Molecular conformation and liquid structure of 2-propanol through neutron diffraction

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Abstract. The neutron diffraction data analysis of deuterated liquid 2-propanol at room temperature to define its molecular conformation is presented. 2-Propanol being a large molecule with twelve atomic sites, the conformation analysis is tricky and an improved method of data analysis is given. The intermolecular structural correlations, i.e., hydrogen-bonded liquid structure, can be modelled accurately to extract the nature of the average hydrogen-bonded molecular association in liquid state at room temperature. Like other alcohols these are mostly hexamer ring chain (HRC) clusters. The cluster analysis of recent X-ray data available in the literature also support the same liquid structure.

Keywords. Molecular conformation; structural correlation; neutron diffraction; X-ray 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 recent years [1–5]. Although alcohols have simple amphiphilic molecular structures, because of the presence of hydrophobic groups, they cannot form tetrahedral structures like water, rather form hydrogen-bonded (HB) chains. X-ray and neutron diffraction techniques have enabled us to obtain direct information on the microscopic average structure and near-neighbour correlations. The computer simulations also provide very useful information about the microscopic structure and dynamics of the hydrogen-bonded systems. Although the general nature of the chain structure suggested by the diffraction results agree well with simulation work, there is a lot of difference in the detailed nature of the chain or cluster that is formed due to hydrogen bonding. In solid and gaseous states, alcohol structures are now well established. In liquid state, however, the question is still open in view of differences in diffraction, simulation and other results [1,2,6–9]. The neutron diffraction is especially useful because it can yield both molecular

conformation including hydrogen positions and intermolecular correlations. The molecular conformation hitherto obtained from X-ray diffraction data [10] has limitation since hydrogen positions cannot be located accurately. The neutrons can accurately see the hydrogen/deuterium positions, but because of the large size of the molecule with a number of atomic sites the separation of the intra- and intercontributions is tricky [4]. Even though the earlier neutron diffraction studies on liquid 2-propanol [11,12] yielded important information on the molecular conformation, there were some uncertainties in the parameters, H-bonded angle in particular, and as such could yield only approximate information about the liquid structure. The important pre-peak could not be explained though chain association of molecules was conjectured. We have however, shown that, like other liquid alcohols at room temperature [1–3,5], the proposition of a dominant cyclic hexamer ring molecular association due to hydrogen bonding works quite reasonably. The proposition has been shown to be also supported by the analysis of recent X-ray data [10]. The conclusion about intermolecular structure, however, depends strongly on the accurate knowledge of the molecular conformation in the liquid state. Therefore, in the present study, we have made detailed analysis of molecular conformation using recent indigenous neutron data available to us. With the number of distances between different atomic sites being comparable with distances between atoms lying on neighbouring molecules, the separation of the intra- and intermolecular terms is quite difficult and therefore a modified technique of data analysis [4,13] has been adopted. In the following sections, we describe the various aspects of our study in details.

2. Experimental

The neutron diffraction measurement of a fully deuterated liquid 2-propanol sample at room temperature was carefully carried out in the high-Q diffractometer at Dhruva, BARC (India) in collaboration with our BARC colleagues. The
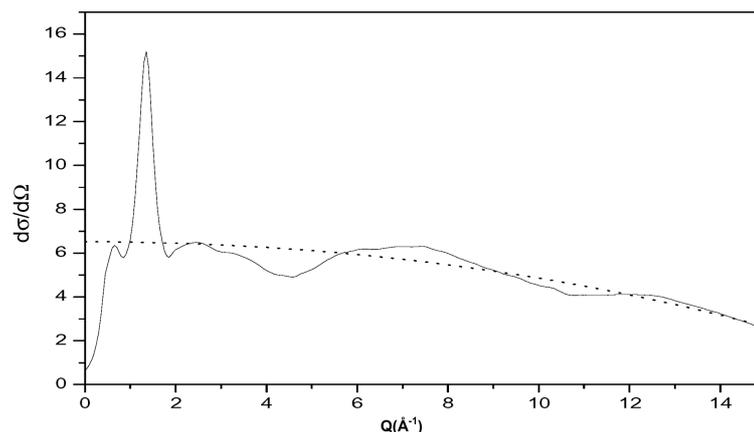

Figure 1. $d\sigma/d\Omega$ vs. Q. (—) Corrected experimental data, (- - -) self-term.

experimental liquid consisted of 99.8% deuterated sample obtained from Aldrich Limited (USA). The sample was held in a vanadium can of 6 mm diameter and 0.1 mm thickness. The conventional neutron diffraction experiment procedure was followed. The data collection, 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. Two incident wavelengths, 0.783 and 1.278 Å, were used and the data were recorded for an angular range of 3° to 125°. The two data sets were clubbed together and the corrected cross-section data evaluated. The cross-section data show a strong pre-peak at a scattering vector, $Q \sim 0.7$ Å (figure 1), similar to the one obtained in the earlier neutron diffraction data [12].

3. Method of analysis

3.1 *General background*

In the following paragraph we present the extraction of total neutron molecular structure function, $H(Q)$, and wherefrom intermolecular or distinct term, $H_\mathrm{d}(Q)$ from our indigenous neutron data. First the corrected cross-section data were extrapolated in the region $0 \le Q \le 0.3$ Å^{-1} and normalized (on high-Q data as well) such that the extrapolation to $Q \to 0$ yields a correct isothermal compressibility. The data are then separated into 'self' and 'interference' terms:

$$\left.\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right|_{\mathrm{expt}} = \left.\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right|_{\mathrm{self}} + \left.\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right|_{\mathrm{int}}. \tag{1}$$

At high-Q, the experimental cross-section data have a 'fall-off' feature. This is due to interaction of incident neutrons with the vibrating scattering sites [4]. This part can be reproduced by appropriate self-scattering term. For an alcohol like 2-propanol, this can be represented by [4]

$$\left.\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right|_{\mathrm{self}} = [3b_\mathrm{c}^2 + b_\mathrm{o}^2 + 8b_\mathrm{d}^2 + 8(\sigma_\mathrm{d}^\mathrm{i}/4\pi)](1 - aQ^2 + bQ^4), \tag{2}$$

where $\sigma_\mathrm{d}^\mathrm{i}$ is the incoherent scattering cross-section for deuterium and a, b are two inelasticity parameters. $b_\mathrm{c}, b_\mathrm{o}, b_\mathrm{d}$ 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 $Q \approx 5.5$–6.0 Å^{-1}) are listed in table 1. The overall normalization constant, estimated from the isothermal compressibility sum rule (taking isothermal compressibility as 11.24×10^{-11} cm^2/dyne) is 0.0591. Figure 1 shows the fitted results between normalized $\mathrm{d}\sigma/\mathrm{d}\Omega|_{\mathrm{expt}}$ and $\mathrm{d}\sigma/\mathrm{d}\Omega|_{\mathrm{self}}$. The data for $\mathrm{d}\sigma/\mathrm{d}\Omega|_{\mathrm{int}}$ are obtained using eq. (1), and they contain both intra- and intermolecular contributions.

The total structure function, $H(Q)$, is defined as

$$H(Q) = \mathrm{d}\sigma/\mathrm{d}\Omega|_{\mathrm{int}}/(\Sigma b_i)^2 \tag{3a}$$

Table 1. Inelasticity and molecular parameters.

Inelasticity parameters: $a = (0.15612 \pm 0.004) \times 10^{-2}$ Å^2; $b = (0.50385 \pm 0.03) \times 10^{-5}$ Å^4.

Molecular parameters	Present BARC, Hi-Q	Holwells *et al* [11,12]		Gas [16] (electron diffraction)	X-ray[a] [10]
		SANDALS	LAD		
r_{CC} (Å)	1.578±0.002	1.51±0.02	1.543±0.004	1.55–1.56	1.526
r_{CO} (Å)	1.258±0.007	1.37±0.03	1.340±0.029	1.40	1.430
r_{CD} (Å)	1.046±0.001	1.09±0.01	1.109±0.007	1.09	1.114
r_{OD} (Å)	1.029±0.009	0.75±0.05	0.876±0.025	0.937	0.965
$\angle C_1OD_1$ (°)	110.52±0.7	76±3	82.6±6.8	105.9	~125.0
φ_{OD} (°)	−44.47±2.0	−15±2	0 (fixed)	–	–
φ_1 (°)	−58.00±0.5	$\varphi_1 = \varphi_2$	$\varphi_1 = \varphi_2$	–	–
φ_2 (°)	36.14±0.9	47±4	−14.4±5.5	–	–

[a]These are parameters used for 2P in ref. [10]; $\lambda_0 = 5.33 \times 10^{-2}$.

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

$$H(Q) = H_{\mathrm{m}}(Q) + H_{\mathrm{d}}(Q), \tag{3b}$$

where

$$H_{\mathrm{m}}(Q) = \frac{(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{intra}}}{(\sum_i b_i)^2} \quad \text{and} \quad H_{\mathrm{d}}(Q) = \frac{(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{inter}}}{(\sum_i b_i)^2}$$

and $H_{\mathrm{m}}(Q)$ in explicit form is

$$H_{\mathrm{m}}(Q) = \frac{\left(\sum_i b_i^2 + \sum_i \sum_{j,i\neq j} b_i b_j j_0(Qr_{ij}) \exp(-\gamma_{ij}Q^2)\right)}{(\sum_i b_i)^2}, \tag{3c}$$

r_{ij} is 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 [14]). i and j sum independently over 12 atomic sites within the 2-propanol molecule with $j_0(x) = \sin x/x$, the zeroth order spherical Bessel function. $H_{\mathrm{m}}(Q)$ is the intrainterference term and gives information about the structure of the molecule, while $H_{\mathrm{d}}(Q)$, the 'distinct' structure function, gives information about the intermolecular or liquid structure. In terms of partial structure functions $H_{ij}(Q)$, $H_{\mathrm{d}}(Q)$ can be written as

$$H_{\mathrm{d}}(Q) = (\sum_i b_i)^{-2} \sum_i \sum_j (2 - \delta_{ij}) b_i b_j H_{ij}(Q). \tag{4}$$

The inverse Fourier transform (IFT) of $H_{\mathrm{d}}(Q)$ gives the liquid r-weighted neutron intermolecular correlation function $d(r)$ and the neutron radial distribution function (RDF), $G_{\mathrm{d}}(r)$, given by

$$d(r) = \frac{2}{\pi} \int_0^\infty Q H_{\mathrm{d}}(Q) \sin(Qr)\mathrm{d}Q \tag{5a}$$

and

$$G_{\mathrm{d}}(r) = 1 + d(r)/4\pi\rho r, \tag{5b}$$

where ρ is the density of deuterated liquid 2-propanol at room temperature. $G_{\mathrm{d}}(r)$ is related to partial distribution functions $g_{ij}(r)$ and is given by

$$G_{\mathrm{d}}(r) = (\sum_i b_i)^{-2} \sum_i \sum_j b_i b_j g_{ij}(r), \tag{5c}$$

where

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

3.2 *Molecular conformation analysis*

In alcohols, the effects of intermolecular hydrogen bonding persist at high Q [15] and as a result $H_{\mathrm{d}}(Q)$ continues to exhibit oscillatory behaviour, positive and negative over $H_{\mathrm{m}}(Q)$. The function $H_{\mathrm{d}}(Q)$ however, tends to vanish more rapidly than the function $H_{\mathrm{m}}(Q)$ and so $H(Q)$ oscillates around $H_{\mathrm{m}}(Q)$ and tends to equalize with $H_{\mathrm{m}}(Q)$ at large Q. This means that for Q greater than some $Q_{\min}$, the experimental total structure function $H(Q)$ comes primarily from intramolecular part. Assuming a model of the molecule from gas phase electron diffraction analysis [16] we can find the atom–atom distances for relevant analysis in liquid phase. We can find $H_{\mathrm{m}}(Q)$ and fit $QH_{\mathrm{m}}(Q)$ to experimental $QH(Q)$ for $Q > Q_{\min}$ by a χ^2-fitting procedure and refine the distances and angles. We then subtract $H_{\mathrm{m}}(Q)$ from experimental $H(Q)$ in eq. (3b) to obtain the first estimate of $H_{\mathrm{d}}(Q)$. The IFT of $H_{\mathrm{d}}(Q)$ yields intermolecular radial distribution function $G_{\mathrm{d}}(r)$ by eq. (5b). Due to limited Q-range ($Q_{\max}$) available in the experiment, a modification function, $W(Q) = \sin(\pi Q/Q_{\max})/(\pi Q/Q_{\max})$ [4] is used in the IFT. Further, we choose $Q_{\max}$ such that $G_{\mathrm{d}}(r = 0)$ is almost zero which means that the contribution of the integral in eq. (5a) beyond $Q = Q_{\max}$ is almost zero. Again, the function $G_{\mathrm{d}}(r)$ is expected to be zero in the range $0 \leq r \leq r_0$ where r_0 is about 1.5 Å because the intermolecular distance cannot be less than this value. Setting $G_{\mathrm{d}}(r) = 0$ for this region a FT of the remaining $G_{\mathrm{d}}(r)$ function would yield a new $QH_{\mathrm{d}}(Q)$. Subtracting this $QH_{\mathrm{d}}(Q)$ from experimental $QH(Q)$ we obtain the corrected $QH_{\mathrm{m}}(Q)$ function. The difference between the corrected $QH_{\mathrm{m}}(Q)$ and original $QH_{\mathrm{m}}(Q)$ is generally small. Varying molecular parameters, the subsequent iteration procedure gives the best fit to this corrected function. A χ^2-fitting is used for the whole range of Q data in steps of 0.01 Å^{-1}. This modified technique of finding molecular conformation of big molecules like alcohols somewhat resembles the method used by Bertagnolli *et al* [13] for neutron data analysis of liquid acetonitrile. The fitted curves are shown in figure 2a. The agreement is very good. The molecular parameters are listed in table 1 along with parameters obtained from electron diffraction (gas phase) and those used in X-ray diffraction (liquid phase).
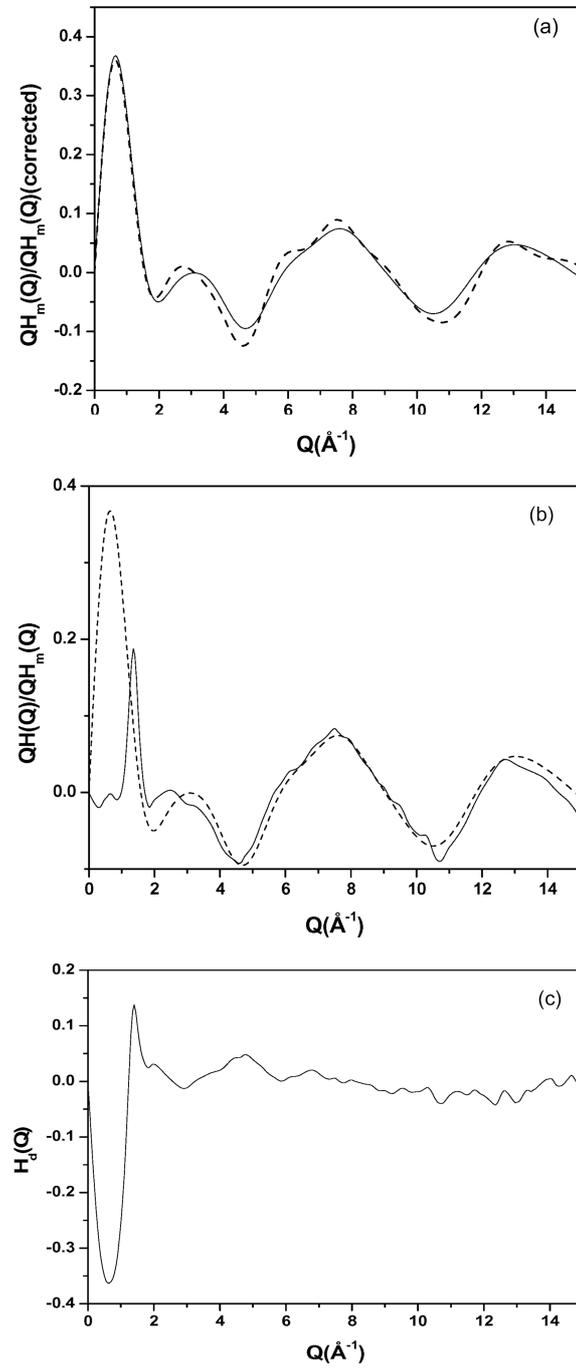
Figure 2. *Q*-weighted structure function vs *Q*: (**a**) (- - -) $QH_m(Q)$ (corrected), (——) $QH_m(Q)$ (model), (**b**) (- - -) $QH_m(Q)$, (——) $QH(Q)$ (experimental) and (**c**) (——) $QH_d(Q)$ (from experimental data).

3.3 *Model of the molecule and intrastructure*

In the X-ray measurement of the alcohols, the scattering data are dominated by carbon and oxygen contributions and important information about the hydrogen positions is not directly accessible [15]. In neutron diffraction with deuterated samples, deuterium atoms scatter the neutron beam significantly and so the positions of the deuterium atoms could be located accurately. Considering all the atomic sites as scattering units, 2-propanol molecule consists of 12 scattering sites. Though it is quite a big molecule, it has good structural symmetry which can be modelled quite comfortably.

The conformation of the molecule is presented in figure 3. Considering its symmetric structure, one can minimize the number of parameters to describe its conformation. We assume C_1C_2 in the X–Z plane and C_1O along the Z-axis. The coordinates of C_3 and D are obtained by $120°$ and $240°$ rotations of C_2 coordinate about Z-axis. We minimize the number of parameters by assuming that CC distances (namely, C_1C_2 and C_1C_3) and also all the CD distances are equal. The initial choice of the parameters is the same as in electron diffraction analysis of the gas phase data. Denoting by D_1 the hydroxyl deuterium, three rotation angles φ_{OD}, φ_1 and φ_2 in addition to $\angle C_1OD_1$ angle and three internal distances r_{CC}, r_{CD} and r_{OD} are treated as variable parameters while the methyl backbones are assumed to have tetrahedral geometry like gaseous phase [16] and liquid X-ray work [10]. The tilt angle of C_1O relative to the methyl groups is assumed zero. We however consider ϕ_{OD}, the rotation angle of OD_1 measured from the plane containing DC_1O while φ_1 and φ_2 are rotation angles of CD_3 groups about C_1C_2 and C_1C_3 lines.

Using the method stated in §3.2 the χ^2-fitting result shown in figure 2a gives molecular parameters (table 1) and these appear very reasonable. The parameters determined by electron diffraction in gas phase and those used in X-ray diffraction in liquid phase are also listed for comparison. The earlier neutron diffraction analysis [11,12] showed quite staggered values in r_{OD} distance and $\angle C_1OD_1$ angle. The previous neutron diffraction analysis parameters are also shown. In the present work the hydroxyl group OD_1 is at a staggered position, as expected. The error estimate for each parameter is done to allow a 1% increase in the χ^2-value. The internal vibrational factors are 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 experimental Q-weighted total structure function $H(Q)$.

3.4 *Intermolecular contribution and liquid structure*

After obtaining the molecular conformation we obtain intermolecular structural contribution $H_d(Q)$ from eq. (3) and 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 Å^{-1} and this implies that our analysis to find the molecular parameters is quite accurate. The intermolecular r-weighted correlation function $d(r)$ is obtained using eq. (5a) and intermolecular RDF $G_d(r)$ obtained from eq. (5b). The $G_d(r)$ curve is shown in figure 5. The window function is used in the IFT to reduce the undesirable ripples arising due
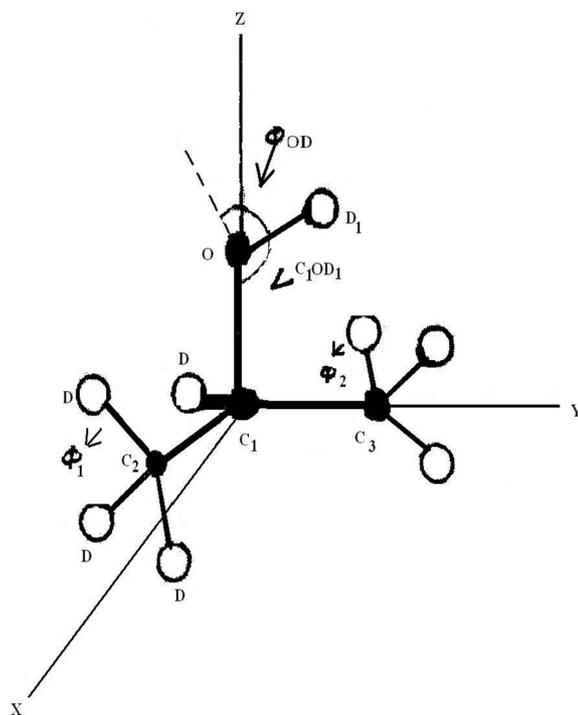
Figure 3. Molecular conformation of 2-P molecule.

to truncation effects. A quadratic interpolation with Filon's quadrature has been used. The results obtained from X-ray data [10] are also shown for comparison. For obvious reason the OD peak is absent in the X-ray result. It is clear that the intermolecular atom–atom correlations can be easily identified. The comparison between neutron and X-ray results also helps to identify the plausible dominant hydroxyl-bonded molecular cluster or association present in liquid state at room temperature. The peak at about 1.6–1.8 Å and hump at about 2.8 Å are clearly due to distances associated with intermolecular OD and OO distances respectively and arising from almost linear hydrogen bonding. The results exhibit a broad oscillatory pattern extending to about 14 Å similar to X-ray result. The general nature is a featured peak at about 5.5 Å whereas the main featured peak for methanol appears at about 4.5 Å [1] and this signifies the comparative largeness of 2-propanol molecule. It is also to be noted that the spurious oscillations in $G_d(r)$ at small r-region (<1.5 Å) are quite small.

3.5 *Intermolecular structure analysis through cluster or association model*

It is clear that the various distances at which peaks and humps occur in $G_d(r)$ curve, as also in X-ray result [10] show the existence of specific molecular association or cluster present in the liquid state. To extract information about the presence of
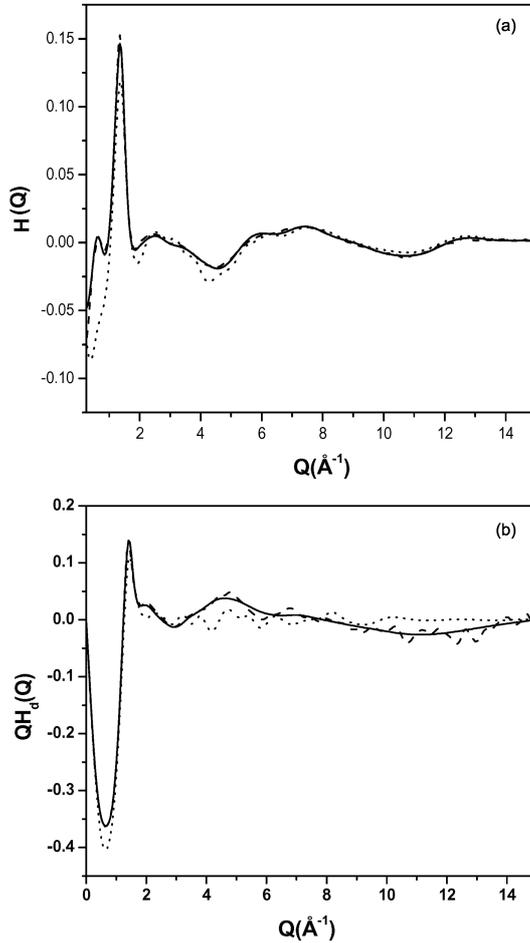
Figure 4. (**a**) $H(Q)$ vs. Q: (- - -) experimental, (—) HRC, ($\cdots$) TLC. (**b**) $QH_\mathrm{d}(Q)$ vs. Q: (- - -) experimental, (—) HRC, ($\cdots$) TLC.

dominant molecular cluster or clusters in liquid state we have done the model analysis based on the theory of molecular clusters developed in this laboratory [1]. In the analysis we follow the same method as in our earlier analysis of liquid 1-propanol and other alcohols [3–5,17,18]. Three assumptions exist in the analysis, namely, (i) there exist distinct molecular cluster or clusters in liquid state due to H-bonding, (ii) the molecules in different clusters are orientationally uncorrelated and (iii) for a large molecule like 2-propanol, the centre structure factor of the liquid can be approximately represented by the Percus–Yevick (PY) single-site hard-sphere model with a suitable core diameter. The expression for $H_\mathrm{d}(Q)$ is given by [3,17,18]

$$H_\mathrm{d}(Q) = H_\mathrm{c}(Q) + F_\mathrm{2u}(Q)[S_\mathrm{c}^\mathrm{hs}(Q) - f_3(Q) - 1], \tag{6}$$

where $S_\mathrm{c}^\mathrm{hs}(Q)$ is the hard sphere centre structure factor, $F_\mathrm{2u}(Q)$, $f_3(Q)$ and $H_\mathrm{c}(Q)$ are respectively the uncorrelated intermolecular form factor, the structure factor of

molecular centre pairs within the cluster and the intermolecular cluster structure function. The relevant expressions are

$$F_{2u}(Q) = \left(\sum_i b_i\right)^{-2} \left[\sum_i b_i j_0(Qr_{ci}) \exp(-\gamma_i Q^2)\right]^2,$$

$$f_3(Q) = N_c^{-1} \sum_{i \neq j} j_0(Qr_{cij}) \exp(-\gamma_{ij} Q^2),$$

$$H_c(Q) = \left(\sum_i b_i\right)^{-2} N_c^{-1} \sum_{ij} b_i b_j j_0(Qr_{ij}) \exp(-\gamma_{ij} Q^2), \tag{7}$$

where N_c indicates the number of molecules in a cluster and i, j the atoms of different molecules within the cluster. In this article two probable widely suggested models for alcohols [1,6], namely, a hexamer ring chain (HRC) cluster and a tetramer linear chain (TLC) cluster of neighbouring molecules are considered. Between these two models, earlier works on other alcohols suggested that HRC is a more probable dominant cluster in liquid state at room temperature. The model clusters are shown in figure 6. Considering all O–D$\cdots$O bonds we can calculate coordinates of all atomic sites. To avoid complication in the calculation, we take $CD_3(\equiv R)$ as a single scattering unit following group scattering concept with appropriate scattering centre and scattering length. Varying the parameters like intermolecular O$\cdots$O distance and the orientation and rotation angles of all C's and R's within the cluster we have fitted the model $QH_d(Q)$ to experimental $QH_d(Q)$ function by χ^2-fitting programme. The fitted curves for these two models are shown in figure 4b. Obviously, the HRC model is far superior to TLC model. The model total structure functions $H(Q)$ obtained from eq. (3b) are also shown in figure 4a along with experimental $H(Q)$. Clearly, HRC model is quite appropriate. The pre-peak in the experimental diffraction pattern, characteristic of chain or cluster [12,17], is nicely generated in the HRC model. The fitted model parameters (for HRC model only) are shown in table 2. It is to be noted that hard core diameter (4.45 Å) and O–O distance parameter (2.68 Å for HRC model) are little bit lower than the corresponding values for liquid t-butanol [5]. Using model $H_d(Q)$ we can obtain intermolecular $G_d(r)$ through eqs (5a) and (5b) and results for HRC and TLC models are shown in figure 5. The agreement between HRC model and experimental data is very good.

3.6 *Testing the model using X-ray data*

Recently, the large angle X-ray scattering was carried out by Takamuku *et al* [10] on liquid 2-propanol and its mixture with water at room temperature. The cross-section data on pure liquid are reported over the range 0.02 Å^{-1} to 14.4 Å^{-1}. The data were digitized using the software 'Digitizeit_win' (screen shot) and were smoothened and obtained at regular interval of 0.1 Å^{-1}. The data were normalized and wherefrom obtained the total X-ray molecular structure function $H(Q)$ and the corresponding intermolecular or distinct X-ray structure function $H_d(Q)$. In $H(Q)$ a strong pre-peak is again observed at about $Q \sim 0.7$–0.8 (figure 7).
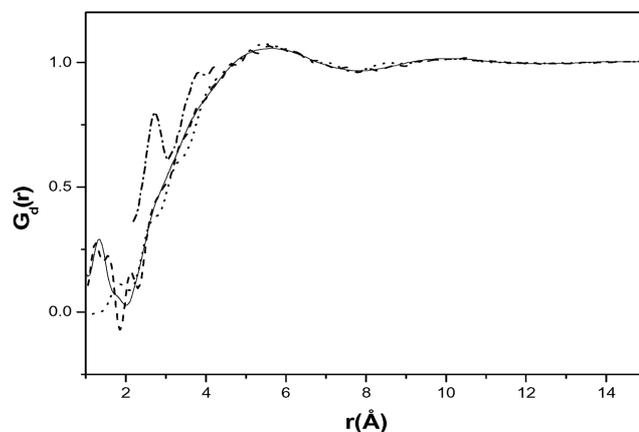
Figure 5. $G_{\mathrm{d}}(r)$ vs. r: (- - -) experimental, (—) HRC, ($\cdots$) TLC, (-·-·-·) experimental (X-ray).
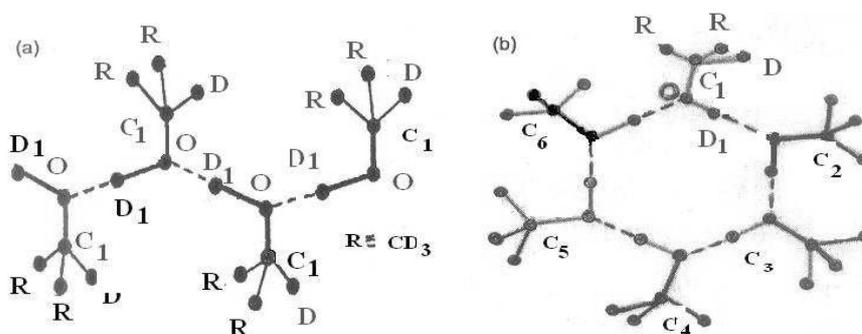

Figure 6. Model clusters. (**a**) TLC, (**b**) HRC.

Table 2. HRC model parameters.

Hardcore diameter, $\sigma = 4.45$ Å; non-planar angle, $\delta = 3°$.

O–O distance	Rotational angles (°) of C's about OD line	Rotational angles (°) of R's about CO line
2.68 Å	(C1) 180.14°	(R1) 18.00°
	(C2) 54.18°	(R2) −114.72°
	(C3) 60.80°	(R3) −11.54°
	(C4) 108.88°	(R4) 68.28°
	(C5) 28.92°	(R5) 1.36°
	(C6) 17.00°	(R6) −11.64°

We have used the parameters (table 2) obtained from neutron data for the calculation of total X-ray structure function $H(Q)$ using HRC model. In the process we have replaced neutron scattering lengths by Q-dependent atomic scattering factors
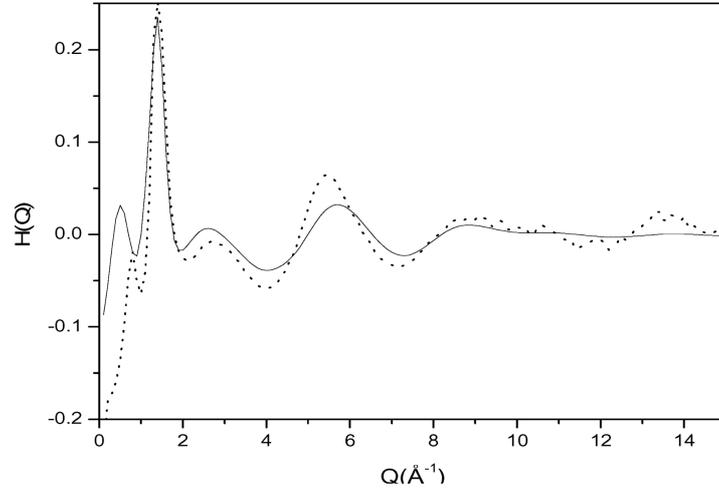
Figure 7. X-ray data: $H(Q)$ vs. Q, (- - -) experimental, (—) HRC.

of the relevant atoms in $H_m(Q)$, $H_c(Q)$, $F_{2u}(Q)$ expressions. The result is shown in figure 7 and agreements appear to be good. Better agreement is expected if the HRC parameters are altered significantly.

3.7 *Intermolecular pair distribution functions using HRC model*

Since agreement of neutron HRC data with experimental data is extremely good, we have thought it appropriate to evaluate intermolecular pair distribution functions $g_{ij}(r)$ from the experimental data using the model. The model analysis enables evaluation of intermolecular partial structure functions $H_{ij}(Q)$ and pair distribution functions, $g_{ij}(r)$ quite easily. We write $H_d(Q)$ as the sum of the partial structure functions as

$$H_{ij}(Q) = H_c^{(ij)}(Q) + F_{2u}^{(ij)}(Q)[S_c^{hs}(Q) - f_3(Q) - 1], \qquad (8)$$

where

$$H_c^{(ij)}(Q) = N_c^{-1} \sum_{l \neq l'} \sum_{i,j} j_0(Q r_{iljl'}) \exp(-\lambda_{iljl'} Q^2)$$

and

$$F_{2u}^{(ij)}(Q) = (2 - \delta_{ij}) j_0(Q r_{ci}) j_0(Q r_{cj}) \exp[(-\lambda_{ci} + \lambda_{cj}) Q^2],$$

where l, l' are two different molecules in the HRC cluster.

The partial distribution functions $g_{ij}(r)$ are given by eq. (5c). 2-Propanol molecule contains four non-equivalent scattering units (C_1, D, R($\equiv CD_3$), D_1) and so it has ten partial structures and pair distribution functions. We have taken, for
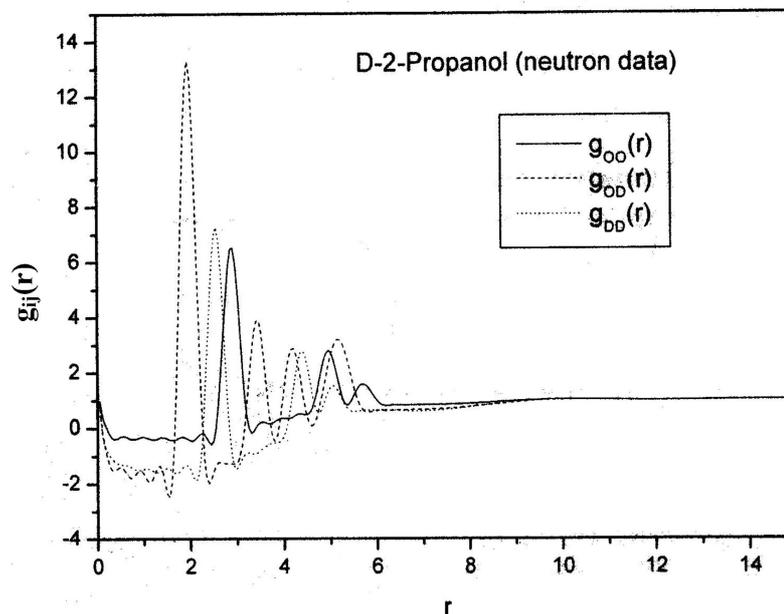
Figure 8. $g_{ij}(r)$ vs. r (from neutron data only): (—) $g_{OO}(r)$, (···) $g_{OD}(r)$, (- - -) $g_{DD}(r)$.

convenience C_1 as the centre of the bonded 2-propanol molecule in the calculation of $f_3(Q)$. We have considered the appropriate core diameter as 4.45 Å for the hard sphere centre structure. Among the ten we report three of them, namely, $g_{OO}(r)$, $g_{OD}(r)$ and $g_{DD}(r)$. From these we have information about H-bonded features. The results are shown in figure 8. The first peak positions are very reasonable and agree well with those for 2-propanol and other alcohols where, in particular, the O–O (X-ray) and OD (neutron) distributions are available [8,10,15,19]. The appropriate neutron isotopic substitution method to evaluate the partials is not available for liquid 2-propanol nor the empirical potential structure refinement model (EPSR) [8] to evaluate the partials is available for this case as yet. We have not obtained partials corresponding to X-ray data as agreement of HRC model here is not that good with parameters (table 2) from neutron data.

4. General remarks and conclusion

In this analysis of neutron diffraction data of liquid 2-propanol at room temperature, we have obtained the molecular conformation as well as intermolecular structural correlations. The analyses give an average conformation and average liquid structure having H-bonded clusters. About the nature of the cluster, we conclude that HRC is definitely the dominant nature of molecular association present in the liquid state at room temperature. The HRC model for methanol was first proposed by

Pauling [20] and was supported by works from this laboratory [1]. The model is applicable to a number of other alcohols [2,3,5]. In the vapour phase of methanol, the existence of closed tetramer rings are known for long while in solid phase a linear chain of infinite length is well known [20]. In the analysis of heats of vapourization and other allied data of alcohols there is a strong support in favour of small cyclic rings, mostly tetramers [9]. The earlier simulation data, however, mostly showed in favour of linear zig-zag open chains of 6–8 molecules for liquid alcohols [7]. It is also important to note here that a recent study on X-ray emission spectra and density functional theory [21] supports the existence of HRC structure in liquid methanol. A very recent simulation work [22] based on a refined H-bonded potential model which includes polarizability, non-additivity and intermolecular relaxation, shows that the presence of HRCs in liquid methanol at room temperature is quite possible. So in pure liquid the actual structural association is still an open question. In methanol, our diffraction as well as heat of vapourization data analyses show the presence of hexamers in dominant form [1]. These clusters are labile and often break and join. It was however suggested [23] that a planar hexamer is energetically not favourable. The present work does suggest that the molecules in the hexamer are not exactly in a plane. Anyway, our present work strongly suggests that diffraction experiments can give specific information about the molecular association in liquid state quite accurately.

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