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A ^{13}C NMR Relaxation Study of Octyltrimethylammonium Salts in D_2O

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Synopsis. The concentration dependence of the ^{13}C spin-lattice relaxation times (T_1) of the alkyl carbons in octyltrimethylammonium salts was analyzed by means of applying the phase separation model. At higher concentration, the $1/T_1$ value deviates from a linear plot and depends on the magnetic field strength. The molecular motions in monomer and micellar states are discussed, along with the overall motions of the molecule and its internal motion.

Micelles formed by surfactants in aqueous media have been the subject of numerous studies involving various techniques. Especially, in studying micellar solutions on the molecular level, NMR spectroscopy has proved to be one of the most useful experimental techniques. Recently, the internal structure and dynamics of micelles have been examined by a ^{13}C NMR study,$^{1-3)}$ since the spin-lattice relaxation times (T_1) for individual carbons of the molecules provide quantitative information concerning the rotational mobility of the corresponding C-H vector. Further, a significant observation in ^{13}C T_1 measurements at different magnetic fields is that the relaxation times are dependent on the magnetic field strength at higher surfactant concentrations.$^{4,5)}$

In the present work, we systematically examined the ^{13}C-T_1 behavior of octyltrimethylammonium salts in D_2O. For these surfactants, the critical micelle concentrations (cmc) are rather high (ca. 0.3 M; 1 M=1 mol dm^{-3}). Therefore, it is feasible to obtain structural information concerning the motions of the alkyl chain segments in surfactant both in monomer and micellar states.

Experimental

Octyltrimethylammonium bromide (C_8TAB) and octyltrimethylammonium chloride (C_8TAC) were used as the surfactants in this study. The preparative procedures for the surfactants have been described elsewhere.$^{6)}$ As a check of the purity of the surfactants, cmc determinations were performed by means of a surface tension method; the cmc's agreed closely with those values from the literature.$^{7)}$

^{13}C NMR spectra and T_1 values were obtained with complete proton decoupling at 22.5 MHz (2.10 T) on a JEOL-FX90QNMR spectrometer. T_1 measurements were also made at 62.9 MHz (5.87 T) using a Brucker-AC250 NMR spectrometer to examine the magnetic field dependence. The deuterium signal from solvent D_2O was used as a lock signal. T_1 values were obtained by the inversion recovery method, using a 180°-τ-90° pulse sequence. The experimental temperature was controlled by a controller unit. It's reliability was monitored by the alternative insertion of a thermister into the sample position. All T_1 measurements were performed at 36 °C.

Results and Discussion

The representative ^{13}C NMR spectrum in a C_8TAB solution at 36 °C is shown in Fig. 1. With C_8TAB, almost all carbons appear as a resolved resonance. For surfactants containing longer alkyl chains, the differences in chemical shifts of the methylene carbons near the center of the chain are insufficient to obtain a complete resolution of the spectrum, as shown in C-4 and C-5 in the figure: hence, an averaged value of T_1 values of these carbons was given. Similar spectral behavior has been observed for C_8TAC. The assignments for the surfactants studied have been given previously.$^{2,8)}$

It is assumed that the ^{13}C spin-lattice relaxation of protonated carbon in large and intermediate sized molecules like an aggregated surfactant system is in general dominated by three kinds of contributions from: (1)the overall motion of micelles, (2)the overall motions of surfactant molecules in a micellar and a bulk phases, and (3)the chain segmentary motion (internal motion) of the hydrocarbon chain in a molecule. Of three, the overall motion of micelle is slow compared with the other two motions and hence it can be neglected.$^{9)}$

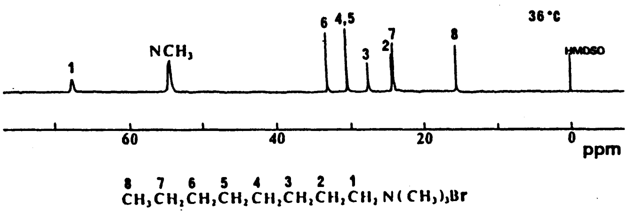

Fig. 1. ^{13}C NMR specturm of C_8TAB in D_2O at 36 °C. Hexamethyldisiloxane (HMDSO) was used as an external reference.

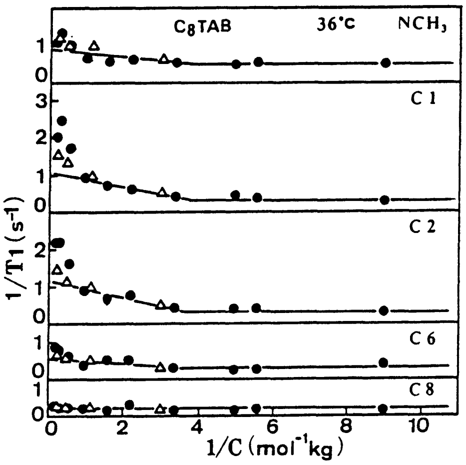

Fig. 2. Plots of $1/T_1$ of carbons for C_8TAB at two different magnetic field strengths against the inverse of surfactant concentration: (△) corresponds to 5.87 T and (●) to 2.10 T. The carbons are numbered as in Fig. 1.

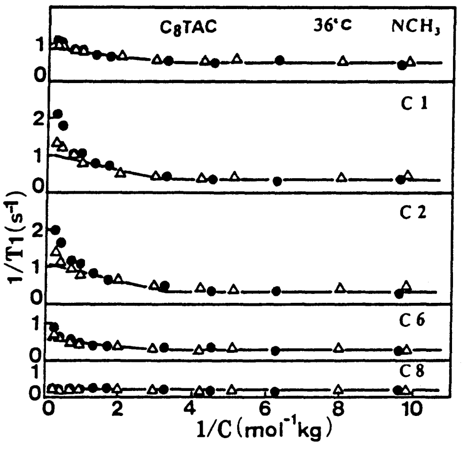

Fig. 3. Plots $1/T_1$ of carbons for C_8TAC at two different magnetic field strengths against the inverse of surfactant concentration: (Δ) corresponds to 5.87 T and (●) to 2.10 T. The carbons are numbered as in Fig. 2.

The observed relaxation rates, $1/T_1$, for alkyl carbons in the C_8TAB and C_8TAC at two different magnetic field strengths are plotted in Figs. 2 and 3, as functions of the inverse of surfactant concentrations (C). It can be seen that relaxation times are almost constant at low concentrations (high values of $1/C$); however, at high concentrations, there is an increase in the relaxation rate for all carbon atoms, except C-8 of the terminal methyl group. The increase in the $1/T_1$ value indicates an increased restriction on the mobility of the entire chain. Similar ^{13}C-T_1 behavior has been observed for aqueous micellar solutions of sodium hexanoate.[10] The changes in $1/T_1$ are due to the formation of micelles. The obtained cmc values are nearly equal to those by the surface tension method: C_8TAB 0.27 mol kg^{-1}, C_8TAC 0.32 mol kg^{-1}. It can be seen that the cmc of C_8TAB is lower than that of the corresponding chloride. As for T_1 values of individual alkyl carbons in the surfactants, there was no striking difference between C_8TAB and C_8TAC, indicating that both of these micelles are of nearly the same size and shape. Considered together with previously published results,[6] these micelles tend to remain nearly spherical up to high concentrations (above the cmc). In the limited range of concentration above the cmc (ca. 0.3—1.0 mol kg^{-1}), an approximately linear relationship exists between $1/T_1$ and $1/C$. We can also see that there is little difference between both T_1 values at 2.10 T and at 5.87 T in this concentraion range, as well as below cmc. Following the phase separation model, the observed relaxation rate $(1/T_1)_{\mathrm{obsd.}}$ is assumed to be a weighted average of the relaxation rates in the micelles and monomers. Then, T_1 in this concentraion range is given by[10,11]

$$\left(\frac{1}{T_1}\right)_{\mathrm{obsd.}} = \frac{\mathrm{cmc}}{C}\left(\frac{1}{T_1}\right)_{\mathrm{mon.}} + \frac{C-\mathrm{cmc}}{C}\left(\frac{1}{T_1}\right)_{\mathrm{mic.}}.$$

This equation suggests that a plot of the $(1/T_1)_{\mathrm{obsd.}}$ against the inverse of the concentration should give two straight lines intersecting at the cmc, as shown in the Figs. 2 and 3. The $1/T_1$ values for all carbons in monomer and micellar states can, therefore, be obtained from the intercepts at cmc and at $1/C=0$, respectively. Thus, the relaxation times obtained for C_8TAB are summarized in Table 1, together with the correlation time (τ_c). In the monomer state, variation of the relaxation along the hydrocarbon chain within a molecule was not large, as compared with those in the micellar state. Precisely, there seems to be a slight increase in the segmentary mobility as one moves away from the polar head. As indicated by the higher T_1 values all along the chain, the overall reorientation motion is faster with a slight degree of segmentary motions along the chain in a molecule, suggesting that the relaxation behavior below cmc is mainly governed by the overall motion of the octyltrimethylammonium ion. From Fig. 2 and Table 1, a marked increase in the $1/T_1$ value above cmc is found along the alkyl chain from C-8 toward C-1 next to the N-methyl head groups. This behavior may be attributed to a severe immobilization at the polar head, because surfactant molecules interact strongly with neighboring molecules, counterions and water molecules at the micellar surface. Accordingly, the overall motion of the molecule becomes more and more restricted, implying that the internal motions become more important for the relaxation behavior. On the other hand, the $1/T_1$ value of N-methyl carbon is rather small, as shown in Table 1. Probably, such N-methyl groups are expected to extend outward from the micellar surface into the solvent. Consequently, they would possess a larger degree of motional freedom than that of the carbons next to the polar group. As for the C-8 carbon, it has a prominent segmentary mobility, irrespective of the surfactant concentration. The micellar interior is likely to have properties that approach those of a liquid-like environment, as already stated by others.[1,12,13] In Figs. 2 and 3 it is remarkable that at the highest concentration range, $1/T_1$ values tend to deviate from the linear plots and the degree of deviation is relatively larger at 2.10 T than that at 5.87 T, suggesting a magnetic field strength dependence for the relaxation behavior. Especially, a marked field dependence is found for the first three methylene car-

Table 1. ^{13}C Spin-Lattice Relaxation Times (T_1) and Correlation Times (τ_c) for the Alkyl Carbons of C_8TAB Solution at 2.10 T

Carbon atom	Micelles		Monomers at cmc	
	T_1/s	τ_c/ps[a)]	T_1/s	τ_c/ps[a)]
N-CH_3	0.99	16	2.0	7.8
C-1	0.73	32	2.6	8.6
C-2	0.78	30	2.4	9.8
C-3	0.87	27	2.4	9.8
C-4,5	1.3	19	2.7	8.6
C-6	1.6	15	3.3	7.0
C-7	2.2	10	3.6	6.5
C-8	4.4	3.6	4.4	3.6

a) Calculated from $1/T_1=N\hbar^2\gamma_C^2\gamma_H^2 r_{CH}^{-6}\tau_c$, where γ_C and γ_H: gyromagnetic ratios of ^{13}C and ^1H, N: number of directly bonded hydrogen, r_{CH}: C-H distance. $\hbar$: Plank's constant.

bons next to the polar head group. For this field dependence, Wennerström et al.[4] have proposed from ^{13}C T_1 measurements on sodium octanoate that the slow micellar motion contributes to the relaxation, particularly for carbons near the polar head. In addition, the deviation from linearity may suggest that some structural change affecting the relaxation occurs in the micelles. From the results presented above, T_1 is found to be magnetic field independent at low concentrations, so that the relaxation is determined by a correlation time τ_c on the order of 10^{-11} to 10^{-12} s based upon the rotational motion of isotropic reorienting molecule, where extreme narrowing condition is fulfilled. At higher concentrations with field dependence, such a surfactant system is expected to have slow motions on the order of 10^{-8} to 10^{-9} s (or longer), such as the rotation of micelle as a single entity and surfactant lateral diffusion along the micelle surface.[14] Further analysis using a two-step model[4,14] from the multifield relaxation data would be necessary to obtain detailed information on both chain dynamics and orientation.

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