CHEMISTRY LETTERS, pp. 933 - 936, 1984.

RAMAN SPECTROSCOPIC STUDY OF NONIONIC SURFACTANTS. MOLECULAR CONFORMATIONS OF TRI- THROUGH OCTAETHYLENE GLYCOL MONODODECYL ETHERS IN THE SOLID STATE

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Raman spectra of $n\text{-C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_m\text{OH}$ with m=3–8 were measured in the solid state. Molecular conformations of these surfactants were examined by utilizing normal coordinate treatment; the conformation of the oxyethylene chain is fundamentally identical with the helical structure of poly(oxyethylene).

Surface activities of surfactants are closely related to their micellar structures and many attempts have been made to reveal the micellar shape by means of various experimental methods.$^{1)}$ Structures of nonionic surfactants have been studied by Kalyanasundaram and Thomas$^{2)}$ and Cooney et al.$^{3)}$ by a Raman spectroscopic method. Some ambiguities are, however, noticed in their spectral interpretations made primarily on an empirical basis. The conclusions drawn are further devalued by their use of polydisperse materials with heterogeneous chain-length distribution. This state of knowledge has prompted us to undertake a systematic investigation on molecular conformations of nonionic surfactants by Raman and infrared spectroscopic methods in combination with normal coordinate calculations. In this letter, the first report of the study, we deal with molecular conformations in the solid state of a series of nonionic surfactants with specified single chain lengths, tri- through octaethylene glycol monododecyl ethers, namely $n\text{-C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_m\text{OH}$ with m=3–8. Although we are eventually interested in molecular conformations of the surfactants in solution, it seems more sensible to start with establishing well-defined conformations in the solid state, since the molecular forms in this state may also be fundamental in solution.

The nonionic surfactants employed in this study, $n\text{-C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_m\text{OH}$, which will be represented by C_{12}E_m, were supplied by Nikko Chemicals Co., Ltd. and were distilled in vacuum prior to the spectroscopic measurements. The Raman spectra of these surfactants, shown in Fig. 1, were measured in the solid state at liquid nitrogen temperature. It is noted that only for C_{12}E_3 two solids giving different spectral features were obtained: one (Type I) obtained by cooling the liquid substance rapidly and the other (Type II) by cooling slowly. The solid of Type I is less stable and is transformed into Type II on annealing.

In the analysis of the observed spectra, attention was paid to the low-wavenumber vibrations associated with deformations of the molecular skeleton, since their wavenumbers are sensitive to the molecular conformation. A look at the spectra in sequence readily points out that the spectrum of rapidly cooled $C_{12}E_3$ (Type I) differs significantly from the rest of them which exhibit rather similar features to one another. For $C_{12}E_3$ (Type I), a dominant band is observed at 126 cm^{-1}, which is most likely assigned to the accordion-like vibration of the planar zigzag part of the molecule. This wavenumber is close to 132 cm^{-1} observed for n-$C_{18}H_{38}$,[4)] suggesting that $C_{12}E_3$ (Type I) has a planar part consisting of approximately 18 backbone atoms (C and O); one of the most plausible chain conformations is $\mathrm{C{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}O\overset{T}{-}C\overset{T}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C{-}OH}$, where T and G denote trans and gauche, respectively. For this molecular form, the terminal O–C–C–O group and the one next to the terminal group retain the basic TGT conformation of poly(oxyethylene),[5)] but the O–C–C–O group adjacent to the n-$C_{12}H_{25}$ group is joined with this alkyl group to form a longer planar zigzag structure. This conformation model will be called γ form. To confirm the molecular conformation, normal coordinate treatment was carried out on this and other possible models by making use of the force constants previously evaluated[6)] with some improvement of their values. The calculated results, as given in Table 1, strongly support the above-mentioned conformation (γ form) for $C_{12}E_3$ (Type I). The atomic displacements in the vibration of 126 cm^{-1} (calculated wavenumber: 127 cm^{-1}) are illustrated in Fig. 2, together with those for other vibrations. A minor peak at 114 cm^{-1} is also attributed to the accordion-like vibration, in which a phase relation of the accompanying out-of-plane displacements to the in-plane displacements is different from that in the 126 cm^{-1} vibration.

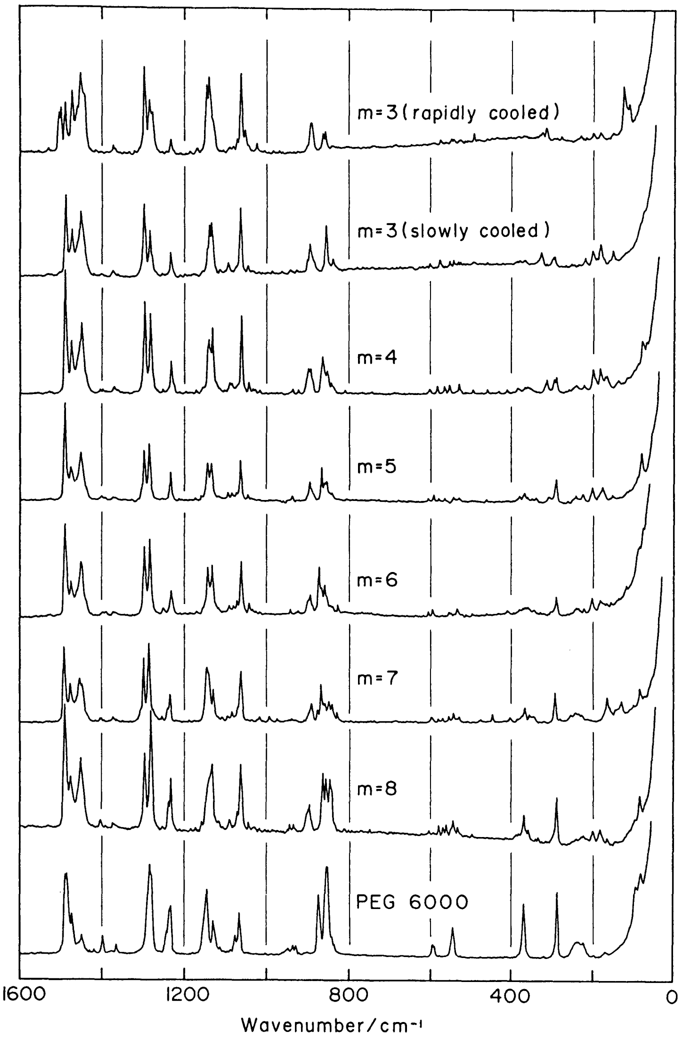

Fig. 1. Raman spectra of n-$C_{12}H_{25}(OCH_2CH_2)_mOH$ and PEG 6000 in the solid state.

For slowly cooled $C_{12}E_3$ (Type II), on the other hand, several bands with similar intensities are observed at 150–220 cm^{-1}, in place of the dominant band at 126 cm^{-1} for Type I. These bands are suggested to be associated with split components of the accordion-like vibrations as coupled with other skeletal deformations. The normal coordinate calculation clarified that the observed wavenumbers and inten-

Table 1. Molecular conformations and observed and calculated wavenumbers of the accordion-like vibrations for n-$C_{12}H_{25}(OCH_2CH_2)_mOH$ in the solid state

Surfactant	Molecular conformation	$\tilde{\nu}_{obsd}/cm^{-1}$	$\tilde{\nu}_{calcd}/cm^{-1}$ α form	β form	γ form
$C_{12}E_3$ (rapidly cooled)	γ form	126 114	153 140 127	198 177 173 159	127 124
$C_{12}E_3$ (slowly cooled)	β form	201 183 175 152			
$C_{12}E_4$	β form	200 183 167	162 144 139	199 179 173 169	125 119
$C_{12}E_5$	β form	200 182 175 152	151 141	195 183 174 172 156	132 125 118
$C_{12}E_6$	β form	201 181 165 155	159 145 140 129	196 177 173 164	127 124
$C_{12}E_7$	α form (tentative)	165 143 128	151 142 126	197 179 173 170 154	135 125 116
$C_{12}E_8$	β form	197 180 162	157 145 140 123	197 174 172 161	131 125 121 115

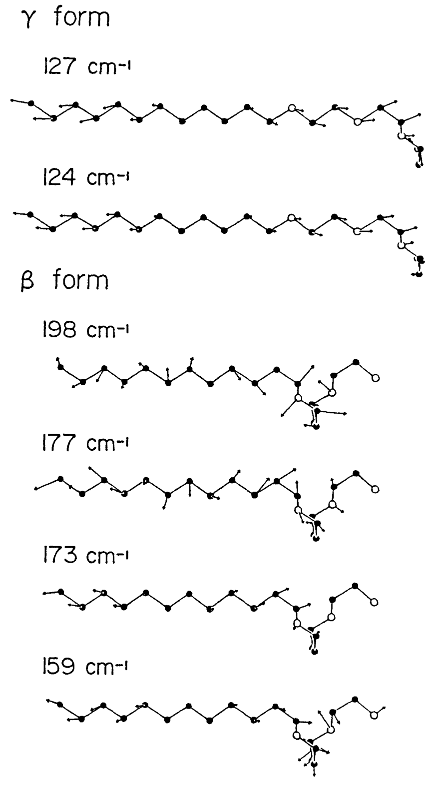

Fig. 2. Atomic displacements in the accordion-like vibrations for n-$C_{12}H_{25}(OCH_2CH_2)_3OH$.

sities for these bands are consistent with the chain conformation, to be called β form, $\mathrm{C{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C{-}OH}$. For this molecular form, all of the C–C bond axes in the n-$C_{12}H_{25}$ group are in the trans conformation with the exceptional gauche CC–CO axis adjacent to the oxyethylene chain, leading to a shorter planar part in the molecule than in Type I. The atomic displacements in the vibrations of 201, 183, 175, and 152 cm^{-1} (calculated wavenumbers: 198, 177, 173, and 159 cm^{-1}) (Fig. 2) are, in fact, distorted significantly from a typical accordion-like vibration, in conformity with the diminished Raman intensities. The third molecular conformation, α form, is deserved considering; this is just a primitive combination of the alkyl and the oxyethylene chains in keeping with their original basic conformations, namely fully planar zigzag for the former and TGT-helical for the latter. However, the spectral feature of neither Type I nor Type II of $C_{12}E_3$ is explained by the α form. The α form is accountable for the conformation of $C_{12}E_1$ (to be reported elsewhere). The three molecular conformations, the α, β, and γ forms, of nonionic surfactants n-$C_nH_{2n+1}(OCH_2CH_2)_mOH$ proposed in this study are schematically shown in Fig. 3.

The spectral feature of $C_{12}E_4$, $C_{12}E_5$, $C_{12}E_6$, and $C_{12}E_8$ in the 150–200 cm^{-1} region resembles that of slowly cooled $C_{12}E_3$ (Type II) which has been shown to take the β form. The normal coordinate analysis indeed revealed that the molecular conformations of these surfactants are the β form (Table 1). In the spectra of $C_{12}E_3$ (Type II) through $C_{12}E_8$, a distinct band is noticed around 300 cm^{-1}, which eventually coincides with the well-defined band of poly(ethylene glycol) (PEG 6000)

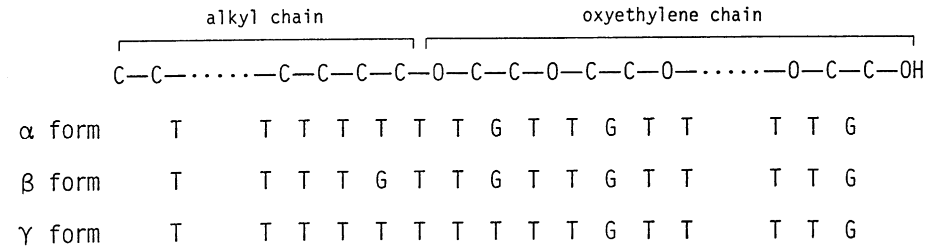

Fig. 3. Molecular conformations of nonionic surfactants n-$C_nH_{2n+1}(OCH_2CH_2)_mOH$ in the solid state.

at 285 cm^{-1} (at liquid nitrogen temperature). This vibration is associated with transverse chain swelling and contracting,[7)] giving rise to considerable Raman intensity, and its wavenumber depends to some extent on the chain length. Accordingly, this Raman band may be used as a measure of helicity of the oxyethylene chain.

The Raman spectrum of $C_{12}E_7$ in the region below 200 cm^{-1} is different from the spectra of $C_{12}E_3$ (Type II) through $C_{12}E_6$ and $C_{12}E_8$; the feature at 170–200 cm^{-1} is missing and appears to be shifted down to 130–165 cm^{-1}. Thus, $C_{12}E_7$ is suggested to have a peculiar conformation. The normal coordinate calculation indicates that the observed spectrum is best explained by the α form among the three (Table 1).

The present study has clarified that there are at least three stable conformations, the α, β, and γ forms, for n-$C_{12}H_{25}(OCH_2CH_2)_mOH$-type surfactants. It is noteworthy that these conformations are fundamentally identical with the basic conformations of n-alkanes (planar zigzag) for the alkyl part and of poly(oxyethylene) (helical) for the oxyethylene part and, for the β and γ forms, only the conformation of the adjoining section to the other part is converted from the respective basic form. These findings suggest that these structures are important in solution as well and the conformational flexibility at the adjoining section may be one of the principal factors for determining the micellar structure.

The conformation of the oxyethylene chain in the solid state has been studied by Rösch.[8)] He interpreted his X-ray diffraction data of polydisperse materials by considering the zigzag and meander models, and claimed that the former conformation of the oxyethylene chain was transformed into the latter with the increase of the averaged chain length. The meander conformation with large steric hindrance is, however, unacceptable in view of the rotational isomeric state. The present work has explicitly shown that the oxyethylene chain of nonionic surfactants takes for the most part the helical structure in the solid state. The spectral interpretation of nonionic surfactants by Cooney et al.[3)] was based on the assumption that there existed the zigzag, meander, and helical conformations; alternative interpretations are perhaps required in that work.

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(Received March 30, 1984)