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ORIGINAL ARTICLE

Synthesis and Surface Activities of Novel Monofluoroalkyl Phosphate Surfactants

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Abstract Two novel environmentally friendly fluorinated surfactants, disodium monofluoroalkyl phosphates were synthesized using phosphorus pentoxide, i.e. $H(CF_2)_6CH_2OPO(ONa)_2$ and $H(CF_2)_6CH_2OCH_2CH_2OPO(ONa)_2$. The novel synthesized fluorinated surfactants have a high thermal stability on the basis of Thermogravimetric Analysis. Their surface properties were also examined with the aim to have similar surface tensions of dilute aqueous solutions when compared with the conventional fluorocarbon surfactants, ammonium perfluorooctanoate. The two synthesized monofluoroalkyl phosphates can respectively reduce the surface tension of water to 23.73 mN/m at 78.3 mmol/L and 21.38 mN/m at 20.93 mmol/L. In addition, the Krafft points are both below 0 °C.

Keywords 1H,1H,7H-dodecafluoroheptanol · Ethylene glycol mono(1H,1H,7H-dodecafluoroheptyl) · Monofluoroalkyl phosphates · Novel fluorinated surfactants · Surface tension

Abbreviation

PFOA	Ammonium perfluorooctanoate

Introduction

Fluorinated surfactants with a fluorocarbon chain as a hydrophobic group reduce the surface tension of water and form micelles at concentrations lower than those for the corresponding hydrocarbon surfactants [1]. Their outstanding chemical and thermal stability expands their applications to extreme conditions which are too severe for hydrocarbon surfactants [2–4]. Yet, they still have shortcomings that need to be overcome, such as their high price and potential environmental hazard. It has been demonstrated recently that perfluorooctanoate of ammonium (PFOA) displayed ubiquity, animal-based toxicity, and some associations with human health [5–7]. With the rising of public awareness for environment protection and extensive attention internationally to biodegradability of the fluorinated surfactants, the use of long-chain ($\geq C_8$) perfluorinated surfactants will be evidently forbidden in future [8].

Because fluorinated surfactants play a very important role in preparation of high performance fluorinated material, exploring novel fluorocarbon surfactants with a good environmental protection function is an important thesis for research workers. There are many research protocols proposed in the literatures, and one of which is that long carbon–fluorine chains of traditional fluorinated surfactants are “diluted” with hydrocarbon chains [9]. While the hydrocarbon content rises in these hybrid surfactants, they still keep the high surface tension lowering ability, characteristic of fluorinated surfactants.

Based on the above points, we expected to synthesize novel fluoroalkyl phosphate surfactants which contain short carbon–fluorine chains. Because phosphate surfactants can show outstanding properties, such as excellent wetting, thermal stability, alkali resistance and antistatic property [10]. What is more, the phosphate surfactants have reduced

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environmental presence of the surfactants themselves because of expected facile biodegradation [11].

This article reports the synthesis of two novel fluoroalkyl phosphate surfactants, disodium mono (dodecafluoroheptyl) phosphate and disodium mono (dodecafluoroheptyl oxyethyl) phosphate, in which single dodecafluoroheptyl acted as a fluorophilic segment, with the aim of obtaining such fluorinated surfactants that are more environmentally friendly than the conventional long-chain perfluorinated surfactants. Comparisons are also made in the article of the surface chemical properties of the newly synthesized surfactants with ammonium perfluorooctanoate, PFOA. Moreover, the effect of the introduction of oxyethylene into the formula was also obtained.

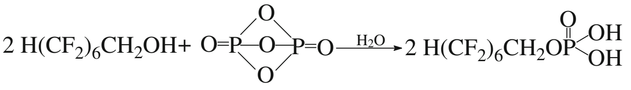
Experimental

Materials

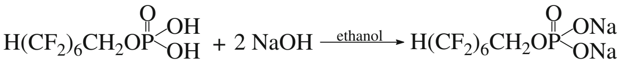
1H,1H,7H-dodecafluoroheptanol was purchased from the China Fluoro Technology Co., Ltd., Shandong China; phosphorus pentoxide was obtained from the Tianjin Chemical Reagent Factory Tianjin China; benzene and toluene were provided by the Tianjin Guangcheng Chemical Reagent Co., Ltd., Tianjin China; ethyl ether was purchased from the Tianjin Kermel Chemical Reagent Co., Ltd., Tianjin China, as well as ethanol and sodium hydroxide. All of those chemicals were analytical reagents (AR) and were used without further purification. Ethylene glycol mono(1H,1H,7H-dodecafluoroheptyl) ether was made by Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, whose purity is up to 96% above. Ammonium perfluorooctanoate, PFOA, was also prepared by Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials.

Synthesis of Disodium Mono(dodecafluoroheptyl) Phosphate

The disodium mono(dodecafluoroheptyl) phosphate was prepared from phosphorus pentoxide and alcohols in accordance with Eqs. 1 and 2.



(1)



$$H(CF_2)_6CH_2O\overset{O}{\overset{\|}{P}}\begin{smallmatrix}OH\\OH\end{smallmatrix} + 2\,NaOH \xrightarrow{\text{ethanol}} H(CF_2)_6CH_2O\overset{O}{\overset{\|}{P}}\begin{smallmatrix}ONa\\ONa\end{smallmatrix} \quad (2)$$

The acid mono(dodecafluoroheptyl) phosphate $H(CF_2)_6CH_2OPO(OH)_2$ was prepared according to methods described in US 2,597,702 [12]. Because of the simultaneous formation of dialkyl phosphates, the content of mono(dodecafluoroheptyl) phosphate in the mixture may be determined by titrimetric procedure [13]. Both organic phosphates and orthophosphoric acid were effectively removed by recrystallization. The finally purified acid mono(dodecafluoroheptyl) phosphate, $H(CF_2)_6CH_2O$-PO(OH), a white solid product, was obtained with a yield of 56.6% of the theoretical based upon the weight of alcohol consumed.

Enough sodium hydroxide/ethanol solution was added dropwise into the ethanol solution of the acid mono(dodecafluoroheptyl) phosphate with continuous stirring for about 2 h. The solid precipitate was collected by vacuum filtration, and then the product was dried in an environment of 50 °C in the vacuum drying oven. The disodium mono(dodecafluoroheptyl) phosphate, a faint yellow solid powder, was finally obtained.

Synthesis of Disodium Mono(dodecafluoroheptyl oxyethyl) Phosphate

The disodium mono(dodecafluoroheptyl oxyethyl) phosphate was synthesized according to the preparation method of disodium mono(dodecafluoroheptyl) phosphate as detailed above, which just used ethylene glycol mono(1H,1H,7H-dodecafluoroheptyl) ether as corresponding fluorine-containing alcohol.

The disodium mono(dodecafluoroheptyl oxyethyl) phosphate was obtained finally, a yellow solid or powder, with a yield 60.5% of theoretical based upon the weight of alcohol consumed.

Characterizations

Fourier transform infrared spectra (FT-IR) on the novel surfactants were performed with the Bio-Rad FTS165 at ambient temperature. ^{1}H-, ^{19}F- and ^{31}P-nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker Avance 400 MHz instrument with tetramethylsilane as an internal standard, using deuteroxide (D_2O) as the solvent. The thermal stabilities of the synthesized fluorinated surfactants were studied by 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 at 50 mL/min.

Surface tension measurements were made at 25 °C on solutions of the synthesized surfactants by the ring method using a tensiometer K 100 (Krüss, Germany) in the following way. Aqueous surfactant stock solutions at given high concentrations were prepared using accurately weighed samples. Each of the stock solutions thus prepared was diluted successively with water to give sample solutions for measurement. The critical micelle concentration (CMC) values of the surfactants were determined from the break point of the γ versus lg$C$ plots.

Krafft point measurements were performed electroconductometrically using a DKK-TOA conductivity meter CM-60G on solutions at given high concentrations placed in a thermostat 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 [14]. The surface concentration, $\Gamma_{\max}$ can be obtained from the slope of a plot of γ versus lg$C$ at constant temperature, as Eq. 3.

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

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 γ is in mN/m. R is the gas constant [8.31 J/(mol K)], $\Gamma_{\max}$ is in mol/1,000 m^2, 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 angstroms is calculated from Eq. 4.

$$a_m^s = \frac{10^{14}}{N_A \Gamma_{\max}} \tag{4}$$

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

$$\Delta G = RT\ln\left(\frac{CMC}{55.5}\right) \tag{5}$$

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

Results and Discussion

Chemical Structure of Novel Monofluoroalkyl Phosphate Surfactants

Figures 1, 2, 3 and 4 show the ^{1}H-NMR, ^{19}F-NMR, ^{31}P-NMR and FT-IR spectra of the disodium mono(dodecafluoroheptyl) phosphate, respectively. ^{1}H NMR (D_2O): $\delta = 6.30$ ppm to $\delta = 6.58$ ppm (m, 1H, *a*), $\delta = 4.10$ ppm to $\delta = 4.19$ ppm (m, 2H, *b*), $\delta = 4.70$ ppm (solvent) for $H^a(CF_2)_6CH_2^bOPO(ONa)_2$; ^{19}F NMR ($D_2O$): $\delta = -138.2$ ppm (s, 2F, *a*), $\delta = -129.9$ ppm (s, 2F, *b*), $\delta = -123.7$ ppm (s, 4F, *c* and *d*), $\delta = -122.4$ ppm (s, 2F, *e*), $\delta = -121.0$ ppm (s, 2F, *f*) for $H(CF_2^aCF_2^bCF_2^cCF_2^dCF_2^e{-}CF_2^f)CH_2OPO(ONa)_2$; ^{31}P NMR ($D_2O$): $\delta = -1.89$ ppm for the only phosphorus atoms in the targeted product; IR (KBr): 2,956 (ν_{C-H}), 1,444 (δ_{C-H}), 1,120 (ν_{C-F}), 1,174 (ν_{P-O-C}), 1,263 ($\nu_{P=O}$), 1,056 (ν_{P-ONa}).

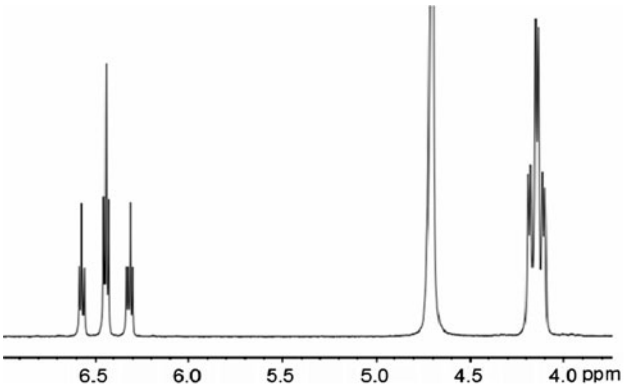


Fig. 1 ^{1}H-NMR spectra of the disodium mono(dodecafluoroheptyl) phosphate

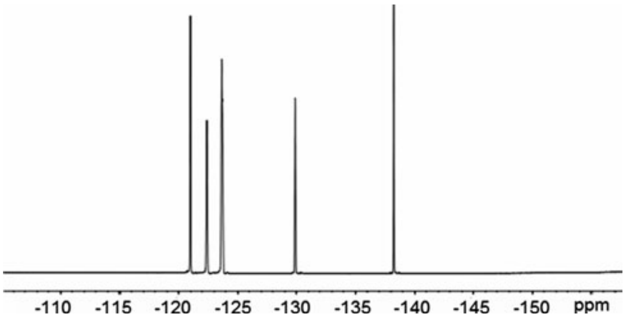


Fig. 2 ^{19}F-NMR spectra of the disodium mono(dodecafluoroheptyl) phosphate

Figures 5, 6, 7 and 8 show the ^{1}H-NMR, ^{19}F-NMR, ^{31}P-NMR and FT-IR spectra of the disodium mono(dodecafluoroheptyl oxyethyl) phosphate, respectively. ^{1}H NMR (D_2O): $\delta = 6.32$ ppm to $\delta = 6.57$ ppm (m, 1H, *a*), $\delta = 4.08$ ppm to $\delta = 4.16$ ppm (m, 2H, *b*), $\delta = 3.76$ ppm (m, 4H, *c* and *d*), $\delta = 4.70$ ppm (solvent) for $H^a(CF_2)_6CH_2^bOCH_2^c{-}\ CH_2^dOPO(ONa)_2$; ^{19}F NMR ($D_2O$): $\delta = -138.2$ ppm (s, 2F, *a*), $\delta = -129.9$ ppm (s, 2F, *b*), $\delta = -123.8$ ppm (s, 4F, *c* and *d*), $\delta = -122.5$ ppm (s, 2F, *e*), $\delta = -120.1$ ppm (s, 2F, *f*) for $H(CF_2^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^f)CH_2OCH_2CH_2OPO(ONa)_2$; ^{31}P NMR ($D_2O$): $\delta = -1.83$ ppm to $\delta = -1.90$ ppm for the only phosphorus atoms in the targeted product; IR (KBr): 2,946 (ν_{C-H}), 1,444 (δ_{C-H}), 1301 (ν_{C-O-C}), 1,136 (ν_{C-F}), 1,198 (ν_{P-O-C}), 1,263 ($\nu_{P=O}$), 1,041 (ν_{P-ONa}).

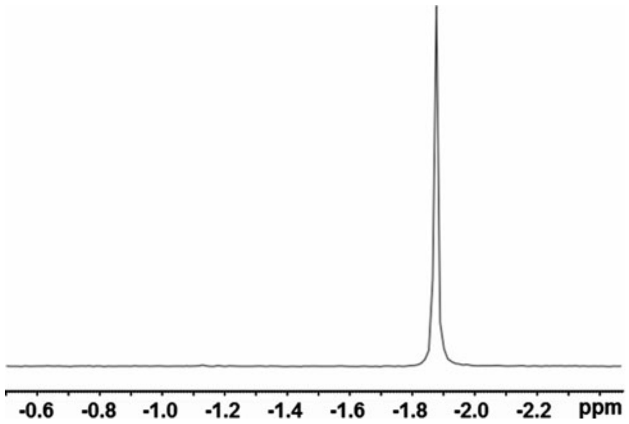


Fig. 3 ^{31}P-NMR spectra of the disodium mono(dodecafluoroheptyl) phosphate

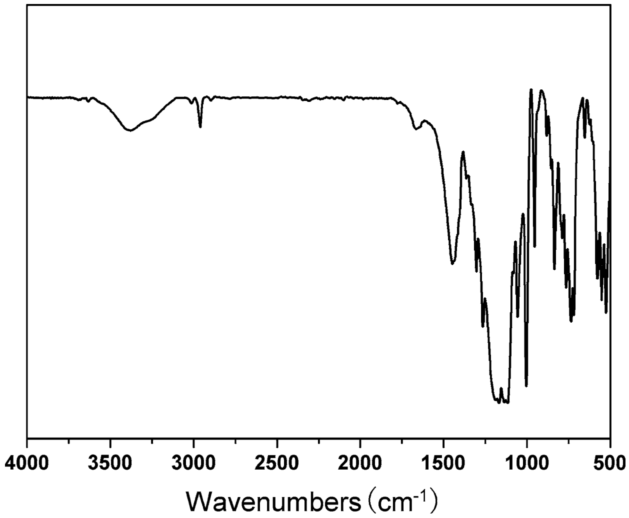


Fig. 4 FT-IR spectra of the disodium mono(dodecafluoroheptyl) phosphate

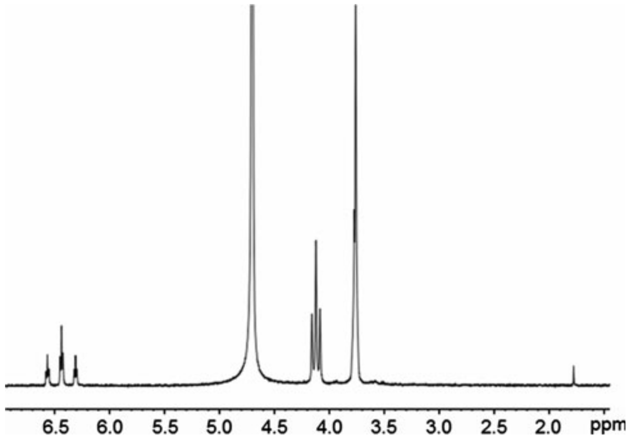


Fig. 5 ^{1}H-NMR spectra of the disodium mono(dodecafluoroheptyl oxyethyl) phosphate

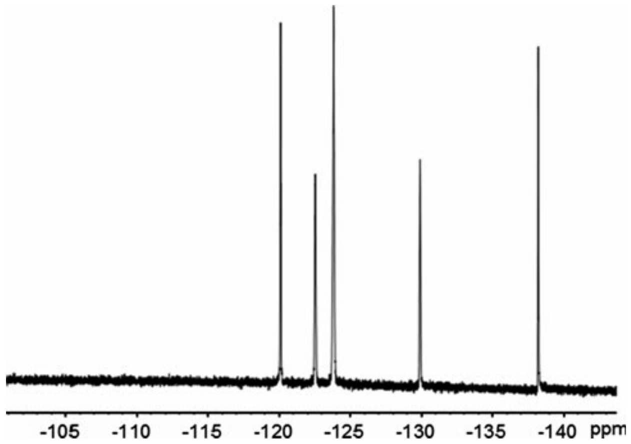


Fig. 6 ^{19}F-NMR spectra of the disodium mono(dodecafluoroheptyl oxyethyl) phosphate

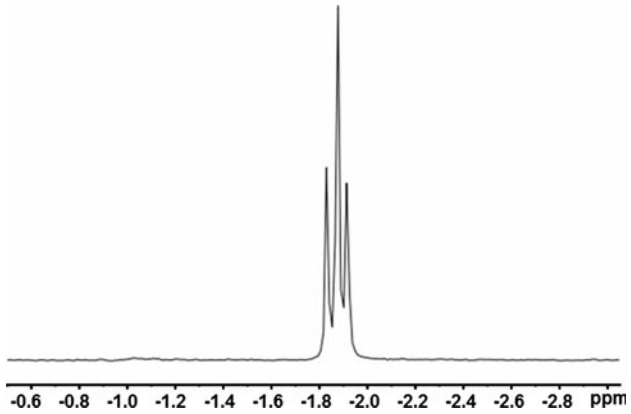


Fig. 7 ^{31}P-NMR spectra of the disodium mono(dodecafluoroheptyl oxyethyl) phosphate

Thermal Stabilities of Novel Monofluoroalkyl Phosphate Surfactants

Figure 9 shows the TGA curves of two novel synthetized surfactants. From the TGA curves, it can be seen that the disodium mono(dodecafluoroheptyl) phosphate begins to degrade at 280 °C and a rapid weight loss occurred at 300 °C attributed to the oxygenolysis of the sample. Finally, complete decomposition was at 350 °C, leaving only a mixture of sodium element oxides and phosphorus pentoxide. The disodium mono(dodecafluoroheptyl oxyethyl) phosphate begins to degrade at 230 °C and decomposes completely at about 320 °C, finally. Thermal stability characteristic of the disodium mono(dodecafluoroheptyl oxyethyl) phosphate is worse than that of the former, which may be caused by the introduction of the oxyethyl group into the molecule. In conclusion, the fluoroalkyl phosphate surfactants have good thermostability to be applied in relatively high temperature state.

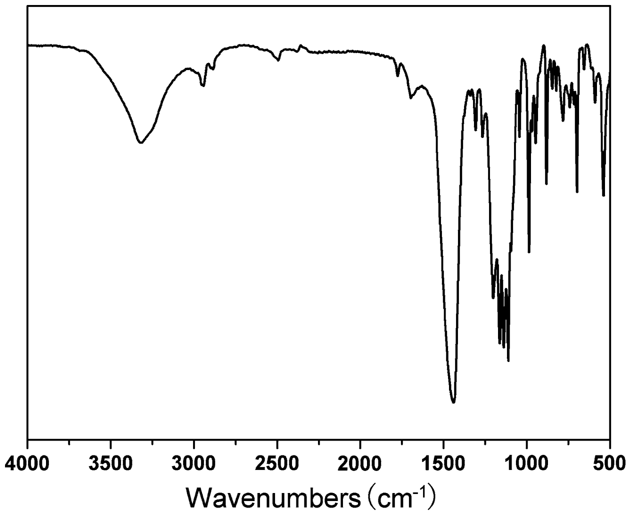


Fig. 8 FT-IR spectra of the disodium mono(dodecafluoroheptyl oxyethyl) phosphate

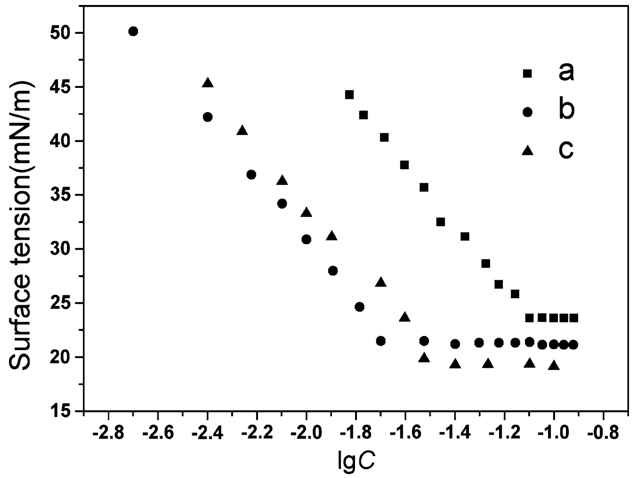


Fig. 10 Surface tension plots of disodium mono(dodecafluoroheptyl) phosphate (*a*), disodium mono(dodecafluoroheptyl oxyethyl) phosphate (*b*) and PFOA (*c*) against concentration at 25 °C

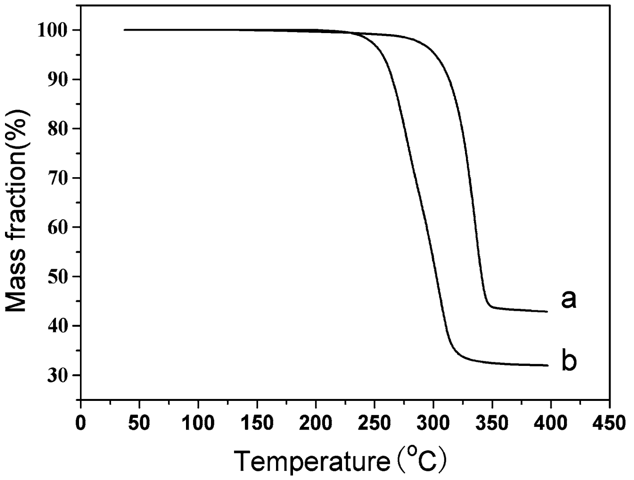


Fig. 9 TGA of the disodium mono(dodecafluoroheptyl) phosphate (*a*) and the disodium mono(dodecafluoroheptyl oxyethyl) phosphate (*b*)

Surface Properties of Novel Monofluoroalkyl Phosphate Surfactants

The surface tension (γ)-bulk concentration (C) dependencies for the studied compounds are presented in Fig. 10. No minimum was observed on the γ-lg$C$ curves of the aqueous synthesized surfactants solution, indicating that there were no impurities brought into our products [15]. Table 1 lists the aqueous surface activities of novel synthesized fluorinated surfactants, PFOA, together with n-$C_7F_{15}SO_3Na$ from the published work [16]. Comparisons of the properties of disodium monofluoroalkyl phosphates with PFOA show that the γ_{CMC} values of the two novel synthetized fluorinated surfactants are close to the that of PFOA, indicting that the two synthesized surfactants possess high surface activities. Both of the newly synthesized fluorinated surfactants have much lower γ_{CMC} than n-$C_7F_{15}SO_3Na$, whose γ_{CMC} is 37.3 mN/m, although all of them possess the same length of fluorocarbon chains.

The CMC of disodium mono(dodecafluoroheptyl) phosphate is a little higher than that of PFOA, which may be attributed to the introduction of a C–H bond into the fluorophilic segment. However, the CMC of disodium mono(dodecafluoroheptyl oxyethyl) phosphate is even lower than that of PFOA, mainly because the introduction of oxyethylene make the hydrophobic group of surfactant lengthen effectively.

The two novel monofluoroalkyl phosphates have outstanding water solubility and their Krafft points are both

Table 1 The Krafft points (K_p), CMC, γ_{CMC}, $\Gamma_{\max}$, a_m^s and ΔG of synthesized surfactants, PFOA and n-$C_7F_{15}SO_3Na$

Surfactants	K_p (°C)	CMC (mmol/L)	γ_{CMC} (mN/m)	$10^{10}\Gamma_{\max}$ (mol/cm^2)	a_m^s (nm^2)	ΔG (kJ/mol)
$H(CF_2)_6CH_2OPO(ONa)_2^a$	<0	78.3	23.73	2.46	0.67	−16.25
$H(CF_2)_6CH_2OCH_2CH_2OPO(ONa)_2^a$	<0	20.93	21.38	2.48	0.68	−19.52
PFOA[a]	<0	33.2	19.51	2.32	0.71	−18.39
n-$C_7F_{15}SO_3Na$	56.5	17.5	37.3	3.1	0.53	–

[a] CMC and γ_{CMC} at 25 °C

below 0 °C owing to the two hydrophilic groups of the surfactants.

Conclusions

Two novel fluorinated surfactants, disodium monofluoroalkyl phosphate [$H(CF_2)_6CH_2OPO(ONa)_2$] and disodium mono(dodecafluoroheptyl oxyethyl) phosphate [$H(CF_2)_6CH_2OCH_2CH_2OPO(ONa)_2$] were successfully obtained as a pale yellow solid or a powder. Studies of the properties of the synthesized fluorinated surfactant showed that the Krafft points are both below 0 °C and the values of surface tension at CMC (γ_{CMC}) are very close to that of PFOA. With the introduction of one mole of oxyethylene into the formula, the CMC of disodium mono(dodecafluoroheptyl oxyethyl) phosphate become lower than that of PFOA. In addition, the fluoroalkyl phosphate surfactants have good thermostability with a starting equilibrium thermal degradation temperature respectively at 250 and 300 °C to be applied under high temperature state. The synthesized fluorinated surfactants may be used as replacement of the traditional long-chain perfluorinated surfactants in order to help construction environment owing to their remarkable biodegradability.

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