

1 Screening Study of Different Amine-Based Solutions as Sorbents for 2 Direct CO₂ Capture from Air

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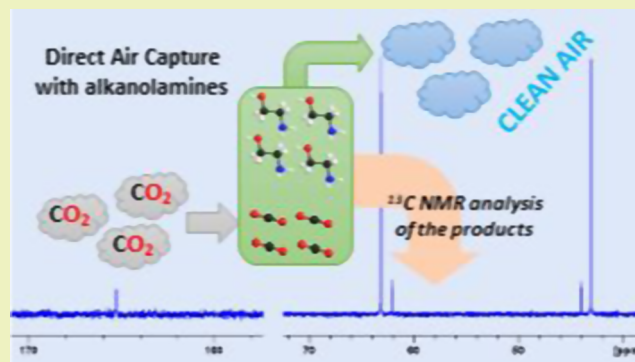


Supporting Information

4 **ABSTRACT:** Direct air capture (DAC) is an emerging technology
5 that can help limit the global temperature rises, as it has the
6 potential to contrast the dispersed CO₂ emissions coming from
7 transport and heating that cannot be captured with traditional CCS
8 methods. Although recent improvements are bringing DAC closer
9 to commercial feasibility, an obstacle to its diffusion is the high
10 regeneration energy required by the most common liquid sorbents,
11 Na or K hydroxides. To develop efficient and more sustainable
12 sorbents, in this screening study, several alkanolamines, particularly
13 those already known for their utilization in CCS, were tested for
14 DAC. The percentage of CO₂ absorbed from compressed air of
15 their 1.5 mol dm⁻³ aqueous solutions was evaluated in 24 h capture
16 experiments, and the species formed were identified and quantified
17 by means of ¹³C NMR spectroscopy. For selected amines, their performance in organic diluents was also evaluated. The correlations

18 between aerial CO₂ absorption, chemical structures of the different amines, and species formed in solution have shown that a high
19 yield production of amine carbamate is the decisive factor for an effective CO₂ capture and that aqueous primary unhindered amines
20 are as efficient as aqueous alkali hydroxides, with the potential of a lower regeneration energy.

21 **KEYWORDS:** carbon dioxide capture, direct air capture, DAC, alkanolamine, ¹³C NMR speciation, amine carbamates



22 ■ INTRODUCTION

23 The recent climate conference COP21 (Paris, 2015) under-
24 lined the need to take actions by most of the world's countries
25 to mitigate climate change and keep the global temperature
26 rise well below 2 °C above preindustrial levels.¹ In addition to
27 the reduction of the combustion of fossil fuels and the
28 improvement of the CO₂ capture from large-point sources, the
29 so-called carbon capture and sequestration (CCS) technol-
30 ogy,^{2,3} a strategy that is emerging as crucial for achieving the
31 ambitious Paris' target, is the development of negative
32 emission technologies (NETs).⁴ NETs relate to CO₂ removal
33 from the atmosphere through techniques such as the direct
34 chemical CO₂ capture from ambient air direct air capture
35 (DAC).⁵ DAC is a developing technology with the potential to
36 contrast the dispersed emissions coming from transport and
37 residential heating, which cannot be captured at their sparse
38 sources and represent approximately half of the annual
39 anthropogenic CO₂ emissions.^{6,7} In the DAC process, large
40 air-adsorbent contactors equipped with many fans blow the air
41 to the absorber, where the ultradiluted CO₂ (approximately
42 410 ppm) is selectively removed and the "clean" air is returned
43 to the atmosphere. Afterward, the sorbent is regenerated and
44 the captured CO₂ is released for disposal or, more
45 interestingly, for direct utilization, as, for example, in the
46 catalytic methanation.⁸ Moreover, DAC systems benefit from

their inherent flexibility of placement, and careful location 47
planning can favor the use of renewable energy and can reduce 48
the cost of CO₂ transportation from the capture site to the 49
storage or utilization sites.⁹ An ideal DAC process should 50
combine a quick and efficient CO₂ capture with low-energy 51
inputs for air handling, sorbent regeneration, and CO₂ release. 52
Although DAC processes were considered prohibitively 53
expensive until a few years ago, with costs in the range 200– 54
1000 \$/ton of CO₂ (10 times higher than conventional capture 55
from flue gas), the most recent economic analyses suggest that 56
with the latest improvements (mainly engineering) the DAC 57
technology is approaching commercial viability, with capturing 58
costs that can be reduced to less than 100 \$/ton of CO₂.^{10–12} 59
In particular, several studies demonstrated that an air–liquid 60
cross-flow scheme, which reduces the pressure drop, can 61
dramatically lower the capture cost.⁹ 62

So far, the main potential technologies involve chemisorbent 63
materials;⁶ in particular, many researchers have focused on the 64

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Table 1. Name, Acronym, and Chemical Structure of the Selected Amines and Organic Diluents

	Name	Acronym	Chemical structure	CAS number
Primary	2-aminoethanol	MEA		141-43-5
	2-(2-aminoethoxy)ethanol	DGA		929-06-6
	1-amino-2-propanol	1A2P		78-96-6
	2-amino-1-butanol	2A1B		96-20-8
	2-amino-2-methyl-1-propanol	AMP		124-68-5
	2-amino-2-methyl-1-3-propandiol	AMPD		115-69-5
	2-amino-2-(hydroxymethyl)-1,3-propanediol	TRIZMA		77-86-1
Secondary	2-(methylamino)ethanol	MMEA		109-83-1
	2-(ethylamino)ethanol	EMEA		110-73-6
	2-(butylamino)ethanol	BUMEA		111-75-1
	2-(tertbutylamino)ethanol	TBMEA		4620-70-6
	Diethanolamine	DEA		111-42-2
	bis(2-hydroxypropyl)amine	DIPA		110-97-4
	Tertiary	2-(dimethylamino)ethanol	DMMEA	
N methyl diethanolamine		MDEA		105-59-9
Diluents	ethylene glycol	EG		107-21-1
	1-propanol	PrOH		67-63-0
	diethylene glycol monoethyl ether	DEGMEE		111-90-0

development of solid-based sorbent systems, especially immobilized amine/silica sorbents or hollow fiber sorbents.^{13–18} Alkaline liquid sorbents have also been taken into consideration for their fast and efficient CO₂ capture in continuous (not batch) processes;⁶ however, their development has so far been limited due to the high costs of regeneration. Aqueous solutions of sodium and potassium hydroxide have been extensively studied as sorbents for DAC processes for their strong alkalinity and their high reaction rate even with ultradiluted CO₂.^{19,20} Despite a good capture efficiency, the process is energy intensive: the sorbent regeneration is based on the formation of CaCO₃ by adding Ca(OH)₂, and the subsequent calcination of CaCO₃ to release pure CO₂ requires very high temperatures (900 °C), which entail high energy costs, up to 180 kJ/mol CO₂.^{9,10,19}

With the aim of developing new liquid sorbents for the efficient capture of ultradiluted aerial CO₂ with a lower regeneration energy compared to KOH and NaOH solutions, we decided to investigate the performance of several amine-based sorbents in DAC systems. Aqueous amines are well-known (and widely investigated) sorbents for the efficient CO₂ capture from large-scale emission points (CO₂ 12–15% v/v), which can be regenerated at $T = 100–120$ °C, a temperature well below that required for the CaCO₃ calcination.^{21,22}

Currently, many researchers are working to develop innovative amine-based absorbents able to combine the most efficient CO₂ capture with the lowest heat of CO₂ desorption,^{23–26} an important parameter for assessing the regeneration energy (the opposite of the heat of CO₂ absorption, usually lower than 90 kJ/mol CO₂ for all of the most studied aqueous amines).^{22,27}

In this screening study, different types of amines have been compared as DAC sorbents under the same operating conditions to identify the chemical peculiarities crucial for a more efficient CO₂ capture from air: several aqueous alkanolamine solutions have been tested in absorption experiments lasting 24 h, and the measured percentages of CO₂ absorbed have been correlated with the chemical properties of the different amines. The carbonated species formed upon the CO₂ uptake and their relative amounts were evaluated by ¹³C NMR spectroscopy, a powerful noninvasive analytical technique that can provide valuable information on the absorption mechanism.^{28,29} The performances of some amines have also been investigated in organic diluents, namely, in diethylene glycol monoethyl ether (DEGMEE) or in a 1:1 (volume scale) mixture of ethylene glycol (EG) and 1-propanol (PrOH). The higher solubility of CO₂ in organic diluents than in water, and the lower heat capacity and vapor pressure of organic diluents compared to water, could enhance

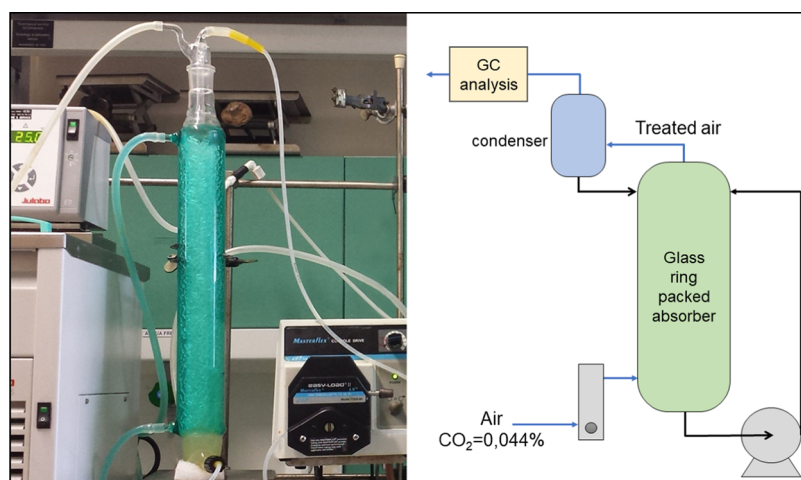


Figure 1. Apparatus for the determination of the percentage of CO₂ absorbed and its schematic flow diagram. Blue lines refer to air and black lines to the liquid sorbent.

113 the CO₂ absorption and reduce the heat required for the
 114 sorbent regeneration: as a matter of fact, several studies have
 115 shown that the use of organic diluents instead of water can
 116 lower the desorption temperature well below 100 °C.^{30–33}
 117 Moreover, we have recently verified that, for the same amine,
 118 the heat of CO₂ desorption in organic solutions is lower than
 119 in aqueous solution.³⁴

120 The CO₂ capture performances of the different alkanolamine
 121 solutions were compared, in the same operating conditions,
 122 with those of aqueous NaOH, sodium carbonate, and
 123 potassium glycinate, some of the most commonly proposed
 124 sorbents in DAC processes. Moreover, some similarities with
 125 general performance trends for amine-based solid sorbents
 126 have been highlighted.

127 ■ MATERIALS AND METHODS

128 **General Information.** All of the organic diluents and the amines
 129 (Sigma-Aldrich) were reagent grade and were used as received
 130 without further purification. A gas controller (Cole Parmer) was used
 131 to measure the flow rate of the compressed air. The concentration of
 132 aerial CO₂ entering and exiting the absorption column was
 133 determined with a Varian CP-4900 gas chromatograph.

134 The CO₂ percentage measured in the compressed air used was
 135 0.044%. Due to the low amount of CO₂ in air, the amine
 136 concentration was fixed at 1.5 mol dm⁻³ for all of the tested solutions
 137 (usually, in the CCS process, the amine concentration is in the range
 138 3–5 mol dm⁻³). In this study, we have considered a large variety of
 139 amines such as primary, secondary, tertiary, and sterically hindered
 140 amines: their names, chemical structures, and CAS numbers are
 141 reported in Table 1, together with those of the used organic diluents.

142 **Experiments of CO₂ Absorption from Air.** The percentage of
 143 CO₂ absorbed from air by the different amine solutions was evaluated
 144 in a home-built glass cylinder with the internal diameter of 56 mm
 145 and the height of 400 mm, equipped with an external jacket (Figure
 146 1). The absorber temperature was kept at 25 °C by circulating a
 147 thermostatted liquid (by means of a Julabo model F33-MC bath)
 148 through the jacket of the column. The gas–liquid contactor column
 149 was packed with glass rings with a diameter of 5 mm and charged with
 150 0.100 dm³ of the sorbent. The packing maximizes the exchange
 151 surface between air and the sorbent and provides the reaction mixture
 152 with a sufficient residence time. The apparatus was designed to
 153 operate in a counter current mode: the compressed air (CO₂ 0.044%
 154 v/v) was continuously introduced from the bottom of the column, at
 155 a flow rate of 46.5 dm³ h⁻¹ (8.36 × 10⁻⁴ mol CO₂ h⁻¹), while the
 156 liquid sorbent was introduced from the top of the column; a peristaltic
 157 pump (Masterflex) allows the sorbent to circulate continuously from

the bottom to the top of the column at the desired flow rate (0.3 dm³
 h⁻¹). The apparatus used and its simplified sketch are reported in
 Figure 1. The CO₂-depleted air, exiting from the top of the absorber,
 was dried by flowing in turn through a condenser cooled at –5 °C,
 a concentrated H₂SO₄ solution, and a gas purification tower filled with
 P₂O₅, to remove all of the possible amine, solvent, and water traces
 before being analyzed by the gas chromatograph. The comparison
 between the amount of CO₂ in inlet and outlet air allowed us to
 continuously evaluate the percentage of CO₂ absorbed (abs %). All of
 the experiments were stopped after 24 h.

¹³C NMR Spectroscopy. ¹³C NMR spectroscopy allows the
 identification of the carbonated species formed in solution after the
 CO₂ uptake and the evaluation of their relative amounts.^{35–39} Here,
 after each absorption experiment, a sample of the solution was
 analyzed with a Bruker Avance III 400 spectrometer operating at
 100.613 MHz using a procedure that has already been described in
 previous studies.^{40,41} Details of the experimental settings and
 procedures are reported in the Supporting Information, together
 with two examples of ¹³C NMR spectra before and after the CO₂
 absorption (Figures S1 and S2). The percentage of carbamate formed
 with respect to the total amine (% Am tot) was calculated as the ratio
 between the area of the carbamate peak and the sum of the areas of
 the carbamate peak and of the peak of the rapidly equilibrating (free
 amine)/(protonated amine). All of the reported spectra refer to 24 h
 of absorption. The spectra relating to 1 h of absorption were not
 reported because the signals of the carbonated species had too low
 intensity to be identified.

■ RESULTS AND DISCUSSION

Aqueous Systems. The reaction of CO₂ with aqueous
 amine solutions entails several equilibria,^{21,22,29,39} shown by
 eqs 1–7, taking a primary amine (R₁NH₂) as an example

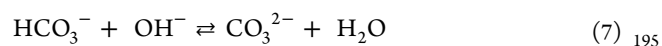
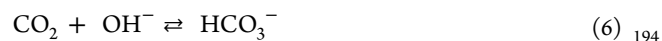
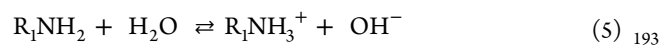
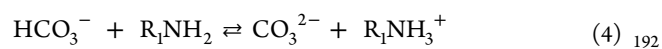
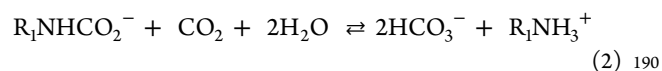
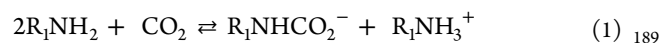


Table 2. Percentage of CO₂ Absorbed (abs%) after 1 and 24 h and Average Values, the Total Amount (mol) of Absorbed CO₂ in 24 h, Absolute (mol) and Relative Amounts of Carbamate Formed (% with Respect to the Total Amount of Amine, % Am tot), and the Percentage of CO₂ Captured as Carbamate^a

entry	amine (or basic species)	pK _b at 25 °C	abs%			CO ₂ abs 24 h (mol)	carbamate		
			at 1 h (%)	at 24 h (%)	average (%)		mol	% Am tot	% CO ₂ abs as carbamate
1	NaOH		86.4	88.3	88.1	0.0177			
2	Na ₂ CO ₃		20.4	11.8	16.9	0.0034			
3	K ⁺ Gly ⁻		89.3	89.3	89.6	0.0180	0.0175	11.7	97.2
4	MEA	4.49 ⁴²	86.9	87.4	87.3	0.0175	0.0164	10.9	93.7
5	DGA	4.38 ⁴³	85.8	84.8	85.5	0.0172	0.0150	10.0	87.2
6	1A2P	4.50 ⁴²	88.8	87.9	88.4	0.0177	0.0177	11.8	100
7	2A1B	4.40 ⁴³	87.7	85.0	87.1	0.0175	0.0167	11.1	95.4
8	AMP	4.29 ⁴²	76.9	65.4	72.3	0.0145			
9	AMPD	5.16 ⁴²	45.7	22.1	32.5	0.0065			
10	TRIZMA	5.78 ⁴³	34.7	10.6	22.2	0.0045			
11	MMEA	4.12 ⁴²	88.4	89.1	88.9	0.0178	0.0143	9.5	80.3
12	EMEA	4.00 ⁴²	86.1	85.1	85.9	0.0172	0.0097	6.5	56.4
13	BUMEA	4.28 ⁴³	85.9	83.5	85.2	0.0171	0.0114	7.6	66.7
14	TBMEA	3.96 ⁴⁴	64.8	48.8	56.3	0.0113			
15	DEA	5.12 ⁴²	78.4	70.2	74.5	0.0150	0.0122	8.1	81.3
16	DIPA	5.12 ⁴²	65.7	50.1	57.8	0.0116	0.0111	7.4	95.7
17	DMMEA	4.43 ⁴²	48.3	36.6	40.8	0.0082			
18	MDEA	5.43 ⁴⁵	41.8	14.2	26.6	0.0053			

^a"/" indicates that the carbamate is not formed. pK_b of the different amines is also reported.

196 where R₁NHCO₂⁻ denotes the carbamate of the amine.

197 The same equations occur with aqueous secondary amines
198 (R₁R₂NH). Equations 1 and 2 do not apply to tertiary amines
199 (R₁R₂R₃N) that are unable to form carbamates due to the lack
200 of hydrogen atoms on the amine functionality.^{29,39}

201 The percentage of CO₂ absorbed (abs%), defined as the
202 ratio between the amount of captured CO₂ and the CO₂ in the
203 air stream, is a useful parameter for evaluating and comparing
204 the absorbent efficiency of the different amine solutions in a
205 DAC system. The determination of the CO₂ captured from air
206 was carried out with the apparatus depicted in Figure 1,
207 charged with 0.100 dm³ of the 1.5 mol dm⁻³ amine solution, at
208 constant T = 25 °C. Abs% was continuously monitored during
209 the whole 24 h experiment by measuring the CO₂
210 concentration in the air exiting from the top of the column
211 with a gas chromatograph. At the end of the absorption
212 experiment, the species present in solution were identified and
213 quantified by means of ¹³C NMR analysis.

214 In Table 2 are reported all of the experimental results
215 obtained with the aqueous solutions tested. The average abs%
216 for the 24 h of the experiment has been reported together with
217 the actual percentages of CO₂ absorbed measured after 1 h and
218 at the end of the experiment (24 h), to evaluate the variation of
219 the capture efficiency over time. For an easier comparison, the
220 actual values of abs% have also been reported in Figure S3 in
221 the Supporting Information. The amount of carbamate formed
222 in solution (mol) and its relative percentage with respect to the
223 total amine in solution (indicated as "% Am tot") have been
224 determined by ¹³C NMR analysis, as previously described. The
225 percentage of the CO₂ captured as carbamate (mol carbamate/
226 mol CO₂ absorbed) has also been reported. The total CO₂
227 absorbed (mol) in 24 h can be calculated from the average
228 value of abs% and the CO₂ flow rate (8.36 × 10⁻⁴ mol CO₂
229 h⁻¹). The amount of bicarbonate/carbonate formed has not
230 been directly determined by ¹³C NMR analysis because the
231 corresponding signal was too weak to provide an accurate

quantitative result, and its value can be deduced from the 232
difference between the total absorbed CO₂ (mol) and the 233
carbamate (mol) found in solution. 234

For comparative purposes, the performances of some 235
commonly proposed sorbents for DAC processes, aqueous 236
solutions of NaOH, sodium carbonate, and potassium 237
glycinate, were tested in the same apparatus with the same 238
operating condition, and the results are reported in Table 2 239
(entries 1–3). 240

As a first general result, the highest values of average abs% 241
were obtained with aqueous solutions of unhindered primary 242
and secondary amines. In particular, the high efficiency of 243
aqueous solutions of MEA, DGA, 1A2P, 2A1B, MMEA, 244
EMEA, and BUMEA was not substantially different from that 245
of aqueous solutions of NaOH and glycinate, and those values 246
were maintained almost unchanged for the whole experiment. 247
The secondary amines DEA and DIPA and the tertiary amines 248
MDEA and DMMEA, as well as the sterically hindered amines 249
AMP, AMPD, TRIZMA, and TBMEA, were the less efficient 250
absorbents. It is noteworthy that these performance trends are 251
almost the same as those found for amine-based solid 252
adsorbents: many studies show that the best adsorption is 253
obtained with immobilized primary amines, while tertiary and 254
sterically hindered amines perform poorly.^{46–48} However, the 255
aforementioned general results deserve more in-depth 256
considerations, to correlate the efficiencies with the chemical 257
structures of the amines used. 258

As a general finding, in the aqueous sorbents with the 259
highest abs% (MEA, DGA, 1A2P, 2A1B, and MMEA), most of 260
CO₂ is captured as carbamate (eq 1). In particular, the amount 261
of carbamate formed corresponds almost entirely (between 80 262
and 100%) to the amount of CO₂ captured in the 24 h of 263
absorption. After 24 h, with an air flow of 46.5 dm³ h⁻¹, 264
approximately 0.02 moles of CO₂ should be passed through 265
the column: consequently, the maximum amount of carbamate 266
that can be produced with a 100% absorption is 0.02 moles (eq 267

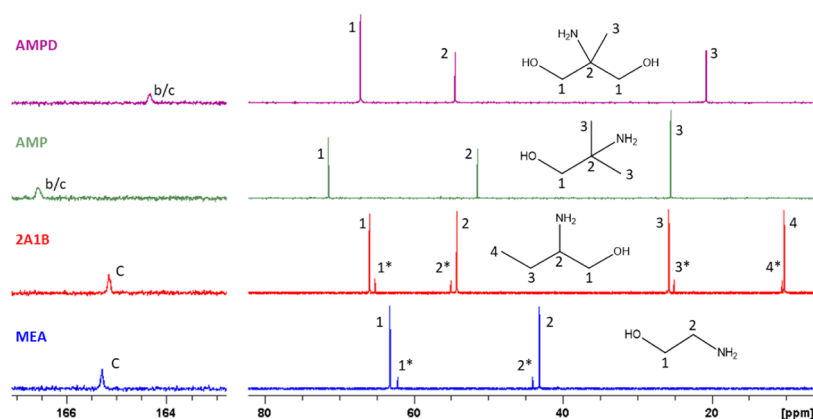


Figure 2. ^{13}C NMR spectra of aqueous MEA, 2A1B, AMP, and AMPD at the end of the absorption experiment. The numbers indicate the carbon atoms referred to both free and protonated amine fast exchanging in the NMR scale. Asterisks denote the chemical shifts of carbon backbones of amine carbamate. C indicates the carbonyl atoms of amine carbamate, while b/c refers to the signal of fast exchanging bicarbonate/carbonate ions. The intensity of the signals at 163–167 ppm is not in scale.

268 1), corresponding to approximately 13.3% of the starting
269 amine (0.15 mol) in the sorbent: at the end of the absorption
270 process, the amount of the amines is always much greater than
271 the absorbed CO_2 .

272 The residual captured CO_2 , which has not been converted
273 into carbamate (20%, at most), is present in solution as
274 bicarbonate/carbonate (eqs 3, 4, and 6). DMMEA and MDEA
275 are tertiary amines and cannot form carbamate, while AMP,
276 AMPD, TRIZMA, and TBMEA are sterically hindered amines
277 and their carbamates are very unstable: the CO_2 absorption in
278 their aqueous solutions produces only bicarbonate/carbonate
279 ions.⁴⁹ Although the bicarbonate formation (overall amine/
280 CO_2 stoichiometry of 1:1) improves the CO_2 solubilization
281 into the amine solution compared to the formation of
282 carbamate (eq 1, overall amine/ CO_2 stoichiometry of
283 2:1),^{36,39} those amines are the least efficient, and quite
284 interestingly, their efficiency strongly decreases with time.
285 Moreover, the abs% order TBMEA > DMMEA > AMPD >
286 MDEA > TRIZMA corresponds to the decrease of the
287 alkalinity (pK_b values from Table 2: 3.96, 4.43, 5.16, 5.43, and
288 5.78, respectively).

289 Very likely, the reaction rate between the sorbent and CO_2 is
290 the most incisive parameter for the efficiency of the capture of
291 CO_2 from the air. We have found in our previous studies on
292 liquid amines^{34,50} that the formation of the carbamate
293 derivatives is more kinetically favored than the bicarbonate/
294 carbonate species, and the same has been found by other
295 researchers during studies on amine-based solid adsorbents for
296 DAC processes.^{16,47} The great excess of unhindered primary
297 and secondary amines in solution compared to the low amount
298 of CO_2 in air favors the rapid formation of carbamate
299 (stoichiometry 2:1) rather than bicarbonate (stoichiometry
300 1:1). Those amines show a much higher reaction rate and
301 consequently greater abs% than the sterically hindered and
302 tertiary amines (Figure S4, Supporting Information). The
303 marked decrease of the abs% over time of these latter amines
304 could be due to the decrease of the OH^- concentration (eq 5)
305 with the increasing protonated amine (R_1NH_3^+) concentration,
306 which decreases the formation of bicarbonate/carbonate. A
307 further confirmation of the importance of the reaction rate
308 comes from the very low percentage of CO_2 absorbed found
309 for the sodium carbonate solution (Table 2, entry 2), in spite
310 of the favorable equilibrium of the reaction



312 It is well known that the main drawback of the carbonate
313 sorbent for CCS processes is due to the low reaction rate,
314 compared to conventional amine- or ammonia-based systems,⁵¹
315 and the same occurs for DAC processes (Figure S4). 315

316 In Figure 2 are reported the ^{13}C NMR spectra of some
317 aqueous primary amines (MEA, 2A1B, AMP and AMPD) at
318 the end of the 24 h absorption. The relative amount of MEA
319 and 2A1B carbamate (carbonyl signal at approximately 165
320 ppm) can be computed from the accurate integration of the
321 peak signal of each $-\text{CH}_2-$ resonance, in the range 10–80
322 ppm. On the contrary, AMP and AMPD cannot form
323 carbamate and the signal in the range 163–167 should be
324 ascribed to bicarbonate/carbonate ions. 324

325 By considering MEA (Table 2, entry 4) as the absorption
326 reference for aqueous primary amines, it is possible to evaluate
327 the influence of groups attached to the carbon adjacent to the
328 amino function (α -carbon) on the percentage of CO_2
329 absorbed. The abs% and the amount of carbamate formed in
330 aqueous DGA, 1A2P, and 2A1B (Table 2, entries 5, 6, and 7
331 respectively) suggest that a single or two alkyl groups attached
332 to the α -carbon do not have significant effects on the CO_2
333 absorption mechanism for carbamate formation and, consequently,
334 for the high CO_2 absorption. 334

335 Instead, the steric hindrance due to the three alkyl groups
336 attached to the α -carbon in AMP, AMPD, and TRIZMA
337 (Table 2, entries 8, 9, and 10, respectively) prevents the
338 formation of the carbamate, and the CO_2 absorption occurs
339 only through the formation of bicarbonate and, to a least
340 extent, carbonate ions (reactions 3, 4, and 6), with a lower
341 reaction rate and abs%. The worse absorption performances of
342 AMPD and TRIZMA, compared to AMP, are presumably
343 related to the number of $-\text{OH}$ (electron attractors) attached
344 to the α -carbon that reduces the electron density of the
345 nitrogen of the amino group, thus affecting the mechanism of
346 the CO_2 reaction. As a matter of fact, their abs% decreases with
347 decreasing alkalinity. It is worth noting that aqueous AMP is
348 among the most efficient sorbents in the conventional CCS
349 process: its poor performance in the DAC process underlines
350 the importance of the kinetic parameter in the CO_2 capture
351 from air. 351

352 As previously stated, in the most efficient amines (primary
353 amines MEA, DGA, 1A2P, 2A1B, secondary amine MMEA, 353

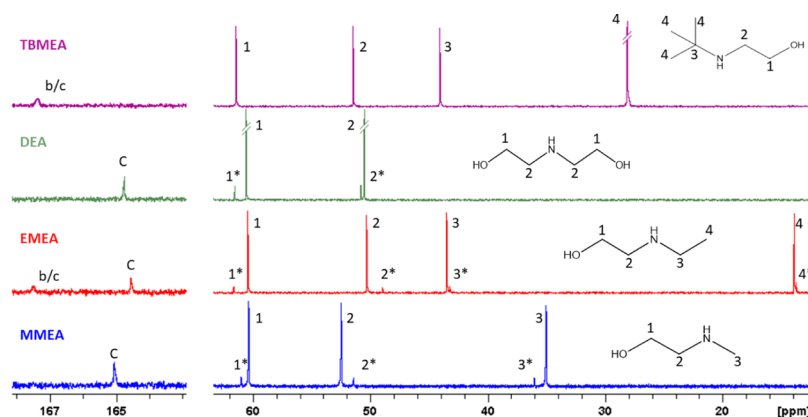


Figure 3. ^{13}C NMR spectra of aqueous MMEA, EMEA, DEA, and TBMEA at the end of the absorption experiment. The numbers indicate the carbon atoms referred to both free and protonated amine fast exchanging in the NMR scale. Asterisks denote the chemical shifts of carbon backbones of amine carbamate. C indicates the carbonyl atoms of amine carbamate, while b/c refers to the signal of fast exchanging bicarbonate/carbonate ions. The intensity of the signals at 163–168 ppm is not in scale.

Table 3. Percentage of CO_2 Absorbed (abs%) of the Different Absorbents Measured after 1 and 24 h and Average Values, the Total Amount (mol) of Absorbed CO_2 in 24 h, Absolute (mol) and Relative Amounts of Carbamate Formed (% with Respect to the Total Amount of Amine, % Am tot), and the Percentage of CO_2 Captured as Carbamate^a

entry	amine	diluent	abs%			CO_2 abs 24 h (mol)	carbamate		
			at 1 h (%)	at 24 h (%)	average (%)		mol	% Am tot	% CO_2 abs as carbamate
1	MEA	H_2O	86.9	87.4	87.3	0.0175	0.0164	10.9	93.7
2		EG/PrOH	85.6	82.4	84.7	0.0170	0.0138	9.2	81.2
3		DEGMEE	89.3	44.9	67.0	0.0134	0.0108	7.2	80.6
4	DGA	H_2O	85.8	84.8	85.5	0.0172	0.0150	10.0	87.2
5		EG/PrOH	87.9	76.1	83.1	0.0167	0.0132	8.8	79.0
6		DEGMEE	85.2	32.7	57.4	0.0115	0.0111	7.4	96.3
7	AMP	H_2O	76.9	65.4	72.3	0.0145			
8		EG/PrOH	52.2	7.6	29.7	0.0060			
9		DEGMEE	13.0	7.4	9.8	0.0020			
10	EMEA	H_2O	86.1	85.1	85.9	0.0172	0.0097	6.5	56.4
11		EG/PrOH	82.4	32.8	57.7	0.0116	0.0063	4.2	54.3
12		DEGMEE	71.3	3.1	28.4	0.0057	0.0030	2.0	52.6
13	BUMEA	H_2O	85.9	83.5	85.2	0.0171	0.0114	7.6	66.7
14		EG/PrOH	79.3	23.7	51.6	0.0104	0.0065	4.3	62.5
15		DEGMEE	65.4	4.8	26.8	0.0054	n.d.	n.d.	

^a“n.d.” relates to a very low amount of carbamate, not detectable with the ^{13}C NMR technique, while “/” indicates that the carbamate is not formed.

354 Table 2), most of CO_2 is converted into carbamate. However,
 355 the features of the secondary amines EMEA, BUMEA, DEA,
 356 and DIPA deserve an explanation because the percentage of
 357 carbamate is not a measure of the percentage of CO_2 absorbed.
 358 The ^{13}C NMR spectra of some aqueous secondary amines at
 359 the end of the experiment are reported in Figure 3.

360 MMEA (Table 2, entry 11) displays both the higher
 361 absorption and the greater amount of carbamate formed: as
 362 shown in the spectral range 163–168 ppm, aqueous MMEA
 363 reacts with aerial CO_2 , producing only carbamate. On the
 364 other hand, aqueous EMEA and BUMEA (Table 2, entries 12
 365 and 13) have high abs% (85.9 and 85.2%, respectively) but a
 366 relatively low carbamate percentage (56.4 and 66.7%,
 367 respectively). The high alkalinity of EMEA and BUMEA can
 368 contribute to their high efficiency, due to the formation of an
 369 appreciable amount of carbonate/bicarbonate (43.6–33.3%,
 370 respectively) as evidenced in the EMEA spectrum in Figure 3
 371 (similar spectrum recorded for BUMEA). On the contrary,
 372 DEA and DIPA (Table 2, entries 15 and 16) have lower abs%
 373 but display a much greater percentage of CO_2 conversion into

carbamate (spectrum of DEA reported in Figure 3, similar
 374 spectrum recorded for DIPA). Those results are due to the
 375 weaker basicity of the two amines that disfavors the formation
 376 of carbonate/bicarbonate, and consequently, most of CO_2 (a
 377 low amount, indeed) is captured as carbamate. Finally,
 378 TBMEA is the worst absorber among the selected secondary
 379 amines (Table 2 entries 14), due to the great steric hindrance
 380 of its tert-butyl group, which prevents the formation of
 381 carbamate and leads to the formation of only bicarbonate/
 382 carbonate, as shown in Figure 3. 383

Nonaqueous Systems. For some significative amines
 384 (MEA, DGA, AMP, EMEA, BUMEA), the percentage of aerial
 385 CO_2 absorbed was also investigated in nonaqueous solutions,
 386 using DEGMEE or a 1:1 mixture of EG and PrOH as diluents.
 387 Recently, we had already studied the advantages of some
 388 nonaqueous solutions of the aforementioned amines as CCS
 389 sorbents,^{34,50} and it seemed interesting to us to evaluate their
 390 capture performance even with ultradiluted CO_2 . The
 391 replacement of water with organic diluents has the potential
 392 of redirecting the reaction between amines and CO_2 toward
 393

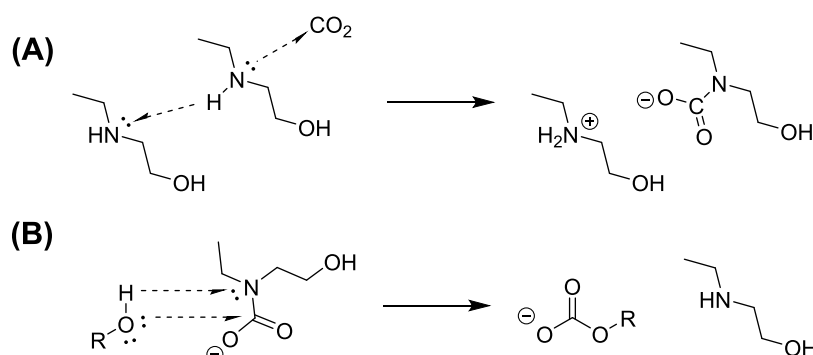
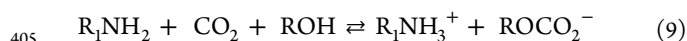


Figure 4. Scheme of the proposed two-step reaction mechanism for the formation of alkyl carbonate in nonaqueous EMEA solutions, including (A) the initial formation of the carbamate of the amine and (B) its subsequent reaction with an alcohol.

394 less stable carbonated species that require lower temperatures
 395 for their regeneration. In the absence of water, the formation of
 396 bicarbonate and carbonate ions (reactions 2–7) cannot take
 397 place and CO_2 reacts with an excess of both primary and
 398 secondary amines to produce the carbamate of the amines
 399 (reaction 1). Moreover, organic diluents with hydroxyl groups
 400 can react with CO_2 in the presence of a base (in this case, the
 401 amine), leading to the formation of alkyl carbonates (in the
 402 following equation, R denotes the alkyl groups
 403 $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$, $\text{HOCH}_2\text{CH}_2-$, or
 404 $\text{CH}_3\text{CH}_2\text{CH}_2-$)^{33,34}



406 In Table 3 are reported the experimental results obtained for
 407 the different solutions tested. For comparison, the result
 408 obtained in its aqueous solution is also reported for each
 409 amine. The experiments were carried out with the same
 410 procedures and operating conditions of the aqueous sorbents.
 411 The amount of alkyl carbonate formed at the end of the
 412 absorption has not been directly determined by ^{13}C NMR
 413 analysis because the corresponding signal was too weak to
 414 provide an accurate quantitative result: its value can be
 415 deduced from the difference between the absorbed CO_2 (mol)
 416 and the carbamate (mol) found in solution. For a simpler
 417 comparison, the actual values of abs% have also been reported
 418 in Figure S5 in the Supporting Information.

419 The data summarized in Table 3 confirm that, in organic
 420 diluents too, the percentage of CO_2 absorbed follows the order
 421 of primary amines > secondary amines > AMP.

422 The primary amines MEA and DGA display similar abs% in
 423 aqueous and EG/PrOH solutions. All of the other sorbents are
 424 less efficient, in particular in DEGMEE solution, and at the end
 425 of the experiments. In DEGMEE, the actual value of abs% at
 426 24 h is more than halved compared to the first hour, whereas
 427 aqueous solutions maintain the same high percentage of CO_2
 428 absorbed during the 24 h experiments. The general order of
 429 abs% as a function of the diluent is $\text{H}_2\text{O} > \text{EG/PrOH} >$
 430 DEGMEE. This trend is particularly evident for the secondary
 431 amines EMEA and BUMEA and for the sterically hindered
 432 AMP.

433 The higher percentage of CO_2 absorbed for all of the amines
 434 in EG/PrOH compared with DEGMEE depends on the
 435 greater reactivity of CO_2 to form the corresponding alkyl
 436 carbonates with EG and PrOH compared to DEGMEE. As
 437 already found in previous studies,^{34,50} the longer the alcoholic
 438 diluent chain, the lower the stability of alkyl carbonate, and

consequently, the abs% in DEGMEE is lower than in EG/ 439
 PrOH. 440

The higher abs% of MEA and DGA in organic diluents with 441
 respect to EMEA and BUMEA is due to the greater amount of 442
 carbamate (about 80%) formed, compared to alkyl carbonate. 443
 As previously reported (Table 2, entries 12 and 13), the 444
 formation of bicarbonate substantially contributes (33–44%) 445
 to the CO_2 capture in aqueous EMEA and BUMEA, in 446
 addition to the formation of carbamate: in the absence of that 447
 contribution in nonaqueous diluents, the percentage of CO_2 448
 absorbed of EMEA and BUMEA solutions must decrease. The 449
 strong abs% reduction over time of the last two amines seems 450
 to indicate that the formation of the alkyl carbonate requires a 451
 large excess of the amine. The proposed mechanism for the 452
 formation of the alkyl carbonate (taking EMEA as an example) 453
 is shown in Figure 4. Initially, EMEACO_2^- (carbamate) and 454
 EMEAH^+ (protonated) are formed, due to the nucleophilic 455
 attack of the amino nitrogen of one EMEA molecule to CO_2 456
 with the consequent deprotonation, promoted by another 457
 EMEA molecule (Figure 4A). In the excess of the amine, 458
 EMEA carbamate can therefore react with the alcoholic 459
 function of the diluent, forming the alkyl carbonate (Figure 460
 4B). The direct reaction between the alcoholic function of the 461
 diluent and CO_2 is likewise hampered by a greater activation 462
 energy. 463

Finally, in nonaqueous AMP solutions, neither bicarbonate 464
 nor carbamate can be formed, and CO_2 can only be captured 465
 as alkyl carbonate (reaction 9): in this case, AMP acts as a base 466
 and allows the diluent with an $-\text{OH}$ group to react with CO_2 . 467

468 ■ CONCLUSIONS

469 With the aim of identifying the most crucial chemical
 peculiarities for the development of new liquid absorbents 470
 for DAC processes, we carried out a screening study on the 471
 performance of different aqueous alkanolamine solutions, 472
 under the same operating conditions: their ability to absorb 473
 CO_2 from an air stream was correlated with their chemical 474
 structure and with the species formed by the absorption 475
 reaction, and useful information on the reaction mechanism 476
 has been obtained. As a general finding, aqueous unhindered 477
 primary amines are the most suitable sorbents for DAC 478
 processes, as they are as efficient as aqueous alkali hydroxides 479
 but with a potential energy saving due to the lower 480
 temperatures required for sorbent regeneration. The formation 481
 of a high yield of amine carbamate seems to be the decisive 482
 factor for an efficient CO_2 capture, but the formation of an 483
 appreciable amount of carbonate/bicarbonate because of the 484

485 strong basicity of some amines (EMEA, BUMEA) can
486 contribute to attain a high percentage of CO₂ absorbed. The
487 amines that are unable to form carbamate have provided poor
488 absorption values. In particular, aqueous AMP, which is a very
489 efficient sorbent in conventional CCS processes, has proven to
490 be poorly suited for the capture of ultradiluted CO₂, due to the
491 lower kinetics of carbonate/bicarbonate formation. These
492 findings highlighted the differences of DAC processes
493 compared to conventional CCS processes and, consequently,
494 the best CCS absorbents cannot be the best choice for the
495 DAC process. The obtained results also showed that aqueous
496 amines are more efficient than the same amines in organic
497 diluents. MEA and DGA in EG/PrOH display slightly lower
498 abs% compared to the aqueous solution by virtue of the high
499 percentage of carbamate formed. In the absence of carbamate
500 formation (as in the case of AMP), CO₂ can only be captured
501 as alkyl carbonate, which is less stable than carbamate and
502 requires a large excess of the free amine as a base. In
503 conclusion, nonaqueous sorbents do not seem suitable for
504 DAC processes, also taking into account that their possible use
505 would entail substantial changes in conventional DAC
506 equipment to limit the solvent loss and consequent environ-
507 mental issues.

508 ■ ASSOCIATED CONTENT

509 ■ Supporting Information

510 The Supporting Information is available free of charge at
511 <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c03800>.

512 ¹³C NMR analysis settings and procedures; comparison
513 of ¹³C NMR spectra before and after CO₂ absorption for
514 aqueous MEA and AMP; comparison of the actual abs%
515 (after 1 and 24 h) of all of the tested aqueous and
516 nonaqueous sorbents; comparison of the reaction rate
517 (reported as abs% vs time) for several aqueous
518 absorbents (PDF)

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538 Notes

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