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Experimental Study on Phase Change Solvents in CO₂ Capture by NMR Spectroscopy

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Abstract

2-(Diethylamino)ethanol (DEEA) and 3-(Methylamino) propylamine (MAPA) in combination may represent a promising absorbent system for CO₂ capture due to high CO₂ loading capacity, high equilibrium temperature sensitivity, low energy requirement for regeneration and relatively high reaction rate.

Three different systems: DEEA-CO₂-H₂O; MAPA-CO₂-H₂O and DEEA-MAPA-CO₂-H₂O were studied quantitatively by NMR spectroscopy and the data are reported in the present work. The main products quantified for these systems are: carbonate-bicarbonate for the DEEA-CO₂-H₂O system; primary, secondary carbamate, dicarbamate for the MAPA-CO₂-H₂O system, and primary/ secondary carbamate, dicarbamate, carbonate/bicarbonate in blended DEEA-MAPA-CO₂-H₂O. The speciation data of the three systems were measured and reported in the present work. The blended system of 5M DEEA-2M MAPA can form two liquid phases after being loaded with CO₂ and both phases were analyzed quantitatively by NMR spectroscopy. The experimental data shows that the lower phase is rich in CO₂ and MAPA while the upper phase was lean in CO₂ and rich in DEEA. The ratio DEEA-MAPA in the lower phase increases with increasing partial pressure whereas for the upper phase the opposite is true.

Keywords: Absorbents, phases change solvents, blended systems, NMR.

1. Introduction

In order to meet the 2°C target on global warming, the total anthropogenic greenhouse gas (GHG) emission levels in 2020 should peak at approximately 39-44 Gt of carbon dioxide equivalents (GtCO₂e). However, CO₂ emissions appear likely to further increase up to 56 GtCO₂e in 2035 (UNEP, 2012).

The Intergovernmental Panel on Climate Change (IPCC, 2012) concluded that global CO₂ emissions must be cut by 50-85% below 2000 levels by 2050 and begin to decrease no later than 2015, in order to avoid the most damaging effects of climate change. Different techniques are suggested for CO₂ capture from power plants, but the most mature technology today is post-combustion removal by chemical absorption.

Single alkanolamines systems, such as primary amines, monoethanolamine (MEA); secondary amines, diethanolamine (DEA), di-isopropanolamine (DIPA); sterically hindered amines, 2-amino-2-methyl-1-propanol (AMP) and tertiary amines, N-methyldiethanolamine (MDEA) have been widely used as chemical absorbents for the removal of acid gases (Astarita et al., 1983; Böttinger et al., 2008; Chakraborty et al., 1986; Kim et al., 2008; Kohl and Nilsen, 1997; Ma'mun et al., 2005; Versteeg et al., 1996) . The major problem using this technology is relatively high operating costs, mainly due to the regeneration of absorbents.

Primary and secondary amines form stable carbamates and have a CO₂ loading limitation of about 0.5 mol of CO₂/mol of alkalinity when carbamate formation is the only reaction (Satori and Savage, 1983). Tertiary amines such as N-methyldiethanolamine (MDEA) or 2-(Diethylamino)-ethanol (DEEA) have higher loading capacity (about 1.0 mol of CO₂/mol of alkalinity) and a low heat of regeneration, If this can be combined with high equilibrium temperature sensitivity, a low heat duty during regeneration can result (Barzagli et al., 2010; Bishnoi and Rochelle, 2002a; Kim, 2009; Svendsen et al., 2011).

Thus, for the development of new cost effective CO₂ capture processes, many research groups have focused on the reduction of regeneration energy by suggesting mixture solvent systems such as mixed amine systems (Aronu et al., 2010; Austgen et al., 1991; Barzagli et al., 2011; Bishnoi and Rochelle, 2002b; Bougie and Iliuta, 2010; Brüder et al., 2012; Dubois and Thomas, 2012; Seo and Hong, 1996).

Recently a new class of solvents called phase change solvents, forming two liquid phases, has been developed (Arshad et al., 2013; Hartono et al., 2013; Liebenthal et al., 2013; Raynal et al., 2011). IFPEN have their DMX™ process which is tested in the EU OCTAVIUS project (Raynal et al., 2011). The DEEA/MAPA system is under development in the EU project *iCap* (Arshad et al., 2013; Liebenthal et al., 2013). Both processes show a potential for large energy savings in the capture process.

2-(Diethylamino)ethanol (DEEA) is a tertiary alkanolamine having good potential for bulk removal of CO₂ from gaseous streams. It contains two ethyl groups replacing the hydrogen atoms of the amino group in MEA. DEEA (2-(Diethylamino)ethanol) can be prepared from agricultural products and/or residues which are renewable resources (Konduru et al., 2010; Vaidya and Kenig, 2007). However, being a tertiary amine, it has low reactivity with respect to CO₂, and to enhance CO₂ capture, an activator is needed such as a primary or secondary amine (Kim and Svendsen, 2007).

3-(Methylamino) propylamine (MAPA) is a di-amine with one primary and one secondary amine group in its structure leading to high CO₂ absorption capacity and high reaction rate (Ciftja et al., 2013b; Ermatchkov et al., 2003; Hartono et al., 2011; Kim, 2009). MAPA has high heat of reaction at stripping conditions and is difficult to strip. This makes this amine less desirable as single absorbent for CO₂ capture (Kim, 2009).

A combination of the primary/secondary (MAPA) and tertiary (DEEA) amines could be an attractive and promising alternative absorbent for CO₂ capture. The systems forms two liquid phases under certain conditions, one lean in CO₂ and one rich in CO₂, and can, after absorption, be separated based on difference in density. As the carbon dioxide concentrates in one of the two phases, only a portion of the total absorbent flow rate has to be sent to the stripper (Aleixo et al., 2011; Liebenthal et al., 2013; Raynal et al., 2011). The energy requirement for regeneration of solvent can be reduced based on low

liquid circulation rate in the stripping section, a potential for high CO₂ pressures in the stripper (stripping at elevated pressure) and operative loadings mainly in the bicarbonate formation and reversion range.

The development of both thermodynamic and kinetic models relies heavily on phase equilibrium measurements and an available tool which can give information about the full liquid speciation of the two phases of the system is Nuclear Magnetic Resonance (NMR) spectroscopy. The important information we can gain is the ability to distinguish between primary, secondary, di- carbamate and carbonate/bicarbonate species. In the present work, the liquid phase speciation of the blended aqueous solution of DEEA/MAPA/CO₂/H₂O, as well as the unblended MAPA/CO₂/H₂O and DEEA/CO₂/H₂O system are presented. Knowing the degree of formation of new species is very helpful to understand the behavior of this solvent and could also be very important information for interpretation of kinetic and equilibrium data.

2. Materials and Methods

2.1. Sample preparation

The chemicals used in this study were CO₂ (AGA, $\geq 99.99\%$ pure), 2-(Diethylamino)ethanol (DEEA) (Sigma-Aldrich 99% pure), 3-(Methylamino) propylamine (MAPA) (Aldrich $\geq 98\%$ pure), and were used without any further purification.

Batch solutions of DEEA and MAPA were prepared and CO₂ was added by purging gas into the solution. The CO₂ amounts added to the DEEA and MAPA systems were in the range of 0.1 - 1 mol CO₂/mol alkalinity. The samples of blended 5M DEEA and 2M MAPA were taken out from a screening apparatus where different CO₂ partial pressures were used (1, 3, 6, 10, 13 and 20 kPa). The screening apparatus and procedure are described in detail by (Aronu et al., 2010).

The loading of CO₂ was estimated from the weight change of the solution after CO₂ bubbling. . The preloaded samples were kept at room temperature for about 24h and then analyzed for CO₂ and amine by titration and compared with the NMR analyses (Ciftja et al., 2013a).

Loaded and unloaded solutions of about 0.4 mL were filled into 5 mm Norrel 507-HP tubes and weighed in a Mettler AE163 digital analytical balance with accuracy of ± 0.0001 g. 1,4-dioxane was added as internal reference standard. About 10 mass % of deuterium oxide (D₂O) solution with 99.9% purity was added to the single amine systems to obtain a signal lock. The blended system of 5M DEEA-2M MAPA turned into two phases after introducing CO₂ to the system and the lower phase was quite viscous. To better understand this system, the phases were separated and the lower phase was diluted with D₂O. This dilution was necessary to avoid shimming problems by the NMR technique due to the high viscosity of the lower phase. Insertion of capillary tubes with D₂O was tested but did not work. The amount of sample and D₂O added to each sample are shown in Table A-4 in the Appendix. A dilution effect of D₂O on the equilibrium cannot be ruled out but is believed to be small as no effect is seen on the CO₂ balance.

A GVLab fixed-speed vortex mixer was used to mix all the contents in the NMR tubes. In order to determine the species in the DEEA-CO₂-H₂O, MAPA-CO₂-H₂O and DEEA-MAPA-CO₂-H₂O systems, qualitative (1D and 2D NMR for assignments) and quantitative ¹³C (for species concentrations) NMR measurements were performed. MestReNova software was used to process the data.

The concentrations of the amines were determined by standard acid-base titration with a 0.1M H₂SO₄ (Kim et al., 2008), while for the CO₂ analysis a BaCl₂ method was used (Ma'mun, 2005). The total alkalinity was calculated as the ratio of mol CO₂/mol alkalinity and compared with the NMR analyses

2.2. NMR experiments

Qualitative NMR experiments. 1D (^1H , ^{13}C) and 2D (H-H COSY, H-C HSQC, H-C HMBC) spectra of loaded DEEA-MAPA solutions were recorded on a Bruker Avance DPX 400MHz NMR spectrometer operating at a frequency 100.62 MHz for ^{13}C with a 5 mm DUAL $^1\text{H}/^{13}\text{C}$ probe head. ^{13}C NMR spectra were recorded at 25°C by applying a one-dimensional sequence with pulse duration, $p_1 = 7\mu\text{s}$, delay time, $D_1 = 2\text{s}$ and number of scans 128. The time needed for qualitative experiments was about 10 minutes.

Quantitative NMR experiments. The parameters used for quantitative experiments were: pulse duration, $p_1 = 7\mu\text{s}$ for 90° pulse, delay time $D_1 = 60\text{s}$ ($\geq 5T_1$), number of scans, $NS = 300$ and acquisition time, $AQ = 1.37\text{s}$. Experimental details on quantitative ^{13}C NMR experiments and the estimated parameters are given by Ciftja et al., (2013)).

2.3. Reaction Mechanisms of Amines

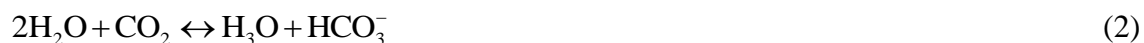
The chemical structures of the amines chosen for this study are shown in Figure 1 and consist of primary, secondary and tertiary amine groups. When CO_2 is absorbed into an aqueous amine solution, the base reactions taking place in the system could be represented in these three steps:

I - The species and reactions involved in the CO_2 -water system are usually taken to be as following:

Dissociation of water:



Dissociation of dissolved CO_2 through carbonic acid:



Dissociation of bicarbonate:

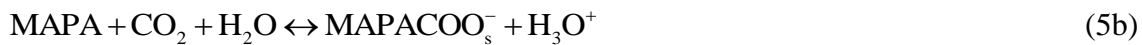
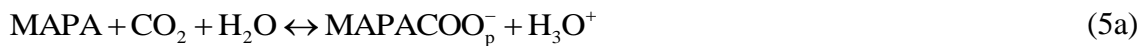


II – The absorption process in primary/secondary amines such as MAPA, compromises several reactions:

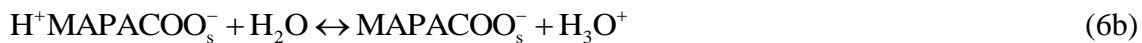
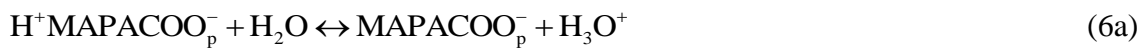
Dissociation of protonated MAPA:



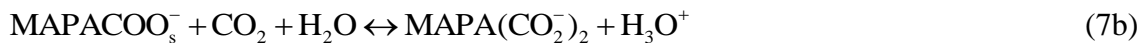
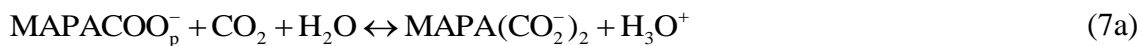
Formation of MAPA carbamates:



Dissociation of protonated carbamates:



Di-carbamate formation:



III – In Tertiary alkanolamines such as DEEA the base reactions could be represented by the following:



The potential species formed in loaded solutions of DEEA; MAPA or blended DEEA and MAPA are DEEA; DEEAH⁺; MAPA; MAPAH⁺; MAPACO₂(_p)⁻ (primary); H⁺MAPACO₂(_p)⁻ (primary); MAPACO₂(_s)⁻ (secondary); H⁺MAPACO₂(_s)⁻ (secondary) and MAPA(CO₂⁻)₂ (dicarbamate). The di-protonated MAPA is unlikely to exist because of the high pH in solution. The molecular structures of the main

species are given in Figure 3. In addition, the following species from Eq.1-3, are present: H_2O , H_3O^+ , OH^- , CO_2 , HCO_3^- , and CO_3^{2-} . Amine-protonated amine, amine carbamate-protonated amine carbamate and bicarbonate-carbonate which involve proton transfers, have very rapid reaction rates with very small relaxation times. Therefore the ^{13}C NMR will average the peaks for these species (Ciftja et al., 2013a; Jakobsen et al., 2005).

3. Results and Discussions

3.1. NMR experiments on the loaded DEEA- CO_2 - H_2O system

A typical ^{13}C NMR spectrum of the loaded aqueous DEEA system is shown in Figure 2 and the corresponding chemical structures with chemical shift ranges are given in Table 1.

DEEA+DEEAH⁺ peaks appeared at $\delta = 59.4$; $\delta = 54.1$; $\delta = 47.4$ and $\delta = 10.9$ ppm. This corresponds to two secondary carbons (-CH₂OH, signal number 7) and (-CH₂-, number 8); to an average peak for two other secondary carbons (number 9), and to an average peak for the two methyl groups ((-CH₃)₂) (number 10) as shown in Figure 2. At loading $\alpha = 0.11$ mol CO_2 /mol alkalinity, a new peak at 165.4 ppm was assigned to carbonate-bicarbonate based on 2D NMR experiments (Sect.2.2). By increasing the carbon dioxide concentration from 0.11 to 0.95 mol CO_2 / mol alkalinity, it was observed that the relative intensity of carbonate-bicarbonate gradually increased.

Increase in acidity (CO_2 content) makes the chemical shift of the DEEA+DEEAH⁺ peak change slightly and, that of the carbonate-bicarbonate peak to also change from 165.4 ppm at loading $\alpha=0.11$ to 161.9 ppm at loading $\alpha=0.95$ mol CO_2 /mol alkalinity. The peak assignments and the chemical shift ranges of the species in this system (in ppm) are listed in Table 1 while the NMR chemical shifts for each of the species are given in Table S1 in the Supporting Information.

Since DEEA is a tertiary amine with no hydrogen atom attached to the nitrogen, no additional peaks, except HCO_3^- - CO_3^{2-} can be observed when the system is pre-loaded with CO_2 .

The quantitative NMR experiments and the parameters used for the system are explained in the literature (Ciftja et al., 2013a). All the data were processed and calculated by the NMR software (MestReNova).

The liquid phase speciations for the unloaded and loaded aqueous DEEA systems calculated directly from the species concentrations on mol fraction basis obtained by NMR are given in Table A-1.

The reaction product in the DEEA-CO₂-H₂O system is carbonate-bicarbonate species and amine-protonated amine. Thus, the carbonate-bicarbonate levels increase rapidly with CO₂ loading whereas the amine-protonated amine levels remain almost constant during the whole absorption process. The speciation data for the liquid phase composition of the DEEA-CO₂-H₂O system are given in Table A-1, Appendix.

3.2. NMR experiments on the loaded MAPA-CO₂-H₂O system

Results from quantitative ¹³C NMR experiments on the MAPA-CO₂-H₂O system at 25 °C are shown in Figure 4. Formation of primary-secondary carbamate and dicarbamate were observed individually as is reported in the literature (Hartono et al., 2011). The high basicity of MAPA (pK_{a1} = 10.74 and pK_{a2} = 8.77, at 25°C (Perrin, 1972) results in carbamate formation immediately after the CO₂ is introduced into the solution. The primary amine group of MAPA (3-(Methylamino) propylamine), due to the high pK_a value, will react first followed by the secondary amine group.

The asymmetric structure of MAPA will result in more species present in this system compared to the DEEA-CO₂-H₂O one (Figure 2). Only four signals that belong to the MAPA+MAPAH⁺ (peaks denoted with blue numbers in Figure 2) are present in the unloaded solution (first spectrum at the bottom of Figure 4).

After introducing a very small amount of CO₂ in the aqueous solution of MAPA, new peaks from primary and secondary carbamate appear. At loading 0.40 mol CO₂/mol alkalinity new peaks were observed and assigned to dicarbamate and confirmed from 2D NMR experiments (Figure 4).

The carbonate-bicarbonate (purple color) peak appears at $\delta = 166.3$ ppm and, with increased loading, shifts to lower frequencies ($\delta = 163.5$ ppm) due to the increased acidity of the system. Carbonate-bicarbonate formation was observed at high loading (0.63 mol CO₂/mol alkalinity). The chemical shifts in ppm for all the species in the unloaded/loaded MAPA - H₂O systems at 25 °C are given in Table S2 in the Supporting Information and the liquid phase concentrations are plotted in Figure 5. As one could expect, the main species formed in this system are: carbamate (primary and secondary), dicarbamate and, at higher loadings, carbonate-bicarbonate. It should be pointed out that the carbamate peaks also contain the protonated carbamates. Similar ionic products were also found in the analogue systems such as 2-[(2-aminoethyl)amino]-ethanol (AEEA) (Jakobsen et al., 2008), diethylenetriamine (DETA) (Hartono et al., 2007) or piperazine (Ermatchkov et al., 2003). A comparison of CO₂ loading based on titration and NMR analysis is given in Figure 9 and shows very good agreement. The speciation data are given in Table A-2 in the appendix.

MAPA, as mentioned previously, is a di-amine with primary and secondary amine groups in its structure (Figure 3) leading to high CO₂ absorption capacity (Ciftja et al., 2013b; Ermatchkov et al., 2003; Hartono et al., 2011; Kim, 2009).

3.3. NMR experiments of blended DEEA-MAPA-CO₂-H₂O

Without CO₂, the blended system is one liquid phase and the corresponding spectrum is shown in Figure 6 (lower red spectrum). Adding CO₂ to the system, a separation of the solvent into two liquid phases was observed. As expected, carbamate-dicarbamate formation in the lower phase took place due to very fast reaction of the primary-secondary amine groups in MAPA, as can be seen in Figure 6.

The CO₂ content was different in the two phases. The CO₂ rich phase (lower phase) and the CO₂ lean phase (upper phase) were separated from each other. The liquid samples from both phases and for each

partial pressure were collected and analyzed by NMR as described in the sample preparation section (Sect. 2.1).

The main product in the upper phase is DEEA. However, the peaks of carbamate, dicarbamate and carbonate-bicarbonate in this phase were very difficult to quantify accurately due to their very low signal intensities. The liquid phase speciations for the upper phase are plotted in Figure 8b and the data are given in Table A-3 in the Appendix. The ^{13}C NMR spectra of loaded aqueous DEEA-MAPA for the upper phase are shown in Figure S1 in the Supporting Information.

Quantitative ^{13}C NMR spectra of the lower phase are shown in Figure 6 where the ranges for the carbamate signals at the highest partial pressures were expanded to make them more visible.

In the lower phase of the DEEA-MAPA system (Figure 6) more peaks were observed due to the formation of carbamate, dicarbamate and carbonate-bicarbonate as was expected.

It was observed that with increasing partial pressure the DEEA-MAPA ratio in the lower phase gradually increased (red symbols, Figure 7), whereas the opposite was observed for the upper phase (blue symbols, Figure 7). Since the upper phase is rich in DEEA, it can further contribute to CO_2 absorption by dissolution into the lower phase while the regeneration of the lower phase will require less energy due to reduced circulation rate in the stripper and mainly the DEEA part being regenerated.

The main products in the lower phase were identified and quantified as the following: primary carbamate, secondary carbamate, both including protonated forms, dicarbamate and bicarbonate-carbonate (see Figure 8a). In the upper phase, the amount of carbamate and dicarbamate were very low while bicarbonate-carbonate was not detected (see Figure 8b). As for the single amine systems, the CO_2 balance was checked. Table 2 and A-3 in the Appendix give the speciation data and CO_2 loadings for the lower and upper phase respectively.

Figure 9 compares the NMR method for determining CO_2 loading with the BaCl_2 precipitation/titration method. Data for loaded aqueous solutions of DEEA and MAPA individually and both phases of the

blended DEEA-MAPA system are shown in Figure 9. As seen, for the DEEA, MAPA and the lower phase from blended DEEA-MAPA, the titration and NMR methods agree very well. This indicates that the sample preparation methods used has not changed the speciation significantly and that the results are representative of the original samples. However, for the very low loadings of the upper phase the uncertainty of particularly the titration method becomes very large and the measurements are also close to the detection limits of the NMR method (Ciftja et al., 2013a). This is the reason for the discrepancies seen for this phase.

Conclusions

Three different systems: DEEA-CO₂-H₂O; MAPA-CO₂-H₂O and DEEA-MAPA-CO₂-H₂O were studied quantitatively by NMR spectroscopy and speciation data are reported in the present work. The main products quantified for these systems are: carbonate/bicarbonate for the DEEA-CO₂-H₂O system; primary/secondary carbamate, dicarbamate for the MAPA-CO₂-H₂O system, and primary/secondary carbamate, dicarbamate, carbonate-bicarbonate in blended DEEA-MAPA-CO₂-H₂O. The blended system of DEEA-MAPA can form two liquid phases after being loaded with CO₂ and both phases were analyzed quantitatively by NMR spectroscopy. The experimental data shows that the lower phase is rich in CO₂ and MAPA while the upper phase was lean in CO₂ and rich in DEEA. The ratio DEEA/MAPA in the lower phase increases with increasing partial pressure whereas for the upper phase the opposite is true.

Abbreviations

<i>AQ</i>	Acquisition time
<i>COSY</i>	Correlation Spectroscopy
<i>HMBC</i>	Heteronuclear Multiple Bond Correlation

HSQC	Heteronuclear Single Quantum Coherence
<i>NS</i>	Number of scans
NMR	Nuclear Magnetic Resonance Spectroscopy

Symbols

D_1	Delay time between two transitions, <i>s</i>
<i>D8</i>	Reference, 1,4-dioxane
p	Primary (carbamate)
p_1	Pulse duration, μs
<i>ppm</i>	Unit, parts per million
s	Secondary (carbamate)
1D	One – dimensional NMR
2D	Two – dimensional NMR
α	Loading, $(\text{mol CO}_2)(\text{mol alkalinity})^{-1}$
δ	Chemical shift, <i>ppm</i>

Acknowledgments

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Appendix

Table A-1 Speciation distribution in mol fraction for DEEA-CO₂-H₂O system at 25 °C.

Loading (mol CO ₂ /mol alkalinity)		DEEA-CO ₂ -H ₂ O	
NMR	Titration	DEEA+DEEAH ⁺	HCO ₃ ⁻ /CO ₃ ²⁻
0.00	0.00	6.58E-02	0.00E+00
0.11	0.11	6.50E-02	6.91E-03
0.18	0.18	6.49E-02	1.14E-02
0.29	0.29	6.46E-02	1.90E-02
0.38	0.40	6.45E-02	2.48E-02
0.43	0.44	6.46E-02	2.76E-02
0.55	0.57	6.37E-02	3.53E-02
0.74	0.74	6.28E-02	4.64E-02
0.95	0.93	6.31E-02	5.91E-02

Table A-2 Speciation distribution in mol fraction for MAPA-CO₂-H₂O system at 25 °C.

(mol CO ₂ /mol alkalinity) Loading		MAPA-CO ₂ -H ₂ O				
NMR	Titration	MAPA+MAPAH ⁺	MAPACO ₂ ⁻ (p) [*] H ⁺ MAPACO ₂ ⁻ (p) [*]	MAPACO ₂ ⁻ (s) ^{**} H ⁺ MAPACO ₂ ⁻ (s) ^{**}	MAPA(CO ₂) ₂	HCO ₃ ⁻ /CO ₃ ²⁻
0.00	0.00	8.59E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00
0.08	0.09	8.07E-02	5.54E-03	1.76E-03	0.00E+00	0.00E+00
0.21	0.22	6.11E-02	1.21E-02	3.66E-03	3.77E-04	0.00E+00
0.40	0.42	5.20E-02	2.32E-02	6.70E-03	1.69E-03	0.00E+00
0.63	0.62	5.04E-02	4.18E-02	1.24E-02	5.25E-03	1.06E-03
0.96	0.94	1.62E-02	5.92E-02	1.66E-02	8.44E-03	3.89E-03

*p-primary carbamate (MAPA)

**s-secondary carbamate (MAPA)

Table A-3 Speciation (in mol fraction) for upper phase of 5M DEEA-2M MAPA system at different partial pressures.

Partial Pressure (kPa)	Loading NMR (mol CO ₂ /mol alkalinity)	DEEA+DEEAH ⁺	MAPA+MAPAH ⁺	MAPACO ₂ ⁻ (p) [*] H ⁺ MAPACO ₂ ⁻ (p) [*]	MAPACO ₂ ⁻ (s) ^{**} H ⁺ MAPACO ₂ ⁻ (s) ^{**}	MAPA(CO ₂) ₂	HCO ₃ ⁻ /CO ₃ ²⁻
unloaded	0.000	3.20E-01	1.26E-01				
1	0.001	5.11E-01	4.70E-03	7.31E-04	0.00E+00	0.00E+00	0.00E+00
3	0.003	6.60E-01	6.07E-03	1.99E-03	0.00E+00	0.00E+00	0.00E+00
6	0.006	6.64E-01	5.25E-03	3.05E-03	1.20E-03	0.00E+00	0.00E+00
10	0.006	6.29E-01	5.28E-03	2.83E-03	1.26E-03	0.00E+00	0.00E+00
13	0.007	6.09E-01	4.50E-03	2.91E-03	1.43E-03	0.00E+00	0.00E+00
20	0.013	6.36E-01	8.49E-03	3.05E-03	3.25E-03	0.00E+00	2.06E-03

*p-primary carbamate (MAPA)

**s-secondary carbamate (MAPA)

Table A-4 Sample preparation for blended system of loaded DEEA-MAPA.

Sample name	Gram sample	Gram D₂O	Gram 1,4-dioxane
Lower Phase			
unloaded	0.4107	0.0357	0.0231
1 kPa	0.1484	0.5006	0.0491
3kPa	0.1811	0.5033	0.0505
6kPa	0.2019	0.4428	0.0431
10kPa	0.1659	0.4913	0.0459
13kPa	0.1711	0.4219	0.0494
20kPa	0.1197	0.4526	0.0441
Upper Phase			
1 kPa	0.3570	0.2049	0.0470
3kPa	0.4492	0.1841	0.0451
6kPa	0.3722	0.1885	0.0435
10kPa	0.4067	0.2004	0.0480
13kPa	0.3552	0.2233	0.0430
20kPa	0.3954	0.2176	0.0484

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Table 1. Chemical shift of the corresponding carbons shown in the DEEA-CO₂-H₂O system.

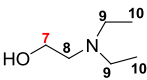
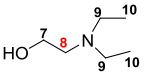
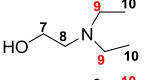
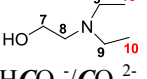
Signal number	Chemical shift	Assignment ^a	Remarks
7	59.4 – 56.3		Secondary carbon of DEEA+DEEAH ⁺
8	54.1- 54.0		Secondary carbon of DEEA+DEEAH ⁺
9	47.4 – 48.0		Two secondary groups of DEEA+DEEAH ⁺
10	10.9 - 8.9		Two methyl groups of DEEA+DEEAH ⁺
HCO ₃ ⁻ -CO ₃ ²⁻	165.4 - 161.9	HCO ₃ ⁻ /CO ₃ ²⁻	Bicarbonate-carbonate

Table 2 Speciation (in mol fraction) for lower phase of DEEA-MAPA system at different partial pressures (loading=mol CO₂/mol alkalinity).

Partial Pressure (kPa)	Loading NMR	DEEA+DEEAH ⁺	MAPA+MAPAH ⁺	MAPACO ₂ p* MAPACO ₂ (p)H ⁺	MAPACO ₂ s** MAPACO ₂ (s)H ⁺	MAPA(CO ₂) ₂	HCO ₃ ⁻ -CO ₃ ²⁻
unloaded	0.000	3.17E-01	1.26E-01	-	-	-	-
1	0.516	2.72E-02	1.82E-01	7.22E-02	2.86E-02	1.60E-02	3.26E-02
3	0.472	4.62E-02	1.55E-01	5.97E-02	2.77E-02	1.66E-02	2.93E-02
6	0.497	6.35E-02	1.80E-01	6.50E-02	2.80E-02	2.24E-02	3.74E-02
10	0.494	6.60E-02	1.58E-01	5.83E-02	2.69E-02	1.98E-02	3.55E-02
13	0.462	9.64E-02	1.79E-01	6.87E-02	2.65E-02	2.03E-02	4.47E-02
20	0.450	1.53E-01	1.55E-01	5.82E-02	1.91E-02	2.19E-02	6.23E-02

* p-primary carbamate (MAPA)

** s-secondary carbamate (MAPA)

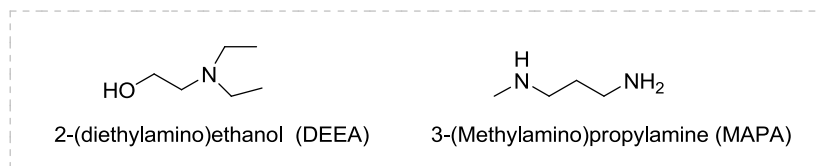


Figure 1. Chemical structures of DEEA and MAPA.

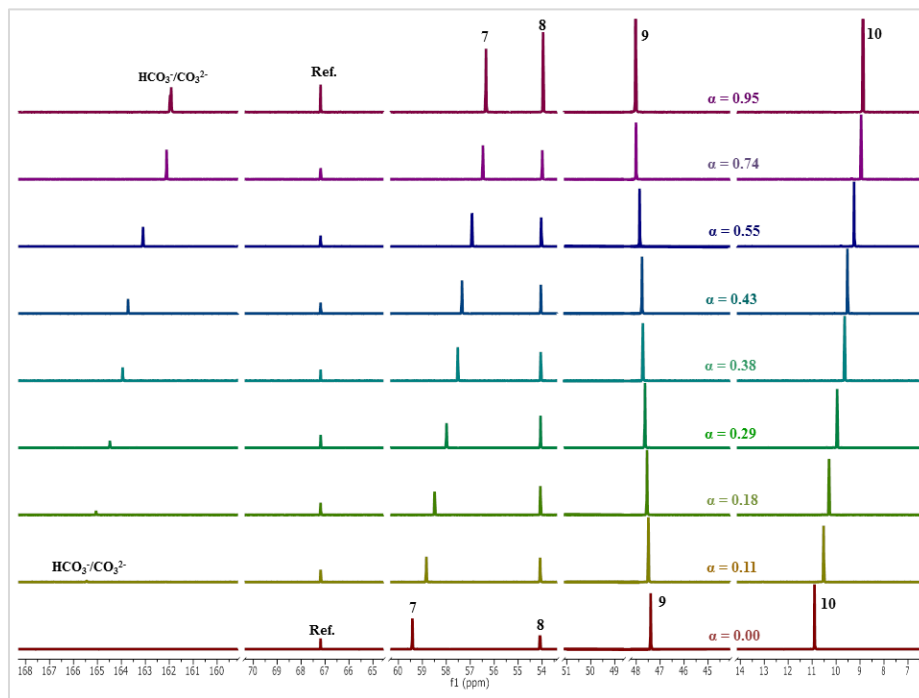


Figure 2. Quantitative ^{13}C - NMR spectra for loaded aqueous solution of DEEA system at 25 °C.

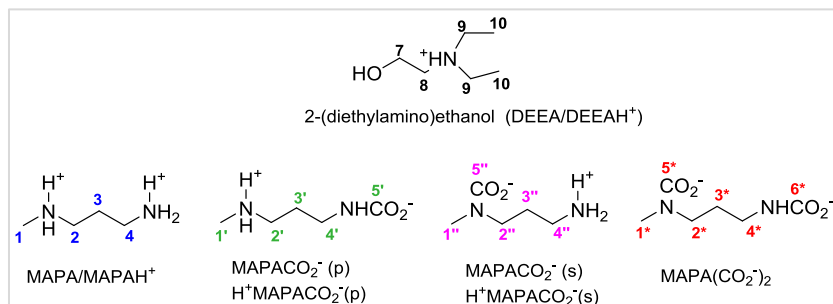


Figure 3. Potential species in loaded aqueous solutions of the blended DEEA and MAPA system.

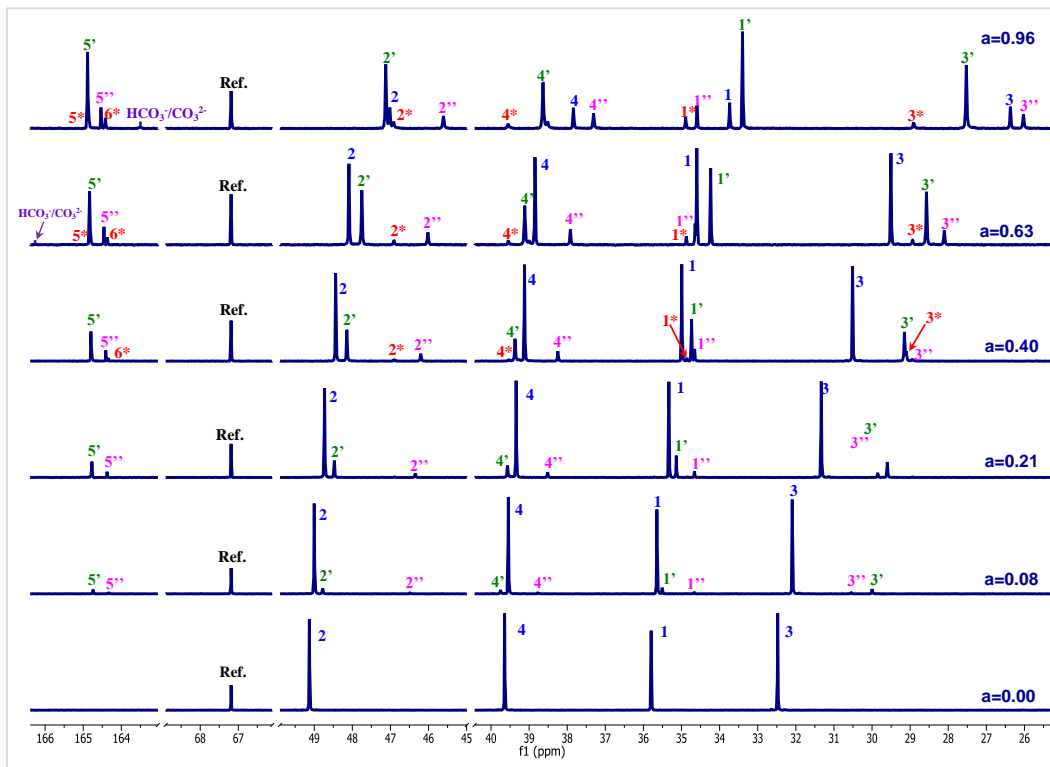


Figure 4. ^{13}C NMR spectra of the MAPA- CO_2 - H_2O system at 25°C .

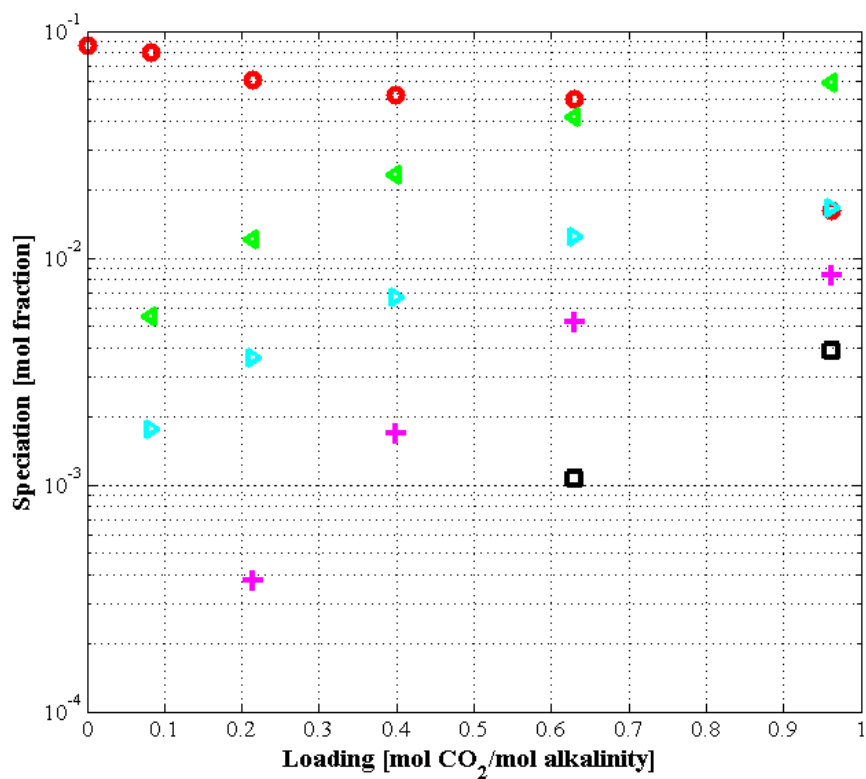


Figure 5. Liquid-phase speciation of MAPA-CO₂-H₂O system at 25 °C. Symbols: ● MAPA+ MAPAH⁺, ◀ MAPACO₂⁻ (p) + H⁺MAPACO₂⁻ (p); ▶, MAPACO₂⁻(s) + H⁺MAPACO₂⁻ (s); +, MAPA(CO₂)₂ ■, HCO₃⁻/CO₃²⁻.

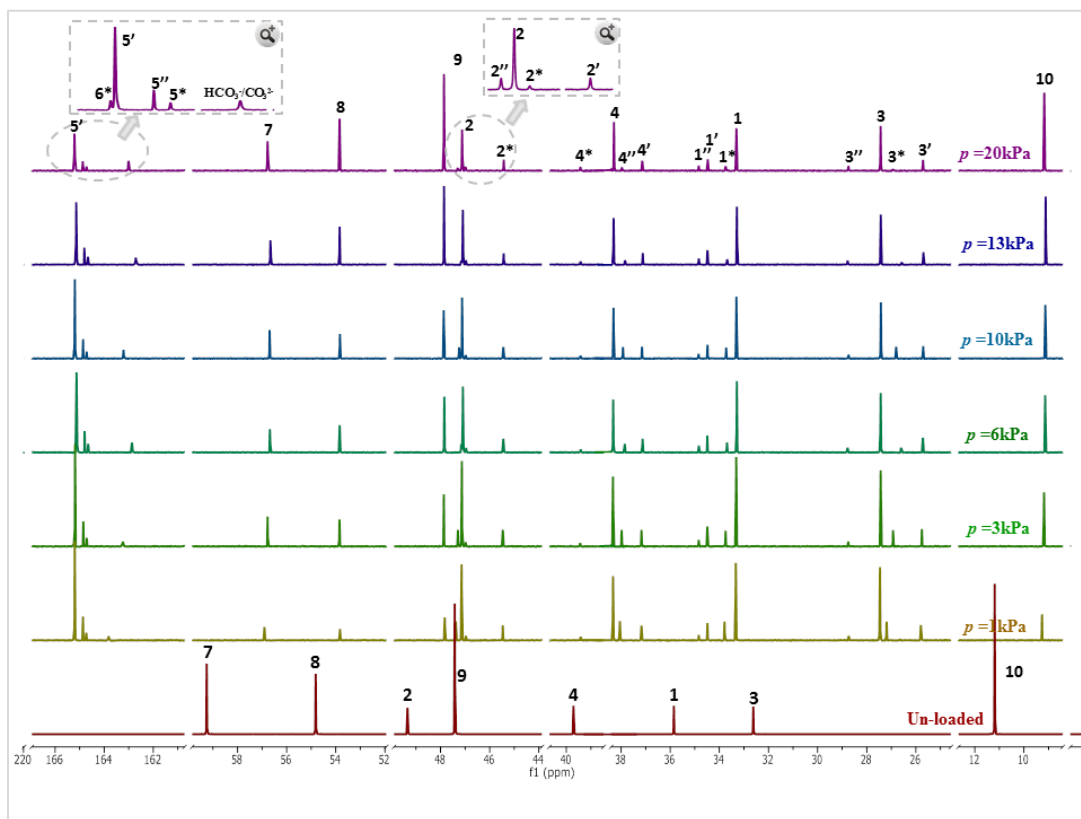


Figure 6. ¹³C NMR spectra of the lower phase of 5M DEEA-2M MAPA-CO₂-H₂O system at partial pressures of 1- 20 kPa (note that the reference at $\delta = 67.2$ ppm is not visible due to expansion of the spectrum).

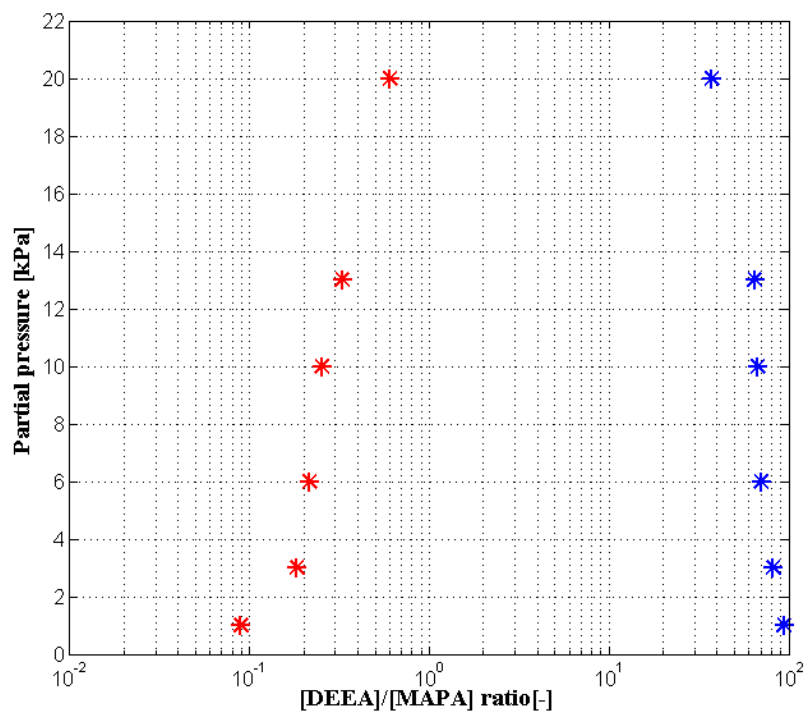


Figure 7. DEEA/ MAPA ratio (in mol fraction scale) in upper and lower phase: * , lower phase; * , upper phase.

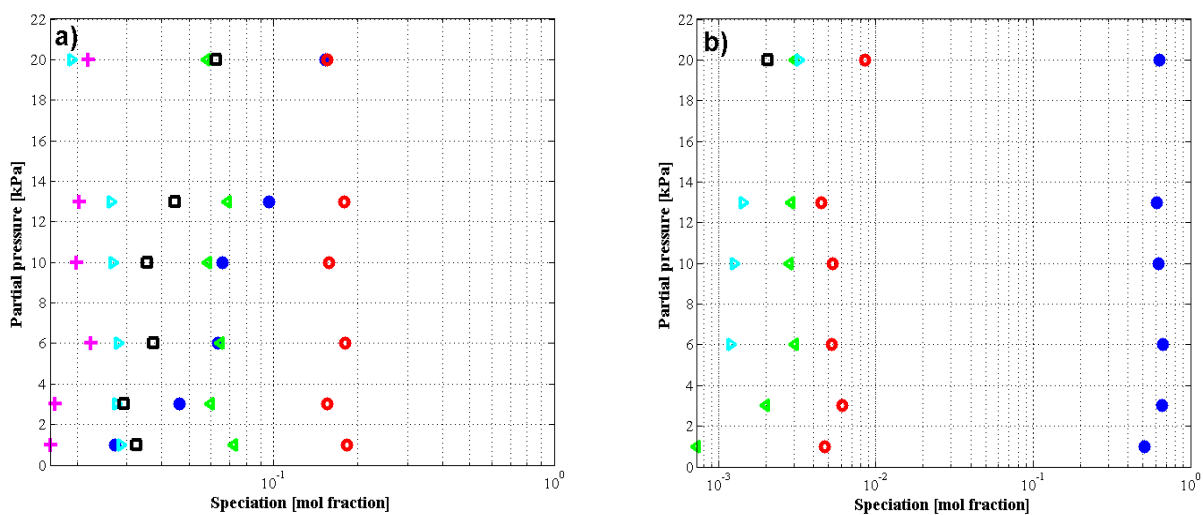


Figure 8. Liquid-phase speciation of 5M DEEA-2M MAPA-CO₂-H₂O system. a) lower phase, b) upper phase. Symbols: ○, MAPA+MAPAH⁺; ●, DEEA+DEEAH⁺; ◀, MAPACO₂⁻ (p) + H⁺MAPACO₂⁻ (p); ▶, MAPACO₂⁻ (s) + H⁺MAPACO₂⁻ (s); +, MAPA(CO₂)₂; ■, HCO₃⁻/CO₃²⁻.

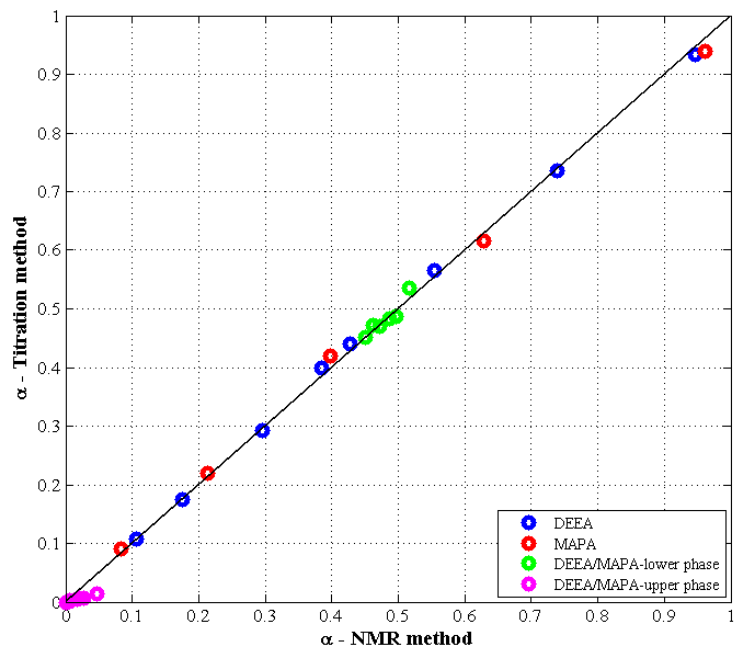


Figure 9. CO₂ loading obtained by NMR and titration method for all the systems studied in the present work at 25°C.