Observation of water in reverse micelles of ionic and nonionic surfactants by using near infrared spectroscopy

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Introduction

A reverse micelle is an aggregate of surfactant molecules formed in a nonpolar solvent (Figure 1). The main interest in reverse micelles comes from their ability to encapsulate water in their core and disperse them into nonpolar solvents.[1] Since the inner diameter of the core is only a few nanometers, the behavior of water in the core might be different from that of bulk water. Their cores are used under various situations, including extraction of proteins, reaction fields and others.[2–3] As a consequence, reverse micelles have been investigated by various methods.[4–7]

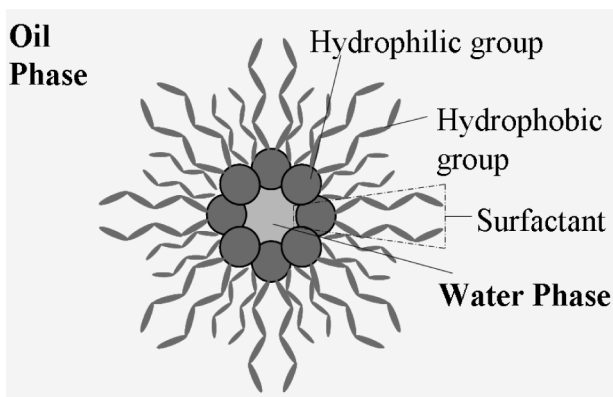

Figure 1. A schematic picture of a reverse micelle.

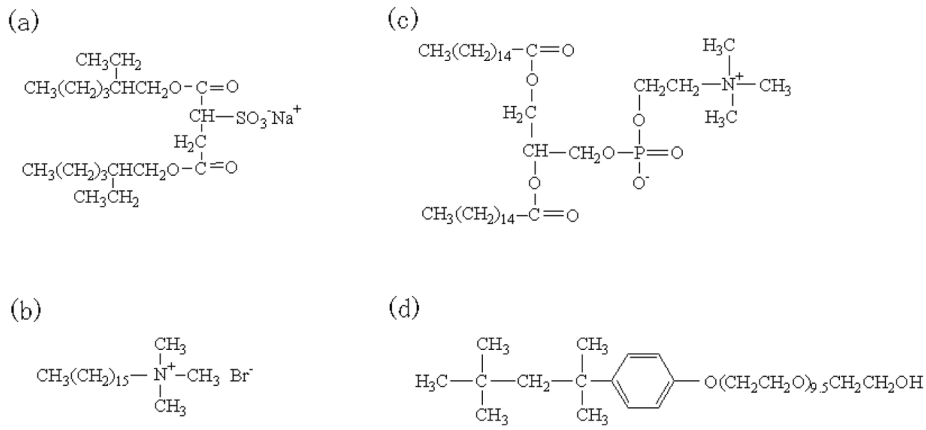

Figure 2. Chemical structure of (a) AOT (b) CTAB (c) lecithin and (d) TX-100 system.

Surfactants forming the micelles can be classified according to the electronic charge that originates when they are dissociated in water. Nonionic surfactants have no charge in their head groups, while the head groups of ionic surfactants carry the net charge. This paper reports hydrogen bonding states of water in reverse micelles in ternary systems of AOT (di-2-ethylhexyl Sodium Sulfosuccinate; anionic)/H_2O/CCl_4, CTAB (cetyltrimethylammonium bromide; cationic)/ H_2O/$CHCl_3$, TX-100 (polyoxyethylene *tert*-octylphenyl ether; nonionic)/H_2O/cyclohexane and lecithin(zwitterionic)/H_2O/isooctane by using NIR spectroscopy. Chemical structures of the four surfactants are shown in Figure 2.

Materials and methods

AOT, CTAB, lecithin, TX-100, carbon tetrachloride, chloroform, cyclohexane and isooctane were purchased from Wako Pure Chemical Industries, Ltd. Ultra pure water (the electric resistivity ratio: 18.2 MΩ·cm) was prepared by using PURELAB ultra (Organo, Japan). The NIR spectra were recorded by a Spectrum One NTS (PerkinElmer, the U. S.) FT-NIR spectrometer equipped with a homemade temperature-controlled water jacket, by using a quartz cell with a 1 mm-path length. All the spectra were recorded at 25°C with different ratios of water, $w = [H_2O]/[\text{surfactant}]$. The raw spectra of the solutions were subtracted by the raw spectrum of the surfactants to eliminate the peaks due to CH vibrations overlapping with the OH band of water. For comparison of spectral shapes, all the spectra were normalised at the peak maxima.

Results and discussion

Figure 3 shows normalised NIR spectra of water in the four reverse micelles with different *w*.

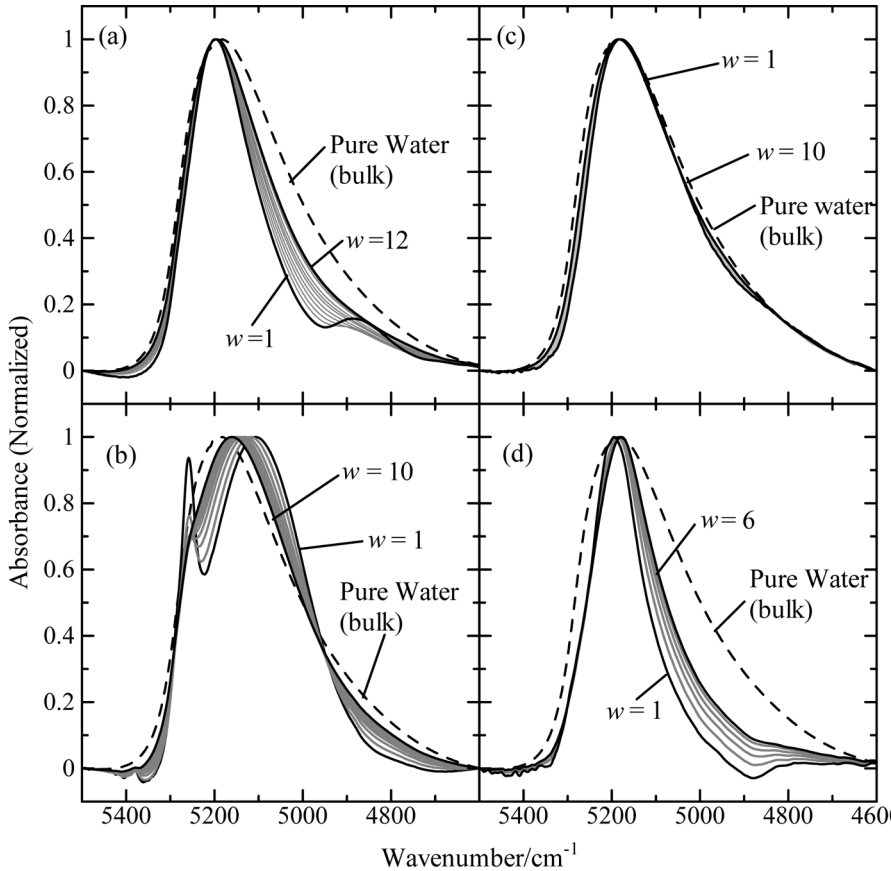

Figure 3. Normalised spectra of water in reverse micelle systems of (a) AOT (b) CTAB (c) lecithin and (d) TX-100 with different water ratios, *w*. The dashed lines indicate spectra of bulk water.

The NIR spectra of water in reverse micelles are given by subtraction of the $w=0$, when the $w=0$ solution contains surfactants and oil only. The broad band observed in the 5500–4600 cm^{-1} region is assigned to the combination of H-O-H stretching and bending vibrations of water. This figure indicates that the hydrogen bonding states of water in each reverse micelle are different from that of bulk water. There are characteristic differences among the four systems. AOT (a) and TX-100 (d) systems show a narrower band than that of bulk water. This narrowing indicates that diversity of hydrogen bonding states has been limited due to the confined nano-space inside the reverse micelles. In the CTAB system (b), two splitting peaks are clearly observed. A sharp peak at about 5265 cm^{-1} may be due to relatively free species. Since an H-O-H band observed in a low wavenumber is generally due to strongly hydrogen-bonded species, the broad band at 5100 cm^{-1} suggests that hydrogen bonds of water especially in the CATB reverse micelles are strengthened. The hydrogen bonding states of the water encapsulated in lecithin micelles (c) is similar to that of bulk water. Moreover, Figures 3(a)–(d) indicate that the water molecules in each reverse micelle

are gradually released from the confined condition and approach bulk water with increasing of the size of the micelles.

Conclusions

The NIR spectra of encapsulated water in the core of AOT, CTAB, TX-100 and lecithin reverse micelles show characteristic spectra. The results indicate that the behaviour of hydrogen bonding of water in the reverse micelle is affected by the hydrophilic group of each surfactant. In all of the systems, with an increase in the ratio of water, the hydrogen bonding state in the reverse micelle approaches that of bulk water. In the AOT and TX-100 system, hydrogen bonding states have been limited, due to the confined nano-space inside the reverse micelles. However, the band in the TX-100 system is sharper than that in the AOT system. This indicates that the negative ion of the hydrophilic group weakens hydrogen bonds. In the CTAB system, encapsulated water obviously has both weak and strong hydrogen-bonded species. The weak hydrogen bond species are due to isolated water pushed against the hydrophobic trimethylammonium group of CTAB. On the other hand, the strong hydrogen bond species may be due to confined water in the nano space at the center of the micelles. In the lecithin system, hydrogen bonding is similar to that of bulk water, although the amount of water is very small in the system. This indicates that the cation and anion compensate each other and make hydrogen bonded water similar to bulk water.

References

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