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Ionic compounds derived from crude glycerol: thermal energy storage capability evaluation

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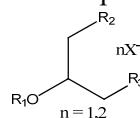
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Abstract

Ionic liquids (diimidazol-1-ium esters) prepared from wastes, crude glycerol and carboxylic acids are investigated as potential phase change materials (PCM). The ionic liquids (IL) with best thermophysical properties were those with also better production yield (higher than 75%).



The chemical composition of those IL was with R₁ being (CH₃)₃CCO, CH₃(CH₂)₁₄CO or C₂H₃CO; R₂ being BIM⁺; R₃ being BIM⁺; and X- being 2 Cl⁻. Phase change of state (solid-liquid) of this IL was 85 °C, 264 °C and 128 °C, which means potential application in different fields such as domestic hot water, solar cooling and industry, respectively. The measured melting enthalpy 328 kJ/kg, 408 kJ/kg, and 660 kJ/kg is much higher in all cases than the usual found in commercial PCM (100 kJ/kg), therefore, these ILs synthesized in this study are proper candidates to be used as PCM because of the huge amounts of energy that they are able to store and their low cost. Moreover, biobPCM are sustainable materials since its obtaining process is based on oil.

Keywords: Ionic Liquids (ILs), Phase Change Materials (PCM), Differential Scanning Calorimetry (DSC), Thermal Energy Storage (TES), synthesis route

32 1. Introduction

33 Renewable chemicals reduce greenhouse gas emissions, along with other pollutant
34 emissions associated with the supply, processing, and use of petroleum and petrochemicals.
35 Consumer demand for renewable goods and the economic competitiveness of biorefining
36 compared to petroleum refining are beginning to pull the market for new biotechnology
37 applications. By 2021, the global market for biobased chemicals and materials alone is expected
38 to increase to \$12.2 billion, accounting for 10.9×10^9 kg of biorefining production [1]. One of its
39 applications is in the preparation of phase change materials (PCM) to be used in thermal energy
40 storage [2-3]. PCM are used in ceiling and wall panels working day and night to stabilize indoor
41 temperatures [4, 5] leading to better indoors thermal comfort; and they have been implementad
42 for cold storage [6], domestic hot water (DHW) [7], solar cooling [8], solar concentrated power
43 plants [9], etc. In 2013, the PCM market was quantified in 480.8 million dollars and is expected
44 to reach 1765.8 million in 2020 with an annual compound growth rate of 20.7% [10]. The
45 market can be segmented by three major product categories: paraffin (45%), salt hydrates (33%)
46 and PCM based on biomass (biobPCM) (22%). There are already several commercial products
47 of the above categories, and all of them have advantages and disadvantages, but their main
48 feature is the heat storage capacity. Those with a latent heat storage capacity (ΔH) higher than
49 100-120 kJ/kg are considered adequate candidates to be used as PCM and this is the typical
50 thermal energy storage capacity of commercial PCM [2-3].

51 BiobPCM is one of the efficient ways of storing thermal energy from abundant bio-based
52 materials and present higher latent heat values than paraffin [11]. Fatty acids and fatty esters are
53 the main components of these materials [12]. Fatty acids and ester can be obtained from various
54 sources such as by-products and wastes from oil-crops, fat and oil industries and meat
55 processing companies. By-products and wastes from oil-crops account for 1×10^9 kg/year
56 worldwide, which means producing 5×10^{11} kg/year oil-crops. Moreover, meat waste in Spain
57 accounts for 2×10^9 kg/year containing roughly 1×10^7 kg/year of animal fats [13]. These wastes
58 typically are more homogenous and constant in composition, when compared to the others and
59 they might be used to prepare biobPCM. The authors of this paper have already shown that
60 crude glycerol and waste fat and vegetable oils can be used to prepare dihalopropyl esters [14-
61 16].

62 Recently, ionic liquids (IL) have also been proposed for thermal storage applications [17].
63 IL are versatile compounds with multiple applications such as solvents [18], in chemical and
64 enzymatic catalysis [19], in carbon dioxide capture and separation, in hydrogen generation, in
65 converting thermal energy into electrical energy, for electrochemical energy storage, and for
66 converting electrical energy into mechanical energy. Moreover, ILs have thermophysical and
67 chemical properties that may be suitable to be used as heat transfer fluid (HTF) in power plants
68 using parabolic trough solar collectors as stated by Van Valkenburg et al. [20]. Moreover,

69 Reddy et al. [21] has studied the thermal stability corrosion effect of ILs when used as HTF.
70 Furthermore, Matic and Scrosati [22], and MacFarlane [17] have recently defined several
71 energy applications of ILs. In addition, depending on the property being investigated, changes
72 in the chemical character of the cation and anion (size, charge distribution, metal complexing,
73 lipophilicity, etc.) and the nature of substituted functional groups can have markedly different
74 effects. This offers various different design points to construct ions with a specific subset of
75 properties [17]. The possibility of performing hydrogen bonds has been proposed as one of the
76 characteristics to consider in the design of IL for thermal storage applications [23]. Recently, we
77 have described the synthesis of the IL 1,1'-(2-hydroxypropane-1,3-diyl)-bis(3-butylimidazol-1-
78 ium) and 1,10-(2-(acryloyloxy)propane-1,3-diyl)-bis(3-butylimidazol-1-ium) salts starting from
79 glycerol derivatives [24].

80 Joining both concepts, preparation of dihalopropyl esters from crude glycerol and wastes as
81 precursors of IL, and the potentiality of IL in thermal energy storage, led to the aim of the
82 present study: assessing the thermal storage capability of these two ionic compounds described
83 above and a new set of ionic compounds prepared also from crude glycerol and various
84 carboxylic acids described in authors their Spanish patent [25]. A preliminary study on the
85 effect of the chemical character of the cation and anion on the thermal storage capability of
86 these new ionic compounds is also presented. This set of compounds and their use as biobPCM
87 are patent pending.

88

89 **2. Materials and methods**

90 **2.1. Materials and reagents**

91 Acrylic, 1-naphtyl carboxylic, palmitic and pivalic acids were purchased from Sigma-
92 Aldrich (Sigma-Aldrich Quimica, S.A., Madrid, Spain). Chlorotrimethylsilane (CTMS) was
93 also from Sigma-Aldrich (Sigma-Aldrich Quimica, S.A., Madrid, Spain). Hexane, methanol,
94 ethanol, acetone, acetonitrile, ethyl ether, isopropanol, and dichloromethane were supplied by J.
95 T. Baker (Quimega, Lleida, Spain). 1,3-Dichloro-2-propanol, N,N-dicyclohexylcarbodiimide
96 (DCC), and potassium hexafluorophosphate (KPF_6) were supplied by Across Organics
97 (Barcelona, Spain). Potassium hydroxide was purchased from Panreac (Barcelona, Spain).

98 Crude glycerol was obtained from a biodiesel industrial supplier that used an alkali-
99 catalyzed alcoholysis procedure (Raluy S.L., Spain). Crude glycerol was neutralized using
100 sulfuric acid, and most of the residual methanol was removed by distillation under vacuum.
101 Finally, the remaining material was centrifuged at 2,600 g and decanted to remove any solids in
102 the suspension. The final product was analyzed using 1H NMR in deuterated dimethylsulfoxide
103 using N,N-dimethylformamide as an internal standard. The final substrate was glycerol rich to
104 c.a. 90%.

105

2.2. Ionic liquids synthesis procedures

2.2.1. General procedure for the syntheses of 2-chloro-1-(chloromethyl)ethyl esters

Carboxylic acid (1 mmol), glycerol (184 mg, 2 mmol) and chlorotrimethylsilane (CTMS) (540 mg, 5 mmol) were added to a reaction vial fitted with a polytetrafluoroethylene-lined cap. The mixture was stirred and heated at 80°C for 48 h. After cooling, an organic solvent was added, and the mixture was washed three times with water. The organic layer was dried over anhydrous MgSO₄ and the solvent was evaporated under vacuum. The residue was purified by crystallization, distillation, or dry flash column chromatography on silica gel. The corresponding compound was identified by ¹H NMR and ¹³C NMR and yield was calculated. This percentage is a common quantitative method to perform quantitative analysis using ¹H NMR where the areas of the peaks of hydrogen atoms observed in the spectrum can be quantitatively compared. Therefore, the purity of a chemical compound can be determined by ¹H NMR using internal standards and following the Eq. 1. The area of a signal corresponding to given hydrogen atoms can be determined and compared with the signal area of hydrogens present in the internal standard. The purity is commonly calculated by the software that controlled the ¹H NMR device.

$$Purity(\%) = \frac{S_{sample}}{S_{st}} \cdot \frac{N_{st}}{N_{sample}} \cdot \frac{m_{st}}{m_{sample}} \cdot \frac{M_{sample}}{M_{st}} \cdot P_{st} \cdot 100 \quad (1)$$

S= Area of the NMR signal used to perform the quantification.

N = Number of atoms (H) responsible of the NMR signal used to perform the quantification.

m = mass used for performing the analysis.

M = molecular weight.

st = parameter corresponding to the internal standard used.

Pst = purity of the internal standard used.

The mentioned compounds were used to prepare N-butylimidazole derivatives, intermediates of the compounds corresponding to samples M1, M5, M7 and M11 in Table 1 as described in 2.2.3.

2.2.2. Procedure for the syntheses of 3-chloro-2-hydroxy-1-propyl 2,2-dimethylpropanoate

A solution of 2-chloro-1-(chloromethyl)ethyl 2,2-dimethylpropanoate (5.08 g, 24 mmol), water (0.7 mL, 38.4 mmol) and sodium carbonate (2.54 g, 24 mmol) in dried 1,4-dioxane (72 mL) was stirred and heated at 115°C for 48 h in a capped reactor. After cooling to room temperature, dichloromethane was added and the mixture was washed three times with water. The organic layer was dried over anhydrous MgSO₄, and the mixture was distilled to yield 2.9 g

140 of the desired compound (62% yield) b.p.: 70°C/ 40 Pa. The compound was identified by ¹H
141 NMR and ¹³C NMR and subsequently used to prepare the corresponding N-butylimidazole
142 derivative, entry M3 in Table 1, following the procedure described in 2.2.3.

143

144 2.2.3. General procedure for the synthesis of M1, M3, M5 and M11 samples.

145 A mixture of the corresponding 2-chloro-1-(chloromethyl)ethyl ester (50 mmol) and N-
146 butylimidazole (12.42 g, 100 mmol) was stirred and heated at 110°C for 48 h in a capped reactor
147 under Ar atmosphere. The mixture was cooled to room temperature and acetonitrile was added
148 until no more product precipitated. The white solid formed was recovered by filtration and
149 washed 3 times with cold acetonitrile. After drying, highly hygroscopic compounds were
150 recovered. The corresponding compound was identified by ¹H NMR and ¹³C NMR. These
151 compounds correspond to samples M1, M3, M5 and M11, and used as well as starting material
152 for the counter ion swap described in 2.2.6 in order to prepare the products corresponding to
153 entries M2, M4, M6, M12 (see Table 1).

154

155 2.2.4. Synthesis of M9 sample.

156 A mixture of 1,3-dichloro-2-propanol (6.45 g, 50 mmol) and N-butylimidazole (12.42 g,
157 100 mmol) was stirred and heated at 110°C for 48 h in a capped reactor under Ar atmosphere.
158 The mixture was cooled to room temperature and acetonitrile was added until no more product
159 precipitated. The white solid formed was recovered by filtration and washed 3 times with cold
160 acetonitrile. After drying 17.36 g of the product (92% yield), a highly hygroscopic compound,
161 were recovered. The compound was identified by ¹H NMR and ¹³C NMR. This compound
162 correspond to sample M9, and this was used also as starting material for the counter ion swap
163 for entry M10 (see Table 1), as described in 2.2.6.

164

165 2.2.5. Synthesis of M13 sample

166 The compound corresponding to sample M13 in Table 1 was synthesized following the
167 Steglich esterification method [26]. In this regard, 80 mL of a dichloromethane solution
168 containing 4 g (55.5 mmol) of acrylic acid, 4.1 g (10.8 mmol) of 3,3'-(2-hydroxypropane-1,3-
169 diyl)bis(3-butyl-3H-imidazol-1-ium) chloride and 35.18 mg (0.288 mmol) of 4-
170 dimethylaminopyridine was added to a 250 mL one-necked round flask equipped with a calcium
171 chloride drying tube. The solution was cooled in an ice bath, and 6.68 g (32.4 mmol) of DCC
172 were added at 0°C for 5 min under stirring. After a further 5 min at 0°C, the ice bath was
173 removed and the reaction mixture was stirred for 24 h at room temperature in a water bath. The
174 reaction mixture was filtered and the precipitate was washed with dry dichloromethane (3x20
175 mL). The organic solutions were combined and evaporated under vacuum giving a final yield of
176 75%. The compound was identified by ¹H NMR and ¹³C NMR. This compound was further

177 used as starting material for the counter ion swap for preparing the compound corresponding to
178 entry M14 (see Table 1) following the procedure described in 2.2.6.

179

180 2.2.6. General procedure for the synthesis of M2, M4, M6, M8, M10, M12 and M14
181 samples

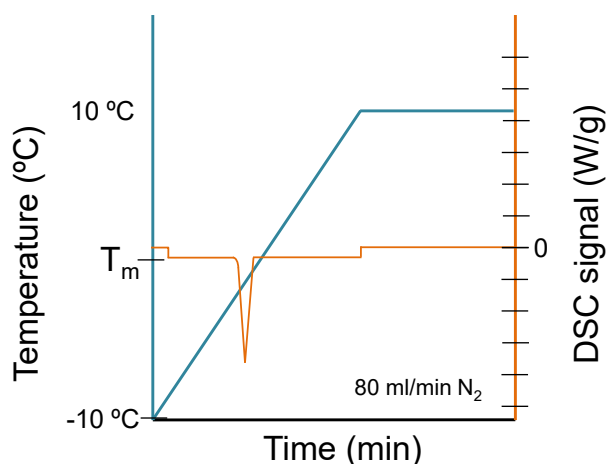
182 The chlorine based ionic liquids obtained in entries M1, M3, M5, M7, M9, M11 and M13
183 (2.0 mmol) were respectively dissolved in water (20 mL) and KPF₆ (828.3 mg, 4.5 mmol) was
184 added. The mixture was stirred for 15 min at room temperature. Then 20 mL of
185 dichloromethane were added and the mixture was gently shaken. The organic layer was
186 recovered and dried over anhydrous MgSO₄. The solvent was evaporated under vacuum and the
187 corresponding compound was identified by ¹H NMR, ¹³C NMR, ¹⁹F and ³¹P NMR. As a
188 consequence the counter ion was swapped giving compounds corresponding to samples M2,
189 M4, M6, M8, M10, M12 and M14.

190

191 2.3. Thermoanalytical methods

192 The equipment used for the thermophysical characterization was the DSC-822e
193 commercialized by Mettler-Toledo. DSC is a technique with full ability of measuring thermal
194 and thermophysical properties of materials and it is widely used to characterize phase change
195 materials. In fact, International Energy Agency experts have started defining a protocol to be
196 followed in order to achieve precise results [27]. This equipment is able to measure the heat
197 flow absorbed/released by the sample in comparison with a sample reference. Taking into
198 account these measured values; the evaluation of the resulting DSC curves was performed with
199 STARe v.11.00 software from Mettler-Toledo. Phase change enthalpy and temperature were
200 obtained from the DSC heat flux signal response by integration of the response area.
201 Specifically, for phase change temperature the peak temperature has been considered as the
202 representative temperature of a phase change material.

203 The sample mass used was around 15 mg using 100 μL aluminum crucibles under a N₂ flow
204 of 80 mL min⁻¹. A dynamic mode was used taking into account the melting temperature (T_m) of
205 the sample. This method is based on a 0.5 K·min⁻¹ heating constant rate. The method used to
206 perform the thermophysical analyses is described in Figure 1.



207
208 **Fig. 1. DSC method performed to characterize the ionic compounds samples under study**
209

210 The measurements of phase change enthalpy present ± 1 kJ/kg error, and the phase change
211 temperature ± 0.1 °C.

212 As a second-step of the thermophysical characterization, the ionic liquids that present th
213 best thermophysical properties have been used to perform a thermal cycling test in order to
214 understand if the material is degraded or not. The thermal cycling is performed in the DSC
215 following the same method described in the Figure 1. The thermal cycling is performed in the
216 DSC following

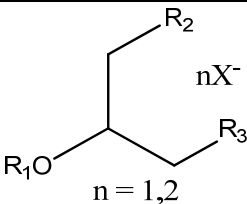
217
218 **3. Results and discussion**

219 Table 1 listed the ^1H NMR, ^{13}C NMR, ^{19}F NMR (376 MHz, DMSO) δ , and ^{31}P NMR (162
220 MHz, DMSO) δ identification of the samples under study.

221 Moreover, Table 1 shows the yields corresponding to each ionic compound. Chloride
222 bidentate ionic esters (M1, M5 and M13) and the alcohol M9 were synthesized in high yields
223 (75 to 91%). The preparation of the aryl ester (M11) and the unidentate chloride ions (M3 and
224 M7) rendered low yields (51 to 28%). The low yield corresponding to the aryl ester indicates the
225 final product yield is highly dependent of the carboxylic acid used. Moreover, the extra step
226 needed to prepare M3 and M7 lowered also the final yields. Similarly, the substitution of the
227 chloride ion for the hexafluorophosphate ion introduces an extra step also lowering up to 20%
228 the final yield.

229

230 **Table 1.** Ionic compounds synthesized and the corresponding yields determined considering the starting
 231 carboxylic acid as limiting reagent of the whole process. ^1H NMR, ^{13}C NMR, ^{19}F NMR (376 MHz, DMSO)
 232 δ , and ^{31}P NMR (162 MHz, DMSO) δ identification of the samples under study

 <p>$n = 1,2$</p>	^1H NMR (400 MHz, DMSO) δ	^{13}C NMR (101 MHz, DMSO) δ	^{19}F NMR (376 MHz, DMSO) δ	^{31}P NMR (162 MHz, DMSO) δ
M1 – Yield 84% R_1 : $(\text{CH}_3)_3\text{CCO}$ R_2 : BIM^+ R_3 : BIM^+ $n\text{X}^-$: 2Cl^-	9.76 (dd, $J = 1.7, 1.6$ Hz, 2H) 8.02 (dd, $J = 1.7, 1.7$ Hz, 2H) 7.93 (dd, $J = 1.7, 1.7$ Hz, 2H) 5.74 (tt, $J = 8.6, 2.8$ Hz, 1H) 4.80 (dd, $J = 14.4, 2.7$ Hz CH_aN , $\text{CH}_b\text{N}'$) 4.54 (dd, $J = 14.4, 8.6$ Hz, CH_bN , $\text{CH}_b\text{N}'$) 4.20 (t, $J = 7.0$ Hz, 4H), 1.72 (m, 4H) 1.20 (m, 4H) 0.94 (s, 9H) 0.84 (t, $J = 7.4$ Hz, 6H)	176.95 (CO) 137.41 (2NarCHarNar) 123.63 (2NarCHarCHarNar) 123.06 (2NarCHarCHarNar) 71.04 (OCH) 49.78 (2CHCH ₂ Nar) 49.05 (2NarCH ₂ CH ₂) 38.66 (CCH ₃) 31.83 (2CH ₂ CH ₂ CH ₃) 27.00 (3CCH ₃) 19.12 (2CH ₂ CH ₃) 13.71 (2CH ₂ CH ₃)	--	--
M2 – Yield 67% R_1 : $(\text{CH}_3)_3\text{CCO}$ R_2 : BIM^+ R_3 : BIM^+ $n\text{X}^-$: 2PF_6^-	9.18 (s, 2H) 7.78 (s, 2H) 7.71 (s, 2H) 5.59 (bs, 1H) 4.64 (d, $J = 12.2$ Hz CHaN , CHaN') 4.41 (dd, $J = 12.2, 8.4$ Hz, CHbN , CHbN') 4.18 (t, $J = 6.9$ Hz, 4H) 1.73 (m, 4H), 1.23 (m, 4H) 0.96 (s, 9H) 0.87 (t, $J = 7.3$ Hz, 6H)	176.99 (CO) 137.14 (2NarCHarNar) 123.65 (2NarCHarCHarNar) 123.18 (2NarCHarCHarNar) 70.14 (OCH) 49.82 (2CHCH ₂ Nar) 49.20 (2NarCH ₂ CH ₂) 38.67 (CCH ₃) 31.80 (2CH ₂ CH ₂ CH ₃) 26.88 (3CCH ₃) 19.10 (2CH ₂ CH ₃) 13.61 (2CH ₂ CH ₃)	70.20 (d, $J = 711.5$ Hz)	105.75 (hept, $J = 711.2$ Hz).
M3 – Yield 51% R_1 : H R_2 : $(\text{CH}_3)_3\text{CCOO}$ R_3 : BIM^+ $n\text{X}^-$: Cl^-	9.40 (dd, $J = 1.7, 1.6$ Hz, 1H) 7.85 (dd, $J = 2.0, 1.5$ Hz, 1H) 7.80 (dd, $J = 2.0, 1.5$ Hz, 1H) 4.38 – 3.91 (m, 7H) 1.74 (m, 2H), 1.22 (m, 2H) 1.13 (s, 9H) 0.86 (t, $J = 7.3$ Hz, 3H).	177.64 (CO) 137.20 (NarCHarNar) 123.63 (NarCHarCHarNar) 122.47 (NarCHarCHarNar) 67.20 (COOCH ₂) 65.58 (CHOH) 52.25 (CHOHCH ₂ Nar) 48.90 (NarCH ₂ CH ₂) 38.71 (CCH ₃) 31.82 (CH ₂ CH ₂ CH ₃) 27.31 (3CCH ₃) 19.20 (CH ₂ CH ₃) 13.72 (CH ₂ CH ₃)	--	--
M4 – Yield 32% R_1 : H R_2 : $(\text{CH}_3)_3\text{CCOO}$ R_3 : BIM^+ $n\text{X}^-$: Cl^-	9.12 (dd, $J = 1.7, 1.7$ Hz, 1H) 7.75 (dd, $J = 1.8, 1.7$ Hz, 1H) 7.70 (dd, $J = 1.8, 1.7$ Hz, 1H) 4.32 – 3.93 (m, 7H) 1.76 (m, 2H) 1.24 (m, 2H) 1.15 (s, 9H) 0.88 (t, $J = 7.3$ Hz, 3H)	177.68 (CO) 137.12 (NarCHarNar) 123.62 (NarCHarCHarNar) 122.54 (NarCHarCHarNar) 67.24 (COOCH ₂) 65.48 (CHOH) 52.42 (CHOHCH ₂ Nar) 48.98 (NarCH ₂ CH ₂) 38.73 (CCH ₃) 31.80 (CH ₂ CH ₂ CH ₃) 27.28 (3CCH ₃) 19.19 (CH ₂ CH ₃) 13.68 (CH ₂ CH ₃)	70.21 (d, $J = 711.5$ Hz)	105.74 (hept, $J = 711.2$ Hz)

<p>M5 – Yield 89%</p> <p>R₁: CH₃(CH₂)₁₄CO</p> <p>R₂: BIM⁺</p> <p>R₃: BIM⁺</p> <p>nX⁻ : 2 Cl⁻</p>	<p>9.65 (s, 2H)</p> <p>7.96 (dd, J = 1.8, 1.6 Hz, 2H)</p> <p>7.88 (dd, J = 1.8, 1.6 Hz, 2H)</p> <p>5.61 (tt, J = 8.3, 2.7 Hz, 1H)</p> <p>4.77 (dd, J = 14.4, 2.6 Hz, CHaN, CHaN')</p> <p>4.47 (dd, J = 14.4, 8.4 Hz, CHbN, CHbN')</p> <p>4.20 (t, J = 7.0 Hz, 4H), 2.28 (t, J = 7.4 Hz, 2H)</p> <p>1.73 (m, 6H), 1.33 – 1.11 (m, 28H),</p>	<p>172.39 (CO)</p> <p>137.45 (2NarCHarNar)</p> <p>123.64 (2NarCHarCHarNar)</p> <p>123.00 (2NarCHarCHarNar)</p> <p>70.72 (OCH)</p> <p>49.75 (2CHCH₂Nar)</p> <p>49.04 (2NarCH₂CH₂)</p> <p>33.29 (CH₂CO)</p> <p>31.84 (2CH₂CH₂CH₃)</p> <p>31.72 (CH₂CH₂CO)</p> <p>29.48 (4CH₂)</p> <p>29.46 (CH₂)</p> <p>29.43 (CH₂)</p> <p>29.30 (CH₂)</p> <p>29.13 (2CH₂)</p> <p>28.76 (CH₂)</p> <p>24.36(CH₂)</p> <p>22.52 (CH₂)</p> <p>19.10 (2CH₂CH₃)</p> <p>14.36 (CH₂CH₃)</p> <p>13.69 (2CH₂CH₃)</p>	<p>---</p>	<p>---</p>
<p>M6 – Yield 89%</p> <p>R₁: CH₃(CH₂)₁₄CO</p> <p>R₂: BIM⁺</p> <p>R₃: BIM⁺</p> <p>nX⁻ : PF₆⁻</p>	<p>9.16 (dd, J = 1.6, 1.5 Hz, 2H)</p> <p>7.79 (dd, J = 1.9, 1.7 Hz, 2H)</p> <p>7.72 (dd, J = 1.9, 1.7 Hz, 2H)</p> <p>5.52 (tt, J = 8.3, 2.9 Hz, 1H)</p> <p>4.60 (dd, J = 14.6, 2.8 Hz, CHaN, CHaN')</p> <p>4.36 (dd, J = 14.6, 8.4 Hz, CHbN, CHbN')</p> <p>4.17 (t, J = 7.1 Hz, 4H)</p> <p>2.25 (t, J = 7.5 Hz, 2H)</p> <p>1.73 (m, 4H)</p> <p>1.36 – 1.13 (m, 30H)</p> <p>0.87 (t, J = 7.4 Hz, 6H)</p> <p>0.83 (t, J = 6.9 Hz, 3H)</p>	<p>172.36 (CO)</p> <p>137.20 (2NarCHarNar)</p> <p>123.68 (2NarCHarCHarNar)</p> <p>123.12 (2NarCHarCHarNar)</p> <p>70.00 (OCH)</p> <p>49.77 (2CHCH₂Nar)</p> <p>49.17 (2NarCH₂CH₂)</p> <p>33.20 (CH₂CO)</p> <p>31.83 (2CH₂CH₂CH₃)</p> <p>31.73 (CH₂CH₂CO)</p> <p>29.48 (4CH₂)</p> <p>29.45 (2CH₂)</p> <p>29.29 (CH₂)</p> <p>29.14 (CH₂)</p> <p>29.12 (CH₂)</p> <p>28.74 (CH₂)</p> <p>24.32 (CH₂)</p> <p>22.53 (CH₂)</p> <p>19.09 (2CH₂CH₃)</p> <p>14.33 (CH₂CH₃)</p> <p>13.64 (2CH₂CH₃)</p>	<p>70.22 (d, J = 711.7 Hz).</p>	<p>105.73 (hept, J = 711.4 Hz).</p>
<p>M7 – Yield 81%</p> <p>R₁: (CH₃)₃CCO</p> <p>R₂: Cl</p> <p>R₃: BIM⁺</p> <p>nX⁻ : Cl⁻</p>	<p>10.56 (dd, J = 1.7, 1.5 Hz, 1H)</p> <p>7.42 (dd, J = 1.9, 1.7 Hz, 1H)</p> <p>7.35 (dd, J = 1.9, 1.7 Hz, 1H)</p> <p>5.46 (m, 1H)</p> <p>5.13 (dd, J = 14.4, 3.0 Hz, CHaN)</p> <p>4.69 (dd, J = 14.4, 8.5 Hz, CHbN)</p> <p>4.29 (t, J = 7.2 Hz, 2H)</p> <p>3.91 (d, J = 4.3 Hz, 2H)</p> <p>1.86 (m, 2H), 1.36 (m, 2H)</p> <p>1.16 (s, 9H)</p> <p>0.95 (t, J = 7.4 Hz, 3H).</p>	<p>137.43 (NarCHarNar)</p> <p>123.64 NarCHarCHarNar)</p> <p>122.99(NarCHarCHarNar)</p> <p>71.17 (OCH)</p> <p>50.15 (CHCH₂Nar)</p> <p>48.99 (NarCH₂CH₂)</p> <p>44.14 (CH₂Cl)</p> <p>38.76 (CCH₃)</p> <p>31.85 (CH₂CH₂CH₃), 27.07 (3CCH₃)</p> <p>19.10 (CH₂CH₃)</p> <p>13.68 (CH₂CH₃)</p>		

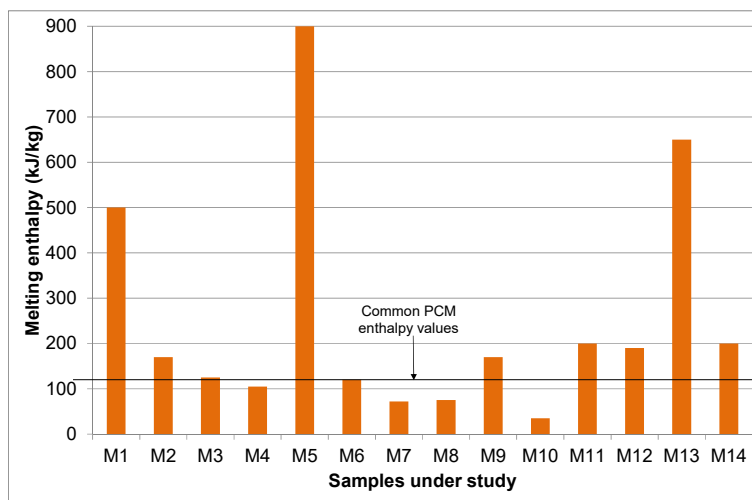
M8 – Yield 28% R ₁ : (CH ₃) ₃ CCO R ₂ : Cl R ₃ : BIM ⁺ nX ⁻ : PF ₆ ⁻	9.22 (dd, J = 1.7, 1.5 Hz, 1H) 7.77 (m, 2H) 5.38 (m, 1H) 4.55 (dd, J = 14.4, 3.2 Hz, CHaN) 4.44 (dd, J = 14.4, 9.0 Hz, CHbN) 4.16 (t, J = 7.0 Hz, 2H) 3.93 (dd, J = 12.1, 3.8 Hz, CHaCl) 3.82 (dd, J = 12.1, 5.8 Hz, CHbCl) 1.73 (m, 2H) 1.21 (m, 2H) 1.06 (s, 9H) 0.87 (t, J = 7.4 Hz, 3H) ---	176.96 (CO) 137.19 (NarCHaRNaR) 123.75 (NarCHaRCHaRNaR) 122.99 (NarCHaRCHaRNaR) 70.87 (OCH) 50.20 (CHCH ₂ NaR) 49.14 (NarCH ₂ CH ₂) 43.93 (CH ₂ Cl) 38.78 (CCH ₃) 31.77 (CH ₂ CH ₂ CH ₃) 27.04 (3CCH ₃) 19.11 (CH ₂ CH ₃) 13.66 (CH ₂ CH ₃) ---	-70.21 (d, J = 711.4 Hz) ---	105.73 (hept, J = 711.4 Hz)-----
M9 – Yield 91% R ₁ : H R ₂ : BIM ⁺ R ₃ : BIM ⁺ nX ⁻ : 2 Cl ⁻	9.53 (s, 2H) 7.92 (dd, J = 1.8, 1.6 Hz, 2H) 7.90 (dd, J = 1.8, 1.6 Hz, 2H) 6.48 (d, J = 5.9 Hz, 1OH) 4.51 (dd, J = 13.3, 2.4 Hz, CHaN, CHaN') 4.28 (bs, 1H), 4.24 – 4.14 (m, 6H) 1.75 (m, 4H), 1.22 (m, 4H) 0.84 (t, J = 7.4 Hz, 6H)	137.25 (2NarCHaRNaR) 123.54 (2NarCHaRCHaRNaR) 122.59 (2NarCHaRCHaRNaR) 68.17 (CHOH) 52.25 (2CHCH ₂ NaR) 48.91 (2NarCH ₂ CH ₂) 31.76 (2CH ₂ CH ₂ CH ₃) 19.22 (2CH ₂ CH ₃) 13.74 (2CH ₂ CH ₃)	--	--
M10 – Yield 45% R ₁ : H R ₂ : BIM ⁺ R ₃ : BIM ⁺ nX ⁻ : 2 PF ₆ ⁻	9.09 (dd, J = 2.0, 1.5 Hz, 2H) 7.77 (dd, J = 2.1, 1.8 Hz, 2H) 7.67 (dd, J = 2.1, 1.8 Hz, 2H) 5.96 (d, J = 5.4 Hz, 1OH) 4.36 (dd, J = 13.3, 2.1 Hz, CHaN, CHaN') 4.17 (t, J = 7.2 Hz, 4H), 4.13 (m, 1H) 4.07 (dd, J = 13.3, 8.1 Hz, CHbN CHbN') 1.76 (m, 4H) 1.25 (m, 4H) 0.89 (t, J = 7.4 Hz, 6H)	137.08 (2N _{ar} CH _{ar} CH _{ar} N _{ar}) 123.49 (2N _{ar} CH _{ar} CH _{ar} N _{ar}) 122.73 (2N _{ar} CH _{ar} CH _{ar} N _{ar}) 67.88 (CHOH) 52.47 (2CHCH ₂ N _{ar}) 49.04 (2N _{ar} CH ₂ CH ₂) 31.80 (2CH ₂ CH ₂ CH ₃) 19.17 (2CH ₂ CH ₃) 13.67 (2CH ₂ CH ₃)	-70.17 (d, J = 711.5 Hz). ---	105.75 (hept, J = 711.5 Hz). ---
M11 – Yield 47% R ₁ : C ₁₀ H ₇ CO R ₂ : BIM ⁺ R ₃ : BIM ⁺ nX ⁻ : 2 Cl ⁻	9.56 (s, 2H) 8.45 (m, 1H) 8.31 (d, J = 7.3 Hz, 1H) 8.25 (d, J = 8.2 Hz, 1H) 8.03 (m, 1H) 7.99 (dd, J = 2.0 1.5 Hz, 2H) 7.82 (dd, J = 2.0 1.5 Hz, 2H) 7.64 – 7.55 (m, 3H) 6.04 (tt, J = 8.7, 2.8 Hz, 1H) 4.92 (dd, J = 14.4, 2.7 Hz, CHaN, CHaN') 4.69 (dd, J = 14.4, 8.6 Hz, CHbN, CHbN') 4.12 (t, J = 7.0 Hz, 4H) 1.56 (m, 4H) 0.94 (m, 4H) 0.59 (t, J = 7.4 Hz, 6H)	165.43 (CO) 137.51 (2NarCHaRNaR) 134.87 (Car) 133.83 (CHaR) 131.76 (Car) 131.02 (COCar) 129.28 (CHaR) 128.58 (CHaR) 126.87 (CHaR) 125.33 (CHaR) 124.97 (CHaR) 124.32 (CHaR) 123.66 (2NarCHaRCHaRNaR) 123.18 (2NarCHaRCHaRNaR) 71.76 (OCH) 49.88 (2CHCH ₂ NaR) 49.08 (2NarCH ₂ CH ₂) 31.68 (2CH ₂ CH ₂ CH ₃) 18.92 (2CH ₂ CH ₃) 13.44 (2CH ₂ CH ₃)	---	---

M12 – Yield 31% $R_1: C_{10}H_7 CO$ $R_2: BIM^+$ $R_3: BIM^+$ $nX^- : 2 PF_6^-$	9.26 (dd, J = 2.1, 1.5 Hz, 2H) 8.47 (m, 1H), 8.25 (m, 2H) 8.03 (m, 1H) 7.83 (dd, J = 2.3, 1.8 Hz, 2H) 7.78 (dd, J = 2.3, 1.8 Hz, 2H) 7.65 – 7.56 (m, 3H) 5.96 (tt, J = 8.6, 2.9 Hz, 1H) 4.82 (dd, J = 14.5, 2.9 Hz, CHaN, CHaN') 4.62 (dd, J = 14.6, 8.6 Hz, CHbN, CHbN') 4.11 (t, J = 7.0 Hz, 4H) 1.55 (m, 4H), 0.98 (m, 4H) 0.60 (t, J = 7.4 Hz, 6H)	165.33 (CO) 137.32 (2NarCHarNar) 135.07 (Car), 133.90 (CHar) 131.49 (Car), 131.07 (COCar) 129.33 (CHar), 128.66 (CHar) 126.96 (CHar), 125.20 (CHar) 124.96 (CHar), 124.24 (CHar) 123.71 (2NarCHarCHarNar) 123.33 (2NarCHarCHarNar) 70.92 (OCH) 49.97 (2CHCH ₂ Nar) 49.19 (2NarCH ₂ CH ₂) 31.70 (2CH ₂ CH ₂ CH ₃) 18.93 (2CH ₂ CH ₃) 13.41 (2CH ₂ CH ₃)	-70.15 (d, J = 711.4 Hz).	105.78 (hept, J = 711.5 Hz)
M13 – Yield 75% $R_1: C_2H_3 CO$ $R_2: BIM^+$ $R_3: BIM^+$ $nX^- : 2 Cl^-$	9.72 (s, 2H) 8.01 (s, 2H) 7.93 (s, 2H) 6.28 (d, J = 17.1 Hz, 1H) 6.06 (dd, J = 17.0, 10.4 Hz, 1H) 5.96 (d, J = 10.7 Hz, 1H) 5.71 (m, 1H) 4.84 (dd, J = 14.3, 2.4 Hz, CHaN, CHaN') 4.56 (dd, J = 14.4, 8.4 Hz, CHbN, CHbN') 4.20 (t, J = 6.9 Hz, 4H) 1.69 (m, 4H) 1.13 (m, 4H) 0.81 (t, J = 7.4 Hz, 6H)	164.62 (CO) 137.49 (2NarCHarNar) 133.79 (CH ₂ =CH) 127.25 (CH ₂ =CH) 123.54 (2NarCHarCHarNar) 123.08 (2NarCHarCHarNar) 71.36 (OCH) 49.67 (2CHCH ₂ Nar) 49.03 (2NarCH ₂ CH ₂) 31.74 (2CH ₂ CH ₂ CH ₃) 19.00 (2CH ₂ CH ₃) 13.67 (2CH ₂ CH ₃)	∥	∥
M14 – Yield 69% $R_1: C_2H_3 CO$ $R_2: BIM^+$ $R_3: BIM^+$ $nX^- : 2 PF_6^-$	9.17 (s, 2H) 7.79 (dd, J = 2.0, 1.6 Hz, 2H) 7.72 (dd, J = 2.0, 1.6 Hz, 2H) 6.27 (dd, J = 16.6, 1.9 Hz, 1H) 6.07 (dd, J = 16.6, 10.4 Hz, 1H) 6.01 (dd, J = 10.4, 1.9 Hz 1H) 5.59 (tt, J = 8.3, 2.9 Hz, 1H) 4.65 (dd, J = 14.6, 2.9 Hz, CHaN, CHaN') 4.42 (dd, J = 14.6, 8.3 Hz, CHbN, CHbN') 4.16 (t, J = 7.0 Hz, 4H) 1.71 (m, 4H), 1.18 (m, 4H) 0.85 (t, J = 7.4 Hz, 6H)	164.57 (CO) 137.24 (2NarCHarNar) 133.92 (CH ₂ =CH), 127.14 (CH ₂ =CH) 123.66 (2NarCHarCHarNar) 123.20 (2NarCHarCHarNar) 70.51 (OCH), 49.74 (2CHCH ₂ Nar) 49.18 (2NarCH ₂ CH ₂) 31.75 (2CH ₂ CH ₂ CH ₃) 19.02 (2CH ₂ CH ₃) 13.64 (2CH ₂ CH ₃).	70.19 (d, J = 711.5 Hz).	105.74 (hept, J = 711.5 Hz).

233

234 The thermophysical characterization of the ionic compounds under study is summarized in
 235 Figure 2. Materials used as PCM have around 120 kJ/kg phase change enthalpy (highlighted in
 236 Figure 2) and this phase change enthalpy is considered as the normal one. These PCM were
 237 listed by Cabeza et al. [2] and the main classification used was dividing the PCM between
 238 organic materials and inorganic materials. The first group is divided as paraffin waxes,
 239 polymers, fatty acids, sugar alcohols, etc. The inorganic-materials are divided as salts, salt
 240 hydrates, aqueous solutions, metals, metal alloys, etc. These materials and their classification
 241 were introduced in a databased developed by Barreneche et al. [3] were commercial materials
 242 are included considering several substances and materials available in the market as commercial
 243 products. Then, the main commercial references of PCM are products commercialized by
 244 Rubitherm® [28], BASF® [29], PCM Products [30], etc. One of the most often used organic-
 245 PCM is paraffin waxes, and RT-90 is a good example of them. This is a commercial paraffin
 246 from Rubitherm presenting 170 kJ/kg melting enthalpy [31]. In addition, SP 90 is a salt hydrate
 247 commercialized by the same company, which is within the most used inorganic-PCM with 150

248 kJ/kg phase change enthalpy. Both are examples that can be used as PCM references in order to
249 compare their thermophysical properties [32]. . Then, some of the ionic compounds under study
250 present high phase change enthalpy becoming more than proper candidate materials to be used
251 as biobPCM.



252
253 **Fig. 2.** DSC results of melting enthalpy for the 14 samples under study.

254

255 M1, M5 and M13 are all bis-imidazole ionic esters with chloride counterions. Fatty
256 acids and fatty esters are the main components of the known biobPCM [4]. Moreover, several
257 ionic liquids had showed PCM capability [17]. In this manuscript the effect of the combination
258 in the same molecule of both approaches is described, which led to a bis-imidazolium ester
259 chlorides set, with interesting energy storage properties. Notice that M9 and M11, which also
260 have chlorides counterions, presented also high thermophysical properties under DSC
261 measurements even though DSC results obtained are lower.

262 However, the substitution of chloride ions by the hexafluorophosphate ions yielded a
263 set of compounds (M2, M6 and M14) with clear lower PCM capability. Nevertheless, the values
264 for these dihexafluorophosphate salts are similar to the ones described for $[N^{+}_{2222}]$
265 hexafluorophosphate ionic liquids [33]. This activity loss was also clearly observed when
266 compound M9 was transformed to M10, which is the same ionic compound synthesized with
267 hexafluorophosphate ions which show lower thermal energy storage capacity. In fact, all
268 hexafluorophosphates derivatives showed lower PCM capability than the corresponding
269 chloride derivatives. The monoimidazole compounds also showed lower thermophysical
270 characteristic than bisimidazole derivatives in spite of the anion present. Most of the
271 bisimidazole chloride salts are the best in terms of melting enthalpies. The substitution of
272 chloride ion by hexafluorophosphate ion yields compounds with low enthalpies in all cases.
273 Monoimidazoles also shows lower energy storage capability in spite of the anion present. The
274 acrylate ester shows better repeatability than palmitate and pivalate esters after three cycles,
275 which indicate good chemical stability of the acrylate ester in the experimental conditions used.

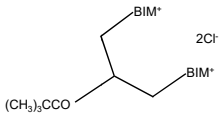
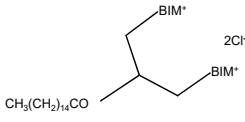
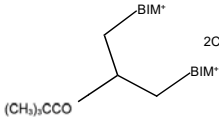
278 Notice that the best candidates for energy storage uses are also the compounds prepared with
 279 higher yield.

288 This behavior can be explained considering that the strength and amount of hydrogen
 289 bonds are key points in improving thermal properties of functionalized ionic liquids [23].
 290 Hence, the increase of imidazole units by molecule unit could improve this parameter. The
 291 formation of H- π bonds between one of the imidazole rings and the neighboring imidazole ring
 292 in the bis-imidazole compounds could be also enhanced in these derivatives contributing to the
 293 results observed [23]. Moreover, the strength of these hydrogen bonds depends also on the
 294 electronegativity of the anion present [23]. In this regarding, the negative charge of Cl^- is larger
 295 than that of the PF_6^- , which could explain the clear higher PCM capability of the chlorine based
 296 ionic liquids. . The presence of this sort of interactions can be also studied considering the NMR
 297 chemical shift of the three imidazolium hydrogens.

293 Since the higher the phase change enthalpy, the better the PCM, samples M1, M5 and
 294 M13 are the best materials to be considered as PCM candidate. So, these are the samples
 295 selected to be thermal-cycled using the DSC. Their thermal cycling stability is a crucial issue to
 296 confirm that this new ILs are able to be applied as PCM [34]. The phase change temperature and
 297 the melting enthalpy are listed in Table 2.

294

295 **Table 2.** DSC results of samples M1, M5 and M13 after 3 thermal cycles

	Phase change temperature (°C)	Melting enthalpy (kJ/kg)
M1:	Cycle 1	85
	Cycle 2	84
	Cycle 3	85
	M5:	Cycle 1
	Cycle 2	264
	Cycle 3	264
	M13:	Cycle 1
	Cycle 2	128
	Cycle 3	128

296

299 Results elucidate that M13 is the sample with highest repeatability after three thermal cycles
 200 because the amount of energy stored is almost constant while M1 and M5 decrease the enthalpy
 201 during the second cycle but this value is almost constant between cycle 2 and cycle 3. This

299 effect is normal in PCM thermophysical properties meaning that after first evaporation of
300 volatiles and synthesis products, the material starts working thermally stable.

301

302 Surprisingly, the acrylate ester (M13) shows better repeatability than palmitate (M5) and
303 pivalate (M1) esters after three cycles, which indicate good chemical stability of the acrylate
304 ester under the experimental conditions used to perform the thermal cycles. Notice that the best
305 candidates for energy storage uses are also the compounds prepared with higher yield.

306

307 **4. Conclusions**

308

309 Due to the high interest to synthesize ILs to be used as biobPCM based on their high energy
310 storage capacity, a set of bisimidazole and monoimidazole chloride and hexafluorophosphate
311 salts were considered to be synthesize from glycerol and carboxylic acids and thermally
312 characterize.

313 Bisimidazole chloride salts are the best in terms of melting and solidification enthalpies.
314 The substitution of chloride ion by hexafluorophosphate ion yields always to compounds with
315 low enthalpies. Monoimidazoles derivatives always show lower energy storage capability in
316 spite of the anion present. The acrylate ester presents better thermal cycling stability than
317 palmitate and pivalate esters, which indicate good chemical stability of the acrylate ester in the
318 experimental conditions used. The best candidates for energy storage uses are also the
319 compounds prepared with higher yield. These results help to improve the understanding of the
320 link between molecular structure and energy storage properties, one of the challenges of this
321 field and ILs are able to be applied as PCM.

322

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334

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