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Intermolecular structure of liquid D-*tert*-butanol by neutron-diffraction data

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Abstract. Neutron-diffraction (ND) measurements are carried out on a high-Q diffractometer for liquid D-*tert*-butanol at room temperature (RT) and the data are analyzed successfully. The molecular structure of the t-butanol molecule is obtained by using an iterative method by making the radial distribution function zero at the core region. Analysis of available X-ray-diffraction data tells us about the dominant presence of a hexamer closed-chain (ring) cluster in liquid t-butanol at RT, similar to liquid methanol and ethanol at RT. We now find that this average intermolecular structure having H-bonding also reproduces very well the ND data and helps us to obtain intermolecular atom–atom partial pair distribution functions that are well comparable with empirical potential structure refinement model results.

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In this article we describe the investigation of the intermolecular structure of the H-bonded liquid monohydric alcohol D-*tert*-butanol at room temperature using neutron-diffraction data. The signature of H-bonded molecular association in diffraction data is the formation of a pre-peak at a scattering vector, $\boldsymbol{Q} \sim 0.7$–$0.8\ \text{Å}^{-1}$, before the main diffraction peak [1]. The pre-peaks of liquid alcohols which are well known in X-ray-diffraction data have been detected in the neutron-diffraction pattern only recently [1]. The comparative study of H-bonded and non-H-bonded liquid structures [2] shows that there exists a cluster correlation between the neighbouring molecules, present in liquid t-butanol.

We have already discussed [3] the liquid structure and intermolecular correlation based on available X-ray-diffraction data [4]. At room temperature a proposition of cyclic hexamer ring molecular association was quite successful. This structure also reproduces quite well the neutron-diffraction data at room temperature, which is shown in a preliminary analysis [5]. In the present study we have analyzed our neutron data to verify the information drawn earlier through X-ray data [3].

In our last communication [6] we have analyzed the neutron data to obtain detailed molecular conformations and intermolecular correlations. In that analysis a technique slightly modified from one used earlier [7] was applied. The intermolecular composite radial distribution function (RDF) obtained from neutron data is compared with one obtained from X-ray data and this helped to identify the intermolecular atom–atom distributions present in the liquid.

1 Experiment

A careful diffraction measurement of a fully deuterated liquid t-butanol sample at room temperature was carried out on the high-Q diffractometer at Dhruva, BARC, India. The liquid used in the experiment consisted of a 99.8% deuterated sample available from Aldrich Ltd. (USA) and 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. The incident wavelengths of 0.783 Å and 1.278 Å were used and the data were recorded for an angular range from 3° to 125°. The corrected cross-section data show a strong pre-peak at $Q \approx 0.71\ \text{Å}^{-1}$, similar to what is observed in the X-ray-diffraction data [4].

2 Analysis

In the analysis we assume that (i) there exist distinct molecular cluster or clusters in the liquid state due to H-bonding, (ii) the molecules in different clusters are orientationally uncorrelated and (iii) for a large molecule like t-butanol the center structure of the liquid can be approximately represented by the Percus–Yevick (PY) single-site hard-sphere model with a suitable core diameter. The molecular structure factor $S_{\mathrm{m}}(Q)$ can be defined as

$$S_{\mathrm{m}}(Q) = F_1(Q) + H_d(Q), \tag{1}$$

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where $F_1(Q)$ contains the coherent self-term and the intramolecular term which gives information about the structure of the molecule. $H_d(Q)$, the distinct structure function gives information about the intermolecular or liquid structure. The intramolecular term can be calculated by knowing the intramolecular separation and atomic orientation. The experimental $S_{\mathrm{m}}(Q)$ can be written as

$$S_{\mathrm{m}}^{\mathrm{ex}}(Q) = F_1(Q) + H_d^{\mathrm{ex}}(Q). \tag{2}$$

$H_d^{\mathrm{ex}}(Q)$ can be obtained from the experimental total structure function minus the intramolecular structure function. The model molecular structure function $S_{\mathrm{m}}^{\mathrm{model}}(Q)$ can be written as

$$S_{\mathrm{m}}^{\mathrm{model}}(Q) = F_1(Q) + H_d^{\mathrm{model}}(Q), \tag{3}$$

where $H_d^{\mathrm{model}} = H_{\mathrm{c}}(Q) + F_{2u}(Q)(S_{\mathrm{HS}}(Q) - f_3(Q) - 1)$, $S_{\mathrm{HS}}(Q)$ is the hard-sphere center structure according to assumption (iii), $H_d^{\mathrm{model}}(Q)$ is the model distinct structure function and $F_{2u}(Q)$ and $f_3(Q)$ are respectively the uncorrelated intermolecular form factor and the structure factor of molecular center pairs within the cluster. $H_{\mathrm{c}}(Q)$ is the intermolecular cluster structure function defined by

$$H_{\mathrm{c}}(Q) = \left(\sum_i b_i\right)^{-2} N_{\mathrm{c}}^{-1} \sum_{i,j} b_i b_j j_0(Qr_{ij}) \exp\left(-l_{ij}^2 \frac{Q^2}{2}\right), \tag{4}$$

with N_{c} the number of molecules in a cluster, i, j the atoms of different molecules within the cluster, l_{ij} the root-mean-square deviation of the local instantaneous atom–atom separation distance, $j_0(x) = x^{-1}\sin x$ and b_i the neutron-scattering length of the ith atom. In this article, we assume that there exists a hexamer intermolecular cluster as shown in Fig. 1. This assumption is based on the previously well-accepted concept of the existence of a plausible intermolecular cluster in the liquid monohydric alcohol series [8]. Considering all six O–H...O bonds lying in a plane, we can calculate coordinates of all atomic sites taking $CD_3(\equiv R)$ as a single scattering unit following the group scattering concept. Varying the parameters like the intermolecular O...O distance and the orientational and rotational angles of all C's and R's within the cluster we have fitted the model $S_{\mathrm{m}}^{\mathrm{model}}(Q)$ to the experimental $S_{\mathrm{m}}^{\mathrm{ex}}(Q)$ data by a chi-square fitting program. The fitted curve is shown in Fig. 2 and the fitted model parameters are shown in Table 1.

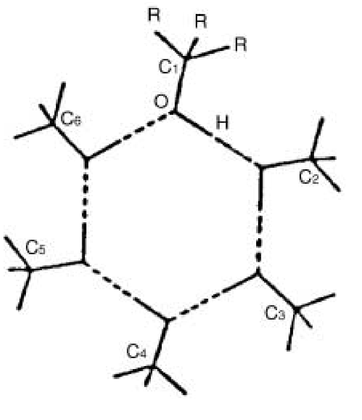

Fig. 1. Hexamer ring cluster of liquid t-butanol

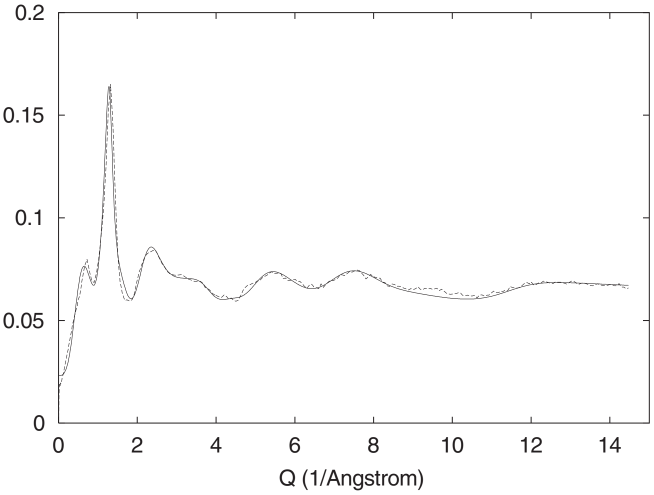

Fig. 2. — $S_{\mathrm{m}}^{\mathrm{model}}(Q)$, - - - $S_{\mathrm{m}}^{\mathrm{ex}}(Q)$

Table 1. Intermolecular cluster parameters (hexamer)

O–O bond length (Å)	Rotational angles (deg.) of C's about OH axes	Rotational angles (deg.) of R's about CO axes
2.82	($C1$) 164.62	($R1$) 359.07
	($C2$) 74.58	($R2$) 318.88
	($C3$) 45.5	($R3$) 77.92
	($C4$) 104.74	($R4$) −188.88
	($C5$) 170.28	($R5$) −93.5
	($C6$) 367.26	($R6$) −128.94

The intermolecular composite r-weighted correlation function $d(r)$ can be calculated with the expression

$$d(r) = 4\pi r\rho(G_d(r) - 1), \tag{5}$$

where $G_d(r) = 1 + \frac{1}{(2\pi^2\rho r)}\int_0^\infty QH_d(Q)\sin Qr\,\mathrm{d}Q$, ρ being the density of liquid t-butanol at room temperature, the value of which is 0.00634 Å^{-3}. Figure 3 shows the comparison between the $d(r)$ obtained through the cluster model and that obtained from the experimental data.

Then we evaluate the intermolecular partial structures and correlations in relation to the intermolecular structural association of liquid t-butanol [9]. To find the partial structure functions for the model, we write the distinct structure function for the model, $H_d(Q)$, as the sum of the partial structure factors according to

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

where

$$H_{\mathrm{c}}^{(\alpha\beta)}(Q) = N_{\mathrm{c}}^{-1} \sum_{l\neq l'} \sum_{\alpha,\beta} j_0(Qr_{\alpha_l\beta_{l'}}) \exp\left(-\lambda_{\alpha_l\beta_{l'}}^2 \frac{Q^2}{2}\right)$$

and

$$F_{2u}^{\alpha\beta}(Q) =$$

$$(2 - \delta_{\alpha\beta}) j_0(Qr_{\mathrm{c}\alpha}) j_0(Qr_{\mathrm{c}\beta}) \exp\left[(-\lambda_{\mathrm{c}\alpha}^2 + \lambda_{\mathrm{c}\beta}^2)\frac{Q^2}{2}\right].$$

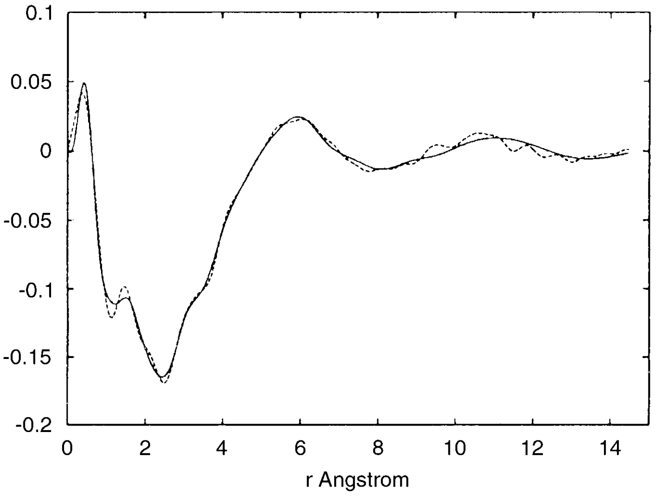

Fig. 3. — model $d(r)$, - - - experimental $d(r)$

The function $g_{\alpha\beta}(r)$ is given by

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2 \rho r} \int_0^\infty Q H_{\alpha\beta}(Q) \sin(Qr) \mathrm{d}Q. \quad (7)$$

The results are shown in Figs. 4, 5 and 6.

3 Discussion of the results

In Fig. 2 we see that the agreement between the model and the experimental data is extremely good and appears to be even better than the X-ray-data interpretation reported earlier. In Fig. 3 the agreement between the experimental data and the model data tells us about the dominant presence of hexamer closed-chain clusters in liquid *t*-butanol at room temperature, similar to liquid methanol and ethanol at room temperature [8].

The *t*-butanol molecule has ten partial structure factors and pair distribution functions, since it contains four non-equivalent scattering units (C, O, D, $R(\equiv CD_3)$). We have taken conveniently carbon as the center of the bonded *t*-butanol molecule in the calculation of $f_3(Q)$. We have considered the appropriate core diameter as 5.174 Å for the hard-sphere center structure. Among the ten, we report three of them, namely, $g_{\mathrm{OO}}(r)$, $g_{\mathrm{OH}}(r)$ and $g_{\mathrm{HH}}(r)$. From these we obtain information about H-bonded features. The distribution functions obtained from both the available X-ray and the present neutron data are compared in Figs. 4, 5 and 6. There is a fair degree of agreement between these two sets of distribution functions. The results of computer simulations on pure liquid *t*-butanol are not available for comparison. The neutron isotopic substitution method for *t*-butanol is now available [10], which has been analyzed by the empirical potential structure refinement (EPSR) procedure. This analysis gives intermolecular atom–atom distribution functions which show in detail the basic features quite in agreement with our present results. The reported H–H partial structure factor and distribution function contain both intramolecular and intermolecular correlation terms and so the results cannot be compared directly with our present results.

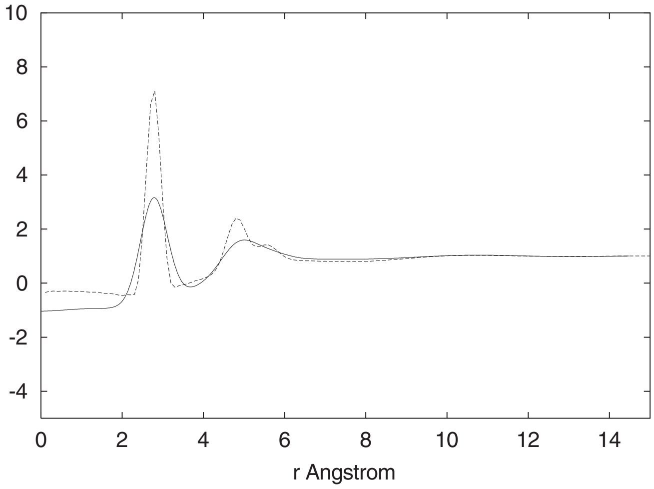

Fig. 4. — $g_{\mathrm{OO}}(r)$ for neutron data, - - - $g_{\mathrm{OO}}(r)$ for X-ray data

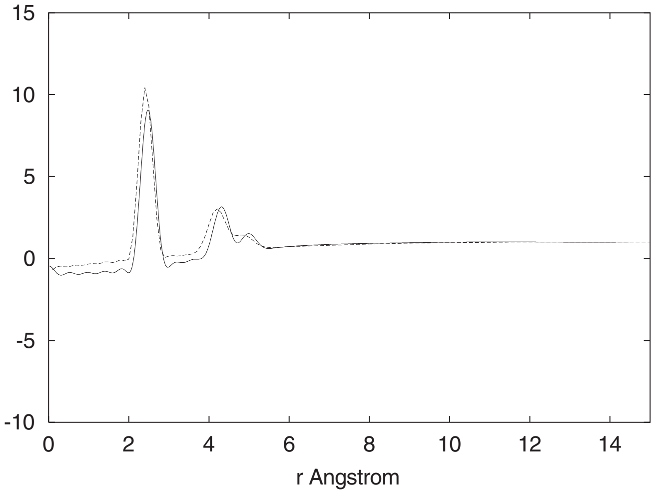

Fig. 5. — $g_{\mathrm{HH}}(r)$ for neutron data, - - - $g_{\mathrm{HH}}(r)$ for X-ray data

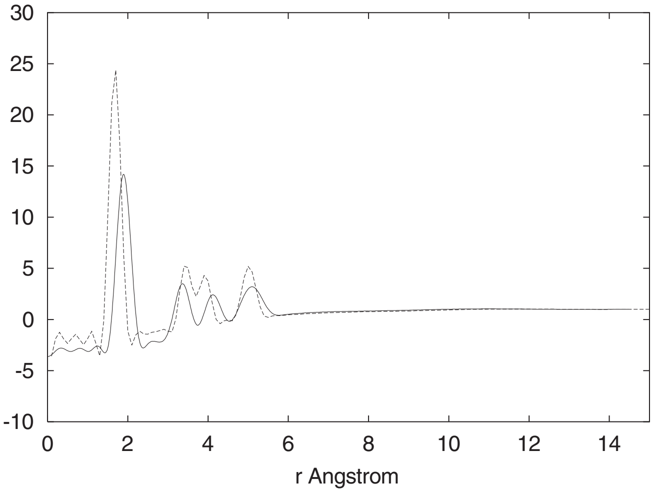

Fig. 6. — $g_{\mathrm{OH}}(r)$ for neutron data, - - - $g_{\mathrm{OH}}(r)$ for X-ray data

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