Deuterium Nuclear Magnetic Resonance Study of Lipophilic Chains in the $C_{12}E_3$/Decane/Water Ternary System

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The order parameters of lipophilic chains in the liquid crystalline phases of the $C_{12}E_3$/decane/water ternary system have been studied by deuterium NMR spectroscopy. The order parameters derived indicate that the decane molecules added to the $C_{12}E_3$/water system penetrate into the lipophilic alkyl layer of the surfactant and make the structure of the lipophilic layer disordered. The lipophilic layers in the reversed hexagonal phase are more disordered than those in the lamellar phase.

Phase behavior of poly(oxyethylene)-type nonionic surfactants in water has been extensively studied.[1–4] Mitchell et al.[5] have examined phase behavior of a number of binary systems of nonionic surfactants, $CH_3(CH_2)_{n-1}(OCH_2CH_2)_mOH$ (abbreviated as C_nE_m) with n = 8–16 and m = 3–12, and water, and have shown that the mesophases observed were the cubic phase of close-packed spherical micelles (I_1), normal hexagonal phase (H_1), normal bicontinuous cubic phase (V_1), lamellar phase (L_α), and reversed bicontinuous cubic phase (V_2). The ternary systems of C_nE_m/oil/water show different phase behavior.[6,7] Kunieda et al.[6] have reported that the self-organizing structures in the $C_{12}E_3$/decane/water ternary system change with increasing decane concentration from the L_α phase to the oily phase like reversed micellar solution phase (O_m) via the V_2 phase and the reversed hexagonal phase (H_2). In this work, we have studied the order parameters of the lipophilic alkyl chains in the $C_{12}E_3$/decane/water ternary system by deuterium NMR spectroscopy. This is the first report on the measurements of quadrupole splittings in the H_2 phase which is not found in the C_nE_m/water binary systems. In our previous work,[8] we have studied using the same method conformational dynamics of alkyl chains in the $C_{12}E_3$/water binary system.[9]

The quadrupole coupling of the deuterium nucleus with the electric field gradient gives rise to splittings of NMR frequencies. The averaged quadrupole splitting for aliphatic C–D bonds in uniaxial liquid crystalline phases such as L_α and H_2 phases can be given by

$$\langle\Delta\nu\rangle = S_{CD}\delta(3\cos^2\alpha - 1)\cdot(1/2)(3\cos^2\beta - 1), \qquad (1)$$

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 magnetic field and the phase axis (the normal of the uniaxial phase surface), β is the angle between the phase axis and the normal of the hydrophobic/hydrophilic interface with a value of 0° for the L_α phase or 90° for the H_2 phase, and S_{CD} is a time-averaged parameter called the order parameter of the C–D bond being given by (1/2) $\langle 3\cos^2\gamma - 1\rangle$ with the angle γ between the normal of the hydrophobic/hydrophilic interface and the principal axis of the electric field gradient tensor, i.e., the C–D bond direction.[10,11] The order parameter S_{CD} thus is a measure of the time-averaged orientation of the C–D bond with respect to the normal of the hydrophobic/hydrophilic interface. The absolute value of the order parameter for uniaxial liquid crystalline phases is obtained from the splitting of the maxima, corresponding to α = 90°, of the doublet spectra as

$$|S_{CD}| = |\langle\Delta\nu\rangle_{90°}/\delta\cdot(1/2)(3\cos^2\beta - 1)|. \qquad (2)$$

Alkyl-deuterated sample $CD_3(CD_2)_{10}CH_2(OCH_2CH_2)_3OH$ (C_{12}-d_{23}-E_3) was synthesized by the method reported previously.[12] Perdeuterated decane (decane-d_{22}) was obtained by stirring undeuterated decane with D_2O, NaOH, and Pd/C catalyst at 180 °C in a high pressure vessel for one month.[13] The deuterium NMR measurements were performed on a Matec pulsed spectrometer using the same procedure as in the previous work.[8] The $\pi/2$ pulse width was 3 μs. The deuterium NMR spectra were measured on the $C_{12}E_3$/decane/water ternary system at 298 K at six compositions; the concentration of decane in the system was changed from 0.0 to 20.5 wt%, while the weight fraction of surfactant to water was fixed at 0.6/0.4.

The deuterium NMR spectra of the deuterated dodecyl chain of the surfactant in the C_{12}-d_{23}-E_3/decane/water system at 298 K are shown in Figure 1. The splittings observed for the decane concentrations 0.0–11.2 wt% are associated with the L_α phase, since the same splittings have been observed for the $C_{12}E_3$/water binary system,[8] which corresponds to the decane concentration 0.0 wt% for the present ternary system. The spectra are composed of several quadrupole splittings associated with the deuterium nuclei at different carbon positions in the dodecyl chain. The observed splittings are assigned, as shown in Figure 1, on the basis of the results of the selectively monodeuterated species of $C_{12}E_3$ in the binary system.[8] The quadrupole splittings of the nuclei at the carbon positions 2 to 7 in the dodecyl chain $-O-C_1-C_2-C_3-C_4-\cdots-C_{11}-C_{12}$ are overlapped with one another. With increasing decane concentration, the splittings gradually decrease; those for the carbon positions 2–7 change

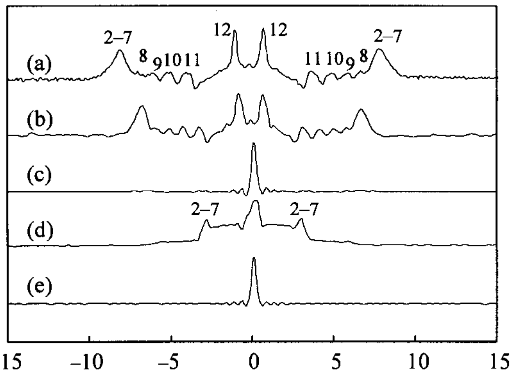

Figure 1. Deuterium NMR spectra of the C_{12}-d_{23}-E_3/decane/water system at 298 K. The splitting of the maxima of the doublet is taken as $\langle\Delta\nu\rangle_{90°}$ in equation 2. The assignments of the splittings to the respective carbon positions in the surfactant dodecyl chain are indicated in the figure. The decane concentrations, in wt%, are (a) 3.8 (L_α), (b) 11.2 (L_α), (c) 16.7 (V_2), (d) 19.4 (H_2), and (e) 20.5 (O_m).

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from 16.1 kHz at 3.8 wt% to 13.4 kHz at 11.2 wt%. At 16.7 wt%, the splittings disappear suddenly and a singlet characteristic of isotropic structure appears. This observation clearly indicates that a phase transition takes place from the L_α phase to the V_2 phase. At 19.4 wt%, the splittings emerge again with a separation of 5.9 kHz, which is nearly half that for the decane concentrations 3.8–11.2 wt%. This spectral change is consistent with a transition from the V_2 phase to the H_2 phase. At 20.5 wt%, the splittings again disappear, in conformity with the transition to the O_m phase at this composition.

The deuterium NMR spectra of decane-d_{22} in the $C_{12}E_3$/decane-d_{22}/water system at 298 K are shown in Figure 2. The quadrupole splittings 4.2 kHz for the decane concentration 3.8 wt% (L_α phase) and 0.6 kHz for 19.4 wt% (H_2 phase) are assigned to the deuterium nuclei at the carbon positions 3–5 in the decane molecule $C_1–C_2–C_3–C_4–C_5–C_{5'}–\cdots–C_{1'}$. These spectral observations indicate that well-defined anisotropic structures of decane are formed in the L_α and H_2 phases. This implies that the decane molecules penetrate into the lipophilic layer of the liquid crystalline phases, in agreement with the result from small-angle X-ray scattering.[6]

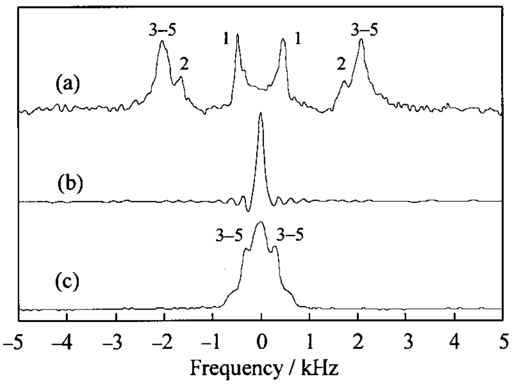

Figure 2. Deuterium NMR spectra of the $C_{12}E_3$/decane-d_{22}/water system at 298 K. The assignments of the splittings to the respective carbon positions in the decane molecule are indicated in the figure. The decane concentrations, in wt%, are (a) 3.8 (L_α), (b) 16.7 (V_2), and (c) 19.4 (H_2).

From the observed quadrupole splittings, the order parameters of the C–D bond, $|S_{CD}|$, at different carbon positions can be evaluated with equation 2. In Figure 3, the absolute values of the order parameters for the dodecyl chain of the $C_{12}E_3$ surfactant and the decane molecule are plotted as a function of the decane concentration in the liquid crystalline phases at 298 K. In the L_α phase, the order parameters for both the surfactant and decane decrease with increasing decane concentration. This shows that the disordering of the lipophilic chains occurs when decane is added to the $C_{12}E_3$/water system. The $|S_{CD}|$ values for the H_2 phase are smaller than those for the L_α phase. The increased disordering of the alkyl chains in the H_2 phase is interpreted to be associated with a high degree of their mobility as a result of the formation of the continuous lipophilic region. The $|S_{CD}|$ values for the H_1 phase of the $C_{12}E_5$/water system, on the other hand, are larger than those for the L_α phase,[14] indicating more ordering of the alkyl chains in the H_1 phase.

On addition of decane molecules to the $C_{12}E_3$/water system, the effective volume of the lipophilic part of one surfactant molecule is increased due to the penetration of the added decane molecules into the lipophilic layer. To minimize the resulting increase in the effective cross-sectional area of one surfactant molecule, the shape of the self-organizing structure changes to the one with a larger packing parameter.[6] Thus the surfactant layer of the self-organizing structure tends to be negative and the sequential phase transitions $L_\alpha–V_2–H_2–O_m$ occur.

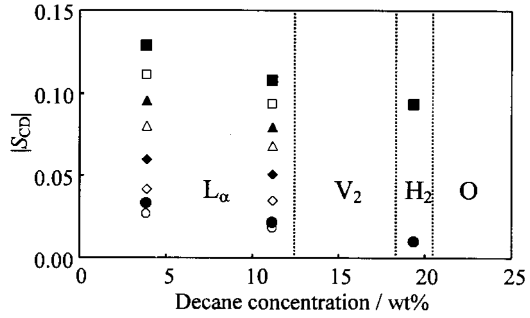

Figure 3. Absolute values of the order parameters, $|S_{CD}|$, for the $C_{12}E_3$/decane/water system at 298 K with different decane concentrations. The carbon positions in the surfactant dodecyl chain are: ■, 2–7; □, 8; ▲, 9; △, 10; ◆, 11; ◇, 12, and the carbon positions in the decane molecule are: ○, 2; ●, 3–5.

Figure 3 shows that the $|S_{CD}|$ values for the carbon positions 2–7 in the dodecyl chain of the surfactant are much larger than the values for the corresponding positions (2 and 3–5) in the decane molecule. This is obviously associated with an effect of the adjoining hydrophilic oxyethylene chain of the surfactant, in that this effect restricts the conformational freedom of the alkyl chain of the surfactant. Decane molecules, on the other hand, can move relatively freely between the lipophilic layers as far as they preserve the anisotropic structures in the liquid crystalline phases.

In conclusion, the present deuterium NMR spectroscopic study has clarified that the decane molecules added to the $C_{12}E_3$/water system penetrate into the lipophilic alkyl layer of the surfactant and make the structure of the lipophilic layer disordered. To minimize the increase in the effective cross-sectional area of the surfactant molecule with addition of decane, the curvature of the surfactant layer tends to be negative and the sequential phase transitions $L_\alpha–V_2–H_2–O_m$ occur. The lipophilic layers in the H_2 phase have been confirmed to be more disordered than those in the L_α phase.

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