Precipitation in amino acid salt CO₂ absorption systems

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Abstract
The solid products precipitating upon a reactive absorption of CO_2 in aqueous solutions of the potassium, sodium and lithium salts of a series of amino acids were identified using CHN analysis, AAS, XRD, ^{13}C and ^{1}H NMR. Among the investigated amino acids were α-aminoisobutyric acid, taurine, l-alanine and 6-aminohexanoic acid. The results from the precipitates identification together with relations between the initial solvent composition and the solid composition are reported.

Keywords: precipitation, CO_2 absorption, amino acid salts, mixtures of compounds

Introduction

Reactive absorption is a common process in the chemical industry, among others in the treatment of CO_2 containing industrial gas streams. In these processes aqueous solutions of alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and their mixtures, as well as sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) are commonly used [1]. In principle, these systems could be used for the removal of the greenhouse gas CO_2 from flue gases, such as from power plants. However, these solvents suffer from a limitation in the CO_2 loading capacity, a relatively high equipment corrosion rate, a high energy consumption for regeneration and from degradation in an oxygen rich atmosphere, commonly encountered in the treatment of such flue gases [2].

Aqueous alkaline salts of amino acids could be an interesting alternative for these alkanolamines. Generally, amino acid salt solutions can be characterized by a higher stability towards oxidative degradation and a chemical reactivity with CO_2 comparable to alkanolamines due to their similar functionality [3]. A further interesting feature is their ability to precipitate when absorbing CO_2. The solid formation was for example reported during the absorption of CO_2 in aqueous potassium taurate solutions [4] and in the potassium salts of N-methylalanine (Alkazid M), dl-alanine, α-aminoisobutyric acid and its sterically hindered derivatives. The precipitate was reported to be the amino acid [4] or the amino acid chemically bonded with carbonate species [5]. As a result of the precipitation the CO_2 equilibrium partial pressure over the resulting slurry remains almost constant for a certain solution loading [6,7]. This can then result in higher solvent loadings, a lower energy consumption for the solvent regeneration and reduction in the gas-liquid contactor size [7].

Due to the novel character of these three-phase CO_2 absorption systems, much is still unclear on for example the character of the precipitate itself, on precipitation kinetics or absorption capacities. This paper aims to shed some light on the chemical composition of the precipitating solid products, which is important for example from the slurry handling point of view and for mechanistic considerations. Different precipitate compositions will probably lead to a different absorption behaviour, affecting for example absorption capacities and regeneration conditions.

Method and materials

The amino acids were converted to their alkaline salts by neutralising the dissolved amino acid with an equimolar amount of the appropriate hydroxide. Subsequently, the solutions were flushed with pure CO_2 to obtain the precipitate, which was then separated, washed and dried.

The amino acids used in this studies were α-aminoisobutyric acid (99%, Fluka), 6-aminohexanoic acid (99%, Sigma), l-alanine (98%, Fluka) and taurine (98%, Aldrich). The hydroxides were KOH (85%, Riedel-de Haën), NaOH (98%, Sigma) and LiOH (98%, Sigma-Aldrich). Deuterium oxide (D_2O, >98%) was used as NMR solvent (Merck). The calibration compounds in the NMR studies were $KHCO_3$ (99.7%, Sigma-Aldrich) and K_2CO_3 (99%, Sigma-Aldrich).

Carbon, hydrogen, nitrogen and sulphur contents were determined by CHN on an Interscience EA 1180. Percentages by weight of the counter-ions were determined using AAS on a Solaar system 939. X-ray diffraction patterns were collected on a Panalitical X'Pert-APD diffractometer equipped with a curved graphical monochromator using Cu Kα radiation. The conditions were: a voltage 50 kV, a tube current 35 mA, a scanning angle $2\theta = 10\text{-}90^o$, a scanning interval 0.01^o, a scanning step time 0.5 s. All NMR spectra were collected on a Bruker Avance 600 MHz spectrometer using an inverse-detection triple nuclei probe, or a broad-band direct detection probe. The ^1H spectra were obtained at 600.13 MHz using presaturation sequences to obtain suppressing of the residual water signal. The ^{13}C spectra were measured at 150.917 MHz using an inverse-gated decoupling pulse sequence in order to minimize coupling patterns. For the molecular composition determination the ratio between the quaternary carbon signals was used.

Results and discussion

The results from elemental analysis of the precipitates obtained from aqueous potassium, sodium and lithium salts of taurine, together with the theoretical composition of taurine, are presented in Table 1. In the last column, percentages by weight of potassium, sodium and lithium in the solids are given, respectively. Clearly, only minor amounts of the alkali metals were present, making it very likely that the solid product formed in all three systems was the amino acid itself. The results were consistent with Kumar at al. [4].

Table 1: Elemental analysis and AAS of the precipitates of taurine and the theoretical composition of taurine.

Compounds	C (wt.%)		H (wt.%)		N (wt.%)		M (wt.%)	
	Theor.	Meas.	Theor.	Meas.	Theor.	Meas.	Theor.	Meas.
Potassium taurate		19.60		5.45		10.64		0.03
Sodium taurate	19.19	19.44	5.63	5.36	11.19	10.48	0.00	0.04
Lithium taurate		19.56		5.45		10.51		0.02

The diffraction pattern of the solid from the potassium salt of α-aminoisobutyric acid showed that the precipitate was α-aminoisobutyric acid (Figure 1) instead of a carbonate containing salt of the amino acid salt as was suggested by Hook et al. [5]. The results were confirmed with elemental analysis; only minor quantity of potassium could be detected in the precipitate (0.12 wt.%). Similar results were found for the solid product precipitating from the potassium salt of l-alanine (Figure 2). As in the previous case, only minor quantity of potassium were found (0.08 wt.%).

The ^{13}C NMR spectrum of the solid product obtained from the sodium salts of α-aminoisobutyric acid revealed two aliphatic and two aromatic signals (Figure 3). The two aliphatic signals at 23.6 and 58.1 ppm corresponded to the amino acid part of the precipitate. The down-field part of the spectrum showed two peaks, of which the one at 178.1 ppm stood for the amino acid. Since the integral area of the carboxyl group ^{13}C NMR signal was increased as compared with the parent

amino acid [10], it was suggested that the amino acid species exist in the crystals in the form of the amino acid salt. The other-downfield signal (160.5 ppm) was located in the region expected for the carbonate/bicarbonate ion in water. The limiting shifts in samples containing solely HCO_3^- or CO_3^{2-} were 160.4 and 168.3 ppm, respectively, suggesting that the signal located at 160.5 ppm belonged to the bicarbonate ion in the precipitate. These values agree well with the values reported by Abbott et al. [8] and Tian et al. [9]. The diffraction pattern of the precipitate (Figure 4) showed that sodium salt of α-aminoisobutyric acid was present in the solid; sodium bicarbonate was also detected. In general, it was concluded that the precipitate was probably a mixture of two compounds, the amino acid salt and sodium bicarbonate.

Relative intensity (a.u.)
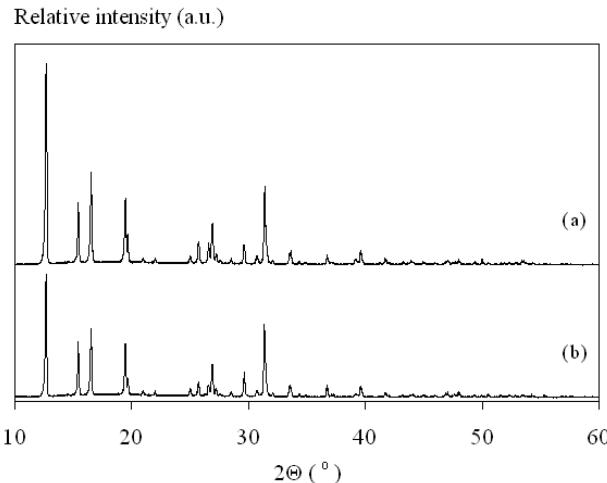
Figure 1: XRD profiles of: (a) α-aminoisobutyric acid, (b) solid precipitated with the potassium salt of α-aminoisobutyric acid.

Relative intensity (a.u.)
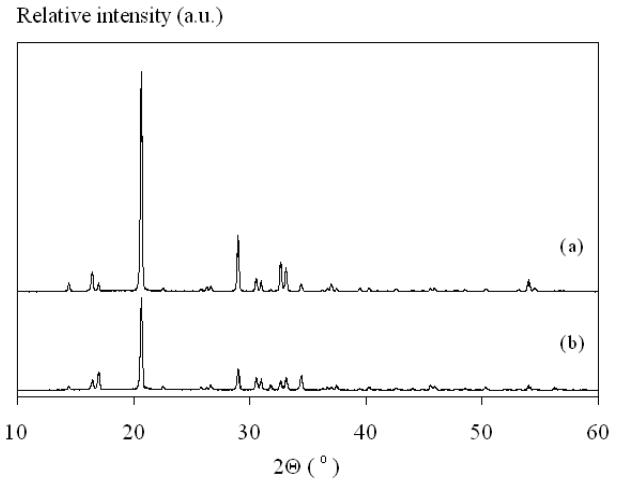
Figure 2: XRD patterns of: (a) l-alanine, (b) precipitate formed with the potassium salt of l-alanine.
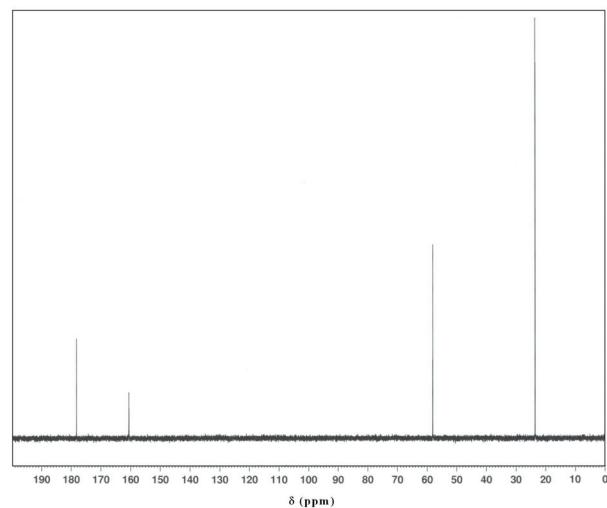
Figure 3: ^{13}C NMR spectrum of the precipitate formed from the sodium salt of α-aminoisobutyric acid.

Relative intensity (a.u.)
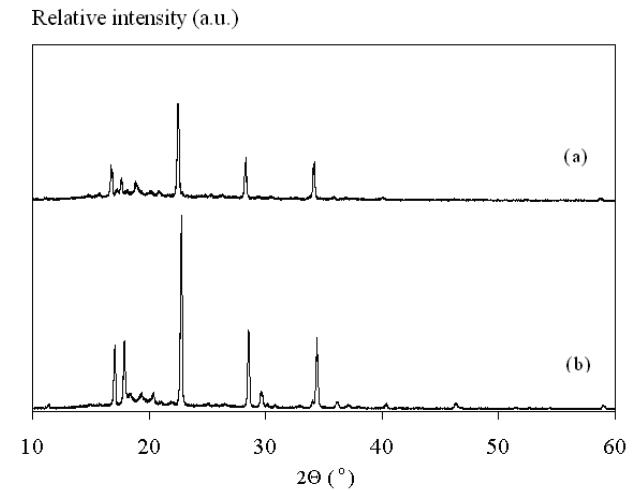
Figure 4: XRD patterns of: (a) sodium salt of α-aminoisobutyric acid, (b) solid formed from the sodium salt of α-aminoisobutyric acid.

In Figure 5, the ^{13}C NMR spectrum of the crystals obtained from the sodium salt of l-alanine is shown. The spectrum revealed more signals than expected if the precipitate was present in the form of a single compound, suggesting that the solid was a mixture of at least two compounds. As in the previous case, apart from the aliphatic and aromatic signals standing for the amino acid part of the precipitate, signals corresponding to hydrated CO_2 species could be found in the down-field part of the spectrum. Based on the integration of the quaternary carbon atom signals and reported 1 to 1

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ratio, it was concluded that two aliphatic signals at 16.2 and 50.5 ppm, combined with the aromatic signal at 176.0 ppm, and the bicarbonate peak at 160.5 ppm, corresponded to the bicarbonate salt of the amino acid salt. The down-field signal at 163.8 ppm was ascribed to sodium bicarbonate, which presence was confirmed with XRD. The two aliphatic singlets at 18.8 and 52.5 ppm, combined with the down-field signal at 182.7 ppm corresponded to a third compound in the precipitate, the amino acid or the amino acid salt. From the ^{1}H NMR spectrum the amount of the latter one was calculated to be around 10%.
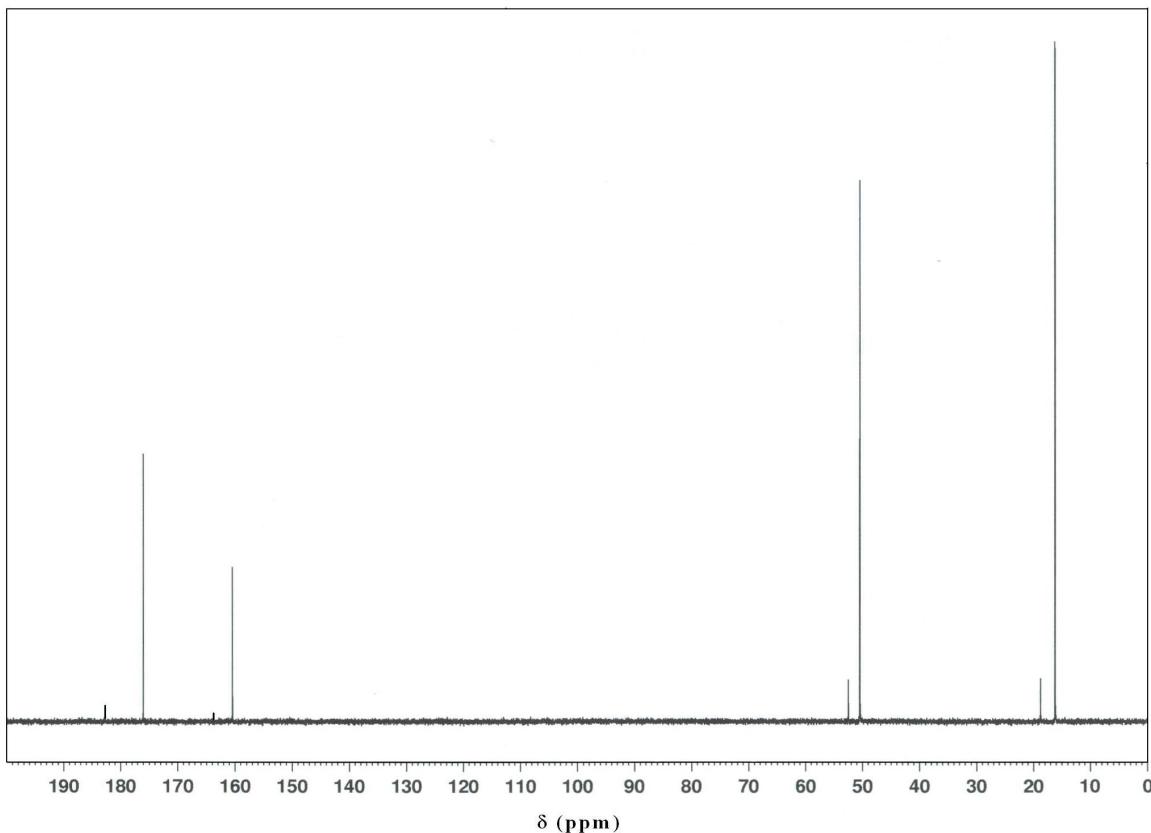

Figure 5: ^{13}C NMR spectrum of the precipitate formed with the sodium salt of l-alanine.

A similar composition pattern was observed for the crystals precipitating from the sodium salt of 6-aminohexanoic acid. The ^{13}C NMR spectra and the XRD diffractogram indicated that the precipitate was a mixture of three compounds. In the ^{13}C NMR spectrum (Figure 6), the aliphatic peaks at 25.2, 25.4, 26.5, 37.2 and 39.3 ppm, combined with the aromatic signal at 183.6 ppm, and the bicarbonate signal at 161.3 ppm, corresponded to the bicarbonate salt of the amino acid salt in the precipitate. This assumption was made based on the observed 1 to 1 ratio between the two quaternary carbon atom signals. Additionally, as the integral area of the carboxyl group signal was increased compared to the amino acid pattern, it was assumed that the amino acid species exist in the precipitate as the amino acid salt [10]. From the ^{1}H NMR spectrum, the amount of this compound was calculated to be around 88% of the solid product. The five remaining aliphatic signals (25.7, 26.0, 29.3, 37.6 and 41.2 ppm) and the carboxylic carbon atom signal at 184.1 ppm corresponded to the amino acid or the amino acid salt. In contrast to the NMR data, the XRD diffractogram showed the presence of some minor quantities of sodium bicarbonate in the crystals.

The type of the precipitate formed in the potassium salt of 6-aminohexanoic acid was significantly different from that of the others. The diffractogram (Figure 7) indicated that the precipitate was predominantly in the form of potassium bicarbonate. Some additional peaks corresponding to the other compound(s) in the crystals could be found. Peaks arising from all the carbon atoms present in the solid are shown in Figure 8. In the spectrum, the signal located at 160.4 ppm corresponded to

potassium bicarbonate, and the aliphatic peaks (25.2, 25.4, 26.5, 37.2 and 39.4 ppm) together with the signal located at 183.7 ppm stood for 6-aminohexanoic acid or its potassium salt. The amount of the latter one was calculated to be less than 2%.
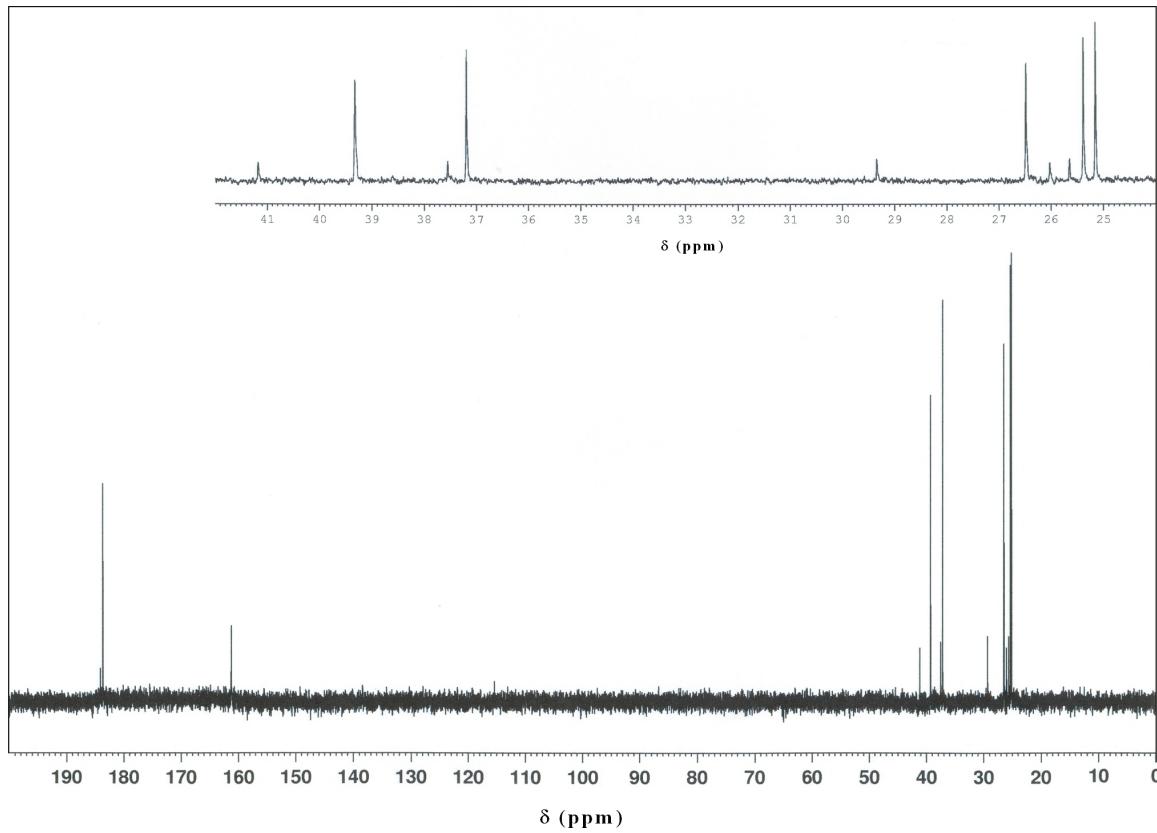

Figure 6: ^{13}C NMR spectrum of the precipitate formed with the sodium salt of 6-aminohexanoic acid.
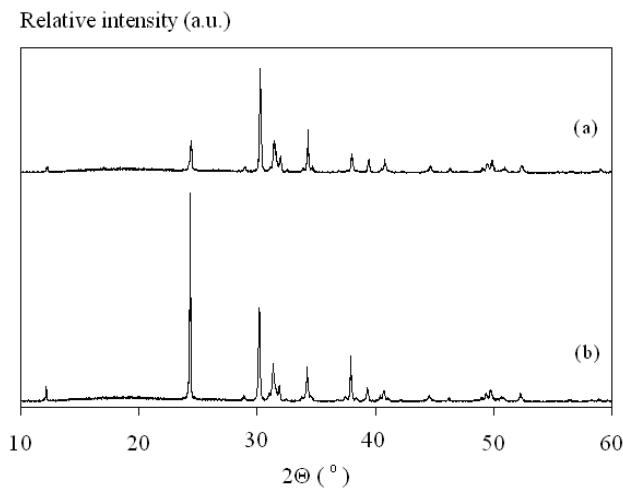

Figure 7: XRD profiles of: (a) KHCO$_3$ (b) solid precipitated with the potassium salt of 6-aminiohexanoic acid.
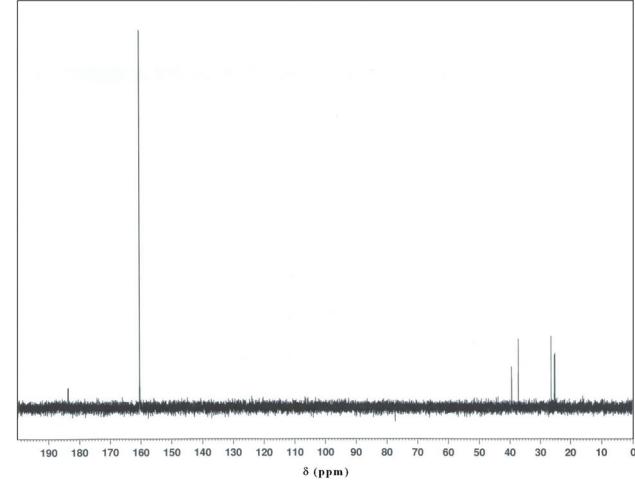
Figure 8: ^{13}C NMR spectrum of the precipitate formed with the potassium salts of 6-aminohexanoic acid.

Conclusions

The solid products formed upon the CO$_2$ absorption in aqueous alkaline salts of amino acid were identified using elemental analysis, AAS, XRD, ^{13}C and ^{1}H NMR. The chemical composition of the precipitates formed from the potassium, sodium and lithium salts of taurine, and the potassium and sodium salts of α-aminoisobutyric acid, l-alanine and 6-aminohexanoic acid showed that the solid

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can be the amino acid or it can contain CO_2 species. The precipitate composition was found to change significantly with the solvent composition or remain the same for the different alkaline salts of the same amino acid. The former one was for example observed for the potassium and sodium salts of α-aminoisobutyric acid, l-alanine and 6-aminohexanoic acid, and the latter one for the taurine based systems. The potassium salts of the amino acids were found to precipitate easier the amino acid, whereas the precipitate formed in the sodium salts more often contains CO_2 species.

Acknowledgement

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