Experimental report

Proposal:	6-02-645

Council: 10/2023

Title: Hydrogen-bond dynamics in 1-propanol and glycerol mixtures in the pressure and temperature dimensions

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: 1-propanol

Deuterated 1-propanol (OD)

1-propanol-(10%) glycerol mixture

Deuterated 1-propanol (OD)-(10%) glycerol (OD)3 mixture

Instrument	Requested days	Allocated days	From	To
IN16B	6	4	14/03/2024	18/03/2024

Abstract:

In this experiment, we shall investigate the dynamics of the hydrogen bond in 1-propanol and propanol-glycerol mixtures under pressure and temperature variation. Neutrons are our only option because techniques like dynamic light scattering and dielectric spectroscopy can't clearly differentiate the contributions from various sample components. We deuterate the sample in order to study the dynamics of the carbon backbone vs. hydrogen bond network since neutrons have a contrast in the density of their scattering lengths for different elements. By creating two different types of samples, one with deuterated propanol and a deuterated combination (propanol-glycerol), and the other entirely protonated, separation can be accomplished. Incoherent scattering will predominate for the protonated component, and the dynamics of that component will be apparent in the data. In order to determine how closely the dynamics of the individual components resemble those of the global alpha relaxation, we shall perform simultaneous dielectric spectroscopy. We will analyze the obtained data to extract the timescales and Q-dependence of the associated dynamics, focusing on the effect of increased pressure.

To investigate the pressure and temperature dependence of the dynamics of hydrogen bonding network in 1-propanol - (10%) glycerol mixture

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This study, associated with proposal number **6-02-645**, focused on conducting pressure- and temperature-dependent measurements on IN16B for two different mixtures: a) a 1-propanol-(10%) glycerol mixture and b) Deuterated 1-propanol (OD)-(10%) glycerol (D8) mixture. The dynamics of both samples were examined through a combination of elastic and inelastic Fixed Window Scans (FWS) at energy offsets of 3 µeV and 6 µeV, during cooling from 320 K to 10 K along two isobars: 0 kbar (ambient pressure) and 3 kbar. Additionally, shorter FWS measurements were carried out along three isotherms (150 K, 220 K, and 270 K), by incrementally increasing the pressure from 0 to 3 kbar at constant temperatures derived from the previous scans.J

IN16B was operated in Doppler mode with Si111 analyzer crystals, configured to high flux settings. This setup provided an energy resolution of 0.75 µeV, a total energy transfer range of ±30 µeV, and a Q range of 0.1–1.8 Å⁻¹. For the protonated sample, full window scans (QENS) were performed at ambient pressure at four temperatures (40 K, 150 K, 220 K, and 270 K), and at 3 kbar at three temperatures (150 K, 220 K, and 270 K). A specialized high-pressure dielectric-neutron sample cell, developed through an earlier collaboration between Roskilde University and the ILL, was used for these measurements. This cell facilitated simultaneous neutron and dielectric spectroscopy measurements at pressures up to 3 kbar. The dielectric measurements were primarily used to monitor the sample's state, specifically to detect any potential crystallization. No crystallization was observed, confirming the sample remained in a supercooled state throughout the experiment.

The experiment, conducted over four days of beam time on IN16B, encountered multiple challenges, particularly in the form of pressure failures caused by leaks. The pressure cell housed a cylindrical capacitor used for dielectric response measurements. Several issues arose as the pressure was increased to 3 kbar, including sample leakage from the pressure seal and damage to the capacitor's connecting pins. As a result, the measurements could not begin until the evening on the first day of beam time. These problems were often identified through dielectric measurements, such as a significant drop in the dielectric signal, which indicated potential damage or disconnection of the capacitor's connecting pins.

The measurement sequence began with an isobaric FWS measurement at 3 kbar, followed by pressure release to ambient conditions. At 150 K, a QENS measurement was performed at ambient pressure, followed by isothermal FWS and QENS measurements at 3 kbar. The pressure was then released, and the sample was heated to 220 K, where the same sequence of ambient and high-pressure measurements was repeated. This process was repeated at 270 K. After completing these measurements, the sample was replaced with a deuterated mixture, and an FWS measurement was conducted at 3 kbar, followed by an ambient pressure FWS isobar measurement.

Figure 1 presents the dielectric spectroscopy data collected during beam time, showing the imaginary part of the dielectric permittivity as a function of frequency. No abrupt intensity increases or peaks were observed, indicating that the sample remained in a supercooled state without unwanted crystallization.
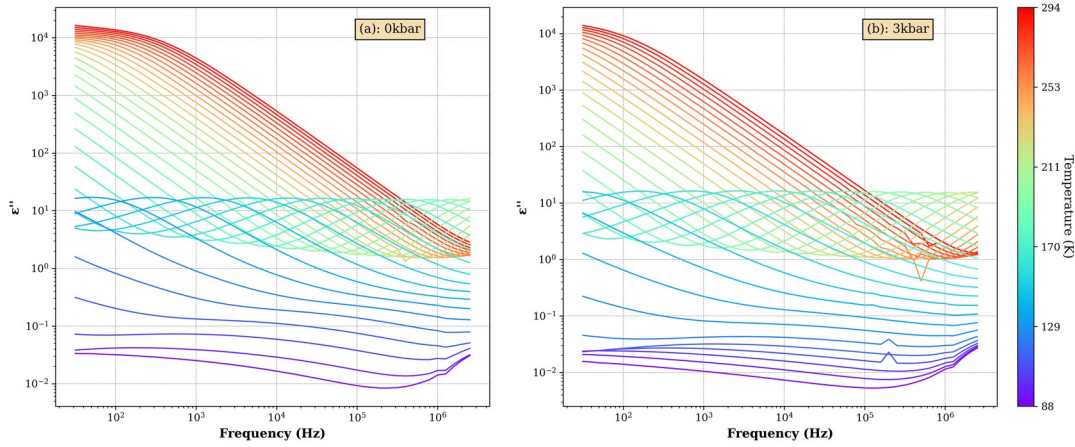
Fig. 1. Imaginary part of the dielectric constant for the protonated mixture at ambient pressure (left) and 3 kbar (right) for different temperatures, measured during beam time concurrently with ambient and 3 kbar isobar FWS measurements. No signs of crystallization were observed.

We observed a significant pressure dependence in the relaxation dynamics of mixture, with the slower relaxation process showing a pronounced response to pressure, while the faster relaxation process remained largely unaffected. This differential pressure dependence suggests the potential for separating the two relaxation processes. Additionally, the samples remained stable in the supercooled state down to 50 K. Figure 2 shows the sum of all q FWS for both protonated and deuterated samples at ambient

pressure and 3 kbar, clearly illustrating the impact of pressure and deuteration on the slower relaxation process.
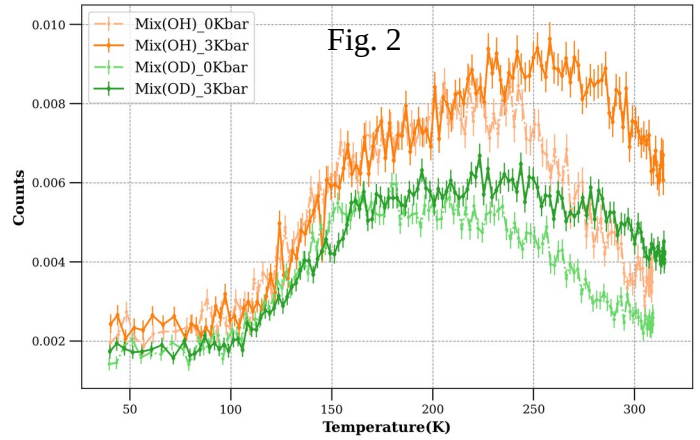
To analyze the data, we performed a q-dependent global fit, considering all q-dependent FWS and QENS spectra across all temperatures. Separate global fits were conducted for the ambient pressure and 3 kbar data. We evaluated various models, with the most significant being: KWW function, 1L + 1L, 1L + 1KWW, and 1KWW + 1L. For each model, we initially fitted the ambient pressure and 3 kbar data separately, followed by a simultaneous fit in which the faster process was kept constant across both pressures, while the slower process was allowed to vary freely. So far, the models **1L + 1KWW** and **1KWW + 1L** provide equally good fits to the data, while the other two models were discarded due to significantly poorer agreement with the experimental data.

Figure 3 presents a simultaneous global fit for the fixed-window scan of the mixture at ambient and 3 kbar pressure, plotted at 3 μeV energy transfer to examine the pressure effect on relaxations. The faster process is assumed to be associated with structural relaxation and is modeled using a

Kohlrausch–Williams–Watts (KWW) function, the Fourier transform of a stretched exponential. The stretching factor, β, characterizes deviations from exponential decay, with β = 1 indicating simple exponential behavior. Similarly, the slower process is attributed to supramolecular structure formation via hydrogen bonding and is represented by a Lorentzian function with a global activation energy and an Arrhenius prefactor γ_0, constrained across all **q** values. The activation energies for both processes and the β parameter of the KWW function are treated as global parameters. Amplitudes for 3 and 6 µeV energy transfers are tied per **q**-value, without imposing constraints between deuterated and protonated samples. The FWHM and γ_0 parameters for QENS data are linked to the corresponding γ_0 and activation energy from FWS data via the Arrhenius law. To ensure consistency between QENS and FWS, the amplitude ratio of the faster to slower processes in FWS is constrained to match the same ratio in QENS. In this model, the faster process is assumed to be pressure-independent.
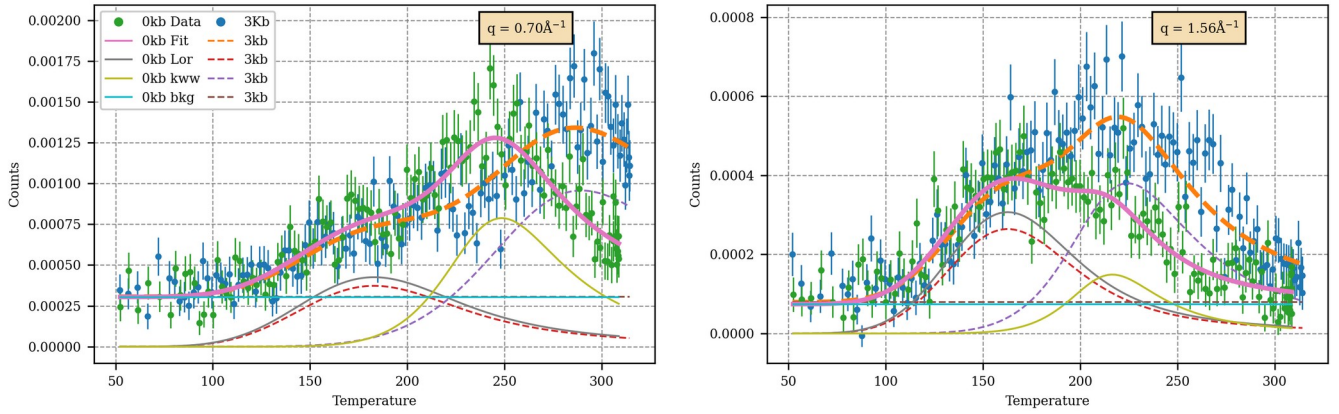

Fig. 3. Simultaneous global fit of fixed window scan (FWS) data for the protonated mixture at ambient pressure and 3 kbar, with a 3 µeV energy transfer, for two different q-values (0.70 Å⁻¹ and 1.56 Å⁻¹). Solid curves represent ambient pressure, and dashed curves represent 3 kbar pressure. The fit quality is indicated by a reduced chi-square value of $\chi^2 = 1.3$.
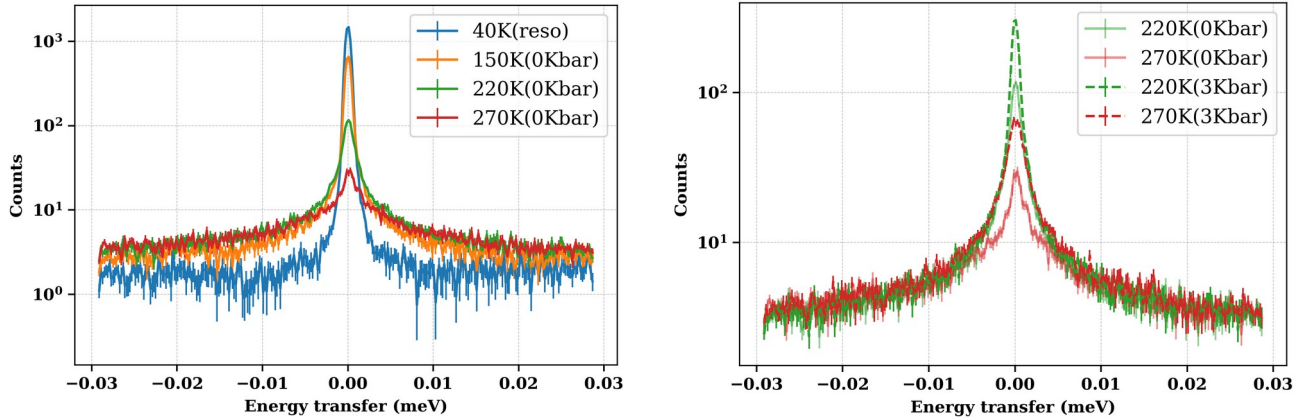

Fig. 4. The left panel shows the QENS spectra for the protonated mixture at four different temperatures under ambient pressure, summed over all q. The right panel compares the QENS spectra at 220 K and 270 K under 3 kbar with the ambient pressure spectrum, also summed over all q.