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Aggregation Behavior of Cationic Fluorosurfactants in Water and Salt Solutions. A CryoTEM Survey

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The aggregation behavior of the cationic fluorocarbon surfactants 1,1,2,2-tetrahydroperfluoroalkylpyridinium chloride and 2-hydroxy-1,1,2,3,3-pentahydroperfluoroalkyldiethylammonium chloride in aqueous solution have been studied using cryo-transmission electron microscopy as the main technique. The effects on aggregate structure of factors such as surfactant and salt concentration, counterion type, and alkyl chain length were investigated. Similar to hydrocarbon surfactants the fluorocarbon surfactants self-assemble into various aggregates such as micelles, threadlike micelles, vesicles, and other lamellar aggregates. A distinctive property of the fluorocarbon surfactants is their tendency to form structures with little curvature, such as cylindrical micelles and bilayer structures. Even a very small reduction of the repulsion between the headgroups is sufficient to accomplish a sphere to rod transition, so that a solution of globular micelles in water is turned into a highly viscous, sometimes viscoelastic solution on the addition of low concentrations of a simple salt. The differences between the fluorocarbon and hydrocarbon surfactants are discussed.

Introduction

The phase behavior and aggregate structures of normal surfactants in water are fairly well understood, and can be successfully rationalized, sometimes even predicted. The surfactant parameter, introduced by Israelachvili and Ninham,[1] or the spontaneous curvature of a surfactant monolayer, are concepts often employed in these connections to explain the effects of parameters, such as surfactant size and shape, changes of interactions through variation of temperature, electrolyte type and concentration, or other solvent properties, and effects of cosurfactants and other additives etc. In comparison, rather little is known about fluorosurfactants, despite the technical interest due to their potential usefulness, with the large hydrophobicity and strong surface activity. The present knowledge of the aggregation behavior and physical chemistry in general of fluorocarbon surfactants was recently reviewed.[2,3] It is mainly the perfluorocarboxylates that have been studied. Nonionic surfactants were dealt with in a series of papers by Ravey.[4,5,6] Very little have been published about cationic fluorosurfactants; in a recent volume about cationic surfactants,[7] fluorinated surfactants were not mentioned at all. One reason is the synthetic difficulties: cationic fluorosurfactants are scarce. Asakawa et al.[8] have recently synthesized and investigated *N*-alkyl-pyridinium surfactants, with the alkyl chain fluorinated except for the two carbons closest to the pyridinium N. Surfactants of this family have been investigated in the present contribution, and in addition a new partially fluorinated cationic surfactant with the following group coupled to the perfluorinated tail: $-CH_2-CHOHCH_2NH(C_2H_5)_2Cl$. These surfactants are also related to a family called DEFUMAC with the headgroup structure: $CH(OH)(CH_2)_2 NH(C_2H_4OH)_2$, for which a few investigations have been published.[9,10,11]

Fluorocarbon surfactants behave in many ways similar to hydrocarbon surfactants, forming micelles of various structures above a critical micelle concentration. They are more hydrophobic than the corresponding hydrocarbon surfactants, which means that a short tail length of the fluorocarbon is enough to give a similar cmc as a longer alkyl tail (by about a factor of 1.5). Solutions of fluorocarbon surfactants above the cmc have much lower surface tensions than hydrocarbon surfactant solutions. The Krafft temperature is often quite high, and lithium or ammonium carboxylates are often utilized for this reason. Hoffmann et al.[12] examined solutions of lithium perfluorononanoate and diethylammonium perfluorooctanoate with small angle neutron scattering and found spherical micelles in the former and vesicles in the latter. The same method indicated short rodlike micelles in a solution of ammonium perfluorooctanoate.[13] A family of phase diagrams were reported by Fontell and Lindman for perfluorononanoate with different counterions.[14] A lamellar phase was found to be the first liquid crystalline phase in many of the systems. These and other results all indicate that the fluorocarbon surfactants are prone to form structures with less curvature than hydrocarbon surfactants with comparable cmc or solubility.

For alkyltrimethylammonium surfactants, and the related pyridinium surfactants, the effects on aggregate structure of factors, such as surfactant and salt concentration, counterion type, and alkyl chain length, have been thoroughly investigated. The aim of the present investigation is to provide an overview of the effects of a similar tuning in the case of cationic fluorosurfactants; a few results for perfluorocarboxylates will also be presented. CTEM, cryo transmission electron microscopy, is the main technique.[15,16] It offers unique possibilities for direct visualization of labile microstructures in dilute aqueous solutions. The samples are examined in the form of thin vitrified aqueous films at liquid nitrogen temperature, without any staining or dehydration.

TABLE 1. The Critical Micelle Concentration, the Surface Tension, and the Interfacial Area per Surfactant Molecule of Several Fluorocarbon and Hydrocarbon Surfactant Systems at 25 °C

surfactant system	CMC (mM)	$\gamma \times 10^{-3}$ (Jm^{-2})	A (Å^2)
$C_6F_{13}CH_2CH_2NC_5H_5\cdot Cl$ (HFOPC)	16.2^a	27.5	61.4
$C_8F_{17}CH_2CH_2NC_5H_5\cdot Cl$ (HFDePC)	2.6	28.6	52.1
$C_8F_{17}CH_2CH_2NC_5H_5\cdot Cl$+50 mM NaCl (HFDePC+50 mM NaCl)	0.4	23.4	28.0
$C_{10}F_{21}CH_2CH_2NC_5H_5\cdot Cl$ (HFDPC)	0.33	25.6	39.8
$C_6F_{13}CH_2CHOHCH_2NH(C_2H_5)_2\cdot Cl$ (I-C9)	18.0^a		
$C_8F_{17}CH_2CHOHCH_2NH(C_2H_5)_2\cdot Cl$ (I-C11)	2.3	17.9	54.9
$C_8F_{17}CH_2CHOHCH_2NH(C_2H_5)_2\cdot Cl$ +30 mM LiCl (I-C11+30 mM LiCl)	0.8	17.4	34.8
$C_{12}H_{25}NC_5H_5\cdot Cl$ (DPC)	15.5	44.4	66.9
$C_{14}H_{29}NC_5H_5\cdot Cl$ (TPC)	4.0	42.2	69.6
$C_{16}H_{33}NC_5H_5\cdot Cl$ (CPC)	1.0	44.9	59.6
$C_{16}H_{33}NC_5H_5\cdot Cl$+50 mM NaCl (CPC+50 mM NaCl)	0.4	38.6	42.5

^{a} Value from conductivity measurements

Experimental Section

Chemicals. C_{16}TAC (cetyltrimethylammonium chloride) was prepared by ion exchange from the bromide salt (Serva, analytical grade). The product was freeze-dried and stored in a desiccator.

The cationic fluorocarbon surfactants 1,1,2,2-tetrahydroperfluorooctylpyridinium chloride (HFOPC), 1,1,2,2-tetrahydroperfluorodecylpyridinium chloride (HFDePC), and 1,1,2,2-tetrahydroperfluorododecylpyridinium chloride (HFDPC) were synthesized as described earlier.[8]

The surfactants 2-hydroxy-1,1,2,3,3-pentahydroperfluorononyldiethylammonium chloride (I-C9), and 2-hydroxy-1,1,2,3,3-pentahydroperfluoroundecyldiethylammonium chloride (I-C11) were synthesized with similar procedures as in refs 17 and 18. The purity of the synthesized surfactants was checked with HPLC. The chromatograms gave no indication of impurities.

Ammonium perfluorooctanoate and perfluorononanoic acid were purchased from Fluorochem Limited, UK, and used as received.

Sodium chloride, sodium chlorate and sodium salicylate, all from Merck, were used as received.

Cryo-Transmission Electron Microscopy. The CTEM investigations were performed with a Zeiss 902 A electron microscope, operating at 80 kV and zero loss bright-field mode. Within a chamber of controlled humidity (98−99% relative humidity) and temperature (25 °C), a drop of the sample solution was placed on a copper grid covered by a holey polymer film. After careful spreading of the drop, excess liquid was blotted away with filter paper. Thin sample films, spanning the 1−8 μm large holes in the polymer film, were formed. After blotting, the samples was plunged into liquid ethane kept just above its freezing temperature. The vitrified sample was transferred under nitrogen atmosphere to the microscope. The temperature was kept below 108 K during the examination.

Dynamic Light Scattering (DLS). The apparatus and technique used were essentially those summarized in ref 19.

Surface Tension. Surface tension was measured in a drop volume instrument.[20]

Results and Discussions

Surface Tension Measurements. Surface tension measurements were performed on solutions of HFDePC, I−C11 and CPC without and with added salt. The critical micelle concentration and the minimum surface tension were determined. The results are presented in Table 1. In analogy to the hydrocarbon surfactants, the critical micelle concentration for fluorocarbon surfactants in aqueous solution depends on the chain length and the salt concentration, the cmc is reduced with increasing chain length and addition of salt. Both the cmc values and the surface tension values are much lower for fluorocarbon surfactants than hydrocarbon surfactants.

We can calculate the area A per surfactant molecule at the interface from the slopes of the linear part by using the simplified Gibbs adsorption equation:

$$\Gamma = -\frac{1}{nRT}\frac{\gamma}{\ln C} \tag{1}$$

$$A = \frac{1}{\Gamma N_A} \tag{2}$$

where Γ is the surface excess, R the gas constant, T the temperature, γ the surface tension, C the molar concentration of surfactant, and N_A Avogadro's number, and $n = 2$ without salt and $n = 1$ in an excess of added salt. The results are presented in Table 1, together with some other parameters deduced from the surface tension results. The value of A is small for the fluorocarbon surfactants; the molecules are packed tightly together.

$$C_XF_{2X+1}CH_2CH_2NC_5H_5Cl; \; X = 6, 8, 10$$

The critical micelle concentration of these surfactants was determined by conductivity and surface tension measurements. The cmc values were obtained as 21.7, 2.6, and 0.33 mM, respectively, for HFOPC, HFDePC, and HFDPC. The cmc values of these fluorocarbon surfactants correspond to those of hydrocarbon surfactants with a longer chain length, by a factor of 1.5, in agreement with the findings of Shinoda et al.[21] for other fluorocarbon surfactants.

The properties of HFDePC were studied earlier.[8] It was found that HFDePC is more surface active than CPC, with a surface tension of 28.6 mN/m above the cmc as compared to 44.9 mN/m for CPC. HFDePC is a fluorescence quencher and this property was utilized to demonstrate the coexistence of two kinds of micelles in mixtures of hydrocarbon and fluorocarbon surfactants.[22] The phase and aggregation behavior of this surfactant is under investigation, using small-angle X-ray-scattering and nuclear magnetic resonance spectroscopy.[23] With increasing surfactant concentration, the following phase sequence was observed: isotropic micellar, hexagonal, at least two intermediate phases, and a lamellar phase.

In the present work, CTEM was used to study changes of the micelle structure induced by increasing salt or surfactant concentrations, and the effects of different counterions and variation of the chain length on the structure in dilute aqueous solution.

Effects of Salt and Surfactant Concentration. With the addition of a simple salt, NaCl, the electrostatic repulsion
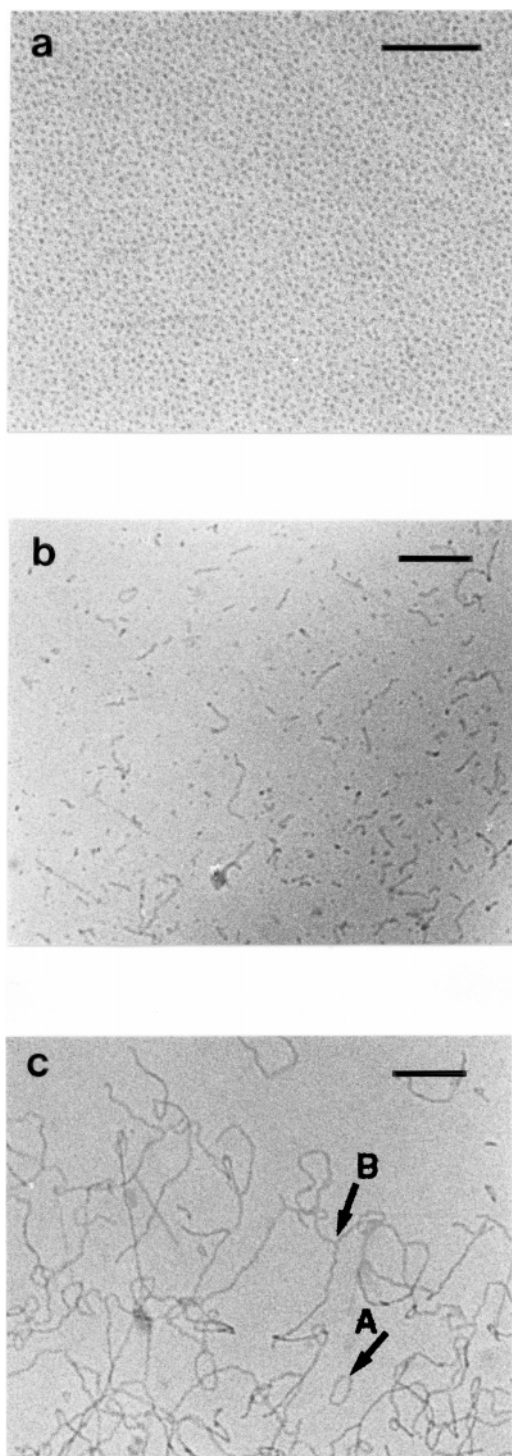
Figure 1. (a) Monodisperse globular micelles are seen in 50 mM HFDePC. Bar = 100 nm. (b) Short threadlike micelles are seen in 8 mM HFDePC with 50 mM NaCl. (c) Long threadlike micelles are overlapping and entangled in 25 mM HFDePC with 150 mM NaCl. **A**: loop. **B**: y-shaped branches.

between the headgroups is reduced and the effective surface area of the surfactant molecule decreases, thus promoting the growth of long cylindrical micelles. Without addition of salt, HFDePC forms small globular micelles in 50 mM solution, as shown in Figure 1a. After addition of only 50 mM NaCl, cylindrical micelles are observed. As shown in the micrographs, Figure 1b,c, short rodlike micelles form first, which at 150 mM NaCl have grown to long and tortuous threadlike micelles. The long threadlike micelles are entangled and overlap in the micrographs. Some true branching points and loops seem to be

present: Y-shaped, three-way junctions in the micrographs are probably real. Similar transitions from spherical to cylindrical and threadlike structures with loops and Y-shaped branches have been observed for cationic hydrocarbon surfactants of the CTAX-family in salt solutions,[24] but the transition for HFDePC occurs at a much smaller amount of added salt. Furthermore, the effect of chloride ion is small on most hydrocarbon cationic surfactants, and it is necessary to use bromide or other more strongly bound ions to induce the transition in CPC and CTAB solutions.[25,26,27]

The micellar elongation can also be induced by increasing the surfactant concentration. Transition from spherical to threadlike micelles occurs in aqueous solution of CTAB and CPB, but not in CTAC and CPC, with increasing surfactant concentration.[28,29] The case of cationic fluorocarbon surfactants is illustrated by the micrographs of Figure 2 which were taken with increasing concentration of HFDePC. The micelles grow, finally resulting in cylindrical micelles, Figure 2c. The long micelles are partially aligned in small domains, indicating that the liquid crystalline phase adjacent to micellar solution is a hexagonal phase consisting of ordered rodlike aggregates. The viscosity of the solution is very high in this case, as is expected for long threadlike micelles, and as is also found in many hydrocarbon surfactant solutions at high concentration. The elongation induced by increasing surfactant concentration comes early and is large for HFDePC, compared with cationic hydrocarbon surfactants such as CPB.[29] Similar findings have also been reported for another family of cationic fluorocarbon surfactants: DEFUMAC.[9] DEFUMAC micelles elongate more effectively than the corresponding cationic hydrocarbon surfactants with chloride counterion.

Effect of Counterions. The effect of different counterions on the aggregation behavior of cationic hydrocarbon surfactants has been much studied.[25,30−41] It is known that long threadlike micelles form in aqueous solutions of many cationic hydrocarbon surfactants above certain surfactant and salt concentrations and that the transition from sphere to rod depends strongly on the nature of the counterion. An illustration of the specificity of the counterions can be found in the light scattering study of Anacker and co-workers[30,31] on micellar solutions of cationic hydrocarbon surfactants with various monovalent counterion. The transition is promoted in the order $F^- < Cl^- < Br^- < ClO_3^- \ll SCN^-, ClO_4^-$. Often the chloride ions are inefficient in promoting micellar elongation,[24,25,27] while the bromide ions promote efficiently.[26,27,32] It was reported earlier that addition of a certain amount of sodium chlorate to CTAC solutions results in the formation of a viscous solution of long threadlike micelles.[33] In the presence of strongly binding counterions, the classical example being salicylate, a striking viscoelasticity is observed. It was found that the viscoelastic behavior of the dilute solutions correlates with the formation of threadlike micellar aggregates.[34−37]

Hoffmann and co-workers[40,41] have demonstrated that the rheological behavior of the solution depends strongly on the chemical structure of the counterion. Extensive investigations of such systems have been made with emphasis on the measurement of the rheological properties.

Similar effects of different counterions were observed for the cationic fluorocarbon surfactants in our study. The effect of $NaClO_3$ on the structure of HFDePC micelles was studied first. In this case the micelles remained globular after the addition of 10 mM $NaClO_3$ to 10 mM HFDePC. Upon the addition of 20 mM $NaClO_3$ to 10 mM HFDePC, the solution becomes viscous. Figure 3a illustrates that micelles have grown into long threadlike micelles. Some branching points and loops can be seen in the micrograph. On adding 60 mM $NaClO_3$ to 10 mM
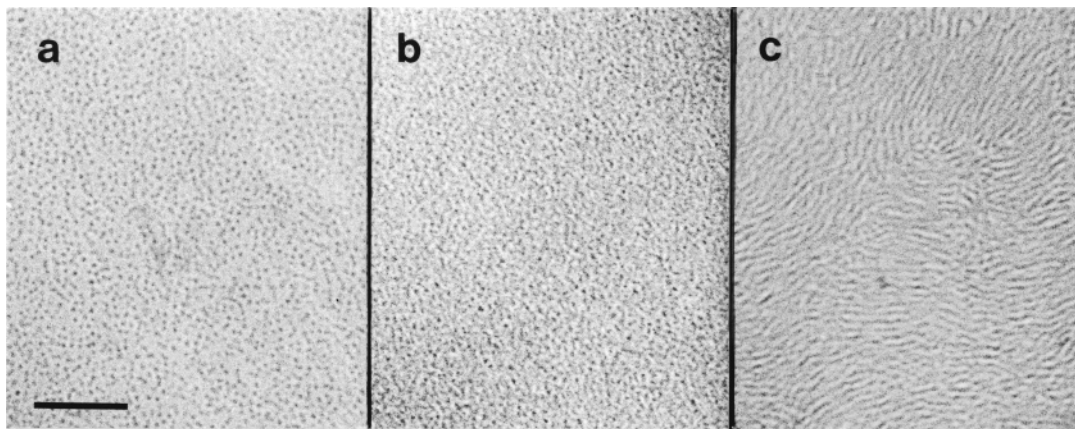
Figure 2. A sequence of CTEM micrographs taken from HFDePC system with increasing surfactant concentration. Bar = 100 nm. Monodisperse globular micelles are observed in (a) 100mM and (b) 150 mM HFDePC. The same structure, globular micelles are seen in 50 mM HFDePC, as shown in Figure 1a. (c) Long threadlike micelles are partially aligned in small domains in 200 mM HFDePC.
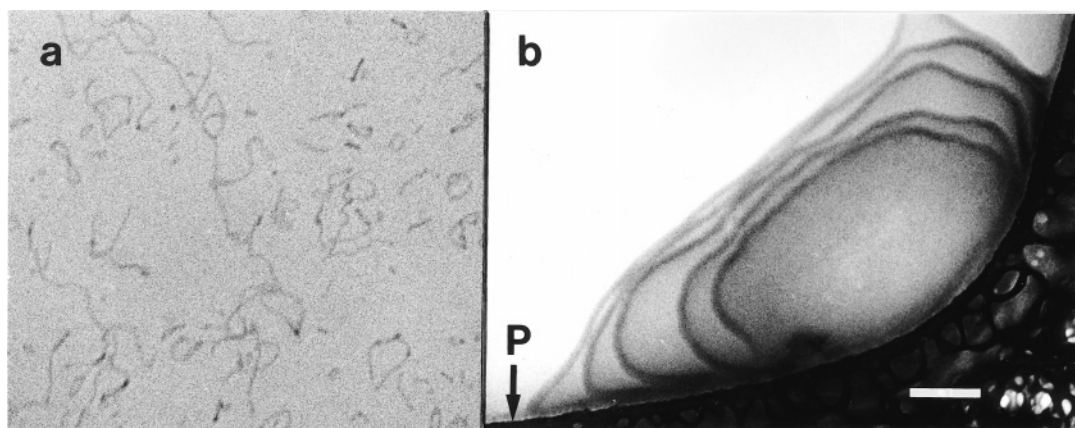
Figure 3. CTEM micrographs taken from HFDePC/NaClO$_3$ system: 10 mM HFDePC with varied NaClO$_3$ concentration. Bar = 100 nm. (a) Threadlike micelles are seen in the presence of 20mM NaClO$_3$. (b) Multilamellar vesicles are observed in the bottom phase of the sample in the presence of 60mM NaClO$_3$. **P**: polymer film.

HFDePC, a phase separation occurs. CTEM micrographs were taken for samples from both phases. Multilamellar vesicles (or a stack of flattend vesicles?) adhering to the wall of the polymer film were observed in the sample from the bottom phase, as shown in Figure 3b, whereas we could not find any structures in the upper phase. A lamellar phase in equilibrium with very dilute surfactant in salt solution is the probable explanation.

Salicylate is even more effective than chlorate in promoting the growth of the micelles. Short threadlike micelles are already formed with the addition of 5mM NaSal to 10 mM HFDePC as shown in Figure 4a. By further increasing the concentration of NaSal, viscoelastic behavior is observed in a solution of 10mM HFDePC with 10 mM NaSal. The viscoelastic effect can be seen by swirling the solution and visually observing the recoil of air bubbles trapped in the solution after the swirling is stopped. Very long threadlike micelles are formed as shown in Figure 4b, similar to the micelles observed by cTEM in a solution of CTAB after addition of NaSal.[37]

From the results above, it is evident that the micellar transition for fluorocarbon surfactant is highly dependent on the nature of the counterions. Strong counterion binding promotes the transition from small to larger aggregate, decreasing the curvature. With anions such as chlorate and salicylate that associate strongly with the surfactant cations, threadlike micelles form already at low surfactant and salt concentrations, and the fluorocarbon surfactants even form vesicles and bilayer structures, which is more unusual for single-tail hydrocarbon surfactants.

Effect of Alkyl Chain Length. We also studied the effect of varied alkyl chain length on the aggregate structure in this family of fluorosurfactants.

It turns out that dilute solutions of both HFOPC and HFDPC of HFDePC contain globular micelles, similar to those in Figure 1a. In the case of HFOPC the micelles remain globular even at 250 mM NaCl. In a solution of HFDPC bilayers are already formed when 9 mM NaCl is added, as shown in the micrograph of Figure 5. Two cylindrical, or slightly conical, bilayer structures with remarkably straight borderlines, are crossing each other. The high contrast of the borderlines come from portions of the bilayers in line with the electron beam. From the different contrast on each side of the border it is clear that the bilayers are folded here, and not making a furrow or a ridge, as has been observed in other systems.[38] In addition to the folded bilayers, there are a number of planar bilayers revealed by less clearly marked borders, some of which are curved. In the central portion of the picture there are at least two such bilayers in addition to four bilayers from the overlapping cylinder structures on top of each others. Evidently, the cylinders must be strongly deflated, with almost planar bilayers but in the folded regions. The sample in this case represents a dispersion of a lamellar phase in solution.

Thus without salt, dilute solutions of the fluorosurfactants form globular micelles. With the addition of salt, the electrostatic repulsion reduces and therewith the effective headgroup area. For HFDePC a transition to long threadlike micelles occurs with the addition of simple salt, whereas the micelles remain globular

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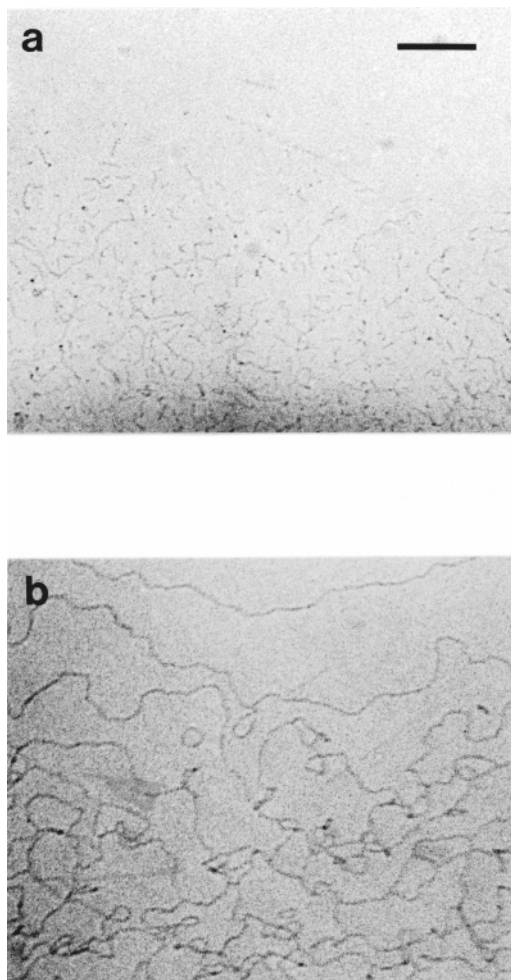
Figure 4. (a) Short threadlike micelles present in 10mM HFDePC with 5mM NaSal. (b) Long threadlike micelles are overlapping and entangled in 10mM HFDePC with 10 mM NaSal. Bar = 100 nm.
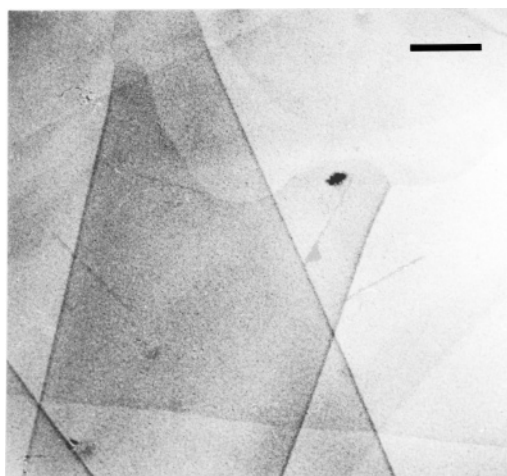
Figure 5. Bilayer structures formed in an aqueous solution of 5 mM HFDPC with 9 mM NaCl. Bar = 200 nm.

for HFOPC and large lamellar structures are observed for HFDPC with longer chain length. In contrast, a much smaller effect of chloride ions were observed for hydrocarbon cationic surfactants.

$$CXF_{2X+1}CH_2CHOHCH_2NH(C_2H_5)_2Cl; \quad X = 6, 8$$

A family of cationic fluorocarbon surfactants with a different headgroup, I, was also studied. The critical micelle concentration

was determined by surface tension and conductivity measurements. The cmc values for I-C11 and I-C9, reported in Table 1, are remarkably close to those of HFOPC and HFDePC, with the same number of fluorocarbon groups. CTEM and DLS measurements showed that bilayer structures were more preferred for the I-surfactants than the PC-surfactants.

Effect of Salt and Surfactant Concentration. With the addition of simple salt (NaCl and LiCl gave similar results), vesicles are formed in a dilute solution of I-C11, as shown in Figure 6. An interesting observation is that two populations of vesicles coexisted in the solution of I-C11 at low salt concentration, one with extremely small vesicles, the other much larger. The small vesicles are so small that they often are not well resolved on the micrographs. They appear as dots without any structure, but larger than usual micelles. Some of the small vesicles in Figure 6b, in particular those inside and in the vicinity of the large vesicle close to the bottom right-hand corner, are resolved well enough to show the typical contour of the vesicle wall. That the small objects really are vesicles is further corroborated by the DLS results presented below, which give a hydrodynamic radius of 6 nm, far too large for a micelle. Equally small vesicles have been observed previously in a mixture of nonionic and cationic surfactants.[39]

When the solution is aged, the large vesicles grow, but the small ones are still present. The solution of 10 mM I-C11 and 30 mM LiCl was freshly prepared by mixing a 20 mM I-C11 solution with a 60 mM LiCl solution. The micrographs presented in Figure 6 show the evolution with time: Shortly after mixing, numerous small vesicles coexisted with few large vesicles. With time the large vesicles grew whereas the small ones remained almost constant in size. Both the number and the size of the large vesicles increased and the size distribution was broad. After 1 day, very large uni- and multi-lamellar vesicles were present with diameters of the spherical ones reaching several hundred nanometers. Larger vesicles were found after the sample had been kept for 1 week, and it is quite possible that even larger structures were present in the solution but sorted out from the thin water films investigated in the CTEM method.

To further investigate this unusual behavior, we made dynamic light-scattering measurements to determine how the radius of hydration of the two populations change with time. Dynamic light-scattering measurements were made on a sample at different times after mixing. Figure 7a shows that there are two populations of vesicles with different size present in the solution. The large vesicles grow with time from $Rh \approx 40$ nm to $Rh \approx 160$ nm after 50 h, whereas small ones remain at constant size, $Rh \approx 6$ nm. As shown in Figure 7b, the fraction of light scattered by the large vesicles increased with time, while the fraction of the small ones decreased.

The main change appears to occur within the population of large vesicles, whereas the small ones seem less affected. In any case, the coexistence of different size vesicles and the growth of the vesicles into larger structures show that the solution is in a nonequilibrium state.

The effect of surfactant concentration was also studied for this surfactant. Globular micelles in coexistence with very long threadlike micelles were observed in dilute solutions of 50 mM I-C11, as shown in Figure 8a. Disklike structures together with very long threadlike micelles were observed at higher surfactant concentration, 100 mM I-C11, as shown in Figure 8b. Viscoelastic behavior was observed in the solutions, which agrees with the presence of threadlike micelles. The alignment of the threadlike micelles in different directions in the micrographs is probably an artifact of the blotting process.
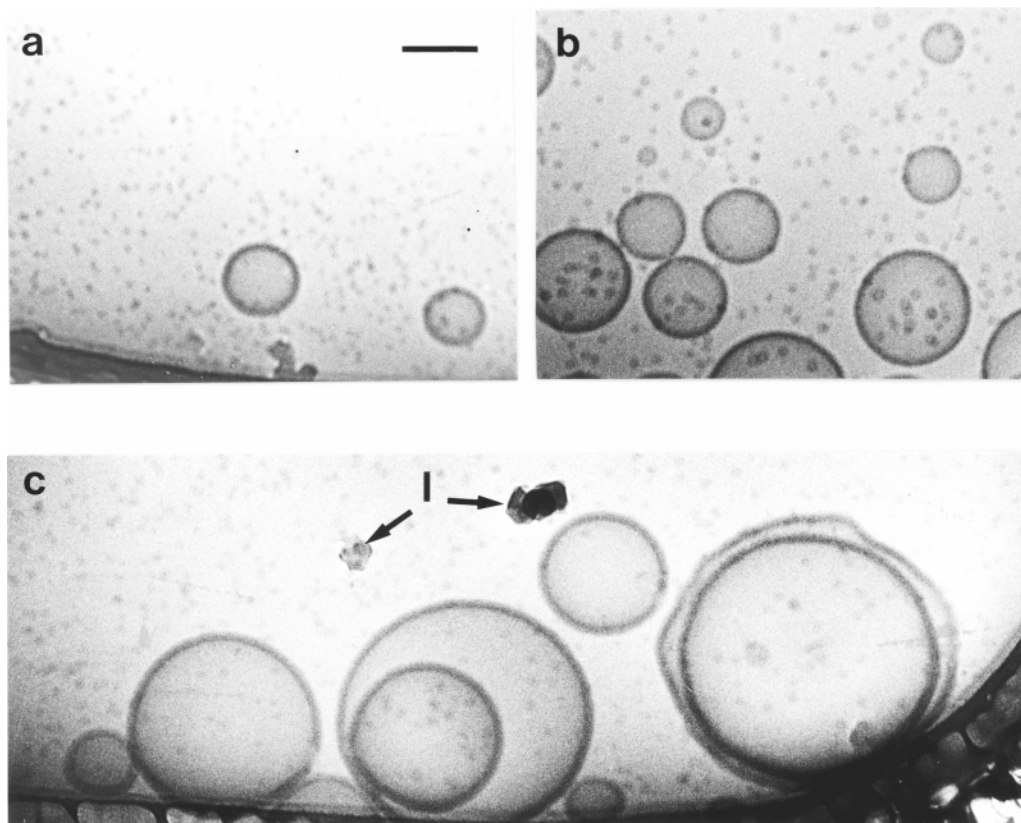
Figure 6. A sequence of CTEM micrographs taken from a sample of 10 mM I-C11 with 30 mM LiCl at different times (a) 8 min, (b) 4 h, (c) 24 h after mixing a 20 mM I-C11 solution with a 60 mM LiCl solution. **I**: ice crystal. Bar = 100 nm.

In the solutions without salt, globular micelles and long threads were found to coexist, and after addition of salt small and large vesicles. It is of course tempting to assume that the two types of vesicles come from the two types of micelles; the reason for the coexistence is obscure in both cases. Note that the surfactant preparation were found to contain only one component according to chromatography tests.

Effect of Counterion Type. The effect of different counterions on the fluorocarbon surfactant I-C11 was studied. Upon the addition of 10 mM $NaClO_3$ to 10 mM I-C11, the solution becomes viscous. Figure 9a illustrates that micelles have grown into long threadlike micelles, which now coexist with probably perforated vesicles and lacelike structures, reminiscent of the defective lamellar phase that was found earlier in other systems.[42] The alignment of the threadlike micelles is again probably an effect from the shear on the sample preparation. Upon the addition of 5 mM NaSal to 10 mM I-C11, viscoelastic behavior was observed in the solution. In the micrographs globular micelles are now seen together with lacelike structures and threadlike micelles, Figure 9b,c.

The lacelike nets seen in Figures 9a,b are strikingly similar to the structures observed on dissolution of the defective lamellar phase of egglecithin/CTAC/0.1 M NaCl[42] and glycerolmonooleate/CTAB/0.1 M NaCl.[43] In the latter system, coexistence of such structures with globular micelles, was also observed. The observation suggests that a defective lamellar phase, at least metastable, occurs also in the fluorosurfactant system with strongly bound counterions. By partial neutralization of surfactants in the bilayer with these counterions, the bilayer may behave as composed of a mixture of a neutral bilayer forming amphiphiles and a charged component that introduces more curvature. Regarded in this way, there is a correspondence to the systems of refs 42 and 43. The coexistence of globular

micelles with structures of less curvature can be understood from a preferential binding of the counterions to the latter.

Effect of Alkyl Chain Length. The effect of salt and surfactant concentration was also studied for the fluorosurfactant I-C9. Globular micelles are formed without salt and long, threadlike micelles are formed with salt, similar to HFDePC, Figure 1. The transition from sphere to thread occurs at lower salt concentration than for HFOPC with the same fluorocarbon chain length. The micelles remained globular with increasing surfactant concentration, as we observed in a micrograph from a concentrated sample at 200 mM I-C9 (not shown).

Perfluorocarboxylic Acids and Carboxylates. Most work on perfluorosurfactants has involved perfluorocarboxylates. Rough phase diagrams of the two-component perfluorononanoic acid ($C_8F_{17}COOH$) and some of its salts in water were reported by Lindman and Fontell.[14] A lamellar phase is the most prominent liquid crystalline phase, which appears already in very dilute solutions of the acid. Figure 10 is a micrograph of 1 wt % $C_8F_{17}COOH$. The solution was viscous. Bilayers with sharp edges are present, and the faceted polyhedral structure indicates that the surfactant molecule within the bilayer are in the gel state, in which the fluorocarbon chains are stiff and closed packed.

Fontell and Lindman also mapped a rough phase diagram for the salt lithium perfluorononanoate (LiPFN), where the solubility in water at room temperature as an isotropic solution is rather high. The aggregation number of LiPFN in the dilute aqueous solution is quite small compare to that of the hydrocarbon surfactant with the same chain length which was determined earlier using the time-resolved fluorescence quenching method.[22] An examination with CTEM also shows spherical micelles in the aqueous solution of LiPFN and multilamellar vesicles at high salt concentration.

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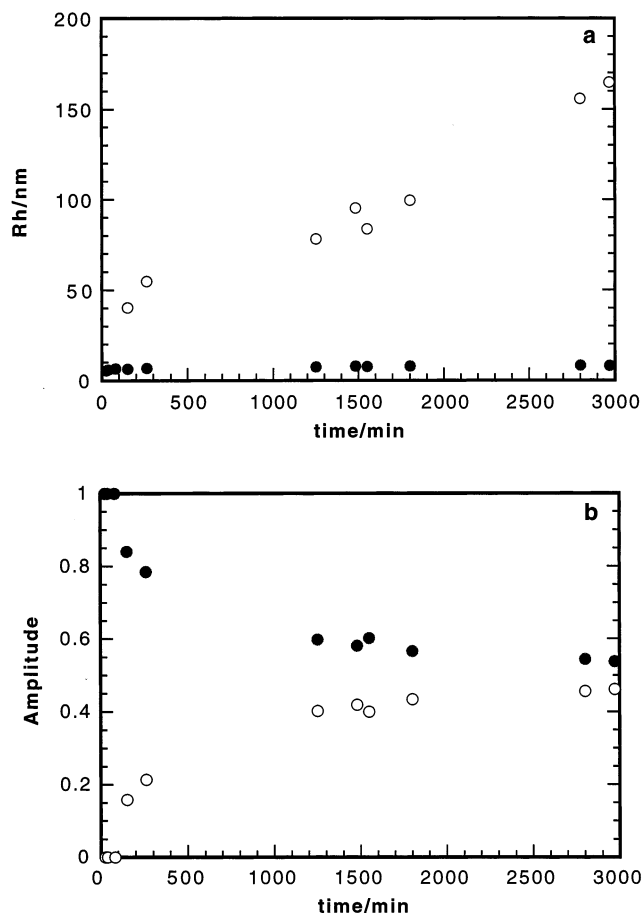
Figure 7. (a) The hydrodynamic radii R_h and (b) the amplitude of the two populations of vesicles in a sample of 10 mM I-C11 with 30 mM NaCl from dynamic light scattering measurements shown as a function of time. (●) small size and (○) big size vesicles.
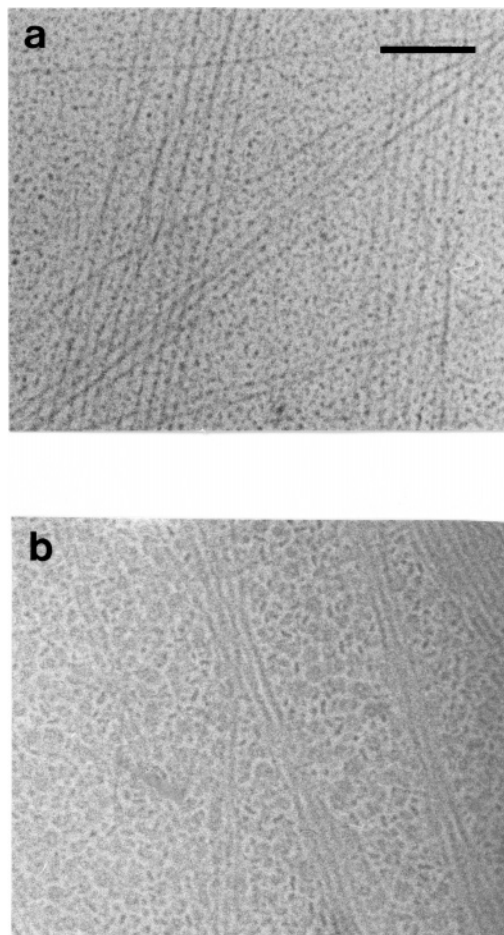

Figure 8. CTEM micrographs taken from I-C11 system with increasing surfactant concentration. Bar = 100 nm. (a) Globular micelles in coexistence with long threadlike micelles are observed in 50 mM I-C11. (b) Disklike structures in coexistence with long threadlike micelles are observed in 100 mM I-C11.

Burkitt et al.[13] studied 0.12 M ammonium perfluorooctanoate (APFO) in NH₄Cl:NH₄OH buffer solutions at pH = 8.8 and an ionic strength of 0.1 M by SANS. They concluded that APFO was present in rodlike micelles, with a radius of 10 Å and length of 48 Å. CTEM investigation of an APFO solution at the same composition showed some short elongated aggregates, but since the contrast was low, the exact shape of the aggregates could not be determined. With the addition of salt APFO micelles grew into bilayers. Figure 11 is a micrograph taken at 90 mM $C_7F_{15}COONH_4$ with 150 mM NH₄Cl. Bilayer sheets, open and closed vesicles, and disklike structures are all present, but no rods.

General Discussions

The main impression from this and other studies of the aggregation of fluorinated surfactants in water is that they form micelles and liquid crystalline phases of similar types, and in the same sequential order, as hydrocarbon surfactants, but with a striking propensity to form bilayer structures, or in general structures with less curvature than the hydrocarbon surfactants.

To understand this disposition, let us consider some of the differences between hydrocarbons and fluorocarbons, and in particular between hydrocarbon and fluorocarbon surfactants.

1. The fluorocarbon surfactants are more hydrophobic than hydrocarbon surfactants (HS). As a rule of thumb, the cmc of an FS corresponds to the cmc of the HS with $1.5^{21}-1.7^4$ as many carbons in the tail. Ravey et al.[5] have studied the chain length dependence of the cmc of nonionic poly(ethylene glycol)

surfactants, both normal and fluorinated, and found an incremental change of the free energy of micellization of $2.8RT$ per CH_2 and $4.8RT$ per CF_2 group, which explains the factor of 1.7. Ravey and Stébé also found that the hydrophobic effect is mainly determined by the volume occupied by the hydrophobic group in water, with the same coefficient for hydrocarbons and fluorocarbons, indicating that the high cohesive energy of water is the main determinant in both cases. For the cationic surfactants of the present study, the cmc values collected in Table 1 suggest an increment in the free energy of micellization of $0.71RT$ for a $-CH_2$-group and $1.05RT$ per $-CF_2$-group (ratio 1.5); the lower values for ionic surfactants than for nonionic being due to the decrease of the electrostatic screening with decreasing cmc values.

2. Fluorocarbon surfactants are more surface active than hydrocarbon surfactants, and reduce the surface tension of aqueous solutions to values that are unreachable with hydrocarbon surfactants. This is obvious from the results in Table 1. In some cases a surface tension as low as $17 \times 10^{-3} J/m^2$ is obtained. Neat hydrocarbon and fluorocarbon liquids show similar differences in surface tension, e.g., $21.6 \times 10^{-3} J/m^2$ for *n*-octane and $13.6 \times 10^{-3} J/m^2$ for the perfluorinated compound.[44] The low surface tension suggests that the cohesive energy density is low, which is also borne out by the fact that the refractive index is very low. The refractive index is related to the polarizability volume, and thereby the strength of dispersion interactions, which determine the cohesive energy
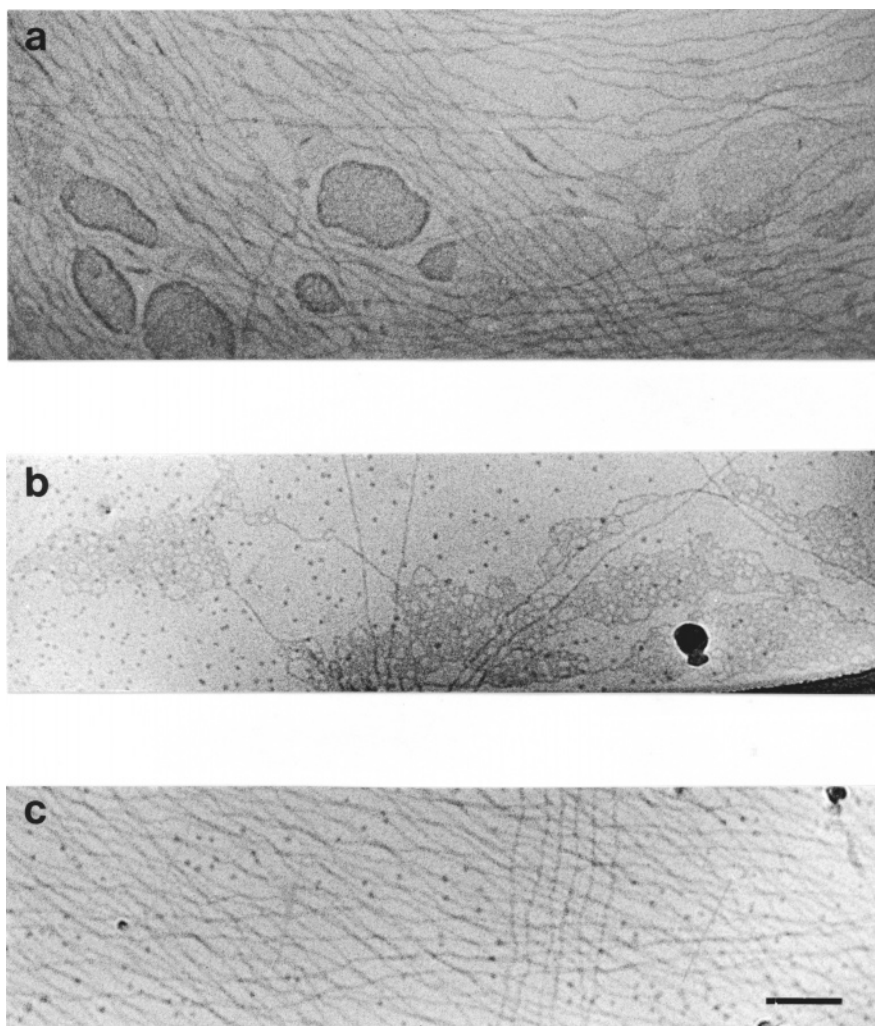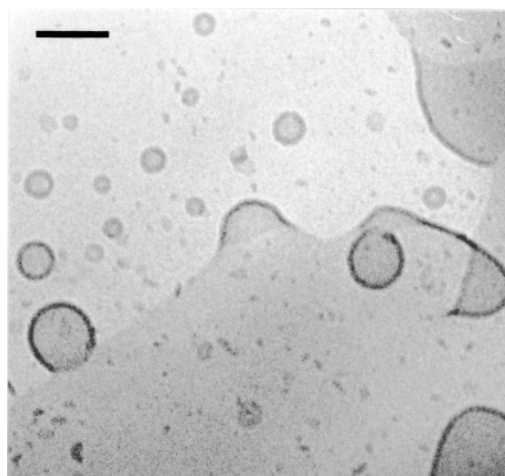
Figure 9. (a) Long threadlike micelles in coexistence with perforated vesicles and some lacelike structures, reminiscent of the defective lamellar phase in 10 mM I-C11 and 10 mM NaClO$_3$. (b, c) Globular micelles together with lacelike structures and threadlike micelles in 10 mM I-C11 and 5 mM NaSal. Bar = 100 nm.
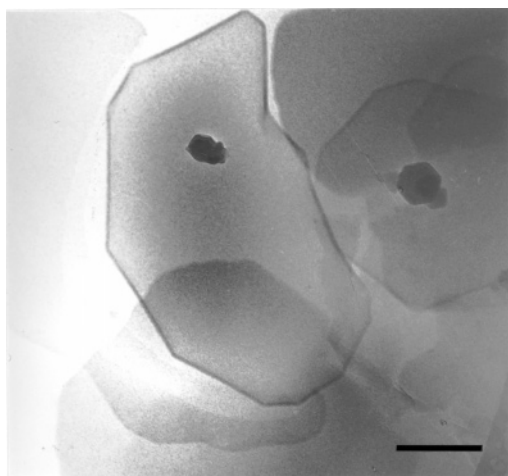
Figure 10. Bilayer structures with sharp edges are present in a solution of 1wt % C$_8$F$_{17}$COOH. Bar = 200 nm.

Figure 11. Bilayer sheets, open and closed vesicles, and disklike structures are formed in a solution of 90 mM C$_7$F$_{15}$COONH$_4$ with 150 mM NH$_4$Cl. Bar = 100 nm.

density of the nonpolar fluorocarbons. A lucid discussion of this point can be found in ref 45.

3. Other observers have suggested that the interchain van der Waals attraction between perfluorinated alkyl chains is much stronger than between hydrocarbon chains. The conclusion comes from experimental studies, simulations, and calculations of lattice energies for the crystalline self-assembly at the air/

water interface of fluorocarbon and hydrocarbon carboxylic acids.[46-48] On spreading of insoluble amphiphiles at the air/water interface, the first aggregation is often a formation of islands of expanded or condensed liquid phase, surrounded by the very dilute surface gas. Such islands of closed packed and condensed, or even crystalline, fluorinated carboxylic acids are

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found at a very low average molecular density at the interface, whereas the corresponding hydrocarbon carboxylic acids assemble as islands first at a much higher surface concentration, and then in a liquid expanded form unless the chains are particularly long. This stronger tendency for aggregation at the air/water interface may be caused by the stronger hydrophobicity of the fluorocarbons. However, lattice energy calculations suggest that the interchain interactions amount to 8.8 and 26.3 kJ/mol per CH_2 and CF_2-group, respectively, for two-dimensional crystals comprising vertical chains of $C_{20}X_{42}$, X = F, H.[46] If these values are correct, the difference is so large that the cohesive energy density must be much larger in the fluorocarbon than in the hydrocarbon crystals, i.e., it is more than a mere size effect. It is hard to reconcile this result with the low refractive index and low surface tension of fluorocarbon liquids, as discussed above, even if we are dealing with fluids in one case and (two-dimensional) crystals in the other (the larger mean separation in the fluid reduces the attractive interaction energy), and consider free energies in the liquid but enthalpies in the crystal.

4. A fluorocarbon chain is stiffer than a hydrocarbon chain. This is to say that the free energy difference between trans and gauche is much larger in the fluorocarbons (4.6 kJ/mol, corresponding to $1.9RT$ at room temperature)[49,50] so that the probability of a C−C bond having a gauche conformation is small. No free rotation about the C−C bonds is shown in the liquid perfluoroalkanes from X-ray data.[51] The hydrocarbon chain in the equilibrium configuration has on average each fourth CH_2 group in a gauche configuration, whereas a much longer part of the fluorocarbon chain is all-trans.[12] It is easier, therefore, to pack fluorocarbon chains closely: less entropy is lost, since the chains are mainly all-trans already in the liquid state.[47]

5. The aggregate structure can often be rationalized by the value of the surfactant packing parameter $v/la_0 = a_{tail}/a_0$.[1,52] Here a_0 is the effective polar headgroup area, v and l the volume and length of the hydrophobic tail, respectively, and a_{tail} the cross sectional area of the hydrophobic tail. From data of the density of fluoroalkanes,[53] a plot of molecular volume vs the number of carbons in the chain was constructed. The regression line suggests that the volume of a CF_2 group is 41 $Å^3$, as compared to 27 $Å^3$ for a CH_2 group in the corresponding alkanes.[54] The volume for the endgroup CF_3 is 84.5 $Å^3$, as compared to 27 $Å^3$ for CH_3, according to Tanford.[54] The contribution per CX_2 to the length of the fully extended (all-trans) tail was given as 1.30 Å in the fluorocarbons[55] and 1.26 Å in the hydrocarbons.[54] The fluorocarbon tail cross-section area would then be 31.5 $Å^2$, compared to 21.4 $Å^2$ for the hydrocarbon; similar values have been deduced by others.[45,55] The surfactant parameter can then be calculated, for fluorocarbon: $a_{tail}/a_0 = 31.3$ $Å^2/a_0$, and for the hydrocarbon analogue 21.3 $Å^2/a_0$. In other words, to have a surfactant parameter of $^1/_3$, which is required for spherical micelles, the effective area of the hydrocarbon surfactant must be 64.5 $Å^2$, which is a normal value for ionic micelles, whereas 94.8 $Å^2$ is required for the fluorocarbon, a value normally not attained. Cylindrical micelles, requiring a surfactant parameter of $^1/_2$, or 62.6 $Å^2$ for the fluorocarbon, would rather form, and bilayer structures would be expected under circumstances giving cylinders for the hydrocarbon surfactants. Thus, the value of the surfactant parameter explains well the fluorocarbon surfactant's preference for structures with little curvature.

6. The stiffness of the fluorocarbon chain, mentioned above, has also an effect on the packing. For hydrocarbon chains, one expects the number of gauche bonds to increase with the number

of carbons in the chain, so that the effective length of the tail is shorter than the all-trans length and that the cross-sectional area is correspondingly larger. Structures with less curvature are then expected to form when the tail-length increases, as is also observed. However, such an effect is also found for the fluorocarbon surfactants, which are already mainly in all-trans form. Other factors must be important as well. Maybe it is simply the fact that with increasing chain length the total attractive van der Waals energy between two molecules increases, so that beyond a certain length there is a net gain in free energy from lining up for optimal interchain interaction.

In general we can conclude that fluorocarbon surfactants behave in a similar way as hydrocarbon surfactants in aqueous solution. The surfactant molecules self-assemble into a variety of structures such as micelles, threadlike micelles, vesicles, lamellar aggregates, and various lyotropic liquid crystalline phases in the solution. The transformation from one structure to another when solution conditions are changed, such as concentration of surfactant or salt occurs in the same order for fluorocarbon and hydrocarbon surfactants, but occurs earlier for the former. Fluorocarbon surfactants have a larger tendency to form structures with less curvature and the micellar elongation induced by increasing concentrations of salt and surfactant concentration is rapid and large, compared with the corresponding hydrocarbon surfactants. The results can usually be explained on the basis of a bigger molecular volume, a larger cross-sectional area and a higher stiffness of the fluorocarbon chain compared to the hydrocarbon analogue.

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