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Understanding Precipitation in Amino Acid Salt systems at Process Conditions

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Abstract

Rapid screening experiment has been used to acquire first-hand information on the precipitation characteristics of 14 aqueous amino acid salt systems. Absorption tests at 40°C have shown that at high concentrations, amino acid salt systems forms precipitate in the presence of CO₂ resulting to 2 or 3 solid-liquid phase formation. Potassium salt of the amino acid salts generally showed better reaction kinetics than their sodium salt counterparts. 5m' KSar and 4.3m' KPro showed significantly higher reaction kinetics while 5m' KSar, 5m' KAla, 4.5m' KSer, 5m' KL-Ala were observed to have an upward shift in absorption rate at some point during absorption resulting to increased loading. Application of the conventional stripping process in the screening test, i.e. heating up the absorption solution to 80°C showed poor desorption characteristics for the precipitating amino acid salt solutions. Qualitative ¹³C NMR studies was used to identify the chemical species in the phases, 3-phase in 5m' KSar and 2-phase in 4.5m' KSer. The NMR results show that each phase contains HCO₃⁻/CO₃²⁻ and carbamate fractions at varying degree.

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1. Introduction

CO₂ capture by absorption technology is the most advanced technology for removal of CO₂ from industrial exhaust gases. The cost of this technology and the environmental aspects of the solvents used in the process remain the bottle necks to its deployment in full scale plant. Alkanolamines have been the most widely tested absorbents for this technology but amino acid salt (AAS) systems have been proposed as a suitable alternative to alkanolamines [1]. This is because of the benefits associated with use of amino acid salt system. Most amino acids are green chemicals, AAS systems are ionic systems thus are

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practically non-volatile systems. Some AAS system has significantly higher CO₂ absorption rates than MEA [2]. The AAS systems also have some drawbacks when used in a conventional CO₂ capture process such as higher desorption energy requirement and precipitation at higher concentrations or at higher CO₂ loadings [2]. Most of the previous works on AAS do not go into the precipitation region of the AAS because they are aimed to be applied on conventional amine process.

This work aims specifically to go into the precipitation region of the AAS. Precipitation allows the driving force to be maintained at increased loading due to shift to higher pH induced by the precipitate. This then gives higher solvent loadings resulting in lower energy consumption for the solvent regeneration [3]. There is however no evidence or any literature that support or showed to prove this claim. The objectives of this work is to carry out screening experimental studies that results to precipitation in AAS systems to gain a first-hand knowledge on the precipitation of amino acid salt systems at process conditions. Further this work will select candidate precipitating AAS systems for further characterization (see Ma'mun and Kim, 2012 [4]). This work equally aims to identify the composition of the precipitate in the selected system by qualitative ¹³C NMR studies.

2. Experimental Section

2.1 Materials and sample preparation

The following amino acids (CAS- nr. given in parenthesis) were screened: ≥ 99% pure Glycine (54-40-6), ≥ 98% pure Sarcosine (107-97-1), 99% pure B-Alanine (107-95-9), ≥ 99% pure Taurine (107-35-7), ≥ 99% pure L-Proline (147-85-3), ≥ 98% pure DL-Serine(302-84-1), 99% pure DL-Valine(516-06-3), ≥ 99% pure L-Alanine (56-41-7). The bases used for neutralization were ≥ 85% pure KOH (1310-58-3) and ≥ 99% pure NaOH (1310-73-2). Amino acid salts were prepared in moles per kg (m') solution using equimolar proportions of the amino acid and the neutralizing base. Partial neutralization was carried out using half the equimolar proportion of the base to react with the amino acid. Final concentration of the solution was crosschecked by titration with 0.2N H₂SO₄. 99.8% 1,4-dioxane was used as an internal reference standard for NMR experiments. The concentrations of the amine and CO₂ were determined by standard total amine and CO₂ analysis and compared with NMR results. Loaded solutions of 0.4 mL were filled into 5 mm Norrel 507-HP tubes and weighed in Mettler AE163 digital analytical balance. Deuterium oxide (D₂O) solution with 99.9% purity was added as a locking agent but.

2.2 Screening Tests

Absorption and desorption experiments were carried out using a rapid screening apparatus described by Aronu (2011) [2]. The equipment is designed to operate at atmospheric conditions and up to 80°C. It is designed to give a fast relative comparison of absorption rate and absorption capacity as well as stripping rate and possible lean loading. Apart from these factors, other properties such as foaming, precipitation and possible discoloration upon CO₂ loading could be observed. The apparatus therefore enables first-hand knowledge on the behavior of solvent systems in a carbon dioxide absorption process. The absorption experiment is the same as described in Aronu (2011)[2]; however the absorber/desorber reactor was modified to a jacket reactor to enable better temperature control, also a magnetic stirrer is used to enhance mixing and mass transfer. A cold trap was inserted to enhance condensation of any amine remaining in the gas phase that could not condense in the coolers. This was necessary to knock out amine or precipitate in the gas phase before getting to the flow meter. A liquid sample was collected for analysis after absorption at 40°C and desorption at 80°C. The comparison provided by the experimental data is semi-quantitative. It was necessary to monitor the behavior of each solvent system since precipitates are expected to form at a certain stage during absorption and also behaviour of the precipitates during heating up to 80°C and during desorption. Possible separation of the aqueous amino acid salt system into two phases at the end of the absorption and stripping was also observed. A re-run of the screening *absorption*

tests was carried out for the selected systems to enable direct study and check the reproducibility of the phase separation and as well as enable the ^{13}C NMR studies of the absorption solution.

2.3 NMR Experiments

Qualitative NMR experiments, 1D (^1H , ^{13}C) and 2D (H-H COSY, H-C HSQC, H-C HMBC and DEPT 90/135) were used for qualitative analysis. Loaded and unloaded solutions were collected from selected systems after the screening absorption experiments. The loaded and unloaded potassium-sarcosine (KSar) and potassium – DL-serine (KSer) solutions were acquired on Bruker Avance DPX 400 MHz NMR spectrometer with a 5 mm DUAL $^1\text{H}/^{13}\text{C}$ probe head. At high loading, the phases formed by the two systems system were viscous, especially in the lower phase; therefore, dilution with D_2O was necessary in order to analyze them with NMR spectroscopy. All the NMR experiments were carried out at 25°C .

3 Results and discussion

The screening results for absorption tests at 40°C for 14 aqueous amino acid salt systems show that most of the precipitating amino acid salt systems absorb more CO_2/l solution than 5M MEA. Potassium salts of proline and sarcosine in particular, maintain both higher absorption rate and absorption capacity than MEA. Sodium salts of the amino acids are found in general to achieve considerably lower absorption rate compared to their potassium salts counterparts. Desorption of the precipitated systems by conventional stripping process i.e. heating up the absorption solution to 80°C showed lower desorption potentials than 5M MEA. It is thus necessary to explore the potentials in separation of the precipitate from the solution before sending to the stripper. The benefit from this will however be anchored on the composition of the precipitate. Majchrowicz et al. (2006)[5] suggests that precipitate from amino acids salt systems are the amino acid, bicarbonate of the amino acid and bicarbonate of the inorganic base. Qualitative ^{13}C NMR analysis was used to identify the chemical composition of the precipitate in the selected amino acid salt systems (see section 3.2). Further characterization by solid-liquid-vapor equilibrium of the selected aqueous amino acid salt system is presented in another work [4].

3.1 Screening

3.1.1 Observed solvent characteristics

The behavior of the solvent systems during CO_2 absorption and mode of precipitate formation were monitored through the glass reactor. It was observed that in general all the amino acid salts at high concentrations easily precipitates upon CO_2 loading which is visible by a light or white coloration. Table 1. gives a summary of the observed behavior of the tested amino salt systems at rapid screening process conditions.

3.1.2 Absorption tests

The result from absorption screening tests is shown in Fig. 1. The figure and the experiments show some features of the precipitating amino acid salt (AAS) systems: Amino acid neutralized using NaOH in general showed lower absorption rate than those neutralized using KOH. Some precipitating AAS (5m' KSar and 4.3m' KPro) systems maintain very high absorption rate and CO_2 loading (higher than 5M MEA) all through the absorption cycle. Some of the AAS systems (2.5m' KVal, 5.5m' NaGly, 6.8m' NaGly), precipitates heavily such that sintered gas line was blocked forcing the absorption to be terminated prematurely. Some of the precipitating AAS solutions (5m' KSar, 5m' KAla, 4.5m' KSer, 5m' KL-Ala) were observed to have an upward shift in the rate at some point resulting in increased loading. This apparent increase in absorption rate may be due to operational problem from blockage of the gas line (less CO_2 in the out let gas flow, giving an apparent higher reaction rate) or due to the solvent property resulting to precipitation of the CO_2 as carbonate/bicarbonate.

Table 1. Observed character of precipitating aqueous amino acid salt systems at rapid screening process conditions.

S/No	Amino acid salt	Composition (mol/kg)	Absorption Characteristics	Desorption Characteristics
1	5m' KSar	5m'KOH + 5m'Sarcosine	Clear mildly viscous (very light yellow) solution. Turns milky white at ~ 7.3 molCO ₂ /l (0.66 vol% CO ₂ out). Absorption rate starts to rise again at ~ 56 molCO ₂ /l (9.12% CO ₂ out). Constant very low absorption rate afterwards and in creased precipitation after the deeping in absorption rate. Absorption completed with solution forming two phases. A less dense white top and a more dense creamy coloured bottom. Upon standing overnight , absorption solution separates into three-phases: white top, clear liquid middle and crystal-like bottom.	Precipitate did not dissolve on heating to 80oC. White color clears gradually as stripping continues.
2	2.5m' KSar	2.5m' KOH + 2.5m' Sarcosine	Non-viscous, very light yellow solution. No precipitation during absorption. Clear solution after absorption.	Solution climbs up condenser during desorption.
3	5m' KSar_partial	2.5m' KOH + 5m' Sarcosine	Non-viscous, very light yellow solution. No precipitate at absorption experiments.	Solution climbed up the condenser during stripping. Solution remain clear after absorption-desorption
4	4m' NaSar	4m'NaOH + 4m'Sarcosine	Clear solution (very light yellow). No precipitate after absorption, no change in solution color. Some crystals (~ 1g, most likely amino acid) were observed at the bottom after absorption.	Stripping at 80oC, no precipitate. Some crystals (~ 1g) were observed at the end of stripping.
5	5m' KGly	5m'KOH + 5m'Glycine	Clear solution before absorption. Turns milky white during absorption. Instant termination of absorption ~ 3.2 molCO ₂ /l (8.0 vol% CO ₂ out from reactor), indicating likely precipitation of amino acid. Absorption solution settles into two phase in not too long time.	Solution become less white at ~ 65oC. White precipitate disappear 80oC. White solution re-appears after cooling to room temperature.
6	6.8m'NaGly	6.8m'NaOH + 6.8m' Glycine	Clear colorless, high viscous solution before absorption. Large bubbles. White precipitate at ~ 5.5% CO ₂ out from reactor. Very thick viscous solution after absorption.	Solution insoluble at 80oC. Unable to strip solution at 80oC.
7	5.5m' NaGly	5.5m'NaOH + 5.5m' Glycine	Mildly viscous clear solution. White precipitate observed at ~ 0.3 molCO ₂ /L (5.3 vol% CO ₂ out). Very viscous white solution forms. Gas flow through the sinter blocked by precipitate. Experiment forced to terminate at 7.4% CO ₂ in the outlet gas from the reactor. White paste solution formed after absorption.	Solids were not dissolved at 80oC. No visible stripping occurred.
8	5m'KAla	5m' KOH + 5m'B-Alanine	Initially very light yellow solution. White cream viscous solution during absorption. More viscous at high loading ~8.9 vol% CO ₂ out from reactor. Absorption rate increased again at ~ 9.2 vol% CO ₂ out. Increased loading at constant (low)absorption rate at about 9.1 vol% CO ₂ out. Absorption forced to terminate at 9.1 vol% CO ₂ out.	Precipitate does not dissolve completely at 80oC. Solution clearer as stripping proceeded.
9	5m'NaB-Ala	5m' NaOH + 5m'B-Alanine	Clear mild viscous solution. White precipitate observed at ~0.33 molCO ₂ /L (5.4 vol%CO ₂ out). Experiment terminated after 300min ~ 90% CO ₂ out .	Clear solution after desorption at 80oC.
10	5m' KL-Ala	5m' KOH + 5m' L-Alanine	Clear mildly viscous solution before absorption starts. Solution starts to turn cloudy at ~ 4.2% CO ₂ out. Low initial rate. Absorption rate increased again at ~ 9.2% CO ₂ out. Solution turn into two phase after absorption. Highly viscous(very thick) top phase and less viscous bottom phase. Only bottom phase was sampled for analysis because of the highly viscous nature of the top.	Poor desorption. Precipitate remain insoluble after desorption at 80oC.
11	4.5m' KSer	4.5m'KOH + 4.5m' Serine	Initially bright yellow non-viscous solution. Solution turns gradually to orange color as absorption proceeds. Low absorption rate. Rate appeared constant at ~7.5vol% CO ₂ outlet gas phase concentration. Absorption experiment re-set to terminate at 90% CO ₂ outlet gas phase concentration due to very low rate. Viscous yellow/white solution after absorption. Upon standing, absorption solution separate into two phase: a clear liquid top and dense solid bottom	Precipitate did not dissolve completely at 80oC as stripping started. On cooling down to 40oC after stripping two phase of yellow top and light yellow bottom formed.
12	4.2m' KTau	4.2m' KOH + 4.2m' Taurine	Clear viscous solution. Solution started turning white at CO ₂ outlet about 4.2 vol%. Very white solution at about 7.7 vol% CO ₂ out.	Precipitate does not dissolve completely at 80oC. White precipitate disappears as stripping continues. Clear solution after desorption. At room temperature overnight, desorbed solution became white and viscous.
12	4.3m' KPro	4.3m' KOH + 4.3m' Proline	Viscous, very light yellow solution. Very high absorption rate observed. Solution turns white at about 0.9vol% CO ₂ out. Absorption curve no disrupted by precipitate.	Precipitate disappears before 80oC. Clear solution after stripping.
14	2.5m' KVal	2.5m' KOH + 2.5m' DL Valine	Yellowish non-viscous solution. Foaming observed as absorption starts. Floating white precipitate observed at ~ 0.48 molCO ₂ /l (3.3vol% CO ₂ out). Gas line to the sinter blocked by precipitate. Floating precipitate climbs up the condenser. Experiment forced to terminate at 32vol% CO ₂ outlet gas concentration. Two layer solution formed. Top layer was a foam/powder precipitate thus was not feasible to sample the top layer.	Bottom layer of solution dissolves at 60oC. Poor desorption at 80oC, probably due to blockage of the gas line in the sinter. White precipitate re-appears upon cooling to 40oC.

Reaction rate of the precipitating AAS systems is observed to decrease considerably towards equilibrium. CO₂ absorption in 5m' KGly terminates suddenly at loading of 3.2 molCO₂/l solvent. This may be due to precipitation of amino acid from solution. 5m' KSar and 4.3m' KPro showed the best CO₂ absorption potential among the precipitating AAS systems tested. A re-run test for some of the precipitating amino acid salt systems (KSar, KSer and KL-Ala) shows that the observed solvent behavior were reproducible as can be seen in Fig 1.

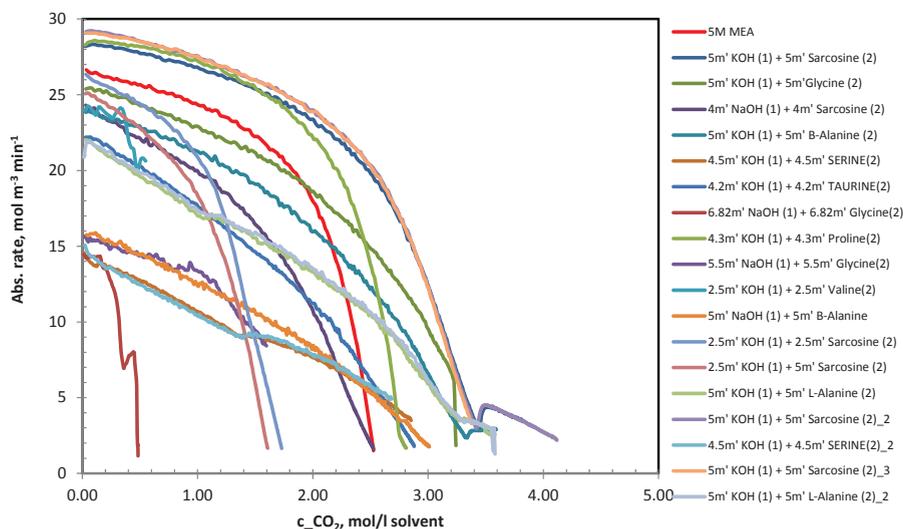


Fig. 1 Precipitating systems absorption curves at 40°C

3.1.3 Desorption tests

The desorption curves at 80°C for the various precipitating AAS systems is shown in Fig 2. It can be observed from the figure and/or the experiments that generally the precipitating AAS systems show poorer desorption at 80°C compared to 5M MEA using this conventional stripping set up. Precipitates in most AAS systems dissolves at 80°C as stripping proceed except in 5.5m' NaGly, 6.8m' NaGly and 4.5m' KSerine. 2.5m' KVal, 5.5m' NaGly, 6.8m' NaGly could not be stripped with the experimental set up mainly due to blockage of sintered gas lines by the precipitate. Two phase formation of liquid top and paste-like bottom were observed in 4.5m' KSer and 5m' KGly systems after desorption. 5m' KSar and 4.2m' KTAu showed the best desorption potential among the precipitating AAS systems tested.

The present work has given first-hand insight into the behavior of the precipitating amino acid salt (AAS) systems. The screening results obtained for the systems show that very high absorption rate and high CO₂ loadings are obtainable by the systems but they exhibit poor CO₂ desorption potentials using the conventional stripping process. 5m' KSar gave the best performance among the tested precipitating amino acid salt systems and it is thus recommended for further characterization. 4.5m' KSer is equally suggested for further characterization based on its behavior (upward shift in absorption curve) during CO₂ absorption since the bottom layer of 5m' KL-Ala which showed similar property was a highly viscous paste.

3.2 Chemical System – NMR

Base on the screening results, the recommended systems 5m' KSar and 4.5m' KSer were further investigated by ¹³C NMR studies to identify the composition of the precipitates and the phases formed. The molecular structures of the two systems and the amino acids are shown in Fig 3. The loaded aqueous solution of KSar from the absorption experiment formed two phases but upon standing overnight further separates into three different phases named lower, middle and upper phase (see Fig 4a). The loaded aqueous solution of KSer formed only two phases, lower and upper phase (see Fig 4b). In the loaded solution, due to fast exchange of protons, the carbonate cannot be distinguished from bicarbonate and, the free amine/amino acid from protonated amine/amino acid [6,7]. The registered chemical shifts for both systems in ppm from the ¹³C NMR spectroscopy are summarized in Table 2.

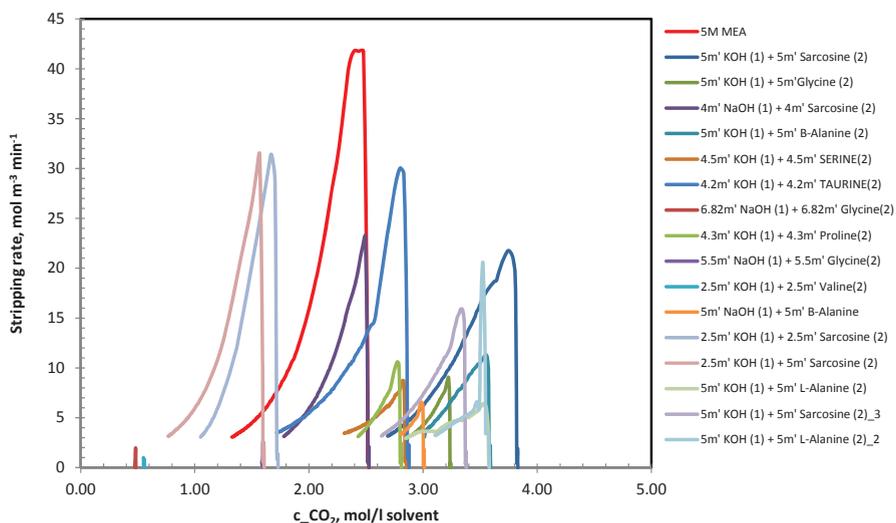


Fig 2. Precipitating system desorption curves at 80°C

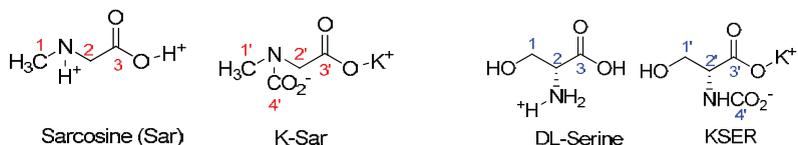


Fig 3. Molecular structure of the amino acids and the amino acid salts used in the present work.

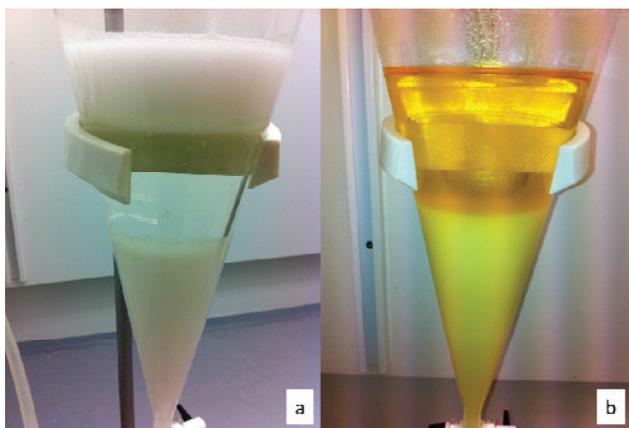


Fig. 4 Precipitation at process condition; (a.) KSar 3-phase formation (b.) KSer 2-phase formation

KSar - system. The main components were identified in the loaded solutions with 2D – NMR techniques (COSY, HSQC, HMBC and DEPT). The assignments for loaded potassium – sarcosine system are shown in Fig 5. In the high field region the four carbons are assigned to free sarcosine (C1 and C2) and carbamate to sarcosine (C1' and C2'). In the low field region of the ^{13}C spectra (Fig 5) the peaks of the quaternary carbon of sarcosine (C3), quaternary carbon of the carbamate form of sarcosine (C3'), carbamate (C4') and of carbonate/ bicarbonate (the common peak) were assigned based on 2D

experiments. In every phase (lower, middle and upper), the dominant species seem to come from carbonate/bicarbonate and carbamate. The peaks in the low field are shifted. This might be due to the change of the pH in different phases.

Table 2. Chemical shift (ppm) for KSar and KSer by ^{13}C NMR spectroscopy.

Sample	C1	C2	C3	C1'	C2'	C3'	C4'	HCO_3^- $/\text{CO}_3^{2-}$
Potassium – Sarcosine System								
KSAR upp.	33.5	51.7	172.3	172.3	53.9	179.7	164.7	161.3
KSAR mid.	33.5	51.8	172.7	172.7	53.9	179.6	164.8	162.2
KSAR low	33.5	51.7	172.2	172.2	53.9	179.7	164.7	161.2
Potassium – DL-Serine System								
KSER upp.	63.8	57.7	179.6	63.9	59.8	179.7	164.7	165.4
KSER low.	62.8	57.4	176.7	63.9	59.7	179.4	164.6	162.8

KSer – system. The same NMR techniques were employed for the assignment of the species in the different phases of loaded potassium – DL-serine system. The ^{13}C NMR spectra for this system are shown in Fig. 6 and the chemical shift is given in Table 1. As one can see in Fig. 6, the peaks are slightly shifted, and again, probably due to the pH change of the phases. A peak for the carbonate/bicarbonate is observed at around 165.4 ppm and 162.8 ppm at the upper and lower phase respectively while for the carbamate the peaks are found at about 164.7 ppm and 164.6 ppm.

The ^{13}C NMR studies have shown the formation of $\text{HCO}_3^-/\text{CO}_3^{2-}$ and carbamate in all the phases formed by KSar (3-phase) and KSer (2-phase). It can also be observed from the peaks in Fig 5 and 6 that $\text{HCO}_3^-/\text{CO}_3^{2-}$ and carbamate are formed at different degrees in the different phases in both systems. Quantification of the amount of species formed in each phase is of interest. Phase containing high proportion of $\text{HCO}_3^-/\text{CO}_3^{2-}$ will be of interest since this has the potential to reduce energy requirement in the stripper. Further work will be focused on quantification of the amount of species present in each phase for each system using ^{13}C NMR.

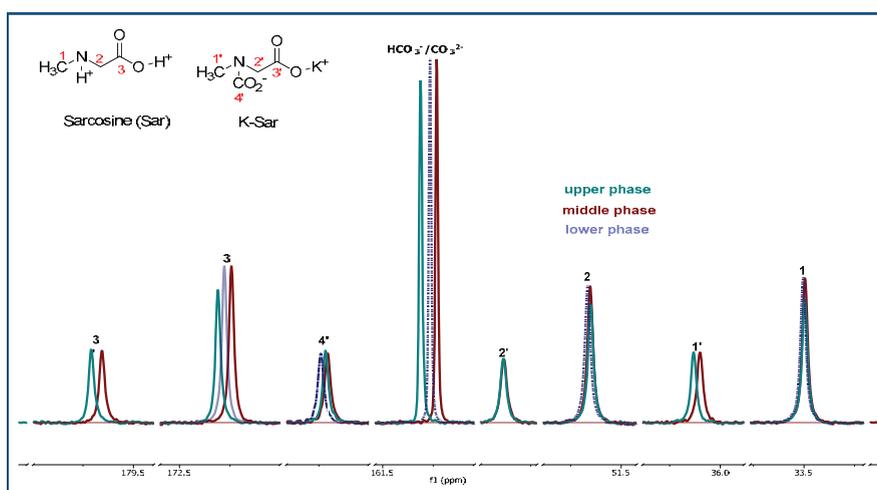


Fig 5 ^{13}C NMR spectra of three phases in loaded K-Sarcosine system.

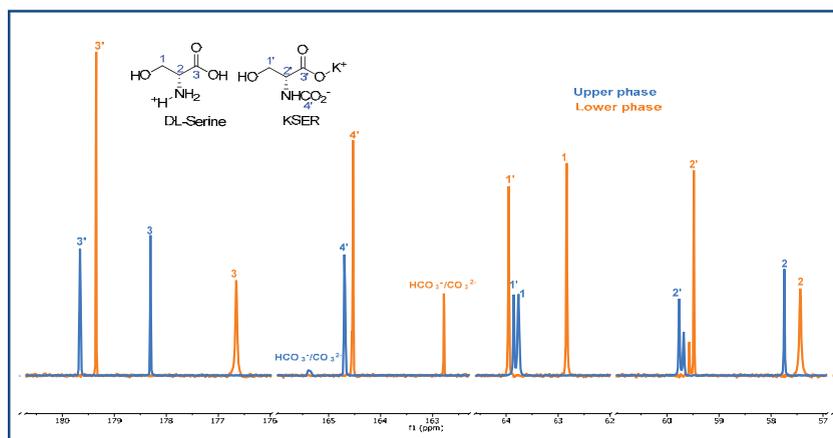


Fig. 6 ^{13}C NMR spectra of two phases in loaded K-DL-serine system.

4 Conclusions

Rapid screening experiment has been used to gain first-hand knowledge on the precipitation characteristics of 14 aqueous amino acid salt systems. Absorption tests at 40°C have shown that at high concentrations, amino acid salt systems precipitates in the presence of CO_2 forming to 2 or 3 solid-liquid phase. Potassium salt of the amino acid salts generally showed better reaction kinetics than their sodium salt counterparts. 5m' KSar and 4.3m' KPro showed significantly higher reaction kinetics while 5m' KSar, 5m' KAla, 4.5m' KSer, 5m' KL-Ala were observed to have an upward shift in absorption rate at some point during absorption resulting to increased loading. Conventional stripping process in the screening tests showed poor desorption characteristics for the precipitating systems. Qualitative ^{13}C NMR studies was used to identify the chemical species in the phases, 3-phase in 5m' KSar and 2-phase in 4.5m' KSer. The NMR results show that each phase contains $\text{HCO}_3^-/\text{CO}_3^{2-}$ and carbamate fractions at varying degree.

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