

# $^1\text{H}$ and $^{19}\text{F}$ NMR Investigation on Mixed Hydrocarbon–Fluorocarbon Micelles

M. E. Amato, E. Caponetti,\* D. Chillura Martino, and L. Pedone

Dipartimento di Chimica Fisica, Università di Palermo, Viale delle Scienze, I-90128 Palermo, Italy, and Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, I-95125 Catania, Italy

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$^1\text{H}$  and  $^{19}\text{F}$  NMR measurements on aqueous solutions of sodium perfluorooctanoate (SPFO) and sodium dodecanoate (SD) mixtures are reported. The surfactant concentration ranged from  $\sim 0.3$  to 10 times the critical micelle concentration ( $\text{cmc} \cong 0.03 \text{ mol L}^{-1}$ ). The cmc of the SD/SPFO/water mixed system obtained from NMR data was in good agreement with that previously obtained by conductivity measurements. Below the cmc, the experimental chemical shift ( $\delta$ ) was independent of the total concentration for both surfactants. Above the cmc, however, the  $\delta$  values for  $^{19}\text{F}$  varied linearly with concentration, whereas the values for the hydrogenated surfactant deviated from linearity. These observations indicate that below the cmc each monomer is not affected by the presence of the others. Above the cmc, on increasing the total concentration, the chemical shift trends indicate that the fluorinated chains begin to aggregate, forming islands among hydrocarbon chain domains. Since the extended chain of the fluorinated surfactant is shorter than the inner micelle radius, some methyl groups of the longer SD must be segregated within the micelle. This patchwork distribution, involving an intramicellar phase separation, prevents the computation of the micelle composition; however, NMR data give information complementary to that obtained by a previous SANS study indicating the existence of mixed micelles having the same composition. Information on the structure of micelles and on the mean distribution of the two components in the system are obtained by SANS, while the NMR technique suggests details on the chemical environment of a single monomer and on the structural organization of the molecules within a micelle. Thus, the patchwork model here proposed is able to explain apparently conflicting data obtained from different techniques.

## Introduction

Aqueous solutions containing a mixture of two different surfactants display properties different from those of solutions containing only one of the two surfactants. Since in most practical applications<sup>1–8</sup> surfactants are seldom used by themselves, studies on mixed systems are potentially instructive.

In particular, mixtures of hydrogenated and fluorinated surfactants are indeed very useful in many practical applications; in addition they provide a useful test for a variety of models. The main question is to verify whether mixed micelles, containing both surfactants in a well-defined proportion, or two kinds of micelles enriched in one of the two components are formed. On the basis of enthalpic factors alone, the formation of mixed micelles is not expected in these systems because of the presence of repulsive interactions between hydrocarbon and fluorocarbon chains. However, micellization is the result of a balance between enthalpy and entropy, and therefore it is necessary to take both contributions into account in order to interpret the experimental results.

Regular Solution Theory (RST), developed to describe the behavior of liquid mixtures, predicts that demixing will occur for  $\beta > 2$ , where  $\beta$  is a parameter accounting for molecule–molecule interactions. RST has been successfully applied<sup>9–11</sup> to several systems containing mixtures of surfactants, and has explained<sup>9</sup> the experimental trend of the critical micelle

concentration (cmc) as a function of the stoichiometric composition,  $\chi$ . Free energy of mixing, calculated from activity coefficient data,<sup>11</sup> indicates that demixing actually occurs for  $\beta > 1.7 \pm 0.1$ .<sup>10,11</sup>

In a solution containing a mixture of two surfactants, if only one kind of mixed micelle exists, Rubingh's approach<sup>9</sup> can be used to predict the micelle composition,  $\alpha$ , as a function of  $\chi$  and of total surfactants concentration,  $C_T$ , as

$$\alpha = \frac{-(C_T - A) + \sqrt{(C_T - A)^2 + 4\chi C_T A}}{2A} \quad (1)$$

where  $A = \gamma_1 \text{cmc}_1 - \gamma_2 \text{cmc}_2$ , and  $\gamma_i$  and  $\text{cmc}_i$  are the activity coefficients and the cmc of the two surfactants. At high concentration, even though mixing is not ideal, the micelle composition approaches the stoichiometric one because the number of free monomers is small. On diluting the system, since the mixing process is not ideal ( $\gamma_1 \neq \gamma_2 \neq 1$ ), the micelle composition will differ from the stoichiometric one even if the cmc values of the two surfactants are the same. The larger is the difference, the bigger is the departure from ideality; it increases when the concentration approaches the cmc.

To test the predictions of RST, one needs to determine experimentally the relative amount of the two surfactants in the micelles. As far as we know, only a few direct determinations of micelle composition have been reported in the literature; the reason for this is that each technique can be applied only to systems having particular features.<sup>12</sup> For example, emf measurements using ion-selective electrodes can be performed only if different ionic headgroups are present. On the other hand, Small-

\* Author to whom correspondence should be addressed. Prof. Eugenio Caponetti, Dipartimento di Chimica Fisica, Viale delle Scienze, Parco D'Orleans II, 90128 Palermo, Italy. Phone: ++39 091 6459842. Fax: ++39 091 590015. E-mail: scatter@unipa.it.

Angle Neutron Scattering (SANS) can be used only if the scattering length densities of the two surfactants are appreciably different.

Among different possible hydrogenated/fluorinated surfactant mixtures, the sodium dodecanoate (SD)/sodium perfluorooctanoate (SPFO)/water system is interesting because the two surfactants are constituted by the same headgroup, the same counterion, and possess chains having roughly the same volume ( $364 \text{ \AA}^3$  for SD and  $384 \text{ \AA}^3$  for SPFO) but different extended lengths ( $15.42 \text{ \AA}$  for SD and  $10.36 \text{ \AA}$  for SPFO) and different stiffnesses; in addition, the two cmc values,  $0.028 \text{ mol L}^{-1}$  for SD and  $0.030 \text{ mol L}^{-1}$  for SPFO,<sup>11</sup> indicate similar hydrophobic–hydrophilic interactions. In 1984, Carlfors and Stilbs<sup>13</sup> investigated this system using the Fourier transform (FT) Nuclear Magnetic Resonance Pulsed-Gradient Spin–Echo (NMR–PGSE) technique in the two extreme regions of composition ( $0.16 < \chi_{\text{SD}} < 0.30$  and  $0.88 < \chi_{\text{SD}} < 0.99$ ). These authors interpreted the observed diffusion coefficient trends by assuming the presence of a mixture of micelles. More recently, the experimental cmc trend of the SD/SPFO/water system has been reproduced using RST;<sup>11</sup> a  $\beta = 1.6 \pm 0.1$  borderline value was obtained, and this implies some uncertainty about the presence of mixed micelles or a mixtures of two kinds of micelles.

We have recently used SANS coupled with the external contrast technique to study the same system.<sup>14,15</sup> Beside obtaining structural parameters such as dimension, shape, and charge of the aggregates, we suggested that, in this system, mixed micelles were present at all the examined stoichiometric mole fractions.<sup>14,15</sup> In addition, the micelle composition was determined by using an appropriate SANS data analysis procedure.<sup>15</sup> On approaching the total cmc, the mixed micelles were always found richer, with respect to the stoichiometric composition, in the component present in solution in greater amount. The agreement between our results and Rubingh's predictions was generally good, although appreciable differences were observed at large SPFO mole fractions. The above results can be considered satisfactory in view of the fact that the different chemical nature of the surfactant tails could not taken into account in the data analysis. In addition, it must be stressed that, since neutrons can only distinguish among large regions characterized by different scattering length densities, just the mean composition of the aggregates can be obtained by SANS.

Structural information on surfactants and their micelles at a molecular level can also be obtained by other techniques such as NMR. This powerful tool takes advantage of the separate observation of the two nuclei present at the same time in mixed solutions and, as a consequence, can provide useful details on the physical-chemical environment of each component.

To gain insight on the microscopic aspects of the micellar miscibility and on the organization of the surfactant molecules within the micelle, in this paper we report  $^1\text{H}$  and  $^{19}\text{F}$  NMR measurements on the SD/water, SPFO/water, and SD/SPFO/water systems.

## Experimental Section

$\text{D}_2\text{O}$  was an Aldrich (99.8 D at. %) product. SPFO was prepared by neutralizing doubly crystallized perfluorooctanoic acid (Fluka) with NaOH (Merck). SD was a Sigma product. Before use, both surfactants were dehydrated under vacuum at  $60^\circ\text{C}$  for 72 h.

$\text{D}_2\text{O}$  stock solutions of SPFO and SD  $0.35 \text{ mol L}^{-1}$  were prepared by weight. By mixing proper volumes of the above solutions, SPFO–SD samples were prepared at the same total surfactant concentration ( $0.35 \text{ mol L}^{-1}$ ) and five different mole

fractions ( $\chi = 0.0, 0.3, 0.5, 0.7, 1.0$ ). Samples at different total surfactant concentration were obtained by diluting with  $\text{D}_2\text{O}$  the appropriate solutions ( $C_{\text{T}} = 0.001, 0.015, 0.03, 0.07, 0.11, 0.17, 0.21, 0.28$ , and  $0.35 \text{ mol L}^{-1}$ ).

$^1\text{H}$  and  $^{19}\text{F}$  NMR were recorded at  $30^\circ\text{C}$  on a Varian Unity INOVA 500 spectrometer equipped with pulse field gradient module (Z axis) using a tunable 5 mm Varian inverse probe. The  $^1\text{H}$  NMR spectra (16K data points) were recorded at 499.88 MHz and the chemical shifts were referred to tetramethylsilane (TMS) as external standard. The  $^{19}\text{F}$  NMR spectra (64K data points) were run at 470.302 MHz. The  $^{19}\text{F}$  chemical shifts are reported relative to external  $\text{CF}_3\text{COOH}$  at 0 ppm. The N-type gradient-enhanced absolute value  $^{19}\text{F}$ –COSY experiments were performed as reported elsewhere.<sup>16,17</sup>

Assignment of the resonances in the  $^1\text{H}$  spectra was reported elsewhere.<sup>18</sup> The  $^{19}\text{F}$  NMR spectra of the fluorocarbon chain were assigned as recently described.<sup>16,19</sup>

## Results and Discussion

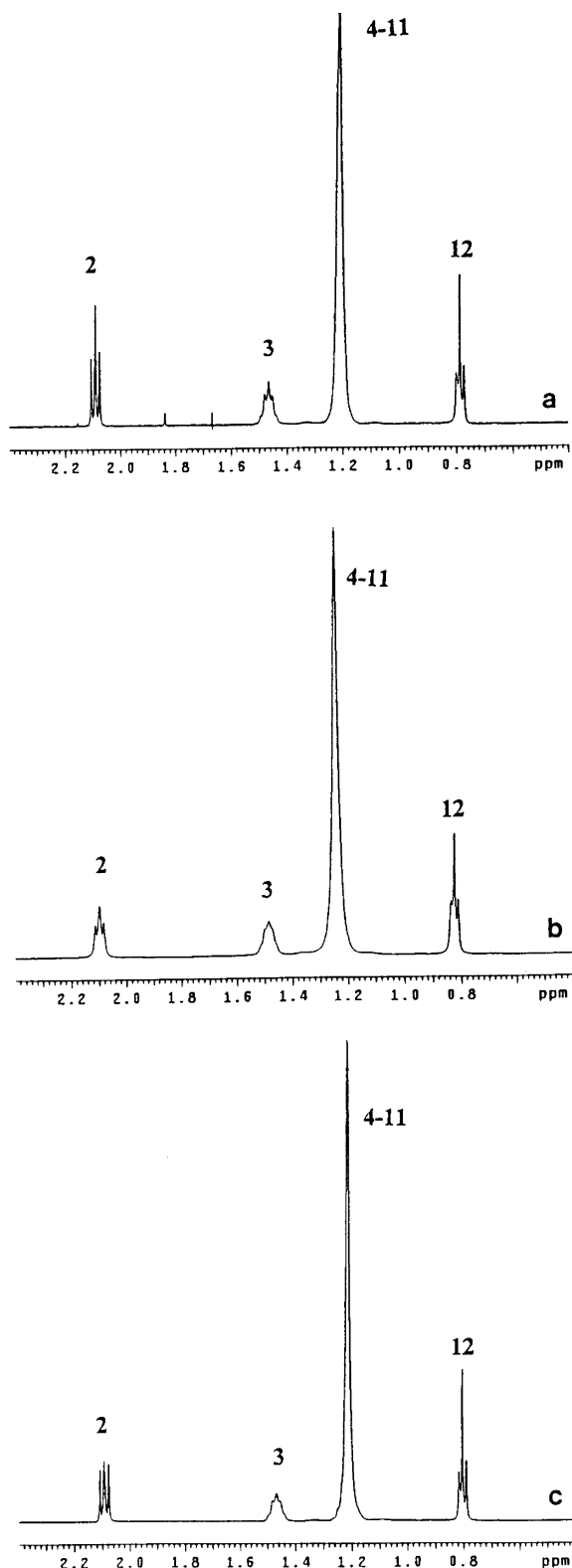
The physical-chemical environment around a surfactant molecule is expected to be quite different if the molecule exists as a free monomer surrounded by water molecules or if it is part of micelles surrounded by other surfactant molecules. In addition, microscopic aspects of intra-micellar environments are expected to be influenced by the formation of mixed micelles, if any.

A large number of  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were collected. In Figures 1 and 2 are shown, as typical examples, the spectrum obtained from SD/water and SPFO/water systems at  $C_{\text{T}} = 0.001 \text{ mol L}^{-1}$  and  $C_{\text{T}} = 0.35 \text{ mol L}^{-1}$  and that from the SD/SPFO/water system at  $C_{\text{T}} = 0.35 \text{ mol L}^{-1}$  and  $\chi = 0.53$ . A single set of sharp resonance signals was observed in each spectrum, indicating that the exchange of surfactant molecules between different states is invariably fast on the NMR time scale; this reflects the time-averaged environment of the surfactant. On comparing the spectra, variations on the  $^1\text{H}$  and of  $^{19}\text{F}$  peaks positions are observed. The shift of the signal can be explained by the variation of the local dielectric constant experienced by each monomer.

**SD/Water and SPFO/Water Systems.** The chemical shifts differences  $\Delta\delta = \delta_{\text{obsd}} - \delta_{\text{mon}}$  are plotted as a function of the reciprocal surfactant concentration in Figure 3a and in Figure 4a for the SD/water system ( $\chi = 0.0$ ) and for the SPFO/water system ( $\chi = 1.0$ ), respectively;  $\delta_{\text{mon}}$  is the chemical shift obtained by extrapolating the measured chemical shift at infinite dilution whereas  $\delta_{\text{obsd}}$  is the  $^1\text{H}$  or  $^{19}\text{F}$  observed chemical shift of each group. The quantity  $\Delta\delta$  was plotted because, in this way, experimental data for each group could be shown on the same scale.

The  $\delta_{\text{obsd}}$  values obtained at concentrations lower than  $0.014 \text{ mol L}^{-1}$  are constant and are not shown in the figures. On increasing the concentration, for each signal the flat trend is followed by a sudden downfield shift for protons in SD chains and an upfield shift for fluorine atoms in SPFO chains. This is expected on the basis of the influence on the observed chemical shift of the local diamagnetic and paramagnetic terms that dominate the shielding of protons and fluorine, respectively. The well-defined break point, observed in all cases, can be attributed to micellization.

The magnitude of the chemical shift variation of each group is related to the distance from the polar headgroup. The methyl and the fluoromethyl groups were the most sensitive to the environment change. The lack of any strong chemical shift variation in addition to that attributable to the micellization



**Figure 1.**  $^1\text{H}$  NMR spectra for SD at (a)  $C = 0.01$  mol/L, (b)  $C = 0.35$  mol/L, (c) in  $\chi_F = 0.53$  mixture at  $C_T = 0.35$  mol/L.

process should suggest that, in water, both perfluorinated and alkyl chains exist primarily in rather extended conformations. This observation is also confirmed by the small broadening (ca. 2–3 Hz) of the line width of each signal passing from the monomeric state to the micellar assembly.

At concentrations larger than the cmc, the chemical shift of C3 protons and, in a greater extent, those of C2 protons which, upon micellization, are closest to the water, follow a non linear

trend reflecting the very complex environment experienced by these sites in the Stern region upon micelle formation.<sup>20</sup>

**SD/SPFO/Water Systems.** The chemical shift differences of proton  $\Delta\delta$  ( $^1\text{H}$ ) and fluorine atoms  $\Delta\delta$  ( $^{19}\text{F}$ ) for each group in the chains for the three compositions are plotted in Figures 3b–d and 4b–d as a function of  $1/C_T$ .

Below the cmc, the chemical shift of each methylene or methyl group of both surfactants is constant and coincident with that observed in the SD/water and SPFO/water systems, respectively. This indicates that hydrogenated and fluorinated monomers do not affect each other. As the total concentration increases, the activity of the species in solution becomes high enough to form micelles. The sudden change in the slope of the  $\Delta\delta$  curves clearly reflects the change in the environment of the observed group upon aggregation. The effect becomes evident at a total concentration very close to the individual cmc's of the pure components. In fact, when the  $^1\text{H}$ - $\delta$  or  $^{19}\text{F}$ - $\delta$  are plotted vs the inverse concentration of each component in the mixture, the aggregation process is anticipated by the presence of the other surfactant.

Above the cmc, for the three molar fractions, on increasing the overall concentration, the  $\Delta\delta$  ( $^{19}\text{F}$ ) of SPFO in the mixtures follows a linear trend (Figure 4b–d). A less-pronounced upfield shift compared with that in SPFO/water system is noticeable. On increasing the hydrogenated surfactant content, the observed shielding decreases, suggesting that all SPFO groups are in contact with the hydrocarbon chains.

In the mixtures, for the three molar fractions, above the cmc the  $\Delta\delta$  ( $^1\text{H}$ ) values (Figure 3b–d) do not follow a linear trend. In particular, for the SD/SPFO/water systems at  $\chi = 0.53$  and  $\chi = 0.73$  (Figure 3c,d), in contrast with the SD/water system, soon after the cmc all signals arising from chain protons are upfield shifted. By increasing the concentration, after a short plateau, a sudden downfield shift is observed. In the mixture rich in SD ( $\chi = 0.33$ , Figure 3b), the  $\Delta\delta$  ( $^1\text{H}$ ) values follow more complex trends.

The observed trends of  $\Delta\delta$  ( $^1\text{H}$ ) are due to the chemical environment variation as a consequence of the micelle formation and the mixing with the fluorinated compound.

By comparing Figures 3 and 4, a different behavior of the two surfactants inside the mixed micelles can be inferred. This aspect will be discussed later.

**The Micellization Process.** Before analyzing the data it is useful to recall that the two most common models used in describing the micellization process are the mass-action and the pseudo-phase transition models. The former considers the micelle formation as a multistep process and it is able to explain the gradual variation of physical properties of the system in the concentration range near the cmc. The latter assumes that micelles are formed in a single process and predicts an abrupt change of the solution physical properties at the cmc.

Despite its simplicity, the pseudo-phase transition model allows a derivation of the thermodynamic functions of micellization by combining the thermodynamic properties of free monomers with those of micelles.

For systems containing just one surfactant, the molecules, either in monomeric or in micellized form, contribute to the observed property,  $A_{\text{obsd}}$ ; weighting the two contributions, the following equation is obtained:

$$A_{\text{obsd}} = (C_{\text{mo}}/C_T) A_{\text{mo}} + (C_{\text{mi}}/C_T) A_{\text{mi}} \quad (2)$$

where  $A_{\text{mo}}$  and  $A_{\text{mi}}$  represent the property related to the free monomers and to the monomers in micelle, respectively;  $C_{\text{mo}}$  and  $C_{\text{mi}}$  are the free surfactant concentration and the micellized

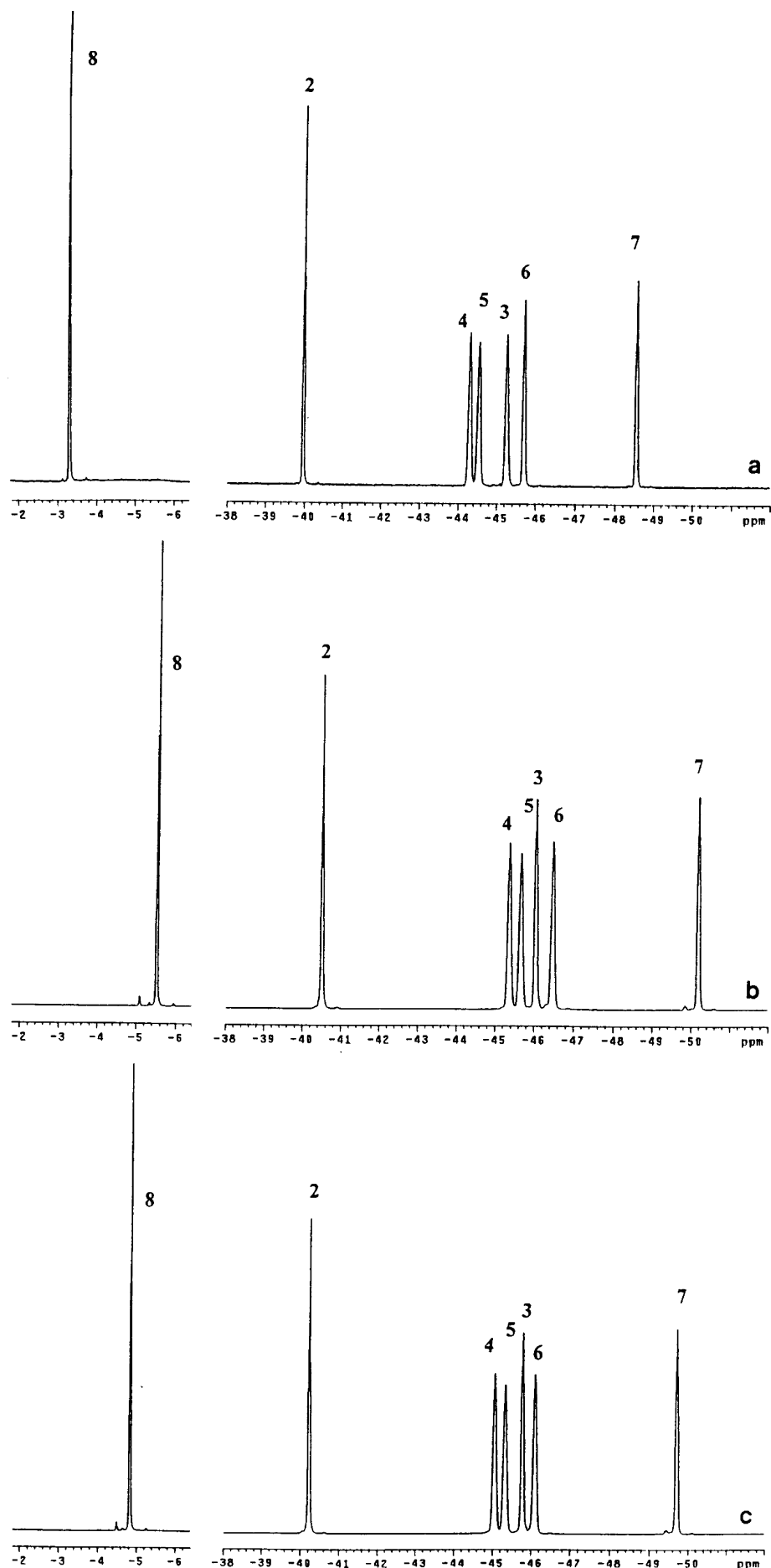
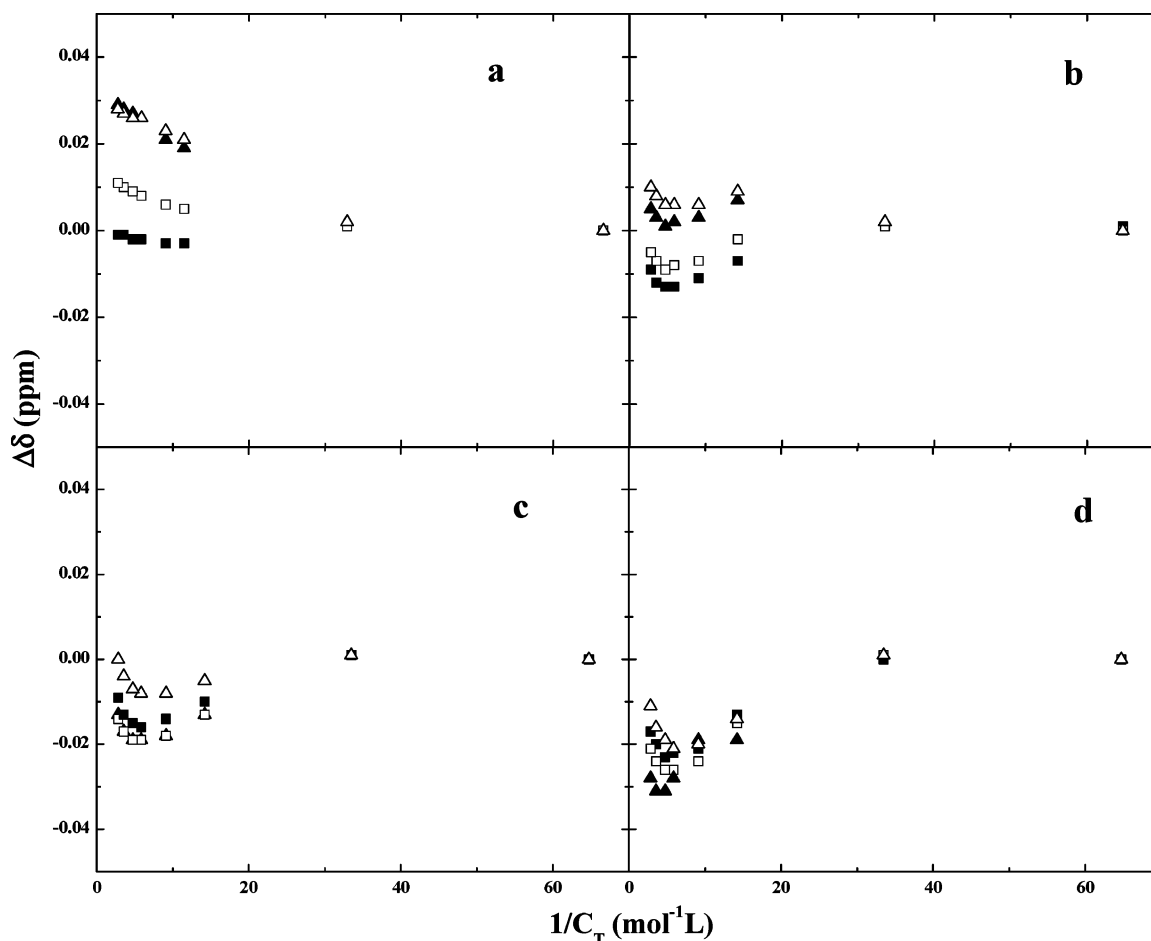


Figure 2.  $^{19}\text{F}$  NMR spectra for SPFO at (a)  $C = 0.01 \text{ mol/L}$ , (b)  $C = 0.35 \text{ mol/L}$ , (c) in  $\chi_F = 0.53$  mixture at  $C_T = 0.35 \text{ mol/L}$ .



**Figure 3.**  $\Delta\delta(^1\text{H})$  vs  $1/C_T$  in the (a)  $\chi_F = 0.00$ , (b)  $\chi_F = 0.33$ , (c)  $\chi_F = 0.53$ , and (d)  $\chi_F = 0.73$  mixtures. ■ C2, □ C3, ▲ C4–C11, △ C12. Data at low concentration are not shown for clarity reasons.

surfactant concentration, respectively, and  $C_T = C_{\text{mo}} + C_{\text{mi}}$  is the total surfactant concentration. Below the cmc, the pseudo-phase transition model predicts that  $A_{\text{mo}}$  remains constant and equal to  $A_{\text{obsd}}$ . Above the cmc and assuming that the free monomer concentration remains constant, eq 2 can be rewritten as

$$A_{\text{obsd}} = (\text{cmc}/C_T)(A_{\text{mo}} - A_{\text{mi}}) + A_{\text{mi}} \quad (3)$$

In a system containing a mixture of two surfactants, the observed property related to each surfactant is given by the sum of monomeric and micellized surfactant contributes

$$A_{\text{obsd}}^i = (C_{\text{mo}}^i/C_T^i)(A_{\text{mo}}^i - A_{\text{mi}}^i) + A_{\text{mi}}^i \quad (4)$$

where the symbols have the same meaning as in eq 3 and the superscript  $i$  alternatively refers to each surfactant. Also in this case, below the cmc,  $A_{\text{mo}}^i = A_{\text{obsd}}^i$  must be constant; above the cmc, a plot of  $A_{\text{obsd}}^i$  vs  $1/C_T^i$  should be linear and the extrapolation at  $1/C_T^i = 0$  should give a value for  $A_{\text{mi}}^i$ .

**Critical Micelle Concentration.** If the pseudo-phase transition model (eq 3) applies, a linear trend of a measured property of the surfactant molecules, such as the chemical shift, either below or above the cmc, is expected. The  $\Delta\delta$  related to each group, reported in Figures 3a and 4a for the SD/water and SPFO/water systems, respectively, indicates that the model is applicable to the two systems, hence the cmc of the two surfactants have been calculated from the intersection of the linear trends in the two regions.

The cmc values, reported in Table 1, are in good agreement with values obtained using other techniques.<sup>11</sup>

In the mixed system, by increasing the concentration, the model is consistent with  $^{19}\text{F}$   $\delta$  trends of each group (Figure 4b–d) but it cannot explain the  $^1\text{H}$   $\delta$  trends of each group related to SD (Figure 3b–d).

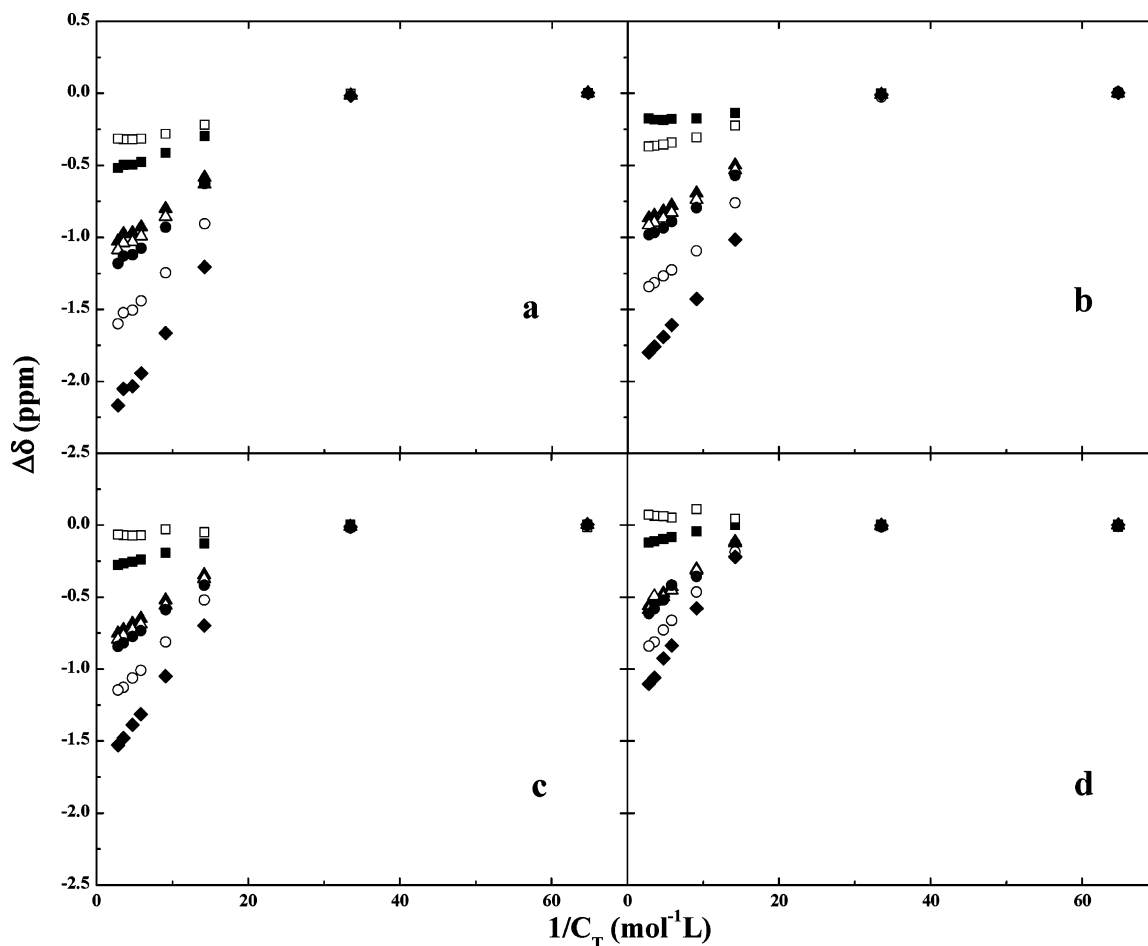
Because of the break in the experimental trends, the mass action model cannot be applied and, therefore, the cmc's of each surfactant were determined from the intersections of the linear trends of  $^1\text{H}$  and  $^{19}\text{F}$   $\Delta\delta$  below and above the cmc. The obtained values, shown in Table 1, in all cases are lower than the cmc of SD/water and SPFO/water systems, suggesting that the aggregation of each surfactant is anticipated by the presence of the other.

At each composition, the sum of the cmc values of the two surfactants gives the total cmc of the SD/SPFO/water system, reported in Table 1. Within experimental errors, these values are in good agreement with those determined by conductivity measurements<sup>11</sup> and reported in the same table for comparison.

The present observations are in agreement with the conclusion obtained by SANS studies<sup>14,15</sup> for the same system where it was concluded that, for each mole fraction and concentration investigated, only one kind of mixed micelles was present. The evidence was that the experimental intensity became zero at one particular isotopic solvent composition; if two kinds of micelles were present, the intensity would have never been zero.

**Micelle Composition.** Since mixed micelles are present, in the hypothesis that the pseudo-phase transition model applies, the micelle composition can be derived from the concentration





**Figure 4.**  $\Delta\delta(^{19}\text{F})$  vs  $1/C_T$  in the (a)  $\chi_F = 1.00$ , (b)  $\chi_F = 0.73$ , (c)  $\chi_F = 0.53$ , and (d)  $\chi_F = 0.33$  mixtures. ■ C2, □ C3, ▲ C4, △ C5, ● C6, ○ C7, ◆ C8. Data at low concentration are not shown for clarity reasons.

dependence of a physical property of the system. Applying eq 4 to the observed chemical shifts it follows that

$$\delta_{\text{obsd}}^i = (C_{\text{mo}}^i/C_T^i)(\delta_{\text{mo}}^i - \delta_{\text{mi}}^i) + \delta_{\text{mi}}^i \quad (5)$$

where the superscript  $i$  refers to either SD or SPFO. The unknown quantities  $\delta_{\text{mo}}^i$ ,  $\delta_{\text{mi}}^i$ , and  $C_{\text{mo}}^i$  in eq 5 depend on  $\alpha$ , that is a function of  $C_T$  on the basis of eq 1; this implies that, to calculate the micelle composition, some assumptions must be made. On the basis of the pseudo-phase transition model, the free monomer concentration above the cmc can be considered constant and equal to the cmc, whereas  $\delta_{\text{mo}}^{\text{F}}$  and  $\delta_{\text{mo}}^{\text{H}}$  can be assumed equal to the values observed below the cmc.

At a given  $\chi$  and total concentration  $C_T = C_{\text{S}}^{\text{H}} + C_{\text{S}}^{\text{F}}$ , where  $C_{\text{S}}^{\text{H}}$  and  $C_{\text{S}}^{\text{F}}$  indicate the stoichiometric SD and SPFO concentrations, respectively, all micelles will have the same composition given by

$$\alpha = \frac{C_{\text{mi}}^{\text{F}}}{C_{\text{mi}}^{\text{H}} + C_{\text{mi}}^{\text{F}}} \quad (6)$$

Combining eq 5 for each surfactant with eq 6, it follows that

$$\delta_{\text{obsd}}^{\text{H}} = \left[ 1 + \frac{\alpha - 1}{\alpha} \frac{\chi}{\chi - 1} \left( 1 - \frac{\delta_{\text{obsd}}^{\text{F}} - \delta_{\text{mi}}^{\text{F}}}{\delta_{\text{mo}}^{\text{F}} - \delta_{\text{mi}}^{\text{F}}} \right) \right] (\delta_{\text{mo}}^{\text{H}} - \delta_{\text{mi}}^{\text{H}}) + \delta_{\text{mi}}^{\text{H}} \quad (7)$$

**TABLE 1: Critical Micelle Concentration**

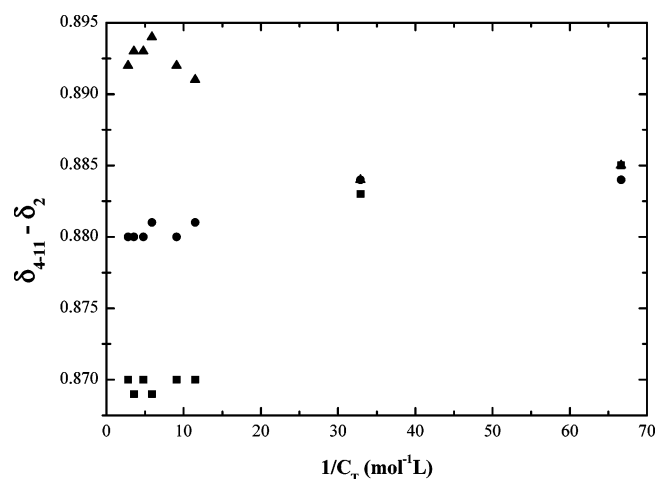
| $\chi_F$ | cmc <sub>H</sub> | cmc <sub>F</sub> | cmc <sub>T</sub> | cmc <sup>a</sup> |
|----------|------------------|------------------|------------------|------------------|
| 0        | 0.028            |                  | 0.028            | 0.028            |
| 0.33     |                  | 0.020            |                  | 0.034            |
| 0.53     | 0.009            | 0.023            | 0.032            | 0.037            |
| 0.73     | 0.014            | 0.025            | 0.039            | 0.036            |
| 1        |                  | 0.034            | 0.034            | 0.030            |

<sup>a</sup> See ref 11 in the text.

Once that  $\delta_{\text{mo}}^i$ ,  $\delta_{\text{mi}}^i$ , and  $\delta_{\text{obsd}}^i$  are determined,  $\alpha$  can be calculated by numerically solving eq 7.

Since the chemical shifts of all hydrogenated surfactant groups do not follow a linear trend above the cmc (see Figure 3b–d), the values of  $\delta_{\text{mi}}^{\text{H}}$  could not be obtained by extrapolation. To bypass this problem we have followed the procedure used by Clapperton and co-workers in the analysis of NMR data from the ammonium decanoate and ammonium perfluorooctanoate mixed micellar system.<sup>18</sup> Accordingly, the chemical shifts of all groups were referred to an internal reference, namely the proton or the fluorine chemical shift from atoms belonging to the C2 group. As mentioned above, this procedure is based on the assumption that, upon micellization, the C2 group environment registers the smallest change and, as a consequence, its chemical shift changes only slightly because this group is nearest to the water.

In principle, the micelle composition can be calculated by using the proton or fluorine chemical shift of any group of the surfactant backbone. In the case of SPFO, the  $^{19}\text{F}$ - $\delta$  related to the fluoromethyl group has been used. In the case of SD, the  $^1\text{H}$ - $\delta$  values related to  $\text{CH}_3$  cannot be used in the calculation



**Figure 5.**  $\delta_{4-11} - \delta_2$  vs  $1/C_T$  in the  $\blacksquare$   $\chi_F = 0.33$ ,  $\bullet$   $\chi_F = 0.53$ , and  $\blacktriangle$   $\chi_F = 0.73$  mixtures.

because, on the basis of geometrical consideration, some of the C12 groups are in contact with each other, forming a hydrocarbon core in the middle of the micelle.

In fact, in a concentration range close to the one here investigated, core radius values of the mixed micelles ranging from 14.4 to 16.7 Å have been obtained by a SANS study.<sup>15</sup> Since SD and SPFO extended chain lengths are 15.42 and 10.36 Å, respectively, it can be concluded that in all cases the fluoromethyl groups cannot reach the inner part of the micelle. Such a situation has been previously observed by Tamori et al.<sup>21</sup> using  $^{13}\text{C}$  NMR in the mixed micellar system containing lithium dodecyl sulfate and lithium perfluorooctansulfonate. It follows that the  $^1\text{H}$ - $\delta$  values related to  $\text{CH}_3$  cannot be used in the calculation.

On the other hand the  $^1\text{H}$ - $\delta$  values related to C3 groups cannot be used because these groups are strongly affected by the C2 environment. As a consequence, the  $^1\text{H}$ - $\delta$  related to C4–C11 groups have been used in the calculation. Using a signal related to many methylenic groups is only a rough approximation and, more important, the trend of  $^1\text{H}$ - $\delta$  values referred to the C2 group plotted vs  $1/C_T$  in Figure 5 never becomes linear in the concentration range above the cmc.

The  $\delta_{\text{mo}}^{\text{H}}$  and  $\delta_{\text{mo}}^{\text{F}}$  have been determined by extrapolation at infinite dilution, as previously stated;  $\delta_{\text{mi}}^{\text{H}}$  and  $\delta_{\text{mi}}^{\text{F}}$  have been determined in the post-micellar region by extrapolation at infinite concentration (for the hydrogenated surfactant, only the linear region has been used).

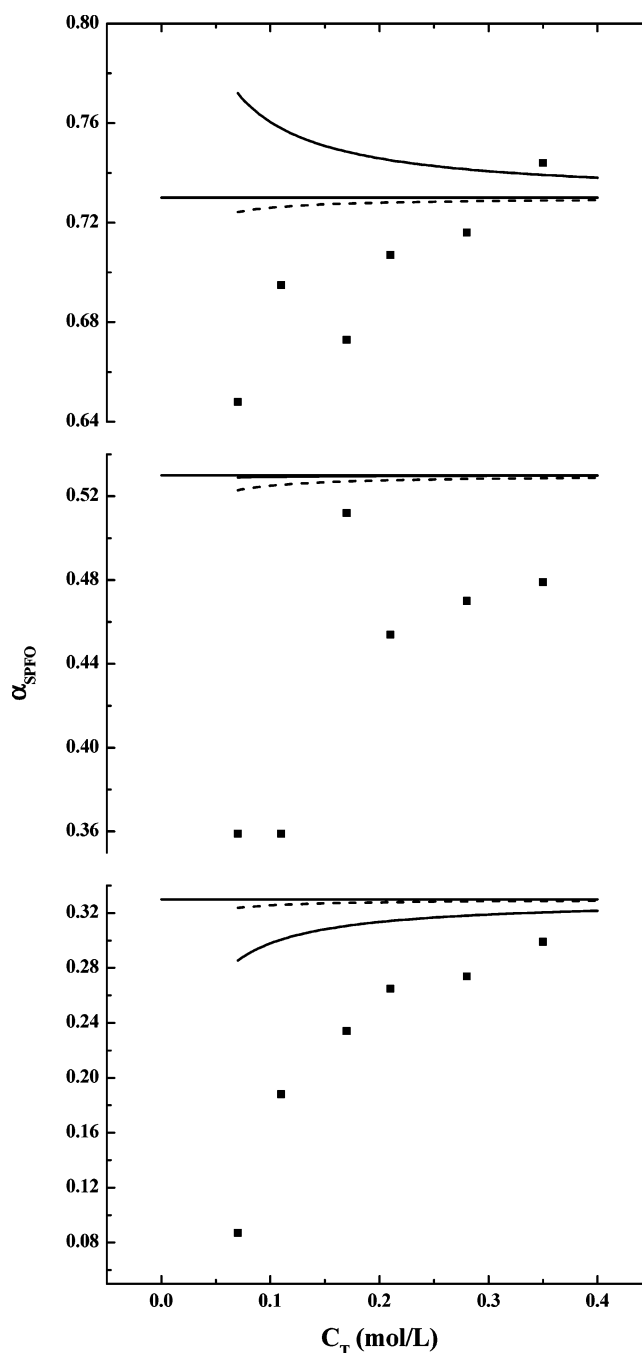
Values of the micelle composition obtained by eq 7 are reported as a function of  $C_T$  in Figure 6 where the lines parallel to the  $x$ -axis represent the  $\chi$  values and the dotted lines represent the  $\alpha$  values calculated on the basis of Rubingh's approach.<sup>9</sup>

At  $\chi = 0.33$ , the micelles are enriched in the component present in greater amount, in qualitative agreement with Rubingh's prediction. At  $\chi = 0.53$ , the micelle composition strongly deviates from the theoretical trend; at  $\chi = 0.73$ , the micelles result enriched in the component present in smaller amount in contrast with Rubingh's prediction.

The procedure was repeated using the perfluoromethylene  $\delta(\text{C6})$  in place of the  $\delta(\text{C8})$ ; the results were worst, even if the qualitative trend remains unchanged.

The compositions, obtained by the above procedure, imply physically unacceptable amounts of free surfactant.

Since  $\alpha$  values calculated from SANS data are in good agreement with the trends predicted by Rubingh's approach,<sup>15</sup> it has been concluded that the procedure suggested for the



**Figure 6.** Micelle composition vs  $C_T$ ;  $\blacksquare$  = experimental values, continuous line = stoichiometric mole fraction, dotted line = Rubingh trend.

analysis of NMR data is not applicable to this system for the reason that will be explained in the next section.

**The Patchwork Model.** Going back to the experimental  $\delta$  trends shown in Figures 3 and 4, some observations can be useful in suggesting why the composition calculated by means of NMR data is not physically acceptable. When in the mixed micelles the SPFO content increases (Figure 3b–d), a radical change in the curves of the chemical shift of  $^1\text{H}$  with respect to the SD/water system (Figure 3a) is observed. The large deviation from linearity can be due either to a micro-phase separation or an intramicellar phase separation. The former implies the coexistence of fluorocarbon-rich and hydrocarbon-rich micelles, the latter implies only one kind of mixed micelle with a non homogeneous distribution of components.

The micro-phase separation model has been used to interpret the behavior of some mixed fluorocarbon/hydrocarbon systems.<sup>22–25</sup> In particular, fluorescence quenching observed from lithium dodecyl sulfate/lithium perfluorononanoate,<sup>23</sup> sodium perfluorooctanoate/sodium dodecyl sulfate<sup>24</sup> and lithium perfluorooctanesulfonate/lithium dodecyl sulfate<sup>24</sup> mixtures, was explained in terms of the coexistence of two kinds of micelles. This interpretation is in agreement with cmc trends and excess free energy calculation obtained for ammonium perfluorononanoate/ammonium dodecyl sulfate mixtures.<sup>26,11</sup>

When SD monomers replace some SPFO molecules in the micelle, the  $^{19}\text{F}$  chemical shift varies (Figure 4 b–d) as a consequence of changes in the dielectric constant within this supramolecular assembly. In particular, above the breakpoint, for the three investigated compositions, the absolute value of  $\Delta\delta$  ( $^{19}\text{F}$ ) regularly decreases, by increasing the amount of hydrogenated component, though the trends are similar to that observed for the SPFO/water system (Figure 4a). This cannot be explained by the micro-phase separation model, hence only one kind of mixed micelles must be present in solution. This hypothesis is in agreement with the conclusion obtained by SANS studies<sup>14,15</sup> about the presence of mixed micelles in the system.

The presence of only one kind of mixed micelles was invoked in the literature to explain the fluorescence quenching<sup>24</sup> and cmc trends<sup>26</sup> observed for sodium perfluorooctanoate–sodium decyl sulfate (SPFO–SDeS) mixture. Excess free energy seems to indicate that both the SPFO–SDeS and SPFO–SD mixtures lie on the edge between miscible and phase-separated systems.<sup>11</sup>

The  $\Delta\delta$  ( $^1\text{H}$ ) trends are consistent with a phase separation, at the same time the  $\Delta\delta$  ( $^{19}\text{F}$ ) trends exclude the micro-phase separation model, and hence the intramolecular phase separation constitutes the only hypothesis that is able to explain the overall system behavior.

This intramolecular phase separation phenomenon is consistent with the fact that, in addition to their typical hydrophobic character, fluorocarbon and hydrocarbon chains also exhibit mutual phobia; moreover, fluorocarbon amphiphiles have a higher self-assembling tendency than the corresponding hydrocarbons.<sup>27</sup> As the overall concentration reaches the cmc, the first mixed micelles forming are composed primarily of the predominant component. On increasing the concentration, the fluorocarbon chains start to aggregate, forming islands among hydrocarbon chains. The mutual phobia between hydrocarbon and fluorocarbon entails a segregation of SD in order to minimize the interfacial area between fluorocarbon and hydrocarbon chains. At higher overall concentrations, hydrogenated chains domains become larger in the micelles. The contribution of these larger islands of hydrocarbon chains to the  $^1\text{H}$  chemical shift is evident and becomes more important by increasing the concentration; in the middle of these islands the dielectric environment approaches that of hydrogenated micelles.

The segregation of the surfactants within the micelles has been suggested, from  $^{19}\text{F}$  NMR line width data, in a cationic surfactant mixture of *N*-(1,1,2,2-tetrahydroperfluorodecyl)-pyridinium chloride and cetyltrimethylammonium chloride at high surfactant concentration and with added salt.<sup>28</sup> In addition, the authors state the coexistence of larger fluorocarbon-rich and smaller hydrocarbon-rich micelles. The latter finding is different from ours, but this is not surprising since it is well-known that different pairs of surfactants can behave quite differently.<sup>22–26</sup>

## Conclusions

The  $^1\text{H}$  and  $^{19}\text{F}$  NMR data related to the two surfactants in the SD/SPFO/water system show that, below the cmc, each monomer is not affected by the presence of the other, being the chemical shifts values coincident with the ones corresponding to the SD/water or SPFO/water systems.

Above the cmc, on increasing the total concentration, the chemical shifts related to the hydrogenated surfactant deviate from linearity and their trends become similar to the one found in the SD/water system in a concentration range far from the cmc, while the values related to fluorinated surfactant show a linear trend. These behaviors have been interpreted assuming that the fluorinated chains always remain in contact with each other, while the hydrogenated chains, at a concentration close to the cmc, experience the contact with the fluorinated moieties and, on increasing the total concentration, get in contact with each other, compensating the effect in the chemical shift due to the presence of the fluorinated surfactant. This distribution, involving an intramolecular phase separation, prevents the computation of the micelle composition from NMR data.

The interpretation of the NMR data is, however, in close agreement with the interpretation of SANS measurements performed on the same system, which indicated the existence of mixed micelles having the same composition and a very narrow size distribution.

Comparing the results of the present study with those obtained by SANS, it is clear that the two techniques give complementary information. Using SANS, we obtain information on the structure of micelles and on the mean distribution of the two components in the system, while using NMR we obtain details on the chemical environment of a single molecule, or on the structural organization of the molecules inside a micelle.

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