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Surfactants having polyfluoroalkyl chains. II. Syntheses of anionic surfactants having two polyfluoroalkyl chains including a trifluoromethyl group at each tail and their flocculation-redispersion ability for dispersed magnetite particles in water

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Abstract

Anionic surfactants having two polyfluoroalkyl chains per molecule, i.e. the sodium salt of bis(1H, 1H, 2H, 2H-heptadecafluorodecyl)-2-sulfosuccinate, $CF_3(CF_2)_7(CH_2)_2OCOCH_2CH(SO_3Na)COO(CH_2)_2(CF_2)_7CF_3$, the sodium salt of bis(1H, 1H, 2H, 2H-tridecafluoro-octyl)-2-sulfosuccinate, $CF_3(CF_2)_5(CH_2)_2OCOCH_2CH(SO_3Na)COO(CH_2)_2(CF_2)_5CF_3$, and the sodium salt of bis(1H, 1H, 2H, 2H-nonafluorohexyl)-2-sulfosuccinate, $CF_3(CF_2)_3(CH_2)_2OCOCH_2CH(SO_3Na)COO(CH_2)_2(CF_2)_3CF_3$, have been prepared from maleic anhydride, the corresponding alcohols possessing a polyfluoroalkyl chain and sodium hydrogen sulfite. The flocculation and redispersion abilities of these surfactants for dispersed magnetic particles in water have been examined to investigate the effect of the chain length. It was found that this ability was enhanced by an increase in the chain length. The contact angles for water for pelleted surface-modified magnetite have been measured. In order to compare this ability and the contact angles, data for other fluorinated surfactant have been obtained. The Krafft point, the surface tension and the pNa of the aqueous surfactant solutions have also been measured.

Keywords: Anionic surfactants; Syntheses; Flocculation-redispersion ability; Magnetite particles; Contact angles; Krafft points; Surface tension

1. Introduction

We have reported previously that anionic surfactants having two polyfluoroalkyl chains in a molecule have high flocculation and redispersion abilities for dispersed magnetite particles in water [1]. In this respect, the ability of the sodium salt of bis(1H, 1H, 2H, 2H)-heptadecafluorodecyl)-2-sulfosuccinate, CF₃(CF₂)₇(CH₂)₂-OCOCH₂CH(SO₃Na)COO(CH₂)₂(CF₂)₇CF₃ (1), was 25-times greater than that of a surfactant with a single polyfluoroalkyl chain containing a terminal CF₃ group, such as sodium pentadecafluoro-octanoate, CF₃(CF₂)₆COONa. These phenomena are assumed to be due to the differences in covering power of the surfactants on magnetite particles. In the case of 1, the molecule contains two spreading fluorocarbon chains in its structure. Thus, the surfactant was a very effective surface-active agent as far as its flocculation and redispersion abilities were concerned. This ability was also greater than those of surfactants containing terminal HCF₂ groups, such as $H(CF_2)_8CH_2OCO-CH_2CH(SO_3Na)COOCH_2(CF_2)_8H$, because the hydrophobicity of CF₃ is higher than that of the HCF₂ group (see Fig. 1 and Table 1).

This paper reports the results of the syntheses and characterizations of anionic surfactants having two polyfluoroalkyl chains containing terminal CF_3 groups, and the effect of the fluorocarbon chain length on the flocculation and redispersion abilities of such surfactants towards dispersed magnetite particles in water.

2. Results and discussion

Surfactants are known to change the surface properties of substances by adsorption. Fig. 1 shows the

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Fig. 1. Comparison of the flocculation and redispersion abilities towards magnetite particles of surfactants having polyfluoroalkyl chain(s). The Rf_a and Rf_b groups listed are for the compounds Rf_aCH₂OCOCH₂CH(SO₃Na)COOCH₂Rf_a and Rf_bCOONa, respectively. Some of the initial points for redispersion were difficult to measure (as shown by the arrows) because of the low solubility of these surfactants.

Table 1

Contact angles for water on surface-modified magnetite treated with surfactants possessing polyfluoroalkyl chain(s)

Surfactant ^a	Contact angle θ (°) of water
Untreated	0
$Rf_a = CF_3(CF_2)_7CH_2 -$	125
$Rf_a = CF_3(CF_2)_5CH_2 -$	102
$Rf_a = CF_3(CF_2)_3CH_2 -$	75
$Rf_a = H(CF_2)_8 -$	106
$Rf_a = H(CF_2)_6 -$	80
$Rf_a = H(CF_2)_4 -$	65
$Rf_b = CF_3(CF_2)_6 -$	119
$Rf_b = H(CF_2)_8 -$	95
$Rf_b = H(CF_2)_6 -$	71
$Rf_b = H(CF_2)_4 -$	64

"Rf_a and Rf_b groups listed are for the compounds Rf_a. CH₂OCOCH₂CH(SO₃Na)COOCH₂Rf_a and Rf_bCOONa, respectively.

regions of flocculation and redispersion of magnetite particles obtained on adding surfactant solutions at various initial concentrations, in comparison with other types of surfactants quoted in the literature [1]. At lower surfactant concentration, the magnetite particles flocculate with increasing surfactant concentration. However, the flocculated magnetite particles are redispersed as the surfactant concentration is increased further. It is concluded that the ability of surfactants with two polyfluoroalkyl chains with respect of flocculation-redispersion is greater than that of surfactants possessing a single polyfluoroalkyl chain, with surfactants having two polyfluoroalkyl chains with terminal CF_3 groups being particularly effective.

The results of the measurement of the contact angle for water with the modified magnetite samples are listed in Table 1. These samples were taken from the midpoint in each flocculation range and pelleted as reported in the literature [1]. Since the amount of adsorbed water associated with the untreated magnetite pellet falls too rapidly to allow the contact angle to be determined, the latter has been described as 0° in this case. With magnetite particles treated with a series of surfactants, the values of the contact angle were found to increase with the chain length of the surfactant.

In the case of surfactants possessing two polyfluoroalkyl chains, compound 1 exhibited the most effective flocculation ability, but its redispersion ability was not very different from that of the sodium salt of bis(1H,1H,2H,2H-tridecafluoro-octyl)-2-sulfosuccinate (2), as shown in Fig. 1. Although the flocculation abilities of 2 and of the sodium salt of bis(1H,1H,2H,2Hnonafluorohexyl)-2-sulfosuccinate (3) were almost the same, the redispersion ability of 2 was slightly superior to that of 3. As expected, the surfactant possessing the longer fluorocarbon chains exhibited a relatively higher flocculation-redispersion ability. The contact angle for water of the modified magnetite surface treated with $CF_3(CF_2)_6COONa$ was higher than that of 2. Flocculation-redispersion abilities were found to be influenced considerably by the covering power of the surfactants on the magnetite surface. A high ability for flocculation-redispersion was associated with high adsorption of the surfactant, as reported in the literature [1].

The Krafft points for the surfactants used are listed in Table 2. The Krafft point of the surfactant increased with increasing fluorocarbon chain length. A similar tendency has been noted for sodium perfluoroalkanoates [2].

Fig. 2 shows the relationship between surface tension and concentration for the surfactants at 30 °C. The surface tension of the surfactant possessing two $CF_3(CF_2)_7CH_2$ - groups was measured at 73 °C because of its high Krafft point as shown in Table 2. In each case, the surface tension decreased with increasing surfactant concentration and attained a constant value at an extremely small CMC (critical micelle concentration). The CMCs listed in Table 3 are considerably smaller than for other fluorinated surfactants such as sodium perfluoroalkanoates [2] and sodium ω -perfluoropropylalkyl sulfonates [3]. In addition, the CMCs increase with a decrease in the fluorocarbon chain length. Moreover, the area of a surfactant molecule at the air/water interface obtained according to the method

Table 2 Kraft points of surfactants possessing two polyfluoroalkyl chains

Surfactant	Krafft point (°C)	
$Rf_a = CF_3(CF_2)_7 CH_2 -$	72	
$Rf_{*} = CF_3(CF_2)_5CH_2$	26	
$Rf_a = CF_3(CF_2)_3CH_2 -$	< 0	



Fig. 2. Plot of surface tension vs. concentration for surfactants having two polyfluoroalkyl chains at temperatures above their Krafft point. \Box : Rf_a = CF₃(CF₂)₇CH₂- at 73 °C; \triangle : Rf_a = CF₃(CF₂)₅CH₂- at 30 °C; and \bigcirc : Rf_a = CF₃(CF₂)₃CH₂- at 30 °C.

Table 3

CMCs of surfactants possessing two polyfluoroalkyl chains at temperatures above their Krafft points

Surfactant	CMC $(\times 10^{-5} \text{ mol } 1^{-1})$
$Rf_a = CF_3(CF_2)_7 CH_2 -$	1.0 (73 °C)
$Rf_a = CF_3(CF_2)_5CH_2 -$	4.5 (30 °C)
$Rf_a = CF_3(CF_2)_3CH_2 -$	72 (30 °C)

Table 4

Area of surfactant molecule at the air/water interface

Surfactant	Å ² molecule ⁻¹
$Rf_a = CF_3(CF_2)_7 CH_2 -$	98.1 (73 °C)
$Rf_a = CF_3(CF_2)_5CH_2$	83.3 (30 °C)
$Rf_a = CF_3(CF_2)_3CH_2 -$	38.1 (30 °C)

Table 5

Degree of ionic dissociation of micelle (α) for surfactants possessing two polyfluoroalkyl chains at temperatures above their Krafft points

Surfactant	α
$Rf_a = CF_3(CF_2)_7CH_2 - Rf_a = CF_4(CF_2)_7CH_2 - Rf_a = CF_4(F_2)_7CH_2 - Rf_4(F_2)_7CH_2 - Rf_4(F_2)_7CH_2$	1.0 (73 °C) 1.0 (30 °C)
$Rf_a = CF_3(CF_2)_3CH_2 -$	0.92 (30 °C)

of Yokoyama et al. [4] from surface tension vs. concentration curves, decreases with decreasing fluorocarbon chain length as shown in Table 4.

The degrees of ionic dissociation of the surfactant micelles as determined by pNa measurements are shown in Table 5. The value of the degree of ionic dissociation

for micelles of surfactants possessing two fluorocarbon chains is almost 1.00, indicating complete dissociation despite the micellar states involved. This is very different from anionic hydrocarbon surfactants such as sodium 3,6,9-trioxaeicosanoate, $C_{11}H_{23}O(CH_2CH_2O)_2CH_2CO-ONa$, [5] and sodium dodecyl sulfate [6].

In conclusion, the abilities of the anionic surfactants possessing two polyfluoroalkyl chains towards flocculation and redispersion of magnetite particles in water are superior to those of surfactants possessing one polyfluoroalkyl chain per molecule. In particular, the sodium salt of bis(1H, 1H, 2H, 2H-heptadecafluorodecyl)-2-sulfosuccinate, which has two terminal CF₃ groups, proved to be the most effective surface-active agent. Furthermore, surfactants possessing two polyfluoroalkyl chains showed good surface activities such as reduction of surface tension, low CMCs and high degrees of ionic dissociation of the micelle.

3. Experimental details

3.1. Materials

The sodium salt of bis(1H, 1H, 2H, 2H)-heptadecafluorodecyl)-2-sulfosuccinate (1) was obtained as described previously [1]. 2H,2H-Tridecafluoro-octanoic acid, CF₃(CF₂)₅CH₂COOH, was donated by Daikin Industries, Ltd. 1H, 1H, 2H, 2H-Tridecafluoro-1-octanol, $CF_3(CF_2)_5(CH_2)_2OH$ (b.p. 63 °C/5.5 mmHg) was prepared by reduction of 2H, 2H-tridecafluoro-octanoic acid with aluminium lithium hydride. 1H, 1H, 2H, 2H-Nonafluoro-1-hexanol, CF₃(CF₂)₃(CH₂)₂OH (b.p. 124 °C) was purchased from PCR Inc. These alcohols were purified by distillation and their purity checked by gas chromatography; no impurities were detected. Reagent grade maleic anhydride (b.p. 63-65 °C/5.0 mmHg) and solvents (toluene, 1,4-dioxane and tetrahydrofuran (THF)) were obtained commercially and purified by distillation. p-Toluenesulfonic acid, sodium hydrogen sulfite, iron(II) chloride and iron(III) chloride were used without further purification. Magnetite particles were made by the method of Shimoiizaka et al. [7], the average particle size being 109 Å (as determined by light scattering).

3.2. Measurements and instruments

FT-IR spectra were measured using a liquid film or the KBr method employing a JEOL JIR-5300 spectrophotometer. Each spectrum was recorded at a resolution of 4 cm⁻¹ with a total of 30 scans. Pulsed Fourier transform 100-MHz ¹H NMR spectra were run in 1,1,2-trichloro-1,2,2-trifluoroethane (F-113) or trifluoroacetic acid with TMS as an internal standard using a JEOL JNR-PX-100 spectrometer at room temperature. Gas chromatography was performed with a

Hitachi 663-30 [G-100 (40 m) column, film thickness 2.0×10^{-6} m, i.d. 1.2 mm, FID] and the intensities measured with a Hitachi D-2500 chromato integrator. The centrifuge was used with a Hitachi himac CR20B2 instrument (10 000 rpm, 10 min at 20 °C). Light scattering measurements were run with Malvern Co. 4700 Submicron Particle Analyzer (argon laser, 4 W, 488 nm). Ultrasonic operations were carried out using a Branson Ultrasonics Corporation model 250 Sonifier Cell Disruptor System (200 W, 20 kHz). The contact angle θ (°) was measured at 23 °C with an Elma-Kougaku Co. Gonio type apparatus. Krafft points were measured with a Rigaku 8240 type high-sensitivity differential scanning calorimeter (DSC). The surface tension was measured with a Kyowa model CBVP-A3 Wilhelmytype surface tensiometer. The pNa value of aqueous solution was measured with a Corning M-130 type pH meter with a Na-glass electrode (Corning Co., A017NA).

3.3. Syntheses of bis(polyfluoroalkyl) maleates

Synthesis of bis(1H,1H,2H,2H-tridecafluoro-octyl) maleate

A mixture of 1H, 1H, 2H, 2H-tridecafluoro-1-octanol (10.0 g, 27.5 mmol), maleic anhydride (1.22 g, 12.4 mmol) and p-toluenesulfonic acid monohydrate (0.23 g, 2.8 mmol) as catalyst in 50 cm^3 of toluene was refluxed with stirring at 110 °C for 15 h. During the reaction, the water liberated was removed azeotropically from the reaction system in order to shift the equilibrium position of the esterification reaction. The reaction was completed when 90% or more of the theoretical water had been formed. After reaction, the mixture was cooled to 70 °C and washed with water at 70 °C to remove p-toluenesulfonic acid and unreacted maleic anhydride. Bis(1H,1H,2H,2H-tridecafluoro-octyl) maleate was obtained as a colorless liquid by fractional distillation (yield 8.08 g, 80.6%); b.p. 133-135 °C/0.08 mmHg. IR (cm⁻¹): 3064; 2978; 2918; 1740; 1653; 1558; 1541; 1504; 1457; 1385; 1365; 1340; 1319; 1211; 1146; 1082; 1007; 914; 897; 895; 843; 810; 781; 733; 708; 698; 652; 633; 606; 567; 532; 436. ¹H NMR (in F-113) δ : 2.54 (4H, t(t), J = 18.3 (6.6) Hz, CH₂CF₂); 4.48 (4H, t, J = 6.6 Hz, OCH_2 ; 6.22 (2H, s, CH) ppm. MS (*m*/*z*) (rel. int.): 808 (0.8) $[M]^+$; 789 (0.6) $[M-F]^+$; 539 (0.6) $[M - C_5F_{11}]^+$; 445 (4.3) $[M - C_8F_{17}CH_2CH_2O]^+$; 99 (100) $[COCH=CHCOO+H]^+$.

Synthesis of bis(1H,1H,2H,2H-nonafluorohexyl) maleate

Procedures and purification techniques were virtually the same as those for the synthesis of bis(1H, 1H, 2H, 2H)tridecafluoro-octyl) maleate. Bis(1H, 1H, 2H, 2H)-nonafluorohexyl) maleate was obtained by the reaction of 1H, 1H, 2H, 2H-nonafluoro-1-hexanol (25.0 g, 94.7 mmol), maleic anhydride (4.20 g, 43.0 mmol) and ptoluenesulfonic acid monohydrate (1.60 g, 8.6 mmol) in 150 cm³ of toluene at 110 °C for 15 h. A colorless liquid product (16.1 g, yield 61.5%) was obtained; b.p. 114–115 °C/0.08 mmHg. IR (cm⁻¹): 3064; 2980; 2916; 1736; 1647; 1464; 1410; 1387; 1358; 1301; 1200; 1130; 1080; 1024; 1022; 1009; 930; 879; 850; 829; 754; 752; 748; 719; 712; 648; 594; 528; 488; 463; 436. ¹H NMR (in F-113) δ : 2.50 (4H, t(t), *J*=18.6 (7.1) Hz, CH₂CF₂); 4.41 (4H, t, *J*=7.1 Hz, OCH₂); 6.14 (2H, s, CH) ppm. MS (*m*/*z*) (rel. int.): 608 (1.0) [M]⁺; 589 (0.5) [M-F]⁺; 439 (0.7) [M-C₃F₇]⁺; 345 (3.8) [M-C₆F₁₃CH₂-CH₂O]⁺; 99 (100) [COCH=CHCOO+H]⁺.

3.4. Syntheses of surfactants having two polyfluoroalkyl chains

Synthesis of the sodium salt of bis(1H,1H,2H,2Htridecafluoro-octyl)-2-sulfosuccinate (2)

To a stirred clear solution of bis(1H,1H,2H,2Htridecafluoro-octyl) maleate (5.00 g, 6.2 mmol) in 85 cm³ of 1,4-dioxane was added 30 cm³ of aqueous sodium hydrogen sulfite solution (0.3 M) at 50 °C. The mixture was refluxed with stirring until foam began to appear after about 10-15 h. The reaction temperature was held at 98 °C for about 30-40 h. The white solid product precipitated was separated from the reaction mixture through a sintered glass disk, washed with 50 cm³ of hot (50 °C) 1,4-dioxane on the disk to remove unreacted bis(1H,1H,2H,2H-tridecafluoro-octyl) maleate. The product was dispersed ultrasonically in 50 cm³ of water. This colloidal dispersion was separated by centrifugation and the upper aqueous layer was decanted off to remove excess sodium hydrogen sulfite. Purification by water washing/centrifugation was repeated three times or more. Products free from sodium hydrogen sulfite were washed with 100 cm³ of THF on a sintered glass disk to remove water. A white powder, 2, was obtained after vacuum drying (yield 3.42 g, 60.5%); m.p. 278 °C. IR (cm^{-1}) : 2980; 2970; 2939; 2927; 2877; 2854; 1734; 1684; 1653; 1576; 1558; 1541; 1506; 1473; 1458; 1236; 1209; 1146; 1053; 654; 418. ¹H NMR (in CF₃COOH) δ: 2.62 (4H, t(broad), J = 19.0 Hz, a and f); 3.46 (2H, broad, c); 4.65 (5H, broad, b, d and e) ppm for C_6F_{13} -CH₂^aCH₂^bOCOCH₂^cCH^d(SO₃Na)COOCH₂^cCH₂^fC₆F₁₃. Elemental analysis: Found: C, 26.19; H, 1.29%. Calc. for C₂₀H₁₁O₇F₂₆SNa: C, 26.33; H, 1.22%.

Synthesis of the sodium salt of bis(1H,1H,2H,2Hnonafluorohexyl)-2-sulfosuccinate (3)

Synthetic methods and purification techniques were virtually the same as those for the preparation of 2. Compound 3 was obtained by the reaction of bis(1H, 1H, 2H, 2H-nonafluorohexyl) maleate (7.00 g, 11.5 mmol) in 100 cm³ of 1,4-dioxan with aqueous sodium hydrogen sulfite [1.80 g (17.3 mmol) in 30 cm³ of water] at 98 °C for 40 h. Compound 3 was obtained as a white powder (5.03 g, yield 61.5%); m.p. 270 °C. IR (cm⁻¹): 2964; 2942; 2872; 2927; 2871; 2858; 1738;

1651; 1622; 1558; 1541; 1460; 1456; 1417; 1358; 1227; 1136; 1084; 1051; 879; 823; 822; 754; 750; 721; 648; 615; 526; 442; 418. ¹H NMR (in CF₃COOH) δ : 2.64 (4H, t(broad), J = 19.0 Hz, a and f); 3.48 (2H, broad, c); 4.63 (5H, broad, b, d and e) ppm for C₄F₉-CH₂^aCH₂^bOCOCH₂^cCH^d(SO₃Na)COOCH₂^eCH₂^fC₄F₉. Elemental analysis: Found: C, 26.87; H, 1.54%. Calc. for C₁₆H₁₁O₇F₁₈SNa: C, 26.98; H, 1.56%.

3.5. Measurement of the flocculation ability

It was confirmed that ultrasonically dispersed magnetite particles in water were not sedimented and that the colloidal precipitate did not appear for 3 d or more, as reported in the previous paper [1]. Surfactant adsorption was achieved by ultrasonic irradiation (200 W, 20 kHz, 15 min) of the magnetite particles (0.100 g) in 40 cm³ of an aqueous solution of the surfactants at various concentrations. The flocculation and redispersion abilities of the surfactants for magnetite particles were observed after allowing the latter to stand for 24 h at room temperature.

3.6. Measurement of contact angles of water on surface-modified magnetite

The surface wettabilities of the modified magnetite were evaluated by measurement of the contact angle θ (°) for water on the pelleted magnetite. Pellets for measurement of the contact angle were prepared as described previously [1]. Contact angles were measured using water drops 1.0×10^{-6} dm³ in volume. Contact angles were evaluated by extrapolating a plot of advancing contact angle θ (°) vs. time to time zero [8].

3.7. Measurement of the Krafft point

DSC experiments to measure the Krafft points were carried out with the apparatus mentioned above by placing the surfactants containing a given amount of water in a high-pressure crucible and heating from -20 °C to 90 °C at a heating rate of 1.0 °C min⁻¹.

3.8. Measurement of the surface tension

The surface tension was measured using aqueous solutions of the surfactants at various concentrations.

3.9. Measurement of the pNa value

The pNa value was measured using aqueous solutions of the surfactants at various concentrations. The degree of ionic dissociation of the surfactant micelle was obtained as in previous papers [5,6].

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