

# Synthesis and Surface Activities of Novel Succinic Acid Monofluoroalkyl Sulfonate Surfactants

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**Abstract** Two environmentally friendly succinic acid monofluoroalkyl sulfonate surfactants were synthesized from maleic anhydride and polyethylene glycol mono(1*H*,1*H*,7*H*-dodecafluoroheptyl) ether, i.e.  $\text{H}(\text{CF}_2)_6\text{CH}_2\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OCOCH}(\text{SO}_3\text{Na})\text{CH}_2\text{COOH}$  (FEOS-1) and  $\text{H}(\text{CF}_2)_6\text{CH}_2(\text{OCH}_2\text{CH}_2)_3\text{OCOCH}(\text{SO}_3\text{Na})\text{CH}_2\text{COOH}$  (FEOS-3). The obtained surfactants were characterized by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR in detail. The synthesized fluorinated surfactants have a high thermal stability on the basis of thermogravimetric analysis. Their surface properties were examined and the results show that FEOS-1 and FEOS-3 surfactants can reduce the surface tension of water to  $25.55 \text{ mN m}^{-1}$  at  $10.25 \text{ mmol L}^{-1}$  and  $21.63 \text{ mN m}^{-1}$  at  $8.33 \text{ mmol L}^{-1}$ , respectively; meanwhile, the introduction of oxyethylene groups enhances the hydrophilicity and micellar forming ability and the longer oxyethylene chains the better surface properties. The Krafft points ( $K_p$ ) of FEOS-1 and FEOS-3 were both below  $0 \text{ }^\circ\text{C}$ , which was lower than perfluoro-*n*-heptanesulfonic acid sodium salt ( $n\text{-C}_7\text{F}_{15}\text{SO}_3\text{Na}$ ,  $K_p = 56.5 \text{ }^\circ\text{C}$ ) at a similar length of fluorocarbon chains. Comparison studies on two surfactants above and the conventional fluorocarbon surfactants, perfluorooctanoate of ammonium (PFOA) show that the

surfactants have comparable properties to PFOA, thus offering an environmentally friendly synthesizing alternatives to PFOA.

**Keywords** Polyethylene glycol mono(1*H*,1*H*,7*H*-dodecafluoroheptyl) ether · Novel fluorinated surfactants · Surface tension · Oxyethylene group

## Introduction

Fluorinated surfactants, containing fluorocarbon chains as hydrophobic groups, have a lot of special properties such as thermal stability, chemical inertness, high surface activity as well as water and oil repellence that offer a lot of advantages [1, 2]. They are more efficient than hydrogenated homopolymers since their surface tensions are lower and the most well-known are perfluorooctanoate of ammonium (PFOA) and perfluorooctane sulfonate ( $\text{C}_8\text{F}_{17}\text{SO}_3\text{X}$ , where  $\text{X} = \text{K}, \text{Na}, \text{H}$ ). In addition, many fluorinated surfactants are well-suited for use under high temperature and pressure conditions where low surface energy performance is critical due to the stability of the carbon–fluorine bond. Therefore, fluorocarbon surfactants have been vigorously applied as emulsifiers of paints, leveling agents for wax, oil fire extinguishing agents, surface modifiers for textiles [3–5] and surfactants for vesicles or cumulative membranes [6]. In addition, PFOA is also frequently used as a surfactant in aqueous media of polymerization of hydrophobic monomers, especially fluorinated monomers such as tetrafluoroethylene and other  $\text{C}_2$ – $\text{C}_3$  alkenes [7].

Whereas, these fluorinated surfactants still have shortcomings that need to be overcome, such as low solubility in water, high price and their accumulation in the

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environment. It has been demonstrated recently that PFOA displays ubiquity, animal-based toxicity, and some associations with human health [8–10]. As a kind of emerging persistent organic pollutant (POP), PFOA has caused global ecosystem pollution, and become a new research topic of POPs. With increasing public awareness for environmental protection and extensive attention internationally to biodegradability of the fluorinated surfactants, the use of long-chain ( $\geq C_8$ ) perfluorinated surfactants will be certainly forbidden in future [11].

Because fluorinated surfactants play a very important role in the preparation of high performance fluorinated material, synthesizing and screening novel fluorocarbon surfactants with a good environmental protection function is an important thesis for research workers [12–16]. There are many strategies for synthesizing non-bioaccumulable alternatives to PFOA, and one of which is that long carbon–fluorine chains of traditional fluorinated surfactants are “diluted” with hydrocarbon chains [17]. While the hydrocarbon content rises in these hybrid surfactants, they still keep the high surface tension lowering ability, characteristic of fluorinated surfactants.

Recently, Guo et al. synthesized sulfate ester-type hybrid surfactants with a hydrocarbon chain and a fluorocarbon chain in their molecule. These surfactants were found to have a surface tension lowering ability as high as that for fluorinated surfactants and a good affinity with water and hydrocarbon. However, they were easily hydrolyzed because a strongly electron attractive fluorocarbon group and hydrophilic sulfate ester group are bound to the same carbon atom. They then needed to be stored in a desiccator at low temperature and the physical properties of their solutions had to be measured within 20 h after preparation, thus making them rather unpractical [18]. Subsequently, the present authors succeeded in synthesizing sulfonate-type hybrid surfactants having a  $-C_6H_4CO-$  or  $-(CH_2)_2-$  group between the hydrophobic and hydrophilic groups as a spacer to improve their chemical stability and solubility in water [19, 20]. Similarly, Kondo et al. [21] synthesized three novel double-tailed anionic fluorocarbon surfactants with the introduction of two oxyethylene units between the hydrophobic and hydrophilic groups as a spacer to enhance the hydrophilicity of the surfactants, since those surfactants which have no oxyethylene units in their molecule are in general poorly water soluble.

This article reports the synthesis of two environmentally friendly succinic acid monofluoroalkyl sulfonate surfactants,  $H(CF_2)_6O(CH_2CH_2O)_nCOCH(SO_3Na)-CH_2COOH$  ( $n = 1,3$ ), in which oxyethylene units are introduced between the hydrophobic and hydrophilic groups as spacers to enhance the hydrophilicity of the surfactants and their chemical stability. Their hydrophilicity and surface active properties in terms of Krafft points, surface tension, and

critical micellar concentration (CMC) are presented and discussed.

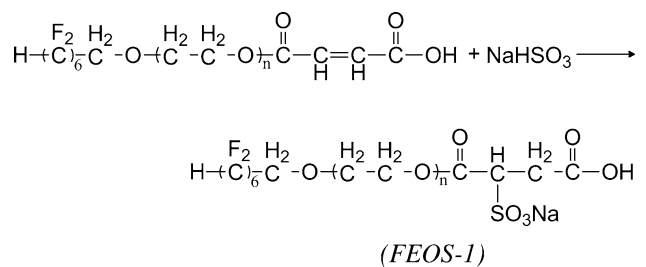
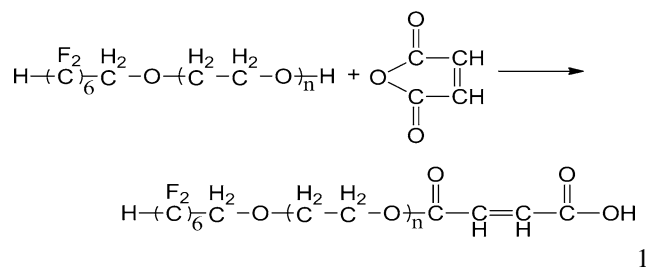
## Experimental

### Materials

1*H*,1*H*,7*H*-Dodecafluoroheptanol was purchased from China Fluoro Technology Co. Ltd., Shandong China; maleic anhydride was obtained from the Tianjin Chemical Reagent Factory, Tianjin China; sodium hydrogen sulfite was purchased from the Tianjin Kermel Chemical Reagent Co. Ltd., Tianjin China; ethanol was provided by the Tianjin Guangcheng Chemical Reagent Co. Ltd., Tianjin China; All of those chemicals were analytical reagents (AR) which were used without further purification. Polyethylene glycol mono(1*H*,1*H*,7*H*-dodecafluoroheptyl) ether was made by the Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, whose purity is up to 99 % and above (by GC). 1,1,2-Trichloro-1,2,2-trifluoroethane and PFOA were also prepared by the Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials.

### Synthesis of Succinic Acid Monofluoroalkyl Sulfonate

The succinic acid monofluoroalkyl sulfonate was prepared from maleic anhydride, polyethylene glycol mono(1*H*,1*H*,7*H*-dodecafluoroheptyl) ether, and sodium hydrogen sulfite in accordance with Schemes 1 and 2.



Maleic anhydride 32.34 g (0.33 mol) was put into a bottle equipped with condenser pipe and a thermometer under

stirring at 80 °C for 1 h. Then maleic anhydride melt, 112.8 g (0.3 mol) of ethylene glycol mono(1*H*,1*H*,7*H*-dodecafluoroheptyl) ether was added dropwise to the system. After 12 h, the product of mono(dodecafluoroheptyl ethoxy) ethanol acetate maleate was obtained as a colorless liquid and then washed several times with distilled water to remove the unreacted maleic anhydride (yield 140 g, 96.5 %).

Then, 100 g aqueous solution of sodium hydrogen sulfite solution (31.3 wt %) was added dropwise into 140 g mono(dodecafluoroheptyl ethoxy) ethanol acetate maleate with continuous stirring at 104 °C for 8 h, a coarse product FEOS-1 was obtained and then washed several times with ethanol to filter the unreacted sodium hydrogen sulfite. The white lardaceous solid product FEOS-1 was collected after removing unreacted ester by washing with 1,1,2-trichloro-1,2,2-trifluoroethane and then further dried under reduced pressure.

#### Synthesis of Sodium Mono(Dodecafluoroheptyl Terethoxy) Ethanol Acetate Sulfonic Acid Maleates (FEOS-3)

The synthesis methods and purification techniques were almost identical to those for FEOS-1. The essential difference between these procedures consisted of using terethylene glycol mono(1*H*,1*H*,7*H*-dodecafluoroheptyl) ether for synthesis of FEOS-3 instead of using ethylene glycol mono(1*H*,1*H*,7*H*-dodecafluoroheptyl) ether for FEOS-1.

FEOS-3: Maleic anhydride 32.34 g (0.33 mol), terethylene glycol mono(1*H*,1*H*,7*H*-dodecafluoroheptyl) ether 139.2 g (0.3 mol), reaction temperature 80 °C for 12 h, yield 155 g, 90.4, 31.3 % aqueous solution of sodium hydrogen sulfite 100 g, mono(dodecafluoroheptyl terethoxy) ethanol acetate maleate 155 g, reaction temperature 108 °C for 8 h, a white lardaceous solid product was finally obtained.

#### Characterizations

Fourier transform infrared (FT-IR) spectra on the novel surfactants were performed with the Bio-Rad FTS165 in the ambient temperature. <sup>1</sup>H-, <sup>13</sup>C- and <sup>19</sup>F-nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker Avance III-400 MHz instrument, using deuterioxide (D<sub>2</sub>O) as the solvent. The thermal stabilities of the synthesized fluorinated surfactants were studied using a Pryris Diamond TG/DTA (Perkin-Elmer Co., USA) in the temperature range from 37 to 400 °C with a heating rate of 10 °C/min under a dynamic nitrogen flow 50 mL/min.

Surface tension measurements were made at 25 °C on solutions of the synthesized surfactants by the ring method

using a tensiometer JK99B (Shanghai Zhongchen Digital Technique Equipment Limited Company, China) according to the procedure described by Wang [22]. Krafft point (*K<sub>p</sub>*) measurements were performed electroconductometrically using a DKK-TOA conductivity meter CM-60G on solutions at given high concentrations placed in a thermostatted bath while gently heating.

For surface-active solutes the surface excess concentration,  $\Gamma_{\max}$  can be considered to be equal to the actual surface concentration without significant error. The concentration of surfactant at the interface may therefore be calculated from surface or interfacial tension data by use of the appropriate Gibbs equation (Eq. 3) [23]. The surface concentration,  $\Gamma_{\max}$  can be obtained from the slope of a plot of  $\gamma$  versus  $\lg C$  at constant temperature.

$$\Gamma_{\max} = -\left(\frac{1}{4.606RT}\right)\left(\frac{\partial\gamma}{\partial\lg C}\right)_T \quad (3)$$

where *C* is the concentration of surfactant,  $\partial\gamma/\partial\lg C$  is the slope in the surface tension isotherm when the concentration is near the CMC, and  $\gamma$  is in mN m<sup>-1</sup>. *R* is the gas constant (8.31 J mol<sup>-1</sup> K<sup>-1</sup>),  $\Gamma_{\max}$  is in mol/1,000 m<sup>2</sup>, and *T* is the absolute temperature.

The area per molecule at the interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecule when compared with the dimensions of the molecule as obtained by use of molecular models. From the surface excess concentration, the area per molecule at the gas–liquid interface  $a_m^s$ , in square ångstroms is calculated from Eq. 4 [23].

$$a_m^s = \frac{10^{14}}{N_A\Gamma_{\max}} \quad (4)$$

and the standard free energy of micelle formation is calculated from Eq. 5 [23].

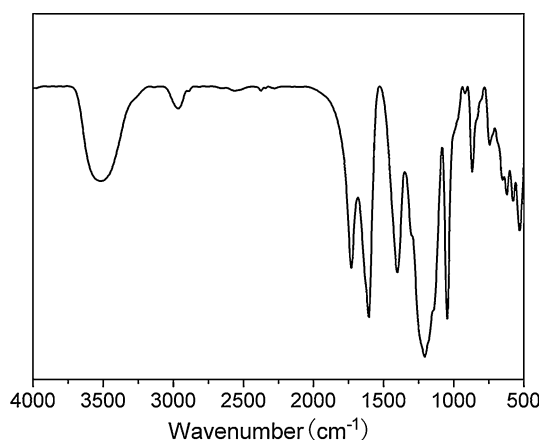
$$\Delta G = RT \ln\left(\frac{\text{cmc}}{55.5}\right) \quad (5)$$

where  $N_A$  = Avogadro's number and  $\Gamma_{\max}$  is in mol/cm<sup>2</sup>.

## Results and Discussion

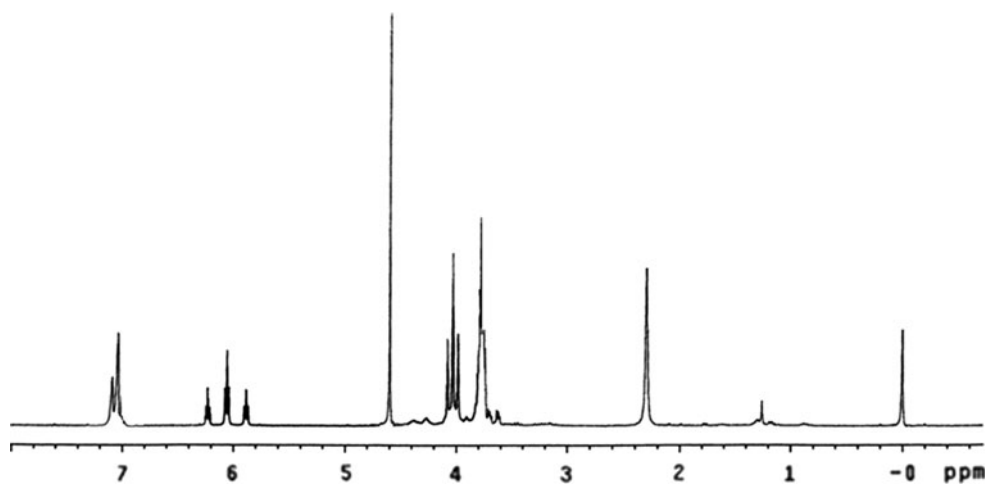
### Chemical Structure of Novel Succinic Acid Monofluoroalkyl Sulfonate Surfactants

Figures 1, 2, 3 and 4 show the FT-IR, <sup>1</sup>H-NMR, <sup>19</sup>F-NMR and <sup>13</sup>C-NMR spectra of succinic acid monofluoroalkyl sulfonate surfactant FEOS-1, respectively. IR (KBr): 3,500 ( $\nu_{\text{OH}}$ ), 2,956 ( $\nu_{\text{CH}}$ ), 1,444 ( $\delta_{\text{CH}}$ ), 1,730 ( $\nu_{\text{C=O}}$ ), 1,600 ( $\nu_{\text{OC=O}}$ ), 1,400 ( $\nu_{\text{SO}_2-\text{O}}$ ), 1,202 ( $\nu_{\text{CF}}$ ), 1,038 ( $\nu_{\text{COC}}$ ). <sup>1</sup>H-NMR(D<sub>2</sub>O):

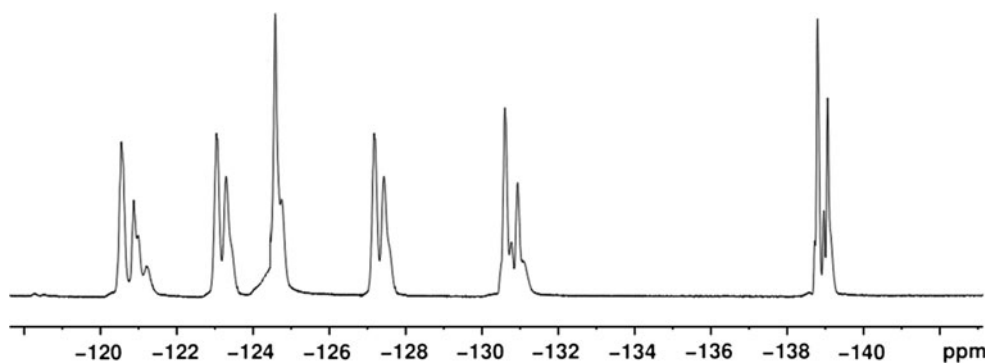


**Fig. 1** FT-IR spectrum of succinic acid monofluoroalkyl sulfonate surfactant FEOS-1

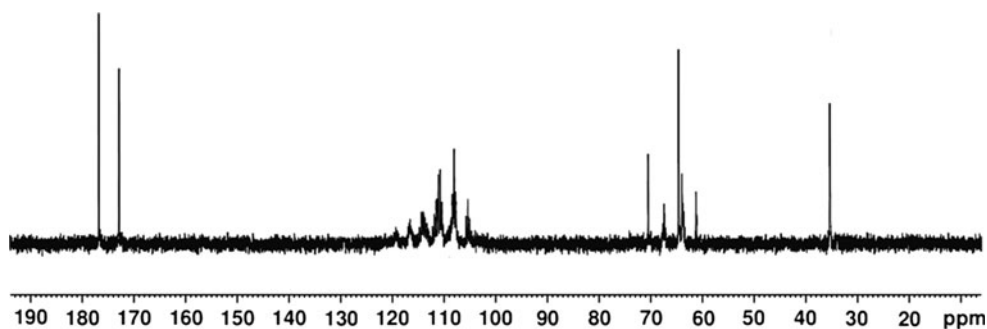
**Fig. 2**  $^1\text{H-NMR}$  spectrum of succinic acid monofluoroalkyl sulfonate surfactant FEOS-1



**Fig. 3**  $^{19}\text{F-NMR}$  spectrum of succinic acid monofluoroalkyl sulfonate surfactant FEOS-1

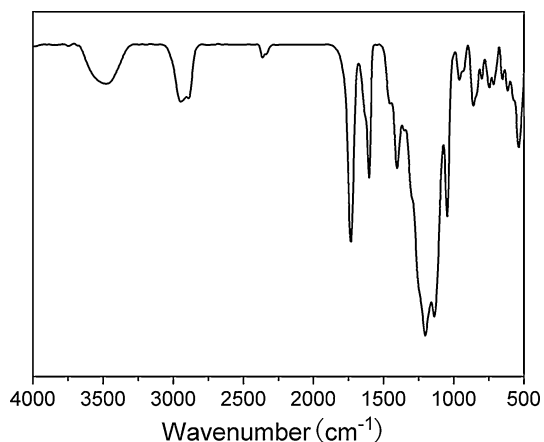


**Fig. 4**  $^{13}\text{C-NMR}$  spectrum of succinic acid monofluoroalkyl sulfonate surfactant FEOS-1



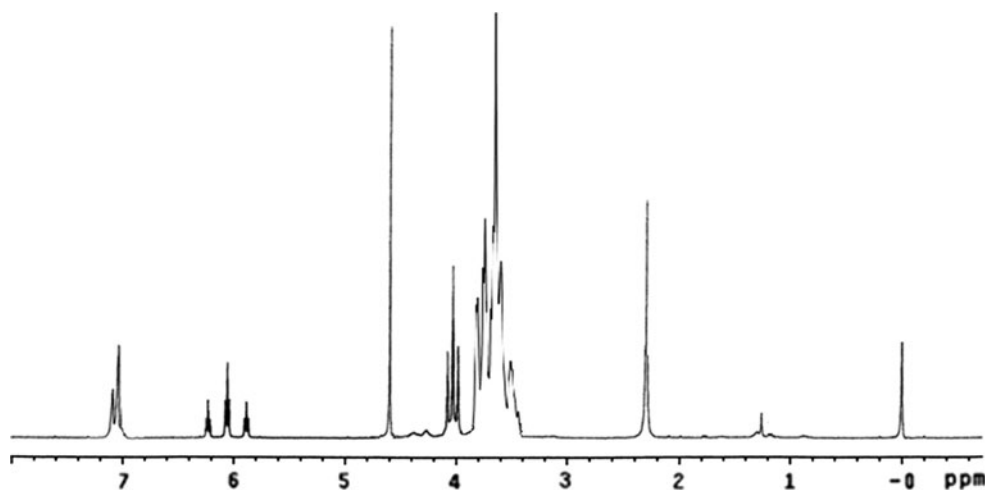
$\delta = 5.84$  ppm to  $\delta = 6.21$  ppm (m, 1H, a),  $\delta = 4.80$  ppm (solvent),  $\delta = 3.96$  ppm to  $\delta = 4.14$  ppm (m, 2H, b),  $\delta = 3.60$  ppm to  $\delta = 3.82$  ppm (m, 4H, c and d),  $\delta = 2.22$  ppm to  $\delta = 2.36$  ppm (m, 3H, e and f),  $\delta = 7.00$  ppm to  $\delta = 7.18$  ppm (m, 1H, g) for  $\text{H}^{\text{a}}(\text{CF}_2)_6\text{CH}_2^{\text{b}}\text{OCH}_2^{\text{c}}\text{CH}_2^{\text{d}}\text{OCOCH}^{\text{e}}(\text{SO}_3\text{Na})\text{CH}_2^{\text{f}}\text{COOH}^{\text{g}}$ ;  $^{19}\text{F-NMR}(\text{D}_2\text{O})$ :  $\delta = -139.20$  ppm (p, 2F, a),  $\delta = -130.80$  ppm (p, 2F, b),  $\delta = -127.50$  ppm (p, 2F, c),  $\delta = -124.50$  ppm (p, 2F, d),  $\delta = -123.20$  ppm (p, 2F, e),  $\delta = -120.80$  ppm (p, 2F, f) for  $\text{HCF}_2^{\text{a}}\text{CF}_2^{\text{b}}\text{CF}_2^{\text{c}}\text{CF}_2^{\text{d}}\text{CF}_2^{\text{e}}\text{CF}_2^{\text{f}}\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCOCH}(\text{SO}_3\text{Na})\text{CH}_2\text{COOH}$ ;  $^{13}\text{C-NMR}(\text{D}_2\text{O})$ :  $\delta = 119.30$  ppm to  $106.20$  ppm (a),  $\delta = 65.90$  ppm (b),  $\delta = 69.80$  ppm (c),  $\delta = 67.10$  ppm (d),  $\delta = 172.00$  ppm (e),  $\delta = 63.00$  ppm (f),  $\delta = 35.00$  ppm (g),  $\delta = 177.00$  ppm (i) for  $\text{H}(\text{CF}_2)_6\text{C}^{\text{b}}\text{H}_2\text{OC}^{\text{c}}\text{H}_2\text{OC}^{\text{e}}\text{OC}^{\text{f}}\text{H}(\text{SO}_3\text{Na})\text{C}^{\text{g}}\text{H}_2\text{C}^{\text{i}}\text{OOH}$ .

Figures 5, 6, 7 and 8 show the FT-IR,  $^1\text{H-NMR}$ ,  $^{19}\text{F-NMR}$  and  $^{13}\text{C-NMR}$  spectra of FEOS-3, respectively. IR (KBr): 3,500( $\nu_{\text{OH}}$ ), 2,956 ( $\nu_{\text{CH}}$ ), 1,444 ( $\delta_{\text{CH}}$ ), 1,730( $\nu_{\text{C=O}}$ ),

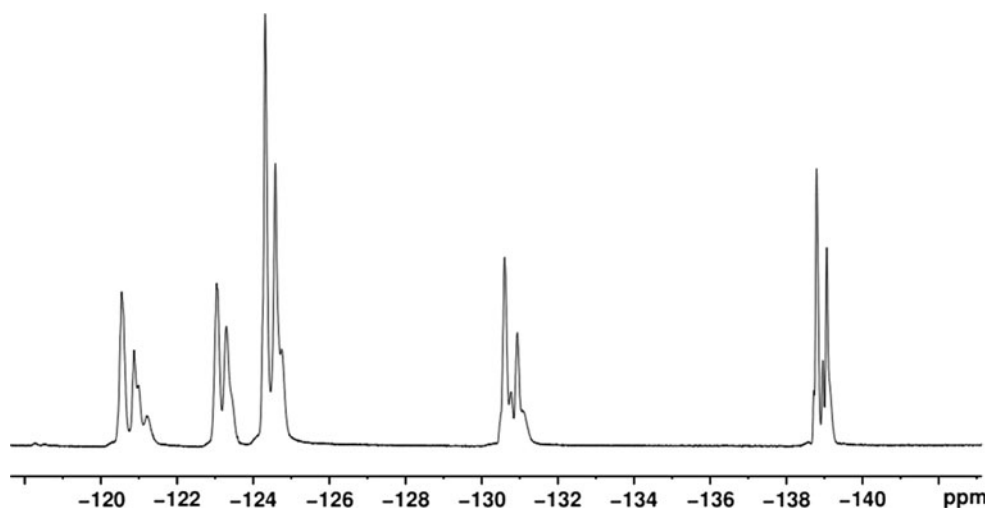


**Fig. 5** FT-IR spectrum of succinic acid monofluoroalkyl sulfonate surfactant FEOS-3

**Fig. 6**  $^1\text{H-NMR}$  spectrum of succinic acid monofluoroalkyl sulfonate surfactant FEOS-3

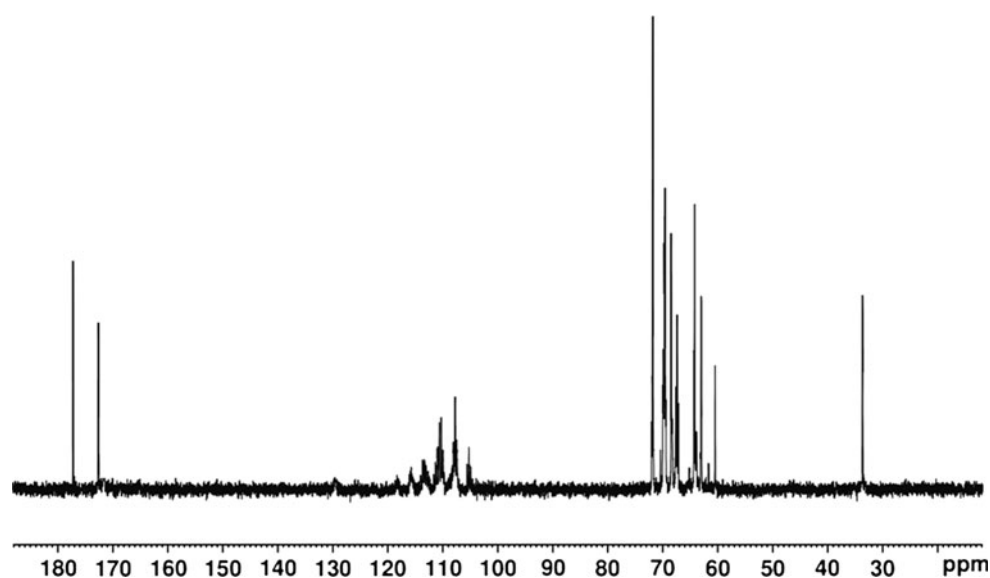


**Fig. 7**  $^{19}\text{F-NMR}$  spectrum of succinic acid monofluoroalkyl sulfonate surfactant FEOS-3



1,600( $\nu_{\text{OC=O}}$ ), 1,400( $\nu_{\text{SO}_2-\text{O}}$ ), 1,202( $\nu_{\text{CF}}$ ), 1,038( $\nu_{\text{COC}}$ ).  $^1\text{H-NMR}(\text{D}_2\text{O})$ :  $\delta = 5.86$  ppm to  $\delta = 6.24$  ppm (m, 1H, a),  $\delta = 4.80$  ppm (solvent),  $\delta = 3.98$  ppm to  $\delta = 4.16$  ppm (m, 2H, b),  $\delta = 3.41$  ppm to  $\delta = 3.86$  ppm (m, 12H, c d e f g and h),  $\delta = 2.24$  ppm to  $\delta = 2.38$  ppm (m, 3H, e and f),  $\delta = 6.96$  ppm to  $\delta = 7.16$  ppm (m, 1H, g) for  $\text{H}^{\text{a}}(\text{CF}_2)_6\text{CH}_2^{\text{b}}\text{OCH}_2^{\text{c}}-\text{CH}_2^{\text{d}}\text{OCH}_2^{\text{e}}\text{CH}_2^{\text{f}}\text{OCH}_2^{\text{g}}\text{CH}_2^{\text{h}}\text{OCOCH}^{\text{i}}(\text{SO}_3\text{Na})\text{CH}_2^{\text{j}}\text{COOH}^{\text{k}}$ ;  $^{19}\text{F-NMR}(\text{D}_2\text{O})$ :  $\delta = -139.10$  ppm (p, 2F, a),  $\delta = -130.60$  ppm (p, 2F, b),  $\delta = -124.40$  ppm (p, 4F, c and d),  $\delta = -123.10$  ppm (p, 2F, e),  $\delta = -120.60$  ppm (p, 2F, f) for  $\text{HCF}_2^{\text{a}}\text{CF}_2^{\text{b}}\text{CF}_2^{\text{c}}\text{CF}_2^{\text{d}}\text{CF}_2^{\text{e}}-\text{CF}_2^{\text{f}}\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCOCH}(\text{SO}_3\text{Na})\text{CH}_2\text{COOH}$ .  $^{13}\text{C-NMR}(\text{D}_2\text{O})$ :  $\delta = 119.40$  ppm to 106.20 ppm (a),  $\delta = 66.20$  ppm (b),  $\delta = 71.50$  ppm (c),  $\delta = 70.90$  ppm (d),  $\delta = 70.90$  ppm (e),  $\delta = 70.60$  ppm (f),  $\delta = 69.80$  ppm (g),  $\delta = 67.10$  ppm (h),  $\delta = 172.00$  ppm (i),  $\delta = 63.00$  ppm (j),  $\delta = 34.00$  ppm (k),  $\delta = 177.00$  ppm (m) for  $\text{H}(\text{CF}_2)_6\text{C}^{\text{a}}\text{H}_2\text{OC}^{\text{b}}\text{H}_2\text{C}^{\text{c}}\text{H}_2\text{OC}^{\text{d}}\text{H}_2\text{OC}^{\text{e}}\text{H}_2\text{OC}^{\text{f}}\text{H}_2\text{OC}^{\text{g}}\text{H}_2\text{OC}^{\text{h}}\text{OC}^{\text{i}}\text{H}(\text{SO}_3\text{Na})\text{C}^{\text{k}}\text{H}_2\text{C}^{\text{m}}\text{OOH}$ .

**Fig. 8**  $^{13}\text{C}$ -NMR spectrum of succinic acid monofluoroalkyl sulfonate surfactant FEOS-3



#### Thermal Stabilities of Novel Succinic Acid Monofluoroalkyl Sulfonate Surfactants

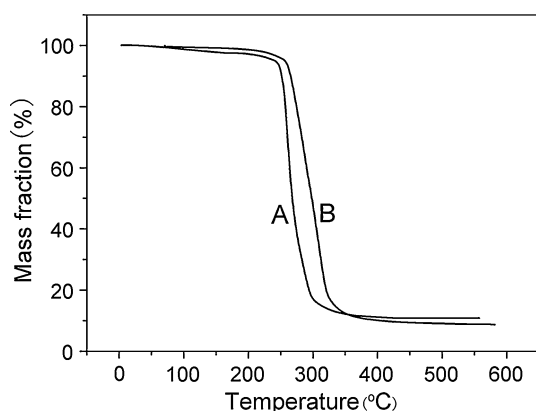
Figure 9 gives the TGA thermograms of the synthesized succinic acid monofluoroalkyl sulfonate surfactants. From TGA curves, it can be seen that FEOS-1 begins to degrade at 240 °C and a rapid weight loss occurs at 260 °C. Finally, complete decomposition was at 340 °C, leaving only sodium element oxides. FEOS-3 begins to degrade at 250 °C attributed to the longer oxyethylene group of the sample and decomposes completely at about 360 °C, finally. Thermal stability characteristic of the FEOS-1 is worse than FEOS-3, which may be derived from the longer molecular main chain. It is well known that the molecular weight of FEOS-3 is a little higher than that of FEOS-1. In conclusion, the succinic acid monofluoroalkyl sulfonate

surfactants have good thermostability to be applied in relatively high temperature state [24, 25].

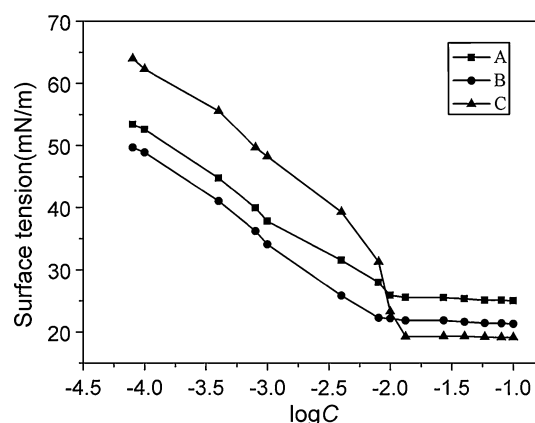
#### Surface Properties of Novel Succinic Acid Monofluoroalkyl Sulfonate Surfactants

The surface tension ( $\gamma$ )-bulk concentration  $C$  dependencies for the studied compounds are presented in Fig. 10. No minimum was observed on the  $\gamma$ - $\lg C$  curves of the aqueous synthesized surfactants solution, indicating that there were no impurities brought into our products [26].

Table 1 lists the aqueous surface activities of FEOS-1, FEOS-3, PFOA, together with  $n\text{-C}_7\text{F}_{15}\text{SO}_3\text{Na}$  from the published work [27]. FEOS-1 and FEOS-3 are highly water-soluble and their Krafft points ( $K_p$ ) are below 0 °C.  $K_p$  values of FEOS-1 and FEOS-3 are lower than those of



**Fig. 9** Thermal gravimetric analysis (TGA) thermograms of the succinic acid monofluoroalkyl sulfonate surfactants FEOS-1 (A) and FEOS-3 (B)



**Fig. 10** Surface tension plots of FEOS-1 (A), FEOS-3 (B) and PFOA (C) against concentration at 25 °C



**Table 1** The Krafft points ( $K_p$ ), CMC,  $\gamma_{\text{CMC}}$ ,  $\Gamma_{\text{max}}$ ,  $a_m^s$  and  $\Delta G$  of synthesized surfactants, PFOA and  $n\text{-C}_7\text{F}_{15}\text{SO}_3\text{Na}$ 

Surfactants	$K_p$ (°C)	CMC (mmol L <sup>-1</sup> )	$\gamma_{\text{CMC}}$ (mN m <sup>-1</sup> )	$10^{10} \Gamma_{\text{max}}$ (mol cm <sup>-2</sup> )	$a_m^s$ (nm <sup>2</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )
FEOS-1	<0	10.25	25.55	1.15	1.45	-21.29
FEOS-3	<0	8.33	21.63	1.20	1.38	-21.80
PFOA	<0	13.30	19.51	1.08	1.54	-20.64
$n\text{-C}_7\text{F}_{15}\text{SO}_3\text{Na}$	56.5	17.5	37.3	3.1	0.53	-

CMC and  $\gamma_{\text{CMC}}$  at 25 °C

$n\text{-C}_7\text{F}_{15}\text{SO}_3\text{Na}$  ( $K_p = 56.5$  °C), indicating that the FEOS-1 and FEOS-3 are more hydrophilic when compared to  $n\text{-C}_7\text{F}_{15}\text{SO}_3\text{Na}$  at the similar fluorocarbon chain length.

Comparisons of the properties of FEOS-1 and FEOS-3 with PFOA show that the  $\gamma_{\text{CMC}}$  values of the two novel synthesized fluorinated surfactants are close to that of PFOA, indicating that the two synthesized surfactants possess high surface activities. Both of the newly synthesized fluorinated surfactants have much lower  $\gamma_{\text{CMC}}$  than  $n\text{-C}_7\text{F}_{15}\text{SO}_3\text{Na}$ , whose  $\gamma_{\text{CMC}}$  is 37.3 mN m<sup>-1</sup>, although all of them possess a similar length of the fluorocarbon chains.

The CMC of FEOS-1 and FEOS-3 are both lower than that of PFOA, mainly because the introduction of oxyethylene units has increased the hydrophobic group of surfactant length effectively. Especially, FEOS-3 are even lower than that of FEOS-1 due to that the functional oxyethylene groups (-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O-) in FEOS-3 molecule make the hydrophobic group of surfactant longer than that in FEOS-1 molecule.

## Conclusions

Two environmentally friendly succinic acid mono-fluoroalkyl sulfonate surfactants, i.e. HCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCOCH(SO<sub>3</sub>Na)CH<sub>2</sub>COOH and HCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>OCOCH(SO<sub>3</sub>Na)CH<sub>2</sub>COOH ( $n\text{FEOS}$ ;  $n = 1, n = 3$ ) were successfully obtained as pale solids. Studies of the properties of the synthesized fluorinated surfactants showed that the Krafft points are both below 0 °C and the values of surface tension at CMC ( $\gamma_{\text{CMC}}$ ) are very close to that of PFOA. The introduction of oxyethylene groups into the synthesized surfactant molecules enhanced their hydrophilicity and micellar forming ability and the longer oxyethylene groups gave better surface properties. In addition, the fluoroalkyl sulfonate surfactants have good thermostability with starting equilibrium thermal degradation temperatures of respectively 240 and 250 °C enabling them to be applied at a high temperature. The synthesized fluorinated surfactants may be used to replace the traditional long-chain perfluorinated surfactants in order to help conserve the environment owing to their outstanding biodegradability.

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