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PREFERENTIAL BENT STRUCTURE OF THE HYDROPHOBIC GROUP OF TRITON X-100 SURFACTANT. A RAMAN SPECTROSCOPIC STUDY

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Structure of the hydrophobic group of Triton X-100 surfactant was studied by a Raman spectroscopic method. The spectral analysis indicated that this group preferentially takes the bent structure with the 1,1,3,3-tetramethylbutyl group in the *gauche* conformation.

Triton X-100 is a polydisperse preparation of α-[*p*-(1,1,3,3-tetramethylbutyl)-phenyl]-ω-hydroxypoly(oxyethylene) with an average of 9.5 oxyethylene units, the chemical formula being represented by $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_{9.5}OH$. This nonionic surfactant has been widely used for separating enzymes and proteins from cell membranes. For understanding the biological function of the surfactant system, physicochemical properties of the system are necessary. In fact, many studies have been made on the size, shape, and hydration of Triton X-100 micelles.[1-5] However, only a few studies have been reported on the conformational state of Triton X-100 molecules, although knowledge of the molecular conformation is essential for comprehensive elucidation of the structural aspect of the Triton X-100 system.

The conformation of the hydrophilic oxyethylene chain in Triton X-100 has been studied by a Raman spectroscopic method,[6,7] but the vibrational assignment of the key bands, used for discussing the conformation, was found to be unreasonable.[8] On the other hand, the conformation of the hydrophobic group has not yet been discussed in spite of its importance in evaluating the length and shape of the surfactant molecule.[3] In this letter, we report the structure of the hydrophobic group of Triton X-100 on the basis of the Raman spectroscopic evidences.

Raman spectra were measured for Triton X-100 and related compounds which include *p*-(1,1,3,3-tetramethylbutyl)anisole (TMBA) $(CH_3)_3CCH_2C(CH_3)_2C_6H_4OCH_3$, *p*-(1,1,3,3-tetramethylbutyl)phenol (TMBP) $(CH_3)_3CCH_2C(CH_3)_2C_6H_4OH$, *p*-(1,1-dimethylpropyl)-anisole (DMPA) $CH_3CH_2C(CH_3)_2C_6H_4OCH_3$, *p*-(1,1-dimethylpropyl)phenol (DMPP) CH_3CH_2-$C(CH_3)_2C_6H_4OH$, *p*-*t*-butylanisole (TBA) $(CH_3)_3CC_6H_4OCH_3$, *p*-*t*-butylphenol (TBP) $(CH_3)_3C$-C_6H_4OH, 2,4,4-trimethyl-2-pentanethiol (TMPT) $(CH_3)_3CCH_2C(CH_3)_2SH$, and α-methyl-ω-hydroxypoly(oxyethylene)s (MHPOE) $CH_3(OCH_2CH_2)_nOH$ with average molecular weights of 350 and 550, respectively, corresponding to approximately 7 and 12 oxyethylene units. Some of the Raman spectra are shown in Fig. 1. TMBA is the closest model compound of the hydrophobic group, *i.e.*, the *p*-(1,1,3,3-tetramethylbutyl)phenoxyl group, of Triton X-100 surfactant and MHPOE's are model compounds of the hydrophilic group. Accordingly, the Raman bands of Triton X-100 arising from the

hydrophobic and hydrophilic groups can be discriminated by comparing the spectra of Triton X-100 with those of TMBA and MHPOE, supplemented by the spectra of the other related compounds. The spectral comparison indicates that the bands assigned to the hydrophobic group are those at 1612, 1454, 1298, 1250, 1214, 1190, 1169, 1102, 923, 874, 805, 752, 686, 641, 590, 321, and 242 cm^{-1} and the bands assigned to the hydrophilic group are those at 1472, 1288, 1067, and 888 cm^{-1}. The bands at 1135 and 843 cm^{-1} are composites of the bands due to the hydrophobic and hydrophilic groups, since TMBA and MHPOE exhibit Raman bands in common at the corresponding wavenumbers. The band of Triton X-100 at 805 cm^{-1}, which has been assigned to the hydrophobic group, is also associated in part with the hydrophilic group, as evidenced by the observation of the 808-cm^{-1} band for MHPOE.

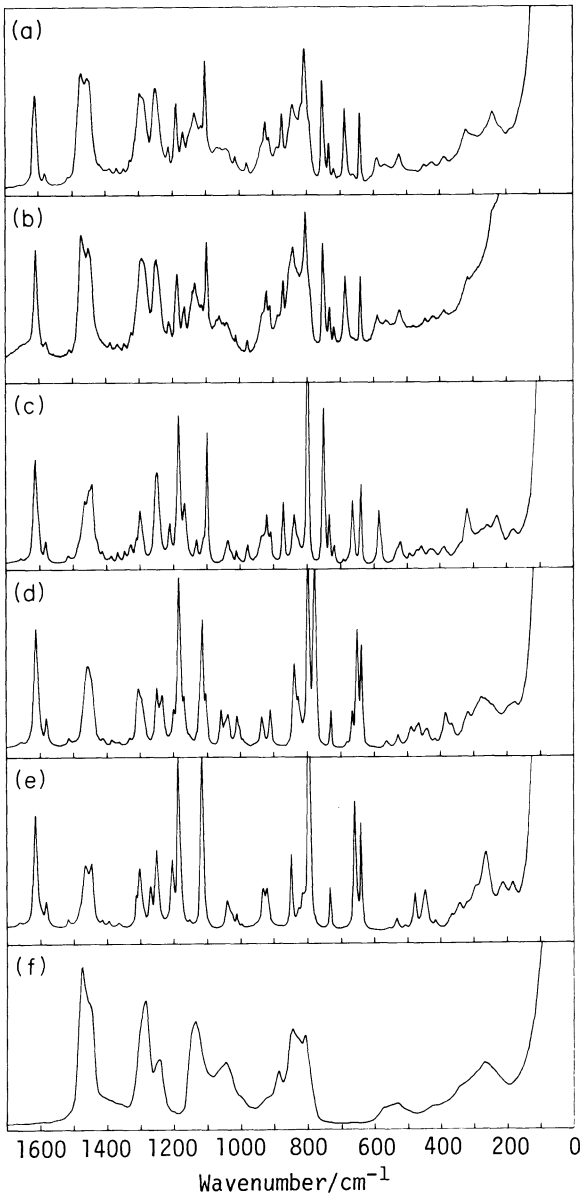

Fig. 1. Raman spectra of Triton X-100 and related compounds; (a) Triton X-100 (liquid), (b) Triton X-100 (20 % aqueous solution), (c) TMBA (liquid), (d) DMPA (liquid), (e) TBA (liquid), (f) MHPOE with average molecular weight of 550 (liquid).

Having examined the vibrational assignment of Triton X-100, we shall discuss the conformation of the hydrophobic group on the basis of the observed spectral feature. The *p*-(1,1,3,3-tetramethylbutyl)phenoxyl group may take various conformations owing to the possible internal rotations about the C_2–C_1, C_1–Ph, and Ph–O bond axes (see Fig. 2). The second and third axes are concerned in the rotation of the phenyl group relative to the C_1–Ph–O axes and accordingly they do not practically affect the overall length of the hydrophobic moiety of Triton X-100. We therefore focus on the conformation about the C_2–C_1 axis in the 1,1,3,3-tetramethylbutyl group. This group is possible to take two conformations, one with the C_3-*t*-butyl group in the *trans* disposition, and the other with this group in the *gauche* disposition, with respect to the phenoxyl group (see Fig. 2). In order to find Raman bands which are characteristic of these conformations, we have examined the spectra of TMPT, in which the 1,1,3,3-tetramethylbutyl group is linked to the mercapto group. Liquid TMPT exhibits strong bands at 732 and 748 cm^{-1},

which have been shown to be due to the totally symmetric C–C stretching vibrations of the *t*-butyl part of the 1,1,3,3-tetramethylbutyl group.[9] On solidification, the 732-cm^{-1} band disappears and only the 748-cm^{-1} band persists, indicating that these two bands are associated respectively with the two possible conformers, the *trans* and *gauche* forms with respect to the CC–CS axis. This molecule also shows the C–S stretching bands at 653 and 598 cm^{-1}, the former being assigned to the *trans* form and the latter being assigned to the *gauche* form on the basis of the correlation between the C–S stretching wavenumber and the conformation about the C–C bond next to the C–S bond, as established for dialkyl sulfide molecules.[9-11] The fact that only the 598-cm^{-1} band is persisting in the solid state shows that this molecule takes the *gauche* form in the solid state and that the C–C stretching band at 748 cm^{-1} is due to the *gauche* form and the band at 732 cm^{-1} is due to the *trans* form. This spectral feature for TMPT, along with the normal coordinate treatment on this molecule,[9] leads to a correlation between the wavenumber for the totally symmetric C–C stretching vibration of the *t*-butyl part of $(CH_3)_3CCH_2C(CH_3)_2X$ and the conformation about the $-\overset{|}{C}C-\overset{|}{C}X$ axis: the wavenumber for the *gauche* conformation is higher than that for the *trans* conformation, if the substituent X is heavier than CH_3, in the light of the fact that the molecule with $X = CH_3$ does not show the *trans-gauche* rotational isomerism because of its chemical structure.

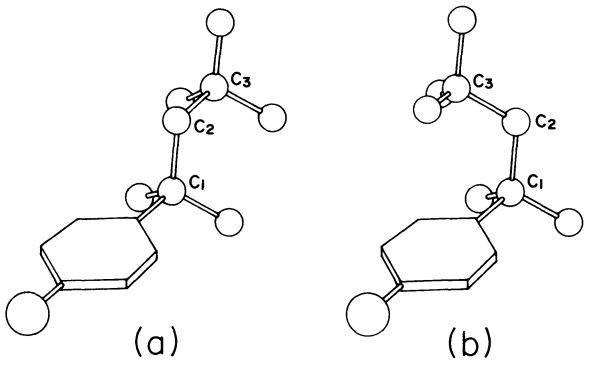

Fig. 2. Schematic structures of the *p*-(1,1,3,3-tetramethylbutyl)phenoxyl group; (a) the *trans* conformation about the C_3C_2–C_1Ph axis, (b) the *gauche* conformation about the C_3C_2–C_1Ph axis.

In the spectral region between 700 and 800 cm^{-1}, Triton X-100, both in the neat liquid state and in aqueous solution, gives a prominent band at 752 cm^{-1} which has been interpreted to be due to the hydrophobic group in comparison with the spectrum of TMBA. TMBP also shows the corresponding band at the same wavenumber but DMPA, DMPP, TBA, and TBP do not show corresponding bands (see Fig. 1). Accordingly, this band is assigned to the 1,1,3,3-tetramethylbutyl group, in accord with the 748-cm^{-1} band of TMPT, in the *gauche* conformation about the C_3C_2–C_1Ph axis. The band at 734 cm^{-1} for Triton X-100 is associated with a vibration of the aromatic group, since the corresponding bands are observed in common for TMBA, TMBP, DMPA, DMPP, TBA, and TBP. A weak band is observed at 720 cm^{-1} for Triton X-100. The corresponding band is found in the spectra of TMBA and TMBP in the liquid state but not in the spectra of the other phenyl-containing compounds. This band is therefore assigned to the 1,1,3,3-tetramethylbutyl group, in accord with the 732-cm^{-1} band of TMPT, in the *trans* conformation about the C_3C_2–C_1Ph axis. It is worthy of note that the 720-cm^{-1} band for TMBA and TMBP disappears on solidification; this indicates that these molecules take only the *gauche* confor-

mation in the solid state.

The spectral evidences given above lead to the conformational state of Triton X-100: molecules of this surfactant take both the *gauche* and *trans* conformations about the C_3C_2–C_1Ph axis in the neat liquid state and in aqueous solution. The normal coordinate treatment on TMPT has indicated that the vibrational modes of the totally symmetric C–C stretching vibrations of the *t*-butyl part of the 1,1,3,3-tetramethylbutyl group in the *trans* and *gauche* conformations resemble each other.[9] This suggests that the Raman scattering intensities, per molecule, for the two vibrations are not largely different. Thus, the relative intensities of the bands due to these vibrations may be used to estimate approximate populations of the two conformations. The observed spectra of Triton X-100 in the liquid state and in aqueous solution show that the *gauche* band at 752 cm^{-1} is 10–15 times stronger than the *trans* band at 720 cm^{-1}. This leads to a conclusion that the 1,1,3,3-tetramethylbutyl group of Triton X-100 molecules is in the *gauche* conformation for the most part, possibly more than 90% as estimated from the relative Raman intensities.

In order to confirm the validity of the preferential *gauche* conformation of the C_3C_2–C_1Ph group, we have surveyed crystallographic data of related compounds which contain the 1,1,3,3-tetramethylbutylated aryl group. Calix[4]arene derived from *p*-(1,1,3,3-tetramethylbutyl)phenol,[12] 2,5-bis(1,1,3,3-tetramethylbutyl)-1,4-benzoquinone,[13] and 1-(1,1,3,3-tetramethylbutyl)-4-phenyl-1,2,4-triazoline-3,5-dione[14] all take the *gauche* conformation in the 1,1,3,3-tetramethylbutyl group with dihedral angles between 55 and 77°. The molecular structures of these compounds are quite consistent with the conformation of Triton X-100 revealed in the present work. In conclusion, the hydrophobic group of the Triton X-100 molecules in the liquid state and in aqueous solution preferentially takes the bent structure, as shown in Fig. 2 (b), with the 1,1,3,3-tetramethylbutyl group in the *gauche* conformation.

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