Experimental report

14/02/2025

Proposal: 6-02-657 **Council:** 4/2024

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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Experimental team:

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Samples: 1-propanol
Deuterated 1-propanol (OD)
1-propanol-(10%) glycerol mixture
Deuterated 1-propanol (OD)-(10%) Glycerol(OD) mixture

Instrument	Requested days	Allocated days	From	To
IN16B	4	3	30/05/2024	02/06/2024

Abstract:

In this experiment, we shall investigate the dynamics of the hydrogen bond in 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 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 and 1-propanol glycerol mixture

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This experiment, associated with proposal number **6-02-657**, is a continuation of proposal number **6-02-645**, which was submitted prior to the execution of the experiment corresponding to proposal 6-02-645. In this study, we conducted pressure- and temperature-dependent measurements on IN16B for bulk 1-propanol and 1-propanol (OD). For both samples, we investigated the dynamics using combined elastic and inelastic Fixed Window Scans (FWS) at 3 μeV and 6 μeV energy offsets during cooling from 320 K to 10 K along two isobars: 0 kbar (ambient pressure) and 3 kbar. Subsequent shorter FWS measurements were performed along three isotherms (150 K, 220 K, and 270 K) by stepwise increasing the pressure from 0 to 3 kbar at constant temperatures determined from the previous scans. During the measurements, IN16B was operated in Doppler mode, equipped with Si111 analyzer crystals and set to high flux settings. This configuration achieved 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 for four temperatures (40 K, 150 K, 220 K, and 270 K) and at 3 kbar for three temperatures (150 K, 220 K, and 270 K). The experiment utilized a specialized high-pressure dielectric-neutron sample cell, developed as part of an earlier LTP collaboration between Roskilde University and the ILL. This cell enabled simultaneous neutron and dielectric spectroscopy measurements at pressures up to 3 kbar. The primary goal of the dielectric measurements was to monitor the state of the sample, particularly to detect any unwanted crystallization during the experiment. No signs of crystallization were observed, confirming that the sample remained in the supercooled state throughout the measurements.

We had four days of beam time on IN16B. At the beginning of the experiment, multiple pressure failures were encountered, primarily due to pressure leaks. Inside the pressure cell, a cylindrical capacitor was mounted to measure the dielectric response. When the pressure was increased to 3 kbar, several issues arose: in some cases, the sample leaked from the pressure seal, while in others, the capacitor's connecting pins were damaged. Due to these difficulties, measurements could only begin 16 hours after the start of beam time. Many of these challenges were identified through dielectric measurements. For instance, a sudden decrease in the dielectric signal by several orders of magnitude indicated that the connecting pins were either damaged or disconnected.

Figure 1(a) shows the imaginary part of the dielectric strength for different temperatures at 1 kHz frequency, for ambient and 3 kbar isobars, with isotherms represented by blue pentagons. The measurement sequence was as follows:

1. **150 K:** Ambient pressure QENS measurement, followed by isothermal FWS and QENS measurement at 3 kbar at the same temperature.
2. Pressure release, followed by heating the sample to 220 K.
3. **220 K:** Ambient pressure QENS measurement, followed by isothermal FWS and QENS measurement at 3 kbar at the same temperature.
4. Pressure release, followed by heating the sample to 270 K.
5. **270 K:** Ambient pressure QENS measurement, followed by isothermal FWS and QENS measurement at 3 kbar at the same temperature.

In principle, the conductivity shown in Figure 1(a) should follow the path indicated by the arrows (a → c → a → e → d → e). However, instead of a smooth transition, the conductivity initially decreased with increasing pressure but then suddenly increased above the ambient pressure value, suggesting a possible contamination of the sample with the pressure-transmitting liquid. A similar trend was observed in the intensity of FWS isotherms measurements at 220 K and 270 K, where a drastic jump occurred at the last three pressure steps. Due to this anomaly, we are excluding the 220 K, 3 kbar QENS data and the 270 K ambient and 3 kbar data from our fitting analysis, as there is a strong possibility that the sample became contaminated during the pressure increase from the 220 K isothermal measurement onward.

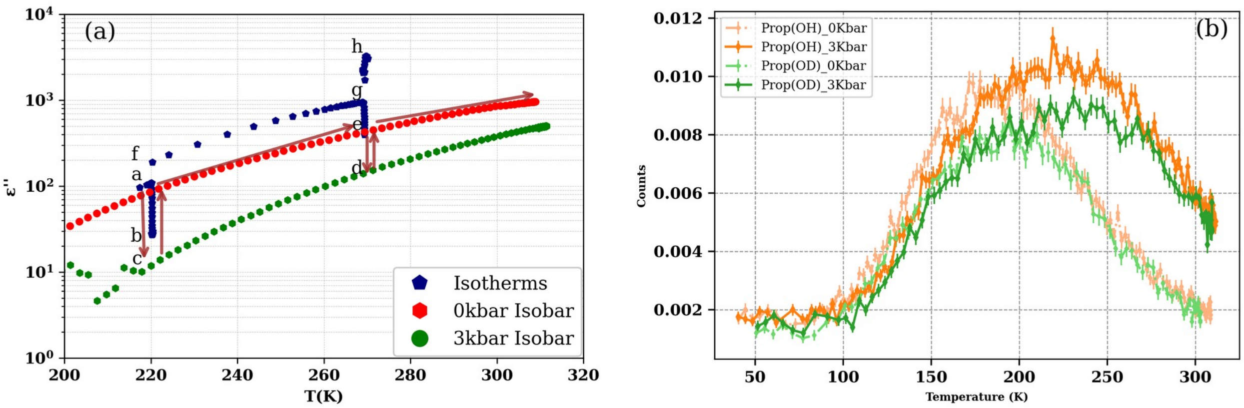

Fig 1. (a) Imaginary part of the dielectric constant at 1 kHz for 1-propanol under different pressure and temperature conditions. The expected behavior under ideal conditions is indicated by the arrow. (b) 3 μeV energy transfer Fixed Window Scan (FWS) for protonated and partially deuterated 1-propanol at ambient pressure and 3 kbar.

We observed a significant impact of pressure on the relaxation dynamics of 1-propanol. Notably, our results highlight a pronounced influence of pressure on the slower relaxation process, while the faster relaxation process remains largely unaffected. This distinct pressure dependence of the two relaxation processes suggests a potential opportunity for their separation. Additionally, we observed that the samples remained stable in the supercooled state down to 80 K.

Figure 1(b) presents the sum over all q FWS for both protonated and deuterated samples at ambient pressure and 3 kbar, clearly illustrating the effect 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. A global fit was conducted separately for ambient pressure and 3 kbar data. Various models were evaluated, among which the most significant were: KWW function, 1L + 1L, 1L + 1KWW, 1KWW + 1L. For each case, we first fitted the ambient pressure and 3 kbar data separately, followed by a simultaneous fit, where the faster process was kept constant across both pressures, while the slower process was allowed to vary freely. So far, two models provide an equally good fit to the data. To fit the FWS spectra, all fitting functions and the background are directly summed, as shown in Equation 1, since the analysis is performed on discrete energy values. However, for the QENS spectra, the model given in Equation 3 is convoluted with the resolution function, Res(Q,ω), which is determined at 40 K. The resulting expression is:

$$S_{\mathrm{IFWS}}(Q,\omega,T) = \mathcal{F}_{1,\mathrm{IFWS}}(Q,\omega,T) + \mathcal{F}_{2,\mathrm{IFWS}}(Q,\omega,T) + B(Q) \quad (1)$$

$$S_{\mathrm{model}}(Q,\omega,T) = \mathcal{F}_{1,\mathrm{QENS}}(Q,\omega,T) + \mathcal{F}_{2,\mathrm{QENS}}(Q,\omega,T) \quad (2)$$

$$S_{QENS}(Q,\omega,T) = [S_{\mathrm{model}}(Q,\omega,T) \otimes Res(Q,\omega)] + B(Q,T) \quad (3)$$

where $F_i(Q, \omega, T)$ represents the individual fitting functions $(i = 1, 2)$, $B(Q, T)$ is the background, and $\otimes$ denotes convolution.

Figure 2 contains fit result obtained from simultaneous global fit of fixed window scan (FWS) and QENS spectrum of 1-propanol data at ambient pressure of 3 μeV energy transfer. The faster process, attributed to methyl group rotation, is represented by a Lorentzian function with global Arrhenius prefactor(γ0) and activation energy. The slower process, associated with the structural relaxation of the entire molecule, is described by a Kohlrausch-Williams-Watts function with a global activation energy and γ0 tied across all q for 3 and 6μeV energy transfers. The fit indicates that at lower q, the intensity of the Lorentzian component is smaller compared to higher q, whereas the slower process exhibits the opposite trend. The fit quality is indicated by a reduced chi-square value, which is $\chi 2 = 1.1$

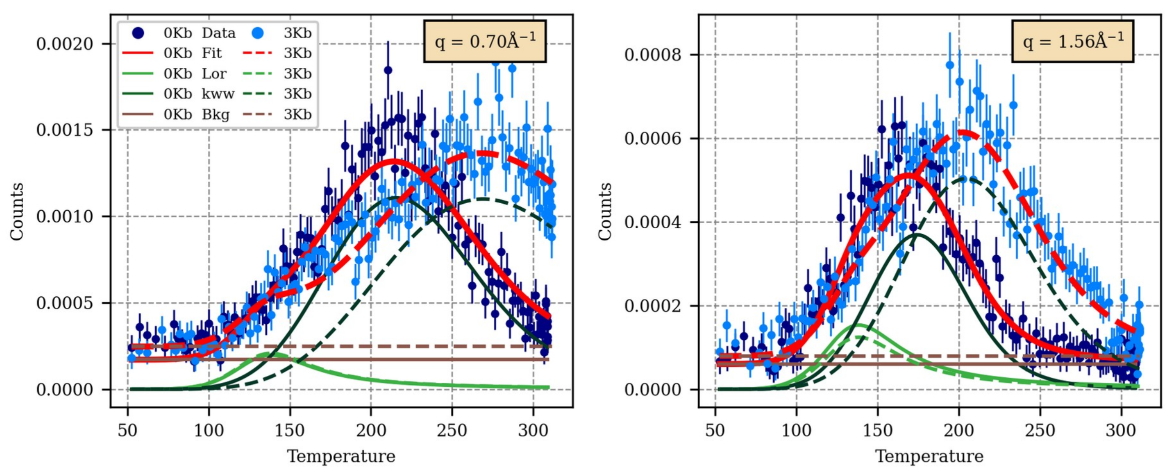

Fig 2. Simultaneous global fit of fixed window scan (FWS) of 1-propanol data at ambient pressure and 3kbar pressure of 3 μeV energy transfer for two different q's (0.59Å^{-1} ,1.47Å^{-1}). Solid curves belongs to ambient pressure and dashed one for 3kbar pressure.

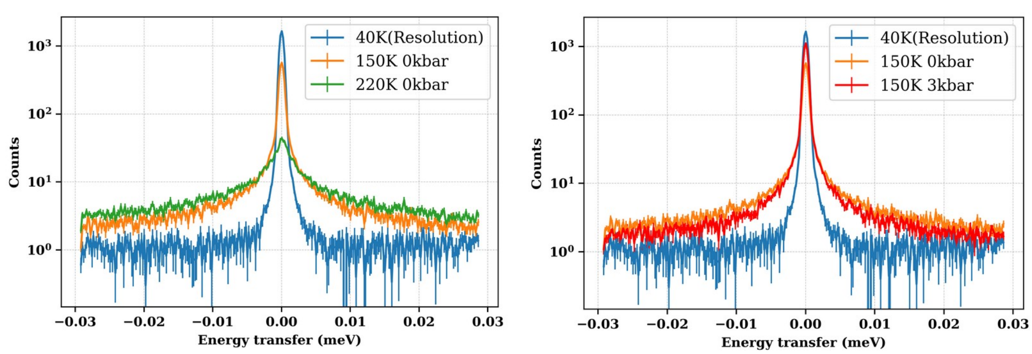

Figure 3. The left panel shows the QENS spectra for protonated 1-propanol at three different temperatures under ambient pressure, summed over all q. The right panel compares the QENS spectrum at 3 kbar with the150K ambient pressure spectrum, also summed over all q. The 40 K ambient pressure data is used as the resolution reference.