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1 Water molecular state in 1-hexylpyridinium hexafluorophosphate: 2 water mean cluster size as a function of water concentration

3
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8 9 Abstract

10 The water sorption behavior of representative pyridinium-based ionic liquid (IL), 1-
11 hexylpyridinium hexafluorophosphate ($[C_6Py][PF_6]$), was studied over the whole range of the
12 water activity a using a continuous gravimetric method. The analysis of the water sorption
13 isotherm using the combination of a two-mode sorption (i.e. Henry-clustering) allowed to
14 better understand $[C_6Py][PF_6]$ -water interactions. At low and intermediate activity ($a \leq 0.8$),
15 the water molecules revealed a very low affinity to $[C_6Py][PF_6]$ and, consequently, the water
16 uptake was rather low. On the contrary, at high water activity ($a > 0.8$), the water uptake
17 increased exponentially and the water clustering easily occurred. The constant of the Henry-
18 clustering equation as well as the water clustering mechanism in $[C_6Py][PF_6]$ were discussed
19 and compared to those of imidazolium-based ILs: 1-hexyl-3-methylimidazolium
20 hexafluorophosphate $[C_6C_{1im}][PF_6]$ (water-immiscible IL) and 1-butyl-3-methylimidazolium
21 tetrafluoroborate $[C_4C_{1im}][BF_4]$ (water-miscible IL). It is shown that the sorption of water
22 molecules by pyridinium-based ILs is controlled not only by the anion's nature, but also by
23 the cation's nature. Moreover, the Zimm-Lundberg theory was used to determine the water
24 mean cluster size (MCS) in $[C_6Py][PF_6]$, $[C_6C_{1im}][PF_6]$ and $[C_4C_{1im}][BF_4]$. The MCS results
25 confirmed the strong capacity of water molecules to be aggregated in $[C_6Py][PF_6]$. In order to
26 have a deeper insight into the water molecular state, infrared spectroscopy measurements
27 were carried out as a function of the relative humidity value and the obtained results were
28 correlated with the results of water sorption isotherms. It is found that at high water activity (a
29 > 0.8), sorbed water molecules are strongly linked with ILs by hydrogen bonds and, therefore,
30 are easily aggregated.

31
32 **Keywords:** room temperature ionic liquids, pyridinium-based cations, water sorption, mean
33 cluster size, water molecular state.

34 **Introduction**

35

36 Room-temperature ionic liquids (RTILs) are becoming an interesting class of solvents
37 for different applications. They possess attractive chemical and physical properties, and
38 present several advantages compared to conventional solvents, such as good chemical and
39 thermal stability, low volatility, non-flammability, and excellent and adjustable solvent
40 properties¹⁻⁴.

41 The most intensively studied class of RTILs is imidazolium-based RTILs.
42 Nevertheless, pyridinium-based RTILs progressively attract attention recently. De los Rios *et al.*
43 studied the use of alkylpyridinium-based cations combined with various anions as reaction
44 media for the direct transesterification of sunflower-seed oil with methanol⁵. Padró *et al.*
45 studied the partition coefficients of several compounds, some of them of biological and
46 pharmacological interest, between water and RTILs based on the imidazolium, pyridinium,
47 and phosphonium cations⁶. Zhang *et al.* showed that uranium formed various complexes with
48 imidazolium- and pyridinium-based RTILs⁷. They came to conclusion that these RTILs might
49 not only be useful in the extraction of uranium, but also showed high potential in the
50 bioremediation of uranium waste stream. Behar *et al.* showed that the pulse radiolysis in
51 alkylpyridinium-based RTILs allowed the production of a variety of radicals and the
52 measurement of absolute rate constants of the reduction and oxidation of different molecules⁸.
53 Siyuthin *et al.* showed that RTILs containing pyridinium cations and [PF₆] anion efficiently
54 catalyzed the asymmetric aldol reaction between aldehydes and ketones in the presence of
55 water to generate aldols with high distereo- and enantio-selectivity⁹. Abdolmohammad-Zadeh
56 *et al.* used 1-hexylpyridinium hexafluorophosphate ([C₆Py][PF₆]) for chemical modification
57 of silica by means of the acid-catalyzed sol-gel processing¹⁰. The obtained RTIL-modified
58 silica was employed as a solid phase extraction sorbent for removal of trace quantity of Fe(III)
59 ions from aqueous samples. [C₆Py][PF₆] was also used as an extractant solvent in the
60 preconcentration of trace quantity of zinc before its determination by flame atomic absorption
61 spectrometry¹¹. The combination of [C₆Py][PF₆]-based dispersive liquid-liquid micro-
62 extraction (RTIL-based DLLME) with stopped-flow spectrofluorometry was applied to
63 evaluate the concentration of aluminum Al(III) in different real samples at trace level¹². Zeeb
64 and Sadeghi proposed an efficient sample preparation method based on the application of
65 [C₆Py][PF₆] as a microextraction solvent to preconcentrate and determine the trace quantity of
66 Terazosin (a selective alpha-1 antagonist used for treatment of symptoms of an enlarged
67 prostate)¹³.

68 However, in all these studies, the water behavior of pyridinium-based RTILs was not
69 investigated, while it is known that the presence of water molecules is important for the
70 separation or extraction capacities of these solvents. [C₆Py][PF₆], an example of RTIL highly-
71 cited in the above studies, was just qualified as hydrophobic RTIL. But it is known that the
72 majority of RTILs is hygroscopic and can absorb water from ambient air despite their
73 hydrophobic character¹⁴⁻¹⁷. Their hygroscopic capacity depends mainly on the nature of their
74 ions (cation and anion), the relative humidity and the temperature. In addition, it is established
75 that the physical and chemical properties of RTILs are very sensitive to water content¹⁴⁻²⁰.
76 Therefore, it is essential to evaluate the possible interactions between water and pyridinium-
77 based RTILs in order to estimate the real potential of this family of RTILs.

78 Numerous studies have already examined the solubility of pyridinium-based RTILs in
79 water. For example, Neves *et al.* determined the solubility of 1-methyl-3-propylimidazolium
80 and 1-methyl-3-propylpyridinium cations combined with the [PF₆] anion in the temperature
81 range from 288.15 to 318.15 K²¹. Freire *et al.* measured the solubility of imidazolium-,
82 pyridinium-, pyrrolidinium-, and piperidinium-based RTILs in combination with different
83 anions (bis-(trifluoromethylsulfonyl)imide, hexafluorophosphate, and tricyanomethane) in
84 water between 288.15 and 318.15 K²². Yang *et al.* studied the solubility of 1-ethylpyridinium
85 hexafluorophosphate in ethanol/water binary solvent mixture from 278.15 to 345.15 K²³.
86 Papaiconomou *et al.* studied the water solubility of RTILs containing 1-octylpyridinium, 1-
87 octyl-2-methylpyridinium, or 1-octyl-4-methylpyridinium cations with various anions in two
88 different experimental conditions, namely in equilibrium with the air and in the liquid water²⁴.
89 The solvatochromic solvent parameters of different RTILs based on imidazolium,
90 hydroxyammonium, pyridinium and phosphonium cations at 298K using UV-Vis
91 spectroscopy were studied²⁵. However, to the best of our knowledge, no attempt has been
92 made to quantify the possible interactions of water molecules and pyridinium-based RTILs in
93 terms of both the water uptake and water behavior over the whole range of water activity.

94 The main objective of this work is to obtain a deeper understanding of the water
95 sorption behavior of representative pyridinium-based RTIL, [C₆Py][PF₆], over the whole
96 range of water activity. The choice of this IL is explained by the fact that this RTIL is among
97 the most commonly used pyridinium-based RTILs in different fields of science. The
98 measurements of water vapor sorption kinetics were carried out using the gravimetric method.
99 The obtained water sorption isotherm was analyzed by using a two-mode sorption (Henry-
100 clustering) in order to describe the water sorption behavior in [C₆Py][PF₆]. This model is
101 based on the dual-model sorption idea, in which an ordinary dissolution (absorption)

102 described by Henry's law is combined with a clustering (aggregation) phenomenon. Water
103 clustering involves multiple self-associated water molecules inside materials and it occurs
104 mainly at high water activity. This model is the most appropriate as in this case the clustering
105 phenomenon may be fitted separately from the Henry's linear part. The difference between
106 the water sorption behavior of [C₆Py][PF₆] and imidazolium-based RTILs, 1-hexyl-3-
107 methylimidazolium hexafluorophosphate ([C₆C₁im][PF₆], water-immiscible RTIL) and 1-
108 butyl-3-methylimidazolium tetrafluoroborate ([C₄C₁im][BF₄], water-miscible RTIL), was
109 discussed. The application of the Zimm-Lundberg theory to water sorption isotherm results
110 made it possible to determine the mean cluster size (MCS) of water molecules in [C₆Py][PF₆],
111 [C₆C₁im][PF₆] and [C₄C₁im][BF₄] as a function of the water concentration (or relative
112 humidity). The infrared spectroscopy is extensively used for understanding the interactions
113 between the water molecules and RTILs¹⁴. Therefore, the results of the water sorption were
114 compared with the infrared spectroscopy results in order to discuss in details the molecular
115 state of water molecules in RTILs.

116

117 **Experimental**

118 1) Materials

119 The chemical structure of RTILs used in this work, i.e. [C₆Py][PF₆], [C₆C₁im][PF₆],
120 and [C₄C₁im][BF₄], is shown in Fig. 1. All RTILs were purchased from Acros Organics (>
121 99% purity) in liquid state and used as received. All water used was Milli-Q water (18.2
122 MΩ/cm at 25 °C, Millipore®). N₂ (99.99% purity, Air Products®) was used as received.

123 2) Sorption studies

124 The water vapor sorption kinetics measurements were carried out using a continuous
125 gravimetric method. The electronic microbalance used was IGAsorp (Intelligent Gravimetric
126 Analyser Sorption moisture) supplied by Hiden Isochema Limited (UK). At the beginning,
127 studied RTIL was placed into a glass sample pan, and retained on one end of the electronic
128 microbalance. The sample environment temperature was controlled by the thermoregulated
129 water bath and fixed at 25.0 ± 0.2 °C. RTIL was dried by the dry flow of N₂ gas until a
130 constant mass m_0 was obtained. Then, the water vapor pressure was increased gradually up to
131 the saturated vapor pressure ($a = 0.95$). At each activity level, the mass gain was continuously
132 measured as a function of time until an equilibrium state was reached. The water vapor
133 sorption isotherm was subsequently deduced by plotting the water content at equilibrium M
134 versus water activity:

135
$$M = \frac{m_{eq} - m_0}{m_0} = f(a) \quad (\text{Eq. 1})$$

136 where m_{eq} is the mass at the equilibrium state for a given water activity a .

137 3) Infrared spectroscopy

138 The infrared measurements were performed using the Fourier transform infrared
139 (FTIR) Nicolet spectrometer (ThermoFischer, Avatar 360 Omnic Sampler) in an attenuated
140 total reflectance (ATR) mode (Ge crystal) with a resolution of 8 cm^{-1} with 200 scans per
141 spectrum in the range of $4000 - 675 \text{ cm}^{-1}$.

142 The FTIR spectra of RTIL equilibrated with water vapors at a given vapor activity a
143 were obtained by means of a home-made apparatus developed for that purpose and explained
144 in details in²⁶. In short, dry RTIL was positioned inside a special hood placed over the sample
145 compartment. The vapor generator was connected to the hood for a few hours, ensuring that
146 RTIL was in the equilibrium state with the water vapor. Dry nitrogen and water-nitrogen
147 flows were controlled with an electronic gas flowmeter (Agilent Technologies, 5067 model).
148 The FTIR spectra were recorded for RTIL equilibrated with the water vapors (from $a = 0$ (i.e.
149 dry RTIL) to $a = 0.95$) and liquid water (i.e. at $a = 1$).

150

151 **Theoretical background**

152 1) Two-mode sorption – Henry-clustering

153 The Flory-Huggins thermodynamic theory is used for correlating the penetrant
154 sorption isotherms²⁷. In this case, the sorption isotherm curve exhibits a quasi linear curve at
155 low ($a \leq 0.2$) and intermediate ($0.2 < a \leq 0.7$) activity and then it is followed by a convex
156 curvature for higher activity ($a > 0.7$). It is noted that this theory is useful for describing the
157 water sorption behavior in a hydrophobic material²⁷. Usually, the Flory-Huggins theory is
158 applied for the organic solvent sorption in rubbery materials, for example, the chloroform
159 sorption in silicone²⁸. Perrin *et al.* showed that the water sorption isotherm in hydrophilic
160 cellulose triacetate could also be well described by the Flory-Huggins theory, but only for the
161 activity less than 0.7 ²⁹.

162 According to this theory, when a penetrant is added to the material solute, an enthalpy
163 change can take place as the penetrant-penetrant and solute-solute interactions are replaced by
164 the penetrant-solute interactions. It should be mentioned that the interactions between the
165 penetrant and solute are assumed to be constant whatever the penetrant activity. However, the
166 clustering phenomenon is not clearly explained as the deviation from the Flory-Huggins

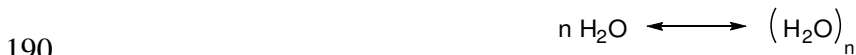
167 thermodynamic theory is observed at high penetrant activity (≥ 0.7). Therefore, in the case of
 168 the RTIL water sorption isotherms with a curve shape similar to the Flory-Huggins sorption
 169 curve shape (i.e. the first linear part followed by the convex shape), it is more judicious to
 170 describe the isotherm by using an approach, which consists of two sorption modes: the
 171 Henry's dissolution and the clustering.

172 In the case of a binary system, the penetrant-penetrant and penetrant-material
 173 interactions are found to be dependent on the penetrant activity value. Thus, in our case it is
 174 assumed that two species of absorbed water molecules contribute to the water concentration in
 175 the material (RTIL): one of these species follows the Henry's law at low and intermediate
 176 water activity ($0 < a \leq 0.7$) (i.e. molecules are randomly sorbed in the medium with no
 177 specific interaction), and the second of the species at higher activity ($a > 0.7$) follows the
 178 water clustering (i.e. part of sorbed molecules from the Henry's sorption due to the
 179 predominant penetrant-penetrant interactions at high water concentration forms a cluster).
 180 Therefore, taking into account these two combined sorption modes, the water sorption
 181 isotherm may be expressed as follows:

$$182 \quad C_{H_2O} = C_{(H_2O)_D} + nC_{(H_2O)_n} = k_D a + nK_a k_D^n a^n, \quad (\text{Eq. 2})$$

183 where C_{H_2O} (g-water/g-RTIL) is the total water concentration, $C_{(H_2O)_D}$ and $nC_{(H_2O)_n}$ are the
 184 water concentration from the Henry's sorption and from the clustered species, respectively, a
 185 is water activity, k_D (g-water/g-RTIL) is the Henry's solubility coefficient representing the
 186 affinity of water molecules to the sample (RTIL), n is the mean number of water molecules
 187 per cluster, and K_a ((g-water/g-RTIL) $^{1-n}$) is the equilibrium constant for the clustering
 188 reaction.

189 The clustering formation corresponds to the next water equilibrium:



191 which is characterized by an equilibrium constant K_a :

$$192 \quad K_a = \frac{C_{(H_2O)_n}}{C_{H_2O}^n},$$

193 where C_{H_2O} is the water concentration of free water molecules ($=k_D a$) and $C_{(H_2O)_n}$ is the
 194 concentration of the water clusters that can be determined as follows:

$$195 \quad C_{(H_2O)_n} = nK_a C_{H_2O}^n = nK_a k_D^n a^n.$$

196 2) Mean cluster size (MCS)

197 The clustering theory of adsorbed molecules was proposed to explain some of the
 198 thermodynamic inconsistencies in sorption first by Zimm et Lundberg^{30,31} and later by
 199 Starkweather³². Water is unique penetrant due to its polar nature, thus, it can create hydrogen
 200 bond with itself and can form clusters. This theory allows us to evaluate the degree of
 201 clustering in binary systems. At this mathematical approach, the clustering function is defined
 202 as:

$$203 \quad \frac{G_s}{V_s} = -(1 - \Phi_s) \left[\frac{\partial(a/\Phi_s)}{\partial a} \right]_{p,T} - 1, \quad (\text{Eq. 3})$$

204 where G_s is the cluster integral, V_s , Φ_s and a are the partial molar volume, the volume fraction
 205 and the activity of penetrant molecules (in our case, water molecules), respectively. The
 206 clustering function $\frac{G_s}{V_s}$ indicates whether clustering takes place or not and it can be easily
 207 determined from the experimental isothermal sorption^{33,34}. A $\frac{G_s}{V_s}$ value equal to -1 (the case
 208 of the ideal solution, i.e. sorption isotherm following the Henry's law) indicates that penetrant
 209 molecules do not affect the distribution of other penetrant molecules. If $\frac{G_s}{V_s} > 0$, penetrant
 210 molecules tend to cluster provided the concentration is higher in their neighborhood as it
 211 would be expected on the basis of non-random mixing, whereas if a $\frac{G_s}{V_s}$ value is greater than
 212 -1, penetrant molecules prefer to remain isolated.

213 The expression $\frac{G_s \Phi_s}{V_s}$ represents the mean number of penetrant molecules in excess
 214 of the mean concentration. Thus, it measures the clustering tendency of penetrant molecules.
 215 The MCS value is hence an estimate of the mean number of molecules which exist in a
 216 cluster:

$$217 \quad MCS = 1 + \left[\frac{\Phi_s G_s}{V_s} \right] \quad (\text{Eq. 4})$$

218 Following Starkweather³², the equation for the mean size of a cluster can be written as:

$$219 \quad MCS = (1 - \Phi_s) \frac{a}{\Phi_s} \left(\frac{\partial \Phi_s}{\partial a} \right)_{p,T} \quad (\text{Eq. 5})$$

220 The volume fraction Φ_s is obtained from the relation:

$$221 \quad \Phi_s = \left(1 + \frac{\rho_s}{M\rho_{IL}} \right)^{-1}, \quad (\text{Eq. 6})$$

222 where ρ_s and ρ_{IL} are the densities of the penetrant (water) and sample (RTIL), respectively.
223 The mass uptake M at the equilibrium and at a given activity a of sorbed species is defined
224 according to Eq. 1. In the case of the Henry-clustering mode, the mass uptake can be
225 expressed according to Eq. 2.

226 In the case of water transport studies, the Zimm and Lundberg theory has been often
227 coupled with the approaches that allow obtaining a mathematical description of the water
228 sorption isotherms. As a result, the MCS value can be expressed from the Henry-clustering
229 parameters as follows:

$$230 \quad MCS = \frac{\rho^2}{M^3 \left(1 + \frac{\rho}{M} \right)^2} (k_D a + n^2 K_a k_D^n a^n), \quad (\text{Eq. 7})$$

231 where $\rho = \frac{\rho_s}{\rho_{IL}}$. The densities of studied RTILs are 1.25 g/cm³ for [C₆Py][PF₆], 1.31 g/cm³
232 for [C₆C₁im][PF₆] and 1.21 g/cm³ for [C₄C₁im][BF₄].

233

234 **Results and discussion**

235 1) Water sorption

236 The sorption kinetics of water vapor into a material depends on numerous factors, such
237 as the chemical composition, the physical and chemical properties, etc. A continuous
238 gravimetric analysis was performed in order to understand possible interactions of water
239 molecules and [C₆Py][PF₆] over the whole range of water activity. Fig. 2 shows that the
240 experimental data of the water vapor sorption kinetics of [C₆Py][PF₆] depend directly on the
241 water activity a . As one can see, the water uptake increases with time to the achievement of
242 the sorption equilibrium after certain period of time. Besides, the maximal amount of sorbed
243 water increases when the water activity a increases. Moreover, the sorption kinetics becomes
244 longer starting from $a = 0.8$. Before this value, the equilibrium state (i.e. gain mass plateau
245 value) is reached rather rapidly (Fig. 2). The sorption kinetics provides a valuable insight into
246 the mechanism involved in the transport of penetrate within a material. In order to get the
247 details of the water sorption kinetics into RTIL, the water vapor sorption isotherm was
248 obtained from the mass gain at the equilibrium state of the sorption kinetics according to Eq. 1

249 (Fig. 3). The water vapor sorption isotherms of imidazolium-based RTILs ([C₆C₁im][PF₆] and
250 [C₄C₁im][BF₄]) (Fig. 1) obtained on the same conditions are added for comparison. The
251 choice of [C₆C₁im][PF₆] is based on the fact that this RTIL is a well-known example of water-
252 immiscible RTILs^{1,2,14,15,19,35} and is known to have very weak interactions with water
253 molecules even at high water activity, whereas [C₄C₁im][BF₄] is water-miscible
254 RTIL^{1,2,14,15,19,35} and is known for its strong water interaction capacity leading to the water
255 clustering at high activity.

256 It can be seen from Fig. 3 that the water uptake by [C₆Py][PF₆] is quasi-linear and
257 non-specific at low and intermediate water activity (up to $a < 0.8$), whereas at high water
258 activity ($a > 0.8$), the water uptake increases exponentially.

259 The analysis of an adequate sorption isotherm model can give important information
260 concerning the water organisation in the material. The water vapour isotherms have been
261 already exploited and treated by classical thermodynamic models such as local-composition
262 models, Group Contribution Methods³⁶, COSMO³⁷ and by other less classical models such as
263 the modified RK EOS³⁸ and the Camper model³⁹. As to the so-called local-composition
264 models, one can find the non-random two-liquid model (NRTL)⁴⁰⁻⁴², the Wilson model⁴³, the
265 UNIQUAC model^{44,45}, and the group contribution model UNIFAC⁴⁶, but also GAB⁴⁷⁻⁴⁹ and
266 Park^{50,51} models. Among all proposed in the literature models, it is admitted that GAB model
267 is mostly used to describe the water sorption by food and food-stuffs. In the case of an
268 exponential increase of the solvent concentration at high vapor pressure (i.e. in the case of the
269 convex form of the isotherm) some other models can be also applied, e.g. Flory-Huggins,
270 ENSIC, or aggregation models. For example, the Flory-Huggins model (usually used for
271 vapor sorption in rubbery-elastomer materials) is not appropriate for polar penetrants such as
272 water molecules (according to hypothesis of Flory-Huggins), so this model cannot be used for
273 the ionic liquid/water system studied in the present work. The convex form of the isotherm is
274 usually attributed to the typical water clustering phenomenon, and the strong increase of the
275 water concentration at high water vapor pressure values is explained by the water/water
276 interactions, which become predominant, compared to the water/substrate interactions. It is
277 well known that such phenomenon occurs mainly in polar systems (i.e. in the case of
278 hydrophilic materials) or in the system containing ionic groups, which are able to interact with
279 water molecules, e.g. polyelectrolyte (Nafion[®]). In addition, as ionic liquids are liquid salts,
280 so ion pairs can be easily solvated by water molecules, thus forming a hydration shell.
281 Recently Zhu et al showed by means of a detailed NMR analysis that imidazolium cations
282 with no or short alkyl chains can form a self-assembled clustering structure in water

283 solution⁵². The authors revealed the presence of the first hydration shell of the polar heads of
284 cations at the water concentration around 60 mol.%. Owing to the high mobility of ionic
285 liquids (i.e. low viscosity compared to polymer material), it is reasonable to imagine that
286 water molecules move and are bonded with each other by strong hydrogen bonds as in bulk
287 liquid water.

288 The presence of water clusters in ionic liquids is the well-known fact and it is
289 confirmed by both theoretical and experimental points of view. Being based on computation
290 studies of three ionic liquid systems containing [BF₄], [PF₆] and [Tf₂N] anions, Maiti et al.
291 revealed that the inclusion of small hydrogen-bonded water clusters was in better quantitative
292 agreement with the experimentally observed water sorption data⁵³. Also, molecular dynamics
293 simulation (MDS) of mixtures of 1,3-dialkyl imidazolium ionic liquids and water performed
294 by Hanke and Lynden-Bell has shown that when the molar proportion of water molecules
295 reached 75%, a percolating network of water and small clusters was formed⁵⁴. Singh and
296 Kumar examined the cation-anion-water interactions in aqueous mixtures of imidazolium
297 ionic liquids over the whole composition range using FTIR spectroscopy⁵⁵. They showed the
298 existence of the hydration shell for [BF₄] anion and deduced the presence of water clusters
299 from the overall broad structure of the -OH band at 2800-3800 cm⁻¹. Moreover, by comparing
300 MDS results with the NMR data, Moreno et al. clearly showed that the ions were selectively
301 coordinated by individual water molecules at low water content, while the ionic network was
302 disrupted by the water clusters at high water content⁵⁶.

303 Taking into account the literature results mentioned above, in the present article the
304 dual-mode (Henry and clustering) was chosen. To evaluate how accurate the fitting was,
305 residual sum of squares (RSS) was used, i.e. the sum of squares of residuals (i.e. deviations
306 predicted from actual empirical values of data). RSS value allows measuring the discrepancy
307 between the experimental data and the estimation model. In each case, very small RSS values
308 were obtained indicating an accurate fit of the model to the experimental data. The fitted
309 model parameters (k_D , K_a and n) (Eq. 2) are gathered in Table 1.

310 At low and intermediate water activity ($a \leq 0.8$), the water uptake by [C₆Py][PF₆]
311 increases linearly with the water activity value, revealing the typical Henry's sorption mode
312 (the first term in Eq. 2), for which interactions between water molecules are not predominant.
313 This sorption mode assumes a random dispersion of sorbed water molecules in RTIL. The
314 Henry's coefficient k_D calculated from the curve slope illustrates the affinity of water
315 molecules and RTIL. The higher is the k_D value, the higher is the water solubility in RTIL.
316 From the thermodynamical point of view, the [C₆Py][PF₆] water uptake is very low and quite

317 similar to that of [C₆C₁im][PF₆] (Fig. 3), thus confirming their hydrophobic character. It can
318 be noted that the k_D values of [C₆Py][PF₆] and [C₆C₁im][PF₆] are rather close (Table 1) that
319 explains the superposition of the water vapor sorption isotherms up to $a = 0.8$ (Fig. 3). It can
320 be seen from Fig. 3 that the amount of water absorbed by [C₄C₁im][BF₄] is largely higher than
321 that absorbed by two [PF₆]-based RTILs at low and intermediate water activity. As a result,
322 the k_D value of [C₄C₁im][BF₄] is almost ten times higher compared to that of [C₆Py][PF₆]
323 (Table 1). Thus, one can conclude that water molecules have very few interactions with
324 [C₆Py][PF₆] at low and intermediate activity, and that the behavior of [C₆Py][PF₆] towards
325 water is very similar to that of [C₆C₁im][PF₆] (water-immiscible RTIL). This fact is in good
326 agreement with the research of Papaiconomou *et al.*²⁴, who studied the water solubility of
327 RTILs containing octylpyridinium-type cations, and found them nearly water immiscible. In
328 addition, numerous studies indicate a weak water miscibility of [PF₆]-based RTILs because of
329 the [PF₆] anion presence^{1,2,14,15,19,35}. Furthermore, it is interesting to note that [C₆Py][PF₆] and
330 [C₆C₁im][PF₆] present almost the same interactions with water molecules up to $a = 0.8$ (Fig.
331 3), although the chemical structure of their cations is different (Fig. 1). It means that at low
332 and intermediate water activity (i.e. at $a < 0.8$) the dialkylimidazolium cations and
333 alkylpyridinium cations have approximately the same influence on the water sorption
334 properties of RTILs (for the same anion). This result is consistent with the study of Neves *et*
335 *al.*²¹, who noted that the water solubility in 1-methyl-3-propylimidazolium and 1-methyl-3-
336 propylpyridinium cations combined with the [PF₆] anion is similar at 30°C.

337 At high water activity ($a > 0.8$), the strong increase in the [C₆Py][PF₆] water uptake
338 reveals the water clustering formation, which occurs also in [C₄C₁im][BF₄] (Fig. 3).
339 Consequently, the values of K_a (the equilibrium constant for the clustering reaction) and n (the
340 mean number of water molecules per cluster) for these two RTILs are significantly higher in
341 comparison with those for [C₆C₁im][PF₆] (Table 1). Moreover, the values of K_a and n for
342 [C₆Py][PF₆] are surprisingly higher than those for [C₄C₁im][BF₄], which is water-miscible
343 RTIL. This means that water molecules are aggregated more easily in [C₆Py][PF₆] than in
344 [C₄C₁im][BF₄]. This result is very interesting, indicating, on the one hand, that the
345 hydrophobicity of the cation increases from imidazolium- to pyridinium-based RTILs^{21,22} and,
346 on the other hand, that the role of anion in the water sorption and clustering in RTILs is a key
347 one^{14-16,18,19,35,44,55}. Indeed, it is well known that the [BF₄] anion, compared to the [PF₆] one,
348 promotes the strong hydrogen bonds with and between water molecules^{14,15,19,55,57}, which
349 explains both the strong water uptake and the formation of the water clusters in [BF₄]-based
350 RTILs, compared to [PF₆]-based RTILs. These literature findings seem not to be valid for all

351 types of RTILs, but they are more suitable only for some classes of RTILs, such as
352 imidazolium-based RTILs (the most extensively studied class in the literature). Consequently,
353 it is not sufficient to take only the anion nature as an indicator of water miscibility in RTILs
354 as it is shown in the present study that [C₆Py][PF₆] which is [PF₆]-based RTIL has the highest
355 values of K_a and n (Table 1) revealing an easier capacity for water molecules clustering
356 compared to [C₄C₁im][BF₄] (which is [BF₄]-based RTIL). This result could be due to the
357 stronger dispersive interactions and, simultaneously, to the decreasing of cohesivity in
358 pyridinium-based RTILs than in imidazolium-based RTILs²⁵. The different kinds of water
359 interactions with the π systems of aromatic cations (pyridinium and imidazolium cations) will
360 be also responsible for this result⁵⁸.

361 The [C₆Py] cation is of importance in the water clustering formation, even in
362 combination with the [PF₆] anion. This fact highlights the strong influence of the cation
363 nature, in addition to that of anion, on the water sorption and clustering in pyridinium-based
364 RTILs. Therefore, it is essential that the cation nature must be also taken into account in the
365 study of interactions of water molecules and pyridinium-based RTILs. On the other hand, it is
366 shown that [C₆Py][PF₆] has a very low affinity towards water molecules at low and
367 intermediate activity (the k_D value (Table 1)). Thus, the behavior of pyridinium-based RTIL
368 towards water molecules can be changed depending on water activity: [C₆Py][PF₆] is water-
369 immiscible RTIL at low and intermediate activity, thus limiting the water sorption, but at high
370 activity ($a > 0.8$) the further sorption of water molecules on already sorbed monolayer
371 moisture favours the water clustering formation as with the water activity increasing
372 water/water interactions are largely stronger than water/RTIL ones. So, starting from a certain
373 water concentration water molecules are self-associated to form clusters. Such behavior has
374 been also observed in the case of the water sorption in low density polyethylene⁵⁹. Indeed, the
375 water cluster formation is revealed in this hydrophobic polymer with very low affinity
376 towards polar molecules. The water clustering is explained by the hydrogen bonds between
377 water molecules themselves confined in the matrix, thus leading to further reducing of the
378 water mobility through the material. Therefore, for each given RTIL application, it is
379 important first to determine the necessary water activity range. If the water presence in
380 [C₆Py][PF₆] is not desired at all, the operating conditions should be in the water activity range
381 less than 0.8 in order to avoid the water sorption and clustering formation as much as
382 possible. On the contrary, if the water presence is required, the RTIL can be applied at the
383 water activity value close to 1. For other applications using pyridinium-based RTILs and
384 where water is the reaction media (or is used in large quantity), the replacement of the [PF₆]

385 anion by others anions is recommended to further improve the water miscibility of RTIL.
386 Popov *et al.*⁶⁰ used *N*-butyl-4-methyl-pyridinium tetrafluoroborate in aqueous solutions to
387 measure the stability constants of crown-ether complexes with alkali-metal ions. This RTIL
388 was qualified by Wang *et al.*⁶¹ as water-soluble RTIL. It was used as a co-solvent with water
389 by Riva *et al.*⁶² to separate aromatic hydrocarbons from a naphtha of very low-aromatic-
390 content (10 wt.%). Indeed, it is known that the different behavior of the [BF₄] and [PF₆]
391 anions is attributed to the fact that the [BF₄] van der Waals volume (48 Å³) is smaller than the
392 [PF₆] one (68 Å³), that gives more space for water molecules to be accommodated in [BF₄]-
393 based RTILs^{16,63}. Papaiconomou *et al.*²⁴ measured the water content of air-saturated and
394 water-saturated pyridinium RTILs, 1-octyl-4-methylpyridinium tetrafluoroborate
395 ([4C₁C₈Py][BF₄]), 1-octyl-2-methylpyridinium tetrafluoroborate ([2C₁C₈Py][BF₄]), 1-octyl-4-
396 methylpyridinium trifluoromethyl sulfonate ([4C₁C₈Py][TfO]), and 1-octyl-4-
397 methylpyridinium dicyanamide ([4C₁C₈Py][N(CN)₂]). At the equilibrium state with liquid
398 water, the water content (in mass fraction) is 11.3, 13.6, 17.2 and 54.9% for [4C₁C₈Py][BF₄],
399 [2C₁C₈Py][BF₄], [4C₁C₈Py][TfO] and [4C₁C₈Py][N(CN)₂], respectively. These values are
400 much higher compared to 10.2% obtained for [C₆Py][PF₆] at $a = 0.95$. These pyridinium-
401 based RTILs are, therefore, more water-miscible than [C₆Py][PF₆] obviously due to the
402 combination of the pyridinium-based cation with such anions as [BF₄], [TfO] and [N(CN)₂].

403 Another question which arises is whether the water clustering mechanism in
404 [C₆Py][PF₆] is the same as in [C₄C₁im][BF₄] (as no clustering is observed in [C₆C₁im][PF₆]
405 (see Fig. 3)). Fortunato *et al.*^{63,64} studied the water uptake of imidazolium-based RTILs after
406 their contact with aqueous solutions. The authors concluded that water molecules began to
407 cluster on the molecular level only when the water content in RTIL exceeded a certain critical
408 concentration. Scovazzo⁶⁵ indicated that the critical concentration for the water cluster
409 formation is easier to reach for the water-miscible RTILs than for the water-immiscible
410 RTILs. Dahi *et al.*⁵⁷ showed that the clustering process was linked to the affinity of water
411 molecules and RTIL already at low and intermediate water activity: the higher the k_D value,
412 the higher the probability of the water clustering at high activity. From the obtained k_D values
413 (Table 1), it is clearly seen that the affinity or interactions of water molecules are very low in
414 the case of [C₆C₁im][PF₆] and rather high for [C₄C₁im][BF₄] at low and intermediate water
415 activity. This result allows us to explain why water molecules easily formed the clusters in
416 [C₄C₁im][BF₄] (high K_a value, Table 1) in contrast with [C₆C₁im][PF₆] (low K_a value, Table
417 1) at high water activity. Indeed, it is known that the [BF₄] anion promotes the strong
418 hydrogen bonds with and between water molecules imidazolium-based RTILs compared to

419 the [PF₆] anion^{14,15,19,44,55,57}, which explains both the strong water uptake and the formation of
420 the water clusters in [C₄C₁im][BF₄] compared to [C₆C₁im][PF₆]. However, in the case of
421 [C₆Py][PF₆] (pyridinium-based RTIL), despite the low affinity with water at low and
422 intermediate water activity (low k_D value (Table 1), water molecules can easily form clusters
423 in this RTIL at high activity, even more easily compared to [C₄C₁im][BF₄] (compare the K_a
424 values (Table 1)). Combining these results with the studies of Fortunato *et al.*^{63,64}, Scovazzo⁶⁵
425 and Dahi *et al.*⁵⁷, it can be pointed out that the water clustering mechanism in [C₆Py][PF₆] is
426 different from that in [C₄C₁im][BF₄]. It seems that in the case of [C₆Py][PF₆], which is
427 alkylpyridinium-based RTIL, the critical concentration for the water clustering formation is
428 much lower in comparison to imidazolium-based RTILs. This fact may be explained by the
429 RTIL cation structure. Wang *et al.*⁵⁸ studied hydrogen bonding interactions of 1-
430 butylpyridinium tetrafluoroborate [C₄Py][BF₄] and water. They stated that water, when it
431 forms the strong anion-HOH-anion complex, could also form H-bonds with aromatic C-H
432 bond on the [C₄Py] cation. This result is different from the case of imidazolium-based RTILs,
433 where the strong anion-cation interaction and steric hindrance from the alkyl chain length
434 prevent water molecules to form H-bonding with aromatic C-H on the imidazolium cation,
435 thus favouring interactions with the anion. This observation supports well the previously
436 mentioned hypothesis about much stronger interactions of water molecules and the π systems
437 of the pyridinium cations than of water molecules and the imidazolium cations.

438 In order to determine the activity from which the water clusters started to form in
439 RTILs, the MCS value (Eq. 7) was calculated in addition to the n parameter (Eq. 2), which
440 represents roughly the number of water molecules per cluster. The calculated MCS values
441 were plotted as a function of the water activity a (Fig. 4). The MCS values are found to be
442 close to unity at low water activity (below $a = 0.6$) for all three studied RTILs and clustering
443 does not take place in this region. Then, the MCS values start to increase rapidly for
444 [C₆Py][PF₆] and [C₄C₁im][BF₄], whereas for [C₆C₁im][PF₆] they stay still very low (~ 2 at $a =$
445 0.95). Such a result is expected as [C₆C₁im][PF₆] is water-immiscible RTIL over the whole
446 range of water activity.

447 According to the Zimm-Lundberg theory, the MCS value greater than one is an
448 indication of the cluster formation^{30,31}. Thus, one can conclude that the water clustering starts
449 from $a = 0.7-0.8$ for [C₆Py][PF₆] and [C₄C₁im][BF₄]. Starting from $a \approx 0.8$, further sorption of
450 water molecules leads to the enhancement of water/water interactions and, thus, to the cluster
451 formation. The formed hydrogen bonds between water molecules promote the rapid formation
452 of a compact hydrogen bond network⁵⁷, which triggers the water clustering. As it can be seen

453 from Fig. 3, at $a = 0.8$ the water sorption obtained for [C₄C₁im][BF₄] (0.1075 g water/g RTIL)
454 is higher than that for [C₆Py][PF₆] (0.017 g water/g RTIL). At the same time, with the
455 increase of water activity above 0.8, the MSC value increases much faster in the case of
456 [C₆Py][PF₆] compared to [C₄C₁im][BF₄] (Fig. 4). It means that the water clustering process is
457 more pronounced in [C₆Py][PF₆] than in [C₄C₁im][BF₄], thus allowing us to obtain rapidly
458 larger water clusters in [C₆Py][PF₆]. This indicates again that the water clustering mechanism
459 in [C₆Py][PF₆] is different from that in [C₄C₁im][BF₄]. The obtained MCS plots based on the
460 Zimm-Lundberg theory agree very well with the results of the Henry-clustering model.
461 Indeed, the MCS value is equivalent to the n parameter (the mean number of water molecules
462 per cluster). However, the n value depends strongly on the quality of the fit of the
463 experimental data and, so, gives only an approximation of the cluster size (i.e. the average
464 value), whereas the MCS value, derived from the statistical mechanics analysis, allows us to
465 determine more precisely the mean size of cluster which varies with the environmental
466 activity. From Fig. 4, one can easily see that the maximum value of MCS (at $a = 0.95$)
467 determined for [C₆Py][PF₆], [C₄C₁im][BF₄] and [C₆C₁im][PF₆] is ~ 22 , 12 and 2, respectively.
468 These values are in good agreement with the calculated n values (25, 19 and 3, respectively,
469 Table 1), thus confirming the same tendency. The highest values of MCS and n are found for
470 [C₆Py][PF₆] indicating a strong trend of water molecules to form clusters of large size (more
471 than 20 water molecules per cluster) in this RTIL at high water activity.

472

473 2) Water molecular state

474 The measurement of the water clustering and interactions in a material is a key factor,
475 however, the proposed structures and/or functions of water differ in many cases, and little
476 consistency can be found among structures. Therefore, the water uptake should be also
477 characterized by direct measurements using the infrared spectroscopy, where -OH bonds for
478 different water populations have distinct bands and can be individually distinguished.

479 The IR bands corresponded to the water stretching vibration modes are widely used to
480 study the molecular state of water dissolved in various solvents^{66,67}. Two characteristic IR
481 bands exist in the region of 3000-3800 cm⁻¹: the antisymmetric (ν_3) and symmetric (ν_1)
482 stretching modes. Their intensity and position are strongly influenced both by the water
483 environment and the water association *via* hydrogen bonding^{14,19,55,57}. For example, in the
484 case of the water vapor when water molecules are distant from each other, the ν_3 and ν_1 bands
485 are situated at 3756 and 3657 cm⁻¹, respectively. In this case, water molecules are free (i.e.

486 they are not associated by hydrogen bonds). On the contrary, in the case of the liquid water,
487 water molecules are linked by hydrogen bonds and these interactions trigger the overlapping
488 of the ν_3 and ν_1 bands leading to a broad and intense band with a maximum at around 3300
489 cm^{-1} .

490 Fig. 5 shows the ATR-FTIR spectra of $[\text{C}_6\text{Py}][\text{PF}_6]$ in the region of the $\nu(\text{OH})$
491 stretching modes of water ($3000\text{-}3800\text{ cm}^{-1}$) obtained at different water activity. At the
492 beginning, $[\text{C}_6\text{Py}][\text{PF}_6]$ was dried by the nitrogen flow ($a = 0$) in order to remove any residual
493 water molecules. As a result, no characteristic IR bands of water were observed in the region
494 $3000\text{-}3800\text{ cm}^{-1}$ (Fig. 5). Then, $[\text{C}_6\text{Py}][\text{PF}_6]$ was progressively equilibrated at various water
495 activity values (from 0 to 1).

496 No significant changes were noticed on the IR spectra up to $a = 0.82$. The absence of
497 the water characteristic bands on the IR spectra of RTIL in the activity range from 0 to 0.8
498 may be explained by the very low water content in $[\text{C}_6\text{Py}][\text{PF}_6]$. This result confirms that
499 $[\text{C}_6\text{Py}][\text{PF}_6]$ is water-immiscible RTIL at $0 < a < 0.8$. On the contrary, when $[\text{C}_6\text{Py}][\text{PF}_6]$ is
500 equilibrated with water vapors at $a = 0.88$, a broad and intense band appears at 3360 cm^{-1}
501 (Fig. 5). The high intensity of this band and rapidity of its appearance proves a rapid and
502 strong increase of the water content in $[\text{C}_6\text{Py}][\text{PF}_6]$ from $a = 0.82$ to $a = 0.88$. The sorption of
503 a higher quantity of water molecules enhances significantly water/water interactions. As a
504 result, sorbed water molecules start to interact together by hydrogen bonds. The shape and
505 position of the band confirm the presence of intermolecular forces between water molecules,
506 as the intense band results from the overlapping of the ν_3 and ν_1 bands^{14,19,55,57}. Therefore,
507 water molecules are well associated by hydrogen bonds at $a = 0.88$. This clustering starts
508 probably even at $a = 0.82$ as the appearance of a large band around 3300 cm^{-1} can be already
509 observed on the spectrum at this water activity value (Fig. 5). This fact means that the activity
510 value around 0.8 marks a crucial point in the behavior of $[\text{C}_6\text{Py}][\text{PF}_6]$ towards water. This
511 observation conforms well to the MCS results (compare Fig. 4 and 5). The formed hydrogen
512 bonds between water molecules promote the formation of a compact hydrogen bond
513 network⁵⁷ and, subsequently, the formation of the water clusters. On the other hand, it does
514 not seem necessary to reach a critical water content in $[\text{C}_6\text{Py}][\text{PF}_6]$ for the water association
515 by hydrogen bonds and the formation of the water clustering since $[\text{C}_6\text{Py}][\text{PF}_6]$ reveals a low
516 water content already at $a = 0.82$ (Fig. 5). This fact confirms the hypothesis proposed above
517 that the water clustering mechanism in $[\text{C}_6\text{Py}][\text{PF}_6]$ is different from that in imidazolium-
518 based RTILs. The increasing of water activity up to 1 promotes the increase of the intensity

519 and width of the water band (Fig. 5), i.e. further strengthening the hydrogen bond network.
520 Consequently, water molecules sorbed in [C₆Py][PF₆] form clusters or even droplets of the
521 bulk liquid-like water at high water activity value. In addition, the shape of the band remains
522 unchanged with the water activity increase, which would indicate that the molecular state of
523 water in [C₆Py][PF₆] is independent of the water concentration. According to numerous
524 studies^{14,17,55,57,68,69}, the intense and broad band in the region around 3400 cm⁻¹ is attributed to
525 water clusters. At high activity ($a > 0.8$), water in [C₆Py][PF₆] shows undoubtedly an easier
526 capacity to be associated by hydrogen bonds until the water clustering formation.

527 The molecular state of water dissolved in different RTILs was studied by means of the
528 infrared spectroscopy as a function of water activity⁵⁷. Water molecules dissolved in
529 [C₄C₁im][PF₆] and [C₆C₁im][PF₆] (water-immiscible RTILs) were found to be not self-
530 associated by hydrogen bonds whatever the water content and, thus, they can be assigned as
531 free water molecules. On the contrary, water molecules sorbed in [C₄C₁im][BF₄],
532 [C₄im][dibutylphosphate], [C₄im][bis(2-ethylhexyl)phosphate] and [Et₃HN][CF₃SO₃] (water-
533 miscible RTILs) were strongly associated with each other by the hydrogen bonds, and could
534 be easily aggregated at high water activity. In the present study, although [C₆Py][PF₆] is
535 [PF₆]-based RTIL like [C₄C₁im][PF₆] and [C₆C₁im][PF₆], its behavior towards water at high
536 activity is similar to that of above-mentioned water-miscible RTILs. The obtained IR results
537 are in good agreement with the gravimetric analysis and the MCS results, and confirm the
538 dual behavior of [C₆Py][PF₆]: water-immiscible RTIL from $a = 0$ to $a = 0.8$, and water-
539 miscible RTIL at $a > 0.8$.

540

541 **Conclusion**

542 The water sorption properties of 1-hexylpyridinium hexafluorophosphate [C₆Py][PF₆]
543 were successfully investigated over the whole range of water activity. The experimental data
544 of the water sorption isotherm were well fitted with the two-mode Henry-clustering model,
545 and compared to those of imidazolium-based RTILs – [C₄C₁im][BF₄] and [C₆C₁im][PF₆]. At
546 low and intermediate water activity ($0 < a < 0.8$), the mass uptake was weak and,
547 consequently, the affinity of water molecules and [C₆Py][PF₆] was rather low. On the
548 contrary, at $a > 0.8$ the water uptake increases exponentially until the water clustering
549 formation. The obtained results revealed that the water clustering mechanism in [C₆Py][PF₆]
550 is different from that in imidazolium-based RTILs. This proves the important influence of the
551 cation structure, in addition to that of anion, on the water sorption of pyridinium-based RTILs.

552 The MCS values calculated according to the Zimm-Lundberg theory for [C₆Py][PF₆],
553 [C₆C₁im][PF₆] and [C₄C₁im][BF₄] were in good agreement with the results obtained by the
554 Henry-clustering model. Both results indicate a strong trend of the water clustering in
555 [C₆Py][PF₆] starting from $a = 0.8$. This trend is much more pronounced than in [C₄C₁im][BF₄]
556 (water-miscible RTIL). It is concluded that the water sorption capacity of [C₆Py][PF₆] varies
557 so much with water activity that it can be considered as water-immiscible RTIL at the low and
558 intermediate activity ($0 < a \leq 0.8$), and water-miscible RTIL at high water activity ($a > 0.8$).

559 The results of the sorption measurements were correlated with the molecular state of
560 water dissolved in [C₆Py][PF₆] studied by the infrared spectroscopy. At low and intermediate
561 activity ($a \leq 0.8$), the water concentration in [C₆Py][PF₆] was found to be low and, hence,
562 [C₆Py][PF₆] showed the behaviour of water-immiscible RTIL. On the contrary, at high
563 activity ($a > 0.8$), the water concentration in [C₆Py][PF₆] significantly increased. Water
564 molecules were strongly associated with each other by the hydrogen bonds leading to the
565 formation of a compact hydrogen bond network. Accordingly, water can easily form clusters.
566 At high activity, [C₆Py][PF₆] showed the behaviour of water-miscible RTIL. Although
567 [C₆Py][PF₆] belongs to [PF₆]-based RTILs, its strong water sorption and the water clustering
568 at high activity must be taken into account for all applications when contact with water is
569 necessary. The present study shows how the water sorption behavior of pyridinium-based
570 RTILs can be modulated and controlled depending on the hydration conditions.

571

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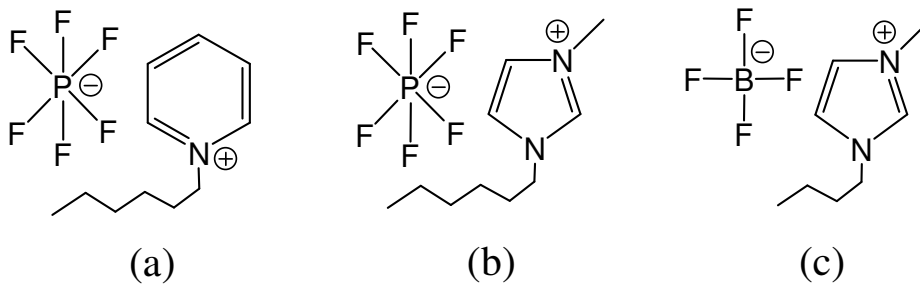
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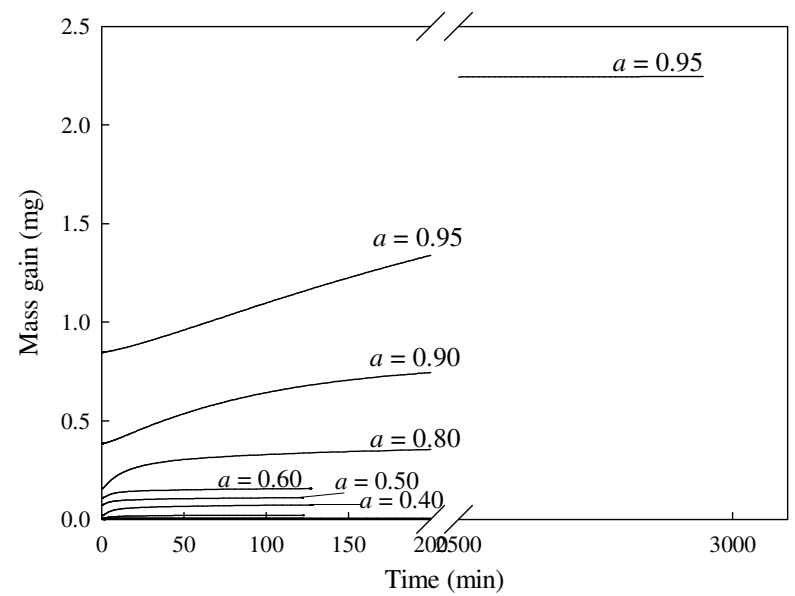
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Fig. 1. Chemical structure of (a) [C₆Py][PF₆], (b) [C₆C₁im][PF₆], and (c) [C₄C₁im][BF₄].



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Fig. 2. Water vapor sorption kinetics of [C₆Py][PF₆] at different water activity values.

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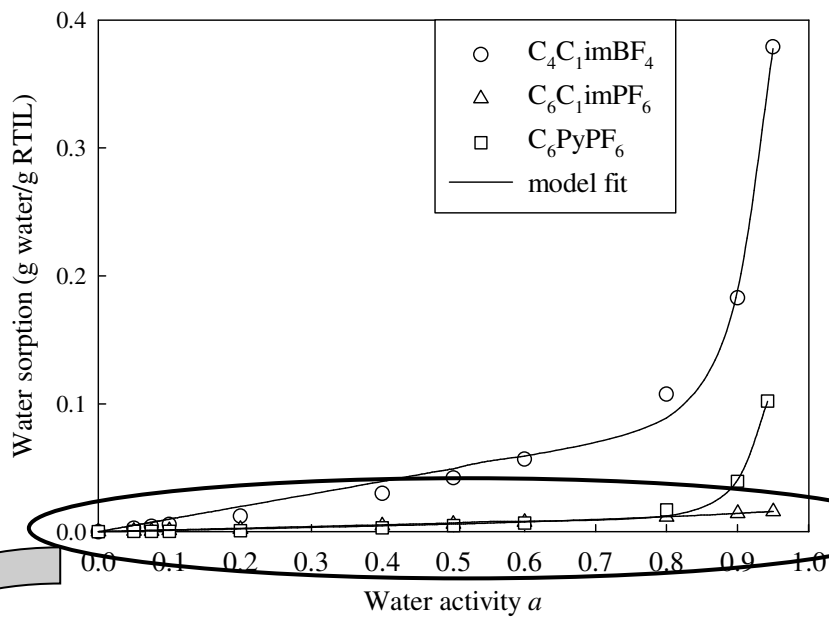
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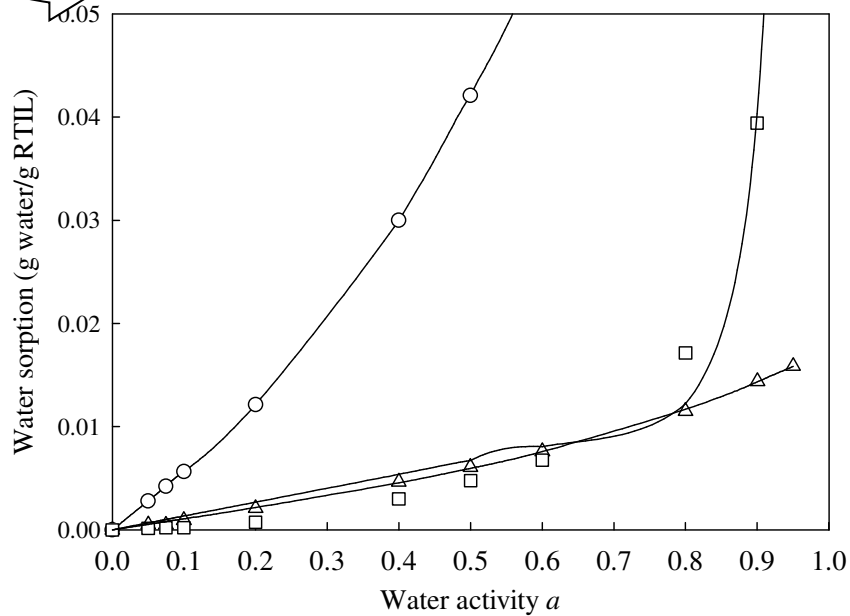
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30 **Fig. 3.** Water vapor sorption isotherms of different RTILs. Solid lines are the fit according to
31 the Henry-clustering model (Eq. 2).

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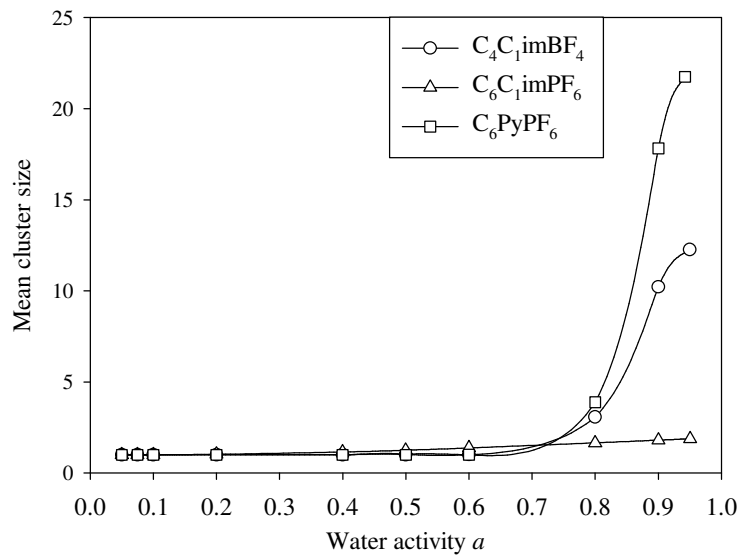
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41 **Fig. 4.** Mean cluster size of $[C_6Py][PF_6]$, $[C_6C_1im][PF_6]$ and $[C_4C_1im][BF_4]$ as a function of
42 water activity.

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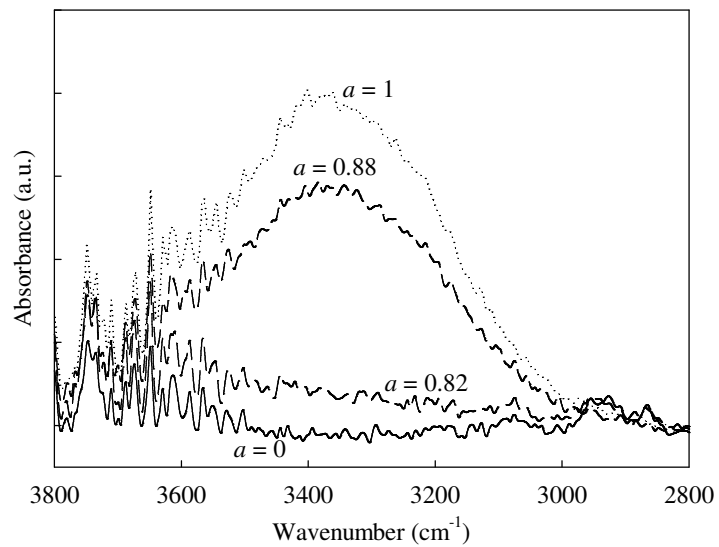
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51 **Fig. 5.** ATR-IR spectra of $[C_6Py][PF_6]$ as a function of water activity a .

52

Table 1. Parameters of the Henry-clustering model (Eq. 2).

RTIL	Parameter			Ref.
	k_D (g water/g RTIL)	K_a ((g water/g RTIL) ¹⁻ⁿ)	n	
[C ₆ Py][PF ₆]	$1.3 \cdot 10^{-2}$	$1.4 \cdot 10^{45}$	25.1	This work
[C ₆ C ₁ im][PF ₆]	$1.1 \cdot 10^{-2}$	$1.2 \cdot 10^4$	3.5	³⁶
[C ₄ C ₁ im][BF ₄]	$9.8 \cdot 10^{-2}$	$1.2 \cdot 10^{18}$	19.3	³⁶