Experimental determination of electron distribution in liquid cyclohexane

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Electron distribution of molecules in the liquid state is certainly affected by strong intermolecular interaction received from neighboring ions and molecules. Although it is difficult to obtain direct information on electron distribution in isotropic liquid structure, combined analysis of X-ray and neutron diffraction data enables us to determine the deviation from the spherical electron density around atoms within the molecule. The X-ray-neutron difference interference term, $\Delta_{XN}(Q)$, can be derived from the difference between intermolecular X-ray interference term, $i_X^{inter}(Q)$, and the sum of intermolecular partial structure factors, $a_{ij}^{inter}(Q)$-1 (determined from neutron diffraction with isotopic substitution method), weighted by "X-ray atomic scattering factors", $i_N^{inter}(Q)$. The Fourier transform of the difference function, $\Delta_{XN}(Q)$, yields the difference distribution function, $\Delta_{XN}(r)$, representing the deviation from the spherical electron distribution of the molecule in the liquid state [1, 2].

In the present study, neutron and X-ray diffraction measurements on liquid cyclohexane have been carried out to obtain direct information on electron distribution of cyclohexane molecule in the liquid state. Neutron diffraction measurements on H/D isotopically substituted three cyclohexane samples, C_6D_{12} (99.6% D, $b_H = b_D$), $C_6^0H_{12}$ (35.8% D, $b_H = 0$) and $C_6^0H_{12}$ (67.5% D, $b_H = b_D/2$) sealed in cylindrical thin-walled vanadium cells have been executed by using the ISSP-4G (GPTAS) diffractometer installed at JRR-3 research reactor. Incident neutron wavelength of $\lambda = 1.082(6)$ Å was employed. Scattering intensities were detected in the scattering angular range of $3 \leq 2\theta \leq 120°$. Intermolecular partial structure factors, $a_{CC}^{inter}(Q)$-1, $a_{CH}^{inter}(Q)$-1 and $a_{HH}^{inter}(Q)$-1, have been derived from the linear combination of neutron intermolecular interference terms

observed for H/D isotopically substituted samples. The intermolecular interference term, $i_N^{inter}(Q)$, was evaluated by the following equation.

$$i_N^{inter}(Q) = \Sigma(2-\delta_{ij})c_ic_jf_i(Q)f_j(Q)[a_{ij}^{inter}(Q)-1]$$
$$\times (\Sigma c_if_i(Q))^{-2} \qquad (1)$$

where, δ_{ij} denotes Kronecker delta function. c_i and $f_i(Q)$ stand for number of atom i in the stoichiometric unit and atomic scattering factor, respectively. Fig. 1 indicates $i_X^{inter}(Q)$, $i_N^{inter}(Q)$ and $\Delta_{XN}(Q)$ terms. Interference feature appearing in the observed $\Delta_{XN}(Q)$ obviously indicates that the deviation of electron distribution from the spherical symmetry around the atomic nuclei actually occurs in the liquid cyclohexane. The difference distribution function, $\Delta_{XN}(r)$, clearly indicates a negative area at $r = 3 \sim 4$ Å, implying that the electron distribution of cyclohexane molecules should be affected by intermolecular interaction received from the neighboring molecules. More detailed structural analyses involving intermolecular configuration among the nearest neighbor molecules are in progress.

[1] Y. Kameda *et al.*, Bull. Chem. Soc. Jpn. **91**, 1586 (2018).
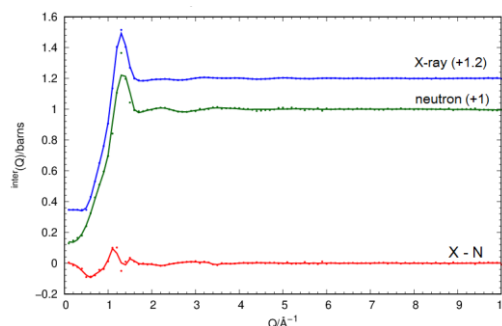[2] Y. Kameda *et al.*, Bull. Chem. Soc. Jpn. **95**, 1680 (2022).

Fig. 1. X-ray and neutron intermolecular interference terms, $i_X^{inter}(Q)$ (blue) and $i_N^{inter}(Q)$ (green) observed for liquid cyclohexane. Difference function, $\Delta_{XN}(Q)$, is shown below (red).