^{13}C-NMR Study of Aerosol OT in Chloroform

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The dynamic structure of Aerosol OT molecules in micellar state was studied by measurements of ^{13}C-NMR spin-lattice relaxation time (T_1) and the effect of a lantanide shift reagent Yb(fod)$_3$ in chloroform at 25 MHz and 40 °C. The results were analyzed on the basis of the conformation and segmental motions of Aerosol OT molecules in micellar state, with the following conclusions: Aerosol OT molecules in the micellar state associate with each other by the polar head groups; their hydrocarbon chains are flexible; the mobility of side chain is restricted to a greater extent than that of the main chain; carbonyl carbon-(2′) is located nearer to the polar group than carbon-(2) in steric conformation.

Studies on the state of surface active agents in solution are of interest from a biological viewpoint, since the amphiphilic behavior of surface active agents such as micelle formation and hydrophobic interaction can also be observed in biological systems. As a suitable substance for the study, Aerosol OT was chosen and thermodynamical studies were carried out on its solution state in water[1)] or in organic solvents[2)] and also its two-phase distribution between water and an organic solvent.[3)] Spectroscopic studies, however, are necessary for more extensive and detailed information.

Recently, solution states of surface active agents in water or organic solvents have been studied by means of NMR.[4)] The dynamic structure of molecules have been studied in the last few years, since the use of Fourier transform NMR made the measurement of relaxation time practicable. Clifford and Pethica studied the properties of micellar solutions of sodium alkyl sulfates in D_2O by ^{1}H-NMR T_1 measurement.[5)] Henriksson and Ödberg studied the micellar structure of heptafluorobutyric acid and sodium pentadecafluorooctanoate in H_2O and D_2O by ^{19}F-NMR T_1 measurement.[6)] Podo *et al.* studied the dynamical structure and hydration of micelle by ^{1}H-NMR T_1 measurement.[7)] However, the study of local mobility or segmental motions by means of ^{1}H- or ^{19}F-NMR is difficult because of the overlap of proton signals and the simplicity of the ^{19}F signal. For this study, ^{13}C-NMR would be most useful. Williams *et al.* and Levy *et al.* studied the local mobility of surface active agents in water and several organic solvents by ^{13}C-NMR.[8,9)] We have applied it to the study of Aerosol OT molecules in the micellar state in chloroform.

Experimental

Materials. Aerosol OT (sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethane-1-sulfonate, American Cyanamid Co., Ltd.) was used. The anhydrous material is claimed to be 99% pure and to contain about 1% of methanol insoluble impurity. The procedure by Higuchi and Misra[10)] was used for purification. The solvents used were as follows: chloroform was distilled twice; chloroform-d_1 (Merck Co., Ltd.) was dried by passing through an alumina gel column. Yb(fod)$_3$ (tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) ytterbium, Nagoya Katayama Kagaku-Kogyo KK).

Methods. ^{13}C nuclear magnetic resonace spectra were recorded on a JEOL-PFT-100 pulse Fourier transform NMR spectrometer at 25 MHz locked on deuterium using 10-mm sample tubes. Chemical shift, δ, was measured relative to tetramethyl silane used as an internal standard by data reduction. For ordinary FT NMR experiments (proton decoupled), pulse angle: 45°, repetition: 2.0 s, data point: 8192, frequency range: 6250 Hz, numbers of scans: 400 (time domain accumulation). For T_1 measurements (proton decoupled), pulse angle: 180°-τ-90°, repetition: 20.0 s, data point: 8192, frequency range: 6250 Hz, numbers of scans: 400. For off resonance experiment, pulse angle: 45°, repetition: 3.0 s, data point: 4096, frequency range: 1000 Hz, numbers of scans: 5000.

Vapor pressure depressions were measured with a molecular weight apparatus (Hitachi Perkin-Elmer Type 115) based on a thermister method.[11)]

Results and Discussion

Vapor Pressure Depression Measurement. Vapor pressure depressions of the solvent were measured for the determination of CMC (critical micelle concentration) and association number of Aerosol OT in chloroform. The thermister bridge reading, ΔR, is plotted against solute concentration (molality) in Fig. 1. Open circles correspond to Benzil as a standard substance and solid circles to Aerosol OT. The insert shows the result of measurement in low concentration. The arrow indicates CMC, 4×10^{-4} M (mol kg^{-1}). By comparison of the slopes of the two straight lines for Benzil and for Aerosol OT, the number average association number was calculated to be 5.

^{13}C-NMR Spectra. ^{13}C-NMR spectra were measured for a solution at 2×10^{-1} M. We see from the results that a large part of Aerosol OT at this concentration is in a micellar state. Spectrum (a) was taken under ^{1}H noise decoupling conditions and spectrum (b) under ^{1}H partial decoupling conditions. Spectrum (c) shows the effect of the addition of a shift reagent and spectrum (d) that of 2-ethyl-1-hexanol whose signals were already assigned.[12)] Almost all the signals in spectrum (a) were assigned to each carbon with reference to spectra (b), (c) and (d). Two peaks of carbonyl carbons at lower fields, however, could not be assigned to either C(2) or C(2′) from only the above reference. We took, therefore, the off resonance spectrum. If the two protons of methylene(1′) are assumed to be magnetically equivalent, it is expected

that under the off resonance conditions the peak of C(2) is split into two peaks by the one proton of methine (1), and that of C(2′) into three peaks by the two protons of methylene (1′). As shown in Fig. 3, the lower-field signal of the two is split into two peaks and is assignable to C(2), while the higher-field signal is split into three peaks and assignable to C(2′). The two methylene carbons (3) and (3′) (Fig. 2-a) also exist in magnetic nonequivalence. However, it is difficult to assign the two signals. It was tentatively assumed that the peak at the lower-field is assigned to C(3) and that at the higher-field to C(3′), by taking into consideration the fact that the carbonyl-carbon peak near a polar group such as ($-SO_3^-$) appears at lower field.

The Influence of a Shift Reagent. The influence of a lantanide shift reagent, Yb(fod)$_3$, on the spectra was examined. Figure 2-(c) shows the spectrum of Aerosol OT on addition of Yb(fod)$_3$ at 0.1 mole ratio. Some peaks become broader and are shifted down field. The chemical shift is plotted against the ratio (La)/(AOT), the molal concentration ratio of lantanide shift reagent to Aerosol OT, in Fig. 6. The Yb(fod)$_3$-induced shift increases in the order of carbons-(2′>1>1′>2>3>3′). For the carbons-(4,4′, 5,5′, 6,6′, 7,7′, 8,8′, 9,9′, 10,10′), no induced shifts were observed. It is probable that the shift reagent coordinates to the polar group, and that carbons nearer the polar group in a spacial distance are more influenced by the shift reagent. It might be

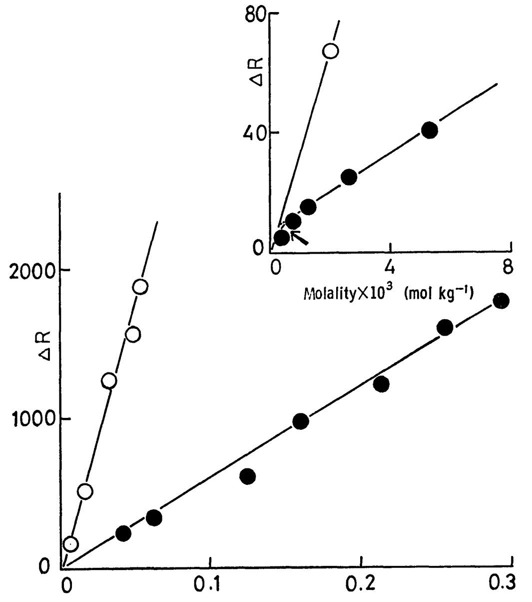

Fig. 1. Thermister bridge reading (ΔR) *vs.* solute concentration in CDCl$_3$.
●: Aerosol OT as solute, ○: Benzil as solute.
The figure inserted in upper right is the result of measurements in dilute concentration. The arrow in the figure indicates CMC.

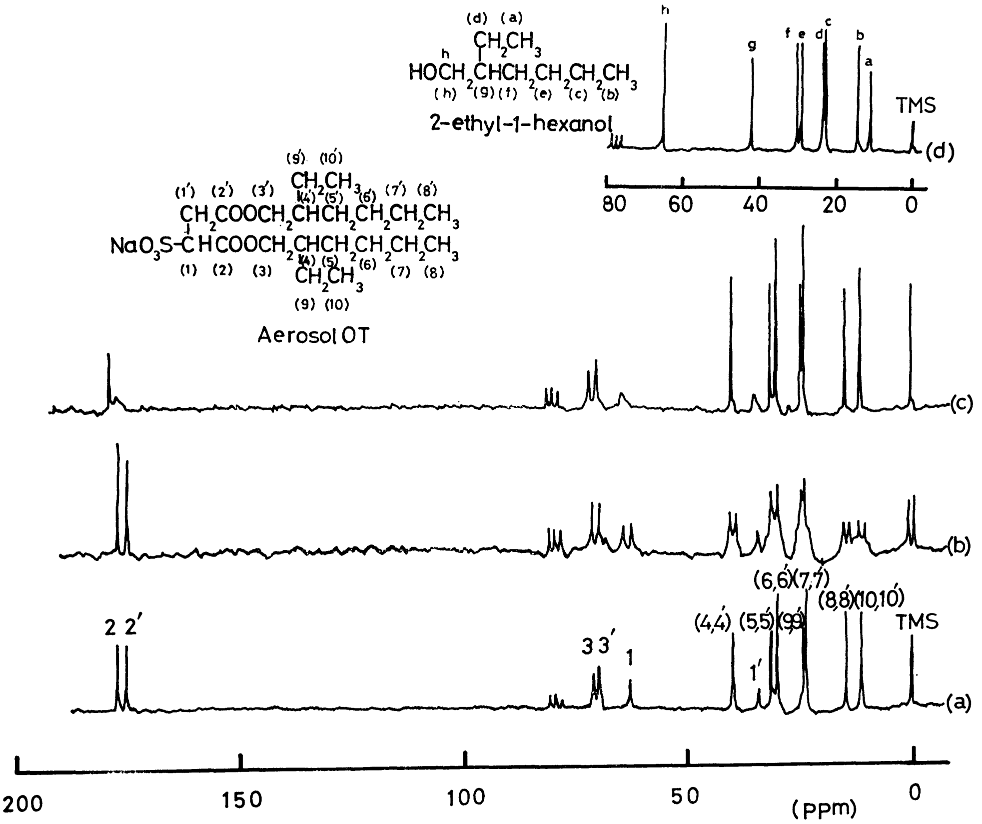

Fig. 2. Natural-abundance carbon-13 NMR spectra.
(a): Proton noise decoupled spectrum of 0.2 M Aerosol OT in CDCl$_3$.
(b): Proton partially decoupled spectrum of 0.2 M Aerosol OT in CDCl$_3$.
(c): Proton noise decoupled spectrum of 0.2 M Aerosol OT in the addition of Yb(fod)$_3$ at 0.1 mole ratio.
(d): Proton noise decoupled spectrum of 2-ethyl-1-hexanol.

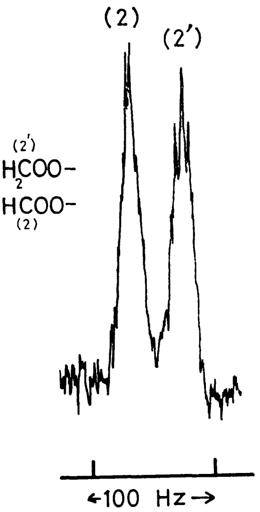

Fig. 3. Two carbonyl carbon signals at the condition of the off resonance.

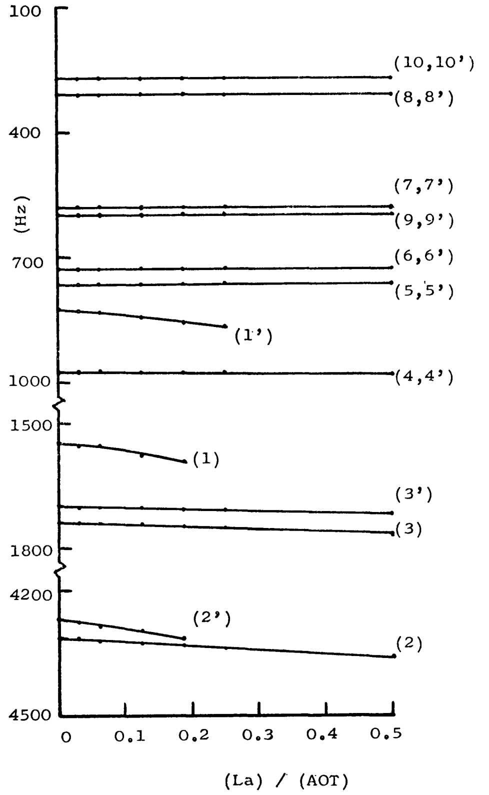

Fig. 4. The chemical shift (Hz) relative to TMS *vs.* the ratio of (La)/(AOT) (the mole ratio of lantanide shift reagent to Aerosol OT).

presumed that carbonyl carbon-(2′) is located nearer the polar group in spacial distance than carbonyl carbon-(2) in spite of the longer distance through chemical bonds. On the contrary, methylene C(3) is nearer to the polar group than C(3′), as expected from the chemical sequence. Carbon-(4,4′, 5,5′, 6,6′, 7,7′, 8,8′, 9,9′, 10,10′) are far from the polar group.

T_1 *Measurement.* Spin-lattice relaxation time T_1 was measured by the 180°-τ-90° pulse sequence method. The sample was dissolved in chloroform-d_1, and the

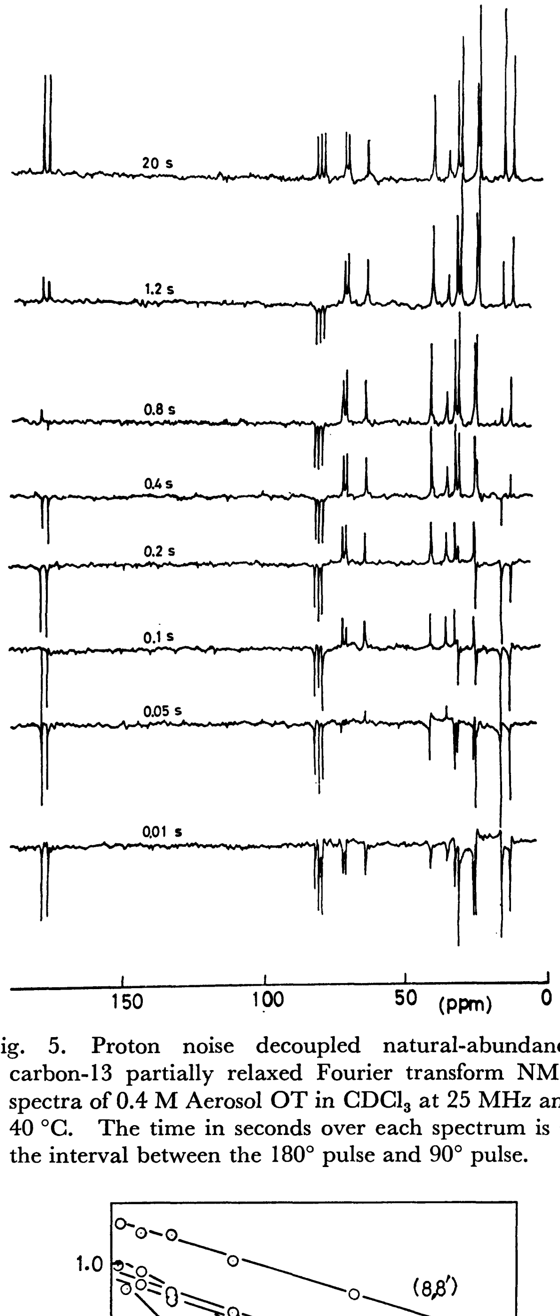

Fig. 5. Proton noise decoupled natural-abundance carbon-13 partially relaxed Fourier transform NMR spectra of 0.4 M Aerosol OT in $CDCl_3$ at 25 MHz and 40 °C. The time in seconds over each spectrum is τ, the interval between the 180° pulse and 90° pulse.

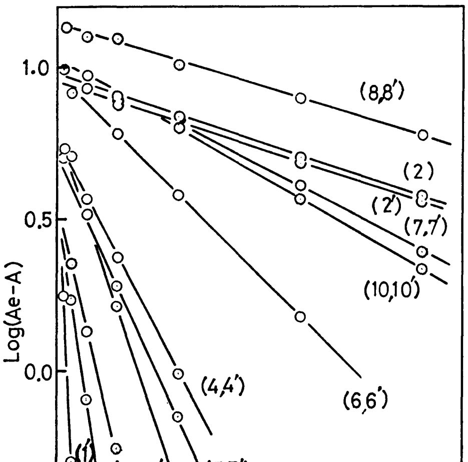

Fig. 6. Log(A_e−A) *vs.* interval τ, where A is the relative peak intensity and A_e is the limited peak intensity when interval τ is long enough.

Table 1. Spin-lattice relaxation time (T_1) and (NT_1) of the ^{13}C nuclei and ^{13}C chemical shift relative to TMS

		T_1(s)	NT_1(s)	δ(ppm)
C=O	(2)	1.39		171.6
	(2′)	1.51		169.7
CH	(1)	0.10	0.10	61.3
	(4,4′)	0.23	0.23	38.6
CH_2	(3)	0.08	0.16	68.5
	(3′)	0.08	0.16	67.5
	(1′)	0.05	0.10	33.1
	(5,5′)	0.21	0.42	30.3
	(6,6′)	0.42	0.84	28.9
	(9,9′)	0.15	0.30	23.5
	(7,7′)	0.85	1.70	23.0
CH_3	(8,8′)	1.39	4.17	14.1
	(10,10′)	1.02	3.06	10.8

* N: The number of protons attached to carbon.

solution was degassed. The concentration was 200 mg/ml, which is sufficiently high to neglect the existence of monomer. Repetition time was 20 s and the peaks were accumulated 400 times in time domain. The results are shown in Fig. 5. In the pulse sequence method, the relative peak intensity A is given by

$$A = A_e(1-2\exp(-\tau/T_1))$$

where τ is the interval between the 180° and 90° pulses and A_e is the limited peak intensity when interval τ is long enough (20 s). In Fig. 6, log (A_e-A) are plotted against τ. T_1 can be calculated from the slopes. The results are given in Table 1 with the corresponding chemical-shift values. The estimated errors in the T_1 measurement were within 10%. We found that when the relaxation was caused by magnetic dipole interaction, most of it was affected by the protons bonded directly to carbon. The relaxation becomes faster with an increase in the number of attached protons. In order to correlate relaxation time to segmental motion, the number of the proton time T_1, *i.e.*, NT_1, is more useful than T_1 itself.

With respect to the main chains, T_1 of carbons gradually becomes greater as they become located far from the polar group ($-SO_3Na$). This implies that segmental mobility increases as the segment becomes located farther from the polar group of the molecule in the miecllar state in chloroform. This is in line with the fact that Aerosol OT in chloroform forms reverse micelles with the aid of dipole interaction among intermolecular polar groups, the hydrocarbon parts far from the micellar core moving freely. This is interesting when compared with the behavior of micelle in water. The relaxation times of main and side chains were compared with each other. T_1 of C(8) is greater than that of C(10), the same relation holding for C(5) and C(9). This indicates that the side chains are restricted in mobility to a greater extent than the main chains in micellar state. It is concluded that (1) Aerosol OT molecules in the micellar state associate with each other by the polar head groups, hydrocarbon chains being flexible, (2) the mobility of side chains is more restricted than that of the main chain, and (3) carbonyl carbon-(2′) is located nearer in spacial distance to the polar group than carbonyl carbon-(2).

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