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Carbamate Formation in Aqueous - Diamine - CO₂ Systems

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Abstract

Qualitative NMR spectroscopy was used to study the species formed during CO₂ absorption in aqueous solution of diamines. Three different systems, consisting of primary (ethylenediamine), primary/secondary (3-(Methylamino) propylamine) and secondary (piperazine) diamines were studied by ¹³C NMR and the main products were identified based on various 1D and 2D NMR techniques. The main compounds were observed and assigned to (primary/ secondary) carbamate, dicarbamate and carbonate/bicarbonate. The highest concentration of carbonate/bicarbonate and dicarbamate were observed in the PZ/CO₂/H₂O followed by MAPA/CO₂/H₂O and EDA/CO₂/H₂O. Both ¹H and ¹³C NMR spectroscopy was used to quantitatively determine the speciation of amines but ¹³C-NMR, although slower, has the potential of being more accurate than the ¹H-NMR. The diamines studied in the present work were found to have high CO₂ absorption capacity compared to other amines described in the literature. This indicates that they are interesting for the further investigation.

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Keywords: carbamate formation, diamine, speciation, NMR, CO₂ capture.

1. Introduction

Aqueous solutions of alkanolamines are the most commonly used chemical absorbents for the removal of acidic gases (H₂S and CO₂) from gas streams. Among them, aqueous monoethanolamine (MEA)

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solutions have been used extensively for this purpose because of the high reaction rate, low cost the solvent, ease of reclaiming, reasonable thermal stability, low molecular weight and hence high absorbing capacity [1].

Diamines could be a more attractive alternative as solvents for carbon dioxide capture than a mono-amine [2] due to possibly faster absorption, higher capacity, lower circulation rate and lower energy requirements [2, 3]. The diamine 2-[(2-aminoethyl)amino]-ethanol (AEEA) as a possibly promising absorbent was identified by Ma'mun et al.[2] through a set of several screening tests focusing on the absorption rate and the capacity of the amines. In their work they showed that AEEA offers a high absorption rate combined with a high net cyclic capacity.

NMR spectroscopy is a powerful tool for fundamental studies of absorption systems and has been frequently employed to distinguish chemical species in amine-CO₂-H₂O solutions [4-8]. Jakobsen et al.[4] investigated loaded aqueous solution of AEEA and identified, primary and secondary carbamate but no dicarbamate formation was found even for high loading. Hartono et al. [5] in their studies found that at high CO₂ loadings in the DETA/CO₂/H₂O system dicarbamate and carbonate/bicarbonate dominate, while no clear evidence was found for tricarbamate formation. The cyclic diamines (such as piperazine) allow an increased solvent capacity and faster CO₂ absorption rates by increasing the concentration of PZ in solution [9].

The objective of this work is to use NMR techniques to determine which species are formed in diamine-CO₂-H₂O systems with different dissociation constants and molecular structures in order to determine the speciation and carbamate formation in these systems. This step is very important to understand the chemistry of the system. ¹H and ¹³C NMR spectroscopy is used for studying the species in solutions of carbon dioxide in aqueous 3-(Methylamino)propylamine (MAPA), ethylenediamine (EDA) and Piperazine (PZ). By employing ¹³C NMR spectroscopy at 25 °C, determinations of the concentrations of the following species are obtained: amine, primary and secondary carbamate and dicarbamate. Due to the fast proton transfer between molecular and protonated amine, only the sum of the concentrations of the amine itself and its protonated forms is determined [5, 10]. Some properties of the diamines used in this study are summarized in Table 1.

2. Experimental part

2.1. Materials and Sample preparation

CO₂ with purity > 99.999 mol % supplied by Yara Praxair AS was used to preload the samples. The chemicals used in this investigation were: 99% Ethylenediamine (EDA) was purchased from Fluka, ≥ 98% 3-(Methylamino)propylamine (MAPA) and 99% Piperazine (PZ) obtained from Sigma-Aldrich. 1,4-dioxane with purity 99.9% obtained from Fluka was used as internal reference standard. All the chemicals were used without further purification.

The aqueous solutions of 30 wt. % of each of the amines were preloaded with CO₂ up to 1 mol CO₂/mol amine and the concentration was estimated from the weight change of the solution after CO₂ bubbling based. The concentrations of amine and CO₂ were analyzed by standard total amine and CO₂ analysis. Loaded solutions of 0.4 mL were filled into 5 mm Norrel 507-HP tubes and weighed in a Mettler AE163 digital analytical balance. About 10 mass % of deuterium oxide (D₂O) solution with 99.96% purity was added as a locking agent. The NMR experiments were divided in two parts, qualitative experiments to assign the species and then quantitative experiments to obtain the speciation of the systems.

2.2. Methods

^1H and ^{13}C NMR spectroscopy was applied to qualitatively investigate the aqueous solutions of 30 wt % of EDA, PZ and MAPA. All the spectra were acquired on a 400 MHz Bruker spectrometer. 1D (^1H , ^{13}C) and 2D (H-H COSY, H-C HSQC, H-C HMBC, DEPT 90/135°) spectra of loaded amine were carried out for the assignments of the species in these three different systems. The parameters and the technique used for this purpose are given elsewhere [11, 12].

3. Chemistry of the System

During chemical absorption of CO_2 in aqueous diamine systems, CO_2 is bound as either bicarbonate/carbonate, carbamate or dicarbamate [13]. The following species are considered to coexist in the liquid phase: Am, AmH^+ , AmCO_2^- , $\text{AmH}^+\text{CO}_2^-$, $\text{Am}(\text{CO}_2^-)_2$, CO_2 , HCO_3^- , CO_3^{2-} , H_2O , H_3O^+ and OH^- . The di-protonated amine is not considered to be present in significant quantities because of the high pH during normal operating conditions. The main chemical equilibrium reactions are:

Protonation of diamine:



Di-protonation of diamine:



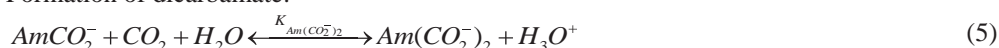
Formation of carbamate:



Carbamate protonation:



Formation of dicarbamate:



The specifications of the diamines studied in the present work are summarized in Table 1.

4. Results and Discussions

4.1. ^1H - NMR experiments

Figure 1 shows the proton NMR spectra of loaded solutions for the three different systems with the respective molecular structures. The chemical shift for the ^1H , δ , is in the range of 0 to 10 ppm (but only the important ranges are shown in Fig. 1). The assignment of the species based on ^1H and the corresponding ^{13}C NMR spectrum for loaded aqueous solution of diamines, are given in Fig. 1 and Fig. 2 respectively. The spectrum of PZ/ CO_2 / H_2O (the green spectrum in Fig. 1) displays the average peak that belongs to PZ/ PZH^+ (marked with no.1 in Fig. 1), peaks 1' and 2' that are assigned to the proton bound in CH_2 carbamate of PZ/ PZH^+ and peak 1* assigned to the proton bound in CH_2 dicarbamate. The separation of signals of each species is very clear, so it is possible to quantify the amine/ carbamate and dicarbamate without using the ^{13}C . The carbonate/bicarbonate is sacrificed as it is not visible by ^1H -NMR [16]. The blue spectrum represents the MAPA/ CO_2 / H_2O system. The peaks 1 to 4 belong to the proton bound to the CH_2 and CH_3 of the free/ protonated MAPA. The peaks denoted with no. 1' and 5' correspond to the primary carbamate and peak no. 1'' and 2'' correspond to the secondary carbamate while dicarbamate is not formed due to low loading ($\alpha = 0.21$ mol CO_2 / mol MAPA).

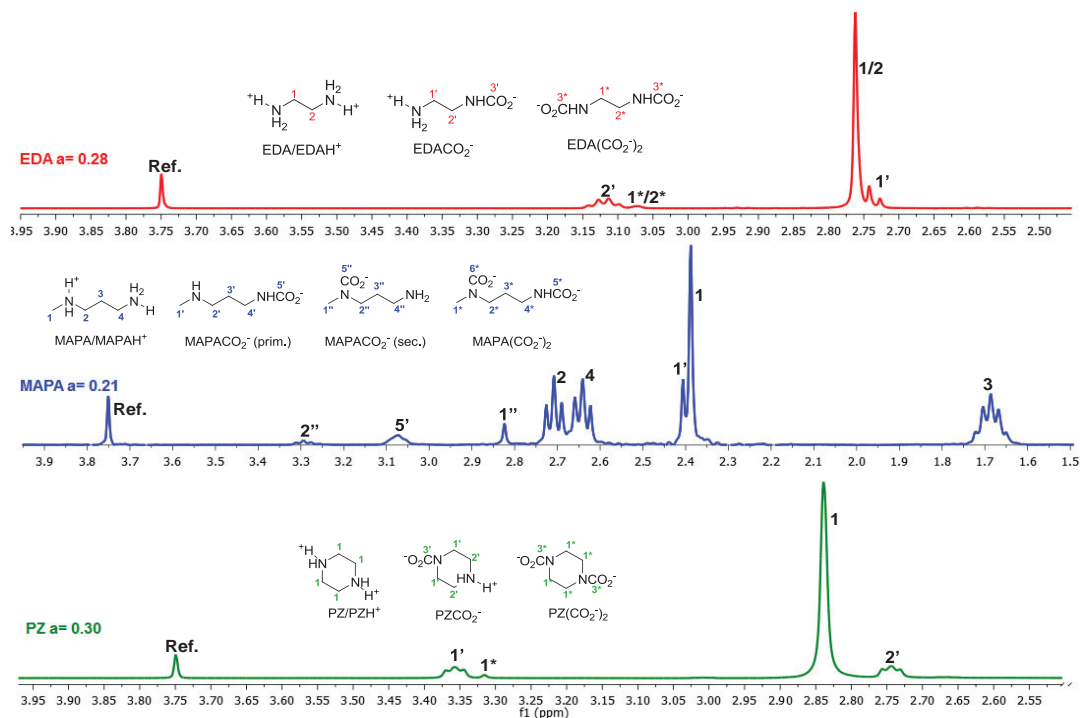


Figure 1. ^1H NMR spectra of loaded aqueous solution of: EDA (red), MAPA (blue) and PZ (green) system with corresponding chemical structures.

The assignments for EDA are shown in the red spectrum. We can see both carbamate and dicarbamate at low loadings and the dicarbamate is found in this symmetrical molecule as a singlet signal.

Use of proton and carbon NMR experiments has advantages and disadvantages. Due to the sensitivity of the NMR and the natural abundance (99.985%), ^1H NMR provides stronger signals than ^{13}C NMR. Also, when it comes to the experiment time required for proton NMR, it is much shorter than for the carbon NMR experiment. This is due to the relaxation time for ^1H which is very short ($>1\text{s}$) compared to ^{13}C (hours). Speciation based on ^1H NMR is used to study different systems such as MEA, PZ etc. [9, 14]. However, due to peak overlapping and chemical shift of the signals at high loadings, it is difficult to distinguish between the species. Thus, for these conditions ^{13}C -NMR has the potential of being more accurate than ^1H -NMR. In addition, the quantification of the carbonate/ bicarbonate species cannot be observed by ^1H -NMR spectroscopy.

4.2. ^{13}C -NMR experiments

The ^{13}C chemical shifts are in the range of 20 – 200 ppm, but only the important ranges are shown in the Fig. 2. Due to the fast exchanging of protons, it is not possible to distinguish signals of protonated and unprotonated (Am/AmH^+) species and of $\text{HCO}_3^-/\text{CO}_3^{2-}$ ([5], [10], [15]). Therefore the observed signals represent the sum of the species in a group. Fig. 2 shows the ^{13}C NMR spectra for each of the loaded systems studied in the present work and the corresponding chemical systems are shown in Fig. 1.

Free piperazine appears at 45.6 ppm as an average peak for four carbons due to the symmetric structure of the molecule (the green spectra in Fig. 2). At loading $\alpha = 0.30$ mol CO_2 /mol amine, new

peaks appear which are assigned to carbamate (1', 2' and 3'), dicarbamate (3*) and carbonate/ bicarbonate based on 2D NMR experiments (see Experimental part). At a CO₂ loading of 0.19 mol CO₂/ mol amine another peak assigned to carbonate/bicarbonate appears. By increasing the CO₂ concentration, it was observed that the relative intensity of carbamate, dicarbamate and carbonate/ bicarbonate gradually increases. However, the chemical shift of the carbamate and dicarbamate did not change. Increase in acidity makes the chemical shift of the PZ/ PZH⁺ peak change from 43.9 ppm to 41.7 ppm and that of the carbonate/bicarbonate peak to change from 166.3 ppm to 161.3.

In the MAPA/CO₂/H₂O system the primary and secondary carbamate were observed individually. This is due to the asymmetrical structure of MAPA and therefore more species were present in this system compared to EDA/CO₂/H₂O or PZ/CO₂/H₂O (see the blue spectrum in Fig. 2). Four peaks that belong to MAPA/MAPAH⁺ are present in the unloaded solution. After introducing a very small amount of the CO₂ in the aqueous solution of MAPA, new peaks coming from primary and secondary carbamate and dicarbamate appear. The carbonate/bicarbonate peak appears at 166.3 ppm and shifts to lower frequency due to the increase acidity of the system.

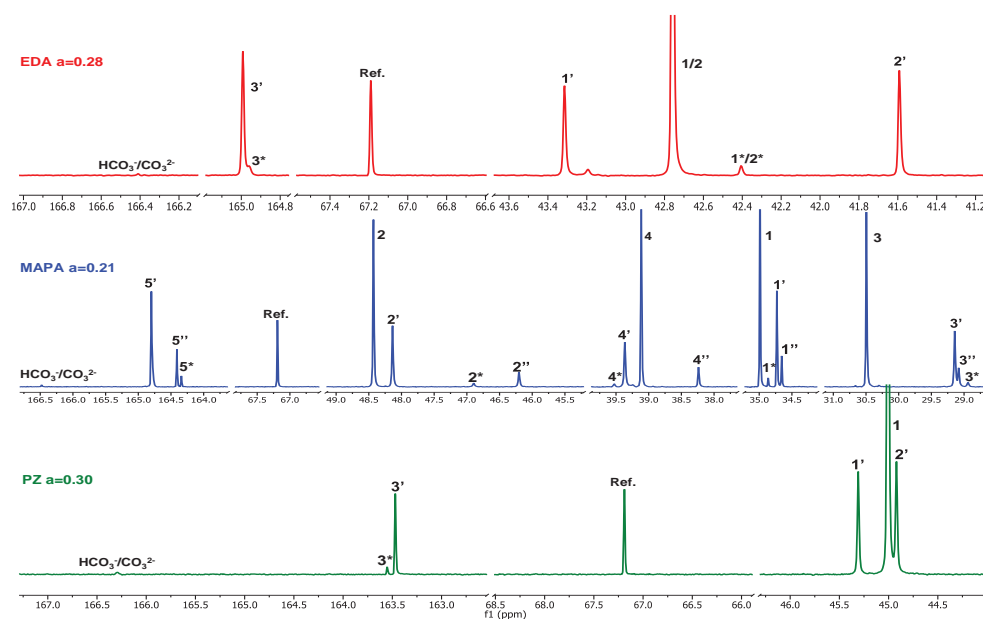


Figure 2. ¹³C NMR spectrum of EDA (red), MAPA (blue) and PZ (green) system. (Note that the peak of the carbonate/bicarbonate is not visible due to the low intensity of the species).

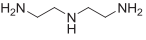
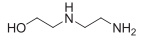
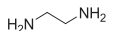
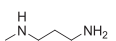

Aqueous solutions of loaded EDA were analyzed qualitatively by ¹³C NMR spectroscopy. In the unloaded solution only one peak was observed and represents both carbons due to the symmetrical structure of EDA. New peaks appear when a small amount of CO₂ is added in the solution ($\alpha = 0.09$). These peaks are identified based on 2D NMR experiments and belong to the primary carbamate (1', 2', and 3'). After increasing the CO₂ amount in the system ($\alpha = 0.28$), new peaks appear due to the formation of dicarbamate of EDA (1*/2* and 3*, in Fig. 2). A common peak for carbonate/ bicarbonate appears in the low field region at $\delta = 166.41$ ppm which shifts to 162.36 ppm due to the pH change.

The level of dicarbamate and carbonate/bicarbonate formation ranges in the order: PZ > MAPA > EDA, while the level of carbamate formation follows almost the same trend for all of the systems presented in this work for a loading about 0.5 mol CO₂/mol amine. The high affinity towards CO₂ for PZ

might be due to the cyclic structure of this compound (see Table 1) compared to the other diamines presented in this work. The diamines are more efficient than monoamines for CO₂ capturing.

It was observed that the dicarbamate formation occurs for loadings higher than 0.2 mol CO₂/mol diamine. Table 1 shows a comparison with available literature for diamine systems such as DETA (diethylenetriamine) and AEEA (2-(2-aminoethylamino)ethanol) at loadings around 0.5 mol CO₂/mol diamine. If we compare DETA (triamine), AEEA (diamine) with MAPA (diamine), all these amines have one primary and one secondary amine group. Still MAPA shows higher carbamate/dicarbamate formation (see Table 1). The same conclusion can be drawn for EDA (with two primary amine groups) and PZ (with two secondary amine groups) which have higher CO₂ capacity than DETA and AEEA.

Table 1. Comparison with literature of the carbamate formation (in mol fraction) in diamine systems.

Diamine	Chemical structure	Loading	pK _a	Carbamate		Dicarbamate	Source
				Prim.	Sec.		
DETA		0.36	10.22 9.75 5.15	1.58E-02	7.00E-04	1.40E-03	[16]
AEEA		0.49	10.05 7.21	2.20E-02	4.00E-03	1.00E-04	[17]
EDA		0.42	9.92* 6.86*	4.00E-02	1.20E-02	2.90E-03	This work
MAPA		0.48	10.74** 8.77**	4.60E-02	-	3.30E-03	This work
PZ		0.48	9.73* 5.33*	-	5.75E-02	8.80E-03	This work

* Perrin 1965 and 1972 [18]

** Aronu 2011 [19]

Based on the pK_a values of these systems it seems that no direct correlation can be suggested between pK_a and CO₂ absorption capacity and that other factor play an important role. From these preliminary results, we observe that piperazine forms more carbamate compared to the other diamines. The same conclusion was drawn in a study by Puxty et al. [20] for 75 different amines at 40 °C (primary, secondary, tertiary and polyamine systems). The absorption capacities were plotted as a function of pK_a. They reported that the primary and secondary amines did not show a strong correlation with pK_a. This is due to the sensitivity of carbamate formation to pH, and thus amine pK_a is dependent on the carbamate stability constant which varies from amine to amine. They also found that the cyclic amines (2-piperidinethanol and 2-piperidinemethanol) have the highest cyclic capacity. This might be the case also in our study where piperazine shows higher CO₂ absorption capacity compared to EDA and MAPA, in spite of the fact that piperazine has lower pK_a (see Table 1). Further work will be focused on quantification of the species concentration present in each systems studied in the present work using ¹³C NMR.

5. Conclusions

This work has demonstrated that ¹³C NMR is more accurate and reliable and is a powerful tool to analyse various systems for CO₂ capture. Three different systems (EDA/CO₂/H₂O, MAPA/CO₂/H₂O and PZ/CO₂/H₂O) were studied by ¹H and ¹³C NMR and the main species were identified based on different

1D and 2D NMR techniques. The main compounds were determined and assigned to (primary/secondary) carbamate, dicarbamate and carbonate/bicarbonate. The highest levels of carbonate/bicarbonate and dicarbamate were observed in the PZ/CO₂/H₂O system followed by MAPA/CO₂/H₂O and EDA/CO₂/H₂O. The preliminary results show that no direct correlation exists between pK_a and CO₂. High CO₂ absorption capacity of piperazine can be attributed to the cyclic structure of this diamine. Further work in quantitative ¹³C NMR is needed for speciation and quantitative characterization of the diamine systems for CO₂ capture.

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