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Effect of temperature on the molecular association in liquid D-methanol using neutron diffraction data

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Hydrogen-bonded cluster analysis of liquid D-methanol data at room and elevated temperatures was carried out and nature of molecular association was extracted. The analysis, based on a choice of suitable centre structure corresponding to an effective pair potential, hardsphere plus a square-well ledge, determines if the H-bonded clusters are broken with the rise in temperature. It is shown that clusters present at room temperature are more or less preserved at elevated temperatures. At low Q (Q being the scattering vector), Ornstein–Zernike behaviour is produced extremely well. The analysis enables the extraction of atom–atom distribution functions, such as $g_{OO}(r)$, $g_{OD}(r)$ and $g_{DD}(r)$, the variation of which with temperature confirm the same observation.

Keywords: neutron-diffraction; molecular conformation; molecular association

1. Introduction

This study on the effect of temperature on the molecular and liquid structures of D-methanol is a continuation of our earlier work [1]. It is a fact that unlike solid and gaseous phases, the hydrogen (H)-bonded liquid structure in this system is still open for discussion [2,3], in particular the effect of temperature on the molecular association/cluster is still not uniquely known. The relevant data in superheated liquids are scarcely available in the literature. The temperature effects on liquid methanol, liquid 2-propanol, etc. were studied by various groups [4] but at temperatures below room temperature (RT) and not at boiling point (BP) and superheated state as in this case. More recently, however, supercritical methanol has been studied using Raman spectra and NMR measurements [5], which indicate decrease in hydrogen-bonding with the rise in temperature. The structure of subcritical and supercritical methanol has also been recently studied by neutron diffraction and analysed by empirical potential structure refinement (EPSR) and spherical harmonic methods [6]. The results show that though H-bonded structures are present, these are mostly linear chain clusters of 3–5 molecules in sharp contrast with ambient methanol structure. This result is also very different from earlier known closed chain tetramer structure found in gaseous phase of methanol [7].

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The presence of a pre-peak or hump in diffraction data at about $Q \sim 0.7\text{--}0.8 \text{ \AA}^{-1}$ (Q being the scattering vector) before the main diffraction peak implies that H-bonded chain association or cluster exists in liquid state [4,8,9]. It is evident that the molecular association affects the thermodynamic and transport properties. It was earlier shown from this laboratory through a detailed analysis of X-ray data [10] that hexamer ring clusters (HRC) are dominantly present in liquid state at RT. It is therefore interesting to see if such liquid structure is also supported by our indigenous neutron data at RT and also to see to what extent this molecular association survives at elevated temperature and pressure. To our knowledge, no similar analysis on superheated liquid methanol exists in the literature.

2. Source of data

The neutron scattering experiment was carried out at RT (20°C), BP (65°C) and 2BP (130°C) on liquid D-methanol sample at Hi- Q diffractometer, Dhruva, BARC (India) in collaboration with BARC colleagues using an indigenously constructed special quartz temperature cell [1]. Hi- Q diffractometer, intended for structural studies of amorphous solids, liquids and high pressure structural phase transitions, is a multi-position sensitive detector (PSD) based instrument located at beam port HS-1019 of Dhruva (100 MW with neutron flux 1.8×10^{14} neutrons $\text{cm}^{-2}\text{s}^{-1}$). A monochromator (usually a large single crystal) housed inside a cylindrical shield (monochromator drum) receives the polychromatic beam from the reactor and produces a monochromatic neutron beam using copper monochromator giving out neutrons with wavelengths depending on chosen crystal planes. The total angular range is up to $2\theta = 140^\circ$ in the scattering plane. The incident neutron energy is of the order of thermal energy. An oscillatory radial collimator (ORC) designed and installed between the sample and the detector shield helps in reducing the general background by 50% and also stops contributions coming from sample environment, namely furnace, etc. Five PSDs each 1 m long are housed in the detector shield. The PSDs are the ideal choice for these diffractometers as they are capable of collecting data for a large angular range simultaneously. The instrument parameters are listed in Table 1. The electronics for the positional coding of the PSD data by charge

Table 1. Instrument parameters.

Beam port	HS-1019
Monochromator	
Cu(220)	$\lambda = 783 \text{ \AA}$
Cu(111)	$\lambda = 1.278 \text{ \AA}$
Take-off angle	35.7°
Scattering angle	$3 < 2\theta < 140^\circ$
Beam size at sample	$4 \text{ cm} \times 1.5 \text{ cm}$
Neutron flux at sample position	2×10^6 ($\lambda = 1.278 \text{ \AA}$) 3×10^5 ($\lambda = 0.783 \text{ \AA}$)
Detector (He^3)	5 overlapping 1-d PSDs each of 1 m length
Q -range	$0.3\text{--}15 \text{ \AA}^{-1}$, $\text{max}^m \sim 24 \text{ \AA}^{-1}$
$\Delta Q/Q$	$\sim 2.0\text{--}2.5\%$

divisional method using digital electronics has been developed in the Electronics Division of BARC and the data collection is controlled by a PC. The data reduction and correction programmes have been incorporated to get the structure factor data on an absolute scale. The reduction programmes take care of the fact that the PSDs are linear and appropriate corrections are applied to the data. The correction programmes take care of the corrections due to background, absorption, multiple scattering, inelasticity effects and normalisation – all programmes follow the prescription given by Egelstaff [11]. The average neutron counts after scattering from the sample (in this case) were $10\text{--}15 \times 10^3$ (arb.units) at various angular points and evidently the data statistics was quite good (statistical accuracy for structure function is smaller than 1%). In all cases calibration was done using a vanadium rod.

The deuterated liquid sample was 99.8% pure and available from Aldrich Ltd, USA. The liquid was confined in the quartz cell properly evacuated in nitrogen atmosphere and sealed, after filling. This arrangement kept the liquid at elevated temperature under pressure and was used in the scattering experiment. It is also to be noted that cell contribution is not more than a small fraction of the sample contribution for all scattering angles. The details about the cell are available in [1]. For elevated temperature measurements, quartz cell has been in use for D_2O (e.g. [12]). Since liquid methanol has low flash point it cannot be heated directly in air contact and so the need for an evacuated cell. Vanadium is not suitable for the purpose. Ti–Zr null alloy cell could however be used for the purpose. The suitable Ti–Zr cell was not available to us (difficulty of evacuation and proper sealing). The Ti–Zr cell used for high temperature and high pressure measurements is usually a bulky container to withstand high pressure and most scattering comes from the pressure cell and as a result very high flux reactor beam is required. Even the Ti–Zr null alloy cell might show problems at high pressure with D-methanol [13]. It is however to be noted here that the RT data obtained using vanadium and also using quartz cell agreed very well including pre-peak and other features.

The corrected cross-section data for two wavelengths were suitably clubbed together. The clubbed data were extrapolated in the region $0 \leq Q \leq 0.3 \text{ \AA}^{-1}$ and were normalised (on high- Q data as well) such that the graphical extrapolation to $Q \rightarrow 0$ yields correct isothermal compressibility of methanol. The cross-section data for three temperatures are shown in Figure 1. There is a pre-peak at all the three temperatures at $Q \sim 0.7\text{--}0.8 \text{ \AA}^{-1}$ similar to what is shown in X-ray data (8) and at low Q , a little bit of the Ornstein–Zernike (O–Z) behaviour is exhibited [14] (critical temperature of normal methanol, 239°C).

3. Analysis

The corrected data were then separated into ‘self’ and ‘interference’ terms

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

At high- Q , the experimental cross-section data have a ‘fall-off’ feature. This is due to interaction of incident neutrons with vibrating scattering sites (deuterium atoms in particular) [15]. This inelasticity effect modifies the self-scattering term. For alcohols,

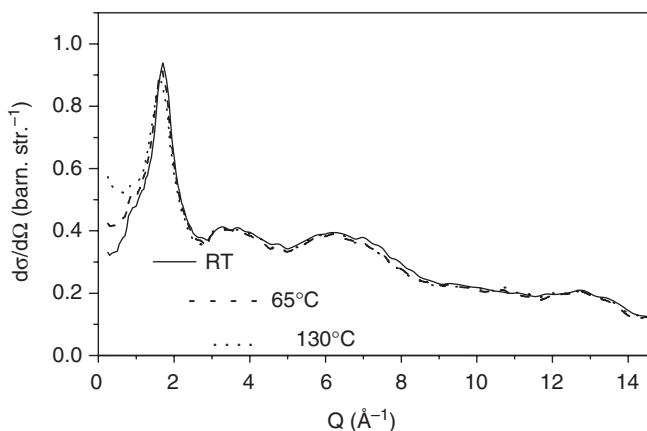


Figure 1. Normalised cross-section of liquid D-methanol, $d\sigma/d\Omega$ vs. Q .

this modification can be represented by a term involving two inelasticity parameters [15]. Thus for D-methanol we have

$$\left. \frac{d\sigma}{d\Omega} \right|_{\text{self}} = \left[b_C^2 + b_O^2 + 4b_D^2 + 4\left(\frac{\sigma_D^i}{4\pi}\right) \right] (1 - aQ^2 + bQ^4), \quad (2)$$

where σ_D^i is the incoherent scattering cross-section for deuterium and a , b are the two inelasticity parameters. b_C , b_O , b_D are the coherent scattering lengths of C, O, D atoms, 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 $Q \approx 5.5$ to 6.0 \AA^{-1}) are listed in Table 2. Subtracting 'self' term from $\left. \frac{d\sigma}{d\Omega} \right|_{\text{expt}}$, we obtain $\left. \frac{d\sigma}{d\Omega} \right|_{\text{int}}$, which contains both intra- and inter-molecular contributions. The total structure function, $H(Q)$ is defined as:

$$H(Q) = \left. \frac{d\sigma}{d\Omega} \right|_{\text{int}} / \left(\sum_{\alpha} b_{\alpha} \right)^2.$$

$H(Q)$ obtained in this way is depicted in Figure 2(b) for all three temperatures. $H(Q)$ is separable into intra- and inter-molecular terms given by:

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

where

$$H_m(Q) = \left. \frac{d\sigma}{d\Omega} \right|_{\text{int}}^{\text{intra}} / \left(\sum_{\alpha} b_{\alpha} \right)^2 \quad \text{and} \quad H_d(Q) = \left. \frac{d\sigma}{d\Omega} \right|_{\text{int}}^{\text{inter}} / \left(\sum_{\alpha} b_{\alpha} \right)^2.$$

$H_m(Q)$ depends on the molecular conformation while $H_d(Q)$ defines inter-molecular or liquid structure. In explicit form, $H_m(Q)$ is given by:

$$H_m(Q) = \sum_{\alpha} \sum_{\beta \neq \alpha} b_{\alpha} b_{\beta} j_0(Qr_{\alpha\beta}) \exp(-\gamma_{\alpha\beta} Q^2) / \left(\sum_{\alpha} b_{\alpha} \right)^2, \quad (4)$$

Table 2. Inelasticity and intra-molecular parameters of liquid CD₃OD molecule.

	<i>RT</i>	65°C	130°C
<i>a</i> (Å ²)	5.556×10^{-3}	5.734×10^{-3}	5.926×10^{-3}
<i>b</i> (Å ⁴)	1.088×10^{-5}	1.171×10^{-5}	1.338×10^{-5}
<i>r</i> _{CO} (Å)	1.460 ± 0.006 1.4246 ^a 1.42 ± 0.004 ^b 1.495 ^c 1.435 ± 0.005 ^d	1.473 ± 0.006	1.512 ± 0.006
<i>r</i> _{CD} (Å)	1.136 ± 0.004 1.0936 ^a 1.070 ± 0.005 ^b 1.09 ^c 1.085 ± 0.005 ^d	1.156 ± 0.004	1.175 ± 0.004
<i>r</i> _{OD} (Å)	1.048 ± 0.010 0.9451 ^a 1.03 ± 0.011 ^b 1.031 ^c 0.990 ± 0.010 ^d	1.006 ± 0.010	1.055 ± 0.01
<i>τ</i> (Tilt)	2.6 ± 1.0 3.27 ^a 3.16 ^b 0 ± 3.0 ^d	1.76 ± 1.0	3.74 ± 1.0
∠COD	103.6 ± 1.1 108.54 ^a 103.4 ± 1.2 ^b 89.2 ^c 112.0 ± 3.0 ^d	106.36 ± 1.1	98.46 ± 1.1
Φ (Twist)	36.2 ± 2.3 15.0 ± 3.0, free ^d	35.88 ± 2.3	37.82 ± 2.3
λ ₀ , constant for Debye–Waller terms	0.001613 ± 0.0003	0.002484 ± 0.0003	0.001412 ± 0.0003
χ ² , agreement factor	0.845×10^{-5}	0.385×10^{-5}	0.292×10^{-5}

Notes: ^aRef. [20]; ^bRef. [15]; ^cRef. [4]; ^dRef. [17].

where $r_{\alpha\beta}$ is the mean distance between the atoms α and β and $2\gamma_{\alpha\beta}$ is the mean square variation in the distance $r_{\alpha\beta}$. We have $\gamma_{\alpha\beta} = \frac{1}{2}\lambda_0^2 r_{\alpha\beta}$, where λ_0 is taken to be a constant for all pairs (similar to Prins relation [16]). For Debye–Waller terms, same procedure was followed by several other workers [17,18]. α and β sum independently over six atomic sites within the methanol molecule. $j_0(x) = \sin x/x$ is the zeroth order spherical Bessel function. $H_d(Q)$, often called ‘distinct’ structure function, can be written in terms of partial structure functions, $H_{\alpha\beta}(Q)$ as

$$H_d(Q) = \left(\sum_{\alpha} b_{\alpha} \right)^{-2} \sum_{\alpha} \sum_{\beta} (2 - \delta_{\alpha\beta}) b_{\alpha} b_{\beta} H_{\alpha\beta}(Q) \quad (5)$$

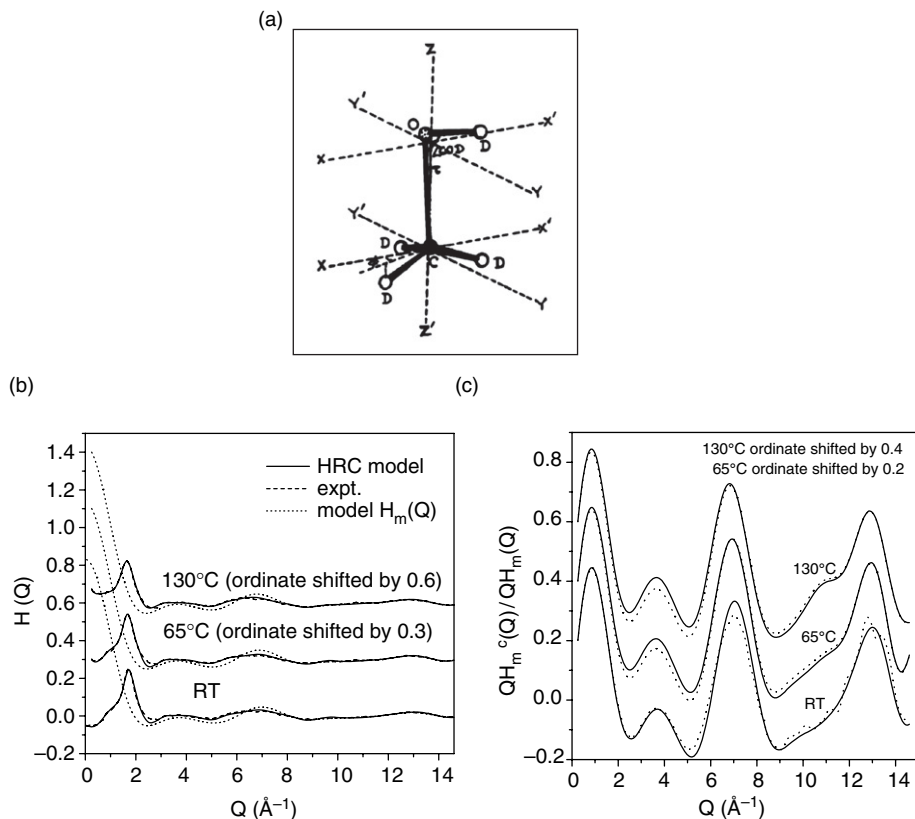


Figure 2. (a) Schematic CD₃OD molecule; (b) total structure function, $H(Q)$ vs. Q at RT, 65°C and 130°C, (c) $QH_m^c(Q)$ and $QH_m^c(Q)$ vs. Q at RT, 65°C and 130°C: $QH_m(Q)$ (...), $QH_m^c(Q)$ (—).

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

$$d(r) = \frac{2}{4\pi} \int_0^{Q_{\max}} QH_d(Q)W(Q) \sin(Qr)dQ \quad (6a)$$

$$G_d(r) = 1 + d(r)/\pi\rho r \quad (6b)$$

where $W(Q)$ is a modification or window function which takes care of the truncation effect of limited Q -range (Q_{\max}) available in the experiment [15] and ρ is the liquid density.

$G_d(r)$ is related to atom-atom pair distribution functions, $g_{\alpha\beta}(r)$ given by

$$G_d(r) = \left(\sum_{\alpha} b_{\alpha} \right)^{-2} \sum_{\alpha} \sum_{\beta} b_{\alpha} b_{\beta} g_{\alpha\beta}(r) \quad (6c)$$

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2\rho r} \int_0^{Q_{\max}} QH_{\alpha\beta}(Q)W(Q) \sin(Qr)dQ \quad (6d)$$

3.1. Molecular conformation

A modified method of analysis for the molecular structure was carried out as in [1] for all three temperatures. In hydrogen-bonded liquids, effects of inter-molecular hydrogen-bonding persist at high- Q [8]. So $H_d(Q)$ continues to show oscillatory behaviour, positive and negative over $H_m(Q)$. $H_d(Q)$, however, tends to vanish gradually and so $H(Q)$ almost equals to $H_m(Q)$ at large Q . This indicates that for Q greater than some Q_{\min} , the value of total structure function comes primarily from intra-molecular part. The molecular structure is characterised by bond lengths r_{CO} , r_{CD} , r_{OD} , hydroxyl angle $\angle\text{COD}$, tilt angle τ (tilt of CO from methyl group symmetrical axis ZZ' , see Figure 2(a)) and the methyl group rotation angle φ while methyl backbone is assumed to have tetrahedral symmetry. The Debye–Waller terms can be obtained in terms of constant λ_0 . The intra-parameters together with Debye–Waller terms determine $H_m(Q)$. Assuming the scheme of the molecule shown in Figure 2(a), we can find the atom–atom distances and calculating $H_m(Q)$ we can fit $QH_m(Q)$ to $QH(Q)$ for $Q > Q_{\min}$ by a χ^2 -fitting method. For this fit, we use an initial set of intra-parameters obtained from X-ray data analysis [8] and electron diffraction analysis of gas phase [18]. Subtracting $H_m(Q)$ from $H(Q)$ we obtain a first estimate of $H_d(Q)$. $G_d(r)$ is obtained from $H_d(Q)$ using Equations (6a) and (6b). The window function, $W(Q) = j_0(Q/Q_{\max})$ [15] was used in the IFT. Further, we choose Q_{\max} such that $G_d(r=0)$ is almost zero and it is assumed that the contribution of the integral in (6a) beyond $Q = Q_{\max}$ is almost zero. Again, $G_d(r)$ is expected to be zero in the range $0 \leq r \leq r_0$ where r_0 is about 1.5 Å, as, in the core region of the molecule, there is little inter-molecular interaction. Setting $G_d(r) = 0$ for this region, Fourier transform (FT) of the resulting $G_d(r)$ would yield a new $QH_d(Q)$. Subtracting this $QH_d(Q)$ from $QH(Q)$ we obtain the corrected $QH_m(Q)$, i.e. $QH_m^c(Q)$. The difference between $QH_m^c(Q)$ and original $QH_m(Q)$ is, however, small. Varying molecular parameters, the subsequent iteration process gives best fit to this corrected function. A χ^2 -fitting is done for the whole range of Q data. This method resembles the method applied by Bertagnolli *et al.* [19]. The fitted curves for all three temperatures are shown in Figure 2(b) and (c). The agreement appears to be very good. The molecular parameters are listed in Table 2. The molecular parameters at elevated temperatures are not available in the literature. The RT molecular parameters are, however, compared with the available data from other workers [4,15,17,20]. It is seen that the intra-molecular structural parameters in liquid phase differ considerably in values obtained by different workers, particularly for the parameters involving atoms participating in the hydrogen bonding. In view of the scatter of the parameter values among different workers the present molecular conformation appears to be quite reasonable. It is also seen that molecular parameters change by not more than 4–5% and this indicates that except some thermal stretching the molecular conformation remains more or less unchanged at elevated temperatures and pressures. This is also more considering the error estimates, which correspond to 10% increase in χ^2 -value. It is to be noted here that the earlier work [4] also showed similar small effect of temperature on the molecular conformation. Since the molecular conformation does not change much at elevated temperatures, the change in the nature of $H(Q)$ data at low and medium Q evidently indicates that the inter-molecular structure changes to some extent at elevated temperatures and pressures (Figure 2(b)).

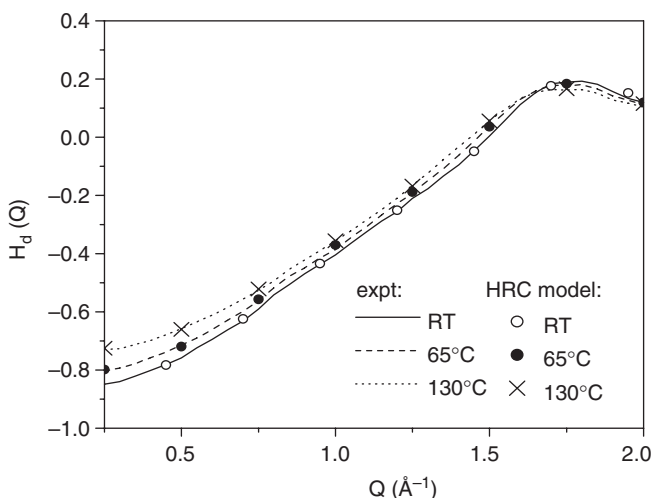


Figure 3. Inter-molecular structure function, $H_d(Q)$ vs. Q .

3.2. Inter-molecular or liquid structure

The inter-molecular structural change is directly represented by $H_d(Q)$. This function is shown in Figure 3 on an extended Q -scale, 0 to 2 \AA^{-1} , the important region representative of liquid structure. The diffraction peak height slowly decreases at higher temperatures with slight shift of the peak to smaller Q . This variation of peak height and position shift is quite in agreement with earlier work on methanol [4]. This shift is however opposite to liquid D_2O where the shift is an indication of H-bond breaking and transition to closed packed non-associative liquid structure [21]. So in methanol the transition, if there be any, must be of different type. Further, for liquid D_2O at high temperature (523 K), unlike that at RT, no oscillations are detectable beyond $Q = 5 \text{ \AA}^{-1}$ and that the main diffraction peak is symmetrical. All these indicate clearly a loss of molecular association in liquid D_2O at 523 K [21]. In liquid methanol however the first $H_d(Q)$ peak is very asymmetric at RT and it is so at BP and 2BP as well. Unlike liquid D_2O at 523 K the oscillations in $H_d(Q)$ continue to large Q for all three temperatures almost in the same fashion. Again, the pre-peak or hump at 0.7 to 0.8 \AA^{-1} , indicative of molecular association or cluster [4,8,9] at RT, remains clearly visible at BP and 2BP as well. All these facts indicate that unlike D_2O , molecular association in liquid methanol prevails in superheated conditions under pressure. At low Q , $H_d(Q)$ goes up at elevated temperatures. This O-Z behaviour is expected with rise in temperature [14]. In Figure 4 we show $G_d(r)$ as a function of r . A comparison of RT result with corresponding X-ray result by Narten and Hebenchuss [8] could identify several inter-molecular atom-atom correlations. The first two peaks appear to occur from inter-molecular OD and OO correlations but occur at little shorter distances than those found in Figure 5b and heights of first peak little bit exaggerated. Both effects might be due to errors in truncation correction. The effect of temperature on $G_d(r)$ is also worth noting. There is an indication of some short of nullifying effects of increasing temperature and pressure on H-bonding in a superheated liquid.

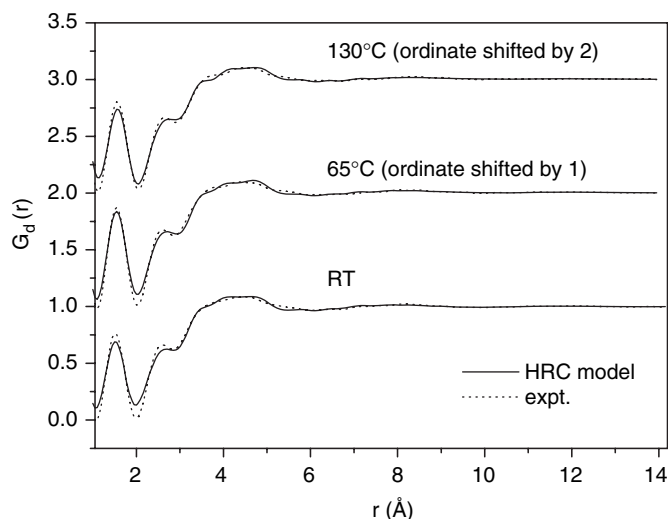


Figure 4. Inter-molecular RDF, $G_d(r)$ vs. r at RT, 65°C and 130°C.

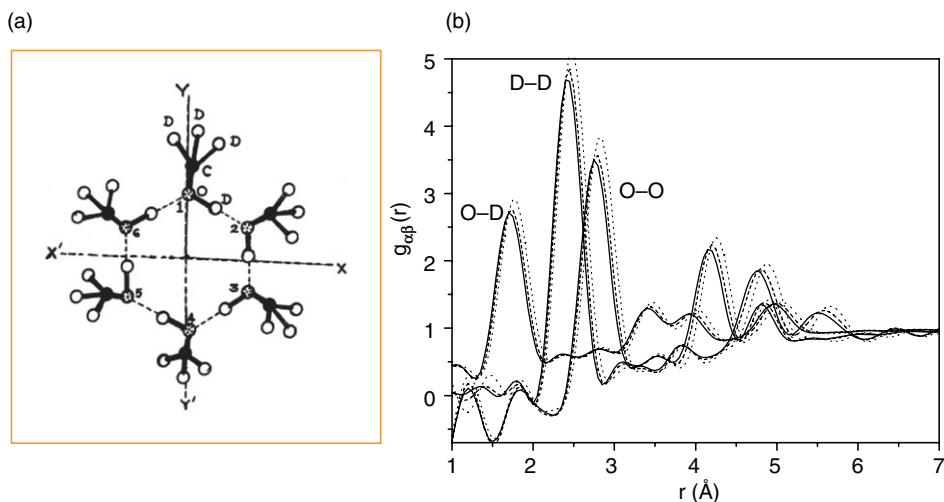


Figure 5. (a) HRC (molecular association) configuration; (b) intermolecular atom-atom RDFs, $g_{OO}(r)$, $g_{OD}(r)$ and $g_{DD}(r)$ vs. r : RT(—), 65°C(---), 130°C(···).

We now present the cluster analysis to extract the nature of the H-bonded chain association or cluster present in liquid state. In our cluster analysis [10,22] we assume that (i) there exist distinct molecular cluster or clusters due to H-bonding, (ii) the molecules in different clusters are orientationally uncorrelated and (iii) for a molecule, such as methanol, we choose the appropriate centre structure factor. In big molecules, such as t-butanol, 1- and 2-propanols the suitable centre structure was one of Percus-Yevik (PY) single site hard-sphere (HS) structure factor with suitable core diameter and damping. In methanol our combined analysis of X-ray

and neutron data [10] yielded a centre structure somewhat similar to that for water [23], which could be approximated by one corresponding to a potential HS plus square-well (SW) ledge. This SW ledge helps to produce the low- Q structure factor very nicely particularly at elevated temperatures i.e. the O-Z behaviour. We also assume that a fraction x of H-bonded clusters are broken as a result of heating. The relevant expression [22] is given by:

$$H_d(Q) = (1 - x)H_c(Q) + F_{2u}(Q)[S_c(Q) - (1 - x)f_3(Q) - 1], \quad (7)$$

where $F_{2u}(Q)$ and $f_3(Q)$ are, respectively, the uncorrelated inter-molecular form factor and the structure factor of molecular centre pairs within the cluster. $H_c(Q)$ is the inter-molecular cluster structure function defined by

$$H_c(Q) = \left(\sum_{\alpha} b_{\alpha} \right)^{-2} N_c^{-1} \sum_{\alpha, \beta} b_{\alpha} b_{\beta} j_0(Qr_{\alpha\beta}) \exp(-l_{\alpha\beta}^2 Q^2 / 2) \quad (8a)$$

with N_c the number of molecules in a cluster, α, β the atoms of different molecules within the cluster, $l_{\alpha\beta}$ the r.m.s. deviation of the local instantaneous inter-molecular atom-atom separation distance $r_{\alpha\beta}$. $S_c(Q)$ is the centre structure factor and the expression for $S_c(Q)$ in random phase approximation (RPA) [24] is given by:

$$S_c(Q) = S_{hs}(Q) / (1 - \rho C_{ld}(Q) S_{hs}(Q) \exp[-\Delta_{ld}^2 Q^2 / 2]), \quad (8b)$$

where $S_{hs}(Q)$ is PY single site HS structure factor, $C_{ld}(Q)$ is FT of the direct correlation function (DCF) corresponding to SW ledge type potential and Δ_{ld} is a parameter representing damping of HS structure factor.

It was earlier shown from this laboratory that the most probable clusters present in liquid state for alcohols at RT are HRCs [10,25]. The linear tetramer open chain, a plausible association in liquid methanol at RT suggested by X-ray data of Magini *et al.* [3] and the tetramer closed chain as in gas phase [7] were ruled out as dominant structural association by a detailed analysis in [10]. Though earlier simulation results did not support such liquid structure, rather supported linear winding chain of 6–8 molecules, a recent study on X-ray emission spectra and density functional theory [26] supports the existence of HRC structure in liquid methanol. The work is based on the fact that the chain and ring structures of methanol molecules have distinguishable electronic structure and the difference can be monitored by resonant soft X-ray emission (SXE) spectroscopy. A recent MC simulation work [27] based on a refined H-bonded potential model, which includes polarisability, non-additivity and intra-molecular relaxation, shows that the presence of hexameric ring clusters in liquid methanol at RT is possible. We have tested here if these hexameric ring clusters, broken by fraction can fit the experimental neutron data at room and elevated temperatures. The conformation of the HRC association model is shown in Figure 5(a). The model is defined by inter-molecular O–O distance, r_{OO} , six rotational angles, φ 's of C's i.e. molecule as a whole about OD axes and six rotational angles, ψ 's of methyl groups about CO axes. The constant for Debye–Waller terms, λ_0 is defined in the same way as for molecular structure case. Using these model variables together with hard sphere plus SW ledge potential parameters we can obtain $H_c(Q)$, $F_{2u}(Q)$, $S_c(Q)$, $f_3(Q)$, etc. and finally obtain $H_d(Q)$. The χ^2 -fitting was

carried out between experimental and HRC model $QH_d(Q)$'s by varying the above mentioned parameters. The best fitted results for $H(Q)$ at three temperatures are shown in Figure 2(b). The model results are also shown in Figures 3 and 4. The HRC and related parameters are listed in Table 3. The value of x is almost zero at all three temperatures. Further, the height of the SW ledge is very small implying that $S_c(Q)$ is very nearly HS like as in our previous studies [25]. It is evident (from the parameters) that the average structure of HRC somewhat changes with increasing temperature.

The cluster model calculations also enable the extraction of inter-molecular atom–atom distribution functions, such as $g_{OO}(r)$, $g_{OD}(r)$ and $g_{DD}(r)$ from experimental data. Since $H_d(Q)$ is expressible in terms of sum of partial structure functions, $H_{\alpha\beta}(Q)$ it is easy to obtain an expression for $H_{\alpha\beta}(Q)$, in terms of partial functions, $H_c^{\alpha\beta}(Q)$, and $F_{2u}^{\alpha\beta}(Q)$ [25]. The expressions of $g_{\alpha\beta}(r)$ are then given by Equation (6d). The results are shown in Figure 5(b). The neutron isotopic substitution method for RT methanol data has been analysed by EPSR simulation method which yields partial distribution functions [28]; the general basic features of the RT data are approximately in agreement with the present results. The ripples that appear in the second peak onwards are similar to those in t-butanol case [25] and may not have much physical meaning. The difference in second peak onwards with EPSR data [28] is also worth noting. This is possible because the basic structural

Table 3. x , fraction of H-bonded clusters broken, HRC (molecular association) model and related potential and other parameters.

		RT	65°C	130°C
Fraction of H-bonded clusters broken	x	~0	~0	~0
Parameters of ledge potential	$\alpha_{hs}(\text{\AA})$	3.366	3.296	3.189
	$\varepsilon/k_B T$	-0.099	-0.116	-0.073
	λ	2.844	2.924	3.00
Damping factor	Δ_{ld}	~0	~0	~0
O–O bond length	$r_{OO}(\text{\AA})$	2.725	2.747	2.784
Rotational angles (deg.) of C's about OD axes	Φ_1	178.40	176.92	181.40
	Φ_2	179.44	176.18	175.90
	Φ_3	202.62	203.34	240.16
	Φ_4	171.46	169.92	173.58
	Φ_5	68.22	79.14	68.00
	Φ_6	-43.82	-25.52	-4.54
Rotational angles (deg.) of methyl group about CO axes	Ψ_1	-20.34	-23.44	-18.12
	Ψ_2	-47.16	-46.10	-47.62
	Ψ_3	15.82	45.84	-6.72
	Ψ_4	23.36	22.74	22.06
	Ψ_5	124.24	96.90	-10.18
	Ψ_6	-101.96	-44.38	-92.66
Constant for Debye–Waller terms	λ_0	0.001951	0.0014385	0.001951
Agreement factor	χ^2	3.33×10^{-5}	2.85×10^{-5}	1.33×10^{-5}

association predicted by two methods are different (in [28] the model is winding linear chain while in our case it is HRC). However, 1.77 ± 0.07 H-bonds per molecule and 5.5 ± 1.0 molecules per chain agree generally with the present results ([2] and [6]).

4. Discussion and general remarks

The present analysis of neutron data of liquid D-methanol at RT and elevated temperatures yields several interesting results. Firstly, the molecular conformation is found to be not highly dependent on temperature except some stretching of the bonds. Secondly, the cluster information, obtained by χ^2 -fitting between Q -weighted experimental and model $H_d(Q)$ function clearly shows that HRC structures are dominantly present not only at RT but also at BP and 2BP. The value of x is almost zero at all three temperatures, which implies that there is little H-bond breaking of the HRC clusters at elevated temperatures. The changes in $H_d(Q)$ with the rise in temperature is entirely due to changes in related HS and SW parameters plus reduction in liquid density. It is true that some changes in the HRC structure occurs at elevated temperatures but the general conformation does not change much. Further, the centre structure factor is nearly HS like (as in other cases of alcohols [25]) except at low- Q values. The low- Q centre structure features resulting from SW ledge potential produces the O-Z behaviour at low Q extremely well. It is to be noted that the low- Q results with HS centre structure are very worse (not shown). Using the compressibility sum rule the values of isothermal compressibility χ_T of liquid methanol based on HS plus SW ledge centre structure appear to be somewhat higher than the observed values (at RT $\chi_T = 1.7 \text{ GPa}^{-1}$ against observed value 1.2 GPa^{-1} and with HS centre structure value is 1.0 GPa^{-1}). This is not unexpected because for H-bonded liquids more appropriate method for χ_T is the thermodynamic perturbation method where H-bonded interaction needs to be considered separately [29]. It is, however, evident that HS plus SW ledge centre structure is quite appropriate.

The extracted $g_{OO}(r)$, $g_{OD}(r)$ and $g_{DD}(r)$ are weakly temperature dependent (Figure 5(b)) which again implies that there is little increase in free H-bonds in the superheated liquid under pressure and the nature of the molecular association or cluster is preserved. In this connection it is relevant to mention that recent diffraction work of Weitkamp *et al.* [13] shows that hydrogen-bonding in liquid methanol is affected little by increase in pressure. Similar is the case with Monte Carlo (MC) simulations [30] though in contrast, molecular dynamics (MD) simulations [31] suggest that hydrogen-bonding increases with rising pressure in glycerol. The NMR spectroscopic works of Wallen *et al.* [2] on liquid methanol suggest that the extent of hydrogen-bonding decreases upon an increase in temperature. Their results for pressure are equivocal, the phenomenological model suggests decrease in hydrogen-bonding upon increasing pressure while MD simulations show an increase in hydrogen-bonding with increasing pressure. The NMR study by Czeslik and Jonas [32] clearly shows a pressure induced strengthening and a temperature induced weakening of hydrogen bonds in clusters of methanol molecules. This apparent cancellation is approximately found to be the case in our results for superheated liquid methanol under pressure.

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