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An FT-IR Study of Micelle Formation of Ionic Surfactants and Water Solubilization in Nonpolar Organic Solvents

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The infrared spectra of the solutions of dodecylammonium propionate (DAP), hexadecyltrimethylammonium bromide (HTAB), and sodium bis(2-ethylhexyl) 2-sulfonatosuccinate (SBSS) in organic solvents were recorded in Fourier transform mode. Difference concentration spectra of DAP in dichloromethane exhibited the change in the stretching bands of the carboxylate ions, which was attributed to the formation of micellar aggregates. Difference hydration spectra were also obtained for water-containing DAP–CH_2Cl_2, HTAB–CH_2Cl_2, and SBSS–benzene systems, and the spectra in the region of 3000—3700 cm^{-1} and 1600—1650 cm^{-1} revealed the existence of free water dispersed in the organic phase and water bound to the micelles. The diffreence spectra also revealed the change in the bands of DAP and SBSS due to hydration of the ionic head groups. The absorption frequency of the O–H stretching bands was discussed in terms of the water-surfactant-interaction.

Recently the studies on the formation and structure of reversed micelles in nonpolar organic solvents have received considerable attention. Reversed micelles can solubilize appreciable amount of water and other polar substances. A variety of techniques have been used for the investigation of the nature of reversed micelles and cosolubilized water. A typical method is the direct observation of the change in the physical properties of the solutes by NMR,[1–8] and another is the use of probe molecules which have physical properties sensitive to the change in the environment of the solubilization sites. Examples of the latter are spin lables,[9–12] absorption and fluorescence probes,[13–19] and positron annihilation techniques.[20,21]

These methods assume that the solubilization of the probe molecules causes little or no change in the structure of the micelles. On solubilization of probes, however, perturbation of the micelle structure is likely to occur because of the small aggregation numbers and hence the small size of the reversed micelles. For example, the mean aggregation number of dodecylammonium propionate (DAP) has been reported to be 4 in carbon tetrachloride[1] and 6 ± 1 in dichloromethane.[3]

In this article we present the results on the Fourier transform infrared (FT-IR) spectroscopic investigation on the micelles of ionic surfactants in organic solvents and the nature of solubilized water in the reversed micellar systems. Infrared spectroscopy is a sensitive method for monitoring the interactions between solutes or between solvents and solutes. Fourier transform technique allows the direct observation of surfactants of low concentrations around critical micelle concentration (cmc) and solubilized water by rapid scan and computation of the difference spectra by subtracting the solvent spectra from those of solutions.

Experimental

DAP was prepared by previously described method[22] and recrystallized from hexane. Hexadecyltrimethylammonium bromide (HTAB) was purified by recrystallization from ethanol–ether, and sodium bis(2-ethylhexyl) 2-sulfonatosuccinate (SBSS) was used as received. All the solvents were of guaranteed grade and used without further purification. Water was solubilized in the surfactant solution by stirring the mixture at room temperature for several minutes and then keeping it standing overnight.

The FT-IR spectra were obtained with a Digilab FT-20C instrument with a 50 μm KRS cell. The spectral resolution was 4 cm^{-1}, and 100 to 1000 scans were accumulated.

Results and Discussion

DAP and HTAB Micelles. The difference spectrum obtained by the subtraction of the dichloromethane spectrum from that of the dichloromethane solution of DAP (15 mM, 1 mM$=10^{-3}$ mol dm^{-3}) exhibits asymmetric and symmetric stretching bands of the carboxylato group around 1580 and 1400 cm^{-1}, respectively. Since the cmc of DAP in dichloromethane obtained by NMR method has been reported to be 27—40 mM,[3] the absorption is considered to be of monomeric DAP dispersed in the solvent. Free carboxylate ions in aqueous solutions have the stretching bands

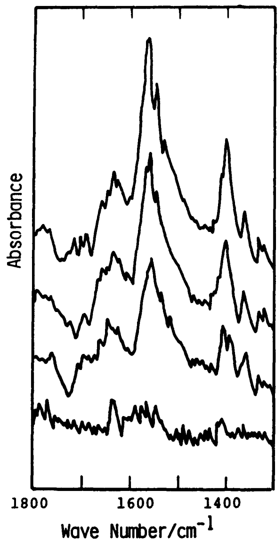

Fig. 1. Difference spectra of DAP in dichloromethane obtained by subtraction of the spectra of 10 mM DAP from those of 20, 30, 40, and 50 mM DAP (from lower to upper). See Ref. 23.

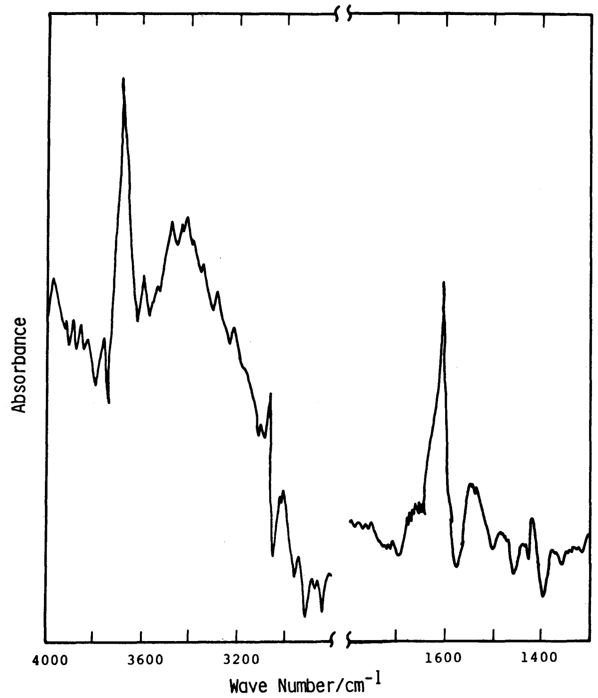

Fig. 2. Difference spectrum obtained by subtraction of the spectrum of anhydrous DAP (50 mM) in dichloromethane from that of the DAP solution of the same concentration containing 200 mM water.

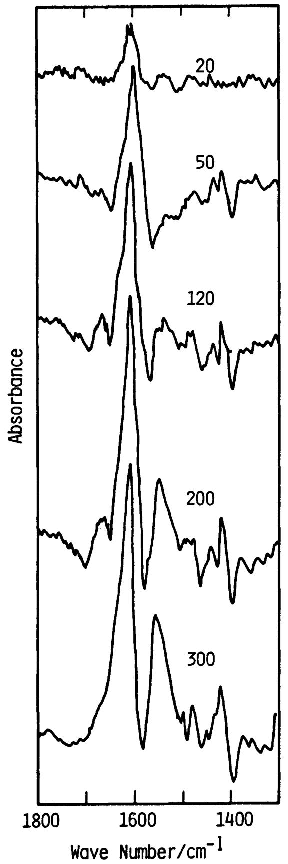

Fig. 3. Difference spectra obtained by subtraction of the spectrum of anhydrous DAP solution (50 mM) in dichloromethane from those of water-containing DAP solutions. Water concentration is indicated in the figure (mM).

around 1550 and 1410 cm^{-1}, and the dispersed DAP is considered to exist as tightly bound ion pairs as suggested by the larger difference between the two stretching bands than free carboxylate ions.

When the concentration of DAP is increased, the carboxylate bands gradually change. The asymmetric band shifts to lower frequencies, while symmetric one shifts to higher frequencies. The change in the spectra is clearly demonstrated by subtracting the spectrum of the solution below cmc from those of the solution above cmc as shown in Fig. 1.[23] With increasing concentration new absorption bands appear around 1550—1570 and 1400—1410 cm^{-1}. These bands are obviously attributed to the formation of DAP aggregates, in which DAP is considered to have more ionic character than monomeric one as suggested by the decrease in the difference between the symmetric and asymmetric stretching bands. The increase in the ionic nature of DAP may be the consequence of the interaction of carboxylato group with two or more ammonium groups. The onset of association seems to fall in the concentration range of 20 to 30 mM, which well agrees with the cmc value obtained by NMR method.[3]

When water was solubilized in a 50 mM DAP solution in dichloromethane, the stretching bands of carboxylate ions shifted in the same direction as that observed in the micelle formation described above. Figure 2 shows the difference spectrum obtained by subtracting the spectrum of DAP–CH_2Cl_2 solution from that of DAP–CH_2Cl_2–H_2O solution. The spectrum exhibits not only the absorption bands of water but also the shift of DAP bands caused by the addition of water. The shift of DAP bands is observed as sigmoid (1550—1570 cm^{-1}) or reversed sigmoid (1400—1410 cm^{-1}) spectra. New DAP bands appear in the regeon closer to that of free carboxylate ions. This may well be understood as a consequence of the formation of water-separated DAP ion pairs due to the hydration of the ionic head groups of the surfactant. The change in the spectra with water concentration is shown in Fig. 3. It is obvious that binding of water to the surfactant occurs even at equimolar concentration of water to DAP.

The spectrum of water saturated in neat dichloromethane exhibited asymmetric (ν_3) and symmetric (ν_1) stretching bands at 3688 and 3600 cm^{-1}, respectively, and bending band (ν_2) at 1604 cm^{-1}. By comparison with this, the sharp absorption bands at 3680, 3600, and 1600 cm^{-1} in Fig. 2 were assigned as that of free water dispersed in bulk organic phase. Since water in gas phase has absorption at 3755, 3654, and 1595 cm^{-1}, while water in liquid phase has absorption at 3430, 3210, and 1650 cm^{-1}, the dispersed water seems to be in a similar state to that in gas phase rather than in liquid phase. The broad bands around 3450 and 1630 cm^{-1} were assigned to the absorption of water bound to DAP micelles. The bands are very close to those of liquid water indicating strong interaction with DAP molecules which is probably a kind of ion-dipole interaction. Although the bands of free and bound water are not fully separated, the competitive solubilization of water seems to occur into the micelles and bulk

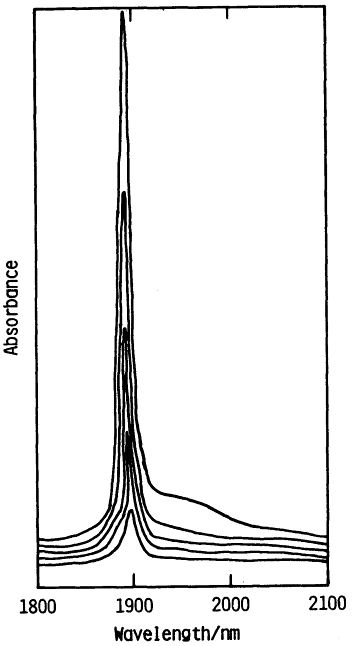

Fig. 4. Near infrared spectra of water-containing DAP solutions (50 mM) in dichloromethane. Water conconcentration is from lower to upper 20, 50, 120, 200, and 300 mM.

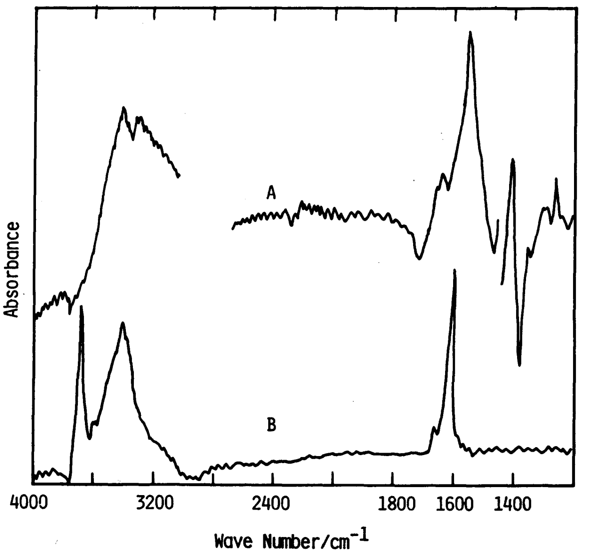

Fig. 5. Spectra of A) water (100 mM) in hexane+DAP (50 mM) and B) water (200 mM) in CH_2Cl_2+HTAB (50 mM).

organic phase.

The existence of free and bound water in this system is confirmed by the near infrared spectra of 1800—2000 nm region due to $\nu_2+\nu_3$ combination mode (Fig. 4). The sharp band at 1890—1900 nm has been ascribed to the free or almost free 1 : 1 complex H–O–H···B in which B denotes a weak base such as dioxane.[24] The position of this band is identical with that of the extremely weakly bonded water in chlorinated hydrocarbons.[24] Furthermore, on the basis of the relationship between the concentration of DAP or waterin chloroform and the absorption intensity of water, the broad band at 1920—1950 nm was assigned towater solubilized in the reversed micelles.[25]

The solution of DAP (50 mM) in hexane afforded a quite similar spectrum to the dichloromethane solution implying the formation of similar kind of DAP aggregates. The shift of the bands of carboxylato group by the addition of water is also quite similar to the dichloromethane solution. In contrast to dichloromethane solution, however, the solubilized water showed no absorption band corresponding to free water (Fig. 5-A), which may be the consequence of low solubility of water in hexane. In addition, the stretching bands of bound water seems to contain lower component around 3300 cm^{-1} than the water in DAP–CH_2Cl_2 system. It has been reported that the cmc of DAP in benzene and cyclohexane is 3—7 mM[1,2] and 1.56 mM,[17] respectively. The lower cmc value in hydrocarbons than dichloromethane[3] or carbon tetrachloride[1,2] implies the formation of more compact and tightly bound aggregates of DAP in hydrocarbons. Although the O–H stretching bands are not well resolved, the band around 3300 cm^{-1} seems to be due to water tightly bound to the ionic head groups of DAP.

In the case of hexadecyltrimethylammonium bromide (HTAB) in dichloromethane, the absorption bands of solubilized water were almost the same as those in DAP–CH_2Cl_2 system (Fig. 5-B), except that the O–H stretching band of bound water appears at slightly lower frequency around 3400 cm^{-1}.

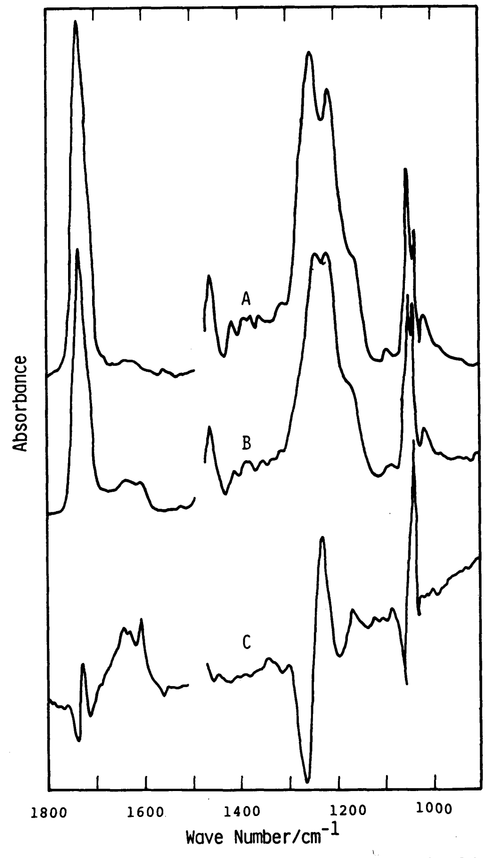

Fig. 6. Spectra of SBSS reversed micelles: A, SBSS 50 mM in benzene; B, SBSS 50 mM+H_2O 100 mM in benzene; C, H_2O 100 mM in (SBSS 50 mM+benzene).

SBSS Micelle. As Fig. 6-A shows the IR spectrum of anionic surfactant SBSS in benzene exhibits SO_3 asymmetric stretching bands at 1252 and 1215 cm^{-1}, and symmetric stretching band at 1050 cm^{-1}. In contrast to DAP in dichloromethane, no effect of the concentration of SBSS on these bands was observed in the range of 2—50 mM. This may indicate the lower cmc of SBSS.

On addition of water, however, distinct change in shape and frequency of SO_3 bands was observed as shown in Fig. 6-B. The change is clearly detected by taking the difference spectrum of solubilized water (Fig. 6-C). The sigmoid spectra around 1250 and 1050 cm^{-1} represent higher shift of 1215 cm^{-1} band and lower shift of 1252 and 1050 cm^{-1} bands due to the hydration of the sulfonato group.

It is interesting to note that the carbonyl band at 1730 cm^{-1} shifts to lower frequency on addition of water as shown in Fig. 6-C. Since the intensity of the new band was found to be almost independent of the water concentration up to 200 mM, the band shift was attributed to the formation of hydrogen bond between the carbonyl oxygen and the water dispersed in bulk benzene phase not in the micelle core. This may be supported by the fact that the bands of water in bulk benzene were observed at 3680 and 1600 cm^{-1}, whose intensity was almost independent of water concentration in the range of 50—200 mM.

TABLE 1. ABSORPTION MAXIMA OF BOUND WATER (cm^{-1}) IN REVERSED MICELLES

Surfactant (Solvent)	IR $\tilde{\nu}/cm^{-1}$	Surfactant (Solvent)	NIR
(H_2O vapor)	3755	(H_2O vapor)	5330
(H_2O in CH_2Cl_2)	3688	(H_2O in CH_2Cl_2)	5280
SBSS (CH_2Cl_2, Benzene)	3500	AOT[a] ($CHCl_3$)	5198[b]
DAP (CH_2Cl_2)	3450	DAP ($CHCl_3$)	5085[b]
HTAB (CH_2Cl_2)	3400	HTAB($CHCl_3$)	5010[b]
DAP (Hexane)	3300		

a) Aerosol-OT. b) From Ref. 8.

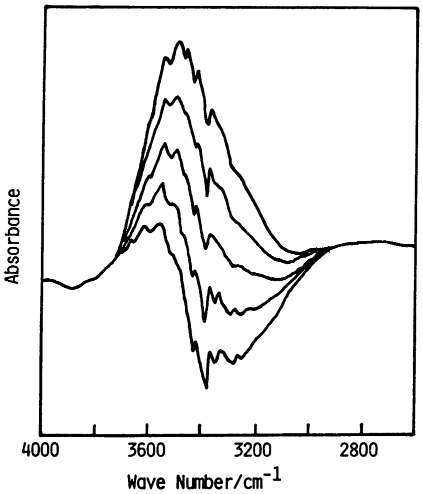

Fig. 7. Difference spectra obtained by subtraction of water spectra from that of 1 M aqueous solution of sodium ethanesulfonate. Scaling factor used in the subtraction is increasing from upper to lower.

O–H Stretching Band of Solubilized Water. The O–H stretching bands of water bound to the micelles are collected in Table 1. Although the spectra are broad and not well resolved, distinct change in the absorption maximum for the different surfactant-solvent system is observed. Assuming that the O–H stretching frequency of the bound water simply reflects the strength of the water-surfactant interaction, the water binding ability of the reversed micelles in dichloromethane is roughly estimated; that is HTAB>DAP>SBSS. The result agrees with that obtained from NIR measurement in chloroform as listed in Table 1.[8)]

In order to obtain better understanding of the interaction of water with surfactants, IR spectra of aqueous solutions of several electrolytes which have analogous structure to the ionic head groups of the surfactants were investigated. As Figs. 7 and 8 show, subtraction of water spectra from those of aqueous solutions of sodium ethanesulfonate or tetrabutylammonium bromide (TBAB) afforded the spectra of water associated with

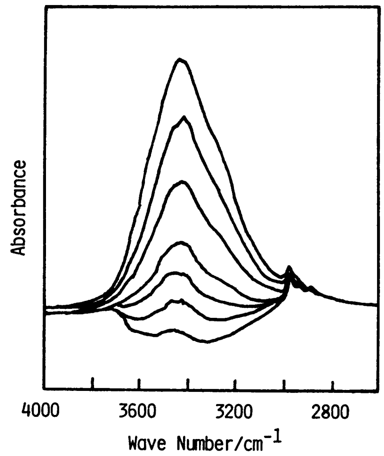

Fig. 8. Difference spectra obtained by subtraction of water spectra from that of 1 M aqueous solution of TBAB. Scaling factor used in the subtraction is increasing from upper to lower.

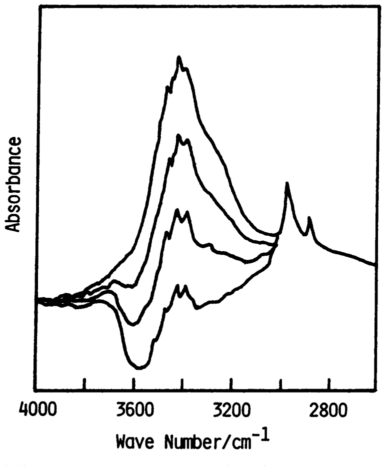

Fig. 9. Difference spectra obtained by subtraction of the spectra of 1 M KBr from that of 1 M TBAB in water. Scaling factor used in the subtraction is increasing from upper to lower.

the electrolytes. It is interesting to note that the maximum frequencies of the bands of water associated with sodium ethanesulfonate and TBAB are close to those in SBSS and HTAB reversed micelles, respectively. This seems to suggest that water in reversed micelles has interaction with ionic head groups of the surfactants like water in the vicinity of electrolytes in aqueous solutions. Further, the difference spectra resulting from the subtraction of the spectra of aqueous sodium bromide solution from that of aqueous TBAB solution allows to estimate approximate frequency of the absorption bands of water associated with sodium and tetrabutylammonium ions, that is around 3560 and 3400 cm^{-1}, respectively. The results indicate that the spectral component of water in HTAB micelles appearing around 3400 cm^{-1} is most likely due to water molecules interacting with ammonium groups. The well established structure-making properties of quaternary ammonium ions may be responsible for the lower shift of O–H stretching band of the water in the reversed micelle core.

Similar technique of difference spectrum has been employed for the study of hydration of ionic species in aqueous solution using the band of HOD near 2500 cm^{-1},[26] and the study on the micelle formation of sodium hexanoate in aqueous solutions.[27]

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