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Time-resolved SAXS studies coupling with pressure jump technique on self-assembled formation process in surfactant solutions

Youhei KAWABATA*, Akimi MATSUNO, Tadashi KATO
Department of Chemistry, Tokyo Metropolitan University
1-1 Minamiohsawa, Hachioji, Tokyo 192-0397, Japan

Introduction

In a binary system consisting of surfactant and water, surfactant molecules self-assemble to form various kinds of structures such as lyotropic liquid crystals, spherical or cylindrical micelles and so on, by changing temperature, pressure and concentration. Recently, much attention has paid kinetics of these structural formations in changing temperature or pressure.

Figure 1 shows the schematic T-ϕ phase diagram of surfactant and water system. As shown in Fig. 1, a micellar phase (L_1) undergoes a phase separation of a gel phase (L_β) and a dilute phase by decreasing temperature or increasing pressure. It has been suggested that the gel phase is a lamellar structure of bilayers whose hydrophilic tails are "solid-like" gel and interdigitated. Therefore, the two-phase coexistence has been often called as "hydrated solid phase", which has a viscoelastic property and its feature is applied in cosmetic industry and so on. So far, we have found that there are big differences in the structural formation of the hydrated solid phase between those of the non-ionic surfactant $C_nH_{2n+1}(OC_2H_4)_mOH$ and water system, $C_{16}E_7$/water and $C_{16}E_6$/water systems. In the $C_{16}E_7$ system, vesicle structures appear, on the other hand, in the $C_{16}E_6$ system, worm-like lamellar domains are formed below the Krafft temperature.

In the present study, in order to investigate the differences in the structures between the $C_{16}E_6$ system and the $C_{16}E_7$ system, we observed the structural formation of the gel phase by using time- resolved small angle X-ray scattering (SAXS) in the binary system after the jump to the hydrated solid phase of the $C_{16}E_7$/water and $C_{16}E_6$/water systems.

Experimental

Measurements were performed on the beamline 15A. The scattered beam was recorded using the CCD area detector covering the scattering vector *q* range from 0.015 to 0.25 Å^{-1}. For the jump experiment, we developed the high pressure cell with a couple of diamond windows whose thickness is 1mm. It was found that the windows were inappropriate for the time-resolved SAXS measurements because the transmission of X-ray to those windows was very low (< 0.2). Therefore, we carried out temperature-jump experiments instead of pressure-jump until the windows are developed. The temperature-jump experiments were performed as shown in Fig. 1 (from 288.9 K to 282.2 K). The concentration of $C_{16}E_7$ is 10 wt.%.

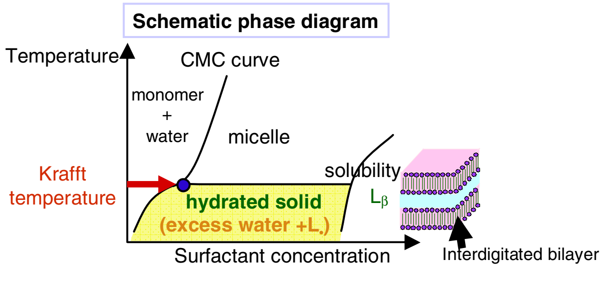

Fig. 1 Schematic T-ϕ phase diagram of surfactant $C_{16}E_7$ and water system.

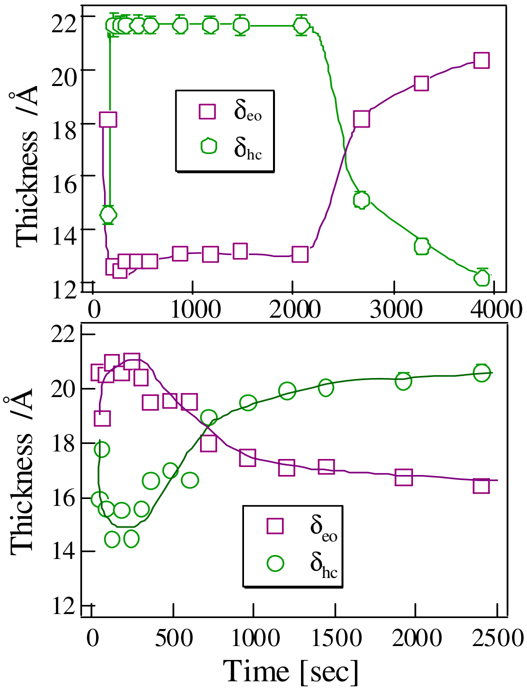

Fig. 2 Time evolution of the length of the hydrophobic tail δ_{hc} and the hydrophilic tail δ_{eo} in the $C_{16}E_7$/water and $C_{16}E_6$/water systems.

Results

We analyzed the SAXS profiles using the form factor of bilayers taking the hydration of hydrophilic parts into account. Figure 2 indicates time evolution of the length of the hydrophobic tail δ_{hc} and the hydrophilic tail δ_{eo} in the $C_{16}E_7$/water and $C_{16}E_6$/water systems. The hydrophilic tails of the $C_{16}E_7$ system are hindered from extending to the full length around ~ 2000 seconds. On the other hand, those of the $C_{16}E_6$ system extend to the all- *trans* conformational length of the $C_{16}H_{33}$.

*youheik@tmu.ac.jp