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Deformation of Onions with Long-Range Orientational Order under Shear and Onion-to-Lamellar Transition in a Nonionic Surfactant ($C_{14}E_5$)/Water System

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1 Introduction

The shear-induced transition from the lamellar phase to the "onion phase" where all the space is filled by multilamellar vesicles alone has been found more than 20 years ago [1]. After that, onion formation has been reported for many surfactant systems. However, conditions and mechanism for the transition have not yet been established. Recently, 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 $C_{14}E_5$/water system (C_nE_m is an abbreviation of $C_nH_{2n+1}(OC_2H_4)_mOH$) by using simultaneous measurements of shear stress/small-angle X-ray scattering (rheo-SAXS) [2]. In the present study, we have performed rheo-SAXS experiments at various shear rates and temperatures to make the temperature-shear rate diagram. It has been shown that onions have a long-range orientational order [3][4] at higher shear rates in a particular temperature range and that deformation of the onion structure occurs with increasing shear rate. We also discuss relations between the deformation of onions and the onion-to-lamellar transition.

2 Experiment

Rheo-SAXS measurements have been performed on the beamline 15A2 by using a rheometer AR550 (TA Instruments). Details of the shear cell have been reported previously [5]. The scattered beam was recorded with the camera length of 2.6 m using the PILATUS 2M.

3 Results and Discussion

First we have performed rheo-SAXS experiments at various temperatures and shear rates in the $C_{14}E_5$/water system (50 wt%). Based on the results of these experiments, we have made the dynamic phase diagram where the temperature and the shear rate are chosen as variables. Comparing this temperature-shear rate diagram with those of the $C_{10}E_3$ system and $C_{16}E_7$ system, we have shown the $C_{10}E_3$ and $C_{16}E_7$ systems exhibits only the upper or lower transition, respectively, whereas both types of transition can be observed for the $C_{14}E_5$ system. This confirms that the $C_{14}E_5$ system is more useful system for studying the lamellae/onion transition.

Next, we have studied the detailed structures of the onion phase. Figure 1 shows azimuthal plots of the diffraction peak intensity at different shear rates at 60 °C. In the range of shear rate between 60 s^{-1} and 400 s^{-1}, the azimuthal plot gives peaks with six fold symmetry, suggesting formation of the onion phase with long-range orientational order both in the radial and tangential configurations. From the change in the relative intensity of these peaks in the range from 60 s^{-1} to 200 s^{-1} in the radial configuration, we can infer that the polyhedral onions are elongated along the neutral direction at the lower shear rates (typically 60 s^{-1}) whereas along the flow direction at the higher shear rates (typically 200 s^{-1}). As can be seen from the results in the tangential configuration, on the other hand, onions are elongated along the neutral direction. After 60 min from the time when the shear rate is increased from 500 s^{-1} to 600 s^{-1}, only the broad peaks are observed for the neutral and the velocity-gradient directions in the radial and tangential configurations, respectively. This indicates that the lamellar structure reappears. These results suggest that deformation of onions is a precursor of the onion-to-lamellar transition.

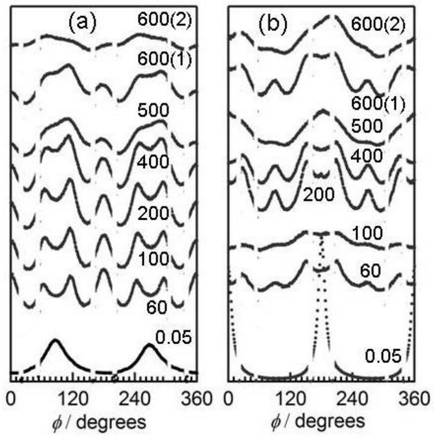

Fig. 1: Azimuthal plots of the diffraction peak intensity from the lamellar phase in the $C_{14}E_5$/water system (50 wt%) at different shear rates indicated by the numbers (in s^{-1}) at 60 °C. The azimuthal angle (ϕ) is defined so that ϕ = 0 indicates the flow and the velocity gradient directions in the radial (a) and tangential (b) configurations, respectively.

References

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