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Conformational Competition between *n*-Alkyl and Oxyethylene Chains in Nonionic Surfactants in the Solid State.
A Raman Spectroscopic Study

Koichi FUKUHARA and Hiroatsu MATSUURA*
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Naka-ku, Hiroshima 730

Raman spectra of 23 nonionic surfactants $CH_3(CH_2)_{n-1}(OCH_2CH_2)_m$-OH were measured in the solid state. The molecular conformation of these compounds was elucidated on the basis of the conformational competition between the *n*-alkyl chain which intrinsically favors the extended structure and the oxyethylene chain which favors the helical structure.

Homogeneous polymers and oligomers are known to have their characteristic conformations in various states of aggregation.[1,2] *n*-Alkane and polyethylene molecules take an all-*trans* extended conformation in the solid state and this conformation is also the most stable in the liquid state. Poly(oxyethylene) $(-OCH_2CH_2-)_m$, on the other hand, is one of the typical polymers that take a helical conformation in the solid state. In this molecular structure, the successive $O-CH_2-CH_2-(O)$ bond axes are in the *trans-gauche-trans* conformation.[3] The molecular conformation of α-*n*-alkyl-ω-hydroxyoligo(oxyethylene)'s, CH_3-$(CH_2)_{n-1}(OCH_2CH_2)_mOH$ (to be abbreviated as C_nE_m), is an interesting subject to study, because these molecules consist of the *n*-alkyl and oxyethylene chains which present, from a conformational standpoint, a striking contrast to each other.

In the course of our systematic study on conformational morphology of nonionic surfactants, we have investigated the conformation of C_nE_m molecules in the solid state by Raman spectroscopy and have reported the preliminary results on some of the compounds.[4,5] In the present work, we have studied the molecular conformation of 23 C_nE_m surfactants with the specified single chain length: n=6, 8, 10, 12, and 16 and m=1–8. Most of the materials were supplied by Tokyo Kasei Kogyo Co., Sigma Chemical Co., and Nikko Chemicals Co., while C_8E_1, C_8E_2, $C_{10}E_1$, and $C_{10}E_2$ were prepared in our laboratory. The Raman spectra of these surfactants were measured in the crystalline solid state at liquid nitrogen temperature. The spectra of the $C_{10}E_m$ series are shown in Fig. 1 for an illustrative purpose. The molecular conformation of the C_nE_m surfactants in the solid state was determined by the spectral analysis based on (1) the accordion vibration[6,7] to estimate an overall conformational state of the molecule, (2) the conformation–spectrum correlations[8] to determine local conformations, and (3) normal coordinate treatment to ascertain the accurate conformation. Detailed procedure of the conformation determination will be reported elsewhere,[9)] but an outline is mentioned below for the $C_{10}E_m$ compounds.

Figure 1 shows that the spectra of $C_{10}E_1$, $C_{10}E_2$, and $C_{10}E_3$ exhibit prominent Raman bands at 176, 155, and 136 cm^{-1}, respectively, which are assigned, on the basis of the results of *n*-alkanes,[10)] to the accordion vibration of the extended planar structure consisting of 14, 16, and 19 backbone atoms. The $C_{10}E_1$ spectrum also shows a shoulder at 183 cm^{-1}, assignable to the accordion vibration of the extended structure of 13 backbone atoms. The strong bands at about 1500 cm^{-1} for $C_{10}E_2$ and $C_{10}E_3$ are due to the OCH_2–CH_2O group in the *trans* conformation, in conformity with a similar band for solid 18-crown-6 containing the same conformational segment.[11)] These findings lead to coexisting molecular conformations of the γ and γ_T forms for $C_{10}E_1$ and a conformation of the γ form for $C_{10}E_2$ and $C_{10}E_3$ (for the molecular forms, see Fig. 2). The spectra of $C_{10}E_4$, $C_{10}E_6$, and $C_{10}E_8$ are similar to one another. The bands at 289–295 cm^{-1} are associated with the helical structure of the oxyethylene chain and the bands in the region below 250 cm^{-1} are consistent only with the CH_2–CH_2–CH_2–O group in the *trans-gauche-trans* conformation. These observations lead to a molecular conformation of the β form with helix dominative structure. The molecular conformations determined for the 23 C_nE_m surfactants are summarized in Table 1.

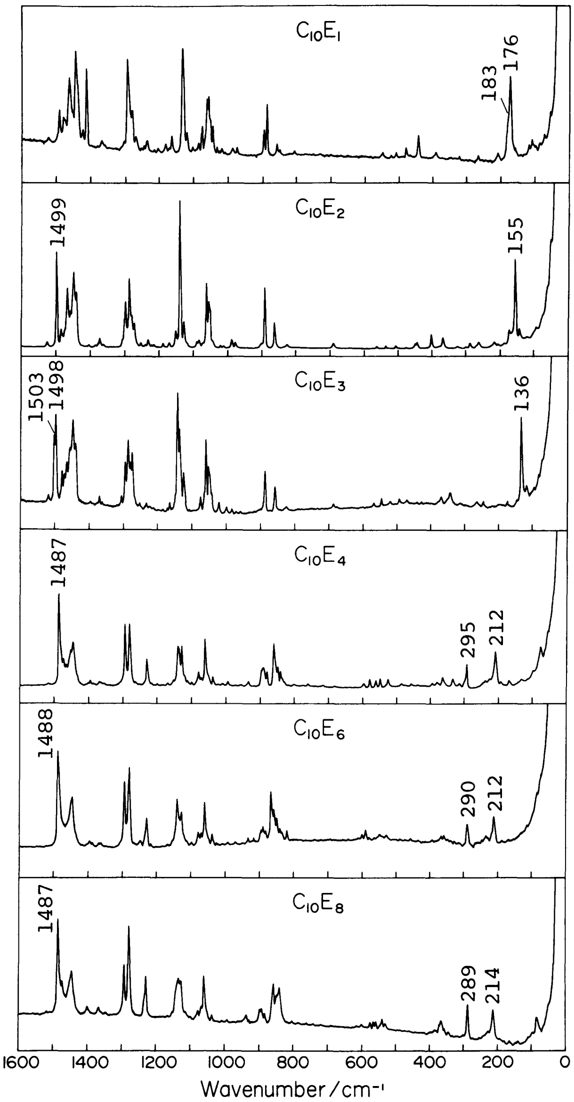

Fig. 1. Raman spectra of $C_{10}E_1$ (γ+γ_T), $C_{10}E_2$ (γ), $C_{10}E_3$ (γ), $C_{10}E_4$ (β), $C_{10}E_6$ (β), and $C_{10}E_8$ (β) in the solid state.

We have found four conformational forms, i.e., the α, β, γ, and γ_T forms, for the solid C_nE_m compounds. These conformational forms are schematically shown in Fig. 2. The α form is a simple combination of an extended zigzag conformation of the alkyl chain and a helical conformation of the oxyethylene chain similar to the 7_2 helix (seven units of OCH_2CH_2 and two helical turns per fiber period) of poly(oxyethylene).[3)] For the β form, part of the alkyl chain at the joining sec-

Table 1. Conformational Forms of the C_nE_m Surfactants in the Solid State

n	m							
	1[a]	2	3	4	5	6	7	8
6	$\gamma+\gamma_T$	γ						
8	$\gamma+\gamma_T$	γ	γ[b], β[c]	β				
10	$\gamma+\gamma_T$	γ	γ	β		β		β
12	$\gamma+\gamma_T$	γ	γ[b], β[c]	β	β	β	α	β
16				β		β		β

a) $\gamma+\gamma_T$ implies that both the γ and γ_T forms coexist in the crystal.
b) Rapid cooling of the liquid. c) Slow cooling of the liquid.

tion to the oxyethylene chain is incorporated into the helical structure of the oxyethylene chain. The incorporated CH_2–CH_2–CH_2–(O) group with the *trans-gauche-trans* conformation corresponds to one unit of the oxyethylene group O–CH_2–CH_2–(O) with the same conformation. The γ form takes a highly extended conformation; the oxyethylene chain is involved, together with the whole alkyl chain, in forming the extended zigzag structure of the molecule.

Table 1 indicates that, as the number of oxyethylene units (m) is increased, the molecular conformation of the C_nE_m compounds changes from the highly extended γ form to the helix dominative β form. This conformational transition occurs around m=3, irrespective of the chain length of the alkyl group. The compounds of C_8E_3 and $C_{12}E_3$ crystallize in fact into either the γ form or the β form depending on the solidification conditions; the rapid cooling of the liquid (with less than 3 min to reach near liquid nitrogen temperature) gives the former, while the slow cooling (with more than 30 min to crystallize completely) gives the latter. These results strongly suggest that four or more oxyethylene units are necessary for establishing the stable helical structure in the C_nE_m molecule. It is important to note that the chain length of four oxyethylene units is practically coin-

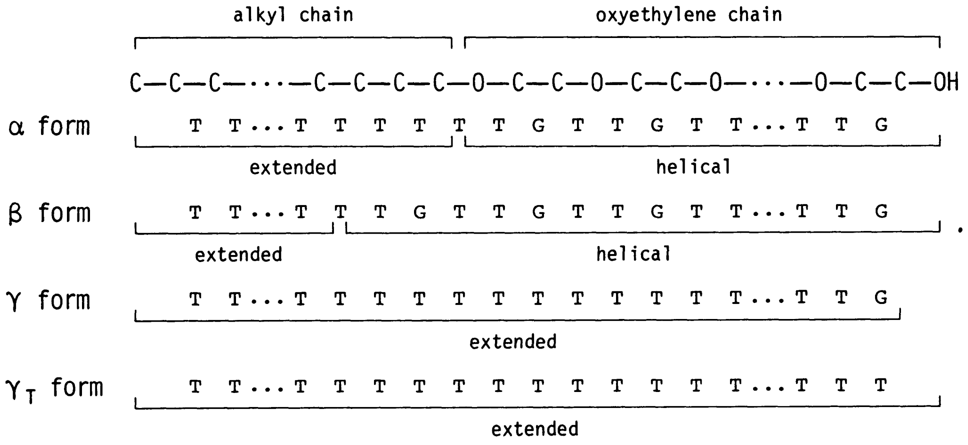

Fig. 2. Schematic representation of the conformational forms of the C_nE_m surfactants. T: *trans*; G: *gauche*.

cident with 3.5 OCH_2CH_2 units per turn of the 7_2 helix of poly(oxyethylene).[3)] This implies that the first full turn is required for stabilizing the helical structure of the oxyethylene chain, when a long alkyl chain is linked to the oxyethylene. The helical nature of the oxyethylene chain, once formed, seems to be influential enough to induce the helix incorporation of the adjoining alkyl chain, as revealed for the β form. The helical conformation of the oxyethylene chain is propagated into the alkyl chain, bringing the conformation of the nearest CH_2–CH_2–CH_2–(O) part into *trans-gauche-trans*, which is now part of the helical structure with the repeated *trans-gauche-trans* conformation. It is worth while to note that this helix incorporation of the alkyl chain does not extend further beyond this point, even if the oxyethylene chain is lengthened up to eight OCH_2CH_2 units (see Table 1). The molecule of $C_{12}E_7$ takes the α form rather than the β form; we refrain from further discussion by the lack of additional evidence to characterize this conformational behavior.

If the oxyethylene part is not sufficiently long ($m \lesssim 3$), the conformation of this part is governed by the dominating alkyl group, and in consequence the oxyethylene chain is joined with the alkyl chain to develope more extensive zigzag structure of the γ form. The influence of the extended conformation of the alkyl chain on the oxyethylene chain is estimated to be rather strong, as this conformation is propagated all the way through the oxyethylene chain but the terminal OCH_2CH_2OH part, although the number of oxyethylene units is limited to at most three. As noted before, if the oxyethylene chain is longer than this, the preferred molecular conformation is determined by the more dominative moiety of the oxyethylene.

The conformational behavior of the C_nE_m surfactants, as summarized in Table 1, has been elucidated on the basis of the conformational competition between the *n*-alkyl and oxyethylene chains with their distinctive conformational characters. The force relevant to the conformational competition may be intramolecular as well as intermolecular by origin, but further experimental studies are necessary for revealing the origin. The conformational competition, as established for a series of *n*-alkyloligo(oxyethylene) surfactants, is most likely one of the basic conformational features of block copolymers and may also be accountable for some aspects of conformational morphology of biological chain molecules.

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