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Amino-Acid-Salt-based Carbon Dioxide Capture: Precipitation Behavior of Potassium Sarcosine Solution

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Abstract. This work studied the precipitation behavior of solids in the aqueous solution of potassium sarcosine (KSar) during the CO_2 capture process with the concentration of 5m' (mol/kg solution). The effect of precipitation on the CO_2 capture capabilities was also studied. The results showed that 5m' KSar gives a comparable result to MEA. The relatively high initial CO_2 absorption efficiency combined with the positive effect of precipitation on CO_2 absorption rate and CO_2 capacity have made the 5m' KSar be a promising solvent for the CO_2 capturing process with precipitation.

1. Introduction

Carbon dioxide (CO2) is produced in large quantities from coal-fired power plants, industrial processes, natural gas processing, and transportation. Amine-based CO2 capture processes have been considered as a leading technology to remove CO2 from various flue gases. Aqueous monoethanolamine (MEA) has been used extensively for this purpose because it offers some advantages such as high reactivity, low solvent cost, reasonable thermal stability, and thermal degradation rate [1]. However, due to its drawbacks, e.g. corrosion of equipment, the high energy requirement for absorbent regeneration, and oxidative degradation [2], development on new solvents are therefore required to overcome these problems.

Amino acid salts (AAS) were previously used in acid gas removal as promoters. However, some research on AAS application in CO2 capture processes was conducted. The AAS may, according to [3, 4], be used as alternative solvents to alkanolamines. Due to the presence of an amino function group, aqueous solutions of AAS have similar performance on CO2 reactivity and capacity to amines [5]. Some potassium salts of amino acid, such as potassium sarcosine (KSar), potassium glycine (KGly), and potassium proline (KPro), show faster reaction rate with CO2 than MEA [6-8]. In addition, the AAS also show good degradation-resistance performance in the oxygenated atmosphere [5]. The ionic structure of the AAS makes its volatility to be relatively low even at a high temperature, therefore, it reduces the solvent vaporization losses.

Precipitation is normally avoided during post-combustion processes. In recent years, however, attention on the precipitating systems has increased, such as chilled ammonia processes [9], carbonate systems [10], and AAS [11, 12]. The AAS solutions may have a promising feature of the solid formation when absorbing CO2. When the formed precipitates contain CO2 species such as carbamate and bicarbonate, the selective removal of solids from a reaction mixture will shift the equilibrium towards the product side, thus it may increase the absorption capacity. It was confirmed that, in the

AAS solutions, the formation of solid may increase the total CO_2 loading and reduce the energy consumption during CO_2 desorption [13-15].

In this work, the concentration of KSar used was 5 m' as this system was also tested by [16]. In order to understand the effect of precipitation on the CO_2 capturing efficiency, a LabMax® system equipped with online probes for in-situ Focused Beam Reflectance Measurement (FBRM) and Particle Vision Measurement (PVM) was used in which both the crystallization behavior and the CO_2 absorption profile can be recorded simultaneously.

2. Materials and Method

2.1. Materials
Sarcosine ($\geq$ 98 wt. %) and KOH ($\geq$ 85 wt. %) were used in this work and were obtained from Sigma Aldric while CO2 (purity $\geq$ 99.99mol %) and N2 (purity $\geq$ 99.999mol %) were obtained from AGA Gas GmbH. The aqueous solution of 5m' KSar was prepared by neutralizing 5 moles of sarcosine with an equimolar amount of KOH in a total solution weight of 1 kg. The actual solution concentration was then determined by potentiometric titration.

2.2. Apparatus and Procedure
The precipitation behavior and absorption rates of CO2 into the AAS solutions were studied in a commercially available automatic laboratory reactor Mettler Toledo LabMax®. FBRM and PVM probes were used to record precipitation behavior during the experiment. FBRM spectra may monitor the onset of crystallization and the chord length distribution (CLD) of the formed solids and PVM was used to observe the morphology of crystals online. The detailed procedure can be found elsewhere [17].

After terminating the process, a liquid sample was collected and the CO2 concentration in the liquid was measured offline by both a GC and the precipitation-titration method as described by [18, 19], whereas the total alkalinity was determined by an automatic titrator Metrohm 905 Titrando. The absorption rate was then calculated by an equation from [1].

3. Results and Discussion
Absorption of CO2 into 5m' KSar was conducted by the use of LabMax®. Figure 1 shows the changes in absorption rate, pH, Tr, and FBRM spectra in the KSar solution after bubbling 10 vol.% CO2 at the flowrate of 5 L/min. The solution temperature was kept at 40.0 °C for at least 20 min to ensure the pH and FBRM spectra stable before loading CO2. The onset of bubbling gases was recorded as time zero. The temperature was maintained at 40.0 °C for the entire experiment with slight fluctuation at the start of loading gas. The pH, with the initial value of 12.6, kept decreasing after loading CO2, accompanying with the decline of absorption rate with the initial absorption rate of $7.96 \times 10{-}4$ mol/(kg·s) which is much higher in comparison to the initial absorption rate in 5m' MEA, i.e. $4.25 \times 10{-}4$ mol/(kg·s) [1, 20]. The onset of precipitation was detected by a sudden increase of FBRM spectra (blue line in figure 1) at 148 min, resulting in an upward shift of CO2 absorption rate (pink line in figure 1). As mentioned by [16], the shift could be due to the blockage of the gas line or by the formation of solids during CO2 capture. Since the tube was used to feed the gas in this work instead of a sparger, the problem of the blockage was avoided; the increase of absorption rate can, therefore, be confirmed as a result of the occurrence of precipitation. This was also confirmed by [17] in which the Vapor-Liquid-Solid Equilibrium (VLSE) data of 5m' KSar at 40°C showed that the CO2 partial pressures decreased in the precipitation region.
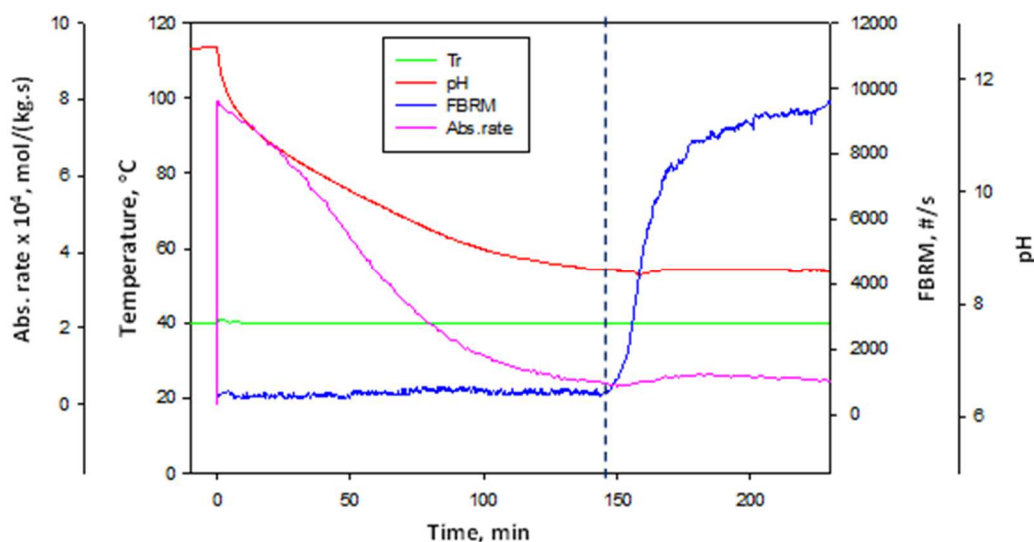
Figure 1. The changes of absorption rate, pH, T_r, and FBRM spectra by absorbing 10 vol.% CO_2
at the gas mixture flowrate of 5 L/min in a 5m' KSar solution at 40.0°C.

When the absorption rate is plotted against the CO_2 loading as shown in figure 2, the change of absorption rate caused by precipitation is clear. Precipitation occurred at the CO2 loading of about 0.56, where the absorption rate showed the lowest point at 0.38×10-4mol/(kg.s), following an evident increase up to 0.68×10-4mol/(kg·s). The crystal growth, taken by PVM, can be seen in figure 3. It should be noted that even though the precipitation led to a rise in the CO2 absorption rate, it took a relatively long time (over 2 hours) to form solids, in which case a very large absorption column would be required. In addition, the absorption rate had reduced to a quite low value before precipitation. These limitations could affect the use of 5m' KSar as a candidate for CO2 capture with precipitation.
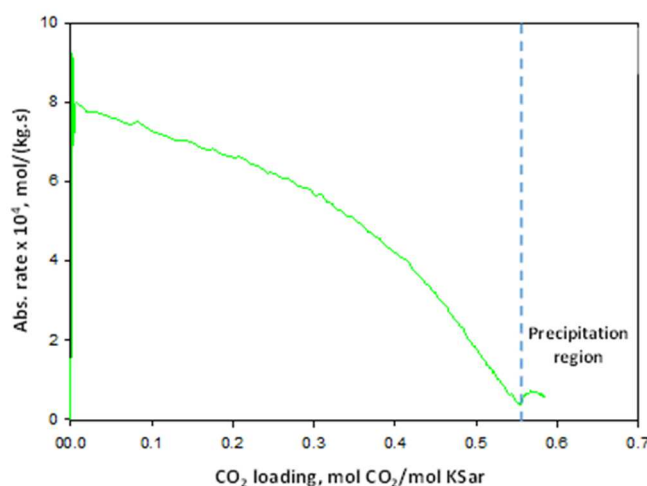
Figure 2. The CO_2 absorption rate as a function of CO_2 loadings in a 5m' KSar solution
by loading a 10 vol.% CO_2 at the gas mixture flowrate of 5 L/min at 40.0°C.
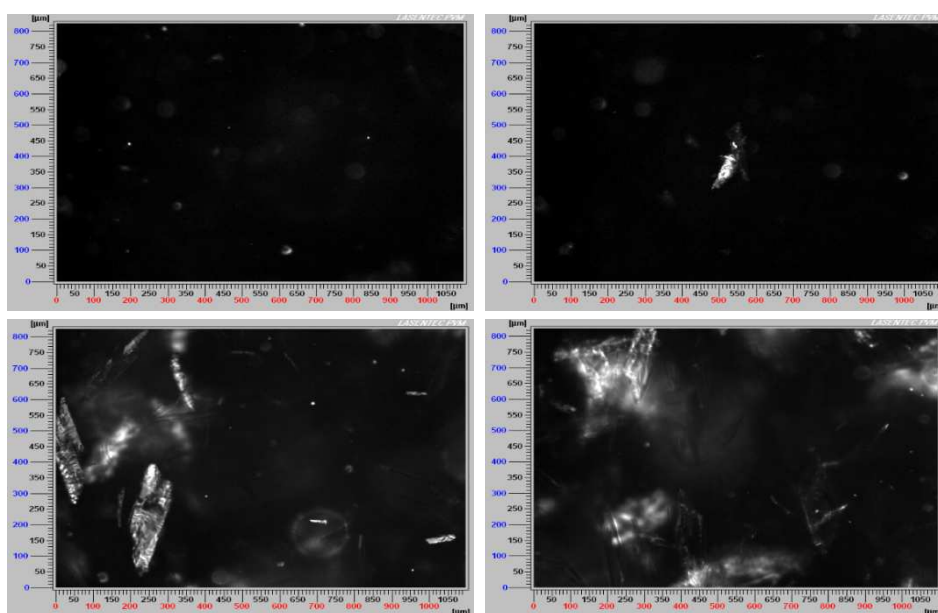
Figure 3. The crystal growth pictures taken by PVM at 40.0°C.

4. Conclusion

This work studied the effect of precipitation in the aqueous solution of 5m' KSar on the CO2 absorption efficiency. It was found that the 5m' KSar solution exhibited a high initial CO2 capture rate in comparison to 5m' MEA solution. Although the occurrence of precipitation led to an upward shift on the absorption rate and CO2 capacity, it would take too long to obtain crystals and the absorption rate at that condition was very low. Thus, the KSar solution was not considered as a good candidate for the CO_2 capture process with precipitation.

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