

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

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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 been paid to kinetics of these structural formations in changing temperature or pressure.

Figure 1 shows the T- ϕ phase diagram of a non-ionic surfactant C₁₆E₇ (C₁₆H₃₃(OC₂H₄)₇OH) and water system. As shown in Fig. 1, a micellar phase (L₁) 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. However, its structure and the structural formation process have not been understood so far. In order to clarify the mechanism of the structural formations of hydrated solid phase, it is important to investigate self-assembled formation processes.

In the present study, 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.

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

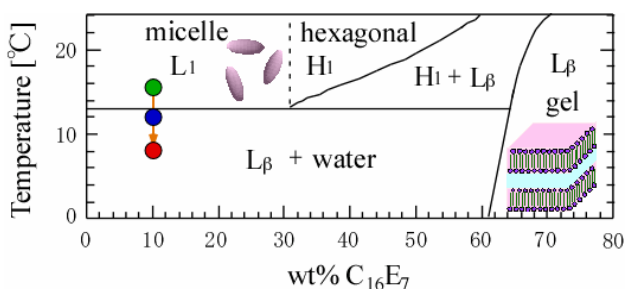


Fig.1 T- ϕ phase diagram of a non-ionic surfactant C₁₆E₇ (C₁₆H₃₃(OC₂H₄)₇OH) and water system

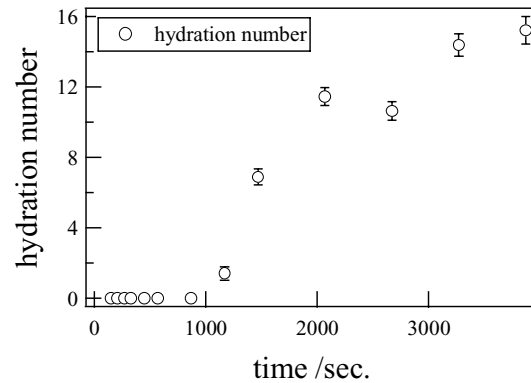


Fig.2 The time evolution of hydration number per C₁₆E₇, which was calculated from the curve fitting to the SAXS profiles measurements because the transmission of X-ray to those windows was very low (< 0.2). Therefore, we carried out temperature-jump experiments instead of pressure-jump until the windows are developed. The temperature-jump experiments were performed as shown in Fig. 1 (from 288.9 K to 282.2 K). The concentration of C₁₆E₇ is 10 wt.%.

Results

From the scattering profiles obtained from SAXS experiments, within 3 minutes after the temperature jump, the peak corresponding to the gel structure appeared. The repeat distance d of bilayers increased up to $d=8$ nm after the temperature-jump. This repeat distance is larger than the value of equilibrium state, which can be estimated the phase diagram. In order to investigate the structural formation process in detail, we analyzed those profiles using the form factor of bilayers taking the hydration of hydrophilic parts into account. Figure 2 indicates the hydration number per molecule, which was estimated from the curve fitting to the scattering profiles. We focused the hydration process and the structure around the hydrophilic parts. To investigate the effects of hydrophilic part, we performed the time-resolved SAXS experiments in the C₁₆E₆/water system, where the hydrophilic part of surfactant is shorter than that of C₁₆E₇. The repeat distance of the C₁₆E₆/water system reached the value of equilibrium state quickly. These results indicate that the hydration structure around hydrophilic parts plays important roles in the structural formation process of the hydrated solid phase.

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