

Structural Analysis of Hybrid Wormlike Micelle

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Wormlike micelles are self-assembled intermolecular aggregates with a large aspect ratio. Typical examples of wormlike micellar systems are aqueous solutions of a cationic surfactant, for example, cetyltrimethylammoniumbromide (CTAB), and organic salts, for example, sodium salicylate (NaSal) or sodium p-toluenesulfonate (NapTS). CTAB itself prefers to form spherical micelles in aqueous solution. However, by adding cosurfactants, such as short chain alcohols, organic salts, or oppositely charged surfactants, the spherical micelles transform to rodlike or wormlike micelles. In this study, we carried out simultaneous measurements of rheology and SANS, that is, Rheo-SANS, on aqueous CTAB and NapTS solutions and constructed a flow behavior diagram as a function of the surfactant (detergent) concentration, CD, and a ratio of the additive (salt) concentration, CS, to CD.

Cetyltrimethylammoniumbromide (CTAB) and sodium p-toluenesulfonate acid (NapTS) were purchased from Wako Pure Chemical Industries, Japan. D2O with 99.9% in purity (CAS 7789-20-0) from Cambridge Isotope Laboratories, Inc. was used as a solvent. Small-angle neutron scattering (SANS) measurements were carried out on the small-angle neutron scattering instrument SANS-U managed by Institute for Solid State Physics, The University of Tokyo, placed in the research reactor, JRR-3, Japan Atomic Energy Agency. The wavelength of the incident beam (λ) was $7 \pm 0.7 \text{ \AA}$, and the sample-to-detector distances (SDDs) were 1, 4, and 8 m. The absolute scattering intensity, $I(q)$, was obtained in the range of $0.005 < q < 0.3 \text{ \AA}^{-1}$.

Figure 1 shows a series of Rheo-SANS pat-

terns for aqueous CTAB/NapTS solution at $CD = 5 \text{ mM}$ and $CS/CD = 0.7$ under flow at several shear rates together with the flow curve (η_{flat} vs d/dt) of the solution. The filled symbols (red) indicate the shear rates at which SANS experiments were carried out. In a low shear rate region up to $d/dt = 50 \text{ s}^{-1}$ (i.e., 10, 20, and 50 s^{-1}), the SANS patterns were isotropic both in radial (r) and tangential (t) configurations. On the other hand, at $d/dt = 100 \text{ s}^{-1}$, a strong anisotropic pattern appeared in the radial configuration with structural orientation along the flow direction. By increasing shear rates, the scattering intensity in the vorticity direction increased, while that in the flow direction decreased. This indicates that the length of formed rodlike micelles became longer and/or the orientation of the micelles became higher.

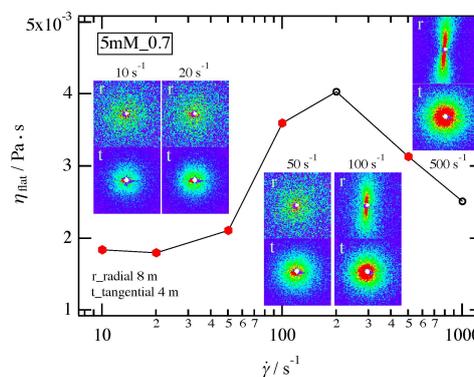


Fig. 1. Fig. 1 Two-dimensional SANS patterns for aqueous CTAB/NapTS solutions at $CD = 5 \text{ mM}$ and $CS/CD = 0.7$ together with flow curves: η_{flat} versus d/dt . Here, r indicates radial configuration (SDD=8 m), and t is tangential (SDD=4 m).