The Raman Spectra and Conformational Change of Simple Sodium Alkylsulfates and Sodium Alkylsulfonates in Aqueous Solution

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In order to study the polar group effect upon conformations about CH_2-CH_2 single bonds, the Raman spectra of simple sodium alkylsulfates and sodium alkylsulfonates were measured. The ethylsulfate ion ($CH_3-CH_2-O-SO_3^-$) in aqueous solution was found to take the trans form about the CH_2-O bond in 0.67–5.41 mol/l. For the n-propylsulfonate ion the Raman line due to the gauche form about the CH_2-CH_2 bond was also observed, the trans form becoming predominant at higher concentrations. For the sulfate and sulfonate ions having butyl and hexyl chains, the concentration dependence of their molecular conformations was also investigated.

Introduction

The Raman spectra in the accordion vibrational region have given direct evidence for conformational changes of the hydrocarbon moiety of simple surfactants [1, 2]. For surfactant molecules having long chains, the Raman bands in the skeletal optical vibration region have been used successfully to discuss the randomness of the alkyl chains [3–5]. Recently, it has been indicated that the Raman spectra of the carbonyl stretching mode of lipids allow for an investigation of the acyl chain conformation at the lipid interface region [6].

Even in the Stern layer of micelles, as well as in the hydrocarbon region, a conformational change has been observed by ^1H NMR spectra for sodium N-acylsarcosinates [7, 8] and O-alkyl-D,L-tyrosines [9].

In this article, the concentration dependence of the Raman spectra is reported for a series of sodium alkylsulfates and alkylsulfonates having ethyl, propyl, butyl and hexyl chains, and the conformations about the CH_2-CH_2 bond near to the polar group are discussed.

Experimental

Materials: Sodium ethylsulfonate (SESu), sodium n-propylsulfonate (SPSu), sodium n-butylsulfonate (SBSu), and sodium n-hexylsulfonate (SHSu) were purchased from the Tokyo Kasei Co. The samples of sodium ethylsulfate (SES), sodium n-propylsulfate (SPS), sodium n-butylsulfate (SBS) and sodium n-hexylsulfate (SHS) were synthesized [10]. *Raman Scattering Measurements:* The Raman spectra of the samples were measured with a JASCO Raman Spectrometer (model R-800, argon ion laser, 400 mW, 488.0 nm) at room temperature.

Results and Discussion

Conformational Change on Micellization – SES, SPS and SPSu: The crystal structure of SES, as analyzed by the X-ray diffraction method [11], has shown that ethylsulfate ion takes the trans form about the CH_2-O bond. The Raman spectra of aqueous and solid SES were found to be much the same; no new Raman lines appeared when the solid was dissolved in water. This observation indicates that the ethylsulfate ion in an aqueous solution exists primarily in the trans form [12]. In the present study, Raman spectral measurements of SES were made at various concentrations. No Raman lines due to the gauche form of ethylsulfate ion were observed in the concentration range of 0.67–5.41 mol/l.

For SPS the peak height of the Raman lines of the gauche form relative to those of the all trans one was also investigated at various concentrations in this study. The peak height of the 839 cm^{-1} line of the all trans form relative to that of the 878 cm^{-1} line of the gauche isomers [12], I_{839}/I_{878}, was found to be 1.0 at 0.87 mol/l and 1.4 at 3.13 mol/l. We conclude that for the n-propylsulfate ion in aqueous solution the all trans form is stabilized at higher concentrations.

The Raman line of the SPSu solution at 900 cm^{-1}, assigned to the gauche form, is not observed in the crystalline state. The Raman intensity of the 915 cm^{-1} line due to the trans form relative to that of the 900 cm^{-1} line was found to increase with increasing concentration, as is seen in Figure 1. In the range of 4.00–5.50 mol/l, the Raman line at 900 cm^{-1} appears as a very weak shoulder. However, at lower concentrations the weak 900 cm^{-1} line is observed as a peak, but its intensity is very small relative to that of the 915 cm^{-1} line. We conclude that the trans and gauche forms coexist in aqueous solution and the predominant transform being preferentially stabilized at higher concentrations. It should be noted that the conformational change with concentration occurs even in a very simple alkylsulfonate ion.

Accordion Vibrational Region – SBS, SHS, SBSu and SHSu: For the accordion vibrations of sodium alkylsulfates ($n \geqq 4$, $n =$ carbon number) and potassium ali-

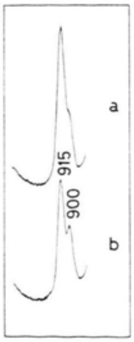

Fig. 1. Concentration dependence of the Raman spectra of SPSu in aqueous solutions (a) 4.60 mol/l; b) 2.30 mol/l) in the 1000 – 700 cm^{-1} region.

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N	SASu	
	soln	solid
3	320	322
4	310	314
6	250	245
8	–	194
12	–	165

Table 1. Accordion frequencies (cm^{-1}) of sodium alkylsulfonates (SASu) in the solid state and aqueous solutions.

phatic carboxylates ($n \geqq 6$), linear relations between the reciprocal number ($1/n$) of C atoms and the accordion frequency in the solid state have been reported by Okabayashi et al. [12]. Recently, for monoalkyl and dialkyl phosphate ions such a linear relation was also found [13]. The accordion frequencies may be observed even in aqueous and liquid crystalline forms, and are useful for studying molecular conformations in aqueous solutions. Especially, for simple surfactants having butyl, pentyl and hexyl chains, the accordion frequency can be easily observed above 230 cm^{-1}, and its intensity relative to gauche bands gives a direct evidence of conformational changes. For a series of sodium alkylsulfonates, the accordion frequencies in aqueous solution and crystal are listed in Table 1. A linear relation between the accordion frequency of the crystal and $1/n$ is also obtained.

For SBSu in aqueous solution, the intensity of the accordion band at 310 cm^{-1} was found to increase with increasing concentration, but that of the gauche band at 374 cm^{-1} decreases. At the concentration of 3.80 mol/l, the relative peak height of the two Raman lines, I_{310}/I_{374}, is about 3.2, but at 1.88 mol/l it is 2.7. This observation in the low frequency region shows that the all trans form of the alkyl group is preferentially stabilized on micellization.

Skeletal Optical Vibrational Region: The Raman spectra of SBS, SHS, SBSu and SHSu in the 1150–1000 cm^{-1} region also reflect the conformational change on micellization. The peak height ratio, I_{1080}/I_{1125}, can be used as a measure of the conformational change of the hydrocarbon chain [3–5].

For SBS and SHS in aqueous solution, no Raman line corresponding to gauche isomers (1080 cm^{-1}) is observed, owing to the very strong 1063 cm^{-1} line assigned to the SO_3^- symmetric stretching vibration [12]. The 1022 cm^{-1} line of SBS and the 987 cm^{-1} line of SHS are assigned to the gauche isomers of the alkyl chains. The I_{1022}/I_{1125} value of SBS decreases above 2.5 mol/l, which was identified with the critical micelle concentration (CMC). For SHS, the I_{987}/I_{1125} value also decreases with increasing concentration above the CMC (1.0 mol/l). The relative intensity changes also imply that the all trans form is stabilized upon micellization.

For the SBSu and SHSu and aqueous solutions, the 1076 cm^{-1} line of SBSu and the 1075 cm^{-1} of SHSu are observed and correspond to the 1080 cm^{-1} line of the gauche isomers of the long hydrocarbon chains. The relative Raman intensities, I_{1076}/I_{1106} for SBSu and I_{1075}/I_{1117} for SHSu, decrease with the micelle formation.

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