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Structure factor of liquid *n*-butanol at room temperature

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Abstract. The structure factor of deuterated liquid *n*-butanol (C₄D₁₀O) has been investigated by neutron diffraction with the aim of exploring the physical nature of the observed pre-peak. The experiment was conducted using two neutron diffractometers: D16 to get a detailed structure factor in the low-*Q* range, and D4 for a high precision structure factor and proper normalization. In this way a total structure factor was determined covering an extended *Q*-range from 0.04 to 23.4 Å⁻¹. A molecular dynamics simulation using the general all-atom ab initio force field COMPASS was also carried out. The agreement between experimental and simulated data is very good, giving a plausible interpretation of the origin of the pre-peak observed at 0.6 Å⁻¹ as coming from the intermolecular ordering in the liquid.

1. Introduction

Alcohols are important compounds widely used as solvents and many of their particular properties are due to the existence of intermolecular hydrogen bonds. The structure of lowest members of the series have in the liquid phase been determined by neutron diffraction, such as methanol, ethanol and iso-propanol [1, 2, 3, 4, 5, 6, 7].

The signature of H-bonded molecular association in diffraction data is the formation of a pre-peak at a scattering vector, $Q \approx 0.7\text{-}0.8 \text{ \AA}^{-1}$, before the main diffraction peak [8, 9]. The pre-peaks of liquid alcohols which are well known in X-ray diffraction data [10], have been detected in the neutron diffraction pattern only recently [8, 9].

The neutron scattering technique, which is sensitive to the positions of both the C and H nuclei, the latter being almost invisible to X-rays. The extremely high value of the incoherent neutron cross section of hydrogen and its exiguous coherent scattering would make it impossible to extract from the total signal the contribution of the partial correlations. We therefore used deuterated *n*-butanol exploiting the much more favorable coherent ($\sigma_{\text{coh}} = 5.592 \text{ b}$, $1 \text{ b} = 10^{-28} \text{ m}^2$) to incoherent ($\sigma_{\text{inc}} = 2.05 \text{ b}$) cross sections ratio of deuterium.

In our study we have determined the structure factor of liquid *n*-butanol at room temperature (300 K). Using molecular dynamics (MD) simulation we can get data of intra- and inter-molecular distances, partial coordination number (CN) and molecular conformational distribution. The theoretical formalism for the extraction of the structural information from a neutron diffraction experiment is presented elsewhere [11].



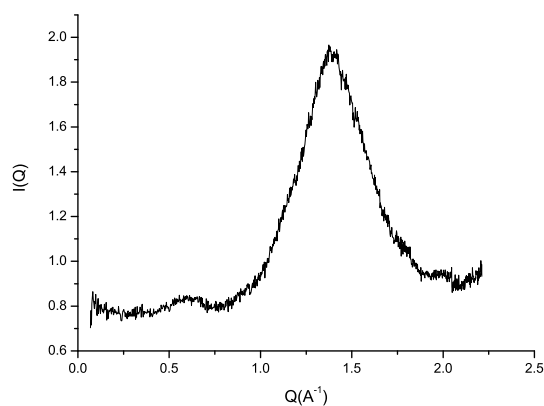


Figure 1. Neutron diffractogram of liquid n-butanol at room temperature as measured in D16. The pre-peak at 0.6 Å is clearly observed.

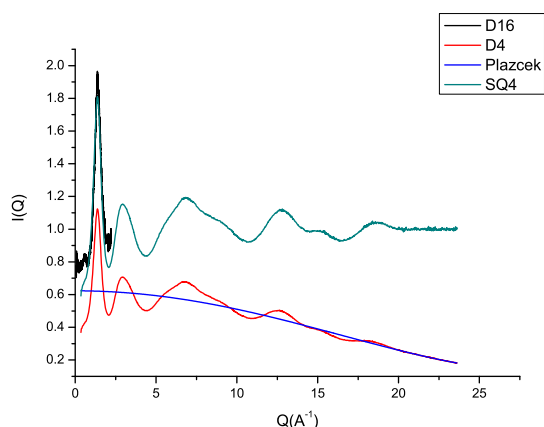


Figure 2. Combined low- and high- Q diffractograms for liquid n-butanol at room temperature as obtained from D4 and D16, after corrections. The corrected D4 (SQ4) data are obtained taking into account the Plazcek contribution.

2. Experimental

A liquid deuterated n-butanol sample of high purity (Aldrich, anhydrous grade, 99.8%) was used for all neutron diffraction experiments. Samples were contained in sealed cylindrical vanadium containers of 6.8/7.0 mm of internal/external diameter. The macroscopic density for liquid deuterated n-butanol at room temperature is 0.92 g/cm³ or 0.0986 at./Å³, and its isothermal compressibility is 1.06×10^{-9} Pa⁻⁹.

For the high- Q region of the diffractogram the experiment was conducted at the hot neutron diffractometer (D4) [12] optimized for structural investigations of liquids and amorphous. The short-wavelength, 0.49667(1) Å, of incident neutrons allows to cover a Q -range of 0.35-23.5 Å⁻¹. This wavelength as well as the zero angle correction (0.0185°) to the scattering angle were determined using a standard Ni powder sample. In addition, diffraction patterns were measured

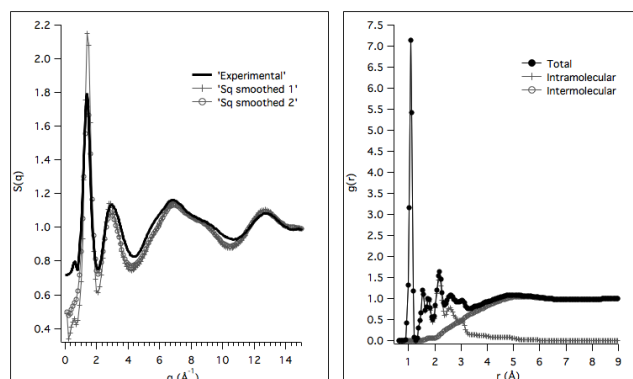


Figure 3. Left: Structure factor as obtained from simulations and its comparison with experimental $S(Q)$. Right: Pair correlation function and the intra- and inter-molecular contributions.

for the sample, the empty sample container, the instrument background and a 6.08 mm diameter vanadium rod, with a beam of $5.0 \times 1.3 \text{ mm}^2$. The low- Q region, $0.01\text{--}2.5 \text{ \AA}^{-1}$ (Fig. 1), was measured on D16 using the same sample and container with an incident wavelength of 4.741 \AA . The beam size at the sample position was $11.9 \times 11.7 \text{ mm}^2$ and the experiment was performed at room temperature for the sample, the empty sample container and the instrument background. The differential cross section was obtained after the raw data were corrected for background, absorption, multiple scattering, inelasticity effects and normalization using CORRECT [13].

The MD simulations were carried out in an NVT ensemble consisting of 1000 flexible molecules with density 0.8098 g cm^{-3} , corresponding to a cubic box of side 53.4 \AA . The equations of motion were integrated with a time step of 1 fs by the Verlet velocity integrator. Non-bonded interactions were calculated with a cutoff of 12.5 \AA for van der Waals forces and using Ewald summation for Coulomb interactions. The equilibrated MD trajectory was recorded for more than 200 ps. The neutron differential cross section was determined using the program package NMOLDYN [14] and the stored MD trajectories obtained using Material Studio.

3. Results

The pre-peak is clearly observed in the low- Q region as measured on D16 (Fig. 1), but on D4 it is more difficult to be observed because its very weak intensity and the low resolution of this instrument. The Fig. 3 shows a preliminary comparison of the structure factors obtained from the numerical simulations and the experimental structure factor, $S(Q)$; in the right frame we observe the comparison of the pair distribution function and the inter- and intra-molecular contributions. The experimental peaks are clearly lower and broader than the simulated ones, because the neighbour distances cannot be resolved and appear as a single peak, contrary to what happens in the simulation. The first and most intense peak of $g(r)$ appears at 1.06 \AA and includes the contribution of D–O and C–D correlations. The following peak at 1.57 \AA is smaller and wider than the previous and is attributed to four contributions, C–O, C–C, D–D, D–O. The third peak at 2.56 \AA is composed by C–D, D–O and D–D (Fig. 3). The positions of the three maxima in X-ray are 0.88 , 1.51 , 2.5 \AA and the first one shows the biggest difference when compared with neutron diffraction [10]. In order to obtain the CN we calculated the total correlation function $T(r)$ by Fourier transformation of the structure factor. The results of Gaussian fits to the peaks are given in Table 1. These data compare very well with X-ray data [10], for which the shortest intra-molecular C–O and C–C distances are 1.41 and 1.52 \AA , and the CN are 1.0 and 1.5 , respectively.

Table 1. Distances and coordination numbers obtained from the simulated structure.

Bond	Distances (Å)	CN	Bond	Distances (Å)	CN
D–O	0.96	0.96	D–O	1.73	1.08
C–D	1.10	2.26	C–D	2.17	6.18
C–O	1.42	0.99	C–O	2.43	1.0
C–C	1.53	1.48	D–O	2.78	1.52
D–D	1.77	1.15			

The total correlation function shows a first inter-molecular shell at 1.73 Å with a CN of 1.08; a second shell is also present at 3.37 Å with a CN of 0.96. For comparison, the first coordination shell for H-bonds for methanol and ethanol are at distances of 1.75 Å and 2.6 Å, respectively, which confirms the decrease of this distance with the number of carbon atoms in the molecule.

Analyzing the O–O intermolecular distances we observe the first- and second-coordination shells at 2.76 Å and 4.83 Å, with CN 1.54 and 3.07, respectively. Comparing with data from X-ray of O–O (2.79 Å, CN= 1.8) [15] we observe that the distance is the same but the CN decreases. The coordination number of O–O describes intermolecular order and suggests that the cluster structures of these alcohols resemble each other.

4. Conclusions

We have measured the structure factor of liquid n-butanol at room temperature over a wide range of scattering vector ($0.01 \text{ \AA}^{-1} < Q < 23.5 \text{ \AA}^{-1}$). By neutron diffraction we can confirm the existence of a pre-peak at 0.6 \AA^{-1} , which was already observed by X-ray diffraction. Thanks to the good agreement with experimental data, the MD simulations allow us to obtain the partial correlation functions and the correlation distances and CN. Our results are comparable to the previous structure obtained by X-ray diffraction.

The position of the pre-peak in reciprocal space corresponds to a distance of 10.5 Å in real space, which is the inter-molecular distance for molecules aligned along the principal axis. In this way the pre-peak is the signature of H-bonding between molecules. Ongoing research on the temperature dependence of the intensity and width of this pre-peak would help in the interpretation of its physical nature.

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