

Lamellar/Onion Intermediate Structure Formed in Low Shear Rate Region in a Nonionic Surfactant (C₁₄E₅)/Water System

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1 Introduction

The lamellar-to-onion transition induced by shear flow has been found more than 20 years ago by the French group [1]. Although the onion formation has been reported for many systems, conditions and mechanism for the transition have been still unclear. A few years ago, we have reported for the first time the re-entrant lamellar/onion (lamellar-onion-lamellar) transition with varying temperature under a constant shear rate in a nonionic surfactant C₁₄E₅/water system (C_nE_m is an abbreviation of C_nH_{2n+1}(OC₂H₄)_mOH) by using simultaneous measurements of shear stress/small-angle X-ray scattering (rheo-SAXS) [2]. We have investigated the change in the lamellar orientation in the lamellar-to-onion and onion-to-lamellar transition processes near the upper and lower transition. The results suggest the existence of intermediate structures depending on the temperature alone at a constant shear rate. In the present study, we have performed rheo-SAXS experiments as a function of the shear rate at a constant temperature paying attention to the intermediate region between lamellar and onion phases.

2 Experiment

Rheo-SAXS measurements have been performed on the beamline 15A2 and 10C by using a rheometer AR550 (TA Instruments). Details of the shear cell have been reported previously [3,4]. The scattered beam was recorded with the camera length of 2.6 m using the PILATUS3 2M. The approximate q range is from 0.1 to 2.4 nm⁻¹. The exposure time was 10 s.

3 Results and Discussion

Figure 1 shows shear-rate dependences of the 2-D SAXS patterns (a, b), the viscosity (c), and the diffraction peak intensities for the three principal directions (d) for the C₁₄E₅/water system (50 wt%, 55°C). The peak intensity has been obtained by averaging over the azimuthal angle $\pm 10^\circ$. In the lower shear rate range below 0.1 s⁻¹, the most lamellae are oriented to the velocity gradient direction. We have observed the shear-thickening in the two regions, i.e., 0.1 - 0.2 s⁻¹ (referred to as the region I) and 1-3 s⁻¹ (the region II). In the region I, the peak intensity for the neutral direction rapidly increases with increasing shear rate. The intensity for the flow direction increases above 0.3 s⁻¹, but still much lower than for these two directions. In the region II, the intensities for these three directions coincide, corresponding to the onion formation.

The enhancement of the orientation to the neutral direction before formation of onions has also been reported by Richtering and coworkers [5,6] in C₁₀E₃/water system by using small-angle neutron scattering. First [5] they have attributed it to the formation of multi-lamellar cylinders as intermediate structures between lamellae and onions and later [6] to either multi-lamellar cylinders or a coherent stripe buckling proposed by Zilman and Granek [7]. The important results in the present study are the existence of two shear thickening regions I and II, and small difference in the diffraction intensity in the shear-thinning region between I and II. These results suggest that the multi-lamellar cylinders are more plausible not as transient structure but as steady state determined by the shear rate.

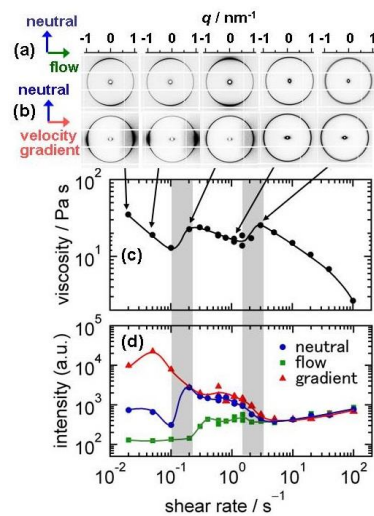


Fig. 1: shear-rate dependences of the 2-D SAXS patterns in the radial (a) and tangential (b) configurations, the viscosity (c), and the diffraction peak intensities for the three principal directions (d) for the C₁₄E₅/water system (50 wt%, 55°C).

References

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