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On the Conformational State of Surfactants in the Solid State and in Micellar Form. A Laser-Excited Raman Scattering Study

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The Raman spectra of a series of cationic, anionic, and nonionic surfactants have been examined as pure solids or liquids, and in aqueous micellar solutions. The spectra show that cationic surfactants such as hexadecyltrimethylammonium bromide (CTAB), dodecylammonium chloride (DAC), and decyltrimethylammonium bromide (DeTAB), along with anionic surfactants such as sodium laurate (NaL) and sodium lauryl sulfate (NaLS) exist in all-trans structures in the crystalline state. Aqueous micellar solution of these surfactants show additional Raman lines which correspond to a liquidlike nature of the micellar core. Raman spectral studies indicate that the ethylene oxide chains in nonionic surfactant such as Igepal CO-880 and Brij 35 assume dihedral helical structures. Nonionic liquid surfactants with shorter ethylene oxide chains such as Triton X-100 and Igepal CO-630 have a major part of the ethylene oxide chain in an open coil form. No significant differences are observed in Brij 35 in H₂O. However, micellization of Igepal CO-630 shows spectra which indicate a partial ordering of the ethylene oxide chains. The phase changes associated with the electrolyte-induced sphere-rod transition in micellar systems have also been examined by Raman spectroscopy. These studies show a greater ordering of the hydrocarbon chain in the rod-shaped compared to the sphere-shaped aggregates.

Introduction

A renewed interest has arisen recently in the study of micellar assemblies.²⁻⁴ Several aspects of the structural and dynamical properties of micellar assemblies such as, the parameters which characterize a micelle, nature of the micellar core, charge on the Stern-layer and counterions binding to it, permeability of the micelle with respect to various species, kinetic aspects of the micellar association equilibria, etc., have been investigated. Of immediate interest is information on the micellar core. It is argued⁵ that the interior or core of micelles must be "liquidlike". (This is based on thermodynamic analysis, on observations that micelles can solubilize a wide variety of hydrophobic organic solutes, and on the ability of surfactants to form mixed micelles.) Strong experimental evidence on the liquidlike core comes from studies of fluorescence depolarization of aromatic probes solubilized selectively in the micellar core. The measured microviscosities of the order of 30 cP agree well with similar values obtained in pure (homogeneous) hydrocarbon liquids.⁶ Quite recently the measurement of carbon-13 spin-lattice relaxation times⁷ for various carbon atoms that form the backbone of the hydrocarbon chains show that the fluidity of the micellar core is probably restricted to a few carbon atoms toward the end of the hydrocarbon chain in the micellar core. Further investigations on these aspects of the micelle are necessary at this point, viz., on the conformational state of the hydrocarbon chain in the micelle core and also studies on the influence, if any, of external additives solubilized in the micellar core on the hydrocarbon chain conformation. Laser Raman spectroscopy is an ideal technique for the study of conformations of molecules, especially in aqueous solutions.

In the first part of the paper, Raman spectra of several cationic, anionic, and nonionic surfactants have been examined as pure solids or liquids and also in aqueous solutions. In aqueous media, above a certain critical micelle concentration (cmc), the surfactants aggregate together to form spherical

micelles. Assignment of the various peaks in these spectra leads to (further) direct evidence for the liquidlike nature of the micellar core. In the second part, the influence of external additives on the micellar core is examined. In particular the phase changes associated with the electrolyte-induced sphere-rod transition in micellar systems have been investigated. These studies provide significant information on the conformational state of the hydrocarbon chains in the solid state and how they are affected following micellization.

Experimental Section

The laser-excited Raman spectra reported in this study were recorded on a Spex Ramalog laser-Raman spectrometer system equipped with a Spectra-Physics Model 164 Ar ion laser and a photon counting system. Typically the laser was operated to give about 200 mW power (for pure solid and liquid samples) and about 700 mW power (for aqueous solutions) of the 5145-Å green line on the sample. The samples were contained in 1-mm melting point capillaries and the scattered light was collected at 90° to the incoming laser light and analyzed in a Spex dual-grating monochromator. The spectra were run with approximately 200-μm slit width corresponding to $\approx 4\text{-cm}^{-1}$ band width. Hence the accuracy in the reported frequencies is estimated to be $\pm 2\text{ cm}^{-1}$. None of the spectra reported in this work are polarized. No interference filters were used in this work.

All surfactants used in this study were of purum grade and were recrystallized several times in ethanol-ether mixtures before recording the spectra. No significant differences, however, were observed in the solid spectra of the samples used before and after crystallization. All spectra reported were recorded at room temperature (25 °C). All electrolytes and additive used were also of AR grade.

Results and Discussion

(1) *Laser-Excited Raman Spectra in Pure and Micellar Form.* (a) *Cationic Surfactants in the Solid State.* The

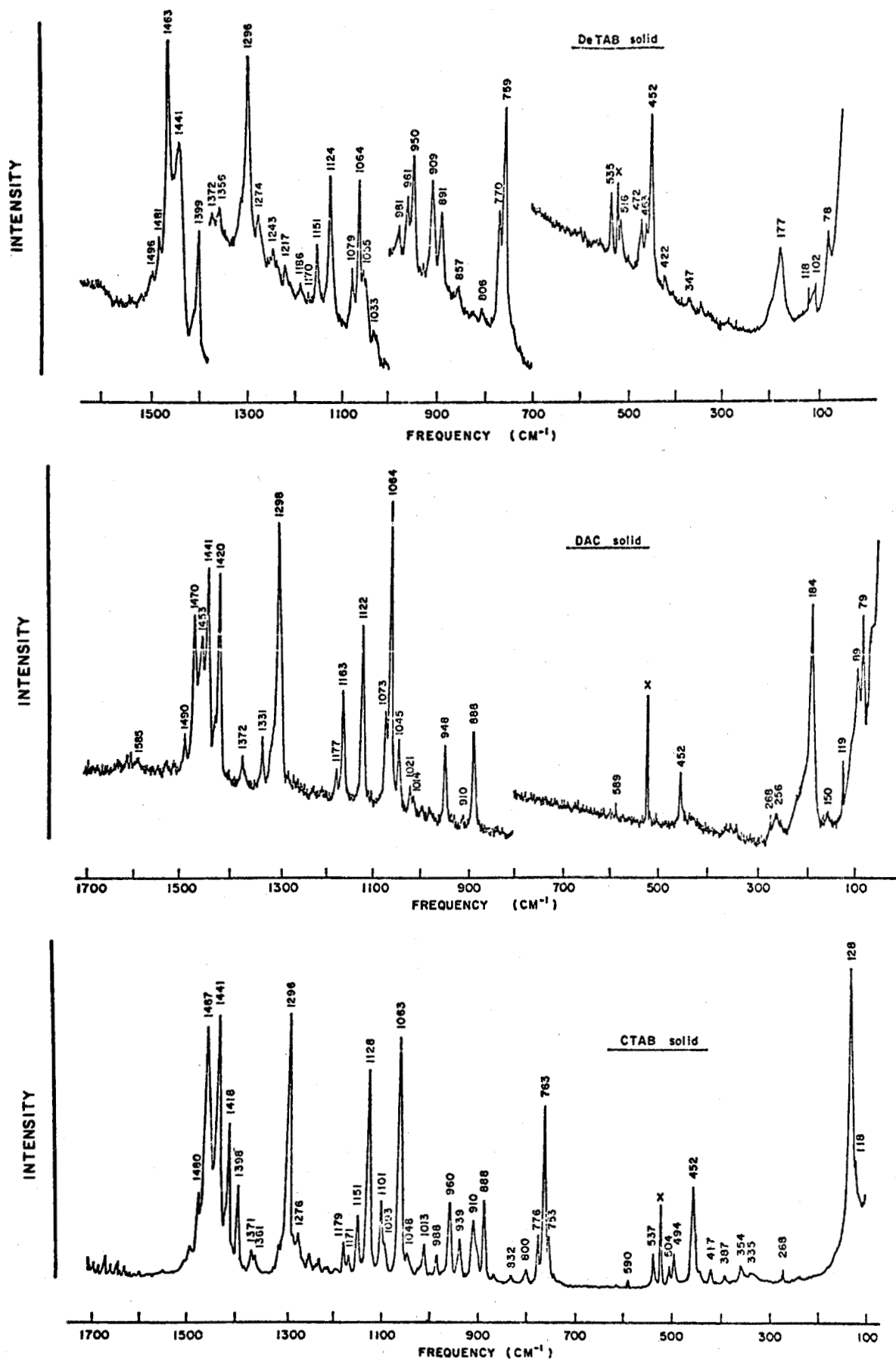


Figure 1. Raman spectra (up to 1700 cm^{-1}) of the crystalline surfactant solids hexadecyltrimethylammonium bromide (CTAB), dodecylammonium chloride (DAC), and decyltrimethylammonium bromide (DeTAB).

TABLE I: Raman Frequencies for the Cationic Surfactant Solids CTAB, DAC, and DeTAB

CTAB	Hexadecane ^a	DAC	Dodecane ^a	DeTAB	Decane ^a	Tentative assignments
128	150	184	194	177	231	Longitudinal accordion modes
		256				
		268				
452		452		452		
				463		
494				472		CH ₃ rock from N ⁺ (CH ₃) ₃ group
504				506		
537				535		
753						
763				759		
776				770		CH ₃ rock (terminal methyl) C-N ⁺ stretch
800				806		
888	888	888	892	891	886	
910		910		909		
939		948		950		
960				961		CH ₂ rock
988				988		
1013		1014		1033		
1048		1045		1055		CH ₂ twist, crystalline C-C sym stretch + CH ₂ wag
1063	1058	1064	1061	1064	1060	
1093		1073		1079		
1101						C-C stretch, crystalline
1128	1135	1122	1136	1124	1136	
1151		1163		1151		
						C-C asym stretch + CH ₂ wag from (TG _m T) with <i>m</i> large CH ₂ rock
1179		1177		1186		
1212					1217	
1229		1224				CH ₂ wag, crystalline
1241		1240		1243		
1276				1274		
1296	1295	1298	1297	1296	1295	CH ₂ twist CH ₂ wag C-CH ₃ sym bending C-H sym bend from N(CH ₃) ₃ group
		1331		1356		
1371		1372		1372		
1398				1399		
1418		1420				-CH ₂ bend -CH ₂ bend -CH ₂ bend, crystalline -CH ₂ bend
1441	1442	1442	1441	1441	1447	
1467	1471	1453	1462	1463	1475	
1480		1470				
2849	2846	2848	2845	2851	2843	
2857		2857		2858		C-H sym stretch of -CH ₂ -
2882	2878	2882	2879	2883	2877	
2889		2888				
2904		2902		2906		C-H asym stretch of -CH ₂ -
2914		2914				
2933	2934	2932	2933	2933	2935	
2944		2950		2943		C-H asym stretch of CH ₃ - C-H sym stretch of CH ₂ -N ⁺ (CH ₃) ₃ group
2972	2963	2973	2964	2965	2964	
2981		2981		2982		

^a Data taken from ref 12.

Raman spectra of the typical cationic surfactants hexadecyltrimethylammonium bromide (CTAB), dodecylammonium chloride (DAC), and decyltrimethylammonium bromide (DeTAB) in the crystalline solid state are shown in Figure 1. The observed Raman frequencies (100–1700-, 2800–3000-cm⁻¹ regions) along with their tentative assignments are summarized in Table I. These assignments are based on a comparative analysis of the spectra of a wide series of surfactants of different chain length and of different head groups and on the basis of the earlier assignments made on the ir and Raman spectra for *n*-paraffin solids and liquids.⁸ For the purpose of comparison we have also included in this table data for solid *n*-hexadecane, dodecane, and *n*-decane.

Chain conformations of solid and liquid long-chain hydrocarbons have been examined already^{8–10} by ir and Raman spectroscopy. Several regions in the Raman spectra are sensitive to conformational changes. The 1000–1200-cm⁻¹ region

corresponds to the skeletal C–C stretching vibration in which the alternate carbon atoms move in the opposite direction. For an extended chain with all-trans structures, there are two intense bands in this region: one at 1064 ± 2 cm⁻¹ and the other around 1130 cm⁻¹. These bands have been assigned to the symmetric or in-phase C–C stretching and the asymmetric C–C stretching, respectively. In addition, there is another additional band at 1075–1100 cm⁻¹ arising from all-trans crystalline structure vibrations. In molten polyethylene and in liquid hydrocarbons a broad intense band centered around 1090 cm⁻¹ is observed in addition to much weaker bands at 1064 and 1130 cm⁻¹. The collapse of the symmetric and antisymmetric C–C stretching into a central spectral maximum implies that an ordered crystalline and extended all-trans chain becomes kinked with the concomitant appearance of a wide distribution of structures which include several gauche rotations. The acoustical mode vibrations due to the presence

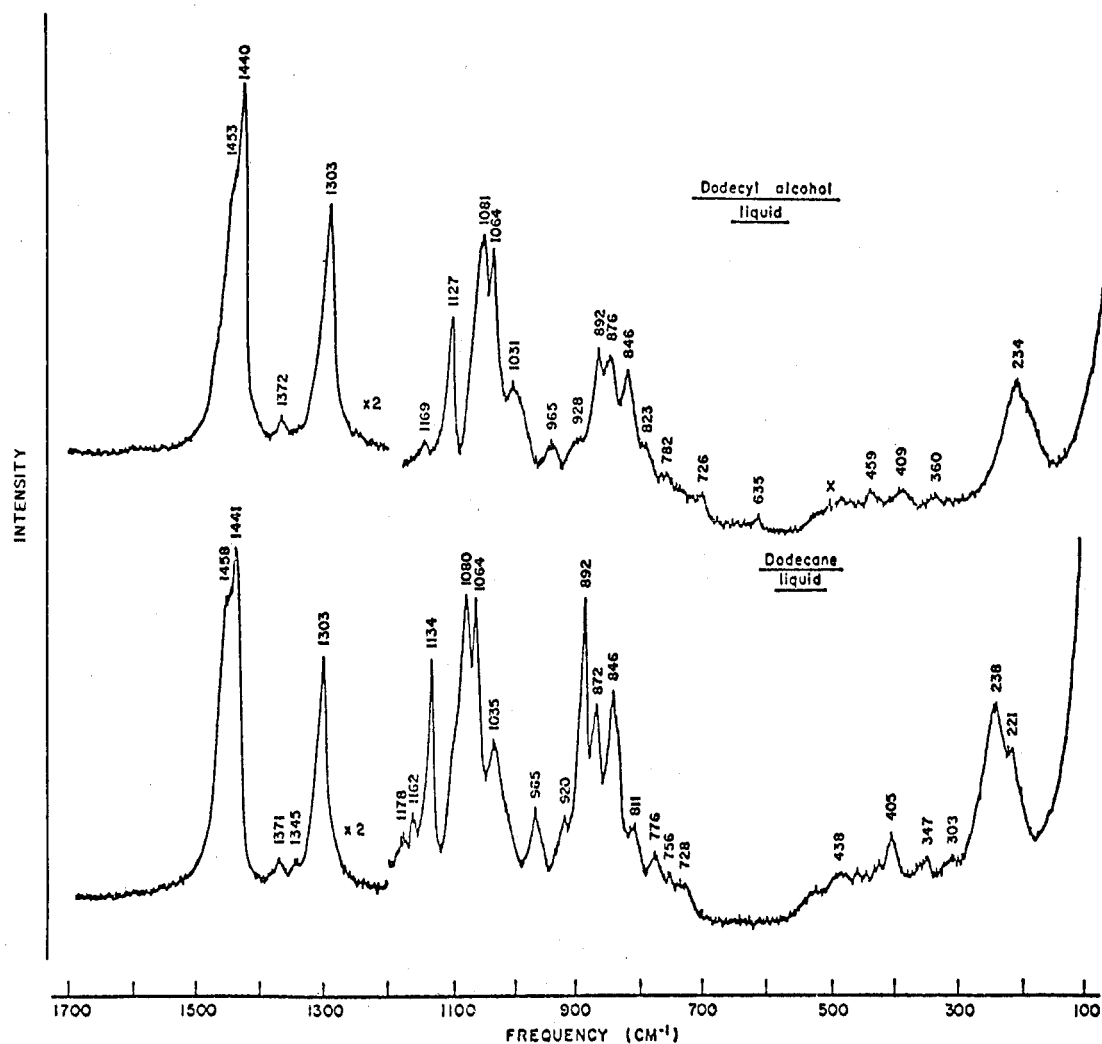


Figure 2. Raman spectra (up to 1700 cm^{-1}) of the hydrocarbon liquids dodecane and dodecyl alcohol.

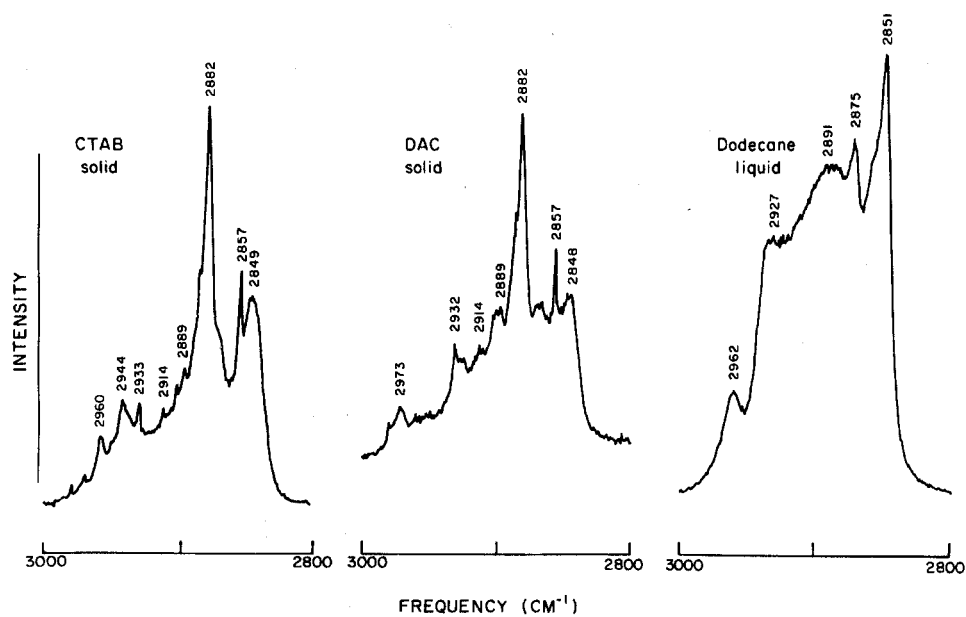


Figure 3. Raman spectra ($2800\text{--}3000\text{ cm}^{-1}$ region) for CTAB solid, DAC solid, and dodecane liquid.

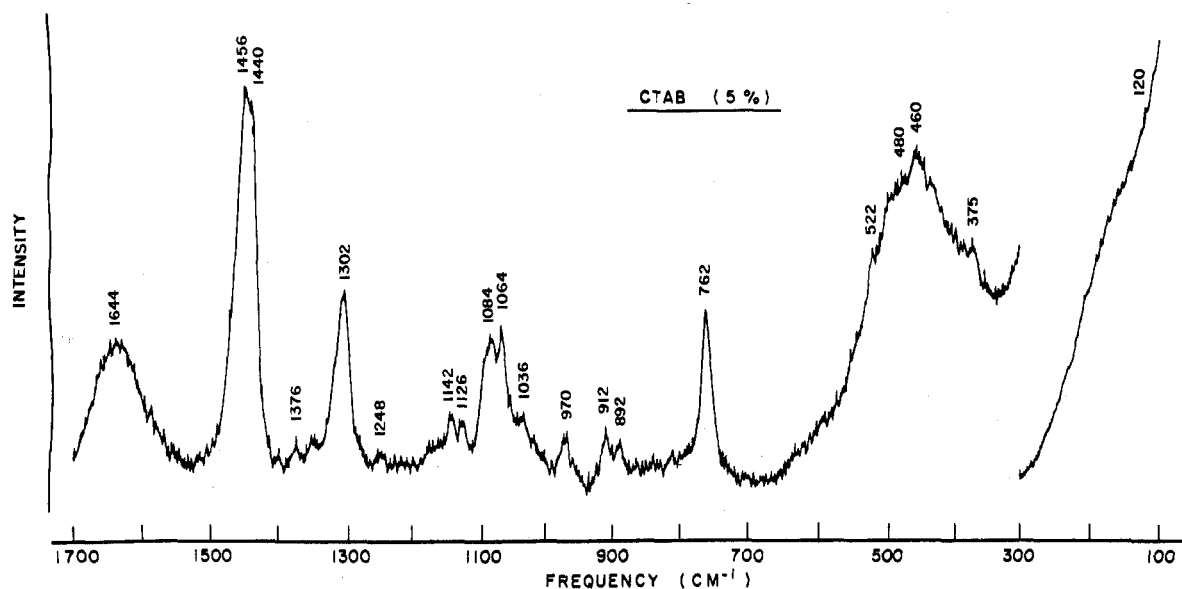


Figure 4. Raman spectrum for a 5% (0.1375 M) micellar solution of CTAB in H_2O .

of random gauche isomers also give rise to a broad band around 230 cm^{-1} (cf. Figure 2). In the C-H stretching region, in the crystalline state the peak around 2880 cm^{-1} due to the symmetric stretch of the CH_3 group is more intense than the symmetric stretch of the CH_2 group at 2850 cm^{-1} . These bands assume equal intensities or even $I_{2880} < I_{2850}$ when several gauche isomers are present.

The Raman spectra of the cationic surfactants CTAB, DAC, and DeTAB, presented in Figure 1, all indicate the existence of an all-trans extended chain structure. All three spectra show intense bands at 1064 and 1124 cm^{-1} (due to C-C symmetric stretching in an all-trans structure), and a weak band around 1100 cm^{-1} . The longitudinal accordion motions of the hydrocarbon chains lead to the peaks at 128 cm^{-1} in CTAB, 184 cm^{-1} in DAC, and 177 cm^{-1} in DeTAB, respectively. The peak at $1296 \pm 2\text{ cm}^{-1}$ and the resolved fine-structure band around 1450 cm^{-1} arise from the methylene twisting and bending modes, respectively. Another salient feature of all three spectra is the occurrence of peaks at constant frequencies of 452 , 888 , and 960 cm^{-1} having their origin in the C-N stretching, CH_3 rocking, and $-\text{CH}_2$ rocking modes, respectively. As the hydrocarbon chain length increases from 10 carbons in DeTAB to 16 in CTAB, the spectrum becomes more and more complex due to the several additional combinatorial vibrational modes of the hydrocarbon chain.

Returning now to Figure 2, which represents the Raman spectra of the pure hydrocarbon liquids dodecane and dodecyl alcohol, one observes two significant differences. As mentioned earlier, the presence of several gauche rotational isomers in these liquids gives rise to new bands at frequencies of about $1080 \pm 2\text{ cm}^{-1}$ and a broad band around 235 cm^{-1} . The peak at 1080 cm^{-1} , due to random liquidlike configurations, has been used earlier to study phase transition in phospholipid dispersions.¹⁰

Further evidence for an extended chain conformation in solid cationic surfactants derives from the nature of the Raman spectrum in the $2800\text{--}3000\text{ cm}^{-1}$ region. The solid state spectra for CTAB, and liquid dodecane, in this region are presented in Figure 3. It is seen that in liquid dodecane the symmetric CH_2 group vibration (at 2851 cm^{-1}) is more intense than the methyl symmetric vibration (at 2882 cm^{-1}) and the

asymmetric vibration of the CH_2 group (at 2927 cm^{-1}). The reverse situation, however, prevails in solid CTAB and DAC. In a rigid crystalline structure, the CH_3 symmetric vibrations are well defined and hence the peaks at 2882 cm^{-1} are more intense.

(b) *Cationic Surfactants in Micellar Form.* In aqueous solutions of about 0.1 M , the cationic surfactants CTAB and DAC aggregate together to form "spherical" micelles. For CTAB Figure 4 represents the Raman spectrum of a 5% (0.1375 M) aqueous solution of this surfactant. The critical micelle concentration of CTAB is $9.2 \times 10^{-4}\text{ M}$ and hence contributions from monomeric surfactants are $<1\%$ and can be safely assumed to be negligible. This situation is also true for all the surfactants examined in micellar form in this study. Micellization of the surfactant in water leads to a simplification of the Raman spectrum. In Figure 4 a new intense band at 1084 cm^{-1} is noted which indicates that the hydrocarbon chains in the micellar core remain "fluid" (kinked) with several gauche isomers present. In contrast to the spectra of liquid hexadecane or molten polymethylenes in this region, the bands at 1064 cm^{-1} (due to C-C symmetrical stretching) and at 1126 cm^{-1} (due to C-C asymmetrical stretching) are still present showing that a significant length of the hydrocarbon chain remains in an all-trans form. In the low frequency region ($<500\text{ cm}^{-1}$), the water scatter background tends to obscure any well-defined spectral structure. However, it is still possible to observe a broad intense band around 460 cm^{-1} and a diffuse band at ca. 150 cm^{-1} due to random gauche configurations.

In *n*-paraffins, it is suggested that as the random character of the hydrocarbon chain increases (either by an increase in chain length or by a phase change, viz., the melting of a solid to the liquid state) and that the accordion motions shift to higher frequencies. Mizushima and Simanouti¹² have calculated the skeletal deformational frequencies for *n*-paraffin solids in the extended form (all-trans) to be around 432 ($n = 4$), 402 ($n = 5$), and 369 cm^{-1} ($n = 6$). Indeed these frequencies have been observed in the spectra of *n*-paraffins. The presence of a broad band in the $350\text{--}520\text{ cm}^{-1}$ region in the micellized CTAB implies that this band should have its origin in the carbon atoms of the hydrocarbon chain that are removed four-six CH_2 units from the polar head group. The polar head

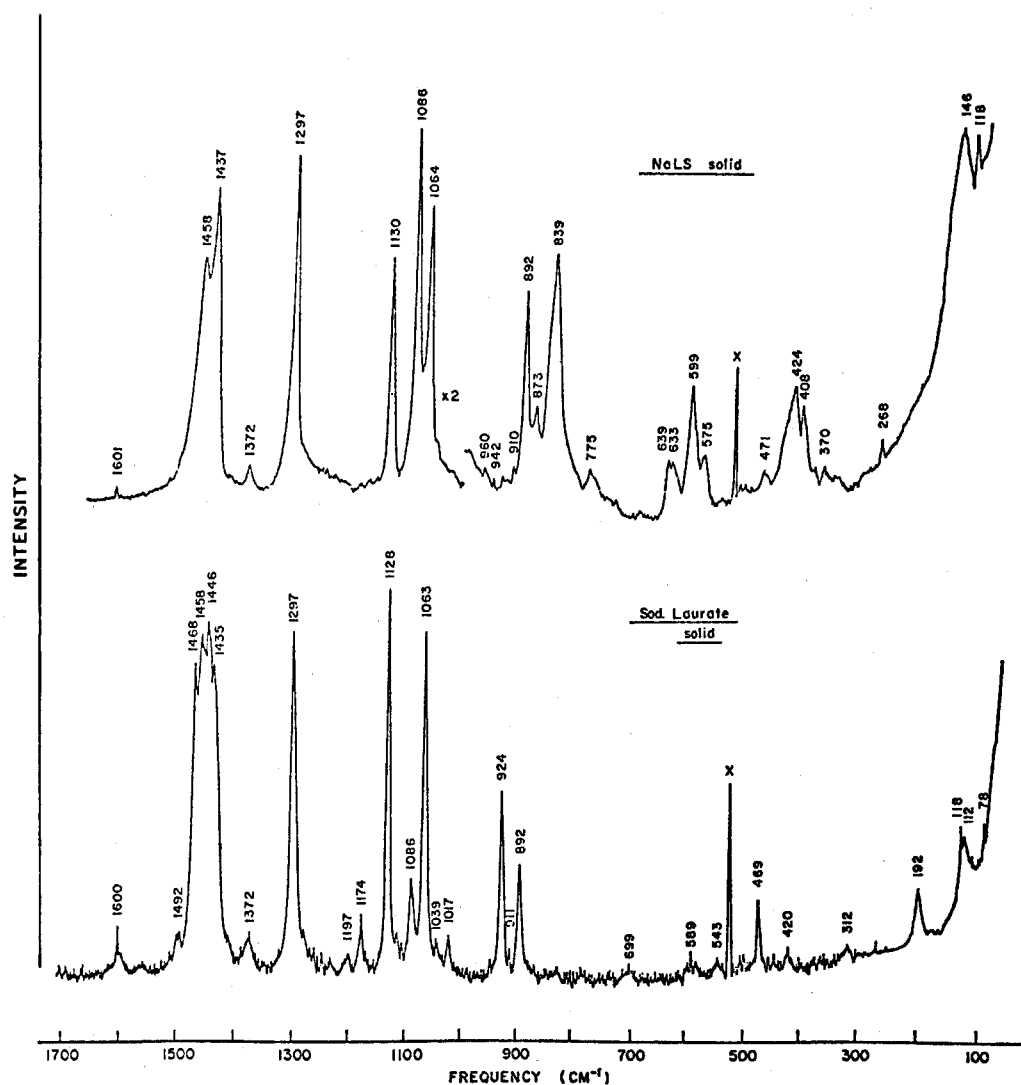


Figure 5. Raman spectra (up to 1700 cm⁻¹) for the crystalline solids sodium laurate (NaL) and sodium lauryl sulfate (NaLS).

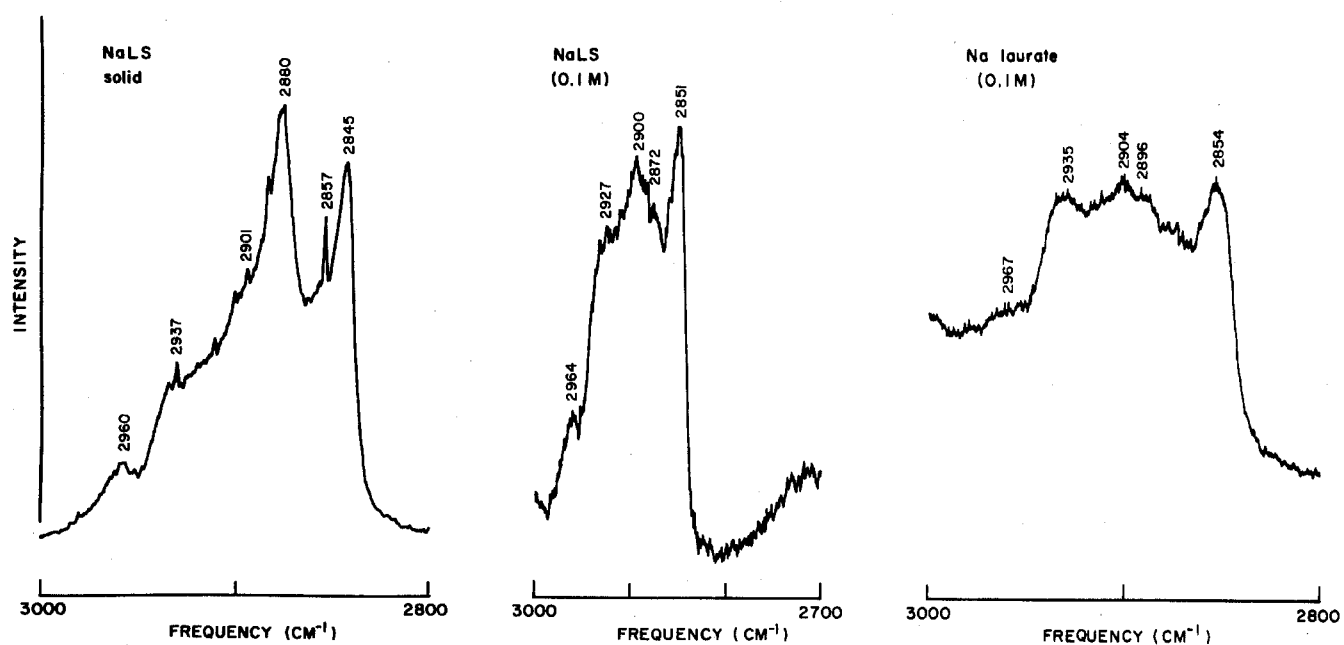


Figure 6. Raman spectra (2800–3000-cm⁻¹ region) for NaLS solid along with those of micellar solutions of NaLS (0.1 M) and NaL (0.1 M).

groups are anchored in the Stern-layer of the micelle. Hence the motion of the hydrocarbon chain subsequent to the head group is considerably restricted.

The identification of exact location of the chain kinking, i.e., the positions of the carbon atoms involved in the formation of "gauche" isomers, requires a complete vibrational analysis similar to those performed by Snyder et al.⁸ For short chain hydrocarbons, ($n < 8$) the Raman frequencies and intensities are calculated for various configurations of the hydrocarbon chain, viz., those with two, three, or four gauche isomers. The most probable configurations are then identified by comparison of the calculated spectra to those observed experimentally. Unfortunately for long-chain surfactants where the number of C atoms is greater than eight, the calculations become prohibitively complex. The experimental task of identifying and observing each of the numerous Raman frequencies is also difficult. In a qualitative sense the Raman spectral data presented above confirm the presence of gauche isomers (fluidity). The data also indicate that the molecular motions of the hydrocarbon chains are *not* as random as observed in pure hydrocarbon liquids such as hexadecane or molten polymethylene.

The above picture for the conformational state of hydrocarbon chains in the micellar core agrees well with the carbon-13 spin-lattice relaxation data.⁷ In micellar solutions of 0.2 M DAC the carbon-13 T_1 values for backbone carbons range from 0.34 to 0.50 s. These data indicate that about eight carbon atoms adjacent to the polar head group are in a rigid structure. The T_1 values, however, show a sharp increase to 2 s for the remaining carbon atoms (three carbons in DAC) at the end of the chains. This T_1 value is comparable to those observed for the various carbon atoms in *n*-paraffin liquids.¹³ It is suggested that the gauche isomers which contribute to the 1081-cm⁻¹ band in the laser-Raman spectrum should arise from the liquidlike structures associated with the carbon atoms toward the end of the chains. The presence of gauche isomers is also indicated by the increased intensities of the methyl and methylene wagging modes of gauche isomers in the 890-cm⁻¹ spectral region (compare Figures 2 and 4).

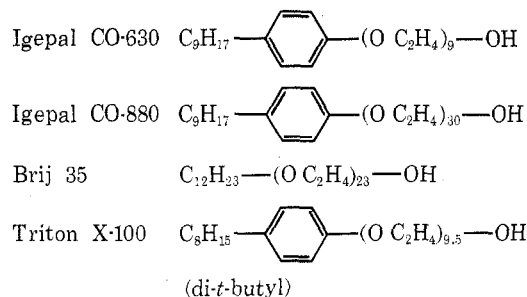
(c) *Crystalline Anionic Surfactants*. The laser-Raman spectra of two representative anionic surfactants, sodium lauryl sulfate (NaLS), and sodium laurate (NaL), in the crystalline state are presented in Figure 5. A similarity is observed on comparing the NaL spectrum to the spectra of the cationic surfactants (Figure 1). The spectrum of NaLS, however, seems to show some apparent anomalies. The sodium laurate spectrum exhibits features characteristic of an extended all-trans chain, viz., (a) intense C-C symmetric and antisymmetric stretching modes at 1063 and 1128 cm⁻¹, (b) a rather sharp and intense methylene twists peak at 1296 cm⁻¹, and (c) intense CH₂ wagging mode frequencies characteristic of trans structures at 592 and 924 cm⁻¹. These features were also observed in cationic solids CTAB and DAC.

Sodium lauryl sulfate is one of the few surfactants which has been studied extensively by a variety of physicochemical techniques. Hence a detailed study of its laser-Raman spectrum was made. It is possible by a comparison of the solid state spectrum of a series of sodium alkyl sulfates [CH₃(CH₂)_{*n*}-SO₄Na with $n = 4, 6, 8, 10, 12, 16$] to assign the various peaks in the Raman spectrum of solid NaLS. As in other long chain hydrocarbon solids, NaLS shows C-C symmetric and antisymmetric stretching frequencies at 1064 and 1130 cm⁻¹. In all sodium alkyl sulfates, the symmetric stretching of SO₃ appears as a strong band around 1080 cm⁻¹. (In NaLS this band appears at 1086 cm⁻¹.) In addition to the Raman

frequencies arising from the hydrocarbon chain, Raman frequencies due to the sulfate head group appear: (a) RO-SO₃ stretch at 839 cm⁻¹, (b) symmetric and antisymmetric deformation modes at 575 and 633 cm⁻¹, and (c) SO₃ rocking at 408 cm⁻¹. In *n*-paraffins Raman spectra are characterized by (a) a broad intense peak at 1086 cm⁻¹, (b) a broad band in the 830-900-cm⁻¹ region, and (c) a broad band in the 600-650-cm⁻¹ region. These imply the presence of extensive gauche forms of the hydrocarbon chains. The appearance of Raman frequencies in these regions due to the sulfate head group¹⁴ obviates clear cut answers on this point. However, the presence of an extended chain with all-trans structures is indicated by several features: (i) presence of sharp intense bands at 1064 and 1130 cm⁻¹ due to C-C stretching; (ii) a sharp peak at 1297 cm⁻¹ as in CTAB and DAC solids and unlike the rather broad peak at 1303 cm⁻¹ in hydrocarbon liquids; (iii) the appearance of the accordion mode frequency at 146 cm⁻¹. The corresponding frequencies for DAC solid and dodecane liquid are 184 and 278 cm⁻¹, respectively. With increasing amounts of gauche isomers, the accordion frequencies shift to higher frequencies; (iv) the nature of the Raman spectrum in the C-H stretching region 2800-3000 cm⁻¹ (Figure 6). The features of this spectrum resemble that of extended chain solids, e.g., CTAB and DAC, as compared to that of liquid dodecane.

(d) *Anionic Surfactants in Micellar Forms*. The laser-Raman spectrum of a 0.1 M aqueous micellar solution of NaLS is presented in Figure 7. The 1000-1200- and 2800-3000-cm⁻¹ regions for micellar NaLS and NaL are specifically compared in Figures 6 and 8. As in the case of cationic surfactants micellization of the surfactant leads to changes in the chain configurations. A predominance of gauche rotomers is observed. This is quite apparent in the case of sodium laurate micelles. The sodium laurate micelles appear to be more fluidlike, as the intensity of the 1081-cm⁻¹ peak is greater than the 1065- and 1123-cm⁻¹ peaks. In the case of NaLS, micellization leads to a considerable reduction in the intensity of the 1084-cm⁻¹ peak (it appears as a shoulder in the 1063-cm⁻¹ peak). In addition there are broad bands around the 828- and 300-500-cm⁻¹ regions, respectively. The spectral features of the 2800-3000-cm⁻¹ region are also in accord with the picture of a micelle with a fluid core. A change in conformation for NaLS following interactions with lysozyme has been noted recently by Lord et al.¹⁵ Presumably the significant drop in the intensity of the 1086-cm⁻¹ peak is due to a freezing of the sulfate head group in the electrical double layer of the micelle.

(e) *Raman Spectra of Pure Nonionic Surfactants*. In addition to examining the Raman spectra of cationic and anionic surfactants, we have also investigated the Raman spectra of a series of nonionic surfactants. In particular we have examined Igepal CO-630, Igepal CO-880, Triton X-100, and Brij



35. The lower members of these polyoxygenated surfactants are viscous liquids at room temperature (25 °C), while the higher member Igepal CO-880 is a waxy solid. Raman spectra

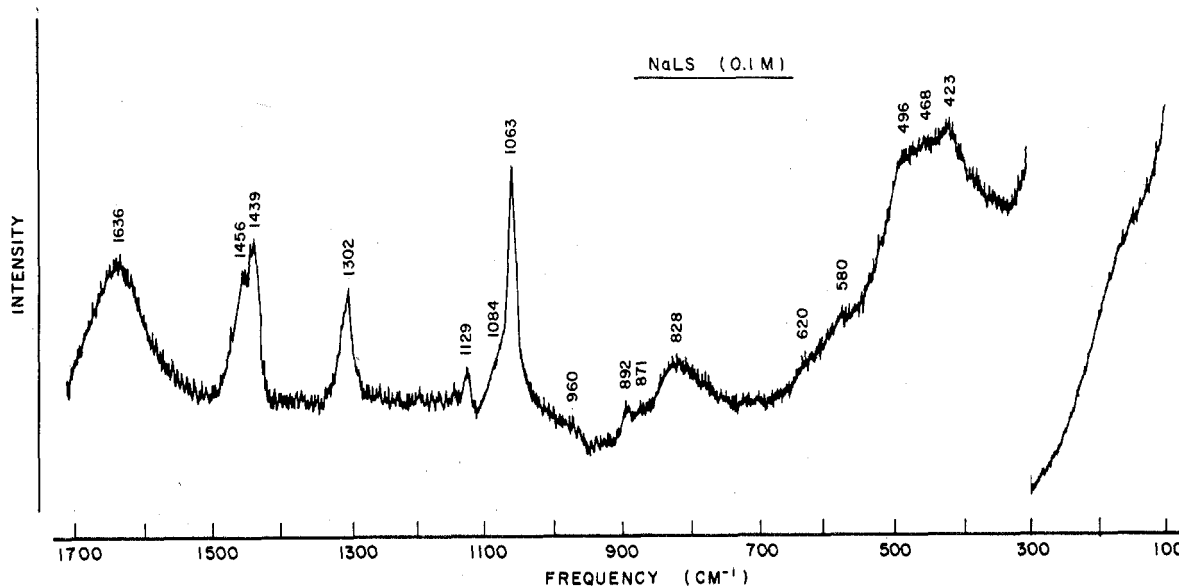


Figure 7. Raman spectrum of 0.1 M micellar solution of NaLS in H_2O .

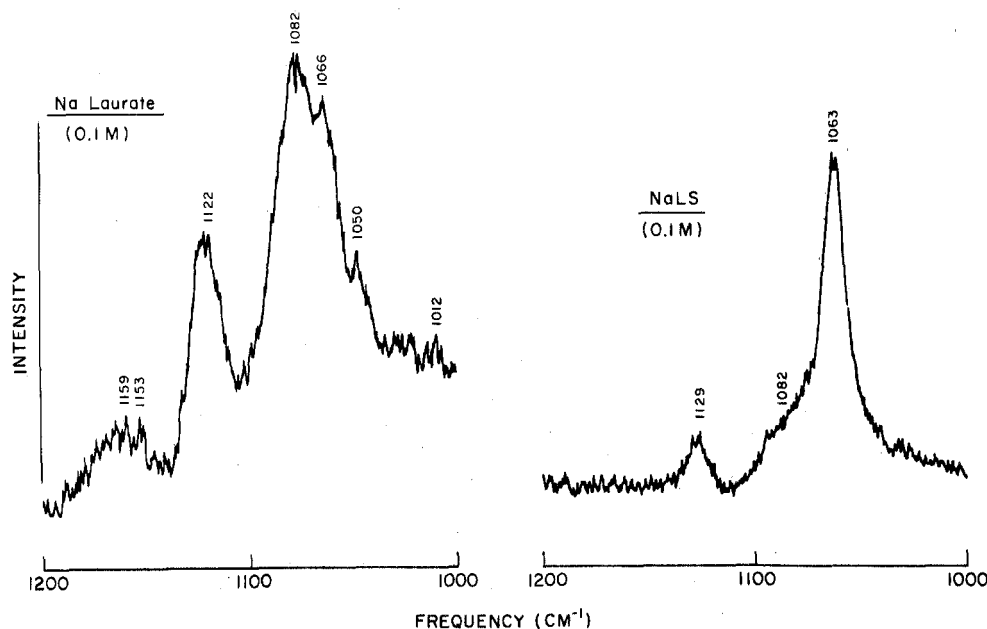


Figure 8. Raman spectra ($1000\text{--}1200\text{-cm}^{-1}$ region) for 0.1 M micellar solution of NaLS and NaL in H_2O .

for Triton X-100 and Igepal CO-630 liquids and Brij 35 and Igepal CO-880 as solids are presented in Figures 9 and 10. The Raman spectra of nonionic surfactants give information on the nature of hydrocarbon core of these micelles. In addition information on the configuration of the ethylene oxide chain is also obtained. Both "zig-zag" and "meander" models for the oxyethylene group have been discussed in the literature.¹⁶ The first model refers to ethylene oxide configurations which are "fully extended" chains in the palisade layer on the exterior of the micelle. In the second model the ethylene oxides assume helical coil forms which twist and wind in the palisade layer from the hydrophobic center to the micellar surface.

Several interesting conclusions can be drawn from examination of the Raman spectra presented in Figures 9 and 10. The Raman spectra in Figures 9 and 10 look entirely different from those of long chain fatty acids, but resemble more those of polyethylene glycols¹⁷ (PEG). This is to be expected as the

hydrocarbon part of the nonionic surfactants examined here are either short or highly branched. The Raman frequencies arising from the alkane chains overlap with those arising from the polyoxyethylene chains. In short the Raman spectra are dominated by vibrations arising from the polyoxyethylene chain, thereby facilitating a direct observation of the conformational state of the hydrophilic part of the micelles formed by these nonionic amphiphiles. In the series Igepal CO-630, Brij 35, and Igepal Co-880, the ethylene oxide (EO) unit increases from 9 to 30. Examination of the Raman spectra show drastic changes from Igepal CO-630 to Igepal Co-880. Brij 35, occupying an intermediate position, shows a spectrum which is an overlap of the spectra of the shorter chain CO-630 and longer chain CO-880.

As mentioned earlier, the Raman spectrum of solid Igepal CO-880 strongly resembles that of solid polyethylene glycol (PEG). Table II summarizes the observed Raman frequencies

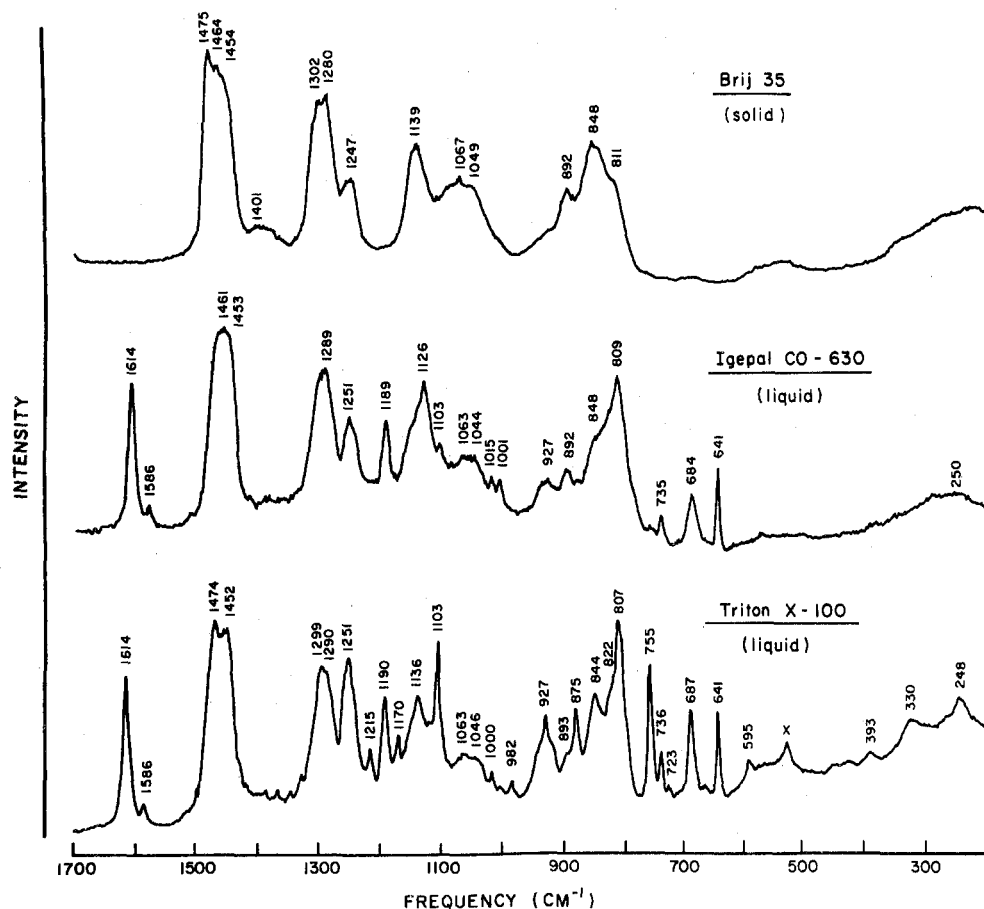


Figure 9. Raman spectra for the nonionic surfactants Triton X-100 liquid, Igepal CO-630 liquid, and Brij 35 waxy solid.

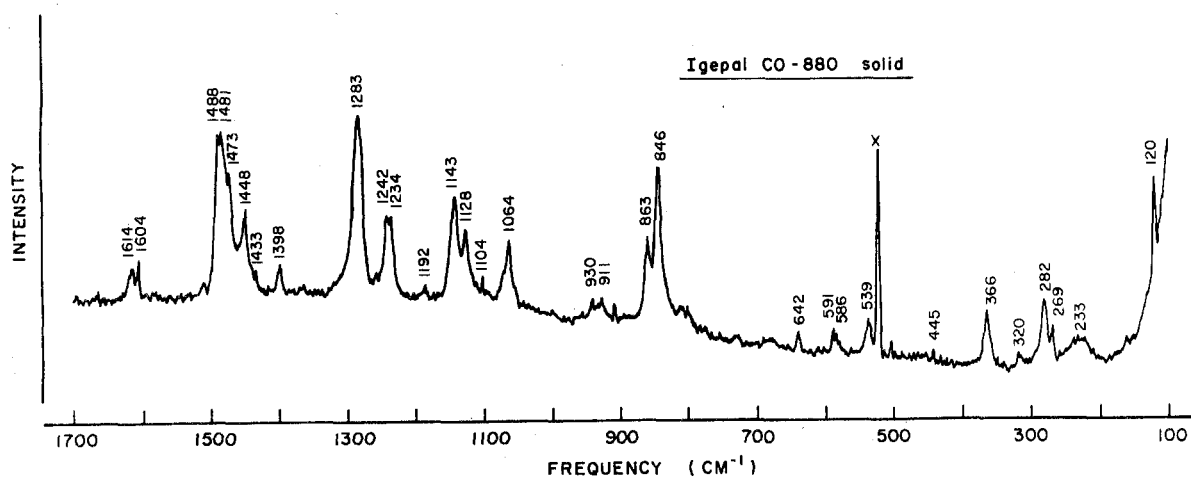


Figure 10. Raman spectrum of Igepal CO-880 solid.

together with their intensities for comparison with solid PEG. The conformational states of the ethylene oxide unit in solid PEG, molten PEG, and PEG in aqueous solution have been examined earlier by Koenig and Angood.¹⁷ Combined (x-ray analysis, ir, NMR, and Raman) studies of PEG have established that PEG has a helical conformation in the crystalline solid with the seven chemical units ($\text{CH}_2\text{-CH}_2\text{-O}$) and two turns in a repeat distance of 19.3 Å. Furthermore the PEG has a dihedral symmetry (i.e., the chain possesses two kinds of twofold axis: one passing through the oxygen atom and the other bisecting the C-C bond). The PEG repeating unit has

a TGT (T = trans, G = gauche) conformation of the $\text{CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O}$ sequence. The dihedral helical conformation is characterized by typical Raman lines and will be discussed below. The striking similarities between the Raman spectra of the 30 (EO) unit nonionic surfactant Igepal CO-880 and that of PEG solid indicate that the long ethylene oxide unit has a helical structure with the dihedral symmetry in the surfactant. However, as the length of the ethylene oxide decreases from 30 EO units to 9 in Igepal CO-630 (the latter is a viscous liquid at room temperature), the helical conformation is no longer preferred. A disordered structure prevails

TABLE II: Raman Frequencies for Igepal CO-880 Solid along with Those of Polyethylene Glycol (PEG) Solid

PEG solid ^a	Igepal CO-880 solid	Tentative assignments
537 s	538 w	(OCC) bending
583	586 w	
	591 w	
	643 w	
	777 vw	
811 w	806 vw	Amorphous (from disordered structures)
846 vs	846 vs	CH ₂ rock
860 m	863 m	CH ₂ , C=O rock
	911 m	
936 vm	929 w	Amorphous (from disordered structures)
947 w	945 w	CH ₂ C=O rock
1065 m	1065 m	C-O stretch, CH ₂ rock
1073 sh	1078 sh	
1125 m	1128 m	C-C stretch, CH ₂ wag
1142 s	1143 s	C-O stretch
1232 m	1232 m	CH ₂ twist
1237 w	1242 m	
1283 vs	1283 vs	
1286 w		
1376 w	1367 w	CH ₂ wag, C-C stretch
1396	1399 mw	
1448 m	1448 m	CH ₂ scissoring
1471 sh	1473 sh	
1481 s	1481 s	CH ₂ scissoring
1486 s	1488 s	

^a Data taken from ref 17: s = strong, w = weak, m = medium, sh = shoulder, vw = very weak.

which includes the presence of several rotational isomers. Table III presents a comparison of the Raman frequencies for liquid Igepal CO-630 and Triton to that of molten PEG. The Raman spectra of lower member short EO chain surfactants resemble that of molten PEG.

As indicated earlier, the Raman spectra of solid Igepal CO-880 and liquid Igepal CO-630 show several differences. In Igepal CO-880 there are two intense bands at 846 and 863 cm⁻¹ in the methylene and methyl rocking regions. In Igepal CO-630, however, there are three peaks at 807, 848, and 892 cm⁻¹, the 807-cm⁻¹ peak being more intense than the other two. For Igepal CO-880 in the methylene rocking region the 1143-cm⁻¹ line is more intense than the 1128-cm⁻¹ line. In Igepal CO-630 these two lines merge together, the 1126-cm⁻¹ line is more intense, and the 1143-cm⁻¹ line appears as a shoulder. The CH₂ bending region also shows significant changes. The four peaks at 1448, 1473, 1481, and 1488 cm⁻¹ of the surfactant Igepal CO-880 merge to two peaks (at 1453 and 1467 cm⁻¹) on reduction of the ethylene oxide unit from 30 to 9. It is also noted that the peaks at 1234 and 1242 cm⁻¹ merge to 1251 cm⁻¹ in CO-630 with a significant increase in the intensity of the 1189-cm⁻¹ line. There is also a considerable reduction in the intensity of the peaks at 945 and 1399 cm⁻¹. The shorter chain surfactants show a more intense band at 1615 cm⁻¹. These spectral differences are also observed in liquid and solid PEG. Based upon the assignments of various peaks (which in turn are based on model vibrational analysis, details are discussed at length in the reference cited above) it is concluded that on the melting of PEG (or on reduction of the EO chain length in the surfactant) that the helical EO structure opens up with the formation of new rotational motions. These motions occur mainly at the C-O bonds rather than around the C-C bonds. According to Koenig et al., this

TABLE III: Raman Frequencies for the Nonionic Surfactant Liquids Igepal CO-630 and Triton X-100 along with Those of PEG Melt

Triton X-100	Igepal CO-630	PEG melt ^a	Tentative assignments
248 w	250 w	261 w	
330 w			
393 vw			
430 vw			
595 w	570 vw	524 w	
641 m	641 m	526 w	
687 m	684 m		
723 vw			
736 w	735 w		
755 s	753 vw		
807 s	809 s	807 m	CH ₂ rock
822 sh			
844 m	848 sh	834 m	
875 m			
893 sh	892 w	884 mw	CH ₂ rock, C-O, C-C stretch
927 m	927 w	919 sh	
982 vw			
1000 vw			
1015 vw	1015 vw		
1046 w	1044 m		
1063 w	1063 sh	1052 m	C-O, C-C stretch
1103 s	1103 sh		C-O, C-C stretch, CH ₂ rock
1136 m	1126 s	1134 s	C-O, C-C stretch
1170 w			
1190 m	1189 m		
1215 s			
1251 s	1251 m		CH ₂ twisting
1290 s	1289 s	1283 s	
1299 s	1295 sh	1291 m	CH ₂ wagging
1351 vw		1352 m	
1371 vw			
1390 vw	1380 w		
1452 sh	1453	1448 sh	CH ₂ scissoring
1474 s	1467 s	1470 s	

^a See footnote a to Table II.

also implies the presence of several additional rotational isomers, with the ethylene oxide configuration changing from a trans-gauche-trans sequence in the solid to a gauche-gauche-trans sequence in the liquid.

The surfactant Brij-35 has an intermediate EO chain length. Here the Raman spectrum shows features of both the longest chain Igepal CO-880 (with 30 EO unit) and that of shortest Igepal CO-630 (9 EO units). With a chain length of 23 EO units significant portions of the polyoxyethylene chains remain in a helical form with a dihedral symmetry, while a small part of the chain exhibits a disordered structure (open coil) with several gauche isomers. The nonionic amphiphile Triton X-100 is a homogeneous mixture of different EO chain lengths, with an average around 9.5. Consequently the Raman spectrum resembles that of Igepal CO-630 except that the Raman lines due to open coils are more intense.

(f) *Nonionic Surfactants in Micellar Form.* Alkyl polyoxyethylene glycol monoethers, such as Brij 35, as well as alkyl phenoxy polyethyleneoxy ethanols, such as Igepals or Tritons, aggregate together in aqueous solution to form spherical micelles. As the molecular chain lengths are quite large, large micelles are formed with aggregation numbers typically around 100-150.^{5a} As in the case of ionic micelles, these non-ionic micelles^{18,19} have a liquidlike hydrophobic core formed by the alkyl chains, while the ethylene oxide units form a hydrophilic palisade layer. NMR studies¹⁹ indicate that the ethylene oxide units are hydrated and that the water mole-

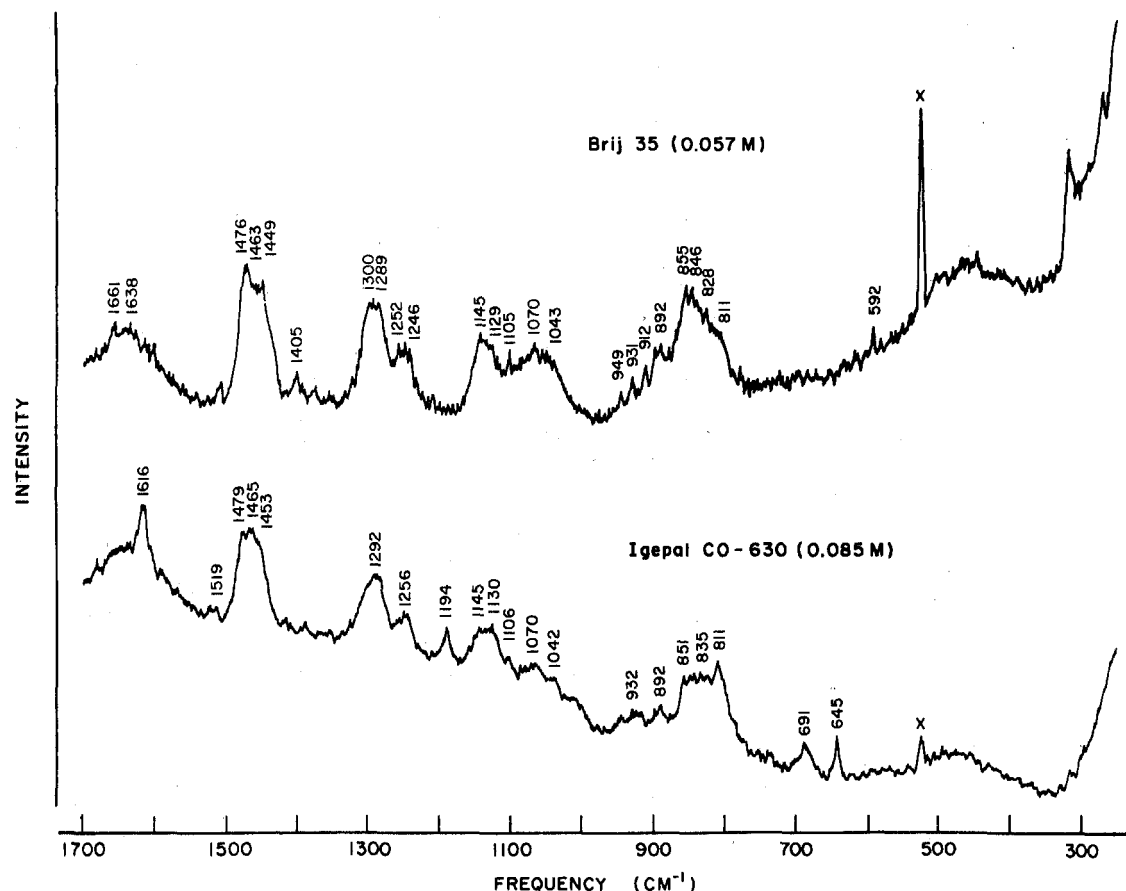


Figure 11. Raman spectra of micellar solution of Igepal CO-630 (0.059 M) and Brij 35 (0.025 M) in H₂O.

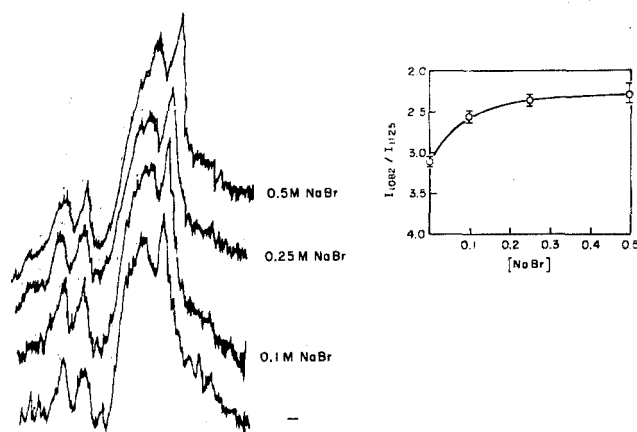


Figure 12. Raman spectrum (1000–1200-cm⁻¹ region) for 0.1 M CTAB in the presence of an increasing concentration of NaBr and a plot of (I_{1082}/I_{1125}) for the series of spectra shown.

cules in the region between the polyoxyethylene chains appear to be partially immobilized. It is of interest to see whether any additional information can be obtained from Raman spectral studies.

The Raman spectra of micellized Igepal CO-630 (0.059 M) and Brij 35 (0.025 M) in H₂O are presented in Figure 11. A comparison of the spectra of Igepal CO-630, in the pure and micellar form, shows instructive differences. In micellar form, the spectrum shows additional peaks at 851, 1194, 1453, 1479, and 1616 cm⁻¹. These features are characteristic of a helical structure as found in solid PEG. The peaks due to the disor-

dered structure, as found in the pure liquid, are still present, indicating that on micellization there is an ordering of the polyoxyethylene units from a random to a more ordered helical structure. For the long chain surfactant Brij 35 there are no significant differences in the Raman spectra in aqueous micellar solutions indicating no significant change in chain conformation.

(2) *Electrolyte-Induced Micellar Phase Changes.* Hitherto the studies have been concerned with Raman spectra of pure surfactants and the spherical micelles formed by these compounds. Raman spectroscopy has also been utilized to probe chain conformations, in CTAB micelles, both spherical and in the bigger rodlike structures, and bilayers which are formed by the addition of electrolytes such as NaBr. The micellar change or growth into larger structures at high concentrations of surfactants, or in the presence of added electrolytes, is a well established phenomenon.

In a decimolar aqueous solution, CTAB exists in the form of "spherical" micelles with an aggregation number around 80. On addition of NaBr, these micelles grow into bigger rodlike structures.²⁰ We recently investigated^{7c} a similar type of electrolyte-induced phase changes for DAC micelles in detail by several physicochemical techniques and observed an increase in the microviscosity of the micellar interior on introduction of the electrolyte.

The increases in the microviscosity of the interior of the CTAB micelles on addition of NaBr is also observed by observing the 1082-cm⁻¹ peak in the laser-Raman spectrum of CTAB. In Figure 12 the ratio I_{1082}/I_{1125} is plotted against the concentration of added NaBr. Due to the highly viscous nature of these solutions, the background scatter increases consid-

erably with increasing concentration of the electrolyte, and this was to be taken into consideration in the measurement of peak intensities. On addition of NaBr, the ratio decreases indicating an increase in rigidity of the micellar hydrocarbon core. A limiting ratio for I_{1082}/I_{1125} is reached at high electrolyte concentration. The presence of the 1082-cm^{-1} peak shows that, even in these larger rod-shaped aggregates (micellar molecular weight $\approx 2\,000\,000$), a significant amount of gauche isomers is still present. The above data are also consistent with the data of Shinitzky et al.⁶ who showed that the microviscosity of the interior of the CTAB micelles increases with increasing NaBr concentration. Presumably in these larger aggregates several carbon atoms at the end of the chains retain their fluidity.

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A Semiempirical Model for the Phase Transition in Polystyrene Latexes

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A simple model for the phase transition in polystyrene latexes has been developed. The model assumes a priori that the transition is fundamentally caused by repulsion between the spherical latex particles, i.e., it is fundamentally hard sphere in nature, but that the hard sphere diameter of the polystyrene particles is in fact ionic-strength dependent. The resulting volume fraction vs. salt concentration phase diagram is in qualitative accord with the experimental phase diagram of Hachisu and co-workers.

Introduction

Modern emulsion polymerization techniques can produce concentrated monodisperse suspensions of spherical polymer particles which, in the freshly prepared state, are typically milky white in color. Luck and coworkers^{1–3} demonstrated that highly concentrated aqueous polystyrene latexes and their dried films exhibit iridescence for a certain range of particle diameters. They showed that the iridescence is due to Bragg diffraction of visible light from ordered layers of particles stacked parallel to the surface of the container.

Vanderhoff et al.⁴ noted that the latex particles are charged and that therefore double-layer interactions should be important in any ordering. They observed that interparticle spacing increases when an iridescent latex is diluted, order being maintained by long-range repulsion between the spheres. Krieger and co-workers^{5,6} studied the diffraction in deionized aqueous latexes and found that the particles remain in a close-packed array down to volume fractions as low as 1%. Deionization of the latex removes excess salt and surfactant, resulting in a suspension of charged spheres interacting in an aqueous environment which contains (ideally) a mobile