



Full Length Article

Direct CO₂ capture from air with aqueous and nonaqueous diamine solutions: a comparative investigation based on ¹³C NMR analysisFrancesco Barzagli^{a,*}, Maurizio Peruzzini^a, Rui Zhang^b^a National Research Council, ICCOM Institute, via Madonna del Piano 10, 50019 Sesto F.no, Florence, Italy^b College of Chemical Engineering, Xiangtan University, Xiangtan, Hunan 411105, P.R. China

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ABSTRACT

Five different diamines, namely 1,2-diaminopropane, N,N-diethylethylenediamine, piperazine, 1-methylpiperazine and N,N,N',N'-tetramethylethylenediamine, have been investigated as liquid sorbents for the direct capture of CO₂ from air (DAC – Direct Air Capture) in both aqueous and non-aqueous solutions, using a 1:1 (volume scale) mixture of ethylene glycol and 1-propanol as an organic diluent. The capture performance of the 1.5 mol dm⁻³ diamine solutions was evaluated on the basis of the CO₂ absorption efficiency from an atmospheric air stream, continuously measured by means of a gas chromatograph during 24-hour bench-scale absorption experiments, carried out in an absorption column maintained at 25°C. The carbonated species formed in solution upon the CO₂ uptake and their relative amounts were evaluated by ¹³C NMR spectroscopy, a powerful non-invasive analytical technique that can provide valuable information on the reaction mechanisms. The correlations between the aerial CO₂ absorption efficiency, the chemical structure of diamines and the carbonated species formed in their different solutions during capture were presented and discussed. Furthermore, the CO₂ capture performance in DAC processes of the diamine solutions was compared to that of some of the more conventional alkanolamine solutions under the same operating conditions.

1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) has identified human influence as the dominant cause of the global warming observed since the mid-20th century, and today the correlation between the resulting climate change and the anthropogenic greenhouse gas (GHG) emissions in atmosphere is worldwide accepted (IPCC, 2014). The development of strategies aimed at reducing anthropogenic emissions of carbon dioxide, the main component of GHGs, should not be further delayed, in accordance with the Paris Agreement of 2015 and the more recent COP26 in Glasgow (2021), which recommend keep the global temperature rise within 1.5°C above the preindustrial level (UNFCCC - United Nations Framework Convention on Climate Change, 2021, 2015). To date, the most impactful actions are: (i) increasingly replacing the use of fossil fuels with renewable energy sources, (ii) improving the efficiency of energy production and utilization, (iii) enhancing the CO₂ capture from large-point sources, the so-called Carbon Capture and Sequestration (CCS) technology (Barzagli and Mani, 2019). Amine-based CCS is considered an effective and mature technology that can be retrofitted at yet working energy and industrial plants (Bui et al., 2018; Chen et al., 2022; El Hadri et al., 2017; Zhang et al., 2017), but, obviously, it cannot be applied to sparse

emissions. Since half of the annual anthropogenic CO₂ emissions comes from dispersed sources, mainly from transport and residential, commercial and service building conditioning, the development of an emerging technology for the removal of CO₂ from the atmosphere, known as Direct Air Capture (DAC), will be crucial for achieving the ambitious Paris' target (Marcucci et al., 2017; Rogelj et al., 2015; Sanz-Pérez et al., 2016).

In DAC processes, the ultra-diluted CO₂ (about 0.044% v/v in air) is selectively removed from the atmospheric air using either a solid or liquid sorbent. The sorbent is subsequently regenerated for its reuse through thermal desorption, with the simultaneous release of a stream of pure CO₂ that can be stored or, more intriguingly, used as raw material for several applications (National Academies of Sciences Engineering and Medicine (NASEM), 2019; Sanz-Pérez et al., 2016). DAC processes are not location-specific, and the capture facilities can be settled anywhere, in areas where carbon-free energy resources are available (e.g., sunny or windy areas), or near CO₂ storage or utilization sites, reducing transport costs significantly (National Academies of Sciences Engineering and Medicine (NASEM), 2019; Sanz-Pérez et al., 2016; Wilcox et al., 2017). On the other hand, the direct CO₂ capture from the atmospheric air requires a large amount of energy compared to CO₂ capture from flue gas (CO₂ about 8–15 % v/v). The very low concentration of aerial CO₂

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reduces the capture efficiency of the conventional sorbents and increases the costs (\$/tonCO₂) of the DAC process which, despite the most recent improvements, remains significantly more expensive than the CCS process (Keith et al., 2018; National Academies of Sciences Engineering and Medicine (NASEM), 2019; Sinha and Realff, 2019).

Although in the last few years some commercial entities have begun to operate in the market planning significant upscales (Erans et al., 2022), DAC is still a technology in the early stages of development, and the formulation of innovative sorbents with high capture performance and low energy demand for regeneration is required to approach to commercial viability.

To date, most of the DAC systems rely on solid sorbents, in particular immobilized amine/silica sorbents, hollow fiber sorbents or metal organic frameworks (MOFs), which are an acceptable compromise between CO₂ capture efficiency (not very high) and operating costs (sustainable) (Darunte et al., 2016; Derevschikov et al., 2014; Lee et al., 2019, 2018; Sabatino et al., 2021; Sadiq et al., 2020; Sujan et al., 2019; Veselovskaya et al., 2020). DAC systems with liquid sorbents have also been developed, in particular with the aqueous alkaline hydroxides KOH and NaOH: these sorbents react with ultra-dilute CO₂ more quickly and efficiently than solid adsorbents, but require very high temperatures for their regeneration (up to 900°C), significantly increasing the energy cost and sustainability of the entire process (Sen et al., 2020; Stolaroff et al., 2008; Zeman, 2007). Aqueous amino acids have recently been proposed as potential liquid sorbents for DAC: although the study is still in an early stage, they are considered very promising as they are inexpensive, low volatile, non-corrosive, non-toxic and exhibit aerial CO₂ capture performance comparable to alkaline hydroxides, but with less energy-intensive regeneration (Brethomé et al., 2018; Custelcean et al., 2021, 2019). Aqueous solutions of alkanolamines could also be considered as alternatives to aqueous alkaline hydroxides, as they are potentially able to maintain the same capture efficiency while requiring lower energy consumption for regeneration, thanks to desorption temperatures of around 100°C. Although they have been thoroughly investigated for CCS processes, amine solutions have not been used in commercial DAC systems to date, mainly due to the high volatility of most of these sorbents, which is not very compatible with the large volume of air that must be treated, resulting in high sorbent evaporation rate. However, the use of aqueous amine sorbents for aerial CO₂ capture has recently been evaluated both experimentally and through techno-economic analysis (Barzagli and Mani, 2021; Hanusch et al., 2019; Kiani et al., 2020; Kothandaraman et al., 2016).

In a recent paper, we have reported a screening study aimed at investigating the performance of several commercial amines as sorbents for DAC processes. Aqueous and non-aqueous solutions of 15 different primary, secondary, and tertiary alkanolamines were used for the CO₂ capture from compressed air in bench scale experiments, and their absorption performances were evaluated and compared each other (Barzagli et al., 2020). The study demonstrated that the fast production of amine carbamate is the key factor for an efficient absorption of aerial CO₂ and, consequently, that primary and secondary unhindered amines are more efficient than tertiary or sterically hindered amines, showing capture performances comparable to NaOH under the same operating conditions.

By extending that investigation, in this paper we report the aerial CO₂ capture performance of several diamine solutions, under the same experimental conditions of the previous screening study (Barzagli et al., 2020). Polyamines have received great attention in CCS processes because of their fast reaction kinetics and loadings, due to their multiple amino groups in each single molecule (Fan et al., 2016; Xiao et al., 2021, 2020). Here, five different diamines, namely 1,2-diaminopropane (1,2-DAP), N,N-diethylethylenediamine (DEEDA), piperazine (PZ), 1-methylpiperazine (MPZ) and N,N,N',N'-tetramethylethylenediamine (TMEDA), were investigated in order to evaluate the relationship amongst their molecular structures, their ability to capture CO₂, and the carbonated species that are formed in solution. The performance of di-

amines as DAC sorbents was evaluated in both aqueous and non-aqueous solutions, using a 1:1 (volume scale) mixture of ethylene glycol (EG) and 1-propanol (PrOH) as the organic diluent. In recent years, many water-lean systems for CO₂ capture have been developed (Wanderley et al., 2021): generally, the greater solubility of CO₂ in organic solutions can increase the reaction rate with the amine compared to aqueous solutions. It has also been shown that the use of organic diluents can lower the regeneration temperature of the sorbent well below 100°C, mainly because organic diluents generally have half the heat capacity of water (Alkhatib et al., 2022; Bhatti et al., 2021; Heldebrant et al., 2017; Karlsson et al., 2020; Svensson et al., 2014). In our previous study we demonstrated that using EG/PrOH as a diluent, the capture efficiency of aerial CO₂ by some unhindered primary amines is comparable to that of their aqueous solutions (Barzagli et al., 2020).

Each diamine solution (1.5 mol dm⁻³) has been screened as sorbent for the direct CO₂ capture from air in a single bench scale 24-hour absorption experiment, carried out in a thermostatted absorption column, kept at 25°C. At the end of the absorption, the CO₂-loaded solution was checked by ¹³C NMR spectroscopy, a powerful non-invasive analytical technique that allowed us to identify and quantify the carbonated species formed upon the aerial CO₂ capture, providing valuable information on the reaction mechanism (Hu et al., 2020; Karlsson et al., 2021; Perinu et al., 2018).

The correlations between the aerial CO₂ absorption efficiency, the chemical structure of diamines and the carbonated species formed in their different solutions during the capture process were presented and discussed in the paper, along with a comparison with the CO₂ capture performance in DAC processes of some of the more conventional alkanolamine solutions under the same operating conditions.

2. Experimental section

2.1. Materials

Ethylene glycol (EG), 1-propanol (PrOH), 1,2-diaminopropane (1,2-DAP), N,N-diethylethylenediamine (DEEDA), piperazine (PZ), 1-methylpiperazine (MPZ) and N,N,N',N'-tetramethylethylenediamine (TMEDA) were reagent grade (Sigma-Aldrich) and were used as received without further purification. Each diamine was evaluated in two different solutions, namely in water and in a 1:1 (volume scale) mixture of EG and PrOH as an organic diluent. In order to compare the results with those of our previous study (Barzagli et al., 2020), the concentration of all diamine solutions was fixed at 1.5 mol dm⁻³. The flow rate of the compressed atmospheric air feeding the absorber was regulated by means of a digital gas mass flow controller (Aalborg) and a gas meter (Cole Parmer). The percentage of CO₂ in air before and after the absorption process was evaluated with a Varian CP-4900 gas chromatograph, equipped with a PoraPLOT U column (Agilent) and a thermal conductivity detector (TCD). The percentage of CO₂ measured in the used compressed air was 0.044%.

2.2. Absorption experiments

The CO₂ capture performance from an air stream of each diamine solution was evaluated in a 24-hour bench scale absorption experiment, following a well-established procedure. Figure 1A shows a simplified diagram of the equipment used. The diamine solution (0.100 dm³) was charged into the absorber, which is a home-built glass cylinder with an internal diameter of 56 mm and a height of 400 mm, equipped with an external jacket that allows the circulation of a thermostatted liquid (Figure 1B). All experiments were conducted at constant temperature of 25°C, maintained by means of a Julabo F33-MC bath. The absorber was packed with 5 mm diameter glass rings, in order to increase the contact surface between atmospheric air and the diamine solution in the column. The apparatus worked in countercurrent: the compressed air was blown from the bottom of the column, at a constant flow rate

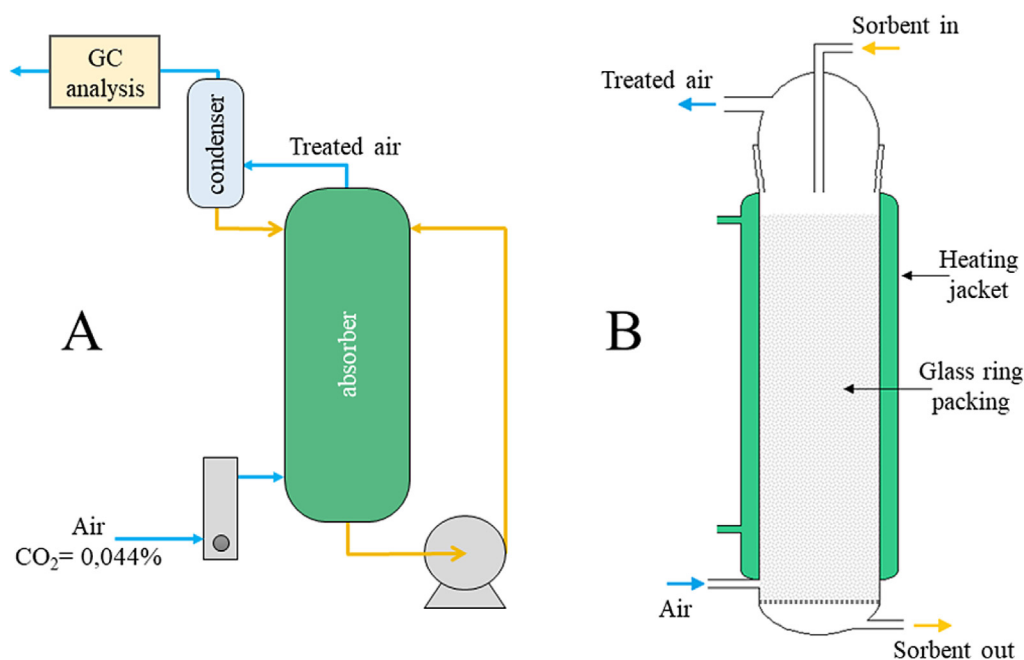


Figure 1. (A) Scheme of the experimental setup and (B) detail of the used absorber. Blue lines are referred to air, orange lines to the liquid sorbent.

of $46.5 \text{ dm}^3 \text{ h}^{-1}$ ($8.36 \cdot 10^{-4} \text{ mol CO}_2 \text{ h}^{-1}$), while the sorbent was fed from the top, by means of a peristaltic pump (Masterflex) which continuously circulated the amine from the bottom to the top of the absorber at a constant flow rate of $0.300 \text{ dm}^3 \text{ h}^{-1}$. The top of the absorber was equipped with a condenser cooled at -5°C : this very low temperature strongly limited the loss of diamines and diluents during the 24 hours of aerial CO_2 capture. The air exiting the condenser flowed through a concentrated H_2SO_4 solution and a gas purification tower filled with P_2O_5 , in order to remove any traces of water and diamine before entering the gas chromatograph. The comparison between the intensity of the GC signal of CO_2 in the air before and after the capture process allowed to continuously measure the CO_2 absorption efficiency (abs%).

2.3. ^{13}C NMR analysis

A Bruker Avance III 400 spectrometer operating at 100.613 MHz was used to record the ^{13}C NMR spectra of the diamine solutions at the end of the 24 hours of aerial CO_2 capture, with a previously reported procedure (Barzagli et al., 2017, 2013). The spectrometer worked with a pulse sequence with proton decoupling and NOE suppression, and with the following acquisition parameters: pulse angle = 90.0° , acquisition time = 1.3632 s , delay time = $2\text{--}30 \text{ s}$, data points = 65K , number of scans = $250\text{--}500$. Tetramethylsilane was used as an external standard, while acetonitrile was used as an internal reference. The signal for the deuterium lock was provided by a sealed glass capillary containing deuterium water (Aldrich) inserted into the NMR tube. The data was processed with Bruker Topspin 3.6.2 software.

After careful peak integration for each $-\text{CH}_2-$ resonance, the percentage of carbamate formed with respect to the total amine was calculated as the ratio between the area of the carbamate peak and the sum of the areas of the peaks of carbamate and of the rapidly equilibrating (free amine)/(protonated amine). 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 $-\text{CH}_2-$ carbon atoms that contain the same number of attached protons (Hook, 1997). The relative amounts of the different carbamates obtainable from the same diamine and of the fast-exchanging bicarbonate/carbonate ion were quantified by integrating the carbon resonances in the range $165\text{--}162 \text{ ppm}$. The ^{13}C atoms of bicarbonate, carbonate and carbamate functionality have no attached

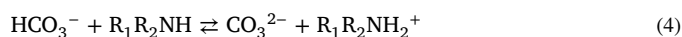
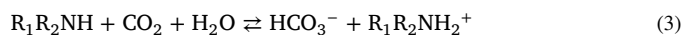
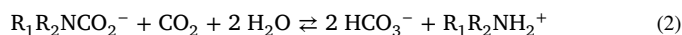
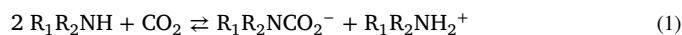
hydrogen, and therefore are characterized by a longer relaxation time compared to that of $-\text{CH}_2-$ groups, with consequent lower resonance intensity; however, an accurate peak integration of the carbon resonances could provide an estimation of the relative amounts of the carbonated species formed.

3. Results and Discussion

3.1. Chemical equilibria in solutions

In order to cover a significative range of different diamine configuration, we have selected 1,2-DAP (two primary N), DEEDA (one primary and one tertiary N), PZ (two secondary N), MPZ (one secondary and one tertiary N) and TMEDA (two tertiary N). Their chemical structures are reported in Figure 2. All the diamines were tested in aqueous and non-aqueous solutions, using a 1:1 (volume scale) mixture of EG and PrOH as organic diluent, with the exception of TMEDA which was only tested in water.

Compared to monoamine, the reaction mechanism between diamine and CO_2 is rather complex. In fact, each of the two amine functionalities of a diamine can independently interact with CO_2 . According to the following main reactions, primary and secondary amine functionalities ($\text{R}_1\text{R}_2\text{H}$, in primary amine $\text{R}_1 = \text{H}$) form the corresponding amine carbamate ($\text{R}_1\text{R}_2\text{NCO}_2^-$) both in water and in organic diluent, while bicarbonate and carbonate are formed only in aqueous solutions (Barzagli et al., 2018; El Hadri et al., 2017; Zhang et al., 2016):



Tertiary amine functionality ($\text{R}_1\text{R}_2\text{R}_3\text{N}$) reacts with CO_2 in aqueous systems to form bicarbonate (equation 6), while it is unable to form

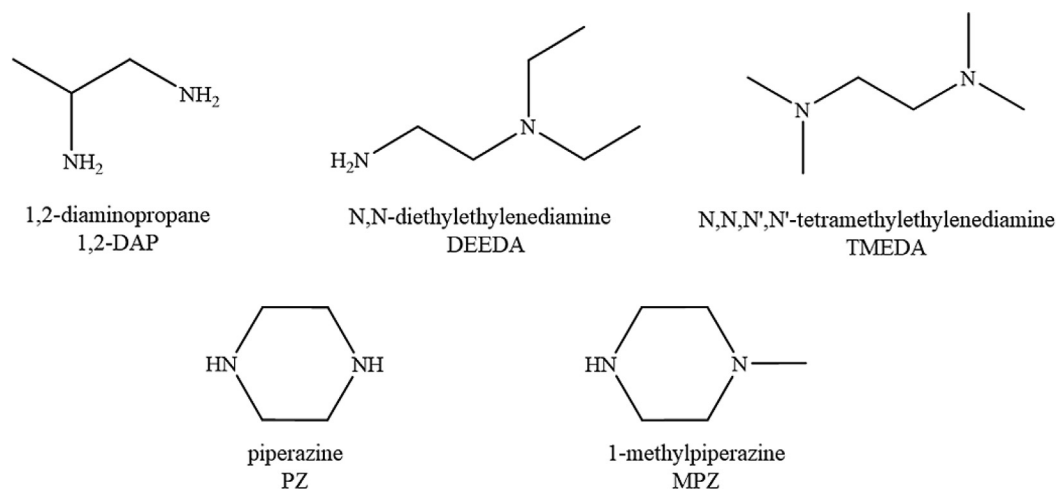
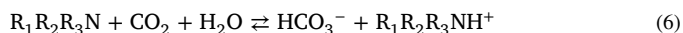
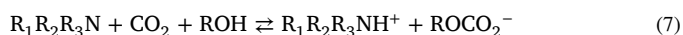


Figure 2. Name, acronym and chemical structure of the selected diamines.

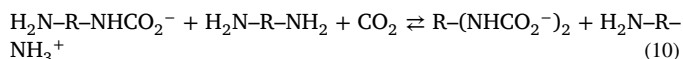
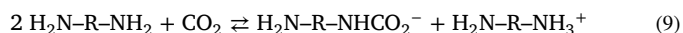
carbamate (equation 1) due to the lack of hydrogen atoms (Hu et al., 2020; Perinu et al., 2018):



Due to the absence of water, non-aqueous systems cannot form bicarbonate and carbonate ions equations 2–(6). However, organic diluents with hydroxyl groups (ROH) can react with both CO_2 and an amine functionality (which acts as a base) to form the corresponding alkyl carbonate ($ROCO_2^-$) (Barzagli et al., 2019; Karlsson et al., 2021):



When two or more amino functionalities of a polyamine react simultaneously, polycarbamate species can be formed (Hartono et al., 2007; Muchan et al., 2017). Consequently, diamines with primary and secondary functionalities have the potential to form a dicarbamate, through the further reaction of a carbamate with CO_2 as reported in equations 8–10:



where $H_2N-R-NH_2$ stands for a generic diamine with two primary amino groups. In our experimental conditions, the formation of the zwitterion species (equation 8) is not probable, because of the large excess of the amines with respect to the CO_2 absorbed. Among the diamines we investigated, 1,2-DAP and PZ can form the corresponding dicarbamate (Barzagli et al., 2013, 2012).

3.2. CO_2 capture from air

The selected diamine solutions (1.5 mol dm^{-3}) were tested as sorbents for DAC systems in a 24-hour absorption experiment, carried out at a constant temperature of 25°C , with the procedure described in section 2.2. The diamines performances were evaluated and compared on the basis of the calculated CO_2 absorption efficiency (abs%), defined as the amount of CO_2 captured with respect to the total amount of CO_2 in the treated air stream (0.044%). The amount of CO_2 captured from the air was continuously monitored by the gas chromatograph during

the experiment. At the end of the 24 hours of absorption, the species in solution were identified and quantified by means of ^{13}C NMR analysis.

The variation of the capture efficiency as a function of time is reported for all the solutions tested in Figure S1 in the Supporting Information, while the main results of the absorption experiments are summarized in Table 1. For all the tested diamine solutions we reported the average CO_2 absorption efficiency together with the actual abs% values measured at 1 and 24 hours, in order to evaluate the variation of the capture efficiency over time (Table 1, entries 1–9). TMEDA has been used only in aqueous solution, because in organic diluent it is not able to capture CO_2 : having only tertiary amino functionalities in its structure, it cannot form carbamates, and in a diluent other than water it cannot even form bicarbonate and carbonate. Table 1 also shows the absorption efficiency values for aqueous and non-aqueous solutions of 2-aminoethanol (MEA) and 2-(butylamino)ethanol (BUEA), and for aqueous 2-(dimethylamino)ethanol (DMMEA), obtained with the same apparatus and under the same operating conditions in our previous DAC study (Barzagli et al., 2020), and here reported for comparative purposes (Table 1, entries 10–14).

The data reported in Table 1 allow some general considerations. As a first finding, for all tested diamines, the actual (at 1 and 24 hours) and average CO_2 absorption efficiency values (abs%) measured in water were always greater than those measured with EG/PrOH as organic diluent. These results are consistent with the MEA and BUEA values also reported in Table 1 and with all the results obtained in our previous screening study with alkanolamines (Barzagli et al., 2020). It should also be noted that the different CO_2 capture efficiency between aqueous and non-aqueous solutions greatly depends on the amine used: 1,2-DAP performed similarly with both diluents (Table 1, entries 1 and 2), while the absorption efficiency of MPZ varied drastically depending on the diluent used (Table 1, entries 7 and 8).

The average capture efficiency of aqueous diamines followed the order $1,2\text{-DAP} \approx \text{DEEDA} > \text{PZ} > \text{MPZ} \gg \text{TMEDA}$ (Table 1, entries 1, 3, 5, 7 and 9). Interestingly, this trend almost corresponds to the decrease in alkalinity, with the exception of TMEDA, (pKa1 values from Table 1: 10.00, 10.02, 9.73, 9.14 and 9.28, respectively), as expected in an acid-base reaction. The comparison of the actual values at 1 and 24 hours shows that the absorption efficiency remained almost constant throughout the duration of the experiment for all aqueous diamines with the exception of MPZ, which showed a significant decrease in abs% over time (from 89.3% to 76.8%, Table 1, entry 7), as also highlighted in Figure S1 in Supporting Information. TMEDA, on the other hand, perform poorly since the beginning of the absorption process (Table 1, entry 9), showing a behavior very similar to that of DMMEA, a tertiary alkanolamine, under the same operating conditions (Table 1, entry 14).

Table 1

Aerial CO₂ absorption efficiency (abs%), reported as measured actual values (at 1 and 24 h) and as calculated total average value. Abs% values for MEA, BUMEA and DMMEA from previous work (Barzagli et al., 2020).

entry	amine	diluent	pKa ₁ (25°C)	pKa ₂ (25°C)	abs %			Reference for pKa
					at 1h	at 24h	average	
1	1,2-DAP	H ₂ O	10.00	7.13	90.1	89.6	89.9	Williams (2011)
2		EG/PrOH			89.2	88.6	89.1	
3	DEEDA	H ₂ O	10.02	7.07	90.0	89.5	89.7	Williams (2011)
4		EG/PrOH			88.3	82.6	85.7	
5	PZ	H ₂ O	9.73	5.35	88.5	87.0	87.3	Khalili et al. (2009)
6		EG/PrOH			88.1	72.9	81.2	
7	MPZ	H ₂ O	9.14	4.63	89.3	76.8	84.0	Khalili et al. (2009)
8		EG/PrOH			88.5	20.0	54.3	
9	TMEDA	H ₂ O	9.28	5.89	51.2	41.9	44.6	Xiao et al. (2020)
10	MEA	H ₂ O	9.51		86.9	87.4	87.3	Gangarapu et al. (2013)
11		EG/PrOH			85.6	82.4	84.7	
12	BUMEA	H ₂ O	9.72		85.9	83.5	85.2	Barzagli et al. (2020)
13		EG/PrOH			79.3	23.7	51.6	
14	DMMEA	H ₂ O	9.57		48.3	36.6	40.8	Gangarapu et al. (2013)

The investigation of the performance of non-aqueous diamines (Table 1, entries 2, 4, 6 and 8) leads to similar considerations. The average absorption efficiency in EG/PrOH diluent has the same trend observed in water, but only 1,2-DAP (Table 1, entry 2) maintained high capture efficiency values for the whole duration of the experiment (Figure S1 in Supporting Information). Noticeable is the drastic drop in absorption efficiency over time of MPZ, from 88.5% to 20.0% (Table 1, entry 8).

All these findings suggest that the efficiency of aerial CO₂ capture by 1,2-DAP and DEEDA is closely related to the presence of at least one unhindered primary amino group in the diamine structure. Compared with PZ (two secondary amino groups) and MPZ (one secondary and one tertiary amino group), 1,2-DAP and DEEDA have higher and, more importantly, almost constant absorption efficiency values for the entire duration of the experiment. Moreover, the effect of any tertiary groups seems negligible. Indeed, comparing these results with those of our previous study (Barzagli et al., 2020), the CO₂ absorption efficiency values obtained for aqueous and non-aqueous solutions of DEEDA (containing a tertiary and a primary unhindered amino group) were very similar to those obtained with the primary unhindered amine MEA (Table 1, entries 3, 4, 10 and 11). Similarly, the performances of the MPZ solutions were consistent with those of the secondary amine BUMEA (Table 1, entries 7, 8, 12 and 13).

In order to better understand the behavior of the different diamines and the mechanisms of the aerial CO₂ capture processes, all the solutions were ¹³C NMR analyzed at the end of the absorption experiment, in order to identify and quantify the carbonated species formed. The integration of the ¹³C NMR signals in the range 160–165 ppm of the spectra allows to calculate the relative amounts (%) of the different products formed during CO₂ capture, as reported in section 2.3. All the results of this speciation study are reported in Table 2.

The ¹³C NMR spectra of the aqueous solutions of the diamines after 24 hours of CO₂ capture from air are reported in Figure 3. The numbers indicate the carbon atoms of both free and protonated amine fast exchanging in the NMR scale, while asterisks denote the chemical shifts of carbon backbones of the amine carbamate.

The reaction between aqueous 1,2-DAP and CO₂ led to the formation of two distinct carbamates, one for each of the two different unhindered primary amino groups, in different percentages. The two carbamates are easily identifiable in the corresponding ¹³C NMR spectrum by the two signals assigned to the carbon atom of the carbonyl group of the carbamates, at 164.5 (C*) and 164.2 ppm (C**), and their relative amount are 83.7 % and 16.3 %, respectively (Table 2, entry 1). In particular, the most abundant carbamate is formed by the amine group adjacent to the –CH₂– group, with the higher electron density and the lower steric hindrance (in Figure 3, the C atom indicated with number 1). Under

the operating conditions of the experiment, 1,2-DAP did not form the dicarbamate species (equation 10), mainly due to the strong excess of amines compared to the total amount of CO₂ treated, which favors the production of the single carbamate. For the same reason, PZ also did not form dicarbamate.

The aqueous solutions of DEEDA and PZ, on the other hand, can form only one type of carbamate: as a matter of fact, DEEDA has only one amino functionality capable of reacting directly with CO₂ (the primary one), while the two secondary amino functionalities of PZ are identical, and therefore give the same carbamate. The single signal of carbamate in the PZ and DEEDA spectra (at 163.7 ppm and 164.4 ppm, respectively) is the clear indication of the formation of a sole carbamate species upon the CO₂ uptake.

It should be noted that the bicarbonate/carbonate signal is not present in the spectra of 1,2-DAP, DEEDA and PZ: due to the excess of amine (1.5 mol) with respect to the total CO₂ that passes in the 24 hours with the flux used (about 0.02 mol), these amines which have two amino functionalities capable of directly binding CO₂ tend to form exclusively carbamate (reaction 1) instead of bicarbonate or carbonate (reactions 2–4).

Differently, MPZ has only one amino group that can form carbamate (signal at 162.8 ppm), but the less intense signal at 163.4 ppm reveals that its reaction with CO₂ also led to the formation of bicarbonate/carbonate ions: from peak integration we calculate that, after 24 hours of experiment, CO₂ was captured for 89.6% as MPZ-carbamate and for the remaining 10.4% as bicarbonate and carbonate (Table 2, entry 7).

Finally, TMEDA cannot form carbamate with its two tertiary amino functionalities, and CO₂ can be captured only as bicarbonate/carbonate, as evident from the broad signal at 164.4 ppm; consequently, the only peaks present in the 10–60 ppm region of the spectrum are those related to the fast-equilibrating (free amine)/(protonated amine).

By comparing the results of the analysis of the spectra of the aqueous diamines with the data reported in Tables 1 and 2, we can assume that the high reaction rate of the carbamate formation is probably the crucial parameter for a higher aerial CO₂ capture efficiency of 1,2-DAP and DEEDA. As a matter of fact, the absorption efficiencies (Abs %) at 1 and 24 hours are substantially similar. Moreover, the formation of carbamate (equation 1) with unhindered primary amino groups is stoichiometrically favored compared to the formation of bicarbonate/carbonate (equations 2–4), due to the large excess of amine with respect to the ultra-dilute CO₂ captured. The carbamate derivatives of the diamines featuring secondary amino groups (PZ and MPZ) are less stable than those of the primary amines (Barzagli et al., 2020), and the slow formation of the bicarbonate cannot be neglected (equation 2). Furthermore, the low bicarbonate/carbonate formation kinetics explains the

Table 2

Total CO₂ captured, calculated from the average absorption efficiency (Abs) in the 24 hours of experiment, and ¹³C NMR speciation of the products formed, reported as relative amount of the different compounds. C* indicates the carbamate, C** refers to the second carbamate (only for 1,2-DAP), b/c indicates the sum of bicarbonate and carbonate ions.

entry	amine	diluent	Abs (%)	CO ₂ captured (mol)	speciation (%)		
					C*	C**	b/c
1	1,2-DAP	H ₂ O	89.9	0.0182	83.7	16.3	0
2		EG/PrOH	89.1	0.0181	83.1	16.9	0
3	DEEDA	H ₂ O	89.7	0.0182	100	0	0
4		EG/PrOH	85.7	0.0174	100	0	0
5	PZ	H ₂ O	87.3	0.0177	100	0	0
6		EG/PrOH	81.2	0.0165	100	0	0
7	MPZ	H ₂ O	84.0	0.0170	89.6	0	10.4
8		EG/PrOH	54.3	0.0110	100	0	0
9	TMEDA	H ₂ O	44.6	0.0090	0	0	100

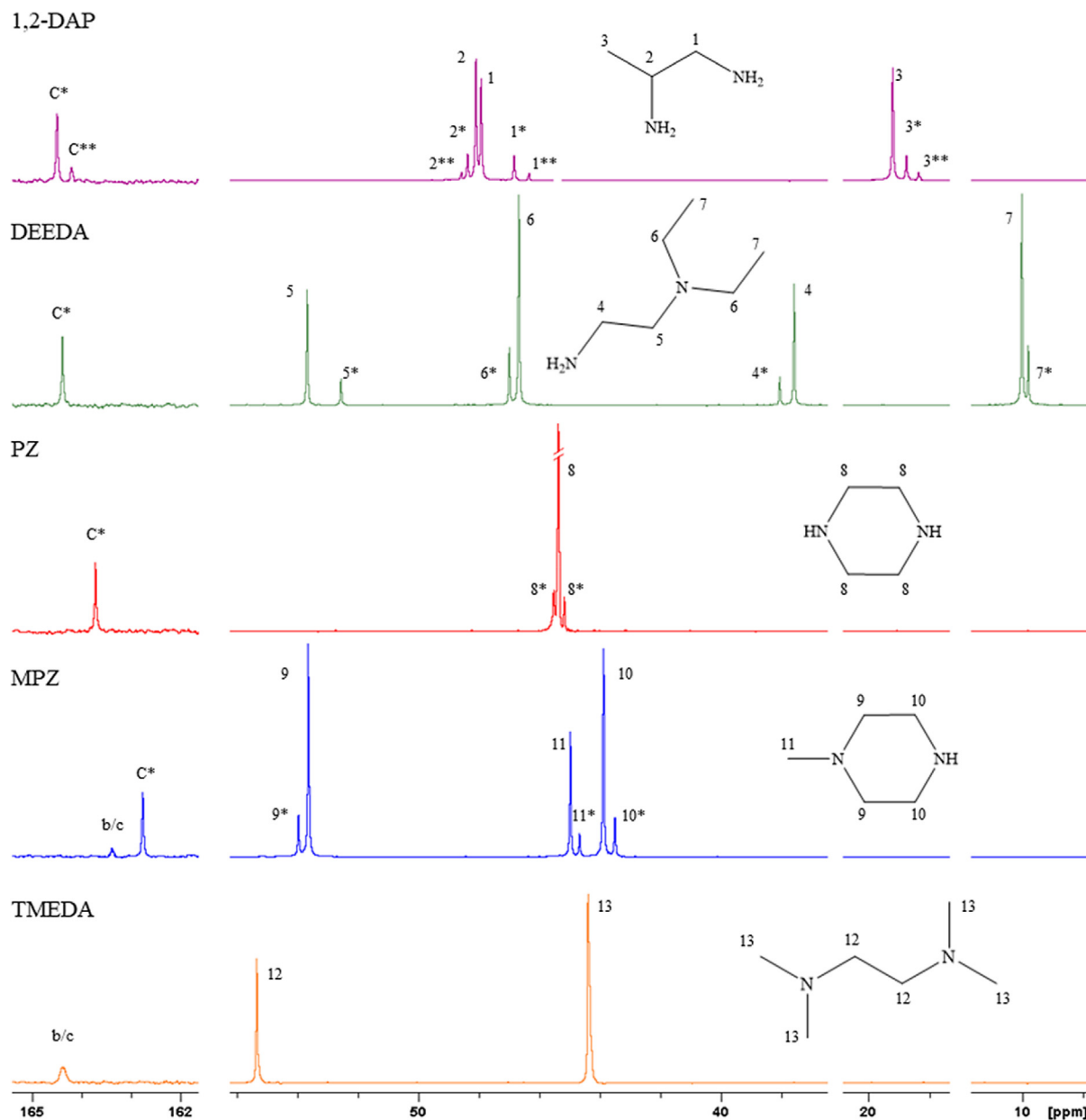


Figure 3. ¹³C NMR spectra of all the aqueous diamines at the end of the absorption experiment. Asterisks (*) denote the carbon backbones of amine carbamate. (**) refers to the second carbamate of 1,2-DAP. C indicates the carbonyl atom of carbamates, b/c indicates the signal of fast exchanging bicarbonate/carbonate ions. The intensity of the signals in the range 162–165 ppm is not in scale.

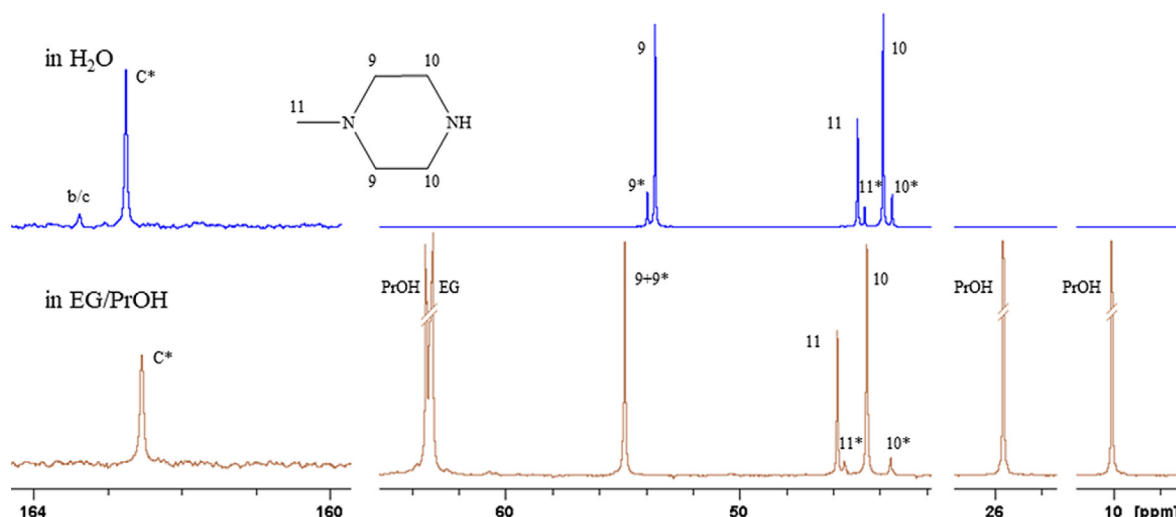


Figure 4. ^{13}C NMR spectra of aqueous and non-aqueous MPZ solutions at the end of the absorption experiment. Asterisks (*) denote the carbon backbones of amine carbamate. C indicates the carbonyl atoms of amine carbamate, b/c indicates the signal of fast exchanging bicarbonate/carbonate ions. The intensity of the signals in the range 160–164 ppm is not in scale.

poor performance of aqueous TMEDA, as these ions are the only products obtainable from the reaction of CO_2 with the tertiary amino groups of this diamine. Similar findings have already been reported in other DAC studies (Foo et al., 2017; Lee et al., 2018).

In the absence of water, bicarbonate can't be produced (equations 2–(6)), and CO_2 can only react with primary or secondary amino groups to form carbamate (Table 2, entries 2, 4, 6 and 8). This is particularly evident from the comparison of the ^{13}C NMR spectra of MPZ in aqueous solution and in organic diluent, shown in Figure 4. On the contrary, the ^{13}C NMR spectra of 1,2-DAP, DEEDA and PZ in EG/PrOH did not show variations of the products with respect to the corresponding aqueous solutions.

The data in Table 2, together with the variation of the CO_2 capture efficiency as a function of time (Figure S1 in Supporting Information), highlight the clear difference in the amount of CO_2 absorbed, which decreases in the order 1,2-DAP > DEEDA > PZ > MPZ. These values confirm the greater stability of the carbamates formed by the primary amino functionalities (1,2-DAP and DEEDA) compared to those formed by the secondary ones (PZ and MPZ). In particular MPZ, which has a single secondary amino functionality, forms an unstable carbamate: while in H_2O the CO_2 absorption could also occur with the formation of bicarbonate (Figure 4), in organic diluent it cannot occur, and the capture efficiency rapidly decreases over time.

Finally, it should be noted that, due to the large excess of amine with respect to CO_2 in air, the formation of the alkyl carbonates of the alcohols used as diluents was not observed in any ^{13}C NMR spectrum of the non-aqueous diamine solutions (equation 7).

4. Conclusions

In the present study we investigated the absorption performance of five different diamines as sorbents for the direct capture of CO_2 from air, in both aqueous and non-aqueous solutions. Their CO_2 capture efficiency from an atmospheric air stream was evaluated in a 24-hour absorption experiment, and the results were correlated with the diamine's chemical structure and with the carbonated species formed during the CO_2 uptake.

As a general finding, the high aerial CO_2 capture efficiency of a diamine solution is closely related to the number of unhindered primary amino groups in its chemical structure. The fast carbamate reaction between the ultra-dilute aerial CO_2 and the unhindered primary amino groups of 1,2-DAP and DEEDA ensures a high absorption efficiency,

both in water and in organic diluents. Also, the diamines with secondary amino groups (PZ and MPZ) showed good absorption efficiency in water, but in organic diluent their performances dropped drastically, because of the decrease of the amine/ CO_2 ratio with absorption time. TMEDA, with two tertiary amino groups, is unable to form carbamate and its aqueous solution has provided poor CO_2 capture efficiency due to the low bicarbonate/carbonate production kinetics.

Comparing the absorption performances of these diamines with those of some common alkanolamines under the same operating conditions, we can conclude that diamines can only be advantageous if they have at least one unhindered primary amino group, otherwise the performances of diamines match those of alkanolamines with similar chemical structure. It was also verified that, for the same amine, the actual (at 1 and 24 hour) and average absorption efficiency values in water were generally higher than those in EG/PrOH: this could suggest that, for DAC processes, the nonaqueous sorbents are less suitable than aqueous ones. However, it should be considered that when the same amine performs equally in the two different types of diluents, as in the case of 1,2-DAP, the use of a nonaqueous diluent can allow significant energy savings for sorbent regeneration in continuous absorption/desorption processes, as already demonstrated also for CCS processes. It is important to underline that this comparative investigation is focused on identifying the diamines potentially most suitable for DAC processes. Evaluations of their possible commercial large-scale use will require further studies conducted with more realistic absorption systems (for example, with a crossflow air-liquid contactor) to determine diamine cyclic capacities, regeneration costs and possible evaporative loss of sorbent.

As a final remark, ^{13}C NMR analysis proved to be a fundamental tool for studying the reactions between ultra-diluted CO_2 and amines in aqueous and non-aqueous systems

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.ccs.2022.100049](https://doi.org/10.1016/j.ccs.2022.100049).

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