isomer relative to the open-chain form. Our results indicate that this does not happen; on the contrary, we found that the ΔE between the lowest-energy isomers of the protonated open-chain and the protonated ring is even greater than the separation between C_{2v} and D_{3h} ozone (48.1 vs 23.2 kcal mol^{-1} at the CCSD level of theory).

The best value for the protonation energy for open-chain ozone in this work is 148 kcal mol^{-1} (CCSDT-1 energy at the CCSD geometry), to be contrasted with the value of 124 kcal mol^{-1} proffered by the early work of Kausch and Schleyer.[41] Extensive search of the experimental literature has failed to reveal a value for the protonation energy of ozone.

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Molecular Conformation of Nonionic Surfactants in the Solid State. A Raman Spectroscopic Study of a Homologous Series of α-*n*-Alkyl-ω-hydroxyoligo(oxyethylene)s

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Abstract: The molecular conformation of a homologous series of nonionic surfactants, α-*n*-alkyl-ω-hydroxyoligo(oxyethylene)s $CH_3(CH_2)_{n-1}(OCH_2CH_2)_mOH$ (C_nE_m) was comprehensively investigated, as the conformational properties are fundamentals of structural and functional aspects of the surfactant systems. Raman spectra of 48 C_nE_m compounds with n = 1–7, 9–11, and 13–16, and m = 1–5 and 7 were measured in the crystalline solid state, and their molecular conformations were determined by a systematic analysis of the spectra. The present results, amalgamated with the previous results for 23 other C_nE_m homologues, show that the molecular conformation of the consecutive C_nE_m surfactants with n = 1–16 and m = 1–8 depends not only on the oxyethylene chain length but also on the alkyl chain length and that there exist at least six distinctive conformational forms. For the compounds with $n \leq 4$, the conformation is basically helical with the predominating oxyethylene chain which intrinsically favors the helical structure. For $n \geq 5$, the molecular conformation greatly depends on the oxyethylene chain length; as the number of oxyethylene units increases, the conformation changes from a highly extended form to a helical/extended diblock form. This conformational transition takes place at m = 3–4. Being coincident with this transition point, C_8E_3, $C_{12}E_3$, and $C_{16}E_3$ crystallize into either the extended form or the diblock form depending on the solidification conditions. The conformational behavior of the C_nE_m compounds is elucidated by a conformational competition between the alkyl and oxyethylene chains whose conformational characters are distinct from each other. The reported thermodynamic quantities of the C_nE_m surfactants are indicative of strong correlations with the conformational behavior of these homologous compounds. The classical model of the meander conformation of the oxyethylene chain is unlikely to exist.

Amphiphilic substances such as surfactants and lipids possess in the same molecule two different types of chemical groups, a hydrophilic group and a hydrophobic group. When these substances are in a medium, some specific interactions are expected to occur between the amphiphilic molecules and the solvent molecules as well as between the amphiphilic molecules and between the solvent molecules. The interactions involved are composed basically of hydrophilic and hydrophobic interactions.[1,2] These interactions are essentially of solvation type and are thereby likely to depend specifically on the structure of the amphiphiles and the solvent molecules. The dual nature of the amphiphilic substances is responsible for these interactions and consequently for the specific surface activity and biological functions.[3,4] These properties of the amphiphiles are thus greatly dependent on the structural aspects of the system. Surfactant and lipid molecules associate, in fact, into a variety of structures in aqueous or nonaqueous solutions. In these systems, conformational properties of the hydrophobic and hydrophilic portions of the amphiphilic molecules are closely related to the geometry of diverse aggregates organized in various macroscopic phases.[5,6] Structural studies of the amphiphilic substances are thus highly challenging in that the knowledge obtained will be eventually correlated with the mechanism of the specific interactions and the functions involved in the biological systems. In spite of this fundamental importance, however, only limited knowledge of the structural problems has in fact been available.

For the purpose of gaining an insight into the structural aspects of amphiphilic systems, we have been working on conformational analyses of fundamental amphiphilic molecules. The substances we have adopted are a series of nonionic surfactants: α-alkyl-ω-hydroxyoligo(oxyethylene)s $R(OCH_2CH_2)_mOH$[7-9] and α-al-

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kylphenyl-ω-hydroxyoligo(oxyethylene)s $RPh(OCH_2CH_2)_mOH$.[10,11] For studying molecular conformations of these nonionic surfactants, we have utilized a vibrational spectroscopic technique that provides plenty of information associated directly with the molecular conformation and its variation with experimental conditions in any state of aggregation (viz., solid, liquid, or gas).[12,13] Hence, the structural information we obtain for one state is applicable immediately to other states in terms of normal vibration frequencies (or wavenumbers), modes of vibrations, force constants, spectral intensities, etc.[14-16]

In a series of our studies on $CH_3(CH_2)_{n-1}(OCH_2CH_2)_mOH$ (C_nE_m), we have focused our attention on the molecular conformation of these compounds in the bulk solid state, since their well-defined rigid conformations are fundamentals of all structural aspects of these surfactant systems. In spite of their substantial importance, no established conformational properties of these surfactants had been available[17,18] until the mid 1980s when we first clarified by Raman spectroscopy the specific molecular conformation of the $C_{12}E_m$ surfactants in the solid state.[7] This preliminary work was followed by more extensive studies on the C_nE_m surfactants with $n = 6$–16 and $m = 1$–8.[8,9] The conformational variation with the chain length has also been examined for a series of triblock compounds $CH_3(CH_2)_{n-1}(OCH_2CH_2)_mO(CH_2)_{n-1}CH_3$,[19] which are composed of a central oxyethylene block and end *n*-alkyl blocks. The conformation and hydration of the oxyethylene chain in aqueous solution have also been studied by Raman spectroscopy and hyper- and ultrasonic techniques.[20-22]

For comprehensive interpretations of the observed vibrational spectra, normal coordinate treatment[23] is a powerful tool, because it provides various vibrational properties which depend on the structure of a molecule. Thus, significant information on the molecular conformation is derived through the normal coordinate analysis from the experimental data of Raman and infrared spectra. The essential physical quantity involved in the normal coordinate analysis is an intramolecular force field or the associated force constants;[15,16] once the relevant force field is established, we can calculate vibrational wavenumbers and modes for any conformational state of the molecule. In light of the fundamental importance of the force constants, we have determined a force field of the oxyethylene chain.[24,25] Making use of the force field derived, we have presented comprehensive conformation–spectrum correlations for the oxyethylene chain.[26] The normal coordinate treatment has been utilized in fact extensively and effectively throughout a series of our conformational studies.

In an earlier Raman spectroscopic study on the C_nE_m surfactants,[9] we have determined the molecular conformation in the solid state for 23 compounds with $n = 6$, 8, 10, 12, and 16 and $m = 1$–8 and shown that the conformation changes from a highly extended form (γ form) to a helix dominative or helical/extended diblock form (β form) as the number of oxyethylene units (m) is increased. In the present work, we have extended the conformational study by Raman spectroscopy of the C_nE_m surfactants in the solid state to an additional 48 homologues which include those with shorter alkyl chains and those with alkyl chains of odd-numbered carbon atoms as well as other homologues previously not adopted, yet of importance. These compounds complete a family of the consecutive C_nE_m surfactants with $n = 1$–16. With a wealth of information available of conformational properties of a total of 71 homologous compounds, we can now discuss comprehensively an overall picture of the conformational aspects of a series of the C_nE_m surfactants in the bulk solid state.

Experimental Section

The materials treated are the following 48 C_nE_m compounds: C_1E_m ($m = 1$ and 3–5), C_2E_m ($m = 3$ and 4), C_3E_m ($m = 3$–5), C_4E_m ($m = 2$–5), C_5E_m ($m = 1$–4), C_6E_m ($m = 3$ and 4), C_7E_m ($m = 1$–4), C_9E_m ($m = 1$–4), $C_{10}E_m$ ($m = 5$ and 7), $C_{11}E_m$ ($m = 1$–4), $C_{13}E_m$ ($m = 2$–4), $C_{14}E_m$ ($m = 1$–4), $C_{15}E_m$ ($m = 2$–4), and $C_{16}E_m$ ($m = 1$–3, 5, and 7). Twenty-two of these were commercially supplied by Tokyo Kasei Kogyo Co. (C_1E_1, C_1E_3, C_2E_3, C_4E_2, and C_4E_3), Kanto Chemical Co. (C_1E_4), Aldrich Chemical Co. (C_1E_5), Sigma Chemical Co. (C_5E_2 and C_6E_3), Bachem AG (C_5E_3 and C_7E_3), and Nikko Chemicals Co. ($C_{10}E_5$, $C_{10}E_7$, $C_{14}E_1$–$C_{14}E_4$, $C_{16}E_1$–$C_{16}E_3$, $C_{16}E_5$, and $C_{16}E_7$). These commercial products were purified by vacuum distillation before the spectroscopic measurements. The other C_nE_m compounds were synthesized in our laboratories. Most of these were prepared by the conventional Williamson ether synthesis, but the homologues of C_2E_4, C_3E_4, C_3E_5, C_4E_4, C_4E_5, C_5E_4, $C_{13}E_2$, and $C_{15}E_2$ were prepared by an improved method of the Williamson synthesis using a phase-transfer catalyst of tetrabutylammonium hydrogensulfate.[27,28] Purity of the synthesized C_nE_m substances was checked by gas chromatography and ^1H NMR.

The Raman spectra of the C_nE_m compounds were measured in the solid state at liquid nitrogen temperature. The crystalline solid was obtained by cooling the liquid substance with liquid nitrogen. The materials which are solid at room temperature were once melted before cooling. The crystallization was performed in two ways; one is rapid cooling with less than 3 min to reach near liquid nitrogen temperature and the other is slow cooling with more than 30 min to reach that temperature. In the latter case, the solidified substance was annealed by warming up to temperature slightly below the melting point and by keeping around this temperature for more than 1 h and was subsequently cooled again down to liquid nitrogen temperature. Of the C_nE_m compounds treated in the present work, a few homologues gave, depending on the solidification conditions, two types of Raman spectra with distinguishing features. The Raman spectra were recorded on a JEOL JRS-400D spectrophotometer equipped with a Hamamatsu R649 photomultiplier, by using 514.5- and 488.0-nm lines of an NEC GLG3200 argon ion laser. A bandpass filter was used to eliminate the laser plasma emission. The neon emission spectrum was utilized for calibration of the Raman spectra observed.

Normal Coordinate Calculations

Normal coordinate calculations were performed on all of the C_nE_m compounds treated in the present work. The calculations were made on most of the possible conformations for each of the molecules consisting of the trans, gauche, and gauche′ conformations around each of the possible internal rotation bond axes.[29] In these calculations, the internal rotation angles were assumed to be 180° for trans and ±60° for gauche or gauche′. The bond lengths and valence angles employed are the same as before.[24,25,30] These structural parameters were taken from the related small molecules.[31] The force fields for the alkyl and oxyethylene chains

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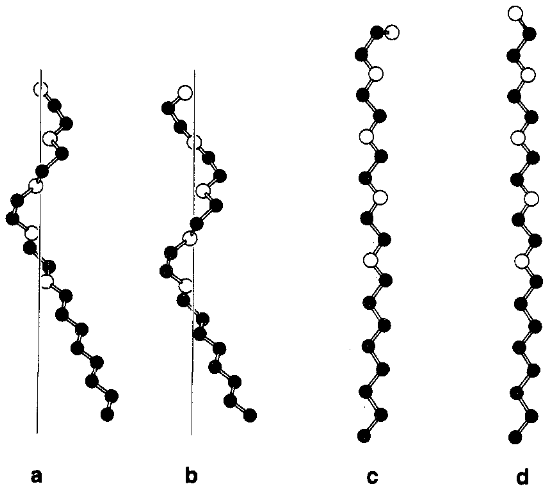

Figure 1. Skeletal molecular models of the C_nE_m compounds: (a) α form, (b) β form, (c) γ form, and (d) γ_T form; ● and ○ represent carbon and oxygen atoms, respectively. The helix axis of the oxyethylene chain is indicated in the figure for the α and β forms.

relevant to the C_nE_m compounds have been established in our previous studies.[24,25,30] In these force fields, the force constants are expressed in terms of the group symmetry coordinates of the atomic groups, such as CH_2 wagging and CH_3 rocking.[16]

The computation was carried out with the program MVIB,[32] which has been developed for calculating normal coordinates of chain molecules. Only minimal input of atomic groupings and a conformation of the molecule suffices for the calculation with this program, the relevant force constants, structural parameters, and other data necessary for the calculation having been prepared as data base. The computation is thus straightforward and almost automatic even for the largest C_nE_m molecules.

Results

Analysis of the Spectra and Determination of the Conformation. (A) Tools for the Spectral Analysis. The Raman spectra of the C_nE_m surfactants were analyzed by utilizing the following tools: (1) the accordion vibration (LAM-1)[33] to estimate an overall conformational state of the molecule, (2) conformation–spectrum correlations for the oxyethylene chain[26] and the alkyl chain[34] to determine local conformations involved, and (3) normal coordinate calculations to ascertain the detailed conformation of the molecule. Although the complete normal coordinate calculation eventually establishes the molecular conformation, the conformation–spectrum correlations are often very useful in identifying conformation-sensitive key bands in the spectra and accordingly in manifesting the local conformations involved in the molecule. The accordion vibration, whose wavenumber is approximately inversely proportional to the length of the extended chain,[33] is a convenient measure to estimate the length of the extended portion of the molecule but is of less use for the shorter C_nE_m homologues since for these molecules the accordion mode is subject to the vibrational coupling with other skeletal deformation modes. This vibration is yet one of the most important clues to deduce an overall shape of the molecule.

In an earlier study,[9] we established four conformational forms for the C_nE_m compounds in the solid state with n = 6, 8, 10, 12, and 16, and m = 1–8. The skeletal models for these forms are shown in Figure 1, and their specific features will be discussed later. In the present conformational analysis of the extended homologous members of the C_nE_m compounds, these known conformational forms and their modifications naturally deserve consideration.

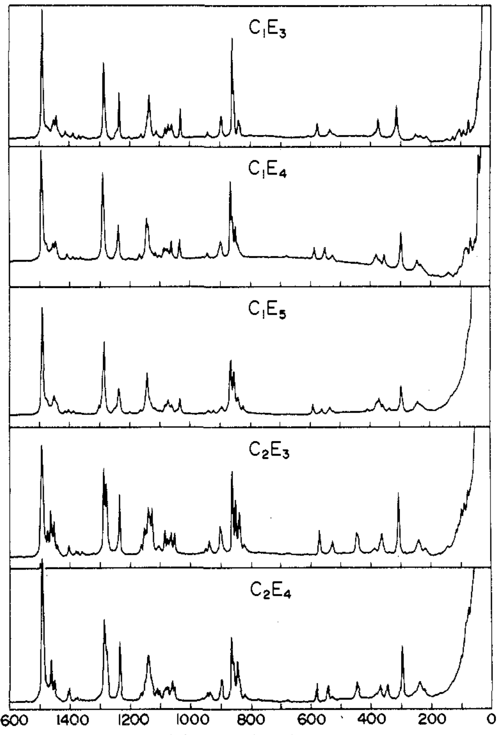

Figure 2. Raman spectra of C_1E_3, C_1E_4, C_1E_5, C_2E_3, and C_2E_4 in the crystalline solid state.

The Raman spectra of a family of C_nE_m surfactants in the crystalline solid state may be classified into several types according to their spectral features and similarities. For the homologues of n = 1–4, the spectra are well correlated with the length of the alkyl chain and are thus classified by n (the number of alkyl carbon atoms). For the homologues of $n \geq 5$, on the other hand, the spectral features depend greatly on the length of the oxyethylene chain rather than that of the alkyl chain, and therefore the classification by m (the number of oxyethylene units) is more reasonable. The classification of the spectral types is another fundamental tool for the analysis of a series of the homologous compounds. The analysis of the spectra and the determination of the molecular conformation for the C_nE_m compounds have been made in accordance with the classification. Since the spectral analysis for the homologues with $n \geq 5$ is analogous to that for the homologues treated in our previous work,[9] detailed descriptions of the analysis will be given below only for the compounds of n = 1–4.

(B) C_1E_m (m = 1 and 3–5) and C_2E_m (m = 3 and 4). Conformational analysis for the C_1E_m and C_2E_m compounds is simpler than that for the homologues with longer alkyl groups, since the rotational isomerism about the alkyl C–C bond is not involved in these short-alkyl molecules. Hence, their conformational properties are expected to be more or less analogous to those of $CH_3(OCH_2CH_2)_mOCH_3$ and $H(OCH_2CH_2)_mOH$,[35,36] whose conformations in the solid state have been found to be similar to the conformation of crystalline poly(oxyethylene) $(-OCH_2CH_2-)_m$; namely, the molecular chain takes a helical conformation with repeated trans–gauche–trans for the bond axes O–CH_2–CH_2–(O).[37]

The Raman spectra of C_1E_m (m = 3–5) and C_2E_m (m = 3 and 4) are shown in Figure 2. For these compounds, several common

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spectral features are noted: (1) a distinct band at 295–315 cm^{-1}, (2) a band progression in the 500–600-cm^{-1} region, (3) weak band(s) at 935–945 cm^{-1}, and (4) prominent bands in higher wavenumber regions at about 1235, 1285–1290, and 1490–1495 cm^{-1}. The C_1E_m compounds also exhibit in common a band at about 1035 cm^{-1}. The C_2E_m compounds show, on the other hand, a characteristic band in doublet at about 445 cm^{-1}, the corresponding band being not found for C_1E_m. In determining the molecular conformation of these compounds, the conformational key bands as established through the conformation–spectrum correlations[26] were utilized. The band at about 1235 cm^{-1} mentioned above is assigned to the antisymmetrical CH_2 twisting mode of the $O{-}C_IH_2{-}C_{II}H_2{-}O$ group in the trans($O{-}C_I$)-gauche($C_I{-}C_{II}$)-trans($C_{II}{-}O$) conformation and corresponds to the 1233-cm^{-1} band of crystalline poly(oxyethylene).[20] This implies that the molecules of C_1E_m and C_2E_m are in the trans–gauche–trans (TGT) conformation with respect to the oxyethylene group. Additional evidence for the TGT-helical conformation is the observation of the band(s) at 935–945 cm^{-1}, which is due to the CH_2 rocking mode of the $O{-}C_IH_2{-}C_{II}H_2{-}O{-}C_{III}H_2{-}C_{IV}H_2{-}O$ group in the gauche($C_I{-}C_{II}$)-trans($C_{II}{-}O$)-trans($O{-}C_{III}$)-gauche($C_{III}{-}C_{IV}$) conformation;[26] the corresponding bands are observed for poly(oxyethylene) at 934 and 948 cm^{-1}.[20] The Raman band of C_1E_m observed at about 1035 cm^{-1} is assigned, on the basis of the normal coordinate analysis, to the terminal $CH_3{-}O$ stretching mode as coupled with the inner skeletal stretching and the CH_2 rocking modes. This vibration is characteristic of the $CH_3{-}O{-}C_IH_2{-}C_{II}H_2{-}O$ group in the trans($O{-}C_I$)-gauche($C_I{-}C_{II}$)-trans($C_{II}{-}O$) conformation.[26] The TGT helix of the oxyethylene chain is further evidenced by the observations of the band at 295–315 cm^{-1} and the band progression in the 500–600-cm^{-1} region. These bands are associated with the ν_{17} and ν_{16} optical branches, respectively, of crystalline poly(oxyethylene) with the TGT-helical structure.[38] These spectral findings confirm that the C_1E_m and C_2E_m molecules are in the TGT conformation with respect to the oxyethylene portion. For the C_2E_m compounds, the distinctive band at about 445 cm^{-1} is important for the determination of the conformation about the C–O bond in the ethoxyl group. The normal coordinate calculation indicates that the observed wavenumber is consistent only with the trans conformation, the calculated wavenumber being 438 cm^{-1} for both C_2E_3 and C_2E_4. This band is interpreted as the accordion vibration of the $CH_3{-}CH_2{-}O{-}CH_2{-}CH_2$ part with the five skeletal atoms (C and O) coplanar. The spectral observations described above now complete the molecular form for C_1E_m

$$\mathrm{C{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}\cdots\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C{-}OH}$$

and for C_2E_m

$$\mathrm{C{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}\cdots\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C{-}OH}$$

where T and G denote trans and gauche, respectively. These conformations for the C_1E_m and C_2E_m compounds belong to the α form (Figure 1) that we have defined in the previous study.[9] The calculated wavenumbers for the α form agree satisfactorily with the observed wavenumbers for these compounds, thus endorsing the determined molecular form.

Examination of the observed wavenumber for the helix characteristic band in the 295–315-cm^{-1} region is of interest, since the wavenumber of this vibration, which is a transverse helix breathing mode of the oxyethylene chain, should decrease as the chain length increases, in accordance with the behavior of the ν_{17} dispersion curve with the phase difference.[38] The observed wavenumbers for this mode are 314 (C_1E_3), 297 (C_1E_4), 296 (C_1E_5), 307 (C_2E_3), and 296 cm^{-1} (C_2E_4), in excellent agreement with the calculated wavenumbers, 310, 297, 293, 304, and 294 cm^{-1}, respectively, and are in conformity with the anticipated behavior with the oxyethylene chain length.

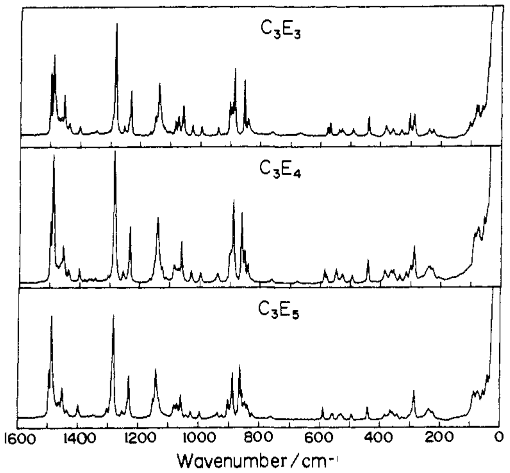

Figure 3. Raman spectra of C_3E_3, C_3E_4, and C_3E_5 in the crystalline solid state.

Determination of the molecular conformation for C_1E_1 is straightforward, since the relevant internal rotation axes associated with rotational isomerism of the molecular skeleton are only two: $CH_3O{-}CH_2{-}CH_2OH$. The normal coordinate analysis has readily established the molecular conformation of this compound to be trans–gauche, corresponding to the α form.

(C) C_3E_m (m = 3–5). The C_3E_m compounds contain a propyl group, which is the shortest alkyl group that shows rotational isomerism about the C–C bond axis. The conformation of the alkyl portion is therefore important for characterizing the conformational state of these molecules. The Raman spectra of C_3E_m are shown in Figure 3. A look at these spectra indicates that there is noticeable similarity among themselves, especially in the wavenumber region above 900 cm^{-1}. The helix characteristic bands that have been pointed out for the C_1E_m and C_2E_m compounds are again distinct features of the C_3E_m compounds: (1) a band progression in the 500–600-cm^{-1} region, (2) a weak band at about 940 cm^{-1}, and (3) a well-defined band at about 1230 cm^{-1}. These spectral observations manifest the conformation of the oxyethylene chain to be a TGT-helical form similar to that for the C_1E_m and C_2E_m homologues. Close spectral examination further reveals that the observed bands, in particular in the region below 600 cm^{-1}, are too many to explain the spectra by a single molecular conformation, as will be discussed later. This implies that molecules of the C_3E_m compounds take more than one conformational form in the crystal; the number of the observed bands is suggestive of two coexisting forms.

There are four possible conformations for the $CH_3CH_2{-}CH_2{-}OCH_2$ group: trans–trans, gauche–trans, trans–gauche, and gauche–gauche. The first and second conformations, when combined with the TGT helix of the oxyethylene chain, give the α form and the β form, respectively.[9] Normal coordinate analysis for these four forms clarified that the observed spectra of C_3E_3, C_3E_4, and C_3E_5 are explained by the coexistence of the first and second conformational forms, i.e., the α form

$$\mathrm{C{-}C\overset{T}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}\cdots\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C{-}OH}$$

and the β form

$$\mathrm{C{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}\cdots\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C{-}OH}$$

Thus, the spectra are composed of the bands due to the two different forms.

The Raman spectra of the C_3E_m compounds are discussed in light of the results of the normal coordinate analysis. For C_3E_3, two well-defined bands are noted at 291 and 306 cm^{-1}, which are assigned to the transverse breathing vibration of the helical chain of the α and β forms, respectively. The calculated wavenumbers for the two forms, 277 and 302 cm^{-1}, are in satisfactory agreement with those observed. In this spectral region, C_3E_4 gives three bands at 287, 300, and 314 cm^{-1}, the first being the most prominent.

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[38] Matsuura, H.; Miyazawa, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 372–378.

Although their assignments are not so straightforward as those for C_3E_3, these bands are interpreted as follows on the basis of the normal coordinate analysis. The bands at 287 and 314 cm^{-1} are attributed to the helix breathing vibration of the α form as coupled with other modes, the calculated wavenumbers being 276 and 306 cm^{-1}, respectively, while the band at 300 cm^{-1} is attributed to a similar vibration of the β form with the calculated wavenumber 293 cm^{-1}. The diminished intensity of the 314-cm^{-1} band is consistent with the more distorted breathing mode than the 287-cm^{-1} band. For C_3E_5, the breathing band is observed at 286 cm^{-1} together with its weaker satellite band. This band is ascribed to both the α and β forms with the calculated wavenumbers 276 and 287 cm^{-1}, respectively.

The C_3E_m compounds (m = 3–5) show in common a distinctive band at about 440 cm^{-1}. This band is associated with the accordion vibration of the CH_3–CH_2–CH_2–O–CH_2–CH_2 part of the α form in the extended conformation. The observed wavenumbers 441, 440, and 439 cm^{-1} for C_3E_3, C_3E_4, and C_3E_5, respectively, are in agreement with the calculated wavenumber of 431 cm^{-1} for the three compounds in common. The m-independent wavenumber of this band is thus in accord with the vibrational assignment given above. The corresponding band for the α form of the C_2E_m compounds was noted at about 445 cm^{-1} as mentioned before. Another characteristic band of the α form of C_3E_m is found at 1029 cm^{-1} for m = 3, at 1030 cm^{-1} for m = 4, and at 1027 cm^{-1} for m = 5. The normal coordinate calculation indicates that this band is due primarily to the terminal CH_3–C stretching vibration, and the calculated wavenumber 1028 cm^{-1} for the three compounds agrees with the observed wavenumbers.

The bands that are characteristic of the β form are found at about 760 and 1000 cm^{-1}. The former is ascribed to the C_IH_2 rocking mode as coupled with the CH_3 rocking of the CH_3–C_IH_2–$C_{II}H_2$–O group in the gauche(C_I–C_{II}) conformation. The latter band, observed at 999, 999, and 997 cm^{-1} for C_3E_3, C_3E_4, and C_3E_5, respectively, is associated with the C–O stretching coupled with the CH_2 rocking and twisting and the CH_3 rocking of the CH_3–C_IH_2–$C_{II}H_2$–O–$C_{III}H_2$–$C_{IV}H_2$–O part with the gauche(C_I–C_{II})-trans(C_{II}–O)-trans(O–C_{III})-gauche(C_{III}–C_{IV}) conformation. The calculated wavenumber for this vibration is 991 cm^{-1}, in agreement with the observed wavenumbers. The weak bands in a pair at 1168 and 1159 cm^{-1} for C_3E_3 are assigned to the alkyl CH_2 rocking mode of the α and β forms, respectively. The corresponding bands are also observed for C_3E_4 and C_3E_5 as well. The above spectral elucidation suffices to conclude that the α and β forms of the molecules coexist in the crystalline solid of the C_3E_m compounds.

(D) C_4E_m (m = 2–5). The Raman spectra of C_4E_2, C_4E_3, C_4E_4, and C_4E_5 are shown in Figure 4. Of these compounds, C_4E_3 gave, depending on the solidification conditions, two types of spectra with different features. One spectrum, called type I, was obtained only by slow cooling for more than 30 min to reach liquid nitrogen temperature, and the other, called type II, was obtained either by rapid cooling for less than 3 min to reach liquid nitrogen temperature or by slow cooling. It should be noted that each of these spectra, once the crystalline solid was formed, did not change to the other on subsequent annealing. For the C_4E_2 substance, on the other hand, the complete crystallization required more than 7 h from the initial growth of crystal nuclei in the liquid phase.

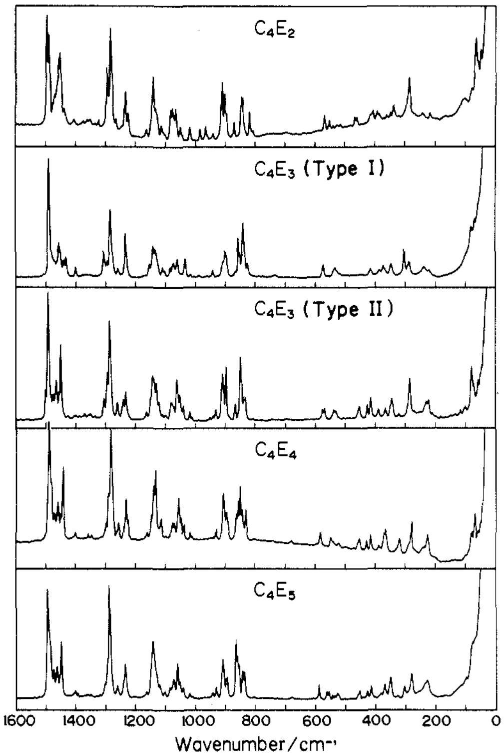


Figure 4. Raman spectra of C_4E_2, C_4E_3 (type I), C_4E_3 (type II), C_4E_4, and C_4E_5 in the crystalline solid state.

The Raman spectra of the C_4E_m compounds may be classified into three types on the basis of their characteristic spectral features. The first type, to which the spectrum of C_4E_2 belongs, is characterized by (1) a well-defined helix breathing band at 287 cm^{-1}, (2) a pair of bands at 808 and 819 cm^{-1}, (3) a weak band at 871 cm^{-1}, (4) a group of three bands at 942, 967, and 986 cm^{-1}, and (5) bands in a pair at 1224 and 1234 cm^{-1}. The second spectral type is given by C_4E_3 (type I) and is featured by (1) a band at 302 cm^{-1}, (2) two weak bands at 534 and 572 cm^{-1}, (3) a weak band at 944 cm^{-1}, and (4) a distinct band at 1233 cm^{-1}. The third type, represented by C_4E_3 (type II), C_4E_4, and C_4E_5, shows spectral features of (1) a distinct band at 280–290 cm^{-1}, (2) a group of three bands at about 415, 428, and 452 cm^{-1}, (3) a weak band at about 930 cm^{-1}, (4) a characteristic spectral pattern in the 1000–1100-cm^{-1} region with the prominent peak at about 1060 cm^{-1}, (5) a couple of bands at about 1230–1240 cm^{-1}, and (6) another characteristic pattern in the 1250–1310-cm^{-1} region containing the bands at about 1260, 1286, 1295, and 1305 cm^{-1}. The spectral characteristics of the three types mentioned above involve those of the TGT-helical conformation of the oxyethylene chain, namely the bands at 1230–1240 and 930–945 cm^{-1} as well as the band progression in the 500–600-cm^{-1} region. These findings thus indicate that, for all the C_4E_m compounds treated, the oxyethylene chain is in the repeated TGT conformation in the solid state. As will be described below, however, unexpected difficulties are encountered in the conformational analysis of some of the C_4E_m compounds, partly because of possible existence of a new conformational form that has not been identified in our earlier study of the C_nE_m compounds.[9]

The spectrum of C_4E_2, the first type of C_4E_m spectra, is analyzed at first by examining the number of the observed bands. It is shown that the bands observed are too many for one conformational form, indicating that more than one conformer coexist in the crystal. Useful key bands to investigate the conformation of the butoxyl group are those at 808 and 819 cm^{-1}. The normal coordinate calculation clarified that the former is associated with the CH_3 rocking and the CH_2 rocking mode of the CH_3–C_IH_2–$C_{II}H_2$–$C_{III}H_2$–O part with the trans(C_{II}–C_{III}) conformation, while the latter is associated with a similar vibrational mode as coupled with the C_I–C_{II} stretching of the same part with the gauche(C_{II}–C_{III}) conformation. If the conformation about the C_{III}–O bond is confined to trans, actually manifested so later, there are four possible conformational forms for C_4E_2:

$$\mathrm{C\!-\!C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\!-\!OH}$$

$$\mathrm{C\!-\!C\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\!-\!OH}$$

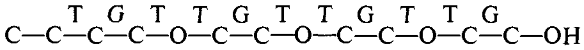
$$\mathrm{C\!-\!C\overset{G}{-}C\overset{T}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\!-\!OH}$$

$$\mathrm{C\!-\!C\overset{G}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\!-\!OH}$$

The first and second are identified with the α and β forms, respectively, of the C_nE_m compounds. The third and fourth may be regarded as modifications of the α and β forms, respectively, in that only the conformation of the CH_3CH_2–CH_2CH_2O group is changed from trans to gauche and will be called accordingly the α' and β' forms, respectively. The normal coordinate calculation on the four conformational forms led to the conclusion that the observed spectrum of C_4E_2 is composites of the bands due to the α and β' forms. Some other spectral features relevant to the conformational characterization will be discussed below.

A distinct band at 287 cm^{-1} is assigned to the breathing mode of the helical oxyethylene group for the α form with the calculated wavenumber 279 cm^{-1}. A close inspection of the spectrum discloses a shoulder band at 293 cm^{-1} on the higher wavenumber side of the 287-cm^{-1} band. This shoulder is ascribed to the distorted breathing mode of the β form with the calculated wavenumber 280 cm^{-1}. In the 500–600-cm^{-1} region, five weak bands are observed and interpreted as follows; the observed wavenumber in cm^{-1} along with the calculated wavenumber and the conformational form shown in parentheses: 514 (514, β'), 527 (528, β'), 538 (532, α), 551 (554, β'), and 567 (577, α). The band at 871 cm^{-1} is due to the skeletal stretching, the CH_2 rocking, and the CH_3 rocking mode of the α form. The bands at 967 and 986 cm^{-1} are due, respectively, to the CH_3CH_2–CH_2–CH_2–O–CH_2 part with the gauche–gauche–trans–trans conformation and the CH_2CH_2–CH_2O part with the gauche conformation. These bands are thus important for characterizing the β' form. These findings for C_4E_2 now ascertain the coexistence of the α and β' forms for this compound in the crystalline solid state.

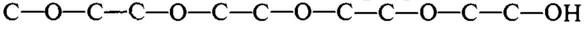
The second type of C_4E_m spectra applies to type I of C_4E_3. As mentioned before, the TGT-helical conformation of the oxyethylene is obvious. Of the possible molecular conformations for this compound, only the following is consistent with the observed spectrum



$$\mathrm{C{-}C\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C{-}OH}$$

where the alkyl C–C bond adjacent to the oxyethylene group is in the gauche conformation. This form is thus identified with the β form. For the determination of this conformation, the helix breathing band at 302 cm^{-1} (calculated wavenumber 296 cm^{-1}) and the broad and sharper bands at 534 and 572 cm^{-1}, respectively (calculated wavenumbers 524, 530, 539, and 572 cm^{-1}), are convincing spectral evidence for the β form.

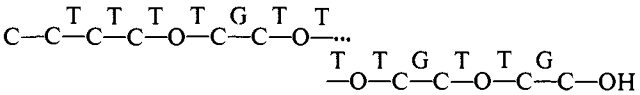
It should be noted here that overall spectral analogy between different compounds consisting of the same number of skeletal atoms (C and O) and having the coinciding skeletal conformation is of great use for the confirmation of the molecular conformation determined. The α form of C_1E_4, as described earlier



$$\mathrm{C{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C{-}OH}$$

is thus analogous in this sense to the β form of C_4E_3. Comparison of the spectra for C_1E_4 (Figure 2) and C_4E_3 (type I) (Figure 4) in fact shows substantial coincidence with each other except for a few bands associated with the alkyl CH_2 and the CH_3O groups.

The Raman spectra of C_4E_3 (type II), C_4E_4, and C_4E_5 belong to the third type of C_4E_m spectra. The conformation–spectrum correlations and the normal coordinate calculation clarify that there are two conformational forms present in the crystalline solid state of these C_4E_m substances. The first form is characterized by a distinct band at 280–290 cm^{-1}, weak bands at about 805 and 1165 cm^{-1}, and a medium-intensity band at about 1295 cm^{-1} on the higher wavenumber side of the predominant peak at 1286 cm^{-1}. According to the conformation–spectrum correlations of the alkoxyl group,[34] the 805-cm^{-1} band is associated with the CH_2CH_2–CH_2O group in the trans conformation and the 1165-cm^{-1} band is associated with the CH_3CH_2–CH_2–CH_2–OCH_2 group in the trans–trans–trans and/or gauche–trans–gauche conformation. The band at about 1295 cm^{-1} is ascribable to the CH_3CH_2–CH_2–CH_2O group in the trans–trans conformation in accordance with the correlations. These conformational assignments of the butoxyl part, when incorporated with the TGT-helical conformation for the oxyethylene part, yield the whole molecular conformation



$$\mathrm{C{-}C\overset{T}{-}C\overset{T}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}\cdots}$$
$$\mathrm{\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C\overset{T}{-}O\overset{T}{-}C\overset{G}{-}C{-}OH}$$

which is the α form as defined previously. The low-wavenumber bands at 287, 280, and 280 cm^{-1} for C_4E_3 (type II), C_4E_4, and C_4E_5, respectively, are assigned, on the basis of the normal coordinate analysis, to the helix breathing mode of the oxyethylene chain for the α form.

The conformational analysis of the second form of C_4E_3 (type II), C_4E_4, and C_4E_5 is not straightforward. The oxyethylene portion is suggested to be helical at least in part, since the characteristic bands relevant to this conformation are noted, as surplus bands to the α form, in the regions, for example, of 500–600 and 1200–1250 cm^{-1}. No observation of bands in the 970–1000-cm^{-1} region and of a strong band at about 1500 cm^{-1} is indicative of no involvement of the extended oxyethylene unit in the molecule. The conformation of the butoxyl group is analyzed by examining the spectral feature in the 700–850-cm^{-1} region. A weak band at about 745 cm^{-1} is assigned, on the basis of the normal coordinate analysis, to the CH_2 rocking mode of the CH_3–C_IH_2–$C_{II}H_2$–$C_{III}H_2$–O group in the gauche(C_I–C_{II}) conformation. Absence of bands at 815–830 cm^{-1} indicates no involvement of the gauche(C_{II}–C_{III}) conformation in the butoxyl group, and hence the trans(C_{II}–C_{III}) is suggested accordingly. As mentioned before, the weak band at about 1165 cm^{-1} is ascribable to the trans(C_I–C_{II})–trans(C_{II}–C_{III})–trans(C_{III}–O) and/or gauche(C_I–C_{II})–trans(C_{II}–C_{III})–gauche(C_{III}–O) conformation of the CH_3–C_IH_2–$C_{II}H_2$–$C_{III}H_2$–O–CH_2 group and has been actually assigned to the first conformation in the α form. Being consistent with these two possible assignments, the 1165-cm^{-1} band may also be assigned to the second conformation with the C_{III}–O axis in the gauche conformation. However, for lack of further spectral evidence available, we refrain from completing the conformation of the whole molecule. Nevertheless, it is almost evident that the second coexisting conformational form for C_4E_3 (type II), C_4E_4, and C_4E_5 is a new form that has not been found so far for our C_nE_m compounds. This indeterminate form will be provisionally called the x form for subsequent discussions. Another remark to be made here is a possibility that the conformational state of this form is distorted considerably from the common trans or gauche state with internal rotation angle in the vicinity of 180° or ±60°, respectively.

(E) Higher C_nE_m Homologues. The Raman spectra of four C_5E_m, two C_6E_m, four C_7E_m, four C_9E_m, two $C_{10}E_m$, four $C_{11}E_m$, three $C_{13}E_m$, four $C_{14}E_m$, three $C_{15}E_m$, and five $C_{16}E_m$ homologues were analyzed on the basis of the accordion vibration, the conformation–spectrum correlations, and the normal coordinate calculations. The Raman spectra of some of these compounds are shown in Figure 5, where the spectrum of C_6E_2 previously reported[9] is also included for reference.

The spectral review indicates that the C_nE_1 compounds (n = 5, 7, 9, 11, 14, and 16) have common features of (1) prominent bands assignable to the accordion vibration in the region below 300 cm^{-1}, (2) a group of three bands in the 860–900-cm^{-1} region, (3) a weak but characteristic band at about 1165 cm^{-1}, and (4) a well-defined band at about 1415–1420 cm^{-1}. These features coincide with those that have been observed previously for the C_nE_1 homologues with n = 6, 8, 10, and 12 (type A and A′ compounds).[9] It is shown therefore that the molecules of the present C_nE_1 compounds take the same conformational state as that for the other C_nE_1 homologues studied before; namely, the molecules in the γ form and the γ_T form (see Figure 1) coexist in the crystal. The compounds of C_nE_2 with n = 5, 7, 9, 11, and 13–16 and C_nE_3 with n = 9, 11, 13–15, and 16 (rapid cooling) present the following spectral features: (1) a prominent accordion band, (2) a weak band at about 690 cm^{-1}, (3) a pair of bands at about 860 and 890 cm^{-1}, (4) a weak band at 970–980 cm^{-1}, and (5) distinct band(s) at about 1500 cm^{-1}. These characteristics are the same as those we have seen previously for the type B compounds,[9] namely C_nE_2 with n = 6, 8, 10, and 12 and C_nE_3 with n = 8 (rapid cooling), 10, and 12 (rapid cooling). The conformation of these homologues

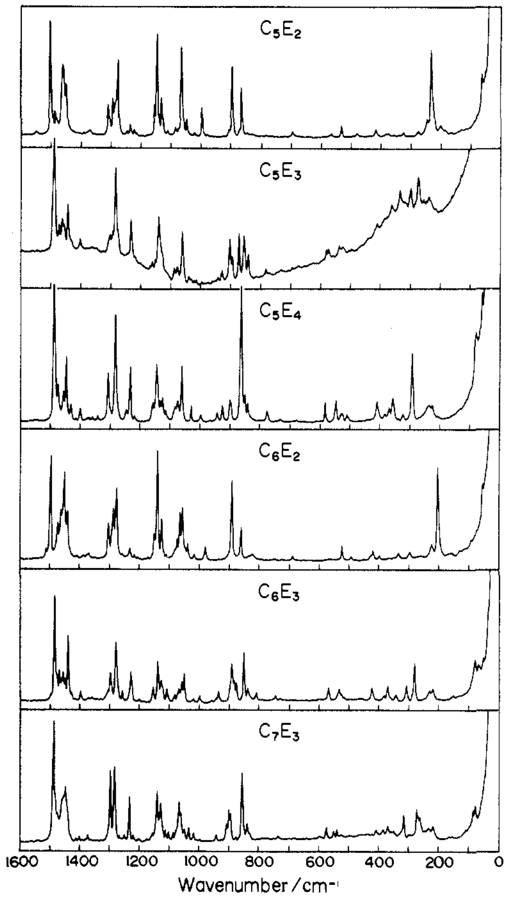


Figure 5. Raman spectra of C_5E_2, C_5E_3, C_5E_4, C_6E_2, C_6E_3, and C_7E_3 in the crystalline solid state.

is thus established to be the γ form.

The Raman spectra of the following compounds are greatly different from those mentioned above. The homologues C_nE_3 with n = 6, 7, and 16 (slow cooling), C_nE_4 with n = 5–7, 9, 11, and 13–15, C_nE_5 with n = 10 and 16, and C_nE_7 with n = 10 and 16 exhibit the following common features: (1) indistinct accordion bands, (2) a band at 285–310 cm^{-1}, (3) a band progression in the 500–600-cm^{-1} region, (4) a weak band at 935–940 cm^{-1}, and (5) a well-defined band at 1230–1235 cm^{-1}. These are in accord with the features of the type C compounds previously discussed,[9] indicating that the conformation of these compounds (except $C_{10}E_7$ and $C_{16}E_7$) is the β form. Close examination reveals that the conformational state of $C_{10}E_7$ and $C_{16}E_7$ is slightly different from the β form and is reasonably explained by the α form, similarly to the case of $C_{12}E_7$. The analysis of the Raman spectrum of C_5E_3 shows that two conformations of the α form and the β form coexist in the crystal. This is the same conformational state as found for C_3E_m (m = 3–5) described before.

(F) Homologues of Unaccomplished Crystalline Solid. We have attempted, in the present work, to obtain Raman spectra of C_1E_2, C_2E_1, C_2E_2, C_3E_1, C_3E_2, and C_4E_1 in the crystalline solid state (the materials were supplied by Tokyo Kasei Kogyo Co., except for C_3E_1 and C_3E_2 which were prepared in our laboratories). In spite of many attempts, we were unable to accomplish crystallization of these lower homologues; we obtained only the supercooled liquid substance.

Established Conformational Forms of the C_nE_m Surfactants. The analysis of the Raman spectra for the 48 C_nE_m homologues with various chain lengths of the alkyl and oxyethylene groups has clarified the conformational forms of these compounds in the crystalline solid state. The present results, together with the previous results for 23 other homologous C_nE_m compounds,[9] are summarized in Table I. For the compounds treated in this work, we have found five conformational forms, i.e., the α, β, β', γ, and γ_T forms, and have also confirmed the existence of another different form (provisionally called the x form) relevant to the C_4E_m compounds, whose exact conformation is, however, not determinate at present. The established conformational forms are schematically represented in Figure 6.

Table I. Conformational Forms of $CH_3(CH_2)_{n-1}(OCH_2CH_2)_mOH$ (C_nE_m) in the Crystalline Solid State[a]

no. of alkyl C atoms (n)	no. of oxyethylene units (m) 1	2	3	4	5	6	7	8
1	α	*	α	α	α			
2	*	*	α	α				
3	*	*	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$			
4	*	$\alpha + \beta'$	β,[b] α + x[c]	α + x	α + x			
5	$\gamma + \gamma_T$	γ	$\alpha + \beta$	β				
6	$\gamma + \gamma_T$	γ	β	β				
7	$\gamma + \gamma_T$	γ	β	β				
8	$\gamma + \gamma_T$	γ	γ,[d] β[b]	β				
9	$\gamma + \gamma_T$	γ	γ	β				
10	$\gamma + \gamma_T$	γ	γ	β	β	β	α	β
11	$\gamma + \gamma_T$	γ	γ	β				
12	$\gamma + \gamma_T$	γ	γ,[d] β[b]	β	β	β	α	β
13		γ	γ	β				
14	$\gamma + \gamma_T$	γ	γ	β				
15		γ	γ	β				
16	$\gamma + \gamma_T$	γ	γ,[d] β[b]	β	β	β	α	β

[a] Results for C_6E_1, C_6E_2, C_8E_1–C_8E_4, $C_{10}E_1$–$C_{10}E_4$, $C_{10}E_6$, $C_{10}E_8$, $C_{12}E_1$–$C_{12}E_8$, $C_{16}E_4$, $C_{16}E_6$, and $C_{16}E_8$ are taken from ref 9. Symbol * implies that the crystalline solid was not accomplished (only the supercooled liquid obtained). Symbol + denotes the coexistence of the two forms indicated. [b] Crystalline solid obtained by slow cooling of the liquid. [c] Crystalline solid obtained either by rapid cooling or by slow cooling of the liquid. [d] Crystalline solid obtained by rapid cooling of the liquid.

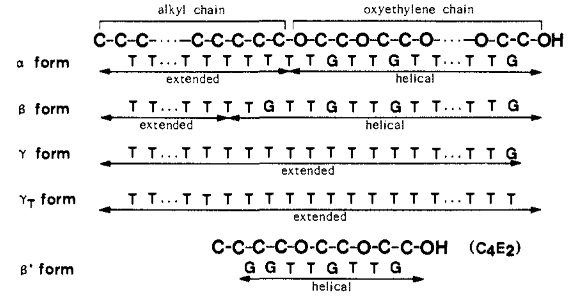


Figure 6. Schematic representation of the conformational forms of the C_nE_m compounds. T and G denote trans and gauche, respectively.

For a comprehensive understanding of the conformational state relevant to the C_nE_m compounds, a description will be given below of the conformational forms determined for a series of these nonionic surfactants. It may be more instructive to recall first the conformation of polyethylene $(-CH_2-)_n$ and poly(oxyethylene) $(-OCH_2CH_2-)_m$ in the crystalline solid state, since they are homogeneous polymers consisting solely of the alkyl group and the oxyethylene group, respectively. These groups are now the two moieties of the C_nE_m molecules. The chain conformation of polyethylene is fully extended all-trans,[39] whereas that of poly(oxyethylene) is helical.[37,40,41] The latter polymer has the 7_2 helical structure (seven units of OCH_2CH_2 and two helical turns per identity period) with the consecutive trans–gauche–trans (TGT) conformation about the O–CH_2–CH_2–(O) bond axes. These two polymers are thus contrasted with each other in chain conformations.

The α form is a simple combination of the fully extended conformation of the alkyl chain and the TGT-helical conformation of the oxyethylene chain. Being uninfluenced by each other's intrinsic conformation, the α form is regarded as the most primitive conformational form of the C_nE_m compounds. The hydroxyl-terminal part of the oxyethylene chain O–CH_2–CH_2–OH is in

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the gauche(C–C) conformation. The β form is a modification of the α form. The difference between the two forms is represented only by the conformation of the C_IH_2–$C_{II}H_2$–$C_{III}H_2$–O part of the alkyl group adjoining the oxyethylene group. This part in the β form is in the trans(C_I–C_{II})–gauche(C_{II}–C_{III})–trans(C_{III}–O) conformation, in place of the trans(C_I–C_{II})–trans(C_{II}–C_{III})–trans(C_{III}–O) conformation in the α form. This implies that part of the alkyl chain is incorporated into the helical structure of the oxyethylene chain in the β form. The incorporated CH_2–CH_2–CH_2–(O) group in the TGT is conformationally equivalent to an oxyethylene unit O–CH_2–CH_2–(O) with the same conformation, so that the helical part of the molecule for the β form is longer by one equivalent oxyethylene unit than for the corresponding α form. The stable gauche conformation for the RCH_2–CH_2O group is consistent with the experimental finding for various alkyl ether compounds that relative stability of the gauche to the trans conformation for the CC–CO bond is much larger than for the CC–CC bond.[42,43] It should be noted here that for the C_1E_m and C_2E_m homologues the α form and the β form denote the same conformation, since the methyl or ethyl group in these molecules does not discriminate between the two forms. The present conformational analysis has revealed the existence of the modified β form, called the β' form, for C_4E_2. This form is characterized by the double-gauche conformation in the butoxyl group CH_3–C_IH_2–$C_{II}H_2$–$C_{III}H_2$–O. The conformation of this group in the β' form is gauche(C_I–C_{II})–gauche(C_{II}–C_{III})–trans(C_{III}–O) instead of trans(C_I–C_{II})–gauche(C_{II}–C_{III})–trans(C_{III}–O) in the β form.

The γ form is notably different from the α, β, or β' form in that the oxyethylene chain takes the extended conformation rather than the helical conformation as found for the other forms. The hydroxyl-terminal part of the oxyethylene chain O–C_IH_2–$C_{II}H_2$–OH is in the trans(O–C_I)–gauche(C_I–C_{II}) conformation for the γ form. The modified form γ_T takes the trans(O–C_I)–trans(C_I–C_{II}) conformation for this part. In the γ and γ_T forms, the alkyl chain takes the intrinsic all-trans conformation. These forms thus have a highly extended structure as a whole in contrast with the α and β forms which involve the helical structure of the oxyethylene chain. The stability of the extended conformation of the oxyethylene chain is in conformity with the fact that poly(oxyethylene) assumes, in addition to the TGT-helical structure, all-trans extended structure in a less stable crystal modification.[44] In uncomplexed 18-crown-6 in the crystalline solid, two of the O–CH_2–CH_2–O groups are in the trans–trans–trans conformation,[45] giving further support to the extended oxyethylene structure. A note is made here that, for the C_nE_1 homologues, the γ form and the α form denote the same conformation.

The sixth conformational form, the x form, was confirmed to exist for C_4E_m with $m = 3$–5, but its full characterization is not possible at present for lack of sufficient spectral information to define the conformation. This indeterminate form seems to have specificity that it invariably exists together with the α form in the crystal. The oxyethylene chain in this form takes, at least in part, the helical structure, and the butoxyl group probably contains the gauche conformation. Possible large conformational distortion might be another factor to make the conformation determination difficult. This possibility implies that the molecule carrying the butoxyl group would be required to take peculiar conformation to optimize molecular packing in the crystal.

Discussion

Chain-Length-Dependent Conformational Behavior. The molecular conformations determined for a total of 71 C_nE_m surfactants including those investigated in the previous work[9] show interesting dependence on the lengths of the oxyethylene and alkyl chains (Table I). The chain-length dependence of the conformation is discussed below.

All of the C_1E_m and C_2E_m compounds treated have a single conformation of the α form independent of the oxyethylene chain length. For the C_3E_m and C_4E_m compounds along with C_5E_3, the molecules assume two coexisting conformational forms, namely the α form and the β, β', or indeterminate x form. In C_1E_m and C_2E_m, the alkyl group is too short, unlike the homologues of $n \geq 3$, to exhibit conformational variety. For the C_4E_m compounds, the molecular conformation is dependent somewhat on the oxyethylene chain length, as seen from Table I. The C_4E_3 compound exhibits interesting conformational behavior of giving two polymorphic phases which depend on the solidification conditions. In one of the phases, the molecule assumes only the β form, while in the other phase it assumes the α and x forms just like the molecules of C_4E_4 and C_4E_5.

For the C_nE_m compounds with $n \geq 5$, the molecular conformation highly depends on the oxyethylene chain length. The conformation of the C_nE_1 compounds is exceptional in the sense that the hydroxyl-terminal part of the oxyethylene group takes two different conformational states in the same crystal, the gauche conformation for the γ form and the trans conformation for the γ_T form. This distinctive conformational property is analogous to that found for a homologous series of 1-alkanol compounds.[46–48] This suggests that the conformational behavior of the CH_2–O–CH_2–CH_2–OH group in the C_nE_1 molecules is similar to that of the CH_2–CH_2–CH_2–CH_2–OH group in 1-alkanol molecules. The conformational form of the C_nE_1 molecules is thus extended as a whole. The molecules of C_nE_2 ($n \geq 5$) all assume the γ form with the extended conformation not only for the alkyl chain but also for the oxyethylene chain except the terminal part. Of the C_nE_3 compounds studied, those with $n \geq 8$ have been shown to take the γ form. It is interesting to note, however, that the second form (the β form) has also been found for C_8E_3, $C_{12}E_3$, and $C_{16}E_3$ under different solidification conditions. It is shown therefore that the highly extended γ form (and the γ_T form) occurs at the oxyethylene chain length $m \leq 2$ for C_5E_m, C_6E_m, and C_7E_m and at $m \leq 3$ for C_8E_m through $C_{16}E_m$. The molecules of the C_nE_m compounds with $m \geq 4$ and $n \geq 5$ all take the helical/extended diblock form, mostly the β form, and, for a few compounds ($m = 7$), the α form. The significance of the α form found only for the homologues of $m = 7$ is not clear. It is interesting to note, however, that seven oxyethylene units coincide exactly with two full turns of the 7_2 helix of the oxyethylene chain.

As discussed so far, the conformational variety of the C_nE_m compounds has been shown to be associated not only with the length of the oxyethylene chain but also with the length of the alkyl chain. Table I indicates that, as the number of oxyethylene units (m) increases, the molecular conformation of the C_nE_m compounds with $n \geq 5$ changes from the highly extended γ form (and the γ_T form) to the helical/extended diblock β form (and the α form). This conformational transition takes place at $m = 3$–4. Being coincident with this transition point, the compounds of C_8E_3, $C_{12}E_3$, and $C_{16}E_3$ crystallize in fact into either the γ form or the β form depending on the solidification conditions. These findings suggest that four or more oxyethylene units are necessary for establishing the stable helical structure in the C_nE_m molecule in competing with the sizable alkyl chain ($n \geq 5$) which favors the extended structure. It is important to note that the chain length of four oxyethylene units practically coincides with 3.5 OCH_2CH_2 units per helical turn of the 7_2 helix of poly(oxyethylene).[40] This implies that the chain length that corresponds to the first full turn is required for stabilizing the helical structure of the oxyethylene chain when a long alkyl chain is directly linked to the oxyethylene. The nature of the oxyethylene helix, 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

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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 worthwhile to note that this helix incorporation of the alkyl chain does not extend further beyond the nearest unit, even if the oxyethylene chain is lengthened up to eight oxyethylene units.

If the oxyethylene part is not sufficiently long ($m \leq 3$) but the alkyl group is still long enough, the conformation of the oxyethylene group is governed by the dominating alkyl group, and in consequence the oxyethylene chain is joined with the alkyl group to develop more extensive zigzag structure in the γ form. The influence of the extended conformation of the alkyl chain on the oxyethylene chain is estimated to be appreciably strong, as this conformation is propagated all the way through the oxyethylene chain except the terminal OCH_2CH_2OH part, although the number of oxyethylene units is confined to at most three ($m \leq 3$). 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.

For the C_nE_m compounds with shorter alkyl chains ($n \leq 4$), the extended conformation is not found possibly because of the too short length of the alkyl group, and the oxyethylene group takes the helical conformation, even incorporating the nearest part of the alkyl group into the helix (the β and β' forms). It is noted that even C_4E_2 with only two oxyethylene units is not transformed into the extended form by the conformational competence of the butyl group. Thus, for the compounds of C_nE_m with $n \leq 4$, the molecules take basically helical conformations, owing to the more dominant oxyethylene moiety, and their conformational properties are substantially not affected by the oxyethylene chain length.

The conformational behavior of the C_nE_m compounds with respect to the chain lengths of the oxyethylene and alkyl groups has been elucidated on the basis of the conformational competition between the two moieties whose conformational characters are distinct from each other. The force relevant to the conformational competition may be intramolecular as well as intermolecular by origin, but further investigations are necessary for revealing the origin. The conformational competition, as established for a series of the C_nE_m surfactants, is most likely one of the basic conformational features of block copolymers and may also be accountable for some aspects of conformational behavior of biological chain molecules.

Conformational Issue of the C_nE_m Surfactants. There have been extensive studies on the conformation of open-chain oxyethylene polymers and macrocycles (crown ethers),[49-52] and it is now well established that the oxyethylene chain assumes several rigid conformations in the crystalline solid, uncomplexed or complexed with other substances. The conformation of the C_nE_m surfactants has, however, not been investigated so much as that of the homogeneous oxyethylene compounds.

The earliest conformational studies on the C_nE_m surfactants in the solid state are those of Rösch, and the results of his extensive experiments were summarized in his review paper.[17] He suggested, on the basis of the powder X-ray diffraction data of polydisperse materials, two conformation models of the oxyethylene chain, an extended zigzag conformation and a meander conformation, and claimed that, on increasing average chain length, the former conformation is transformed into the latter at oxyethylene units of 15–20. The meander conformation, which is based on Staudinger's early model of an alternative conformation of poly(oxyethylene),[53] has been questioned in our previous work.[9] The fatal drawback of this conformation is its inadaptability to the rotational isomeric model,[54] which is now fully accepted for elucidating the conformational state of chain molecules. The meander conformation is therefore thought to be very unstable, owing to the heavy steric hindrance, and is quite unlikely to exist in any conditions. This model has been cited, however, by many authors until recently for elucidating conformational states of the oxyethylene chain in nonionic surfactants. This situation may be due to the facts that there have been no close communications between the fields of surface chemistry and structural chemistry and that it was only recently that structural chemists have interestedly undertaken conformational problems of the nonionic surfactants.

In 1983 Dorset[18] reported the molecular conformation and crystal packing of C_8E_m (m = 1–5) and $C_{12}E_m$ (m = 1–9) in the crystalline solid state. He utilized electron and X-ray diffraction techniques to elucidate the structure of these compounds. According to his results, the C_8E_m and $C_{12}E_m$ homologues with four or more oxyethylene units ($m \geq 4$) are structurally homologous to one another, for which the oxyethylene chain conformation is suggested to be the same as that for poly(oxyethylene) with the TGT-helical structure. For the lower members of $m \leq 3$, on the other hand, the X-ray diffraction data manifest their crystal structure different from that for the higher members. These results of the diffraction experiments are in good agreement with those in the present work; the structure of the higher members corresponds to the β (and α) form and that of the lower members corresponds to the γ (and γ_T) form. A possibility of two polymorphic forms for $C_{12}E_3$ has also been pointed out,[18] in agreement with our finding that this compound gives either the β form or the γ form depending on the experimental conditions. Other results obtained by Dorset such as the growth habit of crystals and the freezing point data are also consistent with the present conformational results for a homologous series of the C_nE_m compounds. The important point to be emphasized is that Dorset's structural information derived from the combined electron and X-ray diffraction experiments is rather complementary to our results obtained by the systematic analysis of the Raman spectra. While the spectroscopic investigation has established the particulars of the conformational state of the molecule, the diffraction study has contributed to the establishment of the crystal packing of the oxyethylene and alkyl chains.[18] The two methods are thus cooperative with each other in elucidating an overall picture of the structural aspects of the C_nE_m surfactants in the solid state.

The *n*-alkyl-oligo(oxyethylene)-*n*-alkyl triblock compounds $CH_3(CH_2)_{n-1}(OCH_2CH_2)_mO(CH_2)_{n-1}CH_3$ ($C_nE_mC_n$) are structurally related to the diblock compounds of the C_nE_m surfactants. Booth and co-workers[55-58] have conducted systematic structural investigations of the triblock compounds by X-ray scattering, infrared spectroscopy, Raman spectroscopy, and other techniques and have shown that the $C_nE_mC_n$ compounds with $m \geq 9$ take the helical conformation in the central oxyethylene block and the extended conformation in the end alkyl blocks. Although these studies did not clarify the full conformational state of the molecule, the model Booth et al. proposed corresponds to our α or β form for the C_nE_m compounds with large m values. More recently, we have studied by Raman spectroscopy the conformation of short homologues of the $C_nE_mC_n$ triblock compounds in the solid state[19] to reinforce the conformational evidence for the C_nE_m compounds. While $C_4E_1C_4$ assumes the all-trans extended conformation, $C_4E_2C_4$ and $C_4E_3C_4$ assume the helical conformation with the end butoxyl groups involved in the helix. These conformations are in accord with the consequence of the conformational competition between the different blocks and are analogous to the γ form and

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the β form, respectively, for the C_nE_m compounds.

The rigid conformation of a homologous series of the C_nE_m surfactants has now been substantially established. It has been demonstrated that vibrational spectroscopy (Raman and infrared) is one of the most powerful techniques to determine conformational details of the molecule, provided that pertinent analysis methods are effectually applied.

Implications of the Conformational Behavior in Other Properties. The conformational behavior of the C_nE_m surfactants in the solid state is likely to have implications in various physical properties of these substances. Examination of the thermodynamic properties of the $C_{12}E_m$ compounds (m = 2–8) in aqueous solution[59] indicates that the entropy of micellization changes much sharply between m = 3 and 4 as compared with the change at other m values. According to the study of the aggregation of the $C_{10}E_m$ homologues (m = 1–7) in heptane,[60] on the other hand, the behavior of their apparent molar heat capacities with decreasing molar fraction of the surfactant is quite different between those of $m \leq 3$ and those of $m \geq 4$. This leads to a break of the linear change, with increasing oxyethylene chain length, of the limiting molar heat capacity between m = 3 and 4. The distinct difference in the behavior of the two quantities mentioned above for the homologues of $m \leq 3$ and those of $m \geq 4$ is certainly associated with the difference of the conformational properties of these substances; the homologues with the shorter oxyethylene chain assume the extended form, whereas those with the longer oxyethylene chain assume the helical/extended diblock form in the solid state.

A study on the thermodynamic quantities of adsorption of $C_{12}E_m$ (m = 2–5)[61] has shown that the partial molar area of the surfactant at the saturated adsorption surface is very small for $C_{12}E_2$ in comparison with the values for the other homologues. The geometrical arrangement of the adsorbed molecules of $C_{12}E_2$ may be interpreted on the basis of the conformational state of this compound in the solid state.

Conclusions

Molecular conformations of a homologous series of 71 C_nE_m compounds in the solid state have been established by Raman spectroscopy (Table I). For the compounds with $n \leq 4$, the conformation is basically helical, though several different forms are found, with the predominating oxyethylene chain which intrinsically favors the helical structure. For $n \geq 5$, on the other hand, the molecular conformation greatly depends on the oxyethylene chain length. As the number of oxyethylene units (m) increases, a conformational transition takes place at m = 3–4 from the highly extended form to the helical/extended diblock form. This conformational behavior of the C_nE_m compounds is elucidated by the conformational competition between the alkyl and oxyethylene chains. The classical model of the meander conformation of the oxyethylene chain is thought to be very unstable owing to heavy steric hindrance and is therefore quite unlikely to exist.

The conformational properties in the solid state should be closely related to various structural aspects of the amphiphilic molecules. Although the structure of the amphiphiles in solvent media is expected to depend on the amphiphile–solvent interaction as well, the conformational properties in the solid state are fundamental in that these properties certainly contain the nature of the amphiphilic molecules themselves. The reported thermodynamic quantities of the C_nE_m surfactants are in fact indicative of strong correlations with the conformational behavior of these homologous compounds.

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Mixed-Dimer Formation between Dimeric Lithium 2,6-Dimethylphenolate and the Lithium Salts of Strong Acids

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Abstract: The ^{13}C, ^7Li, and ^6Li NMR spectra of lithium 2,6-dimethyl-, 4-bromo-2,6-dimethyl-, and 2,4,6-tribromophenolates in 1,3-dioxolane and THF and in the presence of $LiClO_4$, $LiBPh_4$, LiCl, and lithium p-toluenesulfonate are reported for a wide range of temperature and concentration. It is established that all systems give rise to mixed dimers. The extent of mixed-dimer formation is shown to depend on the basicity of the phenolate ion, the cation solvation power of the solvent, and the nature of the anion. ΔH (kcal mol^{-1}) and ΔS (cal mol^{-1} deg^{-1}) for lithium 2,6-dimethylphenolate are 0, 14 ($LiClO_4$/dioxolane); 0, 7 ($LiClO_4$/THF); and −1.2, −1.3 ($LiBPh_4$/dioxolane), respectively. The $^{13}C_{para}$ chemical shifts for mixed dimers of lithium 2,6-dimethylphenolate are strongly dependent on the nature of the anion. The structures of the mixed aggregates are postulated to be ion pairs of the type $[Li_2P]^+X^-$ that are contact, partially solvent separated, or fully solvent separated depending on the nature of X and the solvent. Exchange of X^- between Li_2PX and free salt is rapid on the ^{13}C NMR time scale at −100 °C. Exchange of phenolate between dimeric phenolate and mixed dimer is a slower process that appears to involve the intermediacy of monomeric lithium phenolate.

It is now well-established that organic lithium reagents (organolithium compounds, lithium amides, lithium enolates) form aggregates in weakly polar, aprotic solvents.[1,2] In some cases, at least, these aggregates have been shown to be the primary reactants[3-5] and may therefore be responsible for controlling reactivity as well as regio- and stereochemistry in their reactions with electrophiles. Furthermore, there is an increasing body of evidence to suggest the reactions of these aggregates can be

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