March, 1980] © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **53**, *583—589 (1980)* 583

Microscopic Evaluation of Surfactant–Water Interaction in Apolar Media

Junzo Sunamoto,* Tomiko Hamada, Takafumi Seto, and Shinji Yamamoto
Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852

(Received May 23, 1979)

Under the very limited conditions where the mole ratio of water to surfactant is about unity or so, the tightness of the interaction between various ionic surfactants and water solubilized in apolar media was evaluated using the O–H vibrational mode of water in the near infrared spectral region. Water solubilized in apolar solvents containing surfactant exhibited two absorption bands in the region. One of the two arises from water existing in bulk organic phase and appears around 1900—1910 nm. Another band arises from water bound to surfactant and appears over a range of 1920—2020 nm; it is affected primarily by the ionic head group of surfactant rather than by the counter ion. The cationic surfactants were thought to form more rigid micelles than the zwitterionic or anionic ones. The copper(II) ion cosolubilized in the system hardly altered the O–H vibrational energy of water. The dependence of the near infrared absorption band on water, the chemical shift and line width of water proton resonance in NMR, and the fluorescence intensity of terbium chloride all displayed an inflection at the point where the mole ratio of water to surfactant is about unity. This was interpreted in terms of the two step hydration mechanism.

The term "reversed micelles" describes aggregates of surfactants and polar solutes formed in aprotic media. Although reversed micelles have been investigated intensively, the structure of aggregates remains poorly understood even on the elementary level. Much of the interest in "the aggregates" or "reversed micelles" stems from their use as models of enzyme pockets or cell membranes.

Favorable substrate cosolubilization, orientation, and the unique properties of the system have been proposed to be responsible for the effects on reaction rates, paths, and equilibria occurring in the interior core.[1,2] Aggregates formed in apolar media certainly provide a specific and restricted field. The rigidity-flexibility or hardness-softness of the field is thought to be affected by the kind of surfactants and the amount of water added.[2] Depending on concentrations of surfactant and water added, the tightness of surfactant–water interaction,[2] the size of water pool,[3] the microscopic viscosity[4] and polarity of the interior[5] can be varied over a considerable range. However, the problem of rigidity and tightness of aggregates in conjunction with the structure of surfactants has been not investigated thoroughly thus far. Considering the correlation between the motion of reactants and reaction rates or pathways, we can not discard the problem of the "rigidity" of the reaction field. Certainly, several efforts to rationalize the correlation between the motional freedom and the amount of water added within interior cores have been made through NMR,[4] spin label,[6] and fluorescence studies.[3] However, one has scarecely paid attention to the state and nature of aggregates formed under the very limited condition where the mole ratio of water to surfactant is about unity or less.[7]

Very recently, we found that the configurational change between tetrahedral and octahedral species of cobalt(II) complexes takes place in reversed micelles formed by the several kinds of surfactants.[2] The phenomenon was interpreted in terms of solvochromism and thermochromism which were accompanied by the elimination-addition equilibrium of water between the metal ion and the surfactant.[2] Moreover, it seemed to be certainly connected with the rigidity (or flexibility) of the surfactant–water aggregates. In this work we would like to report the correlation between the structure of surfactants and the tightness of the surfactant-water interaction in apolar media as evaluated using the near infrared O–H vibrational mode of water bound to surfactants. We limited the amount of water to an extremely small extent so that the mole ratio of water to surfactant was about unity or so. It is sure that a portion of water is dispersed in the bulk phase of organic solvent. Of course, the surfactant molecule also may partly exist as the monomeric form in bulk solvent. We do not know, therefore, whether the 1:1 aggregate between water and surfactant in apolar media can be considered as a true reversed micelle.[7]

Experimental

Materials. Surfactants, hexadecyltrimethylammonium bromide (CTAB), dimethyldioctadecylammonium chloride (QD-Cl), egg phosphatidylcholine (EL), dodecylammonium propionate (DAP), and sodium 1,2-bis(2-ethylhexyloxycarbonyl)-1-ethanesulfonate (AOT), were the same as those used in previous studies.[2] 3-(Hexadecyldimethylammonio)-1-propanesulfonate (SB-16:3) was prepared by quarternizing *N*,*N*-dimethylhexadecylamine with propanesultone and purified according to the method described in literature.[8] Hexadecyltrimethylammonium chloride (CTACl) was a gift from Kao Soap Co., Ltd., Tokyo. Sodium dodecylbenzenesulfonate (DBS) was purchased from Wako Pure Chemicals Co., Ltd., Tokyo and purified by recrystallization from benzene prior to the use. Purity of all the surfactants adopted was inspected by TLC or HLC and elemental analysis.

Measurements. All the visible and near infrared spectra were measured on a Hitachi 323 recording spectrophotometer equipped with a thermoregulated cell compartment. NMR studies were run on a JEOL MH-100 spectrometer with TMS as an internal standard. Fluorescence measurements were carried out on a Hitachi 512 fluorospectrometer.

In all runs, the amount of water added was carefully determined every time after the spectroscopic measurements on a Karl-Fischer Moisture Automatic Titration Apparatus Model MK-A (Kyoto Electronics MFG Co., Ltd.) using Karl-Fischer reagent SS "Mitsubishi" (f=0.3 mg/mL) with standard water-methanol solution (f=0.5 mg/mL) for Karl-Fischer reagent, Mitsubishi Chemical Industries Ltd., Tokyo.

Results and Discussion

Near Infrared Spectra of O–H Vibrational Modes. In the near infrared region, water exhibits relatively strong absorption bands due to the ν_2 (scissoring) plus ν_3 (asymmetric stretching) combination mode of vibration.[9] The band observed in vacuum is 5332.0 cm^{-1} (1875 nm) arises from the B_1 species, which corresponds to the band at 5330.6 cm^{-1} (1876 nm) theoretically calculated.[9] This is completely freed from the hydrogen bonding itself. If the water molecule hydrogen-bonds or interacts with other polar molecules or ions, the band will shift toward the lower energy state or the longer wavelength. In pure bulk water the force constant of the O–H bond is compensated owing to the dual character of water as both proton donor and acceptor properties.[10] Bulk water shows, therefore, the band at 5181 cm^{-1} (1930 nm) in the near infrared region. In nonpolar solvents containing ionic surfactants, a part of cosolubilized water locates in the bulk organic phase, where the water molecules are mostly freed from hydrogen bonding themselves, and others interact with the ionic head of surfactant. In the near infrared region, the former exhibits absorption bands around 1900 nm and the latter over a range of 1920—2020 nm.[11,12] Figure 1 shows the near infrared spectra of water in chloroform containing different kinds of surfactant. In chloroform containing anionic surfactants such as AOT or DBS, the position of two bands is close to each other, and at larger amount of water both absorptions overlap to create a broad single band. Intensities of bands in the system containing anionic surfactants are usually stronger than those with zwitterionic and cationic surfactants.

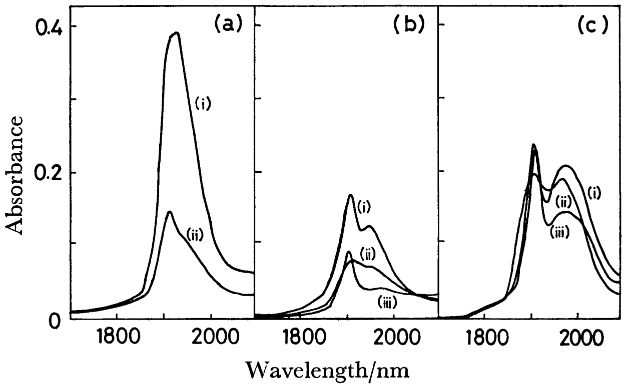

Fig. 1. Near infrared spectra of water solubilized in chloroform containing various kinds of surfactants at 25 °C: (a) anionic surfactants, (i) 0.20 M AOT/0.20 M H_2O and (ii) 0.10 M DBS/0.084 M H_2O; (b) zwitterionic surfactants, (i) 0.040 M SB-16:3/0.037 M H_2O, (ii) 0.045 M EL/0.055 M H_2O, and (iii) 0.20 M DAP/0.20 M H_2O; (c) cationic surfactants, (i) 0.20 M CTACl/0.20 M H_2O, (ii) 0.20 M CATB/0.22 M H_2O, and (iii) 0.20 M QD-Cl/0.18 M H_2O.

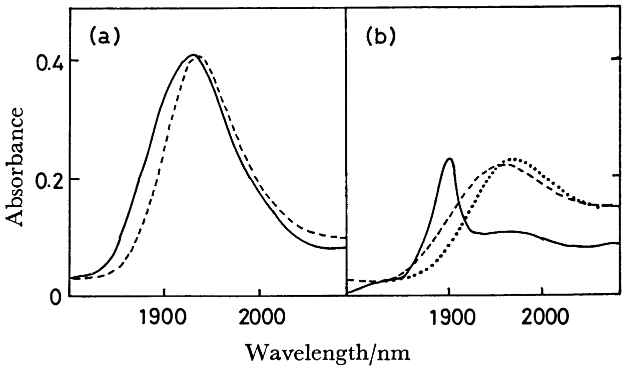

Fig. 2. Effect of bulk solvent on the distribution of water solubilized in apolar solvents containing surfactants at 25 °C: (a) 0.20 M AOT with 0.20 M water in chloroform (——) and 0.20 M AOT with 0.24 M water in carbon tetrachloride (----); (b) 0.20 M DAP with 0.20 M water in chloroform (——), 0.20 M DAP with 0.22 M water in carbon tetrachloride (----), and 0.20 M DAP with 0.22 M water in hexane (······).

Effect of Bulk Solvent. The near infrared spectra of water vary with the bulk solvents as well as the type of surfactants. In chloroform containing surfactants, the O–H vibrational mode in near infrared region separates into two distinct bands as described above. In less polar solvents such as hexane or carbon tetrachloride, only a single absorption band is observable in the corresponding region irrespective of the surfactants (Fig. 2). In hexane containing no surfactants, we could not obtain any reliable spectra because of the extremely low solubility of water in the solvent. Since the dipole moment of the O–H bond depends on the dielectric constant of the field,[13] the intensity of these bands should be affected by the polarity of bulk solvents. Seno and his coworkers also previously observed similar results on the absorption band arising from water dispersed in bulk solvents.[12] That the dipole moment of the O–H bond changes with solvents and/or surfactants means that the quantitative treatment in spectroscopic studies on the system is not feasible.[14] We can, therefore, interpret the data only in a qualitative manner.

Temperature Effect. There exists an equilibrium in the translocation between two different kinds of water existing in bulk solvents and bound to surfactants. Increasing temperature causes a decrease in intensity of the band arising from water bound to surfactants with a concomitant increase in the intensity of the absorption of water in the solvent phase (Fig. 3). A temperature increase enhances the mobility of water bound to surfactants, resulting in easier dispersion into the bulk organic phase. The result coincides with that previously observed on the thermochromism of the cobalt(II) complexes in the reversed micelles.[2]

Effect of Cosolubilized Metal Ion. The energy states of the O–H vibration in three different surfactant systems, AOT, DAP, and CTAB, with or without the copper(II) ion were determined as a function of added water (Fig. 4). The configuration of the copper(II) complexes in reversed micelles is drastically affected by the kind of surfactants and the amount of water present.[2,15] On the other hand, the O–H vibrational energy of water is not so significantly affected by cosolubilizing the copper(II) ion. In three sur-

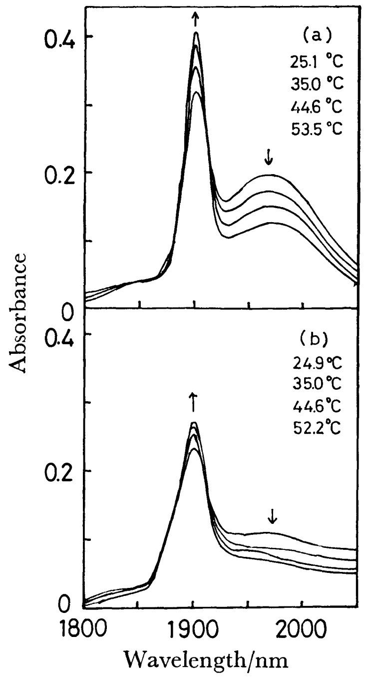

Fig. 3. The near infrared spectra of 0.20 M water solubilized in chloroform containing 0.20 M CTAB (a) and 0.20 M DAP (b) at different temperatures.

factant systems, the energy state of the O–H bond of water changed as a function of water content, giving an inflection around the point where the mole ratio of water to surfactant is about unity. The addition of the metal(II) ion is expected to force water molecules into the interior core of reversed micelles from the bulk phase.[16] However, a concomitant increase of water bound to surfactants was not observed. Because of low solubility of the metal salt under the adopted conditions, it was impossible to cosolubilize more salts. Very recently, we reported solvochromisms of the cobalt(II)[2] and copper(II)[15] complexes in reversed micellar systems, where the configurational change between T_d and O_h takes place when water is added to the system. The present result coincides with those obtained for both the solvochromism of the metal(II) ions[2,15] and the hydrolysis of an amino acid ester as promoted by the copper(II) ion in the AOT/CCl_4 reversed micelles.[15,17]

Effect of Water Content and Tightness of Surfactant–Water Interaction. The interaction of water and various surfactants in apolar media was examined as a function of water amount added using the O–H vibrational modes in the near infrared region (Fig. 5). If water located in bulk solvents were completely free from any interactions with other polar or ionic molecules, the O–H vibrational mode of the water molecule would be identical irrespective of surfactants and/or bulk solvents. Since the band under consideration is affected a little by surfactants, however, the state and nature of water molecules in bulk phase seem to be altered by the solubility of surfactants in the bulk solvent and the polarity of the bulk phase (Fig. 5(b)). On the other hand, the vibrational energy of the O–H bond of water interacting with surfactants depends largely on the head group structure of surfactants (Figs. 1 and 5(a)). If the argument is limited to a series of surfactants under the same conditions, then it is reasonable to postulate that the shift in frequency of the O–H vibration reflects the relative strength of the interaction between water and surfactants.[18] Therefore, we can regard the difference ($\Delta\lambda$) between the theoretically calculated and observed wavelength as a semiquantitative parameter measuring the tightness of the interaction between water and other molecules under consideration:

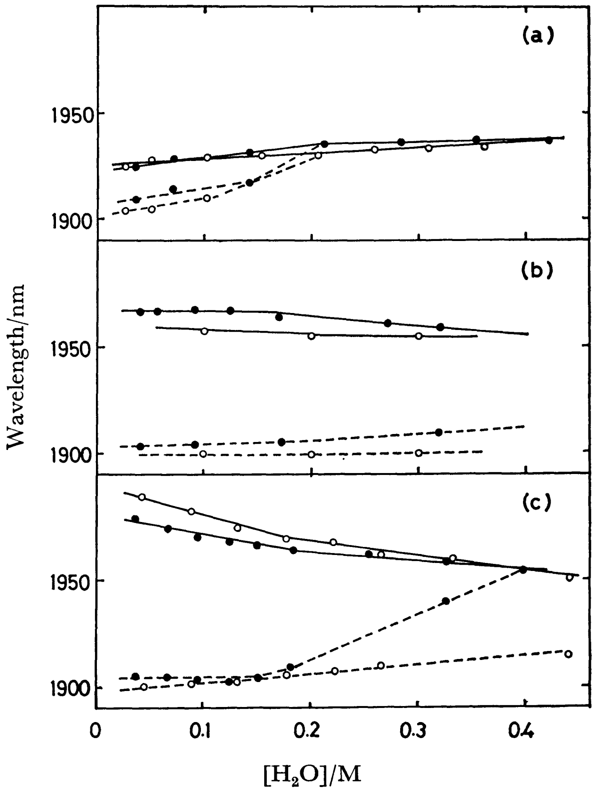

Fig. 4. Effect of the Cu(II)-ion on the near infrared absorption bands of water solubilized in three different surfactants/chloroform system as a function of water added at 25 °C: (a) 0.20 M AOT in chloroform without Cu(II) ion (○) and with 4.6×10^{-4} M Cu(II) ion (●); (b) 0.20M DAP in chloroform without Cu(II) ion (○) and with 2.7×10^{-3} M Cu(II) ion (●); (c) 0.20 M CTAB in chlorofrom without Cu(II) ion (○) and with 5.9×10^{-4} M Cu(II) ion (●). The copper(II) ion was cosolubilized as the aqueous nitrate in all the systems. Solid lines are absorption bands of water bound to surfactant, while broken lines are those of water existing in bulk organic solvent.

$$\Delta\lambda = \lambda_0 - 1876\ (\text{nm}), \qquad (1)$$

where λ_0 stands for the intrinsic absorption band which is graphically estimated, using data given in Fig. 5, by extrapolating the observed wavelength to the point where the mole ratio of water to surfactant is zero. Results are summarized in Table 1.

In dried apolar media, ionic surfactants will exist as intimate ion pairs. The interaction between water and surfactants, therefore, looks like a dipole-dipole interaction, especially under very limited conditions

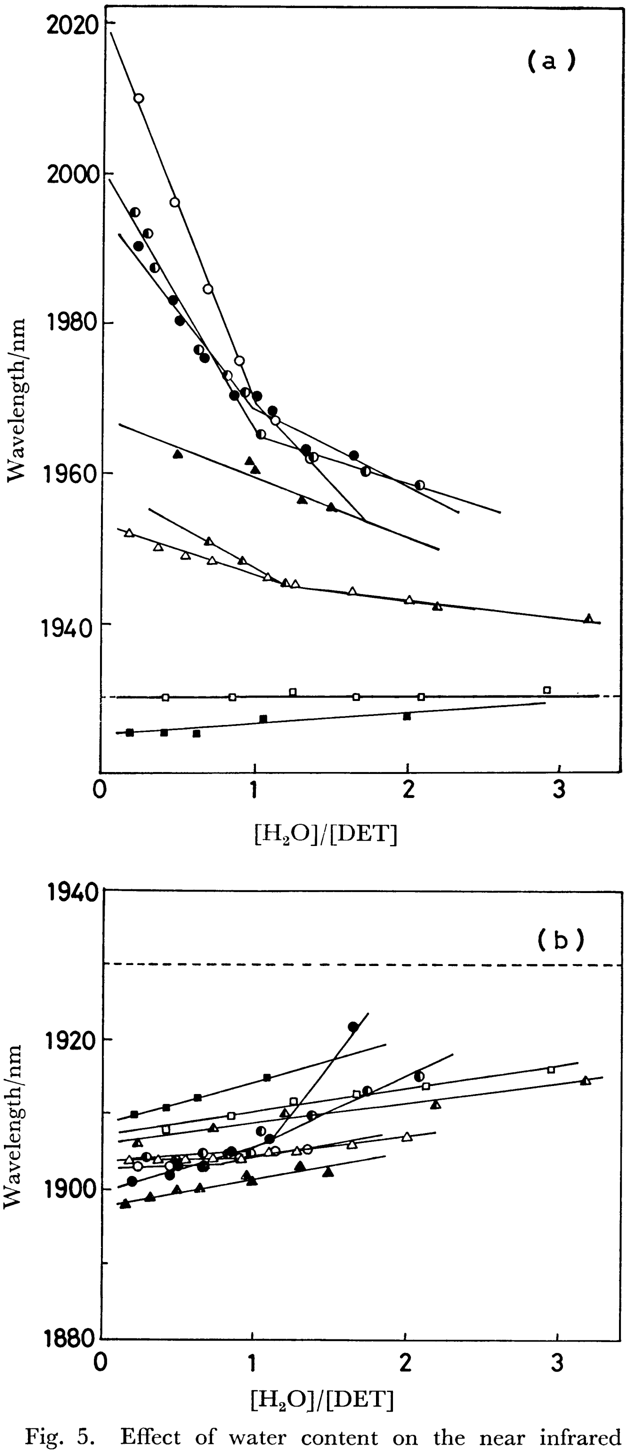

Fig. 5. Effect of water content on the near infrared spectra of water solubilized in chloroform containing various surfactants: (a) the absorption band of water bound to surfactants and (b) the absorption band of free water locating in bulk chloroform containing various surfactants; QD-Cl (○), CTACl (◐), CTAB (●), DAP (▲), EL (◭), SB-16:3 (△), DBS (□), and AOT (■). A broken line in (b) stands for the position of the absorption band of pure water (1930 nm).

TABLE 1. INTRINSIC ABSORPTION BANDS OF FREE WATER LOCATING IN BULK CHLOROFORM AND WATER BOUND TO VARIOUS SURFACTANTS IN THE NEAR INFRARED REGION AT 25 °C a)

Surfactant	Free water		Bound water		$\Delta\lambda_{0,(\mathrm{b-f})}$ b)
	$\lambda_{0,\mathrm{f}}$	$\Delta\lambda_{\mathrm{f}}$ c)	$\lambda_{0,\mathrm{b}}$	$\Delta\lambda_{\mathrm{b}}$ c)	
AOT	1908	32	1924	48	16
DBS	1907	31	1930	54	23
SB-16:3	1904	28	1953	77	49
EL	1906	30	1962	86	56
DAP	1897	21	1967	91	70
CTAB	1901	25	1996	120	95
CTACl	1903	27	2000	124	97
QD-Cl	1903	27	2020	144	117

a) Intrinsic absorption bands were graphically estimated using data given in Fig. 5 (see text). b) Difference between $\lambda_{0,\mathrm{f}}$ and $\lambda_{0,\mathrm{b}}$. Subscripts, f and b, refer to free water and water bound to surfactants, respectively. c) Calculated using Eq. 1.

where the mole ratio of water to surfactants is unity or less. It is of interest to clarify which ion species, the ion head group of surfactants or the counter ion, predominantly affects the interaction with water. Seno and his coworkers deduced that the carboxylato group in the DAP reversed micelles predominantly interacts with water from the shift of stretching frequency of carbonyl group as a function of water added.12) If this is the case, water interacting with QD-Cl and CTACl must exhibit the absorption band at the same wavelength because both surfactants bear same counter anion, Cl$^-$. Furthermore, water interacting with AOT and DBS also will show the same absorption band since both surfactants bear the sulfonato group and sodium ion. Contrary to what would be expected, water interacting with CTACl in chloroform behaves similarly to that interacting with CTAB rather than QD-Cl. Water interacting with AOT exhibits different bands from those interacting with DBS. These results suggest that in apolar media the ion head of surfactant molecules, in spite of being more bulky, predominantly affects the force constant of the O–H bond of water. In order to secure more information of this point, we prepared hexadecylammonium chloride, sulfate, and perchlorate, sodium dihexadecyl phosphate, and potassium salts of anionic surfactants and tried to investigate the effect of small counter ions. Unfortunately, we were unable to utilize these surfactants owing to their diminished solubility in the usual apolar solvents.

Results given in Table 1 and Fig. 5 suggest to us that the tightness of interaction of water with surfactants in apolar media can be roughly classified into three categories depending on the head group structure of surfactants. CTAB, CTACl, and QD-Cl belong to the first category. Of surfactants adopted in this work, these cationic surfactants shift the O–H vibrational energy of the bound water most largely toward the lower energy state (longer wavelength). This means that these cationic surfactants interact tightly with water to reduce the force constant of the O–H bond of water and seem to form the most rigid reversed micelles. The second category includes DAP, EL, and SB-16:3. On the basis of the near infrared data,

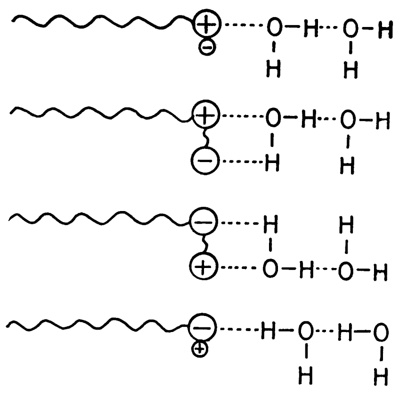

Fig. 6. Schematic representation of the mode of the interaction between water and surfactant in apolar media. From top to bottom, interactions of water with cationic surfactant, two different kinds of zwitterionic surfactants, and the anionic surfactant are shown, respectively.

DAP behaves as a zwitterionic surfactant rather than as cationic or anionic one. The anionic surfactants, AOT and DBS, belong to the different category from above two kinds of surfactants. The anionic surfactants seem to form the softest reversed micelles with water. These three distinct modes of the interaction between water and surfactants are represented schematically in Fig. 6. Assuming that in apolar media water predominantly interacts with the head group of surfactants, the interaction with the anionic surfactants is essentially hydrogen bonding,[19] while that with the cationic ones is the coordination type. In fact, water interacting with the anionic surfactants exhibits the band at the wavelength very close to that of pure bulk water. For the zwitterionic surfactants, two distinct types of interaction will compensate with each other. The difference in the absorption bands between the free water and water bound to surfactants, $\Delta\lambda_{b-f}$, decreases as one goes from cationic to zwitterionic and to anionic surfactant. The larger difference in the energy state between both state of water suggests a greater difficulty in the translocation of water between both states. This means that the surfactant-water aggregate under the circumstances may be relatively rigid. The hypothesis is not inconsistent with results obtained in previous studies on the solvochromism and the thermochromism of the cobalt(II) complexes in reversed micelles.[2] Both bands of free water and water bound to surfactants seem to approach the value of pure bulk water (1930 nm) as increasing the amount of water added (Fig. 5).[19] The state and nature of water in the cationic and the zwitterionic systems drastically change in the region where the mole ratio of water to surfactant is less than unity. The shift of absorption bands as a function of water content reveals an inflection point, where the $[H_2O]/[\text{surfactant}]$ ratio is about unity. The absorption bands of water bound to the cationic and the zwitterionic surfactants shift from the longer wavelength toward the shorter wavelength with increasing the amount of water, while the corresponding bands of the anionic surfactants move in the opposite direction. This reveals that between the cationic and anionic surfactant–water aggregates the nature of interaction of water with surfactants is different.

Evidences for the Two Step Hydration Mechanism. NMR of Water Interacting with Cationic Surfactant in Apolar Media: The chemical shift of the water proton in deuterochloroform containing CTAB was determined as a function of water amount added (Fig. 7 (b)). Over the range of water concentration examined, signals from methyl and methylene protons on the alkyl chain did not move, while *N*-methyl proton signal shifted a little toward the higher magnetic field with an inflection at the point of $[H_2O]/[CTAB] \fallingdotseq 1$. The proton signal of water moved substantially to the lower magnetic field with increasing water content, and again the inflection point appeared around the point where the mole ratio of water to CTAB is nearly unity. Increasing the water content in the system produces more hydrogen bonding between water molecules and causes the paramagnetic shift of the proton signal. The chemical shift of the water proton under consideration seems to finally reach the value of pure water ($\delta = 4.66$ ppm). Extrapolating the chemical shift to the point where the water content is zero gives 2.80 ppm. Water in deuterochloroform containing no surfactants shows a signal at 1.96 ppm. Interaction of the oxygen atom of water with the strongly electronegative cation-head of CTAB causes, therefore, a deshielding effect on the hydrogen atom of water molecule, resulting in the down-field shift of the proton signal. In contrast to the near infrared spectra, only one signal of water proton was observed by NMR. This means that the life time of both water protons, located in bulk phase and interacting with surfactant, is faster than the NMR time scale. In case of the phosphatidylcholine/diethyl ether micelles[20] and the AOT/heptane micelles,[4a] over a range where the mole ratio of water to surfactants is larger than 2, the line width of water proton resonance in NMR decreased as increasing the amount of water. Contrary to previous findings in the anionic and zwitterionic systems,[4a,20] in the present cationic system increasing water broadens the line width (Fig. 7 (a)). Again, we would like to note that the mode of interaction of water with cationic surfactants is different from that with anionic surfactants.

In the present system two possibilities must be considered to elucidate the broadening of the water proton signal: the viscosity of the medium and the proton exchange between free water and water bound to CTAB. Increased viscosity generally leads to line broadening by increasing the correlation time. In the reversed micellar system, in fact, adding a very little amount of water increases the macroscopic viscosity of the medium despite the decrease of the microscopic viscosity in the interior core.[21] Therefore, we can not eliminate the first possibility in interpreting our line broadening. Protons of water interacting with surfactants would have a shorter transversed relaxation time, T_2, than free water protons located in the bulk phase. When the rate of proton exchange between free water and the bound water is sufficiently

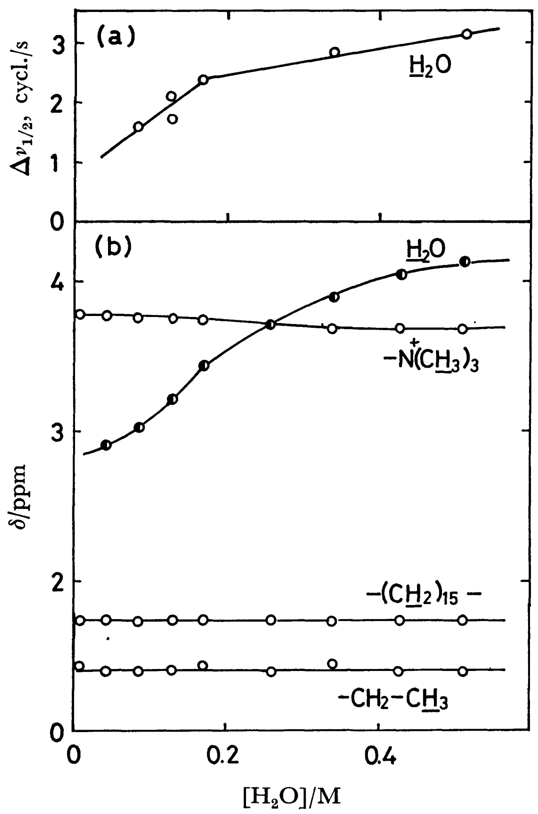

Fig. 7. NMR studies on the interaction of water with 0.20 M CTAB in deuterochloroform as a function of water content at 25 °C: (a) the line width of water proton signal at halfpeak height and (b) chemical shifts of proton signals of water, choline methyl, methylene, and terminal methyl, respectively.

great compared with the reciprocal of the relaxation time, the apparent line width ($\nu_{1/2}=1/T_2$) can be written as

$$1/T_2 = x_f(1/T_2)_f + x_b(1/T_2)_b, \qquad (2)$$

where x is the mole fraction and the subscripts f and b refer to the free and bound water, respectively.[22] Since it is reasonable to assume that $(1/T_2)_b \ll (1/T_2)_f$, the line width will be affected mostly by water bound to surfactants. Increasing the hydrogen bonding of water very probably diminishes the mobility of water molecules and will cause the further line broadening of water proton signals. Anyway, the correlation between the mobility of water bound to surfactant and the strength of interaction of water and surfactant can be discussed only about the same ionic series of surfactants.

Fluorescence Intensity of Tb(III) in DAP Reversed Micelles: The fluorescence emission from the excited Tb^{3+} is strongly quenched in aqueous solution.[23] Removing some of water molecules from its hydration shell tends to enhance the fluorescence emission.[23] We found a significant enhancement of the fluorescence emission from the Tb^{3+}-ion when the concentrated aqueous solution of $TbCl_3$ was cosolubilized in hexane containing DAP. The relative fluorescence intensity decreased with increasing water content and an obvious inflection point was again observed where the mole ratio of water to DAP was about unity. Through the investigation of the state and nature of water interacting with surfactants in apolar media, we always observe an obvious inflection at the point where the mole ratio of water to surfactant is about unity. This is true for the O–H vibrational energy of water molecules in the near infrared spectra, the chemical shift and line width of water proton signal in the NMR, and the fluorescence intensity of terbium chloride. The most plausible explanation is a two step hydration mechanism.[2,15,17,20] When water is first introduced into the specific system, water tends to interact with surfactants irrespective of the presence of other polar or ionic solutes. Upon completion of the first hydration on the surfactants, water molecules start to interact with themselves by the hydrogen bonding or binding to other polar solutes cosolubilized in the interior core. Results obtained in this work coincide with those obtained in previous studies: the solvochromism of the metal(II) ion,[2,15] the hydrolysis of an amino acid ester as promoted by the copper(II) ion in the AOT/CCl_4 reversed micelles,[15,17] and the general acid-base catalysis of DAP on the hydrolysis of alkyl aryl carbonates in apolar media.[24]

We might conclude that in a very restricted field formed by reversed micelles or surfactant-water aggregates the situation closely resembles the hydrophobic pocket of enzymes or biomembranes. And also that the O–H vibrational modes of water in the near infrared region as well as the chemical shift and/or the line width of water proton resonance in NMR[4,20] can give an useful information on the tightness of the interaction of water with polar or ionic groups in the hydrophobic domain.

Professor Fredric M. Menger, Department of Chemistry, Emory University, is profoundly thanked for his reading through the manuscript and beneficial discussion. We are also grateful to Professor Syozaburo Takekiyo, Nagasaki University, for his comments.

References

1) (a) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press, New York (1975); (b) J. H. Fendler, *Acc. Chem. Res.*, **9**, 153 (1976); (c) J. Sunamoto and H. Kondo, *Yukagaku*, **26**, 389 (1977).

2) J. Sunamoto and T. Hamada, *Bull. Chem. Soc. Jpn.*, **51**, 3130 (1978).

3) M. Wong, J. K. Thomas, and M. Grätzel, *J. Am. Chem. Soc.*, **98**, 2391 (1976).

4) (a) M. Wong, J. K. Thomas, and T. Nowak, *J. Am. Chem. Soc.*, **99**, 4730 (1977); (b) K. Tsujii, J. Sunamoto, and J. H. Fendler, presented a paper at the National Meeting of Chemical Society of Japan, Tokyo, April, 1977.

5) F. M. Menger and G. Saito, *J. Am. Chem. Soc.*, **100**, 4376 (1978).

6) F. M. Menger, G. Saito, G. V. Sanzero, and J. R. Dodd, *J. Am. Chem. Soc.*, **97**, 909 (1975).

7) H. F. Eicke and H. Christen, *Helv. Chim. Acta*, **61**, 2258 (1978).

8) E. J. Fendler, C. L. Day, and J. H. Fendler, *J. Phys. Chem.*, **76**, 1460 (1972).

9) G. Herzberg, "Molecular Spectra and Molecular Structure, II, Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand Reinhold Co., New York (1945), pp. 280—282.

10) S. Lewin, "Displacement of Water and Its Control of Biochemical Reaction," Academic Press, New York (1974).

11) O. D. Bonner and Y. S. Choi, *J. Phys. Chem.*, **78**, 1723 (1974).

12) M. Seno, K. Araki, and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, **49**, 899 (1976).

13) A. B. F. Duncan, "Technique of Organic Chemistry, Vol. IX, Chemical Application of Spectroscopy," ed by A. Weissberger, Interscience Publisher, Inc., New York (1956), Chap. III, pp. 187—245.

14) It is difficult to obtain independently the correct molecular coefficients of both absorption bands arisen respectively from water locating in the bulk solvent phase and water bound to surfactants. Therefore, it seems impossible to discuss the equilibrium or the rate of translocation between both water species.

15) J. Sunamoto and T. Hamada, "Fundamental Research in Homogeneous Catalysis," ed by M. Tsutsui, Plenum Publishing Corporation, New York (1979), Vol. 3, p. 809.

16) S. G. Frank, Y. Shaw, and N. C. Li, *J. Phys. Chem.*, **77**, 238 (1973).

17) J. Sunamoto, H. Kondo, and K. Akimaru, *Chem. Lett.*, **1978**, 821.

18) E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961).

19) G. Zundel, "Hydration and Intermolecular Interaction," Academic Press, New York (1969).

20) M. A. Wells, *Biochemistry*, **13**, 4937 (1974).

21) ^{13}C-Spin lattice relaxation time, T_1, of glycine cosolubilized in the DAP/benzene reversed micelles increased as increasing the amount of water added, suggesting the decrease microscopic viscosity around the glycine molecule by increasing water content in the interior core: K. Tsujii, J. Sunamoto, and J. H. Fendler, unpublished results.[4b)]

22) D. E. Gordon, B. Curnutte, Jr., and K. G. Lark, *J. Mol. Biol.*, **13**, 571 (1965).

23) H. F. Eicke, J. C. W. Shepherd, and A. Steinemann, *J. Colloid Interface Sci.*, **56**, 168 (1976).

24) H. Kondo, K. Fujiki, and J. Sunamoto, *J. Org. Chem.*, **43**, 3584 (1978).