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MONODISPERSE PERFLUORO-POLYETHOXYLATED AMPHIPHILIC COMPOUNDS WITH TWO-CHAIN POLAR HEAD - PREPARATION AND PROPERTIES

C. Selve*, J-C. Ravey, M-J. Stebe, C. El Moudjahid,
E.M. Moumni and J-J. Delpuech.

Université de Nancy I - *Campus Victor GRIGNARD* -
Laboratoire d'Etude des Solutions Organiques et Colloïdales. **LESOC** - *Associé au CNRS 406.*
B.P. 239 - **54506** - Vandoeuvre-les-Nancy Cedex - France

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Abstract: *Monodisperse new surfactant molecules with a two-chain polyoxyethylene (EO) hydrophilic head and a perfluoroalkyl hydrophobic moiety linked together through an amide bond are synthesized by methods allowing large-scale production. Surface tension measurements ($\gamma \sim 20$ mN.m^{-1}) show slow organization of the surfactant film at the water/air interface for longer fluorocarbon tail. Values of critical micellar concentrations and comparisons with monosubstituted amide surfactants are consistent with a high hydrophilicity of the amide function, a small influence of branching over hydrophilicity, and a hydrophobicity of each CF_2 unit equivalent to 1.7 methylenes (in the analogous hydrogenated surfactants).*

Introduction

A few years ago, we described a family of nonionic monodisperse fluorinated surfactants which allowed us to obtain for the first time aqueous microemulsions of fluorocarbons[1,2]. These microemulsions retain some of the attractive properties of liquid fluorocarbons, namely their ability to dissolve relatively large quantities of gases, and their great chemical inertness[3,4,5]. These solutions may offer an alternative to commercial macroemulsions presently used as temporary blood substitutes[6] because of their long-term stability and their better solubilization of fluorocarbons, and consequently of molecular oxygen[7]. However it seems that these solutions have short-term toxicity after intravenous infusion to animals, presumably due primarily to membrane-damaging effects from the surfactant[8]. Surfactive molecules synthesized in our laboratory have hydrophilic head and perfluoroalkyl hydrophobic moiety linked together through an ether, ester or amide bond

The first family of surfactant molecules used in our investigations contained a polar head of five to six oxyethylenic units, this represents the required hydrophilic chain length to be coupled to the C_6-C_7 perfluorinated moiety so as to effectively obtain aqueous microemulsions with fluorocarbons such as perfluorodecalin in the vicinity of 37°C[1,3] Recent work from Cserhàti *et al.*[9] shows however that membrane disorganization effects from the surfactant seem to pass through a maximum corresponding to a number of oxyethylenic units close to six. As already pointed out in a preliminary note[10], this has led us to

propose a multihead hydrophilic moiety so as to decrease the number of oxyethylenic units in each branch while keeping the same overall hydrophilic-lipophilic balance (HLB). Besides an expected beneficial effect towards biological membranes, an attractive feature of these compounds is their potential use as multidentate neutral ligands for cation complexation[11,12] in micellar solutions. Among many possible solutions, one of the simplest multi-chain structures involves a double-headed hydrophilic moiety. The necessity for a multifunctional junction unit led us to use amide bonds in the place of ether[1] or thioether[5] bridges in the two series of surfactants previously investigated to prepare fluorinated microemulsions. The new family of fluorinated surfactants synthesized as the first step of a long-term research project has a general formula in which two polyoxyethylenic chains are linked to the nitrogen atom of the amidic junction. However, the first series of compounds thus prepared with terminal hydroxyles suffered a slow degradation easily inferred from their infra-red spectrum which reveals the progressive appearance of an ester band. This degradation is certainly due to the slow reaction of the terminal hydroxyles onto the amide functions, is in line with the similar behaviour of the analogous hydroxyalkanamides which are known to equilibrate with the isomeric aminoesters, that further rearrange into a series of undesired side-products[13]. This led us to protect the terminal hydroxyles by O-methylation. In this way, we prevent equilibration with aminoesters, while the decrease of hydrophilicity is sufficiently small for the surface-active nature of the molecule to be retained. This results in the production of surfactants of high purity - which is required for an easy formulation of microemulsions - and of increased chemical inertness, which is an important factor foı their use as media for chemical or biochemical applications.

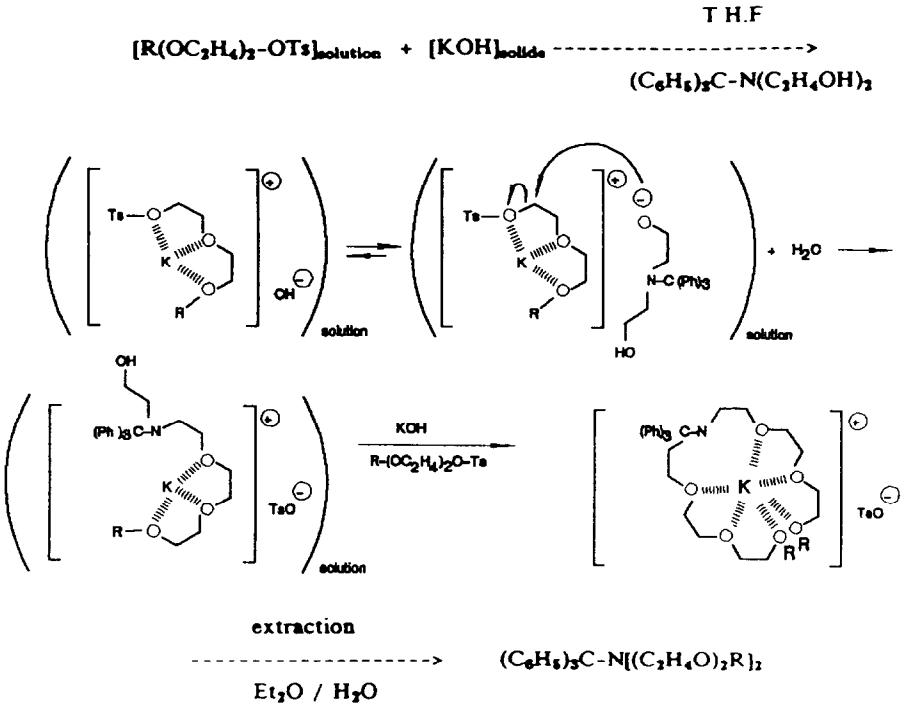
Synthesis

The synthesis was carried out by taking into consideration some requisites for the desired formulation. A simple method for varying the structures of the hydrophilic and hydrophobic moieties; use of expensive perfluorinated acids which requires minimum handling during the experiment; a synthetic pathway which leads to monodisperse surfactants with good yields and from low cost reagents so that large-scale production of these compounds could be envisaged. After trying different possibilities, we have retained the following strategy:

The preparation of the hydrophilic part (ethoxylamine) for which we used two reasonably equivalent pathways in terms of the yields obtained. The preparation of *"activated"* form of the lipophilic part (acid chloride or *"active"* ester) and the condensation of the amine, under this activated form, gives the desired amide.

1) Amines

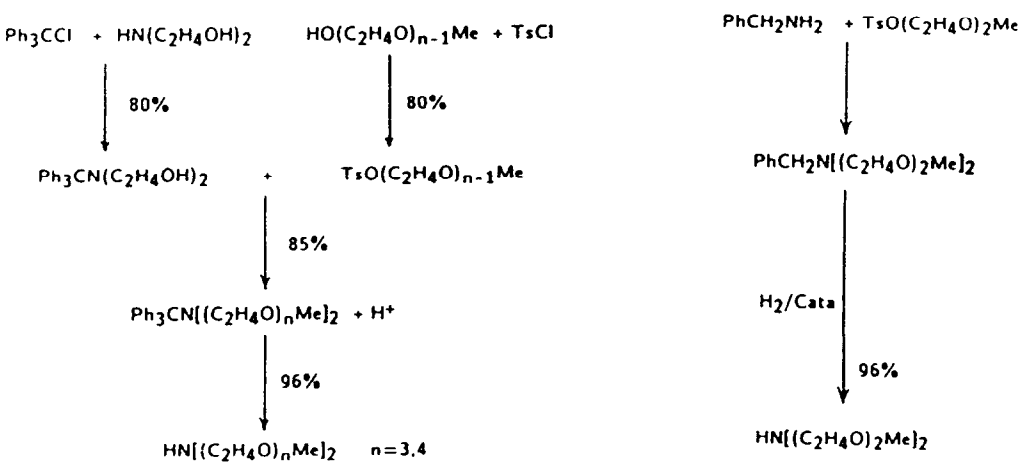
We chose two pathways for preparing the amines: The first possibility uses diethanolamine at the beginning of the reaction which, after protection by tritylation, is condensed on tosyloxyethylenemonoalkylether by either liquid-liquid (50 % NaOH/THF/tetrabutylammonium hydrogensulphate) or solid-liquid[14] phase transfer reaction. The former transfer reaction requires a phase transfer agent and leads to yields inferior to 60 %, while the latter transfer, on the contrary, is carried out in the absence of a catalyst and gives yields superior to 80 %. The latter solid-liquid phase transfer is therefore more interesting in terms of the yields obtained and handling. It is very likely that the tosyloxyethylene-monomethylether plays the role of phase transfer agent by favouring considerably the substitution reaction since an ion pair, between the two species that should react, is susceptible to being formed in the course of reaction The situation would be analogous (scheme I) to that of intermediate complexes proposed by Ouchi *et al*[15] in the synthesis of crown ether (template effect)



Scheme I Proposed mechanism for tosylate substitution in solid-liquid phase transfer

The second pathway uses benzylamine as starting material to which is condensed tosyloxyethylenemonomethylether in the presence of Na_2CO_3 in acetonitrile[16] Debenzylation by catalytic hydrogenation results into the amine

Regardless of the pathway taken, the yields of the desired amines are equivalent (80-90 %) The schemes for the two synthetic procedure are presented in scheme II



Scheme II: Synthesis of ethoxylamines used to obtain the surfactants

2) **Amides**

The prepared amines react with carboxylic acids (perfluorinated or not) under activated form: acid chloride [obtained by treatment with $SOCl_2$] or active ester of hydroxybenzotriazole (HOBT) [formed in situ by reaction with BOP-reagent[17]]:

$RC(O)X + HN[(C_2H_4O)_nMe]_2$ ---> $R - C(O)N[(C_2H_4O)_nMe]_2$ with: X = Cl or N-oxybenzotriazole. This condensation allows the amides to be obtained with good yields. The principal characteristics for these products are shown in table I.

Table I: Monodisperse amphiphilic compounds of the formula:

$$Y-(CF_2)_l-(CH_2)_m-C(O)-N[(C_2H_4O)_nMe]_2$$

N°	code[a] Yl.m.nn	Hydrophobic tail	Rdt%[b]	n_D (20°)	R_F (CCM)[c]	IR(amide) Cm^{-1}
1	*H0.8.33*	C_8H_{17}	65	1.458	0.47	1640
2	*H0.9.33*	C_9H_{19}	70	1.460	0.50	1640
3	*H0.9.44*	C_9H_{19}	80	1.457	0.35	1640
4	*H0.11.22*	$C_{11}H_{23}$	72	1.457	0.57	1640
5	*H0.11.33*	$C_{11}H_{23}$	74	1.458	0.30	1640
6	*H0.11.44*	$C_{11}H_{23}$	76	1.460	0.19	1640
7	F6.1.22	$C_6F_{13}CH_2$	94	1.395	0.57	1650
8	F6.1.33	$C_6F_{13}CH_2$	86	1.405	0.38	1650
9	F6.1.44	$C_6F_{13}CH_2$	84	1.415	0.23	1650
10	F8.1.22	$C_8F_{17}CH_2$	89	1.385	0 55	1650
11	F8.1.33	$C_8F_{17}CH_2$	85	1.398	0.40	1650
12	F8.1.44	$C_8F_{17}CH_2$	85	1.406	0.28	1650
13	F10.1.22	$C_{10}F_{21}CH_2$	80	1.383	0.52	1650
14	F10.1.33	$C_{10}F_{21}CH_2$	87	1.392	0.39	1650
15	F10.1.44	$C_{10}F_{21}CH_2$	83	1.402	0.26	1650
16	*F6.0 22*	C_6F_{13}	63	1.393	0.48	1675
17	*F6.0.44*	C_6F_{13}	57	1.411	0.19	1675

a) Y = H: Hydrogenated amide; Y = F: Fluorinated amide; l: Number of perfluorinated carbons. m: Number of hydrogenated carbons. n: Number of ethoxyl groups (EO = C_2H_4O) per chain in the polar-head.

b) Calculated on the basis of fluoro-acid used during condensation.

c) Thin layer chromatography (ethylacetate).

The amides possessing perhydrogenated hydrophilic chains (compounds 1 to 6) are obtained in good yields (> *ca.* 70%). The same is true for fluoroalkyl surfactants (yields > 80%), only if a separating methylene is present at the junction of the hydrophilic chain (compounds 7 to 15). Compounds 16 and 17 deriving from fully fluorinated acids have special characteristics and the amidification reactions are generally difficult to handle. Fung *et al*[18] used methyl ester with ZnO as catalyst to activate them; the amides were obtained in good yields under these conditions. This procedure, however, necessitates two preliminary steps starting from the acid (preparation of the acid chloride, then its esterification). Our

approach involves a direct *"one-pot"* activation by BOP-reagent[17]; yields with respect to the fluorinated acid (*ca.* ~60% we did not optimize the experimental conditions) are of the same order as those obtained by Fung's method. Compounds 16 and 17 show a major drawback in their use as surfactants: the amide function is relatively unstable. Their hydrolysis is clearly faster than those of alkanolamides, whereas the presence of a methylene separator between the fluorinated moiety and this amide function permits its stabilization by reducing the strong electron-withdrawing effect of the fluorinated moiety, thus a stability equivalent to that of hydrogenated alkanolamides is practically attained. These results led us to essentially select perfluoro structures consisting of at least one methylene group as separator between the perfluorinated and hydrophilic parts. The synthesis of some compounds having a hydrogenated hydrophobic chain allows for interesting comparison with their fluorinated counterparts in terms of their surfactant behaviour. Shinoda[19] indicated in his study of perfluoro ionic surfactants that the CF_2 group has a hydrophobic effect of approximately 1.5 x CH_2. In a recent investigation carried out by Ravey *et al.*[20,21] on fluorinated non-ionic surfactants having an oxyethylene hydrophilic chain, the hydrophobic effect of a CF_2 group is shown be rather equivalent to 1.7 x CH_2 of the corresponding perhydrogenated compounds. This observation led us to synthesize the hydrogenated derivatives H0.11.22 (n° 4), H0.11.33 (n° 5) and H0.11.44 (n° 6) which should be endowed with a hydrophilicity nearly equivalent to C6 perfluorocompounds F6.1.22, F6.1.33 and F6.1.44 (entries 7,8 and 9 of table I). In this way, we can evaluate the similitudes and differences betwen the two series of compounds having exactly the same two-chain head hydrophilic moiety.

Surfactant Properties

Since all these new compounds have been designed in view of their potential use as surfactants, a few of their properties as surface active agents have been examined. Their fundamental characteristic is their ability to lower the surface tension (γ) of their aqueous solutions. Moreover, since they should also be used to promote a water-perfluorocarbon cosolubilization (microemulsions) or to stabilise water-in-oil or oil-in-water emulsions, their hydrophobic-lipophilic balance has to be estimated. A thorough presentation of these data is out of the scope of the present paper. Here, we shall focus mainly on the effect on the length of the fluorinated chain, at fixed hydrophilic head. A comparison with data for the analogous hydrogenated surfactants will also be presented.

- Surface activity

Most of the hydrogenated amphiphiles lower the surface tension of water to about 30-40 mN/m [12]. For fluorinated compounds, that tension generally becomes smaller than 20 mN/m [19,21], ionic amphiphiles being the most effective. As usual, the change of γ with the logarithm of the bulk concentration C (mole/l) has been measured at definite temperatures. This is examplified by the curves of figures 1 and 2, respectively for F6.1.33, F8.1.33 and H0.9.33, H0.9.44.

Such curves exhibit a well defined break for a certain value of C, that is the critical (micellar) concentration (CMC). For C > CMC, γ remains practically constant, and equal to the minimum value of γ attainable with a given amphiphile ($\gamma_{(CMC)}$). Such a behaviour is that of high purity amphiphilic compounds. As expected, $\gamma_{(CMC)}$ for the fluorinated surfactants are about 20 mN/m, while for the hydrogenated ones, they are 10 mN/m higher. (Table II).

A closer examination of the data shows an increase of γ_{CMC} with the number of oxyethylene groups, whatever the type of the amphiphiles (16 and 24, 18 and 24, 27 and 30 mN/m, respectively for F6.1.22 and F6.1.44, F8.1.22 and F8.1.44, H0.11.22 and H0.11.44). On the other hand, there seems to be a minimum of the $\gamma_{(CMC)}$ values when the length of the fluorocarbon tail increases; this is an unusual effect which would then show that the film pressure decreases somewhat when the surfactants becomes highly hydrophobic, suggesting a reduced lability/deformability of the layer of the amphiphilic compounds which gather on the water/air interface.

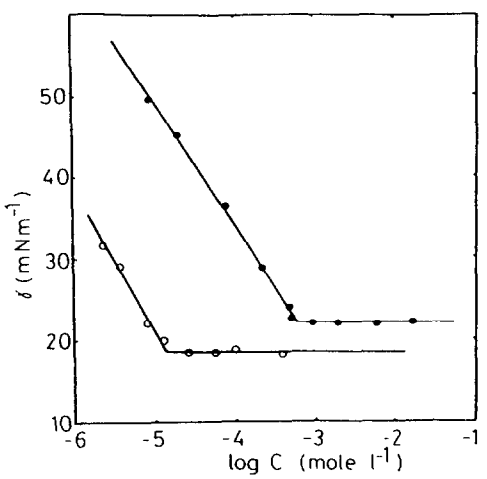


Figure 1. Surface tension *vs* $\log_{10}$ of the concentration (mole dm^{-3}) at 25°C, for compounds F6.1.33 (●) F8.1.33 (○) in aqueous solution.

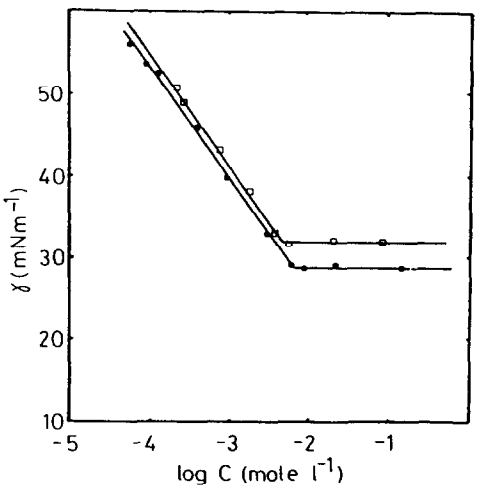


Figure 2. Surface tension *vs* $\log_{10}$ of the concentration (mole dm^{-3}) at 25°C, for compounds H0.9.33 (□) H0.1.44 (●) in aqueous solution.

Table II: Surface Properties of monodisperse amphiphilic compounds at 25°C.

N°	Surfactant code	Mol.W.	H.L.B.[a]	$\gamma_{(CMC)}$[b] $mN.m^{-1}$	CMC[c] ($10^4 mol.dm^{-3}$)	σ[d] A^2
2	*H0.9.33*	463.7	14.5	32	50.2	65
3	*H0.9.44*	551.8	15.3	29	64 1	67
4	*H0.11.22*	403.6	12.3	27	4	53
5	*H0.11.33*	491.7	13.6	28	5.1	61
6	*H0.11.44*	579.8	14.6	30	2 45	65
8	F6.1.33	669.4	10.0	22	5.5	63
11	F8.1.33	769.5	8.74	19	0.12	58
13	F10.1.33	869.4	7.73	22	~0.003	~25

(a) H.L.B. Hydrophilic Lipophilic Balance calculated with Griffin's equation[29].

(b) Surface tension beyond the CMC.

(c) Critical (Micellar) Concentration [CMC] evaluated at the intersection of γ versus $\log_{10}$ [C].

(d) Area per polar head calculated from classical Gibbs equation[22].

Although the data in Table II refer to measurements at 25°C, we may report here that the surface tension decreases with increasing temperature and that its relative change is much larger when the surfactant is more hydrophobic (e.g. $\gamma_{(CMC)}$ changes from 23 to 21 and from 33 to 21 mN/m, respectively for F6.1.33 and F10.1.33, when temperature rises from 5°C to 45°C). This behaviour could effectively be explained by a different structure of the film, whether the hydrophobic chain is longer or shorter, and the temperature is lower or higher, that is the structure which is kinetically attained after a reasonable time. very hydrophobic surfactants seem to be able to adsorb and to spontaneously adopt the classical

fluid palisade monolayer structure only at "higher" temperatures, the more hydrophobic the surfactant the higher the temperature. This kinetic effect is enhanced by a high dilution state of the bulk. Such a behaviour is examplified by the curves of figures 3 and 4, where the change of γ with time is shown for various compounds, concentrations and temperatures. Probably, for low bulk concentrations and low temperatures, when increasing the air/water interface, very hydrophobic surfactants have a so strong tendency to escape the aqueous medium that they form a superficial layer with a rather disordered structure and/or an inhomogeneous thickness. Such a view may be related to kinetics: several minutes, or even several hours, may be necessary before the thermodynamic equilibrium can be attained, i.e. before the surface film reorganizes itself by forming the classical fluid monolayer corresponding to the maximum surface pressure.

- Area per polar head

From the slope of the γ versus logC curve at the CMC, and using the classical Gibbs equation[22], the area per polar head (σ) of one surfactant adsorbed at the air/water interface can be evaluated (Table II). As expected, σ increases with the number of oxyethylene groups, for both the F- and H-series. It should be noted that σ values for H0.9.44 and H0.11.44 are quite similar to those of classical ethoxylated alcohols with the same number of oxyethylene units (EO groups) and the same hydrophobic chain length (75 and 66 A^2, respectively for C_9E_8 and $C_{11}E_8$[23]). On the other hand, for $C_6F_{13}CH_2$-E_6, σ is about 45 A^2 [17], a value markedly lower than 63 A^2 (F6.1.33).

We have shown in a previous paper that for surfactants with a smaller number of oxyethylene units , linear fluorinated surfactants have σ values noticeably smaller than those for the equivalent hydrogenated compounds (i.e. with the same number of EO groups, and similar order of magnitude of their CMC); but for the more hydrophilic nonionic surfactants, they have quite similar σ values whether they are F- or H-exthoxylated alcohols.

Therefore, branching the hydrophilic head lessens the influence of the CF_2 chains, making H- and F-compounds quite alike, i.e. for which $\sigma$is primarily determined by the number of EO groups. Nevertheless, an increase of the hydrophobic chains always leads to a slight decrease of σ : whatever the type of amphiphiles, the larger the "hydrophobic" attractive forces the smaller σ. However, we believe the value given for F10.1.33 reflects in fact some overcrowding of the surfactant in the so called "monolayer" film (i.e., may be, locally bilayered or with heaps).

- Critical concentration (CMC)

As expected, the CMC slightly increases with the number (n) of EO groups and strongly decreases with the length m of the hydrophobic chain. Let us recall that for linear ethoxylated alcohols:

(1) $\log CMC = a + b.m + c.n. + d.m.n$

where d, c << b. Moreover, b(H-surfactant) ~ 1.7 x b(F-surfactant); hence, as far as the CMC is concerned, a given F-surfactant is as hydrophobic as a H-surfactant whose CH_2 chain is *1.7 times longer*[21]; this expresses the very strong hydrophobicity of the fluorinated surfactants (at least with respect to the micellization phenomenon !). Equation (1) shows that the CMC of a H-surfactant is divided by a factor of about 9-10 (let us say 9.5) each time we add one C_2H_4 group in the hydrocarbon moiety. This is exactly what we note when comparing the CMC of H0.9.33 and H0.11.33 (respectively 50 and 5.1 10^{-4} mole/l) and those of H0.9.44 and H0.11 44 (respectively 64 and 6.5 10^{-4} mole/l). On the other hand, let us recall that for the hydrogenated linear ethoxylated alcohols C_9E_8 and $C_{11}E_8$[23] the CMC is respectively: 3 10^{-3} and 3 10^{-4} mole/1. Therefore, although the H-surfactants in table II carry a terminal methyl group on the hydrophilic head, which thus reduces their hydrophilicity (after Tiddy, one OH terminal would be equivalent to two EO groups)[24], their CMC is twice that of linear H-alcohols C_mE_n. Such large values of the CMC must be ascribed to the hydrophilicity of the C(O)N amide group, which should be equivalent to more than five EO groups.

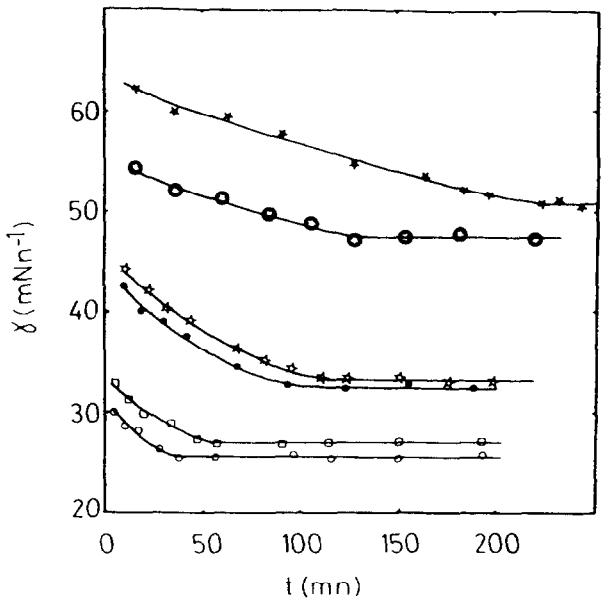


Figure 3. Time effect in the surface tension measurements at 5°C for various concentrations of two surfactants in aqueous solutions: F8 1.33 (●) 3.9 10^{-6}; (□) 8 0 10^{-6}; (○) 1.2 10^{-5} mole dm^{-3} and F10.1 33 (✱) 1.0 10^{-6}, (✪) 1 3 10^{-6}, (✰) 3.5 10^{-6} mole dm^{-3}.

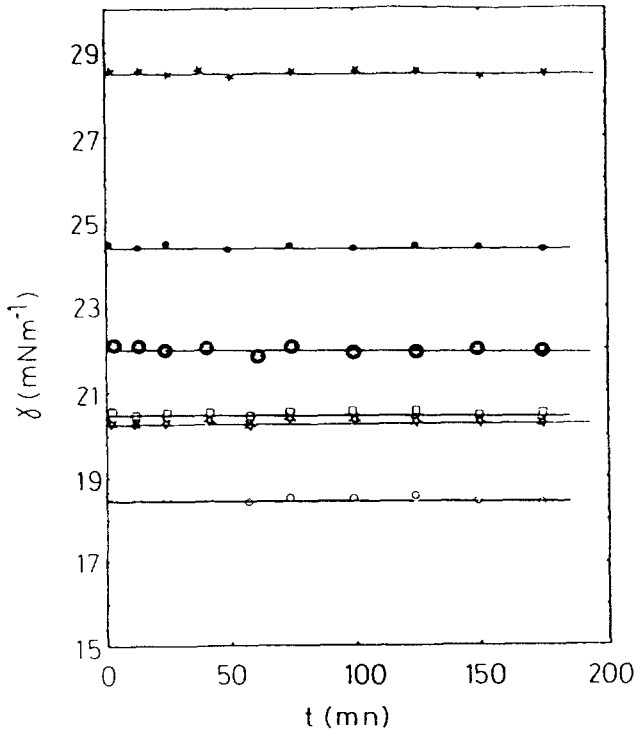


Figure 4. In contradistinction to the measurement at 5°C (cf. fig 3), data at 45°C are practically time independent.

We do not believe that the branching in the polar moiety should contribute anyhow to this enhanced hydrophilicity. This has been checked by studying mono substituted ethoxylated amide surfactants (-C(O)NH-), which are linear molecules (results to be shown elsewhere).

Now, comparing the data for F6.1.33 and F8.1.33, their CMC are in the ratio 1:45, (that is about 9.5 raised to the power of 1.7), as expected from the equivalence rule derived for the hydrophobic part as discussed above. The value given for F10.1.33 is only indicative (i.e. with only the right order of magnitude) due to experimental uncertainties. Nervertheless, it invalidates by no means the eq.(1) when applied to very hydrophobic surfactant. As a last check of this 1.1.7 equivalence rule, we effectively note that both the amphiphiles H0.11.33 and F6.1.33 have very similar CMC values (six CF_2 groups being equivalent to ten CH_2 groups).

- Solubilisation properties

1) Water/surfactant binary systems

Here, let us just mention that the most hydrophobic fluorinated amphiphiles give rise to complicated phase systems, including gels and lamellar liquid crystals. This is clearly apparent for F10.1.33, whose phase diagram is given in figure 5. Although delineations may be only semi-quantitative as far as the gel-water and Lα (lamellar liquid crystal)-water domains are concerned, they clearly remind of the behaviour of very hydrophobic hydrogenated compounds like monopalmitin[25], examplifying the strong tendency for the surfactants to aggregate into bilayers. More quantitative data will be shown elsewhere. However, as noted above (CMC), the present amide derivatives are much more hydrophilic than the oxyethylene alcohols with the same number EO group and the same hydrophobic chain. And this can be seen from their aqueous phase diagrams. For example, the fairly simple diagram for F6.1.33 is shown in figure 6. At low temperature, water and surfactant are totally miscible (L_1 phase). At higher temperature, there is a liquid-liquid consolute curve, with a critical point at T_c = 33°C, the critical concentration being about C_c= 10 % w/w. No liquid crystal can be formed, this may be ascribed to the high spontaneous curvature of the surfactant film in the micelles, i.e. to high hydration of the two-chain polar head (presence of the -C(O)N group), giving rise to a strong repulsion between them: as a result, micelles remain "small" and spherical. Obviously, this behaviour is in sharp contrast with that of the corresponding linear oxyethylene alcohol $C_6F_{13}CH_2$-E_6 (same number of EO groups and same hydrophobic chain as F6.1.33): in this case, classical hexagonal and lamellar liquid crystals are formed for surfactant concentrations above 50 %, at least at lower temperatures[26] (figure 7).

Most interestingly, we also note one liquid-liquid consolute curve with a lower critical point, but with T_c~12°C and C_c~1 %. We ascribe such a difference in the C_c value to the difference in the morphology (anisometry) of the micelles: in the case of the last compound, repulsions between EO groups are somewhat lower than in F6.1.33, allowing for the formation of (more or less) long cylindrical micelles (and the liquid crystals): indeed, the mean attractive forces between the micelles responsible for the phase separation are much more pronounced for cylindrical particles than for spherical ones[27].

2) Oil/water/surfactant ternary systems

When comparable amounts of oil and water are mixed in the presence of a small quantity of surfactant, oil-in-water or water-in-oil emulsions are formed depending on the temperature and the nature of the surfactant and the oil. These emulsions have an optimum stability in the vicinity of the phase inversion process. In a certain range of the values of the parameter, the temperature of the inversion phase (PIT) is related to the structure of the oil and surfactant (in the absence of additives) according to the linear equation[28]:

$$PIT = A + B.\ HLB + C.\ ACN$$

ACN is the equivalent alkane number (for hydrogenated oil), while HLB is the so called hydrophilic-lipophilic balance of the surfactant. Although fluorocarbons are lipophobic, nevertheless the same denomination will be kept to describe the relative hydrophilicity/hydrophobicity (oleophilicity) tendency of the fluorinated amphiphiles[28].

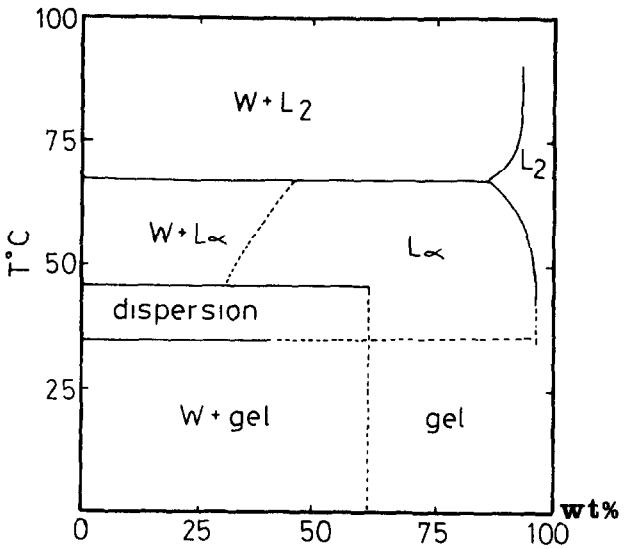


Figure 5. Phase diagram of the F10.1.33/Water system (compositions in weigth % of surfactant). gel is a lamellar gel phase; Lα lamellar liquid crystal; L2 an isotropic phase; W is a water phase.

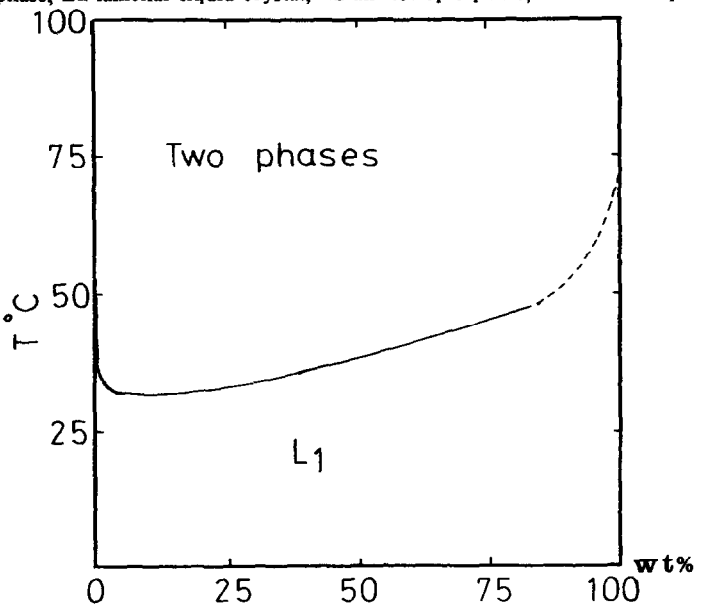


Figure 6. Phase diagram of the F6.1.33/Water system (compositions in weigth % of surfactant).

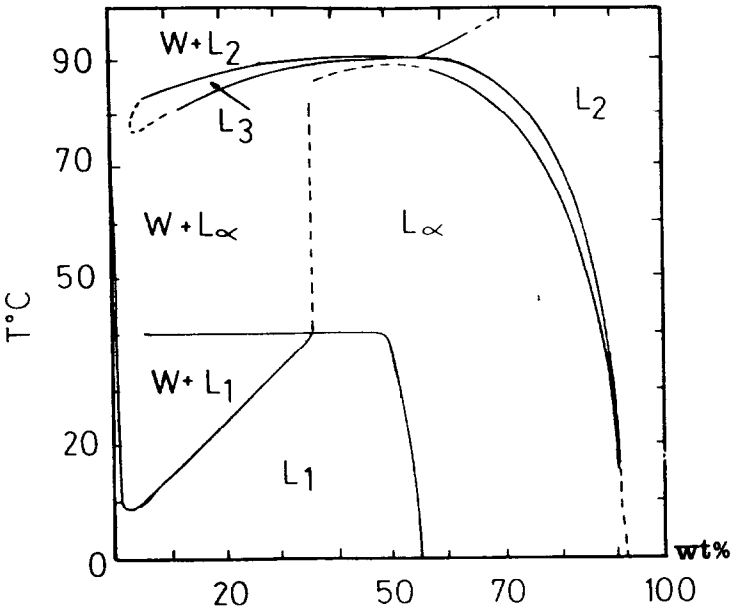


Figure 7. Phase diagram of C_6F_{13}-CH_2-$(OC_2H_4)_6$-OH/Water system (compositions in weigth % of surfactant). L1, L2, L3 are isotropic phases; Lα is a lamellar liquid crystal.

For ethoxylated nonionics, according to Griffin[29], HLB is between 0 and 20 and is proportional to the mass fraction of the polyoxyethylene part. The HLB of any surfactant is evaluated by comparing the optimum stability of the emulsions obtained with both this surfactant and a reference oxyethylated alcohol, using the same oil at the same temperature.

As calculated according to Griffin equation, the HLB is a number which can be used only in comparing various compounds within given series. For example, for hydrogenated compounds and for a PIT of 20°C, the HLB required to get stable emulsions with octane is about 10.6; at 50°C for heptane, it would be 12.6[28,30]. Hence, to each surfactant of the present series (2-chain head, fluorinated tail, one -C(O)N= group, two methyl groups), HLB numbers can be ascribed for each member of the series in the same way as they are calculated for hydrogenated ethoxylated alcohols; but they cannot be mutually compared on a quantitative basis. By studying the PIT of various fluorinated systems, experiments show that the HLB of the present compounds required to stabilize emulsions made of F-heptane, F-octane, or F-decaline at 20-50°C are in the range of 6-8, numbers which are then noticeably lower than those of the range reported above (11-13) for "equivalent" hydrogenated ethoxylated alcohols[28,30,31].

No oil/water cosolubilization experiment has been performed on two-chain H-compounds, and their HLB cannot be directly compared to those of F-amphiphiles, as reported in Table II. For these Fl.m.nn compounds with l= 6, 8, 10 and n= 2, 3, 4, the HLB numbers are in the range 8-11. Therefore, most of these surfactants will lead to the formation of oil-in-water emulsions at room temperature and must be considered rather as hydrophilic, as far as oil/water cosolubilization is concerned. Parallely, for higher surfactant amounts, one isotropic microemulsion phase (oil-in-water microemulsion) can be obtained for oil/surfactant ratios which depend on the temperature (below the PIT). A comprehensive study of these solubilization properties would necessitate full ternary phase diagram determinations, and are out of the scope of the present paper. Nevertheless, in order to examplify the potentialities of the present

surfactants, a few compositions of o/w microemulsions are given in Table III. The surfactant F10.1.33 has the HLB value which leads to the PIT nearest to room temperature; as a result, it allows us to obtain microemulsions containing the largest amount of fluorocarbon as compared to other systems: that optimum oil/water cosolubilization occurs for oil to surfactant ratios in the range of 1-1.5 w/w. F6.1.44 and F8.1.44 are too hydrophilic to allow the formation of a "surfactant phase", their aqueous micelles being unable to incorporate noticeable amounts of oil.

Table III: Composition of microemulsions.

Surfactant code	Surfactants %(weight)	Water %(weight)	Perfluorocarbon %(weight)	Temperature zone T°C to T°C
F6.1.33	14,4	83,2	2,4	5 - 36
F8.1.33	8,3	88,5	3,2	5 - 37
F8.1.33	14,4	82,1	3,5	7 - 34
F10.1.33	3,4	93,6	3,0	7 - 43
F10.1.33	8,7	82,6	8,7	7 - 41
F10.1.33	11,1	70,9	18,0	10 - 36

Conclusion

In this paper we have presented very efficient pathways for the synthesis of new amphiphilic compounds, high yields being obtained by the use of simple experimental procedures which can be applied for large-scale production. These compounds appear rather hydrophilic from their solubilization properties. This results from the fact that such a property is directly related to the mass or volume fraction of the hydrophilic part into the surfactant molecule. But, as far as purely aqueous systems (micelles) are concerned, their hydrophilicity may be very low, because CF_2 groups are very hydrophobic, and such properties essentially depend on the length of the fluorocarbon chain, the exact nature of the polar head being of little importance. Probably, the presence of a two-chain head is not essential for most of the physico chemical properties of these new compounds, although it should somewhat unfavour the formation of non spherical micelles. At any rate, we have to stress the major influence of the very hydrophilic amide group, which largely overcompensates the hydrophobicity of the methyl groups at the end of the EO chains. In that way, we are able to design hydrophilic nonionic surfactant characterized by a quite reduced undesirable reactivity towards the medium (or other surfactant) due to the substitution of the hydroxyl by the methoxy end groups.

In addition to this amphiphilic behaviour, these compounds can have ionophoric properties. Indeed the structures of these derivatives are close to those of acyclic crown ethers[32], of compounds known as phase transfer catalysts (PTC) [for example: tris(polyoxalkyl)amines recently prepared by Soula[33] or substituted triazins presented by Montanari *et al*[34]] and, more specifically, of amides having two oxyethylene chains with a terminal alkyl group (generaly butyl)[35] which are well known to possess good ionophoric properties.

Experimental Section

Tritylation of diethanolamine

To a round-bottomed flask fitted with a dropping funnel was added a solution of 66.6g (2 eq) diethanolamine in 270ml DMF. After cooling at 0°C, 80.2g (1 eq) of trityl chloride in 170ml CH_2Cl_2 were added dropwise for 80mn. The mixture was left at a low temperature (0°C) for 24 hr. This was then washed with 150ml ether and 200ml H_2O. A precipitate was formed after a few minutes ; it was filtered, then crystallized in chloroform/petroleum ether (1/2) to give 88,2g (80%) as a pinkish solid; mp 160°C; R_F= 0,5 (AcOEt/Hexane, 50/50); IR ν_{OH} 3600 - 3200 cm^{-1}; ν_{CH2} 3000 - 2800 cm^{-1}; $\nu_{CH(arom.)}$ 3100 - 3000 cm^{-1}; ν_{C-O-C} 1150 - 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) $(Ph)_3C-N(CH^a_2-CH^b_2-OH)_2$: δ 7,4 ppm (m) $(Ph)_3$; δ 2,5 ppm (t) CH^a_2; δ 3,58 ppm (t) CH^b_2; δ =2,2 ppm (s) OH; Anal. calcd for $C_{23}H_{25}O_2N$: C, 79.51; H, 7.17; N, 4.03; O, 9.20. Found: C, 79.22; H, 7.24; N, 4.10.

Tosylation of oxyethylenemonomethylether

A solution of 3.3 x 10^{-1} mole (1 eq) oxyethylenemonomethylether in 80ml pyridine was introduced to a round-bottomed flask fitted with a dropping funnel. After cooling the mixture to 0°C under constant agitation, 6.6 x 10^{-1} mole (2 eq) of tosyl chloride in 130ml pyridine was added dropwise (90mn) to it. The reaction mixture was then left to attain room temperature. This mixture was diluted with 200ml H_2O after 30mn of reaction and extracted with ether. The organic phase was then washed with an aqueous acid solution (5 % HCl, 100ml). The ether phase was dried over $MgSO_4$, filtered and the ether evaporated under reduced pressure. The resulting oil obtained was used in its crude form. For the purpose of identification is was chromatographed on silica gel, AcOEt/Hexane, 50/50 to afford a yellow oil:

- Tosyl-diethyleneglycol-monomethylether 72g (80%): $CH_3-C_6H_4-SO_2-O(C_2H_4O)_2-CH_3$; n_D^{20}, 1.499; R_F, 0,84 (AcOEt); Anal. calcd for $C_{12}H_{18}O_5S$: C, 52.55; H, 6.60; S, 11.66; O, 29.16; Found: C, 52.19; H, 6.49; S, 11.76.
- Tosyl-triethyleneglycol-monomethylether 79.83g (76%): $CH_3-Ph-SO_3-(C_2H_4O)_3-CH_3$; n_D^{20}, 1.526; R_F, 0.64 (AcOEt); Anal. calcd for $C_{14}H_{22}O_6S$: C, 52.82; H, 6.96; S, 10.06; O, 30.16; Found: C, 52.44; H, 6.97; S, 9.91.

IR: $\nu_{CH(arom.)}$, 3030 cm^{-1}; ν_{CH2}, 3000 - 2800 cm^{-1}; ν_{SO2}, 1200 - 1170 cm^{-1}; ν_{C-O-C}, 1150 - 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ 2.42 (s, 3H); δ, 3.3 (s, 3H); δ, 3.6 [m, $(C_2H_4)_n$]; δ, 4.1 (t, 2H); δ, 7.3-7.7 (m, 4H).

Synthesis of N,N-bis (oxyethylenemonomethylether) tritylamine

- a) Liquid-liquid phase transfer

To a stirred mixture of 30ml (10 eq) solution of 50 % NaOH (aq) and 0.5g (10 %) of tetrabutylammonium hydrogensulfate as catalyst in a round-bottomed flask fitted with a condenser was added a solution of 5g (1 eq) of N-trityldiethanolamine and 15.8g (4 eq) of tosyloxyethylenemonomethylether in 50ml THF. The resulting mixture was refluxed for 18hr with stirring. After reaction, the solution was poured into distilled water (100ml) and extracted with ether. The organic phase was dried over Na_2SO_4, filtered and evaporated to give the crude product which was purified by HPLC (AcOEt/Hexane 50/50)

- b) Solid-liquid phase transfer

To a round-bottomed flask equipped with a condenser and a magnetic stirrer, 1.2 x 10^{-1} mole (12 eq) of finely ground KOH and 20ml dry THF were introduced. A solution of 10^{-2} mole (1 eq) of N-trityldiethanolamine and 4 x 10^{-2} mole (4 eq) of tosyloxyethylenemonomethylether in 70ml THF was added to the KOH. The mixture was refluxed for 16hr under stirring. After reaction, the solution was diluted with 100ml of distilled water, then extracted with ether. The organic phase was dried over Na_2SO_4 and filtered. Vacuum evaporation gave a crude product which was purified by HPLC (AcOEt/Hexane

50/50):

- N,N bis(triethyleneglycol-monomethylether)tritylamine: $(Ph)_3C\text{-}N[(C_2H_4O)_3CH_3]_2$; 4.6g (83%); n_D^{20}, 1.555; R_F, 0.5 (AcOEt/Hexane 80/20); Anal. calcd for $C_{33}H_{45}O_6N$: C, 71.84; H, 8.21; N, 2.53; O, 17.40; Found: C, 71.20; H, 8.03; N, 2.87.
- N,N bis(tetraethyleneglycol-monomethylether)tritylamine: $(Ph)_3C\text{-}N[C_2H_4O)_4\text{-}CH_3]_2$; 5g (78%); n_D^{20}, 1.540; R_F, 0.4 (AcOEt/Hexane 80/20); Anal. calcd for $C_{37}H_{53}O_8N$: C, 69.46; H, 8.34; N, 2.19; O, 20.00; Found: C, 69.55; H, 7.95; N, 2.50.

IR: $\nu_{CH(arom.)}$, 3100 - 3000 cm^{-1}; ν_{CH_2}, 3000 - 28OO cm^{-1}; $\nu_{C\text{-}O\text{-}C}$, 1150 - 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ 2.55 (s, 4H); δ, 3.3 (s, 6H); δ, 3.5 - 3.9 [m, $(C_2H_4)_n$]; δ, 7-7.5 (m, 15H); ^{13}C NMR (400 MHz, C_3D_6O/TMS): δ, 144 (s), 139.5 (d), 127.8 (d), 126.2 (d) (18 $C_{arom.}$); δ, 79 (s C-N); δ, 53.5 (t $N\text{-}C_2$); δ, 70-72 [m $(C_2H_4)_n$]; δ, 58.2 (q CH_3).

Detritylation of polyethoxylamine

To a 20 ml solution of 5 % HCl (aq) contained in a round-bottomed flask fitted with a dropping funnel, 1.34 x 10^{-2} mole (1 eq) of N,N-bis (oxyethylenemonomethylether) tritylamine in 40ml of methanol was added dropwise at room temperature. The mixture was left at ambient temperature for 15mn. The tritylcarbinol formed was filtered, then the solvent was evaporated until the volume of the residue becomes approximately equal to the volume of the initial aqueous phase. It was then extracted with ether (30ml) and the aqueous phase basified with saturated sodium bicarbonate. Water was then evaporated, dichloromethane (50ml) added to the solid residu obtained and the mixture stirred for 15mn. The remaining solid was filtered, the organic phase dried over Na_2SO_4, then evaporated to obtain the final product which is normally pure.

- N,N-bis(triethyleneglycol-monomethylether)amine: $HN[(C_2H_4O)_3\text{-}CH_3]_2$; 3.7g (90%); n_D^{20}, 1.447; R_F, 0.44 (AcOEt/MeOH 80/20); Anal. calcd for $C_{14}H_{31}O_6N$: C, 54.35; H, 10.09; N, 4 52; O, 31.02; Found. C, 54.50; H, 10.05; N, 4.46.
- N,N-bis(tetraethyleneglycolmonomethylether)amine: $HN[(C_2H_4O)_4\text{-}CH_3]_2$; 4.5g (85%); n_D^{20}, 1.458; R_F, 0.32 (AcOEt/MeOH 80/20); Anal. calcd for $C_{18}H_{39}O_8N$: C, 54.39; H, 9.88; N, 3.52; O, 32.20; Found: C, 54.09; H, 9.78; N, 3.23.

IR: $\nu_{N\text{-}H}$, 3500 - 3300 cm^{-1}; ν_{CH_2}, 3000 - 2800 cm^{-1}; $\nu_{C\text{-}O\text{-}C}$, 1150 - 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ, 2.8 (t $N\text{-}CH_2$); δ, ~3 (s 1H); δ, 3.3 ppm (s 6H); δ, 3.5 (t CH_2); δ, 3 6-3.8 [m $(C_2H_4O)_n$].

Condensation of benzylamine on oxyethylenemonomethylether

A solution of 2.5 x 10^{-2} mole (1 eq) of benzylamine in 25ml CH_3CN was added to 5 5 x 10^{-2} mole (2.2 eq) of Na_2CO_3 contained in a round-bottomed flask fitted with a condenser and stirred with a stirring bar. A solution of 5.5 x 10^{-2} mole (2.2 eq) of tosyldioxyethylenemonomethylether in 50ml CH_3CN was added dropwise to the reaction mixture at room temperature. After complete addition, the resulting mixture was refluxed at 62°C for 16hr. It was then filtered and the residue washed with ether in order to recover more of the product. Evaporation of the solvent gave the organic product which was re-dissolved in 50ml of aqueous HCl (2M) and extracted with ether The aqueous phase was basified with saturated $NaHCO_3$, then re-extracted with ether. The organic phase was dried over Na_2SO_4, filtered and the solvent evaporated to give the product in its pure state.

- N,N bis(diethyleneglycol-monomethylether)benzylamine $PhCH_2\text{-}N[(C_2H_4O)_2\text{-}CH_3]_2$: obtained, 5 8g (76%); n_D^{20}, 1.489; R_F, 0.42 (AcOEt/Hexane 80/20); Anal. calcd for $C_{17}H_{29}O_4N$: C, 66.50; H, 9.37; N, 4.65; O, 21.40; Found: C, 64.80; H, 9.31; N, 4.64.

- N,N bis(triethyleneglycol-monomethyl-ether)benzylamine $PhCH_2$-N[$(C_2H_4O)_3$-$CH_3]_2$: obtained, 7.6g (76%); n_D^{20}, 1.487; R_F, 0.30 (AcOEt/Hexane 80/20).

IR: $\nu_{CH(arom.)}$, 3100 - 3000 cm^{-1}; ν_{CH_2}, 3000 - 2800 cm^{-1}; ν_{C-O-C}, 1150 - 1100 cm^{-1}; ν_{C-N}, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ, 2.8 (t NCH_2); δ, 3.3 (s 6H); δ, 3.4 - 3.6 [m $(C_2H_4O)_n$]; δ, 3.7 (s 2H); δ, 7.33 (m Ph).

Hydrogenation of N,N-bis (oxyethylenemonomethylether) benzylamine

To 15ml of ethanol and 10 % ($^w/_w$) of palladium on coal contained in a hydrogen reactor was added 5.4 x 10^{-3} mole (1 eq) of N,N-bis (dioxyethylenemonomethylether) benzylamine. The reactor containing this mixture was purged twice with nitrogen and once with hydrogen. The reaction mixture was left under hydrogen pressure (60 bar) and constant stirring for 4hr, at the end of which it was purged twice again with nitrogen and filtered over celite. The solvent was evaporated under reduced pressure and the product obtained was pure.

- N,N-bis(diethyleneglycol-monomethylether)amine HN[$(C_2H_4O)_2$-$CH_3]_2$: Obteined, 0.95g; (80%); n_D^{20}, 1.449; R_F(AcOEt/MeOH 80/20), 0.34; Anal. calcd for $C_{10}H_{23}O_4N$: C, 54.28; H, 10.46; N, 6.33; O, 28.93; Found: C, 54.40; H, 10.22; N, 6.32.

- N,N-bis(triethyleneglycol monomethylether)amine HN[$(C_2H_4O)_3$-$CH_3]_2$: (76%); identical with similar product prepared with precedent method.

IR: ν_{NH}, 3500 - 3300 cm^{-1}; ν_{C-O}, 1100 - 1150 cm^{-1}; ν_{CH_2}, 3000 - 2800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ, ~2.6 (s H); δ, 2.8 (t NCH_2); δ, 3.3 (s 6H); δ, 3.4 - 3.7 [m $(C_2H_4O)_n$].

Synthesis of two-chain head surfactants

Coupling to Perfluoroalkyl acid chloride:

To a round-bottomed flask fitted with a dropping funnel, 2.26 x 10^{-3} mole (1 eq) of N,N-bis (oxyethylenemonomethylether) amine, 2.26 x 10^{-3} mole (1 eq) of triethylamine or triisopropylethylamine were introduced. After cooling the solution to 0°C, 2.16 x 10^{-3} mole (1 eq) of perfluoroalkyl acid chloride was added dropwise for 15mn. The reaction mixture was kept at 0°C for 3hr with stirring. After reaction, the solution was diluted with 20ml of aq HCl (O.1N), then extracted with ether. The organic phase was then added to 20ml of saturated $NaHCO_3$ aqueous solution and extracted again with ether. The ether phase was dried over Na_2SO_4, then the solvent was evaporated under vacuum. Then traces of impurities are present, the desired product is purified by silica gel column chromatography with AcOEt as eluent.

- F6.1.22 C_6F_{13}-CH_2-C(O)N[$(C_2H_4O)_2$-$CH_3]_2$: obtained, 1.2g (94%); n_D^{20}, 1.395; R_F (AcOEt), 0.55; Anal. calcd for $C_{18}F_{13}H_{24}O_5N$: C, 37.75; H, 4.20; F,42.48; N, 2.42; O, 13.75; Found: C, 37.18; H,4.16; F, 41.93; N, 2.40.

- F6.1.33 C_6F_{13}-CH_2-C(O)N[$(C_2H_4O)_3$-$CH_3]_2$: obtained, 1.2g (86%); n_D^{20}, 1.405; R_F (AcOEt), 0.38; Anal. calcd for $C_{22}F_{13}H_{32}O_7N$: C, 39.47; H, 4.81; F, 36.89; N, 2.09; O, 14.67; Found: C, 39.72; H, 4.77; F, 36.75; N, 2.12.

- F6.1.44 C_6F_{13}-CH_2-C(O)N[$(C_2H_4O)_4$-$CH_3]_2$: obtained, 1.4g (84%); n_D^{20}, 1.415; R_F (AcOEt), 0.23; Anal. calcd for $C_{26}F_{13}H_{40}O_9N$: C, 41.22; H, 5.32; F, 30.90; N, 1.84; O, 20.72; Found: C, 40.99; H, 5.44; F, 30.6; N, 1.83.

- F8.1.22 C_8F_{17}-CH_2-C(O)-N[$(C_2H_4O)_2$-$CH_3]_2$: obtained, 1.3g (89%); n_D^{20}, 1.385; R_F (AcOEt), 0.55; Anal. calcd for $C_{20}F_{17}H_{24}O_5N$: C, 35.25; H, 3.55; F, 47.39; N, 2.05; O, 11.74; Found: C, 36.25; H, 3.72; F, 47.39; N, 2.05.

- F8.1.33 C_8F_{17}-CH_2-C(O)-N[$(C_2H_4O)_3$-CH_3]$_2$: obtained, 1.4g (85%); n_D^{20}, 1.398; R_F (AcOEt), 0.40; Anal. calcd for $C_{24}F_{17}H_{32}O_7N$: C, 37.46; H, 4.18; F, 41.97; N, 1.82; O, 14.57; Found: C, 38.03; H, 4.22; F, 41.94; N, 1.92.

- F8.1.44 C_8F_{17}-CH_2-C(O)N[$(C_2H_4O)_4$-CH_3]$_2$: obtained, 1.6g (85%); n_D^{20}, 1.406; R_F (AcOEt), 0.28; Anal. calcd for $C_{28}F_{17}H_{40}O_9N$: C, 39.21; H, 4.72; F, 37.65; N, 1.63; O, 16.79; Found: C, 39.57; H, 4.63; F, 37.47; N, 1.65

- F10.1.22 $C_{10}F_{21}$-CH_2-C(O)N[$(C_2H_4O)_2$-CH_3)]$_2$: obtained, 1.3g (80%); n_D^{20}, 1.383; R_F (AcOEt), 0.56; Anal. calcd for $C_{22}F_{21}H_{24}O_5N$: C, 33.81; H, 3.09; F, 51.05; N, 1.79; O, 10.23; Found: C, 33.62; H, 3.06; F, 50.88; N, 1.87.

- F10.1.33 $C_{10}F_{21}$-CH_2-C(O)-N[$(C_2H_4O)_3$-CH_3]$_2$: obtained, 1.6g (87%); n_D^{20}, 1.392; R_F (AcOEt), 0.42; Anal. calcd for $C_{26}F_{21}H_{32}O_7N$: C, 37.32; H, 3.87; F, 47.91; N, 1.68; O, 12.88; Found: C, 37.61; H, 3.70; F, 47.81; N, 1.68.

- F10.1.44 $C_{10}F_{21}$-CH_2-C(O)-N[$(C_2H_4O)_4$-CH_3]$_2$: obtained, 1.7g (82%); n_D^{20}, 1.402; R_F (AcOEt), 0.26; Anal. calcd for $C_{30}F_{21}H_{40}O_9N$: C, 37.62; H, 4.21; F, 41.66; N, 1.46; O, 15.03; Found: C, 38.13; H, 4.20; F, 41.66; N, 1.51.

IR: ν_{CH2}, 3000 - 2800 cm^{-1}; ν_{CF3}, 860 - 800 cm^{-1}; $\nu_{C(O)N}$, 1650 cm^{-1}; ν_{CF}, 1250 - 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ, 3.3 (d 6H); δ, 3.4-3.7 [m $(C_2H_4O)_n$]; δ = 3.7 (m 2H); ^{13}C {H} NMR (400 MHz, $CDCl_3$/TMS) $C^a{}_nF_{2n+1}$-C^bH_2-C^c(O)-N[C^dH_2-C^eH_2-O($C^e{}_2H_4O)_n$-C^fH_3]$_2$: δ_a, 110 - 120 (m); δ_b, 110.36 (s); δ_c, 161.80 (s); δ_d, 49.85 (m); δ_e, 67.85 - 71.92 (m); δ_f, 59.02 (s).

Coupling to Hydrogenated acid chloride:

To a solution of 3.75 x 10^{-3} mole (1.1 eq) of N,N-bis (oxyethylenemonomethylether) amine, 3.75 x 10^{-3} mole (1.1 eq) of triethylamine in 15ml of THF contained in a round-bottomed flask, was added a catalytic amount of dimethylaminopyridine (10 % $^w/_w$). After stirring at room temperature, a solution of 3.65 x 10^{-3} mole (1 eq) of desired acid chloride in THF was added dropwise. The reaction was carried out at room temperature with stirring for 14hr. After reaction, the reaction mixture was diluted with 50 ml of distilled water and 10ml of aqueous acid solution (HCl, O.1N), then extracted trice with ether (3 x 30ml). The organic phase was washed again with 20 ml of saturated $NaHCO_3$ (aq), dried over Na_2SO_4, filtered and the solvent evaporated under vacuum. The product is generally pure but in cases where there are impurities, its purification is carried out by column chromatography (silica gel, eluent : AcOEt 95/Hexane 5).

- H0.8.33 C_8H_{17}-C(O)-N[$(C_2H_4O)_3$-CH_3]$_2$: obtained, 1g (65%); n_D^{20}, 1.458; R_F (AcOEt), 0.47; Anal. calcd for $C_{25}H_{47}O_7N$: C, 61.44; H, 10.52; N, 3.12; O, 24.90; Found: C, 61.62, H, 10.45; N, 3.15.

- H0.9.33 C_9H_{19}-C(O)N[$(C_2H_4O)_3$-CH_3]$_2$: obtained, 1.2g (70%); n_D^{20}, 1.460; R_F (AcOEt), 0.50; Anal. calcd for $C_{24}H_{49}O_7N$: C, 62.16; H, 10.64; N, 3.02; O, 24.15; Found: C, 62.40; H, 10.40; N, 3.09.

- H0.9.44 C_9H_{19}-C(O)-N[$(C_2H_4O)_4$-CH_3]$_2$: obtained, 1.6g (80%); n_D^{20}, 1.461; R_F (AcOEt), 0.35; Anal. calcd for $C_{28}H_{57}O_9N$: C, 60.94; H, 10 40; N, 2.53; O, 26.09; Found: C, 61.25; H, 10.20; N, 2.51.

IR: ν_{CH2}, 3000 - 2800 cm^{-1}; $\nu_{C(O)N}$, 1640 cm^{-1}; ν_{C-O-C}, 1150 - 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ, 0.8 (t 3H); δ, 1.2 (m 12H); δ, 1.5 (m 2H); δ, 2.25 (m 2H); δ, 3.4-3.7 [m $(C_2H_4O)_n$]; δ, 3.3 ppm (s 6H).

Coupling of Hydrogenated acids to BOP-Reagent:

A solution of acetonitrile (30 ml) containing 3.68 x 10^{-3} mole (1 eq) of N,N-bis (oxyethylene-monomethylether) amine, 7.36 x 10^{-3} mole (1 eq) of triethylamine. To this solution was added 3.68 x 10^{-3} mole (1 eq) of dodecanoic acid and 3.68 x 10^{-3} mole (1 eq) of BOP-Reagent was introduced to a round-bottomed flask. Stirring was continued at room temperature for 16 hr. After reaction, the solvent was evaporated and the residue was dissolved in ether in order to subject it to a series of acid (0.1N HCl) and base ($NaHCO_3$) washings. After evaporating the solvent under vacuum, a rapid column chromatography (silica gel; eluent: AcOEt) enables the obtention of a very pure product.

- H0.11.22 $C_{11}H_{23}$-C(O)N[$(C_2H_4O)_2$-$CH_3]_2$: obtained, 1g (72%); n_D^{20}, 1.457; R_F (AcOEt), 0.57; Anal. calcd for $C_{22}H_{45}O_5N$: C, 65.47; H, 11.22; N, 3.47; O, 19.81; Found: C, 65.59; H, 11.02; N, 3.38.
- H0.11 33 $C_{11}H_{23}$-C(O)N[$(C_2H_4O)_3$-$CH_3]_2$: obtained, 1.3g (74%); n_D^{20}, 1.458; R_F (AcOEt), 0.30; Anal. calcd for $C_{26}H_{53}O_7N$: C, 63.52; H, 10.85; N, 2.14; O, 22.78; Found: C, 63.62; H, 10.22; N, 2.81.
- H0.11.44 $C_{11}H_{23}$-C(O)N[$(C_2H_4O)_4$-$CH_3]_2$: obtained, 1.6g (76%); n_D^{20}, 1 460; R_F (AcOEt), 0.19; Anal. calcd for $C_{30}H_{61}O_9N$: C, 62.15; H, 10.59; N, 2.41; O, 24.83; Found: C, 62.30; H, 10.35; N, 2.39.

IR:ν_{CH2}, 3000 - 2800 cm^{-1}; ν_{C-O}, 1150 - 1100 cm^{-1}; $\nu_{C(O)N}$, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ, 0.8 (t 3H); δ, 1.2 (m 16H);δ, 1.5 (m 2H); δ, 2.25 (m 2H); δ, 3.4-3.7 [m $(C_2H_4O)_n$]; δ, 3.3 (s 6H).

Coupling of Perfluoroalkyl acids to BOP-Reagent:

A similar protocol as above is used for this coupling; the reaction is effected over 2.4 10^{-3} mole of perfluoroalkylacid. Stirring was continued at room temperature for 24 hr. After reaction, the solvent was evaporated and the residue was dissolved in ether in order to subject it to a series of acid (0.1N HCl) and base ($NaHCO_3$) washings. After evaporating the solvent under vacuum, a column chromatography (silica gel; eluent: AcOEt) enables the obtention of a product, but hydrolysis of amide function is observed and the product is not very pure.

- F6.0.22 C_6F_{13}-C(O)N[$(C_2H_4O)_2$-$CH_3]_2$: obtained 0.82g (60%), purity >95%.
- F6 0.44 C_6F_{13}-C(O)N[$(C_2H_4O)_4$-$CH_3]_2$: obtained 1.01g (57%), purity >95%.

IR:$\nu_{C(O)N}$, 1680 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ, 3.3 (s 6H); δ, 3.6 [m $(C_2H_4O)_n$].

Direct microemulsions; experimental method:

We prepared 1 to 2 ml of a binary water-surfactant solution in phials (thermostatic tubes) which can be sealed hermetically, containing 5 to 15 % weight of the surfactant.

- To these phials, we added increasing amount of fluorocarbon (increment in the region of 2 %).
- After each fluorocarbon addition, the solutions were shaken, then placed in a thermostatic bath. The temperature was varied until we obtained an isotropic solution. The mixture in each phial was observed visually after shaking and in order to verify the isotropy of the solution, the samples were examined between crossed polarizers.

This style of procedure enabled us to roughly estimate the percentage of the constituents as well as the temperature corresponding to microemulsion formation.

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