A ^{13}C NMR Study of Octyltrimethylammonium Bromide Solutions with and without Urea

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Synopsis. The effect of urea on the micelle formation of octyltrimethylammonium bromide (C_8TAB) solution in D_2O was studied by ^{13}C NMR chemical shift and ^{13}C spin-lattice relaxation time. The presence of urea increases the critical micelle concentration (cmc) of C_8TAB solution. In the micellar state, the segmental motions of methylene chain adjacent to the polar head group are strongly affected by urea.

The addition of a low-molecular organic material to aqueous surfactant solutions alters not only the critical micelle concentration (cmc) and the aggregation number of the micelle, but also the micro-environment of the micelle.[1] Many investigations have proved that changes in water structure play an important role in micelle formation. For example, the effect of dissolved urea on the micelle formation and hydrophobic bonding in the micellar core has been interpreted by the structure of water.[2-5] The NMR is one of the most useful techniques in studying micellar solutions on molecular level. This communication reports the effect of urea on the chain dynamics of octyltrimethylammonium bromide (C_8TAB) micelle and the cmc of C_8TAB solution by the NMR method.

Experimental

The preparative procedure of C_8TAB was described in the preceding report.[6] Deuterium oxide (99.85% D) was used as solvent. Urea used was of reagent grade and purified by recrystallization. ^{13}C NMR spectrum was obtained at 22.5 MHz on a JEOL-FX90Q NMR spectrometer operating in the FT-mode. The deuterium signal from solvent D_2O was used as an internal lock signal. The spin-lattice relaxation time (T_1) was measured by the inversion-recovery method, as described earlier.[6] For the ^{13}C chemical shift measurements, hexamethyldisiloxane (HMDSO) was used as an external reference. No susceptibility corrections were applied.

Results and Discussion

The assignment for the ^{13}C NMR spectrum has been given previously.[6] In the ^{13}C spectrum, almost all carbons appear as well-separated signals. The observed relaxation rate, $1/T_1$, for typical alkyl carbons of C_8TAB in D_2O with and without 10 mol kg^{-1} urea is plotted in Fig. 1 as a function of the inverse of total concentration C. In the presence of urea, $1/T_1$ was constant at low concentration region, whereas the $1/T_1$ of all carbon atoms increased with increasing surfactant concentrraion in the cmc region, except C-8, as well as for urea-free C_8TAB solution reported previously.[6] A considerable increase in the $1/T_1$ value in the micellar state was found along the alkyl chain from C-8 to C-1 connecting to the *N*-methyl head group. The addition of urea tends to increase the cmc, which is taken from intersection of two straight line segments of the $1/T_1$ vs. $1/C$ plot. Especially, a marked decrease in the relaxation rate of micelles was observed for C-1, C-2, and C-3 (not shown) carbons next to the polar head group. That is, the methylene carbons adjacent to the polar head group seem to have higher motional freedom in the presence of urea. These results suggest that urea cannot be solubilized within the micelle, but acts on the external environment of the micelle and that it disturbs the micelle formation. On the other hand, $1/T_1$ values in monomers are more or less affected by addition of 10 mol kg^{-1} urea. The increase in the $1/T_1$ value with urea may be due to the rise in viscosity on addition of urea.

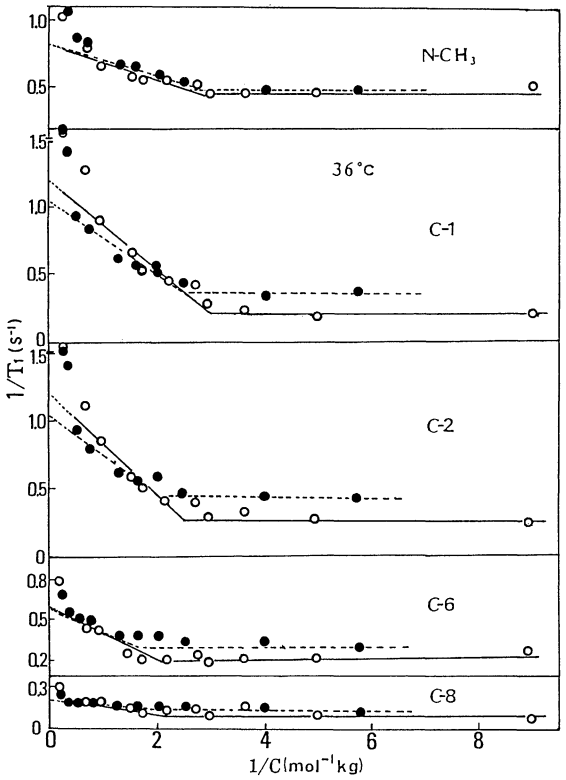

Fig. 1. $1/T_1$ of carbons for C_8TAB with and without urea against the inverse of surfactant concentration: (○): C_8TAB, (●): C_8TAB+10 mol kg^{-1} urea.

In Fig. 2, ^{13}C chemical shifts of C_8TAB in D_2O with and without 3 mol kg^{-1} urea are plotted against $1/C$. At low concentrations of C_8TAB, the shift of the ^{13}C signals was nearly constant. At higher concentrations, the signals shifted progressively with the inverse of the total surfactant concentration. These abrupt

changes in the chemical shifts are due to the formation of micelles. The signals shifted almost linearly to downfield for all carbons except C-1, whereas C-1 shifted upfield. The chemical shifts of C_8TAB with urea of various concentrations showed a concentration dependence similar to that of the system with 3 mol kg^{-1} urea. Furthermore, it is to be noted that urea addition reduced sharpness of the break in the δ vs. $1/C$ plot in the cmc region. This fact suggests that urea disturbs the monomer-micelle equilibrium when the micelle concentration is finite and low. Using the phase separation model, the observed chemical shifts (δ) at concentrations above cmc are assumed to be the weighted average of the shifts of monomer

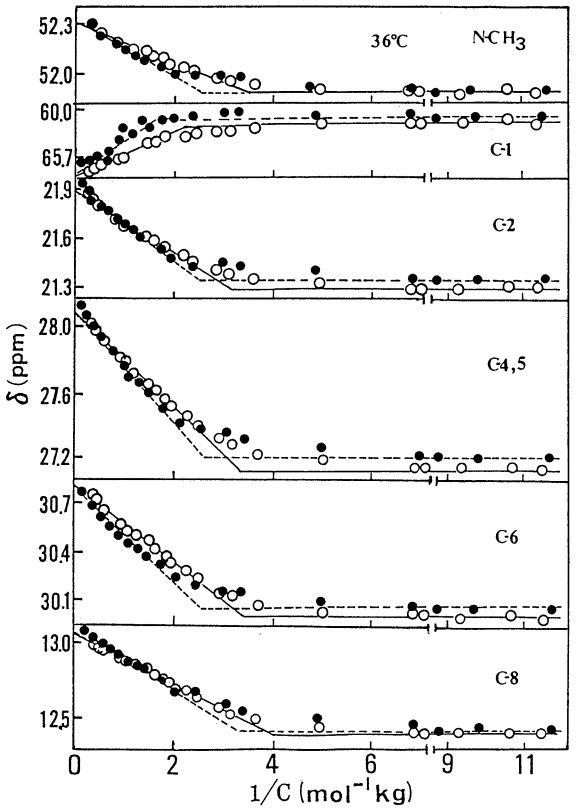

Fig. 2. Variation of the ^{13}C chemical shifts of carbons for C_8TAB with and without urea against the inverse of surfactant concentration. (○): C_8TAB, (●): C_8TAB+3 mol kg^{-1} urea.

(δ_1) and the micellar shift (δ_m) as given by

$$\delta = \delta_m + \frac{\text{cmc}}{C}(\delta_1 - \delta_m),$$

for C>cmc. For C<cmc, the phase separation model implies that $(\delta - \delta_1) = 0$. If δ is plotted against $1/C$, two straight lines are expected to intersect at the point where $1/C$ is 1/cmc. Extrapolating to $1/C$ of 0 the value of δ_m is given, while δ_1 is obtained directly from the measurements for C<cmc. The differences between the micellar and monomer shifts ($\Delta\delta = \delta_m - \delta_1$) except C-1, are summarized in Table 1. These values for all C atoms shifted downfield to the same extent as the corresponding C atoms observed in octyl sulfate.[7] It appears that the downfield shifts by micellization are large in the center of the chain (C-4—C-6), while relatively small at the either polar head or chain end. The significant shift change may be due to the fraction increase of trans conformers in the alkyl chain on micellization.[8,9] On the other hand, the ^{13}C chemical shifts of *N*-methyl head groups would be governed by the environment effect rather than conformation effect, because the methyl group attached to nitrogen atom is considered to project from the micellar surface into solvent.[8] As for C-1 carbon, no sufficient data for $\Delta\delta$ were given, because the estimated error of chemical shift of broad and small peak of the carbon was large. The observed upfield shift of C-1 may be attributed to the steric constraint due to the nature of bulky head groups at micellar surfaces. A similar behavior has also been observed for dodecyldimethylammonium chloride,[8] octyltriethylammonium bromide,[10] and aliphatic sulfates,[7] while the downfield shift of C-1 only for the primary ammonium salt type such as nonylammonium bromide.[9] In addition, particular attention should be paid to electrostatic effect due to the interaction with counter ions. It seems difficult at present to consider these causes as conclusive explanation. From Table 1, it appears that $\Delta\delta$ changes within ca. 0.2 ppm for all C atoms as the urea is added up to 6.0 mol kg^{-1}. Being considered from the fact that all δ_m values are nearly the same ($\pm$0.04 ppm at worst), the observed change of $\Delta\delta$ is probably due to the change in δ_1 of respective carbon. The addition of urea increases δ_1 to some extent for all carbons. Large downfield shifts of ca. 0.2 ppm were observed for C-3 and C-4,5, with smaller

Table 1. Difference between the ^{13}C Chemical Shifts of Monomer and Micelles $\Delta\delta$ (ppm), and Derived cmc Values with and without Urea

Carbon atoms	Urea (mol kg^{-1})							
	0		1.5		3.0		6.0	
	$\Delta\delta$	cmc[a)]	$\Delta\delta$	cmc	$\Delta\delta$	cmc	$\Delta\delta$	cmc
N-CH_3	0.45	0.29	0.48	0.38	0.48	0.42	0.47	0.53
C-2	0.61	0.30	0.64	0.38	0.57	0.43	0.51	0.53
C-3	0.72	0.29	0.64	0.38	0.62	0.43	0.54	0.54
C-4,5	0.98	0.29	0.91	0.38	0.86	0.42	0.75	0.52
C-6	0.80	0.29	0.78	0.37	0.71	0.41	0.67	0.50
C-7	0.66	0.27	0.61	0.36	0.58	0.39	0.51	0.47
C-8	0.61	0.24	0.61	0.28	0.59	0.31	0.55	0.35

a) cmc Values are expressed in mol kg^{-1}.

shifts for the both ends of chain (Fig. 2). Presumably, the shift change of δ_1 with added urea is affected by some solvent-solute interactions involving a structure-breaking effect of urea on water and the change in the dielectric constant. However, such a change in $\Delta\delta$ with urea concentration may be too small to support any tentative interpretation. In contrast, the slope of δ vs. $1/C$ plot above cmc seems to be more sensitive to the urea concentration. With increasing concentration of urea, the slope becomes progressively greater for respective carbons studied. Thus, the derived cmc values for all C atoms, except C-1, are listed in Table 1. In the absence of urea, all cmc values except C-8, are 0.27-0.30 mol kg^{-1}, whereas C-8 signal gives a lower cmc value, as pointed out by Drakenberg and Lindman for sodium octanoate solution.[11] These cmc values are close to 0.22 mol dm^{-3}, obtained by light-scattering method in water at 30 °.[12] From the table, it is seen that the decrease in cmc values along the chain, especially for C-8, is likewise observed on the addition of urea. This suggests that there is some correlation between increasing hydrophobicity of the C-8 terminal group and decreasing cmc. The ratios between the mean cmc with urea and that without urea for all C atoms (except C-8) are evaluated at different urea concentrations as follows: urea concentration and ratio, respectively; 0.5 mol kg^{-1}, 1.1; 1.5 mol kg^{-1}, 1.3; 3.0 mol kg^{-1}, 1.5; and 6.0 mol kg^{-1}, 1.8. Thus, we find that the cmc value for C_8TAB solution tends to increase almost linearly with urea concentration and deviate slightly at 6 mol kg^{-1} urea. As stated by others,[3,4] a possible explanation for this is that urea in the surfactant solutions causes the disruption of water structure to decrease organization around the hydrocarbon chain of the surfactant, reducing the driving forces for micellization. In addition, the importance of other contributions than the change of water structure with increasing concentration of urea should be further investigated.

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