A Carbon-13 Spin-Lattice Relaxation Studies of Simple Alkylsulfates and Alkylsulfonates in Aqueous Solution

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The C-13 spin-lattice relaxation times (T_1) of a series of short-chain *n*-alkylsulfates and sulfonates in D_2O solutions were measured at various concentrations. Even for ethylsulfate and *n*-propylsulfonate ions, inflections, due to association, in the reciprocal of the T_1 *vs.* the inverse concentration plots were observed. The critical micelle concentrations (CMC's) of ethyl and butylsulfates are 3.0 and 2.5 mol/l, respectively, and those of propyl and butylsulfonate 2.3 and 1.9 mol/l, respectively. For the simple alkylsulfates, below the CMC a progressive decrease in T_1 from the terminal methyl group towards the polar group was observed.

Introduction

The CMC's of very simple *n*-alkylsulfates and sulfonates have been determined from the inflections of C-13 NMR chemical shift *vs.* the inverse concentration plots [1]. In the present study, the C-13 spin-lattice relaxation times (T_1) of simple alkylsulfates and sulfonates in aqueous solution were measured to determine the CMC's from the inflections of the $1/T_1$ *vs.* the inverse of the total concentration plots.

Experimental

Materials: Sodium ethylsulfate (SES), sodium *n*-propylsulfate (SPS), sodium *n*-butylsulfate (SBS), sodium *n*-hexylsulfate (SHS), sodium *n*-octylsulfate (SOS) and sodium *n*-dodecylsulfate (SDS) were prepared [2].

Sodium *n*-propylsulfonate (SPSu), and sodium *n*-butylsulfonate (SBSu) were purchased from the Tokyo Kasei Co.

C-13 NMR Measurements: C-13 NMR chemical shift and T_1 measurements were made on a JEOL FX-90Q Fourier Transform Spectrometer at 22.53 MHz. The Inversion Recovery Fourier Transform method [3], pulse sequence 180°, τ, 90°, was employed to obtain T_1.

Results and Discussion

Figure 1 shows the concentration dependence of the C-13 spin-lattice relaxation rate of SES and SBS in D_2O solution. The relaxation rates of all C-13 nuclei of SES and SBS rapidly increase with an increase in the concentrations above 3.0 and 2.5 mol/l, respectively. Similarly, for SPSu and SBSu abrupt changes of the C-13 T_1 values were found at 2.3 and 1.9 mol/l, respectively (not shown). It should be noted that even in the SES and SPSu ions having very short alkyl chains, a marked increase of the relaxation rates is observed.

The reciprocal of the observed T_1 value depends linearly on the inverse of the total concentration above the CMC:

$$(1/T_1)_{\text{obs}} = (\text{CMC}/C_t)\,(1/T_1)_{\text{monomer}} + (C_t - \text{CMC}/C_t)\,(1/T_1)_{\text{micelle}}\,, \qquad (1)$$

where C_t is the total concentration of surfactant, and we assume here that the monomer concentration is constant above the CMC [4, 5].

The observed T_1 values of the sulfate and sulfonate ions are consistent with (1) and our CMC's for SES, SPSu, SBS and SBSu of 3.0, 2.3, 2.5 and 1.9 mol/l, respectively, are very close to the values obtained by the C-13 chemical shift *vs.* the inverse concentration plots (1).

The T_1 values of the alkylsulfate and sulfonate ions in monomer and micellar states are listed in Table 1. In the monomer state they show a progres-

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Table 1. Carbon-13 spin-lattice relaxation times (T_1, s)[a] and effective correlation times (τ_{eff}, picosec)[b] of *n*-alkyl sulfates and sulfonates.

(a) *n*-alkyl sulfates.

No. of carbon atom[c]			1	2	3	4	5	6	7	8	9	10	11	12
SES	Monomer	T_1	6.45	7.19										
		τ_{eff}	3.5	2.1										
	Micelle	T_1	2.63	2.63										
SBS	Monomer	T_1	3.33	3.68	4.88	5.41								
		τ_{eft}	6.8	6.2	4.7	2.8								
	Micelle	T_1	0.75	1.09	2.04	2.86								
SHS	Monomer	T_1	1.96	2.27	2.50	2.70	3.45	5.26						
		τ_{eff}	11.6	10.0	9.1	8.4	6.6	2.9						
	Micelle	T_1	0.56	0.59	0.86	1.10	1.43	2.86						
SOS	Monomer	T_1	1.82	1.85	1.90	1.97	2.03	3.03	4.23	4.84				
		τ_{eff}	12.5	12.3	12.0	11.5	11.2	7.5	5.4	3.2				
	Micelle	T_1	0.57	0.60	0.55	0.66	0.66	0.86	1.28	2.78				
SDS	Micelle	T_1	0.56	0.48	0.44	0.47	0.47	0.47	0.47	0.49	0.49	0.92	1.20	2.90

(b) *n*-alkyl sulfonates.

No. of carbon atom			1	2	3	4
SPSu	Monomer	T_1	2.82	4.00	4.08	
		τ_{eff}	8.1	5.7	3.8	
	Micelle	T_1	1.32	2.56	2.63	
SBSu	Monomer	T_1	2.83	3.53	4.11	4.89
		τ_{eff}	8.0	6.4	5.5	3.2
	Micelle	T_1	0.83	1.14	1.43	3.13

[a] The T_1 values of micelles were obtained from the intercepts at $1/C = 0$.

[b] For the calculation a C−H distance (r_{CH}) of 1.09 Å and the number (N) of protons attached to the C-13 atom were used.

[c] Alkyl carbons are numbered from the CH_2 group adjacent to the polar group to the terminal methyl.

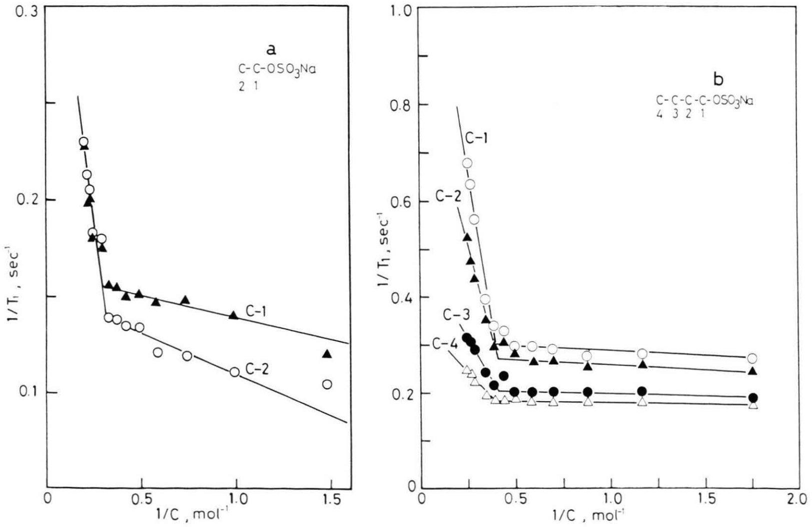

Fig. 1. Carbon-13 spin-lattice relaxation rates as a function of the inverse concentration for (a) SES and (b) SBS in D_2O solution at 32 °C. T_1 values are accurate to ± 5%.

sive decrease from the CH_3 end to the polar group. For SPSu, SBS and SBSu, the relative T_1 values of C-1 to those of the CH_2 carbon nearest to the terminal CH_3 amount to 0.68–0.71, and for the monomer solutions of SHS and SOS the relative ones to 0.43–0.57. These observations show that rotation about the $CH_2{-}O$ or $CH_2{-}CH_2$ bonds nearest to the polar group is restricted in the monomolecular state.

In the T_1 values of the alkylsulfate ions, the effect of conformations about the $CH_2{-}CH_2$ groups nearest to the polar group may be considered because in Raman studies of SES [1a, 6] the ethylsulfate ion has been found to exist primarily in the trans form in 0.67–5.4 mol/l.

For monomeric SPS, SBS, SHS and SOS solutions, a preferential stabilization of the conformation about the $CH_2{-}O$ bond possibly occurs [6]. This causes a restriction of the $CH_2{-}O$ segment, which results in the shortest T_1 of the C-1 atom nearest to the sulfate group.

In the Raman spectra of SPSu the trans and gauche lines have been observed [7]. However, even in the monomer state the trans form predominates. This fact also leads to the restricted state of the $CH_2{-}CH_2$ bond nearest to the SO_3^- group.

The C-13 T_1 of a protonated carbon in a large molecule is dominated by $^{13}C{-}^{1}H$ dipole-dipole interactions and given by the equation

$$1/NT_1 = \hbar^2 \gamma_C^2 \gamma_H^2 r_{CH}^{-6} \tau_{\text{eff}}, \quad (2)$$

where N is the number of directly attached protons, γ_C and γ_H are the gyromagnetic ratios of C-13 atom and H-1, respectively, r_{CH} is the C–H bond length, and τ_{eff} an effective correlation time for rotational reorientation of the C–H relaxation vector [4]. When internal rotations occur, τ_{eff} means an average correlation time. The NT_1 value is inversely proportional to τ_{eff} and gives an indication of rotational mobility and segmental motion of the alkyl chain.

For the observed T_1 values, below the CMC the overall motion of the whole molecule is predominant. However, above the CMC the internal motion of the *n*-alkyl chain and micellar motions are the main cause of the difference observed. Equation (2) is applicable to the T_1-discussion of monomer solutions [4, 5, 8].

For the monomer state of simple alkylsulfate and sulfonate ions, the effective correlation times of all carbon atoms obtained from (2) also indicate that the mobility of the short chains increases gradually from C-1 to the methyl end.

For the SES solution, the internal rotation about the $CH_2{-}O$ bond can be neglected because of the preferential stabilization of the trans form. The effective correlation times of the monomers include only the contribution of the overall reorientational motion. For other simple alkylsulfate ions, the contribution of the internal rotation about the $CH_2{-}O$ bond to the τ_{eff} value can also be neglected.

The transition from monomers to micelles results in a decrease in the T_1 values for all carbon atoms. The T_1 values in the micellar state, listed in Table 1, were obtained from the intercepts at $1/C = 0$. For SOS and SDS, the extent of a decrease in the T_1, the relative T_1 of micelles to that of the monomers, is identical with that of the same surfactants reported by Kragh-Hansen [8]. For SHS, the relative T_1 values of C-1 and C-2 are in accordance with those of SOS. It should be noted that the relative T_1 values of C-1 and C-2 in SES, SBS, SPSu and SBSu are reduced to a considerable extent (0.30–0.47).

For SPSu, SBSu, SBS and SHS in aqueous solution, above the CMC conformational change of the segments has been demonstrated by Raman studies [7]. Such conformational change also becomes a dominant mechanism of the spin-lattice relaxation. However, it is difficult to interpret in detail the carbon-13 T_1 change on micellization in connection with the conformational change.

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