Experimental Report

14/01/2014

Proposal:	**6-02-523**	**Council:**	10/2012
Title:	Dynamics of ionic liquids under confinement		

This proposal is a new proposal

Researh Area: Soft condensed matter

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Samples: O(d17)MIM-Br

Instrument	**Req. Days**	**All. Days**	**From**	**To**
IN11	10	8	13/05/2013	21/05/2013

Abstract:

The propensity of Ionic Liquids (IL) to self-organize in transient nanoscopic domains induces a low ionic conductivity at long time (ms) and large scale (micrometer). We propose to lift the detrimental effect by frustrating the formation of the IL nanometric domains using confinement of the IL within a controlled porous structure. While a prepeak around 0.2-0.4 Å-1 of the confined IL structure factor can be used to quantify (in situ and on line) the extent of the nanosegregation, we will focus on the measurement of the translational self-diffusion coefficient of the center-of-mass of the confined IL molecules. The parasitic quasi-elastic contribution(s) of the IL side-chains will be discarded by use of a specifically deuterated IL.

Obtained results: We obtained 8 days on IN11, so we decided to focus on the fully hydrogenated bulk OMIM-BF$_4$ and the confined one in pores of 35 nm at 300 K. We performed these measurements using 5.5 Å as wavelength and we scanned a dynamical window going from 10 to 1000 ps and from 0.13 to 1.18 Å^{-1}.

From the information about the polarization, we could calculate the structure factor S(Q) of the two samples (Fig. 4).

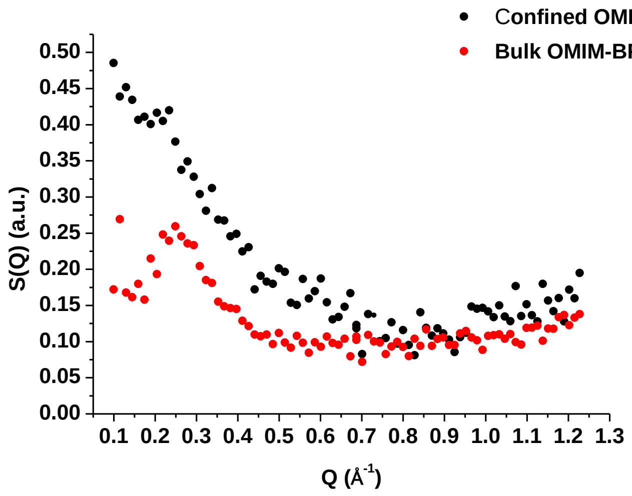

Fig.4: *Structure factor obtained by the measured spectra on IN11 of bulk OMIM-BF4 and the confined one (pore diameter equal to 35 nm) at 300 K. We can note an attenuation of pre-peak due to the confinement.*

As we can see from the plot shown in Fig 4, in the bulk case we can note well the pre-peak in the Q region between 0.2 and 0.4 Å^{-1} due to the auto-organization of the system. At the other hand, when we observe the S(Q) of the confined liquid, we can see a superposition of the pre-peak with a monotonically decreasing signal due to a specific surface contribution of the AAO membrane[4]. We can conclude that there is an attenuation of the peak which reveals a frustration of self-organization behavior due to the confinement.

Then we passed to study the samples dynamics. In figure 5 and 6 are shown the measured intermediate scattering function I(Q,t) at the different values of Q.

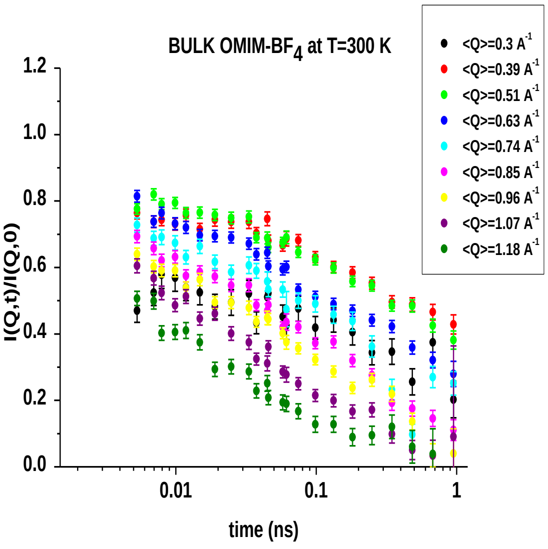

Fig.5: *Intermediate scattering function measured on bulk OMIM-BF4 on IN11 at 300 K.*

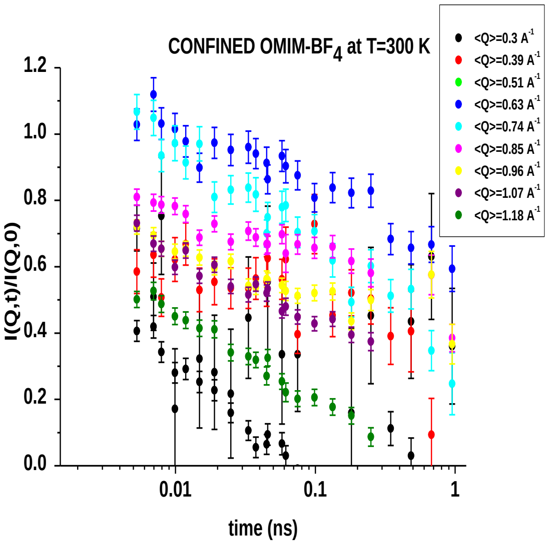

Fig.5: *Intermediate scattering function measured on confined OMIM-BF4 on IN11 at 300 K.*

As we can notice from Figure 6, in spite of the lowest quantity of the sample in the beam (only few mg), we could obtain surprisingly a signal with a quite good statistics.

Seeing the plot shown in figure 5 and 6, we notice that the scattering function displays a relaxation in the time region of 100 ps, and it seems to show another one at smaller time which is not visible because it is outside of the observation window. For confirming this hypothesis we performed on the same samples a time of flight (TOF) experiment on IRIS at ISIS. These measurements allowed us to access to the dynamics in the time region between 1 and 10 ps. The TOF spectra confirmed that there is effectively a second faster relaxation. These results are consistent with other neutron experiments performed on other OMIM ionic liquid[6], which assign the faster relaxation to the localized motion of alkyl chain while the second one to the diffusional motion of the molecular c.o.m.. Because of the presence of the contribution of the chain dynamics it was not possible to determine the self-diffusion coefficient in the two samples. This is compatible with the previous results obtained on the bulk OMIM ionic liquids[7], where it was shown that the chain dynamics strongly affects the determination of self-diffusion coefficient in QENS experiments. Following this previous study, a method for determining this quantity could be doing the same experiment with deuterated chain ionic liquids. In this way the contribution of the chain dynamics would be minimized.

In conclusion we retain that it would be interesting to do the same experiment with O(d17)MIM-BF_4 for completing the characterization of OMIM-BF_4 diffusional properties.

References

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