Conformational Order of the Alkyl Chain in a Nonionic Surfactant α-Dodecyl-ω-hydroxytris(oxyethylene) ($C_{12}E_3$) in Water

Sei Masatoki, Keiichi Ohno, Hiroshi Yoshida, and Hiroatsu Matsuura*
Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739

(Received October 24, 1995)

The conformational order of the alkyl chain in α-dodecyl-ω-hydroxytris(oxyethylene) ($C_{12}E_3$) has been studied by monodeuteration infrared spectroscopy for the lamellar and the isotropic solution phases of the $C_{12}E_3$–water system. The conformational order profiles for the two phases are essentially the same, showing maximum order in the middle of the chain.

Amphiphilic molecules such as surfactants and lipids self-assemble in water and other solvents to form aggregates with supramolecular structures.[1–3] The most typical phases of the supramolecular structures formed by these amphiphiles are the lamellar, the hexagonal, and the cubic phases characterized by long-range order. These molecules form in their isotropic solutions the aggregates lacking long-range correlations, such as spherical micelles, cylindrical micelles, and bilayers. For studying the structure of supramolecular systems consisting of amphiphilic molecules, conformational properties of the molecular chain are important in relation to the phase behavior.[4,5] Despite its fundamental importance, no direct experimental evidence has been reported of the conformational relevance to the phase structure.

In the present work, we have studied one of the typical nonionic surfactants, α-dodecyl-ω-hydroxytris(oxyethylene) $CH_3(CH_2)_{11}(OCH_2CH_2)_3OH$ ($C_{12}E_3$), aiming at establishing the relation between the conformational order of the chain and the supramolecular structure. The $C_{12}E_3$–water system exhibits a phase diagram,[6] in which the liquid-crystalline lamellar phase (L_α) is observed in concentration regions of approximately 45–80 wt % below about 50 °C. In more concentrated regions, an isotropic solution phase (L_2) occurs, which is a phase of liquid surfactant containing dissolved water. In the regions below 45 wt %, the separated phases of $L_2 + L_\alpha$ and $W + L_\alpha$ are observed. We have studied by infrared spectroscopy the conformation of $C_{12}E_3$ in the L_α and L_2 phases and discussed the conformational order in comparison with the order parameters derived from NMR spectra of related systems. This paper presents the first direct observation of the conformational order profiles of the alkyl chain in nonionic surfactants in water.

For studying the conformational state of the alkyl chain, we have used selectively monodeuterated species of $C_{12}E_3$, in which one of the hydrogen atoms in the alkyl chain is substituted by deuterium. Using various monodeuterated species with deuterium introduced into specific sites in the chain, we have observed the stretching vibrations of the isolated C–D bond. This conformational analysis is based on the fact that the wavenumbers of the isolated C–D stretching vibrations are sensitive to the conformation in the vicinity of the C–D bond and are correlated directly to the C–D bond lengths.[7] This method is capable of determining the conformational state of the specifically deuterated part of the chain and eventually, after examining all possible monodeuterated species, the conformational state of the whole chain. Detailed procedure of the conformational analysis will be presented in a separate paper.[8]

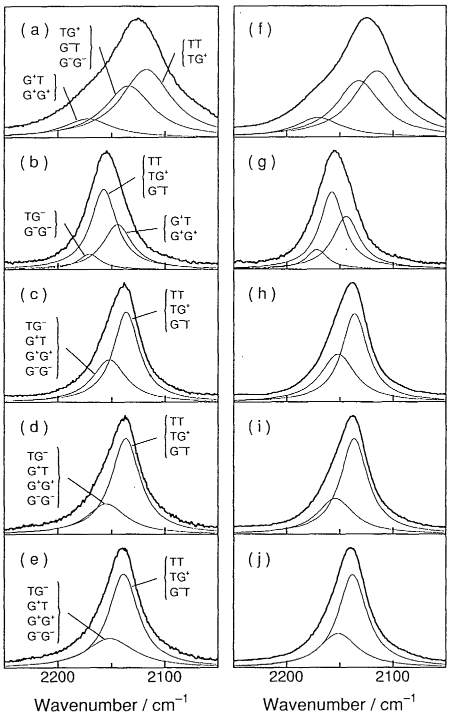

Figure 1. Infrared spectra of 70 wt % (a–e) and 90 wt % (f–j) aqueous solutions at 26 °C of C_{12}-1-d_1-E_3 (a and f), C_{12}-2-d_1-E_3 (b and g), C_{12}-4-d_1-E_3 (c and h), C_{12}-6-d_1-E_3 (d and i), and C_{12}-8-d_1-E_3 (e and j), with conformational assignments of the resolved bands indicated. The conformation designation given applies to the CO–C_1–C_2C_3 bonds for C_{12}-1-d_1-E_3, the OC_1–C_2–C_3C_4 bonds for C_{12}-2-d_1-E_3, and the CC–C–CC bonds for C_{12}-4-d_1-E_3, C_{12}-6-d_1-E_3, and C_{12}-8-d_1-E_3, with the CHD group in the *R*-configuration (T, *trans*; G$^+$, *gauche*$^+$; G$^-$, *gauche*$^-$).

In the present work, we have prepared five monodeuterated species of $C_{12}E_3$, namely $CH_3(CH_2)_{11-k}CHD(CH_2)_{k-1}(OCH_2CH_2)_3OH$ (C_{12}-*k*-d_1-E_3), where k = 1, 2, 4, 6, and 8. Infrared spectra were measured for aqueous solutions of these monodeuterated species with 50, 60, 70, 80, 85, 90, 95, and 100 wt % compositions at 26, 36, 45, 54, and 65 °C. Figure 1 shows the spectra of the C–D stretching vibrations for aqueous solutions of the five monodeuterated species. The observed spectral profiles of the C–D stretching vibrations are resolved into three bands for C_{12}-1-d_1-E_3 and C_{12}-2-d_1-E_3 and into two bands for C_{12}-4-d_1-E_3, C_{12}-6-d_1-E_3, and C_{12}-8-d_1-E_3. These resolved bands are assigned, as shown in Figure 1, to particular conformations around the two adjoining C–C (and C–O) bonds with the substituent deuterium bonded to the central carbon atom.[8]

The experimental data available in this work do not allow to determine all of the conformational populations uniquely, but give only possible ranges of their values. In Figure 2, the *trans* fractions f_T for the O–C_1, C_1–C_2, C_2–C_3, C_3–C_4–C_5, C_5–C_6–C_7, and C_7–C_8–C_9 bonds are displayed for several compositions and temperatures, where the results for the last three bond

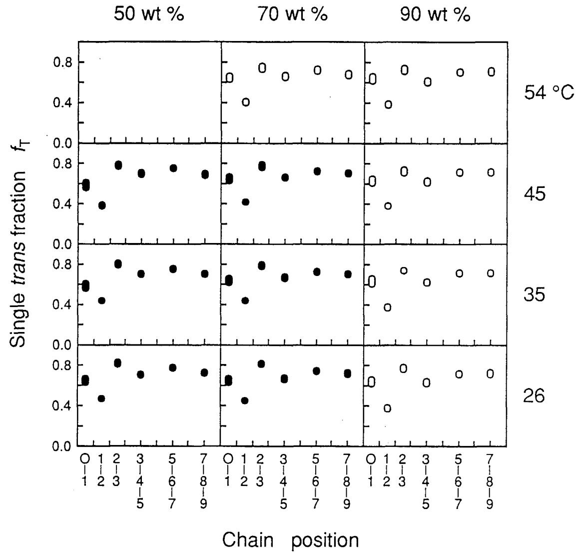

Figure 2. Positional dependence of the single *trans* fraction f_T at different compositions and temperatures. Solid and open symbols are used respectively for the L_α and L_2 phases. Carbon atoms are indicated by their numbers.

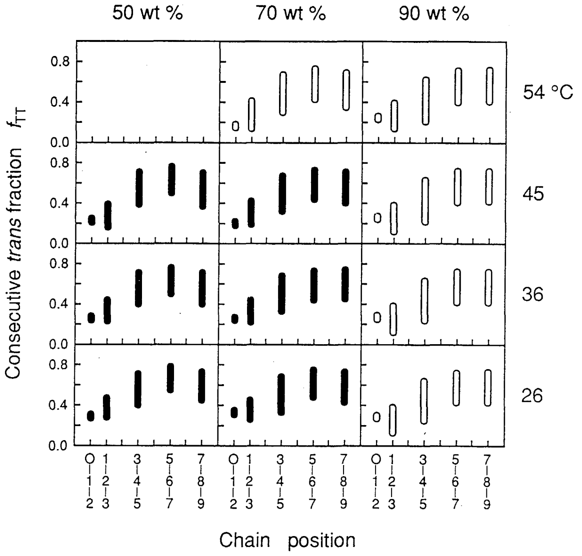

Figure 3. Positional dependence of the consecutive *trans* fraction f_{TT} at different compositions and temperatures. See also the caption for Figure 2.

sequences are averages of the values for the two adjoining bonds. Figure 3 shows the fractions, f_{TT}, of the consecutive *trans* conformations around the two adjoining bonds. These results indicate that the positional dependence of f_T or f_{TT} is not significantly different for different compositions and temperatures. The single *trans* fraction f_T is the highest (0.7–0.8) for the C_2–C_3 bond and is the lowest (0.3–0.5) for the C_1–C_2 bond among the C–C bonds studied. These observations are consistent with the results calculated with the rotational-isomeric state model.[9] The consecutive *trans* fraction f_{TT} shows its maximum at the C_5–C_6–C_7 bonds.

It is reasonable to use the f_{TT} values to represent the conformational order of the alkyl chain, since the disorder originates from the occurrence of the *gauche* segments in the chain. It is remarked that the conformational order is the highest in the middle of the alkyl chain for both the L_α and L_2 phases, but not near the alkyl/oxyethylene interface. Another important finding is that the positional dependence of the conformational order (conformational order profile) is essentially the same for the two phases, although the long-range order should be quite different. Figure 3 indicates that the conformational order in the region of the L_α phase closer to the phase separation into $L_2 + L_\alpha$ or $W + L_\alpha$ decreases more rapidly toward the chain terminal. This observation implies that the conformational transformation from *trans* to *gauche* at the C–C bonds near the chain terminal makes the lamellar structure less stable and leads eventually to the phase separation.

The conformational order determined by infrared spectroscopy may be compared with the order parameters derived from NMR spectra.[10,11] The maximum of the order parameters has been observed at the C_3 to C_5 positions for the L_α phase of $C_{12}E_4$ and at the C_3 to C_6 positions for the neat liquid and the micellar solution phase of $C_{12}E_5$. The conformational order evaluated in the present work is consistent with the order parameters for these surfactants. It should be noticed, however, that the order parameters from NMR spectra are measures of the average bond orientation in all motions faster than about a microsecond, while infrared spectroscopy observes the *trans–gauche* conformational changes on a time scale of 10^{-14} to 10^{-13} seconds.

In conclusion, we have clarified the conformational order of the alkyl chain in the lamellar and the isotropic solution phases; the conformational order profiles for these phases are essentially the same, showing maximum order in the middle of the chain.

References and Notes

1 C. Tanford, "The Hydrophobic Effect: Formation of Micelles and Biological Membranes," 2nd edition, Wiley, New York (1980).
2 "Physics of Amphiphiles: Micelles, Vesicles and Microemulsions," ed by V. Degiorgio and M. Corti, North-Holland, Amsterdam (1985).
3 G. J. T. Tiddy, in "Modern Trends of Colloid Science in Chemistry and Biology," ed by H.-F. Eicke, Birkhäuser, Basel (1985), p 148.
4 G. J. T. Tiddy, *Phys. Rep.*, **57**, 1 (1980).
5 G. Karlström and B. Lindman, in "Organized Solutions," ed by S. E. Friberg and B. Lindman, Dekker, New York (1992), Chapter 5, p 49.
6 D. J. Mitchell, G. J. T. Tiddy, L. Waring, T. Bostock, and M. P. McDonald, *J. Chem. Soc., Faraday Trans. 1*, **79**, 975 (1983).
7 K. Ohno, Y. Takagi, and H. Matsuura, *J. Phys. Chem.*, **97**, 5530 (1993).
8 S. Masatoki, K. Ohno, H. Yoshida, and H. Matsuura, to be published.
9 P. J. Flory, "Statistical Mechanics of Chain Molecules," Hanser, Munich (1989).
10 A. J. I. Ward, H. Ku, M. A. Phillippi, and C. Marie, *Mol. Cryst. Liq. Cryst.*, **154**, 55 (1988).
11 T. Ahlnäs, G. Karlström, and B. Lindman, *J. Phys. Chem.*, **91**, 4030 (1987).