Conformational Dynamics of Alkyl Chains in the Lamellar Phase of a Nonionic Surfactant $C_{12}E_3$ Studied by Deuterium Nuclear Magnetic Resonance

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Deuterium NMR spectroscopy was applied to a study of conformational dynamics of alkyl chains in the lamellar phase of a $C_{12}E_3$ (nonionic surfactant)–water system. The order parameter derived has shown that addition of the surfactant in the lamellar phase causes conformational disordering of alkyl chains, leading to a transition to an isotropic solution phase, while addition of water, which eventually leads to phase separation, causes no substantial disordering of alkyl chains.

Amphiphilic surfactant molecules self-organize in water to form molecular aggregates with different shapes and sizes. These aggregates yield a variety of liquid crystalline phases such as lamellar, hexagonal, and cubic phases, which are characterized by long-range order.[1–3] Nonionic surfactants α-*n*-alkyl-ω-hydroxy-oligo(oxyethylene)s, $CH_3(CH_2)_{n-1}(OCH_2CH_2)_mOH$ (abbreviated as C_nE_m), are typical amphiphilic molecules that form interesting liquid crystalline phases.[4,5] Previously we have studied the conformation of alkyl chains in $C_{12}E_3$ molecules in the lamellar (L_α) and isotropic solution (L_2) phases by infrared spectroscopy and have shown that the conformation changes significantly in the L_α phase when the solution composition or the temperature approaches the region of the phase separation or transition.[6–8] To gain a further insight into dynamical properties of the liquid crystalline phases, relevant studies by nuclear magnetic resonance are important to complement the structural properties elucidated by infrared spectroscopy. We have therefore studied in this work the conformational dynamics of $C_{12}E_3$ in the L_α phase by deuterium NMR spectroscopy.

The quadrupole coupling of the deuterium nucleus with the electric field gradient gives rise to splittings of NMR frequencies.[9] For aliphatic C–D bonds, the electric field gradient is axially symmetric with its principal axis along the bond direction. This makes deuterium NMR spectroscopy an excellent method for studying molecular orientations.[10–12] For uniaxial liquid crystalline phases such as lamellar and hexagonal phases, the quadrupole splitting is time-averaged over the C–D bond orientations because of rapid anisotropic molecular motions, e.g., interconversions between different conformational states, that take place in a time short compared to the inverse of the quadrupole interaction. The averaged quadrupole splitting can therefore be given by

$$<\Delta\nu> = S_{CD}\delta(3\cos^2\alpha - 1), \qquad (1)$$

where δ is 3/4 times the quadrupole coupling constant e^2qQ/h with a value of 167 kHz for aliphatic C–D bonds, α is the angle between the phase axis (the normal of the uniaxial phase surface) and the magnetic field, and S_{CD} is a time-averaged parameter called the order parameter of the C–D bond[10–12] being given by $(1/2)<3\cos^2\beta - 1>$ with the angle β between the principal axis of the electric field gradient tensor, i.e., the C–D bond direction, and the phase axis. The order parameter S_{CD} thus is a measure of the time-averaged orientation of the C–D bond with respect to the phase axis. The absolute value of the order parameter for uniaxial liquid crystalline phases is obtained from the splitting of the maxima, corresponding to $\alpha = 90°$, of the doublet spectra as

$$|S_{CD}| = |<\Delta\nu>_{90°}/\delta|. \qquad (2)$$

In this work, six selectively monodeuterated species of $C_{12}E_3$, namely $CH_3(CH_2)_{11-k}CHD(CH_2)_{k-1}(OCH_2CH_2)_3OH$ (C_{12}-*k*-d_1-E_3), where k = 1, 2, 4, 6, 8, and 10, were synthesized by the method that yields the exclusive monodeuteration at the specified position.[7] The deuterium NMR measurements were performed at a deuterium resonance frequency of 41.6375 MHz on a Matec pulsed spectrometer equipped with a homemade sample probe and a temperature controller. The temperature was varied in a range between 260 and 320 K. The spectra were obtained by a Fourier transformation of free induction decays. The $\pi/2$ pulse width was 4 μs.

The deuterium NMR spectra were measured on the six monodeuterated species of $C_{12}E_3$ in water at three compositions, 50, 60, and 80 wt%. The first composition corresponds to a region of the L_α phase close to the phase separation into W + L_α at lower temperatures (W is a phase of water containing surfactant monomers) or a region close to the phase separation into L_2 + L_α at higher temperatures, the second corresponds to a middle region of the L_α phase, and the last corresponds to a region of the L_α phase close to the transition to the L_2 phase at higher temperatures or a region close to the transition to the solid phase at lower temperatures.[13]

The deuterium NMR spectra of 60 wt% C_{12}-8-d_1-E_3 in water at various temperatures are shown as typical examples in Figure 1. An observation of a sharp singlet peak at 317 K evidences the isotropic L_2 phase at this temperature. With decreasing temperature, the quadrupole splitting emerges at 310 K, indicating a phase transition at this temperature from L_2 to L_α. The decrease of temperature persistently increases the splitting from 11 kHz at 310 K to 20 kHz at 264 K. At 260 K, the splitting suddenly expands to 60 kHz corresponding to $\beta \approx 90°$, being consistent with a phase transition at this temperature from L_α to gel.

From the observed quadrupole splitting for C_{12}-*k*-d_1-E_3 with k = 1, 2, 4, 6, 8, and 10, the order parameter of the C–D bond at each of the six different carbon positions k of the alkyl chain was unambiguously determined. The absolute value of the order parameter is plotted in Figure 2 as a function of the position of the carbon atom for the three compositions in the L_α phase at different temperatures; this plot represents the order profile of the alkyl chain. The results in Figure 2 show that an increase of temperature lowers the order of overall alkyl chains throughout in the L_α phase with conformational conversions

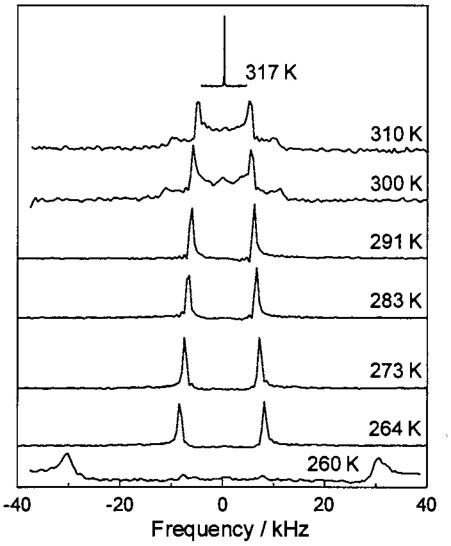

Figure 1. Deuterium NMR spectra of 60 wt% C_{12}-8-d_1-E_3 in water at various temperatures. The splitting of the maxima of the spectra is taken as $\langle \Delta\nu \rangle_{90°}$ in Equation 2. The spectra at 264, 273, 283, and 291 K show the pattern for samples with magnetic field-induced alignment.

from *trans* to *gauche* around the C–C bonds, in agreement with the infrared spectroscopic observations.[6–8]

The order profile given in Figure 2 shows a maximum around C_4 at 270 K, and the maximum shifts toward the alkyl/oxyethylene interface with increasing temperature. The present results are well correlated with a conformational order profile showing a maximum around C_4–C_5–C_6 bonds as deduced by infrared spectroscopy from the population of consecutive *trans* conformations.[6–8] The reduction of the $|S_{CD}|$ values at the positions near the methyl terminal is consistent with a high degree of mobility at the chain terminal due, for the most part, to reduced steric hindrance.

The $|S_{CD}|$ values for the alkyl chain at the positions near the alkyl/oxyethylene interface are larger than those at the positions near the methyl terminal. This is obviously associated with the effect of the adjoining oxyethylene chain. In the hydrophilic layer of the L_α phase, a well-defined hydration structure is formed with the oxyethylene chain favorably incorporated.[14–16] The structuring of the hydrated oxyethylene chain is responsible for restricting the conformational freedom of the alkyl chain near the alkyl/oxyethylene interface.

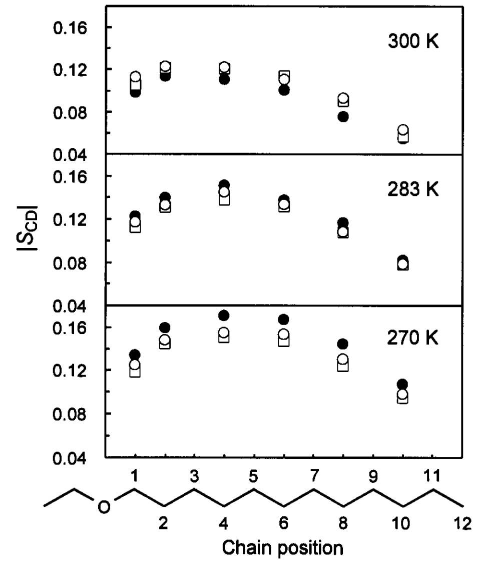

Figure 2. Positional dependence of the absolute value of the order parameter $|S_{CD}|$ for the $C_{12}E_3$–water system in the L_α phase at different temperatures; □: 50 wt%, ○: 60 wt%, and ●: 80 wt%.

The shift of the maximum of the order profile toward the alkyl/oxyethylene interface with increasing temperature is explained as a consequence of the different rates of the reduction in two effects; namely the effect of van der Waals interaction reduces more rapidly than the effect of hydration structuring when the temperature is increased.

With increasing concentration from 60 to 80 wt%, the $|S_{CD}|$ value decreases at 300 K, but it increases at 270 K (Figure 2). This behavior of the order parameter indicates that the alkyl chain in the L_α phase becomes more disordered on approaching the region close to the L_2 phase where the molecules are less ordered than in the L_α phase, whereas it becomes more ordered on approaching the region close to the solid phase where the molecules are more ordered than in the L_α phase. The decrease of the concentration from 60 to 50 wt%, on the other hand, causes no appreciable changes of the $|S_{CD}|$ value at any temperatures. This observation implies that the alkyl chain is not substantially disordered as the concentration approaches the region close to the phase separation into W + L_α or into L_2 + L_α.

The present study has shown that addition of the surfactant in the middle region (60 wt%) of the L_α phase at higher temperatures causes conformational disordering of alkyl chains, leading to a transition to the L_2 phase, while addition of water in the L_α phase causes no substantial disordering of alkyl chains. The observation in the latter process suggests that the water molecules added do not enter much into the hydrophilic oxyethylene layer, but tend to assemble to form regions of water molecules. The expansion of such regions will eventually lead to the phase separation.

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