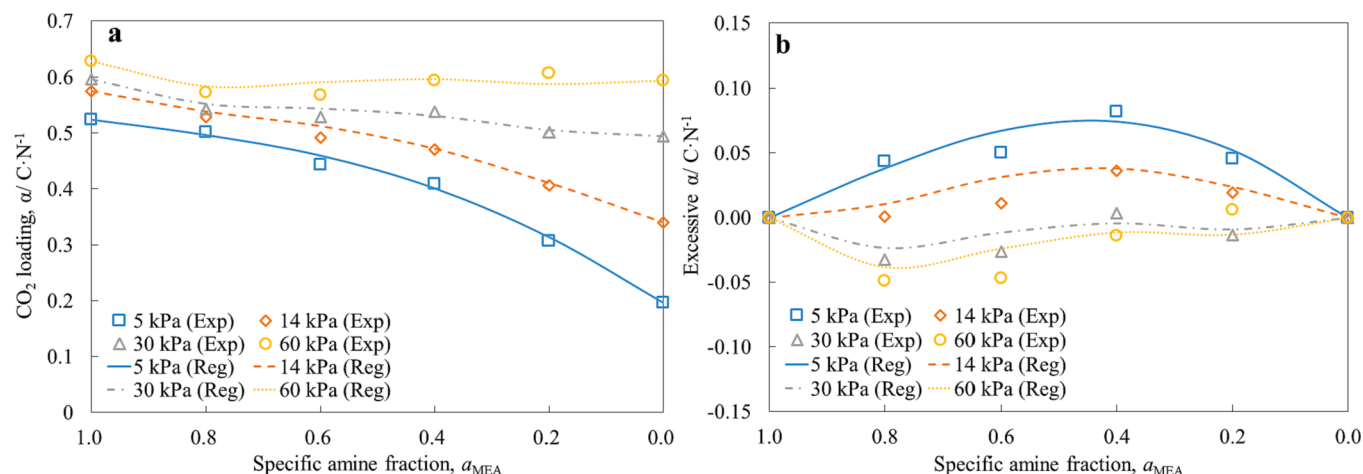
Fig. 7. CO_2 loading of vapor–liquid equilibrium system at 303 K. a: Experimental and regressed data of single MEA, MDEA and their blend solvents; b: Excessive CO_2 loading.

model. The excessive CO_2 loading was described using Redlich-Kister equation with regard to solvent composition. The coefficients of Redlich-Kister equation were then regressed to the temperature and CO_2 partial pressure using polynomial equation. As the excessive analysis normally applies the mole fraction of all components, the simplification that ignores water contribution by using specific mole fraction a_{MEA} will lead to a certain deviation. The CO_2 loading under equilibrium is a function of the amine concentration. In this case, the calculation of excessive CO_2 loading applied the CO_2 loading of 5 mol/L MEA and 5 mol/L MDEA solvent for all solvents. This deviation will be lumped in the correlation for the excessive CO_2 loading. The obtained coefficients are tabulated in Tables 1 to 3. The calculated CO_2 loading under equilibrium and excessive CO_2 loading was summarized in Figs. 6 to 9. Results show that the model captures the trend of excessive CO_2 loading very well at corresponding solvent conditions. The parity plot in Fig. 10 shows that the calculated CO_2 loadings agree well with the experimental data. The average absolute relative deviation between them is 1.7%. The maximum CO_2 loading of MEA and MDEA blended solvents is successfully modelled based on the excessive CO_2 loading under equilibrium.

5. Conclusions

The ideal CO_2 absorbents may be developed by mixing different amines as the single amine can hardly meet the multiple requirements of the cyclic CO_2 capture process. Mixing is a good strategy to take advantages of the parent amines. In this work, we developed the concept of excess CO_2 loading and studied the traditional amine solutions of MEA, MDEA and their blends as an example for applying this concept. It was found that the CO_2 absorption rate decreased with the decrease of a_{MEA}, which also means higher MDEA concentration. NMR results showed that higher MDEA concentration boosted the bicarbonate formation at lower CO_2 loadings. Meanwhile, MDEA would have more weights in amine protonation and facilitated greater portion of MEA to participate carbamate formation. Nevertheless, MEA still played an important role for CO_2 absorption in the blended amine solvent before most of free MEA was consumed. Based on the role transition of MEA, the CO_2 absorption

Table 1
Correlation coefficients for temperature dependent b_i and CO_2 partial pressure dependent B_1.

B_1	b_1	b_2	b_3
k_1	−3.573E + 00	2.043E + 00	−4.707E-02
k_2	2.624E-02	−1.429E-02	3.159E-04
k_3	−4.343E-05	2.469E-05	−5.276E-07

Table 2
Correlation coefficients for temperature dependent b_i and CO_2 partial pressure dependent B_2.

B_2	b_1	b_2	b_3
k_1	−6.832E+01	−1.061E+00	1.988E-02
k_2	4.389E-01	6.947E-03	−1.258E-04
k_3	−7.052E-04	−1.136E-05	1.983−07

Table 3
Correlation coefficients for temperature dependent b_i and CO_2 partial pressure dependent B_3.

B_3	b_1	b_2	b_3
k_1	−8.125E+00	−5.803E+00	1.451E-01
k_2	8.064E-02	3.687E-02	−9.367E-04
k_3	−1.775E-04	−5.859E-05	1.512E-06

in the blended amine solvents at the given CO_2 pressure range could be divided into three stages: 1) MEA protonation and formation of MEA carbamate dominated the increase of CO_2 loading while the protonation of MDEA was relatively slow; 2) MEA and protonated MEA was converted to MEA carbamate while MDEA contributed to amine protonation; and, 3) MEA carbamate formation reached a peak while the conversion of MEA carbamate to $MEAH^+$ and protonation of MDEA jointly drove the further increase in CO_2 loading.

This work tried to provide a new perspective of the mixing rules regarding CO_2 loading under equilibrium of blended amine solvent. Similar as the correlation of Henry's law constant that described physically dissolved CO_2 in binary mixtures, excessive property analysis was firstly applied for CO_2 loading which covered chemically bonded CO_2 simultaneously. The CO_2 loading was measured under equilibrium for the MEA, MDEA and their blended solvents at 298, 303, 313 and 323 K. The CO_2 partial pressure varied at 5, 14, 30 and 60 kPa. The CO_2 loading change in terms of a_{MEA} (1.0, 0.8, 0.6, 0.4, 0.2 and 0.0) implied a shift of underlying CO_2 absorption mechanism. Excessive CO_2 loading that described the CO_2 loading deviation from ideal mixing situation was introduced for the data analysis. The temperature and CO_2 partial pressure dependency was presented, suggesting the concentration of physical dissolved CO_2 as a key factor for the excessive CO_2 loading. Based on the excessive CO_2 loading, an excessive property model was developed for the data correlation. The calculated CO_2 loading agreed well with the experimental value with average absolution relative deviation of 1.7%. It is anticipated that the excessive property analysis method is universal and will not limited by one particular amine
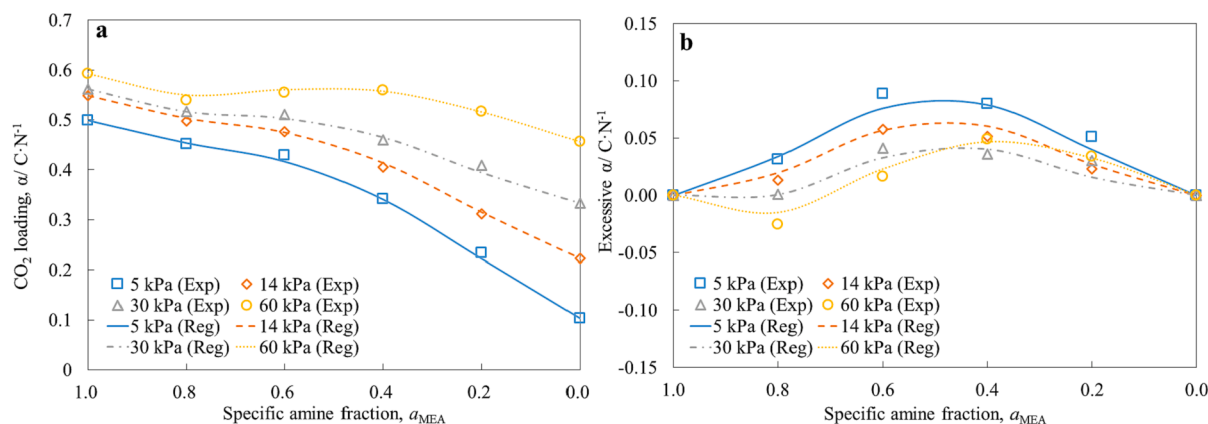
Fig. 8. CO_2 loading of vapor–liquid equilibrium system at 313 K. a: Experimental and regressed data of single MEA, MDEA and their blend solvents; b: Excessive CO_2 loading.
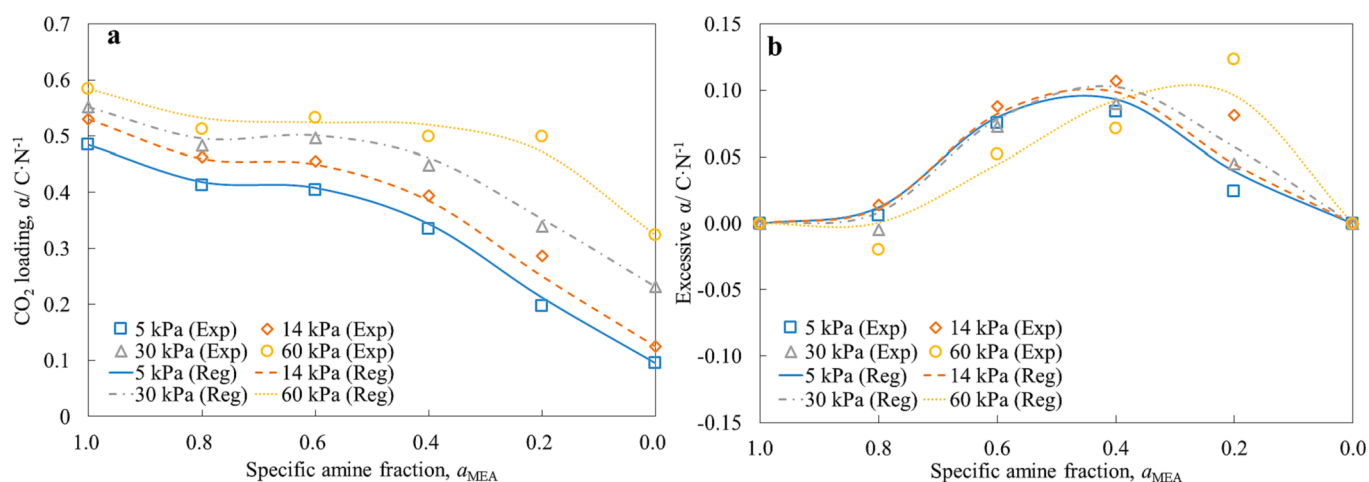

Fig. 9. CO_2 loading of vapor–liquid equilibrium system at 323 K. a: Experimental and regressed data of single MEA, MDEA and their blend solvents; b: Excessive CO_2 loading.
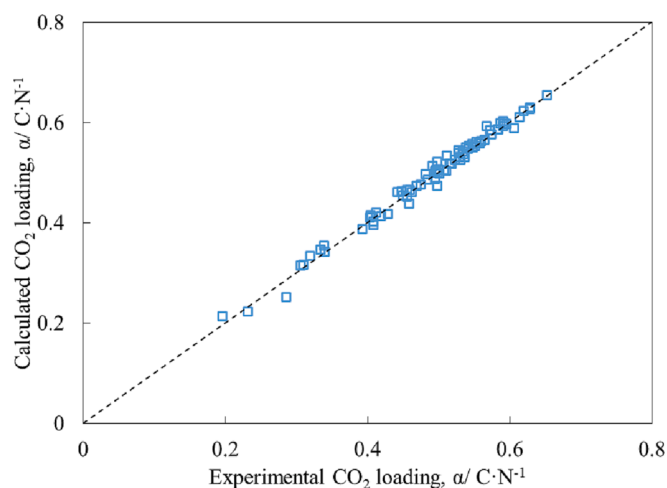

Fig. 10. Calculated CO_2 loading versus experimental CO_2 loading under equilibrium.

blended solvent. In addition, the method may also be applied for correlating different type data e.g. kinetic, mass transfer, absorption heat, etc.

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.

Data availability

No data was used for the research described in the article.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2023.143279.

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