

Reversible carbon dioxide capture by aqueous and non-aqueous amine-based absorbents: a comparative analysis carried out by ^{13}C NMR spectroscopy

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Abstract

The efficiency of CO_2 uptake by the amines 2-(2-aminoethoxy)ethanol (DGA), 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-methyl-1-propanol (AMP), 2,2'-iminodiethanol (DEA) and 2-(butylamino)ethanol (BUMEA) has been investigated either in aqueous and in 2-(2-methoxyethoxy)ethanol (DEGMME) solutions and compared with 30% aqueous MEA. Batch experiments were carried out to measure the CO_2 loading capacity of the different amine solutions and the rate of CO_2 absorption. The ^{13}C analysis has been applied to identify and quantify the carbonated species in solution upon CO_2 uptake. The efficiency of CO_2 (15% in air) capture was measured in continuous cycles of absorption (40 °C) and desorption (110 °C) carried out in packed columns at room pressure. The efficiency of the aqueous absorbents is greater than 90% and overcomes that in DEGMME. The CO_2 absorption heat of aqueous BUMEA and DGA in DEGMME calculated using Gibbs–Helmholtz equation was found to be lower than that of conventional 30% aqueous MEA: the possible advantages of these systems with respect to aqueous MEA as CO_2 absorbents have been discussed.

Keywords

carbon dioxide capture • heat of CO_2 reaction • alkanolamine • ^{13}C NMR speciation • amine carbamates

1. Introduction

Chemical absorption has been recognized as the most efficient technology to separate CO_2 from flue gases and aqueous alkanolamines scrubbing is the most mature technology and the only that has been applied in commercial scale for many years to remove CO_2 from industrial gas streams [1-7]. In particular 30% (wt scale) aqueous MEA is the most proven technique for sequestering large amounts of CO_2 in hydrogen and

ammonia plants, natural gas processing and in the process of post-combustion CO₂ capture and storage (CCS technology) [8-12]. However, the MEA technology suffers of some critical limitations mainly due to the high energy cost of amine regeneration and to the environmental concerns because of the amine thermal and oxidative degradation [13-16]. Therefore, when proposing any new CO₂ capture process, it should be mandatory to reduce the energy costs by adopting absorbent systems capable of minimizing one or more of the drawbacks of aqueous MEA without reducing its advantages. The ultimate goal should be to increase the net balance of CO₂(captured)/CO₂(emitted), where CO₂(emitted) represents the overall amount of CO₂ released by burning fossil fuels to produce all forms of energy (electrical, thermal and mechanical) necessary to sustain the entire CO₂ removal cycle from the production of the absorbing reagents to the final transport of CO₂ and its disposal, which has to be taken into account for a reliable cost-to-benefit assessment. In an effort of formulating new absorbents, we have reported in recent papers some experimental studies on the CO₂ capture by non-aqueous alkanolamines [17-19] and by extending these studies it seemed to us interesting to investigate the features of some selected alkanolamines with the objective of establishing a correlation between the chemical structures of the different amines with their performances and with the chemistry of the CO₂ absorption either in aqueous and in non-aqueous solutions. A deeper understanding of the speciation equilibria in solution can provide useful information about the absorbent behaviour as a function of the structural properties of the amines, of amine/CO₂ ratio, relative CO₂ pressure, temperature and liquid flow rate. To this purpose, in this work we have designed two sets of experiments: (1) batch experiments aimed at measuring the CO₂ loading capacity and the rate of CO₂ capture; (2) continuous cycles of CO₂ absorption and absorbent regeneration carried out in packed columns. We used ¹³C NMR spectroscopy, a powerful non-invasive analytical technique that allowed us to identify and in some cases quantify the carbonated species in the solution equilibria originated by CO₂ absorption [20-23]. The alkanolamines we have selected for the experimental study are 2-aminoethanol (monoethanolamine, MEA), 2-(2-aminoethoxy)ethanol (diethylene glycol amine, DGA), 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-methyl-1-propanol (AMP), 2,2-iminodiethanol (diethanolamine, DEA) and 2-(butylamino)ethanol (BUMEA). The 2-(2-methoxyethoxy)ethanol (diethylene glycol monomethyl ether, DEGMME) was used as non-aqueous solvent because of the solubility of most of the carbonated compounds in this solvent, the high boiling temperature and low viscosity of the solutions. The primary amines MEA, DGA and the secondary amines DEA and BUMEA are expected to react quickly with CO₂ in both aqueous and non aqueous solutions whereas a lower reactivity is anticipated for the more sterically hindered primary amines AMP and AMPD. To maximize the efficiency of any regenerative process of CO₂ capture, it is necessary to combine a high loading capacity with high absorption and desorption efficiency during the continuous absorption-desorption process where neither the regenerated absorbent is saturated by CO₂ nor the carbonated absorbent is fully regenerated and consequently the kinetic features of the different absorbents might prevail over the thermodynamic ones. The heat of absorption of the most performing solutions, aqueous BUMEA and DGA in DEGMME, has been calculated by the Gibbs-Helmholtz equation and compared to that of conventional aqueous MEA solution. To the best of our knowledge the heat of CO₂ absorption, based on experimental data of equilibrium

CO₂ partial pressure at different temperature and at the same CO₂ loadings, has never been determined for non-aqueous systems.

2. Experimental section

2.1. General information

All the amines and the diethylene glycol monomethyl ether (Sigma-Aldrich) were reagent grade and were used as received without further purification. Gas mixture of 15% CO₂ and air (Rivoira Spa) was used to simulate the flue gas. A gas mass flow meters (Aalborg) equipped with gas controllers (Cole Parmer) was used to measure the gas flow rate. The inlet and outlet CO₂ concentrations in the flue gas mixture were measured with a Varian CP-4900 gas chromatograph calibrated with 15% and 40% v/v CO₂/air reference mixture (Rivoira Spa) and 100% CO₂ reference gas (Sapio Sr). Aqueous and organic amine solutions tested were fixed at overall 3.00 mol dm⁻³ and were compared with 30% wt (4.90 mol dm⁻³) aqueous ethanolamine (MEA).

2.2. Batch experiments of CO₂ absorption

The CO₂ loading of the different amine solutions (mol CO₂ captured/mol amine) were determined with a home-made glass cylinder with a diameter of 56 mm and a height of 300 mm, kept at 40 °C by means of a thermostatted bath (Julabo model F33-MC bath). The absorber was charged with 0.100 dm³ of the sorbent and was continuously fed from the bottom with pure CO₂, through a sintered glass diffuser (16-40 μm pores). The absorption was stopped when the solution was saturated and no more CO₂ was absorbed. A cold condenser brought to -5 °C avoids solvent loss during the sorbent carbonatation. From the weight increase of the CO₂ saturated solution, we computed the maximum amine loading capacity.

In order to obtain the heat of CO₂ absorption of aqueous BUMEA and DGA in DEGMME, several experiments to measure the CO₂ equilibrium solubility were carried at CO₂ partial pressures in the range 10.13–101.33 kPa and temperatures in the range 20-40°C. The absorber was charged with 0.025 dm³ of the solution and was continuously fed from the bottom with the gas mixture of N₂ and CO₂ with the planned CO₂ partial pressure. The flow rate of inlet gas was kept at 15.0 dm³ h⁻¹ to avoid the possibility of amine loss or foaming. A cold condenser was equipped to avoid solvent loss during the sorbent carbonatation. The desired temperature was maintained by means of a thermostatted bath. A schematic representation of the apparatus used is shown in Figure 1. The absorption was stopped after 8 hours, to ensure that equilibrium was reached. The CO₂ content of the liquid sample was measured by adding aqueous HCl, using a gastight apparatus which comprises a 0.050 dm³ conical flask containing 0.010 dm³ of the saturated solution. The system was equipped with a pressure-equalising dropping funnel containing 3M HCl solution and connected to two 0.250 dm³ gas burettes equipped with a pressure-equalising device. Both burettes and pressure-equalising

devices were filled with CO₂ saturated water. Through three-way valves, one burette was filled with CO₂ while the other was emptied, thus allowing a continuous collection of gas. The gas pressures inside the burette and the external pressure continuously balanced each other. The total volume measurements were about $\pm 0.005 \text{ dm}^3$ accurate. A duplicate measurement of the CO₂ release was carried out for every solution.

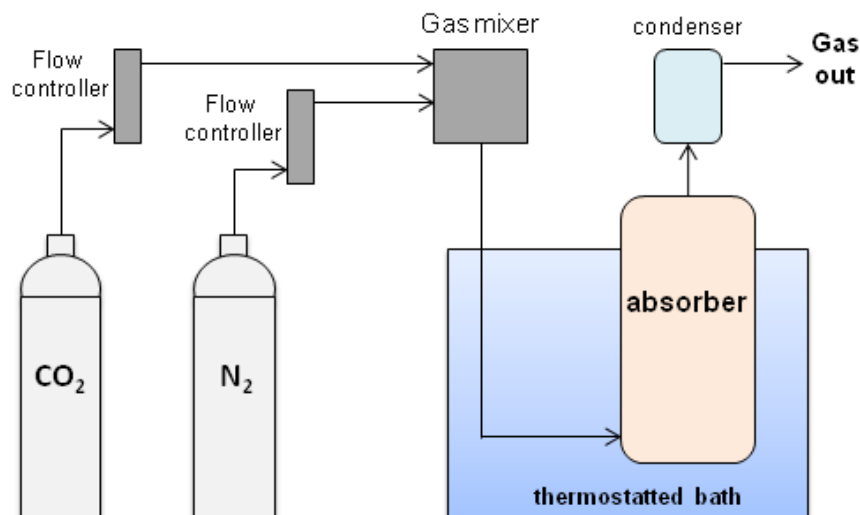


Figure 1. Schematic diagram of the apparatus for the CO₂ equilibrium solubility measurement.

The batch experiments designed to measure the CO₂ absorption as a function of time were carried out with a gastight apparatus which comprises a 2.0 dm³ flask (actual volume 2.295 dm³) equipped with a digital pressure gauge, magnetic stirrer and a pressure-equalizing dropping funnel containing the appropriate amount (0.045 mol) of amine solution (0.0095 dm³ of 30% wt aqueous MEA, 0.015 dm³ of all the other solutions). After the air was removed with a vacuum pump, the flask was filled with pure CO₂ at room pressure. This operation was repeated five times before the final one. After the amine solution was quickly introduced from the funnel into the flask, the stirring was started. The decrease in pressure, measured by the pressure gauge, enabled us to estimate the CO₂ absorption as a function of time. The temperature of the flask was maintained constant to 25 °C during the reaction with a water bath. The experiment was stopped when the pressure did not change with time (about 50 min).

2.3. Continuous cycles of CO₂ absorption-desorption

The apparatus used for the continuous absorption-desorption cycles consists of an absorber and a desorber units connected to each other by means of a double head peristaltic pump (Masterflex), which allows the solutions to circulate continuously at the desired flow rate (in our experiments, in the range between 0.015 and 0.66 dm³ h⁻¹). A simplified scheme is reported in Figure 2. The absorber and desorber devices are two home-built glass cylinders with the internal diameter of 56 mm and height 400 mm, equipped with a jacket. The columns were packed with glass rings (diameter 5 mm). The temperature of both absorber (40 °C) and desorber (110 or 150 °C) was maintained at the appropriate value by circulating a thermostatted liquid (Julabo model F33-MC bath) through the jackets. Due to the endothermic reaction of CO₂ release, the

temperature of the desorption column was 2.5-5.0 °C below that of the heating jacket. The exothermic acid-base reaction allowed to maintain the absorber temperature at the designed values and no cooling was required. The absorber was designed to operate in a counter current mode: the regenerated amine solution was introduced from the top of the packed column while the gas mixture was continuously injected at the bottom of the column. The packing maximizes the exchange surface between the two phases and provides the reaction mixture with a sufficient residence time. The carbonated amine solution exiting from the bottom of the column was preheated by a cross heat exchanger (with hot regenerated amine solution exiting from the desorber which is in turn cooled before being recycled to the absorber) and was sent to the top of the desorber. The desorber was equipped with a water-cooled condenser to reflux the possible overhead vapour to the stripper. The entire apparatus was charged with 0.400 dm³ of each amine solution that had been previously 50% saturated with CO₂. To prepare these solutions, 0.200 dm³ of the appropriate amine solution were pre-saturated with pure CO₂ and, subsequently, mixed with the required volume of the free amine solution to obtain the overall solution.

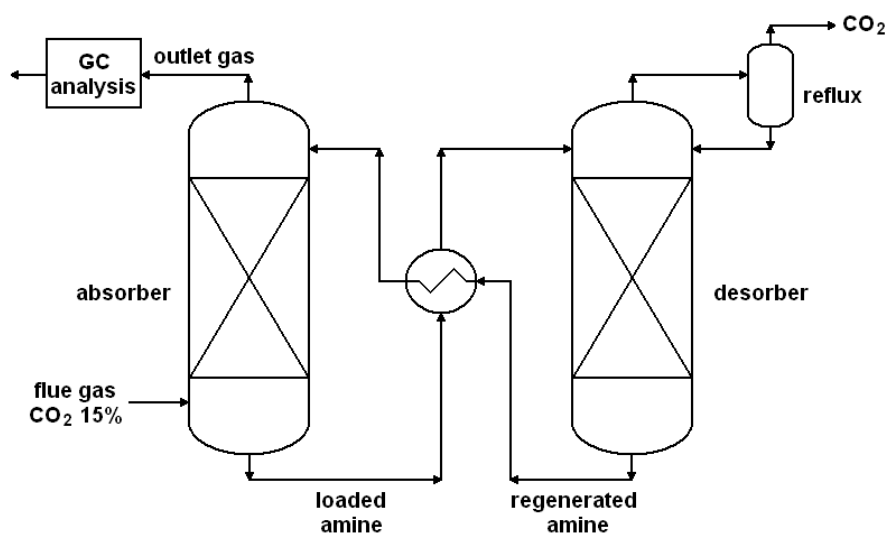


Figure 2. Simplified flow diagram of the absorber–stripper cyclic configuration.

To mimic the flue gas, we used 15% (v/v) CO₂ in air (overall pressure of the gas mixture set at 1.0 bar) which was solvent saturated before being injected into the absorber at a flow rate of 29.0 dm³ h⁻¹ (0.180 molCO₂ h⁻¹ at 22 °C). The vent gas from the top of the absorber was dried by flowing through a condenser cooled at -5 °C, a concentrated H₂SO₄ solution and a tower filled with P₂O₅, before being GC analyzed at intervals of 10 minutes. The stripped CO₂ was not recovered. A complete cyclic experiment lasted 24-36 h and it was stopped when the reactions of CO₂ capture and amine regeneration reached a steady state and the absorption efficiency did not change with time.

2.4. ¹³C NMR Spectroscopy

The ¹³C NMR spectroscopy is a technique that has been well applied in different studies to determine the concentrations of the species in the absorbent solutions [24,25]. In this work, the analysis were performed

with a Bruker Avance III 400 spectrometer operating at 100.613 MHz with a procedure that has been already described [26,27]. Chemical shifts are to high frequency relative to tetramethylsilane as external standard at 0.00 ppm, while CH₃CN was used as internal reference (CH₃, $\delta = 1.47$). To provide a good signal for deuterium lock, a sealed glass capillary containing D₂O (Aldrich) was introduced into the NMR tube with the amine solution. The pulse sequence with proton decoupling and NOE suppression was used to acquire the ¹³C{¹H} with the following acquisition parameters: pulse angle = 90.0°, acquisition time = 1.3632 s, delay time = 2-30 s, data points = 65K, number of scans = 250-500. The data were processed by using Bruker-Biospin Topspin software.

Increasing the acquisition time and/or the relaxation delay (up to 60 s) does not produce substantial changes in the relative peak areas of the –CH₂– carbon atoms that contain the same number of attached protons [28,29]. The relative amounts of carbamate and the rapidly equilibrating (free amine)/(protonated amine) have been estimated by peak integration for each –CH₂– resonance.

In order to quantify the relative amounts of carbamate and fast exchanging bicarbonate/carbonate ion, we carefully integrated the carbon resonances in the range 165–158 ppm. The ¹³C atoms of HCO₃⁻, CO₃²⁻ and of R'-CO₂⁻ functionalities have no attached hydrogen and show relaxation times longer than those of –CH₂– groups, thus resulting in lower intensity resonances. Notwithstanding, integration of the carbon resonances is an estimation (5% deviation) of the relative amounts of the species.

To evaluate the relative amount of carbonate and bicarbonate in solution with a procedure already described [30], reference solutions for calibrating the ¹³C NMR spectra were prepared by dissolving in D₂O pure Na₂CO₃, NaHCO₃, and accurately weighted mixtures of the two salts in different percentages. Chemical shifts of reference solutions are in ppm and the percentages of Na₂CO₃ are reported in parenthesis: $\delta = 168.10$ (100% neat Na₂CO₃); $\delta = 166.08$ (74.9%); $\delta = 164.09$ (50.0%); $\delta = 162.09$ (25.0%); $\delta = 160.25$ (0%, neat NaHCO₃).

The NMR spectra of all the experiments are available in the Supporting Information with the appropriate chemical shifts.

2.5. Heat of CO₂ absorption

The heat of the CO₂ absorption into the absorbent solution can be obtained in two different way: measured by experimental, using a calorimeter, or estimated with the Gibbs-Helmholtz equation [31,32]. As reported also by an increasing number of papers [33-35], in this work the heat of CO₂ absorption in each solution has been calculated by employing the Gibbs-Helmholtz equation using experimental data of CO₂ partial pressure at different temperature and at the same CO₂ loadings, as shown in eq. (1).

$$\frac{d(\ln(P_{CO_2}))}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_{abs}}{R} \quad (1)$$

where ΔH_{abs} represents the heat of CO₂ absorption (J mol⁻¹ of CO₂ absorbed), R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), P_{CO_2} is the partial pressure of CO₂ and T is the experiment temperature.

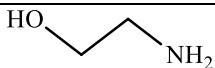
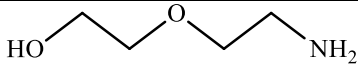
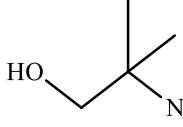
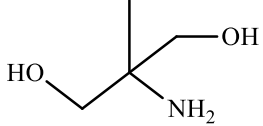
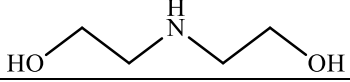
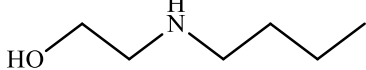
The heat of CO₂ absorption can be obtained from the slope of the plot between ln(P_{CO₂}) and 1/T. To validate the procedure, ΔH_{abs} of aqueous 30% MEA was calculated using this equation: the result value of -83.24 kJ mol⁻¹ well agree with other experimental values reported in literature [36-38].

3. Results and discussion

3.1. Chemical equilibria

The different amine solutions have been formulated to study how the reaction of CO₂ uptake changes with the variation of the solvent used and of the structure of the amine itself. Between the selected amine, 2-aminoethanol (MEA) and 2-(2-aminoethoxy)ethanol (diethylene glycol amine, DGA) are linear primary amines; 2-amino-2-methyl-1,3-propanediol (AMPD) and 2-amino-2-methyl-1-propanol (AMP) are still primary amines but with a steric hindrance near the amine functionality; 2,2-iminodiethanol (diethanolamine, DEA) and 2-(butylamino)ethanol (BUMEA) are secondary amines. The chemical structures of the tested amine are reported in Table 1.

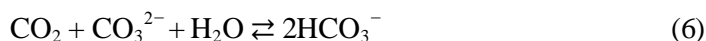
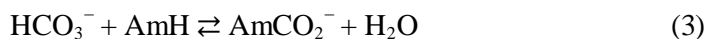
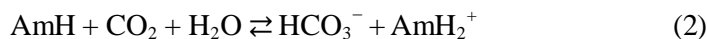
Table 1. Name, acronym and chemical structure of the selected alkanolamine.

2-aminoethanol	MEA	
2-(2-aminoethoxy)ethanol	DGA	
2-amino-2-methyl-1-propanol	AMP	
2-amino-2-methyl-1,3-propanediol	AMPD	
2,2'-iminodiethanol	DEA	
2-(butylamino)ethanol	BUMEA	

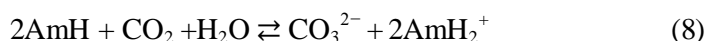
Beside the water, the most commonly used solvent, the choice of 2-(2-methoxyethoxy)ethanol (diethylene glycol monomethyl ether, DEGMME) as non-aqueous solvent was dictated by five main reasons: solubility of the carbonated compounds, high boiling temperature (194 °C), low cost, low viscosity (3.5 cP at 25 °C) and avoidance of foaming problems. As the combustion gases contain water, we have already found in previous studies that amines in organic solvents are tolerant toward moisture up to 5% (on volume scale) of water [39-41].

The concentrations of aqueous and organic amine solutions were fixed at overall 3.00 mol dm⁻³ (27 – 37% wt) and were compared with 30% wt (4.90 mol dm⁻³) aqueous 2-aminoethanol (MEA), the reference absorbent of any CO₂ capture technology. AMPD does not dissolve in DEGMME.

The CO₂ capture with aqueous solutions of amines entails several equilibria, the main reactions are:



where AmH indicates the free amine, AmCO₂⁻ and AmH₂⁺ indicate the amine carbamate and the protonated amine, respectively. The overall reactions (2) and (3) and, respectively, (2) and (4) can be rewritten as:



In the absence of water, only equation (7) can occur and CO₂ reacts with an excess of both primary and secondary amines yielding the amine carbamates.

3.2. Batch experiments of CO₂ absorption

The loading capacities measured by gravimetry (as described in section 2.2) of the different amines and the related variation of pH for aqueous solutions are reported in Table 2. Loading values are congruent with data reported in the literature [32,38].

Table 2. Physical properties of solutions and CO₂ loading measured at 40°C

amine	solvent	wt%	Conc. (mol dm ⁻³)	Density (g cm ⁻³)	Loading 40°C	pH ^a	
						start	end
MEA	H ₂ O	30.0%	4.9	1.005	0.63	12.5	8.1
DEA	H ₂ O	30.8%	3.0	1.030	0.68	11.8	8.0
	DEGMME	30.7%	3.0	1.046	0.52		
BUMEA	H ₂ O	36.7%	3.0	0.960	0.82	11.6	8.3
	DEGMME	36.3%	3.0	0.975	0.53		
DGA	H ₂ O	30.9%	3.0	1.015	0.66	12.5	8.0
	DEGMME	30.7%	3.0	1.031	0.57		
AMPD	H ₂ O	30.3%	3.0	1.049	0.73	10.7	8.1
AMP	H ₂ O	27.0%	3.0	0.982	0.88	12.4	8.0
	DEGMME	27.0%	3.0	0.999	0.49		

^a pH value of aqueous solutions at the beginning (start) and at the end of the loading experiment

As expected, the higher loading values (all > 0.5) are obtained in aqueous solution, thanks to the formation of bicarbonate [equations (2) and (5)] in addition to carbamate [equation (3)]. In the organic solvent, only the carbamate formation can occur, and the loading of each amine is close to the theoretical value 0.5 of the

equation (7); the additional 0.02-0.07 increases can be due either to the formation of small amounts of the neutral carbamic acid or to physical absorption.

In order to evaluate the distribution of the species in solution at the different steps of all the absorption experiments, samples of the solutions were checked by ^{13}C NMR spectroscopy. Figure 3 reports the ^{13}C NMR spectra of the CO_2 saturated aqueous amine solutions.

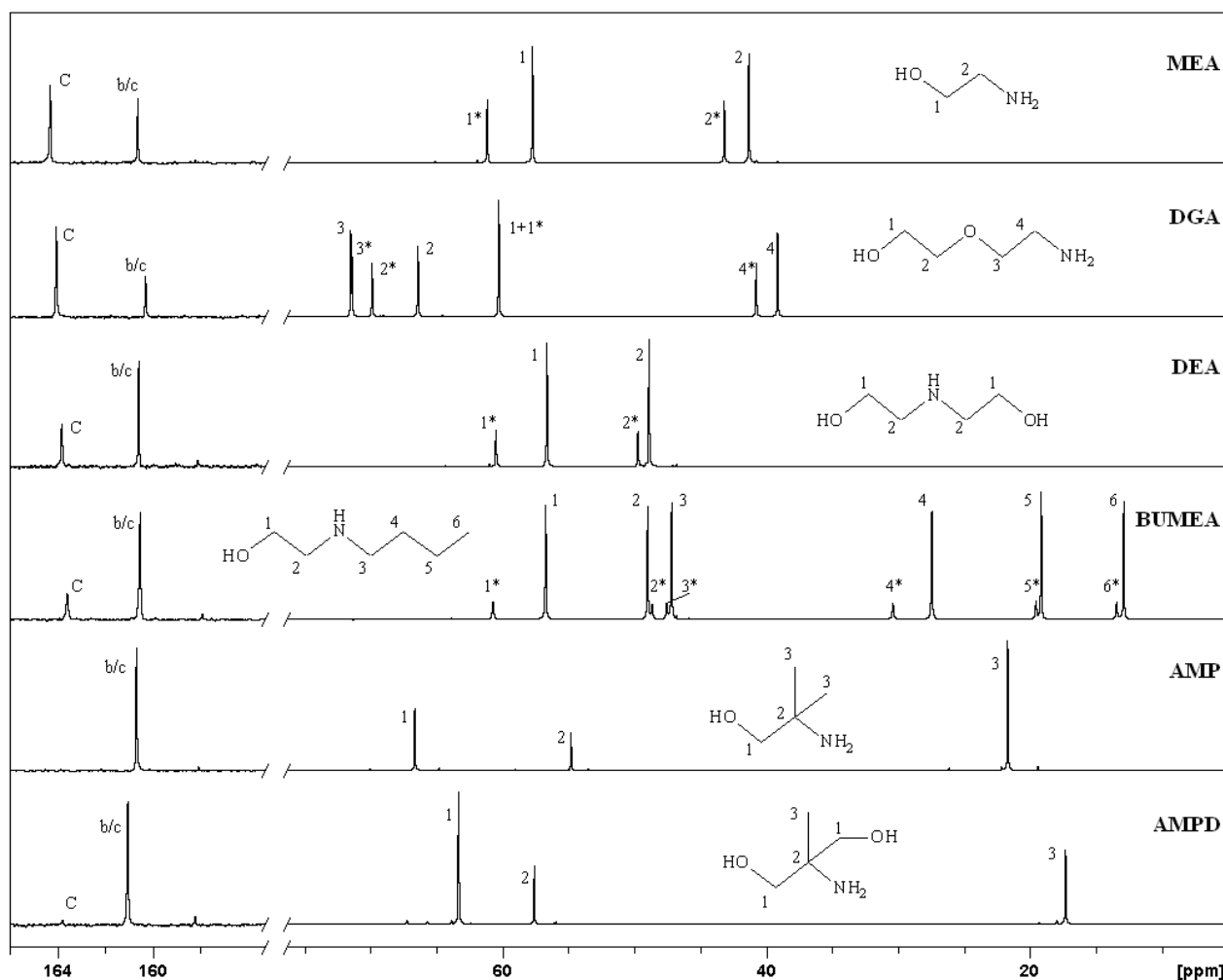


Figure 3. ^{13}C NMR spectra of the different aqueous amine solutions. The numbers indicate the carbon atom referred to both free and protonated amine fast exchanging in the NMR scale, assigned as reported in the relative amine structure. Asterisks denote the chemical shifts of carbon backbones of amine carbamate. C indicates the carbonyl atoms of amine carbamate, while *b/c* is referred to the signal of fast exchanging bicarbonate/carbonate ion. The intensity of the signals at 160-164 ppm is not in scale.

As can be observed from ^{13}C NMR spectra (Figure 3), the aqueous primary amines (MEA and DGA) react with CO_2 to form predominantly the amine carbamates. From the accurate integration of the peak signal of each $-\text{CH}_2-$ resonance we computed a percentage of carbamate ion of 36.7% for aqueous MEA and of 40.5% for DGA with respect to the overall amine. Similarly, from the peak integration of the carbonyl atoms in the range 158-165 ppm, we found 64-74% on molar scale of amine carbamate (MEA = 164.3 ppm; DGA = 164.0 ppm) with respect to the summed carbamate and the fast exchanging bicarbonate/carbonate ion (in the range

160.3-160.6 ppm), even with an excess of carbon dioxide. On the contrary, there is a prevalence of the bicarbonate/carbonate ions (59-77% on molar scale) over the amine carbamate in the aqueous secondary amines DEA and BUMEA. The highest loading of BUMEA (0.82) is the consequence of the formation of about 77% (on molar scale) of bicarbonate, as obtained by the quantitative analysis of the ^{13}C NMR spectra based on the integration of the corresponding signals at about 163.6 and 160.5 ppm, respectively. However, there is no clear relationship between the different loading of BUMEA and DEA with their molecular structures and basic strength that are quite similar to each other.

The absorption of CO_2 in the aqueous solutions of the sterically hindered primary amines AMP and AMPD leads to the formation of almost entirely bicarbonate, with negligible amounts of carbamate, as shown by the respective ^{13}C NMR spectra (Figure 3) and reported in literature [42]. The CO_2 loading of AMP, lower than the theoretical value (0.88 instead of 1.0) may be explained by the thermodynamic equilibrium that decreases on decreasing the pH value because of increasing of the protonated amine. It has been already reported that the CO_2 loading decreased on increasing the amine concentration [43].

The formation of significant amount of carbonate [equation (8)] can be safely ruled out because of the small concentration of residual free amine and by the excess of CO_2 [equation (6)] and is confirmed by the chemical shift at 160.9 ppm indicative of nearly 100% bicarbonate [30] (see section 2.4). The lower loading of AMPD is presumably related at the lower alkalinity of the AMPD solution with respect to AMP solution (Table 2).

In organic solvent, besides the most intense signals due to the carbon backbones of the DEGMME (5 signals, chemical shifts at 72.8, 71.7, 70.0, 60.8 and 58.1 ppm), the peaks of both (free amine)/(protonated amine) and amine carbamate present similar intensity, and the relative percentages of carbamate ion are near to the theoretical value of 50%.

As an example, the spectrum of BUMEA in DEGMME has been reported in Figure 4.

Furthermore, a very weak signal at about 158-159 ppm was observed in the ^{13}C NMR spectra of CO_2 loaded aqueous AMP and AMPD and in either aqueous and organic DEA and BUMEA: this peak should correspond to a very small amount of amine carbonate (AmOCOO^-), formed by the reaction of the hydroxyl group of the amine with CO_2 [44,45].

To evaluate the CO_2 absorption by the different amine solutions as a function of time, the experiments were carried out at 25 °C in a 2.0 dm³ flask containing the same amount (0.045 mol) of the different amines and a fixed amount of pure CO_2 that was in excess (about 2:1) with respect to amine. The airtight flask is equipped with an electronic pressure gauge and a magnetic stirrer. From the pressure decrease during the experiment, the amount of absorbed CO_2 was measured as a function of time. The experiment was stopped after 50 min when the pressure did not change with time and the steady state was reached. The percentage of CO_2 absorbed by aqueous and organic amine solutions with respect to that contained in the flask is reported as a function of time in Figure 5A.

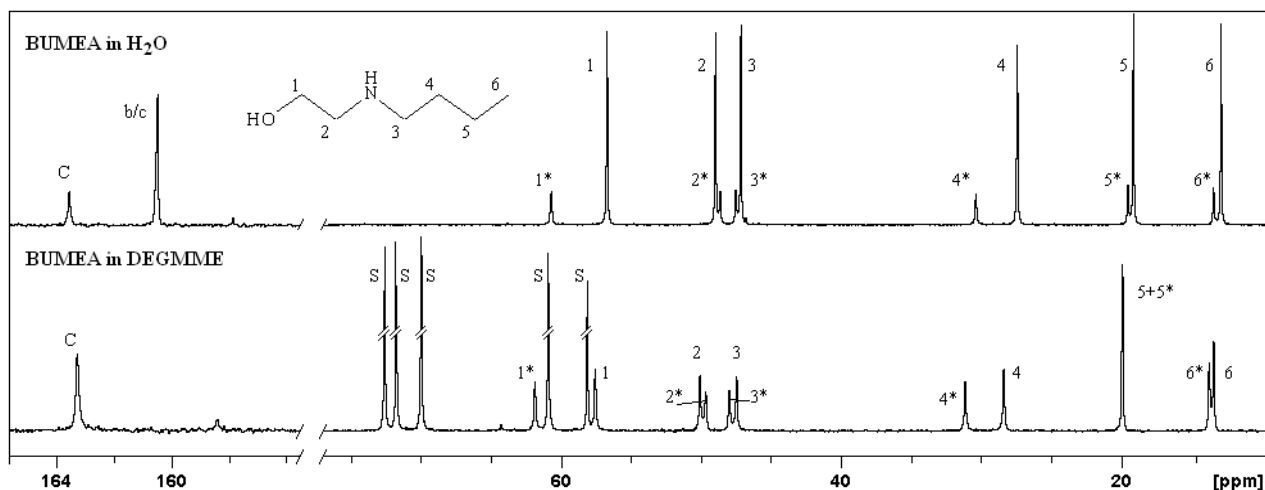


Figure 4. ^{13}C NMR spectra of the BUMEA solutions in water and in DEGMME. The numbers indicate the carbon atom referred to both free and protonated amine fast exchanging in the NMR scale, assigned as reported in the relative amine structure. Asterisks denote the chemical shifts of carbon backbones of amine carbamate. C indicates the carbonyl atoms of amine carbamate, while *b/c* is referred to the signal of fast exchanging bicarbonate/carbonate ion. S indicates DEGMME signals. The intensity of the signals at 160-164 ppm is not in scale.

In general, the rate of CO_2 uptake by the different amines at the beginning of the experiment is rather high with the exception of the aqueous AMPD, AMP and DEA (Figure 5B), and the rate in DEGMME is higher than in water with the exception of BUMEA. The latter result clearly indicates that the formation of the carbamate derivatives is more kinetically favourable than the bicarbonate/carbonate species, and this feature explains the low reaction rate of aqueous AMP and AMPD that form negligible amounts of carbamate derivatives (Figure 3) because of the steric hindrance around the amino functionality. On the contrary, the carbamate of AMP and DEA are stable in DEGMME, whereas the carbamate of AMPD was obtained in the solid state and, consequently, no comparison could be carried out.

It should be noticed that each experiment starts with an excess of the amine with respect to CO_2 so that within about 1 min the carbamate derivatives of MEA, BUMEA, DGA were the sole reaction products in both aqueous and DEGMME solutions and this feature explains their high reaction rate. To get more evidence of the feature at the beginning of the absorption reaction, when the amine is in strong excess with respect to the CO_2 contained in the flask, a similar experiment has been carried out, with the same apparatus and at the same temperature, but with a greater amount of amine with respect to the CO_2 (ratio 10/1). The ^{13}C NMR spectra of the solutions at the end of this absorption experiment (see also Supporting Information) confirmed that the sole product formed was the amine carbamate, both in aqueous and DEGMME solutions, with the exception of aqueous AMP and AMPD.

As the free amine decreases upon the CO_2 uptake, the hydrolysis of carbamates in aqueous solution progressively increases the percentage of bicarbonate [eq. (5)] and, by the consequence, the percentage of CO_2 uptake (Figure 5A) which by far overcomes that in DEGMME at the end of the experiments (50 min). As an example, Figure 6 shows the different composition of the same aqueous DEA solution by varying the amine/ CO_2 ratio. As the bicarbonate is the sole (AMP, AMPD) or the prevailing species (BUMEA, 85%

respect to carbamate), in aqueous solution at the end of CO₂ uptake, the three amines attain the greatest absorption capacity (Figure 5A).

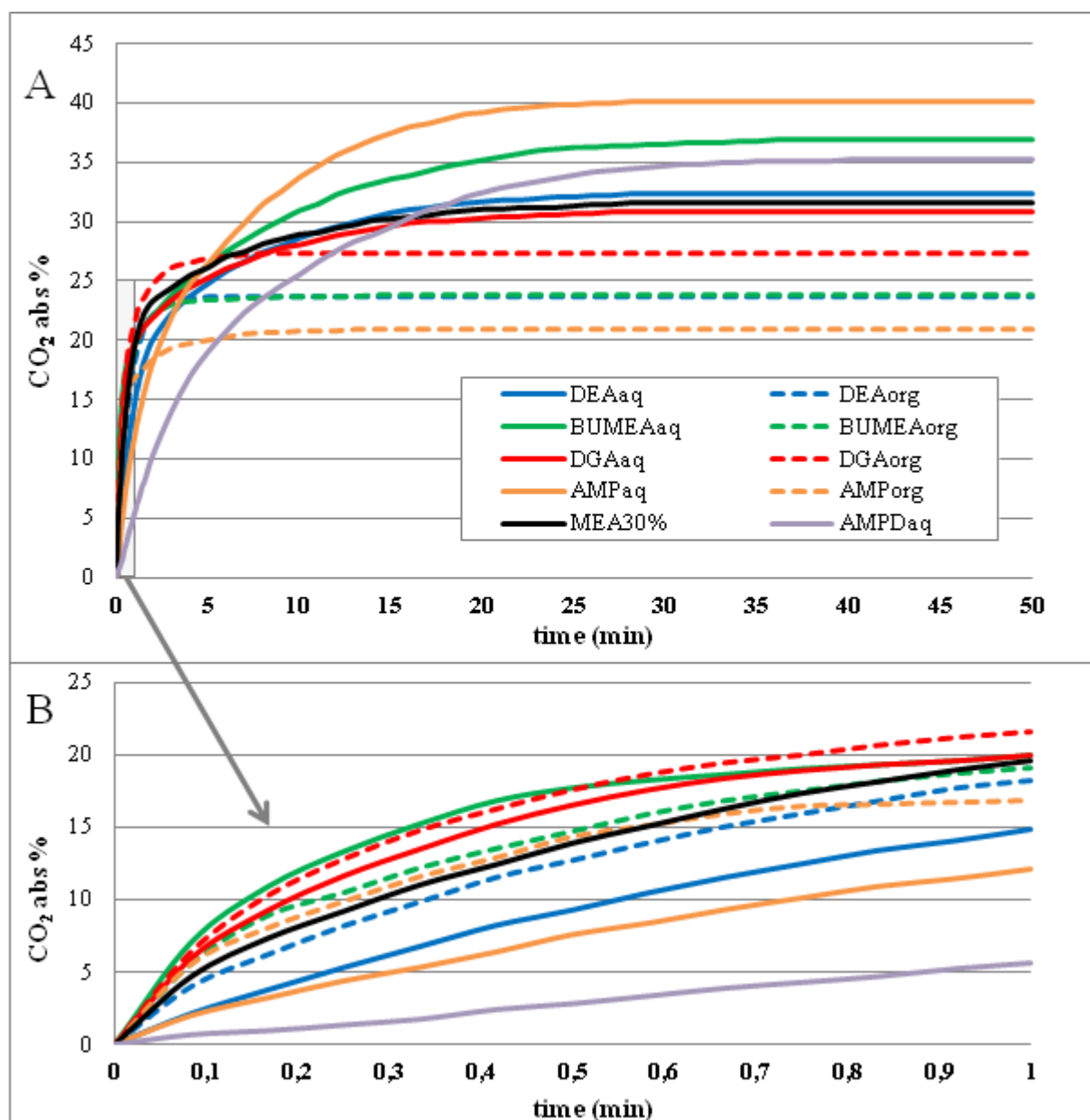


Figure 5. (A) Percentage of CO₂ absorbed with respect to that contained in the flask as a function of time at 25 °C. “aq” indicates aqueous solutions, “org” indicates DEGMME solutions. (B) Enlargement relative to the first minute of absorption, to evaluate the initial CO₂ absorption rate.

The CO₂ uptake by aqueous AMPD lower than aqueous AMP and BUMEA may be due to the formation of a small amount of carbonate [eq. (8)] of the former amine. The relatively lower efficiency of aqueous DEA, MEA, DGA was easily ascribed to the greater carbamate percentage (in the range 32-65% compared to carbonate/bicarbonate). As an example, the advantage of aqueous solution over DEGMME is shown by the absorption efficiency of AMP that increases from 21 % in DEGMME to 40% in aqueous solution (Figure 5A).

In summary, under the same operating conditions, the percentage of CO₂ absorption decreases in the order:

- 1) for the same amine: aqueous solutions > organic solutions
- 2) aqueous solution: AMP > BUMEA > AMPD > DEA ≈ MEA ≈ DGA
- 3) organic solution: DGA > DEA ≈ BUMEA > AMP

The initial CO₂ absorption rate, referred to the first minute of absorption, decreases in the order DGAorg > DGAaq ≈ BUMEAaq > MEAaq > BUMEAorg > DEAorg > AMPorg > DEAaq > AMPaq > AMPDaq.

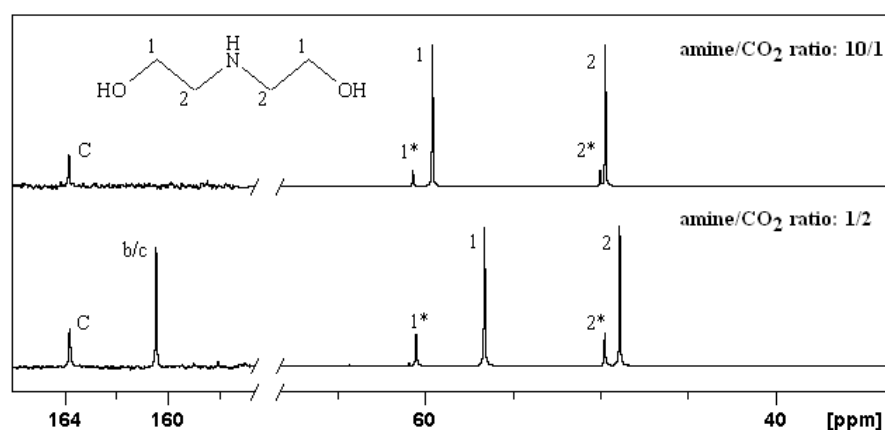


Figure 6. ¹³C NMR spectra of aqueous DEA by varying of the amine/CO₂ ratio from 10/1 to 1/2. The numbers indicate the carbon atom referred to both free and protonated amine fast exchanging in the NMR scale. Asterisks denote the chemical shifts of carbon backbones of DEA carbamate. C indicates the carbonyl atoms of carbamate, while *b/c* is referred to the signal of fast exchanging bicarbonate/carbonate ion. The intensity of the signals at 160-164 ppm is not in scale.

3.3. Continuous cycles of CO₂ absorption-desorption

The experiments aimed at verifying the efficiency of CO₂ capture by the different amine solutions were performed in a closed cycle apparatus for the continuous CO₂ absorption and simultaneous sorbent regeneration as reported in section 2.3.

A summary of the operating conditions is reported in Table 3, while the results of the experiments carried out with the different amine solutions are reported in Table 4. As expected, the efficiency of CO₂ absorption increases with increasing the rate of the absorbent circulation between the absorber and desorber and with increasing the stripping temperature. In most experiments the desorption temperature was fixed at 110 °C to reduce as much as possible the liquid evaporation and amine decomposition. As a general remark, the performances of the aqueous amines overcome those of the same amines in DEGMME. The results obtained with the aqueous absorbents with the flow rate at 0.30 dm³ h⁻¹ and abs/des temperatures at 40-110 °C indicate that the efficiency increases in the order AMPD ≪ AMP ≈ DEA < DGA < BUMEA ≈ MEA. The inefficiency of AMPD would be presumably due to its much lower rate of CO₂ uptake (Figure 5B) compared to the other amines.

Table 3. Operating conditions employed in the continuous absorption-desorption experiments

Solution Volume	0.400 dm ³ (50% carbonated solution)
Absorption Temperature	40 °C
Desorption Temperature / Pressure	110, 150 °C / 1 bar
Overall amine concentration	3.00 mol dm ⁻³ (aqueous MEA 4.90 mol dm ⁻³)
Liquid flow rate	From 0.150 to 1.000 dm ³ h ⁻¹
Gas flow rate	29.0 dm ³ h ⁻¹ (0.180 mol h ⁻¹ at 22 °C)
Gas mixture	15% (v/v) CO ₂ in air

Table 4. CO₂ capture efficiency of the different amine solutions at different sorbent flow rate and desorption temperature (T_{des}). The temperature of the absorber was maintained at 40°C.

amine	solvent	ABS% at different flow rate (dm ³ h ⁻¹). T _{des} 110°C								T _{des} 150°C 0.30	
		0.15	0.18	0.20	0.22	0.25	0.30	0.66	1.0		
MEA	H ₂ O	67.0%		89.5%						99.4%	90.6%
DEA	H ₂ O	71.4%			89.8%					93.5%	
	DEGMME								82.9%	88.6%	
BUMEA	H ₂ O	90.0%	92.9%							99.3%	
	DEGMME									89.6%	
DGA	H ₂ O	64.3%			90.1%					98.6%	
	DEGMME	60.7%					89.4%			94.9%	
AMPD	H ₂ O							67.9%		73.6%	
AMP	H ₂ O					89.8%				93.0%	
	DEGMME									carbamate precipitation	

It should be noticed that in the cyclic experiments, the solutions are continuously circulated between the absorber and the desorber so that neither the regenerated amine is saturated by CO₂ nor the carbonated amine is fully regenerated (see later) and consequently the kinetic constraints prevail over the thermodynamic requirements of the reactions. It should be also noticed that MEA attained the same efficiency of aqueous BUMEA at the expense of a concentration (on molar scale) about 1.6 times greater. The reduction of the absorption flow rate below 0.30 dm³ h⁻¹ reduces the absorption efficiency but the circulation rate of BUMEA at 0.15 dm³ h⁻¹ still achieves 90.0% efficiency while the efficiency of MEA, DEA and DGA is comprised between 64.3 and 71.4 % at the same circulating rate (Table 4). It should be kept in mind that the reduction of the absorbent flow rate sent to the desorber is beneficial to the reduction of the energy consumption for the absorbent regeneration [46-49].

At flow rate of 0.30 dm³ h⁻¹ and abs/des temperatures at 40-110 °C, the efficiency of amines in DEGMME solution increases in the order DEA < BUMEA < DGA, the same order of the increasing reaction rate found in the aforementioned batch experiments (Figure 5B). In particular, the efficiency of DGA in DEGMME is close to that of the most performing aqueous amine solutions (Table 4). On the contrary, it is quite surprising

the low efficiency of non aqueous DEA as it was necessary to increase the desorption temperature up to 150 °C to achieve the 90% CO₂ capture target. To reduce the thermal decomposition of the amines, it is beneficial to attain the 90% efficiency at the lowest possible desorption temperature. The formation of the ionic couples amine carbamate and protonated amine in the solid state prevented the cyclic experiments of AMP in DEGMME.

The ¹³C NMR analysis was carried out in the aqueous and DEGMME solutions that attained 90% CO₂ capture efficiency and allowed us to evaluate the distribution of the species in both loaded (absorber) and regenerated (desorber) absorbents and to correlate the NMR results with the performances of the different amines. All the NMR spectra are reported in Supporting Information. The ¹³C NMR speciation results of each solution are reported in Table 5, with the exception of aqueous AMP and AMPD that do not form quantifiable amounts of carbamate and by the consequence it is not possible to calculate the amount of carbonate/bicarbonate with respect to the total amine. Figure 7 shows the spectra of absorbed and desorbed solutions of aqueous MEA, aqueous BUMEA and DGA in DEGMME.

Table 5. Carbamate percentage with respect to overall amine and relative percentage of carbamate, bicarbonate and carbonate in absorbed and desorbed solutions determined by ¹³C NMR analysis; the data are referred to the sorbents with an efficiency near 90% (operation conditions reported in Table 4).

amine	solv.	% carb vs tot ^a	ABSORBER			% carb vs tot ^a	DESORBER			Cyclic capacity ^c (mol)
			Speciation of products ^b				Speciation of products ^b			
			AmCO ₂ ⁻	HCO ₃ ⁻	CO ₃ ²⁻		AmCO ₂ ⁻	HCO ₃ ⁻	CO ₃ ²⁻	
MEA	H ₂ O	45.2%	99.0%	0.7%	0.3%	25.7%	100%	0%	0%	0.374
DEA	H ₂ O	32.0%	80.1%	13.7%	6.2%	5.1%	100%	0%	0%	0.326
	DEGMME	18.3%	100.0%	0.0%	0.0%	1.0%	100%	0%	0%	0.207
BUMEA	H ₂ O	39.3%	73.2%	20.6%	6.2%	3.8%	100%	0%	0%	0.427
	DEGMME	22.6%	100%	0%	0%	4.1%	100%	0%	0%	0.223
DGA	H ₂ O	43.2%	99.5%	0.3%	0.2%	15.9%	100%	0%	0%	0.325
	DEGMME	38.0%	100%	0%	0%	15.2%	100%	0%	0%	0.274

^apercentage of the carbonated species (carbamate, bicarbonate and carbonate) with respect overall amine;

^brelative percentage of the carbonated species; ^cdifference (mol) between the carbonated and regenerated amine.

The cyclic capacity of an absorbent is defined as the difference between the carbonated and the regenerated amine. The highest cyclic capacity of aqueous MEA and BUMEA have different explanation to each other. MEA shows the maximum loading of the solution exiting from the absorber (45.2% vs. overall amine, Table 5) compared to the other amines, whereas aqueous BUMEA attains the lowest residual carbamate in the desorption step that accounts for less than 4% of the amine, whereas the bicarbonate is entirely decomposed (Figure 7 and Table 5). The latter feature is a further prove of the less energy required by the bicarbonate decomposition with respect to carbamate. The residual 25.7% of MEA carbamate in the desorption step at 110 °C is a clear evidence of its stability compared to that of aqueous DGA (15.9%) and to a greater extent to the carbamates of secondary amines DEA (5.1%) and BUMEA (3.8%) (Table 5).

As a general remark, the percentage of carbonated species in DEGMME is lower than those of the same amines in aqueous solution and the order of efficiency strictly follows the increasing carbamate formation in the absorption step in the order DEA (18.3%) < BUMEA (22.6%) < DGA (38.0%), the same of the cyclic capacity.

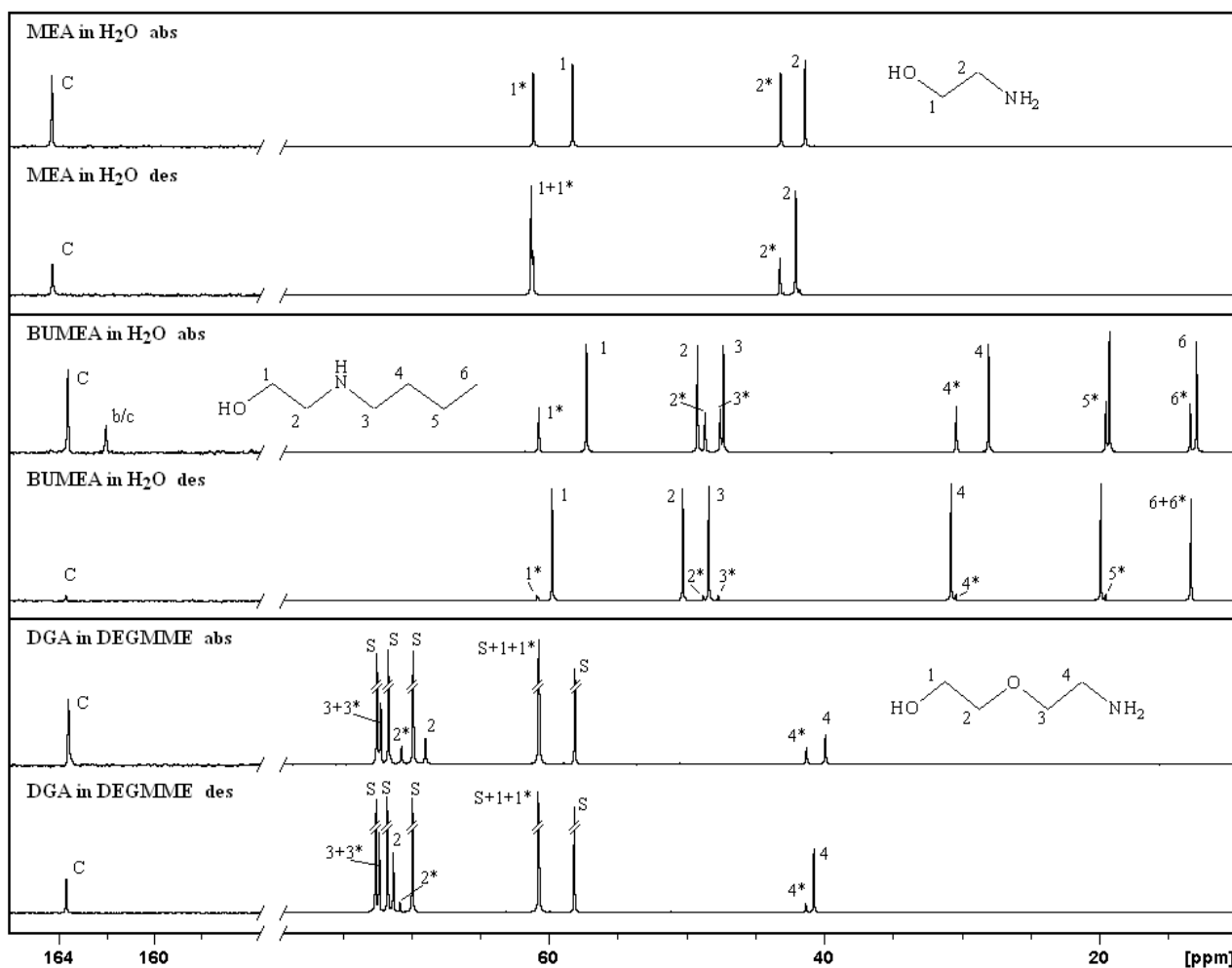


Figure 7. ^{13}C NMR spectra of the solutions recovered from absorber and desorber in continuous cycles experiments of aqueous MEA, aqueous BUMEA and DGA in DEGMME. The numbers indicate the carbon atom referred to both free and protonated amine fast exchanging in the NMR scale, assigned as reported in the relative amine structure. Asterisks denote the chemical shifts of carbon backbones of amine carbamate. C indicates the carbonyl atoms of amine carbamate, while *b/c* is referred to the signal of fast exchanging bicarbonate/carbonate ion. S indicates DEGMME signals. The intensity of the signals at 160-164 ppm is not in scale.

3.4. Regeneration energy demand comparison with MEA

By comparing the results reported in Table 4 and 5 MEA and BUMEA are the most efficient absorbents in aqueous solutions as well as DGA in DEGMME solutions. To evaluate whether aqueous BUMEA and DGA in DEGMME can be considered as alternatives to conventional aqueous 30% MEA, we have decided to determine their heat of CO_2 absorption (ΔH_{abs}), which is a significant parameter to evaluate the overall

energy demand of a CO₂ capture system. The heat required for sorbent regeneration is generally considered as the sum of three terms: the heat of CO₂ desorption from the solution (ΔH_{des}), the sensible heat required (Q_{sens}) to increase the temperature of the solution from the capture to desorption (regeneration) value and the heat of evaporation (Q_{vap}) necessary to produce the stripping steam in the reboiler. By assuming that the desorption of CO₂ from the amine solution in the stripper is the inverse reaction of CO₂ absorption by the amine solution, that is the opposite of equation (7), the heat of desorption (ΔH_{des}) is the same (in absolute value) of the heat of absorption [34,35,38,50]. In this work, the heat of the CO₂ absorption has been computed by employing the Gibbs-Helmholtz equation (section 2.5), from the slope of the plot of CO₂ partial pressure $\ln(PCO_2)$ versus temperature ($1/T$) at the same CO₂ loading (Figure 8). The experimental data of CO₂ equilibrium loading were measured at different temperatures, in the range 20–40°C, and CO₂ partial pressure in the range 10.13–101.33 kPa, until at least three measures under different conditions give the same loading value. The heat of absorption of aqueous BUMEA and DGA in DEGMME are -64.01 and -71.61 kJ mol⁻¹, respectively. Both values are lower than that of aqueous MEA (-83.24 kJ mol⁻¹), which indicates a potential energy saving for the regeneration of the proposed solutions with respect to conventional sorbents.

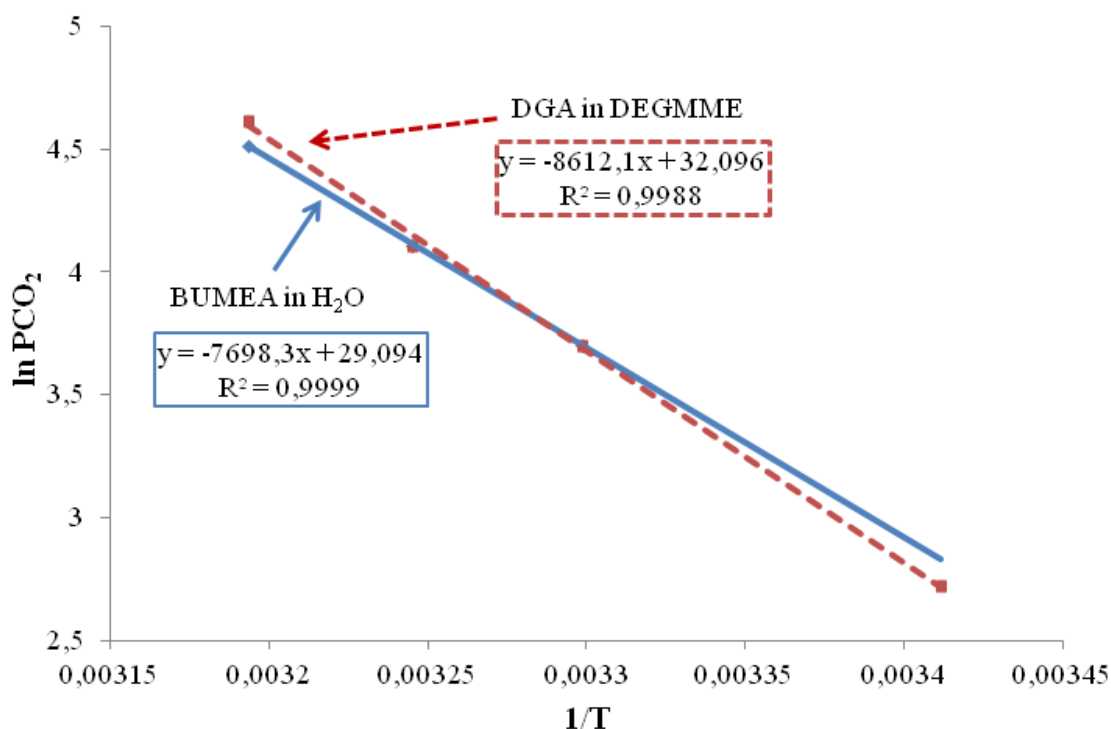


Figure 8. The plot of CO₂ partial pressure $\ln(PCO_2)$ versus temperature ($1/T$) at the same CO₂ loading for aqueous BUMEA (blue line) and DGA in DEGMME (red dashed line); the specific CO₂ equilibrium loading are 0.7527 (± 0.0031), and 0.5139 (± 0.0035), respectively.

4. Conclusions

As a general consideration, by comparing the amine performances measured in the cyclic experiments of absorption-desorption, aqueous BUMEA has potential advantages over aqueous MEA because it attains the

90% efficiency at lower molar concentration (3.0 instead of 4.9 mol dm⁻³) at lower circulation rate (0.15 instead of 0.20 dm³ h⁻¹). Additionally, the formation of about 21% of bicarbonate (on molar scale) reduces the energy consumption of the aqueous BUMEA regeneration because of the lower enthalpy of bicarbonate formation, as indicated by the absolute value of ΔH_{abs} that is lower than that of MEA (section 3.4).

As already stated, the energy required by the amine regeneration comprises the sensible heat to increase the absorbent temperature from the absorption to the desorption steps, in addition to the heat of vaporization of the absorbent and to the heat to decompose the carbonated species.

The process of CO₂ capture by aqueous amines has the disadvantage of the high sensible heat because of the high heat capacity and vaporization heat of water (4.18 kJ kg⁻¹ K⁻¹ and 2.26 kJ g⁻¹, respectively). By increasing the desorption temperature, the CO₂ transfer into the gaseous phase is favoured and less energy is required in the stripping step. In the commercial plants, the desorption temperature of aqueous MEA is limited to 110-120 °C under pressure greater than 1 bar to reduce MEA decomposition and equipment corrosion which are accelerated by the temperature.

On the contrary, by using the DEGMME absorbents, the stripping can be operated up to 150 °C and 1 bar by virtue of the high boiling temperature of DEGMME (198-200 °C) and negligible corrosion due to the absence of water. An additional advantage of DEGMME compared to aqueous absorbents, is the lower sensible heat because of the lower heat capacity of DEGMME (2.26 kJ kg⁻¹ K⁻¹) and to the negligible vaporization of DEGMME at the desorption temperature. On this basis, DGA in DEGMME can be a viable alternative to 30% aqueous MEA due to the lower energy required for solvent regeneration, despite a slightly lower absorption efficiency (94.9% versus 99.4%, at the same liquid flow rate and temperatures, Table 4). The calculated heat of absorption of DGA in DEGMME is -71.61 kJ mol⁻¹, lower (in absolute value) than that of aqueous MEA (-83.24 kJ mol⁻¹); furthermore we easily computed 35% less sensible heat (See Supporting Information) of DGA in DEGMME because of the absence of water when compared with the 30% aqueous MEA. The energy saving should be even greater if we take into account water evaporation [40] compared to the negligible vaporization of DEGMME at the desorption temperature (110 °C). Notwithstanding the results we have reported indicate either aqueous BUMEA or DGA in DEGMME as possible alternative absorbents to the conventional aqueous MEA, their implementation in a commercial plant requires an accurate assessment of costs and benefits of the processes and tests carried out in a pilot plant.

As a final remark, ¹³C NMR spectroscopy has been confirmed to be a valuable tool to evaluate the distribution of the species in solution that give reliable information on the species distribution in the amine/CO₂/solvent systems.

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