Experimental report

13/10/2017

Proposal:	**6-02-572**	**Council:**	4/2016
Title:	Influence of H-bonds on cation dynamics in Protic Ionic Liquids		
Research area:	Physics		

This proposal is a new proposal

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Local contacts:	Jacques OLLIVIER Bernhard FRICK
Samples:	triethylammonium trifluoroacetate methanesulfonate triethylammonium perfluorobutanesulfonate triethylammonium perflurooctanesulfonate triethylammonium

Instrument	Requested days	Allocated days	From	To
IN6	0			
IN16B	3	3	23/09/2016	26/09/2016
IN5	6	5	23/06/2016	28/06/2016

Abstract:

We suggest to perform QENS and fixed energy scan experiments as a function of the temperature to probe the dynamics of 4 different protic ionic liquids (PILs) with an unchanged cation and varying the anion. The series of samples has been selected to change the H-bond interaction between the cation and anion. The aims of our experiment are the following: First we want to study the global dynamics of the cation (TEA, triethylammonium, partially deuterated samples), second we want to investigate the cation's ethyl chain dynamics, and third we want to understand the hydrogen bond dynamics between the cation and the various anions. To accomplish these objectives, we propose to combine results obtained with IN5 and IN16B, respectively.

Influence of H-bonds on cation dynamics in PILs

Proposal No.: 6–02–572

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Instrument: IN5/IN16B **Date:** 23.06.16 – 28.06.16
Instrument Responsible: Jacques Ollivier/Bernhard Frick

Protic Ionic Liquids (PILs) are produced by combining a Brønsted acid and a Brønsted base. Here we present results of the experiments aiming to understand the influence of hydrogen bonding in PILs' dynamics. The PILs investigated have a single cation type but different anions. The cation is a hydrogen rich molecule whereas the anion contains no H-atoms. Partially deuteration of the cation was used as a tag of possible hydrogen bonds. The instrument was set up with a wavelength λ=5.5 Å providing a resolution of ~ 60 µeV and a time window of some picoseconds. The accessible energy range for this setup is between ±1.7 meV, the momentum transfer ranges from 0.4 Å^{-1} to 1.8 Å^{-1}.

cations			
molecular formula	acronym	σ_{coh}	σ_{inc}
$NH(C_2H_5)_3$	$[TEA]^+$	72.42	1284.79
$NH(C_2D_5)_3$	$[d{-}TEA]^+$	1129.95	111.52

Table 1 – *Set of cations their respective scattering cross-sections (given in barn) at* λ=5.5 Å.

anions			
molecular formula	acronym	σ_{coh}	σ_{inc}
$O_2C{-}CF_3$	$[2\,C]^-$	31.88	0.006
$O_3S{-}CD_3$	$[MS]^-$	36.04	6.16
$O_3(CF_2)_4F$	$[PFBS]^-$	72.88	0.02
$O_3(CF_2)_8F$	$[PFBS]^-$	127.49	0.03

Table 2 – *Set anions and their respective scattering cross-sections (given in barn) at* λ=5.5 Å.

The data were analyzed assuming that the signal is dominated by incoherent contributions from the cations, i.e. we neglect the tiny incoherent contributions from the various anions, see Tab.1,2. The partially deuterated cation shed some light on the spatial domain visited by the acidic proton attached to $[d\text{-}TEA]^+$. The measured spectra have to be corrected for the finite instrumental resolution R(Q,E), for processes that are faster that the ones resolved by the actual instrument settings (and thus contribute as a broad background B to the overall signal) and for the Debye-Waller factor, absorbed in a general intensity factor I(Q).

$$S_{\text{observed}}(Q,E) = I(Q)S_{inc}(Q,E) \otimes R(Q,E) + B \tag{1}$$

A simultaneous analysis of the spectra, i.e., a two dimensional fit, was carried out first on $[d{-}TEA]^+$. It turned out, that the model that describes the signal best is the convolution of a jump diffusion [1], characterizing the centre of mass long range diffusion, with a single Gaussian-type restricted dynamics [2], see Fig.1,2.

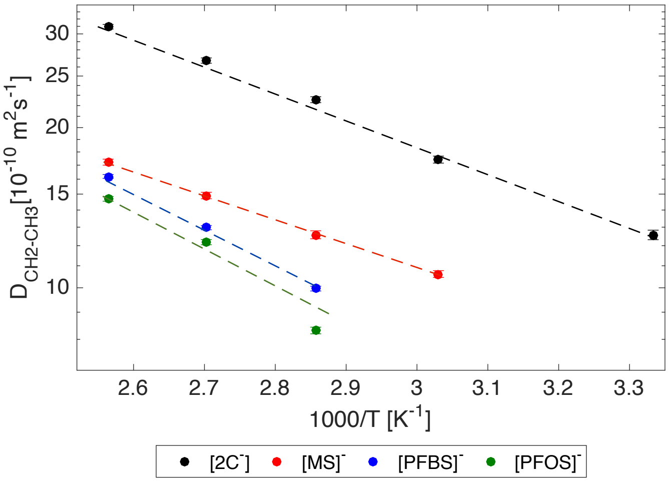


Figure 1 – *Shows the Arrhenius behaviour of the confined diffusion coefficient of the methyl (CH_3) and methylene (CH_2) groups.*

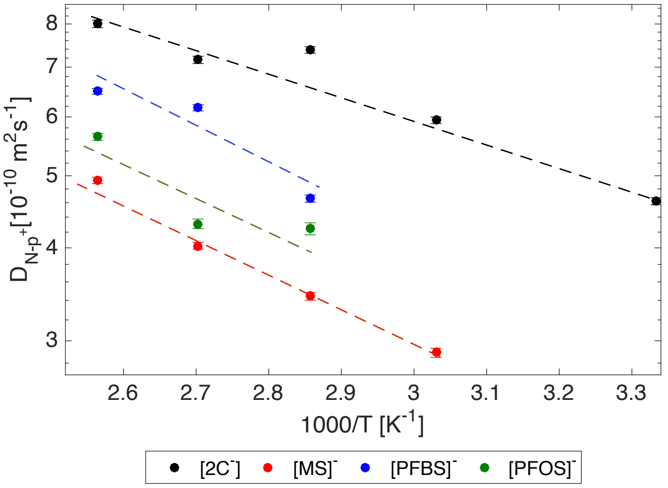


Figure 2 – *The localized diffusion coefficient of the acidic proton directly connected to the nitrogen atom shows an Arrhenius behaviour and is also anion specific.*

In the case of $[TEA]^+$, two extra localized Gaussian-like dynamical components were found. The first one describing the methyl group motions and another accounting for the dynamics of the methylene groups. For all protiated PIL, the results found for the Gaussian process in [d-TEA]$^+$ were added and fixed to the localized self-dynamical structure factor respectively.

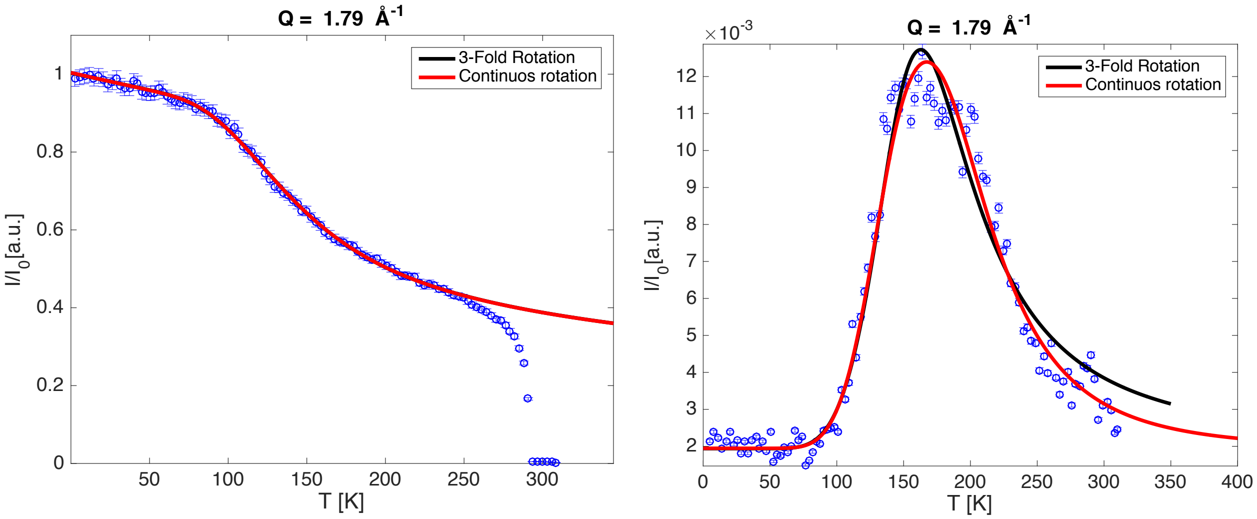
$$S^{TEA}_{local}(Q,E) = \frac{9}{16} S^G_{CH_3}(Q,E) + \frac{6}{16} S^G_{CH_2}(Q,E) + \frac{1}{16} S^{G[d-TEA]^+}_{NH}(Q,E) \tag{2}$$

$$S_G(Q,E) = e^{-Q^2\sigma^2}\left(\delta(E) + \sum_{n=1}^{\infty} \frac{(Q\sigma)^{2n}}{n!} \frac{1}{\pi} \frac{\frac{n\hbar D_{loc}}{\sigma^2}}{(\frac{n\hbar D_{loc}}{\sigma^2})^2 + E^2}\right) \tag{3}$$

IN16B the instrument was set up with a wavelength λ=6.27 Å providing us a resolution of 0.75 µeV and a time window of some nanoseconds. Elastic and inlelastic (at an offset of $E_{\text{off}} = 2\,\mu\text{eV}$) fixed window scans (FWS) were performed simultaneously. The samples were all measured on heating form $2\,\text{K} \leq T \leq 370\,\text{K}$. Two models were considered for the IN16B data, namely, a 3-fold jump rotation and a continuous rotation, accounting mainly for the methyl group rotations.

$$S_{3f}(Q,E) = \frac{1}{3}\left(1 + 2j_0\left(\sqrt{3}QR\right)\right)\delta(E) + \frac{2}{3\pi}\left(1 - j_0\left(\sqrt{3}QR\right)\right) \frac{\frac{3\hbar}{2\tau}}{\left(\frac{3\hbar}{2\tau}\right)^2 + E^2} \tag{4}$$

$$S_{cont}(Q,E) = j_0^2(QR)\delta(E) + \frac{1}{\pi}\sum_{k=1}^{\infty}(2k+1)j_k^2(QR)\frac{\frac{k(k+1)\hbar}{6\tau_r}}{\left(\frac{k(k+1)\hbar}{6\tau_r}\right)^2 + E^2} \tag{5}$$



(a) (b)

Figure 3 – *(a) The fixed window scans FWS for [TEA]$^+$[2 C]$^-$; the lines describe two different kind of data adjustment before the melting transition at ≈ 250 K, namely a 3-fold jump rotation and a continuous rotation; (b) The IFWS show, that exactly where the elastic intensity starts to decrease the inelastic intensity increases.*

The width of the Lorentzian functions in the models are assumed to have an Arrhenius behavior. The fit results are summarized in Tab.3. To get stable fits, it was necessary to fixed the radius R, i.e. the average C–H bondlength to 1.16 Å [3].

Table 3 – *Best fit results for [TEA]$^+$[2 C]$^-$ using the 3-fold jump and the continuous rotation model, respectively.*

fit parameter	3-fold jump rot.	continuous rotation
p_{mob}	0.78 ± 0.07	0.69 ± 0.06
R(Å)	1.16	1.16
t_0(ps)	70.80 ± 32.40	15.6 ± 7.50
E_a(kJ mol^{-1})	4.71 ± 0.47	5.15 ± 0.49

References

[1] C.T.Chudley and R.J.Elliott. *Proc.Phys.Soc.*, 77(2):353, 1961.

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[3] T. Burankova, R. Hempelmann, V. Fossog, J. Ollivier, T. Seydel, and J. P. Embs. *J.Phy.Chem. B*, 119(33):10643–10651, 2015.