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Fluorocarbon Modified Nitroxide: A New Electron Spin Resonance Spin Probe for Micellization of Surfactants

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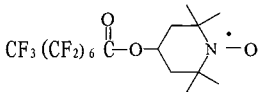
Spin probing in electron spin resonance (ESR) is one of the most effective techniques in the studies of micelles as well as other organized molecular assemblies. It reports information about the polarity of the microenvironment and mimics the molecular dynamics.[1] A variety of the probes were reported including the cationic probe Temp-TMA$^+$ (4-(trimethylammonium)-2,2,6,6-tetramethylpiperidine-*N*-oxyl iodide),[2−4] anionic probe *x*-DSA (*x*-doxyl stearic acid),[5] and nonionic radicals 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO)[6] and its derivatives[7−9] such as 4-hydroxy-2,2,6,6-etramethylpiperidine-*N*-oxyl (H-TEMPO), 4-oxo-2,2,6,6-tetramethylpiperidine-*N*-oxyl (O-TEMPO), octanoyloxy and decanoyloxy derivatives of TEMPO, i.e., C_8-TEMPO and C_{12}-TEMPO, etc. The hydrocabon-modified TEMPOs are more hydrophobic and, consequently, exhibit enhanced partition coefficients between the micelles and aqueous medium.

There have been increasing interests in the studies of physicochemical properties of micellar solutions containing perfluorinated surfactants,[10] as they have numerous applications in industrial and biomedical fields. A variety of techniques including ESR,[4,9] fluorescence spectroscopy,[11−13] small angle neutron scattering,[14] and ^{19}F NMR[15] have been used in these studies. In the studies of micelles by ESR spin probing and fluorescent probing techniques, probes for the micellar environment are required. Conventional probes cannot meet the demand due to their limited solubility in fluorocarbon micelles. Therefore, seeking of more effective probes for fluorocarbon domains has drawn much attention.[11] In our previous work, we found that a fluorocarbon-substituted pyrene, i.e., 1-perfluorooctanoyl-pyrene (PyCORf), showed a better affinity to the fluorocarbon domains and this made it effective in monitoring the association of fluorocarbon-modified water-soluble polymers by fluorospectroscopy.[16−18]

Chart 1. The Structure of F-TEMPO



In this study, a new fluorocarbon-containing nitroxide radical, that is, 4-perfluorooctanoyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (F-TEMPO, Chart 1) was synthesized and used to monitor the micellization of surfactants.

In the experiments, SDS (Unipath Ltd.), ammonium perfluorooctanoate (FC143, 3M Co.), and 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (H-TEMPO, Sigma) were used as received. F-TEMPO was synthesized via direct esterification of H-TEMPO with perfluorooctanoyl chloride[16] in anhydrous diethyl ether. The product was purified by chromatography using petroleum ether/diethyl ether (8/2, v/v) as the eluent followed by recrystallization in cyclohexane twice. Anal. Calcd: F, 50.26; C, 35.98; N, 2.47; H, 2.82. Found: F, 50.52, C, 35.74; N, 2.37; H; 2.91.

ESR spectra of F-TEMPO in different media were recorded on a Bruker SRC 200D ESR spectrometer operating at 20 °C on the X-band of the microwave. The acquisition parameters were as follows: microwave power, 20 mW; central field, 3472 G; sweep width, 100 G; time constant, 0.5 s; sweep time, 100 s; amplitude of modulation, 0.5 G; frequency of modulation, 100 kHz.

The solutions for ESR measurements were prepared as follows. To a surfactant (SDS or FC143) solution of a given concentration in deionized water, a desired amount of F-TEMPO/acetone solution was added using microsyringes. The final probe concentration in the solutions was kept at 4×10^{-4} M. Finally, the solutions were transferred to glass capillary tubes with diameters of ca. 0.9−1.1 mm and sealed.

Table 1 summarizes the solubility of F-TEMPO in water and surfactants (FC143 and SDS) solutions. When the

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Table 1. Solubility Data of F-TEMPO in Water and Surfactant (FC143 and SDS) Solutions[a]

	solubility ($\times 10^4$ M)		
surfactant concn (M)	H_2O	SDS	FC143
	0.74		
0.002		1.51	1.61
0.01		1.38	2.14
0.02		2.58	13.6
0.1		3.62	81.5
0.2		8.45	67.0

[a] The solubility of F-TEMPO was determined by UV−vis spectroscopy. F-TEMPO was mixed into a micelle solution, the solution was then kept in a bath at 30 ± 0.1 °C for about 4 days. After the remaining crystals were removed by filtration, methanol was added to make a final composition of 1/9 (v/v, water/methanol). These solutions were further diluted to desired concentrations before measurements.

surfactant concentrations are very low, e.g., at 0.002 M, the solubility of F-TEMPO in FC143 and SDS solutions is 1.61×10^{-4} and 1.51×10^{-4} M, respectively, comparable to that in water. Then it increases with surfactant concentration. For example, at the surfactant concentration of 0.1 M, it takes the values of 3.6×10^{-4} and 8.2×10^{-3} M in SDS and FC143 solutions, respectively. It was reported[7] that the hydrocarbon analogue of F-TEMPO, i.e., C_8-TEMPO showed a solubility of 2.8×10^{-2} M in SDS solution (5 wt %, ca. 0.2 M), well above that found for F-TEMPO in SDS solutions (8.45×10^{-4} M). This can be attributed to the poor affinity between the hydrocarbon and fluorocarbon chains. F-TEMPO exhibits a much higher solubility in FC143 micelles than in SDS micelles, displaying a favorable effect of introducing the fluorocarbon chain into the probe molecule on its affinity to the fluorocarbon micelles.

It is well-known that ESR spectra of a nitroxide-type spin probe may provide two kinds of information concerning its microenvironment. First, the ^{14}N isotropic hyperfine splitting constant, A_N, of the nitroxide free radical is indicative of the polarity of the solvent as A_N increases with the solvent polarity.[19,20] Second, the rotational correlation time (τ_c) from the ESR spectrum is reflective of the probe mobility and can be used to monitor changes in the microviscosity experienced by the probe.[21−24]

Figure 1 shows A_N and τ_c of F-TEMPO as functions of FC143 concentration. It can be seen that at very low surfactant concentrations, A_N takes a value of 17.00 G, typical for F-TEMPO in water, indicating that the probe molecules are mainly in the aqueous phase. A_N, however, shows a relatively sharp decrease starting at a concentration around 0.02 M, which indicates the onset of FC143 micellization. Finally, it tends to stabilize at ca. 16.67 G. Here, the lowest A_N value of 16.67 G is much higher than that found in organic media such as cyclohexane (15.45 G) and ethanol (16.03 G), indicating that the nitroxide unit experiences a relatively polar environment in FC143 micelles.This probably implys that the reporting groups of F-TEMPO locate at the micelle surface area.

The variance of τ_c with FC143 concentrations also reveals the micellization of FC143 in aqueous solutions. At low surfactant concentrations, the τ_c takes a value of ca. $(3-4) \times 10^{-11}$ s. The τ_c value shows an abrupt increase

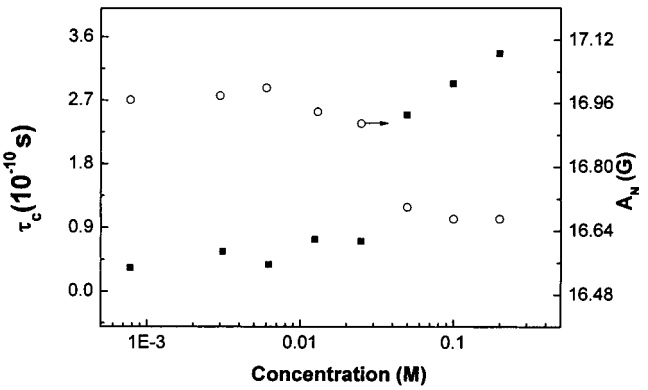

Figure 1. A_N and τ_c of F-TEMPO as a function of FC143 concentration.

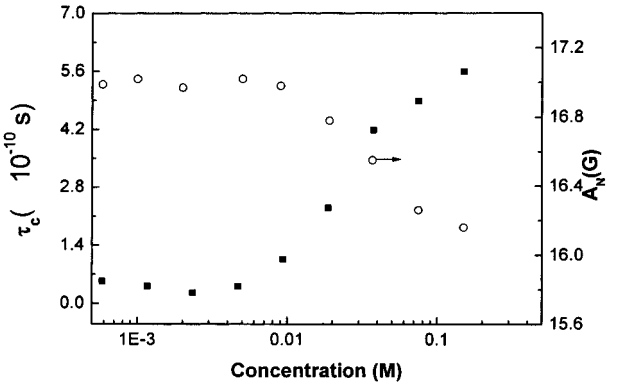

Figure 2. A_N and τ_c of F-TEMPO as a function of SDS concentration.

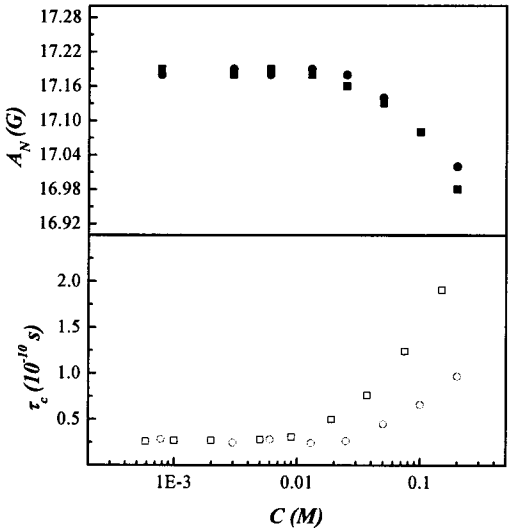

Figure 3. A_N and τ_c of H-TEMPO as a function of FC143 (●, ○) and SDS (■, □) concentration.

at the concentration of about 0.02 M, indicating the onset of micellization. This increase of the τ_c arises from the association of the probe molecules with the surfactant micelles, leading to restriction of its motion. At the surfactant concentration of ca. 0.2 M, τ_c reaches a value about 3.36×10^{-10} s, over 10 times higher than that found in water, indicating that the probe motion is severely restricted.

The dual H/F character of F-TEMPO makes it suitable for use in hydrocarbon surfactants, e.g., SDS as well (see Table 1). Figure 2 shows the variations of A_N and τ_c of F-TEMPO against concentration of SDS, as a representa-

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Table 2. A_N and τ_c Data for F-TEMPO and H-TEMPO in Surfactant Solutions

		F-TEMPO		H-TEMPO	
surfactant	concn (M)	A_N (G)	τ_c ($\times 10^{-10}$ s)	A_N (G)	τ_c ($\times 10^{-10}$ s)
FC143	0.2	16.67	3.36	17.02	0.97
SDS	0.15	16.16	5.59	16.98	1.91
H_2O		16.99	0.29	17.18	0.25

tive of hydrocarbon surfactants. Both curves monitor the micellization. Here, it is interesting to see that the lowest A_N value of 16.16 G in SDS is much lower than that in FC143, i.e., 16.67 G, and the highest τ_c value of 5.59×10^{-10} s in SDS is significantly higher than that in FC143 micelles (3.36×10^{-10} s). The same difference trends have been reported by Martini et al.,[2−4] using the cationic probe Temp-TMA^+, which interacts electrostatically with the negatively charged micelle surface of SDS and FC143 and consequently resides in the surface. Thus the similar results obtained by using Temp- TMA^+ and F-TEMPO reflect the difference in the surface properties between the micelles of FC143 and SDS.

We have also monitored the micellization of FC143 and SDS with H-TEMPO (Figure 3). Both the variances of A_N and τ_c of H-TEMPO against surfactant concentration reveal the micellization of FC143 and SDS. However, the probing ability of H-TEMPO and F-TEMPO is obviously different. As can be seen from the data shown in Table 2, the A_N variance of H-TEMPO is smaller than F-TEMPO. For example, the maximum A_N drops of 0.16 and 0.32 G in FC143 micelles were found for H-TEMPO and F-TEMPO, respectively, and the maximum A_N drops of 0.20 and 0.83 G exist in SDS micelles for H-TEMPO and F-TEMPO, respectively. The results demonstrate that, compared with F-TEMPO, H-TEMPO is less sensitive to micellization of surfactants. The variance of τ_c results in the same conclusion. This is probably due to the low partition coefficients of H-TEMPO between the micelles and water as a result of its hydrophilicity and, consequently, most of H-TEMPO molecules still reside in the aqueous phase even above the critical micelle concentration (cmc).

In our previous work, we confirmed that the fluorocarbon-modified fluorescence probe PyCORf is effective in monitoring the association of fluorocarbon-modified water-soluble polymers.[16−18] In the present work, we demonstrated the effectiveness of the fluorocarbon-modified ESR spin probe F-TEMPO in monitoring the micellization of fluorocarbon surfactants. Thus, in addition to the ionic probes,[11] there is promise in the design of effective fluorinated ESR probes for fluorocarbon microdomains as well. Besides, as has been shown in our previous papers,[16−18] PyCORf is of high hydrophobicity and preferentially solubilized into the micelle core. Thus, its fluorescence spectra usually reflect the characteristics of the micelle core. On the contrary, F-TEMPO is less hydrophobic and the reporting group, i.e., the nitroxide, probably resides at the micellar surface. Thus, the two probes are complementary in exploring the micelles of fluorocarbon surfactants.

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