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NMR techniques and prediction models for the analysis of the species formed in CO_2 capture processes with amine-based sorbents: a critical review

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Abstract:

Carbon dioxide (CO_2) capture by aqueous alkanolamines is among the most mature and efficient technologies to curb the continuous emission of the green-house gas CO_2 into the atmosphere. However, the widespread use of this technology is limited, mostly due to the energy penalty during the CO_2 desorption and the amine regeneration. A key point to develop more efficient sorbents is the knowledge of the species formed in solution after the reaction CO_2 with the amine. Qualitative and quantitative analysis of ions in solutions can help to understand chemical reaction processes and probe chemical reaction mechanisms to discern important information including the rates of CO_2 absorption and desorption rates, the CO_2 capture efficiency, the cyclic capacity, and the energy demand for regeneration, which are essential for the commercialization of this technology. Although many researchers have reported the speciation of primary, secondary and tertiary amines when reacting with CO_2 as determined by nuclear magnetic resonance (NMR) and other methods, a few discussed the state-of-the-art research in this area. This paper aims to review and compare NMR spectroscopy, pH + NMR analysis and model prediction techniques for determining the speciation of CO_2 loaded amine solution, to get information for better understanding the fundamental principles and up-to-date progresses applied in various amine-CO_2 systems.

This review illustrates the applications of these three techniques to observe the morphology of CO_2 loaded amine solutions including single amines, blended aqueous amines and non-aqueous amine solutions. Furthermore, the operating principles are described in detail, and the strengths and weaknesses are discussed carefully. Of the three approaches, NMR spectrometry is proven to be more efficient in determining the proportion of ions in simple amine-CO_2-H_2O systems; however, for more complex systems the process efficiency varies depending on the situation encountered. In sum, these three analytical techniques can help to design efficient amine materials with high CO_2 separation performance and low energy cost.

Keywords: carbon capture, speciation, NMR, pH + NMR, model prediction, quantitative analysis

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■ Introduction

The combustion of fossil fuels (coal, oil, and natural gas) accounts for about 65% of the total greenhouse gas emissions, which contribute to global warming with potentially devastating effects.[1-4] In past decades, the emissions of CO_2 into the atmosphere are dramatically increased owing to the rise of the energy consumption mainly resourced from fossil fuels,[5] simultaneously increasing the earth's surface temperature.[6, 7] As such, the reduction of anthropogenic CO_2 emission is considered one of the most urgent challenges, which demands greater reliance on renewable energies and/or the development of efficient technologies for CO_2 capture and sequestration.[8-11] In order to lower CO_2 emission and mitigate global warming, many efforts have been made by different research groups to develop new and efficient technologies for CO_2 capture and storage (CCS).[12-16]

CO_2 can be captured from large emission sources with three main processes, namely pre-combustion, post-combustion, and oxyfuel combustion, but only the post-combustion carbon capture (PCC), the most mature technology, can be easily retrofitted to plants in operation and worked at commercial scale.[17-21] Chemical capture by aqueous alkanolamines is currently considered the most efficient and relatively less expensive technology for industrial-scale application and for this reason many research activities aim to improve this type of sorbent.[19, 22-24] However, the widespread utilization of this technique is still limited by high operating cost, mainly from the high energy required for CO_2 desorption and amine regeneration.[25, 26]

In order to optimize the efficiency of post-combustion carbon capture by using amine sorbents, an accurate understanding of the chemistry (i.e. reaction mechanism, equilibrium, and speciation) involved in the process of CO_2 capture and release is needed.[27] The types and numbers of ions produced during the different absorption and desorption stages are correlated to amine performances. This correlation is necessary in obtaining accurate parameters of CO_2 absorption and desorption rates, CO_2 absorption efficiencies, cyclic capacities, and regeneration energy requirements.[28, 29] In this regard, to develop a reliable vapor-liquid equilibrium (VLE) model is very useful to explore the reaction mechanism. Specifically, in order to identify which amine achieves the highest CO_2 absorption efficiency and the greatest regeneration capacity, the study for the speciation equilibrium in solution can supply us the information about the absorbent behavior, leading to the optimization of several parameters such as the structural features of the amines, the amine/CO_2 ratio, the liquid flow rate, the CO_2 partial pressure, and absorption temperature.[28, 30]

Various analytical techniques have been used by different scientists to determine the species present in CO_2 - amine reactions: among these, it is worth mentioning the X-ray diffraction (XRD), the Fourier transform infrared spectroscopy (FT-IR) , near-infrared (NIR), and Raman spectroscopy.[31, 32] In the present review, three of the most popular techniques for the study of diluted amine-CO_2 systems, namely nuclear magnetic resonance (NMR) spectroscopy, pH + NMR analysis and model prediction, will be discussed in detail.

NMR spectroscopy is considered a powerful and noninvasive technique.[27, 33, 34] Since its discovery over 70 years ago, the size of the necessary instrumentation for

NMR spectroscopy has been gradually reduced, following the advances in the development of electronics.[35]

The ^{13}C NMR spectroscopy applied to diluted amine-CO_2 systems allows to obtain useful information about the reaction mechanism and to qualitatively and quantitatively determine the species present in solution.[36]

NMR spectroscopy presents several advantages over other techniques, mainly because the peak areas in NMR spectra directly represent the number of nuclei contributing to the signals which makes the quantitative analyses of species possible without calibration requirements.[27, 34]

Previously, ^{13}C NMR spectra of carbon dioxide in water were reported by Abbott et al.[37] and in aqueous NH_3 solutions were discussed by Mani et al.[38] In spite of its practical importance and high potentiality, the application of ^{13}C NMR spectroscopy in the quantification of the species involved in CO_2 loaded aqueous amine- systems[28] has rarely reported due to the convenience of pH + NMR combined analysis.

While the concentrations of CO_2-species can be evaluated by NMR method, the amount of free and protonated amines can be calculated from the K_a and the pH,[39] where the definition of pH is in Eq. 1. Many improvements have been performed on this technique to make it widely applied by researchers. Stadie et al.[40] calculated the total amount of CO_2 as carbamate and bicarbonate in whole blood by using the pH value and the equilibrium constant. Fan et al.[41] calculated the concentration of hydrogen ion from the pH value. However, one of the drawbacks of this method is that it is only suitable for aqueous solutions, and for a restricted range of operating temperatures (293~308

K).[42]

$$pH = -\log([H^+]) \quad (1)$$

The popular thermodynamic models, including Kent-Eisenberg (K-E),[43] Deshmukh-Mather (D-M),[44] and E-NRTL models,[45] can help scientists to predict important parameters for CO_2 capture processes.[46] The K-E model[43] can be employed to calculate the equilibrium constants which is a function of temperature T (Eq. 2),[47] where the vapor-liquid equilibrium（VLE）model is applied to simulate ammonium speciation.[48]

$$\ln K_p = \frac{-5851.11}{T} - 3.3636 \quad (2)$$

In the present review we have decided to discuss and compare critically the utilization of these three popular techniques, namely NMR spectroscopy, pH + NMR combination and model predictions, for the speciation analysis during CO_2 capture processes with amine-based sorbents. This review offers a broad overview of all types of applications of these techniques, evaluating both strengths and weaknesses for various amine systems.

■ Chemical equilibria in amine-CO_2-H_2O systems

Based on the types of ions generated during the reaction of amines with CO_2, the following chemical reactions may occur (where Am denotes a general amine).

Dissociation of water:

$$2H_2O \rightleftarrows H_3O^+ + OH^- \quad (3)$$

Dissociation of dissolved CO_2 through carbonic acid:

$$2H_2O + CO_2 \rightleftarrows H_2CO_3 + H_2O \rightleftarrows H_3O^+ + HCO_3^- \quad (4)$$

Bicarbonate formation:

$$CO_2 + OH^- \rightleftarrows HCO_3^- \quad (5)$$

Carbonate formation:

$$HCO_3^- + H_2O \rightleftarrows CO_3^{2-} + H_3O^+ \quad (6)$$

Protonated amine formation:

$$\text{Am} + H_3O^+ \rightleftarrows AmH^+ + H_2O \quad (7)$$

$$\text{Am} + CO_2 + H_2O \rightleftarrows AmH^+ + HCO_3^- \quad (8)$$

$$AmH^+ + H_3O^+ \rightleftarrows AmH_2^{2+} + H_2O \quad \text{(for diamines)} \quad (9)$$

Zwitterion formation:

$$\text{Am} + CO_2 \rightleftarrows Am^+COO^- \quad (10)$$

Carbamate formation：

$$Am^+COO^- + Am \rightleftarrows AmCOO^- + AmH^+ \quad \text{(H from the amine, tertiary amine cannot form carbamate)} \quad (11)$$

$$AmCOO^- + HCO_3^- \rightleftarrows Am(COO)_2^{2-} + H_2O \quad \text{(for diamines)} \quad (12)$$

Hydrolysis of carbamate:

$$Am(COO)_2^{2-} + 2H_2O \rightleftarrows 2\,HCO_3^- + Am \quad \text{(for diamines)} \quad (13)$$

$$Am(COO)_2^{2-} + H_2O \rightleftarrows HCO_3^- + AmCOO^- \quad \text{(for diamines)} \quad (14)$$

$$AmCOO^- + H_2O \rightleftarrows Am + HCO_3^- \quad \text{(except for tertiary amine)} \quad (15)$$

In amine blends systems, two (or more) amines could have a synergistic interaction during the CO_2 uptake: indeed, after the zwitterion formation (reaction 10) by one of the two amines (here indicated with Am1), the other amine, generally the most alkaline (here indicated with Am2) can work as a acceptor of the proton (H^+) generated and released by Am1, thus promoting the formation of Am1 carbamate:

$$Am1^+COO^- + Am2 \rightleftarrows Am1COO^- + Am2H^+ \quad (16)$$

Typically, Am1 is a primary or secondary amine, whilst Am2 is a sterically hindered or tertiary amine.

■ Single amine-CO_2-H_2O systems

Primary and secondary amine solvents

The reactions of non-hindered primary and secondary amines with CO_2 are quite similar: the amine carbamate represents the main product, while bicarbonate is formed in smaller amounts. Generally, the carbamates formed from primary amines are more stable than those from secondary amines because the nitrogen sites are less hindered from the nucleophilic attack.[33, 49] On the contrary, the reactions of CO_2 with sterically hindered primary and secondary amines such as 2-amino-2-methyl-1-propanol (AMP), produce unstable carbamates, followed by the formation of bicarbonate, as reported in reaction (15). Sterically hindered primary/secondary amines behave similarly to tertiary amines.

Fan et al.[41] performed qualitative and quantitative analyses of the species in the CO_2-MEA-H_2O system using ^1H and ^{13}C NMR spectroscopy: where MEA denotes mono-ethanolamine, the most popular and one of the cheapest amine solvents used for CO_2 capture process.[50, 51] According to their study, the MEA/MEAH$^+$ peaks shift down field while the carbamate peaks shift up field upon CO_2 absorption in the ^1H NMR spectrum due to the acidity increasing. However, the peaks of MEA/$MEAH^+$ in the ^{13}C NMR spectrum shift to higher field, while the carbamate peaks remain almost unchanged.

Lv et al.[52] carried out a detailed investigation on CO_2 absorption and desorption mechanisms within the CO_2-MEA-H_2O system by analyzing the reaction intermediates under different CO_2 loadings using ^{13}C NMR spectroscopy. The authors found the absorption process starting from the formation of MEA-carbamate based on the zwitterionic mechanism and followed by the formation of carbonate and bicarbonate via the hydration of CO_2 and the hydrolysis of the carbamate. The NMR study allowed the authors to analyze the CO_2-MEA-H_2O system over high CO_2 loading values: the lower stability of carbamate was found with the higher CO_2 loading as the carbamate was easily hydrolyzed to carbonate and bicarbonate by H^+ at higher CO_2 loading amount. Similar results have also been found by other authors.[10,19]

A complete species analysis based on ^{13}C NMR in the different amine systems has been performed by Barzagli et al..[28, 53] The amine solutions were tested including MEA, AMP, diethanolamine (DEA), and 2-(methylamino)ethanol (MMEA) with different concentrations. Moreover, the data collected from the spectra has been correlated with the CO_2 capture performances of the different sorbents. García-Abuín et al.,[54] carried out an accurate ^1H and ^{13}C NMR spectroscopic study to evaluate the products formed upon CO_2 uptake in aqueous pyrrolidine solution: as a finding, at the beginning of the CO_2 absorption, the amount of carbonate and carbamate formed indicated a stoichiometric ratio 2:1 (amine:CO_2). The carbamate stability decreased with increasing the CO_2 loading as pyrrolidine is a sterically hindered amine, and more bicarbonate was produced. Consequently, an increase in free amine concentration was observed. Finally, at the end of the process, the stoichiometric ratio was 1:1, and the carbon dioxide capture capacity was enhanced.

Wang et al.[55] used MEA/sulfolane aqueous solvent with a phase interchanging function to capture CO_2: in this kind of sorbents, two immiscible liquid phases (upper and lower phase) are formed after CO_2 absorption. ^{13}C NMR analysis revealed that the most of CO_2 species exists in the upper phase rather than the lower phase.

In order to investigate a new primary amine based solvent, aqueous 4-aminomethyltetrahydropyran (4-AMTHP), Li et al.[56] used potentiometric titrations in the absence of CO_2 to determine the protonation constants (larger protonation constants means better reactivity toward CO_2) for the reaction:

$$4-\mathrm{AMTHP}+H^{+}\rightleftarrows 4-\mathrm{AMTHP}H^{+} \quad (17)$$

The full reaction scheme of the system is described in Figure 1, where RNH_2 represents 4-AMTHP.

Matin et al.[57], taking MEA as an example, employed total alkalinity titration measurement with strong base to measure the concentration of (bi)carbonate, protonated amine, carbamate, total inorganic carbon content and free amine. The presence of bicarbonate in the solution influences the free amine concentration, which is a positive correlation function of CO_2 loading. The investigators also predicted activity coefficient with Aspen Plus ENRTL-RK model, and the results showed that the pH values measured in experiments matched those predicted with the Aspen Plus.[58]

Moreover, total carbon and HCO_3^- calculated by Matin et al.[57] were compatible with the data presented by Jakobsen et al.[59] and with the Aspen Plus predictions[58].

The equilibrium constants K(T) could be obtained with Kent and Eisenberg model[43] to determine the ratio of free and protonated MEA.[41] Luo et al.[60] carried out a comparison between three different models (KE, e-NRTL and UNIQUAC), for the CO_2 loaded aqueous MEA system. The parameters obtained from these models showed good predictions in comparison with experimental data in various conditions. A further test was carried out to evaluate the full and simplified VLE models. The experimental data matched model predictions quantitatively in absolute concentrations instead of relative mole fractions. The results obtained with both models showed a good agreement between experiment and simulation.[61]

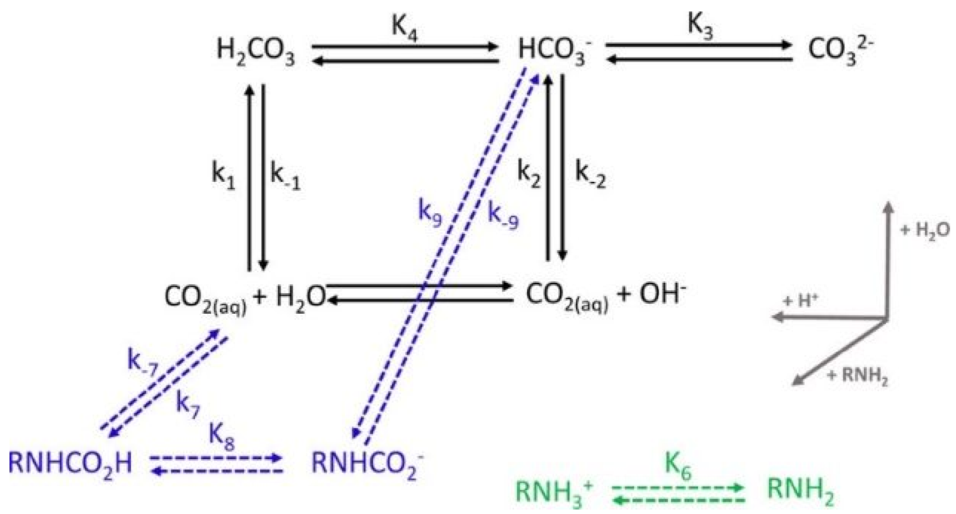

Figure 1. The reaction scheme of the primary amine and CO_2. Reprinted with permission from ref.[56] Copyright 2017 American Chemical Society.

Tertiary amine solvents

Tertiary amines do not have protons on the nitrogen of the amino functionality:

for this reason they cannot form carbamates and the only product of the reaction with CO_2 is (bi)carbonate. Due to their different reaction mechanism, tertiary amines generally present slower CO_2 reaction rates and lower energy requirement for the regeneration compared to primary/secondary amines.[62] It has been proposed by Donaldson et al.[63] that tertiary amines do not react with CO_2 directly but catalyze the hydration reaction of CO_2.[64]

Zhang et al.[65] investigated the HCO_3^- and CO_3^{2-} formation at various CO_2 loadings by mean of ^{13}C NMR method. The concentrations of HCO_3^- and CO_3^{2-} as a function of CO_2 loadings for 1 M aqueous solutions of 1-dimethylamino-2-propanol (1DMA2P) and methyl diethanolamine (MDEA) were plotted. As a result, it was showed that the concentrations of HCO_3^- continuously increased, while that of CO_3^{2-} increased to a maximum value, and then stepped down as the CO_2 loading increased.

Three-dimensional (3D) plots of species formed for the 1DMA2P-CO_2-H_2O system at different temperatures and concentrations were described carefully by Liang et al.[64] by using pH method combined with mass balance, charge balance, and equilibrium constant calculations. As an example of their results, in Figure 2 we report the 3D profile obtained for HCO_3^- concentration.

The Liang et al.[64] used K-E model to predict the CO_2 loadings in tertiary amine systems, while Liu et al.[42] applied K-E model to get equilibrium constant K. The K-E model was also chosen by Luo et al.[60] to predict VLE for the DEEA-CO_2-H_2O system (DEEA = diethyl ethanolamine). The reported models (K-E, Austgen, Li-Sheng, Hu-Chakma, and Liu et al.) well described the equilibrium solubility of CO_2 in 1DMA2P solution, with absolute average deviations (AADs) comprised between 6.3 and 15 %.[66] Among them, the models developed by Hu-Chakma and Liu in separate studies predicted the solubility of CO_2 in 1DMA2P better than others since more parameters were considered. The K-E model applied to calculate CO_2 solubility at equilibrium is plotted in Figure 3.

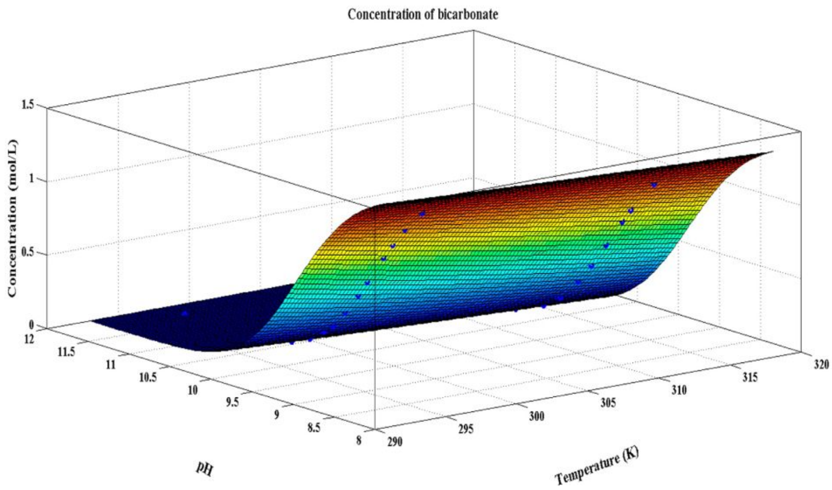

Figure 2. The 3D profile of HCO_3^- concentration in CO_2 loaded 1DMA2P solution. Reprinted with permission from ref.[42] Copyright 2015 American Chemical Society.

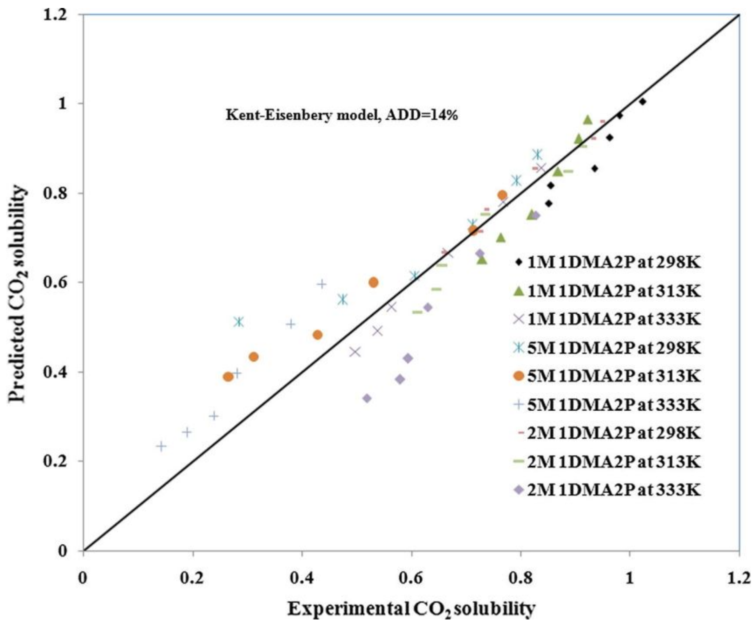

Figure 3. Comparison of the solubility of CO_2 determined by K-E model and experiments. Reprinted with permission from ref.[66] Copyright 2017 ELSEVIER.

Polyamine solvents

The name polyamine identifies a class of compounds containing two or more amino groups. In this review, we mainly discuss diamines.

N-Methylethylenediamine (MEDA) is one of the most common diamines, which contains a primary and a secondary amino groups: the speciation of its aqueous solution after CO_2 uptake was studied by Zhang et al.[67] by using ^{13}C NMR spectroscopy (Figure 4). As a finding, they reported the formation of three different species, in addition to bicarbonate: the primary carbamate which is formed on the primary amino group, the secondary carbamate formed on the secondary amino group, and the dicarbamate. Moreover, the authors observed that both secondary carbamate and dicarbamate convert into primary carbamate (the primary carbamates of some diamines tend to hydrolyze into HCO_3^-) when increasing the CO_2 loading, and the order of the concentration of carbamates follows the order primary-carbamate >> secondary-carbamate > dicarbamate.

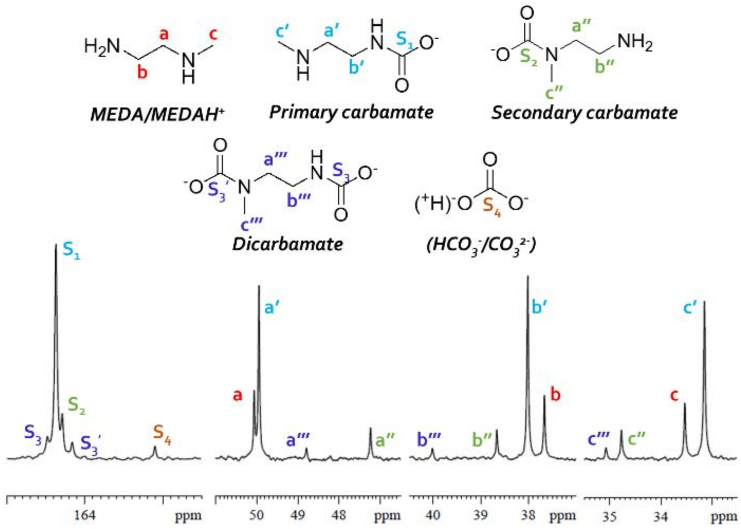

Figure 4. The ^{13}C NMR spectrum of CO_2 loaded MEDA aqueous solution (α=0.93 mol-CO_2/mol-amine). Reprinted with permission from ref.[67] Copyright 2018 ELSEVIER.

The amine-CO_2-H_2O systems for N-Methylethylenediamine (MEDA), N'-Methylpropane-1,3-diamine (MAPA), 2-Dimethylaminoethylamine (DMAEA), and 3-Dimethylaminopropylamine (DMAPA) were also investigated by Zhang et al.[68] using ^{13}C and ^{1}H NMR . Their work indicates that higher CO_2 partial pressures, longer carbon-chain length and more substituent on N-atom favor the formation of bicarbonate in all diamines.

^{13}C NMR analysis was used by Zhang et al.[65] to evaluate the effects of inter- and intra-molecular tertiary amino groups on a primary amino group during the CO_2 capture: in this study aqueous 3-diethylaminopropylamine (DEAPA) and blended MEA-MDEA systems were considered. Their work illustrates that the tertiary amino group of DEAPA (intramolecular) has the effect of improve the absorption rate and the absorption capacity more than the tertiary amino group of MDEA in the aqueous blend of MEA-MDEA (intermolecular) system; moreover, for the latter case, has been observed a greater production of bicarbonate (and a consequent lower production of carbamate) with respect to DEAPA system.

Piperazine (PZ), as one of cyclic amine for CO_2 absorption, is widely applied as a absorption rate promoter in blended amines.[69] Safdara et al.[70] conducted a series of experiments to study the CO_2 solubility in aqueous PZ solution as a function of temperature and pressure. The results revealed that the solubility decreased with the increase in temperature while increased with the increase in pressure. The CO_2 loading capacity for PZ solution improves at high pressure and low temperature. By using NMR spectroscopy, Zhang et al.[71] quantitatively analyzed the species formed (mono-carbamate, dicarbamate, bicarbonate and carbonate) at 298 K in 2M PZ and 2M 2MPZ (2-methylpiperazine) aqueous solutions with different CO_2 loadings (Figure 5).

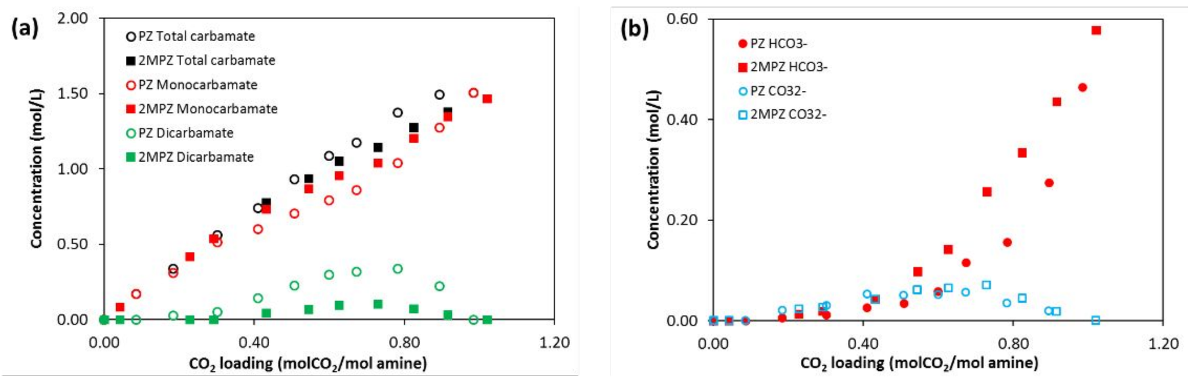

Figure 5. Formation of (a) carbamate, and (b) HCO_3^-/CO_3^{2-} in PZ and 2MPZ solution with different CO_2 loadings. Reprinted with permission from ref.[71] Copyright 2018 American Chemical Society

Figure 5a demonstrates that PZ produces more carbamates (mono-carbamate and dicarbamate summed together) with respected to 2MPZ: in fact, the dicarbamate of 2MPZ is unstable, because of the steric hindrance due to the methyl substituent in the α position. The bicarbonate in solution was mainly generated from the conversion of carbonate and the decomposition of carbamate. As reported in Figure 5b, more bicarbonate was produced from the decomposition of dicarbamate in the 2MPZ system due to its lower stability than PZ dicarbamate. Moreover, the conversion of carbonate is almost negligible, as confirmed by the almost equaled concentrations of carbonates in PZ and 2MPZ solutions, as shown in Figure 5b.

Liu et al.[72] applied ^{13}C NMR spectroscopy to track the specpciation in in aqueous triethylenetetramine (TETA) during the whole CO_2 capture process, including absorption and desorption. As a finding, during the absorption process the NMR peaks of carbamates were between 163.5 and 164.5 ppm, while CO_3^{2-}/HCO_3^- were at 160.3 ppm. The shifts mentioned here were not contributed by single peaks but by peak clusters because TETA has four amine groups. During the desorption, it was observed that the peak intensity of CO_3^{2-}/HCO_3^- decreased until it disappears, while the peak intensities of the carbamates decreased but were still present when the desorption process ended.

According to the pH measurements carried out by Bencini et al.,[73] the pKa_1 of 4-amino-1-methylpiperidine (4-A1MPD) was 10.02, while the pKa_1 of 4-amino-1-propylpiperidine (4-A1PPD) was 10.22. Instead, the pKa_2 was the same for both the amines, 7.46 at 298 K. Although the substituents on both tertiary amines are different, the pKa_1 values only showed a very small difference, and by the consequence the difference in the amount of formed HCO_3^- was negligible. As for linear diamines,[18] the pKa_1 of N, N-dimethyl-1,2-ethanediamine (N,N-DM12EDA) and N,N-dimethyl-1,3-propanediamine (N,NDM13PDA) are 9.69 and 10.34 while the pKa_2 are 6.46 and 8.17, respectively. The lower pKa_2 value for N,N-DM12EDA is due to the shorter distance between amino groups: the first protonated amino group acts as a suppressor for the protonation of the second amino group it is why there is a much lower pKa_2. In comparison with MEA, the cyclic structure significantly reduces the formation of carbamate and boosts the formation of $HCO_3^−$ during CO_2 uptake, which was verified by the species profiles in amine solutions detected with NMR spectroscopy.[18]

Speciation for the CO_2 absorption of at 343.15 K into 0.3 M aqueous PZ solution was conducted by Kadiwala et al.[74] by using Electrolyte-NRTL model. The authors found an interesting correlation between the concentration of the carbonate ion [CO_3^{2-}] in solution and the amount of captured CO_2: [CO_3^{2-}] was high at loading values in the range 0.1-0.6, while it quickly decreased at loading values between 0.6 and 1.5; finally, for loading values higher than 1.5, the carbonate concentration did not vary substantially, indicating that the loading increase was mainly due to physical absorption.

Pashaei et al.[75] justified with the penetration models for the mass transfer flux that the absorption efficiency increased with increasing stirring speed. After investigating five different types of single amines including PZ with K-E modelling, Hwang et al.[76] concluded that the VLEs of the single amines fit well to K-E model. Zhang et al.[68] applied Gaussian software to develop a computational modeling in which the effect of varying chain length on the stability of mono-carbamate was simulated. The results obtained from the experimental, together with the quantum chemistry calculations, proved that carbamates formed from zwitterions with C_2 chains were energetically more difficult than from those containing C_3 chains. In another paper of the same group,[65] the empirical model predictedCO_2 equilibrized solubility at different temperatures with various CO_2 partial pressures within acceptable average absolute deviations compared to the experimental data. In this model, the CO_2 equilibrium solubility was approved as a function of temperature and CO_2 partial pressure.

All researches mentioned in this section are summarized in Table 1.

Table 1. Summary of single amine-CO_2-H_2O systems

Type	Absorbent	Author	Technology	Contribution
Primary/ Secondary amine	MEA	Fan et al.[41]	1. ^1H and ^{13}C NMR 2. K-E model	1. Performed Qualitative, quantitative analysis and ions peak. 2. Determined the ratio of MEA and protonated MEA.
	MEA	Lv et al.[52]	^{13}C NMR	Evaluation of the mechanism on CO_2 absorption and desorption
	MEA, AMP, DEA and MMEA	Barzagli et al.[28, 53]	^{13}C NMR	Preformed species analysis.
	Pyrrolidine aqueous	García-Abuín et al.[54]	^1H and ^{13}C NMR	Developed experiment procedure and the speciation in this reaction.
	MEA + sulfolane	Wang et al.[55]	^{13}C NMR	Qualitative analysis of the two different phases of a phase-change sorbent
	4-AMTHP	Li et al.[56]	Potentiometric titrations	Determined protonation constants.
	MEA	Naser et al.[57]	1. Alkalinity titration measurement 2. Aspen Plus model	1. Calculated the concentration of ions. 2. Predicted speciation was compared with the experimental data.
	MEA	Luo et al.[60]	KE, e-NRTL and UNIQUAC	Carried out a comparison between three different model.
	MEA	Preez, L. J., et al.[61]	Full and simplified version of the VLE model	Predicted the concentrations for all ions.
Tertiary amine	1DMA2P, MDEA	Zhang et al.[65]	^{13}C NMR	Determined the concentration profiles of bicarbonates and carbonates in aqueous solutions.
	1DMA2P	Liang et al.[64] and Liu et al.[42]	1. pH + NMR method 2. K-E model	1. Developed ions (1DMA2P, $1DMA2PH^+$, HCO_3^-, CO_3^{2-}) speciation plots of two-dimensional (2D) and three-dimensional (3D).

				2. Calculated the solubility of CO_2 in tertiary amine systems by Liang et al. 3. Get equilibrium constant K by Liu et al.
	DEEA	Luo et al.[60]	K-E model	Predicted vapor-liquid equilibrium and Henry constant.
	1DMA2P	Liu et al.[66, 77]	Model developed by Kent-Eisenberg, Austgen, Li-Sheng, Hu-Chakma and Liu et al. successively	Determined the equilibrium solubility of CO_2 and the solubility constant of N_2O.
Polyamines	MEDA	Zhang et al.[67]	^{13}C NMR	Analyze the speciation.
	MEDA, MAPA, DMAEA and DMAPA	Zhang et al.[68]	1. ^{1}H and ^{13}C NMR 2. computational model	1. Identified and quantify species. 2. Explained the effect of the chain length on the stability.
	DEAPA	Zhang et al.[65]	1. ^{13}C NMR 2. Empirical model	1. Determined the effect of the intra- and inter-molecular tertiary amino groups. 2. Described the trend observed in experiments.
	PZ and 2MPZ	Zhang et al.[71]	^{13}C NMR	Compared the amount of each ions and analyze the reasons for its difference.
	TETA	Liu et al.[72]	^{13}C NMR	Observed its speciation during the process of CO_2 capture.
	4-A1MPD and 4-A1PPD	Bencini et al.[73]	pH measurements	Establish relationship between pKa and bicarbonate formation.
	N, N-DM12EDA and N, NDM13PDA	Xiao et al.[18]	pH measurements and NMR spectroscopy	Detected species profiles.
	Piperazine solutions	Kadiwala et al.[74]	Electrolyte-NRTL model	Determined Speciation during the absorption process.
	PZ	Pashaei et al.[75]	Penetration models	Determined absorption efficiency.
	Five different types of single amines including	Hwang et al.[76]	K-E models	VLE model matches the K-E models.

	PZ			

■ Blended amine-CO_2-H_2O systems

The wide diffusion and application of the single amine technology is limited due to several drawbacks, in particular the high energy costs in regeneration to regenerate primary/secondary amines and the low reaction rates of tertiary amines.[78] To avoid these shortcomings of single amines, mixtures of primary, secondary, tertiary, and heterocyclic amines attracted attentions.[79] Typically, the blend consists of: (a) a primary or secondary amine, capable of quickly react with CO_2 to form carbamate and (b) a strongly alkaline amine, usually a sterically hindered or tertiary amine, capable of accepting the proton (H^+) generated and released from the reaction of the other amine in its reaction with CO_2, thus promoting the formation of the carbamate (equation 16).

It has recently been demonstrated that dual and trio-solvent blended amines can potentially increase the absorption efficiency and lower the required regeneration energy.[80] For example, the blends of AMP-MDEA (1:2 in molar ratios) and AMP-DEA (2:1 in molar ratios) showed an improvement in absorption efficiency of 7-14% compared to single amines under the same operating conditions.[28] The improved performances of the blended amines in comparison with individual amines were explained on the bases of cooperative effects disclosed by ^{13}C NMR analysis, pH + NMR methods, and model prediction as below.

Dual-amine systems

Liu et al.[72] studied the CO_2 uptake in TETA-AMP-H_2O system by using ^{13}C NMR spectroscopy, they found that both TETA and AMP carbamates were formed at the very early stage of the CO_2 uptake. As the loading increased, the CO_3^{2-}/HCO_3^- signal appeared, grew and moved from 162.9 to 160.6 ppm: this indicates that carbamates (in particular AMP carbamate, with low stability) hydrolyzed to form bicarbonate, which therefore increased its concentration in solution. During the regeneration step, the intensity of CO_3^{2-}/HCO_3^- peak decreased until it disappeared while those of carbamates were still present after the desorption completion.

The species formed in MEA-based blends, in particular MEA-1DMA2P and MEA-MDEA, were investigated at different CO_2 loadings (at 293.15 K) by using ^{13}C NMR spectroscopy by Zhang et al.,[65] and the results compared with the speciation of the single amine solutions. After detailed discussion , it was noted that MEA reacts more easily with CO_2 than tertiary amines. When MEA is added into a tertiary amine system, the production of the CO_3^{2-}/HCO_3^- ions from the tertiary amine is inhibited. Conversely, tertiary amines can promote the formation of CO_3^{2-}/HCO_3^- from MEA at a lower CO_2 loading ratio. HCO_3^- plays an important role in amine regeneration, depending on CO_2 loading, formulation ratio and the operating conditions. Using NMR spectroscopy to determine the species of MEA-4-diethylamino-2-butanol (DEAB) solutions, Yu et al.[81] found that with the rise in temperature from 297 to 363 K, the HCO_3^- concentration demonstrate a remarkable increases, and the ^{13}C signal can be detected at a relative low CO_2 loading stage (0.25).

Ciftja et al.[82] investigated the aqueous DEEA/MAPA blend, a phase-change sorbent, by NMR quantitative speciation. They found that the lower phase was contained most of CO_2 and MAPA (a diamine with a primary and a secondary amine group), while the upper phase was lean in CO_2 and rich in the tertiary amine DEEA. Furthermore, they found that by raising the partial pressure, the DEEA/MAPA ratio increased in the lower phase and simultaneously decreased in the upper phase.

Another phase-change sorbent, aqueous DETA-PMDETA, has been reported by Ye et al.[83] The ^{13}C NMR analysis allowed the identification and quantification of the species in both phases to get information for best understanding to the mechanisms and reaction pathways. They observed that, during the uptake, CO_2 firstly reacted with DETA in the lower phase and then formed bicarbonate and carbonate ions via the protonation of PMDETA.

The quantitative results of MEA-DEAB-CO_2-H_2O system were successfully obtained using pH + NMR analysis: eight samples of the blended amine solutions with different CO_2 loadings were tested at room temperature and the results displayed in Figure 6. The results showed that the pH + NMR method can be applied into a quaternary MEA-DEAB-CO_2-H_2O.[84] The high concentration of carbamate ions was caused by the high fraction of MEA in the solution (MEA was 5.0 M, DEAB 1.25 M). In this system, the free MEA and free DEAB as two available proton acceptors exist at the low CO_2 loading stages, while only MEA-proton-acceptor exists at the high CO_2 loading stages because the free DEAB is consumed.

Used as an addictive in the solutions of AMP, PZ can significantly enhance the CO_2 absorption rate, as confirmed by Sun et al.[85] in hybrid reaction rate modelling. In this model, CO_2 reacts with PZ following a second-order kinetics, while the reaction of CO_2 with AMP fits in the zwitterion mechanism. At higher temperatures and PZ concentrations, the apparent reaction rate constant ($k_{app)}$, increases, with an overall absolute percentage deviation of k_{app} of 7.7%.

The calculation of the concentration of HCO_3^- in MEA-DEAB-CO_2-H_2O system is complicated, but it could be obtained via simulation with. The electrolyte nonrandom-two-liquid model (e-NRTL), suitable for this utilization as it employs multiple equilibria and mass balance rules.[81] Equilibrium behavior in aqueous solutions of MEA, benzylamine (BZA), and their blends was predicted by Conway et al.[86] using a model programmed in MATLAB. The modelling approach undertaken, however, was fundamentally based on the assumption that the individual chemical models for the amines present in the solutions adequately described the absorption chemistry and no additional synergistic behaviors were required.

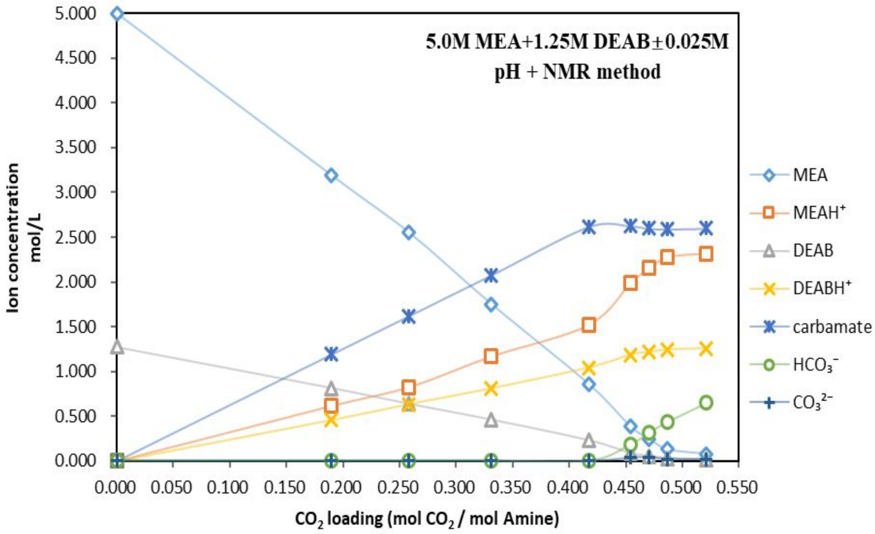

Figure 6. the quantitative results of MEA-DEAB-CO_2-H_2O system by using pH + NMR combined analysis. Reprinted with permission from ref.[84] Copyright 2014 American Chemical Society.

Trio-amine systems

Researches on the formation of species in trio-amine blends are rather scarce,[87] and only a few examples are found in the literature. ^{13}C NMR technique was adopted to analyze CO_2 loaded MEA-AMP-PZ samples with different CO_2 loadings at 298 K: the possible species and the corresponding assignments of ^{13}C peaks were discussed by Zhang et al.[88] A higher AMP/PZ ratio in this trio-amine blends favors the production of more HCO_3^- and less carbamate. Moreover, AMP-carbamates were not found during the CO_2 uptake in any triple-solvent blended systems because the unstable AMP-carbamates can quickly hydrolyze to produce HCO_3^-.

MEA, MDEA and PZ were selected to chosen to compose a trio-amine blends by Zhang et al.[89] for CO_2 capture and release studies. The possibly produced species shown were MEA, $MEAH^+$, MEA-COO^-, MDEA, $MDEAH^+$, PZ, PZH^+, PZ-COO^-, PZ-di-COO^-, HCO_3^- and CO_3^{2-}, which were analyzed by ^{13}C NMR technology together with pH measurements. The PZH_2^{2+} ion, containing two positive charges, was not stable and its concentration was negligible.

The ion concentrations changing with the CO_2 loadings is plotted in Figure 7.

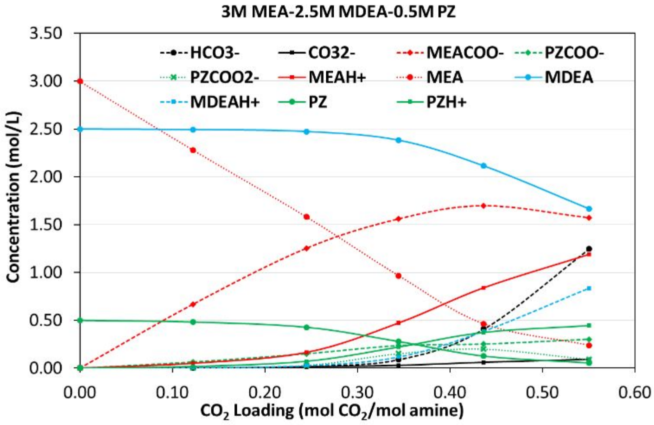

Figure 7. The speciation results of MEA-MDEA-PZ with various of CO_2 loadings. Reprinted with permission from ref.[89] Copyright 2017 ELSEVIER

It has universally been accepted that CO_2 desorption mainly entails the decomposition of HCO_3^- and carbamate ions. Different CO_2-rich solutions could be expressed by CO_2 desorption kinetic model such as Avarami's fractional-order kinetic model which may be the best fitting model. As reported by Liu et al.,[90] the curves generated from the optimized parameters well fit the experimental data. 7% MEA + 3% MDEA + 1% AMP has showed the best performance due to the full interaction between amines. The bicarbonate and carbonate ions produced were more than other mixing proportions.

All researches mentioned in this section are summarized in Table 2.

Table 2. Summary of blended amine-CO_2-H_2O systems

Type	Absorbent	Author	Technology	Contribution
Dual-amine systems	TETA-AMP-H_2O	Liu et al.[72]	^{13}C NMR	The peaks of ions.
	MEA-1DMA2P and MEA-MDEA	Zhang et al.[65]	^{13}C NMR	Ions concentration profiles.
	MEA-DEAB	Yu et al.[81]	^{13}C NMR	Ion speciation plots.
	DEEA-MAPA	Ciftja et al.[82]	^{13}C NMR	Qualitative and quantitative analysis in a phase-change sorbent
	DETA-PMDETA	Ye et al.[83]	^{13}C NMR	Determination of mechanisms and reaction pathways in a phase-change sorbent
	MEA-DEAB	Shi et al.[84]	pH + NMR methods	Speciation plots.
	AMP-PZ	Sun et al.[85]	A hybrid reaction rate model	PZ can significantly increase the CO_2 absorption rate.
	MEA-DEAB	Liu et al.[87]	E-NRTL	Governing the complex CO_2-amine interactions.
	MEA-BZA	Conway et al.[86]	A modelling tool developed in MATLAB	Equilibrium behavior.
Trio-amine systems	MEA-AMP-PZ	Zhang et al.[88]	^{13}C NMR	Speciation during the process of CO_2 capture.
	MEA-MDEA-PZ	Zhang et al.[89]	^{13}C NMR together with pH method	Evaluating possible produced species.
	MEA-MDEA-AMP	Liu et al.[90]	Avarami's fractional-order kinetic model	CO_2 desorption kinetic.

■ Nonaqueous systems

In recent years, interest has grown in using nonaqueous amine solutions as sorbents for the CO_2 capture. The use of organic diluents instead of water redirects the reaction between CO_2 and amine towards less stable carbonated species: consequently, the temperatures required for the regeneration of the absorbent would be lower and the total energy required for the process would decrease. At the same time, lower desorption temperatures also ensure less amine degradation and evaporation.[12, 91-93] Recently, some common organic diluents including methanol, ethanol, ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) have been tested to replace water.[72] As reported in literature, the greater solubility of CO_2 in organic diluents compared to water could enhance the CO_2 absorption, and the lower vapor pressures and heat capacities and of organic diluents with respect to water could reduce the heat required for the sorbent regeneration.[94, 95] Moreover, organic solvents could generally cause less equipment corrosion and avoid foaming problems.[94, 96] As new type of absorbents, a few models are available to predict their solubility, capacity, equilibrium constants, and so on. It should be noted that the pH method cannot be applied in systems without water.

Single nonaqueous organic amines

In TETA-ethanol system, Liu et al.[72] replaced water with ethanol and employed ^{13}C NMR to probe the speciation and reaction mechanism during absorption-desorption processes. The carbamates in this solution were detected at 163.8-164.4 ppm while the peak at 159.9 ppm did not identify to CO_3^{2-}/HCO_3^-, since it could not have formed without the presence of water, but rather referred to the alkyl carbonate of $C_2H_5OCO_2^-$.

Alkyl carbonates in different organic diluents are quite unstable species that could be generated during the absorption, when CO_2 is in significant excess with respect to amine, as demonstrated also from a ^{13}C NMR spectroscopic study carried out by Barzagli et al.[13] As $C_2H_5OCO_2^-$ is an unstable species, it quickly disappears during the desorption process; meanwhile, amine carbamates decrease but still exist.[72] Solutions of AMP in triethylene glycol dimethyl ether (TEGDME) and in N-methyl-2-pyrrolidone (NMP) were investigated by Svensson et al.[97] A precipitate was formed during these experiments which was identified as the AMP carbamate with NMR analysis. The formation of the precipitate could increase the absorption capacity and reduce the energy requirement. The quantitative ^{13}C NMR analysis has been applied by Chen et al.[98] to explore the species distribution in 2-(ethylamino) ethanol (EMEA) + ethanol solutions. The ^{13}C NMR spectrum for a CO_2 loading of 0.547 mol-CO_2/mol-amine is depicted in Figure 8, and the data obtained referring to the amount of different species was plotted in Figure 9 to explain the phenomena appearing in the uptake experiments. Further reactions, such as the formation of $R^1O\text{-}CO_2^-$ (from carbamate with CO_2) and $R^1NHCH_2CH_2O\text{-}CO_2^-$, did not occur, and the final loading value remained low.

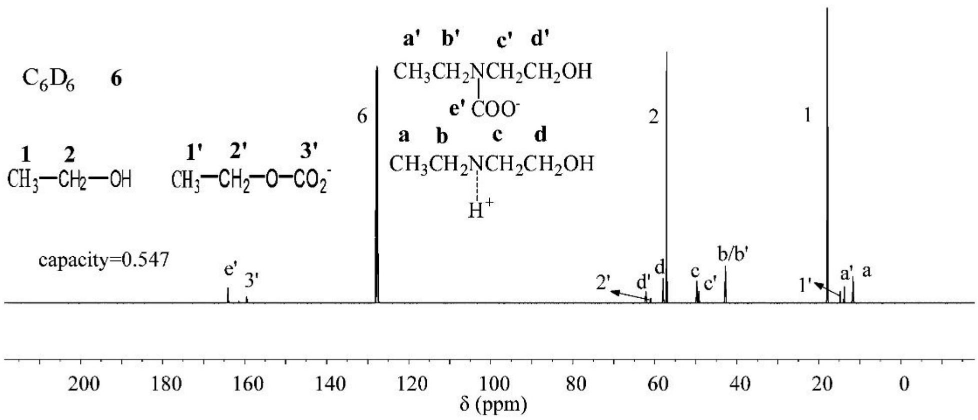

Figure 8. The qualitative analysis of CO_2-loaded EMEA + ethanol solution (CO_2 loading = 0.547). Reprinted with permission from ref.[98] Copyright 2016 ELSEVIER.

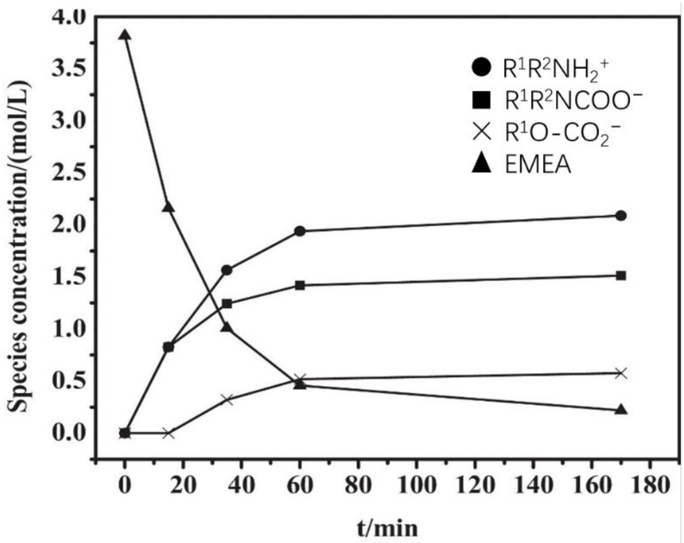

Figure 9. Speciation profile of the CO_2 loaded EMEA- ethanol- at 313 K: ■, $R^1R^2NCOO^-$; ●, $R^1R^2NH_2^+$; ▲, EMEA; ×, $R^1O\text{-}CO_2^-$. Reprinted with permission from ref.[98] Copyright 2016 ELSEVIER.

Barzagli et al.[83] investigated some phase-change nonaqueous sorbents, in particular the secondary alkanolamines MMEA and EMEA in diethylene glycol diethyl ether (DEGDEE) as a diluent. The ^{13}C NMR experiments aimed at determining speciation showed that the upper phase was composed by the diluent DEGDEE as well as the unreacted free amine (traces), while the lower phase contained the ionic couple protonated amine and carbamate (MMEA or EMEA) with a small amount of DEGDEE.

It is worth noting that tertiary amines cannot be used for single nonaqueous systems because they do not form carbamate and cannot produce bicarbonate in the absence of water.

Binary non-aqueous organic amines

To further enhance the performance of the absorbents, binary non-aqueous organic amines were studied. Barzagli et al.[13, 91, 99] devised a technique for chemical CO_2 capture with non-aqueous AMP-based solvents. AMP was blended with DEA, MDEA, MMEA, EMEA, 2-(isopropylamino)ethanol (IPMEA), 2-(tertbutylamino)ethanol (TBMEA) and bis(2-hydroxypropyl)amine (DIPA). The organic diluents used was 1-propanol, EG and diethylene glycol monomethyl ether (DEGMME). ^{13}C NMR analysis was applied to evaluate the distributions of the species in these solutions, and the results indicated that CO_2 was reversibly captured as mono-alkyl carbonates, R-OCO_2^-, (R = CH_3, C_2H_5, CH_2CH_2OH, nC_3H_7), and amine (such as MMEA, DEA, DIPA) carbamates. The carbamates of the amine blended with AMP are always the prevailing species compared to alcohol carbonates, while the carbonate derivatives of DEGMME was negligible and not detectable.

The speciation during absorption process in TETA-AMP-ethanol system, investigated by Liu et al.[72] using ^{13}C NMR, was similar to TETA-ethanol system, however both carbamates of $TETACO_2^-$ and $AMPCO_2^-$ and the alkyl carbonate, $C_2H_5OCO_2^-$, were not found after desorption.

All researches mentioned in this section are listed in Table 3.

Table 3. Summary of nonaqueous systems

Type	Absorbent	Author	Technology	Contribution
Single nonaqueous solutions	TETA-ethanol	Liu et al.[72]	^{13}C NMR	Probed the speciation and reaction mechanism.
	AMP in EG/PrOH or in EG/DEGMME	Barzagli et al.[13]	^{13}C NMR	Observed that alkyl carbonated of different organic diluents are quite unstable species.
	AMP-NMP or TEGDME	Svensson et al.[97]	^{13}C NMR	Observed that a precipitate was formed during these experiments which was identified as the AMP carbamate.
	EMEA in ethanol	Chen et al.[98]	^{13}C NMR	Provided species distribution.
	MMEA or EMEA in DEGDEE	Barzagli et al.[94]	^{13}C NMR	Species distribution in phase-change sorbents
Binary nonaqueous solutions	AMP blends with DEA, MDEA, MMEA, EMEA, IPMEA, TBMEA, DIPA in different organic diluents: EG, PrOH, DEGMME	Barzagli et al.[13, 91, 99]	^{13}C NMR	Evaluated the distribution of the species.
	TETA- AMP in ethanol	Liu et al.[72]	^{13}C NMR	Probed the speciation and reaction mechanism.

■ Applicability of reported methods for speciation

NMR spectrometry

NMR experiments

^{1}H and ^{13}C NMR experiments are convenient techniques for qualitative and quantitative analysis of amine-CO_2-diluent systems. NMR data are provided as spectra containing several peaks: the position of the peaks, called chemical shifts, is characteristic of the nuclei (of H or C) contained in the compound under examination (qualitative information), while the area of the peaks is correlated to the number of equivalent nuclei that contribute to the signal (quantitative information). In this way, it is possible to characterize and quantitatively evaluate even unknown compounds, without the need for standard reference.[27] ^{1}H NMR spectroscopy is fast and reliable, but does not allow to determine some important species, such as carbonate and bicarbonate in aqueous solutions. On the contrary, with ^{13}C NMR spectroscopy is possible to collect direct information on all the interacting carbon-containing species in the systems. Furthermore, ^{13}C NMR is more suitable than ^{1}H NMR to analyze more complex organic systems, because ^{13}C NMR operates in a wider spectral range and without interferences between the peaks (which are usually present in ^{1}H NMR spectra).[27] However, ^{13}C NMR analysis requires more measuring time than ^{1}H NMR, due to the longer the spin-lattice relaxation time for carbon nuclei compared to protons.[34] As reported by Perinu et al,[27] ^{13}C NMR data are particularly suitable for determining the species distributions for the study of the reaction mechanisms of CO_2 absorption/desorption processes in amine-based sorbents. ^{1}H NMR data are usually combined with ^{13}C data for accurate speciation (rarely the speciation is based only on

^{1}H NMR data) or for the development of thermodynamic models.

The single-pulse NMR sequence is a common choice for ^{1}H NMR experiments, while for the acquisition of ^{13}C NMR spectra the pulse sequence with proton decoupling and NOE (Nuclear Overhauser Effect) suppression with a 90° pulse angle is widely used.[27]

To improve the accuracy of qualitative and quantitative analyses of each ion, the relaxation time (T1) needs to be determined in the NMR experiment of each amine solvent. Long enough testing time should be applied to ensure that the peak intensity of each possible ion in the sample can be displayed on the spectrogram. As a general practice, the delay time between each pulse, as a key parameter in the NMR test, should be at least 5×T1 (where T1 is the longest relaxation time of the nuclear spins). ^{13}C NMR experiments require long measuring time due to the long relaxation time of the carbon atom in carboxyl group (carbamates, carbonates and bicarbonates), generally considered in the range 20-30 seconds. Only few T1 values of the different species involved in amine-CO_2-diluent system are reported in literature. Moreover, Ciftja et al.[34] observed that the relaxation time for a particular ^{13}C nucleus does not always remain the same, but could change from single amine system to blended system, due to different chemical environments, such as pH and ionic strength.

Usually, in $^{1}H/^{13}C$ NMR spectroscopic analyzes, deuterated water (D_2O) and hexadecane oxide are applied as solvents. The former is mainly used to lock the field of the signal obtained in optical NMR measurements, while the latter is mainly used as reference to calibrate the chemical shifts of the obtained carbon spectrum because the standard chemical shift of hexadecane oxide in ^{13}C spectrum is 66.79 ppm, as previously reported.[59] Other referent solvents used are: 1,4-dioxane, acetonitrile, 3-(trimethylsilyl)-propionic acid sodium salt or tetramethylsilane.[92]

Validation of NMR spectrometry

The NMR spectrometry was validated by Zhang et al.[65] using 1.5 M aqueous DEAB solution as a reference solvent at 297.65 K. A validation, by formulating the fresh amine and HCl solution with corresponding protonation ratio, was carried out to build the calibration curves for the corresponding carbon atoms. Figure 10 shows the experimental results by Zhang et al.[65] in comparison with those obtained by Shi et al.[100] The figure reveals that the calibration curves generally agreed with the experimental results at 297.65 K, which confirms that the analysis with the NMR spectrometry are accurate and reliable.

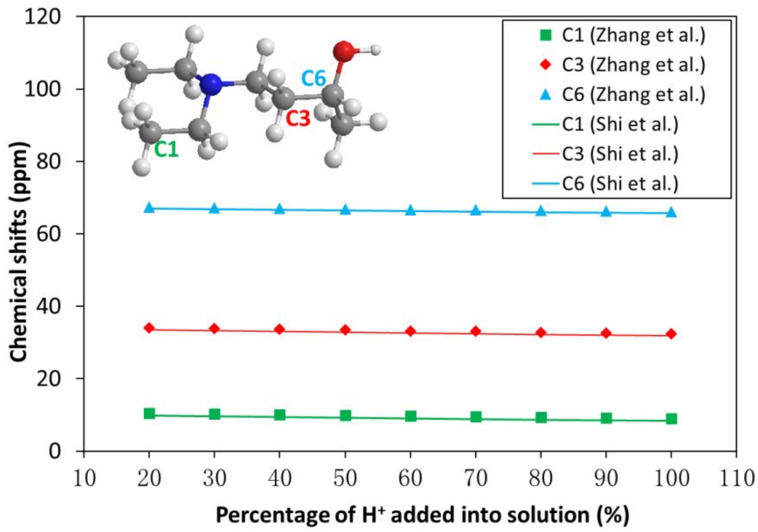

Figure 10. Validation of NMR analysis in 4-diethylamino-2-butanol (DEAB). Adapted with permission from ref.[65] Copyright 2016 American Chemical Society.

The total CO_2 loading is also determined by HCl titration as a reference of ^{13}C NMR method. The HCl titration method for determining the CO_2-loading was originally proposed by Horwitz et al.[101] Moreover, Liu et al.[42] predicted the CO_2 loading in aqueous 1DMA2P with a tolerable average deviation (AAD) of 9.2%. According to the report of Zhang et al.,[68] the total CO_2 loadings calculated from NMR method parallels the results of HCl titration at low loading stage, where the AAD between these two techniques is the acceptable value of 1.98%, as presented in Figure 11.

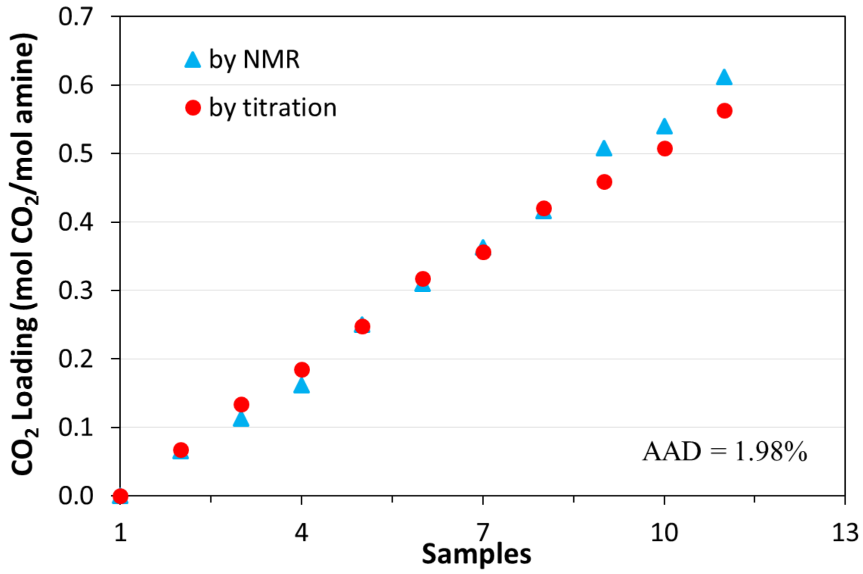

Figure 11. Comparison of the CO_2 loading values between the NMR and HCl titration method. Reprinted with permission from ref.[68]. Copyright 2017 American Chemical Society.

NMR analysis assisted with HCl titration

The main ions produced by reactions between the CO_2 and aqueous amines are: free amines (Am), protonated amines (AmH^+), amine carbamates ($AmCOO^-$, for primary and secondary amines only), HCO_3^- and CO_3^{2-}. The proportions of carbamates, bicarbonate, and carbonate can be calculated directly based on the chemical shifts and peak areas on the NMR spectra. However, for protonated amines and free amines, extra protonation calibration curves and mass balances of amines are required.[102] In the ^{13}C

NMR spectrum of primary amine-CO_2-H_2O systems at 293.15 K,[65] the ion concentrations are calculated with the following equations:[103, 104]

$$\frac{[AmCOO^-]}{[CO_3^{2-}]+[HCO_3^-]} = \frac{S_{carbamate}}{[S_{bicarbonate + carbonate}]} = R \quad (18)$$

$$[AmCOO^-] = \frac{R}{1+R}[CO_2]_0 \quad (19)$$

$$[CO_3^{2-}] = \frac{(\delta - 161.45)}{(168.03 - 161.45)(1+R)}[CO_2]_0 \quad (20)$$

$$[HCO_3^-] = \frac{(168.03 - \delta)}{(168.03 - 161.45)(1+R)}[CO_2]_0 \quad (21)$$

δ denotes the chemical shift of fast exchanging bicarbonate/carbonate (a single peak for the two species), 168.03 and 161.45 ppm represent the chemical shifts of CO_3^{2-} and HCO_3^-, respectively, which are in agreement with the conclusions obtained by Jakobsen et al.[59] also from ^{13}C NMR analysis, within an absolute deviation of 0.27%. $[CO_2]_0$ is the CO_2 capacity (mol) in 1L solution. $S_{carbamate}$ and $S_{bicarbonate+carbonate}$ represent the peak integration of carbamate and of the total value of CO_3^{2-} and HCO_3^-, respectively, in the ^{13}C NMR spectrum. The $[CO_2]_0$ can be calculated from Eq. 22; meanwhile, the concentration of amine and CO_2 loading were calibrated with 1 mol/L HCl solution.[105]

$$[CO_2]_0 = C_{amine} \times \alpha \quad (22)$$

$$\alpha = \frac{V - V_{HCL}}{22.4 \times C_{amine}} \times \frac{273.15}{273.15 + T} \quad (23)$$

where α, V, V_{HCl}, T and C_{amine} represent the CO_2 loading (mol /mol), volume change of trachea (mL), HCl solution volume change (mL), room temperature (°C) and amine solution concentration (mol/L), respectively.

Once the concentration of amine and CO_2 loading were calibrated, the concentrations of ions can be calculated from Eqs. 18 - 21 together with the chemical shifts and peak areas in ^{13}C NMR spectra. Because few carbonate and bicarbonate ions are produced at low CO_2 loading, the ^{13}C intensities of carbonate and bicarbonate are not detectable, so the concentrations in the blended system can be calculated with Eqs. 24 and 25.

$$[AmH^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (24)$$

$$[MEACOO^-] + [HCO_3^-] + [CO_3^{2-}] = [CO_2]_0 \quad (25)$$

Quantification of NMR analysis from carbon classification

The relative amount of the different species in solution can be quantitatively calculated from ^{13}C NMR spectrum. Possible ions in MEA- CO_2-H_2O system, for example, can be classified as in Figure 12a. The peak intensities vary with the related ion concentrations, which are shown in Figure 12b and 12c. The peak area of each aliphatic carbon or carbonyl carbon of corresponding species can be used to determine its ratio (mol species/mol amine). In practice, because of the errors caused by peak area integral, deviations should be considered. Therefore, to avoid this error and improve the accuracy of the quantification, the average of peak areas ((a+a'+b+b')/2) is used as denominator to calculate the relative concentrations of ions (mol species/mol amine), as shown in Eqs. 26 – 28: [68]

$$[HCO_3^- / CO_3^{2-}] = \frac{d}{(a + a' + b + b')/2} \quad (26)$$

$$[MEACOO^-] = \frac{(a' + b')/2}{(a + a' + b + b')/2} \quad (27)$$

$$[CO_2]_0 = \frac{d}{(a + a' + b + b')/2} + \frac{(a' + b')/2}{(a + a' + b + b')/2} \quad (28)$$

When CO_2 completely reacts with amine, it exists in the forms of $MEACOO^-$, HCO_3^-, and CO_3^{2-}. Therefore, the total CO_2 loading in solution should be sum of these three ions, as showed by Eq. 28.

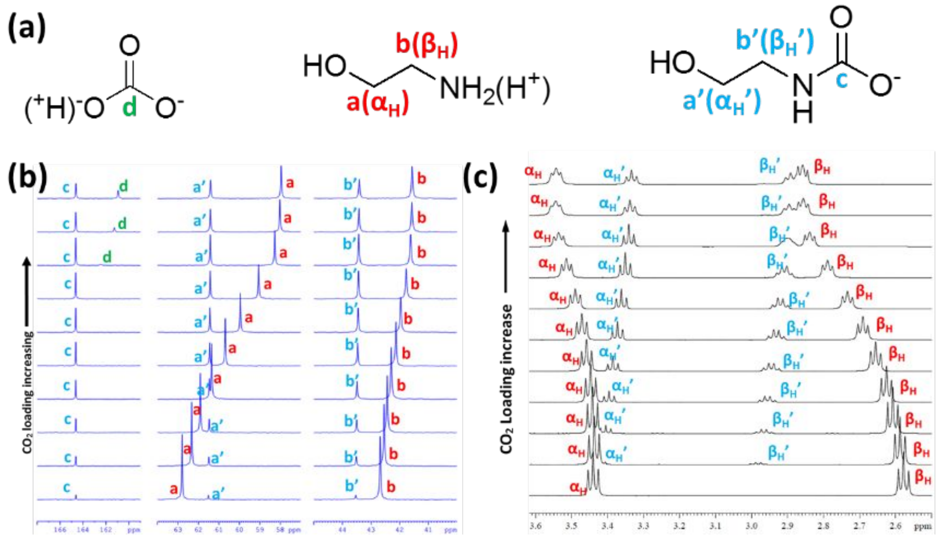

Figure 12. (a) Possible ion classes in CO_2-MEA-H_2O system, (b) stacked ^{13}C NMR and (c) stacked ^{1}H NMR spectrum of the CO_2-MEA-H_2O system. Reprinted with permission from ref.[68] Copyright 2017 American Chemical Society.

The results calculated from ^{13}C spectrum (Figure 12b) and ^{1}H (Figure 12c) should match each other. Moreover, the accuracy of CO_2 loading calculated from Eq. 28 can be validated by HCl titration as well.

The qualitative and quantitative studies of the peak intensities of the ions on NMR spectra mainly depend on the following factors:

a) For the same amine, the peaks of protonated and free amines overlap on ^{13}C NMR spectrum with the peak area decreasing with the increases of CO_2 loading.

b) Due to the fast proton transferring reaction between the CO_3^{2-} and HCO_3^{-}, there is only one single peak between 161 and 169 ppm in the ^{13}C NMR spectra representing the total amount of both of above ions. This peak shifts downward obviously while the peak area increases gradually with the increasing of CO_2 loading in the solution.

c) The peak intensity of carbamate is in the low field of ^{13}C NMR spectrum, and its chemical shift always locates at the same position for the same amine, without correlation with the CO_2 loading.[59]

Calibration curves

The calibration was applied to calculate the exact protonation ratio of the free and protonated amines. Zhang et al.[65] and Shi et al.[100, 102] employed DEAB to build the calibration equations respecting that the chemical shifts (δ) of amines will moves either up- or down-field with different protonation stage.[106] A specific calibration method, based on DEAB and ^{13}C chemical shifts of MEA, was used by Liang et al.[59] Here we report their careful description. Ten tubes containing protonated samples were used with mole ratios of HCl: MEA = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0, respectively. Those ratios were confirmed by titration with standard known concentration of HCl solution. The prepared standard samples were tested at a certain temperature by ^{13}C NMR to get their chemical shifts. Then calibration curves were obtained by taking protonation rates as abscissa and chemical displacements as ordinate. The protonation ratios (H^+/amine) of amine samples could be calculated from the calibration curves using interpolation based on the chemical shifts δ of the selected carbon atom on ^{13}C NMR spectrum.

Calibration curves demonstrate a slightly different for the tested amines at different temperature as the different δ (ppm) obtained. Although these changes are small, they can still affect the accuracy of ^{13}C NMR analytic results.[84] In a more complex system, the application of NMR analysis is illustrated carefully by Shi et al.[84]

pH + NMR combination

Validation of pH + NMR methods

The ion concentrations measured with pH meter matched those analyzed by NMR exploiting the experimental results of Shi et al.,[102] as shown in Figure 13. Therefore, it was confirmed that the ions speciation obtained from the pH measurement are reliable and accurate .

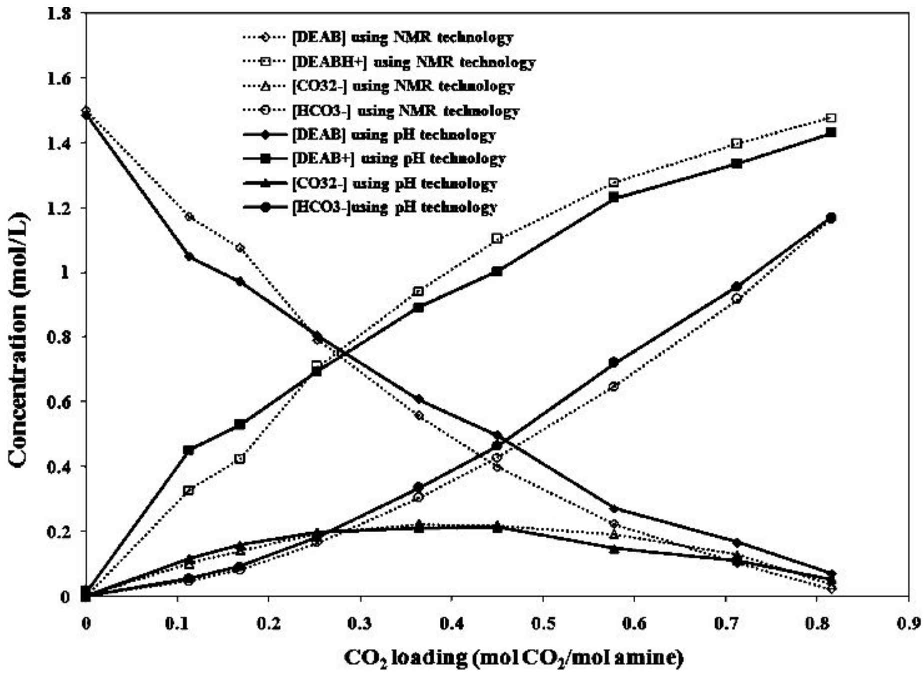

Figure 13. Comparison of the speciation between the pH method and NMR technology. Reprinted with permission from ref.[102] Copyright 2015 American Chemical Society.

The concentrations of free/protonated amines and HCO_3^-/ CO_3^{2-} are calculated from pH measurement by means of reaction equilibrium constants K,[59] while the concentrations of HCO_3^-, CO_3^{2-} and carbamate, are calculated from NMR analysis.[84] Thus, all ion concentrations can be calculated by combining the two techniques. The advantage of this binary method is that it is unnecessary to establish protonation calibration curves to get all main ion's concentration.[84, 107]

Calculation methodology using pH + NMR combination

In this section, the tertiary amine 1DMA2P has been taken as an example[42] to explain pH + NMR combination, the reactions involved in the CO2 capture with aqueous 1DMA2P are as follows:

$$\text{1DMA2P} + H^+ \overset{K_1}{\Leftrightarrow} 1DMA2PH^+ \quad (29)$$

$$CO_2 + \text{1DMA2P} + H_2O \overset{K_2}{\Leftrightarrow} 1DMA2PH^+ + HCO_3^- \quad (30)$$

$$H_2O + CO_2 \overset{K_3}{\Leftrightarrow} H^+ + HCO_3^- \quad (31)$$

$$CO_2 + OH^- \overset{K_4}{\Leftrightarrow} HCO_3^- \quad (32)$$

$$HCO_3^- \overset{K_5}{\Leftrightarrow} H^+ + CO_3^{2-} \quad (33)$$

$$H_2O \overset{K_6}{\Leftrightarrow} H^+ + OH^- \quad (34)$$

where K_i represents the equilibrium constant of reaction i, and the H^+ concentration can be calculated using Eq. 1, from the pH value.

The K-E model[43] has been widely used to predict the VLE data in amine-H_2O-CO_2 systems.[108, 109] This model suggests that the K_i for each reaction can be expressed as follows:[43, 110]

$$K_1 = \frac{[1DMA2P][H^+]}{[1DMA2PH^+]} = exp\left(-7.11 - \frac{4390}{T}\right) = f(T) \quad (35)$$

$$K_5 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = exp\left(-294.74 + \frac{36.4385 \times 10^4}{T} - \frac{1.84157 \times 10^8}{T^2} + \frac{0.41579 \times 10^{11}}{T^3} - \frac{0.354291 \times 10^{13}}{T^4}\right) = f(T) \quad (36)$$

$$K_6 = [OH^-][H^+] = exp\left(39.5554 - \frac{9.879 \times 10^4}{T} + \frac{0.568827 \times 10^8}{T^2} - \frac{0.146451 \times 10^{11}}{T^3} + \frac{0.136145 \times 10^{13}}{T^4}\right) = f(T) \quad (37)$$

In addition, the mass balance and the charge balance in the system cannot be neglected in a amine system,[111] Eq. 38-40 present the balance equations for 1DMA2P system:

Total amine balance:

$$[\text{1DMA2P}]_0 = [\text{1DMA2P}] + [\text{1DMA2P}H^+] \quad (38)$$

Charge balance:

$$[\text{1DMA2P}H^+] + [H^+] = [HCO_3^-] + [OH^-] + 2[CO_3^{2-}] \quad (39)$$

Total carbon balance:

$$\alpha \times [\text{1DMA2P}]_0 = [CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}] \quad (40)$$

where $[\text{1DMA2P}]_0$, α and $[CO_{2(aq)}]$ represents the initial amine concentration, CO_2 loading, and the CO_2 solubility.

Based on the equations 35-40, the main species' concentration in the system can be calculated as below:[42]

$$[\text{1DMA2P}]_0 = f(C) \quad (41)$$

$$[\text{1DMA2P}] = \frac{[\text{1DMA2P}]_0 K_1}{[H^+] + 1} = f(C,T,pH) \quad (42)$$

$$[\text{1DMA2P}H^+] = \frac{[\text{1DMA2P}]_0 [H^+]}{[H^+] + K_1} = f(C,T,pH) \quad (43)$$

$$[HCO_3^-] = \frac{[\text{1DMA2P}]_0 [H^+]^2 + [H^+]^2([H^+] + K_1) + K_6([H^+] + K_1)}{[H^+]([H^+] + K_1)} \times \frac{[H^+]}{2K_5 + [H^+]} = f(C,T,pH) \quad (44)$$

$$[CO_3^{2-}] = \frac{[\text{1DMA2P}]_0 [H^+]^2 + [H^+]^2([H^+]K_1) + K_6([H^+] + K_1)}{[H^+]([H^+] + K_1)} \times \frac{[H^+]}{2K_5 + [H^+]} \times \frac{K_5}{[H^+]} = f(C,T,pH) \quad (45)$$

As described previous equations, ion concentrations depend on temperature, initial amine concentration, and the pH. As for the concentration of carbamate, NMR spectroscopy is useful as has been discussed above.

Model predictions

Prediction using the K-E model can be illustrated by 1DMA2P-H_2O-CO_2 system as an example.[66] The related equilibrium constants for reactions 29 - 34, can be determined as below:

$$K_1 = \frac{[1DMA2PH^+]}{[1DMA2P][H^+]} = \frac{K_2}{K_3} \quad (46)$$

$$K_2 = \frac{[1DMA2PH^+][HCO_3^-]}{[CO_{2(aq)}][1DMA2P]} \quad (47)$$

$$K_3 = \frac{[H^+][HCO_3^-]}{[CO_{2(aq)}]} \quad (48)$$

$$K_4 = \frac{[HCO_3^-]}{[CO_{2(aq)}][OH^-]} = \frac{K_3}{K_1 K_6} \quad (49)$$

$$K_5 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (50)$$

$$K_6 = [H^+][OH^-] \quad (51)$$

Independent correlations exist among the four K_2, K_3, K_5 and K_6, while K_1 and K_4 can be calculated by solving the above equations. Besides above, the $[CO_{2(aq)}]$ normally can be determined by using the Eq.52.

$$P_{CO_2} = He_{CO_2}[CO_{2(aq)}] \quad (52)$$

where P_{CO_2} is the CO_2 partial pressure, and He_{CO_2} represents the Henry's law constant. The He_{CO_2} is the constant of proportionality between absorbed phase and gas phase concentrations, as a function of temperature[112] . The constants of K_3[112], K_5[112], K_6[112] and He_{CO2}[43] within the 1DMA2P-H_2O-CO_2 system can also be calculated with the K-E model. The correlation constant K_2 plays an important role in predicting the CO_2 equilibrium solubility while it can be expressed as Eq. 53:

$$K_2 = exp\left(A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + \frac{E}{T^4}\right) \quad (53)$$

The factors (A – E) for 1DMA2P-CO_2-H_2O system are listed in Table 4.

Table 4. Factors applied for K-E model. Reprinted from ref.[66] Copyright 2017 ELSEVIER.

Factors	A	B	C	D	E
value	-18.41±1.35	-5291±15	-32.95±2.43	0.7903±0.0204	0.05096±0.00123

■ Summary and outlooks

In the present review three of the most popular techniques for the speciation analysis of amine-CO_2-diluent systems, namely NMR spectroscopy, pH + NMR combination and model predictions, have been critically discussed and compared.

^{1}H NMR peaks overlap in most samples, and hence it is difficult to quantify different species by means of ^{1}H NMR, while ^{13}C NMR can be used to quantify most species in a great variety of systems.[33, 113] However, this method consumes much longer analytical time compared to ^{1}H, because of the poor abundance of isotopic ^{13}C and the much longer spin-lattice (or longitudinal) relaxation time of different carbon atoms in a molecule (in particular, carbon atom in carboxyl group) .[104] Nevertheless, the ^{13}C NMR analysis is rather feasible in identifying and quantifying the carbonated species in aqueous and nonaqueous solution.[114] Furthermore, carbamate peaks can be easily located in ^{13}C NMR spectra because their chemical shifts shows almost no changes as the CO_2 loading increased. On the contrary, the NMR chemical shifts of ^{1}H signals for all species in the system vary a lot even within the same process.[104] By comparing the NMR analysis methods, the NMR analysis assisted with HCl titration has lager errors caused by the titration of CO_2 loading, but it is more established. On the other hand, the NMR analysis via carbon classification designed to calculate the relative amounts of ions has higher accuracy, but the concentrations of carbonate and bicarbonate cannot be calculated separately. Nevertheless, both NMR analysis methods need protonation calibration curves and mass balances to calculate the concentrations of protonated and free amines. Without the aid of the pH measurement, NMR technique cannot provide accurate ion speciation as evidenced by Jakobsen et al.[59] and Böttinger et al.[49]

The pH + NMR combination, which has been frequently applied to investigate the VLE profile, exhibits several advantages including not needing to establish protonation calibration curves to get concentrations of all main ions, thus simplifying the operation. In contrast, its applicability for a restricted range of operating temperatures (293~308 K)[42] represents a limitation of which the NMR analysis is not affected. Furthermore, this technique cannot be applied with nonaqueous systems.

The K-E model[43] is considered as a simple model depending only on temperature[115] and it is applied to different systems with good predictions. This model, however, works well only within the given experimental conditions while extrapolating to higher pressure or temperature may lead to significant error due to the increasing system nonideality. When the system is not taken as ideal solution, activity coefficients which account for solution nonideality are needed. For the purpose, the E-NRTL model and the extended UNIQUAC in this case are applied to obtain accurate prediction.[60, 116, 117] Austgen et al.[118, 119] proposed a thermodynamic model to correlate the equilibrium constant to solubility of acid gas. Similar to the K-E model, the Austgen model only varies equilibrium constant with temperature. The Li-Shen to model[115] express equilibrium constant as a function of amine concentration, CO_2 loading, and temperature can also be applied to correlate the solubility of CO_2. Based on this model, Hu and Chakma[120, 121] further proposed a modified mathematical model in which the temperature, the free amine concentration, and the concentration of the gas in the liquid phase are all considered. Counting the physical solubility of CO_2 in 1DMA2P instead of the CO_2 loading amount might be the reason for the lower deviation of Hu-Chakma modelling.[66]

In the present review, many experimental data relating to different amine-CO_2-diluent systems have been reported: these confirm that the three techniques can be successfully applied to provide information on speciation in solution. In simple amine-CO_2-H_2O system, employing the NMR analysis with carbon classification is the most effective in calculating the proportion of ions. However, for complex systems, the situation at hand will dictate the appropriate methodology.

■ Conflicts of interest

There are no conflicts to declare.

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National Department of Education Engineering Research Centre for Chemical Process Simulation and Optimization， National & Local United Engineering Research Centre for Chemical Process Simulation and Intensification.

■ Acronyms

1DMA2P = 1-dimethylamino-2-propanol

2MPZ = 2-methylpiperazine

4-A1MPD = 1-methylpiperidine

4-A1PPD = 4-amino-1-propylpiperidine

4-AMTHP = 4-aminomethyltetrahydropyran

AMP = 2-amino-2-methyl-1-propanol

BZA = benzylamine

DEA = diethanolamine

DEAB = 4-diethylamino-2-butanol

DEAPA = 3-diethylaminopropylamine

DEEA = diethyl ethanolamine

DEGDEE = diethylene glycol diethyl ether

DEGMME = diethylene glycol monomethyl ether

DETA = diethylenetriamine

DIPA = bis(2-hydroxypropyl) amine

DMAEA = 2-Dimethylaminoethylamine

DMAPA = 3-Dimethylaminopropylamine

EMEA = 2-(ethylamino) ethanol

IPMEA = 2-(isopropylamino)ethanol

MAPA = N'-Methylpropane-1,3-diamine

MEA = monoethanolamine

MEDA = N-Methylethylenediamine

MMEA = 2-(methylamino)ethanol

MDEA = methyl diethanolamine

N, N-DM12EDA = N, N-dimethyl-1,2-ethanediamine

N, NDM13PDA = N, N-dimethyl-1,3-propanediamine

PMDETA = N,N,N',N',N''-pentamethyldiethylenetriamine

PZ = Piperazine

TBMEA = 2-(tertbutylamino)ethanol

TETA = triethylenetetramine

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