



13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18
November 2016, Lausanne, Switzerland

Performance of MAPA promoted tertiary amine systems for CO₂ absorption: Influence of alkyl chain length and hydroxyl groups

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Abstract

Absorption and desorption of CO₂ into five aqueous tertiary amine solvents and their blends with MAPA were studied using a screening apparatus. Results showed that MAPA significantly enhanced both CO₂ absorption rate and absorption capacity. The solvent system with the highest CO₂ absorption capacity and cyclic CO₂ capacity was 3M DEEA + 1M MAPA with a CO₂ loading of 2.72 mole CO₂/kg solution and a cyclic CO₂ capacity of 2.06 mole CO₂/kg solution. For both the single and the blended systems, the CO₂ absorption capacity decreased when increasing the number of ethanalamine groups on the tertiary amine (DEEA → EDEA → TEA) and when the alkyl chain length in the tertiary amine was increased (EDEA → BDEA). When the alkyl amine group in the tertiary amine became hindered (BDEA → t-BDEA), the CO₂ absorption capacity increased.

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Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: CO₂ capture; amine solvent; screening; absorption capacity; cyclic capacity

1. Introduction

In light of rising atmospheric CO₂ concentration and that consequences of global warming are steadily becoming more evident, strong mitigation actions are needed. Among the options for CO₂ removal from combustion exhaust gases, amine-based chemical absorption is the most developed method. It is also the method that is dominating the

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current research field [1]. Commonly studied amine solvents are Monoethanolamine (MEA), Methyldiethanolamine (MDEA), Diethanolamine (DEA) and 2-amino-2-methyl-1-propanol (AMP) [2, 3]. MEA is used as a reference solvent due to its fast reaction with CO₂ and relatively low solvent cost. However, a major challenge with this technology is the high energy needed to regenerate the solvent. A solvent system that has shown potential to reduce the specific heat demand is the aqueous solution of 2-(Diethylamino)ethanol (DEEA) and 3-(Methylamino)propylamine (MAPA) [4]. The blended alkanolamine system combines the advantage of high capacity from the tertiary amine and high absorption rate from the diamine [5]. A disadvantage of the DEEA/MAPA system is the relatively high volatility of DEEA. Therefore, it is of great importance to continue developing new solvents for CO₂ absorption.

In this work, absorption rate, absorption capacity and cyclic capacity of single tertiary amine solvents and their blends with 1M MAPA using a screening apparatus were investigated. The work gives insight into the influence of amine alkanol groups (DEEA → N-Ethyldiethanolamine (EDEA) → Triethanolamine (TEA)), alkyl chain length (EDEA → N-Butyldiethanolamine (BDEA)) as well as hindrance in the alkyl chain (BDEA → N-*tert*-Butyldiethanolamine (t-BDEA)) of the tertiary amine part of the MAPA blended systems. The molecular structures of the studied tertiary amines is presented in Figure 1.

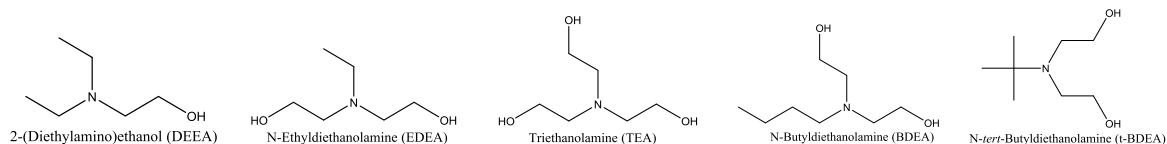


Figure 1. Molecular structure of the studied tertiary amines

2. Materials and Methods

2.1. Materials

Table 1 provide CAS-number, supplier and purity of the chemicals used in this work. All chemicals were used without further purification and the solutions were prepared with deionized water.

Table 1. Details of the chemicals used in this study

Chemical name	CAS-number	Supplier	Mass fraction purity
Monoethanolamine (MEA)	141-43-5	Sigma Aldrich	≥ 0.99
3-(Methylamino)propylamine (MAPA)	6291-84-5	Sigma Aldrich	≥ 0.97
2-(Diethylamino)ethanol (DEEA)	100-37-8	Sigma Aldrich	≥ 0.995
N-Ethyldiethanolamine (EDEA)	139-87-7	Sigma Aldrich	0.98
Triethanolamine (TEA)	102-71-6	Sigma Aldrich	≥ 0.99
N-Butyldiethanolamine (BDEA)	102-79-4	Sigma Aldrich	≥ 0.986
N- <i>tert</i> -Butyldiethanolamine (t-BDEA)	2160-93-2	TCI Europe	≥ 0.97
Nitrogen (N ₂)	7727-37-9	Yara Praxair	0.999
Carbon Dioxide (CO ₂)	124-38-9	Yara Praxair	0.999
Polypropylene Glycol (Antifoam)	25322-69-4	Nalco/Exxon Energy Chemicals L.P.	

2.2. Methods

Absorption and desorption experiments were performed using the screening apparatus (Figure 2) applied in Aronu et al. [6]. The apparatus is designed to operate at atmospheric pressure and at temperatures up to 80 °C. In each experiment, the reactor was filled with about ~124 g of aqueous amine solution. The concentration of the single tertiary

amines and MEA was 3M aqueous solution, while the concentration of MAPA was 1M aqueous solution. The total concentration of the blended MAPA systems was 4M aqueous solution in the molar ratio 3:1, i.e. 3M tertiary amine + 1M MAPA. They were compared to MEA at the same total concentration (4M MEA). As foaming issues were observed for the solutions containing EDEA and BDEA, 1000 ppm antifoam was added to these solutions prior the experiment. Further, CO₂ absorption capacity and CO₂ absorption rates were measured by bubbling a gas mixture, containing 10 vol% CO₂, through the solution at 40 °C. The absorption experiment automatically terminated when the CO₂ concentration in the effluent reached 9.5 vol%, i.e. 9.5 kPa partial pressure of CO₂. Since there was no guarantee that the bubble structure and the interfacial area were the same at each experiment, the resulted absorption rates were only semi-quantitative [7]. The desorption experiment was conducted at 80 °C and terminated when the effluent reached 0.1 vol% CO₂, i.e. 1.0 kPa partial pressure of CO₂.

After each experiment, a liquid sample was taken to determine the CO₂ loading by the precipitation-titration method described in Ma'mun et al. [8]. This method involved to titrate the HCl, which had not been used to dissolve BaCO₃, with 0.1M NaOH using an automatic titrator (Methrohm 809 Titrando). The titrator titrated until it reached the endpoint of pH 5.2. Since the CO₂ liquid analysis is the most accurate method to determine the CO₂ loading in the liquid phase, the CO₂ loadings from the liquid analysis were used in all the calculations. For instance, it was used to correct the final screening CO₂ loading, calculated based on the logged data from the screening absorption experiment, by multiplying the final screening CO₂ loading with the correction factor defined in equation 1.

$$\text{Correction Factor} = \frac{\alpha_{\text{liquid sample}}}{\alpha_{\text{screening, final loading}}} \quad (1)$$

The notation $\alpha_{\text{liquid sample}}$ and $\alpha_{\text{screening, final loading}}$ denotes the CO₂ loading determined by the precipitation-titration method and the final CO₂ loading calculated based on the logged data from the screening absorption experiment, respectively. The CO₂ loading resulted from the liquid analysis was also used to calculate the cyclic capacity by subtracting the lean CO₂ loading from the rich CO₂ loading.

At last, the experimental setup was validated by an experiment using 30 wt% aqueous MEA solution. The obtained CO₂ absorption capacity of 2.53 mole CO₂/kg solution was comparable to literature values [9].

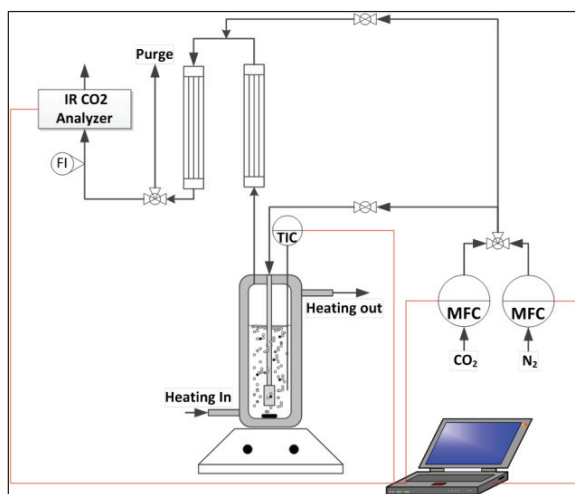


Figure 2. CO₂ absorption screening apparatus [10]

3. Results

3.1. Absorption of CO₂ into single amines

The change in absorption rate for single amine solvents versus CO₂ loading is demonstrated in Figure 3.

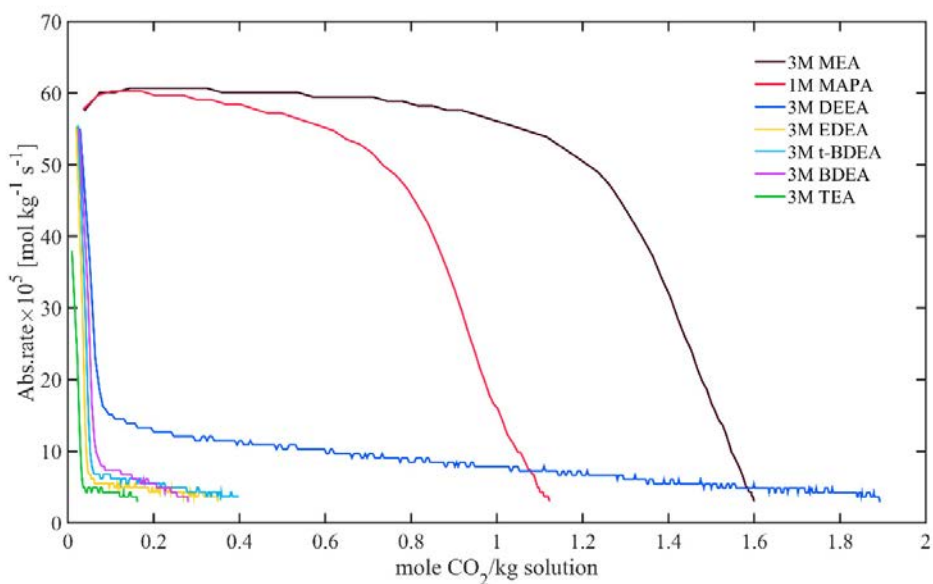


Figure 3. CO₂ absorption rate and capacity for single amine solvents.

For the whole CO₂ loading range, all tertiary amines showed considerably lower absorption rate as compared to 3M MEA and 1M MAPA solutions. This was expected as tertiary amines are known to have lower reaction rates than primary and secondary amines [11]. 3M MEA and 1M MAPA solutions maintained a high absorption rate until about 1.0 mole CO₂/kg solution and 0.6 mole CO₂/kg solution, respectively. At these CO₂ loadings the rates started to decrease rapidly.

Among the studied amines, 3M DEEA solution showed the highest absorption capacity with a CO₂ loading of 1.89 mole CO₂/kg solution. This was 18 % and 69 % higher than for 3M MEA and 1M MAPA solutions, respectively. Monteiro et al. [12] performed VLE studies of 2M DEEA solutions and found a CO₂ loading range from 0.77 to 0.82 mole CO₂/mole amine in the pressure range of 9.25 kPaCO₂ to 16.09 kPaCO₂. This is comparable to our result when taking the higher amine solution concentration into account. Further, the overall trend in increasing CO₂ absorption capacity was TEA < BDEA < EDEA < t-BDEA < MAPA < MEA < DEEA. Thus, the other studied tertiary amines showed poorer performance than both 3M MEA and 1M MAPA solution. As MAPA is a diamine one would have expected MAPA to have a higher CO₂ absorption capacity than MEA [13]. However, due to the lower molar concentration it showed a lower CO₂ loading in unit of mole CO₂/kg solution. Arshad et al. [14] performed calorimetric measurements of 2M MAPA solution and found that the CO₂ loading ranged from 0.94 mole CO₂/mole amine to 1.58 mole CO₂/mole amine in the pressure range of 0.3 kPaCO₂ and 328.5 kPaCO₂. This is in accordance with our result as the CO₂ loading at 1M MAPA was found to be 1.12 mole CO₂/kg solution.

The influence of molecular structure on CO₂ absorption capacity for the tertiary amines was studied in this work. From Figure 3 it can be seen that an increase in the number of ethanolamine groups of the amine (DEEA → EDEA → TEA) decreases the absorption capacity from 1.89 mole CO₂/kg solution to 0.16 mole CO₂/kg solution. Thus, owing to the fact that the hydroxyl group is an electron attractant, an increase in the number of ethanolamine groups led to reduced activity of the nitrogen atom of the amine in the CO₂ absorption environment. El Hadri et al. [15], who performed a CO₂ absorption screening experiment of 30 wt% DEEA and 30 wt% TEA solutions, found the same

trend. Further, the CO₂ absorption capacity also decreased from 0.35 mole CO₂/kg solution to 0.28 mole CO₂/kg solution when the alkyl chain length in the amine was increased (EDEA → BDEA). When the amine alkyl group of the tertiary amine became hindered (BDEA → t-BDEA), the absorption capacity increased from 0.28 mole CO₂/kg solution to 0.40 mole CO₂/kg solution.

3.2. Absorption of CO₂ into MAPA promoted tertiary amines

Figure 4 shows the change in CO₂ absorption rate for MAPA promoted tertiary amines versus CO₂ loading. As mentioned above, the aqueous tertiary amine + MAPA systems were studied in the molar ratio 3:1 and the total concentration was kept constant at a value of 4M aqueous solution.

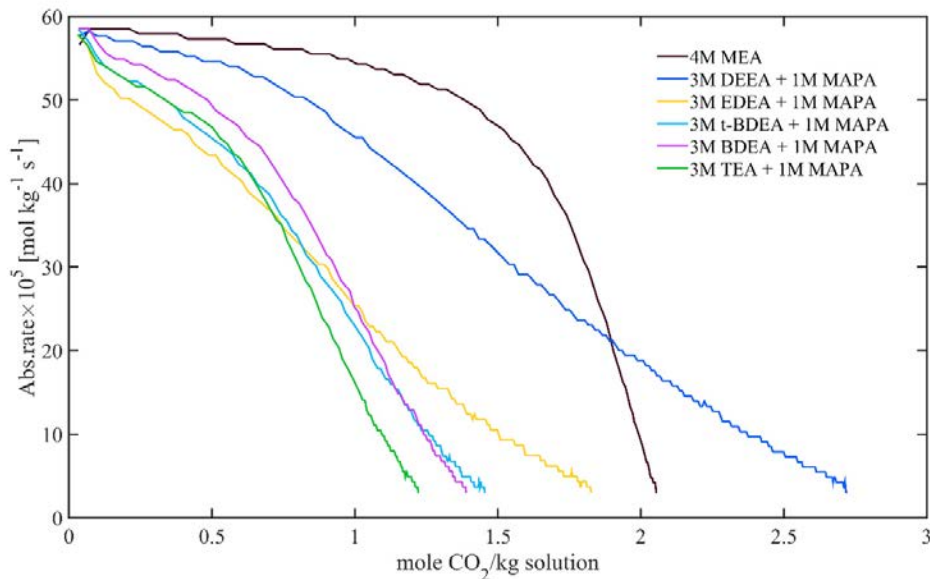


Figure 4. CO₂ absorption rate and capacity for MAPA promoted tertiary amines

The blended systems showed a considerably higher CO₂ absorption rate than the single tertiary amines given in Figure 3. For instance, at CO₂ loading 0.5 mole CO₂/kg solution all the blended systems had an absorption rate that was above 40×10⁻⁵ mol kg⁻¹ s⁻¹. The rate for the single amines were below 20×10⁻⁵ mol kg⁻¹ s⁻¹ in the whole CO₂ loading range. Thus, addition of 1M MAPA significantly enhanced the absorption rate.

Also, the absorption capacity of all the blended systems were considerably improved. For illustration, the absorption capacity of 3M DEEA + 1 M MAPA was 44 % higher than 3 M DEEA given in Figure 3. The blended system with the highest absorption capacity was 3M DEEA + 1M MAPA with a value of 2.72 mole CO₂/kg solution. This was 33 % higher than 4M MEA. The other blended systems showed a lower absorption capacity than MEA. The blended system with highest percentage improvement in absorption capacity, in relation to the single amine, was 3M TEA + 1M MAPA. The blended system obtained an absorption capacity of 1.22 mole CO₂/ kg solution, while 3M TEA (see Figure 3) showed an absorption capacity of 0.16 mole CO₂/kg solution. This was an improvement of 663 %.

In most cases, the single and the blended amine systems followed the same order in terms of increased CO₂ absorption capacity. However, the 3M EDEA + 1M MAPA blend showed a capacity that was 26 % higher than the 3M t-BDEA + 1M MAPA blend. This differed from what was seen for the single amines, given in Figure 3, as 3M t-BDEA performed 14 % better than 3M EDEA. Thus, results indicated that MAPA promoted EDEA to a greater extent than t-BDEA.

Regarding the influence of molecular structure on CO₂ absorption capacity, same trends as discussed for the single tertiary amines were seen for the blended amine systems. However, only a slight improvement (4 %) in CO₂ absorption capacity was observed when the tertiary amine part of the MAPA blend became hindered, i.e. BDEA → t-BDEA. For the single tertiary amine systems, 3M BDEA and 3M t-BDEA, the improvement in CO₂ absorption capacity was 43 %.

3.3. Cyclic capacity of single and blended amines

In Figure 5, the cyclic CO₂ capacity of the single and the blended amine solvent systems are compared. All the blended systems showed a higher cyclic CO₂ capacity than the corresponding single amine systems. The system with the highest cyclic capacity was 3M DEEA + 1M MAPA with a value of 2.06 mole CO₂/kg solution. This was 78 % higher than 4M MEA. Also, the blend 3M EDEA + 1M MAPA and the single system 3M DEEA obtained a higher cyclic capacity than 4M MEA. Especially, 3M EDEA + 1M MAPA seemed to release CO₂ more easily than 4M MEA as it bounded less CO₂ during absorption than MEA (Figure 4).

In case of 3M DEEA + 1M MAPA, addition of 1M MAPA to 3M DEEA improved the cyclic capacity less than the sum of the performance of 1M MAPA (0.38 mole CO₂/kg solution) and 3M DEEA (1.73 mole CO₂/kg solution) on their own. For 3M EDEA + 1M MAPA the situation was different. Addition of 1M MAPA to 3M EDEA seemed to enhance the absorption giving a much higher cyclic CO₂ capacity than the sum of the single parent amines. This blended system also showed the largest improvement in cyclic CO₂ capacity as compared to the single solvent (3M EDEA); the blended system performed 10.5 times better than the single amine solvent.

Furthermore, for the blended amine systems, the order of increasing cyclic CO₂ capacity and the order of increasing CO₂ absorption capacity (Figure 4) was the same. For the single amine systems (Figure 3), the order of increasing cyclic capacity was slightly different as 3M EDEA showed a lower cyclic capacity than 3M BDEA. Thus, increasing the alkyl chain length of the amine (EDEA → BDEA) led to increased cyclic CO₂ capacity.

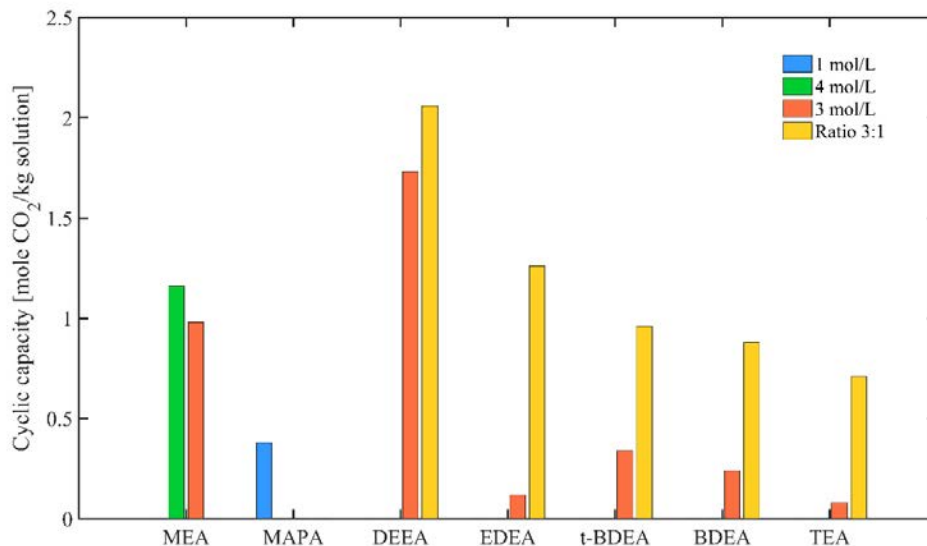


Figure 5. Cyclic CO₂ capacity of single and blended tertiary amine systems

4. Conclusions

In this study, CO₂ absorption rate, CO₂ absorption capacity and CO₂ cyclic capacity of five tertiary amines and their blends with MAPA were studied. The results strongly indicated that both absorption rate and absorption capacity of

the tertiary amine was enhanced by addition of MAPA. Further, both the single and the blended systems showed the same trend in absorption capacity with change in molecular structure of the tertiary amines. For the tertiary amines, increasing the number of hydroxyl groups and the alkyl chain length led to decreased CO₂ absorption capacity. Further, introduction of hindrance in the alkyl chain of the tertiary amine increased the CO₂ absorption capacity. At last, 3M DEEA + 1M MAPA seemed to be the most promising blend due to its high CO₂ absorption capacity (2.72 mole CO₂/kg solution) and cyclic CO₂ capacity (2.06 mole CO₂/kg solution).

Acknowledgements

The work is done under the CLIMIT-program (grant 243620/E20), project Low Energy Penalty Solvents (LEPS). We would like to thank the Research Council of Norway for financial support.

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