Phase change amino acid salt separates into CO₂-rich and CO₂-lean phases upon interacting with CO₂

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1 **ABSTRACT:**

2 Concerns over global climate change have led to strong research emphasis worldwide on reducing the
3 emission of greenhouse gases like CO₂. One avenue for carbon emission reduction is using CO₂ capture
4 and storage from industrial sources. Having low toxicity and low vapor pressure and being resistant to
5 oxidation, natural amino acids could be a better choice over current carbon capture materials. In this
6 study, we pioneered a unique phase change amino acid salt solvent concept in which amino acid salt
7 solution was turned into a CO₂-rich phase and a CO₂-lean phase upon simple bubbling with CO₂ and
8 most importantly, this solution captured the most CO₂ (~90%) in the CO₂-rich phase. Bicarbonate was
9 found to be dominant in the CO₂-rich phase, which had a high CO₂ loading capacity and good
10 regenerability and cycling properties. Such a phase change amino acid salt solvent may provide unique
11 solutions for industries to reduce CO₂ and other harmful emissions.

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13 **Keywords:** *CO₂ capture; phase change solvent; amino acid salt; CO₂-lean phase; CO₂-rich phase*

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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 CO_2 capture and storage is being conducted to mitigate CO_2 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% CO_2 capture rate with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches [10]. The state-of-the-art technology for CO_2 capture is solvent absorption in which an aqueous solution of alkanolamine serving as an absorbent reacts chemically with CO_2 to form soluble carbamates and/or bicarbonates [11]. This process has already been in commercial use; however, this technology requires an inhibitive high amount of regeneration energy, because CO_2 can only be released at quite high temperatures, owing to the strong interactions of CO_2 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 DMXTM 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 monoethanolamine (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 CO₂ 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 CO₂ emissions into regenerable carbamate and bicarbonate, and we identified a unique phase change amino acid salt (**Fig. 1a**), which reacted with CO₂ and underwent a self-concentrating process to form a CO₂-lean phase and a CO₂-rich phase. The CO₂-lean phase could be reused and the CO₂-rich phase could be regenerated.

2. Materials and methods

2.1 Materials

L-alanine (Ala, ≥98%), L-arginine (Arg, ≥98%), L-lysine (Lys, ≥98%), L-serine (Ser, ≥99%), L-aspartic acid (Asp, ≥98%), and sodium hydroxide (NaOH, ≥98%) were purchased from Sigma-Aldrich. Deuterium oxide (D₂O, 99.9%) and tetramethylammonium chloride (≥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

CO₂ absorption was carried out using 100% CO₂ 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 to 220-μm 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 absorption-desorption 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 μ L. The ^1H NMR spectra were obtained with a delay time (D1) of 1 s and the number of scans was 32. The ^{13}C NMR measurements were performed with a delay time of 20 s and number of scans of 64. In the ^{13}C NMR spectra, bicarbonate peak was presented at ~ 161 ppm; Ala carbamate at ~ 164 ppm; Ala/AlaH $^+$ at 18, 50, and 177 ppm; and $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ at ~ 55 ppm. In the ^1H spectra, the D $_2$ O 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. 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 $[(\text{CH}_3)_4\text{N}^+\text{Cl}^-]$ was used as a standard reference. The amounts of species in the samples were quantitatively estimated based on the following equation,

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

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., $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$], and m_a is the amount of a specific specie. The estimated uncertainty associated with these integral values is $\pm 5\%$.

3. Results and discussion

CO $_2$ was bubbled directly (**Fig. 1b**) into solutions of amino acids (e.g. Ala, arginine, lysine, serine, aspartic acid), 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 CO $_2$ bubbling and the two phases (i.e. the clear and milky phases) formed after CO $_2$ bubbling (**Fig. 2**). Before CO $_2$ bubbling, proton signals of free Ala appeared at ~ 1.1 and ~ 3.2 ppm (**Fig. 2b**). After CO $_2$ bubbling, Ala reacted with CO $_2$ to form Ala carbamate ($^-\text{OOCCHCH}_3\text{NHCOO}^-$) 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 ($\text{OOCCHCH}_3\text{NH}_3^+$ or AlaH^+). Note that the peaks of Ala or AlaH^+ shifted to ~1.25 and 3.6 ppm due to the pH change of the solution after CO_2 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 NaHCO_3 (~161 ppm) was confirmed by ^{13}C NMR spectra (**Fig. 2c** and **e**). NMR spectra showed that species of NaHCO_3 , Ala/ AlaH^+ , and Ala carbamate were present in both the clear and milky phases and no Na_2CO_3 was observed (**Fig. 2**).

Using tetramethylammonium chloride [$(\text{CH}_3)_4\text{N}^+\text{Cl}^-$] 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, NaHCO_3 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 NaHCO_3 , Ala/ AlaH^+ , and Ala carbamate were about 19, 50, and 31 wt%, respectively. Furthermore, from the NMR analysis, we found that over 90% of CO_2 was absorbed in the milky phase (therefore designated as CO_2 -rich phase) and about 10% CO_2 was absorbed in the clear phase (designated as CO_2 -lean phase). This means that Ala solution, upon bubbling with CO_2 , self-concentrates into a CO_2 -lean phase and a CO_2 -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-CO₂-H₂O solution at different absorption times using NMR spectroscopic analysis (**Fig. 3a** and Figure S1 in Supporting Information). Ala carbamate was found to form immediately upon CO₂ bubbling, and the amount of carbamate increased sharply with CO₂ bubbling from 0 to 5 min (**Fig. 3a** and Figure S1a in Supporting Information). After this initial increase step, the amount of carbamate that formed decreased with increasing CO₂ 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 CO₂ absorption time (**Fig. 3a** and Figure 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 CO₂ bubbling, Ala interacted with CO₂ first to form Ala carbamate:

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

The species revolution 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**, Figures 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 2-aminoethanol 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

1 solvent which has stable carbamate. Proposed reactions during CO₂ absorption and desorption in Ala-
 2 NaOH-CO₂-H₂O solution as follows:

3

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

14 **Figure 4a** presents the CO₂ uptake performance of Ala-NaOH-CO₂-H₂O solution which indicated
 15 that CO₂ absorption capacity of Ala-NaOH-CO₂-H₂O solution increased quickly within the first 20 min
 16 followed by relatively slower CO₂ absorption. The slow absorption rate at the late stage was associated
 17 with the phase change phenomenon during which the viscosity of the solution increased. A decent CO₂
 18 absorption capacity of [(0.89 mol CO₂)/(mol Ala)] was achieved. This was probably because the
 19 introduction of substituents at the α -carbon atom of amino acids (e.g. Ala) reduces the stability of its
 20 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 CO₂ absorption/desorption process, i.e. phase change solvent process [19-21], where the CO₂-lean phase can be reused without regeneration and the CO₂-rich phase can be regenerated and reused; such a process could significantly 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 CO₂-rich phase in the Ala-NaOH-CO₂-H₂O solution. One can see that the CO₂ release increased sharply within the first 10 min followed by a much slower CO₂ release rate. Most (~80%) CO₂ was released within the first 10 min. Using this regeneration process (i.e. only regenerating the CO₂-rich phase), we obtained a decent working capacity of 0.62 (mol CO₂)/(mol Ala); MEA (30 wt%) had a capacity of [0.25 (mol CO₂)/(mol MEA)] [40].

Absorption-desorption cycles were further performed to evaluate the regenerability of Ala-NaOH-CO₂-H₂O 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 regenerated solutions), the absorption remained substantially constant [0.68 (mol CO₂)/(mol Ala)] during the following absorption-desorption cycles. In the first cycle, a 0.62 (mol CO₂)/(mol Ala) CO₂ was released from the CO₂-rich phase, which is about ~70% of the CO₂ absorbed in the entire solution. It can be seen that decent re-absorption capacities of 0.72, 0.69, and 0.68

(mol CO₂)/(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 CO₂)/(mol MEA) [40].

4. Conclusions

The rationale of developing phase change solvents for CO₂ capture is that phase change solvent technologies, in which the CO₂-rich phase can be regenerated and reused while the CO₂-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 CO₂ bubbling and capture the majority of CO₂ in the CO₂-rich phase. By regenerating only the CO₂-rich phase while reusing the CO₂-lean phase, a working capacity of 0.62 (mol CO₂)/(mol Ala) was obtained. We also found that upon interacting with CO₂, 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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Figure Captions:

Table 1. Species distribution in CO₂-rich and CO₂-lean phases of Ala-NaOH-CO₂-H₂O solution after CO₂ absorption.

Fig. 1. (a) Scheme of the phase change amino acid salt solvent process for CO₂ capture. Ala-NaOH-CO₂-H₂O solution absorbs CO₂ and undergoes a self-concentrating process to form a CO₂-lean phase and a CO₂-rich phase. The CO₂-lean phase is reused and the CO₂-rich phase is sent to the stripper for regeneration. Ala-NaOH-CO₂-H₂O solution (b) before and (c) after CO₂ absorption.

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

Fig. 3. Changes of carbamate and bicarbonate (from NMR spectra) of the entire Ala-NaOH-CO₂-H₂O solution as a function of (a) CO₂ absorption time and (b) CO₂ desorption time. (c) Changes of carbamate and bicarbonate of the CO₂-rich phase as a function of CO₂ desorption time.

Fig. 4. (a) CO₂ uptake performance of the entire Ala-NaOH-CO₂-H₂O solution as a function of CO₂ absorption time. (b) CO₂ release of the entire Ala-NaOH-CO₂-H₂O solution as a function of CO₂ desorption time (only the CO₂-rich phase was regenerated). The CO₂ remaining (including CO₂ in both CO₂-lean and CO₂-rich phases) was presented as well. The amount of alanine salt is based on that in the entire solution. (c) CO₂ absorption/desorption cycling of Ala-NaOH-CO₂-H₂O solution.

Table 1

Phases	CO ₂ loading	Carbamate		Bicarbonate		Ala/AlaH ⁺	
	(%)	mol/(mol Ala)	(%*)	mol/(mol Ala)	(%*)	mol/(mol Ala)	(%*)
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

*Percentage among the species of carbamate, bicarbonate, and carbonate.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Graphical Abstract