BL-15A2/2017G567

Structures of Intermediate Region between Lamellar and Onion Phases in a Nonionic Surfactant ($C_{14}E_5$)/Water System

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1 Introduction

The shear-induced lamellar-to-onion transition in surfactant systems has been found about 25 years ago [1]. Although the onion formation has been reported for many systems, necessary conditions and mechanism for the transition have been still unclear. It has been known that both the lamellar and onion phases show the shear-thinning behaviors whereas shear-thickening behaviors are observed when the lamellar phase is transformed to the onion phase. Recently, we have performed simultaneous measurements of rheology/small-angle X-ray scattering (rheo-SAXS) as a function of shear rate at 55°C [2] for the lamellar phase of $C_{14}E_5$/water system (C_nE_m is an abbreviation of $C_nH_{2n+1}(OC_2H_4)_mOH$)) which exhibits re-entrant lamellar/onion transition with varying temperature [3]. We have found two shear-thickening regions (referred to as the regions I and II) and one shear-thinning region between I and II. In this shear-thinning region, it has been shown that the diffraction intensities for the neutral and gradient directions are relatively close and much larger than that of the flow direction. These results suggest existence of the rodlike vesicles in the region between lamellar and onion phases.

In the present study, we have performed rheo-SAXS experiments by using a new apparatus which can be used both for rheo-SAXS and rheo-SALS (simultaneous measurements of rheology and small-angle light scattering). The SAXS results are analyzed assuming existence of the rodlike vesicles.

2 Experiment

Rheo-SAXS measurements have been performed on the beamline 15A2 by using a rheometer ONRH-1 (Ohna Tech lnc.) with a double cylinder cell made of polycarbonate. The scattered beam was recorded with the camera length of 2.6 m using the PILATUS 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 Azimuthal plots of the diffraction intensity in the radial (a) and tangential (b) configurations at different shear rates and shear rate dependence of the viscosity (c) for the $C_{14}E_5$/water system (50 wt%, 55°C). In the lower shear rate range bellow 0.1 s^{-1}, the most lamellae are oriented to the velocity gradient direction. In the shear-thinning region between I and II, the peak intensity for the neutral and gradient directions are relatively close and much larger than that of the flow direction, suggesting existence of rodlike vesicles. These results are in good agreement with our previous results obtained by using a rheometer AR550 (TA Instruments). We have obtained the axial ratio of the rodlike vesicles defined as $f \equiv (L + D)/L$ where L and D are the length and diameter of the cylindrical part, respectively, from the integrated intensity of the peak for the neutral direction and the base line assuming that the azimuthal plots are composed of two Lorenz functions. Figure 1(d) shows shear rate dependence of f. The axial ratio decreases from about 5 to 1 (corresponding to the onion phase) with increasing shear rate. We have also calculated L and D separately assuming that the volume of the rodlike vesicles is independent of shear rate (Fig. 1(e)). The rod length ($L + D$) decreases with increasing shear rate and follows the power law with an exponent which is nearly equal to that for the diameter of onions ($2R$) obtained from rheo-SALS experiments (see Fig. 1(e)).

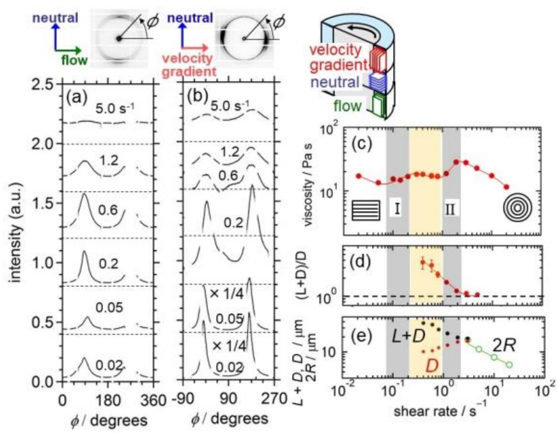

Fig. 1: left: Azimuthal plots of the diffraction intensity in the radial (a) and tangential (b) configurations at different shear rates. Right: Shear rate dependences of the viscosity (c), axial ratio of rodlike vesicles (d), and size of rodlike vesicles and onions (e) for the $C_{14}E_5$/water system (50 wt%, 55°C).

References

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