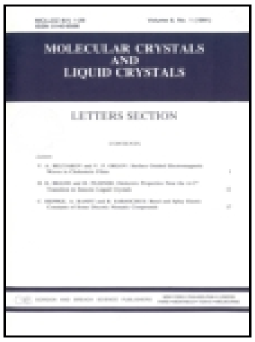

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Study of Translational Diffusion Anisotropy of Ionic Smectogens by NMR Diffusometry

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Thermotropic ionic liquid crystals are considered very promising for a wide range of applications, such as anisotropic conductors as well as electrolytes in dye-synthesized solar cells. Their potential comes from the unique combination of ionic conductivity and high polarizability. In this paper we present a study of the diffusional properties of the ionic smectic A phase formed by the cationic smectogen, N-docecyl-N'-methyl-imidazolium (C12mim), with two different counter ions. Experimental translational diffusion data measured by NMR diffusometry are collected both for cations and anions and discussed in terms of their different anisotropy.

Keywords Ionic Liquid Crystals; Diffusometry; NMR; Pulse Field Gradient NMR; Smectic; Dynamics

Introduction

Thermotropic Ionic liquid crystals (ILCs) combine the typical properties of liquid crystals, i.e. high polarizability and anisotropy with those of ionic liquids, in particular ion conductivity, as well as the possibility of tuning their properties playing on the combination of different ions [1].

In literature, a wide variety of ILCs is reported, mostly formed by an amphiphilic cation, such as imidazolium derivates, with different counter-ions [1]. This combination leads to a class of materials with high anisotropic mobility ionic mobility that let envisage interesting applications in a variety of fields, such as energy storage and conversion, for the realization of high efficiency solar cells [2, 3, 4, 5], organic tuneable photo-luminescent materials [6, 7], as well as high performance lubricants [8, 9]. This wide range of possibilities is however limited by the relatively high temperature of the LC mesophases and recently efforts have been devoted to synthesize room temperature ILCs [10, 11].

The base of the liquid crystalline phase formation is the micro-segregation of ionic moieties and hydrophobic chains in lamellar structures, i.e. smectic A phase, where layers of hydrophobic cationic alkyl chains alternate with anionic layers [1]. These systems,

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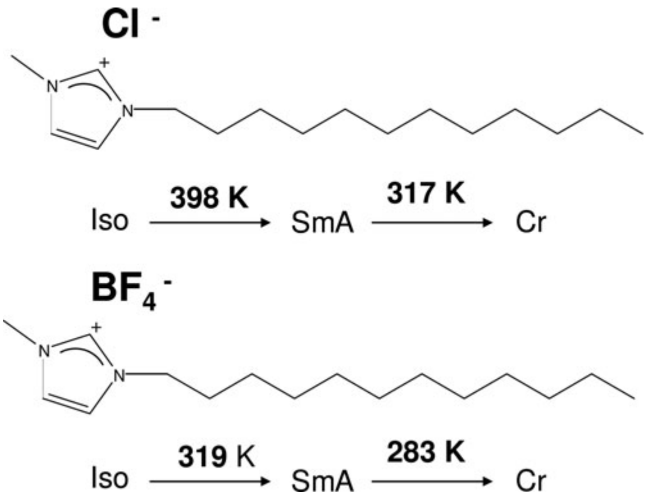

Scheme 1. Molecular structures of the two ionic mesogens and corresponding phase transition temperatures on cooling.

analogously to the non-ionic counterpart, can be easily oriented by means of suitable surface anchoring as well as by magnetic and electric fields.

In order to fully exploit their properties and contribute to the design of innovative ILC-based materials, it is necessary to gain increased understanding of the role of underlying dynamic molecular processes and mechanisms. In this context, Brownian translational diffusion and its anisotropic behaviour play indeed an important role in ionic mobility.

In the present work, we focus on two N-docecyl-N′-methyl-imidazolium (C12mim) salts, the chloride (C12mimCl) and the TetrafluoroBorate (C12mimBF4), respectively. Both mesogens exhibit a smectic A phase. The transition temperature as well as the Smectic A phase temperature range, however, differ significantly for the different counter ions of the C12mim as reported in Scheme 1. These two systems can be hence considered a good "benchmark" to investigate the translation self-diffusion of the ionic moieties, in particular the cationic one and its anisotropy.

Experimental

Mesogens were obtained from Dr. Saielli, and used as received.

Self diffusion measurements have been performed on a 500 MHz Bruker Advance III spectrometer (11.7 T) operating at Larmor Frequency 500.503 MHz and 470.730 MHz for ^{1}H and ^{19}F, respectively.

The micro-imaging probe (MIC5) with gradients strength up to 280 G/cm in three orthogonal directions (x,y,z), generated by the current amplifier GREAT60, has been used to measure diffusion coefficient along and orthogonal to the static magnetic field direction (z). The 90° pulse width was calibrated to 5.9 μs, for both ^{1}H and ^{19}F experiments. Temperature was regulated with an accuracy of ± 0.1°C.

Measurements in the isotropic phase have been carried out with a standard double-stimulated-echo sequence (DSTE) compensated for convectional flow contribution to diffusion decay [12].

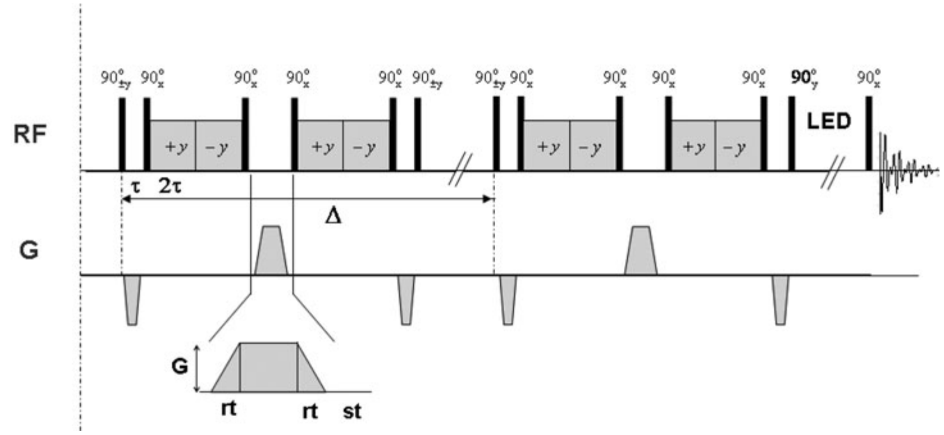

Figure 1. Pulse field gradient STE-ME pulse sequence scheme. During the encoding/decoding time a magic echo decoupling sequence is inserted to extend transverse relaxation time. Trapezoidal gradient shapes were used with ramp time rt and stabilization time st as discussed in the text. Bipolar gradient pulses were applied for cumulative effect of the field gradient and LED delay was inserted to compensate possible eddy current effects on the acquisition.

In the smectic A phase, the NMR transverse relaxation processes become much faster, owing to significant residual dipolar spin interactions induced due to the liquid crystalline structure- Hence, stimulated echo sequence (STE) combined with magic-echo spin decoupling (STE-ME) was applied [13], as shown in Figure 1. ME decoupling delays τ between 300 and 650 μs were used to achieve significant diffusion decays of the stimulated echo in the whole investigated temperature range. Within these conditions the effective maximum gradient pulse length for the experiments was set to 1.0 ms for all experiments.

Trapezoidal gradient shapes have been used with ramp time (*rt*) and supplemented with stabilization delay (*st*) (i.e. rt = st = 50 μs) long enough to avoid transient effects and interferences with r.f. pulses. To compensate for eddy current fields, gradient waveforms were adjusted using preemphasis method [14]. Finally, extension of the sequence with LED (Longitudinal Eddy current Delay) period of 5 ms allowed for suppression of eddy current effect during signal acquisition [15].

Diffusion coefficient along the gradient direction is then measured, by fitting the echo decay with the Stejskal-Tanner equation [16] as the gradient strength increases leaving all the other parameters constant:

$$\begin{aligned} &A\,(\gamma, \delta, G, \Delta) \propto \exp\,(-bD) \\ &b = (\gamma \delta G)^2 (\Delta - \delta/3) \end{aligned} \tag{1}$$

where γ the nuclear magnetogiric ratio, G and δ are the pulse gradient strength and length, respectively, Δ is the diffusion time, and D is the diffusion coefficient along the chosen gradient direction. In Figure 2 a pictorial view of the orientation of the diffusion tensor components is reported and in Figure 3, the typical ME-STE echo decays along z and x are reported.

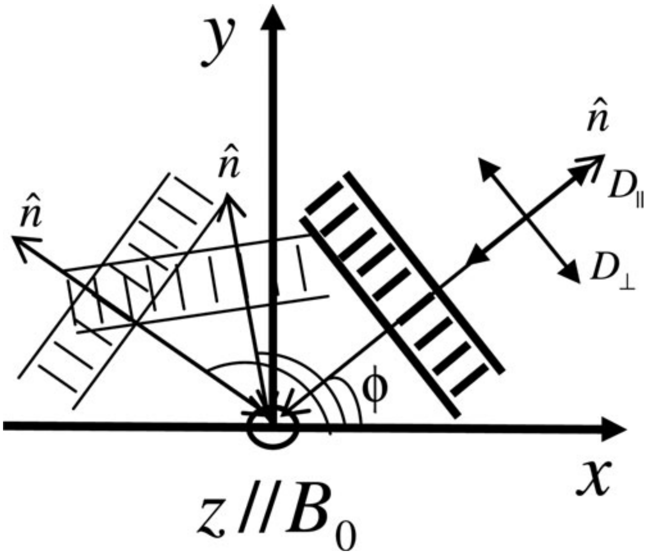

Figure 2. Pictorial representation of the smectic layer distribution in the x,y plane of the laboratory frame. Phase director distributes cylindrically along the z axis (pointing out of the paper plane) and forms arbitrary ϕ angle with the x direction. Diffusion measured along the z direction depends directly on $D_\perp$, while measuring diffusion along the x direction determine a diffusion coefficient that is a combination of $D_{||}$ and $D_\perp$ as discussed in the text.

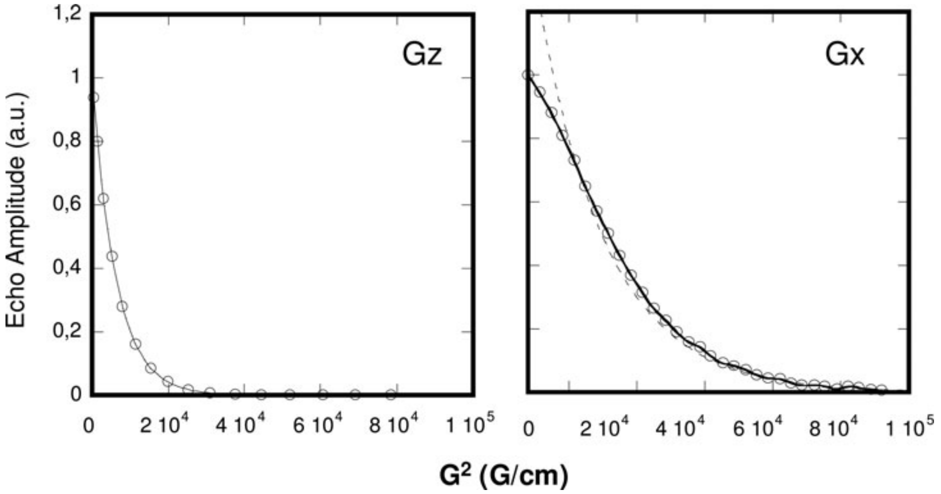

Figure 3. ME-STE echo decay measured at T = 395 K in the smectic A phase of C12mimCl. On the left: measurement along the z direction as a function of the gradient strength; the decay is well fitted with equation (1). On the right: measurement along the x direction. In this case the fitting with equation (1) is unsatisfactory (broken line) and the best result is obtained with equation (5) (full line), as discussed in the text.

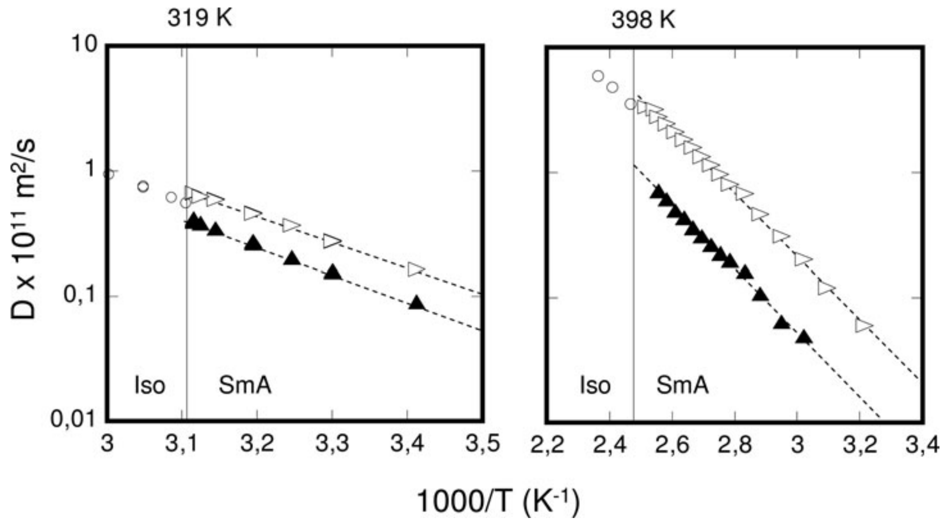

Figure 4. Translational diffusion coefficients D_{iso} (o) $D_{||}$ (▲) and $D_{\perp}$(△) of the cation C12mim of Cmim12BF4 (left side) and C12mimCl (right side) in the isotropic and smectic A phases. Broken lines represent Arrhenius fittings of the diffusion coefficient temperature dependence.

Results and Discussion

Self diffusion in the isotropic phase has been measured with the DSTE experiment cooling the sample in proximity of the Iso-SmA phase transition. The double stimulated echo was used in order to compensate possible convective motions due to small temperature inhomogeneities across the sample. The gradient along the z direction was chosen for the measurements, but also x and y direction have been tested giving the same diffusion coefficient as expected in the isotropic phase. The results are reported in Figure 4.

Measurements in the Smectic A phase were carried out with the ME-STE pulse sequence, as previously discussed. The sequence is not compensated for possible convection flows, however considering the high viscosity of the phase and the short length of the sample (about 3 mm along the z direction), convective motions can be safely neglected.

While measuring diffusion in the isotropic phase is a relatively straightforward task as it does not depend on the gradient direction and normally transverse relaxation time is quite long, in the order of seconds, in the liquid crystalline phases there are complications due to anisotropy [17].

It is well known that the smectic A phase has a uniaxial symmetry around the phase director, that is that in the principal axis frame of the phase, the diffusion second rank tensor is diagonal and can be expressed as [17]:

$$\tilde{D} = \begin{pmatrix} D_{XX} & D_{XY} & D_{XZ} \\ D_{YX} & D_{YY} & D_{YZ} \\ D_{ZY} & D_{ZY} & D_{ZZ} \end{pmatrix} \xrightarrow[PAS]{} \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix}$$

$$\to \begin{pmatrix} D_{\perp} & 0 & 0 \\ 0 & D_{\perp} & 0 \\ 0 & 0 & D_{||} \end{pmatrix} \tag{2}$$

Hence, the two diffusion coefficient $D_{||} = D_{zz}$ and $D_{\perp} = D_{xx} = D_{yy}$, corresponding to diffusion along and perpendicular the phase director have to be measured in order to fully determine the diffusion tensor.

As the C12 mim cation has a long alkyl chain, it has a negative diamagnetic susceptibility $\Delta\chi > 0$. In this case the phase director of the smectic A phase, normal to the smectic layer, aligns orthogonally to the static magnetic field $\mathbf{B_0}$. With this molecular orientation, the phase director $\hat{n}$ is hence cylindrically distributed in the (x,y) plane around the magnetic field direction, as shown in Figure 2.

This orientation in the laboratory frame (x,y,z) implies that measuring diffusion along the magnetic field direction z give direct access to the coefficient $D_{\perp}$, for the in plane diffusion, while measuring the out of plane diffusion coefficient $D_{||}$ is not so straightforward.

The diffusion process occurring along a direction normal to the static magnetic field is a combination of in and out of plane diffusion. Thus, once a specific gradient direction, i.e. x, is chosen, the measured diffusion coefficient along the x direction is

$$D_{xx} = D_{||} \cos\phi + D_{\perp} \sin\phi \tag{3}$$

for an arbitrary phase director orientation forming an azimuthal angle ϕ with the x gradient axis, as shown in Figure 2. Consequently, also the average square displacements along the gradient direction $\langle x^2 \rangle$ has to be rewritten accordingly [18]:

$$\langle x^2 \rangle = 2D_{||}\Delta \cos^2\phi + 2D_{\perp}\Delta \sin^2\phi \tag{4}$$

where Δ is the diffusion time previously defined.

Using equation (4) to rewrite the correct echo decay expression for the ME-STE experiment performed along the x direction gives [18]:

$$A = \exp\left(-(\gamma\delta G)^2 D_{\perp}\right) \times \int_0^1 \exp\left(-(\gamma\delta G)^2 \left(D_{||} - D_{\perp}\right) x^2\right) dx \tag{5}$$

that obviously depends on both the principal diffusion coefficients and can be used to determine the out of plane diffusion $D_{||}$, once the other diffusion coefficient is fixed to the value obtained from the measurement along the z direction.

Equation (5), firstly proposed by Callaghan to measure water diffusion in the endosperm tissue of a single wheat grain [18] and more recently used to also measure ionic diffusion in a liquid crystal columnar phase [19] was then used to determine the diffusion coefficients along the gradient x direction in the smectic A phase of the two smectogens under investigation.

The echo decays measured along the z and x axes at T = 395 K in the smectic A phase of C12mimCl are reported in Figure 3, as example.

As shown in the figure, diffusion along the z gradient direction can be well fitted by equation (1) giving $D_{\perp} = 3.2 \cdot 10^{-11} m^2/s$, while diffusion measured along the x direction is best fitted by equation (5), and $D_{||} = 0.85 \cdot 10^{-11} m^2/s$ was obtained fixing $D_{\perp}$ to the previously obtained value.

Following this approach, ME-STE experiment has been performed along the z and x directions as a function of temperature and the two diffusion coefficients for the C12 mim cation have been determined; the results are reported in figure 4. In order to test the results along the x direction also diffusion along the y direction has been measured, providing the same results within experimental error.

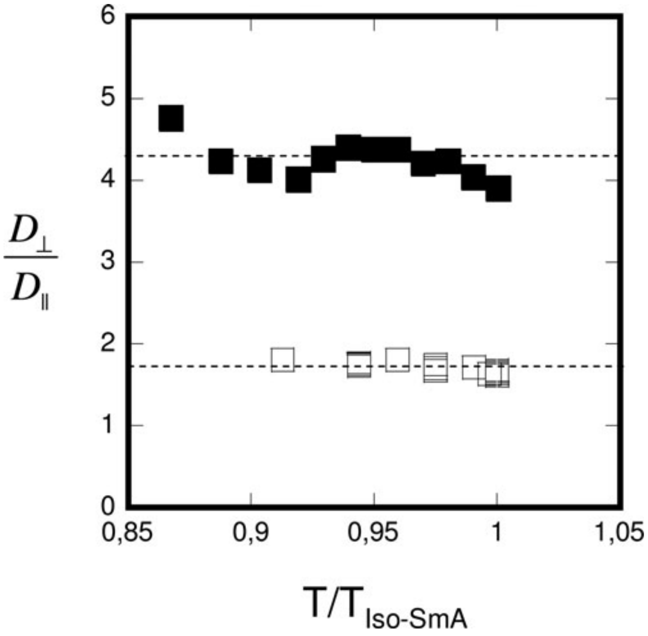

Figure 5. Diffusion anisotropy$D_\perp/D_{||}$ in the smectic A phase of the mesogens C12mimBF4 (□) and C12mimCl (■) as a function of the reduced temperature (T/T$_{\text{Iso-SmA}}$). The broken lines represent the average value.

As shown in the picture, for both samples diffusion in the smectic A phase is characterized by the anisotropy $D_\perp/D_{||} < 1$; the smectic structure hinders the out of plane diffusion in respect to the in plane one. This results are in agreement with previously investigated smectic phases of thermotropic smectogens exhibiting a direct Iso-SmA phase transition [20, 21]. Arrhenius equation

$$D(T) = D_\infty \exp(E_a/RT) \tag{6}$$

is used to fit the temperature dependence of the diffusion process. In our samples, the activation energies E_a for the in plane and out of plane diffusion motions are quite similar. As example, it is $E_a^{||} = 49KJ/mol, E_a^{\perp} = 48KJ/mol$ and $E_a^{||} = 42KJ/mol, E_a^{\perp} = 39KJ/mol$ for the C12mimCl and C12mimBF4 sample, respectively. It is in contrast with non ionic thermotropic smectic A phases, where the activation energy of the out of layer diffusion in typically much higher than the in plane one [20, 21]. This different behaviour, in our opinion, deserves further investigations.

The anisotropies of the cationic diffusion data have been also compared for different counterions as shown in Figure 5. C12mim diffusion anisotropies $D_\perp/D_{||}$are reported as a function of the reduced temperature T/T$_{\text{Iso-SmA}}$, where T$_{\text{Iso-SmA}}$ indicated the Isotropic to Smectic A phase transition. It is clear from the figure that the average anisotropy increases significantly (from about 1.8 to 4.2) as the anion changes from BF4 to Chlorine, putting in evidence an effect of the anion on the smectic structures besides on the phase stability temperature range. Moreover, simulations of the translational diffusion in the Smectic A phase of an ILC have been recently reported on an analogous system [22]. In that case the model takes into account a C16mim chain with a nitrate counter ion and, interestingly, the

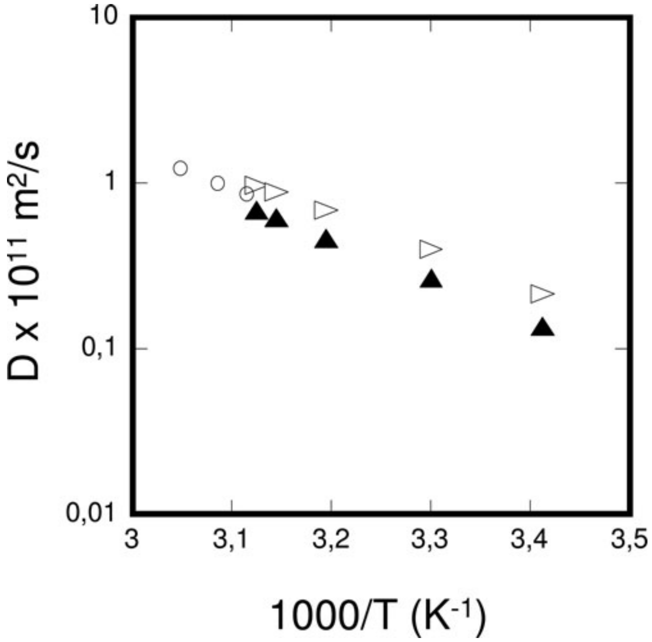

Figure 6. Translational diffusion coefficients D_{iso} (o) $D_{||}$ (▲) and $D_{\perp}$(▷) of BF4 anion of Cmim12BF4 in the isotropic and smectic A phase.

results are in good agreement with the experimental ones here reported both in terms of the order of magnitude of the diffusion coefficients and their anisotropies [22].

In the case of C12mimBF4 also anionic diffusion could be measured exploiting ^{19}F NMR diffusometry on the BF4 moiety. The results are reported in Figure 6.

The measured anionic self diffusion, compared to that for the cationic, is faster in both directions. This behaviour is in agreement with a partial separation of the ionic couple; the smaller and less anisotropic anion moves faster in the more ordered lamellar cationic matrix. Concerning the anionic diffusion anisotropy, $D_{\perp}/D_{||} < 1$ analogously to the cationic one, however it is lower on average, being about 1.2 against 1.8. This again is in agreement with the diffusion of a globular particle in the anisotropic environment of the calamitic C12 mim cations.

Finally, it's interesting to notice that the ratio of cationic and anion diffusion in both direction is again in good agreement with that calculated by coarse grained simulations performed on the smectic A phase of the C16mimNO3 system [22]. Also in this case, anionic diffusion turns to be faster and less anisotropic, as found in our measurements.

Conclusions

In this paper, the possibility of measuring self-diffusion in smectic phases of ionic LC's is demonstrated also in the case of the strongly anisotropic and bulky imidazolium cation. Recent results on translational diffusion in analogous systems were limited to the more symmetric anion as well as to Li cations dissolved in the smectic phase [23]. Here it is the first time that LC cation self-diffusion is reported and its anisotropy evaluated and discussed in terms of a different ionic couple with the same mesogenic cation.

These preliminary results can be hence considered encouraging, showing that the methodology proposed can be exploited to gather information on self-diffusion behaviour of ILCs phases and extended to other similar systems. Collected data can be also useful to validate (or rule out) results obtained by theoretical calculations and simulations.

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