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First Anionic Micelle with Unusually Long Lifetime: Self-Assembly of Fluorocarbon−Hydrocarbon Hybrid Surfactant

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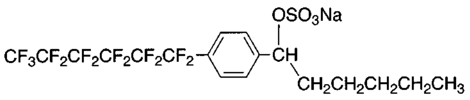
In the mixture of a fluorocarbon surfactant (FCS) and a hydrocarbon surfactant (HCS), FCS-rich and HCS-rich micelles are generally formed because of immiscibility between the fluorocarbon and hydrocarbon chains.[1] To solve this problem, new surfactants having a fluorocarbon chain and a hydrocarbon chain in a molecule, namely a *hybrid surfactant*, have been synthesized.[2] These surfactants formed aqueous micelles, and their critical micelle concentrations (cmc's) followed Kleven's equation, although being unstable to hydrolysis. We have also prepared sulfonate-type fluorocarbon hybrid surfactants ($C_mF_{2m+1}C_6H_4COCH(SO_3Na)C_nH_{2n+1}$; $m = 4,6,8$; $n = 4,6,8$).[3] These surfactants were highly stable to hydrolysis and showed an emulsification ability for the ternary mixture of *n*-octane, (hydrocarbon oil)/perfluoropolyether (fluorocarbon oil)/water, and thus were expected to make it possible to prepare water-based fluoro paints. Further, two specific properties of the hybrid surfactants have been found: one is very high viscosity of the 10 wt % aqueous solution of the surfactant having $m = 6$ and $n = 4$ at 37 °C,[4] and the other is an intramicellar phase separation between the fluorocarbon chain and the hydrocarbon chain.[5] Neither homogeneously double-chained analogues nor general surfactants have such properties.[6] This fact suggests that hybridity of the hydrophobic part in the hybrid surfactant molecule plays an important role in the unique properties. Here we will report another interesting property of a hybrid surfactant (F6H5OS). To our knowledge, this is the first report concerning anionic surfactants on the unusually slow exchange of surfactant between micelle and monomer states on the NMR time scale.



F6H5OS

F6H5OS was synthesized from a ketone having a fluorocarbon chain and a hydrocarbon chain. Details of the synthesis will be described elsewhere.[7] The NMR experiments were all performed at 30 °C on a Bruker Avance DPX-400 spectrometer operating at 400 and 376 MHz for ^{1}H and ^{19}F nuclei, respectively. Samples were prepared in D_2O (purity 99.8%, Merck). Trifluoroacetic acid in D_2O was used as an external reference (−79.45 ppm) for ^{19}F NMR measurement.

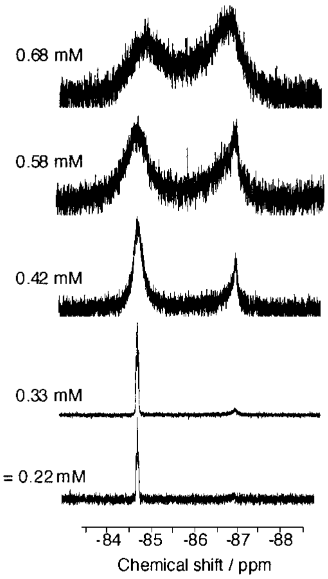


Figure 1. ^{19}F NMR spectra of ω-CF_3 group of F6H5OS in D_2O at different concentrations.

Figure 1 shows the ^{19}F NMR spectra of the ω-CF_3 group in F6H5OS at different concentrations. At 0.22 mM, F6H5OS exhibited one sharp signal that was split into a triplet due to the neighboring fluorine nuclei. As the surfactant concentration increased, an additional signal appeared at the upper magnetic field (−86.91 ppm), and then both signals were broadened. The integrated intensity (I_{up}) of the upfield signal increased rapidly with concentration increasing above 0.30 mM, whereas the downfield signal intensity (I_{down}) almost leveled off (Supporting Information). The threshold value agreed well with the cmc (0.34 mM) obtained by surface tension measurements (Wilhelmy method) for aqueous solutions of F6H5OS. It is thought that the upfield signal comes from the F6H5OS micelles and that the downfield signal corresponds to the surfactant monomer. The lifetime (τ_{mic}) of surfactant micelles is generally in the order of 10^{-5} to 10^{-6} s, and the exchange of surfactant molecules between monomer and micelle states is fast on the NMR time scale,[10] and accordingly a single weight-average signal for the surfactants in both states is observed.[11] The appearance of an original signal of F6H5OS micelle must indicate the slow exchange of the surfactant molecule between the monomer and micelle states on the NMR time scale.

The τ_{mic} value of F6H5OS, estimated from the half width of NMR signals, slightly decreased with increases in the surfactant concentration, indicating that surfactant exchange between the two states became faster (Figure 2). The τ_{mic} value at the cmc, obtained by extrapolating the $\tau_{mic}-c$ curve to 0.30 mM, was 2.0 ms. This

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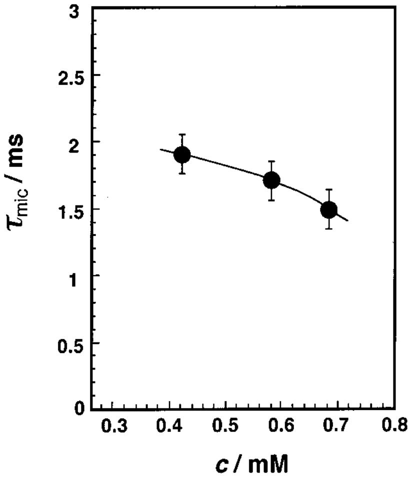

Figure 2. Relationship between the micelle lifetime (τ_{mic}) and the F6H5OS concentration.

indicates that F6H5OS micelles have a lifetime that is about 10^2 to 10^3 times longer than that of general surfactant micelles.

Slow surfactant exchange on the NMR time scale has thus far been found only for cationic gemini surfactants.[13] The gemini surfactants with long alkyl chains such as tetradecyl or octadecyl groups have τ_{mic} of 40−100 ms, and a hybrid gemini cationic surfactant having a dodecyl group and a perfluorooctyl group also yields slow exchange. Although fluorinated nonionic surfactants with an amide bonding also show slow surfactant exchange,[14] they form large aggregates of ca. 220 nm diameter, different from micelles.[10a] Pulsed-gradient spin−echo (PGSE) experiments indicated that F6H5OS forms significantly small micelles with a hydrodynamic radius of 0.6 nm in the concentration range where slow surfactant exchange is observed on the NMR time scale (Supporting Information). Our finding is believed to be the first example of unusually slow exchange of anionic surfactants between monomer and micelle states on the NMR time scale.

On the basis of molecular modeling, the two hydrophobic chains in F6H5OS, tridecafluorohexylphenyl and pentyl chains, are 1.2 and 0.7 nm long, respectively. Surfactant generally forms spherical micelles having a hydrodynamic radius about same as its hydrophobic chain length in dilute aqueous solutions.[15] However, the hydrodynamic radius of F6H5OS micelle was much smaller than the fluoroalkylphenyl chain length. F6H5OS micelles seem to be composed of interdigitated structures of surfactant molecules. Such a structure will sterically hinder dissociation of a surfactant molecule from the micelle, resulting in prolongation of micelle lifetime. The ^{19}F NMR signal for the micelle appeared at ca. 2.3 ppm upfield from that for the monomer, as can be seen in Figure 1. The ^{1}H NMR experiment (not shown) also yielded a signal of the ω-CH_3 group in F6H5OS, (a signal which was a weight-average for the surfactants in both states of monomer and micelle) shifted upfield with the surfactant concentration above the cmc. These facts suggest that the CF_3 and CH_3 groups are shielded more strongly in micelle state than in monomer state, and thus these terminal groups are surrounded by the fluorocarbon chain[2,11]the benzene ring[16] or both in F6H5OS micelles. Such a situation is conceivable in the micelle composed of the interdigitated surfactant structure. On the other hand, the hydrodynamic radius of the F6H5OS micelle at a concentration of 1.30 mM, at which the surfactant showed a fast exchange on the NMR time scale, was 1.1 nm, approximately equal to the length of the fluoroalkylphenyl group (Supporting Information). The looseness of the interdigitation may bring about a shortening of the micelle lifetime, increasing the micelle size. At higher NMR frequency, faster surfactant exchange between monomer and micelle states is detectable as two separate NMR signals because the NMR time scale becomes shorter. Previously, the exchange rate of hybrid surfactants, very analogous to F6H5OS but having no phenylene group, was investigated using a ^{19}F NMR spectrometer operating at 470 MHz, and consequently no slow surfactant exchange on the NMR time scale was observed even for the hydrophobic hybrid surfactant (abbreviated F7H6, see ref 17) whose cmc is lower than that of F6H5OS.[17] On the other hand, we have confirmed that F6H3OS (which is the hybrid surfactant with a hydrocarbon chain shorter than that of F6H5OS by two carbon atoms) also exhibits two separate ^{19}F NMR signals corresponding to the ω-CF_3 groups in monomer and micelle states above cmc. F6H3OS is much less hydrophobic compared to F7H6 and F6H5OS because the cmc of F6H3OS is 0.81 mM. It has been believed that the surfactant exchange rate depends primarily on the hydrophobicity of the surfactants.[10b,13a] However, no one has discussed where the unusually slow behavior of surfactant exchange comes from. We suggest that surfactant interdigitation in micelles could contribute to prolongation of micelle lifetime. Further studies are in progress on the details of the micelle structure of F6H5OS and interactions stabilizing its structure. Such intramicellar interactions may also contribute to the long lifetime.

Supporting Information Available: Procedures of PGSE experiment and micelle lifetime estimation, a figure showing integrated intensity ratio vs surfactant concentration, and a table containing diffusion coefficients and hydrodynamic radii of micelles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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