# Conformational Transformation of Nonionic Surfactants $\alpha$-Decyl-$\omega$-hydroxyoligo(oxyethylene)s ($C_{10}E_m$) in the Solid State with Addition of Water

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(Received December 25, 2000; CL-001152)

Conformational transformation of nonionic surfactants $H(CH_2)_{10}(OCH_2CH_2)_mOH$ ($C_{10}E_m$) ($m$ = 6 and 7) in the solid state with addition of water was studied at –20 °C by IR spectroscopy. For $C_{10}E_7$, the conformation of the alkyl part adjacent to the oxyethylene chain transforms from *trans* to *gauche* with addition of water at about 90 wt% of surfactant. No conformational transformation was observed for $C_{10}E_6$ with addition of water.

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Phase behavior of binary systems of nonionic surfactants $H(CH_2)_n(OCH_2CH_2)_mOH$ (abbreviated as $C_nE_m$) and water has been extensively studied, since the physicochemical properties of these systems with different hydrophile–lipophile balance are governed by their phase structures.[1,2] The structures of anhydrous $C_nE_m$ compounds in the solid state have also been studied systematically by paying attention, in particular, to their dependence on the lengths of alkyl and oxyethylene chains.[3–7] For the $C_nE_m$ compounds with $n \geq 5$, the conformational transition takes place at $m$ = 3–4 from the highly extended $\gamma$ form to the extended/helical diblock $\beta$ form as the number of oxyethylene units increases. These conformational forms for $C_{10}E_m$ are schematically shown in Figure 1. The $\gamma$ form is an all-*trans* conformation except for the terminal $OCH_2–CH_2OH$ part in the *gauche* conformation. The $\beta$ form is a combination of an all-*trans* planar conformation of the alkyl chain except for the $CH_2CH_2–CH_2O$ part in the *gauche* conformation and a helical conformation of the oxyethylene chain with the *trans–gauche–trans* conformation for the successive $O–CH_2–CH_2–O$ bonds. Interestingly, the $\alpha$ form, which is a simple combination of the planar alkyl chain and the helical oxyethylene chain, was found only for the $C_nE_7$ compounds.[6,7] Although the phase behavior of the $C_nE_m$–water systems is reflected by the conformational state of the surfactant molecules, no special attention has been paid to this in previous studies.[8–14] In this work, we have measured the IR spectra of binary systems of $C_{10}E_m$ ($m$ = 6 and 7) and water in the solid state and examined the conformational changes of the surfactant molecules with addition of water.

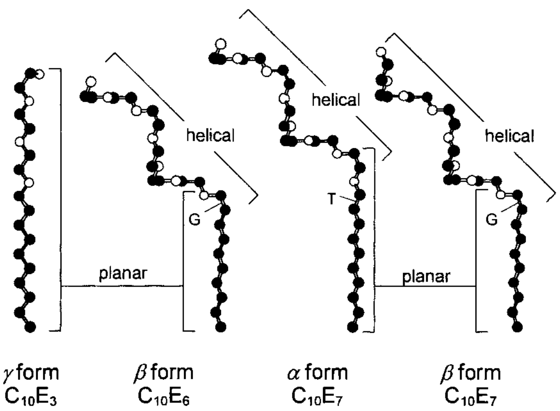

**Figure 1.** Skeletal conformational forms of $C_{10}E_m$ molecules. Black balls represent carbon atoms and white balls represent oxygen atoms. G and T denote the *gauche* and *trans* conformations, respectively.

$C_{10}E_6$ and $C_{10}E_7$ were supplied by Nikko Chemicals and were purified by vacuum distillation before preparing aqueous samples. The IR spectra of the binary systems of $C_{10}E_m$ and water in the solid state were measured at –20 °C by using an IR cryostat cell equipped with a Peltier cooling unit. The spectra were recorded on a JASCO FT/IR-620 Fourier transform spectrometer with a spectral resolution of 2 $cm^{-1}$. Normal coordinate calculations were performed to establish the conformational forms of the $C_{10}E_m$ compounds by using the MVIB program.[15]

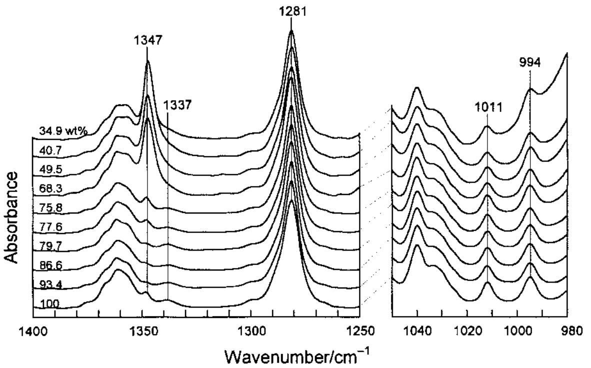

**Figure 2.** IR spectra of the $C_{10}E_6$–water system in the solid state at –20 °C. The compositions of the binary system are indicated in wt% of $C_{10}E_6$.

The IR spectra of the $C_{10}E_6$–water system at –20 °C with various concentrations are shown in Figure 2. As the anhydrous $C_{10}E_6$ molecule assumes the $\beta$ form,[5,6] the bands in the spectra of 100 wt% are all associated with this form. The bands at 1347 and 1281 $cm^{-1}$ are assigned to the $CH_2$ wagging and $CH_2$ twisting modes, respectively, of the helical oxyethylene part, and the wavenumbers of these bands depend on the length of the helical structure of the oxyethylene part.[16] According to normal coordinate calculations, the wavenumbers 1347 and 1281 $cm^{-1}$ are correlated to the (*trans–gauche–trans*)$_7$ conformation of the helical oxyethylene chain with a succession of six $O–CH_2–CH_2–O$ units and a $CH_2–CH_2–CH_2–O$ unit adjacent to the oxyethylene part. The bands at 1338, 1011, and 994 $cm^{-1}$ are assigned to the $CH_3(CH_2)_9O$ part with the (*trans*)$_7$–*gauche* conformation. The intensities of all of the bands observed, except for the band at 1347 cm$^{-1}$, are substantially independent of the water content. Accordingly, the $C_{10}E_6$ molecule retains the $\beta$ form in the studied concentration region 100–30 wt%. The observed intensity change of the 1347 cm$^{-1}$ band, which is assigned to the $a_2$ vibration with dipole moment changes parallel to the helix axis of the oxyethylene chain,[16] can be explained by the different orientations of surfactant molecules with respect to the surface of the IR cell windows.[17]

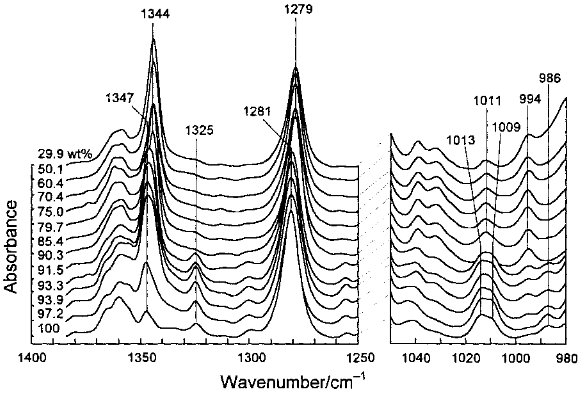

**Figure 3.** IR spectra of the $C_{10}E_7$–water system in the solid state at –20 °C. The compositions of the binary system are indicated in wt% of $C_{10}E_7$.

Figure 3 shows the IR spectra of the $C_{10}E_7$–water system at –20 °C. Sharp spectral changes are observed at about 90 wt%, suggesting a conformational transformation at this concentration. According to normal coordinate calculations, the bands at 1325, 1013, 1009, and 986 cm$^{-1}$ observed in the concentration region 100–90 wt% are assigned to the $CH_3(CH_2)_9O$ part with the $(trans)_8$ conformation. The bands at 1347 and 1281 cm$^{-1}$ in the same concentration region are associated with a succession of seven O–$CH_2$–$CH_2$–O units with the (*trans–gauche–trans*)$_7$ conformation. The fact that the wavenumbers 1347 and 1281 cm$^{-1}$ for $C_{10}E_7$ coincide with the wavenumbers of the bands for $C_{10}E_6$ indicates that the lengths of the helical structures in the $C_{10}E_6$ and $C_{10}E_7$ molecules are the same. These considerations lead to the *a* form as the molecular form of $C_{10}E_7$ in the concentration region above 90 wt%, in agreement with this same molecular form of anhydrous $C_{10}E_7$ established previously.[5,6]

Interesting spectral features are observed for $C_{10}E_7$ in the concentration region below 90 wt%. The bands at 1013, 1009, and 986 cm$^{-1}$ due to the $\alpha$ form observed above 90 wt% disappear, and new bands emerge at 1011 and 994 cm$^{-1}$. The wavenumbers of these bands are the same as those observed for $C_{10}E_6$. Also, the bands observed above 90 wt% at 1347 and 1281 cm$^{-1}$ shift to lower wavenumbers, 1344 and 1279 cm$^{-1}$, respectively, when the concentration is decreased to below 90 wt%. Normal coordinate calculations show that these lower-wavenumber shifts are explained by the elongated helical structure with the (*trans–gauche–trans*)$_8$ conformation, composed of a succession of seven O–$CH_2$–$CH_2$–O units of the oxyethylene chain and an adjacent $CH_2$–$CH_2$–$CH_2$–O part. These conformational characteristics ensure that the molecular form of $C_{10}E_7$ in the concentration region below 90 wt% is the $\beta$ form. It is concluded therefore that the conformation of the $C_{10}E_7$ molecule transforms from the $\alpha$ form to the $\beta$ form with addition of water at about 90 wt% of $C_{10}E_7$. The molecular forms of $C_{10}E_m$ ($m$ = 6 and 7) in the solid $C_{10}E_m$–water systems are summarized in Table 1.

**Table 1.** Molecular forms of $C_{10}E_m$ ($m$ = 6 and 7) in the $C_{10}E_m$–water systems in the solid state at –20 °C

| $C_{10}E_6$ | $C_{10}E_7$ (> ca. 90 wt%) | $C_{10}E_7$ (< ca. 90 wt%) |
|---|---|---|
| $\beta$ form | $\alpha$ form | $\beta$ form |

The previous experimental findings that the $CH_2CH_2$–$CH_2O$ bonds in alkyl ethers assume the *gauche* conformation in the solid state in most cases[18] imply that the $\beta$ form of $C_nE_m$ molecules is more stable than the $\alpha$ form. The stability of the $\alpha$ form of $C_{10}E_7$ in the concentration region above 90 wt% is ascribed in part to the relevant molecular packing requirement in crystals. The conformational transformation of the $C_{10}E_7$ molecule from the $\alpha$ form to the $\beta$ form with addition of water is explained by the relaxation of crystal lattice caused by the penetration of water molecules in the oxyethylene moiety. The transformation concentration, 90 wt%, corresponds to approximately three water molecules per $C_{10}E_7$ molecule, which are responsible for the crystal lattice relaxation. The conformational change observed in this work for the $C_{10}E_7$–water system indicates the presence of a phase boundary, which has not been known, at concentration of about 90 wt% in the solid state.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 10640492 from the Ministry of Education, Science, Sports, and Culture, Japan.

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