# Deuterium NMR and Raman Spectroscopic Studies on Conformational Behavior of Lipophilic Chains in the $C_{12}E_3$ / Decane / Water System

Akimitsu Tonegawa, Ayako Michiue, Takashi Masuda, Keiichi Ohno, Hiroatsu Matsuura, Koji Yamada, and Tsutomu Okuda

Department of Chemistry, Graduate School of Science, Hiroshima University,
Kagamiyama, Higashi-Hiroshima 739-8526, Japan

Reprint requests to Dr. K. O.; E-mail: kohno@sci.hiroshima-u.ac.jp

Z. Naturforsch. **57 a,** 320–326 (2002); received March 2, 2002

*Presented at the XVIth International Symposium on Nuclear Quadrupole Interactions, Hiroshima, Japan, September 9-14, 2001.*

The order parameter and the conformations of the lipophilic chains in the $C_{12}E_3$ / decane / water ternary system have been studied by deuterium NMR and C-D stretching Raman spectroscopy. The order parameter and the trans fraction of the C-C bond of decane molecules decrease steadily or remain nearly constant with increasing decane concentration without noticeable changes at the phase transitions. On addition of decane molecules to the $C_{12}E_3$ / water system, the effective volume of the lipophilic part of a single surfactant molecule increases as a result of the penetration of the added decane molecules into the lipophilic layer, leading to a high mobility of the alkyl chain. To minimize the resulting increase in the effective cross-sectional area of a surfactant molecule, the molecular chains of the surfactant reorient remarkably in the concentration region near the phase transitions, and the shape of the self-organizing structure changes to the one with a larger packing parameter.

*Key words:* $C_{12}E_3$ / Decane / Water System; Conformational Behavior; Phase Transition; Deuterium NMR Spectroscopy; Raman Spectroscopy.

## Introduction

Deuterium NMR spectroscopy has been shown to be a valuable tool for studying molecular orientations, phase transitions, and chain dynamics of liquid crystals [1]. Raman spectroscopy, as well as infrared spectroscopy, is a powerful technique for studying conformations of molecules, giving rich information about structural properties in various states of aggregation. Raman spectroscopy, in particular, is useful for investigations in aqueous solutions [2]. Using selectively monodeuterated species of molecules, we have found that the wavenumbers of the isolated C-D stretching vibrations are sensitive to the local conformation in the vicinity of the C-D bond [3 - 5] and have applied this technique to the study of the $C_{12}E_3$ / water system [6], where $C_{12}E_3$ is the abbreviation of a nonionic surfactant $CH_3(CH_2)_{11}(OCH_2CH_2)_3OH$. The selectively monodeuterated species are also useful in deuterium NMR studies.

Deuterium NMR spectroscopy with a time scale $10^{-5}$ - $10^{-4}$ s provides information of time-averaged conformations of molecules in anisotropic phases, while Raman spectroscopy with a time scale $10^{-14}$ - $10^{-13}$ s provides information of individual conformations of molecules [7]. Thus, a combination of deuterium NMR and C-D stretching Raman spectroscopy is particularly important for comprehensive understanding of conformational properties of molecules in liquid crystalline phases.

Amphiphilic surfactant molecules self-organize in solutions to form molecular aggregates with different shapes and sizes, which yield a variety of liquid crystalline phases such as lamellar, hexagonal, and cubic phases. Kunieda et al. [8] have shown in their small-angle X-ray scattering study that the self-organizing structures in the $C_{12}E_3$ / decane / water ternary system change with increasing decane concentration from the lamellar phase ($L_\alpha$) to the oily phase like reversed micellar solution phase ($O_m$) via the reversed bicon-

0932–0784 / 02 / 0600–0320 \$ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

tinuous cubic phase ($V_2$) and the reversed hexagonal phase ($H_2$). This ternary system gives us an opportunity to investigate conformational behavior of both surfactant and decane molecules in the supramolecular structures by deuterium NMR and C-D stretching Raman spectroscopy.

In this work, we have studied the order parameter and the conformations of the lipophilic alkyl chains in the $C_{12}E_3$ / decane / water ternary system by a combined use of deuterium NMR and Raman spectroscopy. We used the block-deuterated species of $C_{12}E_3$, i. e., $CD_3(CD_2)_{10}CH_2(OCH_2CH_2)_3OH$ ($C_{12}$-$d_{23}$-$E_3$), and the perdeuterated species of decane, i. e., $CD_3(CD_2)_8CD_3$ (decane-$d_{22}$), for NMR studies and the monodeuterated species of decane, i. e., $CH_3CHD(CH_2)_7CH_3$ (decane-2-$d_1$) and $CH_3(CH_2)_3$-$CHD(CH_2)_4CH_3$ (decane-5-$d_1$), for NMR and Raman studies.

## Experimental

$C_{12}$-$d_{23}$-$E_3$ was synthesized from perdeuterated 1-chlorododecane and triethylene glycol by the Williamson method. The synthesis of perdeuterated 1-chlorododecane was reported previously [9]. The product was purified by column chromatography and subsequently by vacuum distillation. Decane-$d_{22}$ was obtained by stirring undeuterated decane with $D_2O$, NaOH, and Pd/C catalyst at 450 K in a high-pressure vessel for one month. Decane-2-$d_1$ and decane-5-$d_1$ were synthesized by the method reported previously [6,10]. The purity of the samples was checked by gas chromatography to be better than 97%.

The deuterium NMR measurements were performed at a deuterium resonance frequency of 41.6375 MHz on a Matec pulsed spectrometer equipped with a homemade sample probe and a temperature controller. The spectra were obtained by a Fourier transformation of free induction decays. The $\pi/2$ pulse width was 3 µs. The deuterium NMR spectra were measured on the $C_{12}E_3$ / decane / water ternary system at 15 compositions at 298 K; the concentration of decane in the system was changed from 0.0 to 20.5 wt%, while the weight fraction of the surfactant to water was fixed at 0.6 / 0.4.

The Raman spectra were measured on a JASCO NR-1800 spectrometer equipped with a Princeton Instruments CCD detector. An NEC argon ion laser GLG 2162 operating at 514.5 nm was used for excitation. The temperature of the samples contained in a sealed ampoule was held constant within 0.2 K during each measurement by an Oxford Instruments Optistat cryostat. Both Raman and deuterium NMR spectra were measured at the same compositions and temperatures. Special care was taken to analyze the Raman spectra of the isotropic and anisotropic liquid-crystalline phases which have different polarization properties as discussed later. The observed spectral profiles of the C-D stretching vibrations were analyzed by fitting with Lorentzian components.

## Results

### NMR Spectroscopy

The quadrupole coupling of the deuterium nucleus with the electric field gradient gives rise to splittings of NMR frequencies. For aliphatic C-D bonds, the electric field gradient is axially symmetric with its principal axis along the bond direction. This makes deuterium NMR spectroscopy an excellent method for studying molecular orientations. For uniaxial liquid-crystalline phases such as $L_\alpha$ and $H_2$ phases, the quadrupole splitting is time-averaged over the C-D bond orientations because of rapid anisotropic molecular motions, e. g., interconversions between different conformational states, that take place in a time short compared to the inverse of the quadrupole interaction. The averaged quadrupole splitting for aliphatic C-D bonds in uniaxial liquid crystalline phases such as $L_\alpha$ and $H_2$ phases can be given by

$$\langle \Delta\nu \rangle = S_{\mathrm{CD}}\delta(3\cos^2\alpha - 1)\cdot\frac{1}{2}(3\cos^2\beta - 1), \quad (1)$$

where $\delta$ is 3/4 times the quadrupole coupling constant $e^2qQ/h$ with a value of 167 kHz for aliphatic C-D bonds, $\alpha$ is the angle between the magnetic field and the phase axis, $\beta$ is the angle between the phase axis and the normal of the hydrophobic / hydrophilic interface, and $S_{\mathrm{CD}}$ is a time-averaged parameter called the order parameter of the C-D bond being given by $(1/2)\langle 3\cos^2\gamma - 1\rangle$ with the angle $\gamma$ between the normal of the hydrophobic / hydrophilic interface and the principal axis of the electric field gradient tensor, i. e., the C-D bond direction [11, 12]. The order parameter $S_{\mathrm{CD}}$ thus is a measure of the time-averaged orientation of the C-D bond with respect to the normal of the hydrophobic / hydrophilic interface. The absolute value of the order parameter for uniaxial liquid crystalline phases is obtained from the splitting of

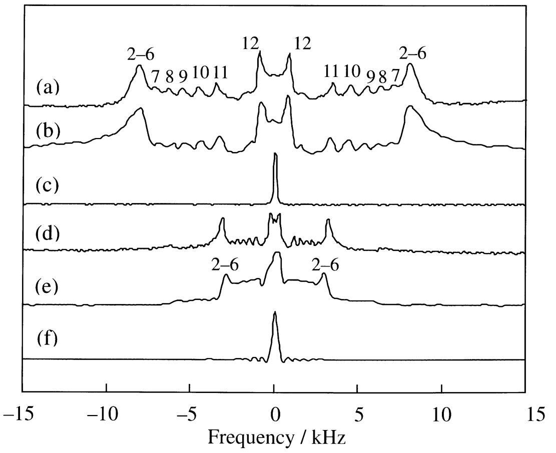

Fig. 1. Deuterium NMR spectra of the deuterated dodecyl chain of the surfactant in the $C_{12}$-$d_{23}$-$E_3$ / decane / water system at 298 K. The splitting of the maxima of the doublet is taken as $\langle\Delta\nu\rangle_{90°}$ in (2). The assignments of the splittings to the respective carbon positions in the surfactant dodecyl chain are indicated in the figure. The decane concentrations, in wt%, and the phases are: (a) 7.1 ($L_\alpha$), (b) 9.1 ($L_\alpha$), (c) 12.5 ($V_2$), (d) 17.9 ($H_2$), (e) 19.4 ($H_2$), and (f) 20.5 ($O_m$).

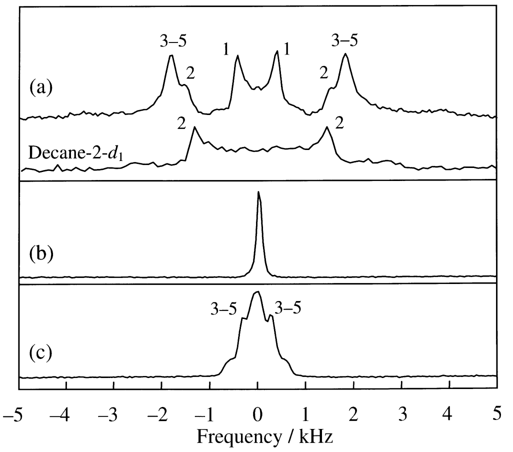

Fig. 2. Deuterium NMR spectra of decane-$d_{22}$ in the $C_{12}E_3$ / decane-$d_{22}$ / water system at 298 K. The assignments of the splittings to the respective carbon positions in the decane molecule are indicated in the figure. Note that the carbon positions 1, 2, ..., and 5 also represent 1', 2', ..., and 5', respectively. The decane concentrations, in wt%, and the phases are: (a) 3.8 ($L_\alpha$), (b) 12.5 ($V_2$), and (c) 19.4 ($H_2$). The spectrum of decane-2-$d_1$ at 298 K with decane concentration 3.8 wt% ($L_\alpha$) is also shown for comparison in (a).

the maxima, corresponding to $\alpha$ = 90°, of the doublet spectra as

$$|S_{\mathrm{CD}}| = |\langle\Delta\nu\rangle_{90°}/[\delta \cdot (1/2)(3\cos^2\beta - 1)]|. \quad (2)$$

The phase axis is parallel to the normal of the hydrophobic / hydrophilic interface ($\beta$ = 0°) for the $L_\alpha$ phase, while it is perpendicular to the normal of this interface ($\beta$ = 90°) for the $H_2$ phase. Accordingly, the $|S_{\mathrm{CD}}|$ value for the $L_\alpha$ phase is half the value for the $H_2$ phase, when the value of the quadrupole splitting is the same. In the isotropic $V_2$ phase or in an isotropic solution phase, the quadrupole splitting disappears and $|S_{\mathrm{CD}}|$ cannot be observed.

Figure 1 shows the deuterium NMR spectra of the deuterated dodecyl chain of the surfactant in the $C_{12}$-$d_{23}$-$E_3$ / decane / water system at 298 K. The splittings observed for the decane concentrations 0.0 - 11.2 wt% are associated with the $L_\alpha$ phase. The spectra are composed of several quadrupole splittings associated with the deuterium nuclei at different carbon positions of the dodecyl chain -O-$C_1$-$C_2$-$C_3$-$C_4$-. . . -$C_{12}$. The observed splittings are assigned, as shown in Fig. 1, on the basis of the spectra of the selectively monodeuterated species of $C_{12}E_3$ in the binary system [13]. With increasing decane concentration, the splittings gradually decrease; those for the carbon positions 2-6 change from 16.1 kHz at 3.8 wt% to 13.4 kHz at 11.2 wt%. At 12.5 wt%, the splittings disappear suddenly and a singlet characteristic of isotropic structure appears. This observation clearly indicates that a phase transition takes place from the $L_\alpha$ phase to the $V_2$ phase at this composition. At 16.7 wt%, the splittings emerge again with a separation of 5.9 kHz, which is nearly half that for the decane concentrations 3.8 - 11.2 wt%. This spectral change is consistent with a transition from the $V_2$ phase to the $H_2$ phase. At 20.5 wt%, the splittings again disappear, in conformity with the transition to the $O_m$ phase at this composition.

Figure 2 shows the deuterium NMR spectra of decane-$d_{22}$ in the $C_{12}E_3$ / decane-$d_{22}$ / water system at 298 K, along with the spectrum of decane-2-$d_1$ in the $L_\alpha$ phase. The splittings of decane-$d_{22}$ are assigned on the basis of the spectra of selectively monodeuterated decane-2-$d_1$. Thus, the quadrupole splittings of 0.9, 3.4, and 4.2 kHz for the decane concentration 3.8 wt% ($L_\alpha$ phase) are assigned to the deuterium nuclei at the carbon positions 1 and 1' (methyl terminals), 2 and 2', and 3-5 and 3'-5', respectively, of the decane molecule $C_1$-$C_2$-$C_3$-$C_4$-$C_5$-$C_{5'}$-. . . -$C_{1'}$, and the splitting of 0.6 kHz for 19.4 wt% ($H_2$ phase) is as-

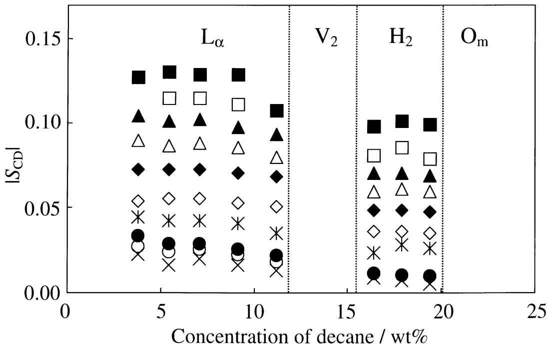

Fig. 3. Absolute values of the order parameter, $|S_{\mathrm{CD}}|$, for the $C_{12}E_3$ / decane / water system at 298 K with different decane concentrations. The carbon positions in the surfactant dodecyl chain are 2-6 (■), 7 (□), 8 (▲), 9 (△), 10 (◆), 11 (◇), and 12 (∗), and the carbon positions in the decane molecule are 1 (×), 2 (○), and 3-5 (●).

signed to the deuterium nuclei at the carbon positions 3-5 and 3'-5'. These observations of the quadrupole splittings indicate that well-defined anisotropic structures of decane are formed in the $L_\alpha$ and $H_2$ phases. This implies that the decane molecules penetrate into the lipophilic layer of the liquid crystalline phases, in agreement with the result from small-angle X-ray scattering [8].

From the observed quadrupole splittings, the order parameters of the C-D bond at different carbon positions can be evaluated with (2). In Fig. 3, the absolute values of the order parameters $|S_{\mathrm{CD}}|$ for the dodecyl chain of the $C_{12}E_3$ surfactant and decane molecules are plotted as a function of the decane concentration in the liquid crystalline phases at 298 K. The $|S_{\mathrm{CD}}|$ values for both surfactant and decane molecules generally decrease with increasing decane concentration. This shows that the disordering of the lipophilic chains occurs when decane is added to the $C_{12}E_3$ / water system. The $|S_{\mathrm{CD}}|$ values of decane decrease steadily with increasing decane concentration without noticeable changes at the phase transitions. On the other hand, the $|S_{\mathrm{CD}}|$ values at the carbon positions 2-6 of the surfactant decrease steeply in the region of the $L_\alpha$ phase close to the phase transition to the $V_2$ phase with increasing decane concentration and show a maximum at the middle region of the $H_2$ phase. The $|S_{\mathrm{CD}}|$ values at the carbon positions 2-12 of the surfactant in the $H_2$ phase are smaller than those in the $L_\alpha$ phase.

Figure 3 shows that the $|S_{\mathrm{CD}}|$ values at the carbon positions near the alkyl / oxyethylene interface of the surfactant are larger than those at the carbon positions near the methyl terminal and are much larger than the values for decane. This is obviously associated with an effect of the adjoining hydrophilic oxyethylene chain of the surfactant, in that this effect restricts the conformational freedom of the alkyl chain of the surfactant. Decane molecules, on the other hand, can move relatively freely between the lipophilic layers as far as part of them preserves the anisotropic structures in the liquid crystalline phases.

### *Raman Spectroscopy*

The phases of the ternary system studied in this work have different polarization properties. Accordingly, special attention should be paid to the polarization problem [14]. The $V_2$ phase is isotropic, whereas the $L_\alpha$ and $H_2$ phases generally consist of very small randomly oriented domains of liquid crystals. In the $L_\alpha$ and $H_2$ phases, the exciting light beam and the Raman scattered light, propagating through the liquid crystals, experience multiple reflections at the boundaries of these domains, which lead to completely depolarized exciting beam and Raman signal, i. e., natural radiation. As a result, the detected signal does not depend on the orientation of the analyzer and its intensity is given by

$$I = I_{\parallel} + 3I_{\perp}. \tag{3}$$

To compare the spectra of the isotropic and anisotropic phases, we register fully depolarized spectra and compare them with the corresponding spectra of the isotropic phase measured on the condition that

$$I_{60} = \frac{1}{4}I_{\parallel} + \frac{3}{4}I_{\perp}, \tag{4}$$

where $I_{60}$ in our experimental arrangement is the intensity of the spectrum recorded with an analyzer oriented at 60° with respect to the polarization of the exciting laser beam. Thus, the spectra recorded for the isotropic and anisotropic phases can be correctly compared.

For studying conformational behavior of the decane molecule, we used the selectively monodeuterated species of decane, i. e., decane-2-$d_1$ and decane-5-$d_1$, and measured the Raman spectra of the isolated C-D stretching vibrations. This method of conformational analysis is based on the fact that the wavenumbers of the isolated C-D stretching vibrations are

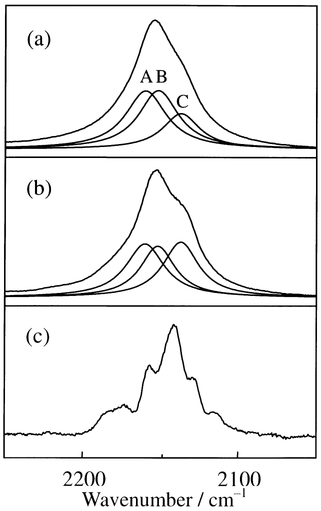

Fig. 4. Raman spectra in the 2050 - 2250 cm$^{-1}$ region of decane-2-$d_1$ in the neat liquid state at (a) 398 K and (b) 298 K and (c) in the solid state.

sensitive to the local conformation of the $C_aC_b$-$C_c$D-$C_dC_e$ segment; namely the wavenumber of the stretching vibration of the isolated $C_c$-D bond trans to the $C_a$-$C_b$ or $C_d$-$C_e$ bond is higher than that of the $C_c$-D bond gauche to the $C_a$-$C_b$ or $C_d$-$C_e$ bond [3 - 5]. For the trans (T) conformation of the $CH_3CHD$-$CH_2CH_2$ segment with the $R$-configuration of decane-2-$d_1$, the isolated C-D bond is gauche with respect to the C-C bond, while, for the gauche$^+$ ($G^+$) and gauche$^-$ ($G^-$) conformations of the same segment with the same configuration, the isolated C-D bond is trans and gauche with respect to the C-C bond. Thus, only one C-D stretching band is expected for the T conformation of the $CH_3CHD$-$CH_2CH_2$ segment, while two C-D stretching bands with different wavenumbers are expected for the G conformation.

Figure 4 shows the Raman spectra of the isolated C-D stretching vibrations of decane-2-$d_1$ in the neat liquid state at 298 and 398 K and in the solid state. The observed spectral profiles of the C-D stretching vibrations in the liquid state can be resolved into three component bands A, B, and C by fitting with the Lorentzian function. In the solid state, band C persists and a band of the accordion vibration associated with the all-trans conformation of the molecule appears at 230 cm$^{-1}$. These results indicate that band C is assigned to the T conformation of the $CH_3CHD$-$CH_2CH_2$ segment and bands A and B are assigned to the $G^{\pm}$ and $G^{\mp}$ conformations, respectively. From the inverse temperature dependence of the logarithm of the intensity ratio $(I_A + I_B)/I_C$ in the liquid state, the apparent enthalpy difference between the gauche and trans conformations is evaluated as $\Delta H$ = 2.34 ± 0.13 kJ mol$^{-1}$, which is comparable to the value 2.1 kJ mol$^{-1}$ for $n$-alkanes [15].

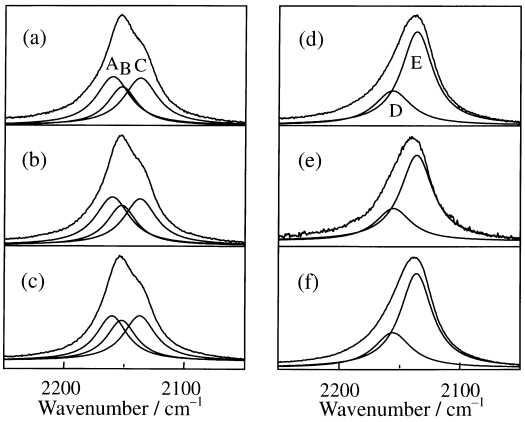

Fig. 5. Raman spectra in the 2050 - 2250 cm$^{-1}$ region of (a-c) the $C_{12}E_3$ / decane-2-$d_1$ / water system at 298 K and (d-f) the $C_{12}E_3$/decane-5-$d_1$ / water system at 298 K. The decane concentrations, in wt%, and the phases are: (a, d) 7.1 ($L_\alpha$), (b, e) 13.5 ($V_2$), and (c, f) 19.4 ($H_2$).

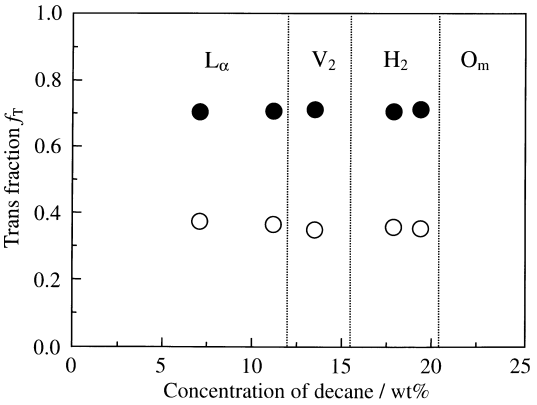

Fig. 6. The trans fraction $f_T$ for the $C_2$-$C_3$ bond (○) and the $C_4$-$C_5$-$C_{5'}$ bonds (●) of decane as a function of the concentration of decane in the ternary system.

Figure 5 shows the Raman spectra of the isolated C-D stretching region of decane-2-$d_1$ and decane-5-$d_1$ in the $L_\alpha$, $V_2$, and $H_2$ phases. The conformational analysis of the $CH_2CH_2$-CHD-$CH_2CH_2$ segment has been discussed previously [6]. According to the interpretation in that work, the C-D stretching profile for decane-5-$d_1$ is resolved into two component bands D and E; the former is associated with the $TG^{\mp}$, $G^{\pm}T$, $G^{\pm}G^{\pm}$, and $G^{\mp}G^{\mp}$ conformations of the $CH_2CH_2$-CHD-$CH_2CH_2$ segment and the latter is associated with the TT, $G^{\mp}T$, and $TG^{\pm}$ conformations. Figure 6 shows the trans fraction $f_T$ for the $C_2$-$C_3$ and $C_4$-$C_5$-$C_{5'}$ bonds of decane as a function of the concentration of decane in the ternary system. The trans fractions for the $C_2$-$C_3$ and $C_4$-$C_5$-$C_{5'}$ bonds are obtained from the intensity ratios $I_C/(I_A + I_B + I_C)$ and $I_E/(I_D + I_E)$, respectively, where the results for the $C_4$-$C_5$-$C_{5'}$ sequences are averages of the values for the two adjoining bonds and the Raman intensity coefficients of the C-D stretching for the T and $G^{\pm}$ conformations are assumed to be the same. For the $C_2$-$C_3$ and $C_4$-$C_5$-$C_{5'}$ bonds of decane, the trans fraction $f_T$ decreases slightly or remains nearly constant with increasing decane concentration. It is noted that no significant conformational changes of the decane molecule occur at the phase transitions. The same results have been reported in the infrared and Raman studies on conformational behavior of the lipophilic alkyl chain of the surfactant in the $C_{12}E_3$ / water and $C_{12}E_5$ / water systems [6, 16].

## Discussion

The results of the deuterium NMR spectra show that the order parameter $|S_{CD}|$ of decane decreases steadily with increasing decane concentration without noticeable changes at the phase transitions, whereas the $|S_{CD}|$ values for the dodecyl chain of the surfactant decrease steeply in the region of the $L_\alpha$ phase close to the phase transition to the $V_2$ phase and the $|S_{CD}|$ values in the $H_2$ phase are lower than those in the $L_\alpha$ phase. The results of the Raman spectra show, on the other hand, that the trans fraction $f_T$ for the $C_2$-$C_3$ and $C_4$-$C_5$-$C_{5'}$ bonds of decane decreases slightly or remains nearly constant with increasing decane concentration without noticeable changes at the phase transitions. This is the same observation as made for the alkyl chain of the surfactant in the $C_{12}E_3$ / water and $C_{12}E_5$ / water systems [6, 16]. The observed changes of the $|S_{CD}|$ values of the surfactant in the ternary system are interpreted as follows.

Phenomena of molecular motions observed by deuterium NMR spectroscopy with its time scale $10^{-5}$ - $10^{-4}$ s are different in principle from those observed by Raman spectroscopy with its time scale $10^{-14}$ - $10^{-13}$ s. Conformational changes of molecules take place in a time scale of $10^{-11}$ - $10^{-10}$ s [7]. The trans fraction $f_T$ is the statistical average of the local conformations of individual conformers. The order parameter $|S_{CD}|$ is, however, a measure of the time-averaged orientation of the C-D bond with respect to the normal of the hydrophobic / hydrophilic interface. The order parameter thus depends not only on the conformational changes, but also on the chain reorientation motion, e. g., the restricted wobbling motion of a whole molecule within an aggregate, with effective correlation time $10^{-9}$ - $10^{-7}$ s [17, 18]. According to the method proposed by Petersen and Chan [18], the order parameter $|S_{CD}|$ in Fig. 3 can be divided into two contributions $|S_{chain}|$ and $|S_{con}|$. The angular deflection of the molecular chain axis with respect to the normal of the hydrophobic / hydrophilic interface is described by the chain order $|S_{chain}|$. The orientation of the C-D bond with respect to the instantaneous molecular chain axis is represented by the conformational order $|S_{con}|$. The chain order $|S_{chain}|$ is likely to decrease in the region near the phase transitions, because the chain reorientation may increase with increasing fluctuations of the hydrophobic / hydrophilic interface as suggested by improper values of the packing parameter [19]. The continuous conformational changes of decane molecules observed in the Raman spectra indicate that the conformational order $|S_{con}|$, as well as the trans fraction $f_T$, of the surfactant may decrease steadily with increasing decane concentration without noticeable changes at the phase transitions, in consideration of the same conformational behavior of the surfactant alkyl chains and the penetrated decane molecules. Thus, the two contributions, $|S_{chain}|$ and $|S_{con}|$, result in the observed changes of the order parameter $|S_{CD}|$ of the surfactant shown in Figure 3.

The decrease of the $|S_{con}|$ values as discussed above indicates the conformational disordering of the alkyl chain in the ternary system. This implies that conformational defects of the alkyl chain such as kink structure with $TG^{\pm}TG^{\mp}T$ conformation, which leaves the direction of the alkyl chain parallel to the surfactant molecular axis, are produced in the $L_\alpha$ phase [18]. With an increase of the effective volume of the lipophilic part of a surfactant molecule on addition of decane molecules, as described below, the kink structure most probably changes into other conformations such as $TG^{\pm}TG^{\pm}T$. This effect brings about the steady decrease of the $|S_{con}|$ values.

On addition of decane molecules to the $C_{12}E_3$ / water system, the effective volume of the lipophilic part of a single surfactant molecule is increased as a result of the penetration of the added decane molecules into the lipophilic layer, leading to a high degree of mobility of the alkyl chain. To minimize the resulting increase in the effective cross-sectional area of a surfactant molecule, the molecular chains of the surfactant reorient remarkably in the concentration region near the phase transitions as indicated by the changes of the $|S_{\text{chain}}|$ values, and the shape of the self-organizing structure changes to the one with a larger packing parameter. Thus, the curvature of the hydrophobic / hydrophilic interface tends to be negative and the sequential phase transitions $L_\alpha$-$V_2$-$H_2$-$O_m$ occur.

[1] J. Seelig, Q. Rev. Biophys. **10**, 353 (1977).

[2] P. C. Painter, M. M. Coleman, and J. L. Koenig, The Theory of Vibrational Spectroscopy and Its Application to Polymeric Materials, John Wiley, New York 1982.

[3] K. Ohno, Y. Takagi, and H. Matsuura, J. Phys. Chem. **97**, 5530 (1993).

[4] K. Ohno, H. Yoshida, and H. Matsuura, Spectrochim. Acta, Part A **52**, 1377 (1996).

[5] K. Ohno, H. Abe, S. Masatoki, H. Yoshida, and H. Matsuura, J. Phys. Chem. **100**, 12674 (1996).

[6] S. Masatoki, K. Ohno, H. Yoshida, and H. Matsuura, J. Phys. Chem. **100**, 8487 (1996).

[7] W. Ziegler and A. Blume, Spectrochim. Acta, Part A **51**, 1763 (1995).

[8] H. Kunieda, K. Ozawa, and K.-L. Huang, J. Phys. Chem. B **102**, 831 (1998).

[9] H. Zimmermann, Liq. Cryst. **4**, 591 (1989).

[10] A. Tonegawa, A. Michiue, K. Ohno, H. Matsuura, K. Yamada, and T. Okuda, Chem. Lett. **2001**, 818.

[11] J. H. Davis and K. R. Jeffrey, Chem. Phys. Lipids **20**, 87 (1977).

[12] K. Abdolall, E. E. Burnell, and M. I. Valic, Chem. Phys. Lipids **20**, 115 (1977).

[13] A. Tonegawa, K. Ohno, H. Matsuura, K. Yamada, and T. Okuda, Chem. Lett. **2000**, 324.

[14] R. Gaufrès, J.-L. Bribes, S. Sportouch, J. Ammour, and J. Maillols, J. Raman Spectrosc. **19**, 149 (1988).

[15] R. L. Jernigan and P. J. Flory, J. Chem. Phys. **50**, 4165 (1969).

[16] A. Tonegawa, A. Michiue, K. Ohno, H. Matsuura, K. Yamada, and T. Okuda, unpublished results.

[17] A. Firouzi, D. J. Schaefer, S. H. Tolbert, G. D. Stucky, and B. F. Chmelka, J. Amer. Chem. Soc. **119**, 9466 (1997).

[18] N. O. Petersen and S. I. Chan, Biochemistry **16**, 2657 (1977).

[19] J. N. Israelachvili, D. J. Mitchell, and B. W. Ninham, J. Chem. Soc. Faraday Trans. **72**, 1525 (1976).