Experimental Report

Proposal: **6-05-934** **Council:** 4/2014

Title: Dynamics in deep eutectic protic ionic liquid-DMSO mixtures

This proposal is a new proposal

Researh Area: Soft condensed matter

Main proposer: **TRIOLO Alessandro**

Experimental Team: TRIOLO Alessandro

Local Contact: FRICK Bernhard

Samples: dimethylsulfoxide
ethylammonium nitrate

Instrument	Req. Days	All. Days	From	To
IN16B	5	3	28/11/2014	01/12/2014

Abstract:

We propose to explore the relaxation processes occurring in deep eutectic binary mixtures of a protic ionic liquid (ethylamonium nitrate, EAN) and dimethyl sulfoxide. Similarly to water-DMSO, EAN and DMSO form mixtures with much lower melting point than the pure compounds. EAN and water have in common the extensive H-bonding network and its interaction with DMSO is presumably responsible for the peculiar thermodynamic behaviour.
Complementing structural (high energy x-ray and neutron scattering) and other dielectric spectroscopic characterization, we propose to use backscattering QENS technique to access the mesoscopic local and diffusive dynamics of the two components.

Report on “Dynamics in deep eutectic protic ionic liquid-DMSO mixtures ” (6-05-934)

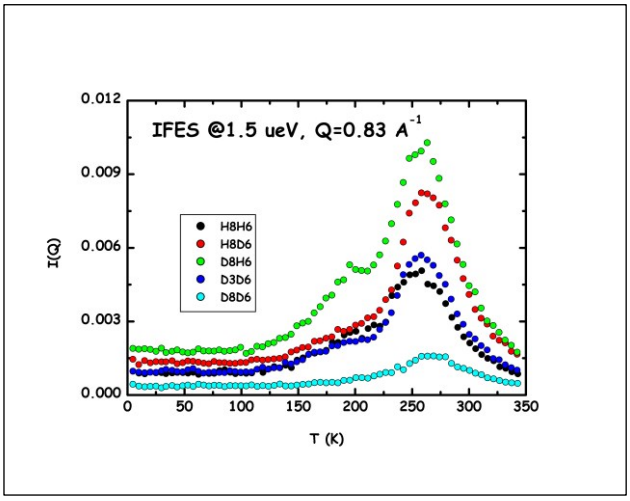
The proposed experiment was awarded with 3 days beam time on IN16B in December 2014. Due to the limited time so far available a more detailed report cannot be provided, but we report these preliminary results, in order to support our request for more beam time at the same beamline on a related series of experiments.

The experiment was successful. We applied for five days beam time, but were awarded with 3 days, with the panel comments of better validating our system before being granted more beamtime. We believe that the present report and the enclosed dielectric spectroscopy evidences provide a sound preliminary dynamic scenario for the explored mixture.

We investigated ethylammonium nitrate-dimethylsulfoxide (EAN-DMSO) mixtures. EAN is a protic ionic liquid, that means an ionic liquid (IL) that is obtained through an acid-base reaction. As such it can stand an extended hydrogen bonding (HB) network, very similar to the water one. Driven by this analogy and considering the peculiarities of H2O-DMSO mixtures, we started to investigate EAN-DMSO mixtures and observed that similarly to the water analogue, they show low (or no) crystallization point. Accordingly we decided to investigate the dynamics of a representative EAN(CH3CH2NH3 NO3):DMSO ((CH3)2SO)=1:3 mixture, using IN16B. We exploited the inelastic fixed energy scan (IFES) option that is now routinely available at the instrument to access detailed information on this mixtures and took advantage of selective deuteration of the two components. Namely we collected IFES from 4 up to 350 K for the following samples:

- h8,EAN-h6,DMSO;
- h8,EAN-d6,DMSO;
- d8,EAN-h6,DMSO;
- d3,EAN-d6,DMSO;
- d8,EAN-d6,DMSO.

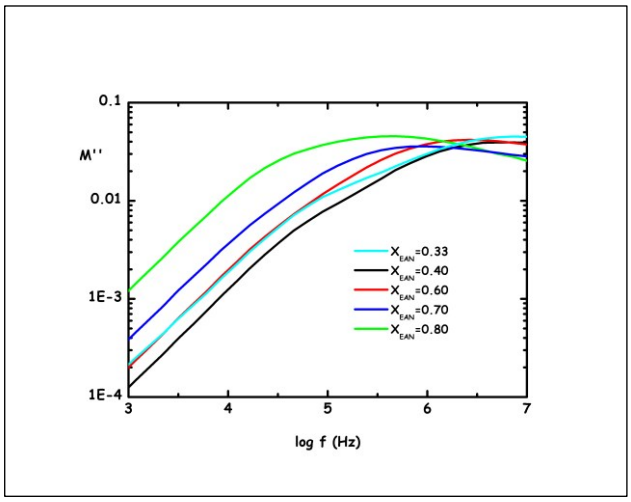
Furthermore the empty cell contribution was collected in a narrower temperature window. All these samples were measured in the IFES option at two inelastic values, namely 1.5 and 5 μeV. Moreover the Elastic fixed energy scan (EFES, with resolution of 1 μeV) was also collected. These measurements provide with a detailed description of the dynamic features, allowing for extracting the relaxation map of the mixture. The use of differentlky deuterium labelled mixtures should allow distinguishing between contributions from either EAN or DMSO, if they are different.



From the structural point of view we found that this mixture is macroscopically homogeneous. Also at mesoscopic level, we did not find evidences of structural heterogeneities, as evidenced by both Small Angle X-ray and Neutron Scattering.

In Figure 1, we show the measured IFES, once subtracted of the background. It can be noticed that in the accessed temperature window all of the IFES data sets (apart from the d8,EAN-d6,DMSO one) show indication of two distinct relaxation processes in the nsec temporal window that is characteristic of the instrumental setup. Consistently with the structural homogeneity, also from the dynamic point of view it seems that the mixtures are homogeneous, as both EAN and DMSO seem to relax in similar way.

We observe however some small difference in the peak position and shape for the relaxation feature observed at high temperature that corresponds to the primary alfa process. This might indicate small, but nevertheless not negligible complexity in the diffusive behaviour of this system.



As a matter of fact we have also preliminary dielectric spectroscopy data that indicate such a possibility. In figure 2 we show the complex modulus for a set of EAN-DMSO mixtures at different concentration at 203 K. It can be appreciated the existence of two components building up the main relaxation peak for these mixtures.

Right now work is in progress to model both the dielectric data and the IFES in terms of two (or more) relaxation processes. In particular, we plan to model the IFES with two different contributions, one a t lower Ts that behaves as an Arrhenius activated process, while the high T process will be described as a Vogel-Fulcher-Tamman process with a non-Debye behaviour.