

Roles of mesoscale dynamics in shear viscosity of high alcohol revealed by γ -ray quasielastic scattering

High alcohols, in which a hydrophilic OH group is attached to an end of a hydrophobic long alkyl chain, are among the simplest amphiphilic molecules. The molecular structure of the high alcohol 3,7-dimethyl-1-octanol (dmOcOH) investigated in this work is drawn in the inset of Fig. 1. In the neat liquid state, the OH groups aggregate through strong intermolecular hydrogen bonding, and the alkyl chains expelled from the hydrogen-bonding network also cluster together. The liquid structure of this high alcohol thus consists of two domains, namely, the polar OH and nonpolar alkyl domains. The domain structure of this high alcohol resembles those of surfactant systems, which are the origin of their large structural viscosity. The shear viscosity of liquids in general has practical applications in chemical engineering, mechanical engineering, and other fields, but its molecular origin is yet to be resolved. It is thus interesting to know how the domain structure of high alcohols is related to their shear viscosity.

The domain structure of high alcohols appears as a low- q peak in the X-ray structure factor. Figure 1 shows the X-ray diffraction pattern of dmOcOH. A strong peak at 13 nm^{-1} , which is hereafter called “main peak,” is common to various liquids in general. In addition, a small peak is observed at 4.5 nm^{-1} , which is hereafter called the “prepeak.” The prepeak originates from the scattering contrast between the polar and nonpolar domains, and it represents the domain structure of the high alcohol.

The shear viscosity of a liquid is a dynamic property reflecting the microscopic structural relaxation. The time scale of the microscopic relaxation responsible for shear viscosity can be evaluated from the frequency-dependent complex shear viscosity, called “viscoelastic relaxation.” On the other hand, the structural relaxation at a given wavenumber is determined through the measurement of the intermediate scattering function at the given wavenumber. From the comparison between the viscoelastic relaxation and the intermediate scattering function, we can infer the length scale of the microscopic structure that governs the shear viscosity. Based on this scheme, a molecular dynamics (MD) simulation study performed by one of us (TY) suggested the significant contribution of domain dynamics to the shear viscosity of high alcohols [1]. In this work, we determine the relaxation times of the intermediate scattering functions of liquid dmOcOH at both the prepeak and the main peak using γ -ray quasielastic scattering spectroscopy, and

compare them with the viscoelastic relaxation times to examine the mechanism suggested by the previous MD study [2].

The γ -ray quasielastic scattering measurement was performed at SPring-8 BL09XU. The Mössbauer γ -ray emitted from the ^{57}Fe nucleus excited by synchrotron radiation was utilized. The energy of the Mössbauer γ -ray of ^{57}Fe is 14.4 keV, whose wavelength, 0.084 nm, is suitable for the structural analysis of molecular systems. Owing to the narrow band width of the Mössbauer γ -ray, 4.7 neV, we can measure the intermediate scattering function in the corresponding time scale of around 100 ns.

A schematic picture of the experimental equipment is drawn in Fig. 2. Thin foils of α - ^{57}Fe are inserted on both the upstream and downstream sides of the sample. The incident beam of the synchrotron radiation, on passing through the ^{57}Fe foil on the upstream side, generates a monochromatic Mössbauer γ -ray, which is then scattered quasielastically by the sample and enters the detector. At the same time, the direct incident beam is scattered by the sample, which also gives a Mössbauer γ -ray on passing through the ^{57}Fe foil on the downstream side. The former γ -ray is broadened by the sample, whereas the latter is not. When the energies of the γ -rays from the upstream and downstream foils are sufficiently different, the interference between these two γ -rays is detected as a beating pattern in the time domain, and the line broadening is used to determine the temporal decay of the beat signal.

Some experimental ingenuity is introduced to improve the measurement efficiency. For instance, magnetic fields of different directions are applied to the ^{57}Fe foils on each side to selectively allow different nuclear excitations between the nuclear energy levels

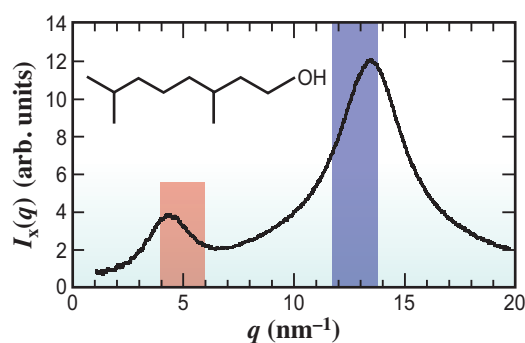


Fig. 1. X-ray structure factor of 3,7-dimethyl-1-octanol, whose molecular structure is indicated in the inset. The q -ranges of the quasielastic scattering measurements are indicated with red (prepeak) and blue (main peak) zones.

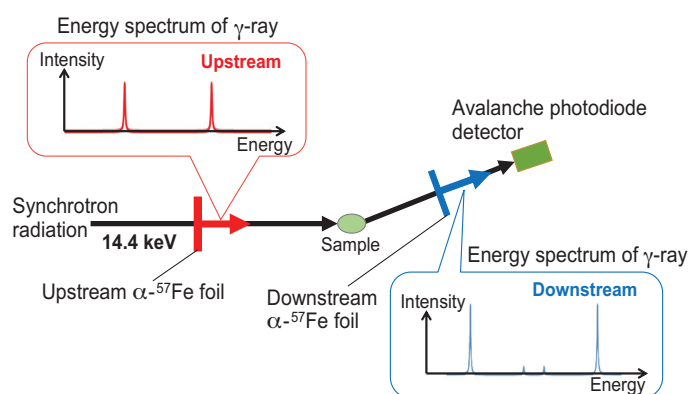


Fig. 2. Schematic picture of γ -ray quasielastic scattering measurement using time domain interferometry.

with the hyperfine splitting. Details of the experiment are given in the literature [3].

The frequency-dependent complex shear viscosity was determined by shear impedance spectroscopy at four different temperatures. In Fig. 3(a), the complex shear viscosity normalized to its zero-frequency limit, η_0 , is plotted against the reduced frequency, $2\pi\nu\eta_0$. The spectra at different temperatures appear to fall on a master curve, indicating that the relaxation frequency is inversely proportional to η_0 . In addition, the spectrum appears to consist of two relaxation modes. The curves in Fig. 3(a) show the fitting using the sum of the Cole-Davidson and the Debye functions, which reproduces the experimental spectra fairly well. From the reduced relaxation frequencies

and the temperature dependence of η_0 , the relaxation times of both modes are determined as the functions of temperature, which are plotted in Fig. 3(b) as the open symbols.

The time-domain interference signal of the γ -ray is analyzed assuming the KWW functional form of the intermediate scattering function, $I(q,t)$, as

$$I(q,t) \propto \exp\left(-\left(\frac{t}{\tau(q)}\right)^{\beta(q)}\right),$$

and the parameters $\beta(q)$ and $\tau(q)$ are determined for both peaks as the functions of temperature. Since the viscoelastic relaxation is related to $I^2(q,t)$ according to the mode-coupling theory, the mean relaxation times of $I^2(q,t)$ are calculated and compared with the viscoelastic relaxation times in Fig. 3(b).

Figure 3(b) demonstrates that the mean relaxation times of $I^2(q,t)$ at the prepeak and the main peak agree well with those of the slow and fast modes of the viscoelastic relaxation, respectively. This suggests that the mesoscale dynamics of the domain structure contributes to the shear viscosity of high alcohols through the slower mode of the viscoelastic relaxation, while the contribution of the short-range dynamics is also present as the faster mode.

Our present study experimentally demonstrated the role of the mesoscopic structure of high alcohols in their macroscopic rheological property for the first time, and we hope that it will be a first step toward controlling the macroscopic shear viscosity by microscopic molecular design.

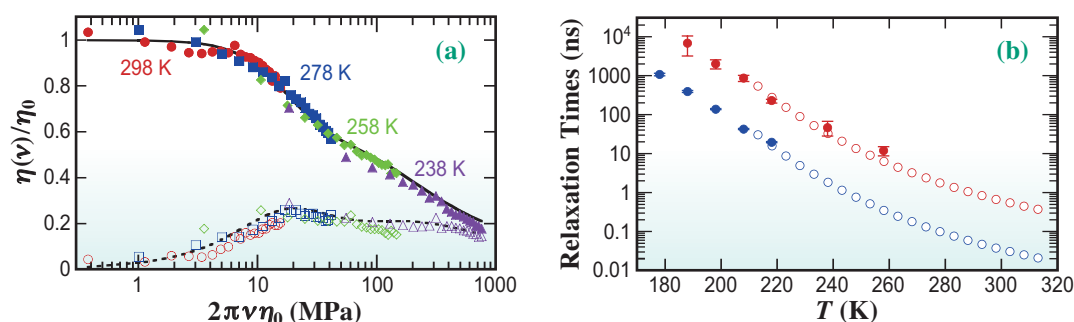


Fig. 3. (a) Frequency dependence of viscosity at four different temperatures. The real and imaginary parts are plotted with the filled and open symbols, respectively. Both axes are reduced to the steady-state shear viscosity, η_0 . (b) The relaxation times of the slower (red) and faster (blue) modes of viscoelastic relaxation, plotted with the open symbols, are compared with those of the squared intermediate scattering functions (filled symbols) at the prepeak (red) and the main peak (blue).

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References

- [1] T. Yamaguchi: J. Chem. Phys. **146** (2017) 094511.
- [2] T. Yamaguchi, M. Saito, K. Yoshida, T. Yamaguchi, Y. Yoda and M. Seto: J. Phys. Chem. Lett. **9** (2018) 298.
- [3] M. Saito et al.: Sci. Rep. **7** (2017) 12558.