

¹⁹F NMR Investigation of Mixed Surfactants Partitioning and Kinetic Stability of Fluorinated Nanodroplets in Water

Stefania Mele,[†] Alba Chittofrati,[‡] Barry W. Ninham,^{§,||} and Maura Monduzzi^{*,†}

Department of Chemical Sciences, CSGI - Cagliari University, S.S. 554 Bivio Sestu, 09042 Monserrato, Italy, Solvay Solexis—R&D Center Physical Chemistry of Interphases, Viale Lombardia 20, 20021 Bollate (Milano), Italy, and Department of Applied Mathematics, Australian National University, Canberra, Australia

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Oil-in-water fluorinated microemulsion aggregates were diluted at high water content, thus taking the system outside the regime of thermodynamic stability. The kinetic stability of aggregates was studied by an analysis of ¹⁹F NMR chemical shifts. The microemulsions were formed from mixtures of three homologous perfluoropolyether (PFPE) sodium carboxylates of high purity. They had a Cl-terminated perfluoroalkyl group and differed in the number of perfluoro-isopropoxy units in the chain. Two PFPE oils having different chain lengths and *n*-perfluorooctane were used to obtain the o/w fluoro-nanodroplets. The partitioning of the individual surfactants between aqueous phase and mixed fluoro-nanodroplets as a function of total surfactant concentration was determined.

1. Introduction

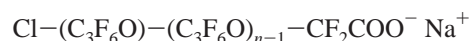
Mixed surfactant systems are of much practical interest.¹ Motivations are several. Manufacturing processes introduce polydispersity in molecular weight and isomerization naturally. Pure surfactants are more expensive to produce than mixtures. Then too, mixed surfactant systems often show better performance and synergic behavior. In industry, deliberate formulations of surfactant mixtures are often made to target physical properties and stability of products.

When two or more surfactants are mixed, both ideal and nonideal mixing can occur.^{1,2} Nonideal behavior, for example, arises from mixing surfactants with different headgroups. Changes of headgroup interactions due to differently charged groups provide a simple example of such phenomena. One example of synergic behavior is the lower cmc values exhibited by mixed surfactants as compared with values expected for pure surfactants alone.

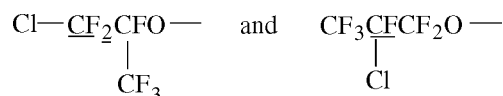
Ideal mixing occurs with homologous surfactants that have the same headgroup but differ in molecular weight.^{3,4} In this case, almost randomly mixed surfactant aggregates will often form. Krafft temperatures of the mixed aggregates tend to diminish. Not much work on mixed micellar systems involving homologous surfactants has been done. One of the few examples is mixed micellar systems of fluorocarbon surfactants. They do exhibit ideal mixing behavior.⁴ However, the behavior of surfactant mixtures in the presence of oil has been somewhat neglected to date, although it is very relevant to emulsion stability.

In a preceding paper,⁵ mixed micellar systems of homologous fluorocarbon Cl-terminated perfluoropolyether (Cl–PFPE) car-

boxylate surfactants with sodium and ammonium counterions were examined. The sodium salts of perfluoropolyether acids, used also in the present work, have the following general structure:^{6–8}



where the ClC₃F₆O group is both in the form⁷



Surfactants having *n* = 2, 3, 4 will be designated n2, n3, and n4, respectively.

The synthesis, purification, and characterization of these homologous perfluoropolyether carboxylic sodium salts, of high purity, were described by Tonelli et al.⁹ Some characterizations of the aqueous micellar systems formed by these surfactants, particularly the shortest chain n2 homologue with both Na⁺ and NH₄⁺ counterions, were reported.^{5,7,10,11} In addition, a detailed study of the binary phase diagrams was performed by means of NMR, SAXS, and optical microscopy,¹² while o/w microemulsions formed by these surfactants with fluorinated oils were investigated by dynamic light scattering.⁷

These mixed micellar systems in water showed almost ideal mixing.⁵ Agreement with theoretical predictions in terms of ideal mixing¹ was found only well above the cmc values of all surfactants in the mixtures. The most reasonable justification of the discrepancy was traced to the high hydrophobicity of PFPE surfactants.^{1,13,14} Also, counterions play an important role. Indeed better agreement was seen for sodium than for ammonium systems. On the basis of previous results obtained for less pure Cl–PFPE surfactants, the differences observed between the sodium and ammonium systems were related to different counterion binding ($\beta_{\text{Na}} < \beta_{\text{NH}_4}$), different hydration (6 water molecules in the first shell for sodium ions and 4 for

* Author to whom correspondence should be addressed: Prof. Maura Monduzzi, Università Cagliari // CSGI, Dip. Scienze Chimiche, S.S. 554 Bivio Sestu, 09042 Monserrato (CA), Italy. Voice: +39 070 675 4385. Fax: +39 070 675 4388. E-mail: monduzzi@unica.it.

[†] Cagliari University.

[‡] Solvay Solexis—R&D Center for Physical Chemistry of Interphases.

[§] Australian National University.

^{||} Visiting Professor Cagliari-Florence University.

the ammonium ions), and to higher solubility in water of the sodium surfactants with respect to the ammonium analogue.⁸

This study focuses on the o/w microemulsions formed from n2, or n2/n3, and n2/n3/n4 mixtures C1–PFPE surfactants with sodium as the counterion. Physical properties of the micellar self-assembly of the surfactant mixtures have been detailed in ref 5. Three different fluorinated oils were used. Two of them belonging to the Galden range by Solvay Solexis were PFPE oils differing for average MW, density, and viscosity (O1 > O2). The third oil was *n*-perfluorooctane (O3). This kind of microemulsion is used in technical applications. These processes require a dilution in water outside the region of thermodynamic stability of the microemulsions. Hence, it is of interest to investigate the effect of surfactant mixtures and the role of oil chain length on the kinetic stability of the fluorinated o/w nanodroplets upon dilution.

From a scientific rather than engineering viewpoint this process corresponds to a transition from a thermodynamically stable system to a highly diluted dispersed system. In other words, a transition from an o/w microemulsion to an o/w emulsion occurs. In the process, all the phenomena related to emulsion stability come together.

The formation and stability of a liquid–liquid emulsion system is related to the interfacial tension ($\gamma_{o/w}$) at the oil–water interface, in consonance with the equation:

$$\Delta G = \Delta A \gamma_{o/w} - T\Delta S$$

where ΔG is the Gibbs free energy, ΔA is the interfacial area variation, and ΔS is the configurational entropy associated with the dispersion process, at a given temperature T . If spontaneous emulsification occurs, the interfacial tension $\gamma_{o/w}$ becomes very low. Hence a thermodynamically stable microemulsion, due to a $\Delta G < 0$, forms. These systems are characterized by small aggregates (diameter around 10–150 nm) and low polydispersity, particularly at low values of the dispersed phase (ϕ_d). If the added surfactant does not produce a sufficiently low $\gamma_{o/w}$, $\Delta G > 0$, and emulsification needs the addition of work. In such cases, emulsions, whose stability relies mainly on kinetics, can form. Typical emulsions are characterized by the presence of aggregates which are polydisperse in size and exceed 150–200 nm (dimensions can usually vary from 200 nm to 100 μ m). Different destabilizing processes such as creaming, sedimentation, flocculation, coalescence, and Ostwald ripening can occur through the involvement of the various hydrodynamic forces, and many of the factors involving intermolecular forces.¹⁵ Polydispersity and solubility of surfactants and oils in water are generally recognized as additional forces that drive destabilization processes.

Our emulsion systems display some peculiar differences from the typical emulsion features. There appear to be three main reasons: (1) The dispersed nanodroplets are formed from fully fluorinated materials (oils and surfactants) of relatively high density and viscosity, and, more importantly, of very high hydrophobicity. These peculiarities induce a very high cohesion of the fluoro-nanodroplet associated with very low water solubility. Not less important, the typical very low interfacial tension of fluorinated surfactants^{16,17} is likely to play a crucial role in the stabilization of the oil–water interface. This is supported by the peculiarly high capacity of spontaneous packing of these surfactants, as assessed by the extent of their liquid crystalline phases in water.⁸ (2) The emulsion forms as a consequence of the dilution process of a microemulsion system. Thus, as suggested by preliminary DLS measurements,⁷ the initial fluoro-nanodroplets have small size (diameter of the

o/w droplets in the microemulsions are around 10–15 nm) and low polydispersity. (3) The emulsion systems investigated have a very low ϕ_d . Thus strong attractive interactions among the nanodroplets can be essentially ignored. Dynamic phenomena determined mainly by Brownian motions in the dilute regime can be expected to dominate. However, the role of dissolved atmospheric gases cannot be neglected. According to recent observations,^{18,19} dissolved gas may favor coalescence through long-distance hydrophobic interactions. Finally, it should be remarked that fluorocarbons (both oils and surfactants) are known to bind dissolved gases strongly, thus producing marked viscoelastic effects.^{16,17} This latter phenomenon swells the oil region changing the effective packing parameter “ v/al ”^{20,21} and turning the micellar particle into ellipsoidal¹⁰ or cylindrical shape.

On the basis of these considerations, it can be expected that fluoro-nanodroplets will have a long shelf life, against density mismatch of neat components. However, the nanodroplets should undergo a slow structural rearrangement toward a phase separation of the fluorinated oil and to the formation of a micellar system. Here, to investigate the kinetic stability of the nanodroplets, a ¹⁹F NMR investigation was performed. The chemical shifts were used to monitor the changes of surfactant binding to different oils with time. This allowed the structural rearrangements of the nanodroplets to be followed as a function of time, type of surfactant (single or mixtures with different chain lengths), and type of fluorinated oil.

The ¹⁹F NMR technique was also used to determine the partitioning of the surfactants in the mixed aggregates, as a function of the total concentration of surfactants.

2. Experimental Section

2.1. Materials. The surfactant samples, their physical characteristics, and examples of their o/w microemulsions have been previously reported.^{5,7,9–11} The sodium salts of perfluoropolyether acids of the general formulas above were provided by Solvay Solexis with a number *n* of perfluoropropyleneoxide units in the chain of 2, 3, or 4. All the surfactant samples were free of any fluorinated precursor and byproduct within analytical sensitivities. Their purity exceeded 99% with respect to the formula, yet including two isomers.⁹ Traces of NaOH or Na₂CO₃ cannot be excluded in the dry salts, although not detectable by pH of the aqueous systems used here. The individual surfactants are indicated by their *n* value, their molecular weight (MW) by NMR and titration agreed within 5% experimental deviation with the value calculated from the formula above, ranging from 484 for Na n2 to the 816 of Na n4.

The two mixtures of these individual surfactants are described in detail in ref 5, but it is worth mentioning that the binary mixture n2/n3 corresponds to an average MW of 539, and the ternary mixture n2/n3/n4 corresponds to an average MW of 580.

At 25 °C, the two perfluoropolyether oils O1 and O2, in the Galden range of Solvay Solexis, have a viscosity of 1.6 cSt (O1) and 0.83 (O2) with a density of 1.77 g/mL (O1) and 1.72 g/mL (O2). The typical average MW values are 740 and 580 for the oils of type O1 and O2, respectively. The technical perfluoro-*n*-octane oil (O3) has boiling point in agreement with the expected value for *n*-C₈F₁₈ (MW 438), although traces of isomers or impurities cannot be excluded. Benzene-*d*₆ 99.5% D, used for lock purpose was from Sigma. Benzotrifluoride 99% used as the reference peak was from Aldrich. Distilled water of Milli-Q grade was used to prepare the microemulsion samples. The microemulsion samples were prepared by weighing appropriate amounts of surfactants, oil, and distilled water.

TABLE 1: Legend of Microemulsion Compositions

		O1 15 wt %	O2 15 wt %	O3 15 wt %
(n2)		1.1	1.2	1.3
surfactants	46 wt %			
water	39 wt %			
(n2/n3 = 60/40)		2.1	2.2	2.3
surfactants	45 wt %			
water	40 wt %			
(n2/n3/n4 = 47/33/20)		3.1	3.2	3.3
surfactants	40 wt %			
water	45 wt %			

Table 1 reports the compositions of the microemulsions examined. The samples were gently mixed to obtain clear solutions, and sufficient time to attain equilibrium was allowed.

2.2. Methods. To investigate the effect of dilution, aliquots of these microemulsions were added to 50 mL of distilled water to obtain the desired dilutions of 2, 10, or 20 g/L of total surfactant concentration. After 10 s of mixing through a Vortex, 0.6 mL of sample was quickly transferred into a 5 mm NMR tube and then inserted into the NMR instrument to ensure the recording of the first spectrum within 20 min from the start of the dilution process. This dilution procedure was performed at least three times for each microemulsion and for each dilution.

^{19}F NMR spectra were recorded at 7.05 T on a Varian VXR-300 spectrometer at an operating frequency of 282.195 MHz. The temperature was kept at a constant value of 25 °C by a standard variable-temperature control unit, with an accuracy of ± 0.5 °C.

An internal coaxial capillary containing a mixture of benzene- d_6 and benzotrifluoride was used inside 5 mm NMR tubes for lock and reference purposes.

The first ^{19}F NMR spectrum was acquired within the minimal time required to set up the experiment (18 min). Then the spectra were acquired every 30 min. A 6 h experiment time was set for the dilution at 2 g/L, and 38 h for those at 10, and 20 g/L.

3. Results and Discussion

3.1. NMR Spectra. Table 1 shows the compositions of the different microemulsions. Before examining the microemulsion spectra, water solutions of n2 surfactant, and n2/n3, n2/n3/n4 mixtures were analyzed by ^{19}F NMR to identify suitable signals for the subsequent investigations. These mixtures were investigated in the previous paper⁵ where it was found that almost ideal mixing occurs above the cmc of the shortest n2 surfactant. Figure 1 (a, b, c) shows ^{19}F NMR spectra of n2, and enlargements of the peaks of interest for the n2/n3 and n2/n3/n4 mixtures, respectively. Each sample had a total concentration of 0.25 mol/L of surfactant(s) in water. The complicated pattern of the spectra arises from ^{19}F – ^{19}F spin–spin coupling. However, the signal relative to the fluorine nucleus nearest to the electro-attractive chlorine can be always distinguished as a single and well-resolved peak. This NMR signal is indicated in Figure 1 as “n2”, “n3”, or “n3 + n4” (n4 does not add any new signal in the spectrum of the ternary n2/n3/n4 mixture; thus the signal “n3” in the three-surfactant mixture is presumably due to both n3 and n4 surfactants). The signals above were chosen for the kinetic study. The ^{19}F NMR signals due to the fluorinated oils do not overlap with these signals even in the case of the PFPE O1 and O2 oils. This is shown in Figure 2a for microemulsion 2.2 and Figure 2b for microemulsion 3.3.

3.2 Kinetic Stability. The three fluorinated n2, n3, and n4 surfactants form a L_1 (micellar) phase in water, the extent of which in the binary phase decreases substantially with increasing

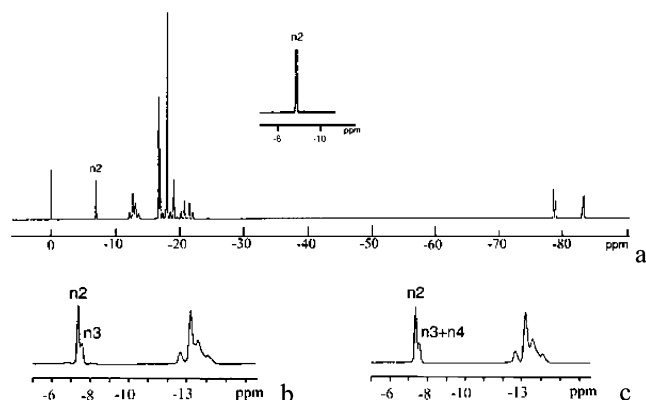


Figure 1. ^{19}F NMR spectra at 25 °C of the Cl–PFPE–Na surfactants and their mixtures, total concentration 0.25 mol/L: (a) n2: the terminal Cl–CF₂– peak chosen for the analysis is indicated as “n2”; (b) enlargement as in the inset of Figure 1a for n2/n3 = 60/40 mixture: the terminal Cl–CF₂– peaks chosen for the analysis are indicated as “n2” and “n3”; (c) enlargement as in the inset of Figure 1a for n2/n3/n4 = 47/33/20 mixture: the terminal Cl–CF₂– peaks chosen for the analysis are indicated as “n2” and “n3 + n4”. (Redrawn from ref. 5.)

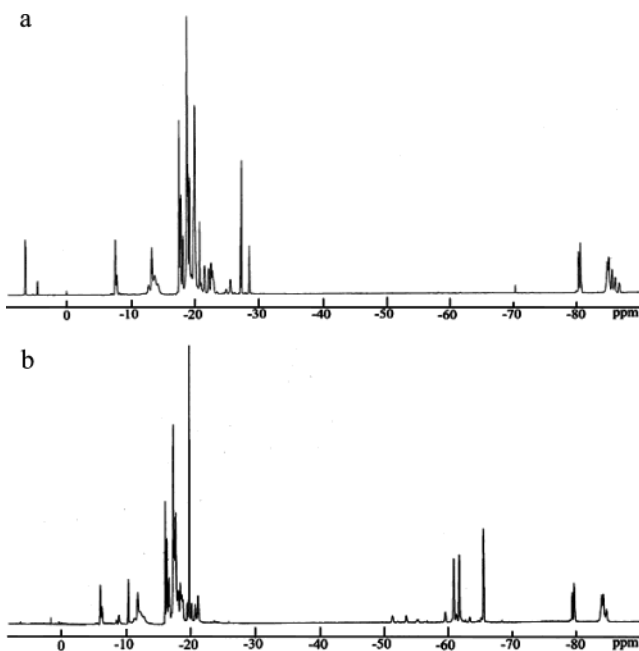


Figure 2. ^{19}F NMR spectra at 25 °C of the microemulsion 2.2 (a) where the PFPE O2 oil produces two new low field NMR signals, around 6 ppm, attributed to terminal CF₃–O– groups; and of the microemulsion 3.3 (b) where the fluoroalkane O3 oil produces a complicated pattern of signals around –60 ppm.

MW. Only the n2 surfactant shows a large micellar region up to about 25 wt % of surfactant in water. For n3 and n4, the L_1 phase coexists with a L_α (lamellar) phase up to about 35 wt % and 82 wt % of surfactant, respectively.¹² However, when n2/n3 and n2/n3/n4 surfactant mixtures are considered, their L_1 phases extend to quite high total surfactant concentrations (about 55 wt %). This phase behavior agrees with expectations, e.g., a significant reduction of Krafft temperature in mixtures (particularly in the presence of n4 term), and, also crucial, a packing parameter “ v/af ”^{20,21} lower than 1 for n2 and close to 1 for n3 and n4 is suggested. When surfactant mixtures are used, the presence of n2 causes a decrease of the effective surfactant parameter “ v/af ”. This favors a positive curvature of the interface with respect to water.^{20,21} Thus a wide region of L_1 -type micelles is observed.

TABLE 2: ^{19}F NMR Chemical Shifts Referred to Benzotrifluoride Signal Set at 0 ppm^a

^{19}F NMR signal	δ_{free} (ppm)	δ_{bound} (ppm)
(n2)		
n2	6.0	7.6
(n2/n3 = 60/40)		$\alpha n2 = 0.6683, \alpha n3 = 0.3317$
n2	6.0	7.6
n3	6.2	7.8
(n2/n3/n4 = 47/33/20)		$\alpha n2 = 0.5633, \alpha n3 + \alpha n4 = 0.4367$
n2	6.0	7.6
n3 + n4	6.2	7.8

^a δ_{bound} and δ_{free} from NMR used to evaluate the molar fraction of the bound surfactants (X_{bound}) with respect to the initial values (αn).

These micellar systems can easily solubilize the fluorinated oils O1–O3 to form oil-in-water microemulsions.^{7,8} Due to their high hydrophobicity, the fluorinated nanodroplets formed from the fluorinated oils and stabilized by the anionic Cl–PFPE–Na surfactants are kinetically stable even upon dilution outside the region of thermodynamic stability of the microemulsions. Indeed, no phase separation is observed within the first 48 h from dilution (within the limits imposed by concentration and refractive index of fluorinated components). Immediately after the dilution, the fluorinated nanodroplets undergo a quick adjustment in surfactant binding to the different oils, particularly in the presence of the mixed surfactant systems. This means that nanodroplets start to release the surfactants molecules immediately after dilution in water. This makes sense entropically. Then a much slower process of reorganization of the aggregates follows. At this step the oil solubility, although very limited, cannot be neglected. Depending on the dilution, a visible phase separation of the fluorinated oils occurs after several days only, whereas surfactants gradually revert to the micelle–monomer equilibria.

The nine microemulsion samples defined in Table 1 were diluted in water to obtain a final concentration of 2, 10, and 20 g/L of total surfactant in water. With surfactant density around 1.8 g/mL, the dilutions correspond to a decrease of the surfactant volume fraction (ϕ_s) of an order of magnitude at least. For instance, in the n2-based microemulsions (1.1 to 1.3) the decrease is from the initial value of $\phi_s \approx 0.36$ (corresponding to 0.47 if oil is included besides the whole surfactant) to $\phi_s \approx 0.001$, 0.006, and 0.011 approximately. The acquisition of a ^{19}F NMR spectrum every 30 min allowed the evolution of the surfactant binding to oils to be followed from the changes of the chemical shifts. It should be noted that no change of the fluorinated oil chemical shifts is seen. This is in agreement with the evidence that no phase separation occurs within a few days from dilution.

For a single surfactant system, a two-site model can be formulated to relate the observed chemical shift (δ_{obs}) to aggregate and monomer states (δ_{bound} and δ_{free} , respectively). The observed chemical shift can be related to the aggregate and monomer chemical shifts and to the molar fraction of the surfactant in the bound and free state (X_{bound} and X_{free}) according to the relation:

$$\delta_{\text{obs}} = X_{\text{bound}} (\delta_{\text{bound}} - \delta_{\text{free}}) + \delta_{\text{free}} \quad (1)$$

If the monomer and aggregate shifts are known, the bound surfactant molar fraction X_{bound} can be calculated at any given surfactant concentration. For an aggregate system it is assumed that each fluorine chemical shift depends on its composition, which generates for each atom an average shielding effect.

To investigate the evolution of this process we considered the initial microemulsion to represent the bound state of the

surfactant in the fluorinated nanodroplets. Thus, the ^{19}F NMR spectra of each microemulsion listed in Table 1 (see as examples Figure 2) were used to evaluate the δ_{bound} of the surfactants in the fluorinated nanodroplets. The values of δ_{free} of each surfactant were obtained by diluting the microemulsions in water at 2 g/L and collecting spectra after 48 h.

Extending the two-site model to mixed surfactant systems allows an evaluation of the particle composition, using the equations:¹⁴

$$\delta_{\text{obsn2}} = \left[1 + \left(\frac{\alpha n2 - 1}{\alpha n2} \right) \left(\frac{Xn2}{1 - Xn2} \right) \left(1 - \frac{\delta_{\text{obsn3}} - \delta_{\text{boundn3}}}{\delta_{\text{freen3}} - \delta_{\text{boundn3}}} \right) \right] \times (\delta_{\text{freen2}} - \delta_{\text{boundn2}}) + \delta_{\text{boundn2}}$$

$$\delta_{\text{obsn3}} = \left[1 + \left(\frac{\alpha n3 - 1}{\alpha n3} \right) \left(\frac{Xn3}{1 - Xn3} \right) \left(1 - \frac{\delta_{\text{obsn2}} - \delta_{\text{boundn2}}}{\delta_{\text{freen2}} - \delta_{\text{boundn2}}} \right) \right] \times (\delta_{\text{freen3}} - \delta_{\text{boundn3}}) + \delta_{\text{boundn3}} \quad (2)$$

Here, n2 and n3 are two different surfactants, e.g., two homologous surfactants differing in the average molecular weight. In this equation, $Xn2$ and $Xn3$ (or $Xn3 + n4$) represent the fractions of n2 and n3 (or n3 + n4) surfactant molecules in the bound state and $\alpha n2$ and $\alpha n3$ (or $\alpha n3 + n4$) are the corresponding molar fractions. At a given mixture composition, the equations can be solved to give $Xn2$ and $Xn3$ (or $Xn3 + n4$), if the values of δ_{bound} and δ_{free} are known. The δ_{bound} and δ_{free} data used to evaluate surfactant binding are given in Table 2.

From the analysis of the ^{19}F NMR chemical shifts given in eq 1 (for microemulsions based on n2 surfactant only), and eqs 2 (for microemulsions based on surfactant mixtures), the degree of surfactant binding was evaluated for the nine microemulsions. Data are shown in Figures 3, 4, and 5. For each microemulsion the surfactant binding is reported for the different dilutions at 2, 10, and 20 g/L. As mentioned above, the most dramatic effect on binding of surfactants occurs immediately after the dilution procedure. The first spectrum of each diluted system reveals significant variations of the chemical shifts of the surfactants, particularly relative to the shortest chain n2. This occurs either for n2 alone or in the mixed surfactant systems. The most significant effects are obviously observed for the highest dilution at 2 g/L. Consequently, different observation times were used to monitor the variations in chemical shifts. No significant chemical shift variations were observed after 3–4 h in most cases. This confirmed the high kinetic stability of the fluoronanodroplets.

From the trends of surfactant binding observed in the various microemulsions, some significant results deserve note. In considering these results, it should be remarked that when systems are diluted at 2 g/L of the total surfactant concentration, the shortest chain n2 surfactant is always below its cmc ($n2 \text{ cmc} = 2 \times 10^{-2} \text{ mol/L} \approx 10 \text{ g/L}^{5,7}$). This factor plays a crucial role, particularly when surfactant mixtures are used. For instance, the dilution at 10 g/L of the n2/n3 mixtures and the dilution at 20 g/L of the n2/n3/n4 mixtures imply a concentration of n2 slightly lower than its cmc ($\approx 1.2 \times 10^{-2}$ and $\approx 1.9 \times 10^{-2} \text{ mol/L}$). n3 surfactant has a concentration of 0.66 g/L, close to its cmc ($n3 \text{ cmc} = 1 \times 10^{-3} \text{ mol/L} = 0.65 \text{ g/L}^{5,7}$), only for the dilution at 2 g/L of the microemulsions based on the ternary n2/n3/n4 surfactant mixtures.

In the presence of n2 surfactant only (see Figure 3), the PFPE O1 oil (highest average MW = 660) always favors higher binding compared to that induced by the PFPE O2 oil (average

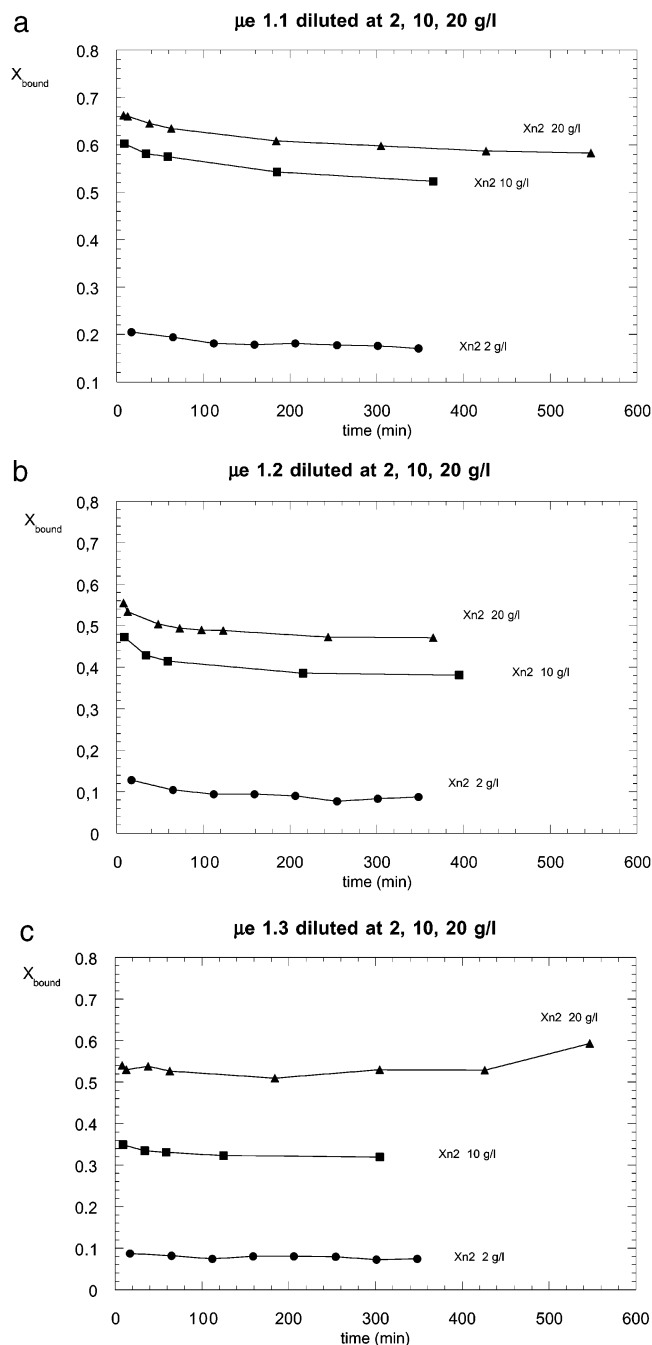


Figure 3. Effect of dilution on the kinetic stability of the n2/water/oil microemulsions. The molar fraction of the bound n2 surfactant is reported vs time (minutes) for the dilutions at 2 (●), 10 (■), and 20 (▲) g/L. (a) O1 oil, (b) O2 oil, (c) O3 oil.

MW = 480) and by the linear fluorocarbon O3. These results agree with the expected effect of the oil chain length and viscosity. Viscosity of O1 ($\eta = 1.65$ cSt) doubles that of O2 ($\eta = 0.83$ cSt) and O3 ($\eta = 0.8$ cSt) oils. Hence, the reduced mobility and low water solubility of O1 favors surfactant binding.

The n2/n3 surfactant mixture produces some counterintuitive results if only oil and surfactant chain lengths are considered (see Figure 4). The surfactant n3 should be expected to always exhibit higher binding than n2. This is true for 2 and 10 g/L dilutions but an opposite trend is found for 20 g/L dilutions, and in the case of microemulsions 2.1 and 2.3 only. It can be surmised that the PFPE O2 oil, having a chain length similar to that of n2, but shorter than that of n3, can easily penetrate

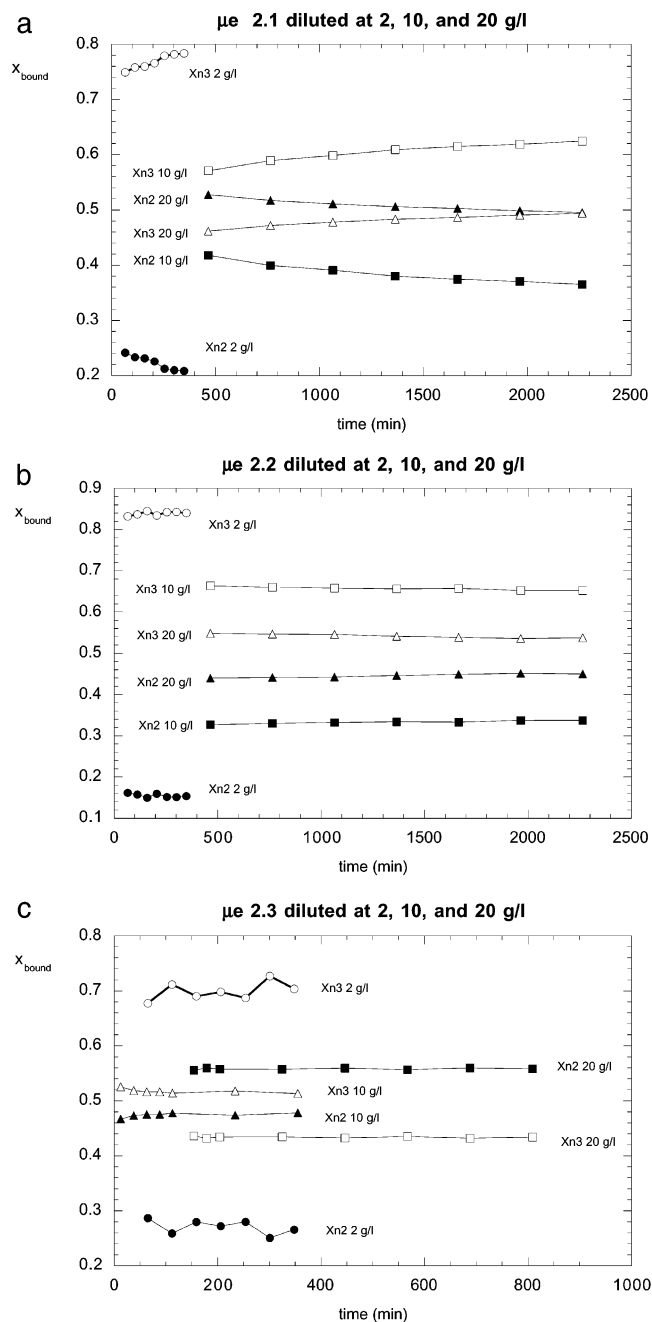


Figure 4. Effect of dilution on the kinetic stability of the (n2/n3)/water/oil microemulsions. The Xn2 and Xn3 molar fractions of the bound n2 and n3 surfactants are reported vs time (minutes) for the dilutions at 2{n2(●), n3(○)}, 10{n2(■), n3(□)}, and 20{n2(▲), n3(△)} g/L. (a) O1 oil, (b) O2 oil, (c) O3 oil.

among n3 chains, thus favoring n3 binding independently of the dilution. Conversely O1 oil, because of its longer chain length, displays a lower degree of penetration, thus favoring an initial unbinding of the surfactant. The oil O3 produces the same effect, but the reasons are different. The linear fluorocarbon chain, because of its helicoidally twist structure, is expected to have less attractive interactions with a PFPE chain, particularly with that of the n3 surfactant. However it is clear that oil penetration influences significantly the binding of the surfactants, thus altering the re-partition equilibria observed for the surfactant mixtures alone.⁵ Indeed a high cohesive energy should be associated with the interactions between PFPE oils (O1, and O2) and PFPE surfactants. The use of the linear fluorocarbon oil O3 should, in principle, decrease the cohesion among the

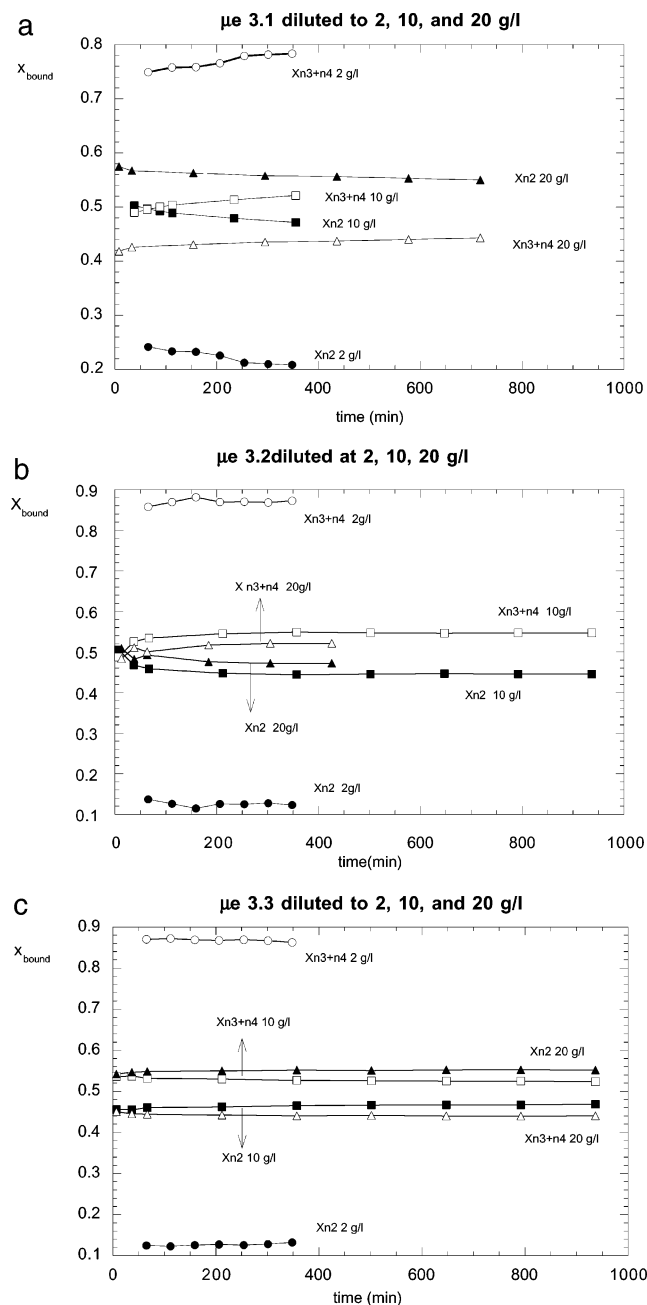


Figure 5. Effect of dilution on the kinetic stability of the (n2/n3/n4)/water/oil microemulsions. The X_{n2} and $X_{\text{n3+n4}}$ molar fractions of the bound n2 and (n3 + n4) surfactants are reported vs time (minutes) for the dilutions at 2 {n2(●), n3 + n4(○)}, 10 {n2(■), n3 + n4(□)}- and 20 {n2(▲), n3 + n4(△)} g/L. (a) O1 oil, (b) O2 oil, (c) O3 oil.

PFPE chains. Nevertheless strong attractive interactions among linear fluorocarbon and PFPE chains still persist as a result of the general high hydrophobicity of all fluorinated chains. For instance, Figure 6a shows the partition of the n2/n3 mixed micellar systems where experimental points agree with ideal mixing predictions (continuous lines).⁵ The cross-over of the binding of the two surfactants occurs around 20 g/L of total surfactant concentration. That is well above the n2 cmc. In the case of O1 and O3 oils, the higher binding of n2 compared to n3 when microemulsions are diluted at 20 g/L (that corresponds to a concentration of n2 around 2.5×10^{-2} mol/L), must involve a slow rearrangement of the composition of the mixed nanodroplets. As for the other dilutions, this trend implies a slow decrease of n2 binding accompanied by a slow increase of n3

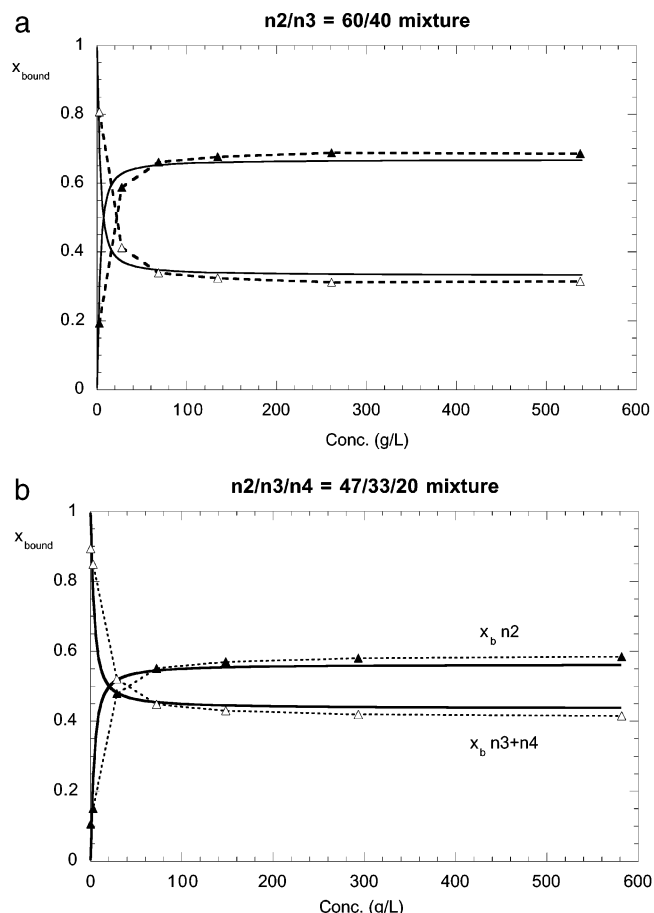


Figure 6. Composition of the Cl-PFPE-Na mixed micelles as a function of the total surfactant concentration C_T (M) obtained from eqs (2); (▲) X_{n2} , and (△) X_{n3} (or n3 + n4). (a) n2/n3 = 60/40 mixture; (b) n2/n3/n4 = 47/33/20 mixture. Data redrawn from ref 5.

binding. Finally the presence of the linear fluorocarbon O3 in all cases favors a high level of preferential binding of n2, almost constant around the molar fractions 0.29, 0.47, and 0.56 for 2, 10, and 20 g/L dilutions, respectively. The effect is evident from the comparison of the trends in Figure 4c, and 5c. Similar trends but lower binding levels were observed for microemulsion 1.3 (see Figure 3c).

The anomalous higher binding of n2 with respect to n3 observed for microemulsions 2.1 and 2.3 is found also for microemulsions 3.1 and 3.3. The partition among surfactants for the ternary mixtures is shown in Figure 6b with a cross-over located around 43 g/L of total surfactant concentration. For microemulsions formed from the n2/n3/n4 mixtures it is worth noticing that the trends of surfactant binding reflect closely that of Figure 6b in the case of microemulsion 3.1 diluted at 10 g/L and microemulsion 3.2 diluted at 10, and 20 g/L. For the n2/n3/n4 based microemulsions, the presence of n4 surfactant tends to mask the marked effect of the oils observed for the other microemulsions, at least in terms of total surfactant binding. Indeed, this long chain PFPE surfactant, due to its very low cmc ($\text{n4 cmc} < 1 \times 10^{-5}$ mol/L), acts more as insoluble oil rather than a true surfactant.

4. Concluding Remarks

Summing up the results in terms of kinetic stability of the mixed surfactant fluoro-nanodroplets, it is remarkable that the O2 oil (2 PFPE units) affects the surfactant binding without altering the trends expected on the basis of cmc and partition

observed in the n2/n3, and n2/n3/n4 mixtures (compare Figure 4b and 5b to 6a and 6b). Re-partitioning of the surfactants occurs within 4–5 h from the dilution procedure. Conversely O1 oil (3 PFPE units) and the linear *n*-fluoroalkane O3 perturb significantly and differently the equilibrium binding of the mixed surfactant/oil nanodroplets depending on the dilution. O3 favors a very rapid re-partitioning of the surfactant mixtures, within 2–3 h after dilution. Then binding levels do not undergo significant modifications for at least 2 days. O1, particularly in the case of mixed surfactants systems produces gradual modifications of the surfactant binding accompanied by a slow re-partition within the aggregates. It should also be mentioned that the anomalous higher binding of n2 with respect to the longer chain surfactants may indicate that eqs 2, which are based on a simple two-site model (free and bound sites), are not fully adequate to describe partition of mixed surfactants at very high dilution. On the other hand it cannot be excluded that shape transitions of the aggregates which are known to occur for micelles with concentration¹⁰ and different oil-surfactant attractive interactions may affect the chemical shift and thus the analysis. Indeed ideal mixing for mixed micelles was ascertained only at high surfactant concentration.

The degree of dilution clearly affects the level of surfactant binding significantly, particularly that of the shortest chain n2 surfactant due to its relatively high cmc. The presence of n4 surfactant tends to point out more the dilution rather than the oil effect.

Ultimately, the kinetic stability of these fluoro-nanodroplets may be prolonged, if of interest, by degassing treatments which should reduce the long-range hydrophobic attractive interactions as ascertained in several cases.^{18,19}

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