

1 A comparative study of the CO₂ absorption in some
2 solvent-free alkanolamines and in aqueous
3 monoethanolamine (MEA)

4 *Francesco Barzagli^{a,b}, Fabrizio Mani^{b*}, and Maurizio Peruzzini^b*

5 ^aUniversity of Florence, Department of Chemistry, via della Lastruccia 3, 50019 Sesto
6 Fiorentino, Italy

7 ^bICCOM CNR, via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

8 *To whom correspondence should be addressed. E-mail: fmani@iccom.cnr.it

9 **KEYWORDS** Regenerative chemical capture of CO₂; switchable solvent-free CO₂ absorbents;
10 room temperature liquid amine carbamates; ¹³C NMR speciation; thermally reversible ionic
11 liquids.

12 **ABSTRACT** The neat secondary amines 2-(methylamino)ethanol, 2-(ethylamino)ethanol, 2-
13 (isopropylamino)ethanol, 2-(benzylamino)ethanol and 2-(butylamino)ethanol react with CO₂ at
14 50-60 °C and room pressure yielding liquid carbonated species without their dilution with any
15 additional solvent. These single-component absorbents have the theoretical CO₂ capture capacity
16 of 0.50 (mol CO₂/mol amine) due to the formation of the corresponding amine carbamates and
17 protonated amines that were identified by the ¹³C NMR analysis. These single-component

18 absorbents were used for CO₂ capture (15 % and 40 % v/v in air) in two series of different
19 procedures: 1) batch experiments aimed at investigating the efficiency and the rate of CO₂
20 capture; 2) continuous cycles of absorption-desorption carried out in packed columns with
21 absorption temperatures brought at 50-60 °C and desorption temperatures at 100-120 °C at room
22 pressure. A number of different amines and experimental setups gave CO₂ capture efficiency
23 greater than 90 %. For comparison purposes, 30 wt % aqueous MEA was used for CO₂ capture
24 under the same operational conditions described for the solvent-free amines. The potential
25 advantages of solvent-free alkanolamines over aqueous MEA in the CO₂ capture process were
26 discussed.

27 INTRODUCTION

28 Amongst the different processes designed to capture anthropogenic CO₂, those based on
29 aqueous alkanolamines represent a mature technology for the CO₂ separation from gas mixtures
30 in hydrogen and ammonia plants, natural gas processing and methane production from landfill
31 wastes.¹⁻⁹ The implementation of this technique into full-size commercial plants, in particular
32 fossil-fuelled power plants as well as steel and cement production plants, entails prohibitively
33 high costs and environmental problems, mainly because of the energy consumption for the amine
34 regeneration¹⁰⁻¹⁷ and of the thermal and oxidative amine degradation and evaporation.¹⁸⁻²⁵ The
35 key challenge in a more efficient process of CO₂ capture should be the development of new
36 absorbent formulations aimed at reducing the main disadvantages of the existing traditional
37 aqueous amines, without reducing their high efficiency.

38 For the replacement of aqueous amines, some groups have recently proposed CO₂ absorbents
39 based on room temperature ionic liquids (RTILs) by virtue of their negligible vapor pressure and

40 high thermal stability. Examples of these organic liquids are “task-specific ionic liquids”
41 (TSILs),^{26,27} alkanol guanidines and amidines,²⁸ tunable basic ionic liquids²⁹ and silylated
42 amines.^{30,31} However, the very high viscosity of the carbonated species or the formation of solid
43 compounds,³² the pressure over 1 bar often required to attain a high CO₂ capacity, the reduced
44 pressure or N₂ flushing sometimes necessary for an efficient CO₂ desorption and the expensive
45 synthesis of these absorbents, prevent their application to a commercial plant.

46 Novel absorbents were recently formulated in our laboratory based on the replacement of
47 water by alcohols^{33,34} or on some secondary amines that reversibly react with CO₂ affording
48 liquid carbonated species.³⁵

49 By continuing these studies with the purpose of developing new absorbents that could combine
50 the good performances of aqueous alkanolamines yet removing, at least in part, their
51 disadvantages, now we report the results of the experimental work on the CO₂ capture by some
52 single component secondary alkanolamines. The alkanolamines we exploited in our experimental
53 study of CO₂ uptake are 2-(isopropylamino)ethanol (IPMEA), 2-(methylamino)ethanol
54 (MMEA), 2-(ethylamino)ethanol (EMEA), 2-(benzylamino)ethanol (BZMEA), 2-
55 (butylamino)ethanol (BUMEA). These single-component absorbents do not require any organic
56 or aqueous diluent because they are liquid before and after the CO₂ uptake at the experimental
57 temperatures. An absorbent which does not require dilution with any solvent should have
58 potential advantages over aqueous amines.^{28,31,32}

59 We have designed batch experiments at room temperature aimed at measuring the CO₂ loading
60 capacity and the rate of CO₂ capture by the different amines. The efficiency of CO₂ absorption
61 was measured in continuous cycles of CO₂ capture at 50-60 °C and amine regeneration at 100-

62 120 °C, carried out in packed columns to room pressure. The ¹³C NMR spectroscopy allowed us
63 to identify the carbonated species originated upon CO₂ capture. The results of these experiments
64 were compared with those obtained with 30 wt % aqueous MEA, the reference of any CO₂
65 capture system from flue gas.

66 A technique of reversible CO₂ capture that does not require the absorbent dilution avoids the
67 sensible and vaporization heat of water that contribute to the overall reboiler duty.^{17,36} Further
68 potential benefits would be the reduced mass of the absorbent (water accounts for 70 wt % of the
69 mass of aqueous MEA) and, consequently, an appreciable reduction of the plant size. As
70 additional, not negligible, benefit, the absence of water strongly reduces the equipment
71 corrosion. Most important, the alkanolamines we used are inexpensive and commercially
72 available.

73 **MATERIAL AND METHODS**

74 **General information**

75 All reagents used were reagent grade (95-98 %) except 2-(isopropylamino)ethanol that
76 contains 30 wt % of the tertiary amine N-isopropyl-2,2'-iminodiethanol. The alkanolamines
77 (Sigma-Aldrich) were used as received without further purification. Mixtures of air and CO₂
78 (15% and 40%; Rivoira Spa) were used to simulate the flue gas. Flow rates were measured with
79 gas mass flow meters (Aalborg) equipped with gas controllers (Cole Parmer). The inlet and
80 outlet CO₂ concentrations in the flue gas mixture were measured with a Varian CP-4900 gas
81 chromatograph calibrated with 15% and 40% v/v CO₂/air reference mixture (Rivoira Spa) and
82 100% CO₂ reference gas (Rivoira Spa).

83 The CO₂ uptake by amines was measured as a function of the reaction time with a gastight
84 apparatus which comprises a 2.0 dm³ flask (actual volume 2.285 dm³) equipped with a digital
85 pressure gauge, magnetic stirrer and a pressure-equalizing dropping funnel containing the
86 appropriate amount of ammine (0.12 mol). After the air was removed with a vacuum pump, the
87 flask was filled with a mixture of air and CO₂ (15% v/v) at room pressure. This operation was
88 repeated five times before the final one. After the amine was quickly introduced from the funnel
89 into the flask, the stirring was started and the pressure decrease shown by the pressure gauge
90 allowed us to measure the CO₂ absorption as a function of time. The temperature of the flask was
91 maintained constant to 22 °C during the reaction with a water bath. The experiment was stopped
92 when the pressure did not change with time (40-90 min).

93 The batch experiments designed to measure the CO₂ loading were carried out with a home-
94 made glass cylinder with a diameter of 56 mm and a height of 300 mm. The absorber was
95 charged with 0.100 dm³ of the amine and the temperature of the reaction was constantly kept
96 under control with a thermostatted bath (Julabo model F33-MC bath), set at 40 °C. Pure CO₂ was
97 continuously fed through a sintered glass diffuser (16-40 μm pores) placed at the bottom of the
98 absorbent. The absorption was stopped when no more CO₂ was absorbed. A cold condenser
99 brought to 0 °C avoids amine loss during the amine carbonatation. From the weight increase of
100 the CO₂ saturated solution, we computed the maximum amine loading capacity.

101 The apparatus used for continuous absorption-desorption cycles was already described³⁷ and
102 comprises the absorber and the desorber units connected to each other by means of a double head
103 peristaltic pump (Masterflex), which allows the solutions to circulate continuously in a closed
104 loop between the absorber and the desorber at the desired flow rate (in our experiments, in the
105 range between 0.060 and 0.300 dm³ h⁻¹). Both the absorber and desorber devices are home-built

106 glass cylinders with the internal diameter of 56 mm and height 400 mm, equipped with a jacket.
107 The columns were randomly packed with glass rings (diameter 5 mm). The temperature of the
108 liquid circulating through the jackets of absorber (40, 50, 60 °C) and desorber (90, 100, 110, 120
109 °C) was maintained at the appropriate value by means of two thermostatted baths (Julabo model
110 F33-MC bath). Due to the endothermic reaction of CO₂ release, the temperature of the desorption
111 column was 2.5-5.0 °C below that of the heating jacket. The exothermic acid-base reaction
112 allowed to maintain the absorber temperature at the designed values and no cooling was
113 required. The absorber operates in a counter current mode: the regenerated absorbent was
114 introduced from the top of the absorber meanwhile the gas mixture was continuously fed into the
115 bottom of the absorber. Some experiments were performed by using two absorbent columns
116 ranged in line. The carbonated absorbent exited at the bottom of the absorbent column(s) and
117 sent to the top of the desorber. The desorber was fitted with a water cooled condenser to reflux
118 the possible overhead vapor to the stripper. The entire apparatus was charged with 0.250 dm³ (in
119 a few experiments the volumes were 0.150 dm³ or 0.350 dm³) of each amine.

120 To mimic the flue gas, we used 15% or 40% (v/v) CO₂ in air (overall pressure of the gas
121 mixture set at 1.0 bar) which was water saturated before being injected into the absorber at a
122 flow rate of 12.0 dm³ h⁻¹ and 29.0 dm³ h⁻¹ (15% CO₂, 0.0743 and, respectively, 0.180 mol h⁻¹ at
123 22 °C; 40% CO₂ 12.0 dm³ h⁻¹, 0.198 mol h⁻¹). The outlet gas from the top of the absorber(s) was
124 dried before being GC analyzed at intervals of 10 minutes. A complete cyclic experiment lasted
125 24-36 h and it was stopped when the reactions of CO₂ capture and amine regeneration reached a
126 steady state and the absorption efficiency did not change with time.

127 The viscosity, of both the free and carbonated amines (the latter were measured at the end of
128 each cyclic experiments) was measured at 50 °C with a Gilmont “Falling Ball Type” Viscometer

129 by using 5 cm³, approximately, of the appropriate amine. The viscometer tube was immersed in a
130 constant temperature bath with a transparent window to observe the fiduciary lines. The proper
131 ball was selected and dropped into the tube using the ball release device. The time of descent
132 between the two sets of fiduciary lines was measured with a stop-watch. The measures were
133 repeated three times, at least, with a reproducibility in the range 0.2– 1.0% depending upon the
134 time of descent. In order to verify the validity of the method, the viscosity of water, ethanol and
135 ethylene glycol was also measured showing relative errors in the range 1.5–3.3% respect to their
136 standard values.

137 **¹³C NMR Spectroscopy**

138 The ¹³C NMR spectra of the neat and carbonated amines were obtained at 25 °C with a Bruker
139 Avance III 400 spectrometer operating at 100.613 MHz with a procedure that has been already
140 described.^{33,34,38,39} Details of the ¹³C NMR experiments are reported in the Supporting
141 information. Chemical shifts are to high frequency relative to tetramethylsilane as external
142 standard at 0.00 ppm. CH₃CN was used as internal reference (CH₃, δ = 1.47). To provide enough
143 signal for deuterium lock, D₂O (Aldrich) contained in a sealed glass capillary was introduced
144 into the NMR tube.

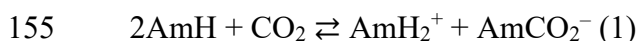
145 **RESULTS AND DISCUSSION**

146 **Batch experiments of CO₂ uptake**

147 The neat secondary alkanolamine 2-(methylamino)ethanol (MMEA), 2-(ethylamino)ethanol
148 (EMEA), 2-(isopropylamino)ethanol (IPMEA), 2-(benzylamino)ethanol (BZMEA) and 2-
149 (butylamino)ethanol (BUMEA) reacted with CO₂ to give carbonated species in the liquid phase

150 notwithstanding the absence of any dilution with an added solvent. The acid-base reactions are
151 thermally reversible thus allowing to recover the free amines and pure CO₂.

152 In anhydrous conditions, CO₂ reacts with the secondary amines to yield the corresponding
153 ionic couples amine carbamate and protonated amine with a theoretical loading capacity of 0.5,
154 according to the reaction (AmH denotes the alkanolamine in the equation)



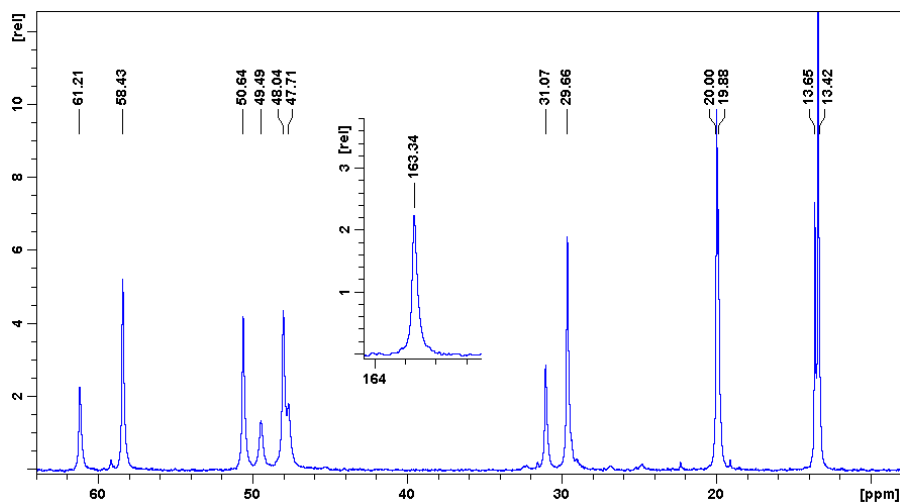
156 To measure the experimental loading capacity of the different amines, pure CO₂ was flowed
157 through 0.100 dm³ of each neat amine maintained at 40 °C until no more CO₂ was absorbed. The
158 loading capacity measured by gravimetry (see General information) of the different amines is
159 quite similar to each other and ranges between 0.48 of BZMEA and 0.52 of MMEA (Table 1),
160 near to the expected theoretical value in the absence of any aqueous or non-aqueous solvent and
161 to 30% aqueous MEA.⁸

162 **Table 1.** Some properties of the alkanolamines used for CO₂ capture.

amine	molar mass (g mol ⁻¹)	T _b (°C)	Density at 20°C (kg dm ⁻³)	viscosity at 50°C (cP)	loading at 40°C
MMEA	75.11	158	0.940	4.39	0.52
EMEA	89.14	170	0.914	4.55	0.50
IPMEA	103.17	182	0.897	9.49	0.49
BUMEA	117.19	199	0.891	5.63	0.50
BZMEA	151.21	156	1.063	15.54	0.48

163

164 The formation of the ionic couple upon the CO₂ uptake was confirmed by the analysis of the
165 ¹³C NMR spectra which allowed us to identify and quantify the carbonated species, with the
166 procedure we have previously described.^{40,41} As an example of the ¹³C NMR spectra of the ionic
167 couples carbamate-protonated amine, the spectrum of BUMEA carbonated by 40% CO₂ is
168 reported in Figure 1.



169
170 **Figure 1.** ¹³C NMR spectrum of BUMEA carbonated by 40% CO₂ in the absorption cycle
171 carried out at 50 °C. The signals (δ, ppm) at 61.21, 49.49, 47.71, 31.07, 19.88 are due to the -
172 CH₂- and 13.65 to the -CH₃ carbon atoms of the amine carbamate. The signal (δ, ppm) at 58.43,
173 50.64, 48.04, 29.66, 20.00 and 13.42 are due to the same carbon atoms of the summed protonated
174 and free amine. The inset reports the raised signal (163.34 ppm) of the carbon atom of the
175 carbonyl group.

176
177 The CO₂ (15 % v/v in air) uptake by the different alkanolamines as a function of time was
178 compared with that of aqueous 30% wt MEA in experiments carried out in a 2.0 dm³ flask (see

179 General information) containing the same amount (about 0.12 mol) of the different amines which
180 were in a large excess with respect to the fixed amount of CO₂ charged in the flask (0.0137-
181 0.0141 mol).

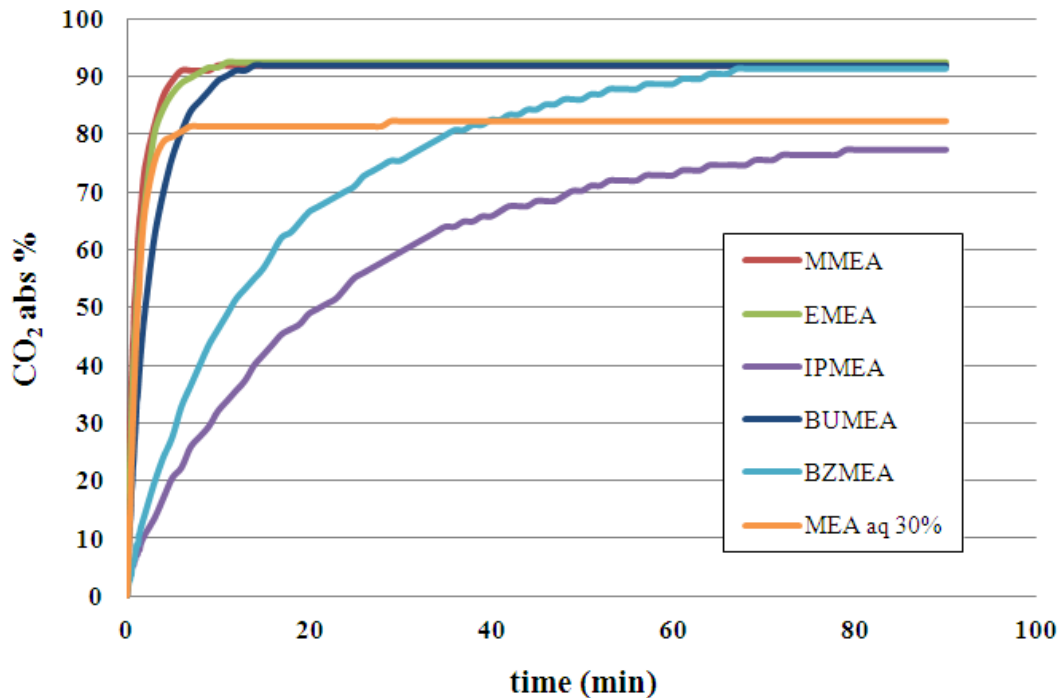
182 **Table 2.** Some data of the batch experiments of CO₂ (15% in air) uptake by neat alkanolamines
183 and 30% aqueous MEA as a function of time.

Amine	vol ^a (dm ³)	mol amine	<i>T</i> (°C) ^b	<i>P</i> (bar) ^c	mol CO ₂	abs % ^d
MMEA	0.0096	0.1201	21	1.0145	0.0141	92.0
EMEA	0.0117	0.1200	24	1.0013	0.0137	92.4
IPMEA	0.0197	0.1199	22	1.0146	0.0140	77.3
BUMEA	0.0158	0.1201	22	1.0173	0.0140	92.0
BZMEA	0.0171	0.1202	21	1.0159	0.0140	91.3
MEA 30%	0.0245	0.1200	25	1.0067	0.0137	82.2

184 ^a volume of the neat alkanolamines and of aqueous MEA; ^b temperature of the gas mixture in
185 the flask; ^c starting pressure of the gas; ^d overall percentage of CO₂ uptake at the end of the
186 experiment.

187
188 After 90 min, no more CO₂ was absorbed and the experiment was stopped. The results are
189 reported in Table 2. The percentage of CO₂ absorbed with respect to that contained in the flask is
190 reported as a function of time in Figure 2. At the end of the absorption experiment, the neat
191 alkanolamines absorbed over 90 % of the CO₂ contained in the flask with the exception of
192 IPMEA (Table 2). It is worth considering that the CO₂ absorption capacity of aqueous MEA was
193 lower, 82 %, notwithstanding aqueous MEA is recognized as a very efficient absorbent.

194



195

196 **Figure 2.** Variation with time of the CO₂ (15% in air) uptake by the different neat
 197 alkanolamines and of 30% aqueous MEA.

198 As far as the rate of CO₂ uptake is concerned, MMEA, EMEA, BUMEA and aqueous MEA
 199 displayed a quite similar behavior and less than 5 minutes were required to reach the respective
 200 equilibrium, whereas the reaction rates of both BZMEA and IPMEA were considerably lower.
 201 Presumably, the steric hindrance of the i-propyl group at the amine function and the presence of
 202 30% of the tertiary amine N-isopropyl-2,2'-iminodiethanol disfavor the insertion of CO₂ and
 203 makes the carbamate derivative less stable, thus disfavoring both the reaction rate and
 204 equilibrium. The relatively low reaction rate of BZMEA, in spite of its high uptake efficiency at
 205 equilibrium, could be explained by its greatest viscosity (15.54 cP at 50 °C) which is a hurdle to
 206 the mass transfer between the gas and the liquid thus lowering the reaction rate. On the contrary,
 207 the low viscosity of the aqueous MEA explains its high reaction rate, but its fairly less CO₂

208 removal efficiency was difficult to explain, unless it was due to the combined effects of the water
209 dilution and of the low pressure of the residual CO₂ which adversely affected the acid-base
210 equilibrium.

211 **Continuous cycles of absorption-desorption**

212 The feasibility and the efficiency of the CO₂ capture by solvent-free alkanolamines were
213 verified by experiments based on continuous cycles of CO₂ absorption and amine regeneration
214 carried out in glass columns packed with glass rings and designed to operate in counter current
215 mode, as previously described for non-aqueous amine absorbents.³⁷ The percentage of CO₂ in the
216 gas mixtures accounts for average CO₂ content of post combustion gas streams (15 %) and of
217 biogas from biomass waste (40 %). A summary of the experimental setup is reported in Table 3.

218 **Table 3.** Operational conditions employed in most of the experiments of CO₂ capture carried
219 out in the continuous cycles of absorption-desorption.

220	Amine volume	0.150, 0.250, 0.350 dm ³
221	Absorption temperature	40, 50, 60 °C
222	Desorption temperature/pressure	100, 110, 120 °C/1 bar
223	Liquid flow rate	from 0.060 to 0.300 dm ³ h ⁻¹
224	Gas flow rate	12.0, 29.0 dm ³ h ⁻¹
	Gas mixture	15%, 40% (v/v) CO ₂ in air
	Pressure of the gas mixture	1.0 bar

225

226 For comparison purposes, analogous experiments were carried out with 30 wt % aqueous
227 MEA, the reference absorbent of any CO₂ capture technology. Each complete experiment lasted
228 24-36 h and was stopped when the process reached a steady state and the CO₂ capture efficiency
229 did not change with time.

230 The choice of the relatively high absorption temperature (50-60 °C) was dictated by the
231 viscosity of the carbonated absorbents at room temperature that was a hindrance to the mass
232 transfer between the two phases thus reducing the rate of CO₂ uptake, even if a high absorption
233 temperature was a detriment to the equilibrium of the exothermic reaction. The viscosity values
234 of the carbonated species at 50-60 °C, are approximately ten times greater than 30% aqueous
235 MEA (except MMEA, Table 4) but they are two order of magnitude lesser than those of most
236 ionic liquids.^{27,30,31} Additional advantages of the absorption temperature at 50-60 °C would be
237 the lower difference between the absorber and the desorber temperatures thereby reducing the
238 sensible heat.^{17,36,39}

239 The results of the experiments carried out with the different amines and operating conditions are
240 reported in Table 4: several combinations of amines and experimental conditions gave efficiency
241 over 90 %. As a general remark, the absorption efficiency of the different amines increased with
242 increasing the desorption temperature and decreasing the absorption temperature. In spite of the
243 enhanced viscosity, the absorber temperature reduction from 60 °C to 50 °C had a beneficial
244 effect on the exothermic reaction as well as on the CO₂ solubility, and the absorption efficiency
245 of all amines increased. In spite of its greater volume (Table 4) that takes into account the 70%
246 content of the pure amine in the commercial product, IPMEA has lowest efficiency, presumably
247 because of its low reaction rate, as shown by batch experiments (Figure 2).

248 **Table 4.** Absorption efficiency of the alkanolamines as a function of the different absorption and
 249 desorption temperatures, absorbent volume, CO₂ percentage and liquid and gas flow rate.

Amine	V^a	mol ^b	viscosity ^c (cP, 50°C)	T^d , 40-100			T^d , 50-100			T^d , 50-110			T^d , 60-110			T^d , 60-120			
	dm ³			15% ^e	15% ^f	40% ^e	15% ^e	15% ^f	40% ^e	15% ^e	15% ^f	40% ^e	15% ^e	15% ^f	40% ^e	15% ^e	15% ^f	40% ^e	
MMEA	0.250	3.13	168.43									95.2	77.7	97.7					
EMEA	0.250	2.56	51.58				94.8	75.4	97.3	98.1	95.4	99.4	96.0	90.8	98.9				
	0.150	1.54											93.1	78.1	96.2				
IPMEA	0.350	2.13	15.85	82.1	59.7	88.0	74.1			79.8	< 50	84.2							
BUMEA	0.250	1.90	21.25				95.6	77.0	97.0	97.8	95.6	99.1	92.6	86.2	97.4	97.0	93.1	99.0	
	0.250 ^g	1.90						91.2	52.0	65.6	96.6	76.3	73.5	85.8	43.0	62.3	91.9	53.6	73.2
	0.150	1.14						94.1	72.0	91.9	97.0	90.4	99.0	92.8	77.0	96.7	96.8	90.7	98.9
BZMEA	0.250	1.76	56.24				84.6	48.6	86.3	95.4	74.3	97.3	89.2	56.9	92.6				

250 ^a volume of the absorbent; ^b amount in mol of the absorbent; ^c viscosity of the carbonated
 251 absorbent measured at 50 °C; ^d absorption and desorption temperatures; ^e flow rate of the gas
 252 mixture: 12.0 dm³ h⁻¹; ^f flow rate of the gas mixture: 29.0 dm³ h⁻¹; ^g flow rate of the absorbent:
 253 0.100 dm³ h⁻¹.

254
 255 Comparison of the amine performances measured in the cycles carried at 60-110 °C (Table 4)

256 indicates that the efficiency decrease in the order EMEA > BUMEA > MMEA > BZMEA.

257 Considering the amount of the amines contained in the fixed volume of 0.250 dm³ that decreases

258 in the order MMEA > EMEA > BUMEA > BZMEA and the viscosity of the carbonated

259 absorbents (measured at 50 °C) that decreases in the order MMEA >> BZMEA > EMEA >

260 BUMEA, the higher efficiency of both EMEA and BUMEA was likewise due to their lower

261 viscosity, rather than to the amount of amine. As a matter of fact, the reduction of the volume of

262 EMEA and BUMEA from 0.250 to 0.150 dm³ (cycles at 60-110 °C, Table 4) did not

263 substantially affect the efficiency of the CO₂ capture.

264 By varying the gas flow rate or CO₂ percentage, the experiment results (Table 4) clearly
265 indicated that 40 % CO₂ was more efficiently captured than 15 % CO₂, most likely because of
266 the increased partial pressure of CO₂ that enhanced its solubility and the reaction rate. As
267 expected, the efficiency decreased if the gas flow rate was increased from 12.0 to 29.0 dm³ h⁻¹,
268 due to the reduced residence time of the gas in the absorber. The reduction of BUMEA
269 circulation resulted in a decrease of the CO₂ capture efficiency, but in most experiments it was
270 over 90 % (Table 4).

271 Based on the efficiency and the highest boiling temperature (i.e. the lowest vapor pressure at the
272 highest operational temperature), as well as on the viscosity values, BUMEA seems to be the
273 most suitable absorbent for its implementation in a full-scale CO₂ capture process.

274 For comparison purposes we carried out experiments of CO₂ capture with 30% aqueous MEA
275 under the same operational conditions of BUMEA. The efficiency of neat BUMEA by far
276 overcomes that of aqueous MEA (Table 5, entries 1 and 3, respectively) by virtue of its higher
277 neat amine circulating rate, notwithstanding the much lower viscosity of the aqueous MEA.

278 It was necessary a mass of aqueous MEA about 1.8 times greater and a threefold increase of its
279 circulation rate (Table 5, entry 4), to attain the same CO₂ capture efficiency of neat BUMEA.. It
280 must be pointed out that the higher is the absorbent circulation rate, the greater is the energy
281 required by the CO₂ desorption process.^{16,28,31,32}

282

283 **Table 5.** Absorption efficiency and working capacity of BUMEA and 30% aqueous MEA; the
 284 fixed operational conditions are: one absorbent column; gas flow rate 12.0 dm³ h⁻¹, 15 % CO₂,
 285 absorption and desorption temperatures 50 °C, and 100 °C.

amine	entry	vol (dm ³)	mass ^a (kg)	mol ^b	liq flow (dm ³ h ⁻¹)	abs (%) ^c	CO ₂ abs ^d (mol h ⁻¹)	amine flow ^e (mol h ⁻¹)	working capacity ^f (mol kg ⁻¹)
BUMEA	1	0.250	0.226	1.90	0.100	91.2	0.068	0.76	0.75
	2	0.150	0.136	1.14	0.300	94.1	0.070	2.28	0.26
30% MEA	3	0.390	0.417	1.90	0.100	49.0	0.036	0.49	0.34
	4	0.390	0.417	1.90	0.300	91.8	0.068	1.46	0.21
	5	0.500	0.535	2.44	0.300	96.6	0.072	1.46	0.22

286 ^a the density of the carbonated absorbents in the absorber at 50°C is: BUMEA 0,904 kg dm⁻³;
 287 30% aqueous MEA 1,070 kg dm⁻³; ^b amount of the amines; ^cCO₂ absorption efficiency; ^d mol of
 288 absorbed CO₂; ^e flow rate of recirculated absorbents; ^f [absorbed CO₂ (mol h⁻¹)]/[absorbent mass
 289 (kg h⁻¹)]

290

291 To have a better comparison of the efficiency of neat BUMEA and aqueous MEA, we have
 292 defined the working capacity of the two absorbents as (mol of CO₂ captured)/(mass of circulating
 293 absorbent). This property seemed to us more appropriate than the cyclic capacity which is based
 294 on the amount of the sole amine (mol CO₂ captured/mol of amine). As a matter of fact, the cyclic
 295 capacity of aqueous MEA would completely neglect the 70% of water that must be pumped and
 296 heated in the desorption step. The results reported in Table 5 (entries 1 and 4) provided
 297 compelling evidences of the disadvantages of aqueous MEA which attained the same CO₂
 298 capture efficiency of neat BUMEA at the expense of a much lower working capacity because of
 299 its greater circulation rate. A volume increase of aqueous MEA had a negligible effect on its

300 working capacity (Table 5, entry 5). As expected, the increased flow rate of BUMEA greatly
 301 reduced its working capacity notwithstanding the decreased volume (Table 5, entry 2).

302 With the purpose of increasing the working capacity without depressing the absorption
 303 efficiency, we designed a different equipment configuration with two packed columns for the
 304 CO₂ capture and absorption-desorption temperatures set at 50-105 °C. The results of the
 305 experiments are reported in Table 6. As a general consideration, the configuration with two
 306 absorbent columns gave a neat advantage in terms either of CO₂ absorption efficiency (Table 6,
 307 entry 2, 80.3%, and Table 4, 52.0%) or working capacity (Table 6, entry 3 and Table 5, entry 1)
 308 which was increased by a factor of 2.1.

309 **Table 6.** Absorption efficiency and working capacity of BUMEA and 30% aqueous MEA; the
 310 fixed operational conditions are: two absorbent columns, absorbent volume 0.250 dm³; gas
 311 mixture 15 % CO₂ and flow rate 29.0 dm³ h⁻¹; absorption and desorption temperatures of 50 °C
 312 and 105 °C.

	entry	liquid flow rate			abs %	CO ₂ abs ^c (mol h ⁻¹)	working capacity ^d (mol kg ⁻¹)
		dm ³ h ⁻¹	kg h ⁻¹ ^a	mol h ⁻¹ ^b			
BUMEA	1	0.060	0.054	0.456	70.1	0.124	2.29
	2	0.090	0.081	0.684	80.3	0.143	1.76
	3	0.120	0.108	0.912	93.5	0.168	1.56
30% MEA	4	0.060	0.064	0.295	67.3	0.121	1.88
	5	0.090	0.096	0.443	85.7	0.154	1.60
	6	0.100	0.107	0.492	93.5	0.168	1.57

313 ^a density as in Table 5; ^b neat amine; ^c amount of absorbed CO₂; ^d defined as in Table 5

314

315 The comparison between the performances of BUMEA and aqueous MEA gives some
316 unexpected results, if we consider the different properties of the two absorbents.

317 The two absorbents have the same CO₂ absorption efficiency (Table 6, entries 3 and 6), and the
318 same working capacity. Presumably, the lower viscosity of aqueous MEA compensates the lower
319 flow rate of the neat amine compared to BUMEA. By reducing the absorbent flow rate below
320 0.100-0.120 dm³ h⁻¹, the working capacity of neat BUMEA and aqueous MEA progressively
321 increased but CO₂ capture efficiency were below the target value of 90%.

322 The energy required by the amine regeneration comprises the sensible heat to increase the
323 absorbent temperature from the absorption to the desorption steps, the heat of vaporization of
324 the absorbent and the heat to decompose the carbonated species, the opposite of the reaction (1)
325 enthalpy.^{17,28,36,39} Even if the reaction enthalpy of neat BUMEA with CO₂ is not available,
326 notwithstanding some qualitative considerations could be drawn. In spite of the presence of
327 water, the ¹³C NMR spectrum of carbonated MEA did not give any evidence of bicarbonate
328 formation. Consequently, the reaction enthalpy of both BUMEA and MEA with CO₂ depends on
329 the relative stability of their carbamates. As we could safely assume that BUMEA carbamate is
330 not more stable of MEA carbamate, the energy required to decompose the two carbamates could
331 be not substantially different to each other. As such, the possible energy saving of BUMEA must
332 come from its lower sensible heat (about 40 % less, see Supporting information) because of the
333 absence of water. Additionally, the vaporization heat of BUMEA is negligible, compared to
334 water, by virtue of its high boiling temperature (198-200 °C). An experiment of water
335 evaporation of aqueous MEA from the desorber (set at 105 °C) in the continuous cycle of
336 absorption-desorption experiment gave a water loss of 80.4 g/mol CO₂ captured.

337 As a final remark, it should be pointed out that, as the combustion gases contain water, our
338 solvent free alkanolamines were found to be tolerant towards moisture as the flux of the moisture
339 saturated gas lasted 36 h did not give a detectable amount of HCO_3^- , as evidenced by ^{13}C NMR
340 spectra of carbonated absorbents (Figure 1), neither gave loss of efficiency. Furthermore no
341 foaming problems were detected in the head of both absorber and desorber during all the
342 experiments.

343 The thermal stability of the neat alkanolamines was tested by their heating at $110\text{ }^\circ\text{C}$ for 40 days:
344 the ^{13}C NMR spectra revealed unidentified decomposition products in the range 1.5-5 % (on
345 molar scale) for all the amines except MMEA where 11 % of by-products were detected.

346 Considering its absorption efficiency, high boiling temperature, thermal stability and moisture
347 tolerance, neat BUEA is the most attractive option and should be the most promising absorbent
348 as a possible substitute for aqueous alkanolamines. The potential advantages of neat BUEA
349 over aqueous MEA would include: i) a reduced mass of the absorbent that must be circulated at a
350 lower rate; ii) no energy is wasted to heat superfluous water in the desorption step; iii) negligible
351 absorbent evaporation by virtue of its high boiling temperature at room pressure; iii) the
352 relatively small difference between absorption and desorption temperatures combined with the
353 reduced equipment size and corrosion.

354 We are well aware that the results we obtained in our small lab-scale equipment cannot be
355 directly scale up to a commercial plant; notwithstanding, the comparison of the performances of
356 neat BUEA and aqueous MEA measured under the same operational conditions gave
357 reasonable indications of the potential advantages of neat BUEA over aqueous MEA.

358

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363

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