Raman Spectra of Benzene, Ethyl Benzene and Dimethyl Phthalate Solubilized in Aqueous Solutions of Surface-Active Agents

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Raman spectral studies were made of benzene, ethyl benzene, and dimethyl phthalate solubilized in aqueous solutions of sodium laurate and of sodium lauryl sulphate. The mechanism of incorporation of the solubilizates in the micelles was discussed on the basis of changes in the half band-width and frequency of their Raman bands on solubilization. It was concluded that solubilized benzene and ethyl benzene were in the same mode of solubilization and located in the hydrocarbon interior of the micelles, whereas solubilized dimethyl phthalate was adsorbed on the surface of the micelles through the hydrogen bond.

INTRODUCTION

Although the mechanism of micellar solubilization has been a subject of much interest in the field of the surface and colloid chemistry, previous studies of solubilization by means of spectroscopy have been very limited in number. Riegelman and coworkers[1] have studied the ultraviolet spectra of various aromatic compounds solubilized in aqueous solutions of surface-active agents, and concluded that, depending upon the polarity of the solubilizates, they were incorporated in the micelles with four different modes of solubilization: (a) Inclusion into the hydrocarbon interior of the micelles, (b) Deep penetration of the palisade layer, (c) Short penetration of the palisade layer, and (d) Adsorption on the surface of the micelles. Mulley and Metcalf[2] and Donbrow and Rhodes[3] have examined the ultraviolet spectra of chloroxylenol and benzoic acid, respectively, solubilized in the micelles of cetomacrogol and suggested the formation of the hydrogen bond between the solubilizates and solubilizers.

It is generally agreed, however, that the ultraviolet spectra are too simple in most cases to afford sufficient information on the complicated mechanism of solubilization, though they should reflect the electron redistribution in aromatic compounds on solubilization. The infrared spectra may be informative, but its application is severely restricted by the solvents and the concentrations with which solubilization takes place. These difficulties are expected to be overcome by the recently developed technique of the laser-excited Raman spectra, which seem to be very promising to inquire into the mechanism of solubilization in aqueous solutions.

In the present paper, we report the Raman spectra of benzene, ethyl benzene, and dimethyl phthalate solubilized in the aqueous solution of sodium laurate and of sodium

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lauryl sulphate. The mechanism of incorporation of the solubilizates in the micelles is discussed on the basis of changes in the half band-width and frequency of their Raman bands on solubilization.

EXPERIMENTAL

All chemicals adopted were the purest grade of commercial origin and used without further purification. Pure water was prepared by redistillation of distilled water which had been passed through an ion-exchange resin column.

The concentrations of the surface-active agents were fixed at *ca.* 0.3 moles in 1000 g of the aqueous solution throughout the work. It is quite beyond the critical micelle concentrations (CMC) which are *ca.* 0.03 for sodium laurate and *ca.* 0.01 for sodium lauryl sulphate, as expressed in moles per 1000 g of the aqueous solution. Benzene, ethyl benzene and dimethyl phthalate were solubilized in these aqueous solutions at various concentrations up to their solubilizing capacities.

Raman spectra of the solubilizates in the aqueous solution were recorded on a Japan Electron Optics Laboratory model JRS-S1 spectrophotometer with the excitation line of 488.0 nm of a Spectra-Physics model 164 argon ion laser. The accuracy of frequency of the spectrometer was less than ± 2 cm^{-1}. The temperature of the aqueous solution was kept at $35 \pm 1°C$ throughout the Raman measurements by the use of a thermostatic cell
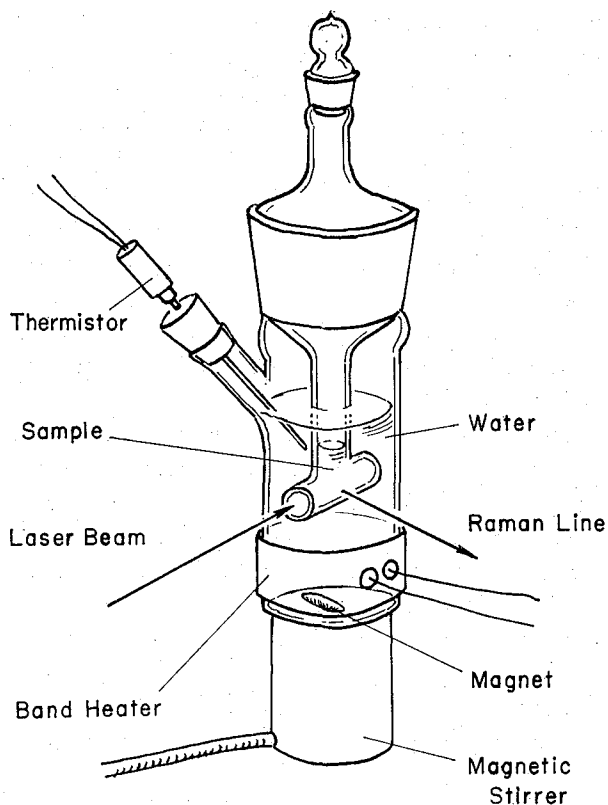

Fig. 1. Thermostatic cell for Raman measurements.

illustrated in Fig. 1. It was made of glass, being composed of two main parts: one was the sample container with the cylindrical Raman tube at its lower end, and the other was the water jacket having the band-heater outside of it. Both parts were jointed together by means of the ground joint so that the Raman tube was dipped into water, temperature of which was controlled by a thermister and band-heater system and slow stirring by a magnetic stirrer. Raman spectra of benzene, ethyl benzene, and dimethyl phthalate were also recorded at the same temperature in liquid and in the octane solution, for references.

RESULTS AND DISCUSSION

The Raman spectra of benzene (0.14 moles) and dimethyl phthalate (1.0 mole) solubilized in 1000 g of the aqueous solution of sodium laurate are represented in Figs. 2 and 3, respectively, as examples. Arrows show the bands due to the solubilizates. It is apparent that except for small frequency shifts, they are merely an addition of the spectra of the three components: solubilizate, sodium laurate, and water. Careful examination
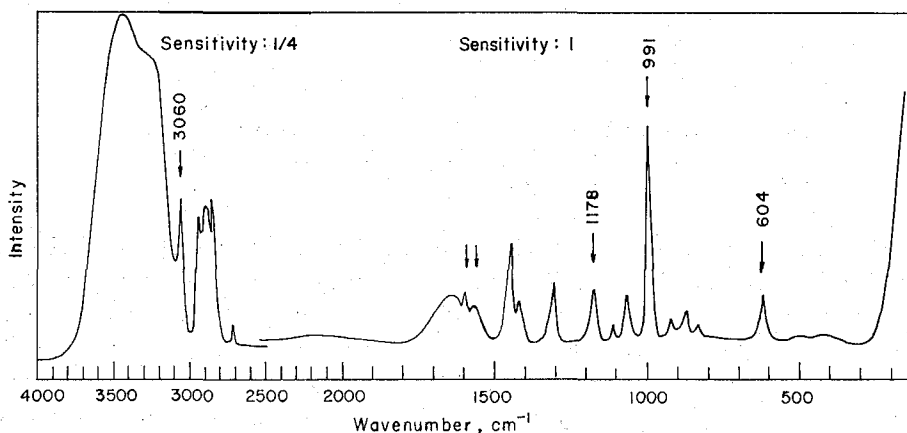

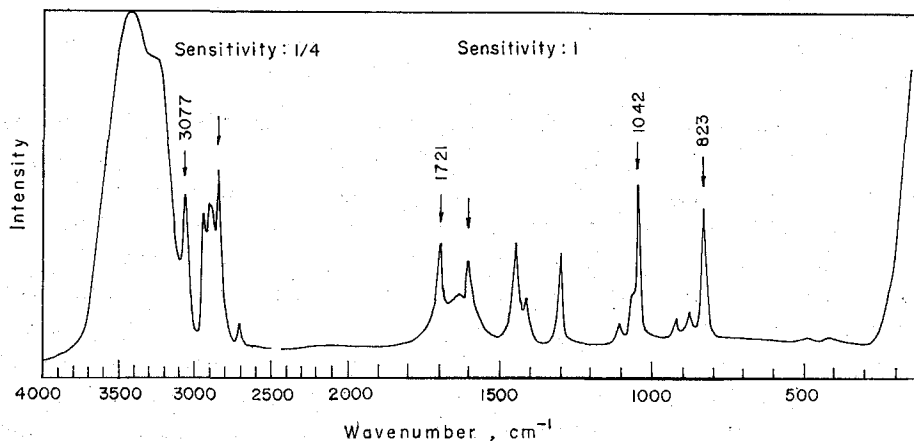Fig. 2. Raman spectrum of benzene solubilized in the aqueous solution of sodium laurate.

Fig. 3. Raman spectrum of dimethyl phthalate solubilized in the aqueous solution of sodium laurate.
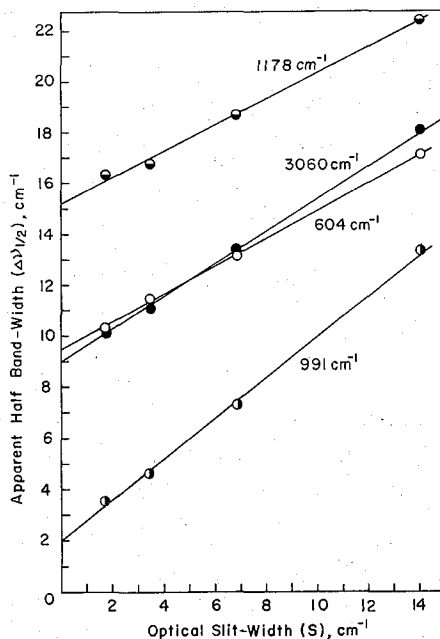
Fig. 4. Apparent half band-width of Raman bands of benzene (0.14 moles) solubilized in the aqueous solution (1000 g) of sodium laurate as a function of optical slit-width.

of the spectra, however, reveals that there is some difference in the band-widths of the aromatic compounds among in liquid, in the octane solution, and in the aqueous solution of the surface-active agents. For the purpose of discussing the modes of incorporation of the solubilizates on this basis, it is convenient to use the half band-width. It can be obtained by measuring the apparent half band-width $\Delta\nu_{1/2}$ at a number of settings of the optical slit-width S. A plot of $\Delta\nu_{1/2}$ versus S is generally linear[4] as shown in Fig. 4, and may be extrapolated to $S=0$ for an estimate of the true half band-width $\Delta\nu^\circ_{1/2}$. The results obtained are summarized in Table I, together with the frequencies of the band maxima.

1. Benzene

Of four Raman bands observed for benzene, two bands near 3060 and 990 cm^{-1} have been assigned to the totally symmetric A_{1g} vibrations of the molecular group D_{6h}, and were found to give rise to nearly the same value of $\Delta\nu^\circ_{1/2}$ in liquid, in the octane solution, and in the aqueous solution. The other two bands near 1180 and 605 cm^{-1} have been assigned to the degenerate E_{2g} vibrations. It was found for these bands that the value of $\Delta\nu^\circ_{1/2}$ was the smallest in liquid, and those in the octane solution and in the aqueous solution were as large as $ca.$ 1.5 times that in liquid. No frequency shift could be observed on solubilization for all bands observed. These facts suggest that the solubilized benzene molecules are in the same environment as in hydrocarbons, where the E_{2g} vibration of benzene is degraded from its degeneracy and shows a tendency of slight splitting, resulting the increase of the $\Delta\nu^\circ_{1/2}$ value. In other words, the solubilized benzene molecules are completely surrounded by the hydrocarbon chains of the micelles and are affected by the

Table I. Frequencies (ν in cm^{-1}) and Half Band-Width ($\Delta\nu^{\circ}_{1/2}$ in cm^{-1}) of Raman Bands of Benzene, Ethyl Benzene, and Dimethyl Phthalate

Aromatic compound	Assignment	Liquid		Octane solution		Solubilized in aq. solution of			
						Sodium laurate		Sodium lauryl sulphate	
		ν	$\Delta\nu^{\circ}_{1/2}$	ν	$\Delta\nu^{\circ}_{1/2}$	ν	$\Delta\nu^{\circ}_{1/2}$	ν	$\Delta\nu^{\circ}_{1/2}$
Benzene (D_{6h})	CH stretch. (A_{1g})	3061	8.3	3060	8.9	3060	9.0	3060	9.1
	CH deform. (E_{2g})	1176	9.8	1178	15.4	1178	15.2	1178	15.5
	CC stretch. (A_{1g})	992	1.9	992	2.0	991	2.0	992	2.2
	CCC deform. (E_{2g})	607	5.6	605	8.9	604	9.5	605	9.3
Ethyl benzene	CH stretch. (Benzene ring)	3053	12.1	3052	15.6	3052	15.9	3051	15.8
	CH stretch. (Ethyl group)	2933	11.2	2933	15.0	2933	14.8	2932	15.1
	CC stretch. (Benzene ring)	1603	7.1	1604	10.1	1601	9.9	1602	10.2
	CH deform. (Benzene ring)	1199	5.9	1199	9.8	1198	10.4	1998	10.3
	CC stretch. (Benzene ring)	{ 1028	3.4	1028	5.6	1028	5.8	1028	5.9
		{ 1001	1.5	999	2.2	1001	2.1	1000	2.4
	CCC deform. (Benzene ring)	767	5.2	768	9.0	767	9.2	766	9.0
Dimethyl phthalate	CH stretch. (Benzene ring)	3076	27.5	3077	30.1	3077	30.5	3076	30.2
	C=O stretch.	1728	18.6	1729	22.2	1721	30.9	1719	31.3
	CC stretch. (Benzene ring)	1040	6.2	1041	9.5	1042	9.3	1041	9.3
	CCC deform. (Benzene ring)	818	6.1	819	9.2	823	9.0	822	9.2

environment so as to lower its D_{6h} symmetry. It seems reasonable to conclude, therefore, that the benzene molecules are located in the hydrocarbon interior of the micelles.[5] This is in conformity with the conclusions arrived at from the X-ray studies.[6~8]

2. Ethyl Benzene

No frequency shift could be observed on solubilization for all bands of ethyl benzene shown in Table I. For these bands, the values of $\Delta\nu^\circ_{1/2}$ were found to be large in the octane solution and in the aqueous solution of the surface-active agents as compared with in liquid. It, therefore, leads to the same conclusion as in the case of benzene that the solubilized ethyl benzene are surrounded by the hydrocarbon environment of the micelles. Riegelman and his coworkers[1] have proposed the same mode of incorporation of ethyl benzene from their ultraviolet studies.

3. Dimethyl Phthalate

The values of $\Delta\nu^\circ_{1/2}$ for the dimethyl phthalate bands were generally large in the octane solution and in the aqueous solution as compared with in liquid. For the C=O stretching vibration band of the carbonyl group at 1728 cm^{-1} (the value in liquid), furthermore, the $\Delta\nu^\circ_{1/2}$ value was larger in the aqueous solution than in the octane solution. In addition, the band shift about 7 to 9 cm^{-1} to the low frequency side was found for this band on solubilization. The similar band broadening and frequency shift of this band were also observed for dimethyl phthalate dissolved in a mixed solvent of water and methyl alcohol. This may indicate that the benzene ring of the solubilized dimethyl phthalate molecule is surrounded by the hydrocarbon environment in the micelles and the methoxycarbonyl groups are bonded with the polar groups of the surface-active agents or with their bound water through the hydrogen bond. It is, therefore, concluded that dimethyl phthalate is located near the surface of the micelles. This is consistent with adsorption as the mode
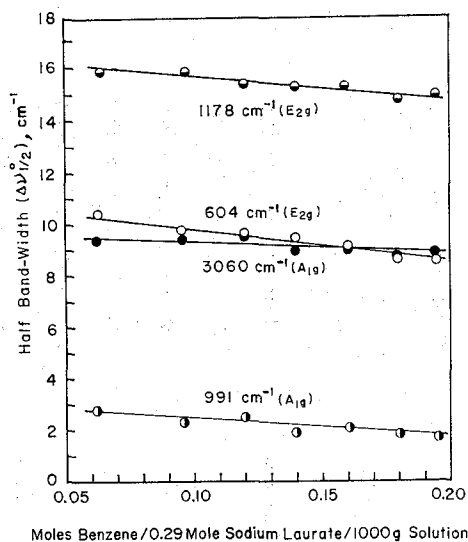

Fig. 5. True half band-width of Raman bands of benzene solubilized in the aqueous solution (1000 g) of sodium laurate as a function of the amount of benzene.

of solubilization as has been postulated by McBain and McHan[9] and Riegelman and coworkers.[1]

It is generally found that the $\Delta\nu^{\circ}_{1/2}$ value decreases linearly with the increase of the amount of the solubilizate. An example is shown in Fig. 5 for benzene. This fact is conceivable by considering that at a small amount of the solubilizate in the aqueous solution, the interaction takes place between the solubilizate and the micelle, while with increasing the amount of the solubilizate, the interaction between the solubilizate molecules becomes predominant, which gives rise to the small value of $\Delta\nu^{\circ}_{1/2}$ as mentioned above. It is apparent from Fig. 5 that the decrease of the $\Delta\nu^{\circ}_{1/2}$ value with the amount of solubilized benzene is more remarkable for the E_{2g} vibration bands than for the A_{1g} vibration bands, as expected.

Although the conclusions drawn in this paper are by no means final, nor entirely unambiguous, the Raman spectra of the solubilizates afford a sensitive method for determining the modes of solubilization.

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