

Molecular conformation and structural correlations of liquid D-1-propanol through neutron diffraction

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Abstract. An analysis of neutron diffraction data of liquid deuterated 1-propanol at room temperature to extract its molecular conformation is presented. Being a big molecule with twelve atomic sites, the analysis is tricky and needs careful consideration. The resulting molecular parameters are compared with electron diffraction (gas phase), X-ray diffraction (liquid phase) and MD simulation results. Information about the hydrogen-bonded intermolecular structure in liquid is extracted and nature of the probable molecular association suggested.

Keywords. Molecular conformation; structure; correlations; neutron diffraction.

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1. Introduction

The present work is a continuation of our studies on hydrogen-bonded liquid alcohols reported from this laboratory during the last 10–12 years. The detailed studies of molecular conformation and liquid structure of H-bonded D-2-propanol through neutron diffraction are available in literature [1–3]. It is now interesting to look at the molecular conformation and structural correlations of liquid D-1-propanol. This study is important because they are isomers and the thermodynamic and other related properties differ significantly. The differences in the conformation and structural correlations would be interesting. The X-ray scattering study to extract the structural parameters of liquid 1-propanol are available in the literature [4–6]. The X-ray data however have limitation of not locating hydrogen sites accurately. The neutron diffraction surely supplements on this point. To our knowledge, there has been no other report on the neutron diffraction technique used for the extraction of molecular structure of D-1-propanol in liquid state. The molecular dynamics (MD) simulation for the molecular parameters of 1-propanol in liquid state has also been

reported recently [6] and the results compare favourably with the X-ray diffraction results. The neutron diffraction data analysis, however, yields more detailed information on molecular conformation with accurate location of hydrogen positions. The analysis is, however, tricky because of largeness of the 1-propanol molecule. With a number of distances between different atomic sites being comparable with intermolecular distances, the separation of the intra- and intermolecular terms is quite difficult and therefore a modified and careful technique [7] of data analysis has to be adopted. In the following sections, we describe the various aspects of our study.

2. Experimental

The neutron scattering measurement of the fully deuterated liquid 1-propanol sample at room temperature was carefully carried out on the high- Q diffractometer at Dhruva, BARC, India in collaboration with the BARC group. The liquid used in the experiment consisted of a 99.8% deuterated sample available from Aldrich Ltd., USA. It was held in a vanadium can of 6 mm diameter and 0.1 mm thickness. The conventional procedure was followed. The data collection and experimental corrections for container scattering, self-attenuation and multiple scattering were done in the usual manner, and the cross-section data were normalized using a standard vanadium rod. Incident wavelengths of 0.783 Å and 1.278 Å were used, and the data were recorded for an angular range of 3° to 125° . The two datasets were clubbed appropriately and the corrected cross-section data are shown in figure 1. The data do not show any significant pre-peak at scattering vector 0.71 \AA^{-1} unlike 2-propanol data [3]. The X-ray data [5,6], however, show a small pre-peak at this scattering vector though the earlier data [4] did not do so.

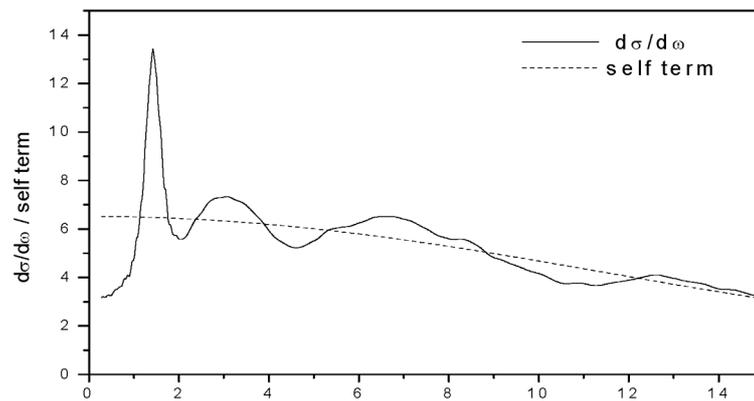


Figure 1. Corrected ($d\sigma/d\Omega$) vs. Q . (—) normalized data, (---) self-term.

3. Method of analysis

3.1 General background

The corrected scattered data were extrapolated in the region $0 \leq Q \leq 0.3 \text{ \AA}^{-1}$ and were normalized (on high- Q data as well) such that the graphical extrapolation to $Q \rightarrow 0$ yields an isothermal compressibility of $12.1 \times 10^{-11} \text{ cm}^2/\text{dyne}$. The data are then separated into ‘self’ and ‘interference’ terms,

$$d\sigma/d\Omega|_{\text{expt}} = d\sigma/d\Omega|_{\text{self}} + d\sigma/d\Omega|_{\text{int}}. \quad (1)$$

At high- Q region, the experimental cross-section data have a ‘fall-off’ feature. This is due to interaction of incident neutrons with the vibrating scattering sites [8]. This part can be reproduced by appropriate self-scattering term. For alcohols this can be represented [8,9] by

$$d\sigma/d\Omega|_{\text{self}} = [3b_c^2 + b_o^2 + 8b_d^2 + 8(\sigma_d^i/4\pi)](1 - aQ^2 + bQ^4), \quad (2)$$

where σ_d^i is the incoherent scattering cross-section for deuterium and a, b are two inelasticity parameters. b_c, b_o, b_d are the coherent scattering lengths of carbon, oxygen and deuterium respectively. The inelasticity parameters a and b , estimated by χ^2 -fitting between the self-scattering term, and the experimental data at high- Q values (starting from $Q \approx 5.5\text{--}6.0 \text{ \AA}^{-1}$) are listed in table 1. The overall normalization constant, estimated from the isothermal compressibility limit, is taken as 0.071. Figure 1 shows the fitted results for the normalized $d\sigma/d\Omega|_{\text{expt}}$ and $d\sigma/d\Omega|_{\text{self}}$. The $d\sigma/d\Omega|_{\text{int}}$, obtained from (1), contains both intra- and intermolecular contributions. The total structure function, $H(Q)$, is defined as

$$H(Q) = d\sigma/d\Omega|_{\text{int}} / \sum (b_i)^2. \quad (3a)$$

$H(Q)$ can be separated into intra- and intermolecular terms given by

Table 1. Room temperature structural parameters for liquid D-1-propanol. Inelasticity parameters: $a = 3.22374 \times 10^{-3} \text{ \AA}^2$, $b = 0.404782 \times 10^{-5} \text{ \AA}^4$. Constant for Debye–Waller terms: $\lambda_0 = 0.0384$, $\chi^2 = 0.134823 \times 10^{-5}$.

Molecular parameters	Present	X-ray [5]	Election diffraction [12] (gas phase)	MD [6]
r_{CC} (Å)	1.477 ± 0.003	1.520	1.540	1.530
r_{CO} (Å)	1.443 ± 0.012	1.420	1.410	1.430
r_{CD} (Å)	1.053 ± 0.002	1.110	1.090	–
r_{OD} (Å)	0.986 ± 0.010	0.940	0.937	0.945
$\angle C_1OD_1$	$110^\circ 25' \pm 5^\circ 43'$	–	$105^\circ 56'$	$108^\circ 30'$
φ_1	$14^\circ 2' 24'' \pm 2^\circ$	–	$\varphi_1 = \varphi_2 = \varphi_3$	–
φ_2	$49' \pm 2^\circ$	–	$= 0.0^\circ$	–
φ_3	$7^\circ 12' \pm 2^\circ$	–	–	–

$$H(Q) = H_m(Q) + H_d(Q), \quad (3b)$$

where

$$H_m(Q) = (d\sigma/d\Omega)_{\text{int}}^{\text{intra}} / \left(\sum_i b_i \right)^2$$

and

$$H_d(Q) = (d\sigma/d\Omega)_{\text{int}}^{\text{inter}} / \left(\sum_i b_i \right)^2.$$

More explicitly, $H_m(Q)$ is given by

$$H_m(Q) = \left(\sum_i b_i \right)^{-2} \sum_i \sum_{j, i \neq j} b_i b_j j_0(Qr_{ij}) \exp(-\gamma_{ij}Q^2), \quad (3c)$$

r_{ij} being the mean distance between sites i and j . $2\gamma_{ij}$ is the mean square variation in the distance r_{ij} . $\gamma_{ij} = (1/2)\lambda_0^2 r_{ij}^2$, where λ_0 is taken to be a constant for all the pairs (similar to Prins relation [10]). i and j sum independently over 12 atomic sites within the 1-propanol molecule. $j_0(x) = \sin x/x$ is the zeroth order spherical Bessel function. $H_m(Q)$ is the intra-interference term which gives information about the structure of the molecule, while $H_d(Q)$, often also called ‘distinct’ structure function, gives information about the intermolecular or liquid structure. In terms of partial structure functions $H_{ij}(Q)$, $H_d(Q)$ can be written as

$$H_d(Q) = \left(\sum_i b_i \right)^{-2} \sum_i \sum_j (2 - \delta_{ij}) b_i b_j H_{ij}(Q). \quad (4)$$

The inverse Fourier transform (IFT) of $H_d(Q)$ gives the r -weighted intermolecular correlation function $d(r)$ and the radial distribution function (RDF), $G_d(r)$ given by

$$d(r) = \frac{2}{\pi} \int_0^\infty Q H_d(Q) \sin(Qr) dQ, \quad (5a)$$

$$G_d(r) = 1 + d(r)/4\pi\rho r, \quad (5b)$$

where ρ is the density of liquid 1-propanol at room temperature.

$G_d(r)$ is related to partial distribution functions, $g_{ij}(r)$ given by

$$G_d(r) = \left(\sum_i b_i \right)^{-2} \sum_i \sum_j b_i b_j g_{ij}(r), \quad (5c)$$

where

$$g_{ij}(r) = 1 + \frac{1}{2\pi^2\rho r} \int_0^\infty Q H_{ij}(Q) \sin(Qr) dQ. \quad (5d)$$

3.2 Determination of molecular conformation

Because of largeness of the molecule, a modified method of analysis has to be used as in the case of other alcohols analysed in this laboratory. In liquid alcohols, hydrogen bonding effects continue to persist at large Q [11] and as a result, $H_d(Q)$ shows decreasing oscillatory behaviour, positive and negative, modulates $H_m(Q)$. $H_d(Q)$, however, tends to vanish gradually and so $H(Q)$ oscillates around $H_m(Q)$ and tends to equalize $H_m(Q)$ at large Q . This implies that for Q greater than some Q_{\min} value, the total structure function $H(Q)$ comes primarily from intramolecular part. To start with, we assume a model of the molecule from electron diffraction in gas phase [12] and evaluate the various atom–atom distances and obtain $H_m(Q)$. Now by varying intramolecular parameters we can fit $QH_m(Q)$ to experimental $QH(Q)$ for $Q > Q_{\min}$ ($Q_{\min} \sim 5.5\text{--}6.0 \text{ \AA}^{-1}$) by a χ^2 -fitting procedure. Now subtracting fitted $H_m(Q)$ from $H(Q)$ in eq. (3b), we obtain the first estimate of $H_d(Q)$. The intermolecular radial distribution function $G_d(r)$ is obtained from IFT of $H_d(Q)$ through eqs (5a) and (5b). The truncation effect of limited experimental data (of maximum $Q \sim 15 \text{ \AA}^{-1}$) is minimized by using a window function and Q_{\max} was chosen such that $G_d(r=0)$ is almost zero as in ref. [7]. Further, $G_d(r)$ is set zero in the core region $0 \leq r \leq 1.5 \text{ \AA}$ and Fourier transform (FT) of the resultant $G_d(r)$ yields a new $QH_d(Q)$ which subtracted from experimental $QH(Q)$ yields corrected $QH_m(Q)$. A χ^2 -fitting is used by varying molecular parameters to have best fit with this corrected function $QH_m^c(Q)$ right from lowest Q . This is our modified method of analysis for big molecules [7]. The fitted curves are shown in figure 2a.

The molecular parameters are listed in table 1. The conformation of the molecule is shown in figure 3. It is evident that the conformation of 1-propanol molecule in liquid state is quite elongated compared to 2-propanol molecule [3]. This is somewhat similar to conformation in solid state [13].

4. Results and discussion

4.1 Model of the molecule and intramolecular structure

The X-ray measurements are dominated by scattering from carbon and oxygen atoms and important information about hydrogen positions are not accurately accessible. In neutron measurement, deuterium atoms scatter neutron beam significantly. Considering all the atomic sites as scattering units, the 1-propanol molecule consists of 12 scattering sites. Though it is a big molecule, it has important symmetry in the structure. Considering the symmetry in the structure one can minimize the number of parameters to describe the possible conformation. We assume C_1C_2 in the X - Z plane and C_1O along the Z -axis. The coordinates of C_3 lie in the X - Z plane. We minimize the number of parameters setting C_1C_2 and C_2C_3 distances equal and all the CD distances kept equal. The initial r_{CC} , r_{CO} and r_{OD} distances are taken as those from gas phase analysis [12]. Denoting D_1 as hydroxyl deuterium, three rotational angles φ_1 , φ_2 , φ_3 in addition to $\angle C_1OD_1$ are treated as variable parameters in the initial fitting. Finally, r_{CC} , r_{CO} and r_{OD} are also fitted. The tilt angle of the methyl group is assumed zero like gas [12] and liquid [5,6] phases. φ_1

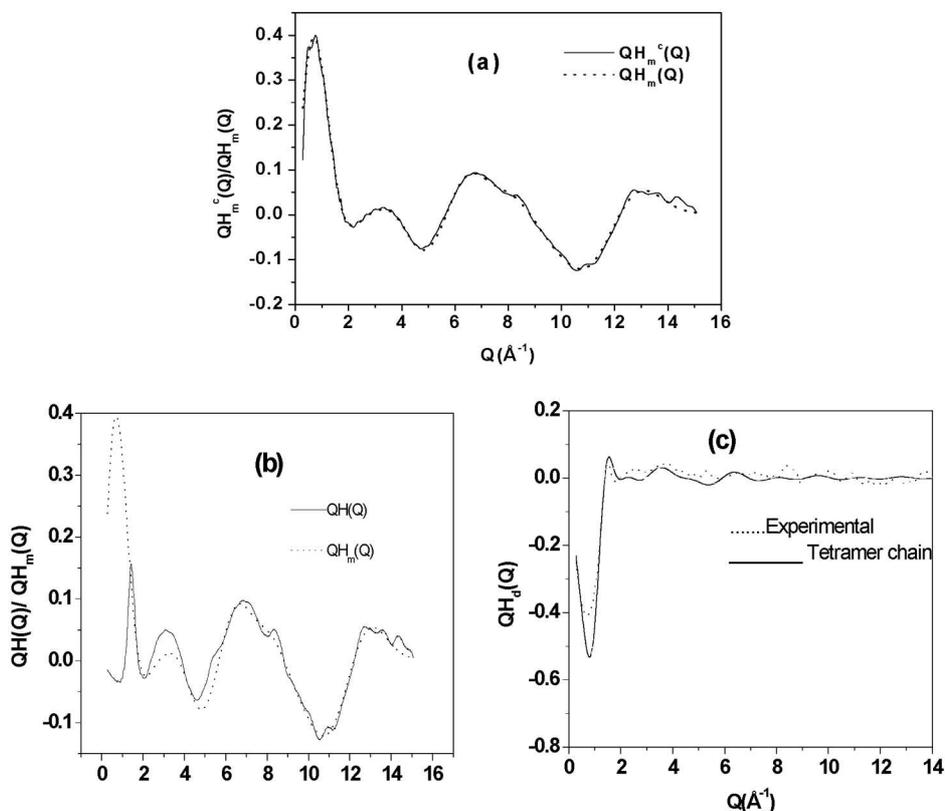


Figure 2. Q -weighted functions vs. Q : (a) (\cdots), $QH_m(Q)$, ($—$) $QH_m^c(Q)$; (b) ($—$) $QH(Q)$, (\cdots) $QH_m(Q)$; (c) (\cdots) exptl $QH_d(Q)$, ($—$) tetramer chain, $QH_d(Q)$.

is the twist angle about C_2C_3 line while φ_2 and φ_3 are twist angles about C_1C_2 line.

Using the procedure stated before the χ^2 -fitting result depicted in figure 2a, gives the molecular parameters (table 1) and these are very reasonable. The parameters determined by electron diffraction (gas phase) [12] and X-ray (liquid phase) [5] are also listed for comparison. The MD simulation distances from ref. [6] are also shown. The error estimate for each parameter is done to allow a 1% increase in the χ^2 -value. The thermal vibration factors were calculated as already stated, and the proportionality constant λ_0 is also obtained by χ^2 -fitting and is listed in table 1. In figure 2b we show the Q -weighted model intrastructure function $H_m(Q)$ along with the total structure function $H(Q)$. The agreement is indeed very good and similar to the one for X-ray diffraction data analyses [5]. In X-ray analysis [5], three conformations were considered, namely, CIS, trans and gauche. The gauche conformation was considered to be more favorable than the other two. In our case, allowing all possible rotations of the consistent group (methyl etc.) inside the molecule we considered and checked trans, gauche conformations as well. Our

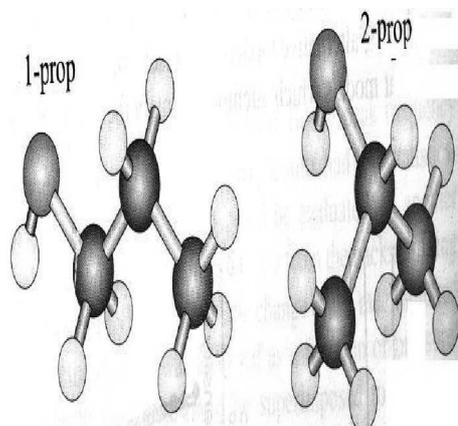


Figure 3. Molecular conformations of 1-propanol and 2-propanol [3].

extracted conformation is nearly a trans conformation (figure 3). This is different from X-ray result. This difference is not unexpected as X-ray fails to locate H-positions accurately. It is also to be noted here that the molecular conformation of 1-propanol is very different from 2-propanol (figure 3).

4.2 Intermolecular contribution and liquid structure

We then use eq. (3) to obtain information about the intermolecular correlations and liquid structure. The Q -weighted $H_d(Q)$ data are shown in figure 2c. The oscillatory behaviour almost vanishes after 9.5 \AA^{-1} and this implies that our analysis to find the molecular parameters is quite accurate. This function and the total structure function, $H(Q)$ are very different for D-2-propanol [3]. The intermolecular r -weighted correlation function $d(r)$ is obtained using eq. (5a) and is shown in figure 4. The intermolecular RDF $G_d(r)$ curve is similar but not shown. The window function is used in the FT to reduce the undesirable ripples arising due to truncation effects. A quadratic interpolation with Filon's quadrature has been used. The results obtained from X-ray data [6] are also shown for comparison. For obvious reason the OD hump at $\sim 1.8\text{--}1.9 \text{ \AA}$ is absent in the X-ray result. It is clear that the intermolecular atom-atom correlations can be easily identified. The comparison also helps to identify the plausible hydrogen-bonded molecular association, if any, in the liquid state at room temperature. Small OD hump is visible in neutron data and, at $\sim 2.8\text{--}3.0 \text{ \AA}$, a clear OO hump is shown in both X-ray and neutron data. It is evident that hydrogen bonding hump is comparatively weak compared to the one in 2-propanol [3]. The near absence of pre-peak in experimental neutron $H(Q)$ data also corroborates this point. The result exhibits an oscillatory pattern extending to about 15 \AA . The several features in the first peak (at about 5 \AA) suggest strong intermolecular correlations. It is also to be noted that the spurious oscillations in $d(r)$ in the low r ($< 1.5 \text{ \AA}$) region is negligible. To look at the difference of liquid structure in relation to liquid 2-propanol, we recall

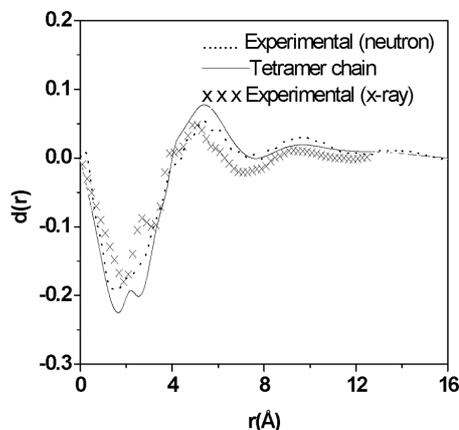


Figure 4. r -Weighted correlation function, $d(r)$ vs. r : (\cdots) exptl (neutron), ($- - -$) tetramer chain, ($\times \times \times$) X-ray, exptl.

the same figure with data for 2-propanol [3]. A lot of difference in liquid structure is evident. The RDF, $G_d(r)$ curve is also quite different from that of 2-propanol and this clearly shows the difference in the nature of molecular association.

We have done some preliminary calculation [14] on the intermolecular modelling of 1-propanol in the liquid state. The absence of significant pre-peak in the $H(Q)$ data eliminates the possibility of cyclic chain cluster (hexamer) as observed in 2-propanol [3] and other alcohols [15]. In our preliminary study we considered linear winding chains (trimer to pentamer) as probable intermolecular association. The best result for tetramer chain is shown in figures 2c and 4. The agreement is not very satisfactory. The X-ray work [5], however, suggests a probable trimer association.

5. General remarks

In this analysis we have studied the molecular conformation of liquid D-1-propanol at room temperature through neutron diffraction. The analysis gives an average conformation of the molecule and shows that it is quite elongated and very different from 2-propanol structure. This molecular conformation is very similar to the one in solid state [13]. The difference in conformation in comparison to 2-propanol molecule affects the intermolecular correlations and so the liquid structure also appears to be significantly different. Like other alcohols [15], 2-propanol in liquid state has been shown to form hexamer chain clusters [3] at room temperature. The H-bonding chain in liquid 1-propanol is different and probably a linear chain of neighboring molecules through H-bonding is a more plausible liquid structure. We have done preliminary calculation [14] in this regard. However, a detailed intermolecular structure analysis using different models is important. This work is being continued and would be reported soon.

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