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The Raman Spectra of Surfactants and The Concentration Dependence of Their Molecular Conformations in Aqueous Solutions[1)]

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The laser Raman scattering by potassium *n*-alkyl carboxylates and sodium *n*-alkyl sulfates was measured in the solid state and aqueous solutions, and the concentration dependence of molecular conformations of these molecules was studied. For aqueous solutions of potassium *n*-hexanoate and potassium *n*-pentanoate, the Raman intensities of the accordion vibrations of the all-*trans* form relative to the skeletal deformation vibrations of the *gauche* isomers were found to increase with an increase in the concentration. This intensity change is remarkable at the critical micelle concentration. A concentration dependence of the intensity of the Raman lines was also observed in the frequency region of 1600—600 cm^{-1}. These observations revealed that the percentage of the all-*trans* form of the surfactant molecules increases with an increase in the concentration above the critical micelle concentration.

The infrared absorption spectra of straight-chain fatty acids and their salts have been extensively studied by many investigators,[2-15)] and the vibrational assignment of the infrared absorption bands has been almost completely established. However, very few Raman studies of these compounds have been reported.

In our preceding paper[16)] on the Raman spectra of a homologous series of sodium *n*-alkyl sulfates and of potassium *n*-alkyl carboxylates, the sulfate ions were found to take the *trans* form about the CH_2–O bond in an aqueous solution. Moreover, it was concluded that the conformational randomness of the *n*-alkyl hydrocarbon skeleton of these surfactant molecules increases with the number of carbon atoms.

In the present study, the concentration dependence of the relative Raman intensities was investigated for aqueous solutions of potassium *n*-alkyl carboxylates and sodium *n*-alkyl sulfates, and the conformation change in the surfactant molecules accompanying the formation of micelles was discussed.

Experimental

The samples of potassium *n*-butanoate (Pn-B), potassium *n*-pentanoate (Pn-P), potassium *n*-hexanoate (Pn-H), and potassium *n*-octanoate (Pn-O) were prepared from the corresponding aliphatic acids and potassium hydroxide, and were purified by recrystallization. The samples of sodium *n*-butyl sulfate (SBS), and sodium *n*-hexyl sulfate (SHS) were prepared from sulfuric acid, *n*-alkyl alcohol, and sodium hydroxide. The purity was checked by elementary analysis. Found for SBS: C, 26.94; H, 5.20%. Calcd for $C_4H_9O_4SNa$: C, 27.27; H, 5.15%. Found for SHS: C, 35.27; H, 6.70%. Calcd for $C_6H_{13}O_4SNa$: C, 35.11; H, 6.39%.

The measurements of the Raman spectra of these surfactants were carried out at room temperature with the use of a JEOL model-02AS Raman spectrometer and the 488.0 nm line of an Ar^+ gas laser. The temperature dependence of the intensities of the Raman lines was measured by the use of a JRS-S1 Raman spectrometer. The Raman spectra of the surfactants in the solid state were obtained by focusing the laser beam into a cavity of the small disk of samples. For the measurements of aqueous solutions, the potassium *n*-alkyl carboxylates were dissolved in a 0.1 M KOH solution to avoid hydrolysis, but the sodium *n*-alkyl sulfates were simply dissolved in water.

Results and Discussion

The Raman spectra of Pn-B, Pn-P, and Pn-H in aqueous solutions are shown in Fig. 1, while the frequencies observed in the solid state and in aqueous solutions are listed in Table 1. The vibrational assignment of these Raman lines was carried out on the basis of the infrared-absorption spectra of fatty acids and their salts.[13-15)]

A weak peak commonly observed at 1550 cm^{-1} in aqueous solutions corresponds to the infrared-absorption band of an aqueous solution at 1550 cm^{-1} and is assigned to the COO^- anti-symmetric stretching vibration. The two Raman lines of the solid surfactants at 1550 and 1580—1600 cm^{-1} may possibly

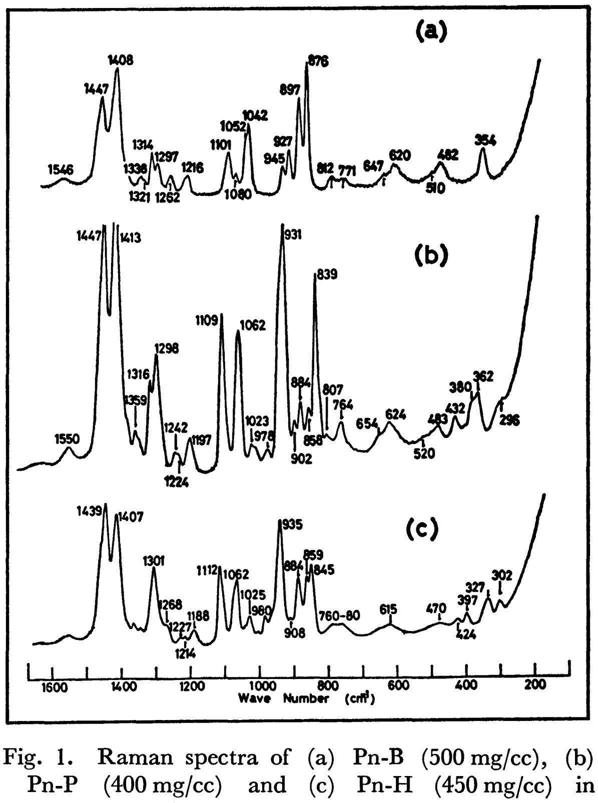

Fig. 1. Raman spectra of (a) Pn-B (500 mg/cc), (b) Pn-P (400 mg/cc) and (c) Pn-H (450 mg/cc) in aqueous solutions.

TABLE 1. RAMAN FREQUENCIES (cm^{-1}) AND RELATIVE INTENSITIES[a)] OF Pn-B, Pn-P, Pn-H, AND Pn-O IN THE SOLID STATE AND AQUEOUS SOLUTIONS

Pn-B		Pn-P		Pn-H		Pn-O	
Solid	Soln	Solid	Soln	Solid	Soln	Solid	Soln
1581 m		1598 w		1582 m		1582 w	
	1546 wb	1550 vwb	1550 wb	1545 vwb	1550 vwb	1545 vw	1551 wb
						1473 sh	
1454 s	1447 s	1464 m	1465 sh	1457 m	1455 sh	1460 vs	1465 vs
		1448 w	1447 s			1445 sh	
1434 sh	1435 sh	1434 vs		1432 s	1439 vs	1435 s	
1420 vs	1408 vs	1406 w	1413 s	1413 s	1407 s	1417 sh	1415 s
1381 vwb	1379 sh	1379 vw	1380 sh	1381 vw	1380 sh	1384 vw	1371 vwb
		1356 vw	1359 w	1363 vwb	1363 vwb	1374 vw	
1345 wb	1338 w	1340 vw	1351 w	1341 vwb	1342 vwb	1345 vwb	1348 vwb
	1321 sh	1319 w			1320 sh		
1310 vwb	1314 m		1316 w				
1288 m	1297 w	1293 s	1298 m	1300 m	1301 m	1288 s	1300 s
				1290 w			
		1275 sh	1275 sh	1262 w	1268 vwb		
1257 w	1262 w					1256 vw	1257 vw
		1236 w	1242 vw			1233 vwb	1240 sh
1224 vwb	1216 w		1224 sh	1222 vwb	1227 vwb		
					1214 vw		
		1204 w	1201 w	1196 vwb		1207 vw	1201 vwb
					1188 wb	1185 vw	1175 w
1108 m	1101 m	1107 s	1109 s	1114 m	1112 m	1120 m	1117 m
						1112 vw	
			1090 sh				
1078 vw	1080 vw			1078 vw	1070 sh		1077 m
		1063 s	1062 m	1060 m	1062 m	1065 m	1064 m
	1052 sh		1058 sh			1050 w	
1040 s	1042 m				1039 sh	1034 w	1036 m
		1024 m	1023 vw	1027 w	1025 w		
			1017 vw				
				1010 vw	1005 vwb	1001 vw	1005 sh
			978 vw	982 sh	980 vw		
				965 vwb	965 sh	963 vwb	960 sh
939 w	945 w		936 sh				
922 vwb	927 m	927 vs	931 s	925 vs	935 s	920 m	926 s
			902 vw		908 vw		
891 vs	897 s	892 m	884 vw	886 w	884 m	896 m	897 m
	876 vs						875 m
858 w			858 vw	861 vw	859 w		
		838 vw	839 m	849 w	845 m	839 vw	844 m
	812 wb	809 vw	807 vwb				
779 vwb	771 vwb			786 vwb	781 vwb	772 vwb	775 wb
			764 w	767 vwb	758 vwb		
		730 vwb	740 sh			731 vw	
698 vwb		692 w		692 wb		695 vwb	
	647 sh		654 sh		650 sh		650 vw
	620 wb		624 wb				622 wb
				610 sh	615 wb		
585 vwb		584 w		587 wb		581 vwb	
		525 w	520 sh				530 sh
503 sh	510 sh						
				495 vw	499 sh		
478 m	482 wb		483 vwb				
				472 vw	470 wb		477 wb
			432 w			442 vw	
				420 w	424 vwb	424 vw	430 sh
					397 w		397 w
			380 sh				
356 m	354 m	355 s	362 m				350 sh
		318 w		325 s	327 m		
							314 vw
			296 sh	296 vw	302 w	293 vwb	
255 vwb		255 vw				248 s	254 sh

a) vs: very strong, s: strong, m: medium, w: weak, wb: weak and broad, vw: very weak, vwb: very weak and broad, sh: shoulder.

be the split components of the COO^- anti-symmetric stretching vibration. A strong Raman line at 1450—1465 cm^{-1} is commonly observed in the solid state and an aqueous solution, and is due to the CH_2 scissoring vibrations. A common Raman line of the surfactant solutions around 1400—1420 cm^{-1} also appears in the solid state; this line corresponds to the infrared-absorption band of the aqueous solutions at 1400 cm^{-1}, and is ascribed to the COO^- symmetric stretching vibration. A Raman line observed at 1380 cm^{-1} in the solid samples and aqueous solutions is due mainly to the terminal-methyl symmetric deformation.

The weak broad Raman line of the solid surfactants at 690—700 cm^{-1} corresponds to the infrared-absorption band at 690—700 cm^{-1}; it is assigned to the COO^- scissoring vibration. This vibrational mode is observed at 650 cm^{-1} in the aqueous solutions, with a considerable shift in the frequencies. A broad Raman line of the aqueous solutions is observed at 615—620 cm^{-1}; in the solid state this Raman line appears at 580—590 cm^{-1}, with a frequency shift, and is attributed to the COO^- wagging vibration. A broad Raman peak is commonly observed at 500—530 cm^{-1} in the solid surfactants and aqueous solutions; it is assigned to the COO^- rocking vibration. These Raman lines do not depend very much upon the chain length. However, there are several Raman lines which are characteristic of each molecule; they are related to the molecular conformations.

In the lower frequency region of the Raman spectrum of each solid sample a strong Raman line is observed, and its frequency is inversely proportional to the number of carbon atoms when it is greater than five. This relationship has been found for the accordion-like skeletal deformation frequencies of *n*-paraffins.[17,18] Accordingly, this line must be ascribed to an accordion vibration of the surfactant molecule. Moreover, in the aqueous solution of each sample there is a medium Raman line which closely corresponds to the accordion vibration observed in the solid state; its frequency is also proportional to the reciprocal number of the carbon atoms. This Raman line should be assigned to the accordion-like vibration due to the extended molecular form in the aqueous solution. This observation is also compatible with the fact that the extended molecular form is abundant in the liquid state for low homologous *n*-paraffins.[17,18])

Potassium n-*Butanoate.* The Raman lines of Pn-B at 812, 876, 1052, and 1321 cm^{-1} are not observed in the solid state; accordingly, these lines are ascribed to the rotational isomer about the CH_2–CH_2 bond. Two Raman lines are observed at 1080 and 1290—1300 cm^{-1} in the solid state and in an aqueous solution. They are not identified in the infrared-absorption spectra of Pn-B.[15] The two Raman lines of the solid Pn-B at 478 and 356 cm^{-1} are also observed at 482 and 354 cm^{-1} in an aqueous solution. These lines correspond closely to the infrared-absorption bands of *n*-butyric acid at 487 and 364 cm^{-1}, which have been assigned to the CCO deformation vibration and the CCC deformation vibration[14] respectively.

Potassium n-*Pentanoate.* The weak Raman lines of the Pn-P solution at 764, 858, 936, 978, 1017, and 1224 cm^{-1} are not found in the spectrum of the solid surfactant; accordingly, they are attributed to the *gauche* isomers about the CH_2–CH_2 bonds. Four Raman lines at 839, 884, 1023, and 1275 cm^{-1} are found for both the solid Pn-P and an aqueous solution, but they are not observed in the infrared-absorption spectra.[15] The accordion vibration of Pn-P is identified at 355 cm^{-1} in the solid state and at 362 cm^{-1} in an aqueous solution. Three Raman peaks of the aqueous solution at 380, 432, and 483 cm^{-1} are not found in the spectrum of the solid state; they are thus ascribed to the skeletal deformation vibrations of the *gauche* isomers.

Potassium n-*Hexanoate.* Three Raman lines of the aqueous solution at 908, 1039, and 1214 cm^{-1} disappear in the solid state and are, therefore, attributed to the *gauche* isomers. The Raman lines of Pn-H are observed at 780—785, 860, 1025—1030, 1070—1080, and 1260—1270 cm^{-1} in both the solid state and an aqueous solution, but none of these lines is observed in the infrared-absorption spectra of Pn-H.[15] The accordion vibration of Pn-H is observed at 325 cm^{-1} in the solid state and at 327 cm^{-1} in an aqueous solution. Since only the Raman peak of the aqueous solution at 397 cm^{-1} disappears in the solid state, it must be assigned to the skeletal deformation vibrations of the *gauche* isomers.

Potassium n-*Octanoate.* The three Raman lines of the aqueous solution at 850, 875, and 1077 cm^{-1} disappear in the solid Pn-O; accordingly, they can serve as indicators of the *gauche* isomers. Three Raman lines of Pn-O are also observed at 960, 1000, and 1120 cm^{-1} in the solid state and in aqueous solution, but these lines do not appear in the infrared-absorption spectra.[16] The accordion vibration of Pn-O gives rise to the Raman lines at 248 cm^{-1} in the solid state and at 250 cm^{-1} in an aqueous solution. The two Raman lines at 430 and 450 cm^{-1} are due to the coupled vibrational modes of the skeletal deformation vibrations and the CCO deformation vibration of the *trans* isomer. The three Raman lines of the aqueous solution at 314, 350, and 397 cm^{-1} are not observed in the solid state; accordingly, they are attributed to the skeletal deformation vibrations of the *gauche* isomers.

Temperature Dependence of Raman Spectra of Aqueous Solutions. Figures 2(a) and (b) show the Raman spectra of Pn-H and Pn-P, respectively, in the aqueous solutions at two different temperatures. The Raman intensity of the accordion vibration of the all-*trans* form seems to decrease as the temperature is raised. In the case of Pn-H, the Raman intensities of the peak at 327 cm^{-1} relative to the peaks at 397, 424, and 470 cm^{-1} are lower at 96 °C, while for Pn-P the intensities of the peak at 362 cm^{-1} relative to other peaks are lower at 96 °C than at 20 °C.

Concentration Dependence of the Relative Raman Intensities of Potassium Aliphatic Carboxylates. Figures 3(a) and (b) show the change in the intensities of Raman lines with the concentration of Pn-H and Pn-P in the skeletal deformation vibration region. The intensities of the Raman lines were found to be con-

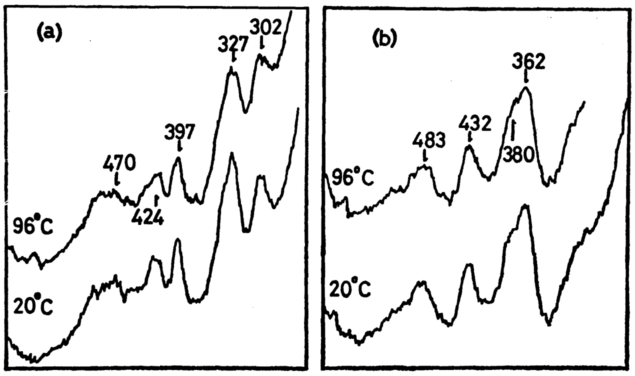

Fig. 2. Temperature dependence of the Raman spectra of (a) Pn-H (450 mg/cc) and (b) Pn-P (400 mg/cc) in aqueous solutions.

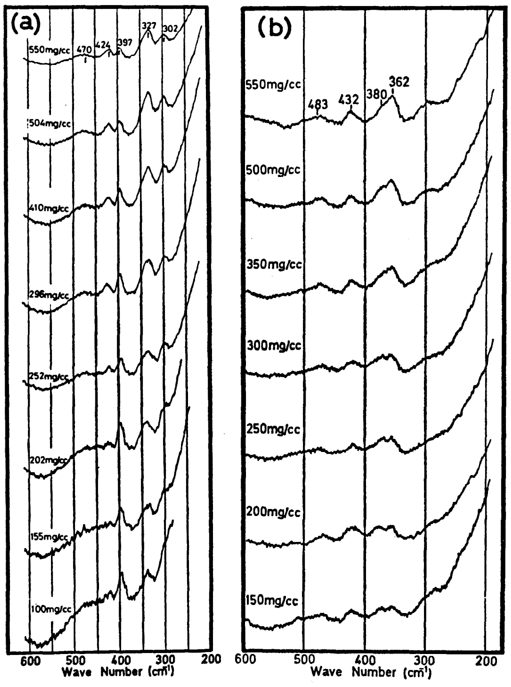

Fig. 3. Raman spectra of (a) Pn-H and (b) Pn-P in aqueous solutions at various concentrations.

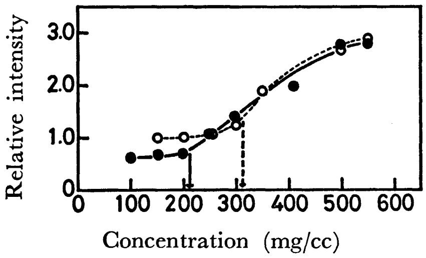

Fig. 4. Concentration dependence of the peak height ratio (I_{327}/I_{397}) of the Pn-H solution (solid line) and that (I_{362}/I_{432}) of the Pn-P solution (broken line). Weak background due to the water spectrum was substracted from the surfactant spectrum using the Raman scattering of distilled water as the base line. Solid and broken arrows indicate the critical micelle concentrations of Pn-H and Pn-P, respectively.

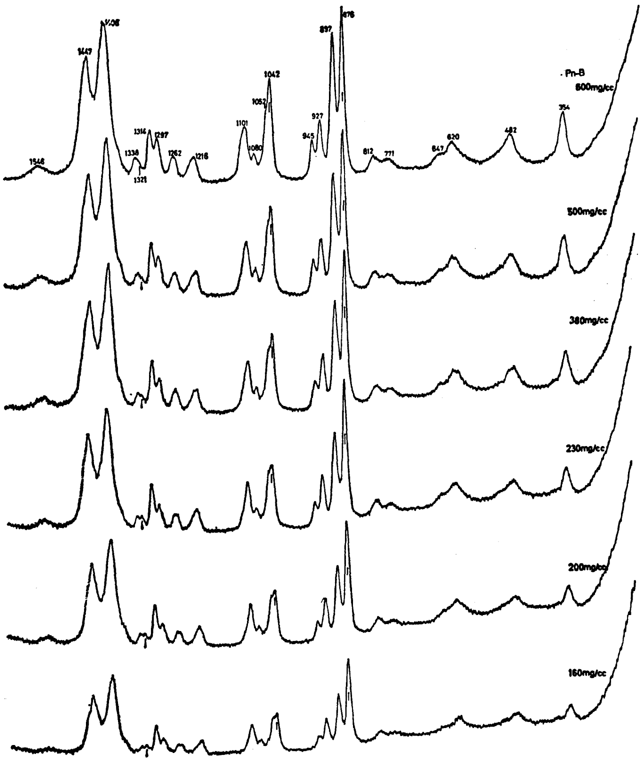

Fig. 5. Raman spectra of Pn-B in aqueous solution at various concentrations.

siderably influenced by the concentration. The relative Raman intensity of the accordion vibration of Pn-H at 327 cm^{-1} increases with an increase in the concentration, while the relative intensity of the peak at 397 cm^{-1} due to the *gauche* isomer decreases. The peak-height ratio of the two Raman lines, I_{327}/I_{397}, is plotted against the concentration in Fig. 4. It is almost constant below ca. 200 mg/cc, but gradually increases with the concentration above this point. Since this intensity change occurs around the critical micelle concentration (CMC), (210 mg/cc),[18] the spectral change is considered to be caused by the formation of micelles.

In the case of Pn-P, the intensity of the accordion vibration at 362 cm^{-1} increases with an increase in the concentration. In Fig. 4, the peak heights of the accordion vibration relative to the skeletal deformation vibration of the *gauche* isomer, I_{362}/I_{432}, are plotted against the concentration. The ratio is unchanged below the CMC (310 mg/cc),[19] but it increases gradually above this concentration. Thus, for Pn-P as well as for Pn-H, the all-*trans* form of the skeletal backbone seems to be more stable in the micelles than in the mono-molecular dispersion state.

For the aqueous solution of Pn-B, the concentration dependence of the relative intensities of the Raman lines was observed in the frequency region of 600—1600 cm^{-1} rather than in the region of 200—600 cm^{-1}. As is shown in Fig. 5, the relative intensities of the Raman lines at 897, 1042, and 1297 cm^{-1} increase with an increase in the concentration, but that of the peak at 1321 cm^{-1} decreases. Since the former three lines exist in the Raman spectrum of the solid

Pn-B, they are ascribed to the all-*trans* form, whereas the latter Raman line disappears in the solid state and is assigned to the *gauche* isomers. In Fig. 6(a), the peak heights of the Raman lines at 897 and 1042 cm^{-1} relative to the peak at 1101 cm^{-1} are plotted against the concentration of Pn-B. In the concentration region below the CMC (440 mg/cc),[18] both I_{897}/I_{1101} and I_{1042}/I_{1101} are constant and then increase above the CMC. On the contrary, the ratio of I_{1321}/I_{1338} decreases slightly above the CMC.

The concentration dependence of the Raman lines of Pn-P and Pn-H was found in the frequency region of 600—1600 cm^{-1} as well as in the low-frequency region. As is shown in Fig. 6(b), the peak heights of the Raman lines of Pn-P at 931, 1109, 1298, and 1447 cm^{-1} relative to the peak at 1062 cm^{-1} increase with an increase in the concentration above the CMC (310 mg/cc).[19] These lines correspond to the Raman lines of the solid Pn-P at 927, 1107, 1293, and 1448 cm^{-1}; therefore, they are attributed to the all-*trans* form. The intensity of the peak at 1224 cm^{-1} relative to that of 1242 cm^{-1} also decreases with an increase in the concentration above the CMC.

A similar variation was also observed for some of the Raman lines of Pn-H. As is shown in Fig. 6(c), the relative peak height of I_{935}/I_{1062} increases with an increase in the concentration above the CMC (210 mg/cc),[18] but that of I_{1214}/I_{1227} decreases. Since the Raman line of the aqueous solution at 935 cm^{-1} corresponds to the very strong line of the solid Pn-H at 925 cm^{-1}, this line must be due to the all-*trans* form.

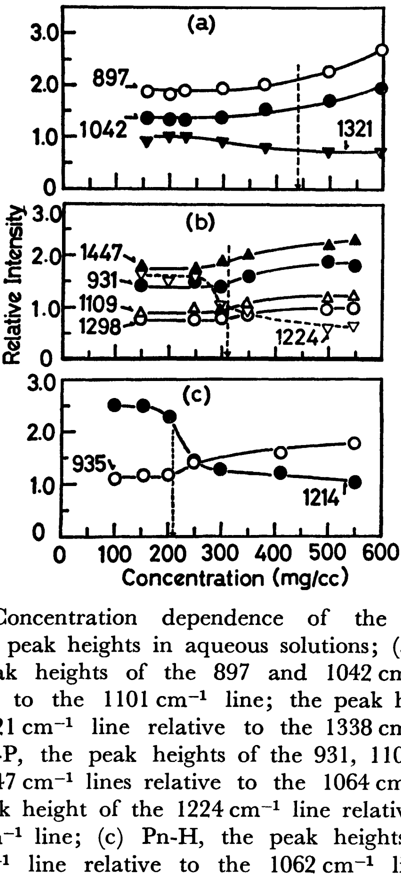

Fig. 6. Concentration dependence of the relative Raman peak heights in aqueous solutions; (a) Pn-B, the peak heights of the 897 and 1042 cm^{-1} lines relative to the 1101 cm^{-1} line; the peak height of the 1321 cm^{-1} line relative to the 1338 cm^{-1} line; (b) Pn-P, the peak heights of the 931, 1109, 1298, and 1447 cm^{-1} lines relative to the 1064 cm^{-1} line; the peak height of the 1224 cm^{-1} line relative to the 1242 cm^{-1} line; (c) Pn-H, the peak heights of the 935 cm^{-1} line relative to the 1062 cm^{-1} line; the peak height of the 1214 cm^{-1} line relative to the 1227 cm^{-1} line.
The baseline was simply drawn from the basin at *ca.* 1500 cm^{-1} to that at *ca.* 700 cm^{-1} in each spectrum.

For the aqueous solution of Pn-O, the relative peak height of I_{844}/I_{897} is almost constant below *ca.* 70 mg/cc, but this ratio decreases with the concentration over this point. On the contrary, the relative intensity of I_{1064}/I_{897} increases in the concentration region above *ca.* 70 mg/cc. Since the Raman line of the Pn-O solution is observed in the solid state, it must be attributed to the all-*trans* form. The concentration of 70 mg/cc is not exactly the CMC, but it is very close to the reported value of the CMC (70—110 mg/cc).[18]

For the surfactant molecules with longer chains, the CMC becomes lower; accordingly, the observation of the precise Raman intensity around the CMC is more difficult. However, it is evident that the formation of micelles causes the intensity change of the Raman spectra and that this spectral change is associated with the conformational changes in the *n*-alkyl hydrocarbon chains.

Concentration Dependence of the Raman Intensities of Sodium n-*Butyl Sulfate and Sodium* n-*Hexyl Sulfate.* In our previous study,[16] the Raman lines of SBS in an aqueous solution at 792 and 947 cm^{-1} were assigned to the CH_2 rocking vibration and the C–C stretching vibration of the *gauche* isomers respectively. The relative peak heights of these Raman lines were also found in the present study to decrease with an increase in the concentration. Similar behavior was observed for the Raman line of the *gauche* isomers at 824 cm^{-1}.

For the aqueous solution of SHS, the two Raman lines of the *gauche* isomers at 806 and 987 cm^{-1} show the concentration dependence of the Raman intensities. The relative peak heights of I_{806}/I_{896} and I_{987}/I_{896} decrease with an increase in the concentration, whereas the ratio of I_{1125}/I_{896} increases. These intensity changes also occur around the CMC (140 mg/cc).[19] The concentration dependence of the relative Raman intensities of sodium *n*-alkyl sulfates are also probably due to the conformation changes in the *n*-alkyl chains.

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