10C/2000G247

Temperature Dependence in Layer Thickness in Lamellar Phase Formed in Nonionic Surfactant $C_{16}E_6$ -Water System

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Introduction

Mixtres of water and polyoxyethylene surfactants $C_nH_{2n+1}(OC_2H_4)_mOH$ (abbreviated as C_nE_m) exhibit a variety of phase behaviors by changing the concentration and temperature without any additive. In the previous study[1], we have measured small angle x-ray scattering (SAXS) on the lamellar phase formed in a $C_{16}E_7$-water system. It has been shown that the repeat distance d follows the power law $d \propto \phi_{hc}^{-s}$ (ϕ_{hc} is the volume fraction of hydrophobic layer) and that the exponent s decreases from unity to 0.65 as the temperature is reduced from 75°C to 55°C. From the line shape analyses of SAXS, the thickness of the hydrophobic layer ($2\delta_{hc}$) has been found to depend on concentration and temperature only slightly. These results suggest that the lamellar phase has some defects in the lower temperature range. In the analyses of the SAXS line shape, we have also shown that the thickness of the hydrophilic layer δ_{eo} decreases with increasing temperature. On the other hand, a Raman scattering study in the micellar phase of the $C_{12}E_8$ system indicate that the fraction of the gauche conformation decreases with increasing temperature [2]. The change in the conformation from gauche to trans corresponds to the increase in the length of the ethylene oxide chain. It should be noted however that the Raman scattering measurements were performed in in the range 0-60°C while the decrease of δ_{eo} in the $C_{16}E_7$ system was observed above 60°C. In the present study, we have determined the layer thickness in a $C_{16}E_6$-water system where the existence temperature of the lamellar phase is lower than that for the $C_{16}E_7$ system from line shape analyses of SAXS.

Experimental

Measurements were performed using SAXS spectrometer installed at the BL-10C instrument at the Photon Factory of the National Laboratory. We used a sample cell made of copper with Kapton windows (thickness = 1mm) whose temperature is controlled by using the DTA/SAXS instrument reported before. All the measurements were made for the sample containing 52wt% of $C_{16}E_6$ in the range 40-55°C where a stable lamellar phase exists.

Analyses

Observed SAXS curves have been analyzed under an assumption that layer displacement fluctuations are independent of the transverse position. In this case, the scattering intensity can be expressed as

$$I(q) = (2\pi/q^2d)P(q)S(q)$$

where $P(q)$ is the form factor of the membrane and $S(q)$ is the structure factor. For the calculation of $P(q)$, we assumed that the membrane is composed of three layers; one hydrophobic layer and two hydrophilic layers. Then the scattering intensity can be expressed as a function of δ_{hc}, the hydration number, and a parameter concerning the amplitude of the layer displacement fluctuations. These parameters have been determined by the least-square fitting of the SAXS intensity.

Results and Discussion

The half-thickness of the hydrophobic layer (δ_{hc}) is around 0.75 nm and almost indepent of temperature. This value is very close to that for the $C_{16}E_7$ system as expected from the fact that both surfactants have the same hydrophobic chain. On the other hand, the thickness of the hydrophilic layer δ_{eo} decreases from 2.25 nm to 2.0 nm as the temperature increases from 40°C up to 55°C. So the decrease of δ_{eo} with increasing temperature is observed not only for $C_{16}E_7$ but also for $C_{16}E_6$. Moreover, these δ_{eo} values are larger than those in the $C_{16}E_7$ system in spite that the number of ethylene oxide groups of $C_{16}E_6$. is smaller than that of $C_{16}E_7$.

These results suggest that the δ_{eo} value is dominated by not the conformation of the ethylene oxide chain but the number of water molecules per ethylene oxide group in the hydrophilic layer which is expected to decrease with increasing temperature. This may result from the fact that in the lamellar phase the mean curvature of the interface between the hydrophobic and hydrophilic parts is much smaller than that in the micellar phase. So the area per surfactant molecule is almost constant throughout the membrane. In the micellar phase, on the other hand, the surface area per surfactant molecule increases with the distance from the interface.

References

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