



The dynamics of cations in pyridinium-based ionic liquids by means of quasielastic- and inelastic neutron scattering



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ABSTRACT

Neutron scattering is an excellent tool to study the dynamics of hydrogen-rich materials. In the present work we subsume our results on pyridinium-based ionic liquids. We have performed inelastic, quasielastic and elastic neutron scattering experiments aiming to understand the different dynamical processes that occur at different temperatures in ionic liquids. Using quasielastic scattering we obtained data that can be described as a superposition of localized dynamical processes and long range diffusion. The localized processes, which originate from the alkyl chain and the pyridinium ring of the cation, have been modelled in terms of the so-called Gaussian model. The influence of the length of the alkyl chain, attached to the cation, on the dynamical processes is discussed in detail. Furthermore we show neutron backscattering data, obtained on partially deuterated samples, that clearly demonstrate the melting of the alkyl chain and the activation of methyl end-group rotations at low temperatures. Finally, the power of deuterium labelling is evidenced for inelastic neutron scattering data.

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1. Introduction

Cold and thermal neutrons have wavelengths that match interatomic distances as well as energies that compare very well to excitation energies in condensed matter. Furthermore, due to the outstanding incoherent scattering cross section of hydrogen, hydrogen-rich materials are very well suited for an investigation using neutron scattering methods. The time scale covered by QENS (quasielastic neutron scattering) ranges from a fraction of picoseconds to nanoseconds and, hence, this method is a valuable tool for studying such processes as diffusion, rotation, libration etc. of molecular and ionic species [1,2]. On the other hand, information about macroscopic dynamics in ionic liquids (ILs) is highly required for their manifold applications, especially, for electrochemical devices [3]. Ion pair formation [4], and existence of long-lived cages [5], and correlated motions [6,7] are some of the currently discussed topics concerning heterogeneous dynamics in ILs. The advantages of QENS has also been used to study these questions [8–11], however, the number of the works on this technique remains limited.

In this paper we summarise our neutron scattering results obtained on pyridinium-based ionic liquids with [Tf₂N] anions. This family of ILs has been selected because of the negligible incoherent scattering cross

section of the anion and the fact that the cation can be easily modified in terms of the alkyl chain length and the possibility to get partially deuterated cations. This latter possibility enables us to *switch on/off* scattering contributions from the different parts of the cations. Moreover, this group of ILs shows some beneficial properties for such applications as dye-sensitized solar cells [12] and ionogels, based on the confinement of an IL in a thermally stable inorganic skeleton [13].

We start with a short description of the preparation and characterisation of our sample, followed by a short introduction into the method of quasielastic neutron scattering (QENS). In Section 3 of this paper we present and discuss our results and we finish this paper with a short outlook.

2. Materials and methods

In this paper we present results on pyridinium-based ILs (See Fig. 1). The list below contains all relevant cations, anions and ILs.

1. C₄H₉–C₅H₅N, protonated [BuPy] cation
2. C₄D₉–C₅D₅N, completely deuterated [Bu_DPy_D] cation
3. N(SO₂CF₃)₂, [Tf₂N] anion
4. IL [C₄H₉–C₅H₅N]⁺[N(SO₂CF₃)₂][–] ([BuPy][Tf₂N])
5. IL [C₄D₉–C₅D₅N]⁺[N(SO₂CF₃)₂][–] ([Bu_DPy_D][Tf₂N])
6. C₁₂H₂₅–C₅H₅N, protonated [C₁₂Py] cation
7. IL [C₁₂H₂₅–C₅H₅N]⁺[N(SO₂CF₃)₂][–] ([C₁₂Py][Tf₂N])

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The efficiency of interaction between an incident neutron and a sample nucleus is represented by means of the quantity called neutron cross section. As the neutron can be either scattered or absorbed by the target, the values of the scattering (σ_{scatt}) and absorption (σ_{abs}) cross sections, respectively, are of relevance for planning a neutron scattering experiment. The scattering cross-section can be further subdivided into coherent (σ_{coh}) and incoherent (σ_{inc}) scattering cross sections, which show whether collective effects or uncorrelated motions will influence the spectrum of the scattered neutrons. Table 1 summarizes the mentioned neutron cross sections for the studied species. We see that the incoherent scattering cross section of the $[\text{TF}_2\text{N}]$ anion can be completely neglected and that the scattering cross section can highly be influenced by exchanging H by D.

2.1. Sample preparation

We used a two-step process to synthesize protonated as well as partially or completely deuterated pyridinium based ionic liquids.

2.1.1. Synthesis of *N*-butylpyridinium bis(trifluoromethylsulfonyl)imide

In the first step we prepared *N*-butylpyridinium bromide. To do so, pyridine was refluxed, in a standard reflux apparatus, fitted with a drying tube, which contained P_2O_5 as drying medium. An equimolar quantity of 1-butylbromide was slowly added and the reaction mixture was refluxed in a dark environment for four days. After cooling to room temperature, the resulting white and shining crystals were purified by recrystallization with ethyl acetate and quickly transferred into a bottle. In the second step, *N*-butylpyridinium bromide was dissolved in distilled water, and an equimolar amount of lithium bis(trifluoromethylsulfonyl)imide was added. The aqueous phase with dissolved LiCl was removed; the remaining ionic liquid was washed 5 times with distilled water and dried 3 days in vacuum at 60 °C, resulting in a colourless viscous liquid with a yield greater than 95%.

2.1.2. Synthesis of $[\text{Bu}_p\text{Py}][\text{TF}_2\text{N}]$, $[\text{BuPy}_d][\text{TF}_2\text{N}]$ and $[\text{C}_{12}\text{Py}][\text{TF}_2\text{N}]$

The partially and fully deuterated ILs were synthesized by the same process detailed above, but with deuterated educts (Butylbromide(d_9)), (Pyridine(d_5)), depending on the cases. The same process was also applied for the $[\text{C}_{12}\text{Py}][\text{TF}_2\text{N}]$, by replacing the *N*-butylpyridinium bromide with *N*-dodecylpyridinium bromide. The water content (<80 ppm) of all the synthesized ionic liquids was determined by means of Karl-Fischer titration. Furthermore, we checked the purity and quality of the partial deuteration ($98.16 < \%D < 99.70$) using NMR-techniques.

2.2. Differential scanning calorimetry, DSC

For the characterization of the studied ionic liquids, determination of the temperatures of phase transitions, DSC measurements have been carried out with a Netzsch DSC 204 F1 System. Measurements were performed on heating and cooling with a rate of 5–10 K/min using 20–30 mg samples encapsulated in standard Al crucibles. An argon stream was used during the whole experiment as a protective gas. The

Table 1

Summary of the neutron scattering and absorption cross sections of the different species mentioned in this paper. σ_{abs} is given for neutrons with 5.75 Å incident wavelength. $1\text{b} = 10^{-28} \text{ m}^2$.

System	σ_{scatt} [b]	σ_{abs} [b]	σ_{inc} [b]	σ_{coh} [b]	$\sigma_{\text{inc}}/\sigma_{\text{scatt}}$ [%]
1	1209.75	21.07	1124.15	85.60	92.9
2	168.43	6.20	29.21	139.22	17.3
3	65.70	9.67	0.52	65.18	0.8
4	1275.45	30.74	1124.67	150.78	88.2
5	234.13	15.87	29.73	204.40	12.7
6	2566.48	38.18	2408.32	158.16	93.8
7	2632.18	47.85	2408.84	223.34	91.5

DSC curves of both samples exhibit a distinct dependence on the temperature history (Fig. 2). Both crystallization and cold crystallization points are affected by the rate of cooling or heating. The onset points for the melting peaks seem to be independent of this parameter (Table 2).

2.3. Quasielastic neutron scattering, QENS

In a QENS experiment the intensities are measured as a function of both, scattering angle 2θ and energy transfer between neutrons and sample, $E = \hbar\omega = \hbar\omega_i - \hbar\omega_f = E_i - E_f$, where E_i and E_f denote the initial and final neutron energy, respectively; this allows for an investigation of the dynamics of a system. QENS [14,1,2,15] investigates small energy exchanges peaked at $E = 0$. Neutrons are electrically neutral and therefore do not interact with the electrons of the atoms/molecules in condensed matter, but are scattered at their nuclei. Since the wavelength and the kinetic energy of cold and thermal neutrons is comparable to interatomic distances and excitation energies in condensed matter, respectively, the diffusion process can be studied on atomic scales of space and time simultaneously, and this feature is unique. For X-rays with wavelengths of a few Å the energies are in the keV range, and for Raman or Brillouin light scattering the energy fits to excitation energies in condensed matter, but the wavelength is far too large.

2.3.1. Neutron scattering basics

The intensity of the scattered neutrons is proportional to the double differential cross-section

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} \left\{ \frac{\sigma_{\text{coh}}}{4\pi} S_{\text{coh}}(\mathbf{Q}, \omega) + \frac{\sigma_{\text{inc}}}{4\pi} S_{\text{inc}}(\mathbf{Q}, \omega) \right\} \quad (1)$$

where k_i is the wave number of the incident neutrons and k_f is the wave number of the scattered neutrons.

Strictly speaking, the scattering process is a quantum mechanical transition and has to be treated in terms of wave functions, transition probabilities, time-dependent perturbation theory etc. and, eventually, ensemble averages. On the other hand, classical particle diffusion in condensed matter is treated in terms of statistical physics. The interface between these quite different types of descriptions is given by thermal averages which can be expressed in terms of so-called van Hove correlation functions, $G(\mathbf{r}, t)$ and $G_s(\mathbf{r}, t)$. The correlation function $G(\mathbf{r}, t) d\mathbf{r}$ is the conditional probability that, given a particle was at time $t = 0$ at the origin $\mathbf{r} = 0$, any particle is found at time t at the position \mathbf{r} in a volume element $d\mathbf{r}$. The self-correlation function $G_s(\mathbf{r}, t) d\mathbf{r}$ is the conditional probability that, given a particle was at time $t = 0$ at the origin $\mathbf{r} = 0$, the same particle is found at time t at the position \mathbf{r} in a volume element $d\mathbf{r}$.

The Fourier transformation of $G(\mathbf{r}, t)$ with respect to space yields the so-called intermediate scattering function $I(\mathbf{Q}, t)$, and a subsequent temporal Fourier transformation yields the dynamical scattering function

$$S(\mathbf{Q}, \omega) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{i(\mathbf{Q}\mathbf{r} - \omega t)} G(\mathbf{r}, t) d\mathbf{r} dt \quad (2)$$

The analogous treatment of the self-correlation function yields, via the self-part of the intermediate scattering function $I_s(\mathbf{Q}, t)$, the incoherent scattering function $S_{\text{inc}}(\mathbf{Q}, \omega)$. With respect to diffusion, $S(\mathbf{Q}, \omega)$ gives access to collective diffusion and $S_{\text{inc}}(\mathbf{Q}, \omega)$ gives access to self-diffusion.

2.3.2. Applications of the QENS method

Concerning the different types of stochastic motions which can be studied by the QENS method we have to differentiate between localized and long-range diffusion. In the case of long-range self-diffusion, $I_s(\mathbf{Q}, t)$ decays to zero for $t \rightarrow \infty$, while for localized motions (like rotations or

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