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1 **Experimental solubility of carbon dioxide in monoethanolamine, or**
2 **diethanolamine or N-methyldiethanolamine (30 wt%) dissolved in deep**
3 **eutectic solvent (choline chloride and ethylene glycol solution)**

4

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14 **Abstract**

15 The success achieved by the COP21 in Paris in 2015 by committing 195 states to reduce the
16 temperature of the planet, shows that it is urgent to find a solution to greenhouse gas
17 emissions especially the CO₂. Monoethanolamine (MEA) in aqueous solution is the reference
18 solvent to capture CO₂ emission based on chemical absorption. However, aqueous solutions
19 present some drawbacks, such as equipment corrosion, loss of solvent and high energy
20 consumption. New and green solvents could be a possible solution to this issue.

21 As part of this study, new experimental data on the solubility of carbon dioxide in
22 monoethanolamine, MEA or diethanolamine DEA or methyldiethanolamine MDEA 30 wt%,
23 dissolved in greener and nontoxic deep eutectic solvent (DES) made of choline chloride
24 (ChCl) and ethylene glycol (EG) with a molar ratio of 1:2 are reported. Measurements were
25 performed at three different temperatures; 298.1, 313.1 and 333.1 K and pressures from 2 Pa
26 up to 800kPa using astatic apparatus with on-line analysis of the gas phase by GC to
27 determine the partial pressure of CO₂. The dissolved CO₂ in the liquid was determined by
28 volumetric method. In a first step, the apparatus and the entire CO₂ isotherm determination
29 protocol were validated by the study of CO₂ absorption in aqueous solution of MEA (reference

30 amine).As no literature data was available, the solubilities of CO₂ in the DES/amine were
31 compared with those obtained from the aqueous media. The two set of measurements are very
32 close.

33 Gabrielsen et al.[44] model of correlation based on the equilibrium constant, initially used for
34 aqueous amine solutions, has been successfully extended to CO₂ capture by nonaqueous
35 solutions.

36 Comparison of heat of absorption values between aqueous amines and in the DES was also
37 investigated.

38 To the best of our knowledge, this is the first time CO₂ isotherms of three classes of amine
39 dissolved in the DES (choline chloride /ethylene glycol) was studied.

40

41 **1. Introduction**

42 The current discussion about global warming and climate change is centered on the
43 anthropogenic greenhouse effect. It is caused by the emission and accumulation of gases such
44 as water vapor, carbon dioxide, methane... Carbon dioxide (CO₂) is the most important
45 anthropogenic greenhouse gas because of its comparatively high concentration in the
46 atmosphere. The combustion of fossil fuels has led mainly to an increase in the CO₂
47 concentration in the atmosphere. CO₂ contributes to more than 60% of the global warming
48 effect [1]. It is therefore essential to develop new technologies to reduce CO₂ emissions from
49 industrial fossil-fueled energy production units (ex: cement plant, refinery, etc...).

50 Post-combustion CO₂ capture technologies are considered to be the most mature technology.
51 Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA),
52 triethanolamine (TEA), 2-amino-2-methyl-1-propanol (AMP), and 2-methylaminoethanol
53 (MAE) in aqueous solutions are the most used as chemical absorbent for CO₂ capture due to
54 their high absorption ability and fast absorption rate [2–7]. However, the problems associated
55 with the aqueous-based absorbents, such as equipment corrosion, high energy consumption,
56 currently make the process not viable [8–13]. Various researches are being carried out in order
57 to define alternative solvents which exhibit high affinity for CO₂ with easier solvent
58 regeneration and reuse, low corrosion of equipment.

59 In recent years, ionic liquids (ILs) have quickly emerged as an alternative of choice. An IL is
60 a molten salt, composed of a cation and an anion which interact via electrostatic forces. They
61 are liquid at room temperature; their melting temperatures are often below 100°C. ILs showed
62 several unusual characteristics such as low volatility, high thermal and chemical stability,
63 strong solvation ability and tunability of chemical and physical properties by choice of the
64 cation/anion combination [14,15]. However, due to expensive raw material chemicals, poor
65 biodegradability, an uncertain toxicity and complicated synthetic processes of ILs, it is still a
66 challenge for their large-scale applications in industry [16,17]. Recently, a new generation of
67 solvent, named Deep Eutectic Solvent (DES), has emerged as a low cost alternative of ILs. A
68 DES is a fluid generally obtained by mixing an organic halide salts with metal salts or a
69 hydrogen bond donor (HBD). These components are capable of self-association, often
70 through hydrogen bond interactions, to form eutectic mixture with a melting point lower than
71 that of each individual component. Most of DESs are liquid between room temperature and
72 70°C [18]. These solvents exhibit similar physico-chemical properties to the traditionally used

73 ILs, while being much cheaper and environmentally friendlier. In fact, they are easily
74 produced at low cost and in high purity. Furthermore, they are non-toxic and most
75 importantly, being made from biodegradable components [19,20].

76 For these reasons, DESs are now of growing interest in many fields of research such as
77 biocatalysis [21,22], electrochemistry [23], pharmaceuticals [24], liquid-liquid extraction [25],
78 gas (NH₃, NO, SO₂ and CO₂) absorption [26– 42] and other chemical and industrial processes.

79 To carry out the solubility of CO₂ in the solvent, a static apparatus with on-line analysis of the
80 vapor phase was designed. Once the apparatus was validated, the solubility of CO₂ in
81 monoethanolamine, MEA, diethanolamine, DEA, or N-methyldiethanolamine, MDEA, at 30
82 mass % in DES medium (choline chloride and ethylene glycol at 1:2 mole ratio) was
83 determined at three different temperatures 298.1, 313.1 and 333.1 K and pressures from 2 Pa
84 up to 800 kPa. CO₂ absorption isotherms were correlated using the model of Gabrielsen et al.
85 [44] which in turn was based on the model developed by Posey et al.[45]. The model was
86 previously established for aqueous solutions. Its transposition to the DES media was
87 successfully carried out in the case of primary and secondary amine. The model proposal for
88 the tertiary amine correlates satisfactorily the experimental measurements up to 35 kPa.

89 2. Experimental section

90 2.1. Materials

91 The chemicals, monoethanolamine (MEA), Diethanolamine (DEA), N-methyldiethanolamine
92 (MDEA), choline chloride (ChCl), ethylene glycol (EG) and hydrochloric acid (HCl, 5N),
93 were purchased from Sigma-Aldrich and were used without further purification. Their purity
94 and source are given in Table 1. High purity deionized water (conductivity = 18 MΩ.cm using
95 a “Purelab” Classic water purification module) was used. The CO₂ was supplied by Air
96 Liquide with mole fraction purity greater than 0.999. A digital balance (Mettler-Toledo
97 AG204) having an accuracy of 0.0001 g was used.

98 2.2. Apparatus

99 The realized apparatus is composed of a glass equilibrium cell of a volume of 396 cm³ with a
100 double envelope for thermoregulated water circulation which ensures a constant temperature
101 of the mixture, Fig.1. The autoclave withstands pressure up to 10 bars, and in order to avoid
102 any overpressure, the lid is equipped with a safety capsule which serves as a valve. In
103 addition, a pumping system allows a vacuum in the entire apparatus when necessary. A

104 calibrated copper-constantan thermocouple, introduced in a glove finger, monitors the
105 equilibrium temperature (absolute uncertainty of $\pm 0.1\text{K}$). Total pressure of the solution is
106 delivered by a Keller type pressure sensor (range: 0 to 10 bars; relative uncertainty of 0.5%).
107 To cushion the effect of CO_2 pressure into the solution, a stainless-steel reserve is placed at
108 the outlet of the gas cylinder. The pressure of CO_2 in the reserve is determined by a
109 supplementary pressure sensor (measurement range: 0 to 10 bar).
110 The solution is homogenized with a self-aspirating hollow stirrer whereas the gaseous phase is
111 submitted to a continuous loop circulation thanks to a peristaltic pump. At the exit of the cell
112 (autoclave), the gaseous phase passes through a sampling loop of 2 mL connected to a gas
113 chromatograph, GC for on-line analysis. As for the liquid phase, an offline volumetric
114 analysis (described below) is carried out. To avoid any vapor condensation upstream GC
115 analysis, the sampling line and the injection valve are maintained at 120°C .
116 Isotherms of absorption are determined by introducing successive additions of CO_2 .

117 *2.3. Preparation of the absorbent*

118 The amine and the DES, (ChCl and EG, 1:2 mole ratio respectively) are prepared separately
119 in a balloon and degassed by heating and submitting each liquid to vacuum. Due to its high
120 hygroscopicity, the DES is prepared inside a glove box. Some argon is finally added in the
121 DES balloon to protect it from ambient air, the time to transport the solution from the glove
122 box to the cell. An exact amount (determined by weighing) of the DES and the amine is
123 introduced into the glass cell. The stirred, homogenous and transparent liquid of about 250
124 mL is finally subjected to moderate heating and purges in order to evacuate the dissolved
125 argon.

126 *2.4. Experimental protocol*

127 Before any new measurement, a vacuum is created in the whole apparatus to ensure that there
128 is no air or CO_2 in the device and to check off an eventual leakage of the system. The
129 equilibrium cell is maintained at constant temperature. The previously prepared solution is
130 then introduced by aspiration into the autoclave via the tube provided for this purpose and
131 stirred (2000 rpm), [Fig.1](#). Once the temperature becomes constant, some CO_2 is added from
132 the one liter tank (containing CO_2 at 3 bars and at room temperature) by opening V_2 and V_3
133 valves. Despite a vigorous mixing of the liquid, the phase equilibrium is reached within 12
134 hours due to the slow absorption kinetic and the viscosity of the solutions of DES/amine. It is
135 monitored by the pressure sensor equipped with online data acquisition system.

136 Prior to the gas phase on-line analysis, in order to determine the partial pressure of CO₂, the
137 GC was calibrated using different compositions of CO₂ and N₂ mixtures. In addition, a sample
138 of the liquid phase is withdrawn and the CO₂ loading, α , is determined by volumetric titration
139 with hydrogen chloride solution, Eq. (1):

$$\alpha = \frac{\text{mol of CO}_2 \text{ in the liquid phase}}{\text{mol of amine}} \quad (1)$$

140 When the equilibrium pressure of CO₂ in the autoclave is under the atmospheric pressure,
141 nitrogen gas (slightly above 1 bar) is introduced into the cell to facilitate the collect of the
142 liquid sample and to transport the vapor phase towards the gas chromatograph via the
143 sampling loop. The next increment of CO₂ is carried out after purging the vapor phase of the
144 cell.

145 **3. Results and discussion**

146 *3.1. Validation of the experimental method*

147 To validate the experimental protocol previously described, solubility of CO₂ in aqueous
148 MEA at 30% (by weight) was determined at three temperatures (298.1, 313.1 and 333.1 K)
149 and at large partial pressures of CO₂ ranging from 1 Pa to 800 kPa, [Table 2](#). The obtained
150 results were compared with literature data [46–48], [Figs.2-4](#). A very good agreement is
151 obtained with Jou et al. [46] and Aronu et al.[48] data whereas a slight deviation is observed
152 with Shen and Li points [47].

153 *3.2. Solubility of CO₂ in the solvent MEA/DES, DEA/DES and MDEA/DES*

154 [A protocol identical to that of aqueous MEA was used to determine CO₂ in the vapor phase](#)
155 [\(by GC\) and CO₂ in the liquid phase \(by volumetry\).](#)

156 The solubility of CO₂ in MEA or DEA or MDEA (30 wt%) dissolved in the DES (ChCl : EG
157 (1:2)) are reported in [Tables 3-5](#). The experimental values expressed as the partial pressure of
158 CO₂ function of the loading, α , are represented in [Figs.5-7](#).

159 As expected, for a given partial pressure of CO₂, the solubility of the gas in term of
160 α decreases with increasing temperature. At the physical absorption range, $\alpha > 0.5$, the
161 influence of temperature on the solubility is negligible for the three amines, the curves
162 overlap. In the same way, for a given temperature and partial pressure of CO₂ (example P_{CO₂} =

163 1 kPa, T= 313.1K), the solubility of CO₂ in term of molality, decreases from MEA (primary
164 amine) to MDEA (tertiary amine). The solubility of CO₂ in the DES (without amine) studied
165 by Leron and Li [20], remains much lower than that of MDEA+DES, Fig. 8, due to the
166 absence of chemical absorption when the amine is missing.

167 On the other hand, the solubilities of CO₂ in the DES/ MEA (15% wt), reported in Table 6,
168 are almost similar with those obtained in the DES/ MEA (30wt%) media, Fig. 9. In the same
169 way, the values of α observed in the aqueous solution of MEA or DEA overlap those obtained
170 in the DES/ amine (30wt%) media, Fig. 10 and Fig. 12. This phenomenon is not observed for
171 MDEA. For example, the solubility of CO₂ at 313.1 K in the DES/MDEA, $\alpha=0.4$, is obtained
172 at a higher pressure ($P_{CO_2} = 100$ kPa) whereas in the aqueous solution for the same $\alpha=0.4$,
173 $P_{CO_2} < 10$ kPa, Fig. 11.

174 Uma Maheswari and Palanivelu [49] carried out the determination of α in the amine (MEA,
175 DEA)/DES (ChCl:EG, molar ratio of 1:2) at 298.1 K and $P_{CO_2} = 200$ kPa. The obtained
176 results, $\alpha = 0.492$ in the case of MEA and $\alpha = 0.301$ in the case of DEA, are in total
177 disagreement with the present study where α is above 0.6 for both amine at the quoted partial
178 pressure of CO₂.

179 *3.3. Correlation model for CO₂ absorption in nonaqueous media- Absorption enthalpy of CO₂*

180 **Correlation**

181 The studied solvent consists of two entities: choline chloride totally ionized and stablishing
182 strong coulombic electrostatic interactions with charged solutes; monoethyleneglycol, like all
183 alcohols, or water ..., is an ampholyte molecular solvent (BH) whose autoprotolysis
184 equilibrium is as follows:



185 The equilibrium constant K_i is:

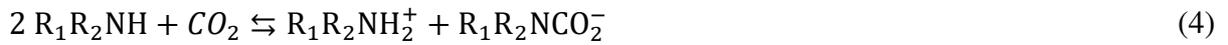
$$K_i = [\text{H}_2\text{B}^+][\text{B}^-] \quad (3)$$

186 It is known that ampholytic solvents could dissolve salts in two solvated forms: free ions
187 (anions A_{sol}^- and cations C_{sol}^+) and ion pairs $(A^-, C^+)_{\text{sol}}$.

188 The molar proportions of these species depend on several parameters (dielectric constant of
189 the solvent, radius and charge of the ions, temperature, solute-solvent interactions ...). As a
190 first approximation when the solvent has a dielectric constant, ϵ_r , higher than 40, the free ions
191 predominate and vice versa. In our case the solvent is a mixture of MEG $\epsilon_r = 37.7$ at 298 K)

192 and Choline Chloride. The dielectric constant of the latter is unknown, but probably very
 193 weak like most ionic species (example $\epsilon_r(\text{KCl}) = 4.86$ at room temperature). The dielectric
 194 constant that results from mixing the two constituents of the solvent should lead to the
 195 coexistence of free species A_{sol}^- and C_{sol}^+ , and ion pairs $(A^-, C^+)_{sol}$. However, it is reasonable
 196 to assume that the presence of the choline chloride, establishing strong coulombic interactions
 197 with charged solutes, favors the predominance of free ions A_{sol}^- and C_{sol}^+ . This is what we
 198 admit in the present study.

199 Kortunov et al.[50] studied the mechanism of the reaction between primary and secondary
 200 amine with CO_2 in nonaqueous media using ^1H and ^{13}C NMR. They confirmed that the same
 201 mechanism occurs in aqueous and nonaqueous media with however a difference in the
 202 stability of the carbamic acid formed intermediately. In nonaqueous medium, carbamic acid
 203 and carbamate, coexist at the chemical equilibrium but their relative proportion depends on
 204 many parameters (the concentration, pressure, molecular structure of the amine, nature of the
 205 solvent, temperature, partial pressure of CO_2 ...). The great similarity of the experimental
 206 absorption isotherms of MEA and DEA in aqueous and non-aqueous medium, [Figs. 10 and](#)
 207 [12](#), leads us to assume that at the absorption equilibrium, carbamate species predominant:



208 Assuming that the activity coefficient is equal to the unity, the equilibrium constant is as
 209 follows:

$$K'_{CO_2} = \frac{[RR'NH_2^+][RR'NCOO^-]}{[CO_2][RR'NH]^2} \quad (5)$$

210 At equilibrium and [by neglecting ions from the autoprotolysis of the solvent](#):

$$[RR'NH_2^+] = [RR'NCOO^-] = a_0\alpha \quad (6)$$

$$[RR'NH] = (1 - 2\alpha)a_0 \quad (7)$$

211 where:

212 α : is the CO_2 loading rate

213 a_0 : the initial concentration of amine

214 The solvated CO₂, [CO₂]_{sol}, follows Henry law, where K_H is the constant:

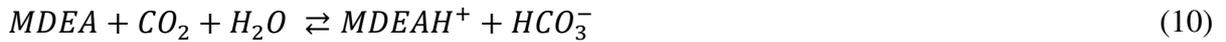
$$P_{CO_2} = K_H [CO_2]_{sol} \quad (8)$$

215 By neglecting the physical absorption of CO₂ in the solvent, Eqs. (5)-(8) leads to the
216 following expression:

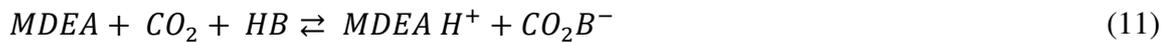
$$P_{CO_2} = K_{CO_2} \frac{\alpha^2}{(1-2\alpha)^2} \quad (9)$$

217 K_{CO₂} includes K'_{CO₂} and Henry constant K_H

218 It is commonly admitted that the absorption of CO₂ by a tertiary amine, in this case MDEA, in
219 an aqueous medium follows the reaction below where the solvent participates in the reaction:



220 CO₂ absorption by MDEA in non-aqueous media (ethanol) has been studied by Kierzkowska-
221 Pawlak and Zarzycki [51]. In the absence of water, the authors expected a limited absorption
222 of CO₂ according Henry's law (physisorption). Actually, the authors observed a solubility of
223 CO₂ much higher than that of NO₂ under the same experimental conditions. NO₂ absorption in
224 water is known to be only physical (do not present chemical reaction). The authors attribute
225 this important solubility of CO₂ to "additional" interactions due to hydrogen bonds with the
226 solvent and also evoke a possible interaction of the nitrogen atom of the amine with CO₂.
227 Ethylene glycol being an amphiprotic solvent, *HB* (like water, alcohol...), we propose the
228 chemical reaction in nonaqueous media,(Eq. (11)). In the same way as for aqueous media, the
229 chemical absorption range is comprised between $\alpha = 0$ and $\alpha = 1$ (different from the case of
230 MEA and DEA where the absorption range is below $\alpha < 0.5$).



231 MDEA H⁺ and CO₂B⁻ are respectively the lyonium and lyate ions. As mentioned previously,
232 we admit that the solvated free ions are predominant compared to the ion pairs.

233 The equilibrium constant of the reaction (10) is:

$$K'_{CO_2} = \frac{[MDEAH^+][CO_2B^-]}{[MDEA][CO_2]} \quad (12)$$

234 According to the same hypothesis as for the primary and secondary amine:

$$P_{CO_2} = K_{CO_2} \frac{\alpha^2}{a_0 (1 - \alpha)} \quad (13)$$

235 In the same way as for primary and secondary amine, K_{CO_2} include K'_{CO_2} and Henry constant
236 K_H .

237 The model used is an extension towards the nonaqueous media of the one proposed by Posey
238 et al.[45] and later used by Gabrielsen et al.[44] for the absorption of CO_2 by the three classes
239 of amine in aqueous phase. The influence of the temperature on the constant of equilibrium is
240 given by the following relation, Eq. (14):

$$\ln K_{CO_2} = A + \frac{B}{T} + C * a_0 * \alpha + D \sqrt{a_0 * \alpha} \quad (14)$$

241 α : is the loading rate (mol of CO_2 /mol of amine)

242 a_0 : initial concentration of amine in the DES

243 K_{CO_2} : combined Henry's law and chemical equilibrium constant for CO_2 partial pressure

244 A, B, C and D: adjustable parameters

245 The model is valid only in the field of chemical absorption: $\alpha < 0.5$ for primary and secondary
246 amines (MEA and DEA) and $\alpha < 1$ for tertiary amines (MDEA).

247 The first two parameters A and B take into account the influence of the temperature on the
248 equilibrium constant. The last parameters C and D, allows a global correction of non-ideality.
249 For primary and secondary amines the expression is truncated to the first two adjustable
250 parameters. Therefore the partial pressure, P_{CO_2} , is independent of the initial concentration of
251 the amine, as for the aqueous phase.

252 The minimized objective function is as follows (Eq. (15)):

$$F = \sum_{i=1}^{NP} \left(\ln \left(\frac{K_{CO_2 cal,i}}{K_{CO_2 exp,i}} \right) \right)^2 \quad (15)$$

253 N is the number of experimental point.

254 The parameters of Eq. (14) are reported in Table 7. As shown in Figs. 13 and 14, the model
255 satisfactorily reproduces the experimental points obtained with MEA and DEA. In the case of

256 MDEA, the model fits well the experimental data for $\alpha < 0.5$ (Fig. 15); beyond this value the
257 model deviates from the experimental points. This phenomenon could be explained by the
258 non-negligible quantity of ion pairs formed during the CO₂/MDEA reaction.

259 Heat of absorption of CO₂

260 From Eq. (14), enthalpy of CO₂ absorption is deduced, using Gibbs-Helmholtz relation:

$$\left[\frac{\partial}{\partial T} \left(\frac{\Delta G}{T} \right) \right]_p = - \frac{\Delta H}{T^2} \quad (16)$$

261 Where ΔG , Gibbs free energy of the reaction, is related to the equilibrium constant K_{CO_2} by:

$$\Delta G = -RT \ln K_{CO_2} \quad (17)$$

262 Assuming that the effect of pressure on K_{CO_2} is negligible, from Eq. (16) and (17) we deduce
263 K_{CO_2} as a function of the temperature:

$$\frac{d(\ln K_{CO_2})}{d\left(\frac{1}{T}\right)} = - \frac{\Delta H}{R} \quad (18)$$

264 The resolution of the derivative function of temperature of equation of Eq. (14) into Eq. (18),
265 gives ($-\Delta H_{absorption}^{average}$):

$$\Delta H_{absorption}^{average} = -BR \quad (19)$$

266 Where R is the universal gas constant.

267 The calculated $\Delta H_{absorption}$ were then compared with those obtained in the aqueous solutions
268 of amines reported by different bibliographic sources, Tables 8.

269 The enthalpy of CO₂ absorption by MEA (30wt%) in (1 ChCl : 2 EG) solution is significantly
270 lower than that of MEA in aqueous medium. The use of MEA in (1 ChCl : 2 EG) would allow
271 an energy saving in the regenerator of the order of 20%. With regard to DEA the nature of the
272 solvent does not have a significant effect on the CO₂ absorption enthalpy. In the case of
273 MDEA, the type of solvent plays an important role: in (1 ChCl : 2 EG) medium the value is

274 clearly lower than in aqueous medium, resulting in a possible saving of energy in the
275 regenerator of almost 40%.

276

277 **4. Conclusion**

278 The three different classes of amine (MEA, DEA and MDEA) were chosen in order to
279 compare their behavior in the DES medium with that in water. With this aim a static apparatus
280 with on-line analysis of the vapor phase was developed. Three temperatures (298.1; 313.1 and
281 333.1 K) with various loading of CO₂ in each solution were explored. The range of the partial
282 pressure of CO₂ investigated is particularly large, from 2 Pa to approximately 800kPa.

283 The study shows that the substitution of water by DES solvents leads to almost the same
284 capacity of CO₂ absorption by the amines except for MDEA where a lower solubility of CO₂
285 is observed comparing to the aqueous medium.

286 The model for primary and secondary amine fits quite well the experimental values obtained
287 with the MEA and DEA. In the case of MDEA, the model deviates from the experimental
288 points when the loading rate is above $\alpha > 0.5$. In the hypothesis of a use of the DES+amine
289 solvent for CO₂ capture in post-combustion, a decrease of the vapor pressure of the solvent
290 (comparing to that of water+amine) has an advantage from the point of view losses by
291 vaporization in the absorber. The second advantage is most likely a lower effect of equipment
292 corrosion, the third positive point is a lower enthalpy of absorption of MEA and MDEA in (1
293 ChCl : 2 EG) comparing to aqueous medium, resulting in a possible saving of energy in the
294 regenerator of almost 40%. However these positives are counter balanced by the increase of
295 the viscosity and by a slower kinetic of the absorption reaction.

296

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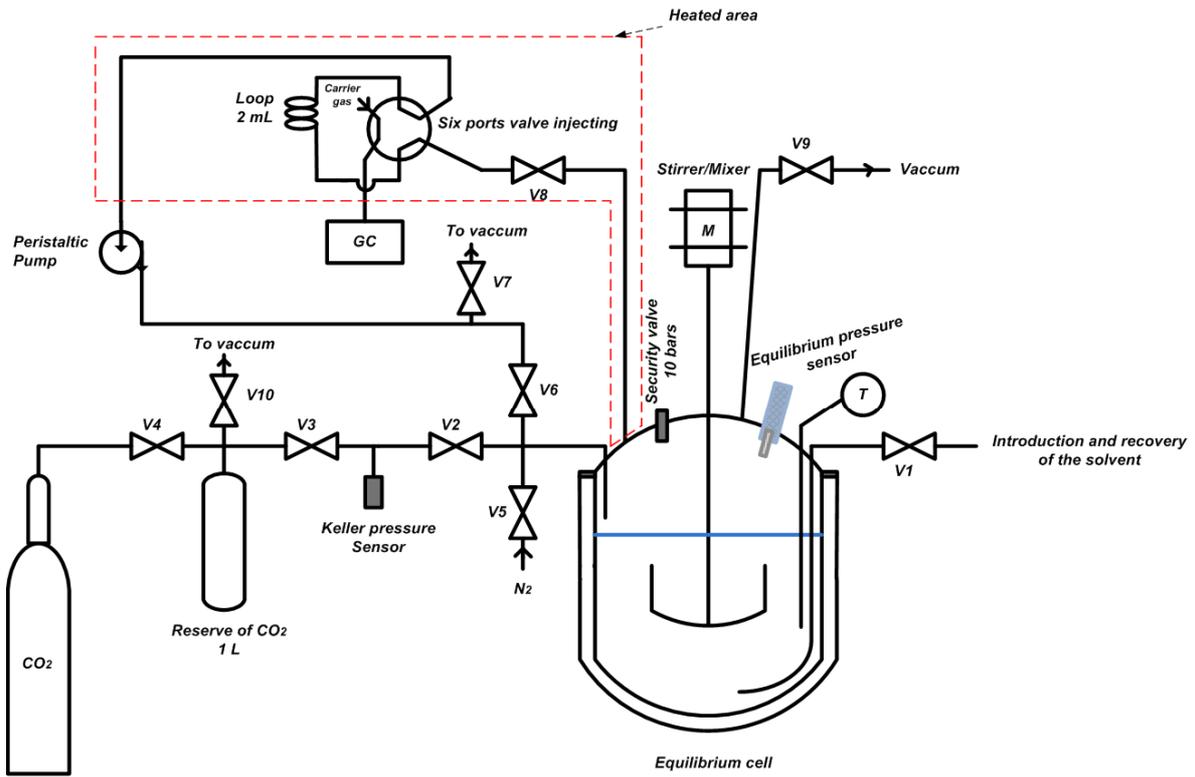


Fig.1. Apparatus for CO₂ absorption.

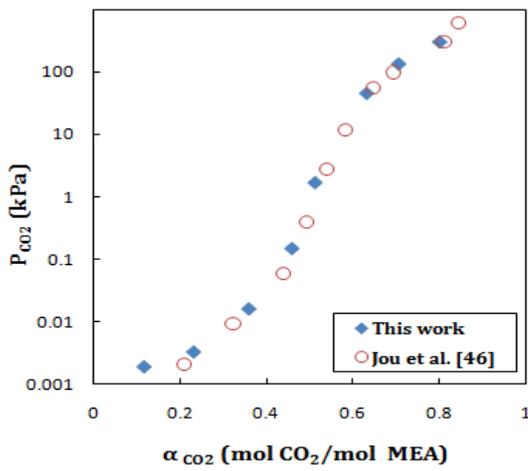


Fig. 2. Solubility of CO₂ in aqueous solution of MEA (30 wt %) at 298.1 K.

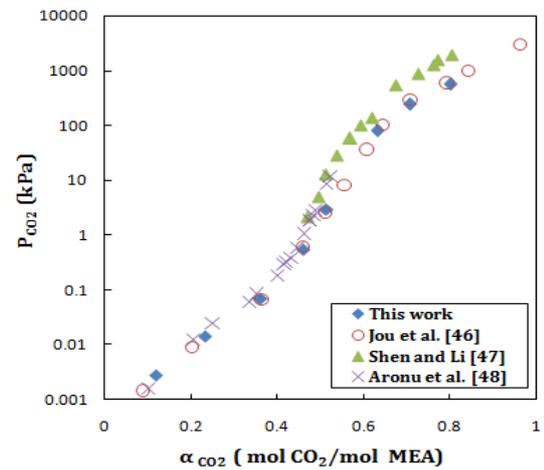


Fig. 3. Solubility of CO₂ in aqueous solution of MEA (30 wt %) at 313.1 K.

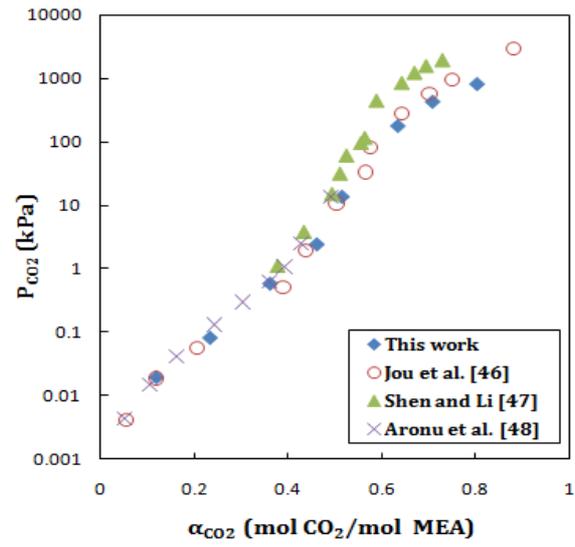


Fig. 4. Solubility of CO₂ in aqueous solution of MEA (30 wt %) at 333.1 K.

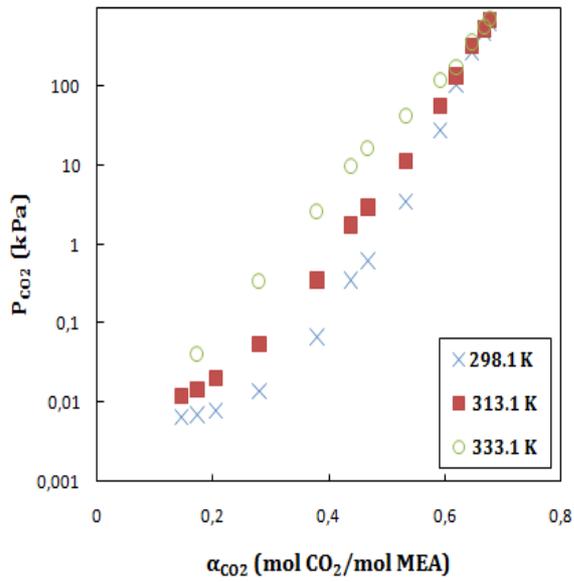


Fig. 5. Solubility of CO₂ in MEA 30 wt% + DES (1 ChCl : 2 EG) at three different temperatures.

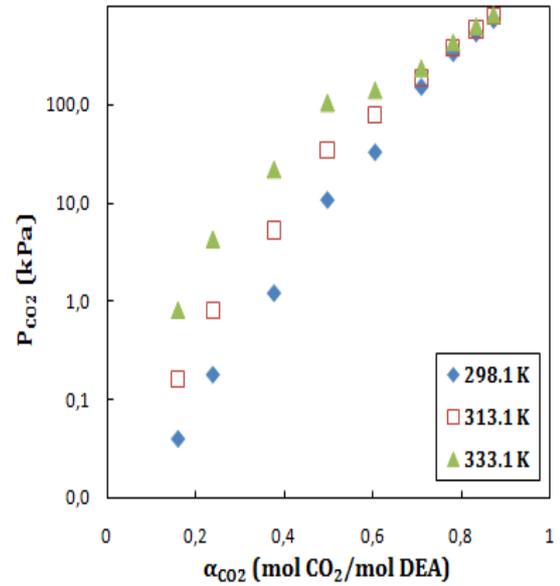


Fig. 6. CO₂ solubility in DEA 30 wt% + DES (1 ChCl: 2 EG) at three different temperatures.

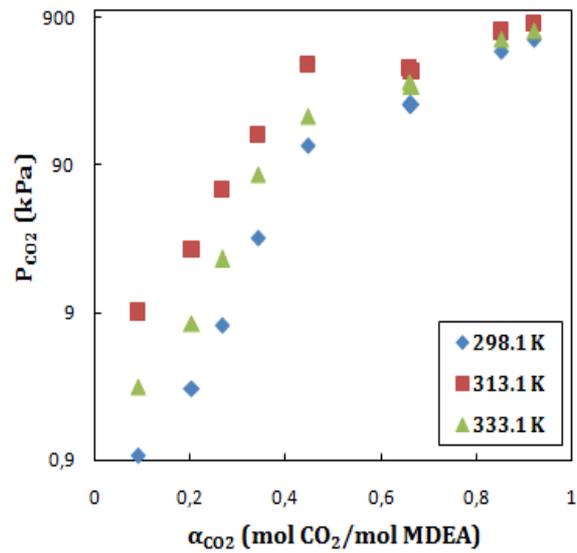


Fig. 7. CO₂ solubility in MDEA 30 wt% + DES (1ChCl:2 EG) at three different temperatures.

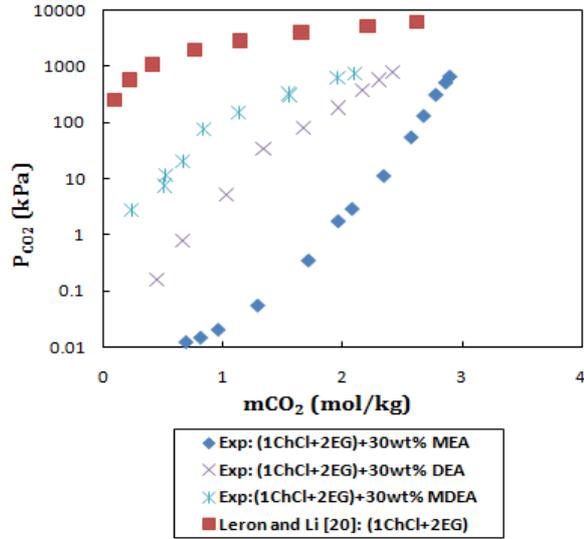


Fig. 8. Comparison of CO₂ solubility at 313.1 K in several solvents: (1 ChCl: 2 EG) + MEA (♦) or + DEA (×) or + MDEA (*); and in (1 ChCl: 2 EG): (■), [20]. Percentage of amine in DES = 30 wt%.

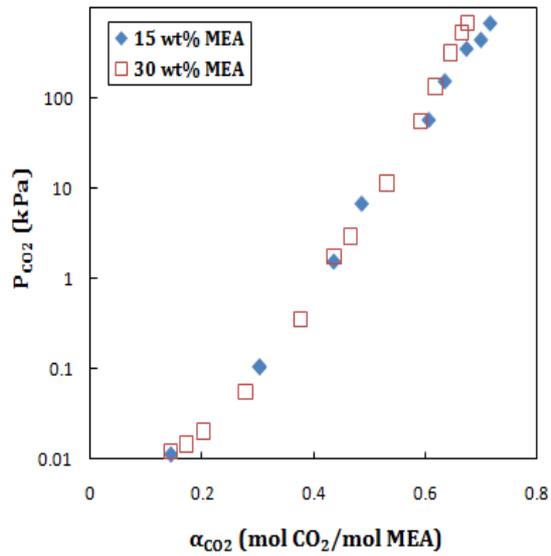


Fig. 9. CO₂ solubility in MEA (15 or 30%) + DES (1 ChCl : 2 EG) at 313.1 K.

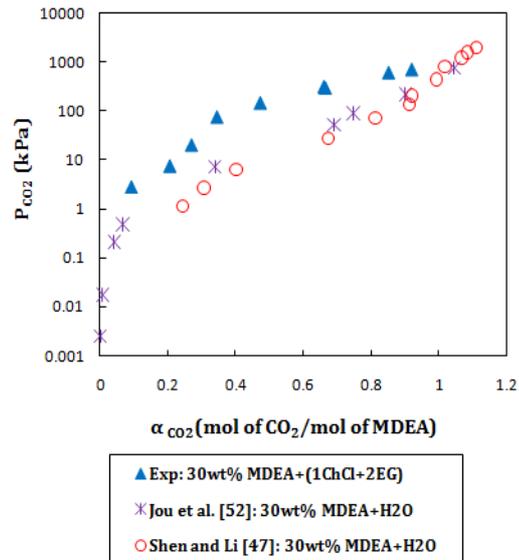
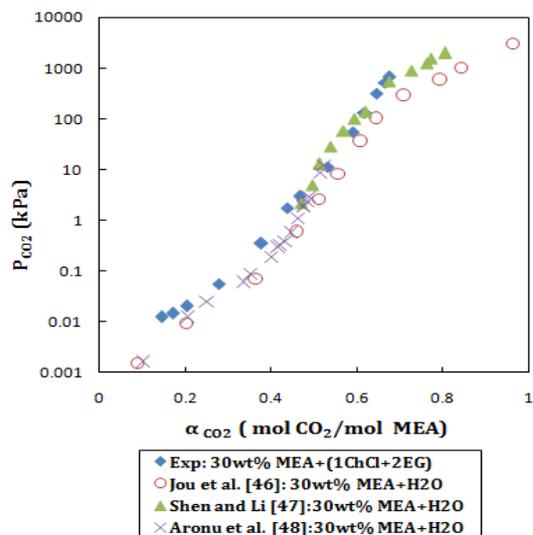


Fig. 10. Comparison of CO₂ solubility at 313.1 K in aqueous and nonaqueous MEA.

Fig. 11. Comparison of CO₂ solubility at 313.1 K in aqueous and nonaqueous MDEA.

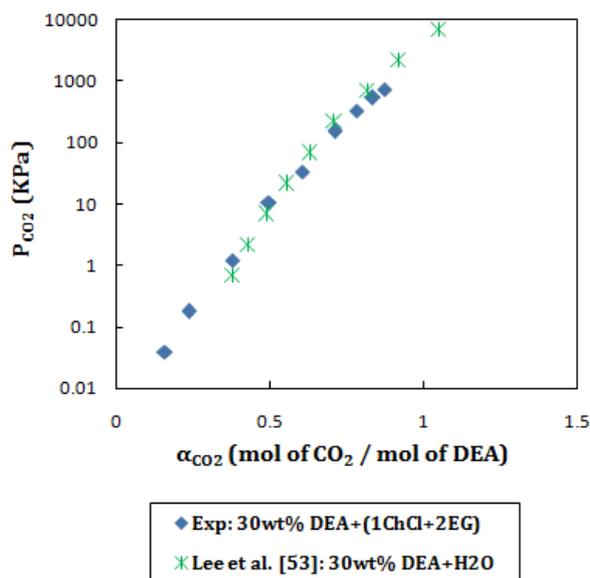


Fig. 12. Comparison of CO₂ solubility at 298.1 K in aqueous and nonaqueous DEA.

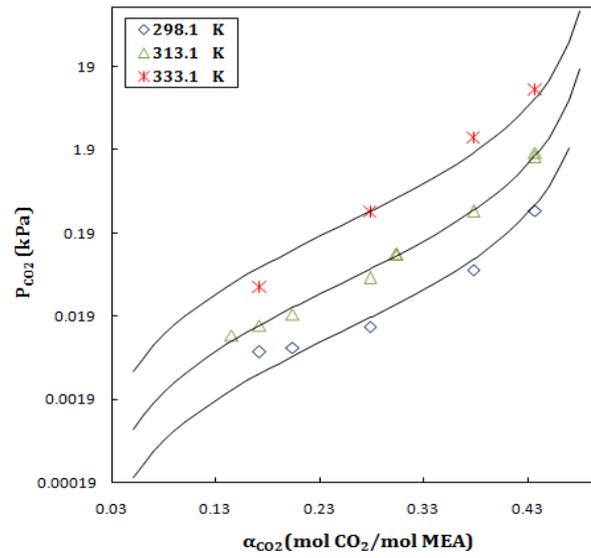


Fig. 13. Comparison between experimental and calculated values (solid lines) of CO₂ solubility in 30 wt% MEA + DES (1 ChCl : 2 EG).

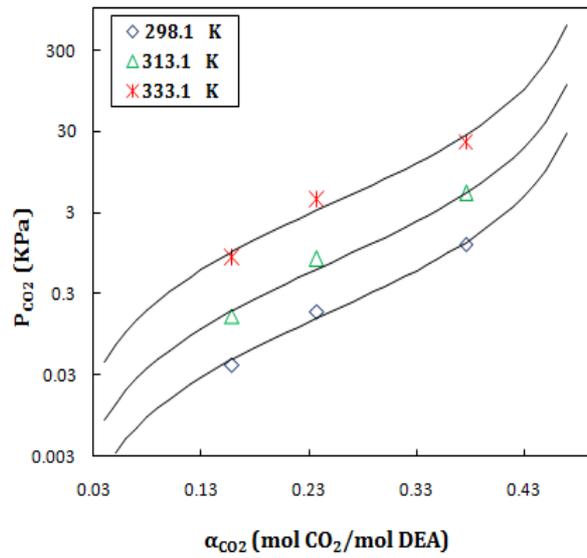


Fig. 14. Comparison between experimental and calculated values (solid lines) of CO₂ solubility in 30 wt% DEA + DES (1 ChCl : 2 EG).

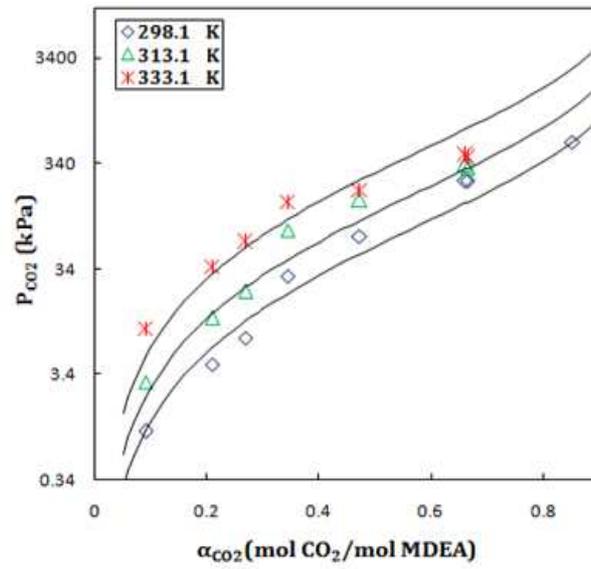


Fig. 15. Comparison between experimental and calculated values (solid lines) of CO₂ solubility in 30 wt% MDEA+ DES (1 ChCl : 2 EG).

Table 1

Chemicals used in this work.

Chemical	Acronym	CASNumber	Purity (mass fraction)	Purity GC	Source
Carbon dioxide	CO ₂	124-38-9	0.999	0.998	Air Liquide
Ethanolamine	MEA	141-43-5	≥0.990	0.990	Sigma Aldrich
Diethanolamine	DEA	111-42-2	≥0.980	0.981	Sigma Aldrich
N-Methyldiethanolamine	MDEA	105-59-9	≥0.990	0.992	Sigma Aldrich
Choline Chloride	ChCl	67-48-1	0.990	-	Sigma Aldrich
Ethylene glycol	EG	107-21-1	≥0.995	0.990	Sigma Aldrich

Table 2Solubility of CO₂, α (mol of CO₂/ mol of amine), in aqueous 30% (w/w) monoethanolamine solution.

α	P_{CO_2} / kPa		
	T = 298.1 K	T = 313.1 K	T = 333.1 K
0.118	0.0019	0.0028	0.0195
0.233	0.0032	0.0145	0.0816
0.361	0.0158	0.0710	0.580
0.460	0.146	0.558	2.41
0.514	1.66	3.01	13.48
0.633	44.75	80.33	174.8
0.707	132.6	243.2	420.1
0.802	297.2	566.7	795.9

Relative standard deviation: $u_r(P_{\text{CO}_2}) = 5\%$ for $P_{\text{CO}_2} < 1$ kPa and $u_r(P_{\text{CO}_2}) = 1\%$ for $P_{\text{CO}_2} > 1$ kPa.

Table 3Solubility of CO₂, α (mol of CO₂/ mol of amine), in DES (1 ChCl : 2 EG) + MEA 30%(w/w) media.

α	P _{CO2} / kPa		
	T = 298.1 K	T = 313.1 K	T = 333.1 K
0.145	0.0066	0.0122	-
0.172	0.0071	0.0146	0.0421
0.204	0.0079	0.0202	-
0.279	0.0141	0.0547	0.34
0.378	0.0677	0.35	2.66
0.437	0.35	1.75	10.13
0.466	0.62	2.91	16.69
0.532	3.43	11.25	42.81
0.591	27.60	55.10	122.9
0.619	102.6	132.8	175.9
0.645	274.4	315.8	369.6
0.667	472.9	521.3	583.7
0.676	616.9	669.7	731.0

Relative standard deviation: $u_r(P_{CO2}) = 5\%$ for $P_{CO2} < 1$ kPa and $u_r(P_{CO2}) = 1\%$ for $P_{CO2} > 1$ kPa.

Table 4Solubility of CO₂, α (mol of CO₂/ mol of amine), in DES (1 ChCl : 2 EG) + DEA 30% (w/w).

α	P _{CO2} / kPa		
	T = 298.1 K	T = 313.1 K	T = 333.1 K
0.159	0.0393	0.16	0.83
0.238	0.18	0.79	4.34
0.376	1.20	5.16	22.20
0.497	10.75	33.96	105.2
0.605	33.01	78.38	141.2
0.710	153.0	184.0	236.0
0.782	337.3	375.8	431.0
0.834	536.4	575.4	629.05
0.874	736.5	777.5	822.9

Relative standard deviation: $u_r(P_{CO2}) = 5\%$ for $P_{CO2} < 1$ kPa and $u_r(P_{CO2}) = 1\%$ for $P_{CO2} > 1$ kPa.

Table 5Solubility of CO₂, α (mol of CO₂/ mol of amine), in DES (1 ChCl : 2 EG) + MDEA 30% (w/w).

α	P _{CO2} / kPa		
	T = 298.1 K	T = 313.1 K	T = 333.1 K
0.092	0.98	2.85	9.06
0.205	2.75	7.68	24.03
0.210	4.19	11.67	35.26
0.269	7.48	20.72	61.48
0.344	28.77	77.90	143.3
0.472	69.09	151.6	186.0
0.660	230.8	327.4	410.0
0.664	230.0	308.4	385.7
0.851	535.2	638.2	725.3
0.920	643.1	740.2	824.7

Relative standard deviation: $u_r(P_{CO_2}) = 5\%$ for $P_{CO_2} < 1$ kPa and $u_r(P_{CO_2}) = 1\%$ for $P_{CO_2} > 1$ kPa.

Table 6

Solubility of CO₂, α (mol of CO₂/ mol of amine), in DES (1 ChCl : 2 EG) + MEA 15% (w/w).

α (313.1K)	P _{CO2} /kPa
0.145	0.0112
0.303	0.107
0.304	0.105
0.436	1.56
0.486	6.84
0.606	58.29
0.635	156.5
0.674	359.2
0.699	450.7
0.716	689.1

Relative standard deviation: $u_r(P_{CO2})= 5\%$ for $P_{CO2} < 1$ kPa and $u_r(P_{CO2})= 1\%$ for $P_{CO2} > 1$ kPa.

Table 7Regressed Parameters of K_{CO_2} *

	A	B	C	D
MEA-CO ₂	25.45	-8355	-1.79	0.00
DEA-CO ₂	29.18	-8655	-1.95	0.00
MDEA-CO ₂	20.04	-4576	0.02	3.50

$$* : \ln K_{CO_2} = A + \frac{B}{T} + C a_0 \alpha + D \sqrt{a_0} \alpha$$

Table 8

Enthalpy of CO₂ absorption in aqueous and nonaqueous (1 ChCl : 2 EG)amine 30wt% - Comparison with literature data.

$\Delta H_{\text{Abs}} \text{ (kJ mol}^{-1}\text{)}$					
MEA + (1 ChCl : 2 EG)	MEA + H₂O				
This work	Literature data				
-68.7	-81/-90 [54] ^a	-90 [52] ^b	-82 [55] ^a	-84/-93 [56] ^a	-95 [57] ^c
DEA + (1 ChCl : 2 EG)	DEA + H₂O				
This work	Literature data				
-72	-69.9 / -71.15 [55] ^a		-55.1 / -74.6 [58] ^a		
MDEA + (1 ChCl : 2 EG)	MDEA + H₂O				
This work	Literature data				
-31	-49/-55 [59] ^a	-48.8 [52] ^b	-49 [55] ^a	-49.8/-58.4 [60] ^a	-40.7/-47.2 [57] ^c

^a: Calorimetry; ^b: Calculated from solubility data, ^c predicted value