NMR Speciation of Aqueous MAPA, Tertiary Amines and their Blends in Presence of CO_2: Influence of pKa and Reaction Mechanisms

Cristina Perinu,[1*] Ida M. Bernhardsen,[2] Diego D. D. Pinto,[2] Hanna K. Knuutila,[2] Klaus-J. Jens[1*]

[1]Department of Process, Energy and Environmental Technology, University College of Southeast Norway, Postbox 235, NO-3603 Kongsberg, Norway
[2]Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

*corresponding authors: cristina.perinu@usn.no; Klaus.J.Jens@usn.no

Abstract

The diamine 3-(Methylamino)propylamine (MAPA) and eight tertiary amines were studied as single and blended aqueous CO_2 absorbents at different concentrations and ratios to investigate the reaction mechanisms. After absorption (40 °C) and desorption (80 °C) experiments, quantitative ^{13}C NMR experiments were performed on each liquid sample.

After absorption, the following CO_2-derived species were identified and quantified: (bi)carbonate in each amine system; primary and secondary MAPA carbamate, and MAPA dicarbamate in MAPA-systems; tertiary amine carbonate in tertiary amine-systems. Concerning desorption, the main CO_2-species removed was (bi)carbonate, followed in the blends by MAPA dicarbamate.

Since, after CO_2 absorption, the concentration of MAPA dicarbamate was negligible in single MAPA and, in the blends, mainly increased at increasing pKa of the tertiary amines, it is concluded that the tertiary amines increase the availability of MAPA species to react further with CO_2. MAPA and tertiary amines appear to influence each other also for the CO_2 release.

1. Introduction

1.1 Background

There is strong evidence that the global warming observed over the past 50 years is attributable to human activities[1] and, to prevent further dangerous anthropogenic interference, the stabilization of greenhouse gas concentrations in the atmosphere is the main objective to be achieved. Carbon dioxide (CO_2) is the greenhouse gas making the largest contribution from human activities and, to reduce its concentration in the atmosphere, processes utilizing aqueous amine solvents for chemical absorption of CO_2 are considered to be a robust separation technology.[2] The amine scrubbing processes absorb CO_2 from flue gases and release it upon heating in a stripper.[3] A wide variety of alkanolamines exist and some of them have been used industrially for a number of years.[4, 5]

Chemical absorption involves different reversible reactions between CO_2 and aqueous amine solutions. Primary (e.g. ethanolamine, MEA) and secondary (e.g. diethanolamine, DEA) amines react mainly with CO_2 to form carbamate (Reaction 1).[6] Tertiary amines (e.g. methyl diethanolamine, MDEA) are instead not able to form carbamate and usually work as bases accepting a proton to produce (bi)carbonate species (HCO_3^-/CO_3^{2-}) (Reaction 2).[7]

$$2\,R_1NH_2 + CO_2 \leftrightarrows R_1NHCOO^- + R_1NH_3^+ \qquad (1)$$

$$R_3N + CO_2 + H_2O \leftrightarrows HCO_3^- + R_3NH^+ \qquad (2)$$

Compared to tertiary amines, primary and secondary amines typically show higher reaction rates, but the absorption capacity (mol_{CO2}/mol_{amine}), limited to approximately 0.5 $mol_{CO2}/mole_{amine}$ (Reaction 1), is lower than the theoretical maximum loading of 1.0 $mol_{CO2}/mole_{amine}$ (Reaction 2).[8] Moreover, the reaction leading to carbamate formation (Reaction 1) is more exothermic than the reaction for (bi)carbonate formation (reaction 2) and, in terms of energy input required for solvent regeneration, it leads to more energy demanding desorption performances.[9] Concerning secondary amines, they form carbamate less stable than primary amines as the nitrogen site for the nucleophilic attack is more hindered. Then, the carbamate hydrolysis is favored and more (bi)carbonate is produced, leading to the stoichiometry observed in reaction (2). [10, 11]

In order to achieve high CO_2 removal efficiency, mixed amines represent an attractive option as the best characteristics of two or more individual amines can be combined and maximized.

Hence, the higher reaction rate offered by primary/secondary amines is usually combined with the higher absorption capacity and the lower heat of regeneration offered by tertiary amines.

One example of a promising absorbent blend for CO_2 capture is the mixed aqueous amine system composed of 3-(Methylamino)propylamine (MAPA), a diamine with a primary and a secondary amino functional groups, and 2-(Diethylamino)ethanol (DEEA), a tertiary amine. This blend has been drawing great attention as it shows high cyclic capacity, high CO_2 pressure during stripping, high equilibrium temperature sensitivity and relatively high reaction rate.[12-15]

NMR spectroscopy is a powerful and non-invasive analytical technique, widely used in chemical laboratories, which allows direct measurements on specific nuclei of the species in solution. The information on the chemical structure, including side-products and/or unknown molecules, and dynamics of compounds can be gathered and, in proper performed NMR experiments, quantitative analyses are possible.

In the field of chemical absorption of CO_2 by aqueous amine solvents, NMR spectroscopy is mainly applied to identify and quantify the species formed in presence of CO_2.[16] By monitoring speciation in CO_2 absorption/desorption processes, information on amine structure relationships, reaction mechanisms, influences of reaction conditions and/or amine capacities can be achieved. Furthermore, the results can be used in rigorous thermodynamic modelling required for process simulations and better understand of the absorption kinetics of blended systems.[16-22] ^{13}C NMR is considered a good option to investigate CO_2 amine absorbents, even though the low abundance of the ^{13}C isotope and the slow relaxation time of the nuclear spin lead to long measuring times, especially for quantitative analyses. ^{13}C NMR gives information about all the components in an amine-CO_2-H_2O system, with the exception of H_2O and its ions. Moreover, due to the broad spectral range and, usually, an absence of interference between peaks, ^{13}C NMR also allows analyses of complex systems, such as amine blends.[16, 23]

In presence of a diamine having both the nitrogen atoms able to bound CO_2, more than one type of amine carbamate can be formed, leading to NMR spectra with several signals.[24, 25] In the context of blended amine solvents for CO_2 capture, Piperazine (PZ) and MAPA are two types of diamine investigated in mixture with tertiary amines by NMR spectroscopy. To the best of our knowledge, several studies are dealing with species distribution, mainly for inputs to thermodynamic models, of PZ in blend with MDEA and/or other tertiary amines, [16, 17, 26] whereas a few publications deal with NMR analyses of blended MAPA.[21, 27] Hartono et al. in 2011[27] reported a qualitative ^{13}C NMR investigation to observe the effect of neutralization of Sarcosine with an organic base, i.e. MAPA. In 2013, Ciftja et al[21] reported speciation data by

^{13}C NMR of the two liquid phases formed by aqueous MAPA 2M-DEEA5M in presence of CO_2.

1.2 Aim and description of the work

Investigations, at molecular level, of the properties that make aqueous blended amine systems promising CO_2 absorbents are necessary to develop even better systems. In particular, the aim of the present work is to understand the reaction mechanisms behind the process of chemical absorption of CO_2 by aqueous MAPA in blend with tertiary amines.

Aqueous solutions of single MAPA, single tertiary amines and their blends, at different concentrations and ratios, were exposed to CO_2 absorption (40°C) and desorption (80°C) in a screening apparatus. After experiments, each liquid sample was analyzed at equilibrium by means of quantitative ^{13}C NMR spectroscopy. The speciation analyses are discussed and highlights of the factors influencing the chemical absorption performances, including hypothesis on the reaction mechanisms, are given.

In literature, several investigations on tertiary amines are reported, in terms of CO_2 equilibrium solubility, reaction rates, absorption heat and structure-activity relationship.[28-35] Some tertiary amines, like e.g. 1-Dimethylamino-2-propanol (1DMA2P), 3-Dimethylamino-1-propanol (3DMA1P), 3-Diethylamino-1-propanol (3DEA1P), 4-Diethylamino-2-butanol (DEAB), 2-(Diethylamino)ethanol (DEEA), are considered promising absorbents, mainly because showing better CO_2 absorption properties than MDEA.[28, 31, 33]

In this study, we selected DEEA as the tertiary amine-base case because of the good CO_2 absorption performances both as single and in blend with MAPA. In Chowdhury et al.,[28] among 24 tertiary amines, DEEA was included in the list of the seven best absorbents, in terms of absorption rate, cyclic capacity and heat of absorption. DEEA belongs to the class of amines having the nitrogen atom (N-) distant 2-3 carbons from the hydroxyl function (OH-) and bounded to ethyl groups, which were found to be key structural features to have good CO_2 capture perfomances. [29, 30]

Structural features (like e.g. inductive, steric, electrostatic, mesomeric effects and others) can influence the electron density on the nitrogen atom and, consequently, the basicity. The pKa is a fundamental property, which affects kinetics, capacity of a solvent and reaction mechanisms.[28, 29, 35-37]

The structure and pKa values[38] of MAPA, DEEA and the other tertiary amines investigated in this study are summarized in Figure 1.

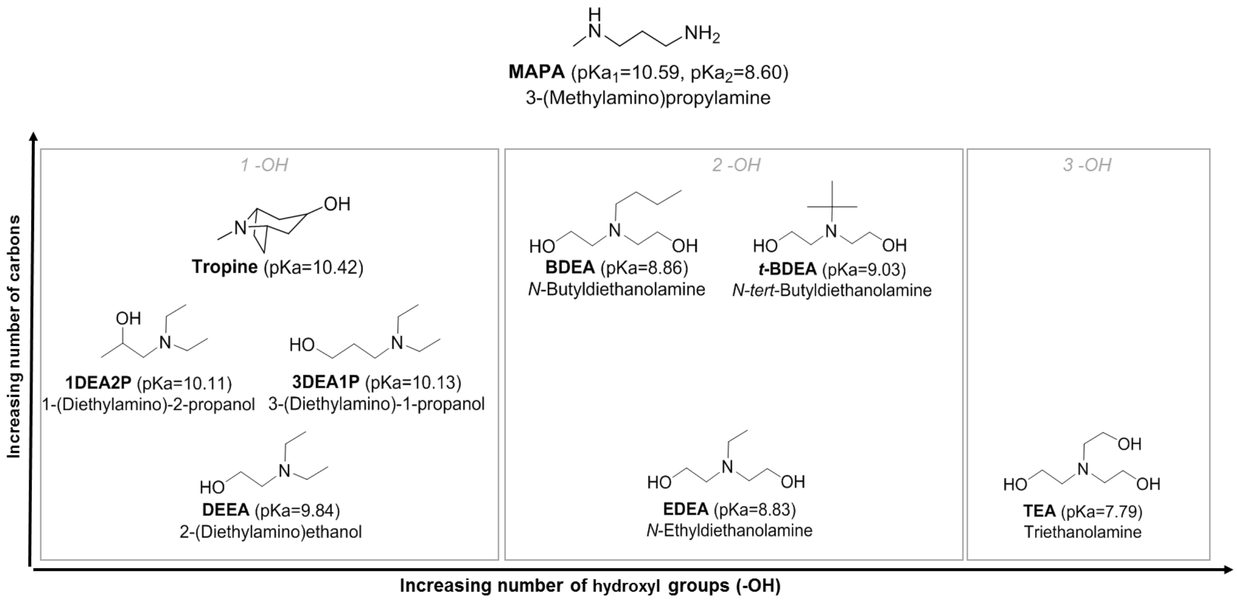


Figure 1. Chemical structure and pKa at 25°C of MAPA and the tertiary amines investigated in this study.

The selected tertiary amines differ from DEEA in the number of –OH groups and/or in the length and structure of their respective carbon chain. In the series, there are two couples of isomers: 1DEA2P/3DEA1P with the –OH differently positioned on the three carbon-chains, and BDEA/*t*-BDEA with the four carbons of the alkyl chain differently structured.

The increasing number of -OH groups in the structure of the tertiary amines results in a pKa value decrease, as the electron withdrawing inductive effect through bonds on the –N atom increases. On the other hand, at increasing number of carbons on the alkyl chain and/or between the -N atom and the –OH group, a pKa value increase is observed. Tropine, a cyclic amine, is indeed the molecule with the highest pKa value as it has a total number of seven carbons between the –N atom and the –OH group. In *t*-BDEA, the $–C(CH_3)_3$ group exerts an electron donating inductive effect slightly higher than the linear $-(CH_2)_3CH_3$ chain in BDEA. The latter has a pKa value similar to EDEA, although it has two carbons more on the alkyl chain.

Concerning the pKa_1 and pKa_2 of MAPA, the secondary amino functional group is expected to be more basic than the primary amino functional group, but the opposite may be true because specific effects (like e.g. intramolecular hydrogen bonds or others) should also be taken into account.[39] In this study, these effects were not measured and, therefore, the pKa attribution was not performed.

Under certain conditions when loaded with CO_2, the MAPA-DEEA-CO_2-H_2O system forms two liquid phases, one rich and one lean in CO_2.[21] In this work, not all of the amines under study have the ability to form two phases and, in order to have a fair comparison of them, chemical conditions giving a single phase in all cases were used. Concentrations and ratios used in this work are reported in Table 1. Tropine and 1DEA2P were studied at concentrations not higher than 1.5M, as this was found to be their solubility limit; and 3DEA1P and DEEA were studied at the same conditions for comparison purposes. The amine solutions containing 1DEA2P after desorption were not investigated in this study as formation of two phases was observed.

Table 1. Concentrations and ratios of the amines investigated in this study.

		Concentration (M=mol/L)		
	Tertiary amine	**Single tertiary amine**	**Single MAPA**	**Blend (tertiary amine + MAPA)**
High concentration	**3DEA1P,** **DEEA,*** ***t*-BDEA,*** **BDEA,*** **EDEA,*** **TEA***	3 M	1 M	3M + 1M (ratio 3:1)*
				2M + 2M (ratio 1:1)
Low concentration	**Tropine,** **3DEA1P,** **1DEA2P,** **DEEA**	1.5M	0.5M	1.5M + 0.5M (ratio 3:1)
				1M + 1M (ratio 1:1)

* Preliminary data on the absorption process (40 °C) are presented in a conference proceeding. [40]

2. Experimental Section

The chemicals used in this study are listed in Table 2. They were utilized without any further purification.

Table 2. Details on the chemicals used to carry out this study.

Chemical name	CAS-number	Purity	Supplier
3-(Methylamino)propylamine (MAPA)	6291-84-5	≥97%	Sigma Aldrich
2-(Diethylamino)ethanol (DEEA)	100-37-8	≥99.5%	Sigma Aldrich
N-Ethyldiethanolamine (EDEA)	139-87-7	98%	Sigma Aldrich
Triethanolamine (TEA)	102-71-6	≥99%	Sigma Aldrich
N-Butyldiethanolamine (BDEA)	102-79-4	≥98.6%	Sigma Aldrich
Tropine	120-29-6	≥97%	Sigma Aldrich
Acetonitrile	75-05-8	anhydrous 99.8%	Sigma Aldrich
Deuterium oxide (Deuterated water, D_2O)	7789-20-0	99.98 atom %±0.01 atom % D	Sigma Aldrich
N-tert-Butyldiethanolamine (*t*-BDEA)	2160-93-2	≥97%	TCI Europe
3-Diethylamino-1-propanol (3DEA1P)	622-93-5	>95%	TCI Europe
1-Diethylamino-2-propanol (1DEA2P)	4402-32-8	≥98%	TCI Europe
Nitrogen (N_2)	7727-37-9	99.9%	AGA
Carbon Dioxide (CO_2)	124-38-9	99.9%	AGA

The aqueous amine solutions were prepared in a volumetric flask: the required amounts of amines were weighed in a Mettler Toledo balance (model MS6002S, d=0.01g), and distilled water was added up to predetermined volume and weighed. Densities of unloaded solutions were measured at 25 ºC using an Anton Paar DMA 4500 M densitometer. The nominal repeatability, as given by the manufacturer, was 0.01 kg/m^3 and 0.01 ºC. A detailed description of the experimental procedure is given in Pinto et al.[41] For each solution, the density measurement was repeated two times and the averaged value is given in the Table S1 of the Supporting Information.

The density of the loaded solutions was not measured in the same apparatus, due to the limited amount of each sample. Instead, 1mL of sample (as measured by Hamilton syringes, model 1001 TLL) was weighted on a Mettler Toledo analytical balance (model ME204, d=0.0001g) at room temperature. The uncertainty of this procedure was determined to be <0.6%. Tables S2 and S3 in the Supporting Information report the g/mL of each CO_2 rich and lean solution, respectively.

The pKa values reported in Bernhardsen et al.[38] were used in this study. Bernhardsen et al. measured the pKa by potentiometric titration at 25°C using a 0.1 mol/L aqueous solution of hydrochloric acid (HCl) to titrate the amine solutions at concentration 0.01 mol/kg H_2O. For each amine, the measurement was performed two times and the average reported as the pKa value.

Bernhardsen et al.[38] conducted absorption tests using a screening apparatus designed to operate at atmospheric conditions and up to 80°C, giving a fast and first-hand knowledge of the performance of each absorbent. Samples for NMR analyses were withdrawn after the absorption process, performed at 40 °C with an inlet gas containing 10kPa partial pressure of CO_2. The absorption screening experiments were terminated when the effluent reached 9.5kPa partial pressure of CO_2. Similarly, a liquid sample for NMR analyses was withdrawn after each screening desorption experiment, conducted at 80 °C and terminated when the effluent reached 1.0 kPa partial pressure of CO_2.

Further details on preparation of solutions, pKa measurements and screening apparatus can be found in Bernhardsen et al.,[38] which also includes the overall absorption and desorption performances, like e.g. absorption capacity, estimation of absorption rates and screening cyclic capacity.

As mentioned above, after each experiment, the liquid samples were analyzed by NMR spectroscopy. Quantitative ^{13}C NMR experiments were performed at 26.85 °C on a Bruker 600 MHz Avance III HD equipped with a 5-mm cryogenic CP-TCI z-gradient probe. To obtain a reliable peak area, the ^{13}C NMR spectra were acquired with the inverse gated decoupling acquisition sequence, using a recycle delay time of 120 s and a pulse width of 11.4 µs (90° pulse angle). The method is described in detail in Perinu, et al. [42] In the current study, the use of a 600 MHz instrument allowed to reduce the number of scans from 512 to 256. Deuterated water was used as “lock” solvent and was inside a coaxial insert, whereas Acetonitrile was chosen as internal reference standard. Acetonitrile (10 µL, as measured by an Hamilton syringe, model 802) was added to 1 mL of sample (as measured by Hamilton syringes, model 1001 TLL) and weighted using a Mettler Toledo analytical balance (model ME204, d=0.0001g). An amount of this solution was inserted in the NMR tube.

The assignment of each signal to the corresponding carbon was performed by means of qualitative 1D, i.e. ^1H and ^{13}C, and 2D NMR experiments, i.e. COSY ($^1J_{H-H}$, Correlation Spectroscopy), HSQC ($^1J_{C-H}$, Heteronuclear Single Quantum Correlation) and HMBC ($^{2-3}J_{C-H}$, Heteronuclear Multi Bond Correlation), on both pure single amines and on CO_2 rich and lean solutions. They were performed on both 600 MHz (above described) and 400 MHz (Bruker 400 MHz Avance III HD equipped with a 5-mm SmartProbe z-gradient probe) NMR apparatuses.

After acquisition of both qualitative and quantitative NMR data, the spectra were processed using MestreNova software v 7.1.1. [42]

3. Results and discussion

3.1 NMR analysis

After absorption of CO_2, the following species were identified:

a) (Bi)carbonate (HCO_3^-/CO_3^{2-}) was formed in all the systems under study;

b) MAPA/MAPA$(H^+)_2$, primary MAPA carbamate (MAPACOO$^-_{(p)}$/MAPAH$^+$COO$^-_{(p)}$), secondary MAPA carbamate (MAPACOO$^-_{(s)}$/MAPAH$^+$COO$^-_{(s)}$), MAPA dicarbamate (MAPA$(COO^-)_2$) were found in both single and blended MAPA solvents;

c) In both single and blended tertiary amines samples, two types of tertiary amines were identified: the tertiary amine (3°Amine/3°AmineH$^+$), as added before loading, and tertiary amine carbonate (3°AmineOCOO$^-$). The latter is formed in basic conditions by the reaction of the hydroxyl group of the tertiary amine with CO_2 .[43-45] In all the systems containing the tertiary amines, it was found to be present in low amount, ranging from 0.01 to 0.13 M. In the solvents containing 1DEA2P, only traces (lower than 0.01 M) were observed.

   Due to overlapping peaks, for some tertiary amines containing 2 and 3 –OH groups (i.e. EDEA in EDEA 2M/MAPA 2M, and BDEA and TEA in all amine systems), it was not possible to establish if mono-, bi- and/or tricarbonate species were formed. In line with the other tertiary amines under investigation, we consider all of them as monoalkylcarbonate species in this study.

The same species listed above were also found after the screening desorption process at 80°C but in different amounts. In particular, the signal corresponding to the (bi)carbonate species was not identified in most of the ^{13}C NMR spectra of the blends. In some cases, the signal assignment was uncertain as the peaks were broadened with the baseline and/or some other similar peaks were also present in the same region (probably, attributable to side-products). It may also be possible that in some cases the corresponding carbon was resonating at the same chemical shift of the carboxylate ion-carbons of the MAPA carbamate species. In any case, if present, the potential amount of (bi)carbonate in these cases is considered to be negligible.

In Figure 2, by way of example, the ^{13}C NMR spectrum of DEEA 3M/MAPA1M-CO_2-H_2O system at equilibrium after the absorption process is reported, together with the structure of the species found in solutions and the signal assignment.

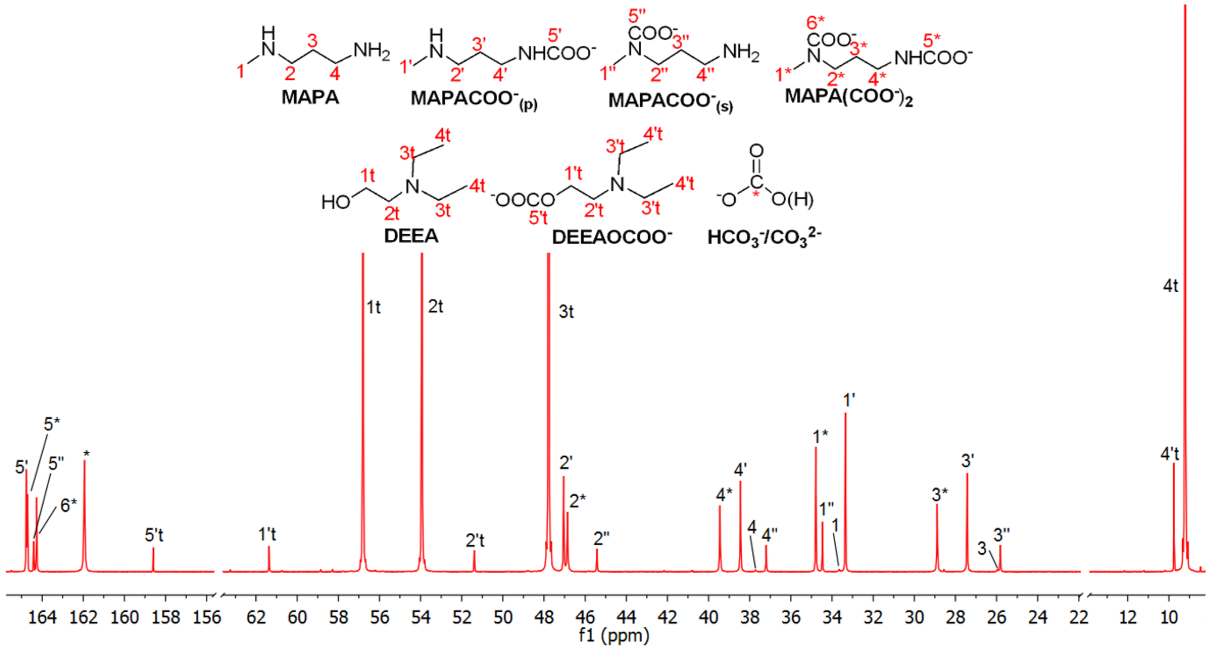


Figure 2. Quantitative ^{13}C NMR spectrum of aqueous DEEA 3M/MAPA1M after absorption at 40 °C. In addition to HCO_3^-/CO_3^{2-}, also the other species are in equilibrium with the corresponding protonated form.

In all of the ^{13} C NMR spectra of the amine systems under study, two main signal exhibiting regions were identified: A high frequency region (circa 158-167 ppm) with signals belonging to deshielded carbon nuclei (carbons of the carboxylate anion, i.e. $–COO^-$, of MAPA carbamates, 3°Amine$OCOO^-$ and HCO_3^-/CO_3^{2-}); and a low frequency region (circa 9-66 ppm) with signals belonging to shielded sp^3 carbons nuclei (-C, -CH, $-CH_2$, $-CH_3$ of MAPA, tertiary amines and their derivatives). The chemical shift values of all the species, including structures and numbering, in each amine solution after both screening absorption and desorption experiments are reported in the Supporting Information (Table S4-S17).

Typical chemical shift values of the carbons in MAPA and its CO_2-derived species are around 33-35 ppm for C-1, 45-48 ppm for C-2, 25-30 ppm for C-3, 37-39 ppm for C-4 and 164-165 ppm for carbons of the $-COO^-$ ion of MAPA carbamates. The signal resonating at about 158-159 ppm is belonging to the C of the $-COO^-$ ion in tertiary amine carbonate.

The fast exchanging proton species (neutral/protonated amines and HCO_3^-/CO_3^{2-}) appear with a common peak in the ^{13}C NMR spectra and the chemical shifts of their carbons depend on the ratio between protonated and neutral form of the species.[16] Various methods could be utilized to distinguish between them but, in this work, they were not applied and the sum of their concentrations is reported.

Usually, the carbons belonging to HCO_3^-/CO_3^{2-} can span from about 161.1 ppm (100% HCO_3^-) to about 168.7 (100% CO_3^{2-}).[42] In this study, in the solutions after absorption, the carbon signal corresponding to HCO_3^-/CO_3^{2-} resonated at a chemical shift value ranging from 160.9 to 162.6 ppm, suggesting that mainly bicarbonate was formed. In the solutions at equilibrium after heating at 80°C, the carbon signal corresponding to HCO_3^-/CO_3^{2-}, if present, was ranging from 161.0 to 166.9 ppm, meaning that in some cases the ratio HCO_3^-/CO_3^{2-} was shifted toward the CO_3^{2-} species.

The same is true for the carbons belonging to tertiary amines, MAPA and its CO_2-derived species. In the current study, from the rich to the lean CO_2 amine solutions, the change in the protonated/neutral form of the species, and consecutively in the chemical shift values of the corresponding carbons, is more evident. The carbons in beta position to the site of protonation (two covalent bonds distant from the –N site) in MAPA, $MAPACOO^-_{(p)}$ and $MAPACOO^-_{(s)}$ (C-3) and in the tertiary amines were shifted most. Within the tertiary amines, the ternary carbon in Tropine and the quaternary carbon in *t*-BDEA, which are both in alpha position to –N, represented an exception. They were influenced by the N-protonation more than the other carbons. On the other hand, the chemical shifts of the carbon signals of MAPA dicarbamate were more constant as all the protonation sites were involved in the covalent bond with CO_2.

To estimate the accuracy of the quantitative analysis, a mass balance check was performed. The error in the concentrations obtained by NMR was estimated by taking into account the concentration of each amine, as measured in the sample preparation. In the solutions after absorption, the average percentage (%) error in the calculated concentrations was estimated to be 3.2% for the tertiary amines and 2.7% for MAPA. Similarly, after desorption, the average % error was found to be 3.7 % for tertiary amine and 3.5% for MAPA.

3.2. Speciation after absorption at 40ºC

3.2.1. Speciation trends

MAPA is composed of a primary and a secondary amino functional groups which, as soon as CO_2 is loaded, transform into carbamate derivatives. In Figure 3, the amounts of MAPA derivative species in each single and blended MAPA-CO_2-H_2O systems are reported.

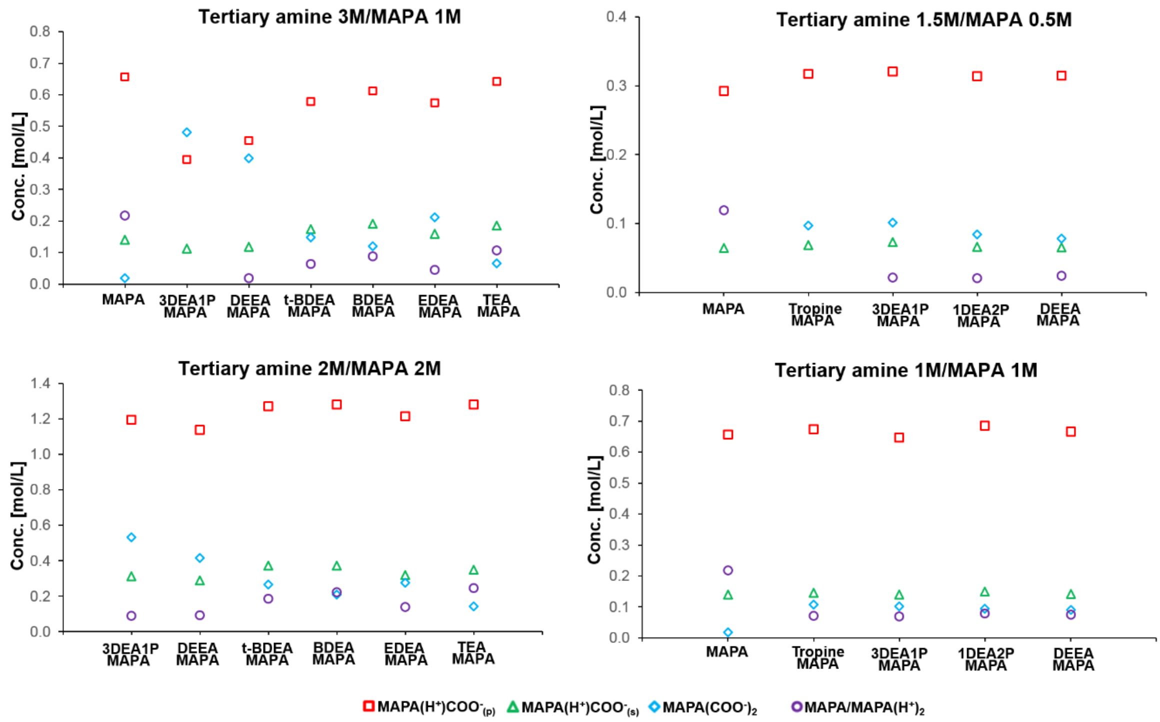


Figure 3. Concentrations at equilibrium of MAPA derivative species in single and blended MAPA after absorption at 40 °C. $MAPA(H^+)COO^-_{(p)}$ and $MAPA(H^+)COO^-_{(s)}$ represent $MAPACOO^-_{(p)}$ and $MAPACOO^-_{(s)}$, respectively, in equilibrium with their protonated form.

In all the amine systems, as expected, primary MAPA carbamate species ($MAPA(H^+)COO^-_{(p)}$) is present in concentrations higher than secondary MAPA carbamate ($MAPA(H^+)COO^-_{(s)}$). Both species, however, increase at increasing concentrations of MAPA and/or when going from 3:1 to 1:1 ratio (tertiary amine:MAPA). Specifically, $MAPA(H^+)COO^-_{(p)}$ is formed in the range of 0.642-0.394 M in tertiary amine 3M/MAPA 1M, whereas it is in the range of 1.28-1.14 M in tertiary amine 2M/MAPA 2M. Similarly, in tertiary amine 1.5M/MAPA 0.5M and in tertiary amine 1M/MAPA 1M it is in the range of 0.321-0.314 M and 0.685-0.647 M, respectively. The same is true for $MAPA(H^+)COO^-_{(s)}$ where in tertiary amine 3M/MAPA 1M it is 0.190-0.112 M and in tertiary amine 2M/MAPA 2M it is 0.373-0.288 M and/or in tertiary amine1.5M/MAPA 0.5M and in tertiary amine 1M/MAPA 1M it is in the range of 0.073-0.066 M and 0.149-0.140 M, respectively. On the contrary, the increase of $MAPA(COO^-)_2$ at increasing MAPA concentrations appears to be less evident. Indeed, in tertiary amine 3M/MAPA 1M the range is about 0.482-0.066 M and in tertiary amine 2M/MAPA 2M around 0.531-0.141 M. In tertiary amine 1.5M/MAPA 0.5M and in tertiary amine 1M/MAPA 1M, it is in the range of 0.101-0.078 M and 0.107-0.090M, respectively. Details on the concentration of the species can be found in the Supporting Information (Table S18-S31).

The trend within the MAPA derivative species in the different amine systems changes as a function of the chemical composition of the sample. In single MAPA, the trend in concentration of MAPA species ($MAPA(H^+)COO^-_{(p)}$ > $MAPA/MAPA(H^+)_2$ > $MAPA(H^+)COO^-_{(s)}$ > $MAPA(COO^-)_2$) is different from that observed in blend with tertiary amines. In particular, in most of the blends, $MAPA(COO^-)_2$ is in amounts higher than $MAPA/MAPA(H^+)_2$. Moreover, at the same starting concentration of MAPA, the amount of $MAPA(COO^-)_2$ increases and the amount of $MAPA/MAPA(H^+)_2$ decreases in presence and at increasing concentration of tertiary amine, i.e. DEEA and 3DEA1P shown in Figure 4.

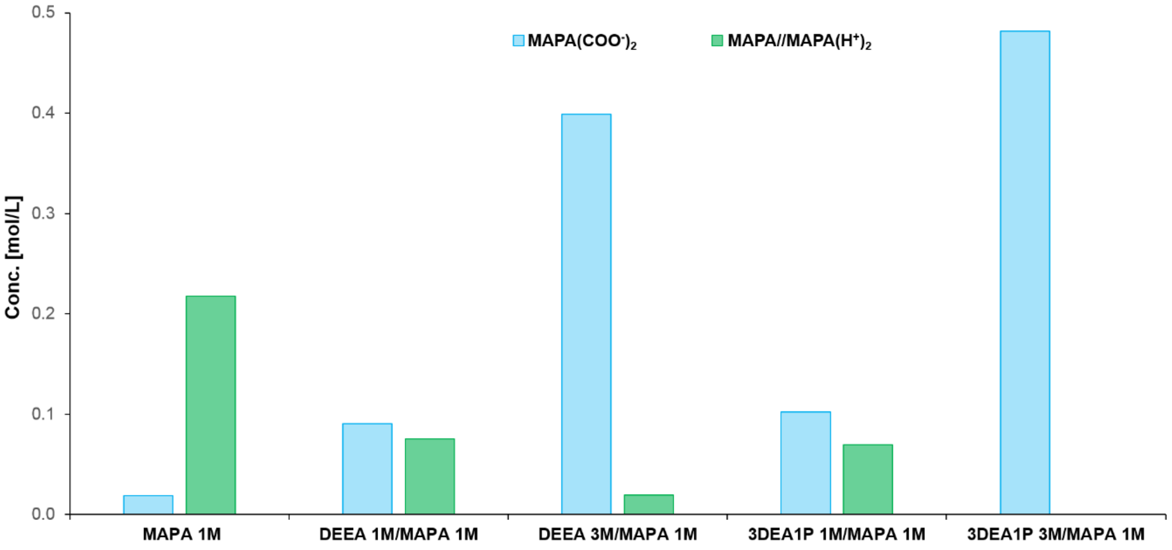


Figure 4. Trend of $MAPA(COO^-)_2$ and $MAPA/MAPA(H^+)_2$ in MAPA 1M and in MAPA 1M blended with DEEA 1M and DEEA 3M, and with 3DEA1P 1M and 3DEA1P 3M.

To understand details of the reaction mechanisms, the concentrations of all the species at equilibrium after the absorption process in both single and blended aqueous tertiary amines are reported as a function of the pKa of the tertiary amines (Figure 5). For comparison, speciation of single aqueous MAPA are also reported and are given as a function of the pKa_1 of MAPA.

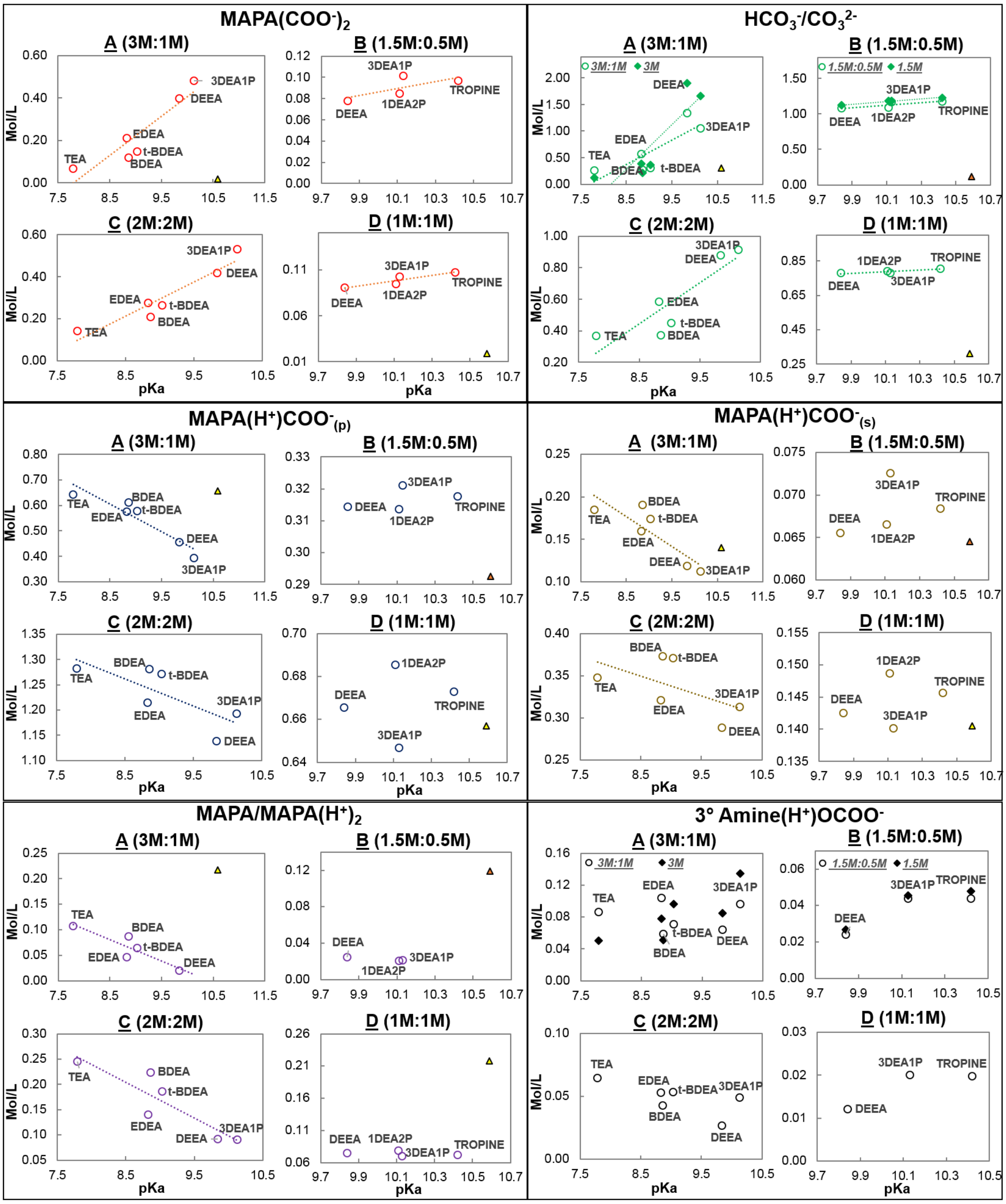


Figure 5. Concentrations of each species, after absorption at 40°C, in A) Tertiary amine3M:MAPA1M (circle) and MAPA 1M (triangle, yellow fill), in B) Tertiary amine 1.5M:MAPA0.5M (circle) and MAPA 0.5M (triangle, orange fill), in C) Tertiary amine2M:MAPA2M (circle) and in D) Tertiary amine1M:MAPA1M (circle) and MAPA 1M (triangle, yellow fill), are reported as function of pKa of tertiary amines for blended amine solvents and pKa$_1$ of MAPA for single MAPA solvents. For HCO_3^- /CO_3^{2-} and 3°Amine(H^+)$OCOO^-$, A) and B) also include the concentrations found in single tertiary amines (3M in A and 1.5M in B, filled diamond).

For each species presented in Figure 5, four graphs are reported (A-D): A and B report the concentrations measured in the blended tertiary amine/MAPA at 3:1 ratio, whereas C and D represent those in the blended systems at 1:1 ratio. Specifically, the concentrations of each species measured in the high-concentration blended solvents (see Table 1) are plotted in A and in C, whereas those measured in the low-concentration systems (see Table 1) are in B and in D. The amount of each species found in single MAPA is reported in A and D for MAPA 1M and in B for MAPA 0.5M, whereas the amount of the species found in single tertiary amines are reported in A and in B of the graph representing HCO_3^-/CO_3^{2-} and 3°Amine(H^+)$OCOO^-$ concentrations.

Among the main species found in all the blends both at 1:1 and at 3:1 ratio (tertiary amine: MAPA), a general tendency can be observed. At increasing pKa of the tertiary amines, the amount of MAPA(H^+)$COO^-_{(p)}$, MAPA(H^+)$COO^-_{(s)}$ and MAPA/MAPA$(H^+)_2$ decreases, whereas the amount of MAPA$(COO^-)_2$ and HCO_3^-/CO_3^{2-} increases. However, above all within the molecules with the same number of –OH groups, some exceptions are observed for both high- and low-concentration systems.

In particular, with respect to MAPA/EDEA, the amine systems containing BDEA and *t*-BDEA appear not to follow this trend exactly (EDEA, BDEA and *t*-BDEA have the same number of –OH and similar pKa values, with *t*-BDEA being slightly more basic). In MAPA/BDEA and MAPA/*t*-BDEA, the amount of MAPA(H^+)$COO^-_{(p)}$, MAPA(H^+)$COO^-_{(s)}$ and MAPA/MAPA$(H^+)_2$ is higher than the amount found in MAPA/EDEA, whereas the amount of MAPA$(COO^-)_2$ is lower. Similarly, the amount of HCO_3^-/CO_3^{2-} is lower than for EDEA, in both blended and single amine systems.

In the high-concentration amine systems, the trends of the species obtained in presence of 3DEA1P are in line with the trend above defined. However, in the tertiary amine2M:MAPA 2M blend, MAPA(H^+)$COO^-_{(p)/(s)}$ species are in concentrations higher than those found in DEEA (same number of -OH, but lower pKa). On the other hand, at 3M concentration, as single and in blend with 1M MAPA (at 3:1 ratio), HCO_3^-/CO_3^{2-} is formed in lower amount.

Moreover, in the amine systems at low concentration (all of them containing tertiary amines with 1 -OH on the amine structure but different pKa values), a clear trend for MAPA(H^+)$COO^-_{(p)}$, MAPA(H^+)$COO^-_{(s)}$ and MAPA/MAPA$(H^+)_2$ can't exactly be defined. The trend is a bit clearer for MAPA$(COO^-)_2$ and (bi)carbonate species where, for MAPA$(COO^-)_2$, the difference between 3DEA1P and 1DEA2P (isomers with similar pKa) appears to be less going from the 3:1 to 1:1 ratio (tertiary amine: MAPA).

A common trend can't be defined for 3°Amine(H^+)$OCOO^-$ but, due to the low amounts found in all solutions, this species is considered not to be of relevance in the current study.

The CO_2 absorption capacity of these amine systems, as reported by Bernhardsen et al.,[38] showed the same general trend observed for the (bi)carbonate and MAPA(COO^-)$_2$ species. It increased at increasing pKa and/or decreasing number of –OH of the tertiary amines in both single and blended tertiary amine systems and was approximately similar within the molecules with the same number of -OH. Xiao et al.[30] similarly reported that the activity of the single tertiary amines increased by decreasing the number of –OH groups in the structure.

3.2.2 Hypothesis on the reaction mechanisms

The increase of MAPA(COO^-)$_2$ at increasing concentration (when keeping constant MAPA concentration, Figure 4) and at increasing pKa of the tertiary amines (Figure 5), and the absence and/or lower amount for single MAPA (Figures 3 and 5), give the bases to theorize that, in addition to charge balancing the formation of HCO_3^-/CO_3^{2-} anions, the tertiary amines may also affect MAPA carbamate formation. The tertiary amines may indeed allow the amino functional groups of MAPA species to be available for further reaction with CO_2, which leads to the formation of more MAPA(COO^-)$_2$. Specifically, protonated MAPA, protonated MAPA$COO^-_{(p)}$ and/or MAPA$COO^-_{(s)}$ may release a proton to the tertiary amines, which, if more basic than MAPA species, lead the protonation process. The activity as Brønsted base of the tertiary amines is supposed to increase at increasing pKa and this may be the reason why, at increasing pKa of the tertiary amines, more MAPA(COO^-)$_2$ is found at the equilibrium (similarly to the (bi)carbonate species). Moreover, complementary to the activity as proton acceptor, the tertiary amines in the protonated form may also act as positive counter-ion of the MAPA carbamates and bicarbonate species.

This hypothesis may also explain the reason why, after absorption, the amount of MAPA/MAPA(H^+)$_2$ at the equilibrium in blend is lower than in the corresponding single MAPA solvent.

The tertiary amines can act as described above, if the tertiary amines pKa is larger than pKa$_1$ and/or pKa$_2$ of MAPA. Therefore, the tertiary amines investigated in this study, which exhibit a pKa value larger than MAPA's pKa values, will accept a proton from the amino functional group of MAPA with pKa$_2$=8.6 and/or will hence prevent its protonation. The exception may be represented by TEA, which has a pKa of 7.79. In MAPA-TEA systems, the amount of MAPA dicarbamate is indeed lower than in the other blends and similar to single MAPA solvent. Moreover, the pKa of the amino functional groups not bounded to CO_2 in MAPACOO^-

$_{(p)}$ and MAPACOO$^-_{(s)}$ may be expected to be different from the corresponding MAPA, as the -NHCOO$^-$ group may have a specific effect through the bonds. In this study, we have not measured the intensity of this effect and/or the pKa of MAPA carbamates and, therefore, it was not possible to neither confirm nor quantify a change in pKa.

A similar mechanism was proposed in literature for monoethanolamine (MEA) in blend with 1-Dimethylamino-2-propanol (1DMA2P) and Methyl diethanolamine (MDEA).[19] In that study, MEA carbamate in the blended amine systems was formed in concentrations higher than MEA-CO_2-H_2O, and this behavior was mainly attributed to the release of a proton from MEAH$^+$ to the tertiary amine.

In Figure 6, the amounts of (bi)carbonate formed in the single and blended amine systems are compared to give a further experimental evidence of the role played by the tertiary amine in the presence of MAPA. The sum of (bi)carbonate formed in the single tertiary amines and single MAPA is higher than the (bi)carbonate amount formed in all of the corresponding blends. If the two amines would react independent of each other in the blends, the amount of HCO_3^-/CO_3^{2-} would be expected to be similar to the combined value of the two single amines. The proposed mechanism also justifies the reason why, in the blend, the amount of (bi)carbonate is lower than in the corresponding single tertiary amines (with the exception of BDEA, EDEA and TEA which have pKa equal to and/or lower than 8.86) (Figure 6). In the blends, due to the large Brønsted basicity of the tertiary amines, the increased availability of the amino functional groups of MAPA species favors the direct reactions of MAPA with CO_2 to the detriment of HCO_3^-/CO_3^{2-} formation.

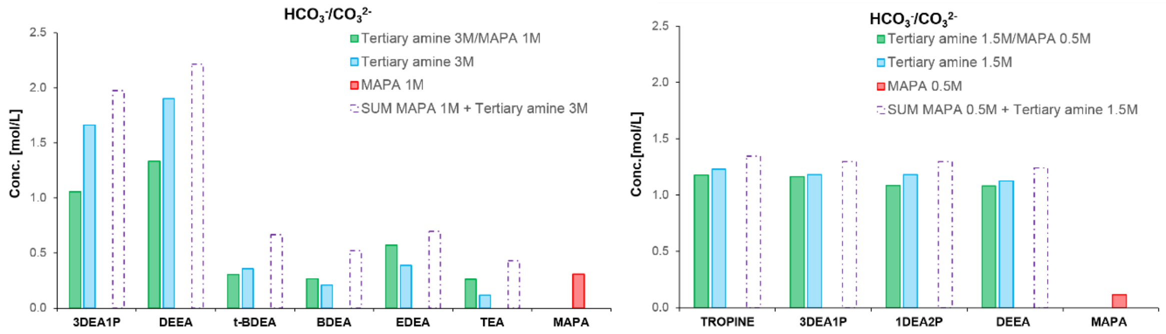
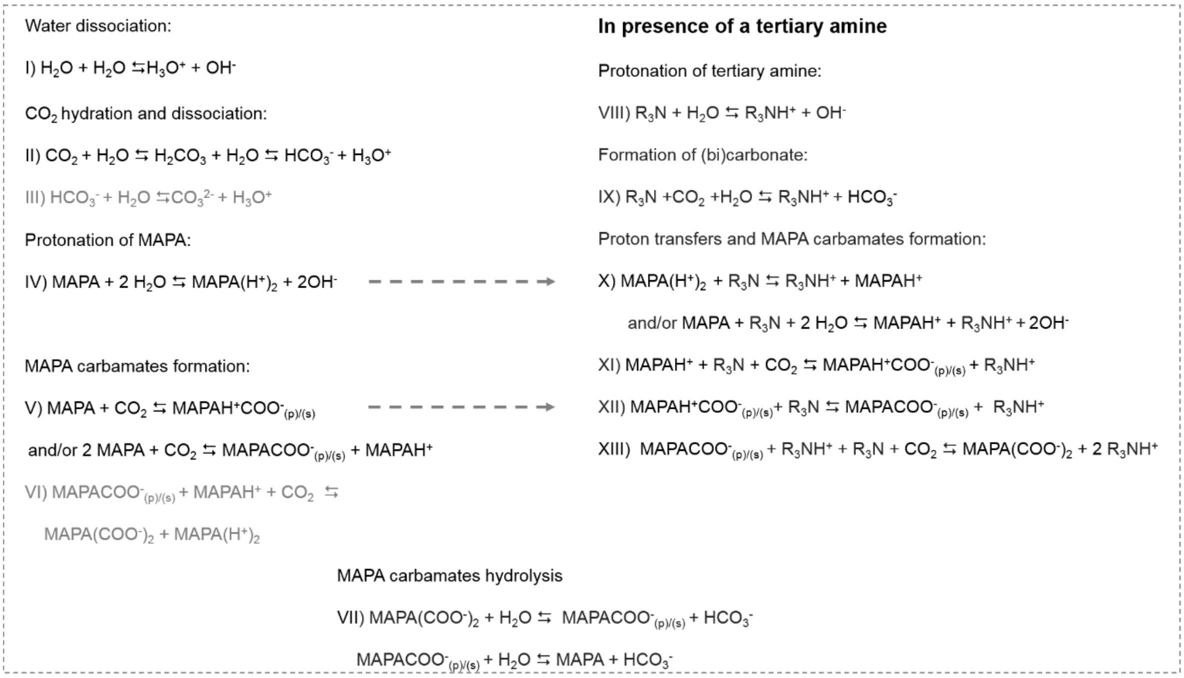


Figure 6. (Bi)carbonate formed in single tertiary amines, single MAPA and their blend at 3:1 ratio.

From the available data so far, the mechanism of (bi)carbonate formation is not clear. However, in the blended MAPA systems containing tertiary amines at pKa equal to and/or lower than 8.86 (BDEA, EDEA and TEA), MAPA may be considered the driving force for the (bi)carbonate formation; and it may do so by means of carbamate hydrolysis and/or by driving the alkalinity of the solutions. The reason is that, in those systems, (bi)carbonate is formed in higher amounts than in the corresponding single tertiary amines.

In the scheme 1, a summary of the main reactions, which may occur in single and blended MAPA and are relevant for the reaction mechanisms, is reported.



Water dissociation:

I) $H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$

CO_2 hydration and dissociation:

II) $CO_2 + H_2O \leftrightarrows H_2CO_3 + H_2O \leftrightarrows HCO_3^- + H_3O^+$

III) $HCO_3^- + H_2O \leftrightarrows CO_3^{2-} + H_3O^+$

Protonation of MAPA:

IV) $MAPA + 2\,H_2O \leftrightarrows MAPA(H^+)_2 + 2OH^-$

MAPA carbamates formation:

V) $MAPA + CO_2 \leftrightarrows MAPAH^+COO^-_{(p)/(s)}$

and/or $2\,MAPA + CO_2 \leftrightarrows MAPACOO^-_{(p)/(s)} + MAPAH^+$

VI) $MAPACOO^-_{(p)/(s)} + MAPAH^+ + CO_2 \leftrightarrows MAPA(COO^-)_2 + MAPA(H^+)_2$

In presence of a tertiary amine

Protonation of tertiary amine:

VIII) $R_3N + H_2O \leftrightarrows R_3NH^+ + OH^-$

Formation of (bi)carbonate:

IX) $R_3N + CO_2 + H_2O \leftrightarrows R_3NH^+ + HCO_3^-$

Proton transfers and MAPA carbamates formation:

X) $MAPA(H^+)_2 + R_3N \leftrightarrows R_3NH^+ + MAPAH^+$

and/or $MAPA + R_3N + 2\,H_2O \leftrightarrows MAPAH^+ + R_3NH^+ + 2OH^-$

XI) $MAPAH^+ + R_3N + CO_2 \leftrightarrows MAPAH^+COO^-_{(p)/(s)} + R_3NH^+$

XII) $MAPAH^+COO^-_{(p)/(s)} + R_3N \leftrightarrows MAPACOO^-_{(p)/(s)} + R_3NH^+$

XIII) $MAPACOO^-_{(p)/(s)} + R_3NH^+ + R_3N + CO_2 \leftrightarrows MAPA(COO^-)_2 + 2\,R_3NH^+$

MAPA carbamates hydrolysis

VII) $MAPA(COO^-)_2 + H_2O \leftrightarrows MAPACOO^-_{(p)/(s)} + HCO_3^-$

$MAPACOO^-_{(p)/(s)} + H_2O \leftrightarrows MAPA + HCO_3^-$

Scheme 1. Main reactions occurring during the absorption of CO_2 at 40°C in single and blended MAPA.

Reaction III (CO_3^{2-} formation) may be considered not relevant for the amine systems investigated in this study because, based on the chemical shift values in the ^{13}C NMR spectra (section 3.1), the formation of HCO_3^- is predominant.

In Reaction V, dealing with $MAPACOO^-_{(p)}$ and $MAPACOO^-_{(s)}$ formation, for the ionic mass balance we could simply consider that, both in $MAPACOO^-_{(p)}$ and $MAPACOO^-_{(s)}$, the -N not bounded to CO_2 is protonated ($MAPAH^+COO^-_{(s)/(p)}$) and acts as counter-ion of the carboxylate ion ($-COO^-$). This would also be in line with the fact that the Reaction VI, which deals with the formation of $MAPA(COO^-)_2$, may be considered a minor one for single MAPA solvent as the amount of MAPA dicarbamate found at the equilibrium is negligible. On the other hand, in presence of tertiary amines, a significant formation of $MAPA(COO^-)_2$ is observed and the reaction in equation XIII leads to its formation, together with the reactions X-XII which represent the increased availability of MAPA species to react with CO_2.

3.3 Speciation after desorption screening at 80 °C

For this series of aqueous amine solvents, Bernhardsen et al.[38] observed that, in both single and blended tertiary amines, the screening cyclic capacity increased at increasing pKa of the tertiary amines (decreasing number of –OH groups) and was approximatively similar among the molecules with the same number of –OH groups. The exception was represented by Tropine, which showed a drop in the cyclic capacity.

The quantitative NMR analyses on the same samples at equilibrium after the desorption screening experiments at 80°C gave an indication of the CO_2 release from the CO_2-containing species. In order to estimate the tendency of each species to deliver CO_2 after heating at 80 °C, the CO_2-containing species removed from the amine systems are reported in percentage (%) with respect to the corresponding amount found at equilibrium after absorption, as follows:

$$\% = \frac{([Abs]-[Des])}{[Abs]} \bullet 100 \qquad (3)$$

[*Abs*] and [*Des*] represent the concentrations of the species in the solutions at equilibrium after absorption and desorption processes, respectively (Supporting Information, Table S18-S31).

In Figure 7, the percentage of (bi)carbonate removed from single aqueous tertiary amines is reported. The removal of this species increases at increasing pKa of the tertiary amines, with the exception of Tropine. Moreover, for the aqueous tertiary amines at 3M concentration the tendency of removing (bi)carbonate is higher than at 1.5 M concentration.

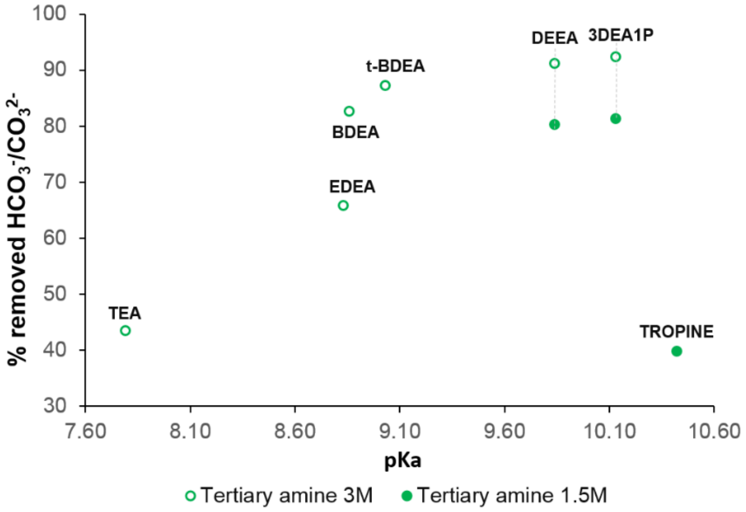


Figure 7. Percentage of (bi)carbonate removed from aqueous single tertiary amine solvents after screening desorption at 80°C.

In Figure 8, the percentage of CO_2-derived species removed from the amine blend solvents and from corresponding single MAPA are reported as a function of the pKa of the tertiary amine and the pKa_1 of MAPA, respectively.

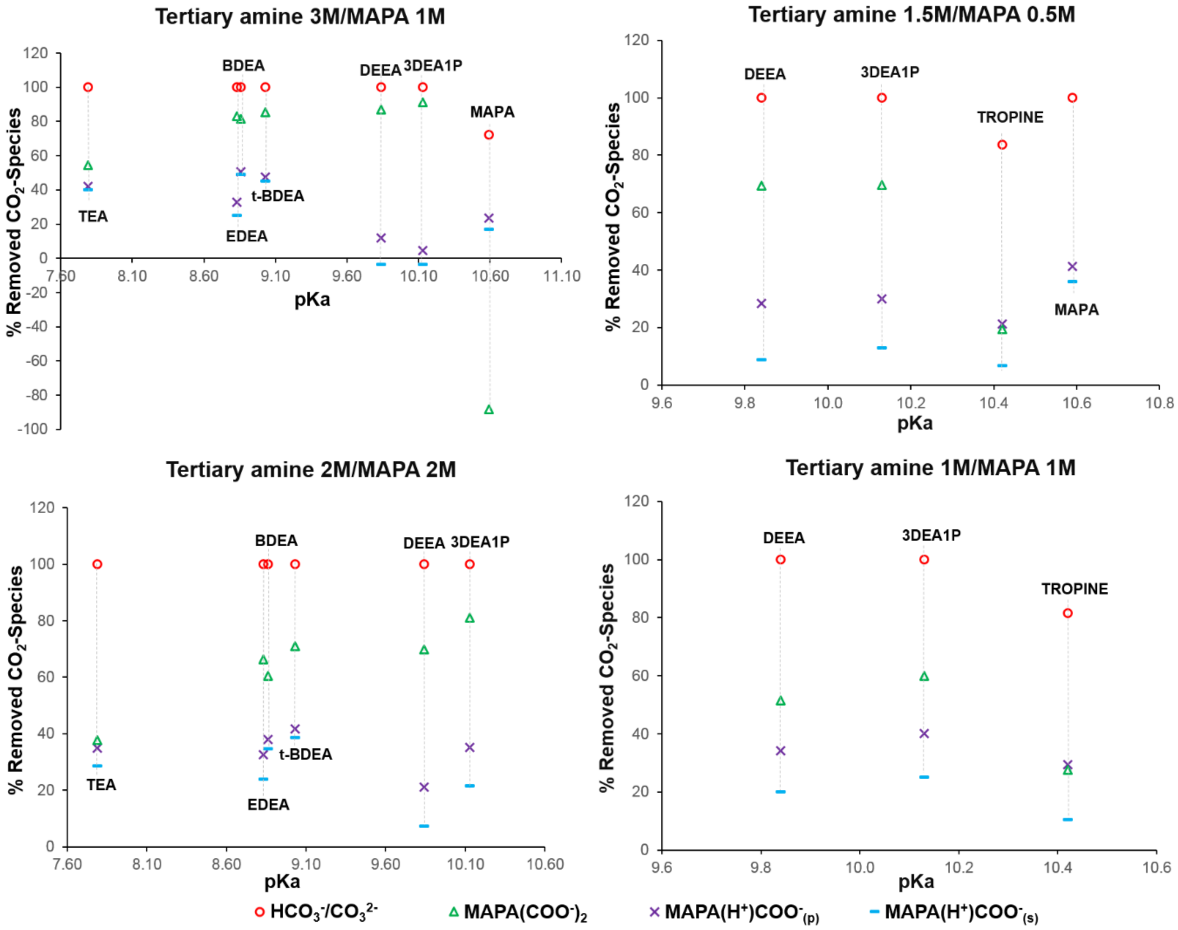


Figure 8. Percentage of CO_2-containing species removed from the single and blended MAPA after screening desorption at 80°C.

In all the systems, (bi)carbonate is the main species removed, followed by $MAPA(COO^-)_2$, $MAPA(H^+)COO^-_{(p)}$ and $MAPA(H^+)COO^-_{(s)}$. However, in single MAPA 1M, the percentage of $MAPA(COO^-)_2$ is negative, meaning that the species is even formed during the desorption (0.02 M and 0.035 M after absorption and desorption, respectively); whereas in Tropine/MAPA blends, $MAPA(H^+)COO^-_{(p)}$ is removed slightly better than $MAPA(COO^-)_2$.

The reactions 4-8 represent the possible pathways to remove CO_2 during heating at 80°C:

$$MAPA(COO^-)_2 + H_2O \leftrightarrows MAPACOO^-_{(p)} + HCO_3^- \quad (4)$$

$$MAPA(COO^-)_2 + H_2O \leftrightarrows MAPACOO^-_{(s)} + HCO_3^- \quad (5)$$

$$MAPACOO^-_{(p)} + H_2O \leftrightarrows MAPA + HCO_3^- \quad (6)$$

$MAPACOO^{-}_{(s)} + H_2O \leftrightarrows MAPA + HCO_3^{-}$ (7)

$HCO_3^{-} + AmineH^{+} \leftrightarrows Amine + CO_2 + H_2O$ (8)

In particular, the reactions 4-7 may explain the reason why, in most of the blended amine systems, the percentages of $MAPACOO^{-}_{(p)}$ and/or $MAPACOO^{-}_{(s)}$ removed from the solutions are lower than $MAPA(COO^{-})_2$. When $MAPA(COO^{-})_2$ is hydrolyzed, $MAPACOO^{-}_{(p)}$ or $MAPACOO^{-}_{(s)}$ (reactions 4 or 5) are the first reaction products, followed by a further hydrolysis process which leads to fully hydrolyzed MAPA (reactions 6-7). The release of CO_2 from the solutions may be expected to occur via the reaction (8). [46]

It is worth to highlight that, in the blends, the percentage of removed $MAPA(COO^{-})_2$ appears to increase at increasing concentration (Figure 9) and, to some extent, at increasing pKa of the tertiary amines, with the exception of Tropine/MAPA blends.

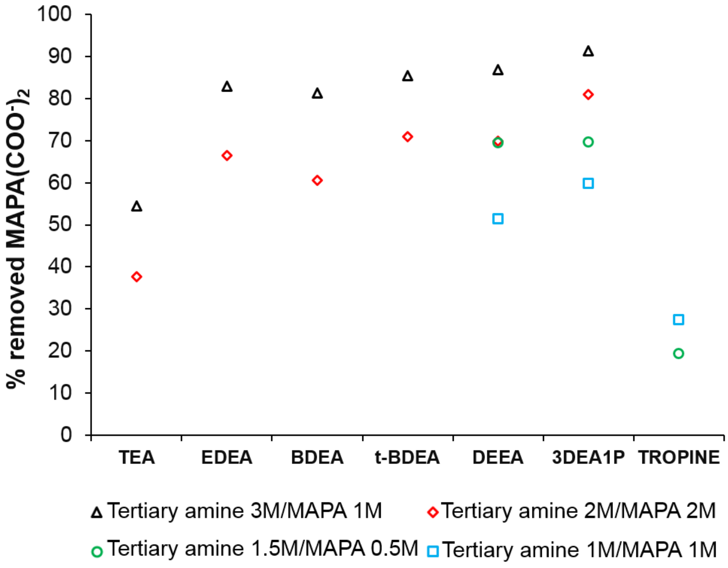


Figure 9. Comparison of the percentage of $MAPA(COO^{-})_2$ removed in the blended MAPA solvents.

Considering that, in most of the blends, (bi)carbonate is mainly removed and the tendency of hydrolyzing $MAPA(COO^{-})_2$ appears to be dependent on the tertiary amine content, it may be hypothesized that MAPA and tertiary amines are influencing each other also during the desorption step. The presence of interactions between MAPA and DEEA has also been suspected by Knuutila and Nannestad.[14]It was observed an increase of the cyclic capacity at increasing MAPA concentration in blends with DEEA at a fixed concentration (3M), and a decrease at increasing MAPA concentration up to 5 M and simultaneously decreasing DEEA concentration up to 1M, indicating that the extend of different reactions happening is dependent on the amounts of DEEA and MAPA in the blends.

The reason why, in presence of Tropine, the removal of CO_2 is lower than in the other amine systems may be attributed to its high basicity. At high pKa, the tendency of an amine to be deprotonated for the CO_2 removal (reaction 8) may be low.

In the current work, the desorption screening experiments conducted at 80°C only gave an indication of the ability of the amines to release CO_2. In order to further investigate the mechanisms of reaction underlying the release of CO_2, the desorption performance of the solvents should be examined further and under more realistic desorption temperature (120°C).[35]

4. Conclusions

The diamine MAPA, composed of a primary and a secondary amine group, and eight tertiary amines (DEEA, 3DEA1P, 1DEA2P, Tropine, *t*-BDEA, BDEA, EDEA, TEA), which differ in the number of hydroxyl groups and length of the carbon chains, were investigated as single and blended aqueous solvents at different amine ratios and concentrations.

The results obtained from the CO_2 absorption tests (40 °C) showed that, in blends, at increasing pKa of the tertiary amine, the amounts of $MAPA(H^+)COO^-_{(p)}$, $MAPA(H^+)COO^-_{(s)}$ and $MAPA/MAPA(H^+)_2$ decrease, whereas the amounts of $MAPA(COO^-)_2$ and HCO_3^-/CO_3^{2-} increase (for the blends containing tertiary amines with the same number of -OH groups, exceptions are found). Moreover, MAPA dicarbamate formed in the single MAPA absorbent was found in a much lower amount (even not found in MAPA 0.5M) than in the corresponding blends, whereas $MAPA/MAPA(H^+)_2$ was found in higher concentrations.

The analyses of the overall trends allowed hypothesizing that, in blend, the tertiary amines may act by increasing the availability of the amino functional groups of MAPA species, which can therefore react further with CO_2.

Concerning the desorption screening tests (80 °C), in the presence of Tropine, which is a cycle and has the highest pKa=10.42 value (within the amines investigated in this study), the removal of CO_2 is lower than in the other amine systems. Specifically, for the single tertiary amines, the percentage of (bi)carbonate removed increases with increasing pKa value and concentration of the tertiary amine, with the exception of Tropine. In most of the MAPA systems (with the exception of single MAPA solvent and of those containing Tropine), (bi)carbonate is the main species removed, followed by $MAPA(COO^-)_2$, $MAPACOO^-_{(p)}$ and $MAPACOO^-_{(s)}$. In particular, the removal of $MAPA(COO^-)_2$ appears to be dependent on the tertiary amines content.

In this study, insights on the role played by the amines in mixture in presence of CO_2 are given. In the field of chemical absorption of CO_2 by amine solvents, this work hence represents a step forward to design new amine solvents with improved CO_2 removal efficiency.

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Associated Content

Supporting Information

The Supporting Information is available in a separate file. Densities, signal assignment, ^{13}C-NMR chemical shift values and concentrations of all the species found in the solutions.

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