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Phase change amino acid salt separates into CO_2 -rich and CO_2 -lean phases upon interacting with CO_2



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HIGHLIGHTS

- Innovative phase change amino acid salt solvent is developed for CO₂ capture.
- Amino acid salt solution is turned into a CO₂-rich phase and a CO₂-lean phase upon simple bubbling with CO₂.
- \bullet The developed solvent captures the most CO_2 (~90%) in the CO_2-rich phase.
- NMR spectroscopy was used to identify the species in the solution.

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GRAPHICAL ABSTRACT



ABSTRACT

Concerns over global climate change have led to strong research emphasis worldwide on reducing the emission of greenhouse gases like CO_2 . One avenue for carbon emission reduction is using CO_2 capture and storage from industrial sources. Having low toxicity and low vapor pressure and being resistant to oxidation, natural amino acids could be a better choice over current carbon capture materials. In this study, we pioneered a unique phase change amino acid salt solvent concept in which amino acid salt solution was turned into a CO_2 -rich phase and a CO_2 -lean phase upon simple bubbling with CO_2 and most importantly, this solution captured the most CO_2 (~90%) in the CO_2 -rich phase. Bicarbonate was found to be dominant in the CO_2 -rich phase, which had a high CO_2 loading capacity and good regenerability and

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Amino acid salt CO₂-lean phase CO₂-rich phase cycling properties. Such a phase change amino acid salt solvent may provide unique solutions for industries to reduce CO₂ and other harmful emissions.

1. Introduction

Currently, over 85% of the global energy demand is being supported by the burning of fossil fuels, which release large quantities of carbon dioxide (CO_2) into the atmosphere [1-4]. Thus, intensive research on CO₂ capture and storage is being conducted to mitigate CO₂ emission which is found to be a major contributor to global climate change [5–9]. Significant progress has been made but unfortunately, none of the current carbon capture and sequestration methodologies can meet the overall fossil energy performance goals set by the U.S. Department of Energy of a 90% CO₂ capture rate with 95% CO₂ purity at a cost of electricity 30% less than baseline capture approaches [10]. The state-of-the-art technology for CO₂ capture is solvent absorption in which an aqueous solution of alkanolamine serving as an absorbent reacts chemically with CO₂ to form soluble carbamates and/or bicarbonates [11]. This process has already been in commercial use; however, this technology requires an inhibitively high amount of regeneration energy, because CO₂ can only be released at quite high temperatures, owing to the strong interactions of CO₂ with such absorbents [12.13].

In order to identify cost-effective approaches for CO_2 capture, new materials and techniques have been studied [1,8,14–18]. In particular, phase change solvents, a new class of solvents, have emerged and been developed into one of the most promising technologies for CO_2 capture. Several experimental studies with absorbents that exhibit phase-change features during the absorption or desorption of CO_2 have shown promise to reduce solvent regeneration energy [19–21]. Such phase change technology removes CO_2 from power plant flue gases using a solvent that, when it reacts with CO_2 , rapidly forms two distinct phases: a CO_2 -rich phase and a CO_2 -lean phase. Only the CO_2 -rich phase will then undergo regeneration. By regenerating only the CO_2 -rich phase, significantly less energy may be needed for the whole process [22].

The current phase change solvents, which often require organic solvents [23], may form liquid–liquid phases or liquid–solid phases upon CO₂ absorption. Phase change solvents that form two liquid phases after CO₂ absorption include the mixed amine systems and DMX[™] process which can be separated based on differences in density [24]. Bruder and Svendsen found that certain blends of 2-(Diethylamino)ethanol/3-(Methylamino)propylamine could form two liquid phases after CO₂ absorption and the cyclic loading could be significantly higher than that of monoethnolamine (MEA) [24]. Phase change solvents that form a liquid phase and a solid phase (due to precipitation during CO₂ absorption) can be found in systems such as alkanolamine/ionic liquids, chilled ammonia, and triethylenetetramine/ethanol solutions. Independent of the precipitate type, the formation of a solid reaction product during absorption and its removal from the solution phase by precipitation may shift the reaction equilibrium toward the production of more products (carbamate or bicarbonate).

Amino acids are of great interest as potential solvents and sorbents for CO_2 capture because they are environmentally friendly, are naturally present in the environment, and have low volatility (due to their ionic nature) [25–31]. In this study, we report, for the first time, the development of phase change solvents based on amino acid salts to convert CO_2 emissions into regenerable carbamate and bicarbonate, and we identified a unique phase change amino acid salt (Fig. 1a), which reacted with CO_2 and underwent a

self-concentrating process to form a CO_2 -lean phase and a CO_2 -rich phase. The CO_2 -lean phase could be reused and the CO_2 -rich phase could be regenerated.

2. Materials and methods

2.1. Materials

L-alanine (Ala, \geq 98%), L-arginine (Arg, \geq 98%), L-lysine (Lys, \geq 98%), L-serine (Ser, \geq 99%), L-aspartic acid (Asp, \geq 98%), and sodium hydroxide (NaOH, \geq 98%) were purchased from Sigma-Aldrich. Deuterium oxide (D₂O, 99.9%) and tetramethylammonium chloride (\geq 98%), used for nuclear magnetic resonance (NMR) measurements, were also obtained from Sigma-Aldrich. CO₂ and N₂ gases from Airgas, Inc. were used as received. Amino acid salt solutions were prepared by adding amino acids and NaOH [e.g. Ala (34 wt% or 4.9 mol/L), NaOH (15 wt%)] at a 1:1 molar ratio in deionized water or D₂O.

2.2. CO₂ absorption/desorption

 CO_2 absorption was carried out using 100% CO_2 in a 25 mL 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- μ m glass frit) was used for CO₂ bubbling, which was inserted in the bottom of the impingers. For desorption, samples were heated to 393 K for 90 min in an oil bath equipped with a condenser. For absorption/desorption cycling runs of phase change amino acid salt solvent, CO₂ absorption was also carried out using 100% CO₂ in a 25 mL glass impinger seating in a water bath of 313 K. The CO₂-loaded phase change amino acid salt solvent with precipitates was centrifuged to speed up the phase separation of the two phases. The clear phase was pipetted out for reuse in the next cycle. The CO₂-rich precipitates in the glass impinger were heated to 393 K and maintained at this temperature for 90 min to release the captured CO₂. The clear phase pipetted out was added back to the impinger with the regenerated solution, and cooled down to 313 K for the next absorptiondesorption cycle. 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.

2.3. Nuclear magnetic resonance (NMR) studies

¹H and ¹³C NMR measurements were performed using Varian INOVA 600 MHz to identify the species in solution and solid samples. The samples were prepared in NMR sample tubes and D₂O was used instead of H₂O. The volumes of the solution (i.e. CO₂-lean phase solution and entire solution) sample and D₂O were 200 µL and 500 µL. The amounts of the CO₂-rich phase and D₂O were 100–200 mg and 700 µL. The ¹H NMR spectra were obtained with a delay time (D1) of 1 s and the number of scans was 32. The ¹³C NMR measurements were performed with a delay time of 20 s and number of scans of 64. In the ¹³C NMR spectra, bicarbonate peak was presented at ~161 ppm; Ala carbamate at ~164 ppm; Ala/AlaH⁺ at 18, 50, and 177 ppm; and (CH₃)₄N⁺Cl⁻ at ~55 ppm. In the ¹H spectra, the D₂O peak was at 4.8 ppm; Ala/AlaH⁺ peaked at ~1.1 and ~3.2 ppm; Ala carbamate at ~1.15 and ~3.75 ppm.

Fig. 1. (a) Scheme of the phase change amino acid salt solvent process for CO_2 capture. Ala-NaOH- CO_2 -H₂O solution absorbs CO_2 and undergoes a self-concentrating process to form a CO_2 -lean phase and a CO_2 -rich phase. The CO_2 -lean phase is reused and the CO_2 -rich phase is sent to the stripper for regeneration. Ala-NaOH- CO_2 -H₂O solution (b) before and (c) after CO_2 absorption.

Note that the peaks may shift to some degree due to the change of pH of the test samples. For NMR quantitative determination of the species, 2 mg tetramethylammonium chloride $[(CH_3)_4N^+Cl^-]$ was used as a standard reference. The amounts of species in the samples were quantitatively estimated based on the following equation,

$$m_a = m_b \cdot rac{N_b}{N_a} \cdot rac{A_a}{A_b} \cdot rac{M_a}{M_b}$$

where *N* is the number of protons responsible for the signals chosen, *A* is the area under appropriate NMR signals, *M* is the molecular weight, m_b is the known amount of the standard reference [i.e., (CH₃)₄N⁺Cl⁻], and m_a is the amount of a specific specie. The estimated uncertainty associated with these integral values is ±5%.

3. Results and discussion

 CO_2 was bubbled directly (Fig. 1b) into solutions of amino acids (e.g. Ala, Arg, Lys, Ser, and Asp), and we found that among the amino acids studied, Ala underwent a unique phase change process and formed two distinct phases, i.e. a clear phase on the top and a milky phase on the bottom (Fig. 1c). The volume ratio between the clear phase and the milky phase was about 1/2.

To gain more insight, NMR spectroscopy was used to identify the species in the Ala solution before CO₂ bubbling and the two phases (i.e. the clear and milky phases) formed after CO₂ bubbling (Fig. 2). Before CO₂ bubbling, proton signals of free Ala appeared at \sim 1.1 and \sim 3.2 ppm (Fig. 2b). After CO₂ bubbling, Ala reacted with CO₂ to form Ala carbamate (⁻OOCCHCH₃NHCOO⁻) in both the clear and milky phases, which resulted in "doubled" signal and another set of two peaks (~1.1 and 3.7 ppm) in the NMR spectra (Fig. 2d and f). Meanwhile, Ala was protonated to give the ammonium ion (-OOCCHCH₃NH₃⁺ or AlaH⁺). Note that the peaks of Ala or AlaH⁺ shifted to \sim 1.25 and 3.6 ppm due to the pH change of the solution after CO₂ absorption. Because of the fast exchange of the proton, it was not possible to distinguish between the amine form and the protonated amine form in the NMR spectra. Thus, the amine and protonated amine peaks were treated as Ala/AlaH⁺ peaks in the NMR spectra. The formation of sodium bicarbonate or NaHCO₃ (~161 ppm) was confirmed by ¹³C NMR spectra (Fig. 2c and e). NMR spectra showed that species of NaHCO₃, Ala/AlaH⁺, and Ala carbamate were present in both the clear and milky phases and no Na₂CO₃ was observed (Fig. 2).

Using tetramethylammonium chloride $[(CH_3)_4N^+Cl^-]$ as an internal reference standard, we quantitatively determined the species amount in each phase based on NMR spectra. The results revealed that, in the milky phase, NaHCO₃ was dominant (~47 wt %) and the amounts of Ala/AlaH⁺ and Ala carbamate were 43 wt% and 10 wt%, respectively (Table 1). In the clear phase, Ala/AlaH⁺ was dominant and the amounts of NaHCO₃, Ala/AlaH⁺, and Ala carbamate were about 19, 50, and 31 wt%, respectively. Furthermore, from the NMR analysis, we found that over 90% of CO₂ was absorbed in the milky phase (therefore designated as CO₂-rich phase) and about 10% CO₂ was absorbed in the clear phase (designated as CO₂-lean phase). This means that Ala solution, upon bubbling with CO₂, self-concentrates into a CO₂-lean phase and a CO₂-rich phase.

Normally, precipitation is considered to be non-beneficial in CO_2 capture processes as it will result in an increase in the viscosity of the solution as well as the plugging and fouling of the reactor. However, if the precipitate contains CO_2 (i.e., carbamate, bicarbonate/carbonate), the driving force may be maintained even with increasing CO_2 loading, so that higher absorption capacity may be obtained and result in lower energy consumption during subsequent regeneration [32].

We examined the evolution of chemical species in Ala–NaOH– CO_2-H_2O solution at different absorption times using NMR spectroscopic analysis (Fig. 3a and Fig. S1 in Supporting Information). Ala carbamate was found to form immediately upon CO_2 bubbling, and the amount of carbamate increased sharply with CO_2 bubbling from 0 to 5 min (Fig. 3a and Fig. S1a in Supporting Information). After this initial increase step, the amount of carbamate that formed decreased with increasing CO_2 bubbling time. Meanwhile, no NaHCO₃ was detected before 5 min, and NaHCO₃ started to form at 5 min and its amount increased almost linearly with increasing CO_2 absorption time (Fig. 3a and Fig. S1b in Supporting Information). At 90 min, there were ~260 mg/(g solution) of NaHCO₃ and ~50 mg/(g solution) of Ala carbamate in the entire solution (Fig. 3a).

These data strongly suggested that during CO_2 bubbling, Ala interacted with CO_2 first to form Ala carbamate:

$$\begin{split} \text{CO}_2(g) + 2^-\text{OOCCHCH}_3\text{NH}_2 &= ^-\text{OOCCHCH}_3\text{NHCOO}^- \\ &+ ^-\text{OOCCHCH}_3\text{NH}_3^+ \end{split}$$

The formed Ala carbamate subsequently hydrolyzed into NaHCO₃, as shown below, due to the low stability of Ala carbamate in aqueous solutions [31,33]:

Fig. 2. (a, c, and e) ¹³C and (b, d, and f) ¹H NMR spectra of Ala–NaOH–CO₂–H₂O solution (a and b) before CO₂ bubbling and (c–f) after CO₂ absorption in the (c and d) CO₂-lean phase and (e and f) CO₂-rich phase. D₂O was used as a solvent and tetramethylammonium chloride [(CH₃)₄N⁺Cl⁻] was used as a standard reference.

Fable 1	
Species distribution in CO_2 -rich and CO_2 -lean phases of Ala–NaOH– CO_2 – H_2O solution after CO_2 absorption.	

Phases	CO ₂ loading (%)	Carbamate		Bicarbonate		Ala/AlaH ⁺	
		mol/(mol Ala)	(% ^a)	mol/(mol Ala)	(% ^a)	mol/(mol Ala)	(% ^a)
CO ₂ -lean phase	10	0.035	31	0.045	19	0.11	50
CO ₂ -rich phase	90	0.09	10	0.74	47	0.67	43

^a Percentage among the species of carbamate, bicarbonate, and carbonate.

Fig. 3. Changes of carbamate and bicarbonate (from NMR spectra) of the entire Ala-NaOH– CO_2 – H_2O solution as a function of (a) CO_2 absorption time and (b) CO_2 desorption time. (c) Changes of carbamate and bicarbonate of the CO_2 -rich phase as a function of CO_2 desorption time.

$-\mathsf{OOCCHCH}_3\mathsf{NHCOO}^- + \mathsf{H}_2\mathsf{O} = -\mathsf{OOCCHCH}_3\mathsf{NH}_2 + \mathsf{HCO}_3^-$

The species evolution of Ala-NaOH-CO₂-H₂O solution with CO₂ bubbling time had the same trend as the species evolution of MEA system, however, no phase change phenomena were observed in MEA systems [34,35]. Note that the formation of bicarbonate instead of carbamate alone during CO2 absorption in the Ala-NaOH-CO₂-H₂O solution has certain advantages: (i) Maximum absorption of CO₂ can be obtained when all of the absorbed CO₂ exists as bicarbonate. This is because the formation of carbamate follows a 1:2 stoichiometry (i.e. one CO₂ molecule reacts with two amino groups), while the formation of bicarbonate follows a 1:1 stoichiometry. (ii) It is expected that a solution containing a higher proportion of bicarbonate will also undergo desorption at a greater rate and produce a "leaner" desorbed solution [36], which was confirmed by the remaining studies in this contribution. It is therefore desirable to achieve high carbamate hydrolysis during CO₂ absorption.

To explore the CO₂ desorption performance and examine the mechanism of CO₂ desorption, we performed NMR studies to investigate species changes in the entire Ala-NaOH-CO2-H2O solution as a function of CO₂ desorption time (Fig. 3b, and Figs. S2 and S3 in Supporting Information). One can see that bicarbonate was easily decomposed by heating, and the decomposition was completed within 10 min. In contrast to the general belief that carbamate decomposes and decreases upon heating solutions like MEA, the amount of Ala carbamate increased sharply from 0 to 250 mg/(g solution) within 10 min and reached the highest value of 268 mg/(g solution) at 30 min. After that, the amount of Ala carbamate decreased slowly from 30 to 90 min. Clearly, the decomposition of bicarbonate led to the formation of carbamate and also the release of CO₂. During this process, the carbamate seems quite stable, with little decomposition/regeneration taking place at 393 K when the bicarbonate was not present. Hook found that carbamate was increased rather than decreased after CO₂ desorption from the potassium glycinate solvent [36]. Similar decomposition and formation of carbamate were observed in aqueous 2aminoethanol and N-methyl-substituted 2-aminoethanol, where Barzagli et al. assumed that the carbamate decomposition and the endothermic reaction that produces carbamate took place to almost the same extent [37,38]. The endothermic formation of carbamate prevailed over its decomposition so that more carbamate was produced at the end of the desorption process than at the end of the absorption step [31,38]. Therefore, upon heating, the bicarbonate in the CO₂ loaded phase change amino acid salt solvent was converted back to carbamate first and then released CO₂. Although some carbamate remained in the final desorbed solution, most absorbed CO2 in the form of bicarbonate was released (Fig. 3b). Bicarbonate decomposes easily and may save energy during regeneration compared to MEA solvent which has stable carbamate. Proposed reactions during CO₂ absorption and desorption in Ala-NaOH-CO₂-H₂O solution are as follows:

Species evolution in the CO2-rich phase of CO2-loaded Ala-NaOH-CO₂-H₂O solution as a function of CO₂ desorption time was further evaluated (Fig. 3c and Figs. S4 and S5 in Supporting Information). Similar to the species changes in the entire CO₂loaded Ala-NaOH-CO₂-H₂O solution, the amount of bicarbonate decreased sharply from 0 to 30 min and was completely decomposed within 30 min. Along with the decrease of bicarbonate, the amount of Ala carbamate increased first until 30 min and then decreased with increasing CO₂ desorption time. At 30 min, there were \sim 274 mg/(g CO₂-rich-phase) of Ala carbamate and no detectable NaHCO₃ in the CO₂-rich-phase solution (Fig. 3c). It should be noted that it took much longer (30 min vs. 10 min) to completely decompose bicarbonate in the CO₂-rich phase compared to that in the entire solution (Fig. 3b). It seems that the existence of the CO₂-lean phase facilitated the decomposition of bicarbonate (Fig. 3b); the underlying reason is unknown.

Fig. 4a presents the CO₂ uptake performance of Ala–NaOH– CO₂–H₂O solution which indicated that CO₂ absorption capacity of Ala–NaOH–CO₂–H₂O solution increased quickly within the first 20 min followed by relatively slower CO₂ absorption. The slow absorption rate at the late stage was associated with the phase change phenomenon during which the viscosity of the solution increased. A decent CO₂ absorption capacity of [(0.89 mol CO₂)/ (mol Ala)] was achieved. This was probably because the introduction of substituents at the α -carbon atom of amino acids (e.g. Ala) reduces the stability of its carbamate resulting in more hydrolysis of carbamate into bicarbonate and thereby allowing high CO₂ absorption. In addition, formation of solid precipitates could shift the reaction equilibrium toward the production of more carbamate or bicarbonate as well as high CO₂ loading capacity.

The unique phase change amino acid salt phenomenon may be exploited to design an energy efficient CO_2 absorption/desorption process, i.e. phase change solvent process [19–21], where the CO_2 -lean phase can be reused without regeneration and the CO_2 -rich phase can be regenerated and reused; such a process could significant reduce the energy penalty associated with regeneration compared to conventional MEA based solvent processes [19–21,39]. Fig. 4b presents the outcome of regenerating only the CO_2 -rich phase in the Ala–NaOH– CO_2 –H₂O solution. One can see that the CO_2 release increased sharply within the first 10 min followed by a much slower CO_2 release rate. Most (~80%) CO_2 was released within the first 10 min. Using this regeneration process (i.e. only regenerating the CO_2 -rich phase), we obtained a decent working capacity of 0.62 (mol CO_2)/(mol Ala); MEA (30 wt%) had a capacity of [0.25 (mol CO_2)/(mol MEA)] [40].

Absorption–desorption cycles were further performed to evaluate the regenerability of Ala–NaOH– CO_2 – H_2O solution using a temperature-swing (*T*-swing) process (Fig. 4c). We carried out four absorption–desorption cycles with each absorption and desorption experiment lasting 90 min. The CO₂-rich phase containing the precipitates could be regenerated by increasing the temperature, driving off the CO₂ and causing the precipitates to re-dissolve. At the beginning, the efficiency of CO₂ absorption was very high as the experiment started with pure amine. Then, after an expected decrease (due to the presence of increased carbamate in the

Fig. 4. (a) CO_2 uptake performance of the entire Ala–NaOH– CO_2 –H₂O solution as a function of CO_2 absorption time. (b) CO_2 release of the entire Ala–NaOH– CO_2 –H₂O solution as a function of CO_2 desorption time (only the CO_2 –rich phase was regenerated). The CO_2 remaining (including CO_2 in both CO_2 –lean and CO_2 -rich phases) was presented as well. The amount of Ala salt is based on that in the entire solution. (c) CO_2 absorption/desorption cycling of Ala–NaOH– CO_2 –H₂O solution.

regenerated solutions), the absorption remained substantially constant [0.68 (mol CO_2)/(mol Ala)] during the following absorptiondesorption cycles. In the first cycle, a 0.62 (mol CO_2)/(mol Ala) CO_2 was released from the CO_2 -rich phase, which is about ~70% of the CO_2 absorbed in the entire solution. It can be seen that decent re-absorption capacities of 0.72, 0.69, and 0.68 (mol CO_2)/ (mol Ala) were achieved during the second, third, and fourth cycle, respectively; in multiple cycling, the capacity of MEA was typically about 0.20–0.25 (mol CO_2)/(mol MEA) [40].

4. Conclusions

The rationale of developing phase change solvents for CO_2 capture is that phase change solvent technologies, in which the CO_2 -rich phase can be regenerated and reused while the CO_2 -lean phase can be reused without regeneration, may significantly reduce the energy penalty associated with regeneration. Our study showed that amino acid Ala salt solution could undergo a phase change process upon CO_2 bubbling and capture the majority of CO_2 in the CO_2 -rich phase. By regenerating only the CO_2 -rich phase while reusing the CO_2 -lean phase, a working capacity of $0.62 \pmod{O_2}$ /(mol Ala) was obtained. We also found that upon interacting with CO_2 , the amino acid Ala was converted to Ala carbamate which subsequently hydrolyzed into bicarbonate, and these reactions were reversed during regeneration.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2015. 09.094.

References

- D'Alessandro DM, Smit B, Long JR. Carbon dioxide capture: prospects for new materials. Angew Chem Int Ed Engl 2010;49:6058–82.
- [2] Figueroa JD, Fout T, Plasynski S, McIlvried H, Srivastava RD. Advances in CO₂ capture technology—The U.S. Department of Energy's Carbon Sequestration Program. Int J Greenhouse Gas Control 2008;2:9–20.
- [3] Wang WL, Xiao J, Wei XL, Ding J, Wang XX, Song CS. Development of a new clay supported polyethylenimine composite for CO₂ capture. Appl Energy 2014;113:334–41.
- [4] Goto K, Yogo K, Higashii T. A review of efficiency penalty in a coal-fired power plant with post-combustion CO₂ capture. Appl Energy 2013;111:710–20.
- [5] Rochelle GT. Amine scrubbing for CO₂ capture. Science 2009;325:1652-4.
- [6] Blanchard LA, Hancu D, Beckman EJ, Brennecke JF. Green processing using ionic liquids and CO₂. Nature 1999;399:28–9.
- [7] Lin L-C, Berger AH, Martin RL, Kim J, Swisher JA, Jariwala K, et al. In silico screening of carbon-capture materials. Nat Mater 2012;11:633–41.
- [8] Li B, Duan Y, Luebke D, Morreale B. Advances in CO₂ capture technology: a patent review. Appl Energy 2013;102:1439–47.
 [9] Markewitz P, Kuckshinrichs W, Leitner W, Linssen J, Zapp P, Bongartz R, et al.
- Worldwide innovations in the development of carbon capture technologies and the utilization of CO₂. Energy Environ Sci 2012;5:7281.
- [10] Liu J, Thallapally PK, McGrail BP, Brown DR, Liu J. Progress in adsorption-based CO₂ capture by metal-organic frameworks. Chem Soc Rev 2012;41:2308–22.
- [11] Shakerian F, Kim KH, Szulejko JE, Park JW. A comparative review between amines and ammonia as sorptive media for post-combustion CO₂ capture. Appl Energy 2015;148:10–22.
- [12] Xiang SC, He YB, Zhang ZJ, Wu H, Zhou W, Krishna R, et al. Microporous metalorganic framework with potential for carbon dioxide capture at ambient conditions. Nat Commun 2012;3:954.

- [13] Zhang MK, Guo YC. Rate based modeling of absorption and regeneration for CO₂ capture by aqueous ammonia solution. Appl Energy 2013;111:142–52.
- [14] Li B, Jiang B, Fauth DJ, Gray MML, Pennline HW, Richards GA. Innovative nano-
- layered solid sorbents for CO₂ capture. Chem Commun 2011;47:1719–21.
 [15] Duan YH, Luebke DR, Pennline HW, Li BY, Janik MJ, Halley JW. Ab initio thermodynamic study of the CO₂ capture properties of potassium carbonate sesquihydrate K₂CO₃ center dot 1.5H(2)O. J Phys Chem C 2012;116:14461–70.
- [16] Hoshino Y, Imamura K, Yue MC, Inoue G, Miura Y. Reversible absorption of CO₂ triggered by phase transition of amine-containing micro- and nanogel particles. J Am Chem Soc 2012;134:18177–80.
- [17] Gao J, Cao L, Dong H, Zhang X, Zhang S. Ionic liquids tailored amine aqueous solution for pre-combustion CO₂ capture: role of imidazolium-based ionic liquids. Appl Energy 2015;154:771–80.
- [18] Jiang B, Kish V, Fauth DJ, Gray ML, Pennline HW, Li B. Performance of aminemultilayered solid sorbents for CO₂ removal: effect of fabrication variables. Int J Greenhouse Gas Control 2011;5:1170–5.
- [19] Hasib-ur-Rahman M, Siaj M, Larachi F. CO₂ capture in alkanolamine/roomtemperature ionic liquid emulsions: a viable approach with carbamate crystallization and curbed corrosion behavior. Int J Greenhouse Gas Control 2012;6:246–52.
- [20] Ciftja AF, Hartono A, Svendsen HF. Experimental study on phase change solvents in CO₂ capture by NMR spectroscopy. Chem Eng Sci 2013;102:378–86.
- [21] Ma'mun S, Kim I. Selection and characterization of phase-change solvent for carbon dioxide capture: precipitating system. Energy Proc 2013;37:331–9.
- [22] Raynal L, Alix P, Bouillon PA, Gomez A, de Nailly ML, Jacquin M, et al. The DMX (TM) process: an original solution for lowering the cost of post-combustion carbon capture. Energy Proc 2011;4:779–86.
- [23] Zheng S, Tao M, Liu Q, Ning L, He Y, Shi Y. Capturing CO₂ into the precipitate of a phase-changing solvent after absorption. Environ Sci Technol 2014;48:8905–10.
- [24] Brœder P, Svendsen HF. Capacity and kinetics of solvents for post-combustion CO₂ capture. Energy Proc 2012;23:45–54.
- [25] Knuutila H, Aronu UE, Kvamsdal HM, Chikukwa A. Post combustion CO₂ capture with an amino acid salt. Energy Proc 2011;4:1550–7.
- [26] Liu AH, Ma R, Song C, Yang ZZ, Yu A, Cai Y, et al. Equimolar CO₂ capture by Nsubstituted amino acid salts and subsequent conversion. Angew Chem Int Ed Engl 2012;51:11306–10.
- [27] Portugal AF, Sousa JM, Magalhães FD, Mendes A. Solubility of carbon dioxide in aqueous solutions of amino acid salts. Chem Eng Sci 2009;64:1993–2002.
- [28] Jiang B, Wang X, Gray ML, Duan Y, Luebke D, Li B. Development of amino acid and amino acid-complex based solid sorbents for CO₂ capture. Appl Energy 2013;109:112-8.
- [29] Wang X, Akhmedov NG, Duan Y, Luebke D, Li B. Immobilization of amino acid ionic liquids into nanoporous microspheres as robust sorbents for CO₂ capture. J Mater Chem A 2013;1:2978–82.
- [30] Wang X, Akhmedov NG, Duan Y, Luebke D, Hopkinson D, Li B. Amino acidfunctionalized ionic liquid solid sorbents for post-combustion carbon capture. ACS Appl Mater Interf 2013;5:8670–7.
- [31] Wang XF, Akhmedov NG, Duan YH, Li BY. Nuclear magnetic resonance studies of CO₂ absorption and desorption in aqueous sodium salt of alanine. Energy Fuels 2015;29:3780–4.
- [32] Feron PH, ten Asbroek N. New solvents based on amino-acid salts for CO₂ capture from flue gases. Proc GHGT 2004;7:5–9.
- [33] Lim JA, Kim DH, Yoon Y, Jeong SK, Park KT, Nam SC. Absorption of CO₂ into aqueous potassium salt solutions of L-alanine and L-proline. Energy Fuels 2012;26:3910–8.
- [34] Fan G-J, Wee AG, Idem R, Tontiwachwuthikul P. NMR studies of amine species in MEA-CO₂-H₂O system: modification of the model of vapor-liquid equilibrium (VLE). Ind Eng Chem Res 2009;48:2717-20.
- [35] Böttinger W, Maiwald M, Hasse H. Online NMR spectroscopic study of species distribution in MEA-H₂O-CO₂ and DEA-H₂O-CO₂. Fluid Phase Equilib 2008;263:131–43.
- [36] Hook RJ. An investigation of some sterically hindered amines as potential carbon dioxide scrubbing compounds. Ind Eng Chem Res 1997;36:1779–90.
- [37] Barzagli F, Mani F, Peruzzini M. A C-13 NMR investigation of CO₂ absorption and desorption in aqueous 2,2'-iminodiethanol and N-methyl-2,2 'iminodiethanol. Int J Greenhouse Gas Control 2011;5:448–56.
 [38] Barzagli F, Mani F, Peruzzini M. A ¹³C NMR study of the carbon dioxide
- [38] Barzagli F, Mani F, Peruzzini M. A ¹³C NMR study of the carbon dioxide absorption and desorption equilibria by aqueous 2-aminoethanol and Nmethyl-substituted 2-aminoethanol. Energy Environ Sci 2009;2:322–30.
- [39] Yan SP, Fang MX, Wang Z, Luo ZY. Regeneration performance of CO₂-rich solvents by using membrane vacuum regeneration technology: relationships between absorbent structure and regeneration efficiency. Appl Energy 2012;98:357–67.
- [40] Brouwer J, Feron P, Ten Asbroek N. Amino-acid salts for CO₂ capture from flue gases. In: Proceedings 4th annual conference on carbon capture and sequestration Alexandria, Virginia, USA; 2005.