Experimental report

06/09/2018

Proposal: **6-05-993**

Council: 4/2017

Title: High-pressure isochronal study on ionic liquid

Research area: Soft condensed matter

This proposal is a new proposal

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Local contacts: Bernhard FRICK

Samples: Pyr14-TFSI (1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide)

Instrument	Requested days	Allocated days	From	To
IN16B	6	4	11/04/2018	15/04/2018

Abstract:

The objective is to study how the alpha relaxation evolves in an ionic liquid (IL) as a function of T and P, especially along an isochrone (constant relaxation time) found from the fixed window scan technique on IN16B, i.e. on nanosecond time scale, while monitoring the conductivity with dielectric spectrocospy (DS) on slower time scales. As predicted by the isomorph theory, we have shown that both the fast and slow dynamics scale along isochrones in a large part of T,P-phase space in the HP DS-NS cell (LTP-6-7) for a van der Waals liquid. In the proposed IL more than 95% of the total scattering will be incoherent scatt. from the cation. This is of interest since the cations form polar domains on mesoscopic length scales. This experiment will provide information on the dynamics of these heterogeneities as a function of T and P along an isochrone. In addition, the cation has both a methyl group and an alkane side chain, which might give contributions that are different in T,P-dependence. Therefore we do not know whether ILs obey the isomorph theory, which predicts that structural and dynamical properties of ALL time scales should be invariant along the same lines in T,P-phase space.

Beamtime report from IN16B, exp_6-05-993, April 2018

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Power: 50 MW
Wavelength: 6.27 Å, Si(111)

Sample: Pyrr14TFSI (1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide)

D0-P14TFSI: fully protonated. Thickness: 0.15 mm, $T \sim 85\%$
D3-P14TFSI: methyl group deuterated. 0.2 mm, $T \sim 85\%$
D9-P14TFSI: butyl chain deuterated. 0.2 mm, $T \sim 88\%$
D12-P14TFSI: methyl group and butyl group deuterated. 0.3 mm, $T \sim 87\%$

All data in **high-pressure cell** are done on **D12-P14TFSI**.

Temperature scans in normal cell

In Fig. 1, the elastic and inelastic ($E_{\text{offset}} = 2\,\mu\text{eV}$) intensity on a temperature scan are plotted for the fully protonated (D0-P14TFSI) and methyl group and butyl chain deuterated (D12-P14TFSI), along with part of the temperature scan of D9-P14TFSI, butyl chain deuterated. These scans were done in the cryo furnace from when the instrument was handed over Wednesday evening to Thursday morning before changing to the 70 mm cryostat for the HP cell.

The rest of the temperature scan for D9-P14TFS and the one for D3-P14TFSI will be done some night at some point in a not too far distance.

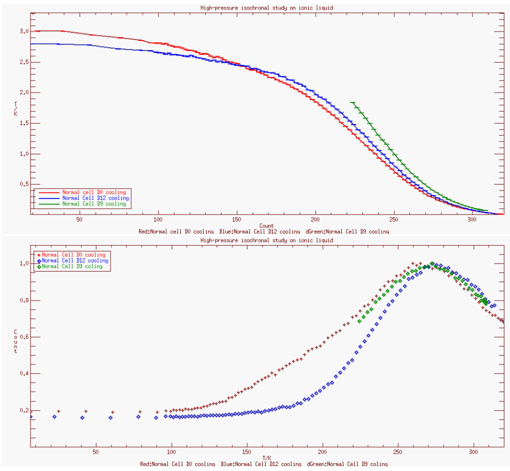

Figure 1: Elastic (top) and inelastic (bottom) fixed window scans with $\Delta E = 0$ and $2\,\mu\text{eV}$, respectively for the fully protonated D0-P14TFSI (red), methyl group and butyl group deuterated D12-P14TFSI (blue), and the part of the temperature scan with butyl chain deuterated D9-P14TFSI (green). Data are here summed over Q.

High pressure fixed window scans

From the pressure scans (Fig. 2) on isotherms there is a nice change in intensity with pressure, however, the inelastic signal is very weak. Increasing the counting time to 10 min did not help much on the errorbars or the fluctuation in signal − this is 5 times as long as what we often have done. The rest of the pressure scans and the temperature scans where therefore only done with elastic fixed windows.

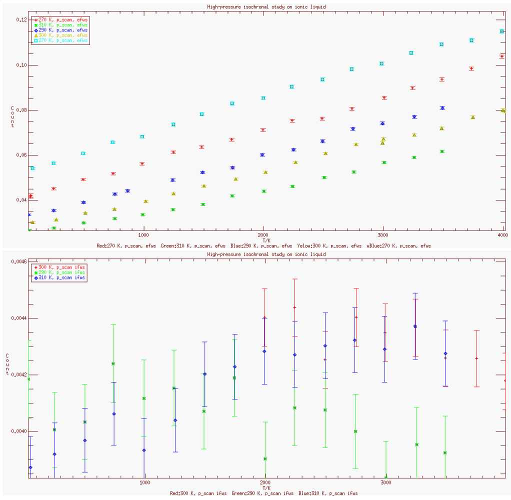

Figure 2: Elastic (top) and inelastic (bottom) fixed window scans with $\Delta E = 0$ and $2\,\mu\text{eV}$, respectively as a function of pressure. Data are here summed over Q and measured on D12-P14TFSI.

The temperature scans (Fig. 3) at ambient pressure and 3 kbar done with a cooling ramp of $0.5\,\text{K}\,\text{min}^{-1}$ are nicely supercooled with glass transition temperatures of 187 K and 217 K, respectively. On fast mode heating, the intensity reproduces nicely, with only a small temperature lack. First crystallisation takes place at 210 K (0 kbar) and 255 K (3 kbar), second crystallisation at 245 K (0 kbar) and 270 K (3 kbar). Melting temperatures at 265 K (0 kbar) and 290 K (3 kbar). Valuable information for the upcoming IN5 beamtime.

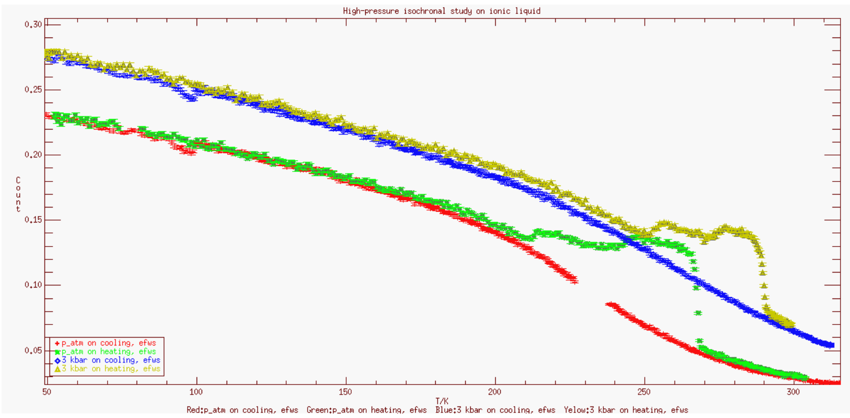

Figure 3: Elastic (top) and inelastic (bottom) fixed window scans with $\Delta E = 0$ and $2\,\mu\text{eV}$, respectively as a function of temperature on cooling and heating. Data are here summed over Q and measured on D12-P14TFSI.

High pressure dielectrics

Fig. 4 show an example of dielectric data along an isotherm, here conductivity.

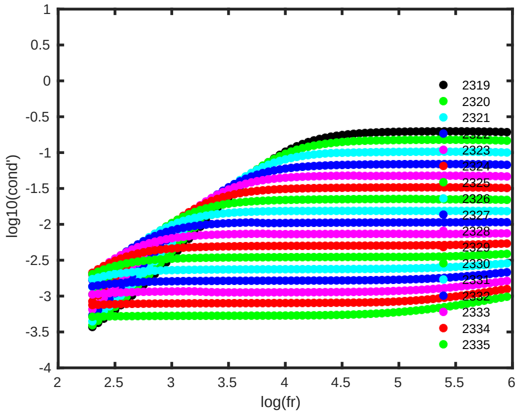

Figure 4: Example of conductivity measurements on a pressure scan at 300 K from ambient pressure to 4 kbar in steps of 0.5 kbar.

High pressure spectra

Full spectra (Fig. 6) obtained along isochronal state points determined from elastic fixed window intensity and in agreement with conductivity measurements (Fig. 5): 270 K Patm and 290 K 1.5 kbar and 310 K 2.75 kbar.

Again, the broadening or inelastic part is quite weak.

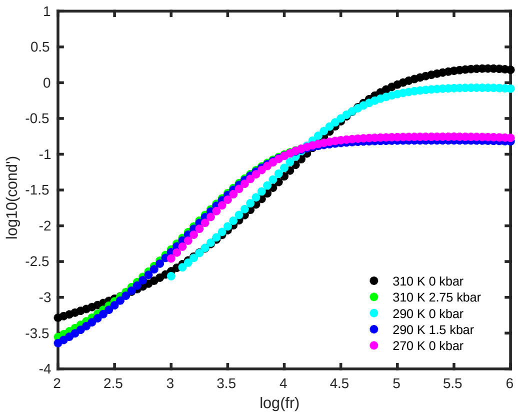

Figure 5: Conductivity of the state points where full sprectra were obtained.

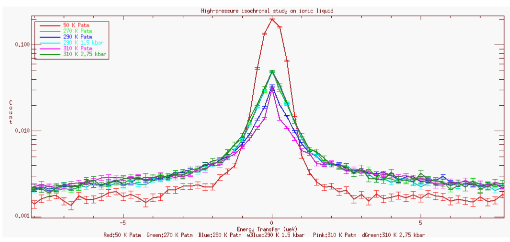

Figure 6: Spectra summed over Q and measured on D12-P14TFSI.