Studies on Molecular Motion in Lyotropic Mesophases of Hexaethylene Glycol Dodecyl Ether-D_2O System by ^{13}C Nuclear Magnetic Resonance

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The ^{13}C spin-lattice relaxation time(T_1) and the resonance line width corresponding to T_2^* were measured for each of the carbons in hexaethylene glycol dodecyl ether–water(D_2O) system, which exists as two distinct lyotropic mesophases(neat and middle phase). The line width is very narrow in the isotropic state, such as in organic solvents and in a lower concentration aqueous solution, whereas in a mesophase and in a higher concentration aqueous solution, the line width of the alkyl chain was broadened. Here the line widths for glycol carbons were about an order of magnitude smaller than for an alkyl chain, demonstrating the difference of molecular motion. The chemical shifts of the alkyl chain in the middle phase were different from those in the isotropic state; this difference was clearly shown in the spectrum of the middle/isotropic coexistent phase. ^{13}C-T_1 was not sensitive enough to differentiate between the isotropic and the lyotropic phase at room temperature. It was found that T_1 did not equal T_2^* for any of the methylene carbons, the difference being most marked for the terminal methyl carbon in the alkyl chain. The orientational order in the phases had an influence on the T_2^* values.

One of the most fruitful techniques used to study lyotropic mesophases is magnetic resonance.[1] Proton nuclear magnetic resonance (^1H NMR) and relaxation measurements have been used to study the interaction of an ester with a polyethylene glycol alkyl ether as a nonionic surfactant.[2] It is difficult by ^1H NMR to measure separately the hydrophilic and hydrophobic parts of a mesophase because of the overlapping and the broadening of resonance lines.[2,3]

^{13}C Nuclear magnetic resonance (^{13}C NMR) has become an important tool in the investigation of the microstructure and molecular dynamics of liquid crystals.[3] The ^{13}C spin lattice relaxation time T_1 can readily be measured for all resolved resonances from partially-relaxed Fourier transform spectra. Ribeiro and Dennis measured ^{13}C NMR and T_1 values in isotropic states for octaethylene glycol dodecyl ether and suggested there were differences in mobility of the various groups in the surfactant.[3] The present study examines the ^{13}C-T_1 and the line width in an aqueous system of hexaethylene glycol dodecyl ether ($C_{12}EG_6$), as a function of aqueous concentration in D_2O and temperature in both the isotropic micellar solution and the mesophase. The $C_{12}EG_6$–water system is known to form two distinct lyotropic mesophases (neat and middle phase).[1,4] The results yield considerable information concerning the motional behavior of the hydrophilic and hydrophobic part of the miceller phases.

Experimental

Samples. Hexaethylene glycol dodecyl ether was obtained from Nikko Chemical Co., Ltd. and used without further purification. Purity of the sample is $\geqq$99% by gas chromatography. NMR measurements were made for an undiluted liquid $C_{12}EG_6$; sample A comprised 90% $C_{12}EG_6$ and 10% D_2O (Merck, Uvasol 99.75%) by weight; sample B was a neat phase comprising 72% $C_{12}EG_6$ and 28% D_2O; sample C contained 65% $C_{12}EG_6$; sample D as a middle phase contained 50% $C_{12}EG_6$, and sample E, 10% $C_{12}EG_6$.[4] These samples were prepared according to the phase diagram established by Clunie *et al.*[4]

NMR Measurements. ^{13}C NMR spectra were measured at 25.03 MHz on a JEOL PFT-100 NMR spectrometer equipped with a PG-100 pulse programmer and a JEOL temperature controller. Samples were studied under conditions of complete proton noise decoupling or the gated decoupling, which minimize the rise of temperature in the sample by proton irradiation. The temperature of the sample in the probe was selected and maintained within $\pm$1 K in accuracy in the range of 301 to 348 K.

Values of T_1 were measured using the inversion recovery method (T-180°-t-90°) over a 2 kHz band width with 8192 time domain data points. The 90° pulse length was calibrated prior to each set of experiments and varied between 20—25 μs. The delay time T was more than 5 times the longest T_1 value. For the relaxation time measurements, the sample was put into a spherical glass, and sealed after being degassed by freezed-thaw cycles. All such sample tubes were equilibrated for more than one weak at room temperature.[1]

Results and Discussion

Assignment of ^{13}C NMR Spectra. In Fig. 1, the ^{13}C NMR spectrum and tentative assignments are shown for the carbons in undiluted liquid $C_{12}EG_6$ at room temperature. The identification of the alkyl

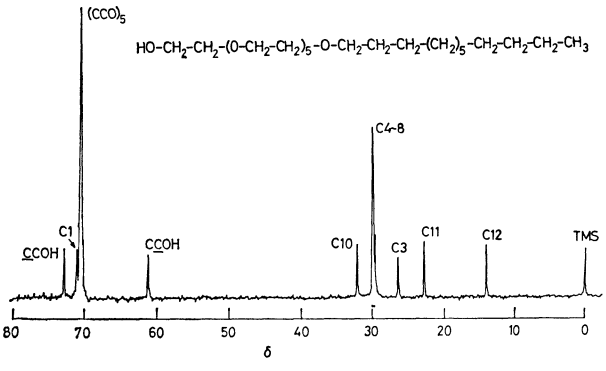

Fig. 1. ^{13}C NMR spectrum and assignment of undiluted liquid of $C_{12}EG_6$ at 301 K.

chain carbons in $C_{12}EG_6$ is based on assignments for $C_{10}OH$ and for other aliphatic compounds. Comparing the $C_{12}EG_6$ spectrum with that of $C_{12}OH$, we find no signal in the $C_{12}EG_6$ spectrum at the position of the C2 carbon of $C_{12}OH$. The C2 signal was shifted upfield and overlapped with the C4—9 signal by an increase of the electron density of C2 in $C_{12}EG_6$, owing to the oxyethylene group. Rebeiro and Dennis have assigned the C2 carbon to the signal which is assigned here to the C3 carbon.[3] The assignment for the carbons of the oxyethylene group has been made by ^{13}C NMR measurements of polyethylene glycol dodecyl ethers ($C_{12}EG_n$, n=1—8) and of compounds with several oxyethylenes and otherwise agreed with that of Ribeiro and Dennis.[3]

^{13}C NMR Spectra in the Mesophase. Sample B was measured by ^{1}H NMR at 100 MHz. At temperatures below the transition point of 343 K, there are two very much broadened peaks of alkyl chain and oxyethylene group in the ^{1}H NMR spectrum. It is difficult by ^{1}H NMR to separate the alkyl chain and the oxyethylene group.[4] In Fig. 2 are shown ^{13}C NMR spectra of a neat phase and of the isotropic phase for sample B. The upper spectrum, corresponding to the neat phase, and the lower spectrum in the isotropic phase at 348 K were obtained from the same solution. The lower spectrum was almost the same as the undiluted liquid spectrum in Fig. 1. In Fig. 3 are shown the ^{13}C NMR spectra of samples A, D, and E. The ^{13}C NMR spectrum in the middle phase for sample D is substantially the same as that in the neat phase in Fig. 2(1).

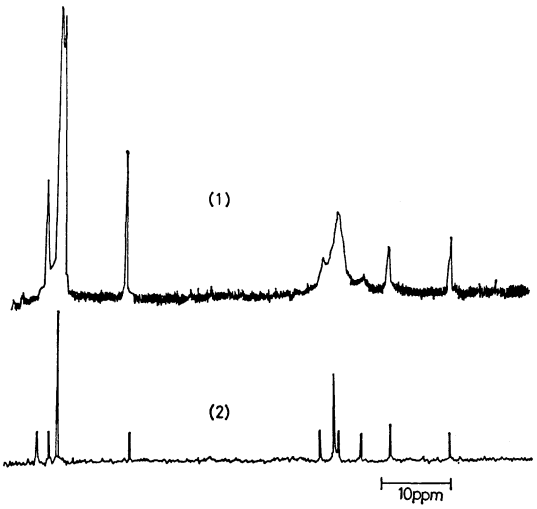

Fig. 2. ^{13}C NMR spectra for $C_{12}EG_6$ 75 w/w% in D_2O.
(1): Neat phase at 338 K, (2): isotropic phase at 348 K.

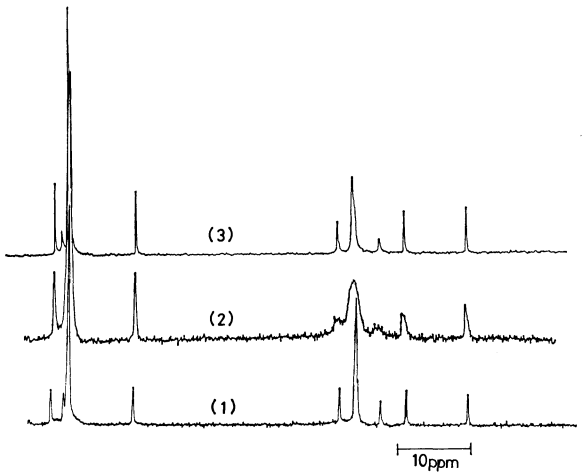

Fig. 3. ^{13}C NMR spectra of $C_{12}EG_6$+D_2O system at 301 K.
(1): 90% $C_{12}EG_6$+D_2O, (2): 50% $C_{12}EG_6$, (3): 10% $C_{12}EG_6$.

In the neat and the middle phase spectra, the peaks arising from the carbons of the alkyl chain are much broader than those of the isotropic phase spectrum. The ^{13}C peaks of the oxyethylene group are slightly broadened. It is considered for mesophases that the alkyl chains overlap and that the paraffinic layer is rigid. The line width narrowing for the oxyethylene group is presumed to be due to a diffusional motion of this group, which is loosely restrained because of a hydration to the oxyethylene group. A low angle X-ray diffraction study on the $C_{12}EG_6$–H_2O system by Corkill et al. supported this assumption.[2] Samples A and E are both in the isotropic phase at room temperature. In the spectrum of sample E, the peaks of the alkyl chain are shown to be slightly broadened and the line shapes are different from those of the neat and middle phase. The spectrum of sample A is similar to that of the undiluted liquid $C_{12}EG_6$ and to that of the isotropic phase of sample B.

Chemical Shift. The data of chemical shifts for all samples are summarized in Table 1. Previously, it was shown that the peaks of the alkyl chain in the isotropic phase are displaced downfield by 0.5 ppm from those in the lyotropic neat and middle meso-

Table 1. The relative ^{13}C chemical shift in sample C

	$(\delta-\delta(C^*COH))$		
Phase	M[a]	M+I[b]	I[c]
Carbon number			
C-12		−46.53	−46.68
	−46.98	−46.92	
C-11		−37.79	−37.88
	−38.29	−38.74	
C-10		−28.46	−28.54
	−29.00	−29.54	
C-4-8		−30.53	−30.65
	−31.51	−31.52	
C-3		−34.14	−34.31
	−34.04	—	
C-1		10.53	10.54
	—	—	
(CCO)		9.50	9.44
	9.23	9.21	
CC*OH	11.47	11.47	11.53

a) M: Middle phase at 300 K. b) M+I: Middle/isotropic coexisting phase at 302 K. c) I: Isotropic phase at 305 K.

phases. On the other hand, ^{13}C chemical shifts of the oxyethylene group do not differ for the lyotropic and isotropic states. In Fig. 4, all oxyethylene group signals except that of terminal oxyethylene for sample C are coincident. But each alkyl carbon signal consists of two resonance lines, as shown in Fig. 4. The lower-field peaks in this region were assigned to the alkyl carbons in the isotropic phase and the upper field peaks to the middle phase, by comparing the chemical shifts in samples B, D, and C. Thus, this spectrum suggests that the state corresponds to a middle/isotropic coexistent phase denoted as an interpenetrated broad boundary in the phase diagram by Clunie *et al.*[4]

Spin-lattice Relaxation Times. In Table 2 are summarized the ^{13}C spin-lattice relaxation times, T_1s, of the undiluted liquid, and samples B and D at several temperatures. At room temperature, samples B and D form the neat and middle phase, respectively. Small differences in magnitude of T_1 values were observed among carbons in the middle phase, indicating that there are small differences in mobility in the molecule. We compared the T_1 values for the phases:

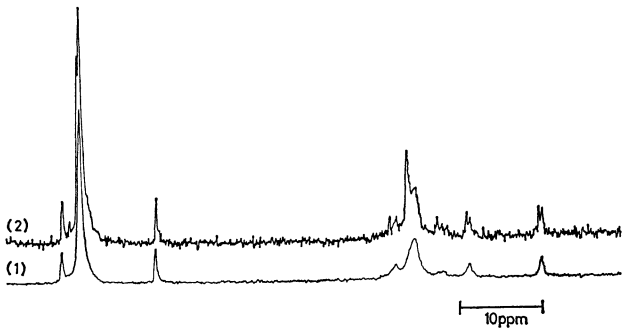

Fig. 4. ^{13}C NMR spectra of 65% $C_{12}EG_6+D_2O$ system (sample C).
(1): Middle phase at 296 K, (2): middle/isotropic coexistent phase at 298 K.

T_1(C12) of the neat phase is smaller than that of the isotropic and the middle phase. The T_1(C*COH) and T_1(CC*OH) values for the carbon (marked by the asterisk) of the middle phase are greater than that of the other phase. However, there is collectively no large difference in the T_1 values between phases. This result suggests that the mobility of a molecule in each phase is similar.

In 1-decanol or decylammonium trifluoroacetate, there is an increase in ^{13}C-T_1 on going from the carbons adjacent to an OH or NH_3 group to the terminal carbon in a molecule chain; this restriction is caused by intermolecular hydrogen bonding.[5,8] The alkyl chain has this tendency in our system. Ribeiro and Dennis had measured ^{13}C-T_1 of $C_{12}EG_8$ in micelles with D_2O as a good hydrogen bonding solvent.[3] They found that all T_1 values in aqueous solution are much smaller than those in the organic solvents.[2] There was little difference in ^{13}C-T_1 values of the corresponding carbons in the $C_{12}EG_6$ undiluted liquid, the neat phase, and the middle phase, as shown in Table 2.

Temperature dependences of T_1(C-11) and T_1(C*COH) for the sample B and the undiluted liquid are shown in Fig. 5. T_1(C-11) plot for sample B has a minimum point at 308 K. The other curves show an inflection at about 301 K. It seems that this temperature is near to that of a minimum point of T_1. The plots of sample B show some scatter between 338 K and 343 K. This scatter agrees with the phase transition point from the neat to the isotropic phase.

Spin-Spin Relaxation Time. If a line shape is Lorentzian, a spin-spin relaxation time T_2^* is generally given by

$$T_2^* = 1/\pi \cdot \Delta\nu,$$

where $\Delta\nu$ is the half-height line width. T_2^* values calculated from this relationship are given in Table 3 T_2^* values of the undiluted liquid are longer than

Table 2. Temperature dependence of ^{13}C spin-lattice relaxation time (T_1)

Phase	T_1(U)/s[a]			T_1(B)/s[b]			T_1(D)/s[c]	
				N		I	M	I
T/K	301	313	348	301	318	348	301	318
Carbon number								
C-12	2.8	2.9	3.6	2.2	2.4	4.3	3.1	3.4
C-11	1.3	1.2	2.6	1.1	1.0	2.5	1.2	1.9
C-10	0.7	0.9	1.9	—	—	—	0.8	1.1
C-4-8	0.3	0.4	0.8	0.4	0.3	0.5	0.4	0.5
C-3	0.4	0.3	0.7	—	—	—	0.6	0.3
C-1	0.4	0.3	0.9	—	—	—	—	0.5
(CCO)	0.3	0.4	1.0	0.3	0.4	0.9	0.4	0.6
C*COH	0.4	0.6	1.7	0.6	0.8	1.8	0.9	1.6
CC*OH	0.5	0.5	1.7	0.6	0.8	1.8	0.9	1.6

N: Neat phase, M: middle phase, I: isotropic phase, U: undiluted liquid, B: sample B (72%$C_{12}EG_6+D_2O$), D: sample D (45%$C_{12}EG_6+D_2O$).
a) Estimated accuracy ±10%. b) Estimated accuracy ±20% in N, and ±10% in I. c) Estimated accuracy ±20% in M, and ±10% in I.

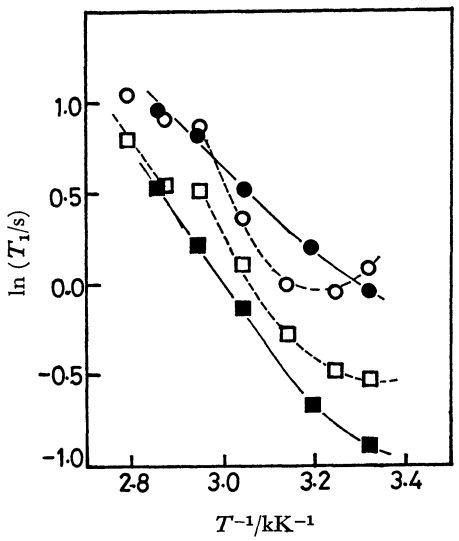

Fig. 5. Temperature dependence of ^{13}C[^{1}H] relaxation time T_1 at 25.03 MHz in $C_{12}EG_6$ (●: C-11, ■: C*COH, ——) and $C_{12}EG_6$ 72 w/w% in D_2O system (○: C-11, □: C*COH, ----).

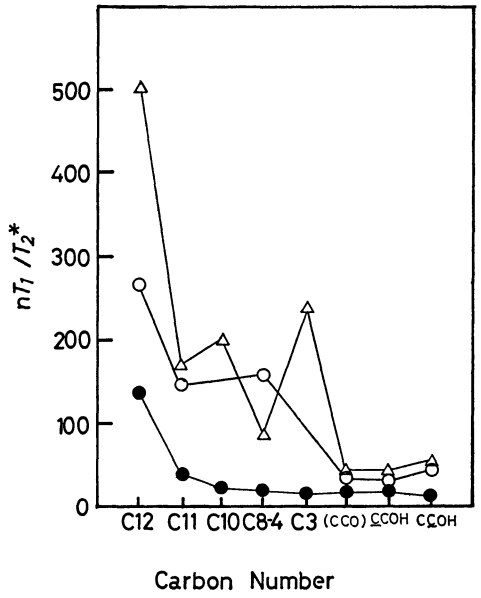

Fig. 6. Ratios of spin-lattice relaxation times (T_1) and spin-spin relaxation times (T_2*) estimated from line width.
●: Undiluted liquid, ○: neat phase, △: middle phase.

those of the other states, but T_2* values of each signal for the neat phase are similar to those for the middle phase. In the undiluted liquid, T_2* values for alkyl carbons were three to eight times greater than those in mesophase, but the values of T_2* for the oxyethylene group do not change between the undiluted liquid and the mesophase.

The Relationship between ^{13}C-T_1 *and* ^{13}C-T_2* *Values.* There is a disparity between the values of ^{13}C-T_1 and ^{13}C-T_2*. Figure 6 shows the nT_1/T_2* ratio for each carbon at 301 K which is close to the temperature of T_1 minimum for the carbons of oxyethylene

Table 3. The values of spin-spin relaxation times estimated from line width(T_2*), at 301 K

Carbon number	T_2*(U)/ms	T_2*(B)/ms	T_2*(D)/ms
C-12	61.0	25.0	18.0
C-11	69.0	15.0	14.0
C-10	57.0	7.0	8.0
C-4-8	30.0	5.0	9.0
C-3	46.0	7.0	5.0
(CCO)	31.0	17.0	18.0
C*COH	41.0	36.0	40.0
CC*OH	54·0	26.0	32.0

U: Undiluted liquid, B: sample B (73%$C_{12}EG_6$+D_2O), D: sample D (45%$C_{12}EG_6$+D_2O).

in the mesophases. In this case the relation of $T_1 > T_2$ should be held acoording to the classical work of Bloembergen *et al.*[9] On the other hand, when the temperature of T_1 minimum for alkyl carbons is higher than 301 K, the T_1 value can be expected to be much greater than the T_2* value. It is found that this expectation is actually valid, as shown in Fig. 6. The ratios of nT_1/T_2* for oxyethylene carbon are almost invariably less than fifty-six, while the ratios of alkyl carbons are more than a hundred.

In contrast to the mesophases, for the undiluted liquid the ratios of both oxyethylene carbons and alkyl carbons, except for terminal ethyl carbons, are almost constant (in the range of about 17 to 25), and less than the value for oxyethylene in mesophases. This result has been attributed to the fact that the undiluted liquid of low viscosity had narrow line widths for all carbons. It is interesting to note that the ratio of methyl carbon is higher than that of the other carbons.

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