Selection of Amine Amino Acids Salt Systems for CO₂ Capture

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Abstract

Several amino acids including Glycine, L-Alanine, Taurine, Sarcosine, L-Serine, L-Proline, blended with monoethanolamine (MEA) in presence of different amounts of CO₂ were qualitatively and quantitatively studied by NMR spectroscopy. 1D and 2D NMR were employed to qualitatively determine the carbamate formation from the amine group of the amino acids. All species were identified and reported in this work. The preliminary quantitative ¹³C NMR have shown that the highest carbamate formation occurs in the loaded taurine – MEA system and the lowest in the loaded L-alanine – MEA system. In the present work, the complete neutralization of sarcosine with MEA did not occur because of the carbamate formation of the amine group of the MEA.

Keywords: amino acid, carbamte, NMR, CO₂ capture.

1. Introduction

The removal of acid gases like CO₂, H₂S, COS from industrial and natural gas streams is an important operation in the process industry. To reduce excessive emissions, several pre- and post-combustion technologies have been introduced in the industry. Among these is gas absorption with chemical reaction using aqueous amines one of the most frequently used methods.

Aqueous amino acids could be an interesting alternative to the currently commercially used alkanolamines. The main advantages of the amino acids are: high stability towards oxidative degradation...
high chemical reactivity with carbon dioxide and low vapor pressure [2]. An additional advantage of amino acids could be their ability to form solid precipitate when absorbing CO₂ [3, 4].

Aronu et al. [5] reported that the amino acid salts formed from the neutralization of amino acids with an organic base such as an amine showed better CO₂ absorption potential than amino acid salts from the neutralization by an inorganic base such as potassium hydroxide. Hartono et al. [6] performed quantitative ¹³C NMR to study liquid speciation of two different systems, potassium sarcosinate (KSAR) and sarcosine blended with equimolar quantities of 3-(methylamino) propylamine (MAPA-SAR). They found that complete neutralization of sarcosine with MAPA did not occur because of the carbamate formation of the primary and secondary amine group of MAPA.

The contribution of an amine into an amino acid system is to activate the amine group by proton transfer from the amine group to the carbonic acid group and also to enhance the carbonate/bicarbonate formation. In order to better understand the mechanisms involved in an amine amino acid system, NMR could be an important analytical method to gather more information for both liquid and solid as a precipitation product.

The present work investigates different mixtures of the organic base monoethanolamine (MEA) and amino acids (Glycine, L-Alanine, Taurine, Sarcosine, L-Serine and L-Proline with different pKₐ values), see Table 1. Qualitative and quantitative NMR experiments were performed at 25 °C to identify the speciation formed in loaded amino acids neutralized by equimolar quantities of monoethanolamine (MEA).

2. Methods and Materials

2.1. Chemicals

Monoethanolamine [141-43-5], Glycine [56-40-6], L-Alanine [56-41-7], L-Serine [56-45-1], L-Proline [147-85-3], Taurine [107-35-7] and Sarcosine [107-97-1] from Sigma-Aldrich were used as supplied. CO₂ gas with purity > 99.999 mol % was supplied by Yara Praxair AS to preload the samples. 1,4-dioxane (~5 mol % of amine) with purity 99.8% supplied by Fluka was used as an internal reference standard. All the solutions were prepared with distilled water.

2.2. Sample preparation.

The solutions were prepared by neutralizing the aqueous amino acid with an equimolar amount of monoethanolamine (MEA – PRO 1:1; MEA – ALA 1.8:1.8; MEA – SER 0.5:0.5; MEA – GLY 2:2; MEA – TAU 0.8:0.8 and MEA – SAR 0.5 : 0.5). The CO₂ was added by bubbling gas into the solutions. The predetermined loading was calculated from the weight change of the solution. The real concentrations of the amine and CO₂ were determined by standard total amine and CO₂ analysis and compared with NMR analyses. Loaded solutions of ~ 0.4 mL were filled into 5 mm Norrel 507-HP tubes and weighed in Mettler AE163 digital analytical balance with accuracy of ±0.0001g. About 10 mass % of deuterium oxide (D₂O) solution with 99.96% purity was added as a locking agent.

2.3. NMR experiments.

Qualitative NMR experiments. In order to confirm the chemical species and their mole fractions the following NMR experiments were performed: 1D (¹H, ¹³C) and 2D (H-H COSY, H-C HSQC, H-C HMBC). Spectra of loaded amine-amino acid solutions were recorded on a Bruker Avance DPX 400 MHz NMR spectrometer operating at a frequency 100.62 MHz for ¹³C with a 5 mm DUAL ¹H/¹³C probe
head. $^{13}$C NMR spectra were recorded at 25°C by applying a one-dimensional sequence with decoupling, 10.5s pulse repetition time, $D_i = 2s$ and number of scans 128. At these conditions, all signals originating from CO$_2$ show a lower intensity compared to those from amine carbons. The time needed for qualitative experiments was about 10 minutes.

**Quantitative NMR experiments.** For these experiments the following parameters were considered: inverse gated decoupling was used to avoid NOE effects, pulse duration, $p_1 = 6.50$ μs, acquisition time, $AQ = 1.37s$, delay time between two transitions was measured for each amino acid and was set longer than 5 times the longest carbon $T_1$, and number of scans, $NS = 300$. To obtain quantitative measurements, the areas under the spectral peaks were integrated and related to the area of the standard peak of 1,4-dioxane (D8) with a chemical shift $\delta = 67.19$ ppm [7]. Peak areas in NMR spectra are directly proportional to the amount of nuclei observed and were integrated by NMR software.

### 3. Chemistry of the system

Amino acids react with CO$_2$ in a similar fashion to amines, i.e. by forming carbamate and bicarbonate. The reactions taking place during the absorption of CO$_2$ in aqueous amino acid salt solutions are:

**Dissociation of water:**

$$2H_2O \xrightleftharpoons{k_{f}} H^+_2O + OH^-$$

**Dissociation of Carbon Dioxide:**

$$2H_2O + CO_2 \xrightleftharpoons{k_{co}} H^+_2O + HCO_3^-$$

**Dissociation of Bicarbonate:**

$$H_2O + HCO_3^- \xrightleftharpoons{k_{bic}} H^+_2O + CO_3^{2-}$$

**Dissociation of Amino Acid in water solvent:**

$$NHR^+_2R_2 + CO_2H + H_3O^+ \xrightleftharpoons{k_{aci}} NH^+_2R^+_2R_2 - CO_2H + H_2O$$

**Dissociation of protonated amino acid:**

$$NH^+_2R^+_2R_2 + CO_2H + H_2O \xrightleftharpoons{k_{aci}} NH^+_2R^+_2R_2CO^2_2 + H_3O^+$$

**Dissociation of zwitterion amino acid:**

$$NH^+_2R^+_2CO^2_2 + H_2O \xrightleftharpoons{k_{aci}} NHR^+_2R^+_2CO^2_2 + H_3O^+$$

**Dissociation of protonated amine:**

$$NH^+_2R^+_2 + H_2O \xrightleftharpoons{k_{aci}} NHR^+_2R_2 + H_3O^+$$

**Zwitterion formation of amine/amino acid:**

$$NHR^+_2R_2 + CO_2H + NHR^+_2R_2 \xrightleftharpoons{k_{aci}} NHR^+_2R^+_2CO^2_2 + NH^+_2R^+_2R_2$$

**Carbamate formation from amino acid:**

$$NHR^+_2R^+_2CO^2_2NH^+_2R^+_2R_2 + CO_2 + H_2O \xrightleftharpoons{k_{aci}} NCO^2_2R^+_2R_2CO^2_2NH^+_2R^+_2R_2 + H_3O^+$$
Carbamate formation from amine:
\[ NHR_2 + CO_2 + H_2O \xrightleftharpoons{K_{sc}}^\text{K} NCO_2 R_2 + H_2O^+ \] (10)

Table 1. Properties of amine and amino acids

<table>
<thead>
<tr>
<th>Amine/Amino acid name</th>
<th>Chemical name</th>
<th>Structure</th>
<th>$pK_{a1}$ [8]</th>
<th>$pK_{a2}$ [8]</th>
</tr>
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<tr>
<td>L-Proline (PRO)</td>
<td>Pyrrolidine-2-carboxylic acid</td>
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<td>L-Serine (SER)</td>
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</tr>
<tr>
<td>Glycine (GLY)</td>
<td>Aminoethanoic acid</td>
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<td>9.78</td>
</tr>
<tr>
<td>Taurine (TAU)</td>
<td>2-Aminoethanesulfonic acid</td>
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</tr>
<tr>
<td>Sarcosine (SAR)</td>
<td>N-Methylglycine</td>
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<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
<td></td>
<td>9.50</td>
<td>-</td>
</tr>
</tbody>
</table>

4. Results and Discussions

4.1. Qualitative and quantitative NMR experiments

The speciation of different amino acids with MEA at different CO₂ loadings (mol CO₂/mol MEA) was studied at 25 °C by NMR spectroscopy. The chemical structure and the properties of each amino acid are summarized in Table 1.

The important factors for the selection of the amino acids subject to this study were based on their chemical and physical properties, aqueous solubility, basicity ($pK_a$) and stability. The detailed qualitative experiments are explained by Ciftja, et al. [9]. In the present work one quantitative experiment for each of the systems was carried out in order to see the full speciation of the systems (the red spectrum in Fig. 1a-f).
Amino acids dissolved in water are in a zwitterion form, which means that the amino group is protonated and hence less reactive towards CO$_2$ at low pH. In order to activate the amino group, an equimolecular amount of base (MEA) was added into the aqueous solution; thereby reaction 8 could occur in the system. This is possible because of the proton transfer from the amine (MEA) which also makes the amino acids highly reactive.

Figure 1 (a – f) shows typical carbon-13 NMR spectra for all the systems used in this study. The blue spectra represent the qualitative NMR experiment which requires about 10 min and is mainly used for assignments. Notice that in a qualitative spectrum, (blue spectrum) the signal intensity is lower than for the quantitative one (red spectrum). In certain cases, some peaks in the qualitative spectrum are not visible, particularly peaks that belong to carbamate, carbonate/bicarbonate in the higher frequencies (see Fig. 1, a – f). This is a consequence of a short relaxation time of these species.

Amino acids, when blended with amines, will, upon addition of CO$_2$, tend to form carbamate either on the acid amino group or the amine amino group depending on the pK$_a$ and carbamate stability of the amino groups. Amino acids with high pK$_a$ will neutralize themselves upon addition of an amine with
lower $pK_a$ and the carbamate may form only on the amine, in this case MEA. This was the case in the SAR-MEA system, where MEA was unable to neutralize sarcosine ($pK_a = 10.1$). Thus, the carbamate from the amine group of MEA dominated. In the special case, PRO – MEA, the carbamate formation from L-proline is higher than that from other amino acids such as L-alanine in spite of the fact that L-proline has a high $pK_a$ ($pK_a = 10.64$). The ability of the NH$_2$- group to form carbamate in L-proline is very strong such as is also found in the relatives, the cyclic amines, piperazine, piperidine and pyrrolidine [10, 11]. Thus, in this case the competition between zwitterion formation, or self-neutralization, and carbamate formation went more in favour of amino acid carbamate formation. It is thus not only the $pK_a$ values of the amino acid versus the amine that determines the favoured carbamate forming position.

The experiments carried out so far showed that the carbamate formation in L-proline system is in the same level as serine. This might be due to the high loading capacity of L-proline (0.89 mol CO$_2$/mol amine) compared to serine (0.70 mol CO$_2$/mol amine), taurine (0.78 mol CO$_2$/mol amine) and glycine (0.70 mol CO$_2$/mol amine) [12]. In some cases, such as L-alanine – MEA system (Fig. 1b) precipitation during CO$_2$ absorption was observed. This resulted in increased CO$_2$ absorption capacity [4], thus making them attractive for future research.

In these preliminary studies, we found that the highest amino acid carbamate formation occurs in the TAU-MEA system, followed by GLY-MEA, SER-MEA/ PRO-MEA, ALA-MEA and SAR-MEA. The opposite trend was observed for HCO$_3^-$/CO$_3^{2-}$ where the lowest carbonate/bicarbonate formation occurs in the TAU-MEA system.

5. Conclusions

The speciation of several amino acids including L-Proline, L-Alanine, L-Serine, Taurine, Glycine and Sarcosine, blended with monoethanolamine (MEA) in presence of different amounts of CO$_2$ was determined in this work. Some conclusions that can be drawn from this investigation are:

1. The carbamate formation from amino acid increases in the order: SAR-MEA < ALA-MEA < SER-MEA = PRO-MEA < GLY-MEA < TAU-MEA.

2. The carbonate/ bicarbonate formation increases in the order: SAR-MEA < TAU-MEA < GLY-MEA < ALA-MEA=PRO-MEA < SER-MEA.

3. Complete neutralization of sarcosine with MEA does not occur and almost only carbamate formation from MEA takes place. This system shows low affinity towards CO$_2$ capture.

4. High loading capacity is observed in the ALA-MEA system, probably due to precipitation in the loaded solution.

NMR spectroscopy is found to be a suitable tool to study and understand the interactions between CO$_2$, amines and amino acids, and the species formed by these systems.

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