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Communication

Synthesis and combined properties of novel fluorinated cationic surfactants derived from hexafluoropropylene dimer

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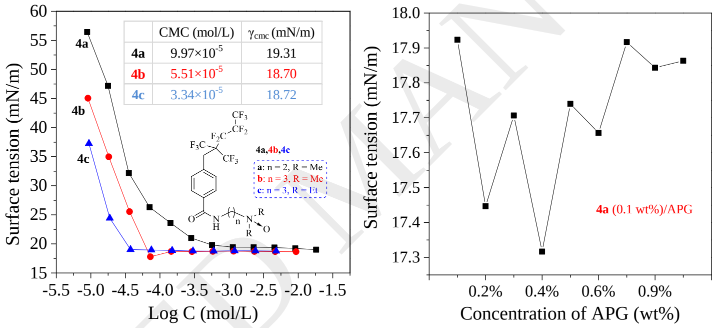
Graphical abstract



	CMC (mol/L)	γ_{cmc} (mN/m)
4a	9.97×10^{-5}	19.31
4b	5.51×10^{-5}	18.70
4c	3.34×10^{-5}	18.72

Three novel fluorinated surfactants with branched short fluorinated tails as hydrophobic groups, ammonium oxide as polar groups are prepared. Surface tension measurement shows that these fluorinated surfactants are ideal compounds to design new formulations in fire-fighting field.

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ABSTRACT

Available online Three novel fluorinated cationic surfactants were prepared by adopting perfluoro-2-methyl-2-pentene as raw substrate. The as-obtained fluorinated cationic surfactants exhibited excellent surface properties, all of them can reduce the surface tension of water to below 20.00 mN/m at the critical micelle concentrations (CMC). The incorporation of SDS, AOS, APG or LAB into 2-(4-(3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl)benzamido)-*N*,*N*-dimethylethana-mine oxide **4a** could generate much lower CMC and surface tension value at the CMC than individual **4a**. Especially, the surface tension values of that combined APG/**4a** can be reduced to 17.31 mN/m. The excellent surface activities and their remarkable compatibility to various types of hydrocarbon surfactants make them as sustainable alternatives to PFOA (perfluorooctanoic acid, $C_7F_{15}CO_2H$) and PFOS (perfluorooctane sulphonate, $C_8F_{17}SO_3X$, with X = K, Na, H).

Keywords:
Fluorinated cationic surfactants
Surface tension
Combined properties
Fire fighting
Aqueous film forming foams

Since the enormous potential of fluorochemical cleaning products were highlighted by 3M company in the 1950s, fluorosurfactants have been extensively exploited over 200 applications in clothing fabrics, electroplating, fire fighting foams, food packaging, petroleum, textile, along with multibillion dollar industries [1, 2]. Aqueous film forming foams (AFFFs), an extinguishing agents to put out polar (alcohols, ketones, esters) or non-polar (hydrocarbons) solvent fire, is one of the most important applications of fluorinated surfactants. The very low apparent density of AFFFs allows them to be spread at the surface of burning liquids [3, 4]. The evaporation of the water resulting from the heat reduces the intensity of the fire and the foam generates a water film at the surface of the solvent which prevents the emission of flammable vapors. In addition, after extinction, the foam prevents the risk of fire burnback [4]. AFFFs are often found where there are large volumes of flammable liquids and the potential for a fire exists. For example, AFFFs are found at military bases, fire departments, and airports [5,6]. Fluorinated surfactants have outstanding chemical and thermal stabilities, and play a crucial role in the formation of the water film at the surface of the solvent.

Featuring the most stable C-F single bond [7], perfluoroalkyl substances recently have awakened the concern in human health (the presence and persistency in fetuses, newborn babies, human milk, and human blood, *etc.*) and social environment [8]. Among of them, fluorinated surfactants that chain lengths of C8 or longer have been revealed more possible to be bioaccumulative and potently toxic [9]. According to the PFOA Stewardship Program, both industrial and academic sectors have set about the deploitation of short-chain based fluorosurfactants (R_f < C6-7) to mitigate their persistent nature of pollution [10].

Hexafluoropropylene dimer containing only C5 main chain is a representative template to synthesize various branched fluorinated surfactants [11-13]. The short chain length makes it is an idea material to preparing non-bioaccumulable alternatives to PFOA/PFOS. On the other hand, hyperbranched hydrocarbon surfactants possess fluorocarbon-like low surface energies than conventional straight chain ones [14], and branched fluorinated surfactants show more efficient at a relatively low concentration than common linear fluorosurfactants [15, 16]. As such, the import of branched chain is a valid strategy to develop surfactants with high performance. So far, to the best of our knowledge, most studies just focused on the preparation of new compound derived from hexafluoropropylene oligomer [11-13,15-17], no report has discussed the application of this kind of branched fluorinated surfactants in the AFFFs field. However, years of employing AFFFs in a variety of situations has resulted in these fire-fighting foam components being directly released to the environment and the contamination of groundwater [5].

In view of those facts mentioned above, this study proposed a novel serious of fluorosurfactants with branched short fluorinated tails as hydrophobic groups, ammonium oxide as polar groups and benzene ring as space units, respectively (Scheme. 1). Four steps led to the compound **4**. First, methyl 4-(bromomethyl)benzoate was changed to compound **1** by a nucleophilic substitution reaction. Second, saponification of the ester **1** followed by acidification led to the carboxylic acid **2**. Then, conversion of the acid **2** into the amide **3** was carried out by treating with EDCI and appropriate diamine. Finally, the title compound **4** was obtained by oxidation with hydrogen peroxide. All the chemicals, instruments used in this work, the experimental details and the key spectra are presented in the Supporting information.

The surface or interface tension of surfactants in individual form or mixed system was tested by the Wilhelmy plate method using a Kruss K100 tensiometer at 25 °C. All the values were the average of three-run measurements. The change trend of surface tension for **4a~c** in aqueous solution upon various concentrations is presented in Fig. 1A. All the CMC of **4a-c** are below 1.0×10^{-4} mol/L and the surface tension at CMC (γ_{CMC}) are below 20 mN/m. Compounds **4b** and **4c** showed better surface activity than **4a**, for instance, the CMC of **4b** reduced from $9.97{\times}10^{-5}$ mol/L to $5.51{\times}10^{-5}$ mol/L at 298 K, along with the simultaneous decrease of γ_{CMC} from 19.31 mN/m to 18.70 mN/m. All the values of surface properties of compounds **4a-c** are lower than that of sodium perfluorooctanoate (about 24.7 mN/m at the CMC of 3.1×10^{-2} mol/L) [18]. Comparisons of surface properties with several fluorinated surfactants (Fig. 1B and synthetic procedure of FO1 see Supporting documents) synthesized from hexafluoropropylene dimmer were summarized in Table 1. The results showed that the compounds we synthesized in this work exhibited the best ability and efficiency to reduce the surface tension of water (The γ_{CMC} of compound **4a**, FCS and FAS, are 19.31 mN/m, 19.68 mN/m, and 21.39 mN/m, respectively, meanwhile, the CMC values of them are $9.97{\times}10^{-5}$ mol/L, $2.50{\times}10^{-3}$ mol/L, $1.04{\times}10^{-4}$ mol/L, respectively).

It is generally acknowledged that lower interfacial molecular areas indicate improved interfacial packing ability [19], the abilities of surfactants to form packed layers on water can be evaluated by the values of A_{CMC} (minimal area per molecule). The occupied area per molecule (A_{CMC}) was derived from the static surface tension *vs.* log(c) curves through the following equation [20, 21]:

$$A_{CMC} = \frac{1}{N_A \Gamma_{\max}} \qquad (1)$$

where N_A is the Avogadro's number and $\Gamma_{\max}$ is the surface excess concentration as defined by:

$$\Gamma_{\max} = -\frac{1}{2.303RT}\log_{c \to c_{CMC}}\left(\frac{d\gamma}{d\lg c}\right) \qquad (2)$$

where R is a gas constant, T is the absolute temperature.

As seen in Table 1, compound **4a** possessed much lower CMC ($9.97{\times}10^{-5}$ mol/L) and A_{CMC} (27 Å^2/mol) than FO1, suggesting that the rigid spacer unit (aromatic spacer) would promote micellization and packing.

AFFFs usually contain fluorinated surfactants, hydrocarbon surfactants, organic solvents, and so on. SDS/AOS/APG/LAB (Fig. 1B) are the most frequently used hydrocarbon surfactants in foam concentrates, determining the formation of foams as well as the reduction of the interfacial tension [3, 4]. We selected compound **4a** to mix with SDS, AOS, LAB or APG to exam the potential application of compound **4a-c** in AFFFs.

Two anion hydrocarbon surfactants sodium dodecyl sulfate (SDS) and sodium C14-16 olefin sulfonate (AOS) were selected. Effects of the total concentration of mixed surfactant with different mass ratios on the surface tension are given in Figs. 2A and 2B. The surface activities of the pure surfactants are summarized in Table 1. Obvious "synergistic" interaction is observed that the CMC decreased with elevated mass ratios of SDS or AOS to **4a,** while the value of γ_{CMC} for mixed systems almost retained unchanged compared to single **4a** solution. It is noteworthy that when the mass ratio of **4a** to SDS is 1:1, the γ_{CMC} is 18.83 mN/m and the CMC is 1.78×10^{-5} mol/L, which are both lower than that of single **4a** or SDS.

The combination systems of **4a** (0.1 wt%) with zwitterionic hydrocarbon surfactant lauroylamide propylbetaine (LAB) and nonionic hydrocarbon surfactant alkyl polyglycoside (APG) were further evaluated (Figs. 2C and 2D). It reveals that a conspicuously low surface tension, which were all below 18.50 mN/m in selected concentration range. In terms of LAB, the lowest surface tension reached to 17.90 mN/m when the concentration is 0.3 wt%. The incorporation of APG exhibited a better "synergistic" interaction than LAB, along with all surface tensions lower than 18.00 mN/m and lowest surface tension of 17.31 mN/m at 0.4 wt%. Compounds **4a-c** not only have great micellization and packing abilities but also have remarkable compatibility to various types of hydrocarbon surfactants, these excellent properties make the application in AFFFs possible. The multicomponent system of AFFFs places the demand of good synergistic effect with additives for fluorosurfactants to guarantee the ability to form water film at the interface. This water film formation occurs when the spreading coefficient (*SC*) of the foaming solution is positive. That spreading coefficient is defined in Eq. (3)[26]:

$$SC = \gamma_S - \left(\gamma_{sl} + \gamma_l\right) \qquad (3)$$

where γ_s is the surface tension of the solvent; γ_{sl} is the interfacial tension between the solvent and the foaming solution and γ_l is the surface tension of the aqueous foaming solution.

The use of fluorinated surfactants provides the foaming solution with a particularly low surface tension (γ_l) and hydrocarbon surfactants reduce the foaming solution/solvent interfacial tension (γ_{sl}). Without an appropriate choice of these two types of surfactants, the spreading coefficient would be negative and extinction impossible. AFFFs usually contains more than one hydrocarbon surfactant to achieve the idea effect [3,4]. Table 1 listed the ternary systems which were comprised by **4a** and two hydrocarbon surfactants. The recipes were designed according to the consequences in the binary systems. The γ_s of the cyclohexane, the γ_l of the aqueous solution and the γ_{sl} between the solvent and the aqueous solution were measured and presented in Table 1. On the basis of resulted surface tension, all the four systems showed better surface activities than single **4a** aqueous solution and the calculated spreading coefficients were positive. The foaming solutions were dropped on cyclohexane to exam the spreading abilities. The results of spreading tests showed all the four aqueous solution could form a water film at the interface of cyclohexane. The excellent performances both in binary and ternary systems of our well-designed compounds further verified **4a-c** can be potential surfactants candidates to develop practical AFFF materials.

In this work, we successfully synthesized three novel branched fluorosurfactants starting from perfluoro-2-methyl-2-pentene. The introduction of aromatic spacer unit can promote micellization in aqueous solution and packing at the air-water interface. The as-obtained compounds not only exhibited excellent ability to reduce surface tension to below 20.00 mN/m but also showed remarkable efficiency to reduce the surface tension of water (the CMC values of compounds **4a-c** in water were less than 1.0×10^{-4} mol/L at 298 K). The CMC decreased obviously with the increased mass ratios of SDS or AOS to **4a**, while the γ_{CMC} of mixed systems were barely changed. Moreover, the combined systems showed even better synergistic interaction when **4a** was mixed with APG or LAB, along with surface tension less than 18.00 mN/m at several mixed conditions. The surface tensions of ternary systems are also less than single **4a** solution. The phenomenon of the foaming solution spread on the cyclohexane means compounds **4a-c** are promising fluorosurfactants to design new formulations in fire-fighting field.

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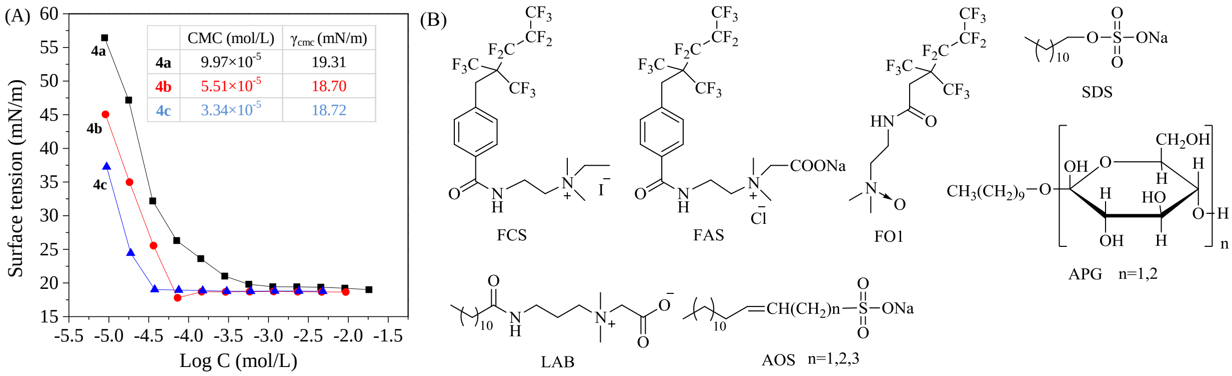


Fig. 1. (A) Surface tension measurements of **4a-c** at 25 °C. (B) Structures of FCS/FAS/FO1 and SDS/AOS/APG/LAB.

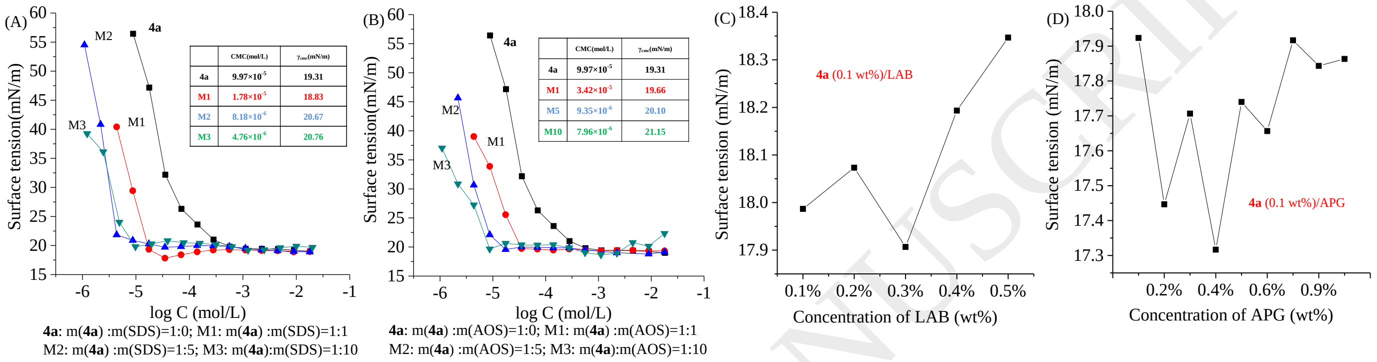
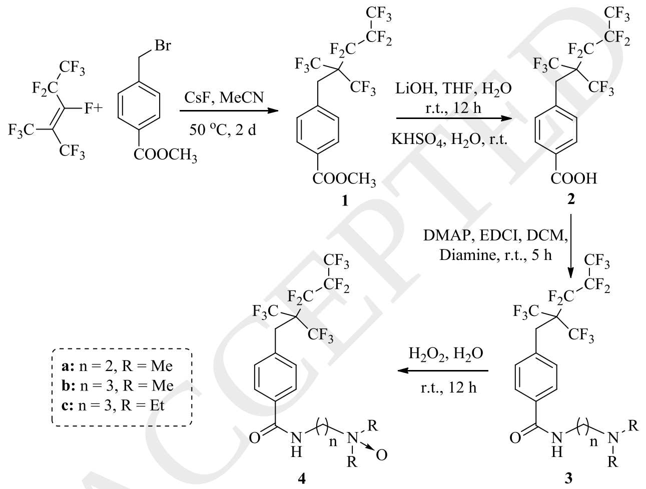


Fig. 2 (A) Effect of the total concentration of mixed **4a** and SDS with different mass ratios on the surface tension at 25 °C. (B) Effect of the total concentration of mixed **4a** and AOS with different mass ratios on the surface tension at 25 °C. (C) Effect of the concentration of LAB on the surface tension of the mixed **4a** and LAB at 25 °C. (D) Effect of the concentration of APG on the surface tension of the mixed **4a** and APG at 25 °C.



Scheme 1. Synthetic route for the branched fluorosurfactants.

Table 1
Static surface and interface properties of different water solutions at 25 °C.

	Systems	CMC	γ_{CMC} (mN/m)	A_{CMC} (Å^2/mol)	γ_l (mN/m)	γ_{sl} (mN/m)	γ_s (mN/m)	*SC*
1	Compound **4a**	9.97×10^{-5} mol/L	19.31	27	-	-	-	-
2 [16]	FCS	2.50×10^{-3} mol/L	19.68	52	-	-	-	-
3 [16]	FAS	1.04×10^{-4} mol/L	21.39	35	-	-	-	-
4	FO1	1.73×10^{-2} mol/L	19.93	49	-	-	-	-
5 [22]	SDS	7.94×10^{-3} mol/L	32.50	-	-	-	-	-
6 [23]	AOS	1.53×10^{-3} mol/L	34.43	-	-	-	-	-
7 [24]	LAB	1.25 g/L	26.76	-	-	-	-	-
8 [25]	APG	0.80 g/L	28.25	-	-	-	-	-
9	**4a** (0.1 wt%)/APG (0.4 wt%)/SDS (0.4 wt%)	-	-	-	19.17	3.89	25.18	2.12
10	**4a** (0.1 wt%)/APG (0.4 wt%)/AOS (0.4 wt%)	-	-	-	19.14	4.15	25.18	1.89
11	**4a** (0.1 wt%)/APG (0.4 wt%)/LAB (0.2 wt%)	-	-	-	18.44	3.21	25.18	3.53
12	**4a** (0.1 wt%)/LAB (0.2 wt%)/SDS (0.4 wt%)	-	-	-	19.08	3.67	25.18	2.43