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Performance of MAPA promoted tertiary amine systems for CO_2 absorption: Influence of alkyl chain length and hydroxyl groups

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Abstract

Absorption and desorption of CO_2 into five aqueous tertiary amine solvents and their blends with MAPA were studied using a screening apparatus. Results showed that MAPA significantly enhanced both CO_2 absorption rate and absorption capacity. The solvent system with the highest CO_2 absorption capacity and cyclic CO_2 capacity was 3M DEEA + 1M MAPA with a CO_2 loading of 2.72 mole CO_2/kg solution and a cyclic CO_2 capacity of 2.06 mole CO_2/kg solution. For both the single and the blended systems, the CO_2 absorption capacity decreased when increasing the number of ethanolamine 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 CO_2 absorption capacity increased.

Keywords: CO_2 capture; amine solvent; screening; absorption capacity; cyclic capacity

1. Introduction

In light of rising atmospheric CO_2 concentration and that consequences of global warming are steadily becoming more evident, strong mitigation actions are needed. Among the options for CO_2 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 CO_2 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 CO_2 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-Ethyldietanolamine (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.
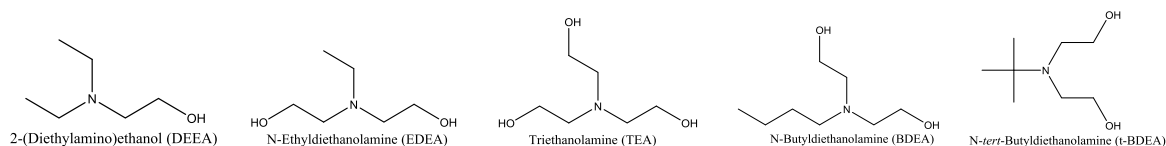

Figure 1. Molecular structure of the studied tertiary amines

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-*tert*-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, CO_2 absorption capacity and CO_2 absorption rates were measured by bubbling a gas mixture, containing 10 vol% CO_2, through the solution at 40 °C. The absorption experiment automatically terminated when the CO_2 concentration in the effluent reached 9.5 vol%, i.e. 9.5 kPa partial pressure of CO_2. 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% CO_2, i.e. 1.0 kPa partial pressure of CO_2.

After each experiment, a liquid sample was taken to determine the CO_2 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 $BaCO_3$, 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 CO_2 liquid analysis is the most accurate method to determine the CO_2 loading in the liquid phase, the CO_2 loadings from the liquid analysis were used in all the calculations. For instance, it was used to correct the final screening CO_2 loading, calculated based on the logged data from the screening absorption experiment, by multiplying the final screening CO_2 loading with the correction factor defined in equation 1.

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

The notation $\alpha_{\text{liquid sample}}$ and $\alpha_{\text{screening, final loading}}$ denotes the CO_2 loading determined by the precipitation-titration method and the final CO_2 loading calculated based on the logged data from the screening absorption experiment, respectively. The CO_2 loading resulted from the liquid analysis was also used to calculate the cyclic capacity by subtracting the lean CO_2 loading from the rich CO_2 loading.

At last, the experimental setup was validated by an experiment using 30 wt% aqueous MEA solution. The obtained CO_2 absorption capacity of 2.53 mole CO_2/kg solution was comparable to literature values [9].
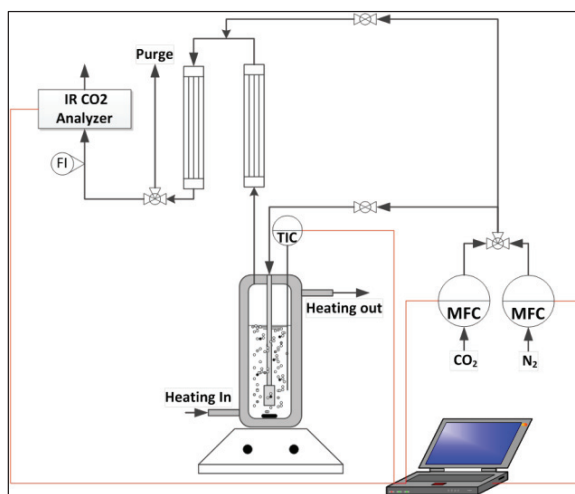

Figure 2. CO_2 absorption screening apparatus [10]

3. Results

3.1. Absorption of CO_2 into single amines

The change in absorption rate for single amine solvents versus CO_2 loading is demonstrated in Figure 3.
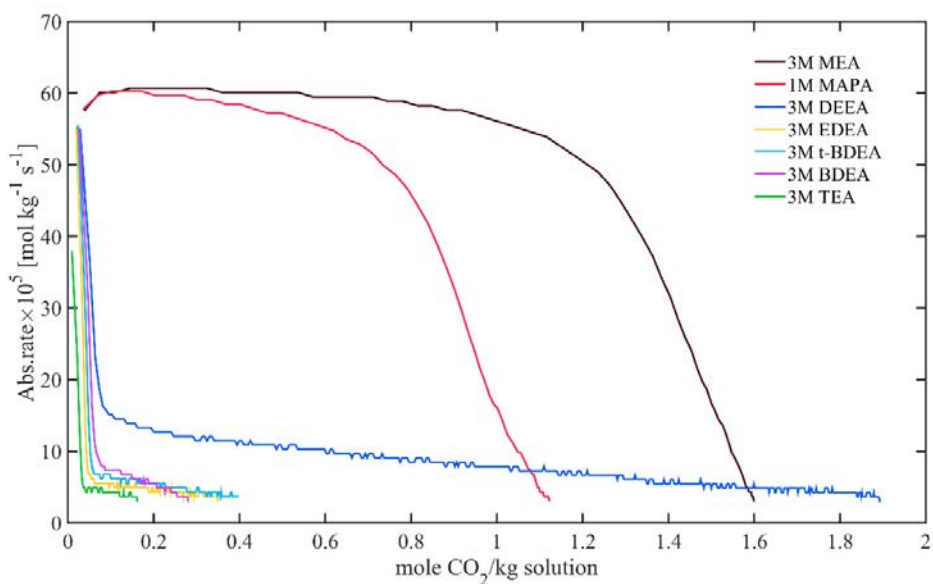

Figure 3. CO_2 absorption rate and capacity for single amine solvents.

For the whole CO_2 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 CO_2/kg solution and 0.6 mole CO_2/kg solution, respectively. At these CO_2 loadings the rates started to decrease rapidly.

Among the studied amines, 3M DEEA solution showed the highest absorption capacity with a CO_2 loading of 1.89 mole CO_2/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 CO_2 loading range from 0.77 to 0.82 mole CO_2/mole amine in the pressure range of 9.25 kPaCO_2 to 16.09 kPaCO_2. This is comparable to our result when taking the higher amine solution concentration into account. Further, the overall trend in increasing CO_2 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 CO_2 absorption capacity than MEA [13]. However, due to the lower molar concentration it showed a lower CO_2 loading in unit of mole CO_2/kg solution. Arshad et al. [14] performed calorimetric measurements of 2M MAPA solution and found that the CO_2 loading ranged from 0.94 mole CO_2/mole amine to 1.58 mole CO_2/mole amine in the pressure range of 0.3 kPaCO_2 and 328.5 kPaCO_2. This is in accordance with our result as the CO_2 loading at 1M MAPA was found to be 1.12 mole CO_2/kg solution.

The influence of molecular structure on CO_2 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 CO_2/kg solution to 0.16 mole CO_2/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 CO_2 absorption environment. El Hadri et al. [15], who performed a CO_2 absorption screening experiment of 30 wt% DEEA and 30 wt% TEA solutions, found the same

trend. Further, the CO_2 absorption capacity also decreased from 0.35 mole CO_2/kg solution to 0.28 mole CO_2/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 CO_2/kg solution to 0.40 mole CO_2/kg solution.

3.2. Absorption of CO_2 into MAPA promoted tertiary amines

Figure 4 shows the change in CO_2 absorption rate for MAPA promoted tertiary amines versus CO_2 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.
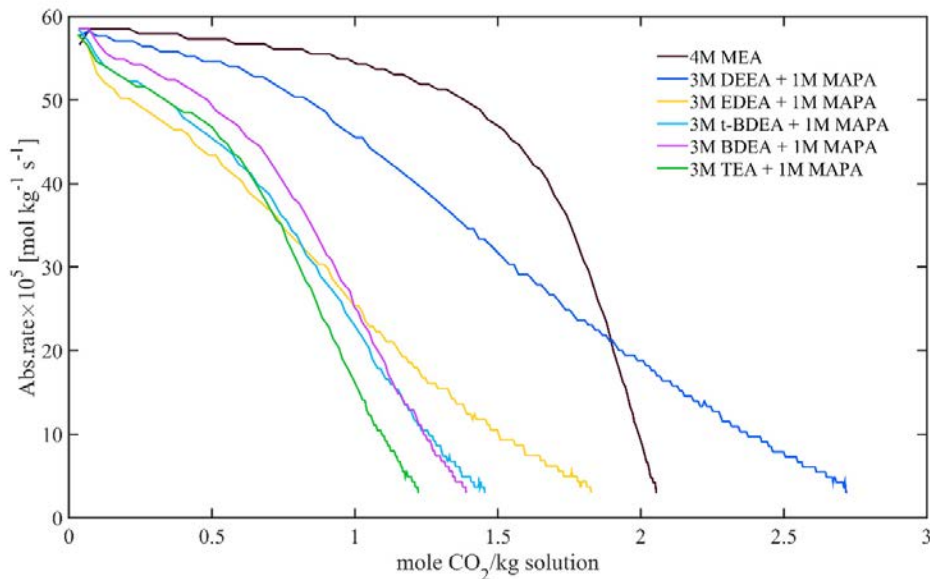

Figure 4. CO_2 absorption rate and capacity for MAPA promoted tertiary amines

The blended systems showed a considerably higher CO_2 absorption rate than the single tertiary amines given in Figure 3. For instance, at CO_2 loading 0.5 mole CO_2/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 CO_2 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 CO_2/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 CO_2/ kg solution, while 3M TEA (see Figure 3) showed an absorption capacity of 0.16 mole CO_2/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 CO_2 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 CO_2 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 CO_2 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 CO_2 absorption capacity was 43 %.

3.3. Cyclic capacity of single and blended amines

In Figure 5, the cyclic CO_2 capacity of the single and the blended amine solvent systems are compared. All the blended systems showed a higher cyclic CO_2 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 CO_2/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 CO_2 more easily than 4M MEA as it bounded less CO_2 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 CO_2/kg solution) and 3M DEEA (1.73 mole CO_2/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 CO_2 capacity than the sum of the single parent amines. This blended system also showed the largest improvement in cyclic CO_2 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 CO_2 capacity and the order of increasing CO_2 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 CO_2 capacity.
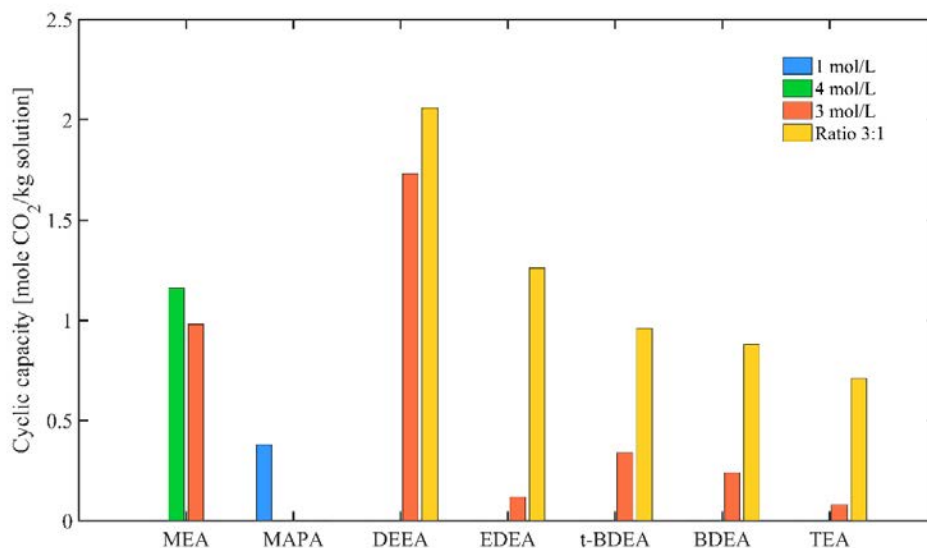

Figure 5. Cyclic CO_2 capacity of single and blended tertiary amine systems

4. Conclusions

In this study, CO_2 absorption rate, CO_2 absorption capacity and CO_2 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 CO_2 absorption capacity. Further, introduction of hindrance in the alkyl chain of the tertiary amine increased the CO_2 absorption capacity. At last, 3M DEEA + 1M MAPA seemed to be the most promising blend due to its high CO_2 absorption capacity (2.72 mole CO_2/kg solution) and cyclic CO_2 capacity (2.06 mole CO_2/kg solution).

Acknowledgements

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