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Nuclear Magnetic Resonance Studies of CO₂ Absorption and Desorption in Aqueous Sodium Salt of Alanine

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Supporting Information

ABSTRACT: For the first time, speciation evolution in aqueous sodium salt of alanine (SSA) solution during both CO_2 absorption and desorption has been investigated via nuclear magnetic resonance (NMR) spectroscopy. Results suggest that amine, carbamate, and bicarbonate are the main species formed in the solvent system. During CO_2 absorption, deprotonated alanine (Ala) reacts with CO_2 first to form carbamate, which subsequently hydrolyzes into bicarbonate. At higher CO_2 loadings (~0.6 mol/mol of Ala), it appears that bicarbonate is dominant. Interestingly, the carbamate concentration in the SSA solution increases first and then decreases slightly during CO_2 desorption, and the amount of carbamate after CO_2 desorption is more than that at the end of the CO_2 absorption, thus reducing the desorption efficiency. Furthermore, the species distributions have also been compared to those of the commercial monoethanolamine (MEA) absorbent, revealing that the main difference between SSA and MEA systems is the hydrolysis rate of carbamate. Determination of the species formed is a first step to understand the chemistry of the solvent system, which may facilitate developing more efficient and energy-saving solvents for CO_2 capture and sequestration.

1. INTRODUCTION

Worldwide use of fossil fuels has resulted in the accumulation of carbon dioxide (CO₂), a major greenhouse gas, which is suspected to cause climate change and global warming over decades.^{1,2} It is thus imperative to explore viable CO₂ capture and sequestration (CCS) technologies to reduce the release of CO₂ and lower its concentration in the atmosphere.^{3,4} Conventional technology for the industrial capture of CO₂ largely relies on employing aqueous amine solutions.^{5–7} However, the drawbacks of high-energy consumption, corrosion, and inefficiency for amine-scrubbing technologies have prompted the development of alternative strategies for CCS.⁸ Significant amounts of research have been conducted to explore advanced CO₂ capture materials;^{9–13} captured CO₂ is proposed to be sequestered by deposition in underground reservoirs.¹⁴

Amino acid salt (AAs) solvents have been evaluated as alternatives for alkanolamines for CO_2 removal because of their superior thermal stability, excellent biocompatibility, and negligible volatility.^{10,15,16} Studies aimed at modeling the molecular chemistry of CO_2 /AAs systems are numerous, but few experimental investigations have dealt with quantitative determination of the solution speciation of real absorbing and desorbing systems based on AAs. A better understanding of the reactions occurring in both absorption and desorption processes through the identification of chemical species produced in the CO_2 /AAs system will facilitate developing

faster and more efficient absorbents for CO_2 capture and sequestration and to make the process less energy demanding. Nuclear magnetic resonance (NMR) spectroscopic analysis is one of the advanced experimental tools that is able to identify chemical species produced by the reaction of CO_2 with different amines.^{17,18} Moreover, this experimental technique can evaluate the amounts of different carbon-containing compounds forming and equilibrating during the reaction. Either ¹H or ¹³C NMR experiments have been used to obtain liquid speciation in several amine $-CO_2-H_2O$ solutions.^{19–22} However, no report has been found about quantitative investigations of species distribution in a CO_2 /alanine system by a NMR technique.

In the present study, quantitative investigations of CO_2 contained species (i.e., carbamate and HCO_3^-) in an aqueous sodium salt of alanine (SSA) system were explored with NMR spectroscopic analysis. Determination of the speciation during both absorption and desorption processes allowed us to quantify the main reactions occurring in the CO_2/SSA system.

2. EXPERIMENTAL SECTION

2.1. Materials. L-Alanine (Ala), sodium hydroxide, monoethanolamine (MEA), deuterium oxide (D_2O , 99.9%), and tetramethylammo-

Received:December 31, 2014Revised:May 26, 2015Published:May 28, 2015

Energy & Fuels

nium chloride were purchased from Sigma-Aldrich. CO_2 (99.99%) and N_2 (99.999%) gases were used as received. SSA solution was prepared by adding Ala (34 wt %) and NaOH (15 wt %) at a 1:1 molar ratio in deionized water or D_2O . MEA solution were prepared by mixing MEA (30 wt %) in deionized water or D_2O .

2.2. CO₂ Absorption/Desorption. The experimental apparatus (see Figure S1 of the Supporting Information) for CO₂ absorption consisted of a CO₂ cylinder for supplying CO₂ at a certain concentration, the reactor (25 mL glass impinger), and the water bath for maintaining the temperatures of the reactor. CO₂ absorption was carried out using 100% CO2 in the glass impinger seating in a water bath of 313 K. Candidate solutions (~18 g) were loaded in the reactor and heated to 313 K. A fritted nozzle with a special nozzle tip $(170-220 \ \mu m \text{ glass frit})$ was used for CO₂ bubbling, and was inserted in the bottom of the impingers. For desorption, the thermal swing approach that has been used for both solvents and sorbents in our previous work was adopted.^{12,23-25} Samples were heated to 383 K in an oil bath equipped with a condenser for 60 min. The amounts of CO₂ absorbed (i.e., mass change before and after CO₂ absorption) and desorbed (i.e., mass change before and after CO₂ desorption) were determined using an analytical balance with an accuracy of 0.0001 g. The CO₂ regeneration efficiency was expressed as a ratio of the amount of CO₂ stripped from the regeneration reactor to the amount of CO_2 in the amine solution during the steady state.

2.3. NMR Studies. The CO₂-loaded solvents were collected and studied by NMR measurements. Initially, SSA-D₂O solution with a temperature of 313 K was thoroughly bubbled with a vigorous nitrogen flux, and the spectra were recorded. Afterward, the solution was flushed for 60 min with CO2 and samples were collected at different bubbling times (0, 1, 2, 5, 10, 20, 30, and 60 min) for NMR characterization. In addition, samples were collected at different CO₂ desorption times (0, 1, 2, 5, 10, 20, 30, 40, and 60 min) for NMR characterization. 1 H and 13 C NMR measurements were performed on a 600 MHz Varian INOVA to identify the species. The samples were prepared in NMR sample tubes with added deuterium oxide (D₂O). The volume of the sample and D₂O were \sim 200/500 µL. The ¹H NMR spectra were obtained with a delay time (D1) of 1 s and the number of scans of 32. The ¹³C NMR measurements were performed with a delay time of 120 s and number of scans of 64. For NMR quantitative determination of the species, ~ 2 mg of tetramethylammonium chloride $[(CH_3)_4N^+Cl^-]$ was used as an external reference standard. Species evolution was quantitatively estimated by NMR spectroscopy based on the following equation:

$$m_{\rm a} = m_{\rm b} \frac{N_{\rm b}}{N_{\rm a}} \frac{A_{\rm a}}{A_{\rm b}} \frac{M_{\rm a}}{M_{\rm b}}$$

where N is the number of protons responsible for the signals chosen, A is the area under the NMR signals, M is the mol weight, m_b is the amount of the known reference substance [e.g., (CH₃)₄N⁺Cl⁻], and m_a is the species amount to be determined.

3. RESULTS AND DISCUSSION

Figure 1 compares the CO_2 absorption performance of SSA and MEA solutions. In comparison to the state-of-the-art aminescrubbing technology, it can be seen that SSA solution reached a CO_2 capacity of 0.73 mol of CO_2 /mol of Ala after 60 min at 313 K and 1.0 bar, higher than the capacity (0.50 mol of CO_2 / mol of MEA) of the 30 wt % MEA solution.

NMR spectroscopy was used to identify the species in CO_2 loaded SSA and MEA solutions. The carbamate and bicarbonate were the products of CO_2 absorption. Figures 2 and 3 present the NMR spectra obtained for CO_2 -loaded solutions of SSA and MEA. For the SSA system, deprotonated Ala reacted with CO_2 to form Ala carbamate, which resulted in a "doubled" signal and another set of two lower peaks, i.e., ~1.25 ppm (CH₃) and ~3.65 ppm (CHN), in the ¹H NMR spectra, while Ala was protonated to give the ammonium ion



Figure 1. CO₂ uptake performance of MEA and SSA solutions.



Figure 2. (a) ${}^{13}C$ and (b) ${}^{1}H$ NMR spectra of CO₂-loaded SSA solution. Note that the peak at 4.63 ppm in panel b corresponds to the semi-deuterated water (HDO).

(Figure 2b). The formation of bicarbonate or NaHCO₃ (~161 ppm) was confirmed by ¹³C NMR spectra (Figure 2a). Similar to the SSA system, the doubled signal (because of the formation of MEA carbamate) and HCO₃⁻ also appeared in the NMR spectra of CO₂-loaded MEA solution (Figure 3). The chemical shifts of MEA were in agreement with those reported in the literature.^{21,22} These results show that amine, carbamate, and bicarbonate were in the CO₂-loaded SSA and MEA solutions.

Species evolution in SSA and MEA solutions as a function of the CO₂ absorption time was further investigated by NMR spectroscopic analysis (Figure 4 and Figure S2 of the Supporting Information). For the SSA system, Ala carbamate formed immediately upon CO₂ absorption and increased sharply with increasing CO₂ absorption time from 0 to 5 min, after which the amount of carbamate decreased with increasing CO₂ absorption time until 60 min (Figure 4). The observed drop off of carbamate after reaching a maximum concentration (~0.3 mol/mol of Ala) after 5 min was due to the hydrolysis of carbamate, which led to the formation of NaHCO₃. NaHCO₃ formation was observed at 5 min, and its concentration increased almost lineally with increasing CO₂ absorption time until 60 min (Figure 4). At 60 min, there were ~0.1 mol/mol of Ala of Ala carbamate and ~0.6 mol/mol of



Figure 3. (a) ¹³C and (b) ¹H NMR spectra of CO₂-loaded MEA solution.



Figure 4. Species changes (from NMR spectra) in SSA and MEA solutions as a function of the CO_2 absorption time.

Ala of NaHCO₃ in the whole solution. These experimental speciations agreed well with those reported for the potassium glycinate solvent²⁶ and MEA system²⁰ and matched with the modeling results,²⁷ which provide confirmatory evidence to support that CO₂ first interacted with the deprotonated Ala in SSA to form Ala carbamate, which subsequently hydrolyzed into NaHCO3 because of its low stability in aqueous solutions.²² For the MEA system, the amount of carbamate formed increased almost linearly with increasing CO2 absorption time in the first 5 min and reached the highest concentration of ~0.4 mol/mol of MEA at 5 min. After that, carbamate showed a slight drop, while a small amount of bicarbonate was produced simultaneously. The main difference between SSA and MEA systems was the hydrolysis rate of carbamate. In the case of MEA, its carbamate has high stability and, therefore, exhibited a low hydrolysis rate and produced a small amount of bicarbonate (~0.1 mol/mol of MEA) at the same CO_2 absorption time. A higher CO_2 capacity can be achieved when absorbed CO2 turns into bicarbonate instead of carbamate. This is because the formation of bicarbonate follows

a 1:1 stoichiometry (i.e., 1 CO_2 molecule reacts with 1 amino group), while the formation of carbamate follows the 1:2 stoichiometry. This explains the lower absorption capacity of MEA compared to SSA.

The CO₂ absorption mechanism of the primary (RNH₂) amine solutions can be expressed as shown below. Dissolved CO₂ quickly reacts with amine and generates carbamate and protonated amine (eq 1).²⁸ In aqueous solutions, carbamate undergoes hydrolysis, resulting in the formation of bicarbonate/carbonate (depending upon the pH of the liquid) and free amine (eq 2).²⁹

$$CO_2 + 2R - NH_2 \leftrightarrow R - NHCOO^- + R - NH_3^+$$
 (1)

$$R-NHCOO^{-} + H_2O \leftrightarrow R-NH_2 + HCO_3^{-}$$
(2)

In the case of MEA, its carbamate has high stability, with the progress of the reaction shown in eq 2 being very slow. Thus, the reaction in eq 1 is dominant, indicating that the amount of CO_2 that can be absorbed by 1 mol of amine is about 0.5 mol.³⁰ In contrast, the result of this study indicated that SSA could quickly initiate the hydrolysis reaction to form bicarbonate as a result of the steric hindrance effect.^{22,31} It is known that substitution at the α carbon atom adjacent to the amino group of an amine reduces the stability of carbamate, resulting in enhanced hydrolysis of the carbamate to bicarbonate/ carbonate.^{32,33} This could explain the relative instability of the carbamate of Ala. Therefore, the overall reaction for SSA solution system can be expressed as eq 3, suggesting that this solvent absorbs CO_2 in a 1:1 stoichiometry (i.e., 1 CO_2 molecule reacts with 1 amino group). Note that the SSA system did not reach equilibrium at 60 min (Figure 1) and higher CO₂ capacity could be achieved when further increasing CO_2 absorption time.

$$CO_{2} + Na^{+}[^{-}OOC - R - NH_{2}] + H_{2}O$$

$$\leftrightarrow ^{-}OOC - R - NH_{3}^{+} + NaHCO_{3}$$
(3)

Stripping of CO_2 from loaded solution of SSA was carried out at 383 K (at atmospheric pressure). The CO_2 release increased with CO_2 desorption time, and ~70% CO_2 was released at 60 min. To explore the CO_2 desorption performance and examine the mechanism of the CO_2 desorption, the composition of CO_2 -desorbed SSA was monitored using NMR spectroscopy at different time intervals (Figure 5 and Figure S3 of the



Figure 5. (a) Species changes in SSA solution as a function of the CO_2 desorption time. (b) CO_2 loading and CO_2 release in solution as a function of the CO_2 desorption time.

Supporting Information). As shown in Figure 5a, bicarbonate was relatively easily decomposed by heating and decomposed completely in 20 min at a significant rate. In contrast to the general viewpoint that carbamate decomposes upon heating, the carbamate concentration in SSA solution increased from 0 to 30 min, reached a maximum value of ~0.32 mol/mol of Ala at 30 min after CO_2 desorption, and then decreased slowly. The increased concentration of carbamate could be ascribed to the endothermic reaction (eq 4) that produces carbamate in the desorption step.

$$^{-}OOC-R-NH_{3}^{+} + 2HCO_{3}^{-}$$

 $\leftrightarrow ^{-}OOC-R-NHCOO^{-} + CO_{2} + H_{2}O$ (4)

This is consistent with the observations by Hook, who also showed an increased level of carbamate after CO_2 desorption from the potassium glycinate solvent.³⁴ For MEA, the carbamate concentration increased at the early stage of the thermal desorption process, and it was assumed that the endothermic formation of carbamate prevails over its decomposition, so that more carbamate is produced at the end of the desorption process than at the end of the absorption.^{21,35} As a consequence of the formation of carbamate, less CO_2 was released and less free amine was regenerated, therefore reducing the desorption efficiency. Note that the endothermic formation of carbamate in the desorption process is a negative element from a thermodynamic point of view, because it increases the energy demand of the process.²¹ Figure 5b shows the CO_2 loading and CO_2 release in SSA as a function of the CO_2 desorption time, indicating that ~0.25 mol of CO_2/mol of Ala remained in the solution after the regeneration process, which means a regeneration efficiency of ~70% was achieved; under the same conditions, MEA–H₂O had a regeneration efficiency of ~50%.

One limitation of this study is that the interpulse delay time used (120 s) was relatively short, while the longitudinal relaxation times of C=O carbons are long (especially in small molecules). This could be a point of inaccuracy, and the results should be taken with caution as semi-quantitative. Also, the effects of contaminants (e.g., SO_2 and NO_2) and temperature on species formation were not studied and will be examined in the future.

4. CONCLUSION

In conclusion, we successfully applied NMR spectroscopy to quantitatively investigate the CO2-contained species in the capture and release of CO₂ from an AAs solvent. Results suggest that amine, carbamate, and HCO₃⁻ species are the main species formed in the solvent system. NMR analysis allowed us to determine the amounts of CO₂ stored in solution as carbamate and HCO₃⁻ and the formation of Ala carbamate and bicarbonate as a function of the absorption or desorption time. Results also suggest that carbamate is one of the main species formed in the system at the beginning of CO₂ loading. At higher CO₂ loadings (~0.6 mol/mol of Ala), it appears that HCO_3^- is dominant. The Ala carbamate concentration increases first and reaches a maximum value of ~0.32 mol/ mol of Ala at 30 min after CO₂ desorption and then decreases slightly. Quantitative determination of the species in the solvent system will facilitate developing more efficient solvents as well as provide insights in developing thermodynamic models of such solvent systems.

ASSOCIATED CONTENT

S Supporting Information

Further information on schematic diagram of homemade CO_2 absorption apparatus (Figure S1) and ¹H and ¹³C NMR spectra for SSA solution at varying absorption and desorption times (Figures S2 and S3, respectively) (PDF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.Sb00535.

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Notes

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and do not necessarily reflect the views of the funding agencies or their institutions.

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

As part of the NETL–RUA, a collaborative initiative of the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) with Carnegie Mellon University, the Pennsylvania State University, the University of Pittsburgh, Virginia Polytechnic Institute and State University, West Virginia University, and URS Corporation, this technical effort was performed under Research and Engineering Services (RES) contract DE-FE0004000. Support was also received from West Virginia National Aeronautics and Space Administration Experimental Program to Stimulate Competitive Research (WV NASA EPSCoR). The authors thank Suzanne Danley for proofreading.

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