



UNIVERSIDADE ESTADUAL DE CAMPINAS  
SISTEMA DE BIBLIOTECAS DA UNICAMP  
REPOSITÓRIO DA PRODUÇÃO CIENTÍFICA E INTELLECTUAL DA UNICAMP

**Versão do arquivo anexado / Version of attached file:**

Versão do Editor / Published Version

**Mais informações no site da editora / Further information on publisher's website:**

<https://pubs.rsc.org/en/content/articlelanding/2019/cp/c8cp07071g>

**DOI: 10.1039/c8cp07071g**

**Direitos autorais / Publisher's copyright statement:**

©2019 by Royal Society of Chemistry. All rights reserved.

DIRETORIA DE TRATAMENTO DA INFORMAÇÃO

Cidade Universitária Zeferino Vaz Barão Geraldo

CEP 13083-970 – Campinas SP

Fone: (19) 3521-6493

<http://www.repositorio.unicamp.br>



Cite this: *Phys. Chem. Chem. Phys.*,  
2019, 21, 2567

## Dealing with supramolecular structure for ionic liquids: a DOSY NMR approach†

Marcileia Zanatta,<sup>id</sup>\*<sup>a</sup> Víctor U. Antunes,<sup>id</sup><sup>b</sup> Cláudio F. Tormena,<sup>id</sup><sup>b</sup>  
Jairton Dupont<sup>id</sup><sup>a</sup> and Francisco P. dos Santos<sup>id</sup>\*<sup>a</sup>

Diffusion-ordered spectroscopy (DOSY) is arguably a powerful method for the NMR analysis of ionic liquids, since the self-diffusion coefficients for cations and anions can be measured straightforwardly. In this work, the dynamic-structural behaviour of imidazolium ionic liquids containing different anions has been investigated by experimental measurements of direct <sup>1</sup>H diffusion coefficients in chloroform and water solutions. The influence of ion structure has been tested by using six IL salts formed by the association of different cations (1-*n*-butyl-3-methylimidazolium, 1,2,3-trimethylimidazolium and tetra-*n*-butylammonium) with different anion structures (prolinate, acetate and *o*-trifluoromehtylobenzoate). The influence of IL concentration (from 0.01 to 0.5 mol L<sup>-1</sup>) was also evaluated for BMI-Pro. The contact ion pairs (or aggregates) are maintained in both chloroform and water within the range of concentrations investigated. In the particular case of 1,2,3-trimethylimidazolium imidazolate (TMI-Im) containing confined water in DMSO the maintenance of the contact ion pairs depends on the water content which may even disrupt the IL supramolecular structure.

Received 15th November 2018,  
Accepted 6th January 2019

DOI: 10.1039/c8cp07071g

rsc.li/pccp

### Introduction

Ionic liquids (ILs) can be formed by almost infinite combinations of different cations and anions. The physicochemical properties of ILs can be modulated according to their structural functionality, which allows the optimization of solvent properties for a given application. Thus, ILs can serve as solutions for a wide variety of applications, *e.g.* electrochemistry, in batteries, CO<sub>2</sub> capture and reuse and as designer solvents for chemical synthesis.<sup>1,2</sup>

Some researchers have demonstrated that many ILs have an internal supramolecular structure. Such structure has been theoretically proved in imidazolium ILs to be responsible for the formation of a polar domain, consisting of the imidazolium ring and the anion, and a nonpolar domain, composed of the alkyl chains. In this kind of ILs, the ions are surrounded by their counter-ions at any given time, forming ion pairs or aggregates.<sup>3</sup> These associations of ions and ion-solvent interactions have been thoroughly researched, because they can affect the applications of ILs due to changes in chemical solubility, reactivity and selectivity.<sup>4-8</sup>

Since ILs are concentrated electrolyte solutions, interpretation of their transport properties is very complicated. Therefore, an

understanding of the transport properties of the ions in the ionic liquids is important for designing new ILs for electrolytes.<sup>9</sup> The combined use of <sup>1</sup>H NMR diffusion ordered spectroscopy (DOSY) and NMR relaxation measurements provides useful alternatives for extracting information concerning the relative molecular motions of ions in solution.<sup>10-12</sup>

Mo and co-workers have measured the self-diffusion coefficients of the cation and anion of tetrabutylammonium tetrahydridoborate (TBA·BH<sub>4</sub>). They observed that the self-diffusion of the anion was only slightly faster than that of the cation. These results indicated that the tight ion pair contact is the primary diffusive species.<sup>10</sup> Likewise, Katsuta and co-workers have measured the aqueous ion pair formation constants for a series of 1-alkyl-3-methylimidazolium salts with different anions. They demonstrated that the stability of the contact ion pair in water increases with increasing alkyl chain length of the 1-alkyl-3-methylimidazolium cation because of the decreased hydration of the cation.<sup>13</sup> Tsuzuki *et al.* calculated the self-diffusion coefficients of ions in 13 ILs, from molecular dynamics simulations, using a refined force field, and compared them with the experimental results.<sup>9</sup>

In other significant studies, imidazolium salts with NTf<sub>2</sub><sup>-</sup> anions have been investigated by <sup>1</sup>H and <sup>19</sup>F NMR self-diffusion techniques. The contact ion pair was reported as the dominant species at low concentrations, while at higher concentrations, the presence of aggregate species was detected.<sup>14</sup> Rollet and co-workers demonstrated an increase in self-diffusion coefficients with increasing water content in BMI-NTf<sub>2</sub>/water systems. The authors suggested that an increased amount of water results in

<sup>a</sup> Institute of Chemistry, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500 Porto Alegre 91501-970 RS, Brazil. E-mail: fpsantos@ufrgs.br, marcizanatta@ufrgs.br

<sup>b</sup> Institute of Chemistry, University of Campinas, UNICAMP, P. O. Box: 6154, 13083-970, Campinas, SP, Brazil

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8cp07071g

the formation of a network of water-rich channels.<sup>15</sup> A similar finding has recently been reported by Cabrita and co-workers. They analyzed the rotational and translational behaviors of ions in BMI-BF<sub>4</sub>/water mixtures and suggested that the incorporation of water in the IL nanostructure pockets maintains the cation/anion interactions present in the neat IL.<sup>16</sup> Recently Zhang and Maginn modified the concept of the ion-pair, stating that the ion-pair remains intact until another anion comes closer to the cation.<sup>17</sup> Scharf *et al.* studied the concentration dependence of the self-diffusion coefficients of both the cation and anion. They concluded that the self-diffusion coefficients (*D*) of the cation and anion would also differ if the IL is completely dissociated.<sup>18</sup> Furthermore, literature reports demonstrated the apparent breakdown of the validity of the Stokes–Einstein equation, which is observed when the translational motion is dominated by the rapid movement of the individual contact ion pairs between the IL aggregates.<sup>11,18</sup>

Despite the current interest in ILs, some important questions, related to the nature of the solvent–solute interactions and the structural changes caused by water solvation, remain unclear.<sup>19–21</sup> Furthermore, although the self-diffusion properties of ILs have been studied by several groups using <sup>1</sup>H and <sup>19</sup>F NMR<sup>14–16,21–24</sup> only a few of them have reported the use of hydrogenated anions for directly comparing the self-diffusion using <sup>1</sup>H NMR.<sup>10,25</sup>

In the present study, the direct self-diffusion coefficients for different ILs (Fig. 1) were determined to study the cation–anion and ion–solvent interactions. The effects of the cation, anion, and water in IL organization and contact ion pair formation have also been studied using a stimulated-echo NMR pulse sequence for diffusion measurements.

## Results and discussion

Since ILs are surrounded by a number of ions, the ion pair concept is hard to define in this case. The “conventional” definition describes an ion pair as a pair of oppositely charged species that acts like a single unit in a water solution. However, in a neat IL, given that each ion is surrounded by a solvation shell of counter-ions, an ion pair is defined by a new concept,

which describes an ion pair as two oppositely charged ions in solution staying together at a separation, *r*, for a time longer than that needed to diffuse over such a distance.<sup>26,27</sup>

For our study, we chose a series of proline ILs with different cations to study their influences on the organization of the ILs and the formation of the contact ion pair by using the self-diffusion coefficient as an experimental parameter. This was followed by testing of the BMI salts with different anions, in order to analyze the anion effect. As a final point, the water pocket effect was also investigated.

Table 1 shows the diffusion coefficients of the cations and the anions of a series of proline ILs in D<sub>2</sub>O and CDCl<sub>3</sub>.

In order to evaluate the strength of the interactions between the cation and the anion, we have defined a parameter *R* as the ratio *D*<sup>+</sup>/*D*<sup>−</sup> (Table 1),<sup>28,29</sup> where the values near to 1 suggest a higher affinity between the ion pair. For chloroform solution similar diffusion coefficient values for the anion and cation are observed (Table 1). For aqueous solution, a weak interaction with the anion is observed for the ammonium salt (entry 1). The comparison between 1-*n*-butyl-3-methylimidazolium (BMI), 1,2,3-trimethylimidazolium (TMI) and tetra-*n*-butylammonium (TBA) (entries 1–3) shows that BMI has a stronger interaction than TMI and TBA with the anion. This can be related to the possibility of H-bonding, between the hydrogen atom of the cation and the oxygen atom of the anion, in BMI. This interaction is not observed in TMI due to the presence of a protecting group (CH<sub>3</sub>). A H-bond donating ability is usually a property of the cation, while the anion acts as the H-bond acceptor, resulting in contact ion pairing or the formation of aggregate structures.<sup>12</sup>

The experimental diffusion coefficients of different ionic liquids show the following trend for the cations: BMI > TMI > TBA in CDCl<sub>3</sub> and TMI > BMI > TBA in D<sub>2</sub>O. The order change may be related to the greater proximity of the cation and the anion in BMI-Pro than in the other ILs, observed by an *R* value close to 1. The fact that the diffusion of the ions in alkyl ammonium based ionic liquids is slower than that in ionic liquids composed of aromatic cations has already been reported in the literature, probably due to the higher hydrodynamic radius.<sup>22,30</sup>

Once the IL is dissolved in an organic solvent, contact ion pairing becomes increasingly likely with the decreasing dielectric constant of the solvent. As demonstrated in Table 1 (see ESI† Fig. S1–S3), for three ILs, the diffusion coefficients were the same for the cations and anions, in CDCl<sub>3</sub>, and different in D<sub>2</sub>O, suggesting the proximity of ions in less polar solvents (Fig. 2).<sup>31,32</sup>

BMI salts with different anions (proline – Pro, acetate – OAc and *o*-trifluoromethylbenzoate – CO<sub>2</sub>BzCF<sub>3</sub>) were tested in order to analyze the anion effect (Table 2).

The diffusion coefficients of the cations and the anions are again essentially indistinguishable in CDCl<sub>3</sub> (Table 2). The opposite behaviour was observed in D<sub>2</sub>O, where dissociation of ions could be detected by the difference in experimental diffusion coefficients, like in the study of the cation’s effect. Taking into account the *R* values in polar solvents (D<sub>2</sub>O), it is possible to predict the ion pair strength according to the anion: Pro > CO<sub>2</sub>BzCF<sub>3</sub> > OAc. The similarity of *D* values for the

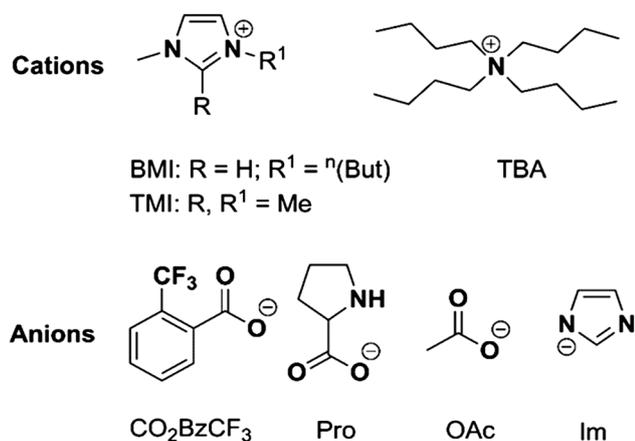
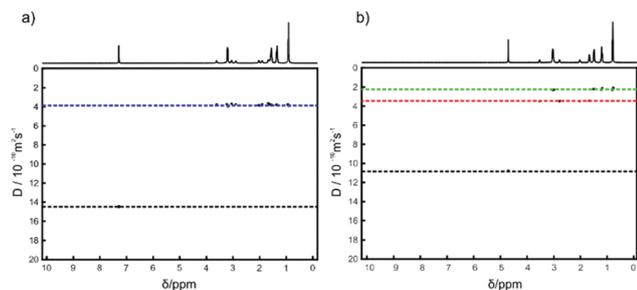


Fig. 1 Chemical structure of the ionic liquids studied.

**Table 1** Diffusion coefficients ( $D^+$  for cation and  $D^-$  for anion) of the prolinatate ILs ( $0.1 \text{ mol L}^{-1}$ ) with different cations, and the ratio  $R$  defined by  $D^+/D^-$ <sup>a</sup>

Entry	IL	CDCl <sub>3</sub>			D <sub>2</sub> O		
		$D^+$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$D^-$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$R$	$D^+$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$D^-$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$R$
1	TBA-Pro	$3.78 \pm 0.02$	$3.78 \pm 0.02$	1.00	$2.21 \pm 0.02$	$3.48 \pm 0.02$	0.64
2	TMI-Pro	$4.60 \pm 0.02$	$4.60 \pm 0.02$	1.00	$5.43 \pm 0.02$	$4.20 \pm 0.02$	1.29
3	BMI-Pro	$5.74 \pm 0.02$	$5.74 \pm 0.02$	1.00	$4.33 \pm 0.02$	$4.05 \pm 0.02$	1.07

<sup>a</sup> Measurements were performed on the TBI probe at 293 K. See ESI (Fig. S1–S3).



**Fig. 2** <sup>1</sup>H DOSY (600.17 MHz, 293 K), with [top] the least attenuated 1D spectrum of  $0.1 \text{ mol L}^{-1}$  of TBA-Pro: (a) in CDCl<sub>3</sub> and (b) in D<sub>2</sub>O. The signal in blue corresponds to the contact ionic pair, in black corresponds to the solvent, in green corresponds to the cation and in red to the anion.

cation and anion in different ILs indicates the presence of a cooperative transport phenomenon, suggesting that the ions move as contact ion pairs.<sup>11,29</sup>

In order to investigate the effect of concentration on the ratio of the anion and cation ( $R$ ) self-diffusion coefficients, *i.e.*, in the spatial proximity between the ion pair, experiments were carried out varying the concentration of BMI-Pro in CDCl<sub>3</sub> and in D<sub>2</sub>O (Table 3).

A decrease in the diffusion coefficients of the ions can be observed when the concentration of BMI-Pro increases, most likely due to the increase in viscosity or an obstruction effect.

For both solvents, the ratios of the coefficients of the contact ion pair did not change with an increase in concentration. In water, the ratio of  $D^-$  and  $D^+$  is around 1.05, suggesting a small separation of the contact ion pairs (solvation effect). In contrast, in CDCl<sub>3</sub>, the  $R$  values equal 1 across the concentration range, suggesting strong contact ion pair interactions. Both of these observations indicate that upon dilution of the IL in these solvents, the cation and anion do not dissociate completely but remain significantly ion-paired or even aggregated.

Water is one of the most commonly occurring impurities in ILs, which may dramatically influence their properties as well as the selectivity and reproducibility of chemical reactions carried out in ILs. The IL structure can be changed by the water molecules due to the water–ion interactions.<sup>19</sup> A previous study reported that a small amount of an impurity in an IL leads to a significant difference in the measured self-diffusion coefficient.<sup>33</sup> For these reasons, 1,2,3-trimethylimidazolium imidazololate (TMI-Im), a hygroscopic IL previously studied by other techniques, was chosen for this study.

In our previous work, we have already proved the formation of a guest@host complex between an IL and water.<sup>34</sup> Here, we would try to understand how this water pocket could influence the diffusion of the ions.

Water can form hydrogen bonding networks within an IL, and depending on its concentration, cause profound effects on

**Table 2** Diffusion coefficients  $D^+$  for the cation and  $D^-$  for the anion of BMI-X ILs ( $0.1 \text{ mol L}^{-1}$ ) with different anions (X) and the ratio  $R$  defined by  $D^+/D^-$  at 293 K

Entry	IL	CDCl <sub>3</sub>			D <sub>2</sub> O		
		$D^+$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$D^-$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$R$	$D^+$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$D^-$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$R$
1	BMI-Pro <sup>a</sup>	$5.74 \pm 0.02$	$5.74 \pm 0.02$	1.00	$4.33 \pm 0.02$	$4.05 \pm 0.02$	1.07
2	BMI-OAc <sup>a</sup>	$7.79 \pm 0.04$	$7.79 \pm 0.04$	1.00	$5.88 \pm 0.03$	$7.20 \pm 0.03$	0.82
3	BMI-CO <sub>2</sub> BzCF <sub>3</sub> <sup>b</sup>	$7.66 \pm 0.04$	$7.66 \pm 0.04$	1.00	$5.52 \pm 0.02$	$4.79 \pm 0.02$	1.15

<sup>a</sup> Measurements were performed on the TBI probe. <sup>b</sup> Measurements were performed on the TBO probe. See ESI Fig. S4 and S5.

**Table 3** Diffusion coefficients  $D^+$  for the cation and  $D^-$  for the anion of BMI-Pro for studying the concentration influence at 293 K

Entry	Concentration ( $\text{mmol L}^{-1}$ )	CDCl <sub>3</sub> <sup>a</sup>			D <sub>2</sub> O <sup>b</sup>		
		$D^+$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$D^-$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$R$	$D^+$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$D^-$ ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$R$
1	10	$8.28 \pm 0.05$	$8.28 \pm 0.05$	1.00	—	—	—
2	25	$8.06 \pm 0.03$	$8.06 \pm 0.03$	1.00	$5.93 \pm 0.02$	$5.71 \pm 0.02$	1.04
3	50	$7.59 \pm 0.03$	$7.59 \pm 0.03$	1.00	$5.85 \pm 0.02$	$5.55 \pm 0.02$	1.05
4	100	$5.74 \pm 0.02$	$5.74 \pm 0.02$	1.00	$5.69 \pm 0.03$	$5.22 \pm 0.02$	1.09
5	200	$5.29 \pm 0.03$	$5.29 \pm 0.03$	1.00	$5.28 \pm 0.03$	$4.94 \pm 0.02$	1.07
6	500	$2.63 \pm 0.05$	$2.63 \pm 0.04$	1.00	$4.61 \pm 0.02$	$4.40 \pm 0.02$	1.05

<sup>a</sup> Measurements were performed on the TBO probe. <sup>b</sup> Measurements were performed on the TBI probe. See ESI Fig. S6 and S7.

**Table 4** Diffusion coefficients  $D^+$  for the cation and  $D^-$  for the anion of ILs for studying the water influence in DMSO- $d_6$  at 298 K

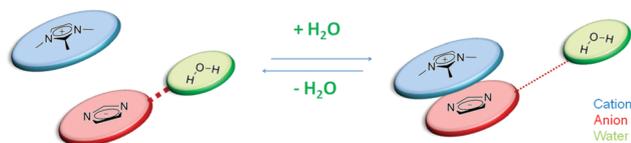
Entry	IL	$D^+$ ( $10^{-10}$ m $^2$ s $^{-1}$ )	$D^-$ ( $10^{-10}$ m $^2$ s $^{-1}$ )	$D_{H_2O}$ ( $10^{-10}$ m $^2$ s $^{-1}$ )	$\delta$ H $_2$ O (ppm)	$R$
1	TMI-Im <sup>a</sup>	2.80 ± 0.02	3.80 ± 0.02	5.50 ± 0.02	4.80	0.74
2	TMI-Im dry <sup>b,c</sup>	2.62 ± 0.02	3.06 ± 0.02	4.00 ± 0.01	6.27	0.86
3	TMI-Im <sup>b</sup>	2.80 ± 0.02	3.07 ± 0.02	4.51 ± 0.03	4.98	0.91
4	TMI-Im wet <sup>b,d</sup>	2.81 ± 0.02	2.98 ± 0.02	5.67 ± 0.08	4.70	0.94
5	—	—	—	9.35 ± 0.02 <sup>e</sup>	3.32	—

<sup>a</sup> 0.1 mol L $^{-1}$ . <sup>b</sup> 1 mol L $^{-1}$ . <sup>c</sup> Dried with molecular sieves. <sup>d</sup> Adding 25  $\mu$ L of water. <sup>e</sup> DMSO containing water. See ESI Fig. S8–S10.

the self-diffusivities of various species.<sup>35</sup> In the case of Im as an anion,  $\pi$  stacking interactions are possible between the aromatic rings, that indicates the small distance among ion. The diffusion coefficient of ions is a result of the balance between cation–anion–water interactions. When analyzing the IL's diffusion coefficients for TMI-Im in DMSO at a concentration of 0.1 mol L $^{-1}$  and 1 mol L $^{-1}$  (Table 4), the approximation of ions is better at the higher concentration.  $R$  increases from 0.74 at the diluted concentration (0.1 mol L $^{-1}$ ) to 0.91 at the higher concentration (1 mol L $^{-1}$ ) (entries 1 and 3). However, due to a strong interaction between the anion and water, a small difference is always observed between  $D^+$  and  $D^-$ .

The  $^1$ H NMR spectra and DOSY (Fig. S8–S11, see ESI $^\dagger$ ) for the 1 mol L $^{-1}$  solution of TMI-Im in DMSO- $d_6$  were evaluated using samples containing different amounts of water (Table 4). The decrease in the diffusion coefficient of H $_2$ O ( $D_{H_2O}$ ) in TMI-Im related to free water in DMSO reinforces the idea of interactions between ions and water. As previously reported by X-ray crystallography and DFT calculations, the nitrogen atom of the anion can strongly interact with the hydrogen from water to form a hydrogen bond.<sup>34</sup> In addition, the water–anion interaction is evident in the chemical shift of the H $_2$ O signal. A higher chemical shift represents more acidic hydrogen and consequently stronger H-bonds.<sup>36</sup> Fig. S11 (ESI $^\dagger$ ) shows the variation of the  $^1$ H NMR chemical shift for the water signal and suggests that the lower amount of water corresponds to a higher frequency in the  $^1$ H NMR spectrum for the water molecule. The addition of water to the IL (Table 4) reduces the water–anion interactions, thereby increasing the cation–anion interactions. Furthermore, the cation and anion diffusion coefficients are similar when a small amount of water (wet IL) is added (Table 4). This suggests that the small amount of water that is naturally present in ILs (including in ILs dried over molecular sieves) forms an extremely strong H-bond with the anion, resulting in the separation of the  $\pi$ -system and a greater difference ( $R = 0.91$ ) between  $D^-$  and  $D^+$ . Similar H-bond formation have been demonstrated by far-infrared difference spectra and DFT-calculations, supporting the present results.<sup>37</sup>

The addition of more water (wet IL) increases the cation–anion interaction due to strengthening of the  $\pi$ -stacking interaction.

**Fig. 3** Interactions between cation–anion–water.

As a result, the ions are closer together, thereby maintaining their organized structure (Fig. 3). In similar studies, a significant change in the diffusivity of ILs has been observed by the addition of water at a concentration slightly higher than one water molecule per one IL molecule; however, further increase in the water concentration leads to a less pronounced effect on the diffusion coefficients of the IL ions.<sup>38</sup>

## Conclusions

Diffusion measurements in different experimental conditions strongly suggest that the dynamics of proline, acetate and *o*-trifluoromethylbenzoate containing ILs follow a universal mechanism governed by the formation or breaking of contact ion pairs.<sup>17</sup> It was also demonstrated that contact ion pair formation although favoured in less polar solvents is also maintained in water in the case of BMI-Pro. The change in the cation (BMI, TMI and TBA) and anion (Pro, OAc and CO $_2$ BzCF $_3$ ) induces some variations in the diffusion coefficient. Even at low concentration (0.01 mol L $^{-1}$ ), BMI-Pro results in the formation of contact ion pairs or aggregates in CDCl $_3$  with similar behaviour in D $_2$ O. This is the first report of the simultaneous measurement of the self-diffusion coefficients for ILs using  $^1$ H NMR DOSY for anions and cations, observing the formation of the water–cation–anion structure. In addition, the amount of water in the IL demonstrates an important contribution to the supramolecular structural organization of the ions.

## Experimental

### Synthesis of ionic liquids

The BMI-Cl salts were prepared according to the literature from 1-methylimidazole and chlorobutane<sup>39</sup> and TMI-I salts were prepared according to the literature from 1-2-dimethylimidazole and iodomethane.<sup>34</sup> TBA-I (tetra-*n*-butylammonium iodide) was purchased from Sigma Aldrich.

BMI-Pro, BMI-OAc, BMI-CO $_2$ BzCF $_3$ , TMI-Pro, TMI-Im and TBA-Pro were prepared by anion exchange of the halogenated salt according to the literature, using an anion exchange resin (AMBERLITE IRA-400 OH (SUPELCO)).<sup>34</sup>

### NMR experiments

NMR spectra were acquired on a 14.08 Tesla Bruker Avance-III spectrometer with a TBI probe and TBO (operating at 600.17 for  $^1$ H), equipped with a  $z$ -gradient coil producing a nominal maximum gradient of 55 G cm $^{-1}$ . Samples containing 0.1 mol L $^{-1}$

or 1 mol L<sup>-1</sup> of each IL in 0.7 mL of solvent (D<sub>2</sub>O, CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub>) in a 5 mm NMR tube were evaluated.

For the <sup>1</sup>H diffusion measurements (DOSY), the experiments were carried out applying a stimulated-echo NMR pulse sequence (Oneshot45)<sup>40</sup> with the delay for gradient recovery (d16) and duration of the gradient purge pulse (p19) at 0.2 and 0.6 ms, respectively. The total diffusion-encoding pulse duration (p30) and diffusion delay Δ (d20) were optimized for each sample. Sixteen nominal gradient amplitudes ranging from 4.8 to 38.4 G cm<sup>-1</sup> were chosen to give equal steps in gradient squared; each FID was acquired using 32 k data points. The <sup>1</sup>H DOSY spectra were constructed in the DOSY Toolbox<sup>41</sup> processing with two zero fillings and line broadening of 5 Hz.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

Thanks are due to the following Brazilian agencies: CNPq (167156/2014-4), (421248/2016-5), (169462/2017-0), CAPES (88881.158804/2017-0), FAPERGS (16/2551-0000), (18/2551-0000561-4), and FAPESP (2015/08541-6) for partial financial support and to CNPq for the fellowship of C. F. T.

## References

- P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA, 2008, pp. 689–704.
- T. Welton, *Coord. Chem. Rev.*, 2004, **248**, 2459–2477.
- B. Kirchner, F. Malberg, D. S. Firaha and O. Hollóczki, *J. Phys.: Condens. Matter*, 2015, **27**, 463002.
- N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.
- J. Dupont, R. F. de Souza and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667–3692.
- H. Olivier-Bourbigou, L. Magna and D. Morvan, *Appl. Catal., A*, 2010, **373**, 1–56.
- J. Dupont, *Acc. Chem. Res.*, 2011, **44**, 1223–1231.
- J. N. A. C. Lopes and A. A. H. Pádua, *J. Phys. Chem. B*, 2006, **110**, 3330–3335.
- S. Tsuzuki, S. Tsuzuki, W. Shinoda, W. Shinoda, H. Saito, H. Saito, M. Mikami, M. Mikami, H. Tokuda, H. Tokuda, M. Watanabe and M. Watanabe, *J. Phys. Chem. B*, 2009, **113**, 10641–10649.
- H. Mo and T. C. Pochapsky, *J. Phys. Chem. B*, 1997, **101**, 4485–4486.
- G. L. Burrell, I. M. Burgar, Q. Gong, N. F. Dunlop and F. Separovic, *J. Phys. Chem. B*, 2010, **114**, 11436–11443.
- H. Weingärtner, *Curr. Opin. Colloid Interface Sci.*, 2013, **18**, 183–189.
- S. Katsuta, R. Ogawa, N. Yamaguchi, T. Ishitani and Y. Takeda, *J. Chem. Eng. Data*, 2007, **52**, 248–251.
- N. T. Scharf, A. Stark and M. M. Hoffmann, *J. Solution Chem.*, 2013, **42**, 2034–2056.
- A.-L. Rollet, P. Porion, M. Vaultier, I. Billard, M. Deschamps, A. Catherine Bessada and L. Jouvensal, *J. Phys. Chem. B*, 2007, **111**, 11888–11891.
- J. Cascão, W. Silva, A. S. D. Ferreira and E. J. Cabrita, *Magn. Reson. Chem.*, 2018, **56**, 127–139.
- Y. Zhang and E. J. Maginn, *J. Phys. Chem. Lett.*, 2015, **6**, 700–705.
- N. T. Scharf and A. Stark, *J. Phys. Chem. B*, 2012, **116**, 11488–11497.
- V. P. Ananikov, *Chem. Rev.*, 2011, **111**, 418–454.
- A. Noda, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2001, **105**, 4603–4610.
- H. Tokuda, K. Hayamizu, K. Ishii, A. Bin, H. Susan and M. Watanabe, *J. Phys. Chem. B*, 2005, **109**, 6103–6110.
- H. Tokuda, K. Ishii, M. A. B. H. Susan, S. Tsuzuki, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2006, **110**, 2833–2839.
- Y. Mao and K. Damodaran, *Chem. Phys.*, 2014, **440**, 87–93.
- H. Tokuda, K. Hayamizu, K. Ishii, M. A. B. H. Susan and M. Watanabe, *J. Phys. Chem. B*, 2004, **108**, 16593–16600.
- W. Shi, K. Damodaran, H. B. Nulwala and D. R. Luebke, *Phys. Chem. Chem. Phys.*, 2012, **14**, 15897.
- Y. Marcus and G. Hefter, *Chem. Rev.*, 2006, **106**, 4585–4621.
- H. K. Stassen, R. Ludwig, A. Wulf and J. Dupont, *Chem. – Eur. J.*, 2015, **21**, 8324–8335.
- V. Mazan and M. Boltoeva, *J. Mol. Liq.*, 2017, **240**, 74–79.
- S. H. Chung, R. Lopato, S. G. Greenbaum, H. Shirota, E. W. C. Jr and J. F. Wishart, *J. Phys. Chem. B*, 2007, **111**, 4885–4893.
- S. Tsuzuki, H. Matsumoto, W. Shinoda and M. Mikami, *Phys. Chem. Chem. Phys.*, 2011, **13**, 5987.
- M. Zanatta, A.-L. Girard, N. M. Simon, G. Ebeling, H. K. Stassen, P. R. Livotto, F. P. dos Santos and J. Dupont, *Angew. Chem., Int. Ed. Engl.*, 2014, **53**, 12817–12821.
- K. Fumino, P. Stange, V. Fossog, R. Hempelmann and R. Ludwig, *Angew. Chem., Int. Ed.*, 2013, **52**, 12439–12442.
- T. Umecky, M. Kanakubo and Y. Ikushima, *Fluid Phase Equilib.*, 2005, **228–229**, 329–333.
- M. Zanatta, A.-L. Girard, G. Marin, G. Ebeling, F. P. dos Santos, C. Valsecchi, H. Stassen, P. R. Livotto, W. Lewis and J. Dupont, *Phys. Chem. Chem. Phys.*, 2016, **18**, 18297–18304.
- W. Shi, K. Damodaran, H. B. Nulwala and D. R. Luebke, *Phys. Chem. Chem. Phys.*, 2012, **14**, 15897.
- M. Zanatta, J. Dupont, G. N. Wentz and F. P. Dos Santos, *Phys. Chem. Chem. Phys.*, 2018, **20**, 11608–11614.
- P. Stange, K. Fumino and R. Ludwig, *Angew. Chem., Int. Ed.*, 2013, **52**, 2990–2994.
- A. Menjoge, J. Dixon, J. F. Brennecke, E. J. Maginn and S. Vasenkov, *J. Phys. Chem. B*, 2009, **113**, 6353–6359.
- R. F. de S. Jairton Dupont, C. S. Consorti and P. A. Z. Suarez, *Org. Synth.*, 2002, **79**, 236–237.
- A. Botana, J. A. Aguilar, M. Nilsson and G. A. Morris, *J. Magn. Reson.*, 2011, **208**, 270–278.
- M. Nilsson, *J. Magn. Reson.*, 2009, **200**, 296–302.