Experimental report

14/02/2025

Proposal: **6-05-1049** **Council:** 4/2021

Title: To probe the strength and correlation of dynamics between the hydrogen bonding network and the carbon backbone of 1-propanol and glycerol.

Research area: Physics

This proposal is a new proposal

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Samples: Glycerol
1-propanol-D1
1-propanol
glycerol-d3
glycerol-d8

Instrument	Requested days	Allocated days	From	To
IN16B	2	0		
WASP	4	4	24/06/2021	28/06/2021

Abstract:

In this proposal we aim to probe the dynamics of mono hydroxy alcohols. Specifically, With the use of deuterated sample, we will look at the carbon backbone versus hydrogen bond network dynamics of 1-propanol and in mixture with glycerol.

In dielectric spectroscopy these mono alcohols exhibit an additional mode, where in glycerol it seems to be mixed with the alpha . Until now, the main interpretation for this mode is that the hydrogen bond "strings" made by the alcohols as having a separate dynamic compared to the alpha relaxation which is believed to be governed by the carbon backbone's Van der Waals interactions. Tools like dielectric spectroscopy or dynamic light scattering can't directly distinguish the different contributions. Neutrons will allow us to make a more direct test for this hypothesis. We aim to look at 1-propanol and mixture of glycerol and 1-propanol. protonated and partially deuterated, either carbon backbone or OH groups, with IN16B and WASP.

To investigate the strength and correlation between the dynamics of the hydrogen-bonding network and the carbon backbone in 1-propanol and 1-propanol-glycerol mixtures

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Monohydroxy alcohols, such as 1-propanol, have been extensively studied due to their distinct relaxation dynamics. Dielectric spectroscopy and depolarized dynamic light scattering have shown that these systems exhibit a prominent Debye-type relaxation process, which is significantly slower than the structural α-relaxation. The Debye process is attributed to the dynamics of hydrogen-bonded supramolecular structures formed in the liquid state, while the α-relaxation corresponds to the structural relaxation of the liquid. In contrast, polyalcohols like glycerol exhibit more complex relaxation behavior. Dielectric spectroscopy studies have identified multiple relaxation processes; however, unlike monohydroxy alcohols, these processes are less distinctly separated. The various relaxation modes in glycerol tend to merge, making it challenging to isolate individual contributions. Understanding these relaxation processes is essential for gaining insights into the molecular dynamics of hydrogen-bonded liquids. The better separation of Debye and structural-relaxations in monohydroxy alcohols provides valuable information about the role of hydrogen bonding in dynamic processes. Meanwhile, the more intertwined relaxation modes in polyalcohols, such as glycerol, highlight the increased complexity introduced by multiple hydroxyl groups.

In this study, a combination of dielectric and neutron spectroscopy was employed to investigate how the dynamics of hydrogen bonds evolve with increasing hydrogen bond concentration and change with temperature in liquid alcohols above the glass transition. The fundamental question driving this experiment was to determine the extent to which the dynamics of the hydrogen-bonding network are coupled to the main relaxation of the liquid and how the different contributions to the dynamics, observed using different techniques, are interrelated.

This study, conducted under proposal number **6-05-1049**, focused on temperature-dependent measurements on WASP for four different systems:

a) 1-propanol (OH) at eight temperatures: [330, 250, 220, 200, 180, 150, 130, 10] K
b) 1-propanol (OD) at eight temperatures: [330, 250, 220, 200, 180, 150, 130, 10] K
c) 1-propanol–(10%) glycerol mixture at eight temperatures: [330, 280, 250, 220, 200, 180, 150, 130] K
d) 1-propanol (OD)–(10%) glycerol (D8) mixture at eight temperatures: [330, 280, 250, 220, 200, 180, 150, 130] K

In this experiments, wide-angle neutron spin-echo (NSE) measurements were conducted using the high-intensity WASP spectrometer to investigate the dynamics of hydrogen-bonded systems. Neutron data were collected with neutron wavelength of $\lambda = 7$ Å, and precise temperature control was achieved through the use of an orange cryostat. The sample geometry was chosen to be cylindrical, with a sample thickness of 0.2 mm for the deuterated samples and 0.1 mm for the protonated samples, which helped optimize scattering conditions. The accessible momentum transfer range covered $0.15 \leq Q \leq 1.36$ Å^{-1}, providing insights into the dynamical properties across various length scales. The Fourier time window spanned from 5.8 ps to 6.2 ns, allowing for the capture of both fast and slow dynamics in the system. Data acquisition at each temperature was conducted for approximately 2.5 hours to ensure adequate statistics. All the data presented in the figures have been corrected for background and empty cell contributions. Data reduction was performed using specialized software developed at the ILL. Simultaneous dielectric spectroscopy measurements were performed across approximately half of the spectrum when covering the shorter Fourier times, to gain complementary information about the sample's state. However, for longer Fourier times, dielectric spectroscopy had to be disabled due to interference from the magnetic field on the analyzer's electronics, which hindered further measurements.

The primary goal of the dielectric spectroscopy was to monitor the sample’s state during the experiment, specifically to detect any potential crystallization. Fortunately, no signs of crystallization were observed throughout the measurements, confirming that the sample remained in a stable supercooled state during the entire experimental run.

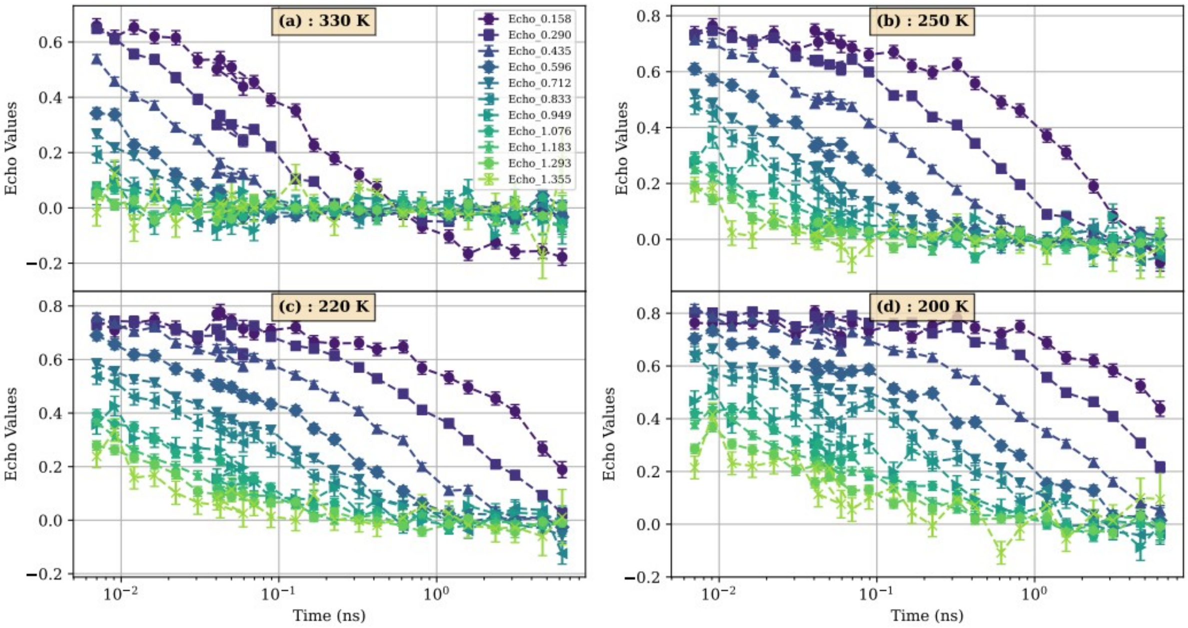

Figure 1: *NSE spectrum for 1-propanol at temperatures [330,250,220,200]K with λ=7 Å neutron.*

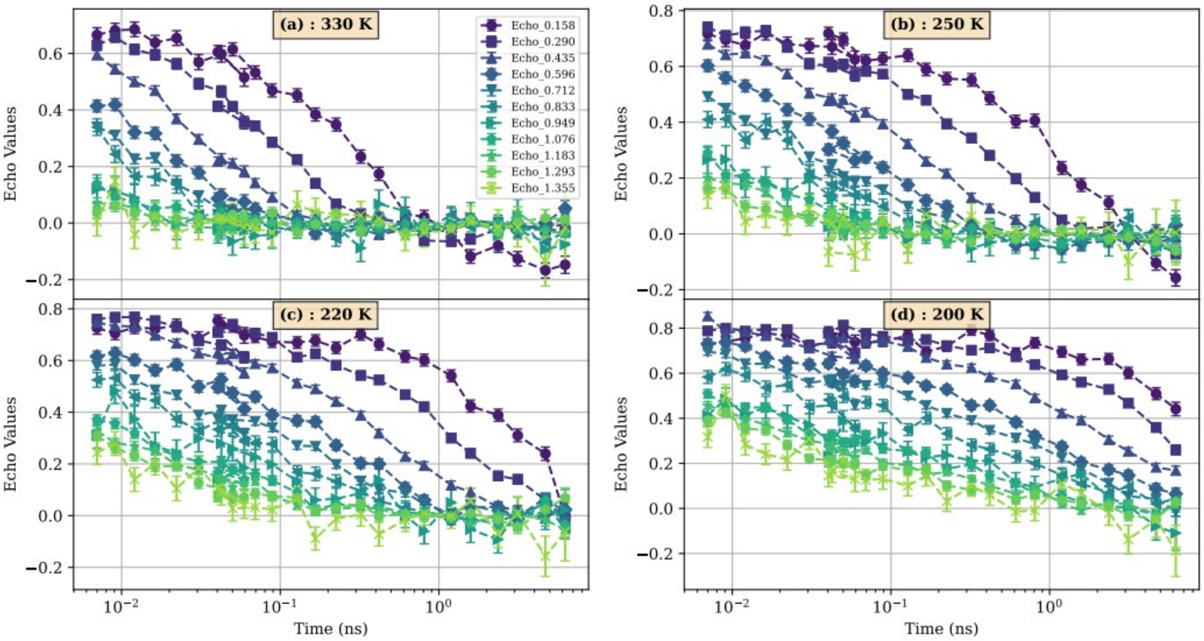

Figure 2: *NSE spectrum for 1-propanol–(10%) glycerol mixture at [330,250,220,200]K with λ=7 Å neutron.*

To analyze the data, we performed a Q-dependent global fit, incorporating all Q-dependent NSE spectra across the entire temperature range. Various models were evaluated, with the most significant being a simple exponential function for the slower process and a stretched exponential function for the faster process. In this model, the faster process is attributed to structural relaxation, while the slower process is associated with the formation of supramolecular structures via hydrogen bonding. The stretching factor, β, quantifies the deviation from a purely exponential decay, where $\beta = 1$ corresponds to simple exponential behavior. Mathematically, the model used to fit the neutron spin-echo data is represented as:

$$I(Q,t) = A_{\kappa}(Q) * \exp\left(-\frac{t}{\tau_{\kappa}(Q)}\right)^{\beta} + A_{\mathcal{L}}(Q) * \exp\left(-\frac{t}{\tau_{\mathcal{L}}(Q)}\right) + B(Q)$$

where τ_k and τ_L are the characteristic timescales of the slower and faster processes, respectively, A_K and A_L are the corresponding amplitudes, β is the stretching factor, and B represents a flat background.