Surface Polyfluorinated Micelles

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Three novel polyfluorinated cationic surfactants and the corresponding three hydrocarbon analogues were synthesized. All of the surfactants formed globular micelles in water. The micellar formation was monitored by five independent methods. The results of the NMR measurements and the other four methods using the anionic dye Rose Bengal (RB) and anilinonaphthalenesulfonic acid as probe molecules agreed well with each other. The polyfluorinated micelles had rather low cmc values, on the order of 10^{-5} M. All of the micelles had similar aggregation numbers around 50−60. Using a detailed NMR relaxation study following addition of paramagnetic Mn^{2+} ions to the bulk water phase, the polyfluorinated micelles were shown to have a very unique microstructure with the perfluoroalkyl chain extending straightforwardly to the bulk water phase. The micropolarity around the ammonium group and the microviscosity in the core of the micelles were estimated using the probe molecules RB and perylene. The local oxygen concentration in the micelles was estimated from the NMR longitudinal relaxation time T_1. The microstructure of water distributed within the micelles is discussed with relation to the observed local oxygen concentration. The rigidity of the micelle is also discussed using the mobility of each nuclei estimated from the T_1 data. The unique protecting effect of the micelles against attack by hydroxide radicals generated in the bulk water phase using Fenton's method was examined using a bleaching reaction of RB as a probe molecule. The surface polyfluorinated micelles exhibited a greater protective effect than either CTAB or the hydrocarbon analogue surfactant micelles. This protective effect is discussed in relation to the unique microstructure of the surface polyfluorinated micelles.

Introduction

Perfluorocarbon, in which all the hydrogen atoms of hydrocarbon are substituted with fluorine atoms, is well-known to form an individual phase upon mixing with water or hydrocarbons owing to its strong hydrophobicity and lipophobicity.[1] Organic polyfluorinated compounds generally have very weak intermolecular interactions with other molecules.[1−3] When they are used as solvent for a chemical reaction, it is thought that solute−solute intermolecular interactions should be relatively strengthened as compared to those in an ordinary solvent, because the solute−solvent interactions should be minimized in a polyfluorinated solvent. In addition to the strong hydrophobicity and lipophobicity, they have the very interesting characteristics of high resistance to oxidation and high solvation of gases as compared to hydrocarbons.[1−3] A polyfluorinated environment, thus, would provide a very unique chemical reaction field.

Amphiphilic compounds having both a hydrophobic group, such as a long alkyl chain, and a hydrophilic one, such as an ammonium group and a carboxylic acid, are well-known to form molecular assemblies such as micelles and vesicles in water.[4] The introduction of a perfluorinated alkyl group into an amphiphilic compound should strongly affect the behavior of the forming molecular assemblies. A surfactant molecule having a short polyfluorinated alkyl chain and a long hydrocarbon chain at both terminal ends of a polar group might form a two-layered molecular assembly in water, having both fluorocarbon and hydrocarbon phases. Utilizing these points, we synthesized novel cationic ammonium surfactants having a short polyfluorinated alkyl chain and a long hydrocarbon chain. We report here that in water these surfactants form surface polyfluorinated micelles as the first examples having very unique microstructures with the polyfluorinated alkyl groups stretching their chains straightforwardly to the bulk water phase.

Results and Discussions

Synthesis of Cationic Polyfluorinated Surfactants. Three kinds of novel polyfluorinated cationic ammonium surfactants with different chain lengths were synthesized according to the Scheme 1. Three corresponding hydrocarbon analogues were also synthesized. *N,N*-Dimethylethylenediamine was treated with perfluoroacyl chloride to form the amide derivative **I**. After the deprotonation of **I**, quaternization with hexadecyl bromide gave the surfactant. According to the chain length of the acyl group, the polyfluorinated surfactants were named C1F-S, C2F-S, and C3F-S. The corresponding hydrocarbon analogue were named C1H-S, C2H-S, and C3H-S. In C*n*F-S and C*n*H-S, the *n*, F, H, and S denote the number of carbons in the acyl group, polyfluorinated surfactant, hydrocarbon analogue, and surfactant type with a single long alkyl chain, respectively.

Micelle Formation. *Critical Micellar Concentration.* When a surfactant with a single long alkyl chain is dispersed in water, micellar formation is generally observed above a critical concentration of the surfactant.[4] Micellar formation and the critical micellar concentration (cmc) are often denoted by drastic changes in the physical properties of a probe molecule sensitive to the microenvironment, i.e., polarity, viscosity, water concentration, etc. Rose Bengal (RB) and 8-anilinonaphthalene-

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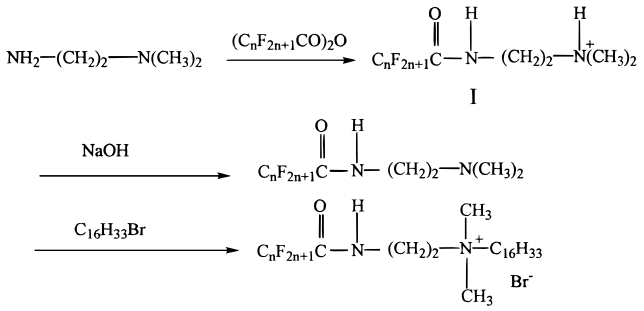
SCHEME 1



sulfonic acid (ANS) were adopted here as probes for micellar formation and the cmc. The λ_{max} of the absorption spectrum of Rose Bengal is sensitive to solvent polarity. The fluorescence polarity measurement of Rose Bengal upon excitation by polarized light reflects the microviscosity of environment. The λ_{max} of the fluorescence spectrum of ANS is also sensitive to solvent polarity.[5,6] The fluorescence intensity of ANS is very sensitive to water concentration; ANS is almost nonfluorescent in aqueous media, while it has a strong fluorescence in a nonaqueous environment.[5,6] By observation of the four independent physical properties, λ_{max} and fluorescence polarity of RB and λ_{max} and fluorescence intensity of ANS, the micellar formation of the six surfactants synthesized here was studied and their cmc's were determined. A well-known cationic surfactant, cetyltrimethylammonium bromide (CTAB), was also studied as a reference.[7] In each case, all four physical properties dramatically changed above a certain surfactant concentration. The concentration of both the RB and ANS probe molecules was fixed at 1×10^{-6} M. When the anionic RB was added to a surfactant aqueous solution with a concentration less than ca. 1×10^{-5} M, an ion association complex with the cationic surfactant precipitated. Above a concentration of 1×10^{-5} M, RB was solubilized with the λ_{max} shifting to blue. The cmc of the surfactant was denoted by the dramatic change of λ_{max}. The fluorescence polarity of RB, upon excitation by polarized light, rapidly increased with increasing surfactant concentration up to a constant value above the critical concentration. The rapid increase in the fluorescence polarity suggests that the viscosity of the microenvironment surrounding RB increases with micellar formation. The fluorescence intensity of ANS also dramatically increased above the critical concentration as anticipated. This strongly suggests that ANS undergoes a dramatic change of its microenvironment from an hydrophilic one to an hydrophobic one. Water molecules surrounding ANS are thought to be excluded upon micellar formation. The λ_{max} of fluorescence exhibited a blue-shifting, which was used to determine the cmc. The cmc's were also measured by observing changes in chemical shifts in ^{1}H NMR without the addition of a probe molecule. The signal from the N$-$CH$_3$ group exhibited the largest shift among the surfactant protons. It shifted to a lower magnetic field position with increasing surfactant concentration. The cmc's were determined from a plot of the changes in the chemical shifts. The obtained cmc's are listed for comparison in Table 1.

The cmc's for the polyfluorinated surfactants, C*n*F-S, were very low on the order of 10^{-5} M. The hydrocarbon analogues, C*n*H-S, had higher values than the polyfluorinated ones but lower than that for CTAB. Very interestingly, the surfactants having a longer acyl group had a lower cmc value among both the polyfluorinated C*n*F-S and C*n*H-S groups. The cmc values follow the order CTAB > C1H-S > C2H-S > C3H-S > C1F-S > C2F-S > C3F-S. The order of the cmc values supposedly

TABLE 1: Cmc (M) of the Polyfluorinated Surfactants C*n*F-S and Hydrocarbon-Type Ones C*n*H-S

surfactant	λ_{max}(RB)[a]	λ_{max}(ANS)[b]	F_p(RB)[c]	I_f(ANS)[d]	NMR
C1F-S	5.2×10^{-5}	3.0×10^{-5}	1.0×10^{-4}	1.3×10^{-4}	8.3×10^{-5}
C2F-S	3.4×10^{-5}	3.2×10^{-5}	6.1×10^{-5}	1.0×10^{-4}	5.9×10^{-5}
C3F-S	2.1×10^{-5}	1.1×10^{-5}	4.4×10^{-5}	2.5×10^{-5}	4.4×10^{-5}
C1H-S	2.0×10^{-4}				
C2H-S	1.7×10^{-4}				
C3H-S	1.1×10^{-4}				
CTAB	2.3×10^{-4}	3.2×10^{-4}	8.0×10^{-4}	9.5×10^{-4}	

[a] Estimated from the λ_{max} of absorption of Rose Bengal. [b] Estimated from the λ_{max} of fluorescence of 8-anilononaphthalenesulfonic acid. [c] Estimated from the fluorescence polarity of Rose Bengal. [d] Estimated from the fluorescence intensity of 8-anilinonaphthalenesulfonic acid.

TABLE 2: Aggregation Number of the Polyfluorinated C*n*F-S Micelles and the Hydrocarbon-Type C*n*H-S Micelles

	micelle						
	C1F-S	C2F-S	C3F-S	C1H-S	C2H-S	C3H-S	CTAB
aggregation no.	48 ± 5	48 ± 5	52 ± 5	61 ± 6	57 ± 6	58 ± 6	54 ± 5

correlates closely with the microstructure of each micelle, as described later. The cmc values obtained by the NMR method were in good agreement with those from the fluorescence polarity measurement of RB and the fluorescence intensity method of ANS. The obtained value for CTAB was in good agreement with that reported in the literature.[7] The λ_{max} methods for absorption in RB and fluorescence of ANS were responsible for the slightly lower values. As described above, RB forms an ion association complex below the cmc, and the λ_{max} method may reflect a premicellar region. The good agreement between data for the NMR method and the probe method indicates that the small amounts of a probe molecule added to the system do not seriously affect micellar formation. Every micelle studied here has an aggregation number around 50$-$60, as described later. The low probe molecule concentration (1×10^{-6} M) relative to the cmc for each surfactant (greater than 2×10^{-5} M (C3F-S)) indicates that 2.5 probe molecules, at most, are solubilized in one micelle of C3F-S at the cmc. In other surfactants, less than one probe molecule is solubilized in one micelle.

Aggregation Number. The aggregation number of each micelle was estimated by the dynamic analysis of the fluorescence decay of pyrene used as a probe molecule, as proposed by Atik et al.[8] When less than one molecule of pyrene is solubilized in one micelle, only monomer fluorescence of pyrene is observed. A characteristic excimer emission is observed in addition to the monomer fluorescence, if the micelle has more than one molecule of pyrene. Assuming a Poisson statistical distribution of pyrene in the micelles, a dynamic analysis of the fluorescence decay affords the aggregation number of the micelle. The obtained aggregation numbers are listed for comparison in Table 2.

The aggregation number of the CTAB micelle used as a reference was also estimated by the pyrene method. The value determined, 54 ± 5, agrees well with the literature value of 61.[7] All of the surfactants form micelles with the aggregation numbers of 50$-$60, similar to that of the CTAB micelle. These results strongly suggest that all of the micelles have a globular structure like that observed for the CTAB micelle.[9]

Microstructure of the Micelle. *Polyfluorinated Micelle.* If the micelle is globular as suggested by the aggregation number, the long alkyl chains of the surfactant undoubtedly form the inner core of the micelle. But a simple question arises here

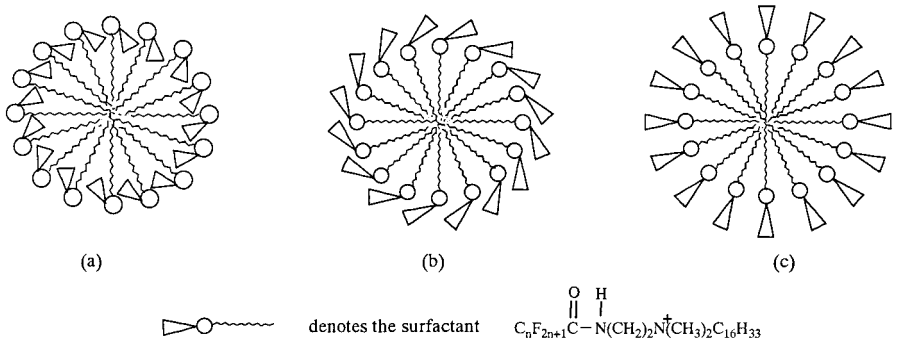


Figure 1. Possible microstructure of the micelle.

regarding the microscopic structure of the micelle, especially the orientation of the perfluoroalkyl group. Perfluoroalkane is well-known to have both very hydrophobic and lipophobic characteristics.[1−3] The perfluoroalkyl group of a C*n*F-S surfactant should try to escape from both the inner long alkyl group and the bulk water phase. How do they orient themselves in the surface area of the micelle? Speculation regarding the assumption of a globular micelle leads to the following three models for the possible microstructure of the micelle, shown schematically in Figure 1.

Figure 1a represents a micelle where the perfluoroalkyl groups are bent into the inner core. In Figure 1b, the perfluoroalkyl groups are bent to cover the surface of the micelle, while in Figure 1c the perfluoroalkyl chains extend their arms straightforward to the bulk water phase.[10] To elucidate the microstructure, we adopted an NMR relaxation method.[11,12] Paramagnetic Mn^{2+} ions in the form of $MnSO_4$ were added to the bulk water phase, and the longitudinal relaxation time (T_1) of each nuclear spin was observed by the inversion recovery method. The effect of the Mn^{2+} ions on T_1 was systematically studied. The longitudinal relaxation from the excited state in NMR is well-known to be strongly enhanced by a paramagnetic species.[13] The relaxation mechanism involves a magnetic dipole−dipole interaction in the Hamiltonian. The rate constant of the relaxation induced by a paramagnetic species is inversely proportional to the sixth power of the internuclear distance.[14] The effect of a paramagnetic species is, thus, very sensitive to the distance; only the nearest nucleus to the paramagnetic species should suffer an enhanced relaxation. When Mn^{2+} ions are added to the micellar aqueous solution, the paramagnetic effect on T_1 should occur with the nuclei located on the surface and facing the bulk water phase, because Mn^{2+} should be in the water phase. If the micelle has a microstructure as in Figure 1a, the *N*-methyl proton should suffer the paramagnetic effect, while the ^{19}F of the perfluoroalkyl group should not. In the microstructure of Figure 1b, both the *N*-methyl protons and all of the fluorine nuclei of the perfluoroalkyl group should be affected by Mn^{2+}, because they are all exposed to the bulk water phase. The microstructure in Figure 1c has a straight perfluoroalkyl chain facing the water phase, and only the terminal trifluoromethyl fluorine nuclei should be affected. Very interesting results were obtained. The T_1 decreased upon addition of Mn^{2+} ions. As a control experiment, the effect of a nonparamagnetic ionic species, Zn^{2+},[15] was also studied, but no effect was observed. The enhanced effect using Mn^{2+} clearly indicates that it is the result of the paramagnetic character of the Mn^{2+} ion. In Figure 2 the reciprocal of T_1 for the *N*-methyl protons of the CTAB micelle versus the concentration of added Mn^{2+} ions is plotted.

A good linear relation is observed. The reciprocal of T_1 represents the relaxation rate constant. The straight line can be represented by the relationship in eq 1, where k_d and k_q denote

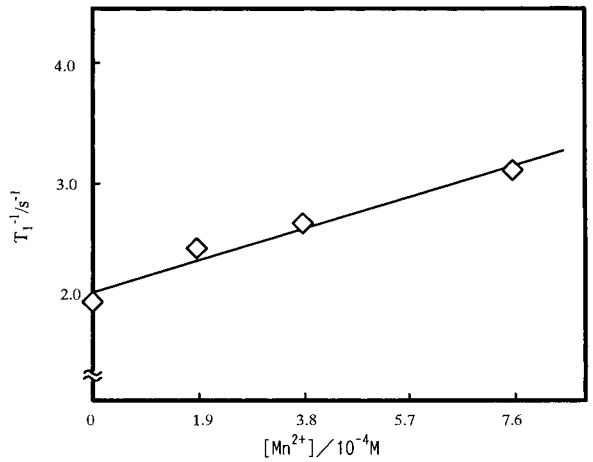


Figure 2. Effect of Mn^{2+} on the longitudinal relaxation time (T_1) of the *N*-methyl protons of the CTAB micelle under aerated conditions at 23 °C with [CTAB] = 2×10^{-3} M.

$$1/T_1 = k_d + k_q[Mn^{2+}] \quad (1)$$

the inherent relaxation rate constant without Mn^{2+} and the rate constant induced by the paramagnetic Mn^{2+} ion, respectively. The results are quite reasonable, because the *N*-methyl groups of CTAB are directly exposed to the bulk water phase. On the other hand, the polyfluorinated C*n*F-S micelles had almost no effect on the relaxation time of the *N*-methyl protons. This clearly indicates that the *N*-methyl groups in the C*n*F-S micelles are not exposed to the water phase. Further interesting results were obtained as shown in Figures 3 and 4.

The T_1 of the terminal trifluoromethyl fluorine nuclei were substantially affected by the Mn^{2+} ions in all of the C1F-S, C2F-S, and C3F-S micelles (Figure 3), while the fluorine nuclei in the α position relative to the amide carbonyl group in the C2F-S and C3F-S micelles were unaffected (Figure 4). All these results clearly indicate that the C*n*F-S micelles have a microstructure like that in Figure 1c, where the perfluoroalkyl chains extend their arms straightforwardly to the bulk water phase. In the microstructure, it could be said that a perfluoroalkyl layer forms on the surface area of the micelle. These C*n*F-S micelles could thus be called "surface polyfluorinated micelles" as the first examples. A simple question then arises again about this very unique micelle microstructure. Why do the polyfluorinated surfactants form such structures? Molecular assemblies such as micelles and vesicles are thought to form via a delicate free-energy balance stabilized or destabilized by hydrophilic and hydrophobic intermolecular interactions.[4] The strong hydrophobic and lipophobic characteristics of the perfluoroalkyl group suggest that the microstructure shown in Figure 1a is rather unstable, because the perfluoroalkyl groups are fully exposed to the lipid environment within the inner core of the micelle.

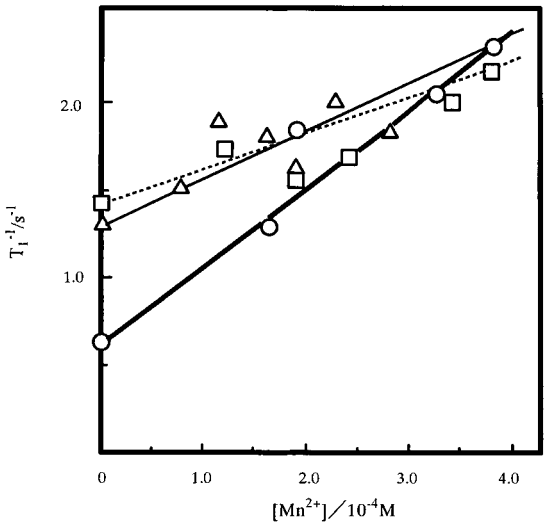


Figure 3. Effect of Mn^{2+} on the longitudinal relaxation time (T_1) of the terminal trifluoromethyl ^{19}F nuclei of the C1F-S (○), C2F-S (△), and C3F-S (□) micelles under aerated conditions at 23 °C with [C*n*F-S] = 2×10^{-3} M.

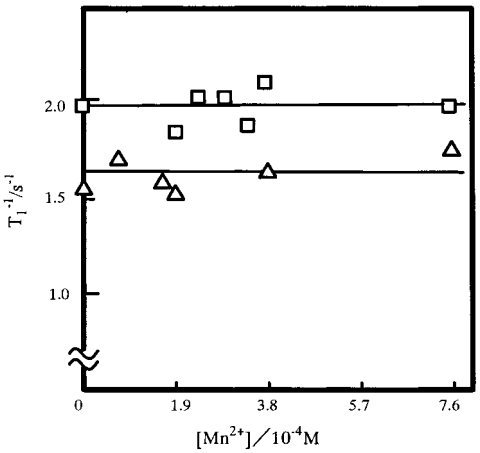


Figure 4. Effect of Mn^{2+} on the longitudinal relaxation time (T_1) of the difluoromethylene ^{19}F nuclei in the α position to the carbonyl group of the C2F-S (△) and C3F-S (□) micelles under aerated conditions at 23 °C with [C*n*F-S] = 2×10^{-3} M.

With the structure in Figure 1b, a destabilization by the lipophobic character of the perfluoroalkyl group would be avoided, but the group is fully exposed to the water phase which also leads to a large destabilization. On the other hand, the microstructure in Figure 1c minimizes the area exposed to both the water phase and the inner core alkyl group enough to be sufficiently stabilized. Therefore among the three possible microstructures for the C*n*F-S micelles, the structure in Figure 1c is thermodynamically the most stable one. Using the plot in Figure 3 and eq 1, the rate constant k_q, induced by Mn^{2+} for the terminal trifluoromethyl fluorine, can be calculated for C1F-S [$(4.3 \pm 2.3) \times 10^4$ M^{-1} s^{-1}], C2F-S [$(2.3 \pm 1.9) \times 10^4$ M^{-1} s^{-1}], and C3F-S [$(1.6 \pm 1.2) \times 10^4$ M^{-1} s^{-1}]. Since the same magnetic relaxation mechanism is thought to operate among the C*n*F-S micelles, a larger k_q indicates a closer distance to the paramagnetic Mn^{2+} ion in the water phase. Thus, the terminal trifluoromethyl fluorine atom in the C1F-S micelle is the most closely facing to the bulk water phase. Since the magnetic relaxation is inversely proportional to the sixth power of the internuclear distance, the relative distances between the water phase and the terminal fluorine atom, normalized to the C1F-S micelle, can be estimated as the sixth root of 4.3×10^4 (C1F-S)/2.3×10^4 (C2F-S) = 1.1 and the sixth root of 4.3×10^4 (C1F-S)/1.6×10^4 (C3F-S) = 1.2. The surfaces of the C2F-S and C3F-S micelles are 10% and 20% more distant from the bulk water phase as compared to C1F-S, respectively. The difference may be due to the stronger hydrophobicity of the longer perfluoroalkyl group. This suggests that the perfluoroalkyl layer in the C3F-S micelle has a strongly hydrophobic character, which is suggestive for designing a perfluoroalkyl layer as a chemical reaction field.

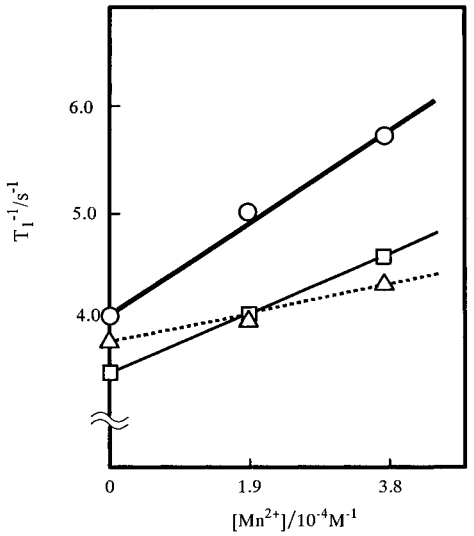


Figure 5. Effect of Mn^{2+} on the longitudinal relaxation time (T_1) of the protons in the *N*-methyl group (○), the terminal acetyl group (□), and the methylene group of the long alkyl chain (△) for the C1H-S micelle under aerated conditions at 23 °C with [C1F-S] = 2×10^{-3} M.

Hydrocarbon-Type Micelles. The microstructures of micelles formed by the hydrocarbon surfactant analogues C1H-S, C2H-S, and C3H-S were also studied by the NMR relaxation method. The effect of Mn^{2+} addition on the relaxation time T_1 was observed. The results for the C1H-S micelle, as a typical example, are shown in Figure 5.

The magnetic relaxation was greatly enhanced in the *N*-methyl protons by the addition of Mn^{2+} ions. Very interestingly, the terminal acetyl protons and even the methylene protons in the long alkyl chain suffered enhanced relaxation by Mn^{2+}, though to a smaller extent. Similar effects were also observed for the C2H-S and C3H-S micelles. These results clearly indicate that all of the protons in the *N*-methyl group, the terminal methyl of the acyl group, and even the methylene are exposed to the water phase. The microstructure which best explains the results is that in Figure 1a, where the short chain acylamide groups are dug into the inner core of the micelle. Since the acylamide group is penetrating the core of the micelle, it induces a lower degree of packing of the surfactant on the surface, accompanied by the incorporation of water into the inner core of the micelle. The microstructure can be rationalized by the lipophilic interaction between the acylamide group and the long alkyl chain.

Microenvironment. The polyfluorinated surfactants C*n*F-S form very interesting surface polyfluorinated micelles as stated above. Using such micelles, especially the surface polyfluorinated area, as novel chemical reaction fields requires a detailed knowledge of the microenvironment. Therefore we examined its micropolarity and microviscosity and the local concentration of oxygen.

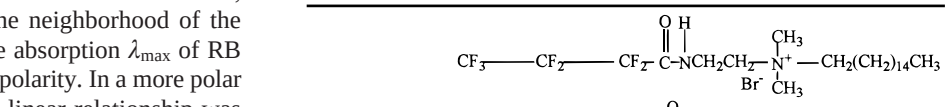
Micropolarity. The anionic dye RB (1×10^{-6} M) was used for probing the micropolarity of the surface polyfluorinated micelles (surfactant concentration: 2×10^{-3} M). As stated above, RB forms an ion association complex which precipitates

below the cmc of the surfactants. The anionic RB supposedly associates with the ammonium groups in the surfactants and, thus, is thought to be solubilized in the neighborhood of the ammonium groups in the micelles. The absorption λ_{max} of RB is well-known to depend on the solvent polarity. In a more polar solvent λ_{max} shifts to the blue. A good linear relationship was observed between the λ_{max} for RB and Lippert−Mataga's solvent parameter P ($\epsilon - 1/\epsilon + 2$).[16−19] Pyridine ($\epsilon$: 12.91), 1-butanol (17.51), 2-propanol (19.92), acetone (20.56), ethanol (24.55), methanol (32.66), and water (78.39)[20] were used for calibrating the relationship. From the λ_{max} for RB in each of the surface polyfluorinated micelles and the calibration graph, the micropolarities in the vicinity of the ammonium groups of the micelles were estimated to be $\epsilon = 21$ for C1F-S, 24 for C2F-S, and 24 for C3F-S. The micropolarity for the CTAB micelle was also examined as a reference and found to be $\epsilon = 20$. The micropolarities determined correspond to those for acetone (C1F-S) and ethanol (C2F-S, C3F-S). The surface polyfluorinated micelles had a polar microenvironment around the ammonium group, similar to that of the CTAB micelle. These results are interesting from the viewpoint of the microstructure of the micelles. As deduced from the model in Figure 1c, the ammonium groups are buried inside of the surface polyfluorinated micelles and are thought to be isolated from the bulk water phase. The micropolarities, however, indicate that the ammonium groups are somewhat exposed to the water as in the CTAB micelle. The micropolarities are closely correlated with the microscopic distribution of water in the micelles estimated from the local oxygen concentration, as described below.

Microviscosity. The microviscosity of the inner core of the surface polyfluorinated micelles was determined from fluorescence polarity measurements using perylene as a probe molecule. Perylene (3×10^{-6} M) was solubilized in the C*n*F-S micelles and the CTAB micelle (surfactant concentration: 2×10^{-3} M). The neutral aromatic compound perylene is thought to be solubilized in the core of the micelles. For calibration data, fluorescence polarity measurements of perylene excited with polarized light were carried out for seven solvents with various viscosities from hexane (viscosity: 0.2942 cP) to 1,4-butanol (71.5 cP),[20] at 20 °C. A reasonably good linear correlation was observed between the fluorescence polarity and the solvent viscosity. From the calibration graph and the measured fluorescence polarity data for the C*n*F-S and CTAB micelles, the microviscosities of the inner cores of those micelles were determined as follows: CTAB (18 cP), C1F-S (34 cP), C2F-S (37 cP), C3F-S (38 cP). The observed viscosity of the CTAB micelle was in good agreement with the literature value (19 cP).[21] The surface polyfluorinated micelles were shown to have significantly higher viscosities than the CTAB micelle. The longer perfluoroalkyl chain seems to induce a higher viscosity in the inner core of the micelles. Aggregative interactions between the surface polyfluoroalkyl chains may be the cause of the higher microviscosity.

Local Concentration of Dissolved Oxygen and Water. Perfluoroalkane is known to have high solubilities for gases such as oxygen. [1−3] It is very curious how oxygen is dissolved in the polyfluorinated area of the micelles. The local concentration of dissolved oxygen should also be a good measure of the local concentration of water, because the solubility of oxygen in water is only about one-tenth of those for organic solvents.[20,22] The local oxygen concentration should be low in the microenvironment surrounded by water, whereas a hydrophobic microenvironment would have higher dissolved oxygen. Because molecular oxygen is paramagnetic, the longitudinal magnetic relaxation

TABLE 3: Longitudinal Relaxation Time, T_1(10^{-3} s), under Nitrogen and Oxygen Atmospheres



Micelle		CF_3—	—CF_2—	-CF_2-$\overset{O}{\overset{\|}{C}}$-	—N^+—CH_3	—$(CH_2)_{14}$—
C3F-S	N_2	636±43	507±29	450±38	129±3.7	305±11
	O_2	407±39	368±40	377±42	119±5.1	238±8.5
	$\Delta(T_1^{-1})/s^{-1}$	0.855	0.745	0.431	0.651	0.985
C2F-S	N_2		649±32	540±39	131±7.9	319±24
	O_2		431±22	425±14	122±4.4	251±14
	$\Delta(T_1^{-1})/s^{-1}$		0.779	0.5012	0.563	0.849
C1F-S	N_2			1324	257	307
	O_2			658	237	250
	$\Delta(T_1^{-1})/s^{-1}$			0.765	0.328	0.743
CTAB	N_2				465±19	372±13
	O_2				441±10	325±7.2
	$\Delta(T_1^{-1})/s^{-1}$				0.117	0.388

in NMR is known to be enhanced under an oxygen atmosphere.[23,24] The enhanced relaxation under an oxygen atmosphere can be expressed as in eq 2, where T_{1O_2} and k_q' denote

$$(1/T_{1O_2}) = k_d + k_q'[O_2] \quad (2)$$

the observed relaxation time T_1 under an oxygen atmosphere and the rate constant enhanced by oxygen. The k_d is the inherent relaxation rate constant that corresponds to the observed T_1 under a nitrogen atmosphere (eq 3).

$$(1/T_{1N_2}) = k_d \quad (3)$$

Subtracting eq 3 from eq 2 results in eq 4.

$$(1/T_{1O_2}) - (1/T_{1N_2}) = k_q'[O_2] \quad (4)$$

Equation 4 indicates that necessary information which is directly proportional to the oxygen concentration can be obtained by observing T_1 under both oxygen and nitrogen atmospheres. As stated above, the enhanced effect on T_1 by a paramagnetic species appears only for the closest nucleus. Observing T_1 for each nucleus will result in a local value of $k_q'[O_2]$ for the microenvironment of the corresponding nucleus. The relaxation times T_1 for each fluorine atom in the perfluoroalkyl group, the *N*-methyl protons, and the methylene protons in the long alkyl chain in the C*n*F-S and CTAB micelles (surfactant concentration: 2×10^{-3} M) were determined under both oxygen and nitrogen atmospheres using the inversion recovery method. Very interesting results were obtained as shown in Table 3.

In the C2F-S and C3F-S micelles, the terminal trifluoromethyl fluorine atoms had larger $k_q'[O_2]$ values than those in the α position of the amide carbonyl group. This indicates that oxygen is dissolved at a higher concentration around the terminal fluorine atoms than it is around those in the α position of the amide carbonyl group. The results also suggest that the amide group is hydrated in the micelles. It should be noted here that the terminal fluorine atoms have a higher oxygen concentration despite their facing directly the bulk water phase. The terminal fluorine atoms in the C2F-S and C3F-S micelles are 10% and 20% further separated from the bulk water phase compared to those in C1F-S micelle, as stated above. The delicate differences may be the cause of the high oxygen concentration and are presumably due to the hydrophobicity of the perfluoroalkyl group. Table 3 indicates that the methylene group has a higher

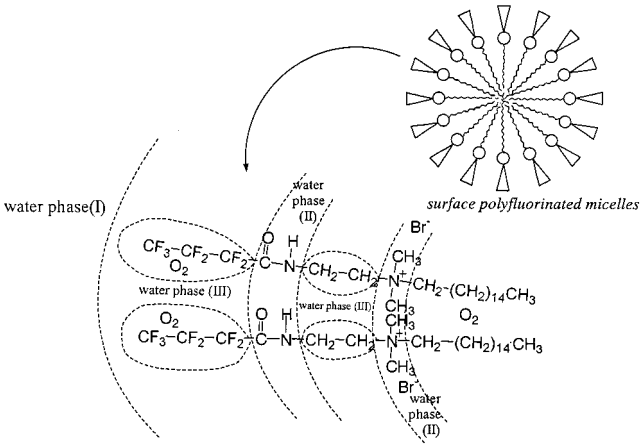


Figure 6. Microscopic structure of the polyfluorinated micelles.

oxygen concentration than the *N*-methyl group in all of the micelles examined. These results clearly indicate that the inner cores of the micelles are sufficiently hydrophobic and the ammonium groups are well-hydrated. The estimated distribution of water in the micelles provide a clue as to why C*n*F-S surfactants can form stable surface polyfluorinated micelles as in Figure 1c. A simple question again arises here. Why do not the surface polyfluorinated micelles, with their strongly hydrophobic perfluoroalkyl groups directly facing the bulk water phase, precipitate instead of being stabilized in water? The data listed in Table 3 partly answer this question. The hydrated water molecules (labeled as phase II in Figure 6) around the ammonium and amide groups may not be isolated from the bulk water phase (phase I) but instead connected with each other through a channellike structure (phase III) as shown in Figure 6.

Because only the terminal fluorine atoms are affected by the Mn^{2+} ions, a solute ion in the bulk water phase should not be able to penetrate the surface polyfluorinated layer. This water structure should also be closely related to the observation that the surface polyfluorinated layer protects against attack by hydroxide radicals in the bulk water phase, as described below. When the data for $k_q'[O_2]$ in Table 3 are compared among the different surfactants, the local oxygen concentration is found to change systematically. The longer perfluoroalkyl group results in an enrichment of the oxygen concentration around the terminal trifluoromethyl group following the order C3F-S > C2F-S > C1F-S. The oxygen concentration around the *N*-methyl group follows the order C3F-S > C2F-S > C1F-S > CTAB. The order should reflect the degree of hydration of the ammonium group. The methylene protons show the same tendency with C3F-S > C2F-S > C1F-S > CTAB. It should be noted here again that the perfluoroalkyl layer in the surface area of the C*n*F-S micelles makes the inner core more hydrophobic.

The values of the relaxation times T_1 themselves also afford crucial information about the mobility of the corresponding nucleus. A higher mobility induces a longer T_1 owing to the better isotropicity of the surrounding magnetic field.[13] The data for T_1 under a nitrogen atmosphere indicate that the mobility of the terminal trifluoromethyl group follows the order C1F-S > C2F-S > C3F-S micelles. The same tendency was also observed for the mobility of the *N*-methyl and methylene groups in the core of the micelles. The longer perfluoroalkyl groups are thought to enhance the degree of packing of the surfactant chains in the surface polyfluorinated micelles. On the other hand, Table 3 shows that the mobilities for the *N*-methyl group and

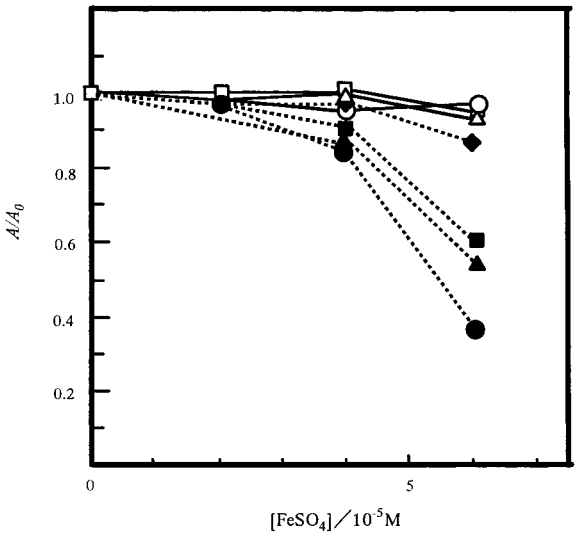


Figure 7. Effect of the micelles (C3F-S (□), C2F-S (△), C1F-S (○), CTAB (◆), C3H-S (■), C2H-S (▲), and C1H-S (●) on protecting Rose Bengal (1×10^{-6} M) against the oxidative attack by the hydroxide radicals generated in the bulk water phase under aerated conditions at 23 °C. The vertical axis denotes the normalized percentage of the residual Rose Bengal estimated from the bleaching at the λ_{max}; [surfactant] = 2×10^{-3} M, and $[H_2O_2] = 0.1$ M.

the methylene groups in the CTAB micelle are higher than those for the polyfluorinated micelles. The lack of a surface polyfluorinated layer may render the CTAB micelle more flexible. The C*n*F-S micelles appear to become more rigid due to the surface polyfluorinated layer. The results are well-correlated with those obtained from the microviscosity measurements described earlier.

Protective Effect of Surface Polyfluorinated Micelles. Because the surface polyfluorinated micelles have very interesting microstructures and water structures, the effect of the surface polyfluorinated layer on a typical oxidation reaction was examined. A strong oxidizing agent, an hydroxide radical, was used as a probing reagent. The hydroxide radical was generated in the bulk water phase using Fenton's method of adding ferrous ion ($FeSO_4$) to a hydrogen peroxide solution as indicated in eq 5.[25]

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+} \qquad (5)$$

The dye RB was chosen as a probe molecule for oxidative decomposition by the hydroxide radical. In an aqueous solution, RB (1×10^{-6} M) is stable in the presence of hydrogen peroxide (0.1 M), while it is easily decomposed by the addition of ferrous ions ($FeSO_4$: 1×10^{-4} M). The bleaching reaction can be monitored by observing the decrease in λ_{max} absorption for RB. The dye RB is thought to be solubilized at the ammonium groups of the micelles, and the surface polyfluorinated layer is expected to protect it against oxidative attack by the hydroxide radical generated in the bulk water phase, because perfluoroalkane is known to be highly resistant to oxidation. The dye RB (1×10^{-6} M) was solubilized in the surface polyfluorinated micelles (C1F-S, C2F-S, C3F-S), CTAB micelle, and hydrocarbon micelles (C1H-S, C2H-S, C3H-S) with a surfactant concentration of 2×10^{-3} M, and hydrogen peroxide (0.1 M) was then added to the bulk water phase. After addition of an aqueous solution of $FeSO_4$ dropwise, the decrease of absorption at λ_{max} for RB was monitored with a spectrometer. Very interesting results were obtained as summarized in Figure 7.

The horizontal axis represents the amount of Fe^{2+} ions added to the micellar solution, which is proportional to the concentra-

tion of the hydroxide radicals generated in the bulk water phase. The vertical axis represents the normalized percentage of the residual RB. When compared with the results for the CTAB micelle, the surface polyfluorinated micelles well-protected RB against oxidative bleaching. The C3F-S micelle had the most protective effect. On the other hand, the hydrocarbon-type micelles (C1H-S, C2H-S, C3H-S) were less protective against bleaching. The protective effect against oxidative attack by the hydroxide radical follows the order C3F-S > C2F-S > C1F-S > CTAB > C3H-S > C2H-S > C1H-S. These results are best explained by the microstructure and distribution of water within the micelles as discussed above. The hydroxide radical in the bulk water phase cannot penetrate into the surface of the polyfluorinated micelles, but it can easily attack the RB solubilized at the ammonium group in the hydrocarbon-type micelles. In the latter, the short acylamide groups are digging into the inner core of the micelle to allow penetration of the water phase as shown in Figure 1a.

As demonstrated by this oxidation reaction experiment, the very unique microstructure of the surface polyfluorinated micelles, especially their surface polyfluorinated area, makes them interesting fields for various chemical reactions.

Experimental Section

Syntheses of the C*n*F-S Series. ((((Trifluromethanoyl)-amino)ethyl)hexadecyl)dimethylammonium bromide (C1F-S) was made as follows: Trifluoroacetic anhydride (61 g) was added dropwise to *N*,*N*-dimethylethylenediamine (24 g) in pyridine (500 mL) below 30 °C to form (((trifluoroacetyl)-amino)ethyl)dimethylammonium trifluoroacetate (**I**). The resulting precipitate (**I**) was filtered out, dissolved in dichloromethane, and washed with aqueous alkaline solution ([NaOH] = 0.2 M). The dichloromethane solution was evaporated and the deprotonated amide (**II**) was purified by distillation under reduced pressure (42 °C at 1 mmHg; yield 65%). A solution of the amide (**II**) (22.8 g) and hexadecyl bromide (100 g) in acetone (550 mL) was stirred for ca. 600 h at ambient temperature. The polyfluorinated surfactant C1F-S precipitated. The crude C1F-S was purified by repeated reprecipitation from dichloromethane solution with hexane. Yield: 57%. FAB-MS: *m*/*e* 410. ^{1}H NMR (δ/ppm) in $CDCl_3$: 0.86 (3H, t), 1.23 (28H, m), 3.3 (6H, s), 3.8 (6H, m). Anal. Found: C, 53.72; H, 9.22; N, 5.78. Calcd for $C_{22}H_{44}N_2OF_3Br$: C, 53.97; H, 9.08; N, 5.72. C2F-S and C3F-S were synthesized by the similar procedures. Data for C2F-S are the following. FAB-MS: *m*/*e* 560. ^{1}H NMR (δ/ppm) in $CDCl_3$: 0.85 (3H, t), 1.22 (28H, m), 3.3 (6H, s), 3.8 (6H, m). Anal. Found: C, 50.31; H, 8.49; N, 5.46. Calcd for $C_{23}H_{44}N_2OF_5Br\cdot{}^1/_2H_2O$: C, 50.36; H, 8.27; N, 5.11. Data for C3F-S are the following. FAB-MS: *m*/*e* 510. ^{1}H NMR (δ/ppm) in $CDCl_3$: 0.84 (3H, t), 1.22 (28H, m), 3.3 (6H, s), 3.8 (6H, m). Anal. Found: C, 47.88; H, 7.46; N, 4.75. Calcd for $C_{24}H_{44}N_2OF_7Br\cdot{}^1/_2H_2O$: C, 48.16; H, 7.58; N, 4.68.

Syntheses of the C*n*H-S Series. C1H-S, C2H-S, and C3H-S were synthesized by procedures similar to those for C*n*F-S surfactants, using the corresponding acid anhydride. Data for C1H-S are as follows. FAB-MS: *m*/*e* 355. ^{1}H NMR (δ/ppm) in $CDCl_3$: 0.9 (3H, t), 1.3 (28H, m), 1.7 (2H, t), 2.1 (3H, s), 3.4 (6H, s), 3.8 (4H, m). Anal. Found: C, 60.46; H, 11.16; N, 6.27. Calcd for $C_{22}H_{47}N_2OBr$: C, 60.66; H, 11.16; N, 6.43. Data for C2H-S are as follows. FAB-MS *m*/*e* 369. ^{1}H NMR (δ/ppm) in $CDCl_3$: 0.9 (3H, t), 1.1 (3H, t), 1.3 (28H, m), 1.4−2.4 (4H, m), 3.4 (6H, s), 3.8 (4H, m). Anal. Found: C, 61.38; H, 11.30; N, 6.15. Calcd for $C_{23}H_{49}N_2OBr$: C, 61.43; H, 11.01; N, 6.23. Data for C3H-S are as follows. FAB-MS; 383. ^{1}H NMR (δ/ppm) in $CDCl_3$: 0.9 (6H, t), 1.3 (28H, m), 1.4−2.4 (4H, m), 3.4 (6H, s), 3.8 (4H, m). Anal. Found: C, 62.16; H, 11.11; N, 6.04. Calcd for $C_{24}H_{51}N_2OBr$: C, 62.21; H, 11.44; N, 5.96.

Measurements. UV and visible absorption spectra were recorded on a Shimadzu UV-210 spectrophotometer. An Hitachi F-4010 was used for the fluorescence spectroscopy. ^{1}H NMR (90 MHz) and ^{19}F NMR (84.7 MHz) were recorded on a JEOL FX-90Q.

Micelle Formation. A designated amount of a stock solution of each surfactant in dichloromethane was placed in a volumetric flask. After the evaporation of dichloromethane, water purified by ion exchange and distillation was added to allow dissolution by stirring or sonication at 20 °C.

References and Notes

(1) Banks, R. E. *Organofluorine Chemicals and their Industrial Applications*; Ellis Horwood Ltd.: Chichester, U.K., 1979.
(2) Negishi, A. *Chemistry of Fluorine*; Maruzen: Tokyo, 1988.
(3) Kitazume, T.; Ishihara, T.; Taguchi, T. *Chemistry of Fluorine*; Kodansya Scientific: Tokyo, 1993.
(4) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975.
(5) Turner, D. C.; Brand, L. *Biochemistry* **1968**, *7*, 3381.
(6) Stryer, L. *J. Mol. Biol.* **1965**, *13*, 482.
(7) Mukerjee, P.; Mysels, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; NSRDS-NBS 36; Superintendent of Documents, U.S. Gov. Printing Office: Washington, DC, 1971.
(8) Atik, S. S.; Nam, M.; Singer, L. A. *Chem. Phys. Lett.* **1979**, *67*, 75.
(9) Ekwall, P.; Mandell, L.; Solyom, P. *J. Colloid Interface Sci.* **1971**, *35*, 519.
(10) The perfluoroalkyl group is known to have a rather rigid conformation and extend its chain straightforwardly owing to the larger van der Waals radius compared to that of the hydrogen atom.[1−3]
(11) Robb, I. D. *J. Colloid Interface Sci.* **1971**, *37*, 521.
(12) Fox, K. K.; Robb, I. D.; Smith, R. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 445.
(13) (a) Jackman, L. M.; Sternhell, S. *Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: Oxford, U.K., 1969. (b) Jackman, L. M.; Cotton, F. A. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1975.
(14) Bloembergen, N.; Purcell, E. M.; Pound, R. V. *Phys. Rev.* **1948**, *73*, 679.
(15) The same amount of $ZnCl_2$ was added in place of $MnSO_4$.
(16) Lippert, E. *Z. Naturforsch.* **1955**, *10a*, 542.
(17) Lippert, E. *Z. Naturforsch.* **1957**, *61*, 962.
(18) Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 690.
(19) Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 465.
(20) Riddick, J. A.; Bunger, W. B.; Skano, T. K. *Techniques of Chemistry, Vol II, Organic Solvents*; John Wiley & Sons: New York, 1986.
(21) Shinitzky, M.; Dianoux, A. C.; Gilter, C.; Weber, G. *Biochemistry* **1981**, *10*, 2106.
(22) Dean, J. A. *Lange's Handbook of Chemistry*; McGraw-Hill: New York, 1985.
(23) Anet, F. A. L.; Bradley, C. H.; Buchanan, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 258.
(24) Becker, E. D.; Feretti, J. A.; Farrar, T. C. *J. Am. Chem. Soc.* **1969**, *91*, 7784.
(25) Walling, C. *Acc. Chem. Res.* **1984**, *8*, 125.