Journal of
Applied
Crystallography
ISSN 0021-8898

Received 16 August 2006
Accepted 21 March 2007

Shear-induced structural transition in the lamellar phase of the $C_{16}E_7/D_2O$ system. Time evolution of small-angle neutron scattering at a constant shear rate

Kyoko Miyazaki, Yuriko Kosaka, Youhei Kawabata, Shigeyuki Komura and Tadashi Kato*

Department of Chemistry, Tokyo Metropolitan University, 1-1 Minamiohsawa, Hachioji, Tokyo 192-0397, Japan. Correspondence e-mail: kato-tadashi@c.metro-u.ac.jp

The time evolution of small-angle neutron scattering is measured for the lamellar phase of a nonionic surfactant $C_{16}H_{33}(OC_2H_4)_7OH$ ($C_{16}E_7$) in D_2O at 48 wt% at 343 K under shear flow. At the shear rates of 0.3, 1 and 3 s^{-1}, a new diffraction peak appears at higher q [where $q = (4\pi/\lambda)\sin\theta$, and λ and 2θ are the wavelength of the neutron beam and the scattering angle, respectively] about 1–2 h after applying shear flow and coexists with the initial diffraction peak. The coexistence of two peaks continues even after 5 h at 0.3 s^{-1} whereas at 1 and 3 s^{-1} the peak at lower q disappears after about 3 h. These results indicate that the repeat distance decreases discontinuously and so suggest some sort of transition. A plot of the repeat distance after 5 h *versus* shear rate shows a minimum at 1 s^{-1}, which is in good agreement with our previous results obtained by increasing the shear rate stepwise.

1. Introduction

In recent years, the effects of shear flow on the structure of surfactant self-assemblies have been studied extensively using microscopy, nuclear magnetic resonance (NMR), and scattering techniques such as small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS) and small-angle light scattering (SALS). Among them, the lamellar phase has become of interest because the shear-induced state is sometimes not simply related to an existing equilibrium. Roux and coworkers have found a transformation from the lamellar phase to the 'onion phase' where multilamellar vesicles are close-packed (Diat *et al.*, 1993, 1995; Sierro & Roux, 1997; Roux, 2000). Following their pioneering study, various types of shear effects have been reported (for example, see Richtreing, 2001).

In the previous study (Kato *et al.*, 2004, 2005), we measured SANS and SALS on the lamellar phase of a nonionic surfactant $C_{16}E_7$ [a surfactant having a chemical formula $C_nH_{2n+1}(OC_2H_4)_mOH$ is abbreviated as C_nE_m] in D_2O at 40, 48 and 55 wt% at 340 K in the range of shear rate 10^{-3}–10 s^{-1}, which is lower than in other published studies. We have found a significant decrease in the lamellar repeat distance (d) at shear rates of 0.3–1 s^{-1}. The minimum value of d is nearly equal to the thickness of the bilayers irrespective of the concentration, suggesting phase separation into concentrated lamellar and water-rich regions, although macroscopic phase separation could not be observed by the naked eye (the outer cylinder of the shear SANS cell is made of quartz). A reduction in the repeat distance by shear flow has been reported by several groups (Yamamoto & Tanaka, 1995; Idziak *et al.*, 2001; Welch *et al.*, 2002). In these experiments, however, the amount of reduction is only a few per cent of the initial repeat distance at rest. In our system, on the other hand, the repeat distance is decreased down to about 40% of the initial one in the case of the 40 wt% sample. Such a large amount of decrease in the repeat distance has not been reported so far and so it is important to elucidate the underlying mechanisms of this phenomenon.

In the present study, the time evolution of SANS patterns has been measured under a constant shear rate in the same system to pursue the change in the lamellar repeat distance as a function of time.

2. Experimental

SANS measurements were carried out at the instrument SANS-U at the Institute for Solid State Physics of the University of Tokyo in JRR-3M at Tokai with a Couette shear cell. The details of the shear cell have been reported previously (Takahashi *et al.*, 2000). Under a constant shear rate (0.3, 1, 3, 10 and 30 s^{-1}), time-resolved two-dimensional SANS patterns have been collected for about 6 h. The exposure times were 3 and 10 min for the radial and tangential configurations, respectively. Measurements have also been made for about 2 h after stopping the shear.

3. Results and discussion

Fig. 1(a) shows the evolution of the two-dimensional SANS pattern after applying shear flow with shear rate of 1 s^{-1}. The pattern in the tangential configuration at rest indicates strong orientation of lamellae to the gradient direction, which may be due to shear caused by lowering the inner cylinder (stator) into the sample in the outer cylinder (rotor). These two-dimensional patterns were reduced to one-dimensional (1D) patterns in the neutral, flow and velocity gradient directions by integrating the scattering intensity over a segment of width $\Delta\phi = \pm 10^\circ$, where ϕ is the azimuthal angle. The 1D patterns for the neutral and velocity gradient directions are shown in

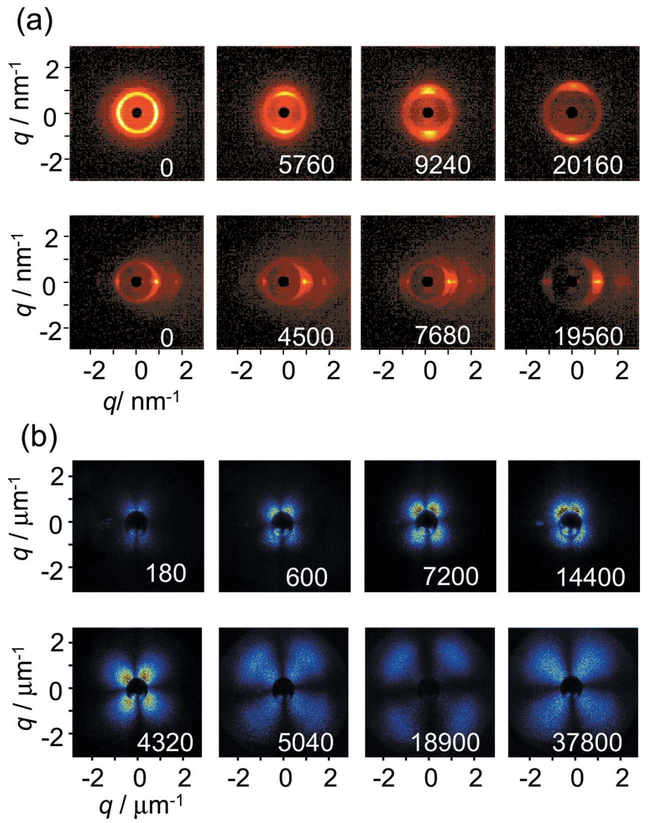

Figure 1
(a) Evolution of two-dimensional SANS patterns after applying shear flow at 1 s^{-1} for the sample containing 48 wt% $C_{16}E_7$ at 340 K for the radial (upper) and tangential (lower) configurations. The numbers indicate the strain. (b) Evolution of depolarized SALS patterns after applying shear flow at 1 s^{-1} (upper) and 3 s^{-1} (lower) for the sample containing 48 wt% $C_{16}E_7$ at 340 K for the radial configurations. The numbers indicate the shear strain.

Fig. 2. This figure demonstrates that a new diffraction peak appears at higher q [q is defined as $(4\pi/\lambda)\sin\theta$, where λ and 2θ are the wavelength of the neutron beam and the scattering angle, respectively] and coexists with the initial diffraction peak at a strain of 7680. At a strain of 17 160, the peak at lower q disappears and the peak intensity at higher q increases. These results indicate that the repeat distance decreases discontinuously, suggesting some sort of transition.

Fig. 3 shows the evolution of the repeat distances (d) for the three principal orientations of lamellae. The discontinuous decrease of d (see the dashed arrows) is observed at the shear rates of 0.3 and 3 s^{-1} as well, although the coexistence of two peaks continues even after 330 min (a strain of about 6000) at 0.3 s^{-1}. At 30 s^{-1}, on the other hand, the repeat distance decreases almost continuously and the amount of the decrease is small compared to the lower shear rates. The discontinuous decrease begins to occur at strains of about 2000, 6000 and 10 000 for the shear rates of 0.3, 1 and 3 s^{-1}, respectively. These results suggest that the strain plays an important role in the transition but the critical strain increases with shear rate.

In Fig. 4, the repeat distance just before stopping shear (after about 6 h) is plotted against the shear rate. This figure demonstrates that the repeat distance takes a minimum at around 1 s^{-1}. In our previous study (Kato *et al.*, 2004), the shear rate increases stepwise (0.03 → 0.1 → 0.3 s^{-1} and 0.3 → 1 → 3 → 10 → 30 s^{-1} for first and second runs, respectively, for the 48 wt% sample). The repeat distance takes a minimum also at around 1 s^{-1}. These results suggest that the shear-rate dependence of the repeat distance in the steady state is almost independent of the shear history.

Nettesheim *et al.* have investigated the effects of shear flow on the lamellar structures in the $C_{10}E_3$ and $C_{12}E_4$ systems. They suggest the formation of an intermediate structure oriented in the flow direction, corresponding to long multilamellar cylinders (or deformed onions) before the formation of spherical onions (Nettesheim *et al.*, 2003). However, the repeat distance remains constant throughout these transition processes. Fig. 1(b) shows the evolution of depolarized SALS patterns after applying shear flow at 1 and 3 s^{-1}. The four-

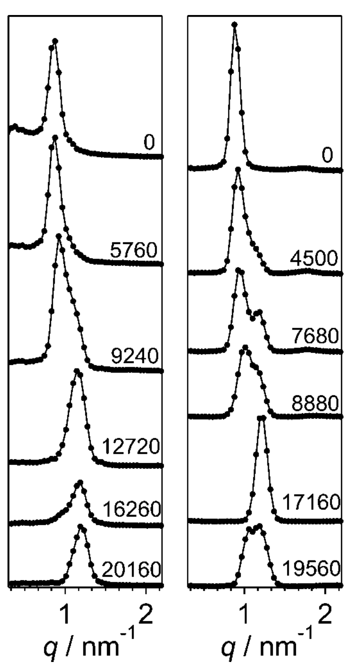

Figure 2
Evolution of 1D SANS patterns after applying shear flow at 1 s^{-1} for the sample containing 48 wt% $C_{16}E_7$ at 340 K for the neutral (left) and velocity-gradient (right) directions. The numbers indicate the shear strain.

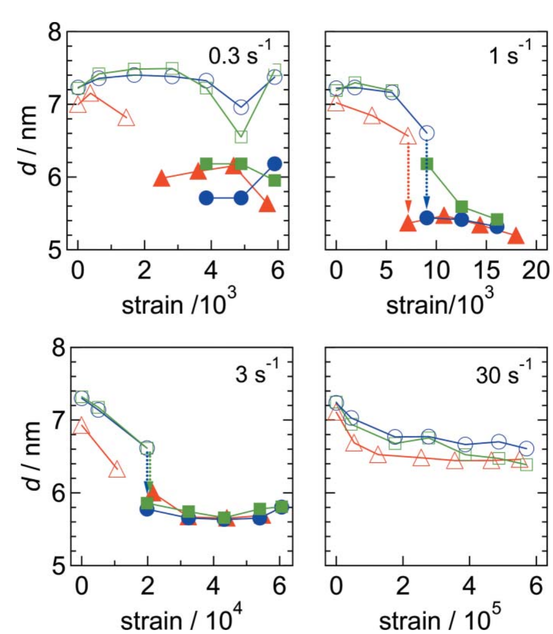

Figure 3
The repeat distance *versus* shear strain at 0.3, 1, 3 and 30 s^{-1} for the sample containing 48 wt% $C_{16}E_7$ at 340 K for the neutral (circles), flow (squares) and velocity-gradient (triangles) directions.

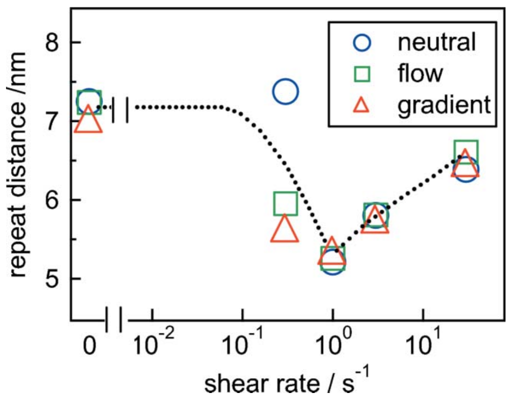

Figure 4
The repeat distance just before stopping shear (after about 6 h) *versus* shear rate for the sample containing 48 wt% $C_{16}E_7$ at 340 K for the neutral (circles), flow (squares) and velocity-gradient (triangles) directions.

lobed pattern with a diffraction peak observed at 3 s^{-1} indicates the existence of onions. So the structural changes on the nanometre scale (reduction in the repeat distance) may be correlated with that on the micrometre scale (onion formation). However, detailed relations between them are not still clear.

Recently, we have also found a change in spacing for a $C_{12}E_5/D_2O$ (35 wt%) system at 0.5–1 s^{-1}. Because the bilayer thickness of $C_{12}E_5$ is about 60% of that of $C_{16}E_7$, the bending constants (κ) for these two systems may be very different from each other. So the results for these two systems suggest that the critical shear rate for the discontinuous change in spacing may depend on κ only slightly. Before drawing conclusions, however, we should perform more systematic experiments for surfactants with different chain lengths, including $C_{10}E_3$ and $C_{12}E_4$.

As has already been shown in the $C_{10}E_3$ system (Le *et al.*, 2001; Oliviero *et al.*, 2003), the fraction of onions under shear flow strongly depends on temperature. In our previous SAXS study on the $C_{16}E_7$ system at rest, we have shown that bilayers in the lamellar phase have water-filled defects below about 341 K and that the fraction of the defects increases with decreasing temperature (Minewaki *et al.*, 2001). Therefore, the time evolution of SANS and SALS patterns as well as the shear stress at different temperatures may give some clue as to the relations between the structural changes on the nanometre and micrometre scales.

This research was partially supported by the Ministry of Education, Science, Sports and Culture of Japan, Grant-in-Aid for Scientific Research (B), 15340140, 2003–2005.

References

Diat, O., Roux, D. & Nallet, F. (1993). *J. Phys. II France*, **3**, 1427–1452.
Diat, O., Roux, D. & Nallet, F. (1995). *Phys. Rev. E*, **51**, 3296–3299.
Idziak, S. H. J., Welch, S. E., Kisilak, M., Mugford, C., Potvin, G., Veldhuis, L. & Sirota, W. B. (2001). *Eur. Phys. J. E*, **6**, 139–145.
Kato, T., Minewaki, K., Kawabata, Y., Imai, M. & Takahashi, Y. (2004). *Langmuir*, **20**, 3504–3508.
Kato, T., Miyazaki, K., Kawabata, Y., Komura, S., Fujii, M. & Imai, M. (2005). *J. Phys. Condens. Matter*, **17**, S2923–S2928.
Le, T. D., Olsson, U., Mortensen, K., Zipfel, J. & Richtering, W. (2001). *Langmuir*, **17**, 999–1008.
Minewaki, K., Kato, T., Yoshida, H., Imai, M. & Ito, K. (2001). *Langmuir*, **17**, 1864–1871.
Nettesheim, F., Zipfel, J., Olsson, U., Renth, F., Linder, P. & Richtering, W. (2003). *Langmuir*, **19**, 3603–3618.
Oliviero, C., Coppola, L., Gianferri, R., Nicotera, F. I. & Olsson, U. (2003). *Colloid Surf. A*, **228**, 85–90.
Richtreing, W. (2001). *Curr. Opin. Colloid Interf. Sci.* **6**, 446–450.
Roux, D. (2000). *Nonequilibrium Dynamics, Metastability and Flow*, edited by M. Cates, M. R. Evans & P. Osborne, ch. 7. Bristol: Institute of Physics Publishing.
Sierro, P. & Roux, D. (1997). *Phys. Rev. Lett.* **78**, 1496–1499.
Takahashi, Y., Noda, M., Naruse, M., Kanaya, T., Watanabe, H., Kato, T., Imai, M. & Matsushita, Y. (2000). *Nihon Reoroji Gakkaishi*, **28**, 187–191.
Welch, S. E., Stezer, M. R., Hu, G., Sirota, E. B. & Idziak, S. H. (2002). *Phys. Rev. E*, **65**, 061511-1–061511-6.
Yamamoto, J. & Tanaka, H. (1995). *Phys. Rev. Lett.* **74**, 932–935.