

Absorption and Desorption Study of Alkylamine Promoted DEEA Solvents for CO₂ Capture

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Three primary and two secondary mono-alkylamines, and a di-alkylamine (3-(Methylamino)propylamine, MAPA) were investigated in blend with a tertiary amine (2-(Diethylamino)ethanol, DEEA). The aim of the study was to understand how structural features of the promoting amine influence CO₂ absorption and desorption performances. The blended systems were studied using a screening apparatus followed by quantitative ¹³C NMR spectroscopy.

Results showed that DEEA/MAPA obtained highest absorption capacity and fastest absorption rate, but also the highest amount of carbamate. Thus, the desorption process may be more energy demanding than for DEEA blended with secondary and sterically hindered alkylamines, which obtained the lowest amount of carbamate and highest amount of (bi)carbonate and amine. Nevertheless, due to high volatility of the alkylamines nonconventional process conditions are needed if they were to be used in an absorption and desorption process.

1. Introduction

Chemical absorption of CO₂ using amine solvents is a robust technology to remove CO₂ from flue gas of coal-fired power plants and from other large point sources such as iron and steel industry, cement production plants and refineries. However, an obstacle to large-scale implementation is the high energy consumption that leads to considerable increase in operating costs (Ho and Wiley, 2016). The energy can be reduced by both process optimization and development of new solvent systems (Neveux et al., 2013). A solvent system that often is proposed to reduce the energy requirement and improve the solvent performance consists in a combination of a tertiary amine and a primary or secondary amine. Tertiary amines are characterized by a slow reaction rate and high theoretical loading of 1 mol CO₂/mol amine (Eq(1)), while primary/secondary amines typically show fast reaction rate and low theoretical loading of 0.5 mol CO₂/mol amine (Eq(2)). Further, since the reaction leading to formation of (bi)carbonate (Eq(1)) is less exothermic than the reaction leading to formation of carbamate (Eq(2)), less energy is needed to regenerate tertiary amines than primary/secondary amines. Moreover, compared to primary amines, secondary and sterically hindered amines form less stable carbamate and, thus, carbamate hydrolysis is favored, which may lead to the stoichiometry observed in Eq(1) (García-Abuín et al., 2014).



In recent years, several tertiary amines have been suggested as potential candidates to be used in blend with primary/secondary amines, which usually work as rate promoters (Liang et al., 2015). However, so far, only a few new promoters have been suggested as potential candidates, indicating how difficult it is to find better promoters than those already known. Especially, two diamines, Piperazine (PZ) and MAPA, have received

great attention as they have shown higher absorption rate than 30 wt% MEA (Monteiro et al., 2014). However, the main drawbacks of MAPA are low resistance towards degradation and toxicity (Eide-Haugmo et al., 2011), whereas PZ suffers from limited solubility, toxicity and tendency to form nitrosamines when exposed to nitrogen oxide in flue gas (Dai et al., 2012). Therefore, there is the need to develop promoters that are more environmentally friendly and, in this regard, it is of high importance to understand how the structure of the promoting amine influences the solvent performance.

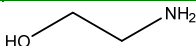
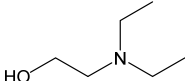
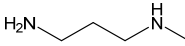
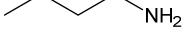
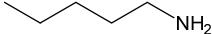

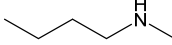
MAPA is a di-alkylamine consisting of both a primary and a secondary amine group, and has previously been used as a promoter for e.g. DEEA (Pinto et al., 2014) and Dimethyl-monoethanolamine (DMEA) (Brüder et al., 2012). The aim of this study is to investigate whether both amine functional groups of MAPA, when blended with DEEA, are necessary to obtain good absorption and desorption performances. In this work, MAPA/DEEA was used as a reference system and DEEA was studied in blend with different mono-alkylamines which have molecular structure similar to MAPA but with only one amino functional group i.e. a primary or a secondary amine (Table 1). The primary amines were Butylamine (BA), Pentylamine (PA) and Isopropylamine (IPA), in which the latter is sterically hindered, and the secondary amines were N-Methylbutylamine (MBA) and N-Methylpropylamine (MPA). The absorption and desorption performances of the amine blends were studied using a screening apparatus and, to obtain speciation data, NMR analyses were performed on each liquid sample withdrawn after the screening absorption experiment.

2. Materials and Methods

2.1 Materials

Chemicals used in this work were used without further purification (Table 1).

Table 1: chemicals used in this work

Chemical name	Structure	CAS	Purity	Supplier
Monoethanolamine (MEA)		141-43-5	≥99 %	Sigma-Aldrich
2-(Diethylamino)ethanol (DEEA)		100-37-8	≥99.5 %	Sigma-Aldrich
3-(Methylamino)propylamine (MAPA)		6291-84-5	≥97 %	Sigma-Aldrich
Butylamine (BA)		109-73-9	99.5 %	Sigma-Aldrich
Pentylamine (PA)		110-58-7	99 %	Sigma-Aldrich
Isopropylamine (IPA)		75-31-0	≥99.5 %	Sigma-Aldrich
N-Methylpropylamine (MPA)		627-35-0	96 %	Sigma-Aldrich
N-Methylbutylamine (MBA)		110-68-9	≥98 %	Merck Millipore
Carbon dioxide (CO ₂)	CO ₂	124-38-9	99.999 %	AGA
Nitrogen (N ₂)	N ₂	7727-37-9	99.998 %	AGA

2.2 Screening apparatus

The different amine blends (1.5M DEEA + 0.5M alkylamine) were studied using the screening apparatus illustrated in Figure 1. The apparatus is designed for atmospheric pressure and temperatures up to 80 °C, and gives information about the solvents CO₂ absorption rate, absorption capacity and cyclic capacity. A detailed description of the apparatus and experimental procedure can be found in a previous publication (Bernhardsen et al., 2018). Briefly, the reactor was filled with around 124 g of aqueous amine solution. Under continuous stirring with a magnet at 450 rpm, the absorption experiment was carried out at 40 °C followed by the desorption experiment at 80 °C. During the absorption experiment, a gas mixture containing 10 vol% CO₂ and 90 vol% N₂ was bubbled into the solution. The gas phase leaving the reactor was cooled and the CO₂ content was determined using a CO₂ analyser. The absorption experiment terminated when the effluent reached around 9.5 vol% CO₂ which represent an absorption process where 95% of the CO₂ is captured. During the desorption experiment, pure N₂ was bubbled into the solution to enhance the CO₂ removal. When the effluent reached 1.0 vol% CO₂, the experiment was terminated. After both the absorption and desorption experiment, a liquid sample was withdrawn for CO₂ and amine analyses. The CO₂ content was determined using the precipitation-titration method and the amine concentration was determined by titrating a diluted liquid sample with H₂SO₄ (see Ma'mun et al., 2006). The CO₂ loading obtained from the liquid analyses were used to

calculate the screening CO₂ cyclic capacity (Eq(3)) and to calculate a correction factor, defined in Eq(4), to correct the screening CO₂ loading calculated purely based on the gas flow rates and the reading in the CO₂ analyser. The average correction factor was 0.98 indicating that trusting CO₂ analyser gives slightly higher CO₂ loadings than the liquid analyser.

$$\text{screening cyclic capacity} \left[\frac{\text{mol CO}_2}{\text{mol amine group}} \right] = \alpha_{\text{abs,liquid sample}}(T=40 \text{ }^\circ\text{C}) - \alpha_{\text{des,liquid sample}}(T=80 \text{ }^\circ\text{C}) \quad (3)$$

$$\text{Correction Factor (CF)} [-] = \frac{\alpha_{\text{liquid sample}}}{\alpha_{\text{screening, final loading}}} \quad (4)$$

Furthermore, the experimental setup was validated by running 30 wt% MEA solution. The obtained CO₂ absorption capacity of 0.51 mol CO₂/mol amine was comparable to literature values (Aronu et al., 2011). At last, it must be emphasized that the absorption rate obtained were only semi-quantitative. This is because it is not possible to ensure that the gas-liquid interfacial area and the bubble structure are the same in all experiments.

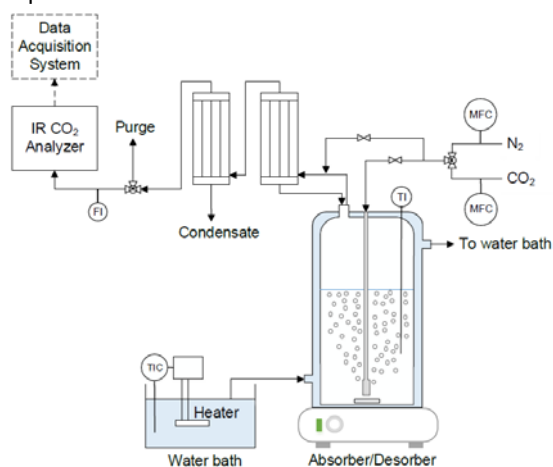


Figure 1: Screening apparatus. Reprinted with permission from Bernhardsen et al. (2018). Copyright © (2018), Elsevier.

2.3 NMR spectroscopy

A certain amount of the liquid sample, collected after the screening absorption experiment, was inserted in an NMR tube for NMR analyses. Each NMR experiment was performed at 300.0 K on a Bruker 600 MHz Avance III HD equipped with a 5-mm cryogenic CP-TCI z-gradient probe. Identification of the structure of the species in the reaction mixtures was performed by means of qualitative 1D and 2D-NMR experiments, whereas the determination of the corresponding concentrations was performed by quantitative ¹³C NMR measurements. The spectra for the quantitative analyses were acquired with the inverse gated decoupling acquisition sequence, using a recycle delay time of 120 s, a pulse width of 11.4 μs (90° pulse angle) and 256 scans. Deuterated water was used as “lock” solvent and was inside a coaxial insert, whereas Acetonitrile was chosen as internal reference standard. The method is described in detail in Perinu et al. (2018). All species identified and quantified in the solutions are reported in Figure 2.

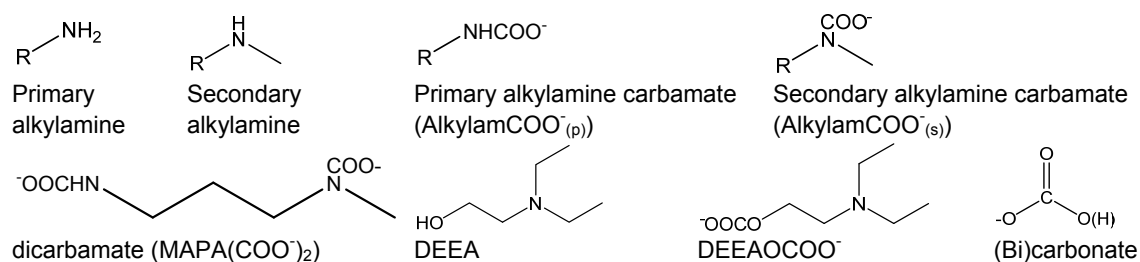


Figure 2: Species identified in DEEA/alkylamine solutions

The fast proton-exchanging species, such as free alkylamine/protonated alkylamine, DEEA/DEEAH⁺, HCO₃⁻/CO₃²⁻ appear as a common peak in the ¹³C NMR spectra because the proton-exchange is faster than the NMR time scale. Then, we here report the concentrations as the sum of free and protonated form of each species.

3. Results and discussion

In Figure 3, the screening absorption capacity and the amount of alkylamine and CO₂ derivative species found in the blended systems after the absorption experiment are reported. Among the mono-alkylamines blended with DEEA, the secondary amines, MPA and MBA, and the sterically hindered amine, IPA, showed similar speciation content and absorption capacity which was higher than that of the primary alkylamines, BA and PA. The amine carbamate in the secondary and sterically hindered alkylamine blends was present in concentration lower than in the primary alkylamine blends, whereas (bi)carbonate and free alkylamines were present in higher concentrations. Thus, for these blends, a higher amount of (bi)carbonate led to higher absorption capacity. Moreover, a higher ratio of (bi)carbonate over carbamate is favourable as it would require less energy to reverse the reactions during the desorption process.

Concerning the reference system DEEA/MAPA, it obtained the highest absorption capacity. This may be due to the two amino functional groups present in MAPA, which can both directly react with CO₂ to form amine carbamate species, i.e. primary MAPA carbamate (AlkylamCOO⁻_(p)), secondary MAPA carbamate (AlkylamCOO⁻_(s)) and the dicarbamate (MAPA(COO⁻)₂).

When comparing the speciation in DEEA/MAPA and DEEA/mon-alkylamines, it can be seen that the amount of AlkylamCOO⁻_(p) and AlkylamCOO⁻_(s) present in the DEEA/MAPA is similar to the amount of the corresponding carbamates present in the other blends; whereas the amount of (bi)carbonate is similar to the primary alkylamine blends. Further, the amount of alkylamine/alkylamineH⁺ after CO₂ absorption is lower in DEEA/MAPA than present in the other blends. This might be related both to the fact that MAPA has two amino functional groups (for the direct reaction with CO₂) and to the basicity of each amine. As reported in Perinu et al. (2018), if the pKa of a tertiary amine is higher than pKa1 or pKa2 of MAPA (pKa1=10.59 and pKa2=8.60) (Bernhardsen et al., 2018), the tertiary amine may lead the protonation process, prompting the increase of the availability of MAPA to further react with CO₂. In DEEA/MAPA, DEEA can react as described as the pKa value of DEEA (9.84) is higher than pKa2 of MAPA (8.60). In the other blends, the pKa value of the alkylamines (~10.60) (SciFinder Scholar™, 2016) is higher than the pKa value of DEEA and, then, compared to DEEA/MAPA, more alkylamines will be protonated and not available for CO₂ reaction.

At last, DEEAOCOO⁻ (DEEA carbonate) were present in all solutions, but due the low amount it was not considered to be relevant in this work.

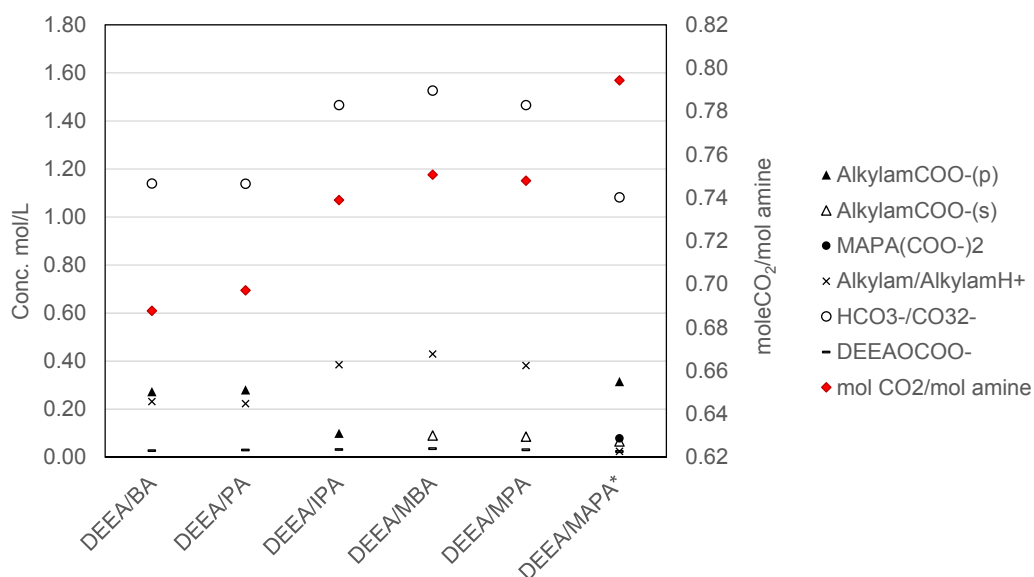


Figure 3: Speciation data and CO₂ loading of DEEA/alkylamine blends. (p) is primary and (s) is secondary. *CO₂ loading and NMR data published in Bernhardsen et al. (2018) and Perinu et al. (2018), respectively.

In Table 2, the screening cyclic capacity of the studied solvents is tabulated. The screening cyclic capacity is calculated as given in Eq(3) and even though a low desorption temperature (80 °C) is used, the method give realistic cyclic capacities for well-known amines like 30wt% MEA (Hartono et al., 2017). However, the screening experiments are mainly used in comparative solvent studies and the absolute values should always be confirmed with more dedicated experiments. During the desorption experiment for DEEA/IPA, DEEA/MBA and DEEA/MPA, the disadvantage of high volatility of alkylamines was clear. After the desorption experiment, the solvent concentration of DEEA/IPA, DEEA/MBA and DEEA/MPA was 15 %, 4 % and 5 % lower, respectively, than their initial starting concentration even though two coolers were used to prevent evaporation (see Figure 1). To overcome the challenge of high volatility process conditions similar to the chilled ammonia process (Han et al., 2013) and/or additional process units to minimize the loss of solvents would be needed. Negligible solvent loss (1-2 %) was instead observed for DEEA/PA, DEEA/BA and DEEA/MAPA. Among them, DEEA/MAPA obtained the highest screening cyclic capacity.

Table 2: screening cyclic capacity of DEEA/alkylamine solvents

Solution	Cyclic capacity [mol CO ₂ /mol amine]
1.5M DEEA + 0.5M PA	0.51
1.5M DEEA + 0.5M BA	0.49
1.5M DEEA + 0.5M IPA	0.54
1.5M DEEA + 0.5M MBA	0.54
1.5M DEEA + 0.5M MPA	0.52
1.5M DEEA + 0.5M MAPA	0.61

Figure 4 shows the CO₂ absorption rate as a function of the CO₂ loading in unit of mol CO₂/mol amine. As mentioned above, the screening absorption rate only gives a rough estimate of how fast solvents react with CO₂. However, it is noticeable that addition of alkylamines to 1.5M DEEA significantly enhanced the CO₂ absorption rate, and that during the CO₂ absorption, DEEA/MAPA obtained the highest average CO₂ absorption rate. Among the other alkylamine blends, the secondary alkylamines showed a slightly higher absorption rate than the primary alkylamines throughout the CO₂ loading range, but lower than the commercially used 30 wt% MEA.

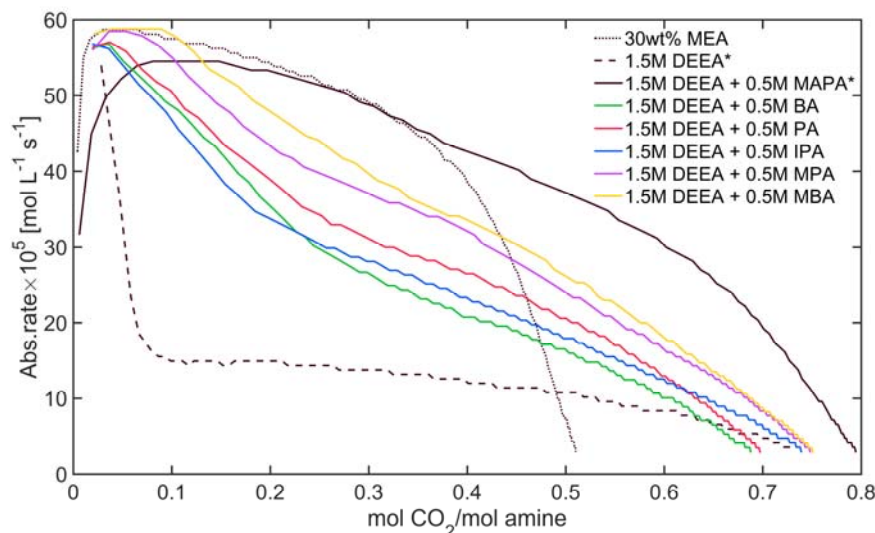


Figure 4: CO₂ absorption rate and absorption capacity at 40 °C. *Published in Bernhardsen et al. (2018)

4. Conclusions

In this study, the influence of the di-alkylamine MAPA and five mono-alkylamines in blend with DEEA on the CO₂ capture performance was studied using a screening apparatus followed by NMR analyses. Among the studied systems, DEEA/MAPA showed greatest CO₂ performance in terms of CO₂ absorption capacity and CO₂ absorption rate, but the desorption process may be the most energy demanding as the amount of carbamate was the highest. Secondary and sterically hindered alkylamines blended with DEEA obtained

lowest amount of amine carbamate and highest amount of (bi)carbonate and amine. However, due to high volatility of the alkylamines, extensive water/acid wash would be needed which increases the operational costs. Also, when exposed to nitrogen oxide in the flue gas, secondary amines form nitrosamines and proper solvent management are required to limit/avoid contaminations.

Acknowledgments

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