Experimental Report

21/06/2013

Proposal:	**6-05-861**	**Council:**	4/2011
Title:	Proton Dynamics in Protic Ionic Liquids		

This proposal is a new proposal

Researh Area: Physics

Main proposer: **EMBS Jan P**

Experimental Team: BURANKOVA Tatsiana
EMBS Jan P

Local Contact: OLLIVIER Jacques

Samples: Triethylammonoin-trifluoromethanesulfonate / NH(C2H5)3-CF3SO3 and NH(C2D5)3-CF3SO3

Instrument	Req. Days	All. Days	From	To
IN5	5	3	03/12/2012	06/12/2012

Abstract:

We propose both, quasielastic as well as inelastic neutron scattering experiments to study the dynamics of the protic ionic liquid TEA-Tf (triethylammonium-triflate). The aim of the proposed quasielastic experiments are as follows: first we intend to study the global dynamics of the TEA-cation, second we want to investigate the ethyl-chain dynamics and finally, we want to understand the hydrogen-bond dynamics between cation and the corresponding anion.

Finally we want to perform experiments in order to investigate the DOS (generalized vibrational density of states) of the corresponding liquids. The aim of these experiments is to study the contributions of different parts of the cation / anion; in collaboration with Prof. Buchner from the University of Regensburg we will compare the outcome of the intended experiment with corresponding results from dielectric spectroscopy.

Proton dynamics as function of deuteration in Protic Ionic Liquids

Proposal No.: 6 – 05 – 861

Experimental team:

Jan Peter Embs[1], Tatsiana Burankova[1,2]
[1]Laboratory for Neutron Scattering, Paul Scherrer Institut, 5232 Villigen, Switzerland
[2]Physical Chemistry, Saarland University, 66123 Saarbrücken, Germany

Instrument: IN5 (03.12.2012 – 06.12.2012)

Local contact: Jacques Ollivier

To study the proton dynamics of triethylammonium trifluoromethanesulfonate (TEA, $[NH(C_2H_5)_3][CF_3SO_3]$) we performed experiments on both totally and partially deuterated samples. The wavelength of incident neutrons of 5.0 Å was chosen as a compromise between a higher neutron flux and a better resolution function to fulfill the requirements of the planned experiments, as our aim was twofold. On one hand we intended to investigate the GDOS of the liquid and to compare the outcome with the corresponding results from dielectric spectroscopy and FIR-measurements. On the other hand the purpose of the QENS measurements was to consider global diffusion of cations, ethyl-chain libration or methyl-group rotation at lower temperatures, dynamics of the single proton in the partially deuterated sample, for which we expected the side-chain contributions to be suppressed.

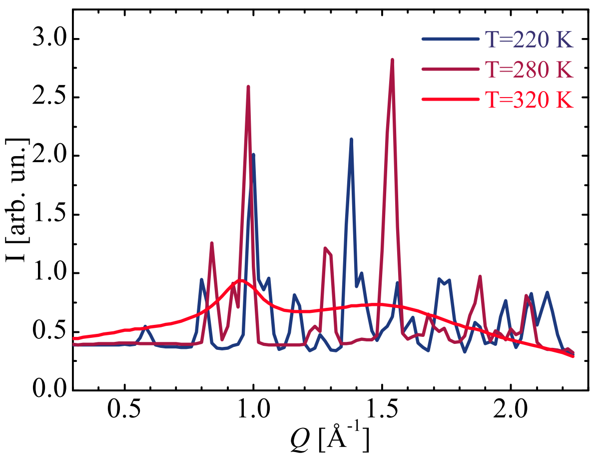

Fig. 1. The changes in the integrated intensity of the partially deuterated sample at the two phase transitions.

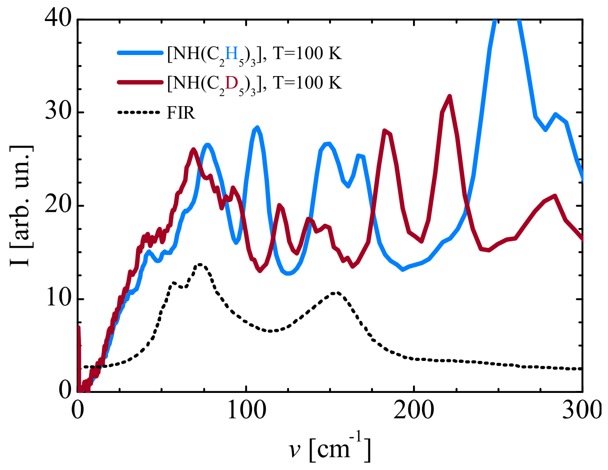

Fig. 2. Generalized density of states of the totally protonated and partially deuterated sample at T=100 K in comparison with the FIR-spectrum.

We studied both samples ($[NH(C_2H_5)_3]$ and $[NH(C_2D_5)_3]$) in the temperature range between 100 K and 440 K. At lower temperatures we focused our attention on the two phase transitions at T_1=227 K and T_2=300 K (as observed by the DSC-measurements) and recorded spectra before and after the melting points. Though the energy window available in the experiment is limited, integrated intensity can give some valuable information about the static structure factor of a sample. We analyzed the latter as a function of temperature (Fig. 1). The phase transition at T_1=227 K is manifested as a slight shift of the peaks as well as an intensity redistribution, some peaks disappearing totally. The narrow lines are smeared when the second phase transition occurs; the pattern exhibits wide maxima typical for molten salts in the liquid state.

The changes in the inelastic spectra can be traced only at the first melting point. Figure 2 presents GDOS of the protonated and partially deuterated samples in comparison with the FIR-spectrum of the totally protonated TEA.

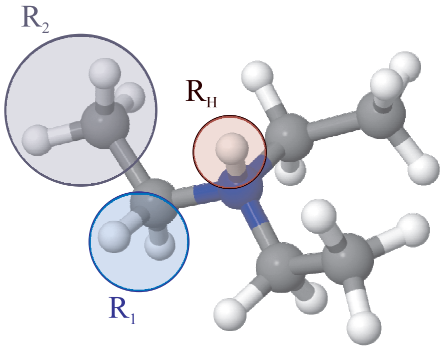

Fig. 3. Cation structure of [NH(C_2H_5)$_3$][CF_3SO_3].

The localized dynamics of the end methyl-groups of the alkyl chains (Fig. 3) turned out to be too slow to be resolved by the instrument (FWHM$_{\rm res}$=0.070 meV, $\Delta t_{\rm obser}$ $\sim$1 ps) at T<180 K. In the temperature range T=250 − 290 K it is possible to fit the spectra of [NH(C_2H_5)$_3$] with the rotational diffusion model under the assumption that only a portion of the protons p_{mob} is involved in the considered motion [1]:

$$S_{rot}(Q,E) = (1-p_{mob})\,\delta(E) + \\ + p_{mob}\cdot\left[j_0^2(QR)\delta(E) + \sum_{k=1}^{\infty}(2k+1)j_k^2(QR)\frac{1}{\pi}\frac{k(k+1)\hbar/6\tau_R}{(k(k+1)\hbar/6\tau_R)^2+E^2}\right] \tag{1}$$

The evaluated value p_{mob} proved to be equal to 0.55 ($\approx$ 9/16); the relaxation time τ_R amounted to $\sim$ 4 ps, the radius of the sphere R increasing gradually from 1.16 Å to 1.45 Å. In the same temperature range the QENS-broadening of the partially deuterated TEA is suppressed, giving another experimental indication that the considered process arises from the alkyl-chains.

In the liquid state the QENS-spectra of both samples can be presented by two Lorentzian curves. From our previous investigation [2] we knew that the narrower Lorentzian is connected with global diffusion. The second broader curve accounts for various types of localized motions. The analysis of [NH(C_2D_5)$_3$] was complicated by a substantial coherent component from both the cation and the anion. The incoherent scattering from the 15 deuterium atoms is also comparable with the contribution from one proton. If we assume that the total scattering of the protonated sample $S_{\rm H}(Q,E)$ is dominated by the incoherent scattering from the ethyl-chains, then the incoherent contribution from the 15 deuterium atoms can be excluded from consideration by subtracting as $S_{{\rm D}corr}(Q,E) = S_{\rm D}(Q,E) - \frac{\sigma_{\rm D}}{\sigma_{\rm H}}S_{\rm H}(Q,E)$. Unfortunately, this correction does not allow to eliminate the coherent scattering, but our recent experiment on separation of coherent and incoherent contributions indicated that interference effects are crucial only for the long-range diffusion [3]. The localized processed turned out to be not influenced by the static structure factor; whereas the converse is true for the linewidthes of the narrower Lorentzian. Taking this into account, we decided not to consider any model for the slower process in the case of [NH(C_2D_5)$_3$] and chose the Gaussian model [4] for describing the localized dynamics of the single proton. The scattering law used for the fits of the partially deuterated sample reads:

$$S_{{\rm D}corr}(Q,E) = S_{glob}(Q,E)\otimes S_{loc}(Q,E;D_H,R_H) \tag{2}$$

$$S_{glob}(Q,E) = \frac{1}{\pi}\frac{\Gamma_{tr}(Q)}{\Gamma_{tr}^2(Q)+E^2} \tag{3}$$

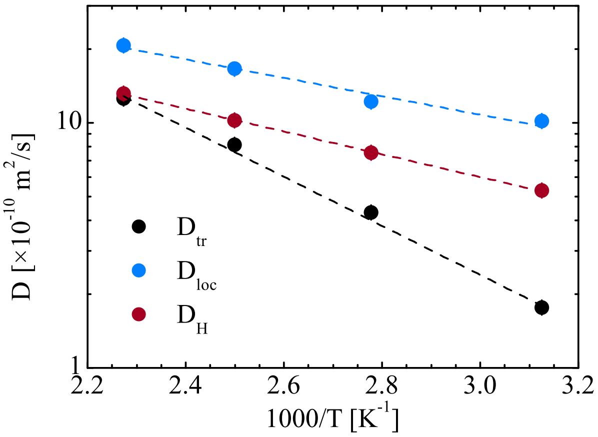

Fig. 4. Temperature dependence of the diffusion coefficients describing the global diffusion and the localized motion of $[NH(C_2H_5)_3]$

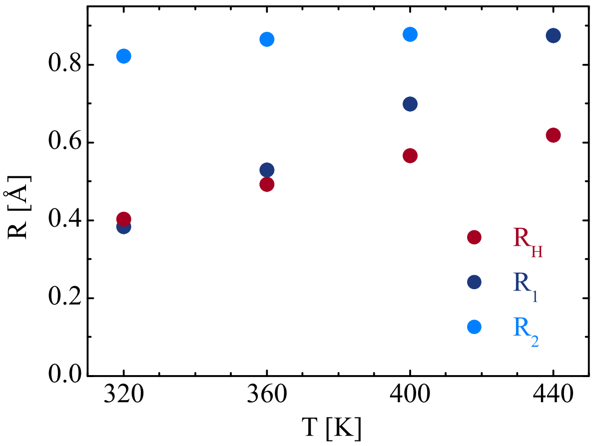

Fig. 5. Temperature dependence of the radii characterizing the localized motion of the different parts of the cation.

$$S_{loc}(Q,E;D_H,R_H) = e^{-Q^2R_H^2}\left[\delta(E) + \sum_{n=1}^{\infty}\frac{(Q^2R_H^2)^n}{n!}\frac{1}{\pi}\frac{\hbar n D_H/R_H^2}{(\hbar n D_H/R_H^2)^2+E^2}\right] \tag{4}$$

In the case of the totally protonated sample it was possible to perform a fitting routine including the jump-diffusion model [5] explicitly for the long-range diffusion:

$$\Gamma_{tr} = \frac{\hbar D_{tr}Q^2}{1+D_{tr}Q^2\tau_0} \tag{5}$$

The localized dynamics was considered for several groups of the protons shown in Figure 3:

$$S_{Hloc}(Q,E) = \frac{1}{16}S_{loc}(Q,E;D_H,R_H) + \frac{6}{16}S_{loc}(Q,E;D_{loc},R_1) + \frac{9}{16}S_{loc}(Q,E;D_{loc},R_2) \tag{6}$$

Figures 4–5 summarize the temperature dependences of the all fitted parameters. Arrhenius plots (Fig. 4) illustrate that the dynamics of TEA in the liquids state is decidedly heterogeneous and characterized by several diffusion coefficients. It is necessary to mention that the value D_{loc} should be different for the first and second groups of the hydrogen atoms; however, introduction of one more parameter renders a fitting routine unstable. Figure 5 gives an idea about the flexibility of the ethyl chain as a function of temperature. At higher temperatures all the protons are fast enough, so that the difference in the domain size is indistinguishable on the time-scale of the experiment.

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