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Reentrant Lamellar-Onion Transition with Varying Temperature under Shear Flow in a Nonionic Surfactant/Water System

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Introduction

In the past 20 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]. 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 and shear stress/small angle X-ray scattering (rheo-SAXS) [2]. We have also found reentrant lamellar-onion (lamellar → onion →lamellar) transition with increasing temperature for a $C_{14}E_4$/ $C_{14}E_6$/water system [3]. In this study, the change in the SAXS intensity is measured in more detail to discuss the transition mechanism .

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 time dependences of the viscosity, temperature, and the intensity of the SAXS peak for each direction for the lamellar-to-onion (a and c) and onion-to-lamellar (b and d) transitions in 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%) at the shear rate of 3 s^{-1}. In this experiment, as shown in Fig. 1, the sample temperature was increased stepwise. It should be noted that the intensity correction for the radial and tangential configurations is not performed and so the intensity for the velocity-gradient direction cannot be compared with those for two other directions. In the lamellar-to-onion transition, the viscosity increases about two orders of magnitude as the temperature increases from 23°C to 26°C. Before the steep increase in the viscosity, the peak intensity for the velocity-gradient direction is further increased. The subsequent increase in viscosity accompanies abrupt enhancement of the neutral as well as abrupt suppress of the gradient peak. Similar results have been obtained in our previous study on the $C_{16}E_7$/ water system. In the onion-to-lamellar transition in the higher temperature range (b and d), the intensity for the neutral direction again takes a maximum followed by the maximum in the intensity for the velocity-gradient direction.

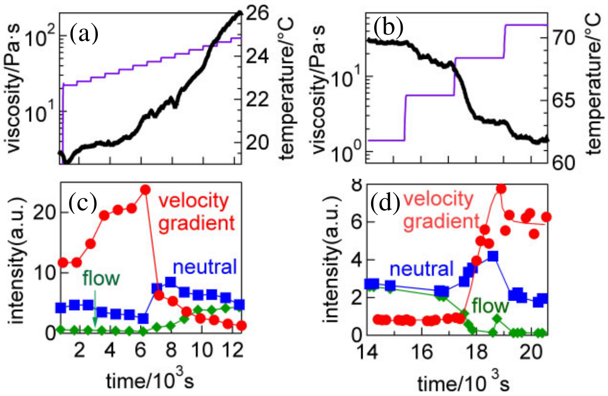

Fig. 1 Time dependences of the viscosity, temperature (a and b), and the intensity of the SAXS peak for each direction (c and d) for the lamellar-to-onion (a and c) and onion-to-lamellar (b and d) transitions in a $C_{14}E_4$/ $C_{14}E_6$/water system (molar ratio of $C_{14}E_4$ to $C_{14}E_6$ = 7/3 and total surfactant concentration is 50 wt%) at the shear rate of 3 s^{-1}.

These results suggest that the onion-to-lamellar transition in the higher temperature range occurs in the reverse pathway for the lamellar-to-onion transition in the lower temperature range. However, the latter transition occurs in the narrower temperature range than in the former transition, which might be due to the difference in the lamellar/onion coexistence region .

References

[1] D. Roux, in "Nonequilibrium Dynamics, Metastability and Flow" ed. by M. E. Cates, M. R. Evans, and P. Osborne, Institute of Physics Publishing, Bristol (2000).
[2] Y. Kosaka, M. Ito, Y. Kawabata, and T. Kato, *Langmuir*, **26**, 3835 (2010).
[3] M. Okamoto, Y. Kawabata, and T. Kato, *Photon Factory Activity Report 2008,* #26, Part B (2009).

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