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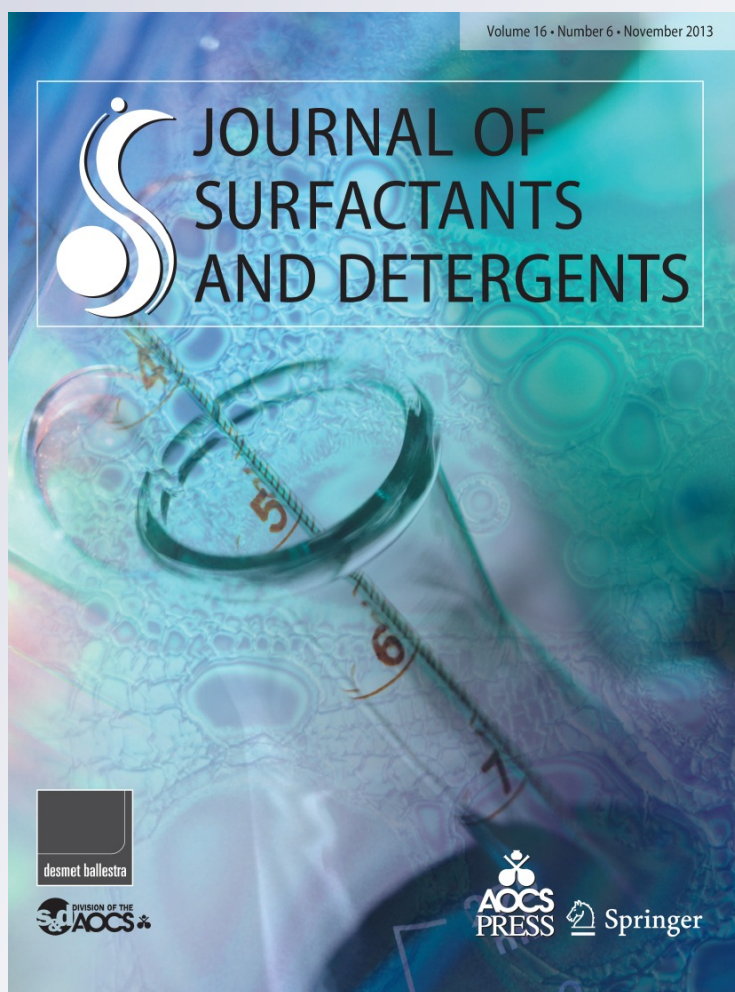
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Abstract The mixed system of an anionic hydrocarbon surfactant, sodium dodecyl sulfate, and a perfluorinated surfactant, perfluorononanoic acid (PFNA), was investigated by a combination of methods. The critical micellar concentrations (CMC) were determined over a wide range of sample compositions by surface tension, conductivity and UV–visible spectrophotometry using N-(4-nitrophenyl)perfluorononanamide as a molecular probe. The values of CMC obtained by different techniques were in good agreement. In addition, the aggregation numbers were determined in the mixtures with a low content of hydrocarbon surfactant, by measuring the fluorescence quenching of pyrene. The hydrodynamic radii of the aggregates were estimated through the diffusion ordered ^{19}F- and ^{1}H-NMR spectroscopy. The values obtained are in agreement with those expected according to the measured aggregation numbers. The analysis of the data with different aggregation models suggests the formation of a non-ideal mixed micelle that is enriched in the perfluorinated surfactant when its mole fraction increases, and that is practically formed by PFNA only at mole fractions higher than 0.8.

Keywords Mixed surfactant systems · Aggregation · Perfluorinated surfactant · ^{19}F nuclear magnetic resonance · Diffusion ordered NMR spectroscopy

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Introduction

Surfactants are compounds of significant interest from a scientific point of view and for industrial applications. The use of amphiphilic molecules as detergents, as dispersion or controlled liberation agents, in areas such as cosmetics, paints, cleaning and biotechnology is particularly important [1]. In most of their practical applications, surfactants are usually mixtures of either homologous compounds or different ionic surfactants. Thus, studies of mixed systems with known composition and structure are potentially instructive for their theoretical and practical implications [2, 3].

Sodium dodecyl sulfate, SDS, either alone or in mixtures with another surfactant, is one of the most widely studied, among ionic surfactants [4], due to its important role in industrial and commercial applications, like the solubilization and stabilization of drugs.

Fluorinated surfactants are characterized by a greater surface activity and chemical stability than that of the corresponding hydrocarbon-type compounds. Because of their unique properties, they prove to be interesting for practical applications and theoretical studies of micellar systems [5–7]. They are used in diverse industrial fields as part of the formulation of fire protection fluids, emulsifiers, cosmetics, or in biological and medical fields [8–10]. Although fluorinated surfactants are superior on surface properties among the surfactants, their extensive use had produced the accumulation of some derivatives in the environment, and so, they are even banned in some developed countries. It would be possible to maintain the properties or even to enhance the performance of fluorinated surfactants, diminishing the concentration used, due to synergistic interaction with conventional hydrocarbon surfactants [11–13].

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The mixtures of perfluorinated and hydrocarbon surfactants are non-ideal in many cases [14, 15]. In recent years an increasing interest in mixtures of fluorocarbon- and hydrocarbon-based surfactants has been noticed for those systems reported to have a limited mutual solubility. Initially, the coexistence of two types of micelles (one fluorocarbon-rich and another hydrocarbon-rich) in mixtures of sodium decyl sulfate (SDeS) and sodium perfluoroctanoate (SPFO) was postulated [16]. The idea of two kinds of micelles has been subsequently supported by others studies [17], however, some authors stated that no demixing occurs in the same mixture [18, 19]. Nordstierna et al. [20] have proposed a single type of micelle with intramicellar segregation where fluorinated surfactants prefer fluorinated neighbors, and hydrogenated surfactants prefer hydrogenated ones. More recently, chemical shift measurements have allowed the calculation of the average fraction of nearest neighbors of each kind of surfactant around a reporter group (the trifluoromethyl group) and a preference for like neighbors was also found [21].

The nonideality of these systems may have significant consequences in: (1) the properties of perfluorocarbon compounds in biological systems, (2) fluorine-labeled molecules for probing or studying hydrophobic environments of proteins, enzymes, or lipid membranes, and (3) surfactants at interfaces where fluorocarbon–hydrocarbon interactions are involved. Those topics, as well as others of interest, motivate chemists to continue studying mixed perfluorocarbon-hydrocarbon systems; they have prompted us to study the mixed micellization of perfluorononanoic acid (PFNA) and sodium dodecyl sulfate (SDS) in aqueous solution at 25 °C in binary combinations. The mixtures of SDS/PFNA were analyzed varying the composition, represented by the mole fraction of the perfluorinated surfactant (α_{PFNA}). For each α_{PFNA} considered, a wide range of total surfactant concentration was analyzed. The mixed system was studied using different techniques that provide tools for their characterization, such as conductivity, surface tension and NMR measurements combined with UV–Visible spectrophotometry and fluorescence spectroscopy in the presence of molecular probes.

Experimental

Materials

Aqueous solutions were made up from water purified in a Millipore apparatus. Acetonitrile HPLC grade (Mallinckrodt or J.T. Baker) was used as received. The D_2O (99.9 atom% D) was purchased from Aldrich.

The molecular probe N-(4-nitrophenyl) perfluorononanamide (1) was synthetized and purified in the laboratory as reported elsewhere [22]. Pyrene (2) (Fluka, 98 %) and
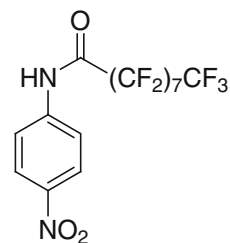
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cetylpyridinium bromide (3) (Aldrich, 98 %) were controlled by NMR to check purity and used without further purification. The surfactants were purchased from Sigma Aldrich (Sigma grade 99–100 %) and controlled by spectroscopic and surface tension techniques to check their purity. Spectroscopic controls included UV visible and NMR techniques. We observed normal surface tension plots for SDS, without the typical deviations of linearity originated by the presence of impurities [4]. All surfactant solutions in water were prepared 24 h before use to ensure that the aggregation equilibrium was reached.

Instrumentation and Techniques

Solvatochromic studies with the molecular probe **1** were carried out adding a very small volume of a stock solution of the probe in acetonitrile (MeCN) to a volumetric flask. Then, the corresponding mixture of surfactants was added. The solutions prepared in this way contained 0.4 % of acetonitrile in water. The critical micellar concentrations (CMC) of the mixtures were determined monitoring changes in the maximum absorption in the UV–visible region of the probe as a function of the total surfactant concentration for each mole fraction of the mixture studied. The measurements were done in a conventional UV–visible spectrophotometer (Shimadzu UV-2101PC) using a 4-cm optical path length quartz cuvette at 25 °C. The amide concentration was maintained constant at 4×10^{-6} mol L^{-1}. The measurements were done 6 h after the preparation of the solutions to ensure that equilibrium had been reached.

Surface tension of the solutions was measured by the ring method using a Du Nöuy ring tensiometer (Cole Parmer Surface Tensiomat 21) at 25.0 °C. The temperature was maintained constant by circulating thermostated water through a jacketed vessel containing the solution. The readings were taken in triplicate to check reproducibility and the averaged values were used for the graphs.

Conductivity measurements were performed at 25.0 °C with a Fisher Scientific Accumet XL20 pH meter/conductimeter, provided with an Accumet conductivity cell. A

standard NaCl solution of $\kappa = 23.8$ μS/cm was used to calibrate the equipment.

All NMR measurements were performed using a Bruker Avance II 400 NMR instrument at 298 K, operating at 400.16 MHz for ^{1}H and 376 MHz for ^{19}F. The solvent was D$_2$O and the external standards used were 3-(trimethyl-silyl)propionic acid sodium salt for ^{1}H NMR and trifluoroacetic acid for ^{19}F NMR. The experiments were carried out at each mole fraction at constant surfactant concentration and following the changes in chemical shifts of the terminal trifluoro-methyl group of the PFNA or the terminal methyl group of SDS.

In the pulse field gradient spin-echo (PFGSE-NMR) experiments the gradient pulse width (δ) and diffusion delay (Δ) were 2.5 and 100 ms for ^{1}H NMR and 2 and 50 ms for ^{19}F NMR respectively. There, we maintained the PFNA concentration as 7×10^{-3} mol L^{-1} that is the maximum concentration allowed by the solubility of this surfactant. The SDS concentration was adjusted to have the desired α_{PFNA}.

Fluorescence measurements were performed using a Perkin Elmer LS 55 fluorescence spectrophotometer using a 1-cm optical path length quartz cuvette. The experiments were done with a constant concentration of the probe (pyrene, $\mathbf{2} = 2.0 \times 10^{-6}$ mol L^{-1}) and quencher (cetyl-pyridinium bromide, $\mathbf{3} = 1 \times 10^{-4}$ mol L^{-1}). As the probe is poorly soluble in water, its solutions were prepared in methanol (HPLC grade, Sintorgan) while the solutions of $\mathbf{3}$ were made in water. After the probe and quencher solutions were added into surfactant solutions, the concentration of which was varied in a range above the CMC, they were shaken for 1 day at 25 °C in a thermostated bath to attain solubilization equilibrium. The final percentage of metha-nol was 0.4 vol %. The excitation wavelengths and scan-ning ranges were 335 and 350–500 nm respectively. The bandwidths of the excitation and fluorescence slides were both set as 3.0 nm. Pyrene concentration was low enough to prevent the excimer formation due to self-assembling [23].

All the determinations were carried out at (25.0 ± 0.1) °C; the temperature was kept constant using an external circulating bath. The experiments were performed without control of the pH. Nevertheless, the total changes in the pH solutions were checked, with the finding that the total change is between 4.5 for the most diluted solution and 2.9 for the most concentrated one. Under all the con-ditions we were working with acid solutions.

Results and Discussion

CMC Measurements

Surface tension (γ) of aqueous solutions of single SDS and mixed SDS/PFNA surfactant systems was measured for a range of concentrations above and below the CMC. In each measurement we waited between 5 and 20 min. The time was longer with the increase in the content of PFNA in the mixture. Pure PFNA could not be measured because its stabilization was too slow; the time necessary between each measurement in these solutions was longer than 2 h. Representative plots are shown in Fig. 1. Table 1 displays the CMC values obtained from the break point of the plots. It is important to take into account that the final value of the surface tension, reached when the micelles are formed, diminished with the increase of α_{PFNA}, and is practically the same from α_{PFNA} 0.4–1.

For the CMC determinations from UV–Visible mea-surements, N-(4-nitrophenyl) perfluorononanamide (**1**) was used as the molecular probe. In a previous work from our laboratory it was shown that **1** aggregates at concentrations as low as 2×10^{-6} mol L^{-1} [22]. Solutions of **1** at con-centrations above 2×10^{-6} mol L^{-1} show a single absorption band at $\lambda_{max} = 270$ nm which is attributed to the aggregated form. Addition of a surfactant to an aqueous solution of **1** at concentrations above its respective CMC causes a breakdown of the aggregates, as evidenced by the disappearance of the peak at 270 nm, and a concomitant appearance of a peak at 304–310 nm (depending on the surfactant) corresponding to the monomer of **1** [24]. Therefore we considered that this probe could be useful to determine CMC values of the mixtures of fluorocarbon–hydrocarbon surfactants. We previously used it to charac-terize the mixture of dodecyl alcohol ethoxylate (with an average of 23EO) with PFNA [25]. In Fig. 2, the values of the maximum absorption wavelength in each spectrum at each total surfactant concentration at $\alpha_{PFNA} = 0.4$ are plotted. The complete graph has a sigmoid shape.

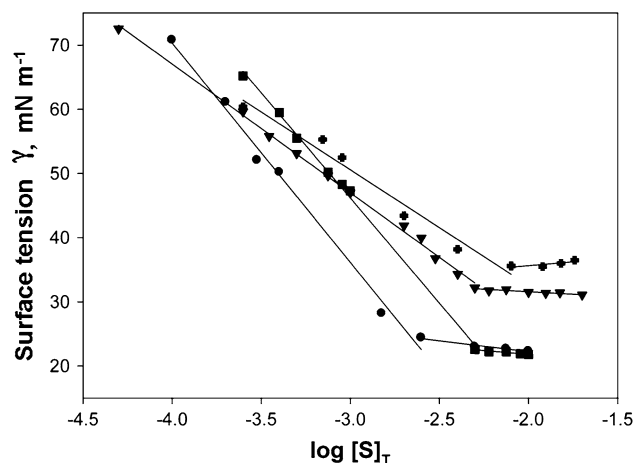**Fig. 1** Surface tension measurements in aqueous SDS/PFNA mix-tures for at $\alpha_{PFNA} = 0.0$ (*plus*), 0.1 (*inverted triangles*), 0.6 (*squares*) and 0.9 (*circles*); $T = (25.0 \pm 0.1)$ °C

Table 1 Summary of the CMC determined for the mixed system SDS/PFNA by different techniques

| α_{PFNA}	Surface tension	UV–visible	Conductivity
0.0	7.06 (8.00[a], 5.50[b])	d	8.25 (7.75[c])
0.1	5.57	9.03	9.62
0.2	d	7.92	8.26
0.3	7.49	7.29	8.63
0.4	8.46	5.46	6.06
0.5	5.48	5.79	5.53
0.6	5.29	4.94	5.06
0.7	4.92	2.97	4.03
0.8	2.90	3.08	3.65
0.9	1.86	2.50	3.10
1.0	d	2.11	3.13

All the concentrations (CMC) are expressed in mmol L^{-1}

Values within brackets are from the literature: [a] Griffiths et al. [48], [b] Zhu et al. [49]. [c] Chatterjee et al. [50]. [d] The absent values were not determined because the systems gave unsatisfactory results
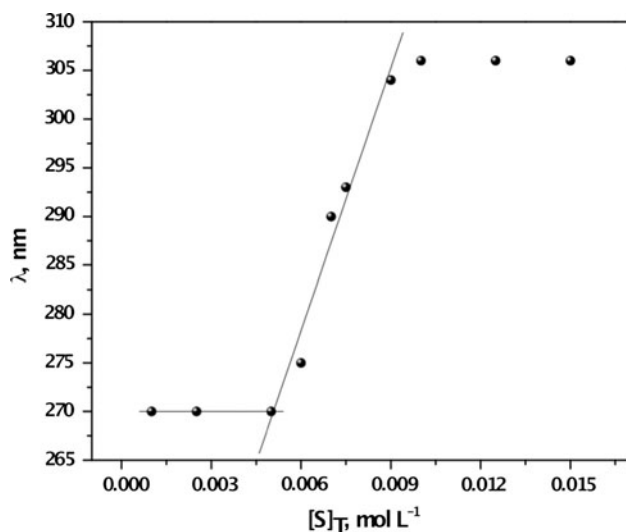
Fig. 2 Plot of λ_{max} of **1** against total surfactant concentration ([S]$_T$) in aqueous SDS/PFNA mixtures at $\alpha_{PFNA} = 0.4$, $T = (25.0 \pm 0.1)$ °C, [**1**] $= 4 \times 10^{-6}$ mol L^{-1}, MeCN $= 0.4$ %

From these plots, we calculated the CMC for the different compositions of the mixture SDS/PFNA using the first break point of the graph according to the methodology proposed by Aguiar et al. [26]. Table 1 shows the results. The values of the CMC are in general lower with this methodology than with the other techniques. This probe interacts readily with the fluorinated surfactant, and may form mixed micelles with it, probably even at concentrations below the true CMC, whereas it does not interact so readily with pure SDS [24].

Conductivity (κ) of aqueous solutions of pure and mixed SDS/PFNA surfactant systems was measured for a range of concentrations above and below the CMC. Some representative
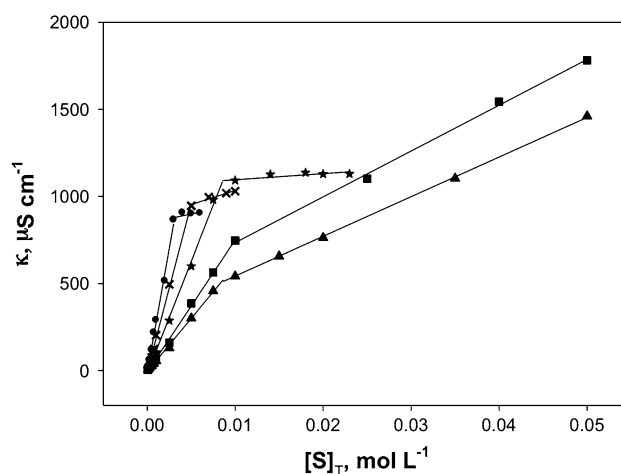
Fig. 3 Conductivity measurements in aqueous SDS/PFNA mixtures at $\alpha_{PFNA} = 0.0$ (*triangles*), 0.1 (*squares*), 0.3 (*stars*), 0.6 (*multiplication signs*) and 1.0 (*circles*); $T = (25.0 \pm 0.1)$ °C

plots are shown in Fig. 3. The CMC values obtained from the break point of the plots are shown in Table 1. As expected, the slope above the CMC is lower than the one below the CMC, as micelles are worse charge carriers when compared to the surfactant monomers.

It is worth noting that despite the fact that the conditions are not exactly the same for the method which involve the use of the molecular probe (UV–Visible) and those that not (conductivity and surface tension), the values of CMC obtained are similar in most cases. Besides, all techniques lead to only one CMC value, in contrast with our previous finding in the system polyoxyethylene (23) lauryl ether (Brij-35)/PFNA [25].

Analyzing the observed CMC we can see that after α_{PFNA} 0.3–0.4, the CMC values diminished with the increase in the mole fraction of the perfluorinated surfactant. At $\alpha_{PFNA} \geq 0.8$ the values were very close to the CMC of pure PFNA.

Determination of Aggregation Numbers

It is well known that the ratio of the intensity of a probe in the presence (I) and the absence (I_0) of a quencher (Q) is related to the aggregation number (N), the concentration of quencher and the total concentration of a given surfactant ([S]$_T$), as shown by Eq. 1 [27, 28].

$$\left[\ln\left(\frac{I_0}{I}\right)\right]^{-1} = \frac{1}{[Q]N}([S]_T - CMC)] \tag{1}$$

Plots of the left-hand side of Eq. 1 (corresponding to the fluorescence of pyrene) against the total surfactant concentration of the mixture at constant Q concentration (Q = cetylpyridinium bromide) were linear and from the slopes the aggregation numbers were determined. As it is
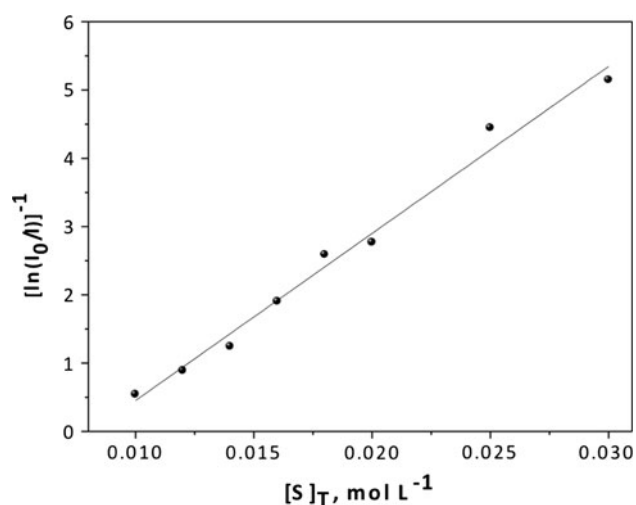
Fig. 4 Plot of $[\ln(I_0/I)]^{-1}$ corresponding to pyrene as a function of total surfactant concentration in aqueous SDS/PFNA mixtures at $\alpha_{PFNA} = 0.2$, $T = (25.0 \pm 0.1)$ °C, $[2] = 2 \times 10^{-6}$ mol L^{-1}, $[3] = 1 \times 10^{-4}$ mol L^{-1}

Table 2 Aggregation numbers (N) and hydrodynamic radii (r_s) for the mixed system SDS/PFNA

α_{PFNA}	N[a]	r_s (^{1}H) (nm)[b]	r_s (^{19}F) (nm)[c]
0.0	60	2.0	
0.1	91	4.0	3.2
0.2	41	3.8	
0.3	34	1.1	
0.4		1.2	1.1
0.5			1.8
0.6			1.1
0.8			1.5
0.9			1.4
1.0	4		1.2

[a] Determined by fluorescence quenching of pyrene in the presence of the quencher cetylpyridinium bromide

[b] Determined by ^{1}H-DOSY measurements

[c] Determined by ^{19}F-DOSY measurements

clear from Eq. 1, it is also possible to obtain the aggregation number at a constant concentration of surfactant by changing the Q concentration. In the present study, however, we employed the former method. A representative plot is shown in Fig. 4. Table 2 summarizes the aggregation numbers obtained in this way.

The value of N obtained for pure SDS, shown in Table 2, is in good agreement with previously reported values, 69 and 64 [29, 30]. At $\alpha_{PFNA} = 0.1$ the aggregation number is higher than that obtained for pure SDS but with the increment in α_{PFNA}, the value of N diminishes. The CMC obtained from these plots (see Eq. 1) are in concordance with the CMC measured from the other techniques.

For instance, from Fig. 4, the CMC determined is 8.16×10^{-3} mol L^{-1} (see Table 1 to comparison).

The measurements at mole fractions between 0.4 and 0.9 gave scattered results; therefore reliable values could not be obtained. This fact could be related to the selective solubilization of the probe depending on the content of hydrocarbon/perfluorinated surfactant in the mixture, as was previously reported [27]. Pyrene has much less affinity for a perfluorinated micelle than for a normal one. The value of N determined for PFNA is very small, so probably a minor part of pyrene is associated with micelles; most pyrene remains in the aqueous subphase and is not strongly quenched by the surfactant quencher. That is one possible explanation of the small value obtained for PFNA. However a small aggregation number in perfluorooctanoate micelles had been previously noted. A value of 7 was reported by Turro et al. [31] and later on, other authors [32] found a value of 26 for a solution of sodium perfluorooctanoate 0.1 mol L^{-1}, with this value decreasing with the square root of surfactant concentration. Although in those cases, the sodium salt of the perfluorooctanoic acid was used, it is known that perfluorinated acids have very low pKa values [33], so in water, PFNA is practically completely dissociated.

NMR Measurements

Pulse field gradient NMR spectroscopy enables one to determine surfactant diffusion coefficients. Diffusion NMR has proved itself to be a powerful method in multiple-component mixture analysis, study of aggregation formation, ligand and receptor recognition, and high-throughput screening of drugs [34]. In particular, diffusion ordered NMR spectroscopy (DOSY) has been used in recent years to characterize micellar systems. In systems containing perfluorinated compounds like this, DOSY is a useful tool for determining the size of aggregates, because light scattering techniques are not adequate due to the similarity between the refractive index of the perfluorinated surfactant with water [35].

The spin echo intensity (I_g) was measured as a function of the gradient strength (g). Using the nonlinear least-squares method, the diffusion coefficient of the aggregate (D_s) in D$_2$O was estimated from Eq. 2, where γ_N is the gyromagnetic ratio of the nucleus measured, I_0 is the spin-echo intensity in the absence of the gradient spin-echo, δ is the length of the gradient pulses and Δ is the diffusion period [36].

$$I_g = I_0 \exp\left(-(\gamma_N \delta g)^2 D_S\left(\Delta - \frac{\delta}{3}\right)\right) \qquad (2)$$

The D_s values were determined by the ^{1}H-NMR signal of the terminal methyl group of SDS and by ^{19}F-NMR signal of the terminal trifluoromethyl group of PFNA using Eq. 2 in both cases.

The diffusion coefficients using ^{1}H measurements could only be obtained for mole fractions of perfluorononanoic acid smaller than 0.5, due to the very small content of H nuclei at higher α_{PFNA}. Using ^{19}F experiments it was possible to determine the D_s values at the remaining mole fractions. The hydrodynamic radii (r_s) of the SDS/PFNA aggregates in the different mixtures were calculated from the D_s values using the Stokes–Einstein Eq. 3 which assumes that the particles are spherical and none interacting:

$$D_s = \frac{k_B T}{6\pi\eta r_s} \tag{3}$$

In Eq. 3 k_B is the Boltzmann constant, T is the absolute temperature and η is the solution viscosity. The results obtained are summarized in Table 2.

The values of r_s determined by ^{1}H and ^{19}F DOSY are in accordance. The value of the hydrodynamic radius of SDS is in agreement with values reported in the literature, 1.8 and 1.75 nm [29, 30].

At $\alpha_{PFNA} = 0.1$ the radius increases and is significantly different to that of pure SDS, as would be expected considering the higher aggregation number. This fact is concordant with the incorporation of fluorinated surfactant in a hydrocarbon micelle of SDS. However, when the content of PFNA continues increasing, the radius diminishes again and between α_{PFNA} 0.4 and 1, it is relatively constant and similar to that obtained for PFNA alone.

Additional evidence of this behavior in the system can be obtained from the chemical shifts of the terminal trifluoromethyl group of PFNA varying α_{PFNA}, but keeping [PFNA] constant at 7×10^{-3} mol L^{-1} to have a considerable signal. The chemical shift of this signal at α_{PFNA} between 0.1 and 0.3 is different from that corresponding to pure PFNA, but after that mole fraction, the signal remains practically constant and equal to that of pure PFNA (Fig. 5). This would be another indication that the aggregate becomes similar to a pure PFNA one, or that there is intramicellar segregation as was suggested in Ref. [20].

Aggregation Models in the Mixed Systems

In the system under study we could detect only one CMC at the different compositions analyzed by the different techniques used. At first, we can consider that in the system one type of mixed micelle is formed. The experimental data can be analyzed considering different possible models of aggregation.

If the phase separation model for micellization is adopted, and a mixed micelle is treated as an ideal mixture of its components and the activity coefficient for free surfactant monomers is assumed to be equal to unity, then it can be shown that the monomer concentration of the fluorinated component is given by Eq. 4 [37],
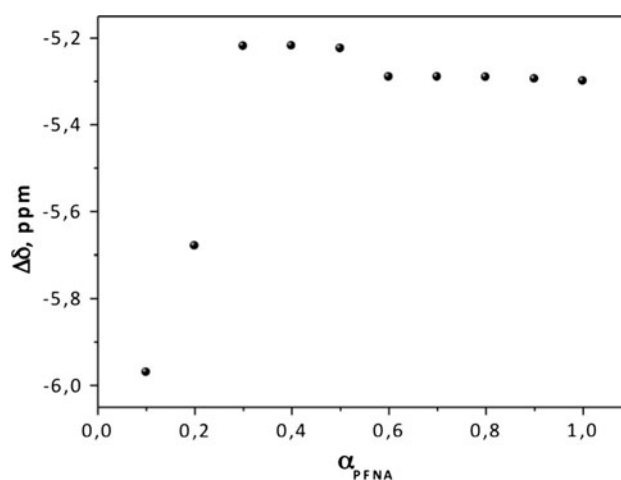

Fig. 5 Chemical shift changes of PFNA terminal trifluoromethyl group signal for the mixture SDS/PFNA with the variation of α_{PFNA}, [PFNA] $= 7 \times 10^{-3}$ mol L^{-1}

$$C_F^m = x_F CMC_F \tag{4}$$

where x_F is the mole fraction of the fluorinated surfactant in the mixed micelle, and the CMC_F is that corresponding to pure PFNA. From Eq. 4, a similar equation for SDS, and a simple mass balance equation, x_F can be eliminated to give Eq. 5.

$$\frac{1}{CMC_i} = \frac{\alpha_F}{CMC_F} + \frac{(1-\alpha_F)}{CMC_H} \tag{5}$$

where CMC_i, is the ideal critical micelle concentration of the mixture, α_F is the stoichiometric fraction of fluorinated surfactant in the mixed solution (α_{PFNA}) and CMC_F and CMC_H are the experimental CMC of the pure surfactants. Figure 6 displays the plot of the values of experimental CMC obtained from conductivity measurements versus α_{PFNA}. The solid line represents the values of CMC_i for each composition of the mixture. The CMC values observed were found to be higher than ideal values until $\alpha_{PFNA} = 0.8$, indicating positive deviation from ideal behaviour for mixed micelle formation. The CMC data used to do the calculations, and shown in Fig. 6, were the obtained from conductivity measurements. However, with the data from surface tension and UV–visible experiments, we obtained very similar plots with the same tendencies (not shown).

To analyze the CMC considering non-ideal mixing, activity coefficients should be introduced for the components within the micelles, thus making Eq. 4 become:

$$C_F^m = x_F f_F CMC_F \tag{6}$$

where the activity coefficient, f_F, is given by the Regular Solution Theory as in Eq. 7 [38]:

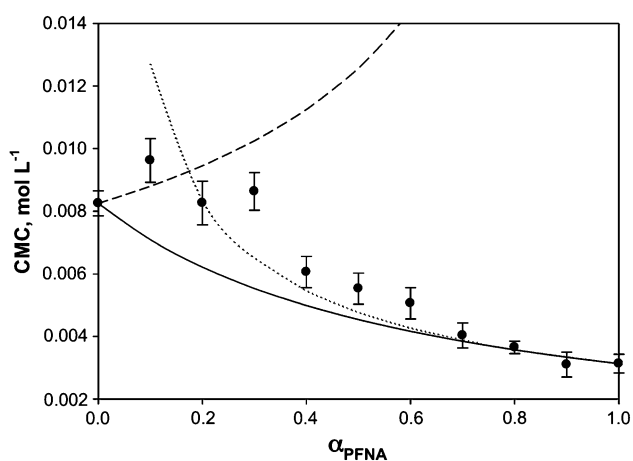$$f_F = \exp\left[\beta(1-x_F)^2\right] \tag{7}$$

Fig. 6 CMC of mixtures of SDS/PFNA determined by conductivity measurements (*symbols*). The curves are theoretical ideal CMC$_i$, (*solid line*), and calculated assuming complete demixing, according to Eq. 12, CMC$_H$ (*dashed line*) and CMC$_F$ (*dotted line*)

with similar expressions for the hydrocarbon surfactant, where β is the interaction parameter.

At the mixed CMC:

$$C_F^m = \alpha_F CMC \tag{8}$$

Hence,

$$x_F \exp\left[\beta(1 - x_F)^2\right] = \alpha_F CMC/CMC_F \tag{9}$$

and

$$(1 - x_F)\exp\left[\beta(x_F)^2\right] = \alpha_F CMC/CMC_H \tag{10}$$

Since we can measure the CMC of the mixture at known α_F, Eqs. 9 and 10 represent two simultaneous equations that can be solved numerically for β and x_F.

Assuming that β has the same value across the whole mole fraction range as is done in Regular Solution Theory, then for any other value of α_F we can solve Eqs. 9 and 10 for x_F and CMC.

In this way, we calculated a value of β equal to 1 with the CMC obtained from conductivity measurements.

In the mixed systems of fluorinated and hydrocarbon surfactants, the value of β is a useful criterion to estimate, at least qualitatively, the degree of compatibility between the two surfactants and whether micellar phase separation does occur or not. The value of β obtained in this work, is positive indicating an unfavorable interaction of the surfactants in these mixtures. It had already been pointed out by other authors that small uncertainties in the CMC values of the pure components and of the mixture, induce substantial errors in the value of β, especially for high $\beta > 2$ [39]. Although the absolute value of β determined here is somewhat questionable, it undoubtedly reflects the strong incompatibility between the two components of the mixture.

Positive values of β are typically found in systems with the same charge in the head group plus a different nature in the alkyl chain and, as mentioned above, in several cases they are related to the formation of two kinds of coexisting micelles [40, 41]. For instance, similar results were found by Clapperton et al. [42] in binary mixtures of two anionic surfactants, ammonium decanoate and perfluorooctanoate. Their experiments showed non-ideal, unfavored mixing of the hydrocarbon and fluorocarbon species in the micelle, with β values between 1.6 and 2.2 depending on the mole fraction. However, they analysed the system, mainly at high mole fractions of the hydrocarbon surfactant, and concluded that independent micellization does not occur in their experimental conditions.

Theoretical CMC can be roughly estimated for non-ionic surfactants using the extreme case of complete demixing. Here, micelle formation occurs when the concentration of one of the surfactants exceeds its CMC value. Then, the two CMC for each surfactant (CMC$_M$) in the mixture are given by Eq. 11 [16].

$$CMC_M = \frac{CMC_0}{\alpha} \tag{11}$$

where CMC$_0$ is the value for the pure surfactant and α is its mole fraction. For ionic surfactants, however, the counterion of one component affects the CMC of the other, and Eq. 11 is modified according to the relation between the CMC of each surfactant in the mixture and the concentration of the counterion of SDS (Na$^+$ in our case) to give Eq. 12 [16].

$$CMC_M = CMC_0 \, anti\log\left(\frac{\log(1/\alpha)}{1 + B}\right) \tag{12}$$

In Eq. 12, B corresponds to the slope in the plot of log CMC versus log [Na$^+$]. This equation must be applied to each component separately. To do the calculations we used the value of B reported previously by Mysels and Kapauan for sodium decyl sulfate, 0.645, as a representative value [43]. As shown in Fig. 6, the experimental CMC were not satisfactorily fitted with the CMC$_M$ calculated according to Eq. 12 until $\alpha_{PFNA} = 0.7$–0.8. Beyond these mole fractions, the values of CMC are in good agreement with a micelle of pure PFNA or an ideal aggregate. The high value calculated for β could be an indicator of demixing that could be expected with these surfactants based on the behavior of systems formed by amphiphilic molecules of similar chain lengths. For instance, the mixture of ammonium perfluorononanoate and ammonium dodecyl sulfate shows only partial mixing at 25 °C [39]. In the systems formed by lithium perfluorooctanesulfonate and lithium dodecyl and tetradecyl sulfate, Villeneuve et al. [44] also found an inaccessible composition domain, indicating micellar segregation for the perfluorinated surfactant and each hydrocarbon detergent.

In systems with shorter chains, such as sodium decyl sulfate and sodium perfluorooctanoate, several authors claimed there were two different micelles. However Nordstierna et al. [20] presented two possible scenes on the bases of detailed [19]F- and [1]H-chemical shift data in combination with self-diffusion coefficients: (1) partial demixing into two distinct micelle types, or (2) no micellar level demixing but local chemically selective coordination within a single micelle type. They incline toward the one-micelle-type scenario because of the low value of the energy of mixing obtained in that work.

The chain length of the hydrocarbon surfactant has a considerable influence on the miscibility of hydrocarbon and fluorocarbon surfactants, either in adsorbed films or in micelles, as was demonstrated by Aratono et al. in the study of sodium and lithium perfluorooctanoates with sodium decyl, lithium dodecyl and lithium tetradecyl sulfates [17, 45, 46]. In these works it was reported that the longer the hydrocarbon chain is, the greater the immiscibility. The number of perfluorinated carbon atoms seems to influence the aggregation process too and in cases where the perfluorinated chain has nine or more carbon atoms, demixing occurs [40]. According to the references mentioned, it would be not so rare to find in the system SDS/PFNA, with twelve and nine carbon atoms respectively, demixing at high α_{PFNA}. Under these conditions (high α_{PFNA}), the SDS concentration is lower than its CMC, so there is no possibility of forming pure SDS micelles. The free monomers of SDS could co-exist with perfluorocarbon micelles or be dissolved in mixed micelles. If the latter occurs, considering the small value of β, their incorporation will most likely not significantly affect the properties of the mixed aggregates, because the experimental results resemble the characteristics of pure fluorocarbon micelles.

Our results are also in very good agreement with those obtained by Nakano et al. [27] who studied the mixture of sodium tetradecyl sulfate (STDS) with sodium perfluorononanoate. Their findings indicated that demixing micelles are almost completely formed at mole fractions of STDS below 0.2, which agrees with the behavior observed in this work at $\alpha_{PFNA} > 0.8$. An interesting point is that fluorocarbon aggregates cannot solubilize any hydrocarbon, whereas hydrocarbon micelles allow the incorporation of some fluorinated molecules. This behavior has already been noticed by other researchers [35].

Conclusions

The mixtures of PFNA and SDS are not ideal as it is usual in many mixed surfactant systems [14, 21, 48]. The CMC of the mixed solutions were found to be dependent on the PFNA composition of the bulk, with CMC values superior to those of the pure surfactants, which indicate repulsion between the components of the blend [16].

The comparison of the values of CMC, aggregation number and size of the aggregates at different compositions of the mixture, allowed us to gain information about the characteristics of the system. The aggregates seem to be enriched in the perfluorinated surfactant with the increase in α_{PFNA}.

Regular solution theory has been applied in the analysis of the mixtures of SDS/PFNA, and the interaction parameter β, has been evaluated, finding a positive value in contrast with the slightly negative values obtained for mixtures of PFNA with the non-ionic surfactant polyoxyethylene (23) lauryl ether [25]. This positive value could be attributed to the same charge in the head group of the surfactants, plus a different nature in their alkyl chains [43]. Although the conditions of the study do not allow the detection of different coexisting aggregates in the mixed system, the analysis of the data indicates that the surfactants show mutual phobia in addition to their hydrophobicity, forming aggregates very rich in PFNA, that beyond $\alpha_{PFNA} = 0.8$ are practically formed by pure PFNA. This conclusion is based on two indirect but coincident pieces of evidence: (1) the CMC values measured at high content of perfluorononanoic acid were very close to those calculated for the complete demixing of both surfactants, and (2) the sizes of the aggregates in those conditions are very close to those obtained in pure PFNA. The observed behavior can be then associated with same charge in the head group of the surfactants, different natures in their alkyl chains, and chains long enough.

The results obtained and the analysis of previous related works [20, 28, 40, 43, 45–47] make it possible to establish a structural border in mixtures of perfluorinated-hydrocarbon systems which, although it is not strict, could serve to predict the behavior of different systems according to the chain length of the surfactants involved.

From the design and synthesis of innovative amphiphilic molecules and due to balanced forces between the hydrogenated and fluorinated repulsions, an extraordinary variety of architectures can be obtained, leading to a number of potential applications. However, the difficulties in their study increase with the complexity of their design, and their understanding should benefit from the progress in the study of mixtures of simpler surfactants.

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