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Lamellar → Onion →Lamellar Transition with Increasing Temperature under Shear Flow in a Nonionic Surfactant/Water System Studied by Rheo-SAXS

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Introduction

In the past 15 years, much attention has been paid to the effects of shear flow on the structure of the lamellar phase. Among them, the most striking result may be the transition from the lamellar phase to the "onion phase" where all the space is filled by multilamellar vesicles alone [1]. Although this type of transition has been reported for various surfactant systems, transition mechanism has not yet been established. Recently, we have found the lamellar-to-onion transition with increasing temperature under a constant shear rate in the lamellar phase of a nonionic surfactant $C_{16}E_7$/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 light scattering (rheo-SALS) and shear stress/small angle X-ray scattering (rheo-SAXS). From time-resolved measurements of rheo-SAXS, we have proposed a mechanism of the transition. On the other hand, the lamellar-to-onion transition with decreasing temperature has been reported for $C_{10}E_3$/water and $C_{12}E_4$/water systems, which is explained in terms of increase (less negative) in the saddle-spray modulus of bilayers with the temperature elevation [2, 3]. In the present study, we have found a system which exhibits lamellar → onion →lamellar transition with increasing temperature by using rheo-SAXS.

Experimental

A rheometer AR550 (TA Instruments) is modified for rheo-SAXS experiments. Details of the cell have been reported previously [2]. Measurements were performed on the beamline 15A. The scattered beam was recorded using the CCD area detector covering the scattering vector range from 0.15 to 2.5 nm^{-1}.

Results

Figure 1 shows temperature dependence of the shear stress and 2-D SAXS patterns (radial configuration) for the lamellar phase of a $C_{14}E_4$/$C_{14}E_6$/water system (molar ratio of $C_{14}E_4$ to $C_{14}E_6$ is 7/3 and the total surfactant concentration is 50 wt%) for the shear rate of 3 s^{-1}. In the lower temperature less than 23°C, the lamellae are oriented to the neutral direction. As the temperature exceeds 25°C, the viscosity increases abruptly and, at the same time, the orientation of lamellae disappears. Between 30°C and 60°C, the viscosity remains high and the isotropic SAXS pattern is observed. When the temperature exceeds 60°C, the viscosity abruptly decreases and again the lamellae are orientated to the neutral direction. These results suggest lamellar → onion →lamellar transition with increasing temperature under a constant shear rate.

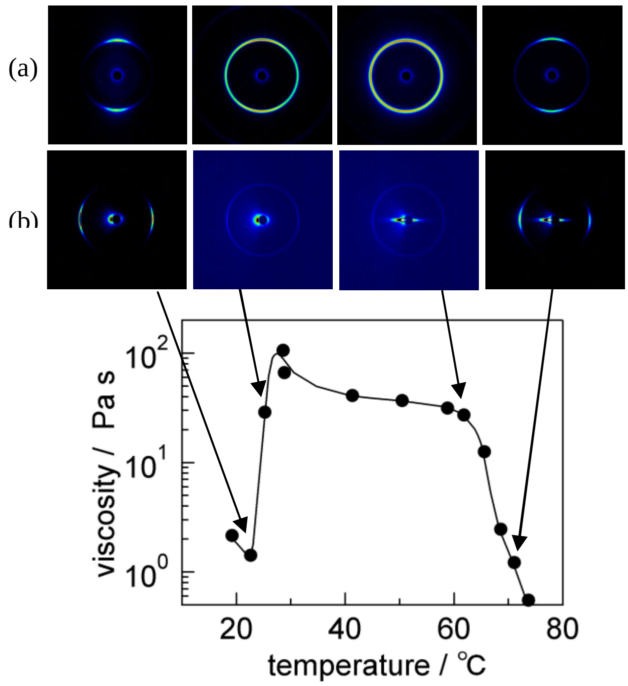

Fig. 1 Temperature dependence of the shear stress and 2-D SAXS patterns for the radial (a) and tangential (b) configurations for the lamellar phase of a $C_{14}E_4$/$C_{14}E_6$/water system (molar ratio of $C_{14}E_4$ to $C_{14}E_6$ = 7/3 and total surfactant concentration is 50 wt%) for the shear rate of 3 s^{-1}. The flow direction is horizontal.

References

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