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# Novel non-aqueous amine solvents for reversible CO<sub>2</sub> capture

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## Abstract

This study describes the chemical capture of CO<sub>2</sub> by AMP and some AMP–alkanolamine blends, namely IPMEA, TBMEA and MDEA, in non-aqueous solvents. The solvents used are a mixture of ethylene glycol and 1-propanol or single diethylene glycol monomethyl ether. A gas mixture containing 15% of CO<sub>2</sub> in air was used for the experiments. We designed two different experimental procedures: 1) batch experiments of CO<sub>2</sub> absorption and desorption aimed at investigating the absorption and desorption properties of the different absorbents; 2) continuous cycles of CO<sub>2</sub> absorption (20 °C) and desorption (90-95 °C) in packed columns in order to investigate the CO<sub>2</sub> absorption efficiency. The CO<sub>2</sub> removal efficiency at equilibrium was in the range 87-95% depending on the operational conditions. The identification and the quantification of the species in solution were obtained from <sup>13</sup>C NMR spectroscopic analysis.

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## 1. Introduction

Chemical capture of CO<sub>2</sub> by aqueous alkanolamines is considered a mature technique for its separation and removal from flue gas of coal-fired power plants. A large numbers of alkanolamines, such as monoethanolamine (MEA, 2-aminoethanol), diethanolamine (DEA, 2,2'-iminodiethanol), methylethanolamine (MMEA, N-methyl-2-aminoethanol), methyldiethanolamine (MDEA, N-methyl-2,2'-iminodiethanol), aminomethylpropanol (AMP, 2-amino-2-methyl-1-propanol), diethylene glycolamine (DGA, 2-(2-aminoethoxy)ethanol), diisopropanolamine

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**Nomenclature**

MEA	2-aminoethanol
DEA	2,2'-iminodiethanol
AMP	2-amino-2-methyl-1-propanol
TBMEA	2-(tert-butylamino)ethanol
IPMEA	2-(isopropylamino)ethanol
MDEA	N-methyl-2,2'-iminodiethanol
EG	ethylene glycol
PrOH	1-propanol
DEGMME	diethylene glycol monomethyl ether

(DIPA, bis(2-hydroxypropyl)amine) and their blends, have been thoroughly studied in lab-scale experiments. [1-4] Aqueous MEA and DEA, in particular, have had industrial scale application to CO<sub>2</sub> capture from natural gas extraction, gas refinery and exhaust gases produced by fossil fuel fired power generation by virtue of their high CO<sub>2</sub> absorption efficiency and loading capacity [5-13]. In spite of the advantages of this CO<sub>2</sub> capture technology, the process entails serious economic and environmental problems, such as the energy cost of the solvent regeneration, the solvent loss by evaporation and its thermal and oxidative degradation because of the high desorption temperature required and equipment corrosion, which have to be addressed before a large scale implementation can become a reality [14-20].

With the aim of taking advantages of the high efficiency of aqueous alkanolamines yet reducing their disadvantages, we have devised the strategy to replace water with organic solvents in order to redirect the reaction of CO<sub>2</sub> capture towards less stable carbonated species which thereby require lower regeneration temperature [21,22]. Additional benefits come from the much lower heat capacity of the organic solvents compared to water, lower ammine degradation and evaporation due to the reduced stripping temperature, and lower corrosion of the equipment. In the experimental study here reported we have investigated an efficient method for the separation of CO<sub>2</sub> from a simulated flue gas containing 15% of CO<sub>2</sub> in air. The absorbents were either single or blended amines (1:1, molar scale), overall 3.0 mol dm<sup>-3</sup>, dissolved in a 1:1 (volume scale) mixture of ethylene glycol (EG) and 1-propanol (PrOH) or in single diethylene glycol monomethyl ether (DEGMME). The selected amines were AMP (2-amino-2-methyl-1-propanol), TBMEA [2-(tert-butylamino)ethanol], IPMEA [2-(isopropylamino)ethanol] and MDEA (N-methyl-2,2'-iminodiethanol).

We have designed two series of experiments:

- CO<sub>2</sub> absorption and, separately, thermal amine regeneration aimed at selecting the most efficient absorbents.
- Continuous cycles of CO<sub>2</sub> absorption-desorption performed in packed columns with the purpose of measuring the efficiency of CO<sub>2</sub> capture.

The carbon containing compounds in the equilibria between alkanolamines, alcohols and CO<sub>2</sub> were analyzed by <sup>13</sup>C NMR spectroscopy [23,24], and were found to be originated from the amine and alcohol carbonation.

Besides our previous studies [21,22], systematic experimental investigations of CO<sub>2</sub> capture by non-aqueous amines are still scarce and have been limited to kinetic and solubility studies of MEA, DEA and MDEA in a variety of organic solvents [25,26]. Recently, equimolar mixtures of alkanolamines and room temperature ionic liquids (RTILs) [27] or CO<sub>2</sub> binding organic liquids (CO<sub>2</sub>BOLs) [28,29] have been tested as effective solvents for reversible CO<sub>2</sub> capture. These absorbents have several advantages over the aqueous alkanolamines, being thermally stable and high-boiling liquids with lower heat capacity than water. However, the expensive synthesis of these absorbents compared to the conventional amines and the huge increase of the absorbent viscosity upon reaction with CO<sub>2</sub>, prevent their possible application to industrial processes.

## 2. Experimental section

### 2.1. General information

All reagents were reagent grade. The alcohols and the amines (Sigma-Aldrich) were used as received without further purification. Gas mixture of 15% CO<sub>2</sub> and air (Rivoira Spa) was used to simulate the flue gas. Flow rates were measured with gas mass flow meters (Aalborg) equipped with gas controllers (Cole Parmer). The inlet and outlet CO<sub>2</sub> concentrations in the flue gas mixture were measured with a Varian CP-4900 gas chromatograph calibrated with 15% v/v CO<sub>2</sub>/air reference mixture (Rivoira Spa) and 100% CO<sub>2</sub> reference gas (Rivoira Spa). The starting amine solutions were fixed at overall 3.00 mol dm<sup>-3</sup>; the amine blends were 1:1 molar ratio and mixed EG/PrOH was 1:1 (v/v).

The CO<sub>2</sub> absorption in the batch experiments was measured with a gastight apparatus which comprises a 2.0 dm<sup>3</sup> flask (actual volume 2.20 dm<sup>3</sup>) equipped with a digital pressure gauge, magnetic stirrer and a pressure-equalizing dropping funnel containing 40.0 cm<sup>3</sup> of the appropriate amine (0.12 mol) solution. The air was removed with a vacuum pump and afterwards the flask was filled with the air-CO<sub>2</sub> mixture 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 and the pressure decrease measured by the pressure gauge enabled us to estimate the CO<sub>2</sub> absorption as a function of time. The experiment was stopped when the pressure did not change with time (about 20 min). The thermal release of pure CO<sub>2</sub> was accomplished with a home-made apparatus which comprises a 250 cm<sup>3</sup> conical flask containing the carbonated solution and connected to two 100 cm<sup>3</sup> gas burettes (Volac) filled with CO<sub>2</sub> saturated water and equipped with a pressure-equalizing device [30]. The desorption rate at 90 °C rapidly decreased with time and a steady state was reached within 60 min.

The apparatus used for the continuous absorption-desorption cycles consists of the absorber and the desorber units connected to each other by means of a double head peristaltic pump (Masterflex), which allows the solutions to circulate continuously in a closed loop between the absorber and the desorber at the flow rate of 0.330 and 0.650 dm<sup>3</sup> h<sup>-1</sup>. 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 (20 °C) and desorber (90, 95 °C) was maintained at the appropriate value by circulating a thermostatted liquid (Julabo model F33-MC bath) through the jackets. The absorber was designed to operate in a counter current mode: the regenerated absorbent was introduced from the top of the packed column while the gas mixture was continuously injected at the bottom of the column below the packing. The carbonated absorbent exited at the bottom of the column and sent to the top of the desorber. The desorber was equipped with a water-cooled condenser to reflux the possible overhead vapor to the stripper. The entire apparatus was charged with 0.400-0.450 dm<sup>3</sup> of amine-alcohol solution that had been previously 50% saturated with CO<sub>2</sub>. To prepare these solutions, 0.200-0.225 dm<sup>3</sup> of the appropriate amine solution were pre-saturated with pure CO<sub>2</sub> and, subsequently, mixed with the required volume of the free amine solution to obtain the overall solution. The flue gas mixture was continuously fed into the bottom of the absorber with a flow rate of 12.2 dm<sup>3</sup> h<sup>-1</sup> (0.0750 mol h<sup>-1</sup> of CO<sub>2</sub> at 24 °C). The vent gas exited from the top of the absorber. The outlet gas was analyzed by the gas chromatograph. A complete cyclic experiment lasted 24-36 h, for each desorption temperature tested, and it was stopped when the reactions of CO<sub>2</sub> capture and amine regeneration were equilibrated to each other.

### 2.2. <sup>13</sup>C NMR Spectroscopy

The <sup>13</sup>C NMR analysis were performed with a Bruker Avance III 400 spectrometer operating at 100.613 MHz. Chemical shifts are to high frequency relative to tetramethylsilane as external standard at 0.00 ppm, while CH<sub>3</sub>CN was used as internal reference (CH<sub>3</sub>, δ = 1.47). To provide a good signal for deuterium lock, a sealed glass capillary containing D<sub>2</sub>O (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 <sup>13</sup>C{<sup>1</sup>H} 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. 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 -CH<sub>2</sub>- carbon atoms that contain the same number of attached protons.[31,32] The <sup>13</sup>C

atoms of  $\text{R-CO}_3^-$  and of  $\text{R}'\text{-CO}_2^-$  functionalities have no attached hydrogen and show relaxation times longer than those of  $-\text{CH}_2-$  groups, thus resulting in lower intensity resonances. Notwithstanding, integration of the carbon resonances of  $\text{R-CO}_3^-$  and of  $\text{R}'\text{-CO}_2^-$  is an estimation (5% deviation) of the relative amounts of the two species.

### 3. Results and discussion

#### 3.1. Separate experiments of $\text{CO}_2$ absorption and desorption

AMP has been selected as the main component of all the absorbents by virtue of its high thermal stability and, on the contrary, the relatively low stability of the corresponding carbamate, as compared, for example, with those of MEA, MMEA and DEA. The choice of the alcohols was dictated by four main constraints: *a*) solubility of the carbonated compounds, *b*) high boiling temperature, *c*) low cost, and *d*) avoidance of foaming problems and immiscible liquid phases. Concerning point *a*), ethylene glycol (EG) was found necessary to avoid the formation of precipitates upon  $\text{CO}_2$  absorption. Unfortunately, pure EG is unsuitable for  $\text{CO}_2$  capture in spite of its high boiling temperature and low cost, because of the high absolute viscosity ( $\mu = 19.9 \text{ mPa s}$ , at  $20 \text{ }^\circ\text{C}$ ) that reduces the mass transfer and consequently lowers the absorption efficiency. Consequently, we employed 1:1 (v/v) mixtures of EG with 1-propanol ( $\mu = 1.07 \text{ mPa s}$ , at  $20 \text{ }^\circ\text{C}$ ) to reduce the viscosity of the solvent yet maintaining a boiling temperature up to  $150 \text{ }^\circ\text{C}$ . For comparison purposes, we also used amine solutions in pure DEGMME. Absorption experiments at  $25 \text{ }^\circ\text{C}$  were carried out into a  $2.0 \text{ dm}^3$  flask containing the absorbent ( $0.040 \text{ dm}^3$ ) and filled with the gas mixture (see experimental) at room pressure. From the pressure decrease measured during the  $\text{CO}_2$  absorption (15% v/v  $\text{CO}_2$  in air at  $25 \text{ }^\circ\text{C}$ ), the amount of absorbed  $\text{CO}_2$  was evaluated as a function of time. When the pressure did not change with time (20 min), the steady state was reached and the experiment was stopped. The percentage of  $\text{CO}_2$  absorbed by single amines or 1:1 (molar scale) blends, overall  $3.0 \text{ mol dm}^{-3}$ , in EG/PrOH 1:1 (v/v) or DEGMME is summarized in Figure 1 as a function of the absorption time. Overall, the absorption efficiency (percentage of  $\text{CO}_2$  absorbed/ $\text{CO}_2$  flowed) decreases in the order:

- AMP > IPMEA > TBMEA > MDEA
- AMP/IPMEA  $\geq$  AMP/TBMEA > AMP/MDEA
- amine blends > single amines (with the exception of AMP)
- EG/PrOH > DEGMME

The absorption efficiency of the single amines decreases with increasing steric hindrance at amine function. The absorption efficiency is comprised between 14% (MDEA-DEGMME) and 100% (several amines, EG/PrOH). For the same experimental conditions, the mixture EG/PrOH has an appreciable advantage over DEGMME because of its greater reactivity towards  $\text{CO}_2$  [see later, reaction (2)]. In particular, the MDEA efficiency increases from 14% in DEGMME to 51% in EG/PrOH. The tertiary amine MDEA is unable to react with  $\text{CO}_2$  in the absence of water and DEGMME is poorly reactive towards  $\text{CO}_2$ , contrary to EG and PrOH. The single amines AMP and IPMEA and the mixed AMP/IPMEA display a greater initial reaction rate irrespective of the solvent employed.

The  $\text{CO}_2$  release during the amine regeneration process was measured at  $90 \text{ }^\circ\text{C}$  using a gastight apparatus (see experimental) connected to two  $100 \text{ cm}^3$  gas burettes. [30] The  $\text{CO}_2$  desorption required a maximum of 60 min. The Figure 2 summarizes the average values of three measurements of  $\text{CO}_2$  absorption and desorption efficiency (the latter is the percentage of the desorbed  $\text{CO}_2$  with respect to that absorbed), after the steady state was reached, according to the different amine solutions. In general, the desorption and the absorption efficiency displays an opposite trend: this feature is particularly evident for DEA.

By considering both absorption and desorption efficiency, the rate of  $\text{CO}_2$  absorption and the absence of solid compounds upon  $\text{CO}_2$  uptake, AMP, AMP/IPMEA and AMP/TBMEA dissolved in EG/PrOH were selected for the experiments in the closed cycles of absorption-desorption where the kinetic constraints, presumably, prevail over the thermodynamic properties.

Analogous experiments carried out for comparison purposes with the amines MEA, DEA, MMEA, gave high absorption efficiency (over 95%) but were discarded for cyclic experiments because of the low desorption efficiency (15-30% at  $90 \text{ }^\circ\text{C}$ ).

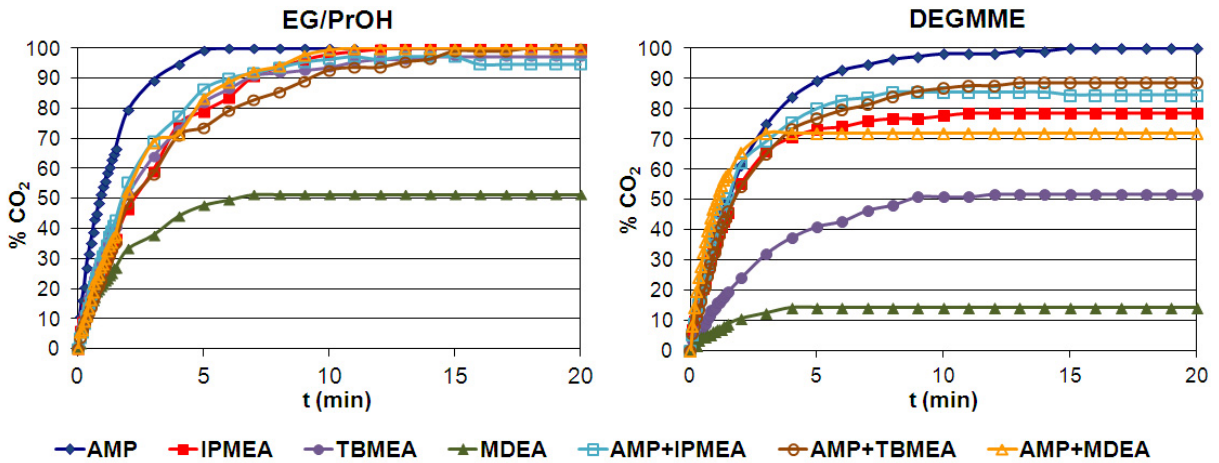


Fig. 1. Variation of the CO<sub>2</sub> absorption efficiency of the different amines in EG/PrOH and DEGMME solutions as a function of time.

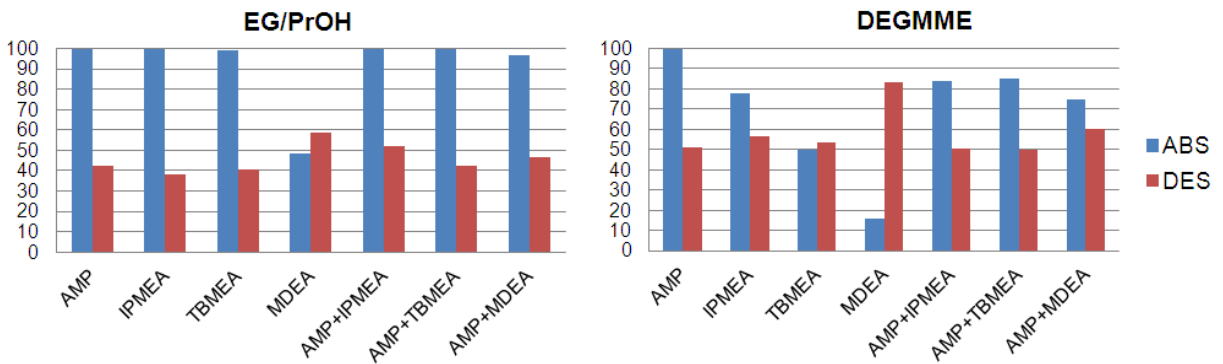
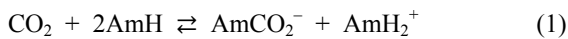


Fig. 2. The CO<sub>2</sub> desorption efficiency of the different amines carbonated by 15% CO<sub>2</sub> in EG/PrOH and DEGMME. The desorption efficiency is compared with the average absorption efficiency in the same solutions

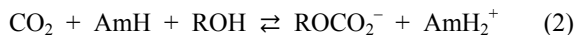
### 3.2. The chemistry of CO<sub>2</sub> absorption in non-aqueous solvents and the analysis of the carbonated species based on <sup>13</sup>C NMR spectroscopy

In the absence of water, CO<sub>2</sub> reacts with an excess of both primary and secondary amines yielding the corresponding amine carbamates [Reaction (1); AmH denotes either primary or secondary amine]



Although tertiary amines such as MDEA cannot react with CO<sub>2</sub> in anhydrous conditions, they can still enter in the CO<sub>2</sub> capture process if they are mixed with primary or secondary amines when the tertiary amines behave as the

base for the carbamic acid deprotonation. Additionally, the alcohol itself could take part to the CO<sub>2</sub> uptake in the presence of a base (*i.e.* the amine) yielding the alkyl carbonate [Reaction (2); R denotes an alkyl group]:



In EG/PrOH and DEGMME, R is CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>–, HOCH<sub>2</sub>CH<sub>2</sub>– and, to a much less extent, CH<sub>3</sub>O(CH<sub>2</sub>)<sub>2</sub>O(CH<sub>2</sub>)<sub>2</sub>–. The reaction (2) has been reported to occur with saturated alcohols in the presence of alkyl bromide and Cs<sub>2</sub>CO<sub>3</sub> [33], dibutyl tin(IV)oxide [34] and of both amidine and guanidine [28]. It also occurs with unsaturated alcohols in the presence of tert-butyl ipiodide [35]. However, the fast CO<sub>2</sub> alkylation promoted by a common amine is noteworthy. Alkyl carbonates formation is prevented by those amines, MEA, MMEA and DEA, that give stable carbamates. The thermal decomposition of stable carbamates is slower than that of alkyl carbonates and, consequently, requires higher temperatures. On the contrary, the amines AMP, TBMEA, IPMEA in EG/PrOH give less stable carbamates with high reaction rate and promote the formation of alkyl carbonates of EG and PrOH. Therefore, these absorbents may be efficient in both absorption and desorption steps.

In order to evaluate the distribution of the species in solution at the end of the absorption experiments, we analyzed the CO<sub>2</sub> loaded solutions by <sup>13</sup>C NMR spectroscopy, as already reported for aqueous solutions.[23,24] The peak assignment was done according to literature data [36]. Besides the most intense signals due to the carbon backbones of the alcohols and of both protonated and free amines that are fast exchanging on the NMR time scale, additional resonances were easily assigned to amine carbamates and to the alkyl carbonates. A couple of resonances in the range 67.70-67.03 ppm and 61.57-60.93 ppm can be assigned to the carbon atoms of the monoalkyl carbonate derivative of ethylene glycol (HO-CH<sub>2</sub>-CH<sub>2</sub>-OCO<sub>2</sub><sup>-</sup>). Furthermore, a resonance at 159.86-159.21 ppm identifies the alkyl carbonate quaternary carbon (R-OCO<sub>2</sub><sup>-</sup>). The resonances ascribable to the alkyl carbonate of 1-propanol are in the ranges 160.44-160.07, 64.96-63.80, 23.40-22.72 and 11.04-10.34 ppm. Finally, the resonances of the carbamate derivative of AMP (164.79-164.64, 72.26-71.60, 53.55-52.72, 22.72-22.17 ppm) and IPMEA (164.77-164.69, 62.52-60.93, 52.27-51.62, 49.65-48.55, 18.48-17.80 ppm) were observed. The <sup>13</sup>C resonances of TBMEA carbamate are very weak. As an example, the <sup>13</sup>C NMR spectrum of carbonated IPMEA in EG/PrOH is reported in Figure 3.

In order to quantify the relative amounts of carbamate and alkyl carbonate, we carefully integrated the carbon resonances of carbamate R-CO<sub>2</sub><sup>-</sup> and carbonate R'-OCO<sub>2</sub><sup>-</sup> falling in the range 164-159 ppm. The quaternary <sup>13</sup>C atoms of R-OCO<sub>2</sub><sup>-</sup> and of R'-CO<sub>2</sub><sup>-</sup> functionalities exhibit much longer relaxation times than –CH<sub>2</sub>– groups, thus resulting in lower intensity resonances. Although some uncertainty in comparing the different integrals is unavoidable (estimated error 5%), nonetheless the method is certainly reliable and provides a first estimation of the concentration changes of the species originating from the adsorbed CO<sub>2</sub> in solution.

The CO<sub>2</sub> capture either as alkyl (EG, PrOH, DEGMME) carbonate or amine (AMP, IPMEA, TBMEA) carbamate is the result of the competition between the relative stability of the alkyl carbonates and amine carbamates. The IPMEA carbamate is the prevailing species in the IPMEA and AMP/IPMEA solutions (70-75%) with respect to the alcohol carbonates. On the contrary, the summed carbonates of EG and PrOH (54 %) prevail over the AMP carbamate in the carbonated solution. In general, the –CO<sub>3</sub><sup>-</sup> signal of EG carbonate is more intense than that of PrOH carbonate. The amount of carbonate derivative of DEGMME is too low to be detected in the <sup>13</sup>C NMR spectra. In summary, the alkyl carbonate stability decreases in the order EG > PrOH >> DEGMME and the carbamate stability decreases in the order IPMEA > AMP > TBMEA. The tertiary amine MDEA is unable to form the corresponding carbamate and, consequently, MDEA-DEGMME is the least efficient absorbent: the small absorption capacity (14%) measured is, presumably, due to a small amount of DEGMME carbonate and to physical absorption.

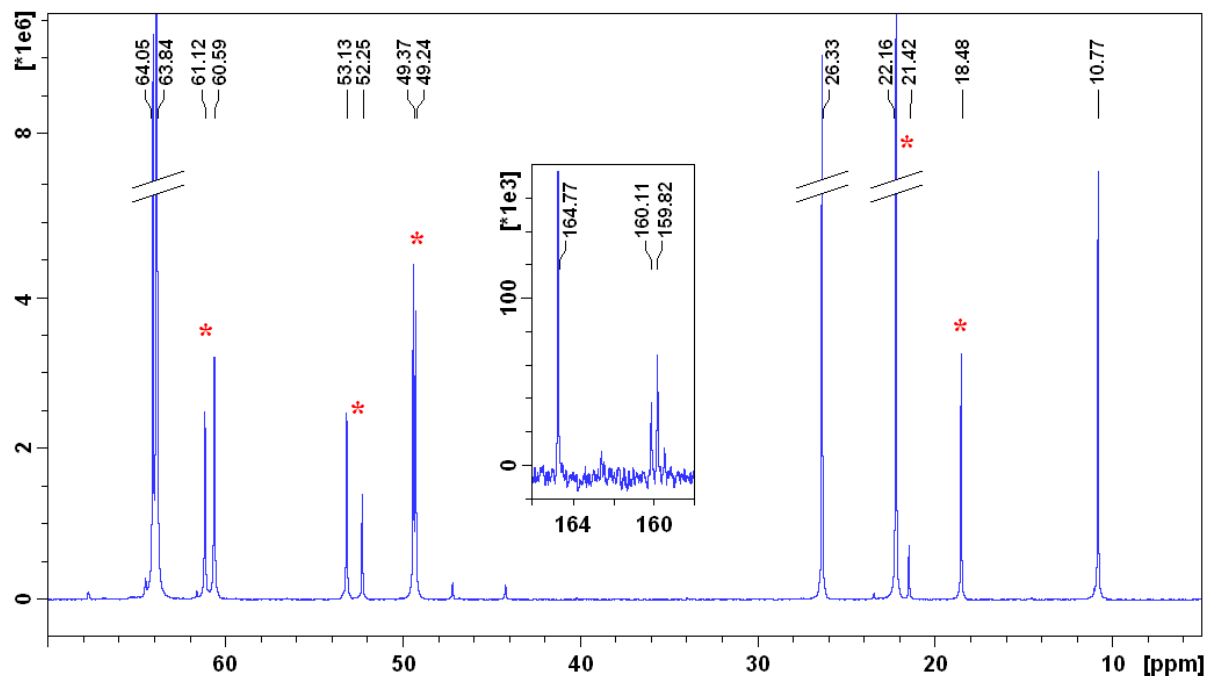


Fig. 3. The  $^{13}\text{C}$  NMR spectrum of IPMEA-EG/PrOH carbonated by 15%  $\text{CO}_2$ . The inset reports the chemical shifts of carbonyl atoms of IPMEA carbamate ( $\delta=164.77$  ppm) and alcohol carbonates ( $\delta=160.11$ - $159.82$  ppm). The asterisk denotes the chemical shifts of carbon backbones of IPMEA carbamate and of both free IPMEA and protonated IPMEA fast exchanging in the NMR scale.

### 3.3. Continuous cycles of $\text{CO}_2$ absorption-desorption

The experiments of  $\text{CO}_2$  absorption efficiency were performed in continuous cycles of  $\text{CO}_2$  absorption and simultaneous solvent regeneration. Both the absorber and desorber, set at the appropriate temperatures, are glass columns packed with glass rings and designed to operate in a counter current mode [21,22]. In such cyclic processes, the hot lean solution exiting from the desorber was cooled and continuously transferred to the absorber for reuse, while the carbonated solution from the absorber was reclaimed back to the desorber for regeneration. The gas mixture of 15% (v/v)  $\text{CO}_2$  in air, simulating the flue gas, was feeding into the base of the absorber coming in contact with the liquid that was fed into the top. The packing maximizes the exchange surface between the two phases and provides the reaction mixture with a sufficient residence time. The outlet gas was dried and purified before being GC-analyzed. Samples of the solutions were checked by  $^{13}\text{C}$  NMR spectroscopy. Each complete experiment lasted 24-36 h and, for each desorption temperature, it was stopped when the reactions of  $\text{CO}_2$  capture and amine regeneration reached a steady state. The stripped  $\text{CO}_2$  was not recovered. Based on the aforesaid batch results, the amines AMP, AMP/IPMEA and AMP/TBMEA in EG/PrOH 1/1 (v/v) were used for the continuous cyclic experiments. A summary of the operating conditions is reported in Table 1 and the results are reported in Table 2.

As expected, the absorption efficiency increases with desorption temperature and with the increased volume of amine solution. The dependence on the liquid flux deserves a comment. The lower flux,  $0.330 \text{ dm}^3 \text{ h}^{-1}$ , increases the residence time of the liquid within the absorber and desorber, thereby enhancing both the absorption and desorption reactions. The higher flux,  $0.650 \text{ dm}^3 \text{ h}^{-1}$  makes a greater amount of the sorbent to come from the desorber to the absorber, and *vice versa*. The higher absorption efficiency was the result of the best compromise between the two opposite features that enabled the greatest amount of both loaded and regenerated absorbent to circulate between the desorber and the absorber. Anyway, an absorption efficiency up to 91-95% was obtained by adopting the best

operational conditions. By increasing the desorption temperatures to 95 °C, the residual carbonated species decreased in all the solutions.

Table 1. Operating conditions employed in the continuous absorption-desorption experiments.

Solution volume	0.400, 0.450 dm <sup>3</sup> of 50 % carbonated solution
Absorption temperature	20 °C
Desorption temperature / pressure	90, 95 °C / 1 bar
Overall amine concentration	3.00 mol dm <sup>-3</sup> (single or 1/1 molar ratio)
Liquid flow rate	0.330, 0.650 dm <sup>3</sup> h <sup>-1</sup>
Gas flow rate	12.2 dm <sup>3</sup> h <sup>-1</sup>
Gas mixture	15% (v/v) CO <sub>2</sub> in air

Table 2. CO<sub>2</sub> absorption efficiency of the amines in EG/PrOH in the continuous absorption-regeneration cycles as a function of the operational parameters

Amine	Liquid flow rate (dm <sup>3</sup> h <sup>-1</sup> )	T abs (°C)	T des (°C)	Efficiency %
AMP	0.330	20	90	91.3
	0.330	20	95	93.3
	0.330	20	95	95.4 <sup>a</sup>
AMP + IPMEA	0.330	20	90	88.9
	0.330	20	95	91.3
	0.330	20	95	89.4 <sup>a</sup>
	0.650	20	95	86.7
AMP + TBMEA	0.330	20	95	91.0 <sup>a</sup>
	0.650	20	95	93.3 <sup>a</sup>

<sup>a</sup> Liquid volume 0.450 dm<sup>3</sup>; in all of the other experiments is 0.400 dm<sup>3</sup>

#### 4. Conclusions

In the present study we have described a technique of CO<sub>2</sub> separation based on chemisorption by non-aqueous solvents containing single AMP, IPMEA, TBMEA, MDEA or their blends and ethylene glycol-propanol mixture or diethylene glycol monomethyl ether. Based on <sup>13</sup>C NMR analysis, CO<sub>2</sub> is reversibly captured in solution as monoalkyl carbonate, R-OCO<sub>2</sub><sup>-</sup>, (R= HOCH<sub>2</sub>CH<sub>2</sub>-, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-) and amine (AMP, IPMEA) carbamate. Due to the lower stability of both monoalkyl carbonates and of amine carbamates with respect to HCO<sub>3</sub><sup>-</sup> and to stable amine (MEA, DEA, MMEA, for example) carbamates that are formed by the conventional aqueous solutions, stripping temperatures of 90-95 °C at room pressure are sufficient to attain CO<sub>2</sub> capture efficiencies up to 95%. The lower heat capacity and evaporation enthalpy of the organic solvents compared to water combined with the lower stripping temperature, all together should co-operate to reduce the energy demand of sorbent regeneration. Additionally, the lower stripping temperatures, as compared with the traditional aqueous alkanolamines (110-140 °C at pressure over 1 bar), should also have beneficial effects by reducing the amine loss by evaporation, their thermal and oxidative degradation and the equipment corrosion rate. As a final remark, notwithstanding the possible advantages offered by the absorbents here reported, we are aware that a large scale application of this technology should require an accurate life cycle assessment to verify the operating and investment costs and benefits of the entire process.



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