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ORIGINAL ARTICLE

Synthesis and Surface Activities of Novel Succinic Acid Double-Tailed Sulfonate Fluorinated Surfactants

Luqing Zhang[1,2,3] · Bing Geng[1,2,3] · Quanxuan Lu[1,2,3] · Anhou Xu[1,2,3] ·
Shuxiang Zhang[1,2,3]

Abstract In this study, four environmentally friendly succinic acid double-tailed sulfonate fluorinated surfactants were synthesized from maleic anhydride, fluoroalkyl alcohols, namely 1-(1H,1H,7H-Dodecafluoroheptyloxy) ethanol, 1-(1H,1H,5H -octafluoropentyloxy) ethanol, 1-(1H,1H,3H-tetrafluoropropoxy) ethanol, and 1-(1H,1H - trifluoroethyoxy) ethanol, and sodium hydrogensulfite. The surfactant structure was characterized by FT-IR, ^{1}H NMR, and ^{19}F NMR . Thermogravimetric results showed that the fluorinated surfactants were stable up to relatively high temperature. The Krafft points of the four novel succinic acid double-tailed sulfonate fluorinated surfactants were all below 0 °C. The lowest CMC value for the synthesized four double-tailed fluorine surfactants is about 0.076 mmol L^{-1}, far less than that of ammonium perfluorooctanoate (PFOA), demonstrating that double-tailed surfactants have higher surface activity than surfactants with one fluoroalkyl chain. The replacement of alkyl groups with oxyethylene groups enhances the hydrophilicity of the obtained fluorinated surfactants. Based on these findings, the synthesized surfactants may be environmentally friendly alternatives to PFOA and exhibit promising potential in industry applications.

Keywords Novel fluorinated surfactants · Surface tension · Double-tailed

✉ Shuxiang Zhang
chm_zhangsx@ujn.edu.cn

1 Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, University of Jinan, Jinan 250022, China
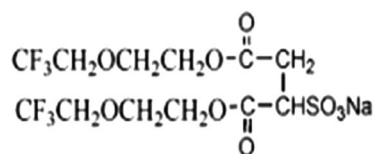
2 School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China

3 Shandong Engineering Research Center for Fluorinated Material, Jinan 250022, China

Introduction

Fluorinated surfactants are more surface active than ordinary hydrocarbon surfactants. They have been extensively investigated and utilized as emulsifying agents for emulsion polymerization, agents for improving wax leveling, flame retardants, surface modifiers for textiles and surfactants for vesicles or cumulative membranes due to their versatile properties, such as thermal stability, chemical inertness, high surface activity as well as water and oil repellence [1, 2]. These properties are affected by the hydrophobic fluorocarbon moieties existing in the molecular structures. It has been reported that their surface tensions are lower than common hydrocarbon surfactants and they form micelles at low concentrations [3].

Two well-known fluorinated surfactants are the ammonium salt of perfluorooctanoate (PFOA) and perfluorooctane sulfonate ($C_8F_{17}SO_3X$, where X = K, Na, H). PFOA plays a key role in the emulsion or dispersion polymerization process to help incorporate hydrophobic monomers into the latex polymer, especially fluorinated monomers such as tetrafluoroethylene and other C_2–C_3 alkenes [4].

Fluorinated surfactants do have shortcomings, such as low solubility in water, high price and environmental concerns that need to be overcome [5]. Recently, PFOA has been found to be persistent, toxic and bioaccumulable because it is difficult to degrade under enzymatic or
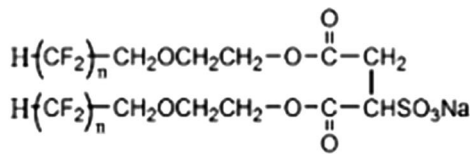
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metabolic decomposition. Its accumulation in the environment has shown some negative associations with human health [6–8].

Since fluorinated surfactants are important for preparing high performance fluorinated materials [9], extensive research on synthesis and screening of novel fluorocarbon surfactants with a good environmental profile has been performed. Many strategies for synthesizing non-bioaccumulable alternatives to PFOA and related perfluorinated surfactants have been reported [10–13].

and their chemical stability [19]. Considering that the ability of surfactants having two fluoroalkyl chains against flocculation-redispersion is superior to that of surfactants having one fluoroalkyl chain, this article reports the synthesis of four environmentally friendly succinic acid double-tailed sulfonate fluorinated surfactants (FEOS*-1, 2, 4, 6). Their hydrophilicity and surface active properties in terms of Krafft points, surface tension, and critical micellar concentration (CMC) are presented and discussed.

$$CF_3CH_2OCH_2CH_2O-\overset{\overset{O}{\|}}{C}-CH_2$$
$$CF_3CH_2OCH_2CH_2O-\overset{}{\underset{\overset{\|}{O}}{C}}-CHSO_3Na$$

FEOS*-1

$$H\!\!\left(CF_2\right)_{\!n}\!\!-CH_2OCH_2CH_2-O-\overset{\overset{O}{\|}}{C}-CH_2$$
$$H\!\!\left(CF_2\right)_{\!n}\!\!-CH_2OCH_2CH_2-O-\overset{}{\underset{\overset{\|}{O}}{C}}-CHSO_3Na$$

FEOS*-n (n=2, 4, 6)

One efficient method is to 'dilute' the long carbon–fluorine chains with hydrocarbon chains and manufacture hybrid surfactants which possess both fluorocarbon and hydrocarbon chains in their molecule. The incorporation of hydrocarbon chains can improve the short comings mentioned previously and still keep the high surface tension lowering ability at same time [14].

Guo et al. firstly reported new 'double tail' type hybrid surfactants composed of hydrocarbon and fluorocarbon chains, both attached to a sulfate group at the head end. Surface tension lowering ability of these surfactants was as high as that for fluorinated surfactants. However, the surfactants were so unstable and had to be stored in a desiccator at −25 °C [15].

Subsequently, Kondo et al. introduced -C$_6$H$_4$CO- or -(CH$_2$)$_2$- groups between a fluorocarbon chain and a hydrocarbon chain in a molecule to successfully synthesize sulfonate-type hybrid surfactants. These surfactants are reported to be very stable in the presence of moisture [16, 17]. The Kondo group also 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 [18]. Recently, the synthesis of gemini-type hybrid fluorinated surfactants with good water-solubility was reported, in which a hydrocarbon group was connected with two fluorinated parts using the Grignard reaction [14]. Unfortunately the overall yield of products is a little low (17–20 wt%).

In our previous work, two environmentally friendly succinic acid monofluoroalkyl sulfonate surfactants were synthesized, in which oxyethylene units were introduced between the hydrophobic and hydrophilic groups as spacers to enhance the hydrophilicity of the surfactants

Experimental

Materials

1H,1H,7H-Dodecafluoroheptanol, 1H,1H,5H-octafluoropentanol, 1H,1H,3H-tetra-fluoropropanol, and 1H,1H-trifluoroethanol were 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). P-toluenesulfonic acid was purchased from the Beijing Yili Fine Chemicals Co Ltd. (Beijing China). The raw materials (AR grade) mentioned above were used as received. 1H,1H,7H-Dodecafluoroheptyloxy ethanol, 1-(1H,1H,5H-octafluoropentyloxy) ethanol, 1-(1H,1H,3H-tetrafluoropropoxy) ethanol and 1-(1H,1H-trifluoroethyoxy) ethanol were self-made at our Key Laboratory of Fluorine Chemistry and Chemical Materials, whose purity is up to 92 % and above (by GC). 1,1,2-Trichloro-1,2,2-trifluoroethane and PFOA were also prepared in our group.

Synthesis of Succinic Acid Double-Tailed Sulfonate Fluorinated Surfactants

The process used to synthesize the succinic acid double-tailed sulfonate fluorinated surfactants is shown in Scheme 1. A mixture of maleic anhydride (0.5 mol), fluoroalkyloxy ethanol (1.1 mol), and a moderate amount of p-toluenesulfonic acid (0.5–0.7 wt%) as a catalyst were put into a bottle equipped with Dean-stark trap and the reaction was performed at 120 °C for 18 h. Given the reaction is an

Scheme 1 Synthetic procedure of the succinic acid double-tailed sulfonate fluorinated surfactants
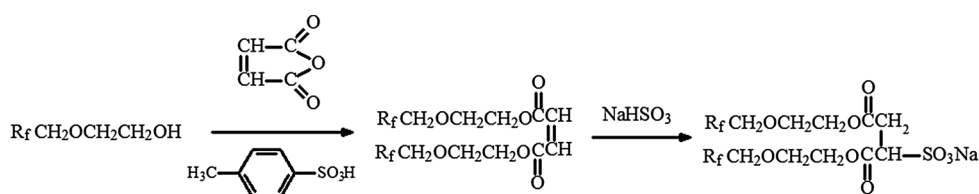
esterification reaction, suitable amounts of water-carrying agents were added to remove the water produced in the reaction process. The proper water-carrying agents (cyclohexane, benzene, toluene and xylene) were chosen depending on the boiling points of fluoroalkyloxy alcohols. After the reaction, the water-carrying agents and the unreacted fluoroalkyloxy alcohols were removed by the vacuum distillation at 160 °C. The vacuum distillation temperature was adjusted accordingly by the boiling points of fluoroalkyloxy alcohols. The bis[2-(2-fluoroalkyloxy ethyl)] maleate product was obtained as a yellow liquid (yields: 74–83 %). Then, an aqueous solution of sodium hydrogen sulfite (0.55 mol) was added dropwise to the bis[2-(2-fluoroalkyloxy ethyl)] maleate with continuous stirring at 104 °C for 8 h. The coarse products FEOS[*]-n (n = 1, 2, 4, 6) obtained were washed several times with ethanol to filter the unreacted sodium hydrogen sulfite. The white lardaceous solid products FEOS[*]-n (n = 1, 2, 4, 6) were collected after removing unreacted ester by washing with 1,1,2-trichloro-1,2,2-trifluoroethane. The overall yield was 67–71 %. The ^{1}H nuclear magnetic resonance (NMR) spectra and the purity of fluoroalkyloxy ethanol measured with gas chromatography were given in Figure S1, Figure S2 and Table S1.

A Bio-Rad FTS165 was used to measure FT-IR spectra of the succinic acid double-tailed sulfonate fluorinated surfactants. ^{1}H-NMR spectra and ^{19}F NMR of the synthesized fluorinated surfactants and intermediate products were obtained using a Bruker Avance III-400 MHz instrument with deuterated chloroform (CDCl$_3$) or deuteroxide (D$_2$O) as solvents and TMS as an internal standard.

A Pryris Diamond TG/DTA (Perkin-Elmer Co., USA) was used to evaluate the thermal stabilities of the fluorinated surfactants. The samples were heated from 37 to 400 °C at a rate of 10 °C/min.

Molar conductivity (Λm) of the prepared fluorinated surfactants was used to determine critical micelle concentrations at 25.0 ± 0.2 °C using a Metrohm 712 conductimeter apparatus with an absolute accuracy up to ±3 %.

A tensiometer JK99B (Shanghai Zhongchen Digital Technique Equipment Limited Company, China) was used to measure the surface and interfacial tension of these fluorosurfactant solutions at 25.0 ± 0.2 °C by the Ring method according to the previous procedure [20].

Critical micelle temperatures (also known as Krafft points) of the synthesized fluorinated surfactants were determined by measuring the electrical conductivity at given high concentrations with a CM-60G(DKK-TOA conductivity meter). The samples were placed in a thermostatted bath with gently heating.

The surface excess concentration at the air/water interface (Γ_{max}) was calculated using the Gibbs adsorption isotherm (Eq. 1) [21]:

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

where R is the gas constant (8.31 J mol^{-1} K^{-1}), T is the absolute temperature and γ is the surface tension of the synthesized fluorinated surfactant aqueous solution, C is the concentration of the synthesized fluorinated surfactant aqueous solution.

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. 2 [21]:

$$a_m^s = \frac{10^{14}}{N_A\Gamma_{max}} \qquad (2)$$

where N_A = Avogadro's number and Γ_{max} is in mol/cm^2. The standard free energy of micelle formation is calculated from Eq. 3 [21]

$$\Delta G = RT\ln\left(\frac{CMC}{55.5}\right) \qquad (3)$$

where CMC is the critical micelle concentration expressed in molar units.

Results and Discussion

Chemical Structure of Novel Succinic Acid Double-Tailed Sulfonate Fluorinated Surfactants

In this work, four environmentally friendly succinic acid double-tailed sulfonate fluorinated surfactants were synthesized from maleic anhydride, fluoroalkyl alcohols, namely
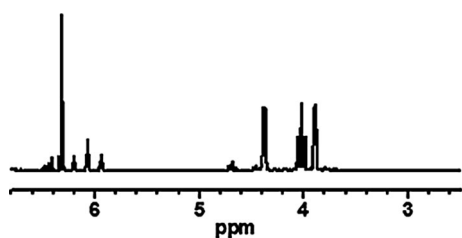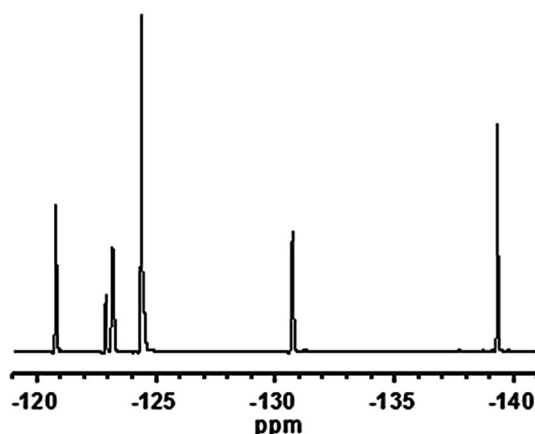
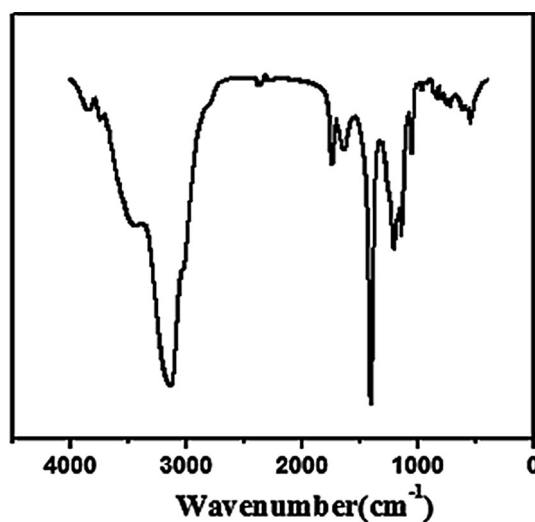**Fig. 1** ^{1}H-NMR spectra of sodium bis[2-(2-1H,1H,7H-dodecafluoroheptyloxy) ethyl] maleate
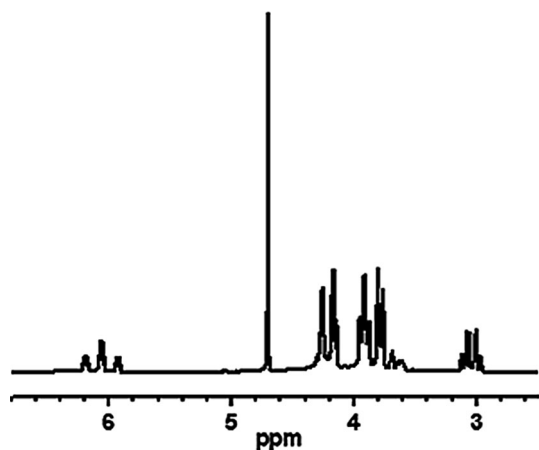
Fig. 2 ^{1}H-NMR spectra of sodium bis[2-(2-1H,1H,7H-dodecafluoroheptyloxy) ethyl]-2-sulfosuccinate surfactant FEOS*-6

sodium bis[2-(2-1H,1H,7H-dodecafluoroheptyloxy) ethyl]-2-sulfosuccinate surfactant (FEOS*-6), sodium bis[2-(2-1H,1H,5H-octafluoropentyloxy) ethyl]-2-sulfosuccinate surfactant (FEOS*-4), sodium bis[2-(2-1H,1H,3H-tetrafluoropropoxy) ethyl] -2-sulfosuccinate surfactant (FEOS*-2), and sodium bis[2-(2-1H,1H-trifluoroethyoxy) ethyl]-2-sulfosuccinate surfactant (FEOS*-1). The structure of the FEOS*-6 was characterized by FT-IR, ^{1}H NMR and ^{19}F NMR and the results are shown in Figs. 1, 2, 3, 4. And the FT-IR, ^{1}H-NMR and ^{19}F-NMR spectra of FEOS*-4, FEOS*-2 and FEOS*-1 are given in the Supplementary Material (see Figure S3).

Figure 1 shows the ^{1}H-NMR spectra of bis[2-(2-fluoroalkyloxy ethyl)] maleate (CDCl$_3$), ^{1}H NMR: $\delta = 5.88$ ppm to $\delta = 6.05$ ppm (m, 2H, a), $\delta = 3.87$ ppm (m, 4H, b), $\delta = 4.01$ ppm (m, 4H, c), $\delta = 4.35$ ppm (m, 4H, d), $\delta = 6.29$ (m, 4H, e) for H^{a} (CF$_2$)$_6$CH$_2^{b}$OCH$_2^{c}$CH$_2^{d}$ OOCCH$_2^{e}$ = CH$_2^{e}$COOCH$_2^{d}$CH$_2^{c}$OCH$_2^{b}$ (CF$_2$)$_6$H^{a}; and Fig. 2 shows the ^{1}H-NMR spectra of FEOS*-6 (D$_2$O), ^{1}H NMR: $\delta = 5.90$ ppm to $\delta = 6.23$ ppm (m, 2H, a), $\delta = 3.75$ ppm to $\delta = 3.85$ ppm (m, 4H, b), $\delta = 3.87$ ppm to $\delta = 3.95$ ppm (m, 4H, c), $\delta = 4.11$ ppm to $\delta = 4.30$ ppm (m, 5H, d and f), $\delta = 3.05$ ppm (m,1H, e) for H^{a} (CF$_2$)$_6$CH$_2^{b}$OCH$_2^{c}$ CH$_2^{d}$OOCCH^{e} (SO$_3$Na) CH$_2^{f}$COOCH$_2^{d}$CH$_2^{c}$OCH$_2^{b}$ (CF$_2$)$_6$H^{a}. The strong peaks at 4.76 ppm is attributed to the D$_2$O.

Fig. 3 ^{19}F-NMR spectra of sodium bis[2-(2-1H,1H,7H-dodecafluoroheptyloxy) ethyl]-2-sulfosuccinate surfactant FEOS*-6


Fig. 4 FT-IR spectra of sodium bis[2-(2-1H,1H,7H-dodecafluoroheptyloxy) ethyl]-2-sulfosuccinate surfactant FEOS*-6

Figures 3 and 4 show the ^{19}F-NMR and FT-IR spectra of sodium bis[2-(2-1H,1H,7H-dodecafluoroheptyloxy) ethyl]-2-sulfosuccinate surfactant FEOS*-6, respectively. ^{19}F-NMR (D$_2$O): $\delta = -120.77$ ppm (p, 4F, a), $\delta = -122.87$ ppm (p, 4, b), $\delta = -123.12$ ppm (p, 4F, c), $\delta = -124.43$ ppm (p, 4F, d), $\delta = -130.67$ ppm (p, 4F, e), $\delta = -139.29$ ppm (p, 4F, f) for HCF$_2^{a}$CF$_2^{b}$CF$_2^{c}$CF$_2^{d}$CF$_2^{e}$CF$_2^{f}$CH$_2$OCH$_2$CH$_2$OOCCH (SO$_3$-Na) CH$_2$COOCH$_2$CH$_2$OCH$_2$CF$_2^{f}$CF$_2^{e}$CF$_2^{d}$CF$_2^{c}$CF$_2^{b}$CF$_2^{a}$H; IR (KBr): 1738($v_{C=O}$), 1637($v_{OC=O}$), 1400(v_{SO2-O}), 1201(v_{CF}), 1049(v_{COC}).

Thermal Stabilities of Novel Succinic Acid Double-Tailed Sulfonate Fluorinated Surfactants
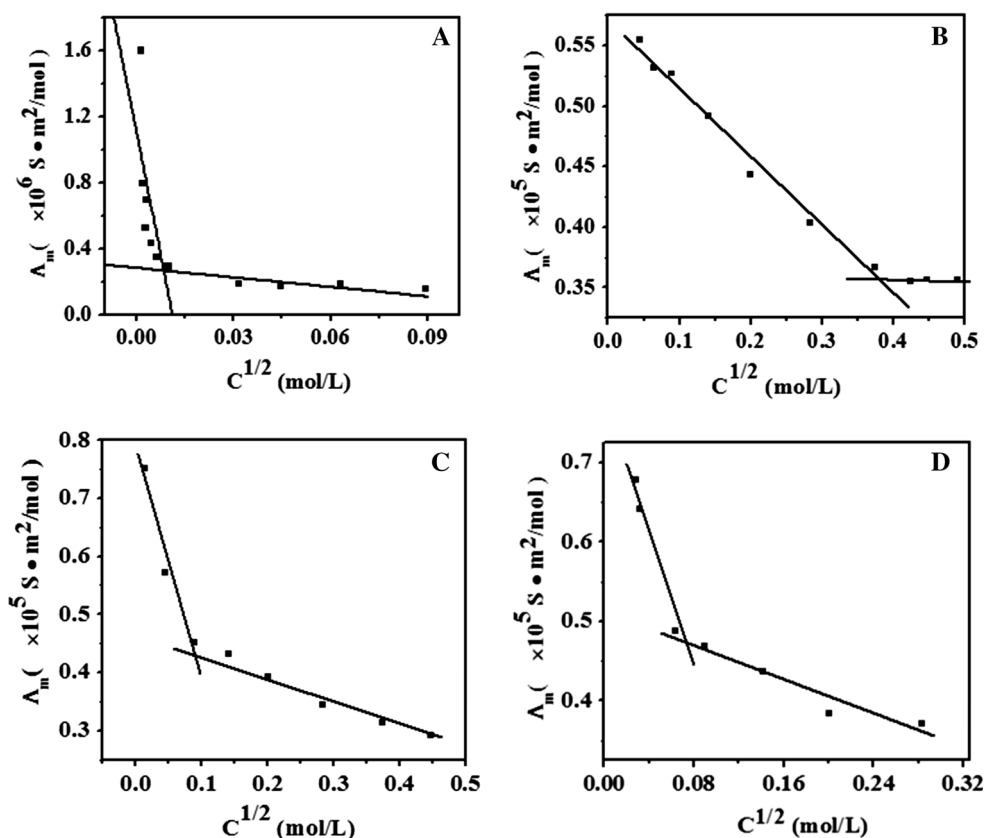
Figure 5 shows the TGA curves of the synthesized fluorinated surfactants. Four novel fluorinated surfactants show
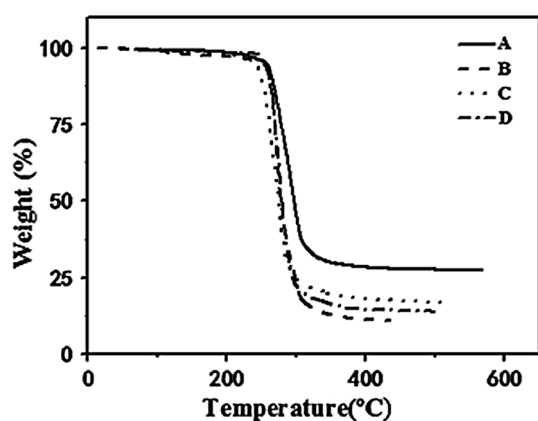
Fig. 5 Thermal gravimetric analysis (TGA) thermograms of the succinic acid double-tailed sulfonate fluorinated surfactants FEOS*-1 (**a**), FEOS*-2 (**b**), FEOS*-4 (**c**) and FEOS*-6 (**d**)

different levels of thermal stability respectively. The basic weight of the fluorine surfactants did not change under 200 °C, while FEOS*-1 began to decompose when the temperature reached 235 °C. With a further temperature increase, FEOS*-1 lost most of its weight (about 83 %) at 430 °C, which verified the surfactant possessed high-temperature resistance. The compounds FEOS*-2 and FEOS*-4 have high thermal decomposition temperatures, and began to decompose when the temperature reached about 248 °C.

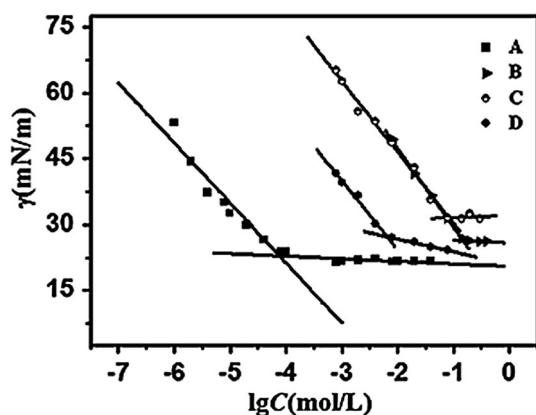FEOS*-2 had broken down 86 % at 438 °C, and the compound of FEOS*-4 showed 89 % decomposition when the temperature reached 432 °C. Therefore, the usage temperature of FEOS*-2 and FEOS*-4 should be controlled below 240 °C. As for product FEOS*-6, the quality of compounds did not change before 248 °C. However, it began to decompose, when the temperature heated to 445 °C (the surfactant had only 23 % left). From the data above, it could be concluded that all four double-tailed fluorine surfactants have thermal-stable properties and could be applied at relatively high temperature. [22, 23]

Surface Properties of Novel Succinic Acid Double-Tailed Sulfonate Fluorinated Surfactants

To investigate the surface properties of the double-tailed fluorinated surfactants, the CMC of FEOS*-6, FEOS*-4, FEOS*-2 and FEOS*-1 were measured by conductivity and are given in Fig. 6. The break points in the curves correspond to the CMC of the prepared fluorinated surfactants. The values of CMC for FEOS*-6, FEOS*-4, FEOS*-2 and FEOS*-1 were 0.0719, 5.42, 80.4 and 143.4 mmol L^{-1}, respectively. The CMC values decreased significantly with increasing -CF$_2$- in the hydrophobic chain. FEOS*-6 exhibited the lowest CMC value, indicating it had better surface properties than the others.

Fig. 6 Variation in the molar conductivity (Λm) with the FEOS*-6 (**a**), FEOS*-1 (**b**), FEOS*-2 (**c**), and FEOS*-4 (**d**) surfactant SQRT concentration at 25.0 ± 0.2 °C

Fig. 7 Surface tension *plots* of the FEOS*-6 (**a**), FEOS*-1 (**b**), FEOS*-2 (**c**), and FEOS*-4 (**d**) logarithm concentration at 25.0 ± 0.2 °C
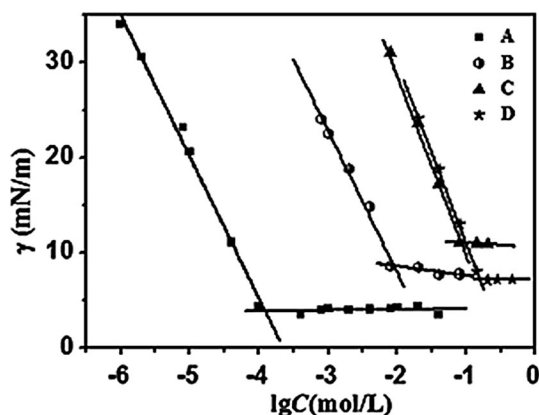
Fig. 8 Interfacial tension *plots* of the FEOS*-6 (**a**), FEOS*-4 (**b**), FEOS*-2 (**c**), and FEOS*-1 (**d**) logarithm concentration at 25.0 ± 0.2 °C

The surface tension (γ)-bulk concentration (C) dependencies for prepared fluorinated surfactants are presented in Fig. 7. No minimum was observed on the γ-lgC curves of the aqueous synthesized surfactants solution, indicating that there were no surface-active impurities in the products

[24]. The surface tension at the CMC of FEOS*-1, FEOS*-2, FEOS*-4 and FEOS*-6 is 26.50, 31.34, 25.43 and 21.63, respectively. In particular, the surface tension of FEOS*-6 has minimum surface tension, comparable to that of PFOA.

Figure 8 shows the interfacial tension of the prepared fluorinated surfactants in cyclohexane and a similar trend in interfacial tension is found in comparison with that of the surface tension. Compared to the interfacial tension of hydrogenated surfactants, perfluoro-surfactants possess higher interfacial tension and lower interfacial activity. For the prepared fluorinated surfactants, the ethoxyl group enhances the interfacial activity of the prepared fluorinated surfactants, hence widening the range of application.

The surface activities of the four novel succinic acid double-tailed sulfonate fluorinated surfactants at 25.0 ± 0.2 °C are summarized in Table 1, together with PFOA and succinic acid monofluoroalkyl sulfonate surfactant (FEOS-1) taken from the previous work [19]. From Table 1, the Krafft temperatures of the four novel succinic acid double-tailed sulfonate fluorinated surfactants are all below 0 °C. The γ_CMC values of FEOS*-4 and FEOS*-6 were close to those of PFOA and FEOS-1, while the CMC values of the former exhibited a lower CMC value and higher micelle forming ability than the latter due to the double-tail molecular structure. A similar tendency was displayed for the gemini-type surfactants and the corresponding mono-type surfactants prepared by Yoshino et al. [14] Our finding suggest that the double-tailed fluorinated surfactants may be good emulsifiers.

Conclusions

In summary, four novel environmentally friendly succinic acid double-tailed sulfonate fluorinated surfactants, FEOS*-n (n = 1, 2, 4, 6), were successfully synthesized. The properties of the synthesized fluorinated surfactants with those of succinic acid monofluoroalkyl sulfonate surfactant and PFOA were tested and all the synthesized fluorinated surfactants showed low Krafft points. The

Table 1 The Krafft points (Kp), CMC, γ_CMC, γ_jCMC, Γ_max, a_m^s, and ΔG of synthesized surfactants, PFOA and FEOS-1

Surfactants	K_p (°C)	CMC[a] (mmol L^{-1})	CMC[b] (mmol L^{-1})	γ_CMC (mN m^{-1})	γ_jCMC (mN m^{-1})	$10^{10}\Gamma_{max}$ (mol cm^{-2})	a_m^s (nm^2)	ΔG (kJ mol^{-1})
FEOS*-1	<0	143	149	26.50	7.14	4.20	0.40	−14.66
FEOS*-2	<0	80.4	84.1	31.34	10.94	3.78	0.44	−16.08
FEOS*-4	<0	5.42	6.45	25.43	7.68	2.26	0.73	−22.44
FEOS*-6	<0	0.071	0.076	21.63	4.03	1.23	1.35	−33.43
PFOA	<0	–	13.30	19.51	–	1.08	1.54	−20.64
FEOS-1	<0	–	10.25	25.55	–	1.15	1.45	−21.29

CMC[a] from conductivity, CMC[b] from surface tension; CMC, γ_CMC, and γ_jCMC at 25.0 ± 0.2 °C

surface tension values of the synthesized succinic acid double-tailed sulfonate fluorinated surfactants at the CMC were similar to those of FEOS-1 and PFOA, while the values of CMC were far less than that of the FEOS-1 and PFOA. In addition, the fluoroalkyl sulfonate surfactants were found to have excellent thermostability with starting equilibrium thermal degradation temperatures of 235 °C, which allows them to be applied at high temperatures. The synthesized novel fluorinated surfactants showed great potential to replace traditional long-chain perfluorinated surfactants due to their outstanding biodegradability. (Have you measured the biodegradability?)

References

1. Kissa E (1994) Fluorinated surfactants synthesis properties applications. Marcel Dekker, New York
2. Shinoda K, Hato M, Hayashi T (1972) Physicochemical properties of aqueous solutions of fluorinated surfactants. J Phys Chem 76:909–914
3. Kunieda H, Shinoda K (1976) Krafft points, critical micelle concentrations, surface tension, and solubilizing power of aqueous solutions of fluorinated surfactants. J Phys Chem 80:2468–2470
4. Kim CU, Lee JM, Ihm SK (1999) Emulsion polymerization of tetrafluoroethylene: effects of reaction conditions on the polymerization rate and polymer molecular weight. J Appl Polym Sci 73:777–793
5. Kostov G, Boschet F, Ameduri F (2009) Original fluorinated surfactants potentially non-bioaccumulable. J Fluorine Chem 130:1192–1199
6. Kawashima Y, Suzuki S, Kozuka H, Sato M, Suzuki Y (1994) Effects of prolonged administration of perfluorooctanoic acid on hepatic activities of enzymes which detoxify peroxide and xenobiotic in the rat. Toxicology 93:85–97
7. Badr MZ, Birnbaum LS (2004) Enhanced potential for oxidative stress in livers of senescent rats by the peroxisome proliferator-activated receptor alpha agonist perfluorooctanoic acid. MechAgeing Dev 125:69–75
8. Kannan K, Corsolini S, Falandysz J, Oehme G, Focardi S, Giesy JP (2002) Perfluorooctane sulfonate and related fluorinated hydrocarbons in marine mammals, fishes, and birds from coasts of the Baltic and the Mediterranean Seas. Environ Sci Technol 36:3210–3216
9. Taylor CK (1999) Fluorinated surfactants in practice. Annu Surfactants Rev 2:271–316
10. Krafft MP, Riess JG (2007) Perfluorocarbons, life sciences and biomedical uses. J Polym Sci A Polym Chem 45:1185–1198
11. Zaggia I, Ameduri F (2012) Recent advances on synthesis of potentially non-bioaccumulable fluorinated surfactants. J Fluorine Chem 17:188–195
12. Guittard F, Geribaldi S (2001) Highly fluorinated molecular organised systems: strategy and concept. J Fluorine Chem 107:363–374
13. Vierling P, Santaella C, Greiner J (2001) Highly fluorinated amphiphiles as drug and gene carrier and delivery systems. J Fluorine Chem 107:337–354
14. Ohno A, Kushiyama A, Kondo Y, Teranaka T, Yoshino N (2008) Synthesis and properties of gemini-type hydrocarbon–fluorocarbon hybrid surfactants. J Fluorine Chem 129:577–582
15. Guo W, Li Z, Fung BM, O'Rear EA, Harwell JH (1992) Hybrid surfactants containing separate hydrocarbon and fluorocarbon chains. J Phys Chem 96:6738–6742
16. Yoshino N, Hamano K, Omiya Y, Kondo Y, Ito A, Abe M (1995) Syntheses of hybrid anionic surfactants containing fluorocarbon and hydrocarbon chains. Langmuir 11:466–469
17. Miyazawa H, Kondo Y, Yoshino N (2005) Synthesis and solution properties of sulfate-type hybrid surfactants with an ethylene spacer. J Oleo Sci 54:167–178
18. Kondo Y, Yokochi E, Mizumura S, Yoshino N (1998) Synthesis of novel fluorocarbon surfactants with oxyethylene groups. J Fluorine Chem 91:147–151
19. Zhang LQ, Shi JH, Xu AH, Geng B, Zhang SX (2013) Synthesis and surface activities of novel succinic acid monofluoroalkyl sulfonate surfactants. J Surfact Deterg 16:183–190
20. Wang Q, Zhang SX, Geng B, Zhang LQ, Zhao JQ, Shi JH (2012) Synthesis and surface activities of novel monofluoroalkyl phosphate surfactants. J Surfactants Deterg 15:83–88
21. Rosen MJ (2004) Surfactants and interfacial phenomena. Wiley, New York
22. Pabon M, Corpart JM (2002) Fluorinated surfactants: synthesis, properties, effluent treatment. J Fluorine Chem 114:149–156
23. Krafft MP, Riess JG (2009) Chemistry, physical chemistry, and uses of molecular fluorocarbon–hydrocarbon diblocks, triblocks, and related compounds unique "apolar" components for self-assembled colloid and interface engineering. Chem Rev 109:1714–1792
24. Xiao JX, Zhao ZG (2003) Application principle of surfactants. Chemical Industry Press, Beijing

Luqing Zhang received his B.Sc. (2007) and M.Sc. (2010) in chemical engineering from the University of Jinan. He is currently a D.Sc. candidate in chemical engineering at the University of Jinan.

Bing Geng is an associate Professor of Chemical and Materials Engineering at the University of Jinan. He received his B.Sc. (1997) from the East China University of Science and Technology, China, and M.Sc. (2003) from the University of Jinan. In 2010, he obtained his Ph.D. in Chemical Engineering from the Beijing University of Chemical Technology.

Quanxuan Lu received his B.Sc. (2013) in chemical engineering from the University of Jinan, China. He is currently an M.Sc. candidate in chemical engineering at the University of Jinan.

Anhou Xu is a lecturer of chemical and materials engineering at the University of Jinan. He received his B.Sc. (2002) from the University of Jinan, China, and his M.Sc. (2005) from the University of Jinan. In 2011, he obtained his Ph.D. in chemical engineering from the Shanghai Jiao Tong University.

Shuxiang Zhang is a professor of chemical and materials engineering at the University of Jinan. He received his B.Sc. (1982) from the Shandong University, China, and his Ph.D. (1997) in chemical engineering from the Beijing University of Chemical Technology, China. His research focuses on fundamental and applied characteristics of fluorinated surfactants and fluorine-containing polymers in industrial and environmental applications. He now leads the study team at Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials (University of Jinan).