



Research paper

X-ray study of molecular association in alcohols having bulky substituents



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ABSTRACT

The formation of globular associate on cooling, which was previously claimed on the basis of small dielectric constant, is supported through measuring X-ray scattering from dicyclohexylmethanol (DCHM). Radial distribution function of the DCHM molecules exhibits strong temperature dependence between 65 °C and 130 °C in contrast to a little change in that of tricyclohexylmethanol (TCHM), which is similar to DCHM but essentially non-associating in experimental conditions (95–160 °C).

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1. Introduction

Molecular association in hydrogen-bonding (H-bonding) systems is ubiquitous and has been believed to play crucial roles in determination of physical properties of the systems. Unique and exceptional properties of water are one of best examples [1]. Although its importance has been identified also in colloidal systems dispersed in aqueous solutions recently [2,3], there exists no consensus concerning its mechanism. In this respect, the study of molecular association in liquid through H-bonds still remains at stages to identify good model systems and to develop new strategies to proceed. Previously, the present authors [4] proposed some alcohols with bulky substituents as candidates of such model systems. In proposed systems, molecules form only a limited number of H-bonds by virtue of the enhanced bulkiness of substituents, resulting in the simplification of the system while keeping interesting properties arising from molecular associations. This work is within this context putting the emphasis on developing new experimental strategy.

Dicyclohexylmethanol [DCHM, (C₆H₁₁)₂CHOH] and tricyclohexylmethanol [TCHM, (C₆H₁₁)₃COH] are primary alcohols substituted with bulky cyclohexyl groups. The crystal structure reports say that a tetramer through cyclic H-bonds and a H-bonded dimer are structural units in crystals of DCHM [5] and TCHM [6,7], respectively. Two compounds however exhibit notable difference concerning H-bonds upon melting. While the H-bond inside a

TCHM dimer starts to break below the melting temperature (94.25 °C) keeping the crystalline form [9], H-bonds in the cyclic tetramer in DCHM survive almost completely up to the melting temperature (64.36 °C) [10]. In the liquid state above normal melting temperatures, the H-bond is broken almost completely in TCHM [8,9] whereas a significant portion of molecules remains involved in H-bond in DCHM [10]. In a previous study [10], the present authors found a pronounced hump in heat capacity and dielectric permittivity of the liquid DCHM. The detailed analyses based on a simple statistical model of these and the temperature dependence of the Fourier transform infrared (FT-IR) spectrum indicated that the humps are due to the reconstruction of the closed tetramers on cooling. Although the model coherently explains all the experimental results, the change in the liquid structure upon temperature variation has not been observed directly. In a previous paper on 1-phenyl-1-cyclohexanol [4], which exhibits similar temperature dependences of heat capacity, dielectric constant and IR spectra to DCHM, ¹H NMR successfully distinguished protons in differently H-bonded states, which supports the presence of plural association state in H-bonds. Unfortunately, however, a similar attempt on DCHM was not successful due to the absence of noticeable structure in the corresponding signal.

The observation of a structure is most directly performed by utilizing some scattering experiments. The intensity of scattered X-ray with the scattering vector \mathbf{q} is given by

$$I(\mathbf{q}) \propto \frac{1}{V} \left| \int_V d\mathbf{R} \rho(\mathbf{R}) \exp(-i\mathbf{q} \cdot \mathbf{R}) \right|^2,$$

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where ρ is the number density of electron. If the liquid consists of only one atomic species, the $I(\mathbf{q})$ can be decomposed into the product of the squared atomic form factor $f(q)$ and the so-called structure factor $S(\mathbf{q})$ as

$$I(q) = f(q)^2 S(q). \quad (1)$$

This structure factor is related to the radial distribution function $g(r) = \rho(r)/\rho_{\text{ave}}$ by [11]

$$g(r) - 1 = \frac{2}{\pi} \int_0^\infty q \sin(qr) [S(q) - 1] dq. \quad (2)$$

It is often the case that the same analysis is performed for systems consisting of plural atomic species putting $f(q) = \sum f_i(q)$ (summation runs over atoms). This procedure may be rationalized by rather similar q -dependences of $f(q)$ except its magnitude (proportional to the atomic number at $q = 0$). However, analyses in this way result in the pursuit of the liquid structure in some atomic length scale. Although this is tractable and useful in simple molecular liquids [12], the experiments up to a high q range is unavoidably necessary because of the length scale l sensed by the X-ray is related to q by $l = 2\pi/q$. Besides, the information concerning the molecular arrangement becomes harder to deduce from the experimental results (intensity of the scattered X-ray) with increasing the complexity of the system. In this work, therefore, a way of the “coarse graining” is attempted. The way taken here is to adopt Eq. (1) assuming a molecule being a scattering particle with a spherically averaged molecular form factor. This is equivalent to assume the independence of orientations of neighboring molecules.

2. Materials and methods

Commercial DCHM (Aldrich) and TCHM (Tokyo Chemical Industry) were purified by fractional sublimation in vacuum. Similar procedure had yielded the purities better than 99.5 mol% in the previous calorimetric study [9]. Purified specimen was sealed in a polyimide tube (1.6 mm in diameter with 0.06 mm thick wall) with epoxy resin. X-ray measurements were performed at BL6A beamline, Photon Factory, KEK, Japan, using PILATUS3 1M and PILATUS 100K detectors (Dectris Ltd.) for small (SAXS) and wide (WAXD) scattering angles, respectively. The wavelength of the X-ray was 1.5 Å. The sample-to-detector distance (ca. 100 cm in SAXS and 230 mm WAXD) and the tilt angles of the detectors were calibrated using a standard sample (silver behenate). The temperature of the sample was continuously decreased at 1°C min^{-1} by a FP82HT temperature controller (Mettler Toledo). The exposure time of each data was 10 s, during which the temperature changed ca. 1.7°C . Intensity of scattered X-ray was corrected for the background (from the polyimide tube, etc.) and the polarization factor. Since there exists a small gap between the ranges of scattering wave vector q covered by SAXS ($0.08 \text{ \AA}^{-1} < q < 0.66 \text{ \AA}^{-1}$) and WAXD ($0.68 \text{ \AA}^{-1} < q < 1.65 \text{ \AA}^{-1}$), the scales of the data sets were adjusted to connect smoothly prior to analyses of liquid structure. Experimental intensities after these corrections are shown in Fig. 1. Both compounds exhibit the symptoms of two peaks in the scattering intensities around $q = 0.7 \text{ \AA}^{-1}$ and $q = 1.1 \text{ \AA}^{-1}$ with reversed amplitude.

The averaged molecular form factors were calculated as a spherical average of the molecular form factor around the molecular center of the electron distribution. The Cartesian coordinates of a monomer and tetramer of DCHM were taken from the supplementary information of the literature [10], which reported those based on quantum chemical calculation. For a TCHM molecule, those used for the calorimetric study [7] were adopted. Atomic form factors were from another literature [13]. Calculated $|f_{\text{av}}(q)|$

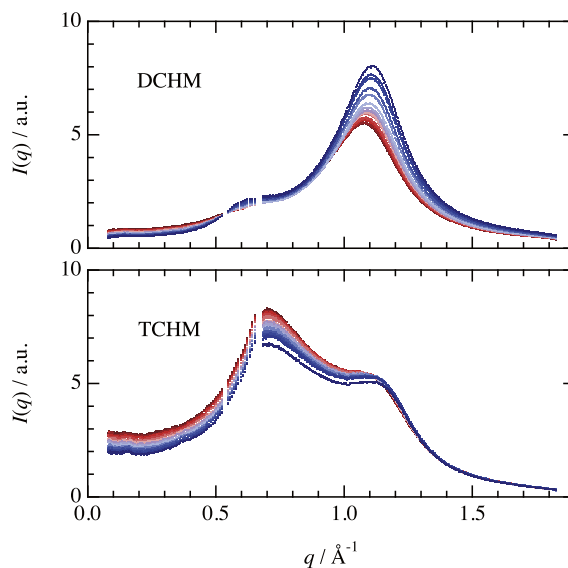


Fig. 1. Experimental scattering intensities after some corrections for DCHM (65–130 °C) and TCHM (95–160 °C). Red to blue color corresponds to high to low temperature at ca. 2°C interval. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

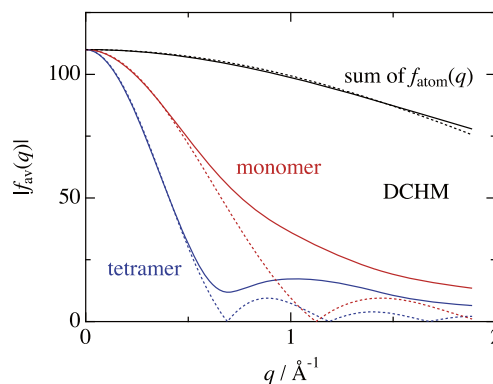


Fig. 2. Spherically averaged molecular form factors of a monomer (red solid curve), tetramer (blue solid curve) and the sum of atomic form factors for DCHM. Dotted curves are form factors of rigid spheres with the radius of 1.0 Å, 4.0 Å and 6.5 Å for comparison with atoms, monomer and tetramer, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

for DCHM are shown in Fig. 2 together with the sum of atomic form factors. Both of calculated $|f_{\text{av}}(q)|$ for monomer and tetramer are quite different from the simple sum. However, form factors of spheres having uniform electron density approximate well the calculated ones if appropriate radii are assumed below $q < 0.5 \text{ \AA}^{-1}$. A comparison of $|f_{\text{av}}(q)|$ calculated for monomer and tetramer indicates that $|f_{\text{av}}(q)|$ does not always resemble that of a rigid sphere though the spherical averaging was certainly performed in the calculation over molecular orientation. The averaged molecular form factor of a TCHM monomer is a monotonic function of q , similarly to that of a DCHM monomer.

3. Results and discussion

The determination of the absolute scale of $S(q)$ is a difficult task in reality. Since the intramolecular part is already taken into the averaged molecular form factor $|f_{\text{av}}(q)|$, the scale was determined assuming $S(q) = 1$ at $q = 1.75 \text{ \AA}^{-1}$ at the highest temperature of a

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