Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Conformational Analysis of Nonionic Surfactants by FT-Raman Spectroscopy Measurements

Takashi Mihara [a] & Naoyuki Koide [a]

[a] Department of Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, JAPAN

Version of record first published: 24 Sep 2006

To cite this article: Takashi Mihara & Naoyuki Koide (2001): Conformational Analysis of Nonionic Surfactants by FT-Raman Spectroscopy Measurements, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 367:1, 605-614

To link to this article: http://dx.doi.org/10.1080/10587250108028681

Mol. Cryst. and Liq. Cryst., 2001, Vol. 367, pp. 605-614
Reprints available directly from the publisher
Photocopying permitted by license only

Conformational Analysis of Nonionic Surfactants by FT-Raman Spectroscopy Measurements

TAKASHI MIHARA and NAOYUKI KOIDE

Department of Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601 JAPAN

A conformational analysis of ethylene oxide and methylene chains for the mixtures of nonionic surfactant (polyethyleneglycol mono n-dodecyl ether, $C_{12}EO_n$, n = 5 ~ 8) with pure water was carried out by FT-Raman spectroscopy measurements to clarify the relationship between the conformation of the methylene or ethylene oxide chain and the aggregate for $C_{12}EO_n$ in the pure water. The trans conformation for C-C bond in the hydrophilic ethylene oxide chain in liquid crystalline phase was less than that in aqueous micellar solution and pure $C_{12}EO_n$. On the other hand, the order of the hydrophobic methylene chain decreased with increasing concentration of $C_{12}EO_n$.

Keywords: nonionic surfactant; lyotropic liquid crystal; FT-Raman spectroscopy

INTRODUCTION

It is well known that lyotropic liquid crystal is consisted of the mixture of amphiphilic molecules with a solvent such as water. The exhibition of

lyotropic liquid crystalline phases like a hexagonal and/or a lamellar phase was mainly dependent upon the concentration of the amphiphilic molecule in the mixture. For example, in high concentration of the mixture of soap such as a sodium stearate with water, lamellar and hexagonal phases were exhibited, while in lower one, micellar solution was formed.

In this study, we paid attention to the conformation of the hydrophilic and hydrophobic groups for the amphiphilic molecules in the lyotropic liquid crystalline phase. Raman spectroscopy measurement was a useful tool for the investigation of conformational analysis for the mixture of amphiphilic molecules with water. In the case of lipids, the phase structure was deeply influenced by the conformation and order (lateral packing) of the hydrophobic methylene chain [1–2]. The conformation and order (lateral packing) of the hydrophobic methylene chain was discussed by the spectral intensity ratio of symmetric and asymmetric methylene stretching peaks. In the case of the lipids, the order of the hydrophobic methylene chain became higher with increasing order of the mesophase structure.

On the other hand, mesophases were also detected for the mixture of nonionic surfactant with water. Nonionic surfactants generally consisted of an ethylene oxide chain as a hydrophilic group and a hydrophobic group like methylene chain or alkylbenzene. The conformation of the ethylene oxide chain for the mixture of nonionic surfactants with water was investigated by Raman spectroscopy measurements. Fukuhara et al discussed conformation of the ethylene oxide chain for nonionic surfactants in the solid phase [3]. However, the conformational analysis of the hydrophobic group was little investigated.

In this report, in order to investigate the relationship between the mesophase structure and the conformation of hydrophilic and hydrophobic group for the nonionic surfactant, Raman spectroscopy measurements of nonionic surfactants were carried out. We discussed mainly the conformation of the hydrophobic group in the nonionic surfactants.

EXPERIMENTAL

Materials

Samples of polyethyleneglycol mono n-dodecyl ether ($C_{12}EO_n$, n = 5 ~ 8) were purchased from Nikko Chemicals Co.. It was used without further purification. Pure H_2O was prepared by Mili Qlabo system.

The mixture of $C_{12}EO_n$ with pure water in various concentrations (in the case of $C_{12}EO_8$, 34, 47, 60, 70, 80, 89 wt%) and pure $C_{12}EO_n$ (n = 5 ~ 8) were prepared in glass tubes. After centrifugation of the mixtures, all samples were permitted to stand in a thermostat for several days.

Thermal properties

In order to obtain a phase diagram of the mixtures of $C_{12}EO_7$ with pure water ($C_{12}EO_7$-H_2O system), we investigated thermal properties of $C_{12}EO_7$-H_2O system by using of polarized optical microscopy (Nikon OPTIPHOTO-POL polarized optical microscopy equipped with a Mettler FP80 controller and a FP82 hot stage), X-ray (Rigaku RINT 2500, 1mm diameter quartz glass capillaries) and differential scanning calorimetry (Mettler DSC 821^e) measurements. Phase diagrams of the mixtures were summarized in Figure 1. The phase diagrams except $C_{12}EO_7$-H_2O system were already reported by Tiddy et al. [4] Raman spectroscopy measurements of $C_{12}EO_n$-H_2O system were carried out based on the phase diagram obtained.

Spectroscopy measurements

Raman spectroscopy measurements of the mixtures and pure $C_{12}EO_n$ were measured at 2 cm^{-1} resolution with a JEOL JIR-7000 spectrometer equipped with RS-RSU200 Raman spectroscopy units. 500 scans were accumulated. Excitation radiation of a cw Nd: YAG laser (1064nm) was used. The laser power was controlled to be constant during Raman spectros-

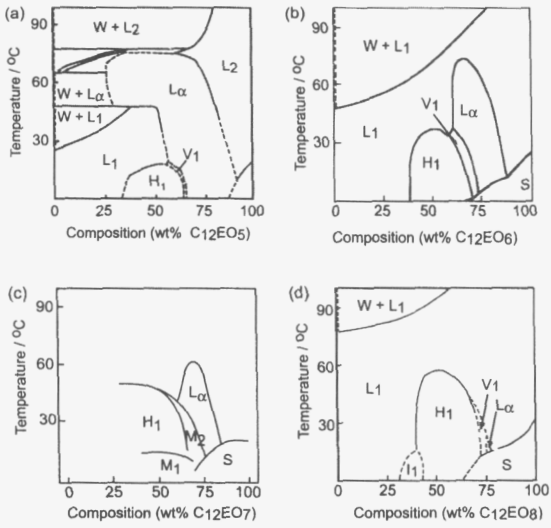
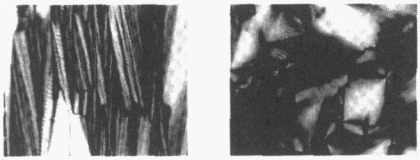


FIGURE 1 Phase diagrams for mixtures of $C_{12}EO_n$ (n = 5 ~ 8) with water: (a) $C_{12}EO_5$, (b) $C_{12}EO_6$, (c) $C_{12}EO_7$, (d) $C_{12}EO_8$: H_1, hexagonal; V_1, bicontinuous cubic; L_1, micellar isotropic; L_2, liquid surfactant containing dissolved water; L_α, lamellar; I_1, closed-packed spherical micelle cubic; M_2, liquid crystalline phase; S, solid phase.

copy measurements. Elevated temperature spectra of FT-Raman were obtained by placing the glass tube in the temperature-controlled cell (Mettler FP-80 temperature controller with a FP82 hot stage). Before each spectral acquisition the temperature was kept constant for about 1 hour to ensure complete temperature equilibration. Measurement temperatures (20~60 or 70 °C) were determined based on the phase diagram already reported by Tiddy et al as shown in Figure 1[4].

RESULTS AND DISCUSSION

Optical micrographs of hexagonal and lamellar phases for $C_{12}EO_7$ were shown in Figure 2. The d-spacings of their phases were summarized in Table 1. In the hexagonal phase, a limited number of Bragg spots were observed on circles whose radii fit the spacing ratios $1 : \sqrt{3}$. The spacing ratio was characteristic of a hexagonal phase. In the lamellar phase, a sharp Bragg diffraction was observed, corresponding to an oriented lamellar phase.



(a) (b)

FIGURE 2 Optical micrographs of $C_{12}EO_7$-H_2O system; (a) 50 wt%, hexagonal phase, (b) 80wt%, lamellar phase.

TABLE 1 d-spacing of $C_{12}EO_7$-H_2O system.

Concentration	d-spacing / Å
50wt%	46.7 , 27.6
80wt%	42.6

A typical Raman spectrum for the mixture of $C_{12}EO_n$ with pure water ($C_{12}EO_n$-H_2O system) was shown in Figure 3. This spectrum consisted of the peaks attributed to various kinds of vibrational modes for hydro-

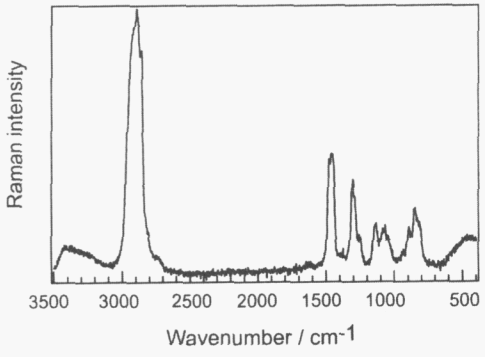


FIGURE 3 Raman spectrum of $C_{12}EO_8$-H_2O system.

philic ethyleneoxide and hydrophobic methylene group. These peaks at 780~950 cm^{-1}, at 1000~1200 cm^{-1}, at 1200~1350 cm^{-1}, at 1400~1550 cm^{-1}, and at 2700~3100 cm^{-1} of $C_{12}EO_n$-H_2O system were assigned to CH_2 rocking, to C-O, C-C stretching and CH_2 rocking, to CH_2 twisting, to CH_2 scissoring, and to CH_2, CH_3 stretching [5~6].

Maxfield et al. investigated the conformation of poly(ethylene oxide): PEO, by Raman spectroscopy measurements [5]. A peak near 809cm^{-1} was attributed to x-t-x conformation for (O-C-C-O) unit in PEO group, while a peak near 851 cm^{-1} was assigned to x-g-x conformation for the unit [7~8] (t and g means trans and gauche conformation, respectively. x indicates t or g.). Therefore the conformation of PEO group in $C_{12}EO_n$-H_2O system can be explained by the intensity ratio of these peaks near 809cm^{-1} and near 851 cm^{-1}. High peak intensity ratio indicated that quantity of (O-C-C-O) unit with x-t-x conformation increased relative to that with x-g-x conformation in PEO group. An increase in x-t-x conformation in PEO group showed that PEO group in $C_{12}EO_n$-H_2O system approached more extended form.

The concentration dependence of the peak intensity ratio was demonstrated in Figure 4. The peak intensity ratios in liquid crystalline state of $C_{12}EO_n$-H_2O system were low compared with those of micellar solution and $C_{12}EO_n$ molten state. These results indicated that (O-C-C-O) unit easily formed x-g-x conformation in liquid crystalline phase compared to micellar solution and $C_{12}EO_n$ molten state. It is known that PEO group forming a helix structure had x-g-x con-

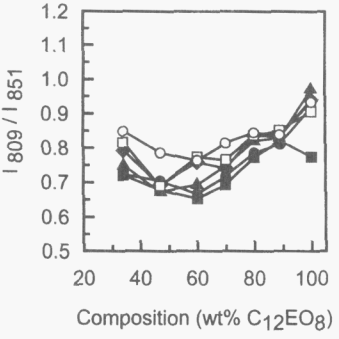


FIGURE 4 Raman intensity ratios (I_{809} / I_{851}) as a function of concentration of $C_{12}EO_8$: 20°C(■), 30°C(●), 40°C(▲), 50°C(◆), 60°C(□) and 70°C(○).

formation for (O-C-C-O) unit. The helix structure of PEO group in micellar solution would be influenced by hydrogen bonding formed between water and oxygen atom in PEO group.

The peak intensity ratios were investigated for polyethyleneglycol (PEG) with same length as hydrophilic PEO group in $C_{12}EO_8$ for comparison with change in the intensity ratios for $C_{12}EO_8$-H_2O system. The peak intensity ratio decreased with decreasing concentration for PEG-H_2O system. This result demonstrated that the x-g-x conformation for (O-C-C-O) unit in PEG increased with decreasing concentration of PEG. We could not observe same changes in the peak intensity ratio for PEG-H_2O system as those for $C_{12}EO_n$-H_2O system. Therefore changes in the conformation for the hydrophilic group in $C_{12}EO_n$-H_2O system would arise from the difference in the state of aggregation (micelle and liquid crystalline phase).

As mentioned above, the relationship between the conformation and order of the hydrophobic methylene chain of lipids was investigated by Raman intensity ratio of the peaks attributed to symmetric and asymmetric stretching vibration in the region of 2700~3100 cm^{-1}. The peak intensity ratio of asymmetric stretching vibration and symmetric stretching vibration displayed the order of the methylene group. The order of the methylene group was higher when the peak intensity ratio became bigger. The peak intensity ratio became bigger when the order of phase structure for the lipids-H_2O system increased with increasing concentration of lipids [1].

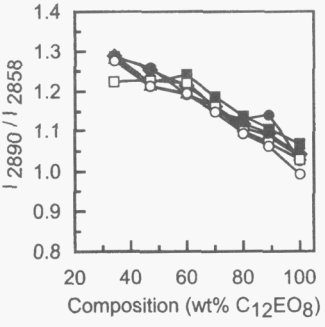


FIGURE 5 Raman intensity ratios (I_{2890} / I_{2858}) as a function of concentration of $C_{12}EO_8$: 20°C(■), 30°C(●), 40°C(▲), 50°C(◆), 60°C(□) and 70°C(○).

We applied this procedure to the investigation for the conformation of the methylene group in nonionic surfactant $C_{12}EO_n$-H_2O system. The intensity ratios of the peaks near 2890 cm^{-1} (assigned to CH_2 asymmetric stretching vibration) and near 2858 cm^{-1} (assigned to CH_2 symmetric stretching vibration) were plotted in Figure 5. The peak intensity ratio decreased with increasing concentration of $C_{12}EO_n$. The order of the methylene group decreased with increasing concentration of $C_{12}EO_n$. Therefore it was considered that the order of the methylene group was dependent upon the concentration of $C_{12}EO_n$ rather than the state of aggregation.

Quantitative analysis of the methylene stretching vibration region was carried out for investigating the order of the methylene group. The methylene stretching vibration region could be divided into five peaks by the curve-fitting procedure as shown in Figure 6. We paid attention to the peak area ratio [(C)/(A)] to estimate the order of the methylene group because the peak area ratio can exactly explain the order of the methylene group compared to the peak intensity ratio.

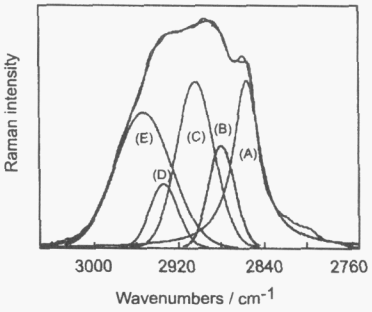


FIGURE 6 Deconvolution of CH_2 stretching region for $C_{12}EO_n$-H_2O system; (A) CH_2 symmetric (alkyl), (B) CH_3 symmetric (alkyl), (C) CH_2 asymmetric (alkyl) and CH_2 symmetric (ethylene oxide), (D) CH_3 symmetric (alkyl) and (E) CH_3 asymmetric (alkyl) and CH_2 asymmetric (ethylene oxide).

The peak area ratios were plotted in Figure 7. The peak area ratios in the low concentration region were dispersed depending on temperature. The peak area ratios decreased with increasing concentration of $C_{12}EO_n$. This result indicated that the order of the methylene group decreased with increasing concentration of $C_{12}EO_n$. This is the same result displayed by the peak intensity ratio mentioned before.

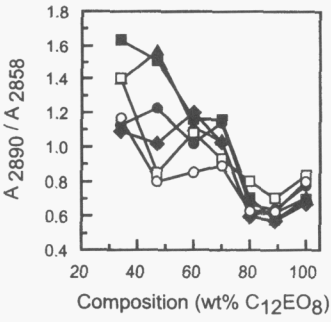


FIGURE 7 Peak area ratios (A_{2890} / A_{2858}) as a function of concentration of $C_{12}EO_8$: 20°C(■), 30°C(●), 40°C(▲), 50°C(◆), 60°C(□) and 70°C(○).

Further, we investigated the order of the methylene group by using of differential spectra between the $C_{12}EO_n$ and PEG as a hydrophilic group. It would be considered that the differential spectra contained the conformational information about the methylene group in the $C_{12}EO_n$. A typical differential spectrum was shown in Figure 8. The differential spectra between $C_{12}EO_8$-H_2O and PEG-H_2O systems were obtained by using of the computer program. We admitted that the differential spectra included some errors because the Raman spectra of the PEG-H_2O system could not contain the information about the state of the aggregation

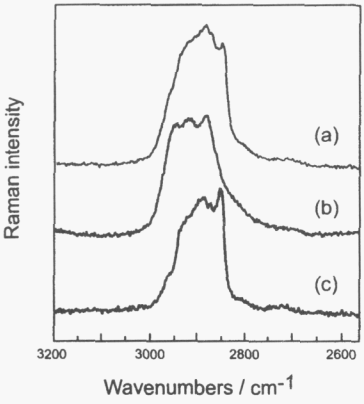


FIGURE 8 Raman spectra of CH_2 stretching region for $C_{12}EO_8$-H_2O system(a), PEG-H_2O(b) and their differential spectrum(c).

like a micelle and liquid crystalline phases. However, it would be worthwhile to estimate the order of the methylene group in the $C_{12}EO_n$-H_2O system by using of the differential spectra.

The peak intensity ratios between CH_2 asymmetric stretching vibration and CH_2 symmetric stretching vibration for the differential spectra were plotted in Figure 9. These intensity ratios decreased with increasing concentration of $C_{12}EO_n$ in the systems. This was the same result that demonstrated by the intensity ratio in the original peak and the area ratio by curve-fitting procedure. The order of methylene chain in the $C_{12}EO_n$-H_2O system decreased with increasing concentration of $C_{12}EO_n$-H_2O. Therefore we concluded that the order of the methylene group decreased with increasing concentration of $C_{12}EO_n$ in the system based on the three methods.

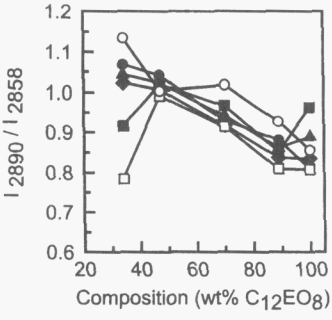


FIGURE 9 Raman intensity ratios (I_{2890} / I_{2858}) as a function of concentration of $C_{12}EO_8$ (Differential spectrum): 20°C(■), 30°C(●), 40°C(▲), 50°C(◆), 60°C(□) and 70°C(○).

References

[1] K. Larsson and R.P. Rand, *Biochim. Biophys. Acta*, **326**, 245 (1973).
[2] B. Gaber and W.L. Peticolas, *Biochim. Biophys. Acta*, **465**, 260 (1977).
[3] H. Matsuura and K. Fukuhara, *J. Phys. Chem.*, **91**, 6139 (1987).
[4] Tiddy D.J. Mitchell, G.J.T. Tiddy, L. Waring, T. Bostock and M.P. McDonald, *J. Chem. Soc., Faraday Trans. 1*, **79**, 975 (1983).
[5] J. Maxfield and I.W. Shepherd, *Polymer*, **16**, 505 (1975).
[6] K. Kalyanasundaram and J.K. Thomas, *J. Phys. Chem.*, **80**, 1462 (1976).
[7] H. Matsuura and K. Fukuhara, *J. Mol. Struct.*, **126**, 251 (1985).
[8] H. Matsuura and K. Fukuhara, *J. Polym. Scie. Part B. Polym. Phys.*, **24**, 1383 (1986).