

# Effect of Nitrile-Functionalization of Imidazolium-Based Ionic Liquids on Their Transport Properties, Both Pure and Mixed with Lithium Salts

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**Abstract** The influence of the presence of a nitrile group in the cation of imidazolium-based ionic liquids on their transport properties was investigated. As these liquids can be used as electrolytes in lithium ion batteries, their mixtures with lithium salts were also considered. 1-Butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide,  $[C_4\text{Im}][\text{NTf}_2]$ , 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide,  $[C_4\text{Im}][\text{NTf}_2]$ , and their mixtures with bis(trifluoromethylsulphonyl)imide lithium,  $\text{Li}[\text{NTf}_2]$ , were studied. Their mass transport properties (viscosity, ionic conductivity, self-diffusion) were experimentally determined. NMR spectroscopy was also used to explore molecular organization and interactions in these systems. The addition of a cyano group increases the viscosity and the ionicity of the liquid. The effect of lithium ion is more pronounced on  $[C_4\text{Im}][\text{NTf}_2]$ , with interactions between  $\text{Li}^+$  and the nitrile group.

**Keywords** Viscosity · Conductivity · Diffusion · Ionicity · NMR spectroscopy · Lithium · Nitrile-functionalization · Ionic liquids

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## 1 Introduction

Lithium batteries are more and more present in the portable electronics and telecommunications market and are indicated as being the most promising option for the next generation of hybrid and electric vehicles. The commercial systems nowadays use mainly electrolytes based on organic carbonates, but these electrolytes are flammable and volatile, inducing serious safety risks [1]. The use of ionic liquids (ILs) is considered to be safer than more conventional organic liquids due to their low volatility and low flammability [2].

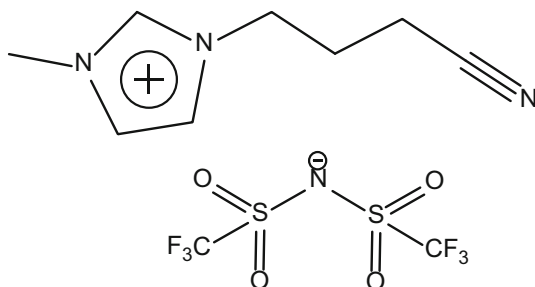
Imidazolium-based ILs have been investigated as electrolyte solvents mixed with conventional Li salts as Li[PF<sub>6</sub>], Li[BF<sub>4</sub>] or Li[NTf<sub>2</sub>] [3–7], but their performance is lower than those of systems containing conventional electrolytes.

Several drawbacks have been identified, mainly linked to the use of graphite or lithium metal as a negative electrode with imidazolium based electrolytes [5]. To address this point, organic additives are often added to the IL for use in graphite-based devices. Acetonitrile or vinylene carbonate have been proposed and show a certain stabilizing effect on graphite electrodes, due to the formation of a film evidenced by scanning electron microscopy [8–11].

Instead of using organic additives, that again render the lithium batteries less safe, the introduction of nitrile or methylcarboxyl groups in the ILs, by functionalizing 1-alkyl-3-methyl imidazolium cations, has been considered as a promising alternative [12, 13]. It has been reported that the incorporation of nitrile groups in imidazolium based ILs results in notable changes in physicochemical and conformational properties on the pure ILs [14]. Furthermore, it has been shown that for nitrile or carbonate-substituted pyrrolidinium-based ILs, the lithium salt strongly coordinates with the functional groups [15, 16]. The effect of the presence of these functional groups will surely have an effect on the properties of the IL as an electrolyte but, as far as the authors are aware of, no systematic study on this effect on the pure IL and on the mixtures IL/lithium salt has been reported.

In order to address this question, we have selected two imidazolium-based ILs, one with an alkyl side chain, [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>], and another with a nitrile functionalized alkyl side-chain, [C<sub>1</sub>C<sub>3</sub>CNIm][NTf<sub>2</sub>] (Fig. 1). We compare their mass transport properties: viscosity, ionic conductivity and self-diffusion when pure or when mixed with Li[NTf<sub>2</sub>], at the concentration of 1 mol·L<sup>−1</sup> corresponding to Li[NTf<sub>2</sub>] mole fraction concentrations of 0.2262 and 0.2216 in [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>] and [C<sub>1</sub>C<sub>3</sub>CNIm][NTf<sub>2</sub>], respectively. In addition, spectroscopic techniques were used to explore the ionicity and molecular organization and intermolecular interactions in these systems.

**Fig. 1** Chemical structure of [C<sub>1</sub>C<sub>3</sub>CNIm][NTf<sub>2</sub>]



## 2 Experimental

### 2.1 Preparation of the Ionic Liquids and of the Mixtures with Li[NTf<sub>2</sub>]

All operations were performed in the strict absence of oxygen and water under a purified argon atmosphere using glovebox (McBraun) or vacuum-line techniques. 1-Methylimidazole (>99 %) was purchased from Aldrich and distilled prior to use. 1-chlorobutane and 4-chlorobutylnitrile (>99 %, Aldrich) was used without further purification. Lithium bis(trifluoromethanesulfonyl)imide salt (>99 %, Solvionic) was used as received.

The ILs [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>] and [C<sub>1</sub>C<sub>3</sub>CNIm][NTf<sub>2</sub>] were synthesized following procedures already described in the literature [17–19] and detailed in the supplementary information. The purity of the ILs (>99 %) was checked using <sup>1</sup>H and <sup>13</sup>C NMR and mass spectroscopy.

A BRUKER AVANCE 300 spectrometer (<sup>1</sup>H 300.1 MHz, <sup>13</sup>C 75.4 MHz) was used with a deuterated solvent (CD<sub>2</sub>Cl<sub>2</sub>) as external standard. The chemical shifts are noted in parts per million (ppm), the coupling constants in Hz.

Mass spectroscopy was used to control the halide content in the samples. High resolution mass spectra (MS QTOF) were recorded in positive and negative ion modes on a hybrid quadrupole time-of-flight mass spectrometer (MicroTOFQ-II, Bruker Daltonics, Bremen) with an electrospray ionization (ESI) ion source. The gas flow of spray gas was 0.6 bar and the capillary voltage is ±4.5 kV. The solutions were infused at 180 μL·h<sup>-1</sup>. The mass range of the analysis is 50–1,000 m·z<sup>-1</sup> and the calibration was done with sodium formate. The chloride contents were 200 ppm and less than 1,000 ppm in [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>] and [C<sub>1</sub>C<sub>3</sub>CNIm][NTf<sub>2</sub>], respectively.

To remove water, the IL samples were kept under primary vacuum (1 Pa) at ambient temperature and under stirring, at least 24 h prior to use. Before each measurement, the water content of the degassed IL was verified with a coulometric Karl Fischer titrator (Mettler Toledo DL32). It was found to be lower than 100 ppm for the two ILs.

To prepare the mixtures, the lithium salt, Li[NTf<sub>2</sub>], was dissolved in [C<sub>1</sub>C<sub>3</sub>CNIm][NTf<sub>2</sub>] and [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>] at a molar concentration of 1.0 mol·L<sup>-1</sup>. The mixtures are referred as [C<sub>1</sub>C<sub>4</sub>Im]Li[NTf<sub>2</sub>] and [C<sub>1</sub>C<sub>3</sub>CNIm]Li[NTf<sub>2</sub>], respectively.

### 2.2 Density Measurements

The liquid densities were measured in a U-shape vibrating-tube densimeter (Anton Paar, model DMA 512) using a procedure already described in the literature [20]. The uncertainty of the density measurements is 10<sup>-4</sup> g·cm<sup>-3</sup>.

### 2.3 Viscosity Measurements

The dynamic viscosity,  $\eta$ , was measured using an Anton Paar Microviscosimeter (AMVn) according to a procedure previously described [21]. The statistical analysis of the results yielded an estimated uncertainty of 1.5 %.

### 2.4 Conductivity Measurements

An AC impedance bridge technique was used to measure the ionic conductivity,  $\kappa$ , as a function of temperature. The detailed procedure can be found in literature [12, 22]. The

precision of the conductivity results is estimated to be 0.6 %. The precision of the calculated molar conductivity values has been estimated (through error propagation analysis) to be 2 %.

## 2.5 NMR Measurements, Diffusion Coefficients

NMR spectra were recorded on a BRUKER AVANCE III 500 spectrometer operating at 500.13 MHz for  $^1\text{H}$ , 470.55 MHz for  $^{19}\text{F}$ , 194.369 MHz for  $^7\text{Li}$  and 50.67 MHz for  $^{15}\text{N}$ . For all the analyses, the pure IL (to avoid interactions with a solvent) was placed in a sealed 3 mm tube centered in a 5 mm tube filled with the locking solvent DMSO- $d_6$  (purity 99.8 %).

The pulsed-field gradient spin-echo NMR technique was used to measure the self-diffusion coefficients of both the cation and anion by observing the  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^7\text{Li}$  nuclei. A 5 mm pulsed-field gradient BBFO probe was used. The sample temperature was controlled within  $\pm 0.1$  K by a variable temperature control unit BVT3200 using a nitrogen gas flow ( $527 \text{ L}\cdot\text{h}^{-1}$ ). The presence of the IL in a sealed 3 mm tube centered in a 5 mm tube filled with the locking solvent DMSO- $d_6$  minimized convection effects at high temperature. These effects are further minimized by using the standard Bruker dstebpgp3s sequence. For each sample and temperature, the probe was carefully tuned, and the 90 pulse evaluated.

For each DOSY experiment, the pulse gradients lengths and diffusion times were optimized to get a signal attenuation of at least 90 % with the contradictory constraints: (i) use the minimum diffusion time to minimize convection, (ii) keep the minimum gradient pulse length to obtain sufficient attenuation, (iii) avoid heating effect of the gradients coil and (iv) keep the highest ratio  $\Delta/\delta$ . The interval between two gradient pulses,  $\Delta$ , was set between 100 and 400 ms, and the duration of the field gradient,  $\delta$ , was varied from 3.5 to 8 ms depending on the temperature. The signals were accumulated 16 times for a linear set of 32 different gradient values distributed from 3 to  $47.5 \text{ G}\cdot\text{cm}^{-1}$ . The relaxation delay was set to 5 s and 16 dummy scans were programmed prior to acquisition. The determination of self-diffusion coefficients used the BRUKER T1/T2 module for each peak. For the imidazolium cation, we took the average of the different available peaks.

## 3 Results and Discussion

The density of the two pure ILs and mixtures with  $\text{Li}[\text{NTf}_2]$  were measured as a function of temperature from 298 to 373 K (Table 1). Due to the high viscosity of some of the samples, a correction to the density was applied, as recommended by the manufacturer of

**Table 1** Experimental densities ( $\rho$ ) of the pure ILs and their mixtures with  $\text{Li}[\text{NTf}_2]$  as a function of temperature at atmospheric pressure

$[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$				$[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$			
Pure		$c_{\text{Li}}[\text{NTf}_2] = 1 \text{ mol}\cdot\text{L}^{-1}$		Pure		$c_{\text{Li}}[\text{NTf}_2] = 1 \text{ mol}\cdot\text{L}^{-1}$	
$T/\text{K}$	$\rho/\text{kg}\cdot\text{m}^{-3}$	$T/\text{K}$	$\rho/\text{kg}\cdot\text{m}^{-3}$	$T/\text{K}$	$\rho/\text{kg}\cdot\text{m}^{-3}$	$T/\text{K}$	$\rho/\text{kg}\cdot\text{m}^{-3}$
297.97	1,434.24	297.70	1,499.74	297.72	1,511.56	297.78	1,570.63
312.59	1,420.21	312.15	1,484.88	312.16	1,498.07	312.16	1,557.30
332.10	1,401.80	331.60	1,465.27	331.59	1,480.21	331.51	1,539.10
351.07	1,384.15	351.08	1,446.57	351.09	1,462.81	351.05	1,521.28
370.64	1,365.85	370.59	1,428.09	370.58	1,445.97	370.53	1,503.90

Standard uncertainties  $u$  are  $u(T) = \pm 0.01 \text{ K}$ ,  $u(\rho) = \pm 0.05 \text{ kg}\cdot\text{m}^{-3}$

the vibrating-tube densimeter. The following equation was considered to calculate the correction factor [23].

$$\frac{\Delta\rho}{\rho} = (-0.5 + 0.45\sqrt{\eta}) \times 10^{-4} \quad (1)$$

where  $\rho$  is the density value obtained from the densimeter calibration and the measured period,  $\Delta\rho$  is the difference between this  $\rho$  value and the “corrected” density value due to the effect of viscosity, and  $\eta$  is the dynamic viscosity of the sample in mPa·s. Only the corrected densities are presented in this paper. For the most viscous sample ([C<sub>1</sub>C<sub>3</sub>CNIm][Li][NTf<sub>2</sub>],  $\eta = 825$  mPa·s at 298 K), a correction factor of 0.1 % of the density was calculated. For the less viscous sample [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>], the correction factor was below the estimated uncertainty of the density measurements (0.01 %, obtained by statistical analysis).

In the temperature range studied, the following equation was used to correlate the density with temperature:

$$\rho = aT + b. \quad (2)$$

The characteristic parameters  $a$  and  $b$  are given in Table S1, together with the standard error of the fit (standard deviation between the experimental and calculated data).

The density of the pure [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>] was already measured by other groups [24–28]. The values reported here are slightly lower (average relative deviation between 0.15 and 0.3 %) than most of the data presented in the literature. They are similar to the data reported by Troncoso et al. [20] (average deviations of 0.05 %). The presence of the nitrile group on the imidazolium cation has a strong effect on the density of the IL causing an increase of 5 % when compared to [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>]. This corresponds to a 3 % decrease in the molar volume. A similar increase (4–5 %) of the density is observed with the addition of Li[NTf<sub>2</sub>] to the IL. This type of result was already observed experimentally with imidazolium [29] and pyrrolidinium-based ILs [32, 33] mixed with a lithium salt. Borodin et al. [30] have predicted, by molecular dynamics simulation, a 5 % increase of the density when mixing pyrrolidinium based ILs with 0.25 mol fraction of Li[NTf<sub>2</sub>].

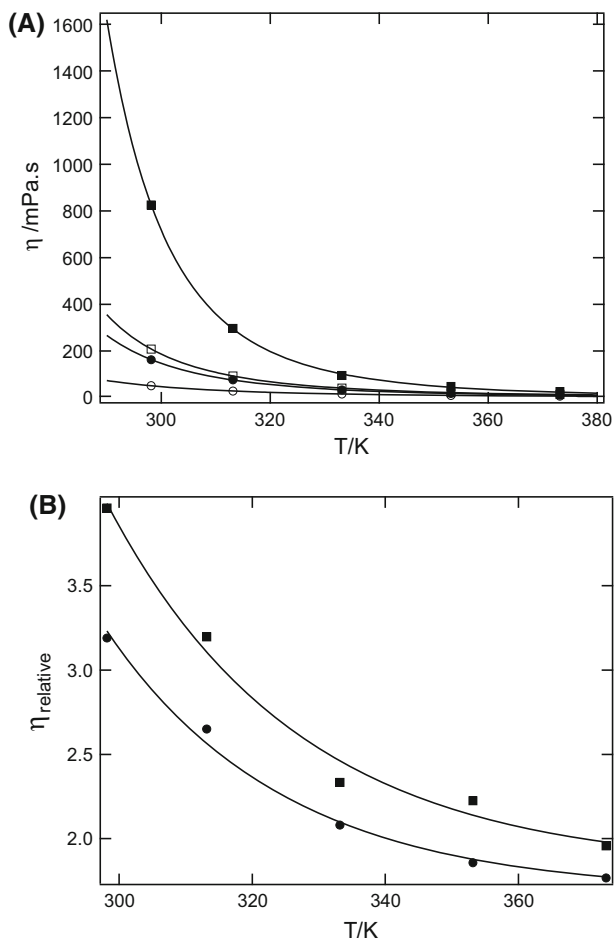
Viscosity is the transport property that characterizes the hydrodynamics of a fluid and its resistance to flow. The viscosity of the two ILs, pure and mixed with Li[NTf<sub>2</sub>], was measured as a function of temperature from 298 to 373 K. The results are presented in Table S2 and in Fig. 2. An important decrease of the viscosity is observed, as expected, for each sample when increasing the temperature [31]. The variation of the viscosity with temperature was correlated using the Vogel–Fulcher–Tamman equation [32–34].

$$\eta = A\sqrt{T} \exp\left(\frac{k}{T - T_0}\right) \quad (3)$$

with  $A$ ,  $k$  and  $T_0$  being adjustable parameters, given in Table S3 along with the standard error of estimation of the fit. Except in the case of the more viscous system [C<sub>1</sub>C<sub>3</sub>CNIm][Li][NTf<sub>2</sub>], the standard error of estimation is below 0.5.

The viscosity measured for [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>] is slightly higher than the data presented in literature [17, 19, 25, 35] (average relative deviations from Jacquemin et al. [25], between 1 and 7 %, except for temperatures higher than 360 K where deviations up to 13 % were found). The data presented by MacFarlane et al. [28] are below the values reported here at temperatures up to 300 K but are above at higher temperatures. These variations are compatible with the presence of significant amounts of water in their samples, eliminated

**Fig. 2** **a**. Viscosity,  $\eta$ , of the pure ILs and their mixtures with Li[NTf<sub>2</sub>] as a function of temperature, from 290 to 380 K: open circle, [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>]; filled circle, [C<sub>1</sub>C<sub>4</sub>Im]Li[NTf<sub>2</sub>]; open square, [C<sub>1</sub>C<sub>3</sub>CNIIm][NTf<sub>2</sub>]; filled square, [C<sub>1</sub>C<sub>3</sub>CNIIm]Li[NTf<sub>2</sub>]. Lines correspond to the fits with Eq. 3. **b** Relative viscosity,  $\eta_{\text{relative}}$ , of the two ILs mixed with Li[NTf<sub>2</sub>] as a function of temperature, from 290 to 380 K: filled circle, [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>]; filled square, [C<sub>1</sub>C<sub>3</sub>CNIIm][NTf<sub>2</sub>]. Lines are guides for the eyes



at higher temperatures. The low densities coupled with the high viscosities measured in our samples could be due to the presence of chloride salts [36]. The chloride measured in our samples was found to be lower than 0.1 % (mol%) as determined by high resolution mass spectra (MS QTOF).

The presence of the nitrile group on the alkyl chain of the imidazolium cation increases the viscosity of the IL, particularly at lower temperatures (viscosity is increased by a factor 4 at 298 K and doubled at 373 K). This effect was already reported in the literature on [C<sub>1</sub>C<sub>3</sub>CNIIm]<sup>+</sup> associated with different anions ([BF<sub>4</sub>]<sup>−</sup>, [PF<sub>6</sub>]<sup>−</sup>, [NTf<sub>2</sub>]<sup>−</sup>) [9] and can probably be explained by increased hydrogen bonding interactions in the ionic liquid with the nitrile group [9, 37].

The presence of the lithium salt increases the viscosity of the medium, particularly at the lower temperatures studied. The viscosity increases by a factor of 3 for [C<sub>1</sub>C<sub>4</sub>Im]Li[NTf<sub>2</sub>], by a factor 4 for [C<sub>1</sub>C<sub>3</sub>CNIIm]Li[NTf<sub>2</sub>] at 298 K, and doubles in both cases at 373 K. This behavior is depicted in Fig. 2b where the relative viscosity (viscosity of the mixture Li[NTf<sub>2</sub>] + IL/viscosity of the pure IL) is shown for the two ILs as a function of

temperature. For  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$ , the relative viscosity is 3.2 at 298 K, while it decreases to 1.8 at 373 K. The same trend was observed by Tsuzuki [21] for  $[\text{C}_1\text{C}_2\text{Im}][\text{NTf}_2]$  mixed with  $\text{Li}[\text{NTf}_2]$  with relative viscosities of 1.9 at 290 K and of 1.4 at 360 K.

The ionic conductivity of a medium is a measure of the number and mobility of available charge carriers and is of critical importance for electrochemical applications. Although ILs are composed entirely of ions, they are in general significantly less conductive than concentrated organic electrolytes. The lower-than-expected conductivity of ILs can be attributed to the reduction of available charge carriers due to ion pairing or other forms of aggregation [38].

The ionic conductivity of the two ILs with and without  $\text{Li}[\text{NTf}_2]$  was measured as a function of temperature from 298 to 373 K. The results are presented in Fig. 3 and are listed in Table S4.

A conductivity of  $4.01 \text{ mS}\cdot\text{cm}^{-1}$  was measured for pure  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  at 298 K, 1 % lower than the value of  $4.06 \text{ mS}\cdot\text{cm}^{-1}$  measured by François et al. [39] and 4 % lower than the value of  $4.16 \text{ mS}\cdot\text{cm}^{-1}$  previously measured by our group [30] on another sample of  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$ . The  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$ , which is more viscous, has a smaller conductivity ( $1.25 \text{ mS}\cdot\text{cm}^{-1}$  at 298 K). The addition of the lithium salt dramatically decreases the conductivity in the solutions of the two ILs. This is attributed to the increase of the viscosity, as generally reported in the literature [5, 40–42].

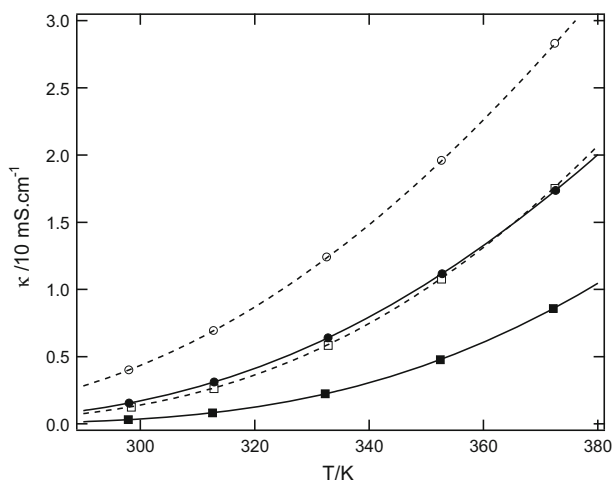
The variation of the conductivity with temperature was correlated using the Vogel–Fulcher–Tamman equation, the adjustable parameters  $A'$ ,  $k'$  and  $T'_0$  being given in Table S5 along with the standard error of the fit.

The molar conductivity measured by impedance,  $A_{\text{imp}}$ , can be calculated from the ionic conductivity,  $\kappa$ , and the IL concentration,  $c_{\text{IL}}$ , according to:

$$A_{\text{imp}} = \kappa / c_{\text{IL}}. \quad (4)$$

In the case of ILs mixed with lithium, the ionic conductivity was divided by the total concentration of charged species (IL + lithium salt). The molar conductivities measured by impedance are presented in Table S4. For all the considered systems an increase with temperature was observed.

**Fig. 3** Ionic conductivity,  $\kappa$ , of the pure ILs and their mixtures with  $\text{Li}[\text{NTf}_2]$  as a function of temperature, from 290 to 380 K: open circle,  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$ ; filled circle,  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$ ; open square,  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$ ; filled square,  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$ . Lines correspond to the fits with the equation of Vogel, Fulcher and Tamman



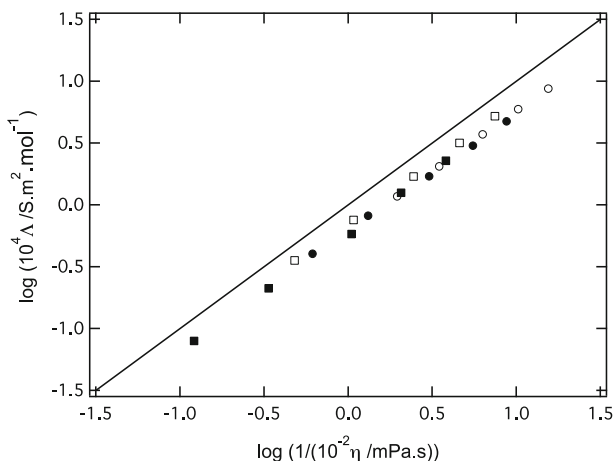
The relationship between ionic conductivity and viscosity is illustrated by the qualitative approach first developed by Walden for aqueous electrolytes [33]. In this graphical representation ( $\log_{10} A_{\text{imp}}$  as a function of  $\log_{10} \eta^{-1}$ ), the diagonal 1:1 line represents the ideal Walden line, obeyed by a  $0.01 \text{ mol}\cdot\text{L}^{-1}$  aqueous solution of KCl, considered to be fully dissociated. Angell et al. [43] have proposed classifying ILs on their ionicity, defined as the effective fraction of ions available to participate in conduction. The vertical distance  $\Delta W$  of the data points to the reference KCl line is a measure of the deviation of IL media from electrolytic ideality i.e. of its (loss of) ionicity. Components that lie close to this line are said to be ionic (good ILs), whereas subionic (poor) ILs are below this line. It must be stressed that such comparisons and classifications are mainly qualitative due to the fundamental differences between a diluted electrolyte solution ( $0.01 \text{ mol}\cdot\text{L}^{-1}$  aqueous KCl solution) and an IL.

Walden plots for the pure ILs and when mixed with  $\text{Li}[\text{NTf}_2]$  are represented, as a function of temperature, in Fig. 4. The four systems fall slightly below the reference line. This corresponds to incompletely ionized systems but these systems can be considered as good ILs following the classification of Angell. The experimental points corresponding to  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$  are slightly above the ones of  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$ . The latter is thus less ionic (stronger anion–cation association). For  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$ , the addition of the lithium salt increases the deviation from the reference line corresponding to a stronger ionic association in the presence of  $\text{Li}^+$ . This is not observed for  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$ .

The pulse-field gradient spin echo DOSY NMR constitutes another tool to estimate the transport properties in these systems. The diffusion coefficients of the anion  $[\text{NTf}_2]^-$  and of the cations ( $[\text{C}_1\text{C}_4\text{Im}]^+$ ,  $[\text{C}_1\text{C}_3\text{CNIm}]^+$  and  $\text{Li}^+$ ) were measured by  $^{19}\text{F}$   $^1\text{H}$  and  $^7\text{Li}$  NMR, respectively, from 278 to 353 K, in the pure ILs and in the ILs mixed with  $\text{Li}[\text{NTf}_2]$ . The results are presented in Tables 2 and 3.

All the diffusion coefficients increase with increasing temperature, following an Arrhenius law. In pure  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  at 313 K,  $D_{[\text{C}_1\text{C}_4\text{Im}]}^+$  and  $D_{[\text{NTf}_2]}^-$  were found equal to  $5.82$  and  $4.48 \times 10^{-11} \text{ m}^2\cdot\text{s}^{-1}$ , respectively. These values agree with those reported in the literature to within the mutual experimental uncertainties [19, 44]. Given the relative sizes of the ions, it can be surprising to observe that the cation diffuses faster than the anion. This fact, also observed in the literature, can be explained by the boardlike shape of the imidazolium ring being more appropriate for fast diffusion [19, 45].

**Fig. 4** Walden plots of the pure ILs and their mixtures with  $\text{Li}[\text{NTf}_2]$  as a function of temperature from 290 to 380 K: open circle,  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$ ; filled circle,  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$ . Open square,  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$ ; filled square,  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$





**Table 2** Self-diffusion coefficients of  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  and its binary mixture  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$  at  $1 \text{ mol}\cdot\text{L}^{-1}$  of  $\text{Li}[\text{NTf}_2]$ 

$T/\text{K}$	$[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$			$[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$		
	$D_{\text{ion}} \times 10^{-11}/(\text{m}^2\cdot\text{s}^{-1})$			$D_{\text{ion}} \times 10^{-11}/(\text{m}^2\cdot\text{s}^{-1})$		
	$D_{[\text{C}_1\text{C}_4\text{Im}]^+}$	$D_{[\text{NTf}_2]^-}$	$D_{\text{Li}^+}$	$D_{[\text{C}_1\text{C}_4\text{Im}]^+}$	$D_{[\text{NTf}_2]^-}$	$D_{\text{Li}^+}$
298	2.04	2.32	–	1.19	0.59	0.33
313	5.82	4.48	–	2.79	1.46	0.79
333	10.53	8.47	–	6.05	3.44	1.69
353	17.06	14.06	–	11.39	6.21	3.11

Standard uncertainties  $u$  are  $u(T) = \pm 0.1 \text{ K}$ ,  $u(D) = \pm 5 \times 10^{-12} \text{ m}^2\cdot\text{s}^{-1}$

**Table 3** Self-diffusion coefficients of  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$  and its binary mixture  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$  at  $1 \text{ mol}\cdot\text{L}^{-1}$  of  $\text{Li}[\text{NTf}_2]$ 

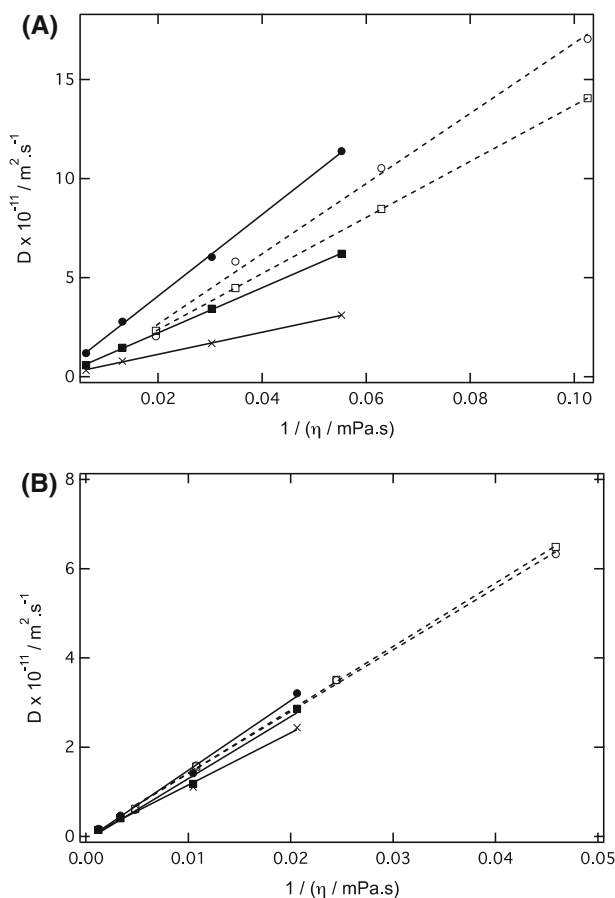
$T \text{ (K)}$	$[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$			$[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$		
	$D_{\text{ion}} \times 10^{-11}/(\text{m}^2\cdot\text{s}^{-1})$			$D_{\text{ion}} \times 10^{-11}/(\text{m}^2\cdot\text{s}^{-1})$		
	$D_{[\text{C}_1\text{C}_3\text{CNIm}]^+}$	$D_{[\text{NTf}_2]^-}$	$D_{\text{Li}^+}$	$D_{[\text{C}_1\text{C}_3\text{CNIm}]^+}$	$D_{[\text{NTf}_2]^-}$	$D_{\text{Li}^+}$
298	0.6	0.62		0.17	0.15	0.15
313	1.59	1.57		0.47	0.41	0.42
333	3.50	3.51		1.42	1.18	1.11
353	6.33	6.49		3.21	2.86	2.44

Standard uncertainties  $u$  are  $u(T) = \pm 0.1 \text{ K}$ ,  $u(D) = \pm 5 \times 10^{-12} \text{ m}^2\cdot\text{s}^{-1}$

In  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$  at 313 K, the diffusion coefficients of the two ions are similar and lower than in the previous IL ( $1.59$  and  $1.57 \times 10^{-11} \text{ m}^2\cdot\text{s}^{-1}$ , respectively), which can be attributed to its higher viscosity.

In both binary systems  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$  and  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$ , the diffusion coefficients of  $([\text{C}_1\text{C}_4\text{Im}]^+, [\text{C}_1\text{C}_3\text{CNIm}]^+ \text{ and } [\text{NTf}_2]^-)$  are lower than in the pure ILs, which is consistent with the observed increase in viscosity reported above and shown in Fig. 2. In  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$ , the relative order of the diffusivities is  $D_{[\text{C}_1\text{C}_4\text{Im}]^+} > D_{[\text{NTf}_2]^-} > D_{\text{Li}^+}$ . Molecular dynamics simulations [24] and experimental studies [35, 46–48] have proved that the lower value of  $D_{\text{Li}^+}$  can be explained by a coordination between  $\text{Li}^+$  and  $[\text{NTf}_2]^-$  leading to aggregates typically formed by clusters of one  $\text{Li}^+$  and at least 2  $[\text{NTf}_2]^-$ .  $D_{[\text{NTf}_2]^-}$  is also dependent of the coordination of the  $[\text{NTf}_2]^-$  anion [49]. In  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$ , the diffusion coefficients of the three ions are lower than those of  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$ , and the three ions have comparable diffusion coefficients.

The plots of  $D$  versus the fluidity ( $\eta^{-1}$ ), for both pure ILs and their mixtures with lithium salts, show an excellent linearity suggesting that the Stokes–Einstein relationship is followed (Fig. 5). The comparison of the slope of the curve  $D_{[\text{NTf}_2]^-}$  versus  $\eta^{-1}$  between pure IL  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  and its mixture with  $\text{Li}[\text{NTf}_2]$  shows a lower drop in the mixture with the lithium salt. This could indicate agreement with high interactions between  $[\text{NTf}_2]^-$  and  $\text{Li}^+$  [19–23]. Contrarily, in  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$  and its binary mixture with  $\text{Li}[\text{NTf}_2]$ , the slopes for all ions are similar (Fig. 5b). This could mean that, in the mixture with the lithium salt, both  $[\text{C}_1\text{C}_3\text{CNIm}]^+$  and  $[\text{NTf}_2]^-$  interact with  $\text{Li}^+$ .



**Fig. 5** Diffusion coefficients plotted as a function of  $\eta^{-1}$  for all the ions. **a** In  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  and  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$ . Open circle,  $\text{C}_1\text{C}_4\text{Im}^+$  in  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$ ; filled circle,  $\text{C}_1\text{C}_4\text{Im}^+$  in  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$ ; open square,  $\text{NTf}_2^-$  in  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$ ; filled square,  $\text{NTf}_2^-$  in  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$ ;  $\times$ ,  $\text{Li}^+$  in  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$ . **b** In  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$  and  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$ . Open circle,  $\text{C}_1\text{C}_3\text{CNIm}^+$  in  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$ ; filled circle,  $\text{C}_1\text{C}_3\text{CNIm}^+$  in  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$ ; open square,  $\text{NTf}_2^-$  in  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$ ; filled square,  $\text{NTf}_2^-$  in  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$ ;  $\times$ ,  $\text{Li}^+$  in  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$

From the diffusion coefficients measured by NMR spectroscopy, the molar conductivity can be calculated according to:

$$\Lambda_{\text{NMR}} = N_{\text{A}} e^2 \frac{D^+ + D^-}{kT} \quad (5)$$

with  $N_{\text{A}}$  being Avogadro's number,  $e$  the electronic charge on each ionic carrier,  $D^+$  and  $D^-$  the diffusion coefficients of the cation and anion, respectively,  $k$  the Boltzmann constant and  $T$  the absolute temperature.

When lithium salts are added to the ILs,  $\Lambda_{\text{NMR}}$  is calculated according to:

$$A_{\text{NMR}} = \frac{N_A e^2}{kT} \left( \frac{n_{\text{cation}}}{n_{\text{cation}} + n_{\text{Li}^+}} D^+ + \frac{n_{\text{Li}^+}}{n_{\text{cation}} + n_{\text{Li}^+}} D_{\text{Li}^+} + D^- \right) \quad (6)$$

with  $n_{\text{cation}}$  being the quantity of IL and  $n_{\text{Li}^+}$  the quantity of lithium salt.

This conductivity,  $A_{\text{NMR}}$ , corresponds to the transport of all species of the system (charged and non-charged). It can be compared to  $A_{\text{imp}}$ , which corresponds to the transport of the charged species in the system. The ratio  $A_{\text{imp}}/A_{\text{NMR}}$  represents the proportion of charged species contributing to ionic conduction and is a quantitative measurement of the ionicity of the system.

The ionicities of the pure ILs and IL/lithium salt mixtures (Fig. 6) are between 0.55 and 0.80. For pure  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  this value is in agreement with the literature data (0.6) [19]. Pure  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  exhibits a lower ionicity (higher ionic association) than pure  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$ , in agreement with their relative positions in the Walden plots (Fig. 4) [50].

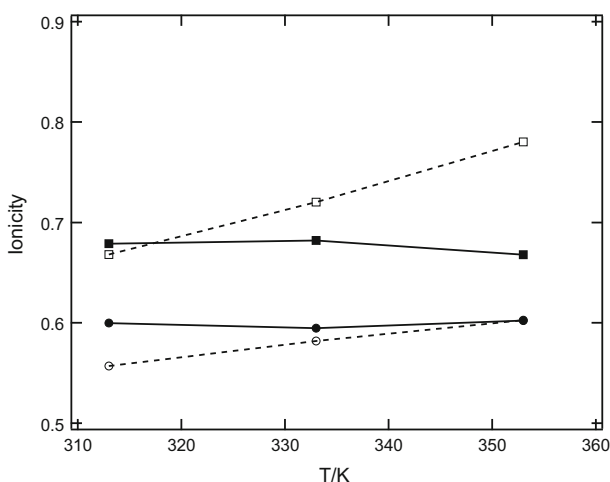
The ionicities of  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  and  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$  are similar and slightly increase with temperature. On the contrary, the presence of lithium has an effect on the molecular organization of  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$ , the ionicity of  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$  being higher than the ionicity of  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$ . This result suggests a probable higher structuration of both  $[\text{C}_1\text{C}_3\text{CNIm}]^+$  and  $[\text{NTf}_2]^-$  around  $\text{Li}^+$ .

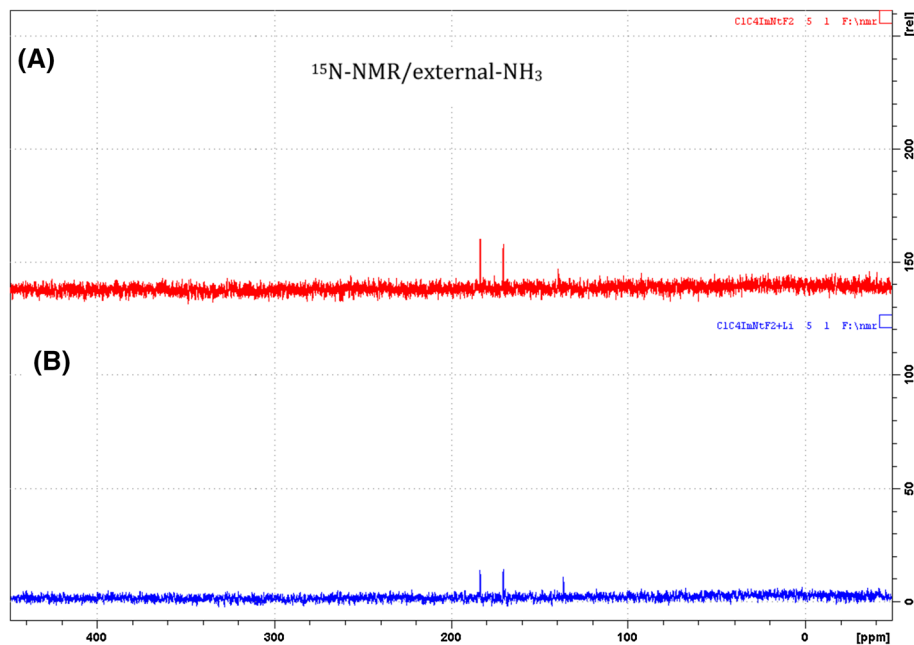
To gain more information about the molecular organization and intermolecular interactions involving lithium and nitrogen atoms,  $^7\text{Li}$  and  $^{15}\text{N}$  NMR spectra have been studied in these systems at 298 K.

As can be observed from Fig. 7, the  $^{15}\text{N}$  NMR spectra of  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  and  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$  show no differences. In this IL, the presence of lithium induces no major modification of the electronic environment of the nitrogen atoms.

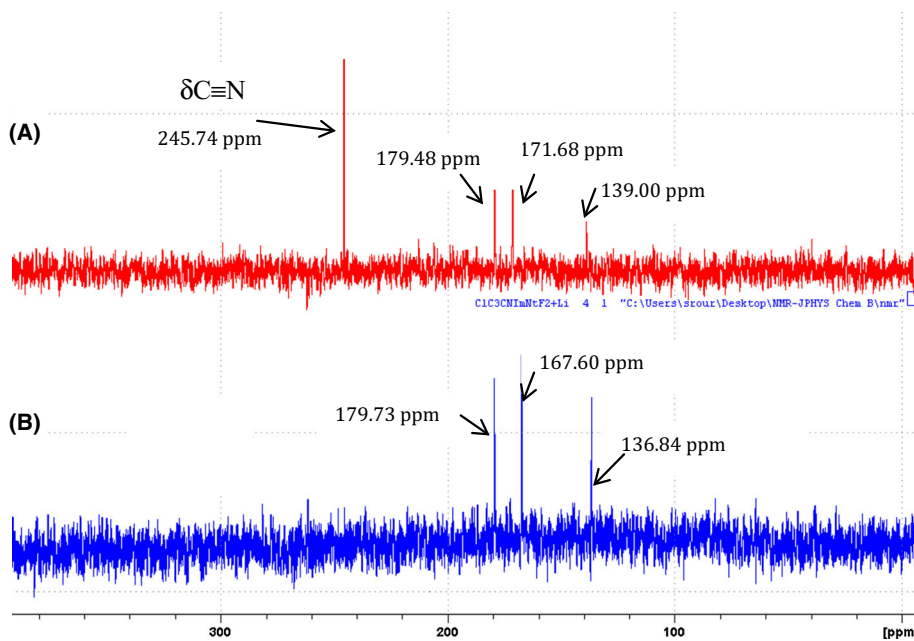
In the  $^{15}\text{N}$  spectrum of  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$  (Fig. 8) the resonance at 139 ppm/ $\text{NH}_3$  (i.e.,  $-242.6$  ppm/ $\text{CD}_3\text{NO}_2$ ) is assigned to the nitrogen atom of the  $[\text{NTf}_2]^-$  anion, while the other 3 chemical shifts  $\delta\text{N}-\text{C}_1$ ,  $\delta\text{N}-\text{C}_3\text{CN}$  and  $\delta\text{C}\equiv\text{N}$  at 171.68, 179.48, and 245.74 ppm/ $\text{NH}_3$ , (i.e.  $-209.9$ ,  $-202.12$  and  $-135.86$  ppm/ $\text{CD}_3\text{NO}_2$ ) are assigned to the nitrogen atoms of the imidazolium cation and of the  $\text{C}\equiv\text{N}$  group, respectively [51].

**Fig. 6** Ionicity of the pure ILs and their mixtures with  $\text{Li}[\text{NTf}_2]$  as a function of temperature from 290 to 380 K: open circle,  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$ ; filled circle,  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$ ; open square,  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$ ; filled square,  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$

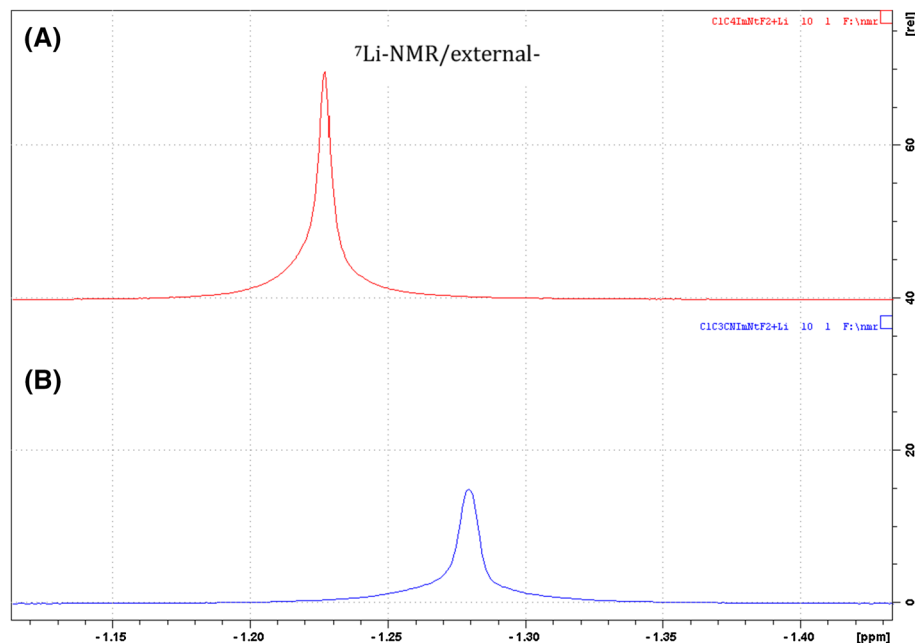




**Fig. 7**  $^{15}\text{N}$ -NMR spectra of **a**  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  and **b**  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$  recorded at room temperature



**Fig. 8**  $^{15}\text{N}$ -NMR spectra of **a**  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$  and **b**  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$  recorded at room temperature and using  $\text{NH}_3(\text{liq})$  ( $-381.6 \text{ ppm}/\text{MeNO}_2$ ) as external standard



**Fig. 9**  $^7\text{Li}$ -NMR spectra of **a**  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$  and **b**  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$  recorded at room temperature

In the  $^{15}\text{N}$  spectrum of  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$  (Fig. 8), both  $\delta\text{N} - \text{C}_1$  and  $\delta\text{N} - \text{C}_3\text{CN}$  are slightly deshielded (179.73 versus 179.48 ppm and 167.60 versus 171.68 ppm, respectively), indicating a change in the negative charge on this nitrogen atom. In the presence of lithium, no more resonance of  $\text{C}\equiv\text{N}$  is observed, probably reflecting a dynamic process between the free and coordinated population of the nitrile group with the lithium salt.

In the  $^7\text{Li}$  spectra of  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$  and  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$  (Fig. 9), we observe a shift (resonance at  $-1.28$  ppm in  $[\text{C}_1\text{C}_4\text{Im}]\text{Li}[\text{NTf}_2]$  versus  $-1.23$  ppm in  $[\text{C}_1\text{C}_3\text{CNIm}]\text{Li}[\text{NTf}_2]$ ) corresponding to a modification of the molecular environment of the lithium ion in both systems.

These analysis of the NMR spectra, together with the Walden plots and the study of the ionicity and of the evolution of the diffusion coefficients as a function of the fluidity, are compatible with coordination of the lithium ion by the functionalized IL as already observed in the literature [24, 36, 37].

## 4 Conclusions

To estimate the potential of ILs as electrolytes in lithium batteries, the effect of the presence of lithium salts and of a nitrile functionalization in an imidazolium-based IL, on the transport properties and molecular organization of these mixtures, was studied. Both the presence of nitrile group and the addition of  $\text{Li}[\text{NTf}_2]$  increase the viscosity of the liquid.  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$  was found to be more ionic than  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$ . The addition of lithium salt has no effect on the ionicity of  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  while it increases the anion-cation association of  $[\text{C}_1\text{C}_3\text{CNIm}][\text{NTf}_2]$ .

The use of spectroscopic techniques confirm the more important modifications of the molecular organization in  $[C_1C_3CNIm][NTf_2]$  in the presence of lithium salts, compared to  $[C_1C_4Im][NTf_2]$ . In particular, interactions between the nitrile group of the  $[C_1C_3CNIm][NTf_2]$  and the lithium ion were observed. This is compatible with possible coordination of the lithium ion by functionalized IL that was observed in the literature.

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