NOTE

Effect of D₂O Solvent on the Micellization Behavior of 2-Hydroxy-1,1,2,3,3-pentahydroperfluoroundecyldiethylammonium Halides

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Abstract: Solvent isotope effects on the micellization behavior of fluorosurfactants have been investigated. The critical micelle concentration and the micelle ionization degree for 2-hydroxy-1,1,2,3,3-pentahydroperfluoroundecyldiethylammonium halides in D₂O were lower than those in H₂O. The stronger hydrogen bonding in D₂O enhanced the micelle growth accompanying counterion binding.

Key words: solvent isotope effect, fluorosurfactant, fluorescence probe, critical micelle concentration, micelle ionization degree

1 Introduction

The hydrophobic interaction related to hydrogen bonding plays an important role in micelle formation of surfactants. The solvent effect of D₂O on micellization has been investigated by conductivity, light scattering, and SANS measurements (1-3). Several physical properties of D₂O are significantly different from those of H₂O. The length of the hydrogen bonds in D₂O (2.766 Å) and H₂O (2.765 Å) are essentially identical, while the energy of a hydrogen bond in D₂O is 0.24 kcal/mol, which is about 5% larger than that in H₂O (4). D₂O is a more structured solvent than H₂O as judged from the higher temperature of maximum density in D₂O. The stronger hydrogen bonding in D₂O leads to the lower cmc and larger micelle size. The effects on micelles increases with increasing chain length of the surfactant

owing to the increased hydrophobic interaction in D₂O.

2 Experimental

2.1 Materials

6-Methoxy-N-(3-sulfopropyl)quinolinium (SPQ) and pyrene were purchased from Molecular Probes, Inc., and Aldrich, respectively, and used without purifications. n-Hexadecylpyridinium chloride (CPC) was obtained from Tokyo Kasei Kogyo Co., Ltd. and was purified by the repeated recrystallization from acetone-ethanol mixtures. 1,1,2,2-Tetrahydroheptadecafluorodecylpyridinium chloride (HFDePC), 1,1,2,2-Tetrahydroheptadecafluorodecylpyridinium bromide (HFDePB), 2-hydroxy-1,1,2,3,3-pentahydroperfluoroundecyldiethylammonium chloride (FC₈DAC) and 2-hydroxy-1,1,2,3,3-pentahydroperfluoroundecyldiethylammonium

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bromide (FC₈DAB) were prepared as reported previously (5). Fluorosurfactants were purified by the repeated recrystallization from acetone.

2.2 Measurements

The 1.0×10^{-6} M SPQ probe aqueous solutions were made up in doubly distilled water. The fluorescence intensities of surfactant solutions were measured at 440 nm by the excitation at 345 nm using a Hitachi F-2000 spectrophotometer. The fluorescence intensity without quencher (I_0) was used as a standard. The fluorescence spectra of 1.0×10^{-7} M pyrene were measured with scanning from 350 nm to 450 nm by the excitation at 335 nm using Hitachi F-3010 spectrometer. The ratio of first and third peaks has a value of 1.88 in water. All experiments were performed at 25°C.

3 Results and Discussion

The cmc of surfactant has been estimated by the abrupt changes in the fluorescence spectrum or yield of selected probes upon micelle formation (6). The halide sensitive fluorescence probe, 6-methoxy-N-(3-sulfo-propyl)quinolinium (SPQ), provides a direct approach for measurement of halide concentrations dissociated from the surfactant (7). When the fluorescence intensity of SPQ is measured as a function of surfactant concentration, the variation of fluorescence intensity is related to the concentration of quencher [Q], $I_0/I = 1 + K_{SV}[Q]$, where I_0 and I are the fluorescence intensities in the absence and presence of quencher, respectively, and K_{SV} is the Stern-Volmer constant.

As shown in **Fig. 1**, the fluorescence of SPQ is quenched by chloride ions with a linear Stern-Volmer relation below the cmc of FC₈DAC. Since the quenching occurs by the collision of SPQ with chloride ions,

Fig. 1 Stern-Volmer Plots of SPQ Fluorescence Quenching in H₂O and D₂O.

the slope below the cmc in D₂O was smaller than that in H₂O because the viscosity of D₂O is 23% higher than that of H₂O at 25°C (4). The Stern-Volmer plot gave a distinct break at the cmc owing to the binding of chloride counterion to the micelles. The slope above the cmc in D₂O was significantly smaller than that in H₂O. The micelle ionization degree, α , was taken as the ratio of the values of K_{SV} above and below the cmc. **Table 1** shows the cmc and α values for cationic surfactants with both chloride and bromide as counterion. The cmc value of CPC decreased to some extent in D₂O, while that of HFDePC remained almost constant. The solvent isotope effect was virtually abolished in small micelles such as HFDePC. This finding is in accord with the finding that the effect increases with alkyl chain length for alkyltrimethylammonium micelles (2), and that no

Table 1 Cmc and Micelle Ionization Degree from the SPQ Fluorescence Quenching Method at 25°C.

surfactant	CMC (mM)		α	
	H ₂ O	D ₂ O	H ₂ O	D ₂ O
C ₁₆ H ₃₃ NC ₅ H ₅ Cl (CPC)	1.10	0.95	0.32	0.28
C ₈ F ₁₇ CH ₂ CH ₂ NC ₅ H ₅ Cl (HFDePC)	2.70	2.69	0.34	0.36
C ₈ F ₁₇ CH ₂ CH ₂ NC ₅ H ₅ Br (HFDePB)	2.06	1.95	0.23	0.19
C ₈ F ₁₇ CH ₂ CHOHCH ₂ NH(C ₂ H ₅) ₂ Cl (FC ₈ DAC)	2.20	1.66	0.28	0.18
C ₈ F ₁₇ CH ₂ CHOHCH ₂ NH(C ₂ H ₅) ₂ Br (FC ₈ DAB)	1.85	1.43	0.18	0.09

isotope effect was observed for octyl- β -malto-pyranoside (8), while a significant effect was observed for nonyl- β -D-glucoside (9). A lower degree of water penetration between the headgroups is suggested for larger micelles. We note that some decrease in the values for HFDePB was observed in D₂O probably owing to the lower degree of water penetration with bromide ion binding. The largest solvent isotope effects were observed for perfluoroundecyldiethylammonium halides. Almost 25% decrease in cmc was observed for FC₈DAC as well as FC₈DAB. The α values were significantly decreased in D₂O suggesting larger micelles.

Fluorosurfactants are prone to form large aggregates of low curvatures when the electrostatic repulsion of the headgroups is suppressed (10,11). They exhibit a tendency to form cylindrical or threadlike micelles as a result of the larger molecular volume as well as the greater rigidity compared to hydrocarbon surfactants. We previously reported that FC₈DAC surfactants self-assemble into vesicles with the addition of salt (5). The large aggregates can be expected to lead to significant differences in solvent isotope effect. Pyrene fluorescence has been widely used for the determination of micelle micropolarity using the ratio of the intensity of the first and third vibronic peaks (12). The I_1/I_3 ratio in D₂O was 1.98 in contrast to 1.88 in H₂O, suggesting that the high solvent polarity may originate from the stronger hydrogen bonding between D₂O molecules. We measured the I_1/I_3 ratios as a function of surfactant concentration. The cmc is usually found at the inflection point of the decrease in the I_1/I_3 ratio (13). However, no inflection point was observed upon micelle formation of FC₈DAC or FC₈DAB.

Thus the fluorescence intensities of pyrene were plotted against concentration as shown in **Fig. 2**. The I_3 values were almost constant below the cmc. The I_3 values increased above the cmc of FC₈DAB in D₂O, whereas they decreased around the cmc in H₂O and then slightly increased above the cmc. Since bromide counterions are known to act as quenchers of pyrene fluorescence, the increases in I_3 values suggest the solubilization of pyrene into the micelles. The solubilization site has been shown to interact with ammonium head groups (14). The observed high micropolarity suggests that the location of pyrene will be close to the micelle surface, but pyrene molecule can penetrate into the palisade layer which contains hydroxy group in the FC₈DAB for D₂O system as judged by the increase in I_3 values.

Fig. 2 Variations of Pyrene Fluorescence Intensities in H₂O and D₂O.
Note that pyrene concentration in D₂O was 1.6 times that in H₂O (1×10^{-7} M).

4 Conclusion

As compared with perfluorodecylpyridinium halides, perfluoroundecyldiethylammonium halides self-assemble into larger aggregates owing to the stronger binding of counterions. The large aggregates having lower curvature will result in significantly stronger deuterium isotope effects. The micellar counterion binding was confirmed to be larger in D₂O than in H₂O. Chou *et al.* reported a lower dissociation degree of the surfactant headgroups in D₂O owing to the difference in hydration degree of D₂O and H₂O (15). The hydration of surfactant ions and counterions is likely to affect the packing of surfactant monomers at the aggregate surface. Thus the aggregates comprised of perfluoroundecyldiethylammonium halides were thoroughly dehydrated at the palisade layer in D₂O. It was anticipated that the hydrogen bonding between hydroxy groups of perfluoroundecyldiethylammonium molecules would be enhanced in D₂O. The hydrogen bonding is expected to decrease the area per headgroup. That is to say, perfluoroundecyldiethylammonium halides are prone to form large aggregates of low curvatures.

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