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CO₂ Capture by Aqueous 3-(Methylamino)propylamine in Blend with Tertiary Amines: an NMR Analysis

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Abstract

Aqueous 3-(Methylamino)propylamine (MAPA) in blend with 2-(Diethylamino)ethanol (DEEA) and other tertiary amines, which mainly differ from DEEA in the number of hydroxyl functions (-OH) and/or in the length and structure of their alkyl chain, are investigated. After absorption of carbon dioxide (CO₂) at 40°C, quantitative ¹³C NMR experiments are performed to calculate the concentration of the species in each blend at equilibrium, together with qualitative NMR experiments for signal assignment. Speciation and absorption capacity data are discussed in terms of chemical structure and basicity of the tertiary amines.

In general, it is observed that, at increasing pK_a of the tertiary amines (decreasing number of -OH on the structure), there is a decrease of MAPA and primary and secondary MAPA carbamates, and an increase of MAPA dicarbamate, (bi)carbonate and of the absorption capacity. Within the molecules with the same number of -OH but differently branched, some exceptions are found.

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1. Introduction

Among various commercial processes available for separating carbon dioxide (CO₂) from gas mixtures, chemical absorption of CO₂ into aqueous amine solutions is the most common technology [1]. However, the energy penalty and the costs represent an issue of concern [2].

Chemical absorption involves one or more reversible reactions between CO₂ and aqueous amine solutions. Tertiary amines act as bases accepting a proton to form (bi)carbonates (bicarbonate/carbonate species), whereas primary and secondary amines can act as both nucleophiles and bases to form carbamates and (bi)carbonates [3]. Primary and secondary amines typically show reaction rates higher than tertiary amines, but the reaction with CO₂ is more exothermic.

In order to improve the efficiency of the CO₂ absorption process, aqueous mixed amine solvents are of great interest as they offer the possibility of combining the best characteristics of the two or more single amines [4-6]. A blended amine system is usually based on the combination of the higher reaction rate of a Lewis base (nucleophile), i.e. a primary or a secondary amine, and the higher equilibrium capacity, lower reaction enthalpy and relatively improved CO₂ desorption performances of a tertiary amine.

The aqueous system composed of 3-(Methylamino)propylamine (MAPA) (Figure 1) and 2-(Diethylamino)ethanol (DEEA) (Figure 2) is a promising absorbent for CO₂ capture because of its high cyclic capacity, high CO₂ pressure during stripping, high equilibrium temperature sensitivity and relatively high reaction rate [7].

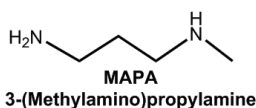


Figure 1. Chemical structure of MAPA, a diamine with one primary and one secondary amino group.

Although a lot of data on MAPA, DEEA and their mixture are available in the literature [7-10], experimental insights at molecular level on the properties of these molecules are needed to support the development of even better systems.

Nuclear Magnetic Resonance (NMR) is a non-invasive analytical method that allows direct measurements of specific nuclei of species. Depending on the type of NMR experiments, interpretation of NMR data gives information on chemical structure and dynamics of the molecules and, with some care, quantitative analyses are also possible. Several NMR studies on amine-CO₂-H₂O systems have been reported [11] and speciation of CO₂ loaded aqueous 2M MAPA and 5M DEEA, as both single amines and in blend, were also carried out [12].

The aim of the present work is to investigate the mechanisms of reactions underlying the process of chemical absorption of CO₂ by aqueous MAPA in blends with DEEA and other tertiary amines. In particular, the influence of the tertiary amines on the formation of bicarbonate and of MAPA carbamates is explored, together with the effect on the absorption capacity.

The tertiary amines investigated in this study mainly differ from DEEA in the number of hydroxyl functions (-OH) and/or in the length and structure of their alkyl chain (Figure 2). It is known that structural features (like e.g. inductive, steric, electrostatic, mesomeric effects and others) influence the electron density on the nitrogen (-N) and, consequently, the basicity. Here, the increasing number of -OH in the structure of the tertiary amines results in an increase of the electron withdrawing inductive effect through bonds on the -N, leading to a pK_a decrease. The opposite is somehow true for the tertiary amines at increasing number of carbons on the alkyl chain. In *t*-BDEA, the -C(CH₃)₃ group exerts an electron donating inductive effect, more than the linear -(CH₂)₃CH₃ chain in BDEA (Figure 2).

After CO₂ absorption experiments, the solutions at equilibrium are systematically analyzed by NMR spectroscopy. Quantitative ¹³C NMR experiments are performed to calculate the concentration of the species in solution, whereas structural characterizations are carried out by means of qualitative 1D and 2D NMR experiments.

Data on speciation and absorption capacity are presented and some hypotheses on the mechanism of the reactions between aqueous MAPA, tertiary amines and CO₂ are formulated.

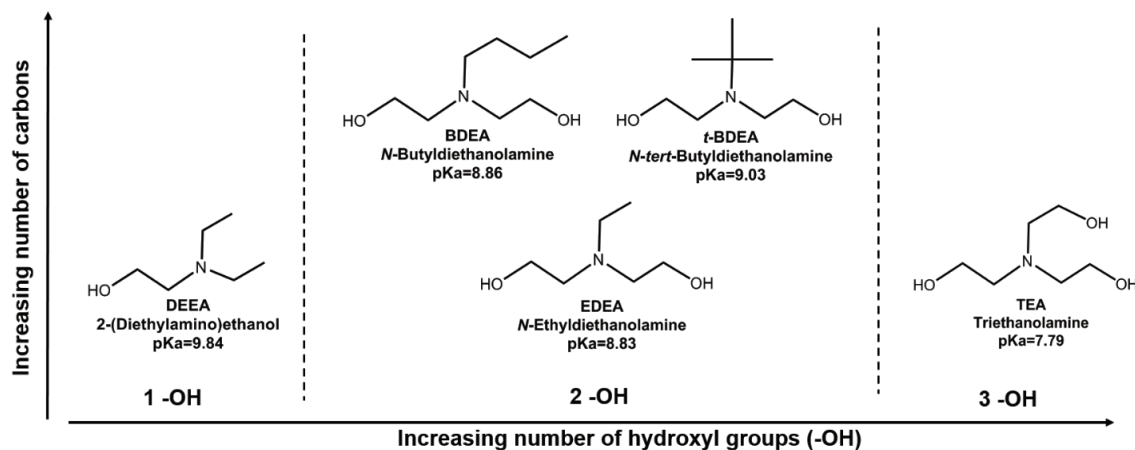


Figure 2. Chemical structure and pKa of the tertiary amines investigated in this study.

2. Materials and methods

The following chemicals were used in the current study: 3-(Methylamino)propylamine ($\geq 97\%$, CAS: 6291-84-5), 2-(Diethylamino)ethanol ($\geq 99.5\%$, CAS:100-37-8), *N*-Ethyldiethanolamine (98%, CAS:139-87-7), Triethanolamine ($\geq 99\%$, CAS: 102-71-6), *N*-Butyldiethanolamine ($\geq 98.6\%$, CAS:102-79-4), Acetonitrile (anhydrous 99.8%, CAS: 75-05-8) and Deuterium oxide (Deuterated water, 99.98 atom % ± 0.01 atom % D, CAS: 7789-20-0) from Sigma Aldrich; *N*-tert-Butyldiethanolamine ($\geq 97\%$, CAS:2160-93-2) from TCI Europe; Nitrogen (99.9%, CAS:7727-37-9) and Carbon Dioxide (99.9%, CAS: 124-38-9) from Yara Praxair. They were utilized without any further purification.

Screening absorption tests were conducted 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 for each absorbent. In this work, we report data on the absorption process which was performed at 40°C with an inlet gas containing 10kPa partial pressure of CO₂. The experiments were terminated when 95% of the CO₂ was captured, i.e. 9.5kPa partial pressure of CO₂. Further details can be found in Bernhardsen et al. [13].

The pKa values of the amines were measured by potentiometric titration at 25°C using the same apparatus as Kim et al. [14]. A 0.1 mol/L aqueous solution of HCl was used to titrate the amine solutions at concentration 0.01 mol/kg H₂O. For each amine, the measurement was performed two times and the average reported as the pKa value.

After the absorption experiments, NMR experiments were performed at 300.0 K on a Bruker 600 MHz Avance III HD equipped with a 5-mm cryogenic CP-TCI z-gradient probe. For the determination of the concentrations of the species formed in the equilibrated reaction mixtures, quantitative ¹³C NMR experiments were performed by setting appropriate acquisition and processing parameters to obtain reliable area integrals. The ¹³C 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. [15]. In this 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.

After ¹³C NMR acquisition, the spectra were processed using MestreNova software v 7.1.1, as described in Perinu et al. [15].

The assignment of each signal to the corresponding carbon was performed by means of qualitative 1D (i.e. ¹H and ¹³C) and 2D NMR experiments, i.e. COSY (¹J_{H-H}, Correlation Spectroscopy), HSQC (¹J_{C-H}, Heteronuclear Single Quantum Correlation) and HMBC (²⁻³J_{C-H}, Heteronuclear Multi Bond Correlation), on both pure single amines and on MAPA-tertiary amine-CO₂-H₂O systems.

3. Results and discussion

Under certain conditions when loaded with CO₂, the MAPA-DEEA-CO₂-H₂O system forms two liquid phases, one rich and one lean in CO₂[12]. In this work, MAPA and the tertiary amines were studied in blends at 1:3 ratio, at 1M and 3M concentrations, respectively, which give a single phase in all cases. This allowed fair comparison of all the amine systems under study, as not all of them have the ability to form two phases.

After absorption of CO₂ at 40°C, by means of qualitative 1D and 2D NMR experiments, the following species were identified for all the blends at equilibrium: MAPA, primary MAPA carbamate (MAPACOO⁻_(p)), secondary MAPA carbamate (MAPACOO⁻_(s)), MAPA dicarbamate (MAPA(COO⁻)₂), tertiary amine (3°Amine), tertiary organic amine carbonate (3°AmineOCOO⁻) and (bi)carbonate. Each species is in equilibrium with the corresponding protonated form (Figure 3).

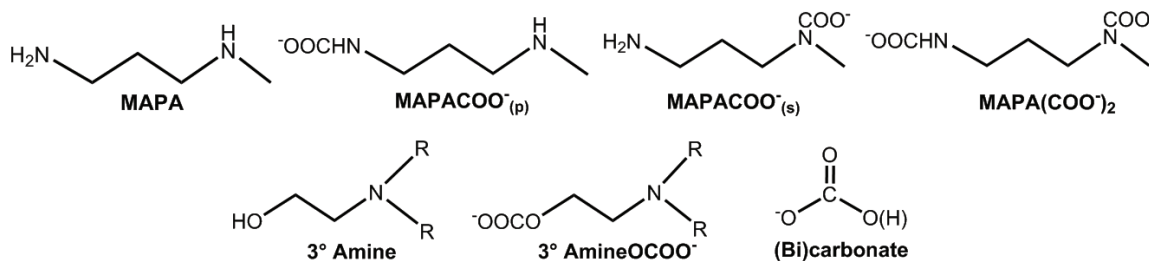


Figure 3: Species formed in the blended amine systems (MAPA 1M/ 3°Amine 3M) after absorption of CO₂ at 40°C. Each species is in equilibrium with the corresponding protonated form.

The fast exchanging proton species (neutral/protonated amines and carbonate/bicarbonate) appear with a common peak in the ¹³C NMR spectra and the sum of their concentrations can be obtained. Various methods [11] could be utilized to distinguish between them but, in this work, they were not applied. However, for all of the blends, the carbon signal corresponding to carbonate/bicarbonate (CO₃²⁻/HCO₃⁻, (bi)carbonate) resonates at a chemical shift value ranging from 161.2 to 162 ppm, suggesting that mainly bicarbonate is formed [15].

In Figure 4, the concentration (obtained from quantitative ¹³C NMR experiments and expressed in mol/L) of each species formed in the different amine systems is reported.

In each blend, a small amount of organic amine carbonate (3°AmineOCOO⁻), ranging from 0.059 to 0.104 mol/L, was found. Due to overlapping peaks, for BDEA and TEA containing 2 and 3 hydroxyl functional groups respectively, it was not possible to establish if mono-, bi- and/or tricarbonates were formed. In line with the other amines under study, we here give the concentrations as monocarbonate. Organic carbonate comes from the direct reaction of CO₂ with the -OH of the tertiary alkanolamines. This species can be formed at extremely high pH values (higher than 12)[16, 17] and there are some studies where they were found to be constant at increasing CO₂ loadings [18-20]. In our opinion, this suggests that the organic carbonate is formed at the beginning of the CO₂ absorption process where the pH is still high. At decreasing pH (increasing CO₂ loading), the reaction between CO₂ and the tertiary amines is towards (bi)carbonate formation.

Looking at the main species at equilibrium and at the structure of the tertiary amines, it is possible to define a trend (for some species more evident than in others).

Concerning MAPACOO⁻_(p), MAPACOO⁻_(s) and MAPA, a decrease in their concentrations at decreasing number of -OH and at decreasing number of carbons in the alkyl chain of the tertiary amine structure is observed. Specifically, the trend is: MAPA-TEA > MAPA-BDEA > MAPA-*t*-BDEA > MAPA-EDEA > MAPA-DEEA, where MAPA-*t*-BDEA ≥ MAPA-EDEA for MAPACOO⁻_(p). An exception is MAPA-BDEA ≥ MAPA-TEA for MAPACOO⁻_(s) species.

On the contrary, $\text{MAPA}(\text{COO}^-)_2$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$ decrease at increasing number of -OH and at increasing number of carbons in the alkyl chain of the tertiary amine structure, following this trend: $\text{MAPA-DEEA} > \text{MAPA-EDEA} > \text{MAPA-}t\text{-BDEA} > \text{MAPA-BDEA} > \text{MAPA-TEA}$ (specifically, $\text{MAPA-BDEA} \geq \text{MAPA-TEA}$ for (bi)carbonate species).

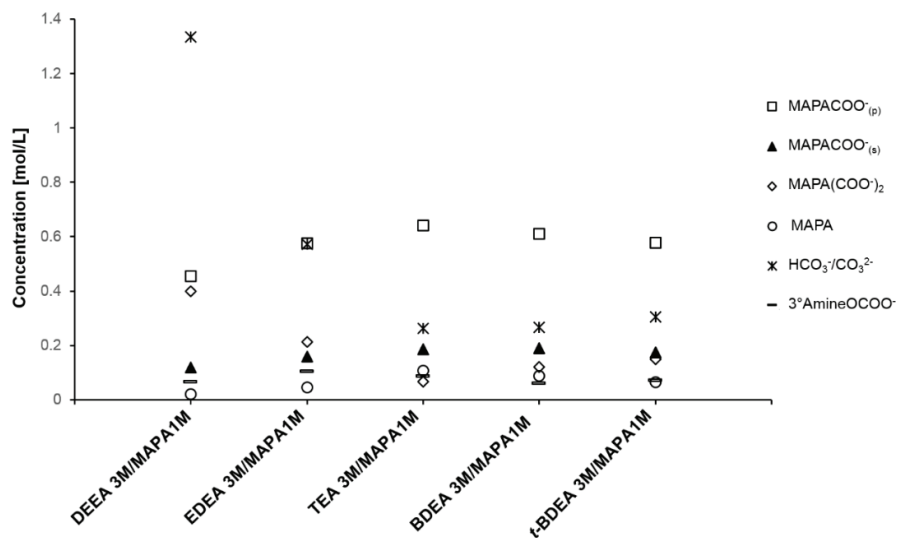


Figure 4. Amount of the species at equilibrium in aqueous MAPA 1M/ 3°amine 3M after CO_2 absorption at 40°C .

In Figure 5, the pKa value of the tertiary amines are plotted as function of the concentration of the main species at equilibrium in each blend after the absorption process.

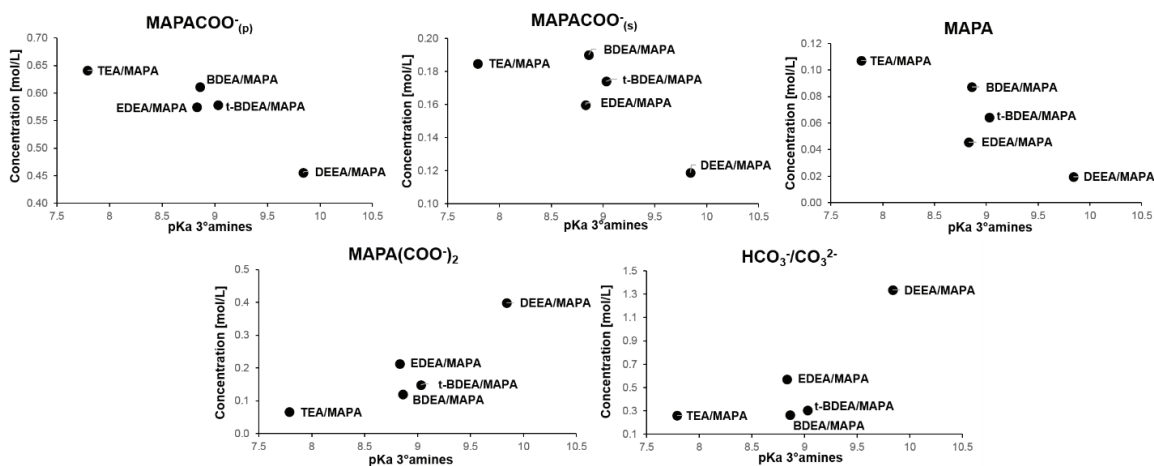


Figure 5: pKa of the tertiary amines as function of the concentration of the main species at equilibrium in each blend after CO_2 absorption at 40°C .

As a general tendency, it can be observed that at increasing pKa of the tertiary amine, the amount of $\text{MAPACOO}^-_{(p)}$, $\text{MAPACOO}^-_{(s)}$ and MAPA decreases, whereas $\text{MAPA}(\text{COO}^-)_2$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$ increase. However, BDEA/MAPA and *t*-BDEA/MAPA appear not to exactly follow this trend. This may probably be attributed to the structure of BDEA and *t*-BDEA which have a $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ chain and a tertiary carbon $-\text{C}(\text{CH}_3)_3$ group bound to the amino functional group. These features may influence the activity of the -N site.

The absorption capacity for each blend, calculated by NMR analyses and expressed in mole CO₂/mole amine groups, is reported in Figure 6. The trend is the same as for (bi)carbonate and MAPA(COO)₂ formations, both in terms of chemical structure and basicity of the tertiary amines (MAPA-DEEA>MAPA-EDEA>MAPA-t-BDEA>MAPA-BDEA>MAPA-TEA).

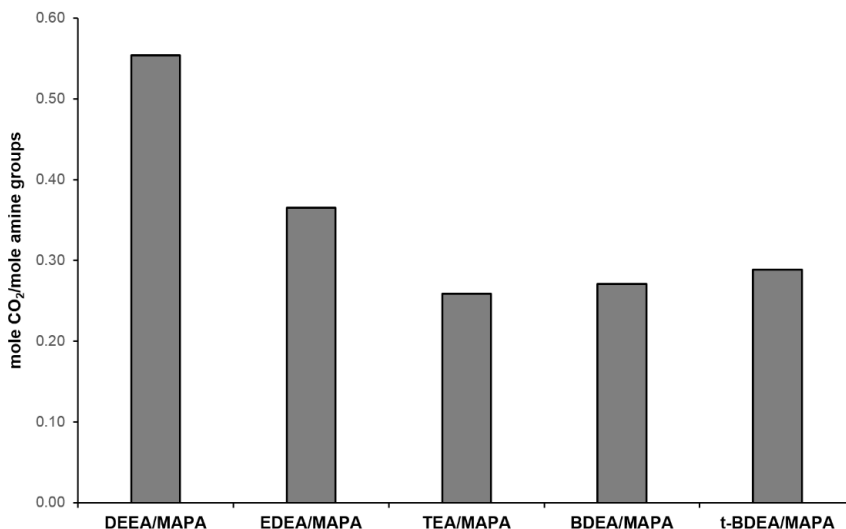


Figure 6: Absorption capacity for each MAPA 1M/3°amine 3M-CO₂-H₂O system.

The absorption capacity and (bi)carbonate formation are somehow connected. With respect to the carbamate formation reactions, the (bi)carbonate formation allows capturing more moles of CO₂ per moles of amines leading to a larger absorption capacity. Based on the generic trend observed in this study (increase of MAPA(COO)₂, HCO₃⁻/CO₃²⁻ and absorption capacity at increasing pKa), it could be hypothesized that, in addition to charge balancing the formation of HCO₃⁻/CO₃²⁻ anions, the tertiary amines may also affect MAPA carbamate formation. They may do so by accepting a proton from protonated MAPA and from protonated MAPACOO⁻_(p/s) and/or by acting (in the protonated form) as a counter ion of the MAPA carbamates species. In both cases, this would make the amino functional groups of MAPA, MAPACOO⁻_(p) and MAPACOO⁻_(s) available for reaction with CO₂, and could be the reason why, at increasing pKa of the tertiary amines, more MAPA(COO)₂ is formed.

These hypotheses need to be validated by further studies on the same molecules and with a larger selection of tertiary amines. For the development of improved amine systems, it is pivotal to investigate the role played by the basicity and the structure of the tertiary amines and to understand if they interact with the primary/secondary amines in the mechanism of CO₂ capture.

4. Conclusions

In this work, five tertiary amines at 3M concentration in blend with MAPA 1M were investigated. After CO₂ absorption screening experiments, quantitative ¹³C NMR experiments were performed on each blend at equilibrium to calculate the concentration of the species, together with qualitative NMR experiments for signal assignment. The following species were identified: MAPA, MAPACOO⁻_(p), MAPACOO⁻_(s), MAPA(COO)₂, 3°Amine, 3°AmineOCOO⁻ and (bi)carbonate. Each species is in equilibrium with the corresponding protonated form.

In general, it is observed that, at increasing pKa of the tertiary amines (decreasing number of -OH on the structure), there is a decrease of MAPACOO⁻_(p), MAPACOO⁻_(s) and MAPA and an increase of MAPA(COO)₂, HCO₃⁻/CO₃²⁻ and of the absorption capacity. Within the molecules with the same number of -OH but differently branched alkyl groups, some exceptions are found.

Further studies are needed to deeply focus on the mechanism of reaction and design new amine solvent systems with improved properties.

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