Experimental report

17/02/2020

Proposal: 6-05-1008 **Council:** 4/2019

Title: How independent is water dynamics in liquid glycerol-water mixtures?

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: HEAVY WATER
glycerol fully protonated
glycerol fully deuterated

Instrument	Requested days	Allocated days	From	To
IN16B	7	3	20/01/2020	23/01/2020

Abstract:

This proposal focuses on the dynamics in glycerol-rich glycerol water mixtures. In this region of the phase diagram there is no structural or thermodynamic signs of phase separation. However, based on the slow dynamics studied with dielectric and mechanical spectroscopy, we have seen indications that the dynamics of water becomes independent of the glycerol dynamics [PCCP., 20, 1716 (2018)]. In the proposed experiment we will study the pressure and temperature dependence of glycerol and water dynamics independent of each other by studying the mixtures in two version where one of the components is deuterated, i.e. one sample with deuterated glycerol and one with heavy water. In these samples the incoherent scattering of the protonated component will dominate and the dynamics of this component will be visible in the data. By this approach we will be able to evaluate whether the water and glycerol dynamics are linked or independent. We will perform simultaneous dielectric spectroscopy in order to see to which extend the dynamics of the individual components mimic that of the global alpha relaxation.

Dynamics of glycerol rich water-glycerol mixtures, 0.4 deuterated sample

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This experiment used simultaneous dielectric spectroscopy (Novocontrol alpha/beta analyzer) and quasi elastic neutron scattering (IN16B). The aim was to study the dynamics of glycerol water mixtures in the glycerol rich region. This experiment focused on the moderately glycerol rich region (glycerol molar ratio = 0.4). The sample is glycerol $(OD)_3$-D_2O. And we redid some more experiment on a fully protonated sample

Experiment on IN16B

On IN16B for the deuterated sample, we performed a cooling ramp isobar at 0.4 K/min (Patm) and 2 isotherms from atmospheric pressure to 4 kbar (310 K, 297 K) with fixed window scan at 0, 3 μeV and 6 μeV. We also did 5 full QENS spectrum at 6 state points (310 K Patm, 310 K 2.5 kbar, 310 K 4 kbar, 297 K Patm, 297 K 2.5 kbar and lastly 40 K Patm). For the protonated sample, 2 cooling ramp isobar at 0.4 K/min (Patm and 4 kbar), 1 isotherm at 310 K and 3 full QENS spectrum at 3 state points (310 K Patm, 310 K 4 kbar and 293.5 K Patm).

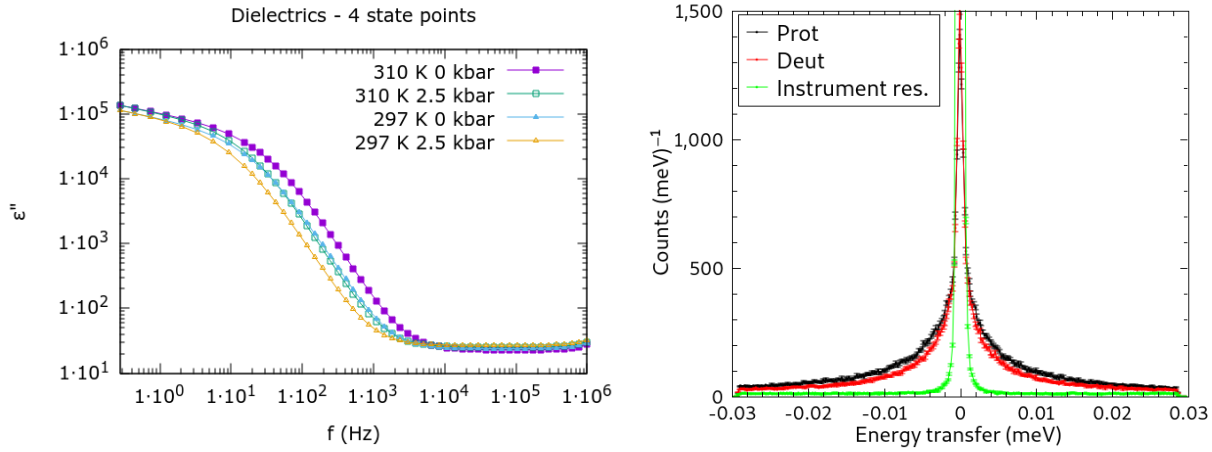

Figure 1: Dielectrics spectroscopy of glycerol water 0.4 molar ratio taken during the 4 state points QENS full spectrum.

Results

Comparing protonated and deuterated samples QENS, figure 1 right, we clearly see a drop in the inelastic signal, which is expected since most of it at high temperatures should come from the free water. The QENS of 310 K 2.5 kbar and 297 K Patm do overlap very well, figure 2 left, as they did for fully protonated sample. this is a good indication that the deuteration did not change the pressure behavior of the dynamics with the isotopic substitution. Having gone this time to higher pressure, 4 kbar instead of 2.5 kbar, we see that the relationship pressure/temperature effect is not linear. We find an isochrone at 4 kbar of $\sim$16.5 K, 4.1 K/kbar compared to 5.2 K/kbar at 2.5 kbar.

The sample of protonated glycerol water matches very well the same mixture done during experiment 6-05-998, seen in figure 2 right, comforting reproducibility. and comparing the 4 kbar isobar with the atmospheric pressure one, we see a slight broadening of the peak with pressure, which is also seen in dielectrics for the alpha relaxation.

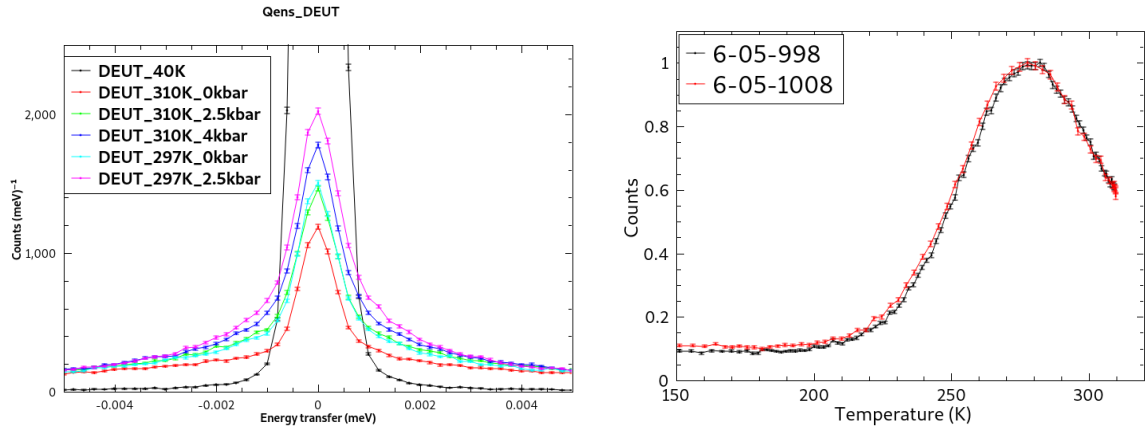

Figure 2: left: QENS full spectrum done at 310 and 297 K, and Patm and 2.5 kbar. in black taken at 40 K for instrument resolution. Right, 3 μeV fixed window scan of glycerol and 0.3, 0.4 and 0.7 glycerol molar ratio in water. using non pressur cells

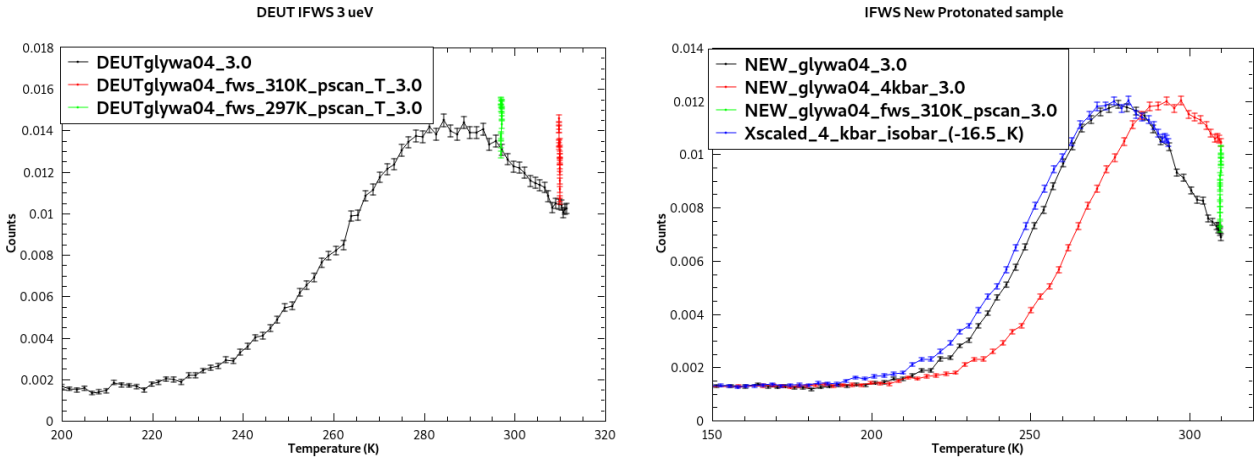

Figure 3: Fixed window scan. Elastic on the left and inelastic at 3 μeV on the right

During the second isotherm, at 297 K, while increasing pressure, the pressure cell failed at 3.5 kbar and the pressure fluid polluted the sample. Background was done then while preparing for a new sample. Decision was made to get some more information on the protonated sample at higher pressure. On the last morning, after releasing pressure then heating up from 40 K to 293.5 K, the cylindrical capacitor was crushed and a short could be seen in the dielectrics.

The next step is to look into the concentrated glycerol rich region (0.7 molar ratio), starting with experiment 6-05-1012 and check why there is a drift of the conduction band in dielectrics when coming back up to room temperature from 40 K.