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Effect of water on the transport properties in protic and aprotic imidazolium ionic liquids. An analysis of self-diffusivity, conductivity, and proton exchange mechanism.†

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In this paper we report on the transport properties of protic and aprotic ionic liquids of the imidazolium cation (C₂C₁Im⁺ or C₂HIm⁺) and the TFSI⁻ or TfO⁻ anion as a function of added water. We observe that the self-diffusion coefficient of the ionic species increases upon addition of water, and that the cation diffuses faster than the anion in the entire water concentration range investigated. We also observe that the overall increase of anionic and cationic diffusion coefficients is significant for C₂HImTfO while it is rather weak for C₂C₁ImTFSI, the former being more hydrophilic. Moreover, the difference between cationic and anionic self-diffusivity specifically depends on the structure of the ionic liquid’s ions. The degree of ion-ion association has been investigated by comparing the molar conductivity obtained by impedance measurements with the molar conductivity calculated from NMR data through the Nernst-Einstein equation. Our data indicate that the ions are partly dissociated (\(\Lambda/N_{\text{Imp}}\) in the range 0.45–0.75) but also that the degree of association decreases in the order C₂HImTfO > C₂HImTFSI ≈ C₂C₁ImTfO > C₂C₁ImTFSI. From these results, it seems that water finds different sites of interaction in the protic and aprotic ionic liquids, with a strong preference for hydrogen bonding to the –NH group (when available) and a stronger affinity to the TfO anion as compared to the TFSI. For the protic ionic liquids, the analysis of \(^1\)H NMR chemical shifts (upon addition of H₂O and D₂O, respectively) indicates a water-cation interaction of hydrogen bonding nature. In addition, we could probe proton exchange between the –NH group and deuterated water for the protic cation, which occurs at a significantly faster rate if associated to the TfO anion as compared to the TFSI.

1 Introduction

During the last decades ionic liquids (ILs) have attracted considerable attention due to their unique properties such as negligible vapor pressure, non-flammability, low melting point, and wide windows of thermal and electrochemical stability. The areas for ionic liquid applications are many and include dissolution of cellulose, nuclear fuel processing and organic reactions, among others.\(^1\) While the non-volatility of ILs is interesting in organic syntheses offering a mean to reduce the use of volatile organic compounds (VOC), the non-reactivity towards many acids and bases have made ILs very interesting compounds for use in green chemistry.\(^1\) ILs are exceptionally good solvents, able to dissolve both organic and inorganic compounds and, by having very low melting points, they can be used in many chemical processes where the reaction products and the solvent can readily be separated and recycled, as in the case of biodiesel production.\(^2\) The low emission policy adopted in many countries in the last years, has definitely contributed in highlighting ionic liquids as the future solvents for sustainable chemical processes.

In particular, ILs are widely investigated as electrolytes for energy conversion devices like the lithium-ion battery and the fuel cell.\(^3\) In the former, non-flammability is the crucial property whilst in the latter non-volatility brings along a main advantage with respect to the issues of dehydration and thus reduced operational temperature, encountered with hydrated Nafion membranes.\(^3\) In fact, the use of protic ILs (PILs) in fuel cells allows for operational temperatures higher than 120 °C,\(^5\) hence reducing the amount of platinum catalyst at the electrodes and enhancing the overall fuel cell efficiency.\(^4\)–\(^6\) However one should consider that as a result of the electrochemical reaction at the cathode, water is produced that can back-diffuse into the membrane and mix with the electrolyte. Hence, from the viewpoint of real fuel cell applications it is crucial to understand not only the properties of PILs, but also

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§ Which is also the target set by the U.S. Department of Energy (DOE) to promote the implementation of intermediate-temperature fuel cells in, for instance, the transport sector.
those of H$_2$O-IL mixtures. Although water has long been
considered an undesired impurity that affects the properties of
ionic liquids, more recently the approach to deliberately add
water to ILs has increased significantly. Thence, the issue of
understanding the chemical and physical properties of H$_2$O-IL
binary systems in the entire composition range has come to the
attention of several researchers. Nevertheless, since this is
an emerging field of research, many issues are still unclear and
vividly debated.

From the studies reported so far, it seems that water mainly
bonds to the anion but we believe that this must also de-
pend on the basicity of the anion considered. Perfluorinated
anions like bis(trifluoromethanesulfonyl)imide (TFSI) and tri-
flate (TfO) are poorly basic and thus expected not to strongly
interact with water; however it has been reported that the
strength of hydrogen bond between water and triflate (TfO)
is slightly higher than that of TFSI. Although aprotic ILs
like C$_2$C$_1$ImTFSI have been reported to be immiscible with
water, the protic counterpart can promote water miscibility.
C$_2$C$_1$ImTfO and C$_2$HImTfO, on the other hand, are totally
miscible with water. The issue of miscibility and hydrophilic-
ity in IL/water mixtures has to date not been addressed exten-
sively. A general result, however, is that longer alkyl chains
on the cation reduce hydrophilicity. Furthermore, Kohno et
al. have found that while [N$_{4444}$]$^-$ based ionic liquids asso-
ciated to [TsO]$^-$, [DMBS]$^-$ or [CF$_3$COO]$^-$ are miscible with
water, the [P$_{4444}$]$^-$ analogous undergo LCST-type phase tran-
sition. As discussed by Kohno et al. “The strength of the
hydrogen bonding between ILs and water should also be ca-
ble of predicting the degree of hydrophobicity of ILs, which
would be related to the energy of interaction between the ILs
and water molecules.” However, this relationship may not
straightforward. In this context, a direct interaction between
water and ammonium based cations is manifested by increased
H-bonding. On the other hand, the nature of interaction be-
tween water and imidazolium based ionic liquids has been
investigated to a limited extent and, to the best of our
knowledge, no reports are available on the effect of added wa-
ter on the ionic mobility in imidazolium ionic liquids.

In this study we thoroughly investigate the transport prop-
erties in a series of imidazolium based ionic liquids, where
the cation is varied from aprotic to protic and the anion from
less to more hydrophilic. By employing pulsed field gra-
dient nuclear magnetic resonance (PFG NMR) spectroscopy we
investigate to what extent water promotes the mobility of
the different molecular species and, in this context, the influ-
ence of cationic protonation and anionic hydrophilicity. A
wide water-to-IL composition range is analyzed and, where
relevant, the mechanism of proton exchange is also investi-
gated. In addition, to address the issue of ionic association the
$\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$ ratio is analyzed, where $\Lambda_{\text{NMR}}$ is calculated ap-
plying the Nernst-Einstein equation to the self-diffusion coef-
ficients obtained by PFG NMR, and $\Lambda_{\text{imp}}$ is the molar conduc-
tivity independently obtained by impedance measurements.

2 Experimental

2.1 Material

$\text{1-Ethyl-3-methylimidazoliubis(trifluoromethanesulfonyl)}$
$\text{-}$
$\text{imide (C$_2$C$_1$ImTFSI), 1-Ethyl-3-methylidazoliumtrifluoro-
$\text{methanesulfonate (C$_2$C$_1$ImTFO), 1-Ethylidazoliubis}$
$\text{(trifluoromethanesulfonyl)imide (C$_2$HImTFSI) and}$
$\text{1-Ethylidazoliumtrifluoromethanesulfonate (C$_2$HImTFO)}$
$\text{were purchased from litiitec Germany and stored in a}$
$\text{glove box until use. The cationic and anionic molecular}$
$\text{structures, along with the proton labeling used in this}$
$\text{work, are shown in Figure 1. H$_2$O-IL mixtures were}$
$\text{prepared with different H$_2$O-to-IL mole ratios,}$
$\text{with}$
$\text{x varying in the range}$
$0 \leq x \leq 1$. H$_2$O-IL samples were analyzed immediately after
preparation.
2.2 PFG NMR

Pulsed field gradient nuclear magnetic resonance (PFG NMR) experiments were performed on a Bruker Avance 600 spectrometer. The stimulated echo pulse sequence was employed to determine the self-diffusion coefficient of the molecular species. All diffusion measurements were performed at 30 °C, at which all samples are in the liquid state. The NMR tubes containing the liquids were thermally equilibrated for 30 minutes before the measurement. Self-diffusion coefficients were obtained by fitting the decay of the echo signal with the Stejskal-Tanner expression,

\[ I = I_0 \exp\{-(\gamma G D \Delta - \frac{D \Delta^2}{3})\} \]

where \( I \) is the signal intensity, \( I_0 \) is the signal intensity of spin-echo at zero gradient, \( G \) is the gradient strength, \( D \) is the diffusion coefficient, \( \Delta \) the length of the gradient pulse, and \( \Delta \) is the diffusion time. The applied linear gradient was varied in the range 0–1200 G/cm, while the diffusion time \( \Delta \) and the pulse duration \( \delta \) were set to 150 and 0.6 ms respectively. The number of acquisitions in each experiment was 16 and the relaxation delay was 12 s. To ensure that thermal convection did not affect our results, we run the diffusion NMR experiments for different \( \Delta \) values (100, 150, 200 ms) whereby the self-diffusion coefficients were observed not to depend on \( \Delta \). The magnetic field gradients were calibrated using a 50/50 mixture of HDO and D\(_2\)O. The consistency of the measured diffusion coefficients from \(^1\)H and \(^19\)F PFG NMR experiments was verified using the reference sample trifluoroethanol (CF\(_3\)CH\(_2\)OH).

2.3 Proton exchange and chemical shift analyses

\(^1\)H NMR spectra were collected for proton exchange and chemical shift analyses on a Varian 400 MHz spectrometer using 5 mm NMR tubes with inserted capillaries filled with octamethylcyclotetrasiloxane as a chemical shift reference. In order to study the proton exchange between water and the ionic liquid, D\(_2\)O-IL mixture were prepared at various concentrations.

2.4 Conductivity measurements

Conductivity measurements were performed on a CDM 210 conductivity meter instrument. Consistently with the procedure used for diffusion measurements, the samples were equilibrated for 30 minutes at 30 °C before collecting data. A dosimeter was used to carefully control the amount of water added to the ionic liquid. The instrument was calibrated with aqueous KCl at a concentration of 0.01 M.

\[ \text{Fig. 2 Single pulse } ^1\text{H NMR spectra of the investigated pure ionic liquids. From bottom to top: } \text{C}_2\text{HImTfO}, \text{C}_2\text{HImTfO}, \text{C}_2\text{HImTfO}, \text{C}_2\text{HImTfO}. \text{The proton resonance of the reference molecule octamethylcyclotetrasiloxane is also indicated.} \]

\[ \text{The NMR peaks assignment is according to the labeling in Fig. 1.} \]

3 Results and discussion

3.1 Effect of water on ionic mobility

Figure 2 shows the single pulse \(^1\)H NMR spectra of the four pure ionic liquids investigated. All proton resonances are well resolved whereas the self-diffusion of different protons could be analyzed independently. Our analysis reveals that all imidazolium protons diffuse at the same rate, with a deviation of only 0.1–1.5 percent, hence we define the self-diffusion of the whole imidazolium molecule as the mean value obtained from the distinct proton resonances. Note that in Figure 2 the resonance of the –NH proton is clearly visible for both C\(_2\)HImTfO and C\(_2\)HImTfO, at 11.04 and 11.99 ppm respectively.

Figure 3 shows the self-diffusion coefficients of the cation (\(D^+\)), the anion (\(D^-\)), and water (\(D_{\text{water}}\)) in the four H\(_2\)O-IL binary systems. We observe that the diffusivity of all molecular species decreases upon addition of water, which is rationalized by an overall decrease of viscosity. An increase in diffusivity with added water had already been observed for ethylmethylimidazolium-ethylsulfate (\(\text{C}_2\text{C}_1\text{Im}^+\text{EtSO}_4^-\)) and ethylmethylimidazolium-triflate (\(\text{C}_2\text{C}_1\text{Im}^+\text{TfO}^-\)), that

\[ \text{§ Note, however, that } D_{\text{water}}, \text{not necessarily is the diffusion coefficient of water but that of the signal corresponding to water protons and other exchangeable protonic protons in the system.} \]
apparently correlates with a decrease of the activation energy when self-diffusion is described by the Arrhenius equation as recently discussed by Menjoge et al.\textsuperscript{19} Similar results have also been discussed for pyrrolidinium hydrogensulfate (Pyrr\textsuperscript{+}HSO\textsubscript{4}\textsuperscript{−}), pyrrolidinium trifluoroacetate (Pyrr\textsuperscript{+}CF\textsubscript{3}COO\textsuperscript{−}),\textsuperscript{8} and ethylmethylimidazolium methanesulfate (C\textsubscript{2}H\textsubscript{5}Im\textsuperscript{+}MeSO\textsubscript{3}−).\textsuperscript{8,19,21,24} Another observation is that the self-diffusivity in pure ionic liquids \textit{(i.e.} at x=0) is lower for the protic ionic liquids as compared to their aprotic analogues, which is consistent with their higher viscosity. It is also interesting to note that in the entire concentration range investigated the cation diffuses faster than the anion. This behavior has previously been observed in pure ionic liquids\textsuperscript{19,24,25} and becomes an anomaly when the cationic size exceeds that of the anion. Indeed, according to the classical Stokes-Einstein relation larger molecules should diffuse slower than smaller molecules, and \textit{vice versa}.	extsuperscript{8} This relation does not hold in some ionic liquids,\textsuperscript{25} which thus do not behave as classical hydrodynamic fluids. In this context, Tokuda \textit{et al.} have found that the \( c \) factor in the Stokes-Einstein relation must be assumed to be smaller than 6 to fit the experimental data from ionic liquids of the C\textsubscript{2}C\textsubscript{1}Im\textsuperscript{+}cation,\textsuperscript{26} and that this factor is smaller for cations than for anions despite their similar van der Waals radii. This intriguing behavior has been ascribed to some degree of anisotropy in the cationic motion, with "\textit{the motion on the ring plane and almost perpendi-\textsuperscript{cular to the 1-alkyl chain being the less hindered one}''}.\textsuperscript{27} The reported van der Waals radii for the ionic species considered in the present study are 0.303 nm (C\textsubscript{2}C\textsubscript{1}Im\textsuperscript{+}), 0.267 nm (TfO\textsuperscript{+}), and 0.327 nm (TFSI\textsuperscript{−}).\textsuperscript{28} The radius for C\textsubscript{2}HIm\textsuperscript{+} is not reported in the literature but can be assumed to be comparable to, or smaller than, that of C\textsubscript{2}C\textsubscript{1}Im\textsuperscript{+}. So, from ionic radii considerations only, it is a 'hydrodynamic anomaly' that the C\textsubscript{2}C\textsubscript{1}Im and C\textsubscript{2}HIm cations diffuse faster than their associated TfO anion.

As mentioned above, one effect of adding water to ionic liquids is the decrease of the self-diffusion activation energy, as revealed by MD simulations.\textsuperscript{19} These simulations, however, also indicate that this decrease becomes less significant at higher water concentrations, more specifically at concentrations with more than 0.7 water molecules per cation:anion pair, \textit{i.e.} for x \( \geq 0.7 \). In good agreement with these findings, we also observe that the effect of water on self-diffusion is stronger at lower concentrations and becomes weaker as more water is added. The behavior displayed in Figure 3 by the system based on C\textsubscript{2}C\textsubscript{1}ImTFSI is slightly different from the others, with plateau values for D\textsuperscript{+} and D\textsuperscript{−} observed for x \( \geq 0.4 \). Upon further addition of water no changes at all are appreciated, which we attribute to the occurrence of phase separation due to the immiscibility of this aprotic ionic liquid with water. For C\textsubscript{2}C\textsubscript{1}ImTfO, that has a more water affine anion, the increase of both D\textsuperscript{+} and D\textsuperscript{−} is observed in the whole concentration range, similarly to the cases of C\textsubscript{2}HImTFSI and C\textsubscript{2}HImTfO.

The issue whether proton transport in ionic liquids can occur \textit{via} the Grotthuss mechanism is currently vividly debated, yet

\begin{center}
\textbf{Fig. 3} Self-diffusion coefficients of cations (D\textsuperscript{+}, ○), anions (D\textsuperscript{−}, ■) and water (D\textsubscript{water}, ▲) as a function of added water in the four investigated ionic liquids. A: C\textsubscript{2}C\textsubscript{1}ImTFSI/water; B: C\textsubscript{2}C\textsubscript{1}ImTfO/water; C: C\textsubscript{2}HImTFSI/water, and D: C\textsubscript{2}HImTfO/water. Dotted lines are guides for the eye.
\end{center}
Fig. 4 Normalized self-diffusion coefficients with respect to the bulk values for the cation (\(D^+/D_{\text{neat}}^+\), ○) and the anion (\(D^-/D_{\text{neat}}^-\), ■) as a function of added water. Dotted lines are guides for the eye.

not conclusively verified. While Noda et al. claim that the proton conduction behavior in non-equimolar mixtures of imidazole and HTFSI follows a combination of Grothuss- and vehicle-type mechanism,\(^{29}\) Blanchard et al. bring to the researchers attention the possibility of an overestimation of self-diffusion values as a result of fast proton exchanges between water (impurities) and protic sites in the time-frame of the diffusion experiments.\(^{30}\) Moreover, Anouti et al. also believe that the proton conduction in water-added pyrrolidinium (protic) ionic liquids can follow a combination of Grothuss- and vehicle-type mechanism, at least in the water-rich domain.\(^{8}\) Achieving a unifying picture is made even more complicated by the fact that the above-mentioned studies concern ionic liquids of very different structures: imidazolium,\(^{29}\) ammonium,\(^{30}\) and pyrrolidinium, respectively.\(^{8}\) Nevertheless, one method to assess the occurrence of the Grothuss mechanism is to verify that the \(D_{\text{NH}}/D_{\text{cation}}\) ratio is significantly higher than unity.\(^{29}\) In the present study, the \(D_{\text{NH}}/D_{\text{cation}}\) ratio for the \(\text{C}_2\text{HImTFSI}\) system shows to be close to one for all water concentrations, see Table 1. This indicates that the main transport mechanism is of vehicular type and that the imidazolium cation keeps its native structure with an intact amine group, at least in time scale of the delay time in diffusion experiment, \(\approx 150\) ms. The latter observation is of key importance for the discussion below, since it tells that the only charges present in solution are the ionic liquid’s cation and anion, excluding the formation of long-lived \(\text{H}_3\text{O}^+\) ions. The \(D_{\text{NH}}/D_{\text{cation}}\) ratio for the \(\text{C}_2\text{HImTfO}\) system could not be calculated due to fast proton exchange during the time scale of the NMR experiment, wherefore the NMR signals of \(-\text{NH}\) group and water are merged into one signal and \(D_{\text{NH}}\) can not be analyzed independently.

Table 1 Excess self-diffusion values expressed as \(D_{\text{NH}}/D_{\text{cation}}\) as a function of added water for \(\text{C}_2\text{HImTFSI}\).

<table>
<thead>
<tr>
<th>mole_{water}: mole_{IL}</th>
<th>(D_{\text{NH}}/D_{\text{cation}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.01</td>
</tr>
<tr>
<td>0.02</td>
<td>1.01</td>
</tr>
<tr>
<td>0.05</td>
<td>1.01</td>
</tr>
<tr>
<td>0.1</td>
<td>0.99</td>
</tr>
<tr>
<td>0.2</td>
<td>1.00</td>
</tr>
<tr>
<td>0.4</td>
<td>1.00</td>
</tr>
<tr>
<td>0.6</td>
<td>0.95</td>
</tr>
<tr>
<td>0.8</td>
<td>0.98</td>
</tr>
<tr>
<td>1</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

A particularly interesting aspect in this context is the concentration dependence of the self-diffusion of water. It increases with \(x\) in the binary systems and by different amounts depending on the ionic liquid’s structure\(^{§}\) \(D_{\text{water}}\) increases only slightly in \(\text{C}_2\text{C}_1\text{ImTFSI}\), while it depends much more strongly on concentration in \(\text{C}_2\text{HImTFSI}\). Indeed, as shown in Figure 3C, water self-diffuses associatively to the \(\text{C}_2\text{HIm}\) cation at very low concentrations (\(x<0.1\)). This associative behavior has not been reported before and may find a plausible explanation in a specific water-cation interaction. Nevertheless, upon more added water (\(x\geq 0.1\)) \(D_{\text{water}}\) increases steeply and water appears to self-diffuse at its distinct rate. For the \(\text{C}_2\text{HImTfO}\), the self diffusion of water could not be independently evaluated for any \(x\) value, due to the merged signals of

\(^{§}\) The self-diffusion coefficient of water does not change in \(\text{C}_2\text{C}_1\text{ImTFSI}\) for \(x\) greater than 0.4, since water and \(\text{C}_2\text{C}_1\text{ImTFSI}\) become immiscible.
–NH group and water, as discussed above.

The different degree by which the self-diffusion of cations and anions is affected by added water can be appreciated from the analysis of the \( D^+ / D^- \) ratio, as also suggested by Stark et al.\(^{21} \) In agreement with the results of Menjoge et al.\(^{19} \) we also find that \( D^+ / D^- \) steadily decreases upon addition of water in C\(_2\)C\(_1\)ImTfO, indicating that the cation is more affected than the anion. But we here also observe that this ratio is almost constant in C\(_2\)C\(_1\)ImTfSi and C\(_2\)HImTfO, while it increases in C\(_2\)HImTfSi for concentrations higher than \( x \geq 0.6 \) (see Figure SI-1\(†\)). Nevertheless, to better understand the diffusional properties on a molecular level, we here propose to analyze the excess ionic diffusivity by expressing the relative self-diffusion coefficients \( D^+/D^+_{\text{neat}} \) and \( D^-/D^-_{\text{neat}} \), as summarized in Figure 4 (where \( D_{\text{neat}} \) is the self-diffusion coefficient measured in the pure ionic liquid).

Even though an overall increase of \( D/D_{\text{neat}} \) is observed as a result of lower viscosity, more subtle differences can be appreciated that depend on the ionic liquid’s molecular structure. The highest increase (four-fold) with respect to the neat ionic liquid is observed for C\(_2\)HImTfO, followed by C\(_2\)C\(_1\)ImTfSi / C\(_2\)HImTfSi (three-fold), and C\(_2\)C\(_1\)ImTfSi (less than two-fold). For C\(_2\)C\(_1\)ImTfSi the effect is limited to concentrations of \( x \leq 0.4 \). Another small but intriguing feature is that while in H\(_2\)O/C\(_2\)HImTfSi at 1:1 concentration \( D_{\text{cation}} \) exceeds \( D_{\text{anion}} \) (Fig. 4C), the opposite is observed at the analogues concentration in C\(_2\)C\(_1\)ImTfO (Fig. 4B).\(^5\)

A plausible explanation of this effect may be that water interacts with the ionic liquid through specific sites, most probably through the –NH group in protic ionic liquids and through the –SO\(_3\) in the TFO anion, that by a drag effect can in turn result in a selective self-diffusion enhancement.\(^5\) This speculation would also explain why \( D^+ \) and \( D^- \) are equally and more greatly enhanced in the ionic liquid C\(_2\)HImTfO, which offers both type of interaction sites. Our hypothesis is in line with recently reported MD simulations and experimental works that reveal the possibility of water-anion hydrogen bonding. These works reveal that while hydrophobic anions like TFSI are not most favorable for strong and directional hydrogen bonds,\(^1\) those with a higher water affinity like TFO do show a tendency to form water-anion complexes.\(^7\) While the nature of water-anion interaction will be investigated in more detail in a separate work with focus on vibrational spectroscopy,\(^8\) the issue of water-cation interaction is further discussed in the next sections.

### 3.2 Effect of water on chemical shift

To further investigate the nature of H\(_2\)O···cation interactions we have analyzed the chemical shifts, \( \delta \) (ppm), in the \(^1\)H NMR spectra of water/IL binary systems, see also Figure SI-2\(†\). While the chemical shifts of imidazolium hydrogens (aromatic and aliphatic) and of water are insignificantly changed upon addition of water to the aprotic C\(_2\)C\(_1\)ImTfSi and C\(_2\)C\(_1\)ImTfO based systems (Figure SI-2A and SI-2B\(†\)), the chemical shifts of the hydrogen in –NH and of water (H\(_2\)O) considerably shift down-field and up-field, respectively in C\(_2\)HImTfSi (Figure SI-2C\(†\)). These shifts are a consequence of lower electron density (deshielding) for the –NH group and higher electron density (shielding) for water,\(^{19,31} \) a clear evidence for a specific C\(_2\)HIm\(^+\)–water interaction through the –NH group, which we now can describe being of hydrogen bonding nature. The effect of hydrogen bonding on the chemical shift of the –NH proton has previously also been discussed for diethylmethylammonium trifluoromethanesulfonate (dem\(^+\)TFO\(^−\))/water and imidazole/HTfSI non-equimolar mixtures.\(^9,29\)

The scenario for C\(_2\)HImTfO is different (Figure SI-2D\(†\)). The \(^1\)H resonances of the –NH proton and of water appear merged and broad at all water concentrations, wherefore the reported chemical shifts assigned to the –NH group are in fact an average of all –NH and water protons as these undergo fast exchange on the time scale for the NMR experiment. This merged peak continuously shifts up-field upon increased water content, while the chemical shift for the other imidazolium hydrogens remains unaltered.

### 3.3 Proton exchange

Having established the existence of hydrogen bonding between water and protic cations, we now investigate the proton exchange mechanism between these two molecular species. To this end, we have analyzed the \(^1\)H NMR spectra of D\(_2\)O/C\(_2\)HImTfSi and D\(_2\)O/C\(_2\)HImTfO systems for increasing D\(_2\)O concentrations, see Figure 5A and 5B respectively. The chemical shift of the –NH group in C\(_2\)HImTfSi, \( \delta_{\text{NH}} \), shifts down-field upon increased D\(_2\)O content, consistently with the results obtained for the H\(_2\)O/IL systems. Moreover, the relative decrease of the \(^1\)H NMR signal intensity assigned to –NH with increasing D\(_2\)O indicates the occurrence of complete proton exchange between the imidazolium protic site –NH and deuterated water. In fact, the complete exchange between –NH and D\(_2\)O in C\(_2\)HImTfSi occurs on a time scale longer than 0.5 ms,\(^5\) in fact longer than 150 ms, which is the time scale of the diffusion experiment. In C\(_2\)HImTfO this proton exchange is so fast that the NMR signals associated to the

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\(†\) The reader should note that in C\(_2\)C\(_1\)ImTfO the deviation of \( D^- \) from \( D^+ \) is considerable in the whole concentration range, as opposed to the other three systems.

\(‡\) That the –SO\(_3\) in TFO interacts with water is indicated by Raman spectroscopic data which will be presented in a separate paper.

\(§\) Yaghini et al., in preparation.

\(\dagger\) This time is calculated as the inverse of the difference in chemical shift (in Hz) multiplied by magnetic field strength.
Fig. 5 $^1$H NMR spectra of D$_2$O/C$_2$HImTFSI (A) and D$_2$O/C$_2$HImTfO(B) for different D$_2$O/IL mole ratios. The $^1$H resonances assigned to DOH (or DOH/H$_2$O) are marked by circles.

Fig. 6 A: Chemical shift map from $^1$H NMR experiments for D$_2$O/C$_2$HImTFSI and B: D$_2$O/C$_2$HImTfO mixtures at different D$_2$O-to-IL mole ratios. Numbers "1(H), 2, 3, 4, 5, 6" correspond to the NMR peaks of Figure 2.

−NH and water are broad and merged for all D$_2$O concentrations here investigated, see Figure 5B.

In Figure 6 we have summarized the chemical shift evolution as a function of added D$_2$O for the two protic ionic liquids. In C$_2$HImTFSI the chemical shift of the −NH proton, $\delta_{1/(H)}$, shifts downfield and decreases in intensity upon added water, while the opposite is observed for the chemical shift of deuterated water, $\delta_{\text{DOH}}$, Figure 6A. This trend is in agreement with that shown in Figure SI-2C and is attributed to a direct NH···OD$_2$ (or ND···OHD) interaction through hydrogen bonding.

The chemical shift and NMR intensity analyses for the D$_2$O/C$_2$HImTfO system reveal a slightly different scenario, Figure 6B. The single broad and merged −NH/DOH $^1$H resonance shifts up-field upon addition of D$_2$O (see also Figure 5B) and its intensity evolution as a function of added D$_2$O also indicates a proton exchange between the C$_2$HImTfO cation and deuterated water. In this case however, due to the merged character of the $^1$H resonance, a quantitative estimation of the proton exchange would require further analyses, which is outside the scope of this work. We limit our discussion to the observation that the proton exchange between water and C$_2$HImTfO is much faster than in the analogues C$_2$HImTFSI system, i.e. faster than 0.5 ms.
For a comparison of the state of water in the different binary systems, the chemical shift of the \( ^1\text{H} \) resonance associated to water as a function of concentration is shown for all ionic liquids in Figure 7. This plot reveals different states of water that depend on the surrounding cation:anion pairs. While \( \delta_{\text{H}_2\text{O}} \) has a low value and is almost unaltered in aprotic ionic liquids, it is more concentration dependent in the protic ones. Indeed, at any concentration the chemical shift of water increases in the order C\(_2\)C\(_1\)ImTFSI < C\(_2\)C\(_1\)ImTFO < C\(_2\)HImTFSI < C\(_2\)HImTFO, \(^*\) which is also the order in which hydrophilicity increases. This trend indicates that water is found in a more hydrogen bonded state in the protic ionic liquids as well as in the presence of the TfO anion, consistently with an increased hydrophilicity of the ionic liquid (see order above). We can anticipate that this behavior is consistent with the frequency shift observed in the water sensitive range 3200–4000 cm\(^{-1}\) of infrared spectra (not shown here). This behavior also indicate a more intimate mixing of water with the protic ionic liquids, which is also reflected by self-diffusion values of water presented in Figure 3. Here, the reader should recall that the chemical shift values given for C\(_2\)HImTFO in fact also include contributions from the –NH group. Thus, to qualitatively compare the state of water in the two protic ionic liquids we have calculated the population averaged chemical shift for C\(_2\)HImTFSI, \( \delta_{\text{calc}} = p\delta_{\text{water}} + (1-p)\delta_{\text{NH}} \), where \( p \) is the fraction of water protons in the system, i.e. \( n_{\text{water}}/(n_{\text{water}} + n_{\text{NH}}) \). The result is shown in Figure 7 as red asterisks. The good overlapping of the observed average chemical shift for C\(_2\)HImTFO with the calculated one for C\(_2\)HImTFSI indicates that the state of water in the two systems is very similar, and so should the proton exchange mechanism also be, the difference being mainly in the kinetics of the exchange process. We deduce that the faster exchange process observed for C\(_2\)HImTFO is induced by the TfO anion. With this respect, it is also interesting to note that as can be deduced from the chemical shifts in the pure ionic liquids (11.99 ppm in C\(_2\)HImTFO and 11.04 ppm in C\(_2\)HImTFSI), the proton in the –NH group is more ’acidic’ when associated to the TfO anion. This difference can also explain the small but appreciable deviation between the observed and calculated averaged chemical shift curves at very low water contents, see Figure 7.

### 3.4 Effect of water on ionic conductivity

In addition to the self-diffusion coefficients and the chemical shifts, we have also measured the ionic conductivity in order to achieve a more thorough picture of the transport properties in these water-added ionic liquid systems. The experimentally measured ionic conductivities are shown as a function of composition in Figure 8.

At very low water concentrations (\( x<0.2 \)) the ionic conductivities in C\(_2\)C\(_1\)ImTFSI and C\(_2\)C\(_1\)ImTFO are comparable, and higher than those of C\(_2\)HImTFSI and C\(_2\)HImTFO (see Figure 8A). The lower conductivity observed in the protic ionic liquid based systems qualitatively agrees with the trend observed from diffusion NMR experiments (see Figure 3). Furthermore, while the ionic conductivity in C\(_2\)HImTFSI, C\(_2\)HImTFO, and C\(_2\)C\(_1\)ImTFO based systems steadily increases with water concentration, that in C\(_2\)C\(_1\)ImTFSI shows no changes for \( x>0.4 \) as a result of phase separation, and in agreement with the self-diffusion trend (see section 3.1). Figure 8 also shows that the relative increase in conductivity with respect to the neat ionic liquid (\( x=0 \)) is more enhanced for the TfO based ionic liquids. The overall increase in ionic conductivity with water content is in agreement with the data reported by Anouti et al. for the ionic liquids (PyrHSO\(_4\)) and (PyrCF\(_3\)COO),\(^8\) and has been tentatively attributed to a more dissociative character of the ionic species in solution.

However, the issue of ionic dissociation is more properly investigated by analyzing the molar conductivity ratio \( \Lambda_{\text{imp}}/\Lambda_{\text{NMR}} \) also referred to as ”ionicity”, where \( \Lambda_{\text{imp}} \) is the molar conductivity obtained from impedance experiments and \( \Lambda_{\text{NMR}} \) is the molar conductivity calculated from NMR self-diffusion coefficients. Indeed, while impedance

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\(^*\) To remind, however, that for the latter the chemical shift of water is merged with that of –NH.

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\(^8\) Anouti et al.
Fig. 8 A: Ionic conductivity measured at 30 °C for the water added ionic liquids. B-E: Concentration dependence of molar conductivity obtained from diffusion NMR and impedance measurement.

experiments probe the mobility of charged species only, by diffusion NMR any species in motion is detected regardless its complexation state. \( \Lambda_{\text{NMR}} \) can be estimated from self-diffusion values using the Nernst-Einstein (NE) equation \( \Lambda_{\text{NMR}} = \frac{F^2}{RT} \left( D_{\text{cation}} + D_{\text{anion}} \right) \) where \( F \) is the Faraday constant and \( R \) is the universal gas constant.\(^{32} \) The equation mentioned above is derived for non-interacting ions in infinite dilute electrolyte solutions, assuming that all ionic mobile species contribute to molar conductivity.\(^{32} \) However, Harris et al.\(^{33} \) and Hayamizu et al.\(^{34} \) have recently proposed a slightly modified form of this equation to better suit the complexity of electrolyte solutions and ionic liquids. Anywise, in the field of ionic liquids the \( \Lambda_{\text{imp}}/\Lambda_{\text{NMR}} \) ratio is extensively used as an indicator of the dissociation degree in ionic liquids.\(^{35–37} \)

Figure 8B-E shows that \( \Lambda_{\text{imp}} \) is smaller than \( \Lambda_{\text{NMR}} \) in all ionic liquids at all water concentrations. A value of \( \Lambda_{\text{imp}}/\Lambda_{\text{NMR}} \) smaller than unity (Figure 9) means that part of the ionic species are associated and do not contribute to ionic conductivity. Interestingly, the ionicity in the investigated ionic liquids follows the order \( \text{C}_2\text{C}_1\text{ImTFSI} > \text{C}_2\text{C}_1\text{ImTfO} \approx \text{C}_2\text{HImTFSI} > \text{C}_2\text{HImTfO} \), at least at very low (or zero) water concentrations. This trend is consistent with the results recently discussed by Tokuda et al. who observed that for identical cations the ionicity is higher for TFSI as compared to TfO.\(^{26} \) The \( \Lambda_{\text{imp}}/\Lambda_{\text{NMR}} \) values reported for the pure ionic liquids \( \text{C}_4\text{C}_1\text{ImTFSI} \) and \( \text{C}_4\text{C}_1\text{ImTfO} \) are also indicated in Figure 10 for comparison (red symbols). This comparison shows that keeping the same anion, the ionicity is lower in \( \text{C}_4\text{C}_1\text{Im}^+ \) cations as compared to the \( \text{C}_2\text{C}_1\text{Im}^+ \) counterpart. It is also interesting to note that the protonation of the imidazolium cation reduces the ionicity of the system, as reflected by lower \( \Lambda_{\text{imp}}/\Lambda_{\text{NMR}} \) values. This may be a result of stronger ion-ion interaction in protic ionic liquids, as also discussed by Miran et al.\(^{36} \) Upon addition of water, the ionicity of the protic ILs increases suggesting that water is capable of interfering with the native cation-anion coulombic forces, consistently with the observed cation-water interactions discussed above. By contrast, the ionicity of \( \text{C}_2\text{C}_1\text{ImTFSI} \) and \( \text{C}_2\text{C}_1\text{ImTfO} \) are much less affected by added water.

### 4 Conclusions

In this work we have investigated the transport properties in water/ionic liquid binary systems by performing PFG-STE NMR and conductivity measurements. To better understand...
how the molecular structure influences the local dynamics, we have investigated different ionic liquids with a systematic variation of aprotic/protic cations (C2C1Im+ and C2HIm+) and more or less hydrophilic anions (TfO− and TFSI−). Overall, the addition of water enhances the mobility of all ionic species, which results in higher self-diffusion coefficients and ionic conductivities. However, the degree by which cation and anions are individually affected strongly depends on their molecular structure.

In C2C1ImTFSI, which is representative for hydrophobic and water immiscible ionic liquids, the dynamical effects are limited to a narrow concentration range, beyond which phase separation occurs. In this system, cations and anions are equally affected and no specific water-ion interaction is suspected. For its protonated counterpart, C2HImTFSI, an associating diffusional behavior is detected for water and cation at very low water concentrations, whereas at high water contents the imidazolium cation is speeded up more than the anion. By contrast, in C2C1ImTfO the anion is the species most affected at high water contents, while in C2HImTfO both ions are affected in a similar way. These findings suggest preferential interaction sites for water, that are the −NH group in protic ionic liquids and the −SO3 group in the TfO anion, a scheme of interaction that can explain the selective self-diffusion enhancements that we observe. In the protic ionic liquids the interaction between water and the −NH group on the imidazolium is manifested by proton exchange, which is much faster in C2HImTfO as compared to C2C1ImTfO. Moreover, the analysis of the molar conductivity obtained by impedance measurements and from diffusion NMR reveals that the ionicity (λimp/λNMR) is lower in the protic ionic liquids than in the aprotic, in longer chain cations than in shorter, and for cations in association with TfO than with TFSI. This trend further proofs the tendency for complexation once sites of interaction are provided.

Altogether these results represent a considerable step forward with respect to a better understanding of the structure-property relationship in water added ionic liquids. In addition, our results provide new and important indications for the design of ionic liquid based electrolytes in which the addition of water can selectively enhance the mobility of specific ionic species.

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