1     **Title:** Carbon dioxide capture using water-imidazolium ionic liquids-amines ternary systems

2     **Running Head**: Absorption of $CO_2$ in ternary systems

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13     **Highlights**

14     Solubility of $CO_2$ in ternary systems of IL-amines-water evaluated

15     DBU promotes the fixation of $CO_2$ in [emim][OcSO$_4$]

16     Facile regeneration of DBU-[emim][OcSO$_4$] system at 60°C

17     Mechanism of absorption confirmed by $^{13}C$ NMR and MS

18     Some systems display non-Newtonian behavior after $CO_2$ absorption

19

20     **Keywords:** carbon dioxide, ionic liquids, amines, absorption, ternary mixtures, DBU

21     **Abstract:**
22     Ionic liquids (ILs) mixtures with water, amines and other solvents have been receiving
23     attention as alternative $CO_2$ absorbents that could offer energy savings comparing with
24     traditional aqueous MEA processes and mitigate high cost or viscosity of pure ionic liquids.

In this work, mixtures of two ionic liquids (1-butyl-3-methylimidazolium acetate [bmim][OAc], 1-ethyl-3-methylimidazolium octylsulphate [emim][OcSO$_4$]) and five amines (1,1,3,3-tetramethylguanidine (TMG), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), triethylamine (TEA), and 2,2'-aminodiethanol (DEA)) were used for $CO_2$ capture. In total ten model systems were investigated. Generalized patterns of composition-$CO_2$ absorption relationships were identified depending on underlying mechanism of absorption. Viscosities and regeneration potential of selected systems were determined. DBU-[emim][OcSO$_4$] systems showed the temperature of regeneration as low as 60°C. The viscosity of all systems was greatly reduced by addition of water. Some $CO_2$-reach solutions displayed non-Newtonian behavior. Mechanism of $CO_2$ absorption in imidazolium ionic liquids in the presence of DBU was confirmed based on $^{13}C$ NMR.

**NOMENCLATURE/LIST OF SYMBOLS**

| | |
|---|---|
| $a_i$ | empirical parameter of Eq. (1) |
| $b_i$ | empirical parameter of Eq. (1) |
| $c_i$ | empirical parameter of Eq. (1) |
| $d$ | empirical parameter of Eq. (1) |
| DABCO | 1,4-diazabicyclo[2.2.2]octane |
| DBU | 1,8-diazabicyclo[5.4.0]undec-7-ene |
| DEA | 2,2'-aminodiethanol |
| IL | ionic liquids |
| MEA | 2-aminoethan-1-ol, monoethanolamine |
| TEA | triethylamine |
| TMG | 1,1,3,3-tetramethylguanidine |
| $x_i$ | mass fraction of component $i$ |
| [bmim][OAc] | 1-butyl-3-methylimidazolium acetate |
| [emim][OcSO$_4$] | 1-ethyl-3-methylimidazolium octylsulphate |

**1. Introduction**

Separation of $CO_2$ from industrial gases is a topic engendering significant scientific interest (Theo et al., 2016). It is due to a current policy of mitigation of anthropogenic impact on climate by reducing greenhouse gases emission. It was implemented by The United

56 Nations Framework Convention on Climate Change in 1997 which was an international treaty

57 widely known as Kyoto Protocol. The ultimate objective of this agreement was to reduce the

58 emission of greenhouse gases of which $CO_2$ was the main target. A current stage of

59 development of the civilization is largely dependent on fossil fuels, hence a viable concept of

60 achieving Kyoto targets is separation of $CO_2$ from flue gases and its underground or deep-

61 ocean storage (Azar et al., 2006; Kihm et al., 2019). The demand for effective $CO_2$ absorbents

62 also exists due to its unwanted but common presence in natural gas. It typically causes

63 corrosion, clogging and decreases the heating value (Liu et al., 2016).

64 Currently available, technologically mature methods suitable for $CO_2$ capture are

65 absorption processes which utilize liquid absorbents. They were initially developed for natural

66 gas sweetening and were not intended for a large scale operations required by $CO_2$

67 sequestration (Yuan et al., 2019). The main drawback being high cost of operation which, if

68 implemented in a typical coal-power plant, would reduce its energy output by 30% (Harkin et

69 al., 2012). Such high economical cost stimulated intensive research for modern cost-effective

70 methods of possible industrial scale applications (Sheridan et al., 2018). For example, a

71 typical aqueous alkanolamine process being the best available technology requires large

72 amount of energy during desorption stage, mainly because large enthalpy of reaction between

73 alkanolamines and $CO_2$, enthalpy of vaporization and heat capacity of water (Ma et al., 2018;

74 Shiflett et al., 2010). Traditional absorbents have also disadvantages such as high volatility

75 leading to solvent loss, high rate of corrosion of equipment, and high rate of degradation in

76 the presence of oxygen (Cuccia et al., 2019).

77 In recent years ILs have gained considerable attention as alternative absorbents. The

78 topic was extensively reviewed by various authors (Aghaie et al., 2018; Zeng et al., 2017).

79 Pure ILs offer high physical $CO_2$ solubility under pressure and potential for $CO_2$

80 chemisorption after functionalization with reactive groups such as amines (Luo and Wang,

81 2016). Other advantages of ILs are modifiable properties, low volatility, inflammability,

82 stability, and low heat capacity leading to lower absorbent regeneration costs (Ma et al.,

83 2018).

84 On the other hand ILs have high viscosity, approximately 1-3 orders of magnitude

85 greater than that of water (Liu et al., 2016). In the case of amino-functionalized or amino acid-

86 derived ILs the viscosity after absorption of $CO_2$ often increases by several orders of

87  magnitude (Chen et al., 2018; Zhang et al., 2017). Such properties may lead to low rates of

88  absorption (Zareie-kordshouli et al., 2016) and poor economic performance of absorption

89  processes based on pure IL (Mota-Martinez et al., 2018). The environmental impact of IL

90  production is also substantially higher comparing with MEA (Cuéllar-Franca et al., 2016).

91  Nevertheless, numerous successful results especially for high $CO_2$ content in feed gas were

92  reported by various authors (Nguyen and Zondervan, 2018; Zhai and Rubin, 2018). Overall

93  energy savings may reach 31% using IL-based solvents compared with 30% aqueous MEA

94  (Ma et al., 2017; Zareiekordshouli et al., 2018).

95  In order to mitigate above mentioned problems and utilize numerous benefits of

96  application of ILs in the industrial processes several approaches have been proposed. They

97  either relied on synthesis of low viscosity IL or blending ILs with low-viscosity solvents such

98  as polyethylene glycols (Zhang et al., 2017) or alcohols (Huang et al., 2018; Usman et al.,

99  2016). Addition of amines (Yu et al., 2016) is another option that allows to achieve high $CO_2$

100 absorption capacity (Zacchello et al., 2017). Application of ternary mixtures water-ionic

101 liquid-amine (Damanafshan et al., 2018) was also investigated (Huang et al., 2017; McCrellis

102 et al., 2016; Yang et al., 2017). In this case lowering of absorption capacities of ILs by water

103 is possible due to deactivation of ions participating in $CO_2$ capture process (Avelar Bonilla et

104 al., 2019; Huang et al., 2019).

105 The main advantages of 3-component systems are their low viscosity due to the

106 presence of water or other solvents, high capacity of absorption determined by amine content,

107 reduced cost comparing with pure ILs, corrosion inhibition (Rafat et al., 2016), higher

108 reaction rate between $CO_2$ and an amine (Fu et al., 2017; Haider et al., 2016; Orhan and

109 Alper, 2017), and potential of lower regeneration cost due to reduced heat capacity

110 (Afsharpour and Haghtalab, 2017) and lower solvent loss (Wang et al., 2018).

111 The aim of this work was to establish a general relationship between the composition

112 of water-ionic liquid-amine ternary mixtures and their $CO_2$ absorption capacity and to identify

113 the most promising composition of aqueous hybrid solvents in terms of the balance between

114 properties such as capacity, viscosity, and regeneration potential.

115

116 **2. Experimental methods**

The ionic liquids used were commercial products: 1-butyl-3-methylimidazolium acetate ([bmim][OAc]) (Fluka, Steinheim, Germany) and 1-ethyl-3-methylimidazolium octylsulphate ([emim][OcSO$_4$]) (Merck, Darmstadt, Germany). The amines 1,1,3,3-tetramethylguanidine (TMG), 2,2'-aminodiethanol (DEA), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triethylamine (TEA), 1-methylimidazole and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from (Acros Organics, Geel, Belgium).

$CO_2$ absorption was performed in a gasometric apparatus described previously (Baj et al., 2013). It consists of a gas burette of 50 mL volume connected with a vessel filled with ethylene glycol. Before each measurement the apparatus was evacuated with vacuum pump and the burette was flushed with $CO_2$. Samples of 1 mL of absorbents were magnetically stirred. All runs of experiments were prepared according to the special cubic design. In all cases a varied number of additional points were added to the standard plan (Gozálvez and García-Díaz, 2006) depending on the complexity of the system and the minimal number of regression coefficients that adequately predict the absorption capacity. All experimental points are indicted in Fig. 1. The absorption was measured once for each composition. Because DABCO is not fully soluble in water or in ILs it was impossible to measure absorption in all possible composition ranges. The results were presented in mmol of $CO_2$ per 1 g of an absorbent.

Statistical evaluations of the results were performed using Experimental Design module of STATISTICA 13.1 software. The experimental behavior of various water-IL-amine mixtures was fitted to general Scheffe polynomial given by Eq. (1) (Maherani et al., 2012). Statistically insignificant coefficients were excluded.

$$Q = \sum_{i=1}^{3} a_i x_i + \sum_{i=1,j=2,i\neq j}^{i=2,j=3} b_i x_i x_j + \sum_{i=1,j=2,i\neq j}^{i=2,j=3} c_i x_i x_j (x_i - x_j) + d x_1 x_2 x_3$$

**(1)**

Regeneration of IL after $CO_2$ absorption was performed by heating of post-absorption sample with a magnetic stirrer in an oil bath at 120 or 60°C under reflux at atmospheric pressure for 60 min. The appropriate amount of water was added afterwards to maintain constant composition between cycles of absorption-desorption

145        Viscosity of absorption systems was measured at 20°C using RST Cone Plate

146    Rheometer (Brookfield) equipped with the RCT-75-1 cone spindle. The shear rate ramp 100 –

147    3000 – 100 s$^{-1}$, with the step 100 s$^{-1}$ and measuring time of 15 s for each point was applied. In

148    the case of [bmim][OAc]and DBU-[emim][OcSO$_4$]mixtures, the RCT-25-2 cone spindle with

149    smaller diameter was used.

150        The evaluation of degradation of selected hybrid solvents was performed by heating of

151    samples (0.5 g) containing water amine and [emim][OcSO$_4$] (1:1:1 mass ratio) in sealed glass

152    vials for 100 h at 80°C. One set of samples was saturated with $CO_2$ before sealing. The

153    quantitative analysis was performed by $^1$H and $^{13}$C NMR while the structure of the products

154    was confirmed by HR-MS. Besides substances identified earlier by other authors (Hyde et al.,

155    2019; LaFrate et al., 2012) 1,4-diazabicyclo[2.2.2]octane, 4-aza-1-azoniabicyclo[2.2.2]octane

156    as the alkylation product of DABCO by [emim][OcSO$_4$], ($C_{14}H_{29}N_2^+$ of m/z = 225.2333

157    (observed) vs 225.2331 (predicted)) was detected.

158    **3.   Results and discussion**

159    *3.1. Mechanistic consideration*

160        The utilization of ternary mixtures introduces another layer of complexity and also a

161    virtually unlimited number of possible combinations of ILs and amines, hence the selection

162    and optimization of composition is a daunting problem. However, it is possible to greatly

163    simplify the task considering the number of possible mechanisms involved in $CO_2$ absorption

164    (Scheme1 and Scheme 2).

165        Mechanism shown in Scheme 1 is valid only for imidazolium ILs bearing acetate or

166    other carboxylate anions (Hollóczki et al., 2013). It involves the formation of imidazolium

167    C(2)-$CO_2$ bond. The newly formed carboxylic group is stabilized by a second imidazolium

168    ring. The proton displaced from imidazolium ring is coordinated solely by one or two acetate

169    anions. The mechanism correspond to empirical data which shows that pure [bmim][OAc]

170    absorbs 1 mol of $CO_2$ per 2 mol of IL and that the addition of water reduces the volume of

171    $CO_2$ absorbed (Zhang et al., 2013) due to hydrolysis (Baj et al., 2015).

172

173    **Scheme 1.** Mechanism of $CO_2$ absorption in 1,3-dialkylimidazoilium acetate (Zhang et al.,

174    2013)

175
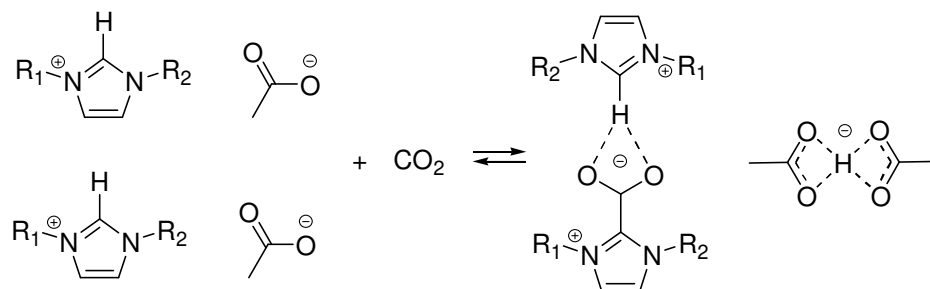


176    Similar process is also possible in other ILs containing highly basic anions such as

177    DBU which can coordinate proton displaced from imidazolium ring (Gao et al., 2019; Wang

178    et al., 2010; Zhu et al., 2017).

179    Absorption of $CO_2$ in amines is possible through two different mechanisms. First

180    one, which is valid for primary and secondary amines, involves the formation of a carbamic

181    acid salt according to Scheme 2a. Possible molar ratio of absorbed $CO_2$ to amine is equal to

182    0.5. Similarly, amines such as TMG can maximally absorb 1 mol of $CO_2$ per 1 mol of an

183    amine (Scheme 2b).

184    **Scheme 2.** Reactions of $CO_2$ with amines



185    (c)    $R_1R_2R_3N + CO_2 + H_2O \rightleftharpoons R_1R_2R_3NH^{\oplus} + HCO_3^{\ominus}$
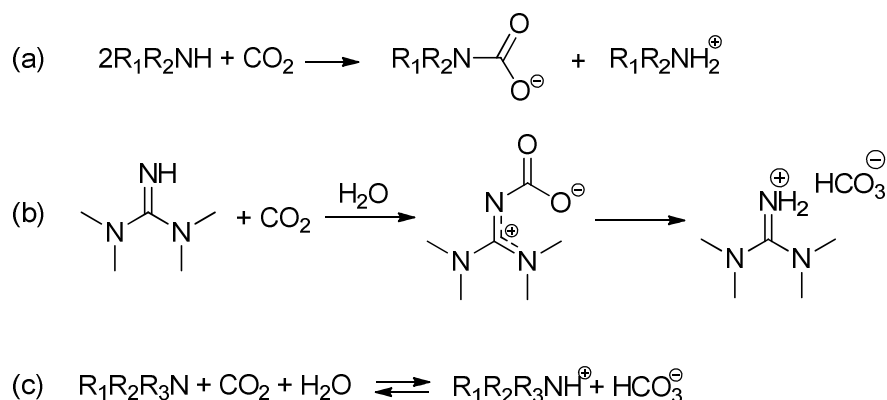
186    In contrast, tertiary amines and amines such as DBU react with $CO_2$ in the presence of

187    water to form bicarbonate (Scheme 2c) where absorption capacity depends on the basicity of

188    the amine. In the case of TMG the mechanism involves the formation of carbamate in the

189    presence of water with subsequent formation of bicarbonate (Cuéllar-Franca and Azapagic,

190    2015; Gurau et al., 2011; Pereira et al., 2008).

191     Regardless of chemisorption mechanism all solvents possess small capacity of

192 physical absorption. At atmospheric pressure ILs are capable of absorbing approximately 0.1

193 mol of $CO_2$ per $dm^3$ of IL (Ramdin et al., 2012). This value does not considerably exceed

194 results for water or other solvents and is negligible comparing with chemisorption of

195 functionalized ILs or amines.

196

197 *3.2. Experimental solubility of $CO_2$ in aqueous IL-amines hybrid solvents*

198     In order to investigate how various ternary mixtures behave as $CO_2$ absorbents we

199 decided to focus on each combination of selected amines and ILs displaying different

200 chemisorption properties. Entire possible domain of concentrations was covered. Two ILs

201 from imidazolium-based family were used. First one, [bmim][OAc], is able to react directly

202 with $CO_2$. The second one, [emim][OcSO4], is inert towards $CO_2$ but presumably may also

203 follow the mechanism given in Scheme 1 in the presence of strongly basic amines that could

204 abstract the proton from imidazolium ring. Primary and tertiary amines of a wide range of

205 basicity were selected. Each of them follows one of possible mechanisms of $CO_2$ absorption

206 (Scheme 2): DBU (pKa = 13.5), TMG (13.0) (Kaupmees et al., 2014), TEA (10.8) (Riddick et

207 al., 1986), DABCO (8.7) (Benoit et al., 1987), and DEA (8.88) (Khalili et al., 2009). In total

208 ten distinct ternary mixtures were investigated. Absorption properties of MEA-based mixtures

209 were a subject of our earlier publication (Baj et al., 2013).

210     Experimental points for each mixture were distributed according to simplex-centroid

211 design (Maherani et al., 2012) with various numbers of additional experiments. Eq. (1) was

212 fitted to the experimental data collected for all investigated systems. In each case an empirical

213 model that describes the measured property Q (in our case mmol of $CO_2$ $g^{-1}$) as a function of

214 mass fractions of components $x_i$ were calculated using standard regression methods. Eq. (1)

215 was simplified by elimination of statistically insignificant coefficients ($p > 0.05$). No more

216 than 8 coefficients $a_i$, $b_i$, $c_i$, $d$ were required. Good agreement between experimental points

217 and predicted values was observed (linear relationship, average slope = 0.98 and $R^2$= 0.976).

218 The data were collected in Table 1 and Table 2 and in Fig. 1.

219

**Fig. 1.** CO$_2$ absorption capacity of ternary mixtures of water-IL-amine at 25°C. A-E [bmim][OAc], F-J [emim][OcSO$_4$]. Composition given in mass fractions.
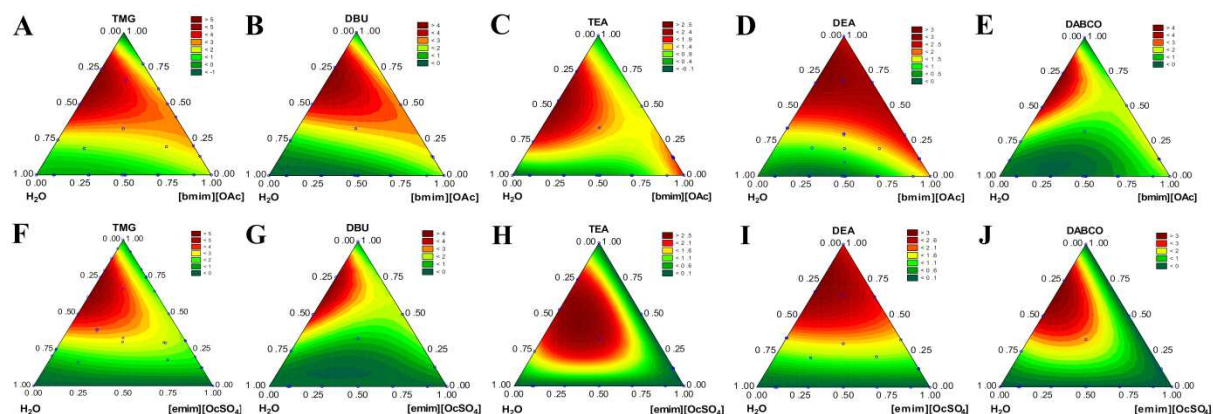


**Table 1.** Calculated coefficients of Eq. (1) for [emim][OcSO$_4$] systems (25°C, p = 1 bar).

| Coefficients | TMG | DBU | DABCO | TEA | DEA |
|---|---|---|---|---|---|
| $a_1$ (H$_2$O) | 0.07±0.22 | 0.11±0.14 | 0.09±0.14 | 0.06±0.06 | 0.08±0,09 |
| $a_2$ (IL) | -0.03±0.21 | 0.09±0.11 | 0.1±0.1 | 0.098±0.4 | 0.08±0,07 |
| $a_3$ (amine) | 0.69±0.22 | 0.62±0.23 | 0.13±0.25 | 0.06±0.09 | 2.31±0,11 |
| $b_{12}$ | - | - | - | - | - |
| $b_{13}$ | 17.79±0.9 | 14.2±0.9 | 15.2±1.0 | 10.2±0.4 | 5.5±0.5 |
| $b_{23}$ | 7.36±0.9 | 6.7±0.9 | - | - | 3.7±0.5 |
| $c_{12}$ | - | - | - | - | - |
| $c_{13}$ | -18.3±1.5 | -17.2±1.9 | -14.0±2.3 | -3.7±0.9 | -4.6±1.2 |
| $c_{23}$ | 5.0±1.5 | - | - | - | - |
| d | - | -44±7 | 22±8 | 37.8±3.2 | - |

**Table 2.** Calculated coefficients of Eq. (1) for [bmim][OAc] systems (25°C, p = 1 bar).

| Coefficients | TMG | DBU | DABCO | TEA | DEA |
|---|---|---|---|---|---|
| $a_1$ (H$_2$O) | 0.16±0.15 | 0.26±0.20 | 0.24±0.31 | -0.16±0.15 | 0.36±0.17 |
| $a_2$ (IL) | 1.53±0.14 | 1.75±0.15 | 1.72±0.18 | 1.88±0.08 | 1.75±0.09 |
| $a_3$ (amine) | -1.1±0.5 | 0.71±0.28 | 0.12±0.34 | 0.23±0.17 | 2.38±0.13 |
| $b_{12}$ | -2.7±0.6 | -3.5±0.8 | -3.4±1.1 | -2.7±0.5 | -3.7±0.5 |

9

| | | | | | |
|---|---|---|---|---|---|
| $b_{13}$ | 21.5±1.3 | 13.4±1.1 | 14.6±1.5 | 10.6±0.8 | 4.5±0.6 |
| $b_{23}$ | 10.2±1.3 | 6.5±1.2 | 4.3±1.5 | - | 2.5±0.6 |
| $c_{12}$ | - | - | - | 3.1±1.1 | - |
| $c_{13}$ | -21.4±2.0 | -17.4±2.4 | -14.6±2.5 | - | -4.7±0.6 |
| $c_{23}$ | - | - | - | - | - |
| d | -16±6 | - | -36.0±2.7 | - | - |

227

228    The investigated systems could be arranged into the categories depending on the
229    properties of the amine and IL. It was in the agreement with the expected number of
230    combinations of possible $CO_2$ absorption mechanisms of ILs and amines.

231    In the case of amines that reacts according to Scheme 2a, 2b (MEA, DEA) the
232    maximum absorption was possible in 100% amine solution and decreased with the dilution
233    with either amine or water. In the case of TMG the water presence was also crucial for $CO_2$
234    absorption. In pure TMG no absorption of $CO_2$ was observed.

235    In the case of amines which do not form carbamates (TEA, DBU, DABCO) but
236    follow Scheme 2c mechanism the maximum $CO_2$ absorption was observed in the binary
237    mixture containing only amine and water. The composition of the optimal mixture (in terms
238    of maximal capacity) in those cases could be determined by the position of the equilibrium in
239    the $CO_2$ saturated solution of aqueous amine (Scheme 2c). In the case of highly basic amines
240    the optimal molar ratio of amine:water was close to 1 and gradually increased with the
241    decrease of amine basicity (Fig. 1, amine-water side).

242    The effect of ILs structure and concentration on $CO_2$ absorption was minor but two
243    patterns could be identified. In the case of [emim][OcSO4], a gradual decrease of the amount
244    of $CO_2$ absorbed in a binary aqueous amine solution or in pure amine with the addition of IL
245    was observed. Due to the relatively large capacity of pure [bmim][OAc] the dilution effect
246    was smaller. Also, mixtures close to IL vertex or binary amine-[bmim][OAc] mixtures had
247    substantial absorption capacities as well.

248    Another identified feature of [bmim][OAc] mixtures was strong negative impact of
249    water on the absorption capacity of binary IL-water mixtures. The reason for this is an unique
250    absorption mechanism valid for imidazolium ILs with basic anion (Shi et al., 2012). However,

251 the $CO_2$ absorption in [emim][OcSO$_4$] was not affected by water presence and in most cases

252 [emim][OcSO$_4$] and water can be replaced with each other without the effect on the

253 absorption capacity. In such cases it was determined by the amine content in a ternary system.

254    Clear synergistic effect was apparent (Fig. 1B, 1G) when a highly basic amine such

255 as DBU was used with both investigated ILs. The reason is the possibility of DBU may act as

256 a proton acceptor and promote the carboxylation of imidazolium ring. The mechanism of

257 chemisorption in DBU systems was confirmed by means of $^{13}$C NMR studies (Fig. 2 A, B,

258 Table 3). A formation of a signal at 120.5 ppm which corresponds to the newly formed

259 carboxylic group attached to C2 carbon of imidazolium ring was identical to the observed

260 signal in [bmim][OAc] systems. In the presence of water the signal gradually decreased and in

261 DBU-[emim][OcSO$_4$]-H$_2$O mixture $CO_2$ reacted only towards bicarbonate.

262    Interestingly, TMG did not showed the ability to promote carboxylation of

263 imidazolium ring by $CO_2$ in [emim][OcSO$_4$] mixtures despite only 0.5-1 units lower basicity

264 than DBU (Kaupmees et al., 2014). This was confirmed by $^{13}$C NMR studies where no 121

265 ppm signal was detected in TMG-[emim][OcSO$_4$] solutions but only 159 ppm derived from

266 carbamate anion (Table 3). This probably results from preferred formation of the carbamate

267 instead of proton abstraction from imidazolium ring by TMG. Such behavior indicates that

268 only highly basic tertiary amines can promote carboxylate formation in imidazolium ILs with

269 neutral anions. In the case of TMG we were not able to detect $HCO_3^-$ anion which confirms

270 the preferred fixation of $CO_2$ to carbamate by this amine.

271    In the case of [emim][OcSO$_4$] which is chemically inert towards $CO_2$ the model

272 derived from Eq. (1) was relatively simple with 3-7 coefficients (Table 1) depending on the

273 nature of the amine. In all cases coefficients $a_1$ and $a_2$ corresponding to absorption of $CO_2$ in

274 pure water or IL were very low and statistically insignificant. Coefficients $a_3$ were high in the

275 case of reactive amine (TMG, DEA) and were equal to the amount of $CO_2$ absorbed by 1 g of

276 an amine. In the case of TMG (MW 115.18) the theoretical value was 8.7 mmol $CO_2 \cdot g^{-1}$, and

277 in the case of DEA (MW 105.14) 4.75 mmol $CO_2 \cdot g^{-1}$ which indicates 90% and 50% yield of

278 absorption in pure amines, respectively. For comparison the coefficients $a_2$ for MEA was 8-

279 8.35 (Baj et al., 2013) indicating nearly quantitative yield. In the case of DEA this is due to

280 the formation of solid products which limited the contact with $CO_2$ and prevented quantitative

281 yields. The effect was negligible for MEA. Dilution DEA with an IL or water prevented the

solidification of reaction mixture and increased the amount of $CO_2$ absorbed (Fig 1D). It is especially visible in solutions of DEA (Fig. 1E). Coefficients $b_{13}$ were significant in all investigated cases. High values were observed only for tertiary amines where it describes the position of optimal composition of a binary mixture. In the case of DEA it was probably determined by solubility of amine or carbamate salt which affected the yield of reaction with $CO_2$. Coefficient $d$ was significant for DABCO, TEA and DBU. High positive values suggest complex interactions between three components. The most likely is the possibility of shifting the reaction equilibrium given in Scheme 2c depending on the relative concentration of water and IL.

The models for [bmim][OAc] presented in Table 2 are more complex. In all cases coefficient $a_1$ was insignificant whereas $a_3$ was high for TMG, DEA. Coefficients $b_{13}$ were high for all amines in both ILs indicating either chemical equilibrium or improvement of yield due to dissolution of solid products. This is especially visible for DEA where absorption in pure amine was difficult but the dilution with water or IL leaded to better solubility of $CO_2$.

In contrast with [emim][OcSO$_4$] $a_2$ value for [bmim][OAc] was high and $b_{13}$ was negative. This reflects the detrimental effect of water on the chemisorption capacity of [bmim][OAc]. The value of $a_2$ for [bmim][OAc] in the range of 1.53-1.88 was roughly 2/3 of the theoretical value. For the IL of MW 198.3 the theoretical value equals $\approx 2.5$ mmol $CO_2$ g$^{-1}$. The lower result was mainly caused by non-quantitative yields of absorption and to a lesser extent due to mismatched fitting of experimental data to Schaffe polynomial for points lying close to the corner of the experimental domain. High positive value of $b_{23}$ in the case of TMG, DBU, DABCO indicates a synergy between [bmim][OAc] and the amines that improve the capacity of the system. In the case of [emim][OcSO$_4$] $b_{23}$ was also high for TMG and DBU.

The ^{13}C NMR investigation (Table 3, Fig. 2) of selected systems confirmed the postulated mechanisms of absorption. Comparing with the literature the relative chemical shifts of carbamate and HCO$_3^-$ signals might differ depending on the solvent and amine (Umecky et al., 2019). For example Liu et al. (Liu et al., 2017) reported 164.1 ppm and 159.1 ppm respectively while Zhou (Zhou et al., 2017)163.82 ppm and 160.72 ppm.

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**Table 3.** Chemical shifts of $CO_2$-derived signals in various absorbents. Spectra registered after dilution 1:5 with DMSO containing 5% of DMSO-$d_6$. Mass ratio of components was given in brackets.

| Sample name | $HCO_3^-$ | Imidazolium carboxylation | Carbamate |
|---|---|---|---|
| NaHCO$_3$ | 162.6 | - | - |
| DBU:H$_2$O (1:1) | 165.5 | - | - |
| DBU:[bmim][OAc] (1:1) | 165.5 | 121.1 | - |
| DBU:[bmim][OAc]:H$_2$O (1:1:1) | 165.5 | 121.5 | - |
| DBU:[emim][OcSO$_4$] (1:1) | 162.3 | 120.5 | - |
| DBU:[emim][OcSO$_4$]:H$_2$O (1:1) | 165.5 | - | - |
| TMG:H$_2$O (1:1) | - | - | 158.7 |
| TMG:[bmim][OAc] (1:1) | - | 121.3 | 159.2 |
| TMG:[bmim][OAc]:H$_2$O (1:1:1) | - | 121.0 | 159.2 |
| TMG:[emim][OcSO$_4$] (1:1) | - | - | 158.7 |
| TMG:[emim][OcSO$_4$]:H$_2$O (1:1) | - | - | 159.4 |
| [bmim][OAc] | - | 121.5 | - |
| [emim][OcSO$_4$] | - | - | - |
| TEA:H$_2$O (1:1) | 161.8 | - | - |
| DABCO:[bmim][OAc]:H$_2$O (1:1:1) | 165.5 | - | - |
| MEA:H$_2$O (1:1) | 165.5 | - | 162.2 |
| DEA:H$_2$O (2:1) | 165.5 | - | 162.2 |

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**Fig. 2.** $^{13}C$ NMR spectra of selected pre- and post-absorption mixtures.



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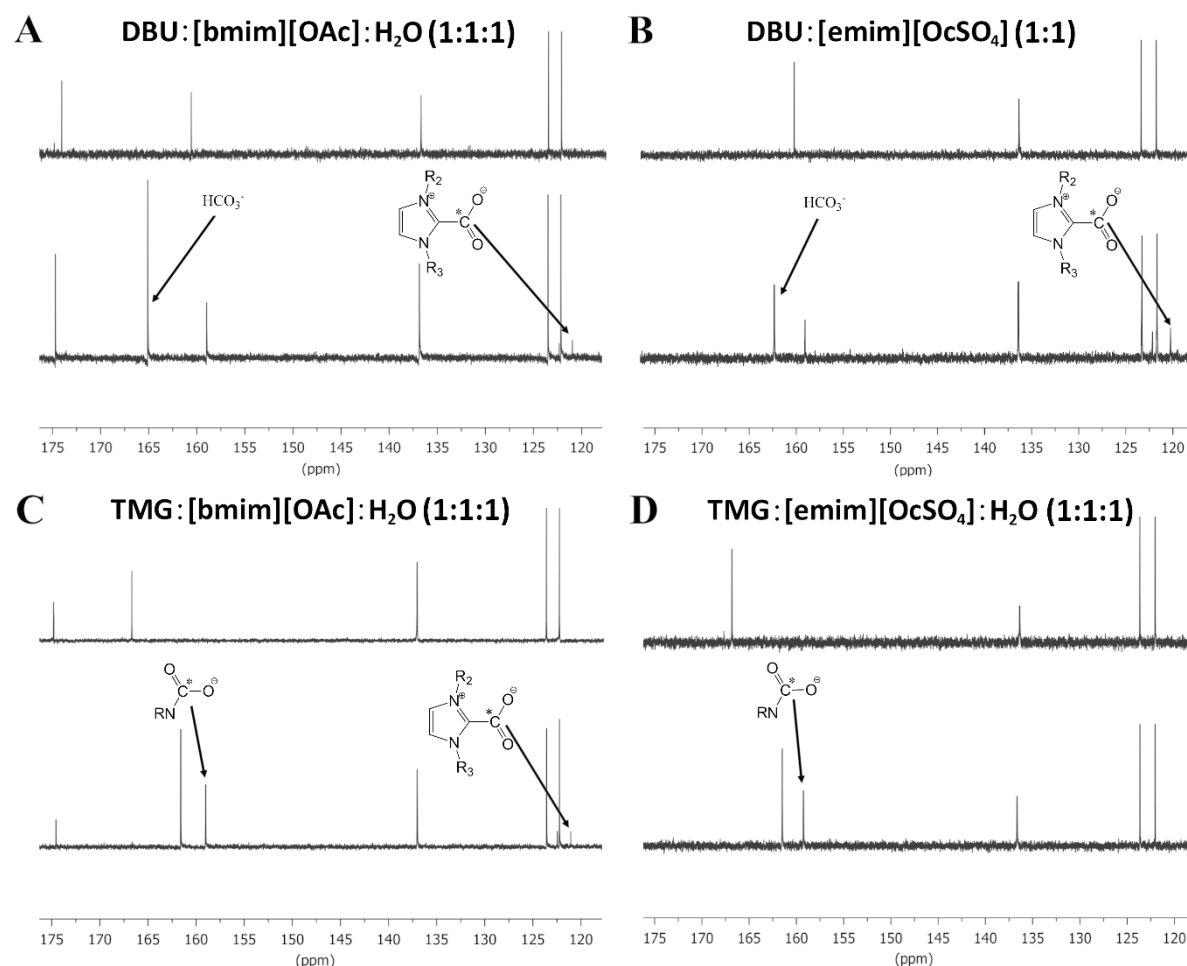
The selection of liquid absorbent of most suitable properties can be guided based on the observed solubility of $CO_2$ and the pattern of absorption. The following conclusions could be drawn: a) the optimal water:amine proportion in terms of $CO_2$ solubility is between 2:1-1:2 depending on the amine; b) in the case of DEA and similar amines capable of forming of carbamates water can be replaced with an IL; c) for tertiary amines reacting towards bicarbonate the aqueous amine solution of desired amine:water ratio can be diluted with IL which leads to slower decrease of overall $CO_2$ solubility than dilution with water only; d) the

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use of [bmim][OAc] or DBU with imidazolium IL leads to considerable absorption by means of carboxylation of imidazolium ring and to synergy between the amine and an IL. Because DBU has low volatility it is an attractive component of ternary absorbents containing imidazolium ILs.

*3.3. Viscosity of hybrid solvents*

A practical application of discussed hybrid solvents would be possible if they had a favorable viscosity prior and after absorption. Earlier publications reported PEG-ILs systems as $CO_2$-absorbents exhibited viscosity in the range of 30 to 78 mPa·s – 10 times lower than for pure IL (Zhang et al., 2017). The impact of addition of water was clearly visible by examining the kinetics of absorption (Fig. 3). In the case of [emim][OcSO$_4$] the presence of 33% water resulted in nearly 300% of increased absorption rate comparing with 1:1 amine:IL solution. In the case of [bmim][OAc] the effect was smaller and no more than 50% of increased rate was achieved by the addition of water.

A series of solvents were investigated using Cone Plate Rheometer to obtain exact values of viscosity prior and after $CO_2$ absorption. The results for selected mixtures of high absorption capacity are presented in Table 4.
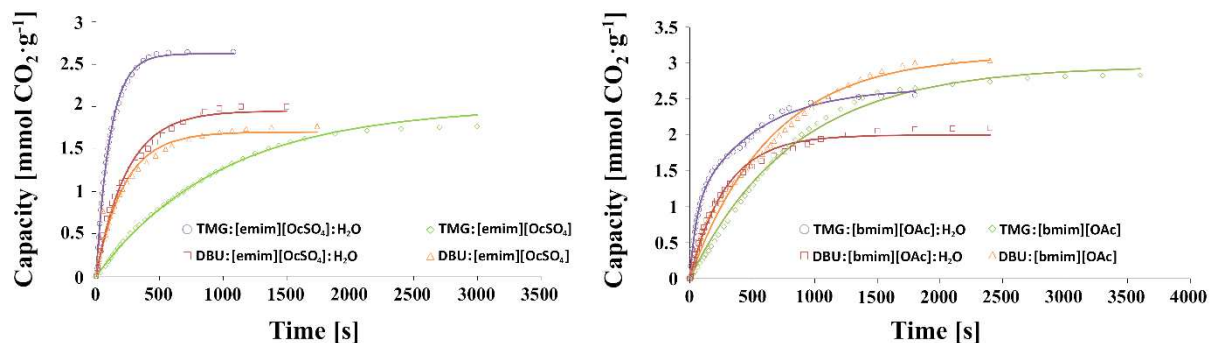


**Fig. 3.** Comparison of the course of $CO_2$ absorption in hybrid solvents. T = 25 °C, 1000 rpm, p = 1 bar. 1 g of reaction mixture of 1:1 or 1:1:1 weight proportions.

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**Table 4.** Viscosities of selected hybrid. Shear ramp 100-3000-100 $s^{-1}$, T = 20°C. *Ranges indicates non-Newtonian fluids.

| Composition of the absorbent [wt. %] | | | Viscosity before absorption [mPa·s] | Viscosity after absorption [mPa·s] | $CO_2$ solubility | |
|---|---|---|---|---|---|---|
| IL | Amine | Water | | | [mmol·g$^{-1}$] | molar ratio $CO_2$:amine |
| - | MEA (30%) | 70% | 2.91±0.16 | 4.36±0.19 | 3.26±0.23 | 0.73±0.20 |
| - | MEA (100%) | - | 24.4±0.4 | 6700±130 | 9.0±0.7 | 2.18±0.30 |
| - | TEA (75%) | 25% | 67.0±1.2 | 111.2±3.2 | 2.12±0.17 | 0.29±0.09 |
| - | DBU (50%) | 50% | 13.8±0.5 | 28.7±1.2 | 3.27±0.21 | 1.04±0.11 |
| [bmim][OAc] (33%) | DBU (33%) | 33% | 25.9±0.5 | 61.0±0.9 | 2.32±0.18 | 1.06±0.14 |
| [emim][OcSO$_4$] (33%) | DBU (33%) | 33% | 32.2±0.5 | 52.4±0.5 | 0.96±0.12 | 0.44±0.04 |
| [emim][OcSO$_4$] (50%) | DBU (50%) | - | 86.2±8.1 | 700-2480* | 1.98±0.17 | 0.60±0.09 |
| [emim][OcSO$_4$] (33%) | TMG (33%) | 33% | 12.11±0.32 | 140-270* | 2.93±0.20 | 0.17±0.02 |

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Comparing with traditional 30% MEA solution the viscosities of studied absorbents were at least one order of magnitude higher. A reasonable values were possible with the addition of 33% water which limited the increase of viscosity of post-absorption mixtures above 270 mPa·s$^{-1}$. The results indicate that mixtures containing [bmim][OAc] are more attractive as the viscosity is similar to [emim][OcSO$_4$] but the absorption capacities are higher with the same composition.

Some post-absorption mixtures showed an interesting non-Newtonian feature (Fig. 4) where viscosity was highly affected by the shear rate. In the case of aqueous TMG and DBU in [emim][OcSO$_4$] the viscosity decreased with the increasing shear rate. The drop was as

high as 50-60%. This could be interesting from technical point of view as flow resistance might be lowered by increasing flow rate.
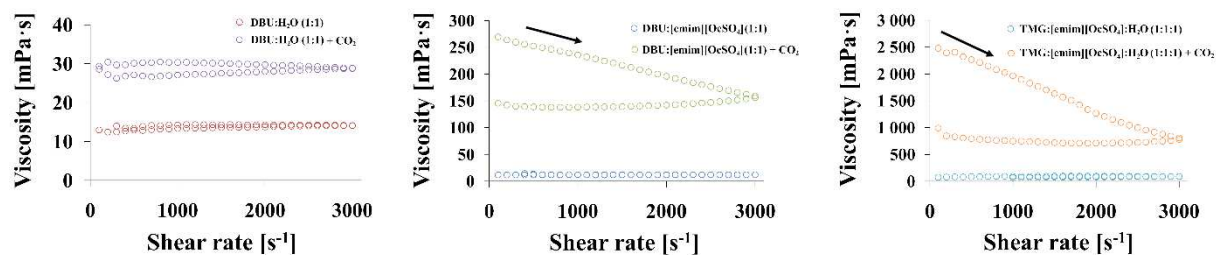


**Fig. 4.** Impact of shear rate on the viscosity of hybrid solvents. Arrow indicate the ramp direction.
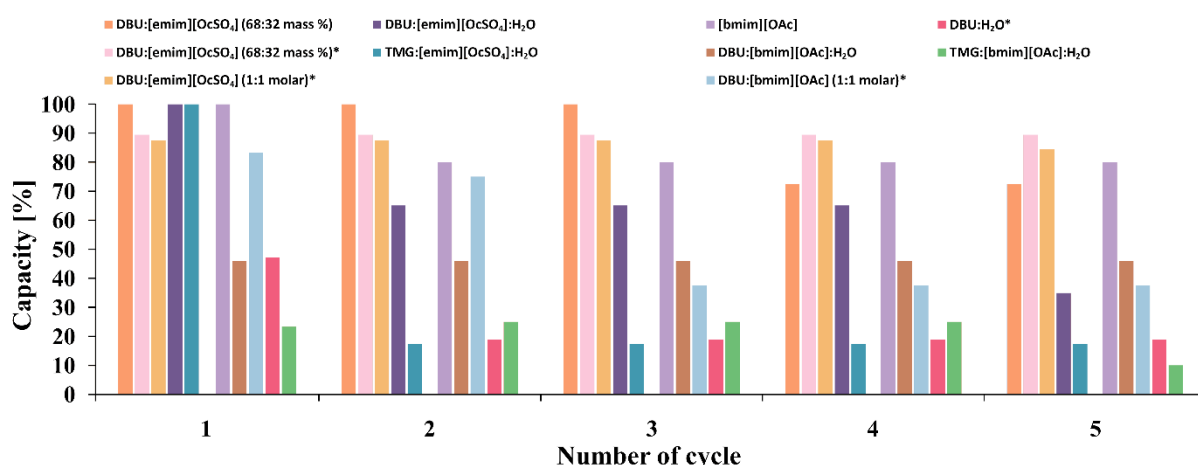
*3.4. Regeneration of selected hybrid solvents*

A various means of regeneration were proposed in the literature for liquid $CO_2$ absorbents. In most cases, including industrial MEA-based process heating to 100-120°C allows full regeneration (Aaron and Tsouris, 2005). Some authors applied a combination of heating and vacuum desorption (Nii et al., 1995) or purging with inert gas (Z. Li et al., 2019). Because the cost of regeneration increases with the heat capacity of absorbent and with the temperature of regeneration the possibility of utilization of IL-based absorbents with smaller water content is economically beneficial (Chowdhury et al., 2009; Kim and Svendsen, 2011). We decided to apply thermal desorption and varied temperature to identify the most promising absorbents. Up to 5 cycles of thermal desorption was performed (Fig. 5).

The most difficult regeneration was observed for TMG-based absorbents where 2nd and further cycles showed only 20% of initial capacity. At 120°C the regeneration of [bmim][OAc] either in the mixture with DBU or water was difficult and no more than 80% of capacity was retained by pure [bmim][OAc] and 40-50% by mixture with water or DBU. On the other hand mixtures of [emim][OcSO4] with DBU underwent facile regeneration at only 60°C and 90% of initial capacity was retained. At increased temperature during 4th and 5th cycles only a 10% loss of capacity was observed.

The rationale for observed efficiencies is the difference in the reaction type of $CO_2$ occurring during absorption. If $HCO_3^-$ is formed the regeneration is more difficult comparing

with carboxylation of imidazolium ring. The latter is the main product for [bmim][OAc] or [emim][OcSO$_4$]-DBU mixtures. The presence of water in DBU-containing mixtures allowed the formation of HCO$_3^-$ which reduced the possibility of full regeneration at 60°C which was possible for binary [emim][OcSO$_4$]-DBU but not possible for binary [DBU]-H$_2$O. The observations are in line with experimental enthalpies of CO$_2$ fixation in various solvents reported in the literature. In the case of amines the average values were 80, 70 and 60 kJ mol$^{-1}$ for primary, secondary and tertiary amines respectively (Kim and Svendsen, 2011), 55-90 kJ mol$^{-1}$ for amino acids-derived functionalized ILs (Luo and Wang, 2016) while only 40-54 kJ mol$^{-1}$ for absorption involving carboxylation of imidazolium ring (Shaahmadi et al., 2019; Song et al., 2019) or 10-20 kJ mol$^{-1}$ for physical absorption in ILs (Carvalho et al., 2010; Y. Li et al., 2019). Such data indicate that imidazolium carboxylation is a very attractive mechanism because of low heat of absorption and large theoretical 1:2 or 1:1 molar ratio of CO$_2$ fixated per imidazolium ring.



**Fig 5.** CO$_2$ absorption capacity after cyclic regeneration in different/hybrid solvents T$_{absorption}$=25°C, T$_{regeneration}$ = 120°C (*60°C), regeneration time = 60 min.

*3.6. Degradation of selected hybrid solvents*

The stability of solvents for CO$_2$ capture is an important feature considering feasibly of industrial applications. The issue has been extensively studied by various authors in the case of thermal degradation of ILs and very good stability up to at least 200°C was demonstrated in most cases (Zeng et al., 2017). Another important issue is slow oxidation of amines leading

420 to numerous products. So far there is little data available besides classic aqueous amine
421 solvents (Chahen et al., 2016; Saeed et al., 2018). Such studies require long (1000 h)
422 oxidation under realist conditions. In the case of an aqueous piperazines blend 39 oxidation
423 products was identified responsible for irreversible loss of 0.06-0.2% of amines per day of
424 operation in absorption/stripping columns (Cuccia et al., 2018). Similar studies with
425 MEA/MDEA identified 22 products and daily loss of 0.03% of amines (Widger et al., 2019).

426 Another route of much faster degradation that could be important for presented hybrid
427 solvents was amine alkylation by octylsulfate ion (LaFrate et al., 2012) and hydrolysis of
428 amidine and guanidine bases leading to aminoureas and aminolactams (Hyde et al., 2019). In
429 order to quantitatively asses the loss of amines due to those processes a 100 h long heating
430 (80°C) in a sealed glass tubes without the presence of oxygen was performed. The results
431 were summarized in Table 5 and Fig. 6.

432

433 **Table 5.** Amine loss by alkylation or hydrolysis in the amine:[emim][OcSO$_4$]:H$_2$O (1:1:1
434 mass) hybrid solvents. T$_{aging}$=80°C, aging time= 100 h. Letter in brackets indicate structures of
435 identified products showed in Fig. 5.

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| Amine loss [%] and the product of degradation | | |
|---|---|---|
| amine | without CO$_2$ | with CO$_2$ |
| MEA | 2 (A) | 0.5 (A) |
| DEA | 3.5 (B) | 0.7 (B) |
| TMG | 7 (C); 93 (D) | 20 (C); 9 (D) |
| DBU | 4 (E); 2 (F) | 4 (E); 2 (F) |
| DABCO | 4 (G) | 4 (G) |

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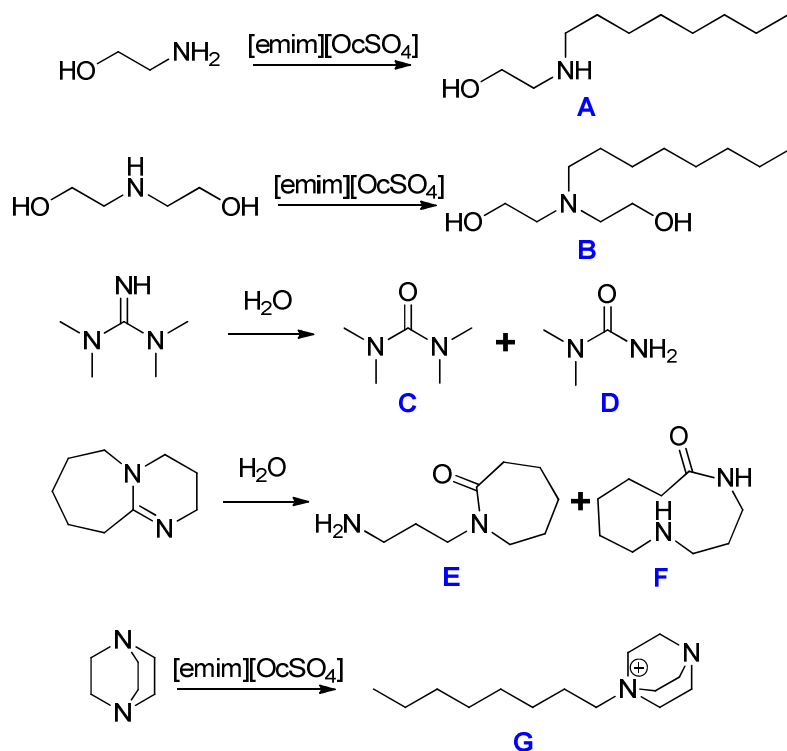
**Fig. 6** Alkylation of MEA, DEA, DABCO by [emim][OcSO$_4$] and hydrolysis of TMG and DBU observed during the 100 h aging process.

In the case of MEA, DEA and DABCO the alkylation by octylsulfate ion leads to 0.5-3.5% loss of amine. It occurs about much faster in the absence of $CO_2$ in MEA and DEA and no difference was detected for DABCO between rich and lean solvent. The observed differences are most likely the result of formation of carbamates of DEA and MEA upon $CO_2$ absorption which inhibits the alkylation. The impact of pH on the alkylation rate is also a possible contribution factor. Considering the lower rate (0.5%) it corresponds to ≈0.1% daily loss amine which is comparable or higher to the oxidation rate observed by other authors. As the ILs is also consumed its loss is 3-5 times higher. No alkylation products of TMG or DBU was detected.

The apparent rate of hydrolysis of DBU was higher to the alkylation rate of DEA and MEA but was independent on the presence of $CO_2$. Two products were identified which corresponds to a daily amine loss of 1.5%. In the case of TMG the loss was almost quantitative without $CO_2$ and the product of hydrolysis (1,1-dimethylurea) formed a precipitate. Approximately only 0.4% of TMG remained in the solution. The presence of $CO_2$

reduced the rate of hydrolysis and favored the formation of tetramethylurea but the daily loss of amine reached as much as 8% which is consistent with the rate of hydrolysis proportional to the pH of the solution (Hyde et al., 2019).

The data are consistent with the results of regeneration experiments where the capacities of solvents containing TMG quickly upon recycles while DBU-based solvents allowed multiple recycles with minimal loss of capacity. It is likely, that the degradation of amines and [emim][OcSO$_4$] can be mitigated by optimization of temperature of desorption, careful monitoring of desorption progress and avoiding excessive and prolong heating of solvent streams.

## 4. Conclusions

Ternary mixtures of water-IL-amine are interesting absorbents for $CO_2$. Their behavior is dependent on the amine and IL type. Two types of quantitative relationship patterns were identified with respect to amine and two with respect to an IL. The observation could be useful in designing absorption processes and the most promising experimental domains for optimization purposes.

The most promising ternary systems include ionic liquids of chemisorption capacity with a highly basic amine such as DBU. Their low volatility comparing with typically used amines and their ability to offset the effect of water on IL reactivity towards $CO_2$ are the most important benefits which potentially reduce the cost of IL-based absorbent and the energy demand for regeneration. DBU also showed relatively low hydrolytic instability comparing with TMG. Moreover, its decomposition does not consume [emim][OcSO$_4$] which is significant in the case of MEA-, DEA- and DABCO-based hybrids.

Moderate viscosity of systems containing only 33% of water together with high capacities of amine and low volatility of ILs makes them attractive alternatives for traditional binary aqueous amine absorbents.

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