The Raman Spectra and Molecular Conformations of Surfactants in Aqueous Solution and Crystalline States

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The Raman spectra were measured for sodium alkyl sulfates and potassium aliphatic carboxylates in the solid state and aqueous solutions. Vibrational assignments of Raman lines were made, and characteristic Raman lines of the alkyl sulfate ion were identified. The ethyl sulfate ion in the aqueous solution was found to exist predominantly as the *trans* form about the CH_2–O bond. For higher alkyl sulfate ions in aqueous solutions, Raman lines due to rotational isomers with *gauche* CH_2–CH_2 bonds were observed. Longitudinal accordion frequencies of the solid state and aqueous solutions were compared in order to discuss the conformations of hydrocarbon chains in solution.

The physicochemical properties of aqueous solutions of surfactants have been extensively studied. For more detailed investigations of surfactants, conformation studies of surfactant molecules in aqueous solutions are highly desirable. Laser Raman spectroscopy is useful for conformation studies of molecules, especially in aqueous solutions. However, the Raman spectra of surfactants in aqueous solutions have not been reported on.

In the Raman spectra of long-chain *n*-paraffins in the crystalline state, very strong Raman lines due to "accordion" vibrations have been observed; the frequencies of these accordion vibrations have been found to be inversely proportional to the number of carbon atoms.[1,2] Accordion vibrations of *n*-paraffins have also been observed in solution, and molecular conformations in solution have been discussed.[1,3,4]

In the present study, the Raman spectra of a homologous series of sodium alkyl sulfates and of potassium aliphatic carboxylates were measured. The characteristic Raman lines of alkyl sulfate groups were identified. Raman lines due to accordion vibrations were observed in order to study molecular conformations in aqueous solutions.

Experimental

The samples of sodium methyl sulfate (SMS), sodium dodecyl sulfate (SDS), and potassium aliphatic carboxylates ($C_{n-1}H_{2n-1}CO_2K$, $n=3$, 4, 6, 8, 10, and 12) were obtained from the Tokyo Kasei Co. and were purified by recrystallization. However, the samples of sodium ethyl sulfate (SES), sodium *n*-propyl sulfate (SPS), sodium *n*-butyl sulfate (SBS), sodium *n*-hexyl sulfate (SHS), sodium *n*-octyl sulfate (SOS), and sodium *n*-decyl sulfate (SDeS) were prepared from sulfuric acid, *n*-alkyl alcohol, and sodium hydroxide.[5]

The Raman spectra of sodium alkyl sulfates and potassium aliphatic carboxylates in the crystalline state and in an aqueous solution at room temperature were measured with a JEOL Raman spectrometer (JRS-O2AS, argon ion laser, 488.0 nm). The sodium alkyl sulfates were dissolved (30—50 wt%) in water, but the potassium aliphatic carboxylates were dissolved (30—50 wt%) in a 0.1 M KOH solution.

Results and Discussion

The Raman spectra of SDS, SDeS, SOS, SHS, SBS, and SPS in aqueous solutions are shown in Fig. 1. In the Raman spectra of surfactants (SDS, SDeS, and SOS), common Raman lines are observed at 890

Table 1. Raman frequencies (cm^{-1}), relative intensities,[a] and vibrational assignments of PMS (potassium methyl sulfate), SMS and SES in the solid state and aqueous solution and of the series from SPS to SDS in aqueous solution

PMS[b] soln	SMS soln	SMS solid	SES soln	SES solid	SPS–SDS soln	Assignments
273 w	272 w	271 w		263 w		C–O–S deform.
			345 s	350 m		C–C–O deform.
413 m 438 m	415 m 435 m	411 m 444 m	421 m	423 m	417—420 m	$-SO_3$ rock.
559 m	561 m	566 m	574 m	578 m	580—584 m	$-SO_3$ sym. deform.
615 m	591 w 617 m	593 w 614 m	622 w	590 w 623 w	619—625 w	$-SO_3$ asym. deform.
781 s	785 s	763 s 799 m	795 s	793 s 816 s	822—839 s	RO–SO_3 stretch.
			913 w	933 w		CH_3–CH_2 stretch.
1006 s	1004 s	1016 m				CH_3–O stretch.
			1013 s	1010 w		CH_2–O stretch.
1063 vs	1063 vs	1081 vs	1063 vs	1079 vs	1062—1065 vs	$-SO_3$ sym. stretch.

a) vs: very strong, s: strong, m: medium, w: weak. b) Ref. 7.

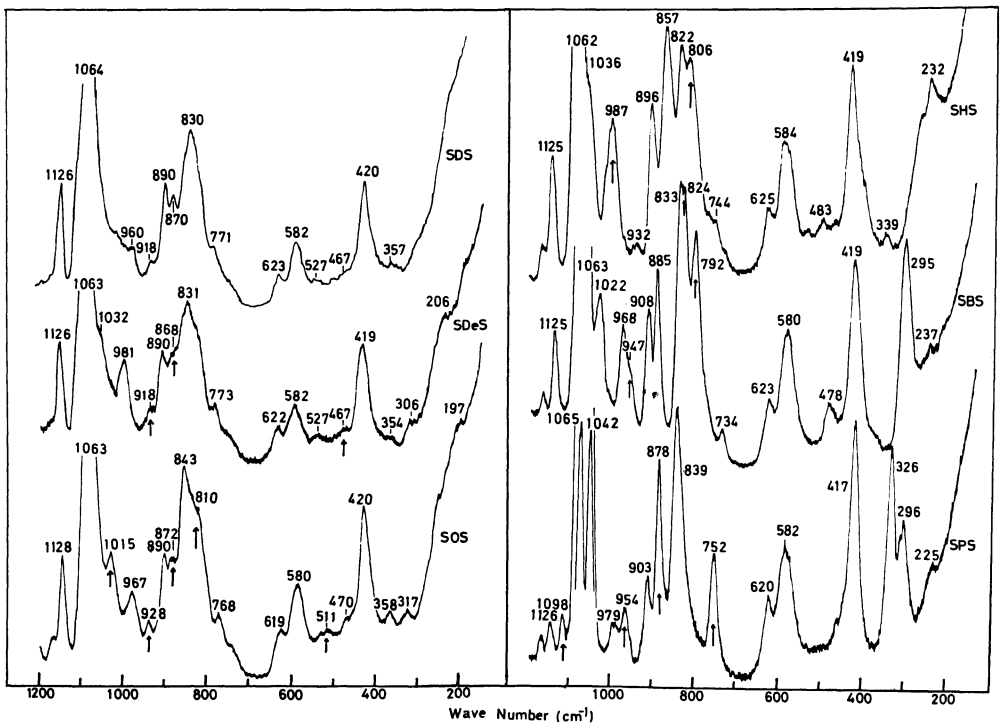

Fig. 1. Raman spectra of SDS (30 wt %), SDeS (35 wt %), SOS (40 wt %), SHS (45 wt %), SBS (50 wt %), and SPS (50 wt %) in aqueous solution at room temperature. Excited with an argon ion laser (488.0 nm). Raman lines marked with arrows are not observed in the crystalline state.

and 1131 cm^{-1}; these lines correspond to the Raman lines of long-chain *n*-paraffins[1] at about 900 and 1135 cm^{-1} and are thus assigned to the terminal-methyl rocking vibration and C–C stretching vibrations[6] respectively. For the series from SPS to SDS, common Raman lines are also observed at 417—420, 580—584, 619—625, 822—839, and 1062—1065 cm^{-1} (see Fig. 1 and Table 1). The assignment of these Raman lines was made with reference to the Raman spectra of PMS (potassium methyl sulfate)[7] and SMS.

Sodium Methyl Sulfate. The Raman frequencies of SMS in an aqueous solution are listed in Table 1, together with the Raman frequencies (and vibrational assignments) of PMS[7] in an aqueous solution. The band of PMS at 615 cm^{-1} was resolved into two components (591 and 617 cm^{-1}) in the Raman spectra of SMS. In other respects, the Raman lines of SMS closely correspond to the Raman lines of PMS; accordingly, the vibrational assignments of SMS were made following those of PMS.[7] The Raman lines due to the rocking (or asym. deform.) modes are split into two components, since there are two modes, symmetric or antisymmetric, with respect to the CH_3–O–S plane. There are two strong Raman lines at 1063 and 1004 cm^{-1}. However, the line at 1063 cm^{-1} is characteristic of alkyl sulfates; accordingly, the line at 1004 cm^{-1} is assigned to the stretching vibration of the CH_3–O bond. The weak broad line at 272 cm^{-1} can reasonably be assigned to the C–O–S deformation vibration.

The Raman line of solid SMS at about 781 cm^{-1} is split into two components. In other respects, the Raman lines of SMS in an aqueous solution closely correspond to the Raman lines in the solid state, indicating that the molecular structures of SMS in solution and in the solid state are similar.

Sodium Ethyl Sulfate. The crystal structure of SES was analyzed by the X-ray diffraction method. The ethyl sulfate ion (CH_3–CH_2–O–SO_3^-) was found to take the *trans* form in the crystalline state.[8] In solution, the *gauche* form may well be expected to appear. However, the steric repulsion between the terminal CH_3 group and oxygen atoms of the $-SO_3^-$ group possibly makes the *gauche* form much less stable than the *trans* form. In fact, the Raman spectra of the aqueous solution and the solid were found to be much the same except for the splitting of the Raman lines at about 810 and 610 cm^{-1} in the solid state, and no new lines appeared when the solid was dissolved in water. Accordingly, the ethyl sulfate ion in an aqueous solution may be concluded to exist primarily in the *trans* form.

The Raman spectra of SES were compared with those of SMS (Table 1) for vibrational assignments. The Raman lines of SES at 913 and 345 cm^{-1} were readily assigned to the CH_3–CH_2 stretching and C–C–O deformation vibrations respectively.

Sodium Propyl Sulfate. The Raman lines of SPS at 903 and 1042 cm^{-1} (Fig. 1) correspond to the infrared bands of propane at 899 and 1049 cm^{-1}, and are assigned to the methyl rocking and C–C stretching vibrations[9] respectively. The three lines of the aqueous solution at 752, 878, and 954 cm^{-1} are not observed in the solid state and are assigned to the *gauche* form about the CH_2–CH_2 bond.

Sodium Butyl Sulfate. The Raman lines of SBS

Table 2. Accordion frequencies (cm^{-1}) of sodium alkyl sulfates (SAS), potassium aliphatic carboxylates (PAC) in the solid state and aqueous solutions and of *n*-paraffins

Number of carbon atoms	SAS		PAC		*n*-Paraffin[a)]	
	soln	solid	soln	solid	liquid	solid
3	326	340	496	496		
4	295	315	349	353	429	425
6	232	236	327	325	370	373
8	197	196	254	248	279	283
10	206	169	243	208	250	231
12			222	181	239	194

a) Ref. 1.

at 792 and 947 cm^{-1} disappear in the solid state. These lines closely correspond to those of the *gauche* isomer of *n*-butane at 788 and 956 cm^{-1}, and are assigned to the methylene rocking and C–C stretching vibrations[9] respectively.

Sodium Alkyl Sulfate. The Raman lines of SHS at 806 and 987 cm^{-1} disappear in the solid state; accordingly, they must be due to rotational isomers having *gauche* CH_2–CH_2 bonds. The Raman intensities of these lines relative to other lines were found to be concentration-dependent. This observation allows some detailed studies of the molecular conformations of surfactant molecules in solution (to be reported separately).

For SOS and SDeS, the Raman lines shown with arrows in Fig. 1 disappear in the solid state and are due to rotational isomers other than the all-*trans* form.

Accordion Vibrations. The accordion frequencies of sodium alkyl sulfates and potassium aliphatic carboxylates are listed in Table 2, together with those of *n*-paraffins. For the example of $n=6$, the accordion frequencies become lower in the order of: $CH_3(CH_2)_4$–$CH_3 > CH_3(CH_2)_4$–$CO_2^- > CH_3(CH_2)_4$–CH_2–OSO_3^-. These frequency differences are possibly due to the greater mass of the terminal groups of aliphatic carboxylates and alkyl sulfate ions.

For the accordion vibrations of sodium alkyl sulfate ($n \geq 4$) and potassium aliphatic carboxylate ($n \geq 6$), there are linear relations, as is shown in Fig. 2, between the reciprocal number ($1/n$) of carbon atoms and the accordion frequencies in the solid state. However,

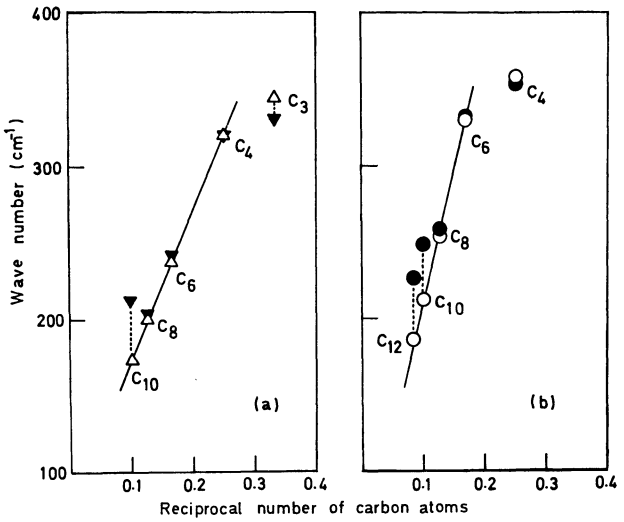

Fig. 2. Number of carbon atoms and accordion frequencies of (a) sodium *n*-alkyl sulfates (R–O–SO_3Na) and (b) potassium aliphatic carboxylates in the crystalline state (open mark) and aqueous solution (full mark).

for $n>8$, the accordion frequencies in an aqueous solution are apparently higher than those in the solid state. Similar observations were previously made of *n*-paraffins in the liquid and solid states.[3,4] Observations of these higher-frequency accordion vibrations indicate that the randomness of *n*-alkyl hydrocarbon chains is increased with the number of carbon atoms.

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