5160 *J. Phys. Chem. A* **2009,** *113,* 5160–5162

The Probable Molecular Association in Liquid D-1-Propanol through Neutron Diffraction

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Received: September 26, 2008

The neutron scattering data of liquid D-1-propanol at room temperature has been carefully analyzed to extract the probable molecular association. The molecular conformation (quite elongated) being very different from its isomer 2-propanol (somewhat spherical) would suggest a different type of molecular association in 1-propanol. The probable molecular associations like open chain trimer (as in recent X-ray work) to pentamer (winding) as in earlier X-ray analysis in addition to hexameric ring clusters (as reported in 2-propanol and other alcohols) are compared. It is surprisingly seen that hexameric rings are most probable molecular association in 1-propanol too.

Introduction

The extraction of H-bonded molecular association or cluster information in liquid D-1-propanol is indeed very interesting. This is first because its molecular conformation is quite elongated in shape unlike its isomer 2-propanol which is somewhat spherical.[1,2] Second, the prepeak at scattering vector, $Q \sim 0.7-0.8$ Å^{-1}, so prominent in 2-propanol and other alcohols in both X-ray and neutron diffraction is almost absent (or very weakly present) in 1-propanol neutron data. In X-ray data, however, a small prepeak is present.[3] From the diffraction analysis, the most probable H-bonded molecular association in liquid 2-propanol happens to be hexameric ring clusters (HRCs)[4] as recorded in other alcohols.[5] In liquid 1-propanol, while earlier X-ray diffraction analysis suggested a linear open pentamer chain,[6] a recent X-ray diffraction analysis suggests a probable linear trimer molecular association.[3] In view of these differences in X-ray diffraction analysis results and also neutron diffraction results vis-à-vis its isomer 2-propanol, we think that the question of probable molecular association in liquid 1-propanol at room temperature is still open and, therefore, needs a careful cluster analysis. Thus in this presentation, we consider four model clusters, namely, open linear winding trimer, tetramer, and pentamer chain associations and also a HRC molecular association similar to that in 2-propanol and compare the results with experimental data. We see that agreement with a trimer or tetramer model is so so, but agreement in the case of the HRC is far better. This is a little bit surprising in view of its marked different molecular conformation compared to its isomer 2-propanol.

Source of Data

The room temperature neutron diffraction data were procured from a Hi-Q diffractometer at Dhruva (BARC) in collaboration with our BARC colleagues. The data collected for two wavelengths (0.783 and 1.278 Å) were grouped together, normalized, and latter analyzed[1] to obtain the molecular conformation and total structure function, $H(Q)$, and intermolecular term, $H_d(Q)$ shown in Figures 1 and 2.

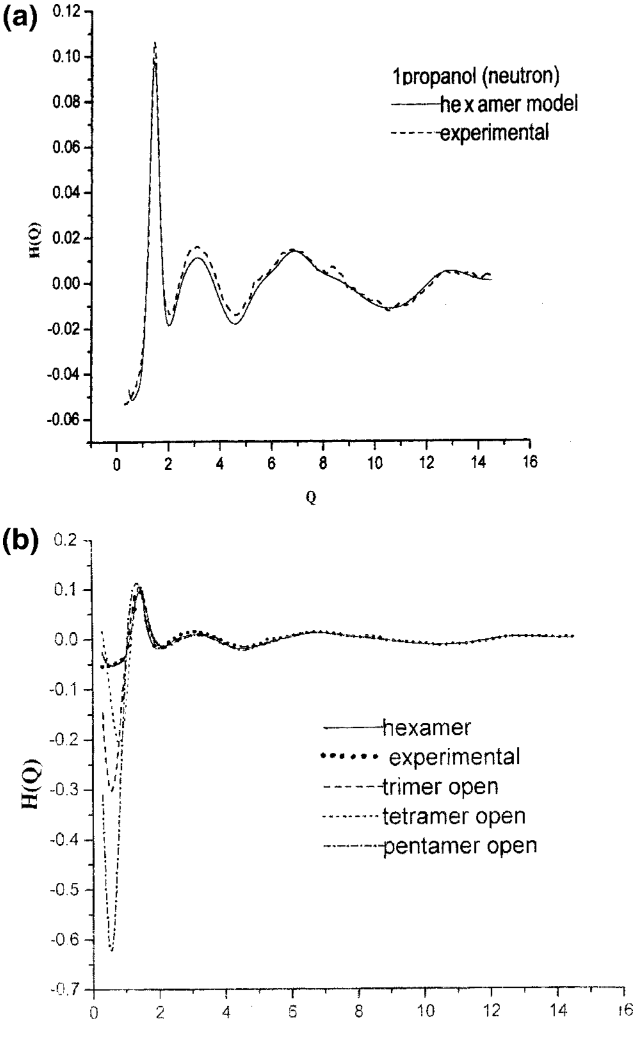

Figure 1. (a) $H(Q)$ vs Q. Experiment and HRC model. (b) $H(Q)$ vs Q. Experiment and HRC, trimer, tetramer, and pentamer models.

Cluster analysis and Results

The details of the analysis of molecular clusters due to H-bonding[4,5] are not discussed here. In the cluster analysis, we

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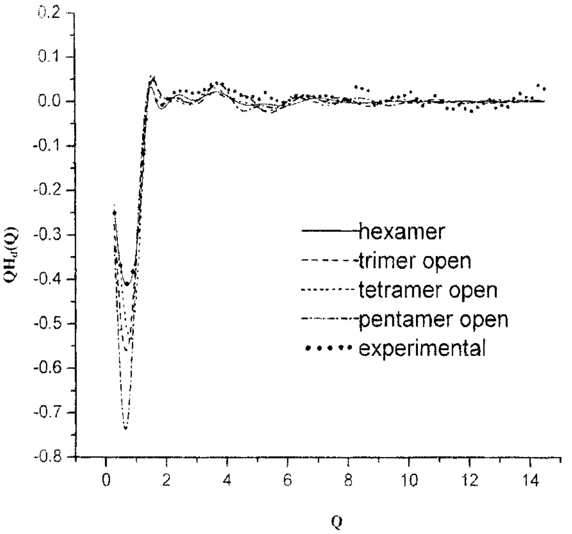

Figure 2. $QH_d(Q)$ vs Q: experiment, HRC, and trimer to pentamer chains.

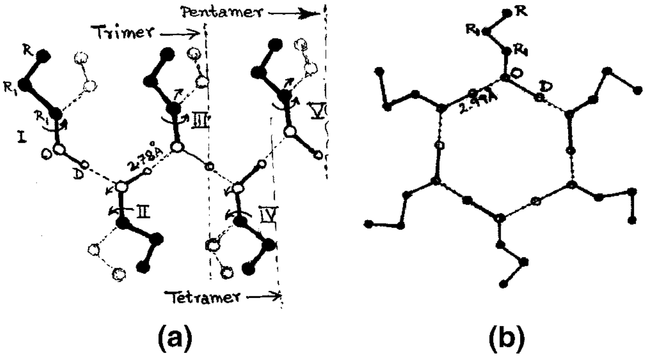

Figure 3. Probable (a) trimer to pentamer. (b) HRC structures.

make plausible assumptions like the following: (i) in liquid there exists distinct molecular association or cluster due to H bonding, (ii) the molecules in different clusters are orientationally uncorrelated, and (iii) for a large molecule like 1-propanol the center−center correlation represented by center structure factor $S_c(Q)$, is obtainable from a PY single site hard sphere model with suitable core diameter and damping. Thus, the expression for model $H_d(Q)$ is given by[5]

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

where $H_c(Q)$ is the intermolecular cluster structure function, $F_{2u}(Q)$ is the uncorrelated intermolecular form factor, and $f_3(Q)$ is the structure factor of molecular center pairs within a cluster.

In line with X-ray diffraction analysis works[3,6] and our experience with other alcohols,[4,5] we test four probable molecular associations, namely, three probable open chain clusters and HRC (Figure 3). The winding of the chains was allowed for chain clusters and winding of the molecules from the plane of hexameric ring is considered. Considering these model clusters, we can obtain the coordinates of all the atomic sites taking $CD_3(\equiv R)$ and $CD_2(\equiv R_1)$ as single scattering sites following a group scattering idea.[5,11] Replacing CD_3 and CD_2 groups by effective single scattering sites with appropriate location and scattering lengths keeps the calculation simple and avoids inclusion of a few more parameters in the model clusters. Further, D’s in CD_3 and CD_2 are symmetrically located relative to the 1-propanol molecular geometry (see Figure 3 of ref. 1) which means that when D’s are treated separately, flexible rotations of D’s about corresponding C−C bonds would not contribute very differently to the intermolecular cluster structure function, $H_c(Q)$, involving several molecules. This is evident because here we are interested in the intermolecular contribution only where, in general, larger distances are involved and almost symmetrically located D’s with C’s in CD_3 and CD_2 would not contribute much differently if CD_3 and CD_2 are replaced by appropriate scattering sites. In the analysis of molecular conformation, however, where smaller distances are involved, we need to consider all D locations separately.[1] So in this cluster analysis, where intermolecular structural contributions are important, for simplicity, we have assumed CD_3 and CD_2 groups as single units with appropriate location and scattering length.[5,11]

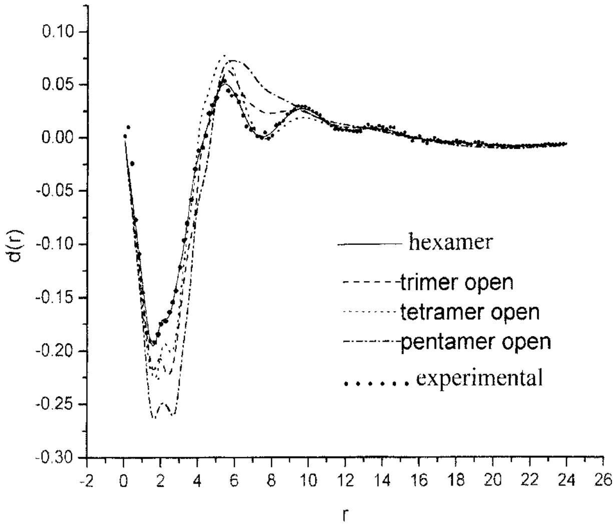

Figure 4. $d(r)$ vs r: experimental, HRC, and trimer to pentamer chains.

Now, varying the parameters like hardsphere diameter, damping factor, intermolecular O−O bond length, and in the case of chain clusters the rotational angles of all R_1R_1R and winding of the chain, i.e., twist of OR_1’s, etc., within a cluster and in the case of HRC, the rotational angles of all R_1R_1R about OD axes and all twist angles of R_1R about R_1R_1 within a cluster, we have fitted Q-weighted model $H_d(Q)$ data with experimental $H_d(Q)$ data by a χ^2-fitting routine. The fitted curves are shown in Figures 1b and 2. The agreement in the case of HRC is indeed very good. For linear winding trimer and tetramer, the agreement is so so. But it is clear that HRC is surely a better model for liquid structure in 1-propanol like 2-propanol and other alcohols.[4,5] The details of HRC model result are shown in Figure 1a. Evidently the agreement is very good.

The intermolecular r-weighted correlation function $d(r)$ obtained from $QH_d(Q)$ by inverse Fourier transform is given by

$$d(r) = (2/\pi) \int_0^\infty QH_d(Q) \sin(Qr) \, dQ \qquad (2)$$

The computed values for all model clusters are shown in Figure 4. It is very clear that HRC is a far superior model than linear chain models for 1-propanol liquid structure.

Discussion

About HRC it is however to be noted that though both X-ray and neutron diffraction analyses[4,5] of liquid alcohols at room temperature suggest such structure, the simulation results[7] so far did not support such clusters, rather they were in favor of linear winding chains of six to eight molecules, though all the simulation results predict about 1.8−1.9 H-bonds per molecule nearly in agreement with 2, which is for hexameric rings. It is true that the molecular orbitals of the six unit ring methanol structure[8] show similarity to those of benzene rings indicating that H-bonding in the methanol ring has a significant amount of covalent contribution. Further, the electronic structure of methanol dimer is as polarized as the other chain structures and it is completely different from rings, and as such the molecular dynamics based on potentials derived from methanol dimmer does not predict ring structures.[8] So it is expected that potentials which take into account the unique covalent contribution to H-bonding need to be used in simulation works for generating ring structures like hexameric rings as observed in the different studies of alcohols. This has been clearly pointed out in studies on X-ray emission spectra and density functional theory analysis.[8] As suggested in ref 8, MC simulation work with refined H-bonding potential, which includes polarizability, nonadditivity, and intramolecular relaxation, has been carried out recently[9] where the authors show that presence of hexameric ring structures in liquid methanol is possible like that of linear chains.

Further, for liquid methanol, the EPSR method[10] based on neutron diffraction data predicts 1.77 ± 0.07 H-bonds per molecule and 5.5 ± 1.0 molecules per chain cluster, and these generally agree with the HRC results (2 and 6). In this connection, we would also like to mention that though in this case we have not tested other closed ring clusters like tetramer, pentamer, etc., we in fact previously tested closed chain tetramer, etc., for liquid methanol, ethanol, and *tert*-butanol and our observations[5,12] clearly show that these are not probable molecular association in these liquids. The closed chain tetramer could be a likely possibility in view of the fact that in methanol, in vapor phase, this is seen to be the most likely structure.[13] The transition from liquid structure assuming mostly HRC to vapor structure assuming mostly cyclic tetramer chains involves an energy change which agrees reasonably well with the heat of vaporization of methanol.[5] An analysis via heat of vaporization and other thermochemical data of various alcohols indicates the possibility of cyclic structures.[14] Anyway, it is evident from the present neutron diffraction analysis that the most probable H-bonded clusters or dominantly present H-bonded molecular association in liquid 1-propanol at room temperature is likely to be hexameric rings.

Acknowledgment. The authors are thankful to Dr. P. S. R. Krishna SSPD, BARC for assistance in procuring neutron data. They are also grateful to UGC-DAE-CSR (BARC) and CSIR (New Delhi) for financial support.

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JP8107717