

Structural formation process of hydrated solid gel structure in a surfactant solution

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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 paid kinetics of these structural formations in changing temperature or pressure. Below the Krafft temperature, where hydrophobic tails of surfactants extended to those full lengths (all-trans), a micellar phase (L_1) undergoes a phase separation of a gel phase (L_β) and a dilute phase. The gel phase is a lamellar structure of bilayers whose hydrophilic tails are "solid-like" gel and interdigitated. We have ever found that in non-ionic surfactant $C_{16}E_7$ [$C_nH_{2n+1}(OC_2H_4)_mOH$] and water system, hollow vesicles are formed below the Krafft temperature [1], as shown in Fig.1. The formation process of vesicles strongly depend on quenched temperature, and at the quenched temperature is 10°C, vesicles are transformed to string-like formations.

In the present study, in order to investigate the temperature dependence of vesicle formations in the $C_{16}E_7$ system, we observed the structural formation of the gel phase by using time-resolved small and wide angle X-ray scattering (SAXS, WAXS) in the binary system after the jump to the various quenched temperature.

Experimental

Measurements were performed on the beamlines 15A and 9C. At 15A, the scattered beam was recorded using the CCD area detector covering the scattering vector q range from 0.015 to 0.25 \AA^{-1} . At 9C, we used PSPC detectors for wide and small angle X-ray scattering. The q range of the wider angle is 0.3 to 6.0 \AA^{-1} . For the temperature jump, DTA/SAXS instrument with Kapton windows [2]. The temperature was changed from 16 to 14, 12, 10, 8 and 6°C, and scattered X-rays were detected after the temperature jump. The concentration of $C_{16}E_7$ is 10 wt. %.

Results

Figures 2 are SAXS and WAXS profiles obtained at 15A and 9C. For the SAXS profiles, after the temperature jump, the broad peaks corresponding to the micellar phase disappear earlier, as the quenched temperature is lower. Furthermore, for the WAXS profiles, the Bragg peak corresponding to the a-type crystal which surfactant molecules arrange in hexagonal array, become sharp at the lower temperature. This indicates that hydrophobic

tails are strongly interdigitated and molecules in plane are densely packed at low temperature. Combining with SAXS and WAXS results, we can conclude that micellar concentration decrease earlier and surfactant bilayers which constitute vesicles become rigid as the quenched temperature is lower. On the other hand, at the higher temperature, micelles disappear slowly, which it takes about 1 hour, and bilayers are flexible. As a result, it would be considered that vesicles are deformed by osmotic pressure due to micellar concentration difference between inside and outside of vesicles. This assumption has been confirmed by the confocal microscope observation, that is to say, after the temperature jump to the higher quenched temperature, there are the micellar concentration difference between inside and outside of vesicles.

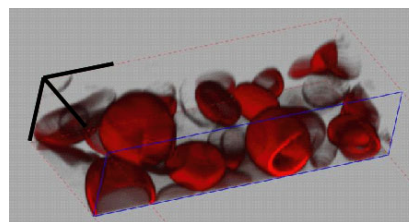


Fig.1 3D image of vesicles obtained from confocal microscope observation.

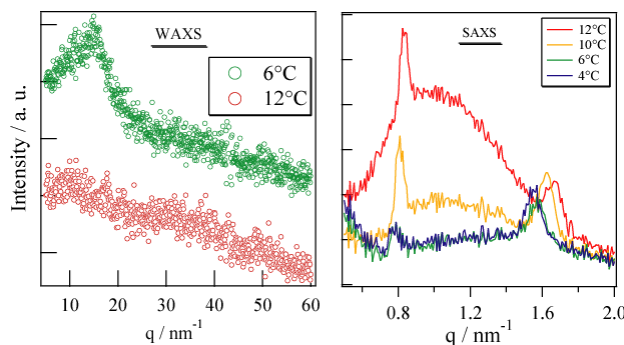


Fig.2 WAXS and SAXS profiles obtained at BL-15A and 9C. The Bragg peak of WAXS corresponds to the a-type crystal which surfactant molecules arrange in hexagonal array, and those of SAXS profiles correspond to the lamellar structures of L_β phase.

References

- [1] Y. Kawabata et al., *J. Phys. Chem B*, 113, 5686 (2009).
- [2] H. Yoshida et al., *Thermochim. Acta* 264, 173 (1995).

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