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**NMR techniques and prediction models for the analysis of the species formed in CO<sub>2</sub> capture processes with amine-based sorbents: a critical review**

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# NMR techniques and prediction models for the analysis of the species formed in CO<sub>2</sub> capture processes with amine-based sorbents: a critical review

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7  
8 **Abstract:**

9  
10 Carbon dioxide (CO<sub>2</sub>) capture by aqueous alkanolamines is among the most mature  
11 and efficient technologies to curb the continuous emission of the green-house gas CO<sub>2</sub>  
12 into the atmosphere. However, the widespread use of this technology is limited, mostly  
13 due to the energy penalty during the CO<sub>2</sub> desorption and the amine regeneration. A key  
14 point to develop more efficient sorbents is the knowledge of the species formed in  
15 solution after the reaction CO<sub>2</sub> with the amine. Qualitative and quantitative analysis of  
16 ions in solutions can help to understand chemical reaction processes and probe chemical  
17 reaction mechanisms to discern important information including the rates of CO<sub>2</sub>  
18 absorption and desorption rates, the CO<sub>2</sub> capture efficiency, the cyclic capacity, and the  
19 energy demand for regeneration, which are essential for the commercialization of this  
20 technology. Although many researchers have reported the speciation of primary,  
21 secondary and tertiary amines when reacting with CO<sub>2</sub> as determined by nuclear  
22 magnetic resonance (NMR) and other methods, a few discussed the state-of-the-art  
23 research in this area. This paper aims to review and compare NMR spectroscopy, pH +  
24 NMR analysis and model prediction techniques for determining the speciation of CO<sub>2</sub>  
25 loaded amine solution, to get information for better understanding the fundamental  
26 principles and up-to-date progresses applied in various amine-CO<sub>2</sub> systems.

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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<sub>2</sub>-H<sub>2</sub>O 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<sub>2</sub> 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.<sup>1-4</sup> In past decades, the emissions of CO<sub>2</sub> into the atmosphere are dramatically increased owing to the rise of the energy consumption mainly resourced from fossil fuels,<sup>5</sup> simultaneously increasing the earth's surface temperature.<sup>6, 7</sup> As such, the reduction of anthropogenic CO<sub>2</sub> 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<sub>2</sub> capture and sequestration.<sup>8-11</sup> In order to lower CO<sub>2</sub> emission and mitigate global warming, many efforts have been made by different research groups to develop new and efficient technologies for CO<sub>2</sub> capture and storage (CCS).<sup>12-16</sup>

CO<sub>2</sub> 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.<sup>17-21</sup> 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.<sup>19, 22-24</sup> However, the widespread utilization of this technique is still limited by high operating cost, mainly from the high energy required for CO<sub>2</sub> desorption and amine regeneration.<sup>25, 26</sup>

In order to optimize the efficiency of post-combustion carbon capture by using

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4 amine sorbents, an accurate understanding of the chemistry (i.e. reaction mechanism,  
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6 equilibrium, and speciation) involved in the process of CO<sub>2</sub> capture and release is  
7  
8 needed.<sup>27</sup> The types and numbers of ions produced during the different absorption and  
9  
10 desorption stages are correlated to amine performances. This correlation is necessary in  
11  
12 obtaining accurate parameters of CO<sub>2</sub> absorption and desorption rates, CO<sub>2</sub> absorption  
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14 efficiencies, cyclic capacities, and regeneration energy requirements.<sup>28,29</sup> In this regard,  
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16 to develop a reliable vapor-liquid equilibrium (VLE) model is very useful to explore  
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18 the reaction mechanism. Specifically, in order to identify which amine achieves the  
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20 highest CO<sub>2</sub> absorption efficiency and the greatest regeneration capacity, the study for  
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22 the speciation equilibrium in solution can supply us the information about the absorbent  
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24 behavior, leading to the optimization of several parameters such as the structural  
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26 features of the amines, the amine/CO<sub>2</sub> ratio, the liquid flow rate, the CO<sub>2</sub> partial  
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28 pressure, and absorption temperature.<sup>28,30</sup>  
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38 Various analytical techniques have been used by different scientists to determine  
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40 the species present in CO<sub>2</sub> - amine reactions: among these, it is worth mentioning the  
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42 X-ray diffraction (XRD), the Fourier transform infrared spectroscopy (FT-IR) , near-  
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44 infrared (NIR), and Raman spectroscopy.<sup>31,32</sup> In the present review, three of the most  
45  
46 popular techniques for the study of diluted amine-CO<sub>2</sub> systems, namely nuclear  
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48 magnetic resonance (NMR) spectroscopy, pH + NMR analysis and model prediction,  
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50 will be discussed in detail.  
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56 NMR spectroscopy is considered a powerful and noninvasive technique.<sup>27,33,34</sup>  
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58 Since its discovery over 70 years ago, the size of the necessary instrumentation for  
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4 NMR spectroscopy has been gradually reduced, following the advances in the  
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6 development of electronics.<sup>35</sup>  
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9 The <sup>13</sup>C NMR spectroscopy applied to diluted amine-CO<sub>2</sub> systems allows to obtain  
10  
11 useful information about the reaction mechanism and to qualitatively and quantitatively  
12  
13 determine the species present in solution.<sup>36</sup>  
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16  
17 NMR spectroscopy presents several advantages over other techniques, mainly  
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19 because the peak areas in NMR spectra directly represent the number of nuclei  
20  
21 contributing to the signals which makes the quantitative analyses of species possible  
22  
23 without calibration requirements.<sup>27, 34</sup>  
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26  
27 Previously, <sup>13</sup>C NMR spectra of carbon dioxide in water were reported by Abbott  
28  
29 et al.<sup>37</sup> and in aqueous NH<sub>3</sub> solutions were discussed by Mani et al.<sup>38</sup> In spite of its  
30  
31 practical importance and high potentiality, the application of <sup>13</sup>C NMR spectroscopy in  
32  
33 the quantification of the species involved in CO<sub>2</sub> loaded aqueous amine- systems<sup>28</sup> has  
34  
35 rarely reported due to the convenience of pH + NMR combined analysis.  
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40 While the concentrations of CO<sub>2</sub>-species can be evaluated by NMR method, the  
41  
42 amount of free and protonated amines can be calculated from the K<sub>a</sub> and the pH,<sup>39</sup> where  
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44 the definition of pH is in Eq. 1. Many improvements have been performed on this  
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46 technique to make it widely applied by researchers. Stadie et al.<sup>40</sup> calculated the total  
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48 amount of CO<sub>2</sub> as carbamate and bicarbonate in whole blood by using the pH value and  
49  
50 the equilibrium constant. Fan et al.<sup>41</sup> calculated the concentration of hydrogen ion from  
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52 the pH value. However, one of the drawbacks of this method is that it is only suitable  
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54 for aqueous solutions, and for a restricted range of operating temperatures (293~308  
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4 K).<sup>42</sup>  
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$$6 \quad \text{pH} = -\log([H^+]) \quad (1)$$

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9 The popular thermodynamic models, including Kent-Eisenberg (K-E),<sup>43</sup>  
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11 Deshmukh-Mather (D-M),<sup>44</sup> and E-NRTL models,<sup>45</sup> can help scientists to predict  
12  
13 important parameters for CO<sub>2</sub> capture processes.<sup>46</sup> The K-E model<sup>43</sup> can be employed  
14  
15 to calculate the equilibrium constants which is a function of temperature T (Eq. 2),<sup>47</sup>  
16  
17 where the vapor-liquid equilibrium (VLE) model is applied to simulate ammonium  
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19 speciation.<sup>48</sup>  
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23

$$24 \quad \ln K_p = \frac{-5851.11}{T} - 3.3636 \quad (2)$$

25  
26  
27 In the present review we have decided to discuss and compare critically the  
28  
29 utilization of these three popular techniques, namely NMR spectroscopy, pH + NMR  
30  
31 combination and model predictions, for the speciation analysis during CO<sub>2</sub> capture  
32  
33 processes with amine-based sorbents. This review offers a broad overview of all types  
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35 of applications of these techniques, evaluating both strengths and weaknesses for  
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37 various amine systems.  
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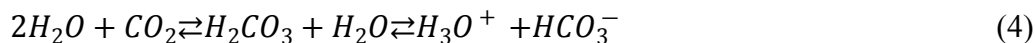
## 43 ■ Chemical equilibria in amine-CO<sub>2</sub>-H<sub>2</sub>O systems

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46  
47 Based on the types of ions generated during the reaction of amines with CO<sub>2</sub>, the  
48  
49 following chemical reactions may occur (where Am denotes a general amine).  
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53 Dissociation of water:



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58 Dissociation of dissolved CO<sub>2</sub> through carbonic acid:  
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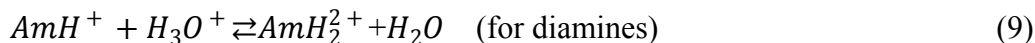
Bicarbonate formation:



Carbonate formation:



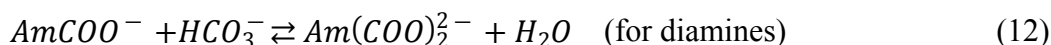
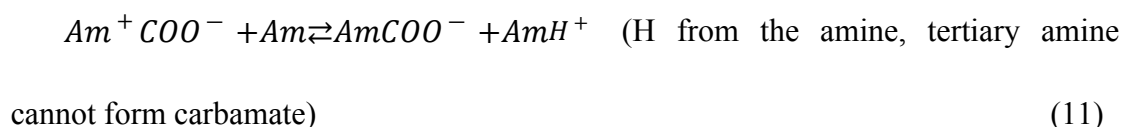
Protonated amine formation:



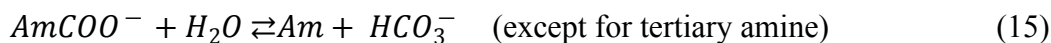
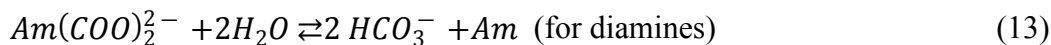
Zwitterion formation:



Carbamate formation:

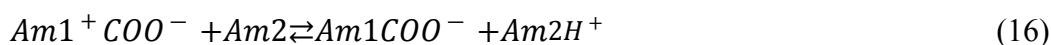


Hydrolysis of carbamate:



In amine blends systems, two (or more) amines could have a synergistic interaction during the CO<sub>2</sub> 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<sup>+</sup>) generated and released by Am1, thus promoting the formation of Am1 carbamate:



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

## ■ Single amine-CO<sub>2</sub>-H<sub>2</sub>O systems

### Primary and secondary amine solvents

The reactions of non-hindered primary and secondary amines with CO<sub>2</sub> 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.<sup>33, 49</sup> On the contrary, the reactions of CO<sub>2</sub> 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.<sup>41</sup> performed qualitative and quantitative analyses of the species in the CO<sub>2</sub>-MEA-H<sub>2</sub>O system using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy: where MEA denotes mono-ethanolamine, the most popular and one of the cheapest amine solvents used for CO<sub>2</sub> capture process.<sup>50, 51</sup> According to their study, the MEA/MEA<sup>+</sup> peaks shift down field while the carbamate peaks shift up field upon CO<sub>2</sub> absorption in the <sup>1</sup>H NMR

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4 spectrum due to the acidity increasing. However, the peaks of MEA/MEA<sup>+</sup> in the <sup>13</sup>C  
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6 NMR spectrum shift to higher field, while the carbamate peaks remain almost  
7  
8 unchanged.

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11 Lv et al.<sup>52</sup> carried out a detailed investigation on CO<sub>2</sub> absorption and desorption  
12 mechanisms within the CO<sub>2</sub>-MEA-H<sub>2</sub>O system by analyzing the reaction intermediates  
13  
14 under different CO<sub>2</sub> loadings using <sup>13</sup>C NMR spectroscopy. The authors found the  
15  
16 absorption process starting from the formation of MEA-carbamate based on the  
17  
18 zwitterionic mechanism and followed by the formation of carbonate and bicarbonate  
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20 via the hydration of CO<sub>2</sub> and the hydrolysis of the carbamate. The NMR study allowed  
21  
22 the authors to analyze the CO<sub>2</sub>-MEA-H<sub>2</sub>O system over high CO<sub>2</sub> loading values: the  
23  
24 lower stability of carbamate was found with the higher CO<sub>2</sub> loading as the carbamate  
25  
26 was easily hydrolyzed to carbonate and bicarbonate by H<sup>+</sup> at higher CO<sub>2</sub> loading  
27  
28 amount. Similar results have also been found by other authors.<sup>10,19</sup>

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38 A complete species analysis based on <sup>13</sup>C NMR in the different amine systems has  
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40 been performed by Barzagli et al.<sup>28,53</sup> The amine solutions were tested including MEA,  
41  
42 AMP, diethanolamine (DEA), and 2-(methylamino)ethanol (MMEA) with different  
43  
44 concentrations. Moreover, the data collected from the spectra has been correlated with  
45  
46 the CO<sub>2</sub> capture performances of the different sorbents. García-Abuín et al.,<sup>54</sup> carried  
47  
48 out an accurate <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic study to evaluate the products formed  
49  
50 upon CO<sub>2</sub> uptake in aqueous pyrrolidine solution: as a finding, at the beginning of the  
51  
52 CO<sub>2</sub> absorption, the amount of carbonate and carbamate formed indicated a  
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54 stoichiometric ratio 2:1 (amine:CO<sub>2</sub>). The carbamate stability decreased with increasing  
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4 the CO<sub>2</sub> loading as pyrrolidine is a sterically hindered amine, and more bicarbonate was  
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6 produced. Consequently, an increase in free amine concentration was observed. Finally,  
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8 at the end of the process, the stoichiometric ratio was 1:1, and the carbon dioxide  
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10 capture capacity was enhanced.  
11  
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13  
14 Wang et al.<sup>55</sup> used MEA/sulfolane aqueous solvent with a phase interchanging  
15  
16 function to capture CO<sub>2</sub>: in this kind of sorbents, two immiscible liquid phases (upper  
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18 and lower phase) are formed after CO<sub>2</sub> absorption. <sup>13</sup>C NMR analysis revealed that the  
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20 most of CO<sub>2</sub> species exists in the upper phase rather than the lower phase.  
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23  
24 In order to investigate a new primary amine based solvent, aqueous 4-  
25  
26 aminomethyltetrahydropyran (4-AMTHP), Li et al.<sup>56</sup> used potentiometric titrations in  
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28 the absence of CO<sub>2</sub> to determine the protonation constants (larger protonation constants  
29  
30 means better reactivity toward CO<sub>2</sub>) for the reaction:  
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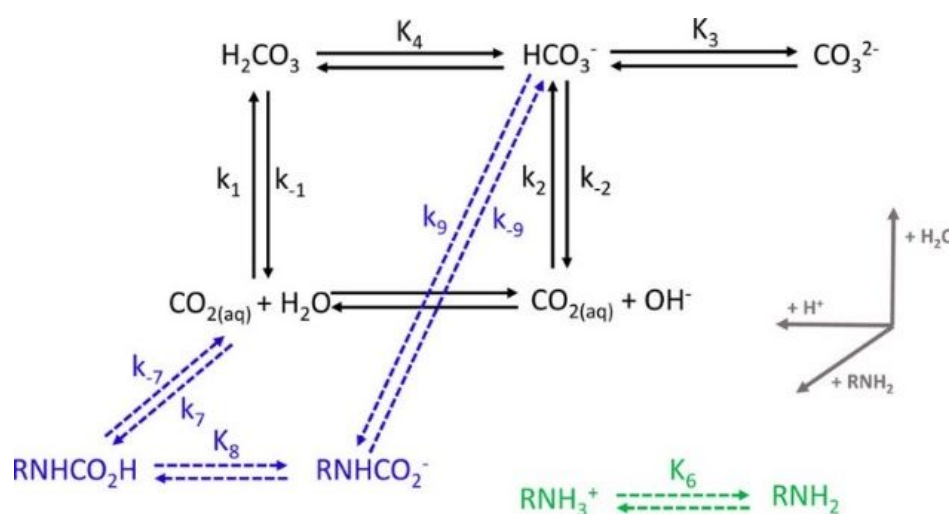


34  
35 The full reaction scheme of the system is described in Figure 1, where RNH<sub>2</sub> represents  
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37 4-AMTHP.  
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43 Martin et al.<sup>57</sup>, taking MEA as an example, employed total alkalinity titration  
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45 measurement with strong base to measure the concentration of (bi)carbonate,  
46  
47 protonated amine, carbamate, total inorganic carbon content and free amine. The  
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49 presence of bicarbonate in the solution influences the free amine concentration, which  
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51 is a positive correlation function of CO<sub>2</sub> loading. The investigators also predicted  
52  
53 activity coefficient with Aspen Plus ENRTL-RK model, and the results showed that the  
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55 pH values measured in experiments matched those predicted with the Aspen Plus.<sup>58</sup>  
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Moreover, total carbon and  $\text{HCO}_3^-$  calculated by Matin et al.<sup>57</sup> were compatible with the data presented by Jakobsen et al.<sup>59</sup> and with the Aspen Plus predictions<sup>58</sup>.

The equilibrium constants  $K(T)$  could be obtained with Kent and Eisenberg model<sup>43</sup> to determine the ratio of free and protonated MEA.<sup>41</sup> Luo et al.<sup>60</sup> carried out a comparison between three different models (KE, e-NRTL and UNIQUAC), for the  $\text{CO}_2$  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.<sup>61</sup>



**Figure 1.** The reaction scheme of the primary amine and  $\text{CO}_2$ . Reprinted with permission from ref.<sup>56</sup> Copyright 2017 American Chemical Society.

## Tertiary amine solvents

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

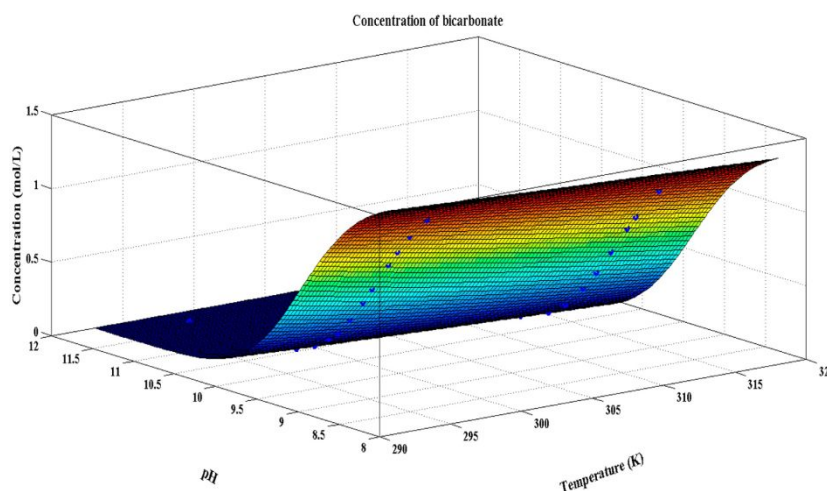
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4 for this reason they cannot form carbamates and the only product of the reaction with  
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6 CO<sub>2</sub> is (bi)carbonate. Due to their different reaction mechanism, tertiary amines  
7  
8 generally present slower CO<sub>2</sub> reaction rates and lower energy requirement for the  
9  
10 regeneration compared to primary/secondary amines.<sup>62</sup> It has been proposed by  
11  
12 Donaldson et al.<sup>63</sup> that tertiary amines do not react with CO<sub>2</sub> directly but catalyze the  
13  
14 hydration reaction of CO<sub>2</sub>.<sup>64</sup>  
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19  
20 Zhang et al.<sup>65</sup> investigated the HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> formation at various CO<sub>2</sub> loadings  
21  
22 by mean of <sup>13</sup>C NMR method. The concentrations of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> as a function of  
23  
24 CO<sub>2</sub> loadings for 1 M aqueous solutions of 1-dimethylamino-2-propanol (1DMA2P)  
25  
26 and methyl diethanolamine (MDEA) were plotted. As a result, it was showed that the  
27  
28 concentrations of HCO<sub>3</sub><sup>-</sup> continuously increased, while that of CO<sub>3</sub><sup>2-</sup> increased to a  
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30 maximum value, and then stepped down as the CO<sub>2</sub> loading increased.  
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36 Three-dimensional (3D) plots of species formed for the 1DMA2P-CO<sub>2</sub>-H<sub>2</sub>O  
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38 system at different temperatures and concentrations were described carefully by Liang  
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40 et al.<sup>64</sup> by using pH method combined with mass balance, charge balance, and  
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42 equilibrium constant calculations. As an example of their results, in Figure 2 we report  
43  
44 the 3D profile obtained for HCO<sub>3</sub><sup>-</sup> concentration.  
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49 The Liang et al.<sup>64</sup> used K-E model to predict the CO<sub>2</sub> loadings in tertiary amine  
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51 systems, while Liu et al.<sup>42</sup> applied K-E model to get equilibrium constant K. The K-E  
52  
53 model was also chosen by Luo et al.<sup>60</sup> to predict VLE for the DEEA-CO<sub>2</sub>-H<sub>2</sub>O system  
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55 (DEEA = diethyl ethanolamine). The reported models (K-E, Austgen, Li-Sheng, Hu-  
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57 Chakma, and Liu et al.) well described the equilibrium solubility of CO<sub>2</sub> in 1DMA2P  
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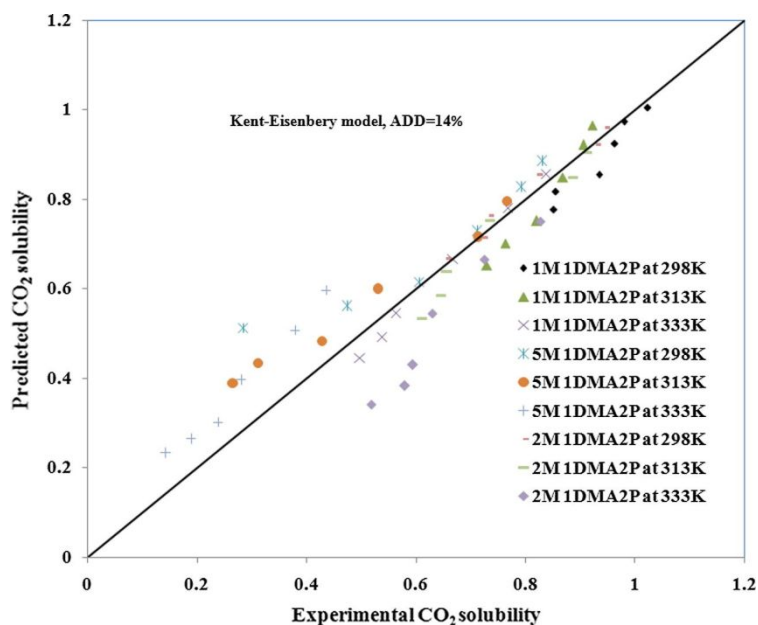
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4 solution, with absolute average deviations (AADs) comprised between 6.3 and 15 %.<sup>66</sup>  
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7 Among them, the models developed by Hu-Chakma and Liu in separate studies  
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9 predicted the solubility of CO<sub>2</sub> in 1DMA2P better than others since more parameters  
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11 were considered. The K-E model applied to calculate CO<sub>2</sub> solubility at equilibrium is  
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13 plotted in Figure 3.



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33 **Figure 2.** The 3D profile of HCO<sub>3</sub><sup>-</sup> concentration in CO<sub>2</sub> loaded 1DMA2P

34 solution. Reprinted with permission from ref.<sup>42</sup> Copyright 2015 American Chemical

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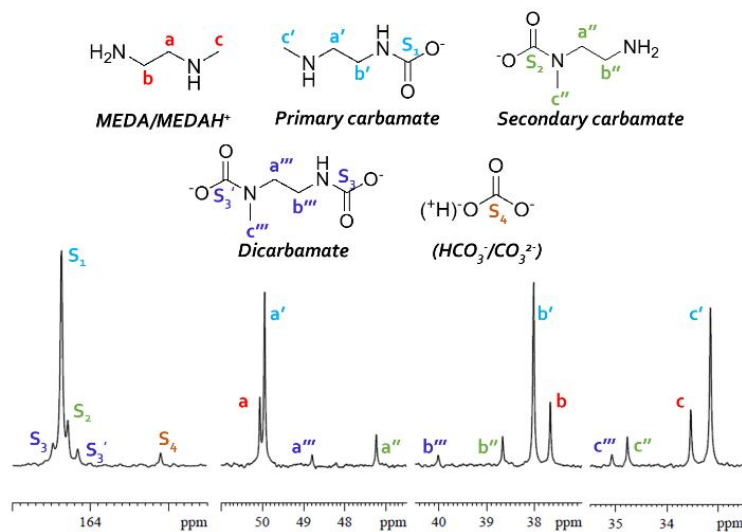
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4 **Figure 3.** Comparison of the solubility of CO<sub>2</sub> determined by K-E model and  
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6 experiments. Reprinted with permission from ref.<sup>66</sup> Copyright 2017 ELSEVIER.  
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## 10 **Polyamine solvents**

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14 The name polyamine identifies a class of compounds containing two or more  
15 amino groups. In this review, we mainly discuss diamines.  
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18  
19 N-Methylethylenediamine (MEDA) is one of the most common diamines, which  
20 contains a primary and a secondary amino groups: the speciation of its aqueous solution  
21 after CO<sub>2</sub> uptake was studied by Zhang et al.<sup>67</sup> by using <sup>13</sup>C NMR spectroscopy (Figure  
22 4). As a finding, they reported the formation of three different species, in addition to  
23 bicarbonate: the primary carbamate which is formed on the primary amino group, the  
24 secondary carbamate formed on the secondary amino group, and the dicarbamate.  
25  
26 Moreover, the authors observed that both secondary carbamate and dicarbamate convert  
27 into primary carbamate (the primary carbamates of some diamines tend to hydrolyze  
28 into HCO<sub>3</sub><sup>-</sup>) when increasing the CO<sub>2</sub> loading, and the order of the concentration of  
29 carbamates follows the order primary-carbamate >> secondary-carbamate >  
30 dicarbamate.  
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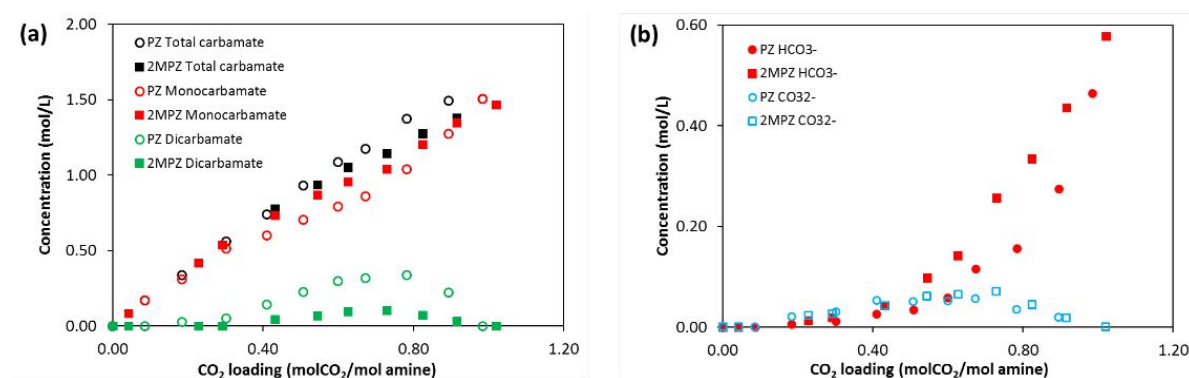
**Figure 4.** The  $^{13}\text{C}$  NMR spectrum of  $\text{CO}_2$  loaded MEDA aqueous solution ( $\alpha=0.93$  mol- $\text{CO}_2$ /mol-amine). Reprinted with permission from ref.<sup>67</sup> Copyright 2018 ELSEVIER.

The amine- $\text{CO}_2$ - $\text{H}_2\text{O}$  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.<sup>68</sup> using  $^{13}\text{C}$  and  $^1\text{H}$  NMR. Their work indicates that higher  $\text{CO}_2$  partial pressures, longer carbon-chain length and more substituent on N-atom favor the formation of bicarbonate in all diamines.

$^{13}\text{C}$  NMR analysis was used by Zhang et al.<sup>65</sup> to evaluate the effects of inter- and intra-molecular tertiary amino groups on a primary amino group during the  $\text{CO}_2$  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<sub>2</sub> absorption, is widely applied as a absorption rate promoter in blended amines.<sup>69</sup> Safdara et al.<sup>70</sup> conducted a series of experiments to study the CO<sub>2</sub> 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<sub>2</sub> loading capacity for PZ solution improves at high pressure and low temperature. By using NMR spectroscopy, Zhang et al.<sup>71</sup> quantitatively analyzed the species formed (monocarbamate, dicarbamate, bicarbonate and carbonate) at 298 K in 2M PZ and 2M 2MPZ (2-methylpiperazine) aqueous solutions with different CO<sub>2</sub> loadings ( Figure 5).



**Figure 5.** Formation of (a) carbamate, and (b) HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> in PZ and 2MPZ solution with different CO<sub>2</sub> loadings. Reprinted with permission from ref.<sup>71</sup> Copyright 2018

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4 Figure 5a demonstrates that PZ produces more carbamates ( mono-carbamate and  
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6 dicarbamate summed together) with respected to 2MPZ: in fact, the dicarbamate of  
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8 2MPZ is unstable, because of the steric hindrance due to the methyl substituent in the  
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10  $\alpha$  position. The bicarbonate in solution was mainly generated from the conversion of  
11  
12 carbonate and the decomposition of carbamate. As reported in Figure 5b, more  
13  
14 bicarbonate was produced from the decomposition of dicarbamate in the 2MPZ system  
15  
16 due to its lower stability than PZ dicarbamate. Moreover, the conversion of carbonate  
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18 is almost negligible, as confirmed by the almost equaled concentrations of carbonates  
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20 in PZ and 2MPZ solutions, as shown in Figure 5b.  
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27 Liu et al.<sup>72</sup> applied  $^{13}\text{C}$  NMR spectroscopy to track the specciation in in aqueous  
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29 triethylenetetramine (TETA) during the whole  $\text{CO}_2$  capture process, including  
30  
31 absorption and desorption. As a finding, during the absorption process the NMR peaks  
32  
33 of carbamates were between 163.5 and 164.5 ppm, while  $\text{CO}_3^{2-}/\text{HCO}_3^-$  were at 160.3  
34  
35 ppm. The shifts mentioned here were not contributed by single peaks but by peak  
36  
37 clusters because TETA has four amine groups. During the desorption, it was observed  
38  
39 that the peak intensity of  $\text{CO}_3^{2-}/\text{HCO}_3^-$  decreased until it disappears, while the peak  
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41 intensities of the carbamates decreased but were still present when the desorption  
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43 process ended.  
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51 According to the pH measurements carried out by Bencini et al.,<sup>73</sup> the  $\text{pK}_{\text{a}1}$  of 4-  
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53 amino-1-methylpiperidine (4-A1MPD) was 10.02, while the  $\text{pK}_{\text{a}1}$  of 4-amino-1-  
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55 propylpiperidine (4-A1PPD) was 10.22. Instead, the  $\text{pK}_{\text{a}2}$  was the same for both the  
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57 amines, 7.46 at 298 K. Although the substituents on both tertiary amines are different,  
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4 the pKa<sub>1</sub> values only showed a very small difference, and by the consequence the  
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6 difference in the amount of formed HCO<sub>3</sub><sup>-</sup> was negligible. As for linear diamines,<sup>18</sup> the  
7  
8 pKa<sub>1</sub> of N, N-dimethyl-1,2-ethanediamine (N,N-DM12EDA) and N,N-dimethyl-1,3-  
9  
10 propanediamine (N,NDM13PDA) are 9.69 and 10.34 while the pKa<sub>2</sub> are 6.46 and 8.17,  
11  
12 respectively. The lower pKa<sub>2</sub> value for N,N-DM12EDA is due to the shorter distance  
13  
14 between amino groups: the first protonated amino group acts as a suppressor for the  
15  
16 protonation of the second amino group it is why there is a much lower pKa<sub>2</sub>. In  
17  
18 comparison with MEA, the cyclic structure significantly reduces the formation of  
19  
20 carbamate and boosts the formation of HCO<sub>3</sub><sup>-</sup> during CO<sub>2</sub> uptake, which was verified  
21  
22 by the species profiles in amine solutions detected with NMR spectroscopy.<sup>18</sup>  
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30 Speciation for the CO<sub>2</sub> absorption of at 343.15 K into 0.3 M aqueous PZ solution  
31  
32 was conducted by Kadiwala et al.<sup>74</sup> by using Electrolyte-NRTL model. The authors  
33  
34 found an interesting correlation between the concentration of the carbonate ion [CO<sub>3</sub><sup>2-</sup>]  
35  
36 in solution and the amount of captured CO<sub>2</sub>: [CO<sub>3</sub><sup>2-</sup>] was high at loading values in the  
37  
38 range 0.1-0.6, while it quickly decreased at loading values between 0.6 and 1.5; finally,  
39  
40 for loading values higher than 1.5, the carbonate concentration did not vary  
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42 substantially, indicating that the loading increase was mainly due to physical absorption.  
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48 Pashaei et al.<sup>75</sup> justified with the penetration models for the mass transfer flux that  
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50 the absorption efficiency increased with increasing stirring speed. After investigating  
51  
52 five different types of single amines including PZ with K-E modelling, Hwang et al.<sup>76</sup>  
53  
54 concluded that the VLEs of the single amines fit well to K-E model. Zhang et al.<sup>68</sup>  
55  
56 applied Gaussian software to develop a computational modeling in which the effect of  
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4 varying chain length on the stability of mono-carbamate was simulated. The results  
5  
6 obtained from the experimental, together with the quantum chemistry calculations,  
7  
8 proved that carbamates formed from zwitterions with C<sub>2</sub> chains were energetically more  
9  
10 difficult than from those containing C<sub>3</sub> chains. In another paper of the same group,<sup>65</sup>  
11  
12 the empirical model predicted CO<sub>2</sub> equilibrated solubility at different temperatures with  
13  
14 various CO<sub>2</sub> partial pressures within acceptable average absolute deviations compared  
15  
16 to the experimental data. In this model, the CO<sub>2</sub> equilibrium solubility was approved as  
17  
18 a function of temperature and CO<sub>2</sub> partial pressure.  
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24 All researches mentioned in this section are summarized in Table 1.  
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**Table 1.** Summary of single amine-CO<sub>2</sub>-H<sub>2</sub>O systems

Type	Absorbent	Author	Technology	Contribution
Primary/ Secondary amine	MEA	Fan et al. <sup>41</sup>	1. <sup>1</sup> H and <sup>13</sup> 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. <sup>52</sup>	<sup>13</sup> C NMR	Evaluation of the mechanism on CO <sub>2</sub> absorption and desorption
	MEA, AMP, DEA and MMEA	Barzagli et al. <sup>28, 53</sup>	<sup>13</sup> C NMR	Preformed species analysis.
	Pyrrolidine aqueous	García-Abuín et al. <sup>54</sup>	<sup>1</sup> H and <sup>13</sup> C NMR	Developed experiment procedure and the speciation in this reaction.
	MEA + sulfolane	Wang et al. <sup>55</sup>	<sup>13</sup> C NMR	Qualitative analysis of the two different phases of a phase-change sorbent
	4-AMTHP	Li et al. <sup>56</sup>	Potentiometric titrations	Determined protonation constants.
	MEA	Naser et al. <sup>57</sup>	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. <sup>60</sup>	KE, e-NRTL and UNIQUAC	Carried out a comparison between three different model.
	MEA	Preez, L. J., et al. <sup>61</sup>	Full and simplified version of the VLE model	Predicted the concentrations for all ions.
Tertiary amine	1DMA2P, MDEA	Zhang et al. <sup>65</sup>	<sup>13</sup> C NMR	Determined the concentration profiles of bicarbonates and carbonates in aqueous solutions.
	1DMA2P	Liang et al. <sup>64</sup> and Liu et al. <sup>42</sup>	1. pH + NMR method 2. K-E model	1. Developed ions (1DMA2P, 1DMA2PH <sup>+</sup> , HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> ) speciation plots of two-dimensional (2D) and three-dimensional (3D).

				<ol style="list-style-type: none"> <li>2. Calculated the solubility of CO<sub>2</sub> in tertiary amine systems by Liang et al.</li> <li>3. Get equilibrium constant K by Liu et al.</li> </ol>
	DEEA	Luo et al. <sup>60</sup>	K-E model	Predicted vapor-liquid equilibrium and Henry constant.
	1DMA2P	Liu et al. <sup>66, 77</sup>	Model developed by Kent-Eisenberg, Austgen, Li-Sheng, Hu-Chakma and Liu et al. successively	Determined the equilibrium solubility of CO <sub>2</sub> and the solubility constant of N <sub>2</sub> O.
Polyamines	MEDA	Zhang et al. <sup>67</sup>	<sup>13</sup> C NMR	Analyze the speciation.
	MEDA, MAPA, DMAEA and DMAPA	Zhang et al. <sup>68</sup>	<ol style="list-style-type: none"> <li>1. <sup>1</sup>H and <sup>13</sup>C NMR</li> <li>2. computational model</li> </ol>	<ol style="list-style-type: none"> <li>1. Identified and quantify species.</li> <li>2. Explained the effect of the chain length on the stability.</li> </ol>
	DEAPA	Zhang et al. <sup>65</sup>	<ol style="list-style-type: none"> <li>1. <sup>13</sup>C NMR</li> <li>2. Empirical model</li> </ol>	<ol style="list-style-type: none"> <li>1. Determined the effect of the intra- and inter-molecular tertiary amino groups.</li> <li>2. Described the trend observed in experiments.</li> </ol>
	PZ and 2MPZ	Zhang et al. <sup>71</sup>	<sup>13</sup> C NMR	Compared the amount of each ions and analyze the reasons for its difference.
	TETA	Liu et al. <sup>72</sup>	<sup>13</sup> C NMR	Observed its speciation during the process of CO <sub>2</sub> capture.
	4-A1MPD and 4-A1PPD	Bencini et al. <sup>73</sup>	pH measurements	Establish relationship between pKa and bicarbonate formation.
	N, N-DM12EDA and N, NDM13PDA	Xiao et al. <sup>18</sup>	pH measurements and NMR spectroscopy	Detected species profiles.
	Piperazine solutions	Kadiwala et al. <sup>74</sup>	Electrolyte-NRTL model	Determined Speciation during the absorption process.
	PZ	Pashaei et al. <sup>75</sup>	Penetration models	Determined absorption efficiency.
Five different types of single amines including	Hwang et al. <sup>76</sup>	K-E models	VLE model matches the K-E models.	



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## ■ Blended amine-CO<sub>2</sub>-H<sub>2</sub>O 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.<sup>78</sup> To avoid these shortcomings of single amines, mixtures of primary, secondary, tertiary, and heterocyclic amines attracted attentions.<sup>79</sup> Typically, the blend consists of: (a) a primary or secondary amine, capable of quickly react with CO<sub>2</sub> to form carbamate and (b) a strongly alkaline amine, usually a sterically hindered or tertiary amine, capable of accepting the proton (H<sup>+</sup>) generated and released from the reaction of the other amine in its reaction with CO<sub>2</sub>, 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.<sup>80</sup> 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.<sup>28</sup> The improved performances of the blended amines in comparison with individual amines were explained on the bases of cooperative effects disclosed by <sup>13</sup>C NMR analysis, pH + NMR methods, and model prediction as below.

### Dual-amine systems

Liu et al.<sup>72</sup> studied the CO<sub>2</sub> uptake in TETA-AMP-H<sub>2</sub>O system by using <sup>13</sup>C NMR spectroscopy, they found that both TETA and AMP carbamates were formed at the very early stage of the CO<sub>2</sub> uptake. As the loading increased, the CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup> signal appeared, grew and moved from 162.9 to 160.6 ppm: this indicates that carbamates (in

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3 particular AMP carbamate, with low stability) hydrolyzed to form bicarbonate, which  
4 therefore increased its concentration in solution. During the regeneration step, the  
5 intensity of  $\text{CO}_3^{2-}/\text{HCO}_3^-$  peak decreased until it disappeared while those of carbamates  
6 were still present after the desorption completion.  
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12 The species formed in MEA-based blends, in particular MEA-1DMA2P and  
13 MEA-MDEA, were investigated at different  $\text{CO}_2$  loadings (at 293.15 K) by using  $^{13}\text{C}$   
14 NMR spectroscopy by Zhang et al.,<sup>65</sup> and the results compared with the speciation of  
15 the single amine solutions. After detailed discussion, it was noted that MEA reacts  
16 more easily with  $\text{CO}_2$  than tertiary amines. When MEA is added into a tertiary amine  
17 system, the production of the  $\text{CO}_3^{2-}/\text{HCO}_3^-$  ions from the tertiary amine is inhibited.  
18 Conversely, tertiary amines can promote the formation of  $\text{CO}_3^{2-}/\text{HCO}_3^-$  from MEA at  
19 a lower  $\text{CO}_2$  loading ratio.  $\text{HCO}_3^-$  plays an important role in amine regeneration,  
20 depending on  $\text{CO}_2$  loading, formulation ratio and the operating conditions. Using NMR  
21 spectroscopy to determine the species of MEA-4-diethylamino-2-butanol (DEAB)  
22 solutions, Yu et al.<sup>81</sup> found that with the rise in temperature from 297 to 363 K, the  
23  $\text{HCO}_3^-$  concentration demonstrate a remarkable increases, and the  $^{13}\text{C}$  signal can be  
24 detected at a relative low  $\text{CO}_2$  loading stage (0.25).  
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42 Ciftja et al.<sup>82</sup> investigated the aqueous DEEA/MAPA blend, a phase-change  
43 sorbent, by NMR quantitative speciation. They found that the lower phase was  
44 contained most of  $\text{CO}_2$  and MAPA (a diamine with a primary and a secondary amine  
45 group), while the upper phase was lean in  $\text{CO}_2$  and rich in the tertiary amine DEEA.  
46 Furthermore, they found that by raising the partial pressure, the DEEA/MAPA ratio  
47 increased in the lower phase and simultaneously decreased in the upper phase.  
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56 Another phase-change sorbent, aqueous DETA-PMDETA, has been reported by  
57 Ye et al.<sup>83</sup> The  $^{13}\text{C}$  NMR analysis allowed the identification and quantification of the  
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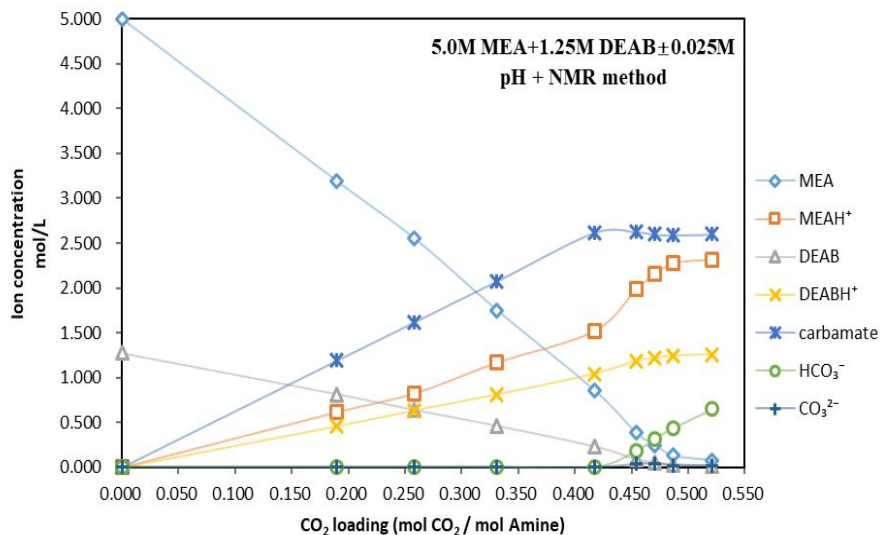
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3 species in both phases to get information for best understanding to the mechanisms and  
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5 reaction pathways. They observed that, during the uptake, CO<sub>2</sub> firstly reacted with  
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7 DETA in the lower phase and then formed bicarbonate and carbonate ions via the  
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9 protonation of PMDETA.  
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12 The quantitative results of MEA-DEAB-CO<sub>2</sub>-H<sub>2</sub>O system were successfully  
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14 obtained using pH + NMR analysis: eight samples of the blended amine solutions with  
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16 different CO<sub>2</sub> loadings were tested at room temperature and the results displayed in  
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18 Figure 6. The results showed that the pH + NMR method can be applied into a  
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20 quaternary MEA-DEAB-CO<sub>2</sub>-H<sub>2</sub>O.<sup>84</sup> The high concentration of carbamate ions was  
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22 caused by the high fraction of MEA in the solution (MEA was 5.0 M, DEAB 1.25 M).  
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24 In this system, the free MEA and free DEAB as two available proton acceptors exist at  
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26 the low CO<sub>2</sub> loading stages, while only MEA-proton-acceptor exists at the high CO<sub>2</sub>  
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28 loading stages because the free DEAB is consumed.  
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33 Used as an additive in the solutions of AMP, PZ can significantly enhance the  
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35 CO<sub>2</sub> absorption rate, as confirmed by Sun et al.<sup>85</sup> in hybrid reaction rate modelling. In  
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37 this model, CO<sub>2</sub> reacts with PZ following a second-order kinetics, while the reaction of  
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39 CO<sub>2</sub> with AMP fits in the zwitterion mechanism. At higher temperatures and PZ  
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41 concentrations, the apparent reaction rate constant ( $k_{app}$ ), increases, with an overall  
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43 absolute percentage deviation of  $k_{app}$  of 7.7%.  
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47 The calculation of the concentration of HCO<sub>3</sub><sup>-</sup> in MEA-DEAB-CO<sub>2</sub>-H<sub>2</sub>O system  
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49 is complicated, but it could be obtained via simulation with. The electrolyte nonrandom-  
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51 two-liquid model (e-NRTL), suitable for this utilization as it employs multiple  
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53 equilibria and mass balance rules.<sup>81</sup> Equilibrium behavior in aqueous solutions of MEA,  
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55 benzylamine (BZA), and their blends was predicted by Conway et al.<sup>86</sup> using a model  
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57 programmed in MATLAB. The modelling approach undertaken, however, was  
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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.



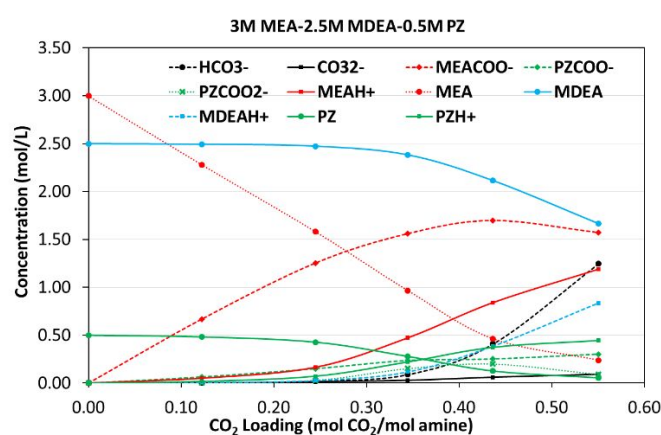
**Figure 6.** the quantitative results of MEA-DEAB-CO<sub>2</sub>-H<sub>2</sub>O system by using pH + NMR combined analysis. Reprinted with permission from ref.<sup>84</sup> Copyright 2014 American Chemical Society.

## Trio-amine systems

Researches on the formation of species in trio-amine blends are rather scarce,<sup>87</sup> and only a few examples are found in the literature. <sup>13</sup>C NMR technique was adopted to analyze CO<sub>2</sub> loaded MEA-AMP-PZ samples with different CO<sub>2</sub> loadings at 298 K: the possible species and the corresponding assignments of <sup>13</sup>C peaks were discussed by Zhang et al.<sup>88</sup> A higher AMP/PZ ratio in this trio-amine blends favors the production of more HCO<sub>3</sub><sup>-</sup> and less carbamate. Moreover, AMP-carbamates were not found during the CO<sub>2</sub> uptake in any triple-solvent blended systems because the unstable AMP-carbamates can quickly hydrolyze to produce HCO<sub>3</sub><sup>-</sup>.

MEA, MDEA and PZ were selected to compose a trio-amine blends by Zhang et al.<sup>89</sup> for CO<sub>2</sub> capture and release studies. The possibly produced species shown were MEA, MEAH<sup>+</sup>, MEA-COO<sup>-</sup>, MDEA, MDEAH<sup>+</sup>, PZ, PZH<sup>+</sup>, PZ-COO<sup>-</sup>, PZ-di-COO<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, which were analyzed by <sup>13</sup>C NMR technology together with pH measurements. The PZH<sub>2</sub><sup>2+</sup> ion, containing two positive charges, was not stable and its concentration was negligible.

The ion concentrations changing with the CO<sub>2</sub> loadings is plotted in Figure 7.



**Figure 7.** The speciation results of MEA-MDEA-PZ with various of CO<sub>2</sub> loadings. Reprinted with permission from ref.<sup>89</sup> Copyright 2017 ELSEVIER

It has universally been accepted that CO<sub>2</sub> desorption mainly entails the decomposition of HCO<sub>3</sub><sup>-</sup> and carbamate ions. Different CO<sub>2</sub>-rich solutions could be expressed by CO<sub>2</sub> desorption kinetic model such as Avrami's fractional-order kinetic model which may be the best fitting model. As reported by Liu et al.,<sup>90</sup> 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<sub>2</sub>-H<sub>2</sub>O systems

Type	Absorbent	Author	Technology	Contribution
Dual-amine systems	TETA-AMP-H <sub>2</sub> O	Liu et al. <sup>72</sup>	<sup>13</sup> C NMR	The peaks of ions.
	MEA-1DMA2P and MEA-MDEA	Zhang et al. <sup>65</sup>	<sup>13</sup> C NMR	Ions concentration profiles.
	MEA-DEAB	Yu et al. <sup>81</sup>	<sup>13</sup> C NMR	Ion speciation plots.
	DEEA-MAPA	Ciftja et al. <sup>82</sup>	<sup>13</sup> C NMR	Qualitative and quantitative analysis in a phase-change sorbent
	DETA-PMDETA	Ye et al. <sup>83</sup>	<sup>13</sup> C NMR	Determination of mechanisms and reaction pathways in a phase-change sorbent
	MEA-DEAB	Shi et al. <sup>84</sup>	pH + NMR methods	Speciation plots.
	AMP-PZ	Sun et al. <sup>85</sup>	A hybrid reaction rate model	PZ can significantly increase the CO <sub>2</sub> absorption rate.
	MEA-DEAB	Liu et al. <sup>87</sup>	E-NRTL	Governing the complex CO <sub>2</sub> -amine interactions.
Trio-amine systems	MEA-BZA	Conway et al. <sup>86</sup>	A modelling tool developed in MATLAB	Equilibrium behavior.
	MEA-AMP-PZ	Zhang et al. <sup>88</sup>	<sup>13</sup> C NMR	Speciation during the process of CO <sub>2</sub> capture.
	MEA-MDEA-PZ	Zhang et al. <sup>89</sup>	<sup>13</sup> C NMR together with pH method	Evaluating possible produced species.
	MEA-MDEA-AMP	Liu et al. <sup>90</sup>	Avarami's fractional-order kinetic model	CO <sub>2</sub> desorption kinetic.

## ■ Nonaqueous systems

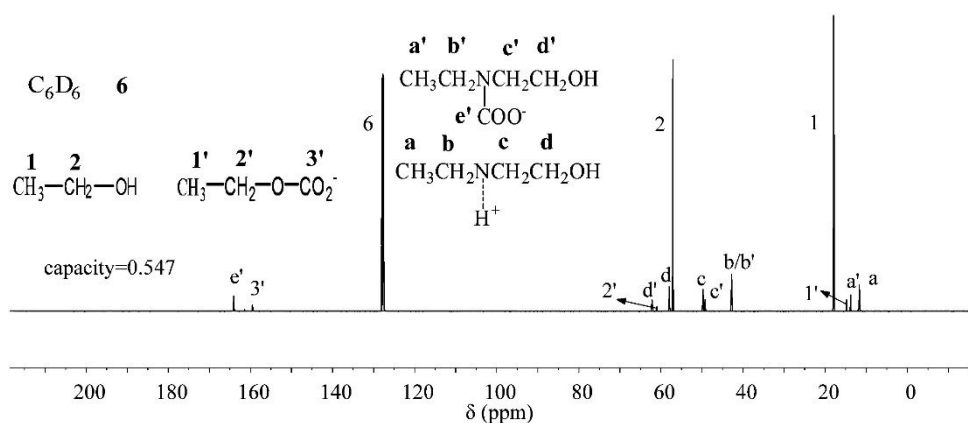
In recent years, interest has grown in using nonaqueous amine solutions as sorbents for the CO<sub>2</sub> capture. The use of organic diluents instead of water redirects the reaction between CO<sub>2</sub> and amine towards less stable carbonated species: consequently, the temperatures required for 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.<sup>12, 91-93</sup> Recently, some common organic diluents including methanol, ethanol, ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) have been tested to replace water.<sup>72</sup> As reported in literature, the greater solubility of CO<sub>2</sub> in organic diluents compared to water could enhance the CO<sub>2</sub> 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.<sup>94, 95</sup> Moreover, organic solvents could generally cause less equipment corrosion and avoid foaming problems.<sup>94, 96</sup> 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

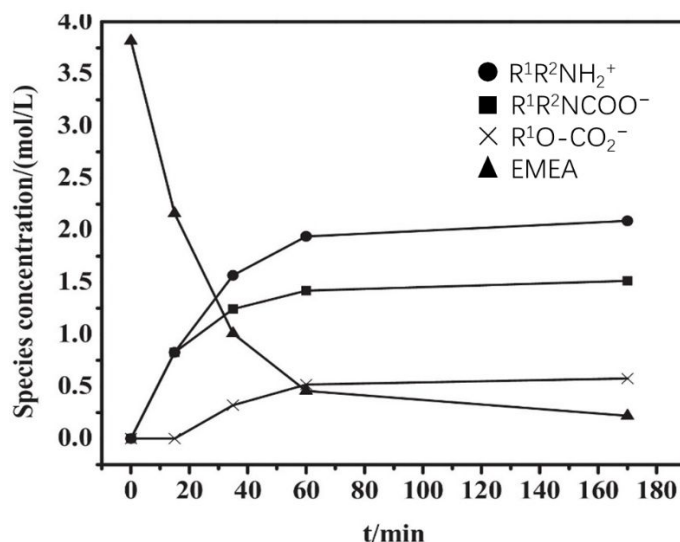
In TETA-ethanol system, Liu et al.<sup>72</sup> replaced water with ethanol and employed <sup>13</sup>C NMR to probe the speciation and reaction mechanism during absorption-desorption processes. The carbamates in this solution were detected at 163.8-164.4 ppm while the peak at 159.9 ppm did not identify to CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup>, since it could not have formed without the presence of water, but rather referred to the alkyl carbonate of C<sub>2</sub>H<sub>5</sub>OCO<sub>2</sub><sup>-</sup>.



Alkyl carbonates in different organic diluents are quite unstable species that could be generated during the absorption, when CO<sub>2</sub> is in significant excess with respect to amine, as demonstrated also from a <sup>13</sup>C NMR spectroscopic study carried out by Barzagli et al.<sup>13</sup> As C<sub>2</sub>H<sub>5</sub>OCO<sub>2</sub><sup>-</sup> is an unstable species, it quickly disappears during the desorption process; meanwhile, amine carbonates decrease but still exist.<sup>72</sup> Solutions of AMP in triethylene glycol dimethyl ether (TEGDME) and in N-methyl-2-pyrrolidone (NMP) were investigated by Svensson et al.<sup>97</sup> 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 <sup>13</sup>C NMR analysis has been applied by Chen et al.<sup>98</sup> to explore the species distribution in 2-(ethylamino) ethanol (EMEA) + ethanol solutions. The <sup>13</sup>C NMR spectrum for a CO<sub>2</sub> loading of 0.547 mol-CO<sub>2</sub>/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<sup>1</sup>O-CO<sub>2</sub><sup>-</sup> (from carbamate with CO<sub>2</sub>) and R<sup>1</sup>NHCH<sub>2</sub>CH<sub>2</sub>O-CO<sub>2</sub><sup>-</sup>, did not occur, and the final loading value remained low.



**Figure 8.** The qualitative analysis of CO<sub>2</sub>-loaded EMEA + ethanol solution (CO<sub>2</sub> loading = 0.547). Reprinted with permission from ref.<sup>98</sup> Copyright 2016 ELSEVIER.



**Figure 9.** Speciation profile of the CO<sub>2</sub> loaded EMEA- ethanol- at 313 K: ■, R<sup>1</sup>R<sup>2</sup>NCOO<sup>-</sup>; ●, R<sup>1</sup>R<sup>2</sup>NH<sub>2</sub><sup>+</sup>; ▲, EMEA; ×, R<sup>1</sup>O-CO<sub>2</sub><sup>-</sup>. Reprinted with permission from ref.<sup>98</sup> Copyright 2016 ELSEVIER.

Barzagli et al.<sup>83</sup> investigated some phase-change nonaqueous sorbents, in particular the secondary alkanolamines MMEA and EMEA in diethylene glycol diethyl ether (DEGDDE) as a diluent. The <sup>13</sup>C NMR experiments aimed at determining speciation showed that the upper phase was composed by the diluent DEGDDE 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 DEGDDE.

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.<sup>13, 91, 99</sup> devised a technique for chemical CO<sub>2</sub> 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). <sup>13</sup>C NMR analysis was applied to evaluate the distributions of the species in these solutions, and the results indicated that CO<sub>2</sub> was reversibly captured as mono-alkyl carbonates, R-OCO<sub>2</sub><sup>-</sup>, (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, CH<sub>2</sub>CH<sub>2</sub>OH, nC<sub>3</sub>H<sub>7</sub>), 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.<sup>72</sup> using <sup>13</sup>C NMR, was similar to TETA-ethanol system, however both carbamates of TETACO<sub>2</sub><sup>-</sup> and AMPCO<sub>2</sub><sup>-</sup> and the alkyl carbonate, C<sub>2</sub>H<sub>5</sub>OCO<sub>2</sub><sup>-</sup>, 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. <sup>72</sup>	<sup>13</sup> C NMR	Probed the speciation and reaction mechanism.
	AMP in EG/PrOH or in EG/DEGMME	Barzagli et al. <sup>13</sup>	<sup>13</sup> C NMR	Observed that alkyl carbonated of different organic diluents are quite unstable species.
	AMP-NMP or TEGDME	Svensson et al. <sup>97</sup>	<sup>13</sup> C NMR	Observed that a precipitate was formed during these experiments which was identified as the AMP carbamate.
	EMEA in ethanol	Chen et al. <sup>98</sup>	<sup>13</sup> C NMR	Provided species distribution.
	MMEA or EMEA in DEGDEE	Barzagli et al. <sup>94</sup>	<sup>13</sup> 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. <sup>13, 91, 99</sup>	<sup>13</sup> C NMR	Evaluated the distribution of the species.
	TETA- AMP in ethanol	Liu et al. <sup>72</sup>	<sup>13</sup> C NMR	Probed the speciation and reaction mechanism.

## ■ Applicability of reported methods for speciation

### NMR spectrometry

#### NMR experiments

$^1\text{H}$  and  $^{13}\text{C}$  NMR experiments are convenient techniques for qualitative and quantitative analysis of amine- $\text{CO}_2$ -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.<sup>27</sup>  $^1\text{H}$  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  $^{13}\text{C}$  NMR spectroscopy is possible to collect direct information on all the interacting carbon-containing species in the systems. Furthermore,  $^{13}\text{C}$  NMR is more suitable than  $^1\text{H}$  NMR to analyze more complex organic systems, because  $^{13}\text{C}$  NMR operates in a wider spectral range and without interferences between the peaks (which are usually present in  $^1\text{H}$  NMR spectra).<sup>27</sup> However,  $^{13}\text{C}$  NMR analysis requires more measuring time than  $^1\text{H}$  NMR, due to the longer the spin-lattice relaxation time for carbon nuclei compared to protons.<sup>34</sup> As reported by Perinu et al.,<sup>27</sup>  $^{13}\text{C}$  NMR data are particularly suitable for determining the species distributions for the study of the reaction mechanisms of  $\text{CO}_2$  absorption/desorption processes in amine-based sorbents.  $^1\text{H}$  NMR data are usually combined with  $^{13}\text{C}$  data for accurate speciation (rarely the speciation is based only on

<sup>1</sup>H NMR data) or for the development of thermodynamic models.

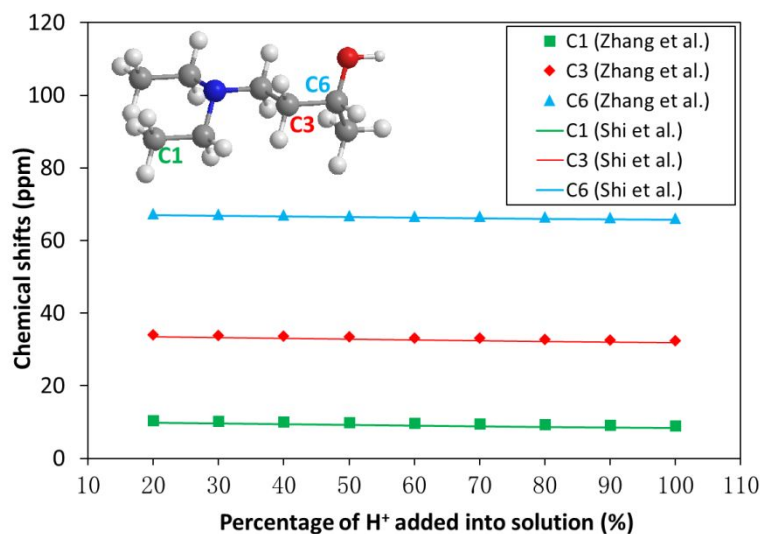
The single-pulse NMR sequence is a common choice for <sup>1</sup>H NMR experiments, while for the acquisition of <sup>13</sup>C NMR spectra the pulse sequence with proton decoupling and NOE (Nuclear Overhauser Effect) suppression with a 90° pulse angle is widely used.<sup>27</sup>

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). <sup>13</sup>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<sub>2</sub>-diluent system are reported in literature. Moreover, Ciftja et al.<sup>34</sup> observed that the relaxation time for a particular <sup>13</sup>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 <sup>1</sup>H/<sup>13</sup>C NMR spectroscopic analyzes, deuterated water (D<sub>2</sub>O) 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 <sup>13</sup>C spectrum is 66.79 ppm, as previously reported.<sup>59</sup> Other referent solvents used are: 1,4-dioxane, acetonitrile, 3-(trimethylsilyl)-propionic acid sodium salt or tetramethylsilane.<sup>92</sup>

## Validation of NMR spectrometry

The NMR spectrometry was validated by Zhang et al.<sup>65</sup> 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.<sup>65</sup> in comparison with those obtained by Shi et al.<sup>100</sup> 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.

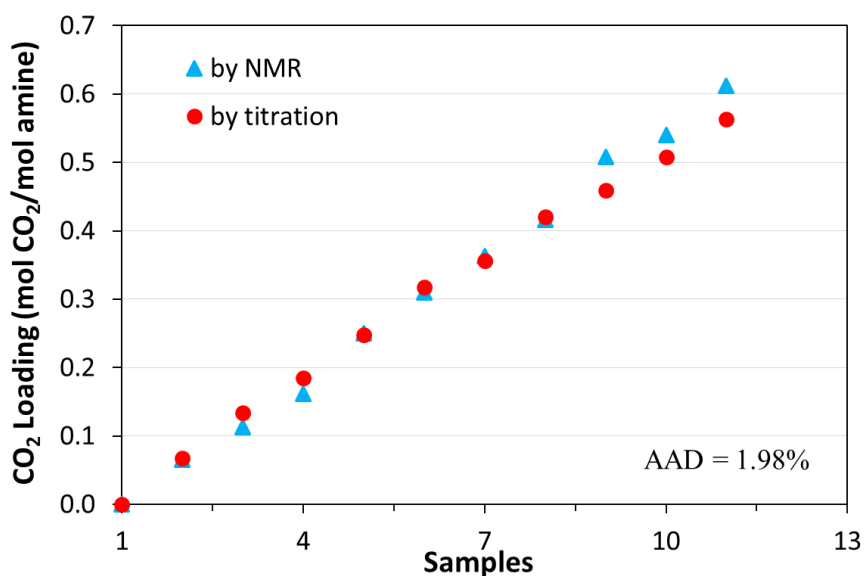


**Figure 10.** Validation of NMR analysis in 4-diethylamino-2-butanol (DEAB).

Adapted with permission from ref.<sup>65</sup> Copyright 2016 American Chemical Society.

The total CO<sub>2</sub> loading is also determined by HCl titration as a reference of <sup>13</sup>C NMR method. The HCl titration method for determining the CO<sub>2</sub>-loading was originally proposed by Horwitz et al.<sup>101</sup> Moreover, Liu et al.<sup>42</sup> predicted the CO<sub>2</sub> loading

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3 in aqueous 1DMA2P with a tolerable average deviation (AAD) of 9.2%. According to  
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5 the report of Zhang et al.,<sup>68</sup> the total CO<sub>2</sub> loadings calculated from NMR method  
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7 parallels the results of HCl titration at low loading stage, where the AAD between these  
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9 two techniques is the acceptable value of 1.98%, as presented in Figure 11.



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33 **Figure 11.** Comparison of the CO<sub>2</sub> loading values between the NMR and HCl  
34 titration method. Reprinted with permission from ref.<sup>68</sup>. Copyright 2017 American  
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### 43 NMR analysis assisted with HCl titration

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The main ions produced by reactions between the CO<sub>2</sub> and aqueous amines are: free amines (Am), protonated amines (AmH<sup>+</sup>), amine carbamates (AmCOO<sup>-</sup>, for primary and secondary amines only), HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. 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.<sup>102</sup> In the <sup>13</sup>C



NMR spectrum of primary amine-CO<sub>2</sub>-H<sub>2</sub>O systems at 293.15 K,<sup>65</sup> the ion concentrations are calculated with the following equations:<sup>103, 104</sup>

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

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

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

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

$\delta$  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<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>, respectively, which are in agreement with the conclusions obtained by Jakobsen et al.<sup>59</sup> also from <sup>13</sup>C NMR analysis, within an absolute deviation of 0.27%. [CO<sub>2</sub>]<sub>0</sub> is the CO<sub>2</sub> capacity (mol) in 1L solution. S<sub>carbamate</sub> and S<sub>bicarbonate+carbonate</sub> represent the peak integration of carbamate and of the total value of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>, respectively, in the <sup>13</sup>C NMR spectrum. The [CO<sub>2</sub>]<sub>0</sub> can be calculated from Eq. 22; meanwhile, the concentration of amine and CO<sub>2</sub> loading were calibrated with 1 mol/L HCl solution.<sup>105</sup>

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

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

where  $\alpha$ , V, V<sub>HCl</sub>, T and C<sub>amine</sub> represent the CO<sub>2</sub> 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<sub>2</sub> loading were calibrated, the concentrations of ions can be calculated from Eqs. 18 - 21 together with the chemical shifts and peak areas in <sup>13</sup>C NMR spectra. Because few carbonate and bicarbonate ions

are produced at low CO<sub>2</sub> loading, the <sup>13</sup>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

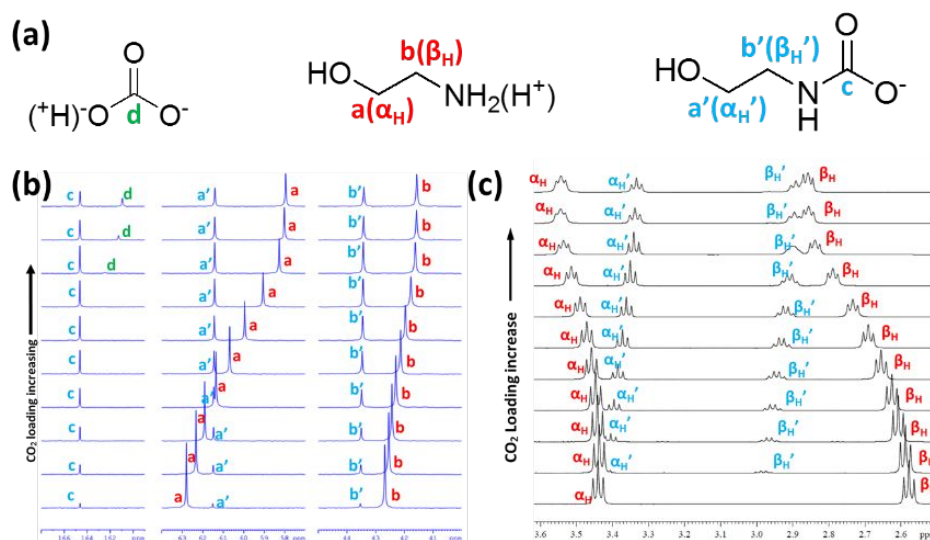
The relative amount of the different species in solution can be quantitatively calculated from <sup>13</sup>C NMR spectrum. Possible ions in MEA- CO<sub>2</sub>-H<sub>2</sub>O system, for example, can be classified as in Figure 12a. The peak intensities vary with the related ion concentrations, which 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:<sup>68</sup>

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

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

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

When CO<sub>2</sub> completely reacts with amine, it exists in the forms of MEACOO<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>. Therefore, the total CO<sub>2</sub> 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  $^1H$  NMR spectrum of the  $CO_2$ -MEA- $H_2O$  system. Reprinted with permission from ref.<sup>68</sup> Copyright 2017 American Chemical Society.

The results calculated from  $^{13}C$  spectrum (Figure 12b) and  $^1H$  (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

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3 its chemical shift always locates at the same position for the same amine, without  
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5 correlation with the CO<sub>2</sub> loading.<sup>59</sup>  
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### 8 9 **Calibration curves**

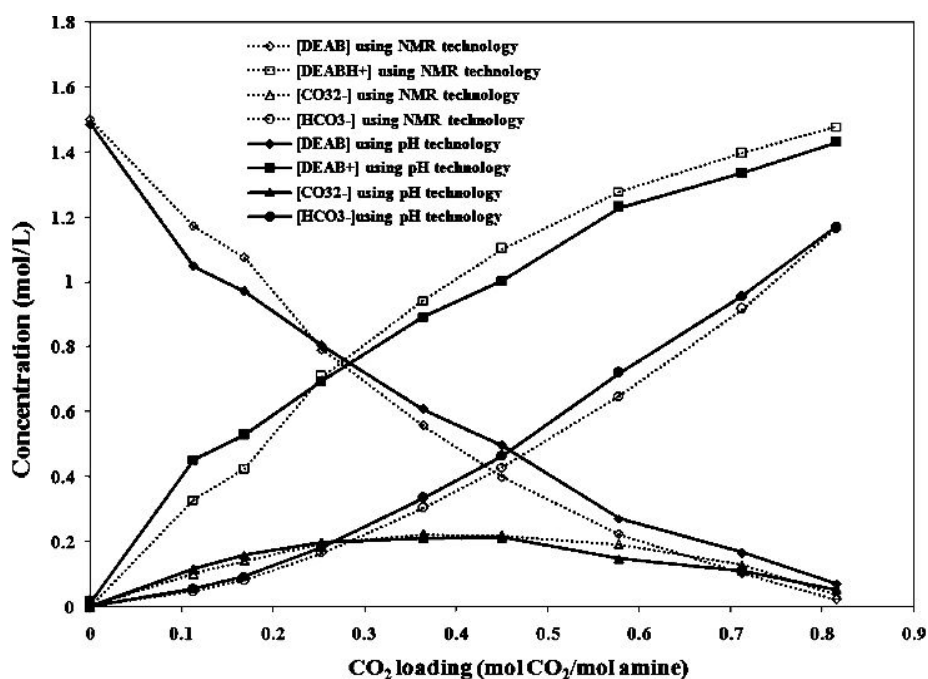
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12 The calibration was applied to calculate the exact protonation ratio of the free and  
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14 protonated amines. Zhang et al.<sup>65</sup> and Shi et al.<sup>100, 102</sup> employed DEAB to build the  
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16 calibration equations respecting that the chemical shifts ( $\delta$ ) of amines will moves either  
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18 up- or down-field with different protonation stage.<sup>106</sup> A specific calibration method,  
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20 based on DEAB and <sup>13</sup>C chemical shifts of MEA, was used by Liang et al.<sup>59</sup> Here we  
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22 report their careful description. Ten tubes containing protonated samples were used  
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24 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,  
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26 respectively. Those ratios were confirmed by titration with standard known  
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28 concentration of HCl solution. The prepared standard samples were tested at a certain  
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30 temperature by <sup>13</sup>C NMR to get their chemical shifts. Then calibration curves were  
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32 obtained by taking protonation rates as abscissa and chemical displacements as ordinate.  
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34 The protonation ratios (H<sup>+</sup>/amine) of amine samples could be calculated from the  
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36 calibration curves using interpolation based on the chemical shifts  $\delta$  of the selected  
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38 carbon atom on <sup>13</sup>C NMR spectrum.  
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45 Calibration curves demonstrate a slightly different for the tested amines at  
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47 different temperature as the different  $\delta$  (ppm) obtained. Although these changes are  
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49 small, they can still affect the accuracy of <sup>13</sup>C NMR analytic results.<sup>84</sup> In a more  
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51 complex system, the application of NMR analysis is illustrated carefully by Shi et al.<sup>84</sup>  
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## 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.,<sup>102</sup> as shown in Figure 13. Therefore, it was confirmed that the ions speciation obtained from the pH measurement are reliable and accurate .



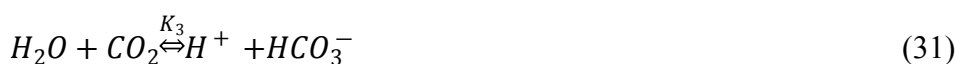
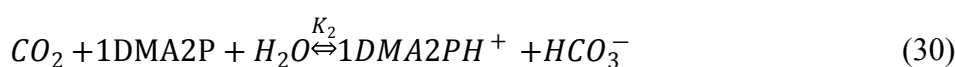
**Figure 13.** Comparison of the speciation between the pH method and NMR technology. Reprinted with permission from ref.<sup>102</sup> Copyright 2015 American Chemical Society.

The concentrations of free/protonated amines and HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> are calculated from pH measurement by means of reaction equilibrium constants  $K$ ,<sup>59</sup> while the concentrations of HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and carbamate, are calculated from NMR analysis.<sup>84</sup> 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.<sup>84, 107</sup>

### Calculation methodology using pH + NMR combination

In this section, the tertiary amine 1DMA2P has been taken as an example<sup>42</sup> to explain pH + NMR combination, the reactions involved in the CO<sub>2</sub> capture with aqueous 1DMA2P are as follows:



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

The K-E model<sup>43</sup> has been widely used to predict the VLE data in amine-H<sub>2</sub>O-CO<sub>2</sub> systems.<sup>108, 109</sup> This model suggests that the  $K_i$  for each reaction can be expressed as follows:<sup>43, 110</sup>

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

$$K_5 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = \exp\left(-294.74 + \frac{36.4385 \times 10^4}{T} - \frac{1.84157 \times 10^8}{T^2} + \frac{0.41579 \times 10^{11}}{T^3} - \frac{0.354291 \times 10^{13}}{T^4}\right) = f(T) \quad (36)$$

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

In addition, the mass balance and the charge balance in the system cannot be

neglected in a amine system,<sup>111</sup> Eq. 38-40 present the balance equations for 1DMA2P system:

Total amine balance:

$$[1\text{DMA2P}]_0 = [1\text{DMA2P}] + [1\text{DMA2PH}^+] \quad (38)$$

Charge balance:

$$[1\text{DMA2PH}^+] + [H^+] = [HCO_3^-] + [OH^-] + 2[CO_3^{2-}] \quad (39)$$

Total carbon balance:

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

where  $[1\text{DMA2P}]_0$ ,  $\alpha$  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:<sup>42</sup>

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

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

$$[1\text{DMA2PH}^+] = \frac{[1\text{DMA2P}]_0 [H^+]}{[H^+] + K_1} = f(C, T, pH) \quad (43)$$

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

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

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<sub>2</sub>O-CO<sub>2</sub> system as an example.<sup>66</sup> 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<sub>2</sub> 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<sup>112</sup>. The constants of  $K_3$ <sup>112</sup>,  $K_5$ <sup>112</sup>,  $K_6$ <sup>112</sup> and  $He_{CO_2}$ <sup>43</sup> within the 1DMA2P-H<sub>2</sub>O-CO<sub>2</sub> system can also be calculated with the K-E model. The correlation constant  $K_2$  plays an important role in predicting the CO<sub>2</sub> 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<sub>2</sub>-H<sub>2</sub>O system are listed in Table 4.



**Table 4.** Factors applied for K-E model. Reprinted from ref.<sup>66</sup> Copyright 2017

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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<sub>2</sub>-diluent systems, namely NMR spectroscopy, pH + NMR combination and model predictions, have been critically discussed and compared.

<sup>1</sup>H NMR peaks overlap in most samples, and hence it is difficult to quantify different species by means of <sup>1</sup>H NMR, while <sup>13</sup>C NMR can be used to quantify most species in a great variety of systems.<sup>33, 113</sup> However, this method consumes much longer analytical time compared to <sup>1</sup>H, because of the poor abundance of isotopic <sup>13</sup>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).<sup>104</sup> Nevertheless, the <sup>13</sup>C NMR analysis is rather feasible in identifying and quantifying the carbonated species in aqueous and nonaqueous solution.<sup>114</sup> Furthermore, carbamate peaks can be easily located in <sup>13</sup>C NMR spectra because their chemical shifts shows almost no changes as the CO<sub>2</sub> loading increased. On the contrary, the NMR chemical shifts of <sup>1</sup>H signals for all species in the system vary a lot even within the same process.<sup>104</sup> By comparing the NMR analysis methods, the NMR analysis assisted with HCl titration has larger errors caused by the titration of CO<sub>2</sub> 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.<sup>59</sup> and Böttinger et al.<sup>49</sup>

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)<sup>42</sup> represents a limitation of which the NMR analysis is not affected. Furthermore, this technique cannot be applied with nonaqueous systems.

The K-E model<sup>43</sup> is considered as a simple model depending only on temperature<sup>115</sup> 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.<sup>60, 116, 117</sup> Austgen et al.<sup>118, 119</sup> 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<sup>115</sup> express equilibrium constant as a function of amine concentration, CO<sub>2</sub> loading, and temperature can also be applied to correlate the solubility of CO<sub>2</sub>. Based on this model, Hu and Chakma<sup>120, 121</sup> further proposed a modified mathematical model in which the temperature, the free amine concentration, and the concentration of the gas in the liquid

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3 phase are all considered. Counting the physical solubility of CO<sub>2</sub> in 1DMA2P instead  
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5 of the CO<sub>2</sub> loading amount might be the reason for the lower deviation of Hu-Chakma  
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7 modelling.<sup>66</sup>  
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10 In the present review, many experimental data relating to different amine-CO<sub>2</sub>-  
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12 diluent systems have been reported: these confirm that the three techniques can be  
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14 successfully applied to provide information on speciation in solution. In simple amine-  
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16 CO<sub>2</sub>-H<sub>2</sub>O system, employing the NMR analysis with carbon classification is the most  
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18 effective in calculating the proportion of ions. However, for complex systems, the  
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20 situation at hand will dictate the appropriate methodology.  
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## 27 ■ Conflicts of interest

28  
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31 There are no conflicts to declare.  
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39  
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54 Research Start-up Foundation of Xiangtan University (19QDZ05). Hunan Key  
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5 Simulation and Optimization, National & Local United Engineering Research Centre  
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8 for Chemical Process Simulation and Intensification.  
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## 14 ■ Acronyms

17 1DMA2P = 1-dimethylamino-2-propanol

19 2MPZ = 2-methylpiperazine

21 4-A1MPD = 1-methylpiperidine

23 4-A1PPD = 4-amino-1-propylpiperidine

25 4-AMTHP = 4-aminomethyltetrahydropyran

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

29 BZA = benzylamine

31 DEA = diethanolamine

33 DEAB = 4-diethylamino-2-butanol

35 DEAPA = 3-diethylaminopropylamine

37 DEEA = diethyl ethanolamine

39 DEGDEE = diethylene glycol diethyl ether

41 DEGMME = diethylene glycol monomethyl ether

43 DETA = diethylenetriamine

45 DIPA = bis(2-hydroxypropyl) amine

47 DMAEA = 2-Dimethylaminoethylamine

49 DMAPA = 3-Dimethylaminopropylamine

51 EMEA = 2-(ethylamino) ethanol

53 IPMEA = 2-(isopropylamino)ethanol

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3 MAPA = N'-Methylpropane-1,3-diamine  
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5 MEA = monoethanolamine  
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7 MEDA = N-Methylethylenediamine  
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9 MMEA = 2-(methylamino)ethanol  
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11 MDEA = methyl diethanolamine  
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13 N, N-DM12EDA = N, N-dimethyl-1,2-ethanediamine  
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15 N, NDM13PDA = N, N-dimethyl-1,3-propanediamine  
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17 PMDETA = N,N,N',N',N''-pentamethyldiethylenetriamine  
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19 PZ = Piperazine  
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21 TBMEA = 2-(tertbutylamino)ethanol  
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23 TETA = triethylenetetramine  
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50  
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52  
53  
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55  
56  
57  
58  
59  
60

## ■ References:

1. Li, J.; Chen, B., Review of CO<sub>2</sub> absorption using chemical solvents in hollow fiber membrane contactors. *Sep. Purif. Technol.* **2005**, 41, (2), 109-122.
2. Yeh, J. T.; Pennline, H. W., Study of CO<sub>2</sub> Absorption and Desorption in a Packed Column. *Energy Fuels* **2001**, 15, 274-278.
3. Chen, X.; Huang, G.; An, C.; Yao, Y.; Zhao, S., Emerging N-nitrosamines and N-nitramines from amine-based post-combustion CO<sub>2</sub> capture – A review. *Chem. Eng. J.* **2018**, 335, 921-935.
4. Team, C. W.; Pachauri, R. K.; Meyer, L. A., Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. *Climate Change 2014 Synthesis Report* **2014**.
5. Qiao, W.; Huang, K.; Azimi, M.; Han, S., A Novel Hybrid Prediction Model for Hourly Gas Consumption in Supply Side Based on Improved Whale Optimization Algorithm and Relevance Vector Machine. *IEEE Access* **2019**, 7, 88218-88230.
6. D'Alessandro, D. M.; Smit, B.; Long, J. R., Carbon dioxide capture: prospects for new materials. *Angew. Chem. Int. Ed. Engl.* **2010**, 49, (35), 6058-82.
7. Mann, M. E.; Bradley, R. S.; Hughes, M. K., Global-scale temperature patterns and climate forcing over the past six centuries. *Nature* **1998**, 392, (6678), 779-787.
8. Barzagli, F.; Mani, F.; Peruzzini, M., From greenhouse gas to feedstock: formation of ammonium carbamate from CO<sub>2</sub> and NH<sub>3</sub> in organic solvents and its catalytic conversion into urea under mild conditions. *Green Chem.* **2011**, 13, 1267-1274.
9. Mondal, B. K.; Samanta, A. N., Equilibrium solubility and kinetics of CO<sub>2</sub> absorption in hexamethylenediamine activated aqueous sodium glycinate solvent.

1  
2  
3 *Chem. Eng. J.* **2019**.

4  
5 10. Gao, H.; Liu, S.; Gao, G.; Luo, X.; Liang, Z., Hybrid behavior and mass transfer  
6 performance for absorption of CO<sub>2</sub> into aqueous DEEA/PZ solutions in a hollow fiber  
7 membrane contactor. *Sep. Purif. Technol.* **2018**, 201, 291-300.

8  
9  
10  
11 11. Hu, X.; Mangano, E.; Friedrich, D.; Ahn, H.; Brandani, S., Diffusion mechanism  
12 of CO<sub>2</sub> in 13X zeolite beads. *Adsorption* **2014**, 20, (1), 121-135.

13  
14  
15  
16 12. Barzagli, F.; Lai, S.; Mani, F., A new class of single-component absorbents for  
17 reversible carbon dioxide capture under mild conditions. *ChemSusChem* **2015**, 8, (1),  
18 184-91.

19  
20  
21  
22  
23 13. Barzagli, F.; Giorgi, C.; Mani, F.; Peruzzini, M., Comparative Study of CO<sub>2</sub>  
24 Capture by Aqueous and Nonaqueous 2-Amino-2-methyl-1-propanol Based  
25 Absorbents Carried Out by <sup>13</sup>C NMR and Enthalpy Analysis. *Ind. Eng. Chem. Res.*  
26  
27  
28  
29  
30  
31 **2019**, 58, (11), 4364-4373.

32  
33 14. Hu, X.; Liu, L.; Luo, X.; Xiao, G.; Shiko, E.; Zhang, R.; Fan, X.; Zhou, Y.; Liu,  
34 Y.; Zeng, Z.; Li, C. e., A review of N-functionalized solid adsorbents for post-  
35 combustion CO<sub>2</sub> capture. *Appl. Energy* **2020**, 260, 114244.

36  
37  
38  
39  
40 15. Hu, X.; Brandani, S.; Benin, A. I.; Willis, R. R., Development of a Semiautomated  
41 Zero Length Column Technique for Carbon Capture Applications: Study of Diffusion  
42 Behavior of CO<sub>2</sub> in MOFs. *Ind. Eng. Chem. Res.* **2015**, 54, (21), 5777-5783.

43  
44  
45  
46  
47 16. Hu, X.; Brandani, S.; Benin, A. I.; Willis, R. R., Development of a Semiautomated  
48 Zero Length Column Technique for Carbon Capture Applications: Rapid Capacity  
49 Ranking of Novel Adsorbents. *Ind. Eng. Chem. Res.* **2015**, 54, (26), 6772-6780.

50  
51  
52  
53 17. Liang, Z.; Rongwong, W.; Liu, H.; Fu, K.; Gao, H.; Cao, F.; Zhang, R.; Sema, T.;  
54 Henni, A.; Sumon, K.; Nath, D.; Gelowitz, D.; Srisang, W.; Saiwan, C.; Benamor, A.;  
55 Al-Marri, M.; Shi, H.; Supap, T.; Chan, C.; Zhou, Q.; Abu-Zahra, M.; Wilson, M.;  
56  
57  
58  
59  
60

1  
2  
3 Olson, W.; Idem, R.; Tontiwachwuthikul, P., Recent progress and new developments  
4 in post-combustion carbon-capture technology with amine based solvents. *Int. J.*  
5 *Greenhouse Gas Contro* **2015**, 40, 26-54.  
6  
7

8  
9  
10 18. Xiao, M.; Cui, D.; Yang, Q.; Liang, Z.; Puxty, G.; Conway, W.; Feron, P.,  
11 Advanced designer amines for CO<sub>2</sub> capture: Interrogating speciation and physical  
12 properties. *Int. J. Greenhouse Gas Contro* **2019**, 82, 8-18.  
13  
14

15  
16 19. Wang, L.; Liu, S.; Wang, R.; Li, Q.; Zhang, S., Regulating Phase Separation  
17 Behavior of a DEEA–TETA Biphasic Solvent Using Sulfolane for Energy-Saving CO<sub>2</sub>  
18 Capture. *Environ. Sci. Technol.* **2019**, 53, (21), 12873-12881.  
19  
20

21  
22 20. Liu, H.; Xiao, M.; Luo, X.; Gao, H.; Idem, R.; Tontiwachwuthikul, P.; Liang, Z.,  
23 Modeling of CO<sub>2</sub> equilibrium solubility in a novel 1-Diethylamino-2-Propanol Solvent.  
24 *AIChE J.* **2017**, 63, (10), 4465-4475.  
25  
26

27  
28 21. Liu, L.; Chen, H.; Shiko, E.; Fan, X.; Zhou, Y.; Zhang, G.; Luo, X.; Hu, X., Low-  
29 cost DETA impregnation of acid-activated sepiolite for CO<sub>2</sub> capture. *Chem. Eng. J.*  
30 **2018**, 353, 940-948.  
31  
32

33  
34 22. Rao, A. B.; Rubin, E. S., Identifying Cost-Effective CO<sub>2</sub> Control Levels for Amine-  
35 Based CO<sub>2</sub> Capture Systems. *Ind. Eng. Chem. Res.* **2006**, 45, (8), 2421-2429.  
36  
37

38  
39 23. Bernhardsen, I. M.; Knuutila, H. K., A review of potential amine solvents for CO<sub>2</sub>  
40 absorption process: Absorption capacity, cyclic capacity and pKa. *Int. J. Greenhouse*  
41 *Gas Contro* **2017**, 61, 27-48.  
42  
43

44  
45 24. Xiao, M.; Liu, H.; Idem, R.; Tontiwachwuthikul, P.; Liang, Z., A study of  
46 structure–activity relationships of commercial tertiary amines for post-combustion CO<sub>2</sub>  
47 capture. *Appl. Energy* **2016**, 184, 219-229.  
48  
49

50  
51 25. Zhang, X.; Liu, H.; Liang, Z.; Idem, R.; Tontiwachwuthikul, P.; Jaber Al-Marri,  
52 M.; Benamor, A., Reducing energy consumption of CO<sub>2</sub> desorption in CO<sub>2</sub>-loaded  
53  
54  
55  
56  
57  
58  
59  
60



- aqueous amine solution using Al<sub>2</sub>O<sub>3</sub>/HZSM-5 bifunctional catalysts. *Appl. Energy* **2018**, *229*, 562-576.
26. Zhang, R.; Zhang, Y.; Cheng, Y.; Yu, Q.; Luo, X.; Li, C. e.; Li, J.; Zeng, Z.; Liu, Y.; Jiang, X.; Hu, X. E., New Approach with Universal Applicability for Evaluating the Heat Requirements in the Solvent Regeneration Process for Postcombustion CO<sub>2</sub> Capture. *Ind. Eng. Chem. Res.* **2020**, *59*, (7), 3261-3268.
27. Perinu, C.; Arstad, B.; Jens, K.-J., NMR spectroscopy applied to amine-CO<sub>2</sub>-H<sub>2</sub>O systems relevant for post-combustion CO<sub>2</sub> capture: A review. *Int. J. Greenhouse Gas Contro* **2014**, *20*, 230-243.
28. Barzagli, F.; Mani, F.; Peruzzini, M., Continuous cycles of CO<sub>2</sub> absorption and amine regeneration with aqueous alkanolamines: a comparison of the efficiency between pure and blended DEA, MDEA and AMP solutions by <sup>13</sup>C NMR spectroscopy. *Energy Environ. Sci.* **2010**, *3*, (6), 772.
29. Ling, H.; Gao, H.; Liang, Z., Comprehensive solubility of N<sub>2</sub>O and mass transfer studies on an effective reactive N,N-dimethylethanolamine (DMEA) solvent for post-combustion CO<sub>2</sub> capture. *Chem. Eng. J.* **2019**, *355*, 369-379.
30. Barzagli, F.; Giorgi, C.; Mani, F.; Peruzzini, M., Reversible carbon dioxide capture by aqueous and non-aqueous amine-based absorbents: A comparative analysis carried out by <sup>13</sup>C NMR spectroscopy. *Appl. Energy* **2018**, *220*, 208-219.
31. Puxty, G.; Bennett, R.; Conway, W.; Maher, D., A comparison of Raman and IR spectroscopies for the monitoring and evaluation of absorbent composition during CO<sub>2</sub> absorption processes. *Int. J. Greenhouse Gas Contro* **2016**, *49*, 281-289.
32. Wong, M. K.; Bustam, M. A.; Shariff, A. M., Chemical speciation of CO<sub>2</sub> absorption in aqueous monoethanolamine investigated by in situ Raman spectroscopy. *Int. J. Greenhouse Gas Contro* **2015**, *39*, 139-147.

- 1  
2  
3 33. Perinu, C.; Bernhardsen, I. M.; Pinto, D. D. D.; Knuutila, H. K.; Jens, K.-J., NMR  
4 Speciation of Aqueous MAPA, Tertiary Amines, and Their Blends in the Presence of  
5 CO<sub>2</sub>: Influence of pKa and Reaction Mechanisms. *Ind. Eng. Chem. Res.* **2018**, *57*, (5),  
6 1337-1349.  
7  
8  
9  
10  
11  
12 34. Ciftja, A. F.; Hartono, A.; Svendsen, H. F., <sup>13</sup>C NMR as a method species  
13 determination in CO<sub>2</sub> absorbent systems. *Int. J. Greenhouse Gas Contro* **2013**, *16*, 224-  
14 232.  
15  
16  
17  
18  
19 35. Blümich, B., Beyond compact NMR. *Microporous Mesoporous Mater.* **2018**, *269*,  
20 3-6.  
21  
22  
23  
24 36. Barbarossa, V.; Barzagli, F.; Mani, F.; Lai, S.; Vanga, G., The chemistry of  
25 resorcinol carboxylation and its possible application to the CO<sub>2</sub> removal from exhaust  
26 gases. *J. CO<sub>2</sub> Util.* **2015**, *10*, 50-59.  
27  
28  
29  
30  
31 37. Abbott, T. M.; Buchanan, G. W.; Kruus, P.; Lee, K. C., <sup>13</sup>C nuclear magnetic  
32 resonance and Raman investigations of aqueous carbon dioxide systems. *Can. J. Chem.*  
33 **2011**, *60*, (8), 1000-1006.  
34  
35  
36  
37  
38 38. Mani, F.; Peruzzini, M.; Stoppioni, P., CO<sub>2</sub> absorption by aqueous NH<sub>3</sub> solutions:  
39 speciation of ammonium carbamate, bicarbonate and carbonate by a <sup>13</sup>C NMR study.  
40 *Green Chem.* **2006**, *8*, (11), 995-1000.  
41  
42  
43  
44  
45 39. Liang, Z.; Fu, K.; Idem, R.; Tontiwachwuthikul, P., Review on current advances,  
46 future challenges and consideration issues for post-combustion CO<sub>2</sub> capture using  
47 amine-based absorbents. *Chin. J. Chem. Eng.* **2016**, *24*, (2), 278-288.  
48  
49  
50  
51  
52 40. Stadie, W. C.; O'Brien, H., The Carbamate Equilibrium. *J. Biol. Chem.* **1937**, *112*,  
53 (2), 439-470.  
54  
55  
56  
57 41. Fan, G.; Wee, A. G. H.; Idem, R.; Tontiwachwuthikul, P., NMR Studies of Amine  
58 Species in MEA-CO<sub>2</sub>-H<sub>2</sub>O System: Modification of the Model of Vapor-Liquid  
59  
60

- Equilibrium (VLE). *Ind. Eng. Chem. Res.* **2009**, 48, 2717-2720.
42. Liu, H.; Luo, X.; Liang, Z.; Tontiwachwuthikul, P., Determination of Vapor–Liquid Equilibrium (VLE) Plots of 1-Dimethylamino-2-propanol Solutions Using the pH Method. *Ind. Eng. Chem. Res.* **2015**, 54, (17), 4709-4716.
43. Kent, R. L.; Eisenberg, B., Better Data for Amine Treating. *Hydrocarbon Process* **1976**, 87.
44. Deshmukh, R. D.; Mather, A. E., A mathematical model for equilibrium solubility of hydrogen sulfide and carbon dioxide in aqueous alkanolamine solutions. *Chem. Eng. Sci.* **1981**, 36, (2), 355-362.
45. Chen, C.; Britt, H. I.; Boston, J. F.; Evans, L. B., Local composition model for excess Gibbs energy of electrolyte systems. Part I: Single solvent, single completely dissociated electrolyte systems. *AIChE J.* **1982**, 28, (4), 588-596.
46. Rayer, A. V.; Sumon, K. Z.; Sema, T.; Henni, A.; Idem, R. O.; Tontiwachwuthikul, P., Part 5c: Solvent chemistry: solubility of CO<sub>2</sub> in reactive solvents for post-combustion CO<sub>2</sub>. *Carbon Manage.* **2014**, 3, (5), 467-484.
47. Lee, H.; Seo, M.; Kang, J.; Yang, D., Measurement and Correlation of the Solubility of Carbon Dioxide in the Mixtures of Aqueous Monoethanolamine Solution and Benzoic Acid. *J. Chem. Eng. Data* **2012**, 57, (57), 3744–3750.
48. Ahn, C. K.; Lee, H. W.; Lee, M. W.; Chang, Y. S.; Han, K.; Rhee, C. H.; Kim, J. Y.; Chun, H. D.; Park, J. M., Determination of ammonium salt/ion speciation in the CO<sub>2</sub> absorption process using ammonia solution: Modeling and experimental approaches. *Energy Procedia* **2011**, 4, 541-547.
49. Böttinger, W.; Maiwald, M.; Hasse, H., Online NMR spectroscopic study of species distribution in MEA-H<sub>2</sub>O-CO<sub>2</sub> and DEA-H<sub>2</sub>O-CO<sub>2</sub>. *Fluid Phase Equilib.* **2008**, 263, (2), 131-143.

- 1  
2  
3 50. Heldebrant, D. J.; Koech, P. K.; Glezakou, V. A.; Rousseau, R.; Malhotra, D.;  
4  
5 Cantu, D. C., Water-Lean Solvents for Post-Combustion CO<sub>2</sub> Capture: Fundamentals,  
6  
7 Uncertainties, Opportunities, and Outlook. *Chem. Rev.* **2017**, 117, (14), 9594-9624.  
8  
9  
10 51. Bara, J. E., What chemicals will we need to capture CO<sub>2</sub>? *Greenhouse Gases: Sci.*  
11  
12 *Technol.* **2012**, 2, (3), 162-171.  
13  
14 52. Lv, B.; Guo, B.; Zhou, Z.; Jing, G., Mechanisms of CO<sub>2</sub> Capture into  
15  
16 Monoethanolamine Solution with Different CO<sub>2</sub> Loading during the  
17  
18 Absorption/Desorption Processes. *Environ. Sci. Technol.* **2015**, 49, (17), 10728-10735.  
19  
20 53. Barzagli, F.; Mani, F.; Peruzzini, M., A <sup>13</sup>C NMR study of the carbon dioxide  
21  
22 absorption and desorption equilibria by aqueous 2-aminoethanol and N-methyl-  
23  
24 substituted 2-aminoethanol. *Energy Environ. Sci.* **2009**, 2, (3), 322.  
25  
26 54. García-Abuín, A.; Gómez-Díaz, D.; Navaza, J. M.; Rumbo, A., CO<sub>2</sub> Capture by  
27  
28 Pyrrolidine: Reaction Mechanism and Mass Transfer. *AIChE J.* **2014**, 60, (3), 1098-  
29  
30 1106.  
31  
32 55. Wang, L.; Zhang, Y.; Wang, R.; Li, Q.; Zhang, S.; Li, M.; Liu, J.; Chen, B.,  
33  
34 Advanced Monoethanolamine Absorption Using Sulfolane as a Phase Splitter for CO<sub>2</sub>  
35  
36 Capture. *Environ. Sci. Technol.* **2018**, 52, (24), 14556-14563.  
37  
38 56. Li, L.; Clifford, S.; Puxty, G.; Maeder, M.; Burns, R.; Yu, H.; Conway, W., Kinetic  
39  
40 and Equilibrium Reactions of a New Heterocyclic Aqueous 4-  
41  
42 aminomethyltetrahydropyran (4-AMTHP) Absorbent for Post Combustion Carbon  
43  
44 Dioxide (CO<sub>2</sub>) Capture Processes. *ACS Sustainable Chem. Eng.* **2017**, 5, (10), 9200-  
45  
46 9206.  
47  
48 57. Matin, N. S.; Remias, J. E.; Neathery, J. K.; Liu, K., Facile Method for  
49  
50 Determination of Amine Speciation in CO<sub>2</sub> Capture Solutions. *Ind. Eng. Chem. Res.*  
51  
52 **2012**, 51, (19), 6613-6618.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 58. Zhang, Y.; Que, H.; Chen, C.-C., Thermodynamic modeling for CO<sub>2</sub> absorption in  
4 aqueous MEA solution with electrolyte NRTL model. *Fluid Phase Equilib.* **2011**, 311,  
5  
6 67-75.  
7  
8  
9  
10 59. Jakobsen, J. P.; Krane, J.; Svendsen, H. F., Liquid-Phase Composition  
11 Determination in CO<sub>2</sub>-H<sub>2</sub>O-Alkanolamine Systems: An NMR Study. *Ind. Eng. Chem.*  
12  
13 *Res.* **2005**, 44, (26), 9894-9903.  
14  
15  
16 60. Luo, X.; Chen, N.; Liu, S.; Rongwong, W.; Idem, R. O.; Tontiwachwuthikul, P.;  
17 Liang, Z., Experiments and modeling of vapor-liquid equilibrium data in DEEA-CO<sub>2</sub> -  
18  
19 H<sub>2</sub>O system. *Int. J. Greenhouse Gas Contro* **2016**, 53, 160-168.  
20  
21  
22  
23 61. Preez, L. J. d.; Motang, N.; Callanan, L. H.; Burger, A. J., Determining the Liquid  
24  
25 Phase Equilibrium Speciation of the CO<sub>2</sub>-MEA-H<sub>2</sub>O System Using a Simplified in  
26  
27 Situ Fourier Transform Infrared Method. *Ind. Eng. Chem. Res.* **2018**, 58, (1), 469-478.  
28  
29  
30 62. Zhang, R.; Yang, Q.; Yu, B.; Yu, H.; Liang, Z., Toward to efficient CO<sub>2</sub> capture  
31  
32 solvent design by analyzing the effect of substituent type connected to N-atom. *Energy*  
33  
34 **2018**, 144, 1064-1072.  
35  
36  
37 63. Donaldson, T. L.; Nguyen, Y. N., Carbon dioxide reaction kinetics and transport in  
38  
39 aqueous amine membranes. *Ind. Eng. Chem. Fundam.* **1980**, 19, (3), 260-266.  
40  
41  
42 64. Liang, Y.; Liu, H.; Rongwong, W.; Liang, Z.; Idem, R.; Tontiwachwuthikul, P.,  
43  
44 Solubility, absorption heat and mass transfer studies of CO<sub>2</sub> absorption into aqueous  
45  
46 solution of 1-dimethylamino-2-propanol. *Fuel* **2015**, 144, 121-129.  
47  
48  
49 65. Zhang, R.; Liang, Z.; Liu, H.; Rongwong, W.; Luo, X.; Idem, R.; Yang, Q., Study  
50  
51 of Formation of Bicarbonate Ions in CO<sub>2</sub>-Loaded Aqueous Single 1DMA2P and  
52  
53 MDEA Tertiary Amines and Blended MEA-1DMA2P and MEA-MDEA Amines for  
54  
55 Low Heat of Regeneration. *Ind. Eng. Chem. Res.* **2016**, 55, (12), 3710-3717.  
56  
57  
58 66. Liu, H.; Gaoa, H.; Idem, R.; Tontiwachwuthikul, P.; Liang, Z., Analysis of CO<sub>2</sub>  
59  
60

1  
2  
3 solubility and absorption heat into 1-dimethylamino-2-propanol solution. *Chem. Eng.*  
4  
5 *Sci.* **2017**, 170, 3-15.

6  
7  
8 67. Zhang, R.; Luo, X.; Yang, Q.; Yu, H.; Puxty, G.; Liang, Z., Analysis for the  
9  
10 speciation in CO<sub>2</sub> loaded aqueous MEDA and MAPA solution using <sup>13</sup>C NMR  
11  
12 technology. *Int. J. Greenhouse Gas Contro* **2018**, 71, 1-8.

13  
14  
15 68. Zhang, R.; Yang, Q.; Liang, Z.; Puxty, G.; Xue, Y., Toward Efficient CO<sub>2</sub> Capture  
16  
17 Solvent Design by Analyzing the Effect of Chain Lengths and Amino Types to the  
18  
19 Absorption Capacity, Bicarbonate/Carbamate and Cyclic Capacity. *Energy Fuels* **2017**,  
20  
21 31, (10), 11099-11108.

22  
23  
24 69. Nainar, M.; Veawab, A., Corrosion in CO<sub>2</sub> Capture Process Using Blended  
25  
26 Monoethanolamine and Piperazine. *Ind. Eng. Chem. Res.* **2009**, 48, (20), 9299-9306.

27  
28  
29 70. Safdara, R.; Thanabalana, M.; Omara, A. A., Solubility of CO<sub>2</sub> in 20 Wt %  
30  
31 Aqueous Solution of Piperazine. *Procedia Engineering* **2016**, 148, 1377-1379.

32  
33  
34 71. Zhang, R.; Jiang, W.; Liang, Z.; Luo, X.; Yang, Q., Study of Equilibrium Solubility,  
35  
36 Heat of Absorption, and Speciation of CO<sub>2</sub> Absorption into Aqueous 2-  
37  
38 Methylpiperazine (2MPZ) Solution. *Ind. Eng. Chem. Res.* **2018**, 57, (51), 17496-17503.

39  
40  
41 72. Liu, F.; Jing, G.; Zhou, X.; Lv, B.; Zhou, Z., Performance and Mechanisms of  
42  
43 Triethylene Tetramine (TETA) and 2-Amino-2-methyl-1-propanol (AMP) in Aqueous  
44  
45 and Nonaqueous Solutions for CO<sub>2</sub> Capture. *ACS Sustainable Chem. Eng.* **2018**, 6, (1),  
46  
47 1352-1361.

48  
49  
50 73. Bencini, A.; Bianchi, A.; Garcia-España, E.; Micheloni, M.; Ramirez, J. A., Proton  
51  
52 coordination by polyamine compounds in aqueous solution. *Coord. Chem. Rev.* **1999**,  
53  
54 188, (1), 97-156.

55  
56  
57 74. Kadiwala, S.; Rayer, A. V.; Henni, A., High pressure solubility of carbon dioxide  
58  
59 (CO<sub>2</sub>) in aqueous piperazine solutions. *Fluid Phase Equilib.* **2010**, 292, (1), 20-28.

- 1  
2  
3 75. Pashaei, H.; Ghaemi, A.; Nasiri, M., Experimental investigation of CO<sub>2</sub> removal  
4 using Piperazine solution in a stirrer bubble column. *Int. J. Greenhouse Gas Contro*  
5  
6 **2017**, 63, 226-240.  
7  
8  
9  
10 76. Hwang, S.; Kim, H.; Lee, K., Prediction of VLE for aqueous blended amines using  
11 VLE models of single amines. *Int. J. Greenhouse Gas Contro* **2016**, 49, 250-258.  
12  
13  
14 77. Liu, H.; Idem, R.; Tontiwachwuthikul, P., Novel models for correlation of  
15 Solubility constant and diffusivity of N<sub>2</sub>O in aqueous 1-dimethylamino-2-propanol.  
16  
17  
18  
19  
20  
21  
22 78. Shi, H.; Huang, M.; Wu, Q.; Zheng, L.; Cui, L.; Zhang, S.; Tontiwachwuthikul, P.,  
23 Study of Catalytic CO<sub>2</sub> Absorption and Desorption with Tertiary Amine DEEA and  
24 1DMA-2P with the Aid of Solid Acid and Solid Alkaline Chemicals. *Molecules* **2019**,  
25  
26  
27  
28  
29  
30  
31 79. Sakwattanapong, R.; Aroonwilas, A.; Veawab, A., Behavior of reboiler heat duty  
32 for CO<sub>2</sub> capture plants using regenerable single and blended alkanolamines. *Ind. Eng.*  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60
80. Idem, R.; Wilson, M.; Tontiwachwuthikul, P.; Chakma, A.; Veawab, A.;  
Aroonwilas, A.; Gelowitz, D., Pilot Plant Studies of the CO<sub>2</sub> Capture Performance of  
Aqueous MEA and Mixed MEA/MDEA Solvents at the University of Regina CO<sub>2</sub>  
Capture Technology Development Plant and the Boundary Dam CO<sub>2</sub> Capture  
Demonstration Plant. *Ind. Eng. Chem. Res.* **2006**, 45, (8), 2414-2420.
81. Yu, Z.; Jiang, L., The Role of Bicarbonate in Ion Speciation Plots in DEAB and  
Blended MEA-DEAB Systems, an NMR Study. *Key Eng. Mater.* **2017**, 727, 870-877.
82. Ciftja, A. F.; Hartono, A.; Svendsen, H. F., Experimental study on phase change  
solvents in CO<sub>2</sub> capture by NMR spectroscopy. *Chem. Eng. Sci.* **2013**, 102, 378-386.
83. Ye, Q.; Zhu, L.; Wang, X.; Lu, Y., On the mechanisms of CO<sub>2</sub> absorption and

1  
2  
3 desorption with phase transitional solvents. *Int. J. Greenhouse Gas Contro* **2017**, *56*,  
4 278-288.  
5

6  
7  
8 84. Shi, H.; Naami, A.; Idem, R.; Tontiwachwuthikul, P., 1D NMR Analysis of a  
9 Quaternary MEA–DEAB–CO<sub>2</sub>–H<sub>2</sub>O Amine System: Liquid Phase Speciation and  
10 Vapor–Liquid Equilibria at CO<sub>2</sub> Absorption and Solvent Regeneration Conditions. *Ind.*  
11 *Eng. Chem. Res.* **2014**, *53*, (20), 8577-8591.  
12  
13

14  
15  
16 85. Sun, W.; Yong, C.; Li, M., Kinetics of the absorption of carbon dioxide into mixed  
17 aqueous solutions of 2-amino-2-methyl-1-propanol and piperazine. *Chem. Eng. Sci.*  
18 **2005**, *60*, (2), 503-516.  
19  
20  
21

22  
23  
24 86. Conway, W.; Beyad, Y.; Feron, P.; Richner, G.; Puxty, G., CO<sub>2</sub> absorption into  
25 aqueous amine blends containing benzylamine (BZA), monoethanolamine (MEA), and  
26 sterically hindered/tertiary amines. *Energy Procedia* **2014**, *63*, 1835-1841.  
27  
28  
29

30  
31 87. Liu, Y.; Zhang, L.; Watanasiri, S., Representing vapor-liquid equilibrium for an  
32 aqueous MEA-CO<sub>2</sub> system using the electrolyte nonrandom-two-liquid model. *Ind. Eng.*  
33 *Chem. Res.* **1999**, *38*, 2080-2090.  
34  
35  
36

37  
38 88. Zhang, X.; Zhang, R.; Liu, H.; Gao, H.; Liang, Z., Evaluating CO<sub>2</sub> desorption  
39 performance in CO<sub>2</sub>-loaded aqueous tri-solvent blend amines with and without solid  
40 acid catalysts. *Appl. Energy* **2018**, *218*, 417-429.  
41  
42  
43

44  
45 89. Zhang, R.; Zhang, X.; Yang, Q.; Yu, H.; Liang, Z.; Luo, X., Analysis of the  
46 reduction of energy cost by using MEA-MDEA-PZ solvent for post-combustion carbon  
47 dioxide capture (PCC). *Appl. Energy* **2017**, *205*, 1002-1011.  
48  
49  
50

51  
52 90. Liu, Y.; Fan, W.; Wang, K.; Wang, J., Studies of CO<sub>2</sub> absorption/regeneration  
53 performances of novel aqueous monoethanolamine (MEA)-based solutions. *J. Cleaner*  
54 *Prod.* **2016**, *112*, 4012-4021.  
55  
56  
57

58  
59 91. Barzagli, F.; Lai, S.; Mani, F.; Stoppioni, P., Novel Non-aqueous Amine Solvents  
60



- 1  
2  
3 for Biogas Upgrading. *Energy Fuels* **2014**, 28, (8), 5252-5258.  
4  
5  
6 92. Barzagli, F.; Lai, S.; Mani, F., CO<sub>2</sub> Capture by Liquid Solvents and their  
7  
8 Regeneration by Thermal Decomposition of the Solid Carbonated Derivatives. *Chem.*  
9  
10 *Eng. Technol.* **2013**, 36, (11), 1847-1852.  
11  
12 93. Barbarossa, V.; Barzagli, F.; Mani, F.; Lai, S.; Stoppioni, P.; Vanga, G., Efficient  
13  
14 CO<sub>2</sub> capture by non-aqueous 2-amino-2-methyl-1-propanol (AMP) and low  
15  
16 temperature solvent regeneration. *RSC Advances* **2013**, 3, (30), 12349.  
17  
18 94. Barzagli, F.; Mani, F.; Peruzzini, M., Novel water-free biphasic absorbents for  
19  
20 efficient CO<sub>2</sub> capture. *Int. J. Greenhouse Gas Contro* **2017**, 60, 100-109.  
21  
22  
23 95. Barzagli, F.; Mani, F.; Peruzzini, M., A Comparative Study of the CO<sub>2</sub> Absorption  
24  
25 in Some Solvent-Free Alkanolamines and in Aqueous Monoethanolamine (MEA).  
26  
27 *Environ. Sci. Technol.* **2016**, 50, (13), 7239-46.  
28  
29  
30 96. Barzagli, F.; Vaira, M. D.; Mani, F.; Peruzzini, M., Improved solvent formulations  
31  
32 for efficient CO<sub>2</sub> absorption and low-temperature desorption. *ChemSusChem* **2012**, 5,  
33  
34 (9), 1724-31.  
35  
36  
37 97. Svensson, H.; Edfeldt, J.; Velasco, V. Z., Solubility of carbon dioxide in mixtures  
38  
39 of 2-amino-2-methyl-1-propanol and organic solvents. *Int. J. Greenhouse Gas Contro*  
40  
41 **2014**, 27, (8), 247–254.  
42  
43  
44 98. Chen, S.; Chen, S.; Zhang, Y.; Qin, L.; Guo, C.; Chen, J., Species distribution of  
45  
46 CO<sub>2</sub> absorption/desorption in aqueous and non-aqueous N -ethylmonoethanolamine  
47  
48 solutions. *Int. J. Greenhouse Gas Contro* **2016**, 47, 151-158.  
49  
50  
51 99. Barzagli, F.; Mani, F.; Peruzzini, M., Efficient CO<sub>2</sub> absorption and low temperature  
52  
53 desorption with non-aqueous solvents based on 2-amino-2-methyl-1-propanol (AMP).  
54  
55 *Int. J. Greenhouse Gas Contro* **2013**, 16, (4), 217-223.  
56  
57  
58 100. Shi, H.; Liang, Z.; Sema, T.; Naami, A.; Usubharatana, P.; Idem, R.; Saiwan,  
59  
60

C.; Tontiwachwuthikul, P., Part 5a: Solvent chemistry: NMR analysis and studies for amine-CO<sub>2</sub>-H<sub>2</sub>O systems with vapor-liquid equilibrium modeling for CO<sub>2</sub> capture processes. *Carbon Manage.* **2012**, 3, (2), 185-200.

101. Horwitz, W.; Chichilo, P.; Reynolds, H., Official methods of analysis of the Association of Official Analytical Chemists. *J. Pharm. Sci.* **1970**, 60, (4), 414-414.

102. Shi, H.; Sema, T.; Naami, A.; Liang, Z.; Idem, R.; Tontiwachwuthikul, P., <sup>13</sup>C NMR Spectroscopy of a Novel Amine Species in the DEAB-CO<sub>2</sub>-H<sub>2</sub>O system: VLE Model. *Ind. Eng. Chem. Res.* **2012**, 51, (25), 8608-8615.

103. Holmes, P. E.; Naaz, M.; Poling, B. E., Ion Concentrations in the CO<sub>2</sub>-NH<sub>3</sub>-H<sub>2</sub>O System from <sup>13</sup>C NMR Spectroscopy. *Ind. Eng. Chem. Res.* **1998**, 37, (8), 3281-3287.

104. Hu, X.; Yu, Q.; Cui, Y.; Huang, J.; Shiko, E.; Zhou, Y.; Zeng, Z.; Liu, Y.; Zhang, R., Toward Solvent Development for Industrial CO<sub>2</sub> Capture by Optimizing the Catalyst-Amine Formulation for Lower Energy Consumption in the Solvent Regeneration Process. *Energy Fuels* **2019**, 33, (11), 11507-11515.

105. Horwitz, W.; Chichilo, P., Official methods of analysis of the Association of official analytical chemists (AOAC) methods. *Association of Official Analytical Chemists* **1975**.

106. Liu, H.; Idem, R.; Tontiwachwuthikul, P.; Liang, Z., Study of Ion Speciation of CO<sub>2</sub> Absorption into Aqueous 1-Dimethylamino-2-propanol Solution Using the NMR Technique. *Ind. Eng. Chem. Res.* **2017**, 56, (30), 8697-8704.

107. Li, M.; Liu, H.; Luo, X.; Tontiwachwuthikul, P.; Liang, Z., Development of Ion Speciation Plots for Three Promising Tertiary Amine-CO<sub>2</sub>-H<sub>2</sub>O Systems Using the pH Method and the <sup>13</sup>C NMR Method. *Energy Fuels* **2017**, 31, (3), 3069-3080.

108. Yang, Z.; Soriano, A. N.; Caparanga, A. R.; Li, M., Equilibrium solubility of

1  
2  
3 carbon dioxide in (2-amino-2-methyl-1-propanol + piperazine + water). *J. Chem.*  
4  
5 *Thermodyn.* **2010**, 42, (5), 659-665.

6  
7  
8 109. Tourneux, D. L.; Iliuta, I.; Iliuta, M. C.; Fradette, S.; Larachi, F., Solubility of  
9  
10 carbon dioxide in aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol.  
11  
12 *Fluid Phase Equilib.* **2008**, 268, (1), 121-129.

13  
14  
15 110. Chang, Y.; Leron, R. B.; Li, M., Equilibrium solubility of carbon dioxide in  
16  
17 aqueous solutions of (diethylenetriamine + piperazine). *The Journal of Chemical*  
18  
19 *Thermodynamics* **2013**, 64, 106-113.

20  
21  
22 111. Xiao, M.; Cui, D.; Zou, L.; Yang, Q.; Gao, H.; Liang, Z., Experimental and  
23  
24 modeling studies of bicarbonate forming amines for CO<sub>2</sub> capture by NMR spectroscopy  
25  
26 and VLE. *Sep. Purif. Technol.* **2020**, 234, 116097.

27  
28  
29 112. Dang, H.; Rochelle, G. T., CO<sub>2</sub> Absorption Rate and Solubility in  
30  
31 Monoethanolamine/Piperazine/Water. *Sep. Sci. Technol.* **2003**, 38, (2), 337-357.

32  
33  
34 113. Yang, X.; Rees, R. J.; Conway, W.; Puxty, G.; Yang, Q.; Winkler, D. A.,  
35  
36 Computational Modeling and Simulation of CO<sub>2</sub> Capture by Aqueous Amines. *Chem.*  
37  
38 *Rev.* **2017**, 117, (14), 9524-9593.

39  
40  
41 114. Barzagli, F.; Mani, F.; Peruzzini, M., Carbon dioxide uptake as ammonia and  
42  
43 amine carbamates and their efficient conversion into urea and 1,3-disubstituted ureas.  
44  
45 *J. CO<sub>2</sub> Util.* **2016**, 13, 81-89.

46  
47  
48 115. Li, M.; Shen, K., Calculation of equilibrium solubility of carbon dioxide in  
49  
50 aqueous mixtures of monoethanolamine with methyldiethanolamine. *Fluid Phase*  
51  
52 *Equilib.* **1993**, 85, 129-140.

53  
54  
55 116. Chen, C.-C.; Evans, L. B., A local composition model for the excess Gibbs  
56  
57 energy of aqueous electrolyte systems. *AIChE J.* **1986**, 32, (3), 444-454.

58  
59  
60 117. Na, S.; Hwang, S. J.; Kim, H.; Baek, I.-H.; Lee, K. S., Modeling of CO<sub>2</sub>

1  
2  
3 solubility of an aqueous polyamine solvent for CO<sub>2</sub> capture. *Chem. Eng. Sci.* **2019**, 204,  
4 140-150.  
5

6  
7  
8 118. Austgen, D. M.; Rochelle, G. T.; Xiao, P.; Chen, C., Model of Vapor-Liquid  
9 Equilibria for Aqueous Acid Gas-Alkanolamine Systems Using the Electrolyte-NRTL  
10 Equation. *Ind. Eng. Chem. Res.* **1989**, 28, (7), 1060-1073.  
11  
12

13  
14  
15 119. Austgen, D. M.; Rochelle, G. T.; Chen, C. C., Model of vapor-liquid equilibria  
16 for aqueous acid gas-alkanolamine systems. 2. Representation of hydrogen sulfide and  
17 carbon dioxide solubility in aqueous MDEA and carbon dioxide solubility in aqueous  
18 mixtures of MDEA with MEA or DEA. *Ind. Eng. Chem. Res.* **1991**, 30, 543–555.  
19  
20  
21

22  
23  
24 120. HU, W.; CHAKMA, A., Modelling of equilibrium solubility of CO<sub>2</sub> and H<sub>2</sub>S  
25 in aqueous amino methyl propanol (AMP) solutions. . *Chem. Eng. Commun.* **1990**, 94,  
26 (1), 53-61.  
27  
28

29  
30  
31 121. HU, W.; CHAKMA, A., Modelling of equilibrium solubility of CO<sub>2</sub> and H<sub>2</sub>S  
32 in aqueous diglycolamine (DGA) solutions. *The Canadian Journal of Chemical*  
33 *Engineering* **1990**, 68, 523–525.  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
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