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Precipitation regime for selected amino acid salts for CO₂ capture from flue gases

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Abstract

The tendency of alkaline (sodium, potassium and lithium) salts of taurine, β-alanine, sarcosine and L-proline to form precipitates under varying operational conditions of CO₂ absorption has been investigated. CO₂ absorption experiments have been performed at 293.15 and 313.15 K, at partial pressures relevant for capturing CO₂ from flue gas conditions and amino acid salt concentrations up to the saturation concentration. In addition to this ‘window of operation’ for the (non-) precipitation regime, the identity of precipitates formed was revealed and relevant properties like density of the saturated aqueous amino acid salt solutions at 293.15 K have been determined.

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1. Introduction

Absorption with chemical reaction is a common process in the chemical industry and it is used among others in the treatment of the industrial gas streams containing acid gases like H₂S, NO_x and CO₂. In these gas treating processes, aqueous solutions of particularly alkanolamines are commonly used, especially monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and their mixtures (with or without “activators” like piperazine added to the mixture), as well as sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) [1]. In principle, these systems could be used for the removal of the greenhouse gas CO₂ from flue gases, such as from power plants in a regenerative absorption-desorption process. However, these solvents have a limited cyclic CO₂ loading capacity, they lead to a relatively high equipment corrosion rate, require high energy consumption for regeneration and suffer from solvent losses by evaporation, and from degradation in an oxygen rich atmosphere, as commonly encountered in the treatment of such flue gases [2]. Aqueous alkaline salts of amino acids could be an interesting alternative for these alkanolamine solutions. Generally, amino acid salt solutions can be characterized by the more favourable properties like a low volatility (due to ionic nature) and higher surface tension, higher stability towards the oxidative degradation and as a consequence smaller production of toxic degradation

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products, while having (due to similar functionality) a comparable or even higher chemical reactivity towards CO₂ as compared to alkanolamines [3].

A further interesting feature of aqueous amino acid salt solutions is their ability to form solid precipitates when absorbing CO₂, which depending on the process requirements can be more or less desirable feature. The precipitate formation was reported, for example, during absorption of 100% CO₂ gas stream in 2.5 M aqueous potassium salts of N-methylalanine, DL-alanine, α -aminoisobutyric acid (and its sterically hindered derivatives) at 295 ± 0.5 K [4]. The precipitation of one the reaction products was reported as well when absorbing the diluted CO₂ gas streams (CO₂ partial pressure up to 6 kPa) in aqueous solutions of potassium taurate (0.5 - 4 M) at 298 and 313 K [5]. A significant advantage is that as a result of the precipitate formation the CO₂ equilibrium partial pressure over the resulting slurry remains almost constant for a certain solution loading-range, which can then result in higher solvent loadings, a lower energy consumption for the solvent regeneration and reduction in the gas-liquid contactor size [6]. Also, chemical composition of the precipitate formed creates new possibilities for the (temporarily) storage of CO₂ [7].

When designing a new (regenerative) gas separation process for CO₂ removal, utilizing the features of either a precipitating or non-precipitating amino acid salt solutions, knowledge is required on the operational window in order to know whether or not precipitation will occur within the process at the operating conditions under consideration. In this paper, the results are presented from an experimental investigation in which the operating conditions for the CO₂ absorption process (like absorption temperature, CO₂ partial pressure, chemical composition and concentration of the amino acid salt, etc.) are varied to determine the precipitation regime (or the “window of operation”) for a series of non-volatile amino acid salts.

2. Method and materials

2.1 Chemicals

The CO₂ (min. 99.995 mol%) and N₂ (min. 99.999 mol%) gases used were obtained from Linde Gas. The amino acids were purchased from Sigma-Aldrich and were used without further purification. Those selected were taurine [2-aminoethanesulfonic acid, H₂N(CH₂)₂SO₃H], β -alanine [3-Aminopropionic acid, NH₂CH₂CH₂COOH], sarcosine [N-Methylglycine, CH₃NHCH₂COOH] with their reported purity not less than 98%, and L-proline [(S)-Pyrrolidine-2-carboxylic acid, C₅H₉NO₂] with the reported purity not less than 98.5%. Alkaline hydroxides utilized for the amino acid salts preparation (all supplied from Sigma-Aldrich) were potassium hydroxide ($\geq 98.5\%$), sodium hydroxide ($\geq 99\%$) and lithium hydroxide (≥ 98). Water content in these chemicals was determined by titration.

Chemical solvents were prepared by neutralizing the amino acid dissolved in deionized, distilled water which was further purified by vacuum distillation, with an equimolar quantity of an appropriate alkaline hydroxide. All amino amino acid salt solutions were prepared by mass using a balance with a precision of $\pm 1 \times 10^{-4}$ g. The concentration of these solutions was cross-checked by titrating with a standard HCl solution.

2.2 Physical properties of saturation concentrations

The saturation concentrations of aqueous amino acid salt solutions were determined by dissolving in deionized, distilled water an excess of equimolar quantities of amino acid and alkaline hydroxide, subsequently filtrating the solution to remove the solid phase and titrating the filtrated solution with a standard HCl solution. The densities of these amino acid salt solutions were determined at 293.15 K using a 10 mL Gay-Lussac pycnometer. The experimental method was in accordance with the ASTM D3505 standard test method [8]. Temperature of the water bath was controlled within ± 0.05 K. Calibration runs were performed at 293.15 K using pure degassed, deionized water. The calibration measurements were compared with the literature data [9].

2.3 Screening apparatus

The windows of operation for the taurine, β -alanine, sarcosine and L-proline absorption systems were investigated with respect to the precipitate formation during CO₂ absorption using the screening apparatus shown on Figure 1. The apparatus was designed to operate at atmospheric pressure and absorption temperatures up to 333.15 K consists of thirty glass test tubes, a Sick Maihak IR CO₂ analyzer, two Tamson water bath (model T1000), two PT

100 temperature sensors and Brooks mass flow controllers for pure N_2 and CO_2 gas streams (model 5850 TR). The data acquisition system uses LabView.

Before starting a screening experiment, a continuous dilute CO_2 gas stream of known composition was prepared by mixing desired flowrates of pure CO_2 and N_2 using the mass flow controllers. This mixed gas stream was passed through a water saturator and then through the thirty test tubes (arranged in parallel), each filled with an amino acid salt solution of different concentration and/or composition. The outlet gas stream from the test tubes was led to a cold trap to condense water vapor and the CO_2 concentration in the gas stream leaving the cold trap was analyzed using the IR gas detector. Before every experiment the CO_2 concentration in the feed gas was determined by bypassing the set of test tubes. After that, the feed gas was led to the distributor, through the various parallel test tubes, to the collector and subsequently to the IR detector to measure the (collective) outlet concentration. The test tubes with amino acid salt solutions were immersed in a water bath which temperature was regulated to within ± 0.1 K. The saturator temperature was regulated by a second water bath and was operating at a slightly higher temperature than the actual absorption temperature. This temperature was chosen such that evaporation losses for distilled water in a single test tube were negligible (less than 0.15 % per hour). The temperature difference between saturator and water bath for the test tubes was around 294.85 K when operating at 293.15 K and around 316.05 K when working at 313.15 K. The experiment was stopped when the CO_2 concentration in the inlet and the outlet gas streams were the same. All the experimental data were collected by the LabView data acquisition system. The samples were visually inspected for crystals formation just after the experiment termination and after staying overnight in the water bath.

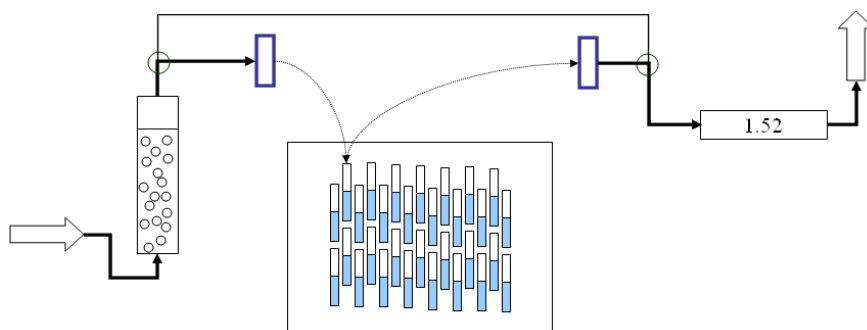


Figure 1. Screening apparatus for precipitation during CO_2 capture

3. Results and discussion

3.1. Density determination

When investigating the operational conditions at which the amino acid salt based CO_2 absorption systems tend to precipitate, it is required to know the saturation concentration (maximum solubility) of these chemical solvents. To our best knowledge, no such experimental data for taurine, β -alanine, sarcosine, L-proline have been published in an open literature and were therefore determined experimentally in this work. In addition to the maximum solubility in water, the corresponding density as measured and is reported in Table 1.

Table 1. Saturation concentration and density of aqueous amino acid salt solutions determined at the maximum solubility at 293.15 K

Compound	C, $kmol \cdot m^{-3}$	ρ , $g \cdot cm^{-3}$
k, taurine	6.56	1.4688
k, β -alanine	7.50	1.3767
k, sarcosine	6.98	1.3147
na, sarcosine	4.64	1.1934
li, sarcosine	2.10	1.0658

k, L-proline	5.56	1.2927
na, L-proline	4.05	1.1984
li, L-proline	1.84	1.0708

All measurements were performed at 293.15 K. Each data point reported was taken as an average of at least three readings. The accuracy of measured densities was verified by determining the density of pure degassed, deionized water. The uncertainties of the measured densities were estimated to be $\pm 0.0001 \text{ g}\cdot\text{cm}^{-3}$ on the basis of comparison with the literature data. In general, it can be noticed that the saturation concentration decreases in the order potassium > sodium > lithium.

3.2. Screening experiments

A tendency of alkaline salts of taurine, β -alanine, sarcosine, L-proline to form solid products under the varying operational conditions of CO₂ absorption processes has been investigated using the experimental set-up presented in Figure 1. Absorption experiments have been performed at 293.15 and 313.15 K, CO₂ partial pressure in the range of 1 up to 10 kPa as well as at atmospheric pressure (101 kPa). The concentration of amino acid salt was varied up to the saturation concentration. Prior to the absorption experiments, water evaporation tests (using tubes filled with water) have been performed at both temperature levels used in the experiments in order to fine-tune the saturator temperature. After this, it was found that changes in the solvent composition due to evaporation losses are negligible.

Figure 2 presents the window of operation for the potassium taurate CO₂ absorption system. The empty symbols indicate the experimental conditions without precipitate formation and the filled ones indicate precipitation during the absorption process. Experimental data from this study for 293.15 and 313.15 K are compared with the literature data for 298.15 and 313.15 K [10]. Results obtained at 298 K during the screening experiments match well with the literature data with respect to the operational conditions at which the solid formation takes place. Comparing the data at 313 K with those at 298 K, it can be seen that for constant CO₂ partial pressure the solubility limit (as expected) shifts to higher concentrations. The sensitivity of the solubility limit for the temperature can be appreciated from Figure 2.

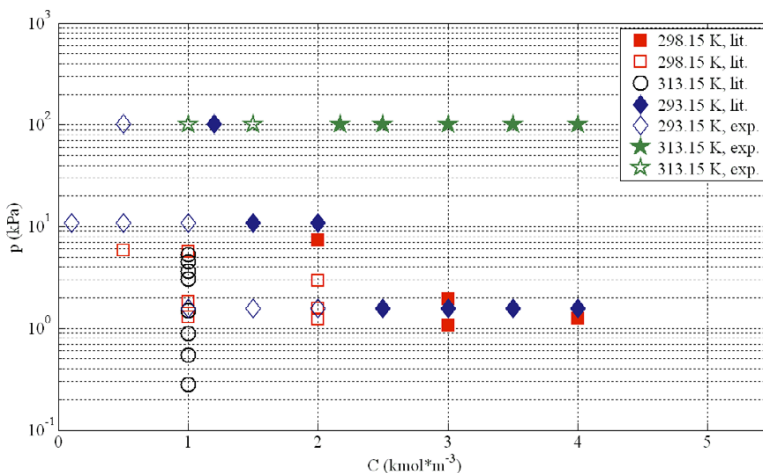


Figure 2. Window of operation for precipitate formation for the potassium taurate CO₂ capture process.

In general, it can be observed that the critical point at which a boundary exists between the non-precipitating and precipitating system strongly depends on the amino acid salt concentration, absorption temperature and CO₂ partial pressure. At constant temperature, the critical point shifts to lower CO₂ partial pressure with increasing amino acid salt concentration. Alternatively, at constant CO₂ partial pressure, the critical point shifts to higher amino acid salt concentration with increasing temperature. This system behaviour can be explained by an influence of the

absorption temperature and of the chemical speciation in the liquid phase on the solubility product of the solid formed, which in case of taurine was reported to be the amino acid itself [5,7]. A series of systematic studies on the effect of anions, acids and bases on solubility of amino acids and related complex compounds have been reported in the literature [11,12,13]. Experimental investigation of the effect of a counter ion on precipitation (or its lack) in amino acid salt CO₂ absorption systems have been performed at 293.15 K and 101 kPa for sarcosine and L-proline. The results are presented in Table 2, where the last column gives number of phases which is equal to two for non-precipitating and three for precipitating gas-liquid systems. In general, it was found that the ionic systems studied follow the same trends as found for the solubility of amino-acids in simpler salt (-acid,-base) systems. For example, no precipitation could be observed at lower (amino acid) salt concentrations whereas at higher concentrations of the ions the precipitate formation occurs, due to formation of complexes and the “salting out” effect of the ions on solubility of the solid products.

Table 2. Window of operation for precipitate formation for alkaline salts of sarcosine and L-proline, temperature = 293.15 K and P(CO₂) = 101 kPa

Compound	sarcosine		proline	
	C, kmol·m ⁻³	Np.	C, kmol·m ⁻³	Np
potassium salt	2.5	2	2.5	2
	3.0	3	3	3
sodium salt	1.5	2	1.5	2
	2.0	3	2	3
lithium salt	2.098	2	1.837	2

At higher (amino acid) salt concentrations, the solubility product of the precipitate is higher in the presence of potassium- than for sodium counter ions and the (amino acid) salt concentration required for the solid to precipitate out of the solution differs from one amino acid to another. The latter system behaviour can also be observed in Table 3, where the experimental data from CO₂ absorption in aqueous potassium salts of taurine, β-alanine, sarcosine, L-proline at 293.15 K are presented.

Table 3. Window of operation for solid formation of potassium salts of taurine, β-alanine, sarcosine and L-proline at 293.15 K

Compound	P (CO ₂), kPa	C, kmol·m ⁻³	Np
taurine	1.57	2.0	2
	1.57	2.5	3
	10.86	1.0	2
	10.86	1.5	3
	101	0.5	2
β-alanine	101	1.0	3
	1.57	5.0	2
	1.57	5.5	3
	10.86	3.0	2
	10.86	3.5	3
sarcosine	101	2.5	2
	101	3.0	3
	1.57	5.0	2
	1.57	5.5	3
	10.86	3.5	2
L-proline	10.86	4.0	3
	101	2.5	2
	101	3.0	3
	1.57	5.56	2
	10.86	3.0	2
	10.86	3.5	3
	101	2.5	2
	101	3	3

4. Conclusions

The tendency of alkaline salts of taurine, β -alanine, sarcosine and L-proline to form solid products under varying operational conditions of CO₂ absorption has been investigated. CO₂ absorption experiments have been performed at 293.15 and 313.15 K, at partial pressures relevant for capturing CO₂ from flue gas conditions and amino acid salt concentrations up to the saturation concentration. Densities of aqueous amino acid salt solutions at the saturation concentration at 293.15 K have been determined.

It was found that the location of the boundary between the non-precipitating and precipitation region does vary from one amino acid salt CO₂ absorption system to another, although some general rules seem to hold:

- (1) higher temperatures and lower CO₂ partial pressures lead to higher solubility limits
- (2) at higher amino acid salt concentration precipitation starts at lower CO₂ partial pressures.
- (3) the effect of the counter ion on the solubility limit appears to be: potassium > sodium > lithium
- (4) the precipitates formed can be the amino acid itself (as in the case of taurate), or more complex (CO₂-containing) species (as for proline, sarcosine and β -alanine). Each leading to different opportunities for process optimization.

A more fundamental model of the (gas-) liquid-solid equilibria, including liquid phase speciation, is required for better understand of the interaction between CO₂ absorption and precipitation, which will be subject of further study.

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