A ^{14}N NMR Relaxation Study of Aqueous Alkyltrimethylammonium Salt Solutions

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Synopsis. ^{14}N spin-lattice and spin-spin relaxation times were measured in a series of alkyltrimethylammonium salts at higher concentrations above the critical micell concentration. Octyltrimethylammonium bromide and dodecyltrimethylammonium chloride form spherical micelles at all concentrations, while decyl- and dodecyltrimethylammonium bromides form larger and rodlike micelles such as the hexadecyltrimethylammonium bromide suggested previously.

The transition of the shape of micelles in aqueous solutions is known to occur for various surfactants. In connection with this phenomenon, a change from spherical to rodlike micelles at higher concentrations has, also, been observed by macroscopic techniques, such as light scattering, viscosity and electron microscopic observation etc.[1-3] The significance of the spectroscopic work is evident for the dynamical study of the micellar phenomenon at the molecular level. Here, nuclear magnetic resonance (NMR) is a very powerful tool; thus, that many ^{1}H, $^{2}H(D)$, and ^{13}C studies have been reported in this field.[4-6] It has been shown that the longitudinal relaxation time, T_1, and the transverse relaxation time, T_2, can give information about the intensity of molecular motions. The time scale of the molecular motions is usually characterized by the parameter τ_c, the rotational correlation time. Recently, a study of ^{14}N relaxation times, T_1 and T_2, of hexadecyltrimethylammonium bromide (CTAB) and chloride (CTAC) micellar solutions has been reported by Henriksson et al.,[7] suggesting a change from spherical to rodlike form for the CTAB micellar shape.

With the aim of further documenting changes in the micellar shape, we have undertaken a systematic study of a series of alkyltrimethylammonium systems using the applicability of ^{14}N NMH.

The surfactants used in this study were alkyltrimethylammonium bromides with 8, 10, and 12 carbon atoms in the aliphatic chain, and dodecyltrimethylammonium chloride (DTAC). Dodecyltrimethylammonium bromide (DTAB), decyltrimethylammonium bromide (DeTAB) and DTAC were supplied from Kanto Chemical Inc. and purified through several recrystallizations from an ethanol-ether mixture. Octyltrimethylammonium bromide (OTAB) was synthesized by reacting equimolar quantities of trimethylamine and octyl bromide in ethanol at −3 °C for 5 d. 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.[8] Deuterium oxide was used without further purification. ^{14}N relaxation times were measured at 6.42 MHz by a JEOL-FX90QFT NMR. The experimental temperature was 27 °C. Its reliability was monitored by the alternative insertion of a thermister into the sample position; the temperature was found to be ±0.5 °C. Spectra were recorded in the FT mode and T_1 was obtained by the 180°—τ—90° pulse sequence. T_2 was calculated from the half-width of the absorption signal in the fourier transform spectrum using the relation $(\pi\ T_2)^{-1}=\Delta\nu-\Delta\nu_{inhom}$, where $\Delta\nu$ is the experimental line width and $\Delta\nu_{inhom}$ is the contribution to the line width from magnetic field inhomogeneities. $\Delta\nu_{inhom}$ was determined from the spectrum of an aqueous solution of ammonium nitrate, which has a negligible contribution to the line width from relaxation.

The observed ^{14}N relaxation times, T_1 and T_2, for several alkyltrimethylammonium bromides are plotted in Fig. 1 as functions of the surfactant concentration. For a comparison, the result at 28.5 °C for CTAB reported by Henriksson et al.[7] is also given in the Fig. 1. All measurements obtained here have been performed at concentrations well above the cmc. When the concentration is increased, there is a gradual decrease in the relaxation times, and both T_1 and T_2 values initially have the same values, as are those for normal micellar solutions which extreme narrowing condition is fulfilled. At higher concentrations, T_2 still continues to decrease with increasing concentration, while T_1 becomes rather larger compared with T_2; consequently, T_1 differs from T_2, except for OTAB. For DTAB, a broader minimum in T_1 was

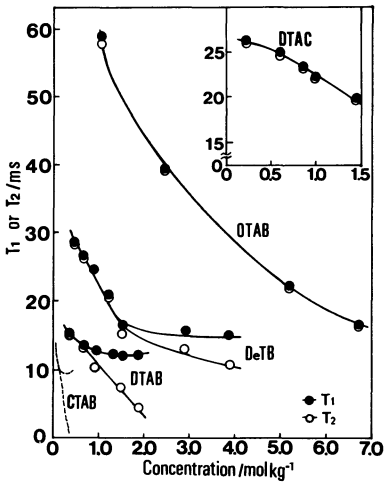

Fig. 1. ^{14}N relaxation times T_1 and T_2 vs. concentration at 27 °C for various surfactants. For comparison, the result for CTAB at 28.5 °C by Henriksson et al.[7] is included as the dashed curve.

also observed at $c \approx 1.5$ mol kg^{-1}, just as that for CTAB.[7] In such a case, it was suggested that the rotational motion about the principal axis of the electric field gradient at the nitrogen nucleus, the N–C$_\alpha$ bond, would not be described by a single correlation time based upon the rotational motion of isotropically reorienting molecule. Henriksson et al.[7] explained this observation by assuming that two kinds of molecular motions are effective for the relaxation. One is a local fast anisotropic motion of the molecule and the other is a slower motion over a distance of the order of micellar dimensions. For the fast motion which makes approximately constant contribution to the relaxation, the correlation time is $\tau_c^f = 4.5 \times 10^{-10}$ s at 27 °C in DTAB micelles.[9] On the other hand, the correlation time for the slow motion, τ_c^s, increases rapidly with the concentration.[7] This can be regarded as the slow motion that is tied to the distribution of aggregation numbers of the micelles, implying that the overall motion becomes more important for the relaxation. The calculation with τ_c^s value in DTAB micelles gives approximately 1.53×10^{-8} s[9] at $c = 1.5$ mol kg^{-1}, which is obviously much larger than τ_c^f. These values are of similar magnitude to those calculated for CTAB micelles by Henriksson et al., indicating that the same types of larger micelles are present in both systems. As the alkyl chain length is shortened, the discontinuous change tends to be shifted to the higher-concentration region and the relaxation times become larger. At the same time, it is suggested that T_1 gradually approaches T_2.

On the other hand, the relaxation behavior for OTAB seems to be different from the other surfactants and $T_1 = T_2$ holds throughout the concentration range examined. The differences in micellar size and shape would bring about a different relaxation behavior. This result is certainly expected since the concentrated solution of OTAB consists of spherical micelles.[2] Also, the behavior in aqueous solutions of DTAB and DTAC in Fig. 1 is found to be quite different and the relaxation times are about twice as long for the DTAC as for the DTAB solutions. The most likely explanation is that bromide ions can lower the electrostatic repulsion between the cationic head groups in the DTAB micelles and make a closer packing and tighter binding of the surfactant molecules on the micellar surface.[7] This seems to be caused by a phase change in the molecular packing accompanied by a phenomenon similar to that of the transition from spherical to rod-shaped micelles at high concentrations. In analogy with the above discussion, no change in the micellar shape occurs with DTAC and the micelles tend to remain spherical over all the concentration range, as already noted by Ozeki and Ikeda.[11] Accordingly, these results can be best explained by the occurrence of both rodlike (in which $T_2 < T_1$) and spherical (in which $T_1 = T_2$) micelles.

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