

Temperature effects on the structure of liquid D-methanol through neutron diffraction

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Abstract. The study of changes in the structure (H-bonded) of liquid alcohols at elevated temperatures is rare probably due to low flash points of these liquids. An indigenously devised special quartz cell is now used to carry out the structural studies of these liquids at elevated temperatures through neutron diffraction. Here, the liquid consists of deuterated methanol and neutron data was collected on the high- Q diffractometer at Dhruva, BARC. The corrected data at elevated temperatures (BP (boiling point) and double the BP) show that there is a large change in the H-bonded structure of this liquid. The pre-peak or hump, known to be signature of H-bonded clusters appears to be present at all the three temperatures studied. In the low- Q (scattering vector) data Ornstein–Zernike (OZ) behaviour is also observed. It is, however, seen that the intramolecular structure does not change very much at higher temperatures. A detailed model analysis is in progress and would be reported later.

Keywords. Structure; correlation; D-methanol; neutron diffraction.

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1. Introduction

The present work is a continuation of our series of works on hydrogen-bonded molecular liquids [1]. Though the nature of molecular association in solid and gaseous states is well-established [2] there is still some uncertainty about the exact nature of average molecular association in liquid state in view of differences in simulation, diffraction and other results [1,3]. The formation of a pre-peak or hump at about $Q \sim 0.7\text{--}0.8 \text{ \AA}^{-1}$ before the main diffraction peak of liquid alcohols is now known to be a signature of hydrogen-bonded molecular chain association [1,4]. Of course in neutron data it is detected only recently [1,5]. The distinct molecular association should affect the thermodynamic and transport properties. The change in the molecular association with rise in temperature evaluated from diffraction data is surely an interesting problem. Probably due to low flash points of liquid alcohols no attempt has been made so far to carry out studies on the changes in the molecular association at elevated temperatures. We have however indigenously constructed a special quartz cell which keeps the liquid at elevated temperature

under pressure and used it for the scattering experiment. Since methanol is the simplest member in the alcohol series we have made our first study on liquid D-methanol at room temperature (RT), at BP and at twice the BP. Very interesting information are obtained about the molecular and liquid structure.

2. Experiment

Careful neutron diffraction measurements of fully deuterated liquid methanol sample were carried out on the upgraded high- Q diffractometer at Dhruva, BARC, Mumbai, India. The liquid methanol sample (99.8% deuterated) was available from Aldrich Ltd, USA and was held in an indigenously constructed special quartz cell of 5 mm inner diameter and 7 mm outer diameter properly evacuated in nitrogen atmosphere and sealed. A block diagram is shown in figure 1. Two nozzle heaters are used to vary the temperature and it can be kept constant with a temperature controller within an accuracy of less than 1°C . For the data collection conventional procedure was used. The experimental corrections for container scattering, self-attenuation and multiple scattering were done in the usual manner and the cross-section data was normalized. The incident wavelengths of 0.783 Å and 1.278 Å were used and the data were recorded for an angular range of 3° – 125° . The corrected cross-section data for two wavelengths were suitably clubbed and the data are shown in figure 2 for all three temperatures. It is evident that there is a large change in the structure with clear pre-peaks or humps at scattering vector $Q \sim 0.7$ – 0.8 \AA^{-1} similar to what is seen in X-ray data of liquid methanol [4].

3. Analysis

The corrected scattered data were normalized such that graphical extrapolation to wave vector $Q \rightarrow 0$ yields a correct isothermal compressibility of methanol. The data then separated into ‘self’ and ‘interference’ terms. The inelasticity parameters

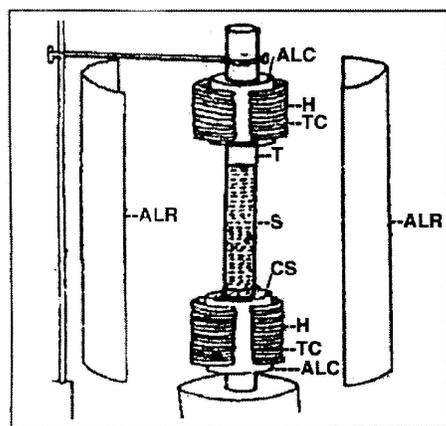


Figure 1. Heating cell, T: quartz tube; S: liquid; CS: Cu ring; H: heater; ALC: Al core; TC: to temperature controller; ALR: Al reflector.

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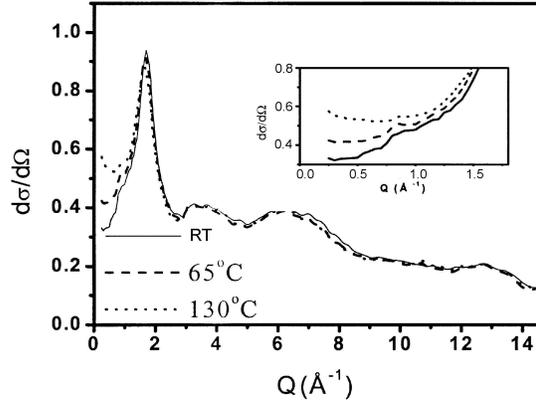


Figure 2. $d\sigma/d\Omega$ at three temperatures. Inset shows the pre-peak region on enlarged scale.

in ‘self’ term were estimated by χ^2 -fitting on high Q data. The parameters (table 1) defined for D-methanol in ref. [6] change slightly at higher temperatures. The ‘interference’ term contains intra and intermolecular contributions and defines the total structure function, $H(Q)$ given by

$$H(Q) = H_m(Q) + H_d(Q). \quad (1)$$

$H_m(Q)$ is defined by molecular conformation while $H_d(Q)$, called ‘distinct’ structure function defines the intermolecular or system structure. The inverse Fourier transform (FT) of $H_d(Q)$ gives r -weighted intermolecular correlation function, $d(r)$ and pair distribution function, $G_d(r)$ given by

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

$$G_d(r) = 1 + d(r)/4\pi\rho r \quad (2b)$$

$G_d(r)$ is related to atom–atom partial pair distribution functions, $g_{\alpha\beta}(r)$, where $\alpha \equiv C, O, D$ and $\beta \equiv C, O, D$ respectively.

Table 1. Inelasticity and intraparameters at RT. Inelasticity parameters: a : $5.556 \times 10^{-3} \text{ \AA}^2$; b : $1.088 \times 10^{-5} \text{ \AA}^4$.

Intraparameters:	
r_{CO} (Å): 1.460 ± 0.006	τ (Tilt angle): $(-2.6 \pm 1.0)^\circ$
r_{CD} (Å): 1.136 ± 0.004	\angle COD (H-bond angle): $(103.6 \pm 1.1)^\circ$
r_{OD} (Å): 1.048 ± 0.01	Φ (Rotational angle): $(36.2 \pm 2.3)^\circ$
Debye–Waller constant	χ^2 : 0.845×10^{-5}
γ_0 : 0.00337 ± 0.0003	

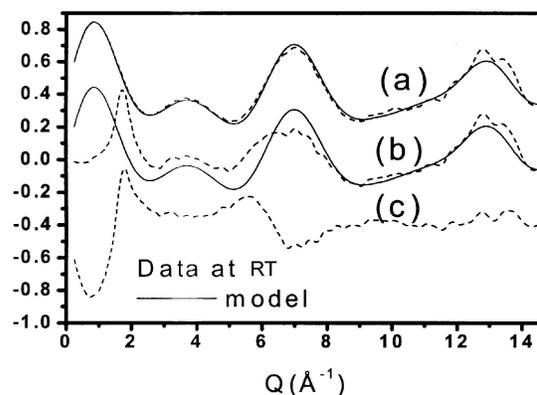


Figure 3. (a) $QH_m(Q)$ (---), $QH_m^c(Q)$ (—) on Y-axis (+0.4); (b) $QH(Q)$ (---), $QH_m(Q)$ (—) on Y-axis; (c) $QH_d(Q)$ (---), $QH_m(Q)$ (—) on Y-axis (−0.4).

Molecular conformation: In H-bonded liquids effect of intermolecular H-bonding persists at high Q [4] and so $H(Q)$ is expected to be generally oscillatory around $H_m(Q)$ and the difference tends to vanish gradually. We adopt here an improved method of analysis for extraction of molecular conformation somewhat similar for big molecules like *t*-butanol and *iso*-propanol [1,7]. In the method first $H(Q)$ and model $H_m(Q)$ are fitted at high Q by χ^2 fitting. $H_d(Q)$ is then extracted and transformed to $G_d(r)$. Now $G_d(r)$ is made zero within $0 < r < r_0$, where r_0 is about 1.3 Å. This restriction generates a correct $H_m^c(Q)$ which is not very different from the original $H_m(Q)$. Varying molecular parameters in an iteration process gives best fit to this corrected function. A χ^2 -fit is used for the whole range of Q -data. The fitted curves for RT are shown in figure 3 and molecular parameters in table 1. The parameters agree well with those obtained by other workers. The errors correspond to 10% increase in χ^2 value. At elevated temperatures, the molecular parameters do not change more than 4–5% which show that the conformation does not change substantially at elevated temperatures and pressures.

Intermolecular or liquid structure: In figure 4a we show $H(Q)$ vs low Q for all the three temperatures and for comparison we plot $H^{\text{sym}}(Q)$ for uncorrelated methanol molecules with hardcore center structure [1]. It is evident that there is a large change in the structure at superheated conditions under pressure. To see it more prominently we also show $H_d(Q)$ vs Q at all temperatures (for Q up to 2.1 Å^{−1}). Three basic features are to be noted. Firstly, the first diffraction peak height is gradually decreasing at higher temperatures with slight shift of the peak to smaller Q . This is opposite to liquid D₂O where it is an indication of H-bond breaking and transition to closed packed structure [8]. In methanol the transition must be of different type. The nature of the dominant form of cluster or molecular association may change. Secondly, the existence of clear pre-peak or hump at all the three temperatures indicates that the molecular association or cluster is present at higher temperatures also. The magnitude of the pre-peak however gradually decreases which might indicate the change in the nature of the dominant form of cluster (e.g. transition from hexamer to tetramer chains). But a detailed model

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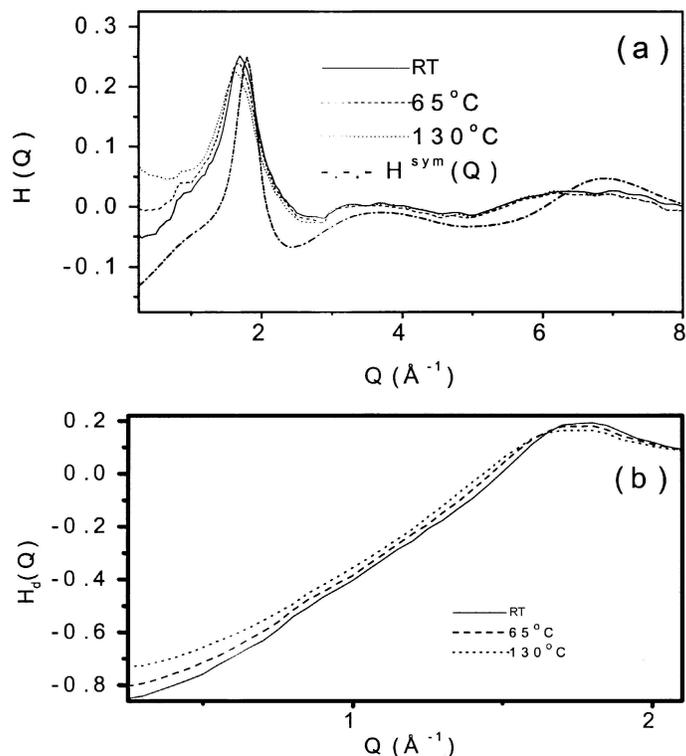


Figure 4. (a) $H(Q)$ vs Q for three temperatures with $H^{\text{sym}}(Q)$ for RT only, (b) $H_d(Q)$ vs Q for three temperatures.

analysis is required to support such a proposition. Thirdly, a clear OZ behaviour is observed at low Q [9]. The critical point of normal methanol is 239°C . With the present set-up, study of critical behaviour of liquid D-methanol is possible. The interpretation in terms of detailed modelling is however absolutely essential.

In figure 5 we show r -weighted correlation function, $d(r)$. A comparison with X-ray data [4] clearly identifies the various intermolecular atom-atom correlations and helps to identify the probable H-bonded cluster or clusters present. The major $d(r)$ peak indicates a possibility of slightly different type of dominant clusters at higher temperatures.

4. General remarks

The neutron scattering data at elevated temperatures (in superheated conditions under pressure) are surely one of its kind. The data show several interesting features. Here, in this report there is ample evidence that the molecular conformation does not change much at elevated temperatures. The intermolecular association or cluster structure definitely changes. There is however little indication of drastic

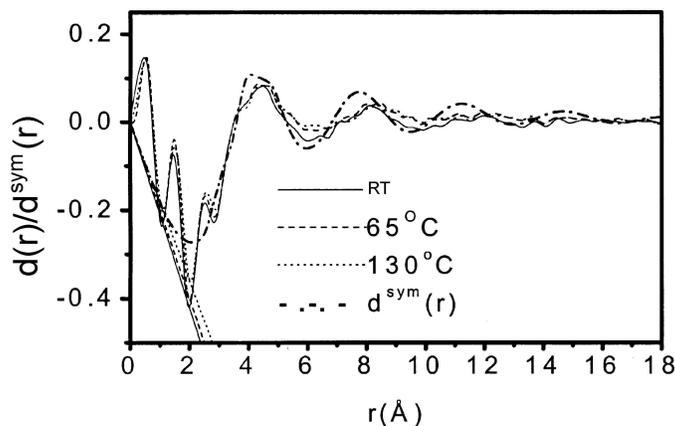


Figure 5. $d(r)$ for three temperatures with density lines and $d^{\text{sym}}(r)$ for RT.

increase in free H-bonds at high temperatures. A thorough model analysis is required to understand this in detail. Work in this direction is in progress and would be reported soon in a detailed paper.

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