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ESR study of aqueous micellar solutions of perfluoropolyether surfactants with the use of fluorinated spin probes

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Abstract

Fluoroalkyl esters of 3-carboxy pyrroline nitroxide, FP*n* ($n = 8$ and 12), containing $(n-2)$ CF_2 groups in the side-chain, were used as novel ESR spin probes of fluorinated micellar systems. The method was applied to study aqueous solutions of perfluoropolyether surfactants of the general formula $Cl(C_3F_6O)_2CF_2COOX$, consisting of two perfluoroisopropoxy units and the counterion $X = Na^+$ or NH_4^+. By measuring the change of ^{14}N hyperfine splitting with surfactant concentration the critical micellar concentration of the ammonium salt was determined at temperatures of 297, 313 and 333 K. The ESR line shape was also examined as a function of surfactant concentration and of temperature in the range 120–360 K. The results are discussed in terms of solubilization and local environment of the probes in micelles of different size and shape, depending on the surfactant concentration and the kind of the counterion.

Keywords: Perfluoropolyether surfactants; Micellar solutions; ESR spectroscopy; Fluorinated spin probes

1. Introduction

The self-assembly of perfluorinated amphiphiles on the nano- and mesoscale is a topic of increased recent interest, both in terms of a fundamental understanding of the process as well as of established and potential applications of fluorinated materials [1]. Use of a variety of experimental techniques is an advantage, because of the complementary information that these methods can provide.

A useful tool for examining molecular self-assembled systems is electron spin resonance (ESR) spectroscopy using nitroxide radicals as spin probes. The method is based on the sensitivity of the nitroxide ESR line shapes to the local viscosity, molecular packing and ordering, and of the ^{14}N hyperfine splittings to the polarity of the medium. Depending on the probe hydrophobicity, charge, and, in the case of amphiphilic probes, length of the alkyl chain and position of the nitroxide group with respect to the polar head-group, different regions of the self-assembled systems can be identified and studied [2].

Previous studies of aqueous solutions and water-swollen membranes of ionomers indicate that location of protiated amphiphilic probes in fluorinated systems may be quite different than in protiated systems, due to incompatibility of fluorocarbon and hydrocarbon chains [3]. It is thus desirable to examine the behavior of fluorinated spin probes in fluorinated hosts.

Recently, fluoroalkyl esters of the carboxylic derivative of pyrroline nitroxide, FP*n* ($n = 8$, 12 and 18), cf. Chart 1, have been synthesized and proposed as spin probes of the perfluorinated ionomer Nafion [4]. In the present study we apply two of these probes ($n = 8$ and 12) for examining micellar solutions of chlorine terminated perfluoropolyether surfactants, $Cl(C_3F_6O)_2CF_2COOX$ (PFPE–X, cf. Chart 1), consisting of two perfluoroisopropoxy units and the counterion $X = Na^+$ or NH_4^+.

Micellization of the PFPE–X surfactants in water has been studied by surface tension [5], conductivity [6], ^{19}F NMR [7], SANS [8–10], and fluorescence quenching of a cationic pyrene-based probe [11]. It has been found that spherical micelles

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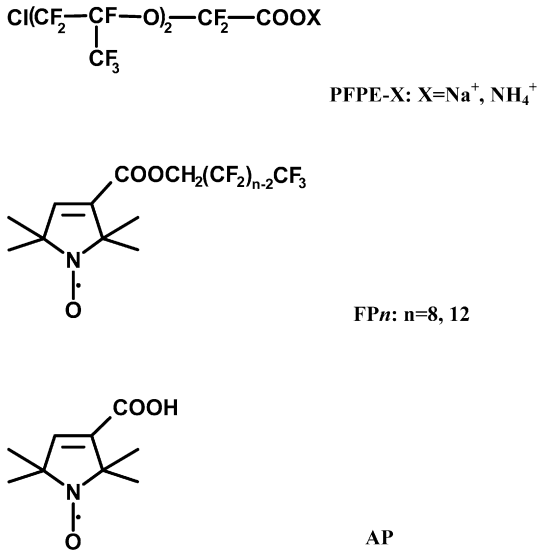

Chart 1. Perfluoropolyether surfactants (PFPE–X), fluorinated probes (FP*n*) and the precursor paramagnetic acid (AP) used for their synthesis.

formed at the critical micellar concentration (CMC) grow in size and transform into ellipsoidal aggregates with increasing surfactant concentration. A counterion effect has been observed: at a given PFPE–X concentration, aggregation numbers, N, are higher for the ammonium salt than for the sodium salt [8–11].

Micellar solutions of PFPE carboxylate mixtures with narrow molecular weight distributions, as well as those of ammonium perfluorooctanoate (APFO), were examined earlier by ESR with the use of protiated nitroxide probes; see the review papers [12]. The results indicate that the small cationic nitroxide CAT1 can be used to estimate CMC at room temperature, but its derivative with a long alkyl substituent, CAT12, has a strong perturbation effect on the host systems if the probe concentration is not much lower than surfactant concentration. This perturbation effect was not observed for neutral amphiphilic probes, C12- and C16-TEMPO, and for doxylstearic acids, *n*-DSA, with the doxyl group attached to different carbon atoms of the chain, $n = 5$, 12 or 16. The examined TEMPO derivatives, however, were not found suitable for the host CMC determination, because they themselves form micelles at low concentrations (CMC $= 1.6 \times 10^{-6}$ and 4.7×10^{-7} mol/dm^3 for C12- and C16-TEMPO, respectively) [13–15]. Electron spin echo modulation study of *n*-DSA probes in APFO micelles [16] indicated that the protiated probe chains do not penetrate deeply into the micellar core but are largely tilted and occupy regions with relatively easy water accessibility.

The probes with fluorinated alkyl chains are expected to be more compatible with the perfluorinated host. Such probes, however, are not available commercially and have been rarely used. Ristori et al. synthesized the radical PFPE–tempamide and used it in the study of mixed vesicles of PFPE carboxylate with *n*-dodecylbetaine [17]. The probe was found to be preferentially located in the PFPE rich domains of the aggregates. Based on the ESR line shape simulations in pure lamellar PFPE dispersions the authors concluded that the probe tail was well intercalated between fluorinated host chains. Zhou et al. synthesized fluorinated C8-TEMPO radical (F-TEMPO) and compared its behavior with that of the protiated analogue (H-TEMPO) in APFO and sodium dodecyl sulfate micellar systems [18]. Their results indicate that F-TEMPO is much better solubilized in fluorinated than in protiated surfactant micelles, and in both systems it is more sensitive to micellization compared to less hydrophobic H-TEMPO.

The aim of the present work is to evaluate the usefulness of the above mentioned FP*n* probes for an in-depth ESR investigation of micellar systems of short-chain fluorinated surfactants; in particular, we address key questions on whether the probes are suitable for CMC determination in a wide temperature range, and sensitive to structural transformations of the aggregates. Our results may help to extend the scope of the spin probe studies to other fluorosurfactant-based colloid systems, e.g. reverse micelles or microemulsions.

2. Experimental

2.1. Materials

PFPE–X surfactants of purity ca. 99% (with respect to the formula given in Chart 1) were supplied by Solvay Solexis—Research & Technology, Bollate (Milano), Italy. Their synthesis and chemical analysis has been described by Tonelli et al. [19]. FP*n* probes were synthesized as described earlier [3]. Millipore deionized water was used for preparation of solutions.

2.2. Methods

Stock solutions of the probes were prepared in chloroform. A proper amount of the respective stock solution was transferred to a vial and the solvent was evaporated under nitrogen. The film thus obtained was dried in vacuum in order to remove last traces of the solvent, and then stirred with the aqueous surfactant solution. The probe concentration in the examined solutions was $\leqslant 0.1$ mmol/dm^3. Probe/surfactant solutions were deaerated by bubbling with argon (at least 40 min). The samples for ESR measurements (in capillary tubes or in 3 mm i.d. quartz tubes, depending on the temperature range of the measurement) were prepared in the glove box, sealed there with parafilm, and flame sealed.

ESR measurements were done with a Bruker X-band ESR 200D-SRC spectrometer operating at 9.7 GHz with 100 kHz magnetic field modulation, on line with an ESP 3220-200SH system for data acquisition and processing. The spectrometer was equipped with a home-made cold gas (N_2) flow cryostat driven by the ITC-4 temperature controller (Oxford Instruments Ltd.). The spectra were recorded at selected temperatures in the range 120–360 K using the following parameters: microwave power 2 mW, time constant 20.48 ms, conversion time 49.96 ms, number of scans 5–10, resolution 2048 points; modulation amplitudes in the range 0.5–2 G depending on the line width of the spectrum; and sweep width in the range 70–140 G. The samples examined at low temperatures were initially quenched in liquid nitrogen.