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A Class of Efficient Short-Chain Fluorinated Catanionic Surfactants

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There have been many attempts to find suitable replacements for fluorinated surfactants due to problems related to their bioaccumulation and resistance to biodegradation. Meeting the exceptional performances of these compounds, however, remains largely an unaccomplished challenge. Currently, a solution might be found through synthesis of new classes of fluorinated compounds that possess reduced environmental impact by following recommended strategies for their greener and safer design. In this article we report a novel approach by designing a family of catanionic fluorinated surfactants that shows a potential for improved degradation, good water solubility, and low Krafft points. Furthermore, these surfactants exhibit excellent surface activity with one of the highest effectiveness of surface tension reduction and fluorine efficiency reported to date in the literature.

Fluorinated surfactants are generally superior to their hydrocarbon analogues in terms of their surface activity, thermal and chemical stability.[1, 2] Additionally, they have a unique property of being both hydrophobic and lyophobic. Since the size of CF_2 group is significantly higher than size of CH_2 group (38 *vs* 27 Å^3)[3] steric hindrances cause fluorinated chains to adopt helical rather than zig-zag conformation characteristic of hydrocarbon chains (see Figure 1). Fluorosurfactants are used as additives for paints, coatings, and fire extinguisher foams, wetting agents, cleaners for hard surfaces, plane hydraulic fluids, emulsifying and dispersing agents, surface protectors, *etc*. Besides the broad current usage of fluorosurfactants, there is also significant ongoing research on novel fluorinated structures with potential bio-medical and pharmacological applications,[4, 5] applications in the field of emulsion stabilisation,[6-8] liquid crystals,[9] self-cleaning surfaces,[10] solar cells,[11] and templating agents[12, 13]. The presence of both hydrophilic head and fluorinated chain(s) in their structures makes some fluorosurfactants also efficient in stabilisation of water-in-CO_2 microemulsion.[14-21]

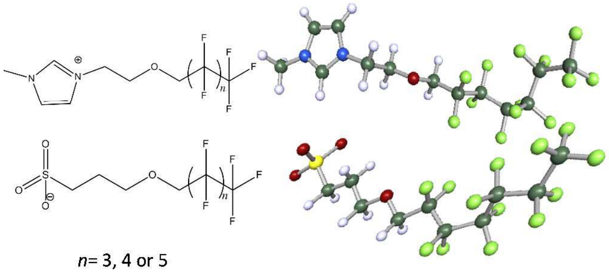

Figure 1. General structure of synthesised fluorosurfactants and equilibrium geometry calculated with Spartan'14 using the HF/6-311G++(d,p) *ab-initio* method.

The most investigated fluorinated surfactants are anionic[21-23] and non-ionic[24]. The cationic types of fluorinated surfactants are much less studied, mainly because of difficulties in their syntheses, and in particular the troublesome purification steps. It was shown, however, that some cationic surfactants with branched structures have very good water solubility and surface activity.[25] In the recent literature, hybrid double-chain surfactants having either two semi-fluorinated chains[21], or one hydrocarbon and one partially- or fully-fluorinated chain, have been also reported.[26-29] Those double-chain surfactants are very efficient in surface tension reduction and have a potential to solubilise both hydrocarbon and fluorocarbon compounds. Unfortunately, a disadvantage of these structures is that their Krafft points are usually higher compared to single chain amphiphiles which often makes them water insoluble at room temperature.[21] Catanionic surfactants are the least explored type of surfactant structures. They can be formed by mixing the oppositely charged surfactants when the resulting mixture contains two starting surfactants, the catanionic surfactant salt, and the simple salt formed from the counterions. These systems are prone to precipitation at equimolar ratio of

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cationic and anionic surfactants, particularly if the monomers possess chains longer than eight carbon atoms.[30, 31] Recently, an excellent review on the self-assembly and interactions of hydrocarbon and fluorocarbon surfactants including catanionic mixtures was published.[32] The examples of salt-free catanionic mixtures, which are considered 'true' catanionic surfactants, are rare in the literature.[33-35] Pasc-Banu *et al*. have described synthesis and morphology of the aggregates formed by salt-free catanionic mixtures of fluorinated/hydrogenated surfactants.[36]

Surprisingly, salt-free catanionic surfactants with fluorinated chains incorporated in both the cation and anion, have not been systematically studied so far; probably because of presumed poor water solubility. In this paper, we have synthesised, to the best of our knowledge for the first time, a family of salt-free catanionic surfactants where both the anion and the cation have a short fluorinated chain in their structures. An ether unit was built into both the cation and the anion in order to improve water solubility. Importantly, it also provides a 'weak' link for cleavage and degradation of the molecule making this class of fluorosurfactants more environmentally friendly.[37]

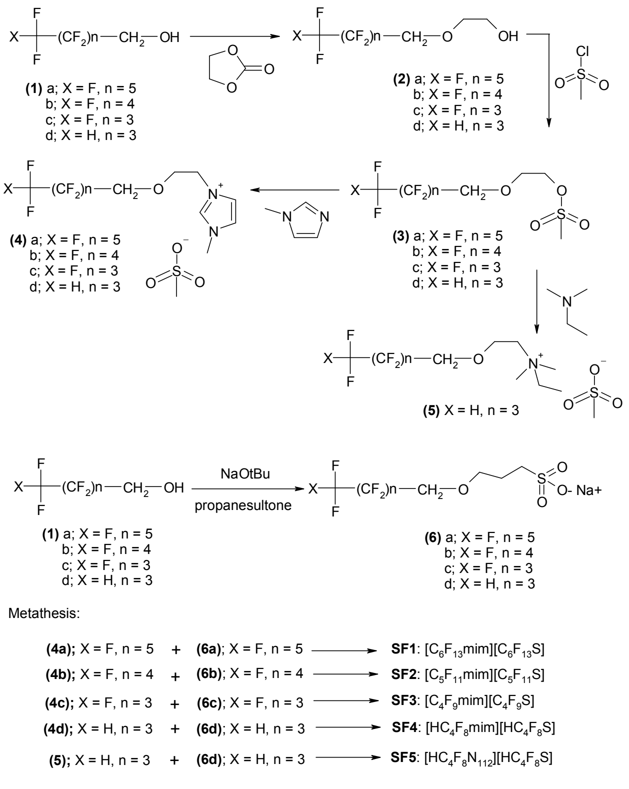

Figure 2. General synthetic procedure and abbreviations of fluorosurfactants used in this study.

This work has demonstrated that the applied design strategy offers the most efficient way to achieve very low limiting surface tension in an aqueous solution approaching to the surface tension of neat fluorocarbons, while keeping high fluorine efficiency. Design of efficient short-chain fluorinated surfactants as replacement products for C_8-perfluorinated compounds has become a particularly important and challenging task, since both US Environmental Protection Agency[38] and European Parliament[39] have launched programmes to reduce and ultimately eliminate long chain fluorosurfactants that have optimal surface activity in majority of applications. The eight main manufacturers of fluorochemicals and the Environmental Protection Agency made clear that perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and their associated compounds should be replaced with shorter perfluoroalkyl chemicals until more sustainable solutions are found.[40] Several scientific reports confirmed that shorter fluorosurfactants containing 6 or 4 CF_2 units have low bioaccumulation potential and consequently better environmental safety profiles.[40-42] Design of short-chain fluorosurfactants that does not compromise their performances is addressed in this communication.

Syntheses and characterisation in terms of surface activity for five fluorosurfactants are described and a general synthetic scheme is shown in the Figure 2.

Details on the surfactant synthesis and characterisation, melting points, surface tension measurement, mass spectroscopy, ^{1}H NMR and ^{19}F NMR spectroscopy, can be found in the Electronic Supplementary Information (ESI)†.

Table 1. Critical micelle concentration (CMC) measured by interfacial tension (IFT) and ^{19}F NMR spectroscopy, limiting surface tension (γ_{CMC}) at 23°C of aqueous solutions, and fluorine efficiency expressed as g of F per dm^3 of solution at CMC of the synthesised fluorosurfactants. For comparison purposes literature data of PFOA is also included.

Surfactant	CMC/mM		γ_{CMC} / mN m^{-1}	g F /dm^3 at CMC
	IFT	^{19}F NMR		
[C_6F_{13}mim][C_6F_{13}S]	0.08-0.11	0.045-0.065	13.5	0.05
[C_5F_{11}mim][C_5F_{11}S]	0.7	0.69	15.3	0.3
[C_4F_9mim][C_4F_9S]	4.5	4.5	16.1	1.5
[HC_4F_8mim][HC_4F_8S]	Ph. separ.	-	-	
[$HC_4F_8N_{112}$][HC_4F_8S]	30	-	26	9.1
PFOA[37]	8.5		20	2.4

Our approach to structural design of the compounds described herein was based on synergistic effect in catanionic mixtures. This synergism caused by strong electrostatic attraction between polar heads is well established in literature.[33, 34] There are several consequences of the strong electrostatic interaction between polar heads in such mixtures: i) composition of the mixed aggregate is close to equimolar in almost entire range of surfactant composition of the mixture[43], ii) the occurrence of precipitation[33], iii) in the mixtures of oppositely charged fluorinated and hydrocarbon surfactants the strong electrostatic attraction overcomes 'animosity' between fluorinated and hydrocarbon chains leading to formation of mixed aggregates[44] rather than micellar demixing (segregation)[45]. The precipitation is a common phenomenon in the mixture of cationic and anionic surfactants, since the presence of inorganic salt formed by counterions shields the surface charges and leads to extensive micellar growth and formation of bulk aggregates.[46] This phenomenon is even more pronounced for a very delicate hydrophilic-hydrophobic balance present in aqueous solutions of fluorosurfactants. In order to keep highly hydrophobic oppositely charged fluorocarbon moieties in an 'active' form in solution in a reasonable concentration range, it was required in this approach to remove counterions and to build in an oxygen link that promotes interaction with water leading to better solubility.

Following the described design the fluorosurfactants were obtained mainly as soft gels or viscous liquids; they exhibited low melting or glass transition temperatures (reported in the ESI) and can be considered room temperature ionic liquids. Thus, the problems related to the formation of solid crystalline phases and high Krafft points often found in the fluorinated surfactants[32], do not play a role for this family of surfactants.

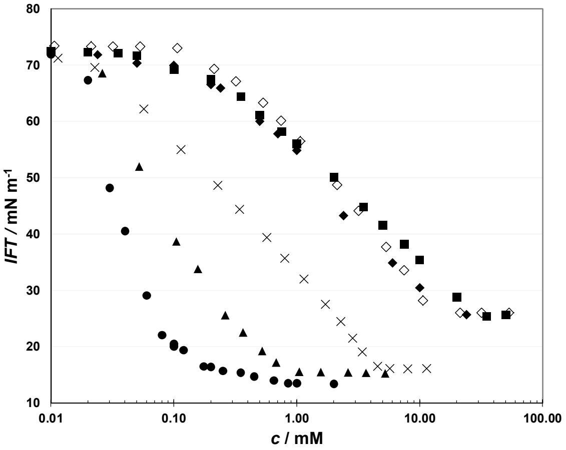

Figure 3. Surface tension of aqueous solution *versus* fluorosurfactants concentration data: (•) [C_6F_{13}mim][C_6F_{13}S], (▲) [C_5F_{11}mim][C_5F_{11}S], (✕) [C_4F_9mim][C_4F_9S], (◆) [HC_4F_8mim][HC_4F_8S], (■) [$HC_4F_8N_{112}$][HC_4F_8S], (◇) [C_8H_{17}mim][C_8H_{17}S][34].

Self-aggregation of the fluorosurfactants in water over the low concentration regimes was studied by surface tension and ^{19}F NMR spectroscopy. Surface tension measurements were performed in order to study monolayer formation, and to determine critical micelle concentration, CMC, and limiting surface tension in the plateau region, γ_{CMC}. The surface tension *versus* concentration curves for [C_6F_{13}mim][C_6F_{13}S], [C_5F_{11}mim][C_5F_{11}S], [C_4F_9mim][C_4F_9S], [HC_4F_8mim][HC_4F_8S], and [$HC_4F_8N_{112}$][HC_4F_8S] are presented in the Figure 3. For the comparison purposes the literature data[34] for a structurally similar non-fluorinated catanionic surfactant with eight carbon atoms in both the cation and the anion, [C_8H_{17}mim][C_8H_{17}S] (the structure given in the ESI), is also included in the Figure 3. From the surface tension *versus* log concentration graph, CMC and the surface tension at CMC, γ_{CMC}, were determined and reported in Table 1. In the case [C_4F_9mim][C_4F_9S] and [C_5F_{11}mim][C_5F_{11}S] a sharp change of the slope of the surface tension *versus* the surfactant concentration curve was found and CMCs were defined unambiguously. In contrast, for [C_6F_{13}mim][C_6F_{13}S] a smooth change of the slope was obtained and consequently, CMC had to be reported as a concentration range rather than a single point. A possible reason for this is discussed in more details below. Nevertheless, it is obvious from the presented graph that both the formation of monolayer and micellisation are strongly controlled by the length of the fluorocarbon segment. The surface tension values obtained for [C_6F_{13}mim][C_6F_{13}S], [C_5F_{11}mim][C_5F_{11}S], and [C_4F_9mim][C_4F_9S] show that the increase of the length of the fluorinated chain by one CF_2 unit in the cation and the anion, decreases CMC roughly by one order of magnitude and the limiting surface tension approximately by 1.5-2.0 mN·m^{-1} (Figure 3 and Table 1). Thus, the surface tension value obtained for [C_6F_{13}mim][C_6F_{13}S] is one of the lowest value reported for an ionic fluorosurfactant and it approaches to the surface tension of neat perfluoroalkanes.[47] Comparable low limiting surface tension data were reported in literature for a family of fluoro derivatives of sodium bis(2-ethylhexyl) sulfosuccinate where the minimum surface tension of 15.5 mN·m^{-1} was recorded for the structure bearing two $CF_3(CF_2)_5CH_2$- chains in place of 2-ethylhexyl chains.[21] However, a direct comparison between the two fluorosurfactant families is not possible since the surface tension values of the sulfosuccinate based fluorosurfactants were reported at different temperatures because of their relatively high Krafft points.

Both adsorption and micellisation are negatively affected by replacement of one fluorine atom with hydrogen on the terminal carbon atom; this phenomenon was previously studied and described by Eastoe *et al.*[48] The huge impact of the aforementioned phenomenon on this family of surfactants can be seen by comparing data for [C_4F_9mim][C_4F_9S] and [HC_4F_8mim][HC_4F_8S]. Clearly, [HC_4F_8mim][HC_4F_8S] is surface active and able to form a monolayer at the water-air interface, but has limited solubility and phase separates into two liquid phases before micellisation occurs. Thus, considering surface activity of the non-fluorinated surfactant [C_8H_{17}mim][C_8H_{17}S] with similar length of the alkyl chains as [HC_4F_8mim][HC_4F_8S], we can conclude that the partial fluorination of the terminal carbon atom in the surfactant molecule had a negative impact on the surface activity. It has made such fluorosurfactant, surprisingly, inferior to non-fluorinated analogue. Finally, comparison of the results obtained for [HC_4F_8mim][HC_4F_8S] and [$HC_4F_8N_{112}$][HC_4F_8S] indicates that imidazolium and ammonium groups have similar behaviour, *i.e.* type of polar head group has only a minor influence on surface activity. It also appears that ammonium based cation offers slightly better water solubility, which may lead to conclusion that it would be more reasonable to synthesise a similar family based on cheaper ammonium, rather than imidazolium group in the structure. Therefore, we can conclude that the described design maximises the affinity of the surfactant for the adsorption and the micellisation.

For comparison purposes literature surface activity data obtained for pefluorooctanoic acid is also presented in Table 1.[37] In an attempt to present surface activity of different structural types of fluorosurfactants in a more comparable way taking also into account environmental aspect of the problem, we have decided to express the concentrations at

CMC as grams of fluorine per dm^3 of solution. The reported data show that compounds $[C_6F_{13}mim][C_6F_{13}S]$, $[C_5F_{11}mim][C_5F_{11}S]$, $[C_4F_9mim][C_4F_9S]$ have both the higher effectiveness of surface tension reduction and the fluorine efficiency in comparison to PFOA. The compound $[C_6F_{13}mim][C_6F_{13}S]$ has the fluorine concentration at CMC 50 times as low as PFOA.

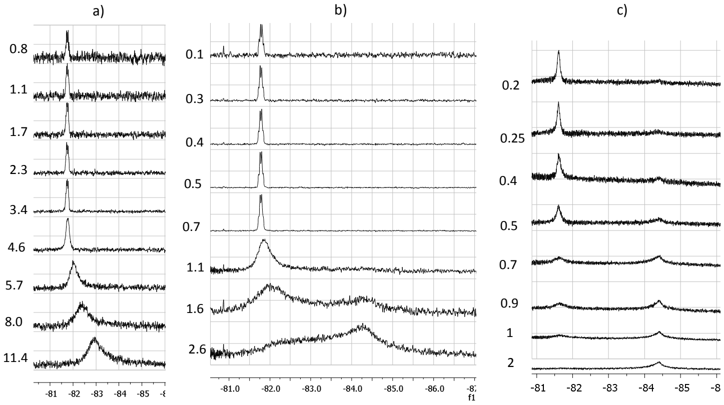

Figure 4. Aggregation process in aqueous solution studied by ^{19}F NMR spectroscopy: changes in chemical shift of terminal CF_3 groups for a) $[C_4F_9mim][C_4F_9S]$, b) $[C_5F_{11}mim][C_5F_{11}S]$, and c) $[C_6F_{13}mim][C_6F_{13}S]$. The surfactant concentrations associated with each spectrum are given in mM.

^{19}F NMR spectroscopy was used to study aggregation of $[C_6F_{13}mim][C_6F_{13}S]$, $[C_5F_{11}mim][C_5F_{11}S]$, and $[C_4F_9mim][C_4F_9S]$ surfactants. This study shows a rare example that one family displays three characteristic NMR responses upon micellisation: chemical shift of the terminal group signals, broadening of the signals, and finally appearance of a peak attributed to the formation of aggregates and complete disappearance of the peak corresponding to monomers. Although, these phenomena have been reported separately in literature, this is the first case that they are all present just in one family of surfactants. It enables a systematic study of the effect of change of surfactant hydrophobicity on micellar kinetics by simple ^{19}F NMR experiments. It is well known that NMR chemical shift of a terminal group is affected by intermolecular interactions imposed by the surroundings and that micellisation causes shifting of the peak upfield.[49-51] Generally, exchange of surfactant molecules between free monomeric state and micellar phase is very fast on NMR time scale, and NMR spectrum practically records only one set of signals whose chemical shifts are weight average of monomeric and micellar signals. This is the most common behaviour, and it is typical for single-chain surfactants. This behaviour was also found for the short-fluorocarbon chain surfactant $[C_4F_9mim][C_4F_9S]$ (Figure 4a). CMC was determined from the sharp change of the slope in the dependence terminal CF_3 group chemical shift *versus* the surfactant concentration (the values reported in Table 1, see also the ESI). Increasing the length of the fluorocarbon chain to five carbon atoms, as in $[C_5F_{11}mim][C_5F_{11}S]$, leads to the stronger interaction and, consequently, the higher micellar stability and longer life-time. Hence, for this surfactant both broadening of the signals and appearance of an additional signal corresponding to micelles were found (Figure 4b). The presence of both the free monomer and the micelle signals means that the process of interconversion is slow. CMC in this case was found based on analysis of the monomeric half-peak width *versus* the surfactant concentration, and it is reported in Table 1 (the graph given in the ESI). This phenomenon of very slow exchange rate was reported previously for a hybrid hydrocarbon/fluorocarbon surfactant[23] and some long-chain gemini surfactants[51]. Finally, for $[C_6F_{13}mim][C_6F_{13}S]$ was found that as the surfactant concentration increases an additional signal corresponding to micelles appears, while the signal attributed to monomers completely disappears (Figure 4c). Similar behaviour was described recently for fluorinated zwitterionic micelles.[52] It means that $[C_6F_{13}mim][C_6F_{13}S]$ micelles are closely packed and kinetically more stable with long life-times. These micelles might behave as ‘sink of monomers’. It would inevitably hinder the process of adsorption by effecting the number of molecules diffusing to interface.[53] This phenomenon is currently under investigation in our lab.

Conclusions

Contrary to the aggregate structures formed by hybrid hydrocarbon/fluorocarbon systems where an intramicellar phase separation normally occurs,[54] fluorocarbon/fluorocarbon surfactant aggregates described here have shown better stability and longer life-time. The packing density and rigidity in the monolayer and in the self-assembly structures will be also increased by attractive electrostatic interactions between oppositely charged heads. Hence, these fluorosurfactants in the presented or in slightly modified forms might be useful in applications such as encapsulation, templeting or surface protection. Furthermore, bearing in mind the well-known correlation between water/air surface tension and the potential in stabilising water/CO_2

interface[55], the very low surface tension at CMC found for this family of catanionic surfactants could be an indication of their potential emulsifying ability in $scCO_2$. Nevertheless, at the current stage prior considering any potential applications, there is an urgent need for a detailed characterisation of the size and the morphology of this new family of colloidal self-assemblies. Work on these aspects is currently in progress.

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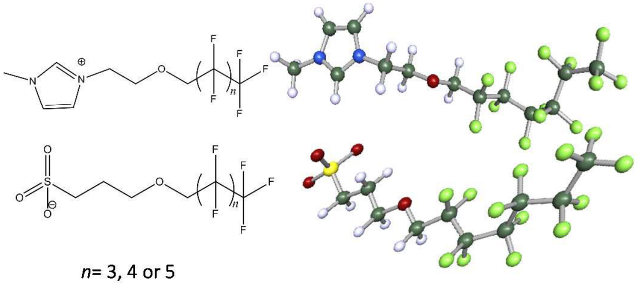

A FAMILY OF SHORT-CHAIN CATANIONIC FLUORINATED SURFACTANTS WITH POTENTIAL FOR REDUCED ENVIRONMENTAL IMPACT, EXCELLENT SURFACE ACTIVITY AND FLUORINE EFFICIENCY.