

Syntheses of novel fluorocarbon surfactants with oxyethylene groups

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Abstract

Three anionic fluorocarbon surfactants with oxyethylene groups, sodium bis[2-(2-(perfluoroalkyl)ethoxy)ethyl] 2-sulfosuccinate $C_nF_{2n+1}-CH_2CH_2OCH_2CH_2OCOCH_2CH(SO_3Na)COOCH_2CH_2OCH_2CH_2C_nF_{2n+1}$ (*n*FEOS; *n* = 4, 6, or 8), were prepared from ethylene carbonate, maleic anhydride, corresponding alcohols having a polyfluoroalkyl chain, and sodium hydrogensulfite. The surfactants were highly water-soluble, and their Krafft points (K_p) were below 0°C. The K_p values of *n*FEOS were lower than those of conventional fluorocarbon surfactants, sodium bis[2-(perfluoroalkyl)ethyl] 2-sulfosuccinate $C_nF_{2n+1}CH_2CH_2OCOCH_2CH(SO_3Na)COOCH_2CH_2C_nF_{2n+1}$ (*n*FS; *n* = 4, 6, or 8). The surface tension at cmc (γ_{cmc}) of *n*FEOS showed very low values, and the cmcs of 4FEOS and 6FEOS were smaller by about one order of magnitude than those of *n*FS surfactants at the same fluorocarbon chain length *n*. It should be noted that the introduction of oxyethylene groups enhances the hydrophilicity and micellar forming ability of *n*FEOS compared to *n*FS. © 1998 Elsevier Science S.A. All rights reserved.

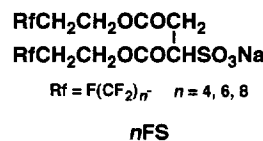
Keywords: Synthesis; Novel fluorocarbon surfactants; Oxyethylene groups

1. Introduction

Surfactants with fluorocarbon chains as a hydrophobic region exhibit (1) greater efficiency in reducing the surface tension of aqueous solutions, (2) high stability in chemicals and heat, and (3) surface activity, even for organic solvents such as alcohols and ethers, when compared to hydrocarbon surfactants [1,2]. Therefore, fluorocarbon surfactants have been vigorously applied as emulsifiers of paints, leveling agents for wax, oil fire extinguishing agents and surface modifiers for textiles [3–5]. Furthermore, fluorocarbon surfactants have been recently developed as vesicles or cumulative membranes [6,7].

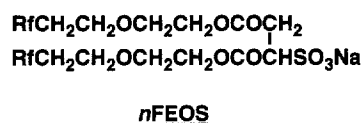
However, the hydrophilicity of fluorocarbon surfactants is generally poorer than that of hydrocarbon surfactants [8,9]. This feature has restricted the use of fluorocarbon surfactants for long time.

Previously, we synthesized double-tailed fluorocarbon surfactants (*n*FS) and reported that



the compounds have a great flocculation and redispersion ability on magnetite particles in water. However, these surfactants tend to exhibit a low solubility in water [10].

In this study, the introduction of oxyethylene units to conventional fluorocarbon surfactants has been attempted to enhance the hydrophilicity of the surfactants. We will report the syntheses of new surfactants (*n*FEOS), which



have two oxyethylene groups in a molecule, and will discuss their hydrophilicity and surface active properties in terms of Krafft points, surface tension, and critical micellar concentration (cmc).

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2. Experimental details

2.1. Materials

The fluorocarbon compounds $F(CF)_nCH_2CH_2OH$ ($n = 4, 6, \text{ or } 8$) were purchased from Daikin Industries, and used without further purification. Reagent grade maleic anhydride (Kanto Chemical) and ethylene carbonate (Nacalai Tesque) were used as received. Tetra-*n*-butylammonium iodide, *p*-toluenesulfonate monohydrate and sodium hydrogensulfite were purchased from Kanto Chemical and employed without further purification. Toluene (Kanto Chemical) was used after desulfurization with concentrated sulfuric acid, followed by dehydration by calcium hydride and then distilled. The reagent grade acetone, 1,4-dioxane and diethyl ether were commercially obtained and employed as received.

2.2. Measurements and instruments

FT-IR spectra were measured in a liquid film or using the KBr disk method with a Nicolet 510T-IR spectrophotometer. Pulse FT 1H -NMR (300 MHz) and ^{13}C -NMR (75 MHz) were run in $CDCl_3$ or trifluoroacetic acid (TFA) with TMS as an internal standard using a Bruker AC-300D spectrometer at room temperature. The FT mode 280 MHz ^{19}F -NMR was recorded at room temperature on a Bruker AC-300D in $CDCl_3$ or TFA with $CFCl_3$ as an external standard. The assignments of the ^{19}F -NMR spectra were based on spectra reported in other literature [11]. Mass spectra (MS) were measured (70 eV) with a Hitachi M-80A GC/MS spectrometer, and the data were analyzed with a Hitachi M003 data processing system. Gas chromatography (GLC) was performed on a Hitachi 063-30 (G-100 40 m column, film thickness 2.0×10^{-6} m, i.d. 1.2 mm, FID) and intensities were measured with a Hitachi D-2500 chromatointegrator.

The Krafft point was measured by the naked eye for each 1 wt.% aqueous solution of the surfactant. The surface tension (γ) was measured using the Wilhelmy method (KRÜSS surface tensiometer) with a platinum plate at 30°C. The micellar forming concentration (cmc) and the surface tension at the cmc (γ_{cmc}) were determined from the break point of each γ -surfactant concentration plots.

2.3. Synthesis of 2-[2-(perfluoroalkyl)ethoxy]ethanols (*n*FEOA)

2.3.1. 2-[2-(Perfluorobutyl)ethoxy]ethanol (4FEOA)

A mixture of 2-(perfluorobutyl)ethanol $F(CF_2)_4CH_2CH_2OH$ 25.0 g (95.0 mmol), ethylene carbonate and tetra-*n*-butylammonium iodide (TBAI) 0.7 g (1.9 mmol) as a catalyst was refluxed under stirring at 170°C for 72 h. In this mixture, 12.5 g (142.0 mmol) of ethylene carbonate was added to the system at three different reaction times of 0, 24 and 48 h. After the reaction, diethyl ether (50 cm³) and water (50 cm³) were added to the system, and the resultant mixture was stirred vigorously for 5 min. The ether layer was sepa-

rated and washed several times with a saturated NaCl aqueous solution to remove the unreacted ethylene carbonate and the catalyst. After evaporation of ether, the product 2-[2-(perfluorobutyl)ethoxy]ethanol was obtained as a colorless liquid by distillation (yield 4.9 g, 19.3%); bp 31–33°C/17 Pa; IR (cm⁻¹) 3388 (ν_{OH}), 2933, 2889 (ν_{CH_2}), 1252 (ν_{CF_2}); 1H -NMR ($CDCl_3$) δ 2.00–2.70 (a, m (multiplet), 3H), 3.40–3.90 (b, m, 6H) for $C_4F_9CH_2^aCH_2^bOCH_2^cCH_2^dOH^a$; MS (m/z) (rel. int.) 308 (1) [M]⁺.

2.3.2. 2-[2-(Perfluorohexyl)ethoxy]ethanol (6FEOA) and 2-[2-(perfluorooctyl)ethoxy]ethanol (8FEOA)

The synthesis methods and purification techniques were almost identical to those for 4FEOA.

6FEOA: 2-(perfluorohexyl)ethanol 20.0 g (55.0 mmol), TBAI 0.41 g (1.1 mmol), ethylene carbonate 7.26 g (82.5 mmol) (3 times, tot. 21.78 g), reaction temp. 170°C for 72 h; a colorless liquid product 4.6 g (19.3%) was obtained; bp 50–51°C/27 Pa; IR (cm⁻¹) 3346 (ν_{OH}), 2964, 2910 (ν_{CH_2}), 1243 (ν_{CF_2}); 1H -NMR ($CDCl_3$) δ 2.10–2.70 (a, m, 3H), 3.40–3.90 (b, m, 6H) for $C_6F_{13}CH_2^aCH_2^bOCH_2^cCH_2^dOH^a$; MS (m/z) (rel. int.) 408 (0.1) [M]⁺.

8FEOA: 2-(perfluorooctyl)ethanol 20.0 g (43.3 mmol), TBAI 0.40 g (1.1 mmol), ethylene carbonate 11.4 g (129.3 mmol) (3 times, tot. 34.2 g); reaction temp. 160°C for 72 h; a colorless liquid product 12.8 g (58.0%) was obtained; bp 96–100°C/665 Pa; IR (cm⁻¹) 3381 (ν_{OH}), 2933, 2890 (ν_{CH_2}), 1240 (ν_{CF_2}); 1H -NMR ($CDCl_3$) δ 2.10–2.70 (a, m, 3H), 3.40–3.90 (b, m, 6H) for $C_8F_{17}CH_2^aCH_2^bOCH_2^cCH_2^dOH^a$; MS (m/z) (rel. int.) 508 (2) [M]⁺.

2.4. Synthesis of bis[2-(2-(perfluoroalkyl)ethoxy)ethyl] maleates (*n*FEOA)

2.4.1. Bis[2-(2-(perfluorobutyl)ethoxy)ethyl] maleate (4FEOA)

A mixture of 4FEOA 8.0 g (26.0 mmol), maleic anhydride 1.2 g (12.0 mmol) and *p*-toluenesulfonic acid monohydrate 1.0 g (5.3 mmol) as a catalyst in 100 cm³ toluene was refluxed with stirring at 110°C for 120 h. During the reaction, the water liberated, was removed azeotropically from the reaction system to shift the equilibrium of the esterification reaction. After the reaction, the mixture was washed sufficiently with a saturated NaCl aqueous solution to remove *p*-toluenesulfonic acid and excess maleic anhydride. A colorless liquid, bis[2-(2-(perfluorobutyl)ethoxy)ethyl] maleate (4FEOA), was obtained by fractional distillation (yield 6.2 g, 69%); bp 120–124°C/10 Pa; IR (cm⁻¹) 2961, 2894 (ν_{CH_2}), 1736 (ν_{CO}), 1239 (ν_{CF_2}); 1H -NMR ($CDCl_3$) δ 2.10–2.70 (a, m, 4H), 3.40–3.90 (b, m, 8H), 4.20–4.42 (c, m, 4H), 6.26 (*cis*) and 6.86 (*trans*) (d, s (singlet), 2H) for $C_4F_9CH_2^aCH_2^bOCH_2^cCH_2^dOCOCH^e = CH^fCOOCH_2^gCH_2^hOCH_2^iCH_2^jC_4F_9$; MS (m/z) (rel. int.) 696 (0.4) [M]⁺, 290 (100) [$C_4F_9CH_2CH_2OCH_2CH_2 - H$]⁺.

2.4.2. *Bis[2-{2-(perfluorohexyl)ethoxy}ethyl] maleate (6FEOD) and bis[2-{2-(perfluorooctyl)ethoxy}ethyl] maleate (8FEOD)*

The synthesis methods and purification techniques were virtually the same as those for the preparation of 4FEOD.

6FEOD was obtained by the reaction of $C_6F_{13}CH_2CH_2OCH_2CH_2OH$ 7.2 g (17.5 mmol), maleic anhydride 0.8 g (8.0 mmol), and *p*-toluenesulfonic acid monohydrate 0.7 g (3.7 mmol) in 100 cm³ of toluene at 110°C for 120 h. A colorless liquid product 5.4 g (76%) was obtained; bp 164–166°C/40 Pa; IR (cm⁻¹) 2961, 2894 (ν_{CH_2}), 1731 (ν_{CO}), 1241 (ν_{CF_2}); ¹H-NMR (CDCl₃) δ 2.10–2.90 (a, m, 4H), 3.60–4.10 (b, m, 8H), 4.20–4.70 (c, m, 4H), 6.26 (*cis*) and 6.86 (*trans*) (d, s, 2H) for $C_6F_{13}CH_2^aCH_2^bOCH_2^cCH_2^dCOOCH^e=CH^dCOOCH_2^cCH_2^bOCH_2^bCH_2^aC_6F_{13}$; MS (*m/z*) (rel. int.) 896 (1) [M]⁺, 390 (100) [$C_6F_{13}CH_2CH_2OCH_2CH_2-H$]⁺.

8FEOD: $C_8F_{17}CH_2CH_2OCH_2CH_2OH$ 7.8 g (10.5 mmol), maleic anhydride 0.7 g (7.0 mmol), and *p*-toluenesulfonic acid monohydrate 0.6 g (3.2 mmol) in 100 cm³ of toluene at 110°C for 120 h. A solid white product 6.2 g (81%) was obtained; bp 152–160°C/11 Pa; IR (cm⁻¹) 2920, 2850 (ν_{CH_2}), 1710 (ν_{CO}), 1230 (ν_{CF_2}); ¹H-NMR (CDCl₃) δ 2.10–2.70 (a, m, 4H), 3.40–3.90 (b, m, 8H), 4.00–4.45 (c, m, 4H), 6.08 (*cis*) and 6.75 (*trans*) (d, s, 2H) for $C_8F_{17}CH_2^aCH_2^bOCH_2^cCH_2^dCOOCH^e=CH^dCOOCH_2^cCH_2^bOCH_2^bCH_2^aC_8F_{17}$; MS (*m/z*) (rel. int.) 1096 (0.3) [M]⁺, 490 (100) [$C_8F_{17}CH_2CH_2OCH_2CH_2-H$]⁺.

2.5. *Synthesis of sodium bis[2-{2-(perfluoroalkyl)ethoxy}ethyl] 2-sulfosuccinate (nFEOS)*

2.5.1. *Sodium bis[2-{2-(perfluorobutyl)ethoxy}ethyl] 2-sulfosuccinate (4FEOS)*

Aqueous sodium hydrogensulfite [1.5 g (14.0 mmol) of NaHSO₃ in 25 cm³ water] was added to a stirred clear solution of 4FEOD 3.3 g (4.7 mmol) in 100 cm³ 1,4-dioxane. The mixture was refluxed under stirring for 50 h, and then 1,4-dioxane and water were removed by evaporation. The residual products were extracted using Soxhlet with acetone to remove excess NaHSO₃, and the crude product of 4FEOS was obtained by evaporating acetone. Subsequently, the product was dispersed ultrasonically in 1,4-dioxane. This colloidal dispersion was separated to a 1,4-dioxane layer and jelly-like 4FEOS by centrifugation and the upper 1,4-dioxane layer was decanted off to remove the unreacted ester (4FEOD). Purification by centrifugation was repeated several times and a white surfactant jelly was obtained after vacuum drying (yield 3.7 g, 53%); IR (cm⁻¹) 2971, 2902 (ν_{CH_2}), 1738 (ν_{CO}), 1248 (ν_{CF_2}), 1050 (ν_{SO_2}); ¹H-NMR (TFA) δ 2.10–3.00 (a, m, 4H), 3.50 (d, d (doublet), 2H, *J* = 6.0 Hz), 3.80–4.40 (b, m, 8H), 4.40–5.00 (c, m, 5H) for $C_4F_9CH_2^aCH_2^bOCH_2^cCH_2^dCOOCH^e=CH^dCOOCH_2^cCH_2^bOCH_2^bCH_2^aC_4F_9$; ¹³C-NMR (trifluoroacetic acid (TFA)) δ 34.72 (a), 37.18 (b), 66.37 (g), 68.23 (c), 69.15 (d), 70.14 (d'), 72.89 (f), 173.39 (e), 177.64 (e')

for $C_4F_9C^aH_2C^bH_2OC^cH_2C^dH_2OC^eOC^fH_2C^gH(SO_3Na)-C^eOOC^dH_2C^cH_2OC^bH_2C^aH_2C_4F_9$; ¹⁹F-NMR (TFA) δ -83.39 (a, s, 6F), -127.75 (b, s, 4F), -126.27 (c, s, 4F), -115.58 (d, s, 4F) for $CF_3^aCF_2^bCF_2^cCF_2^dCH_2CH_2OCH_2CH_2OCOCH_2CH(SO_3Na)COOCH_2CH_2OCH_2CH_2CF_2^dCF_2^cCF_2^bCF_3^a$; MS (*m/z*) (rel. int.) 777 (100) [M - Na]⁺, 441 (9) [M - Na - C₄F₉CH₂CH₂OCH₂CH₂OCO - H]⁺.

2.5.2. *Sodium bis[2-{2-(perfluorohexyl)ethoxy}ethyl] 2-sulfosuccinate (6FEOS) and sodium bis[2-{2-(perfluorohexyl)ethoxy}ethyl] 2-sulfosuccinate (8FEOS)*

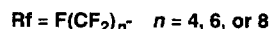
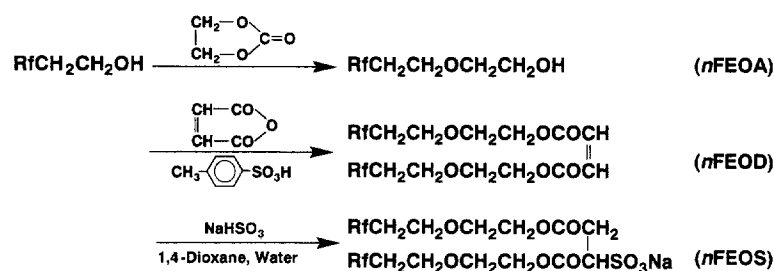
The synthesis methods for 6FEOS and 8FEOS were almost the same as those for the preparation of 4FEOS. The surfactants were purified by recrystallization using acetone.

6FEOS: 6FEOD 5.0 g (5.6 mmol), sodium hydrogensulfite 1.7 g (16.7 mmol) (in 25 cm³ water), 1,4-dioxane 100 cm³, reaction time 50 h; a white solid product 4.2 g (75%) was obtained; IR (cm⁻¹) 2964, 2894 (ν_{CH_2}), 1735 (ν_{CO}), 1239 (ν_{CF_2}), 1057 (ν_{SO_2}); ¹H-NMR (TFA) δ 2.20–2.90 (a, m, 4H), 3.30 (d, d, 2H, *J* = 8.0 Hz), 3.80–4.40 (b, m, 8H), 4.30–4.72 (c, m, 5H) for $C_6F_{13}CH_2^aCH_2^bOCH_2^cCH_2^dCOOCH^e=CH^dCOOCH_2^cCH_2^bOCH_2^bCH_2^aC_6F_{13}$; ¹³C-NMR (TFA) δ 34.83 (a), 37.21 (b), 66.42 (g), 68.30 (c), 69.19 (d), 70.16 (d'), 72.91 (f), 173.45 (e), 177.41 (e') for $C_6F_{13}C^aH_2C^bH_2OC^cH_2C^dH_2OC^eOC^fH_2C^gH(SO_3Na)C^eOOC^dH_2C^cH_2OC^bH_2C^aH_2C_6F_{13}$; ¹⁹F-NMR (TFA) δ -83.16 (a, s, 6F), -127.99 (b, s, 4F), -125.26 (c, s, 4F), -124.34 (d, s, 4F), -123.20 (e, s, 4F), -115.35 (f, s, 4F) for $CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCH_2CH_2OCH_2CH_2OCOCH_2CH(SO_3Na)COOCH_2CH_2OCH_2CH_2CF_2^fCF_2^eCF_2^dCF_2^cCF_2^bCF_3^a$; MS (*m/z*) (rel. int.) 977 (100) [M - Na]⁻, 541 (11) [M - Na - C₆F₁₃CH₂CH₂OCH₂CH₂OCO - H]⁺.

8FEOS: 8FEOD 2.5 g (2.3 mmol), sodium hydrogensulfite 0.5 g (4.5 mmol) (in 35 cm³ water), 1,4-dioxane 100 cm³; reaction time 70 h; a white solid product 2.0 g (71%) was obtained; IR (cm⁻¹) 2966, 2904 (ν_{CH_2}), 1737 (ν_{CO}), 1250 (ν_{CF_2}), 1059 (ν_{SO_2}); ¹H-NMR (TFA) δ 2.07–3.02 (a, m, 4H), 3.41 (d, d, 2H, *J* = 6.0 Hz), 3.77–4.30 (b, m, 8H), 4.30–4.95 (c, m, 5H) for $C_8F_{17}CH_2^aCH_2^bOCH_2^cCH_2^dCOOCH^e=CH^dCOOCH_2^cCH_2^bOCH_2^bCH_2^aC_8F_{17}$; ¹³C-NMR (TFA) δ 34.84 (a), 37.20 (b), 66.40 (g), 68.31 (c), 69.19 (d), 70.17 (d'), 72.91 (f), 173.41 (e), 177.39 (e') for $C_8F_{17}C^aH_2C^bH_2OC^cH_2C^dH_2OC^eOC^fH_2C^gH(SO_3Na)C^eOOC^dH_2C^cH_2OC^bH_2C^aH_2C_8F_{17}$; ¹⁹F-NMR (TFA) δ -83.21 (a, s, 6F), -127.96 (b, s, 4F), -125.26 (c, s, 4F), -124.27 (d, s, 12F), -123.38 (e, s, 4F), -115.40 (f, s, 4F) for $CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCH_2CH_2OCH_2CH_2OCOCH_2CH(SO_3Na)COOCH_2CH_2OCH_2CH_2CF_2^fCF_2^eCF_2^dCF_2^cCF_2^bCF_3^a$; MS (*m/z*) (rel. int.) 1177 (12) [M - Na]⁺, 643 (7) [M - Na - C₈F₁₇CH₂CH₂OCH₂CH₂OCO + H]⁺.

3. Results and discussion

The synthetic process of fluorocarbon surfactants with oxyethylene groups is shown in Scheme 1. Fluorinated alcohols



Scheme 1.

Table 1
Properties of double-tailed fluorocarbon surfactants

Surfactant	cmc/mol l ⁻¹	γ_{cmc} /mN m ⁻¹	Krafft point/°C	Surf. [9]	cmc/mol l ⁻¹	γ_{cmc} /mN m ⁻¹	Krafft point/°C
4FEOS	5.7×10^{-5}	21.0	<0	4FS	8×10^{-4}	16.3	<0
6FEOS	2×10^{-6}	15.8	<0	6FS	5×10^{-5}	22.0	26
8FEOS	1.2×10^{-5}	16.0	<0	8FS	1×10^{-5} ^a	12.8 ^a	72

^a 73°C.

with an oxyethylene group (*n*FEOA) were prepared using the reaction of corresponding alcohols with ethylene carbonate. The yields of *n*FEOA were not very high (Section 2). Heilmann et al. reported that the oxyethylation of 1*H*,1*H*-perfluoro-1-alkanols by ethylene carbonate gives oxyethylated alcohols with a satisfactory yield (ca. 85%) [12] under the similar conditions to this work. The oxyethylation yields of this reaction step are strongly dependent on the acid–base interaction between the carbonyl oxygen in ethylene carbonate and an acidic hydrogen of the alcohols. At the same fluorocarbon chain length, 1*H*,1*H*,2*H*,2*H*-perfluoro-1-alkanols should be less acidic than 1*H*,1*H*-perfluoro-1-alkanols. The low yields of *n*FEOA in this work are due to the weak acidity of the starting alcohols.

The diesters of *n*FEOD were obtained by the esterification of *n*FEOA with maleic anhydride in high yield.

6FEOS and 8FEOS were purified by recrystallization using acetone and obtained a white solid, while 4FEOS was a colorless jelly compound and highly soluble in acetone. Therefore, recrystallization with acetone was undesirable in purifying 4FEOS.

The solution properties of *n*FEOS at 30°C are summarized in Table 1, along with the reported data [9] for conventional double-tailed fluorocarbon surfactants (*n*FS). 4FEOS, 6FEOS and 8FEOS are highly water-soluble, and their Krafft points (K_p) are below 0°C. K_p values of *n*FEOS are lower than those of *n*FS, indicating that the *n*FEOS are more hydrophilic when compared to *n*FS at the same fluorocarbon chain length (*n*). It is clear that the introduction of oxyethylene units to *n*FS enhances the water-solubility of the surfactants containing a fluorocarbon chain, *n*FEOS.

Fig. 1 represents the surface tension of the *n*FEOS solution as a function of the concentration at 30°C. The surface tension decreases with an increase in surfactant concentration and

inflects at their cmcs. Table 1 and Fig. 1 show that the values of γ_{cmc} (surface tension value at cmc) for *n*FEOS are very low, especially at *n* = 6 (15.8 mN/m) and *n* = 8 (16.0 mN/m).

It should be noted that the cmcs of 4FEOS and 6FEOS are smaller by about one order of magnitude than those of *n*FS with the same *n*. On the other hand, a discussion about 8FEOS is fruitless because datum for 8FS was obtained at 73°C. It is known that the sulfate group SO_4^- and/or the sulfonate group SO_3^- of anionic surfactants interact attractively with oxyethylene parts of non-ionic surfactants through water molecules [13,14]. This interaction will contribute to the surfactant molecular aggregation, in other words, micellar formation. The *n*FEOS have both a sulfonate group and oxyethylene units in a molecule. Accordingly, the very low cmc values of *n*FEOS result from the intermolecular force working between the oxyethylene units of one *n*FEOS molecule and the SO_3^- group of another *n*FEOS molecule.

It was also determined that the cmc values of *n*FEOS exhibit a minimum at a medium fluorocarbon chain length,

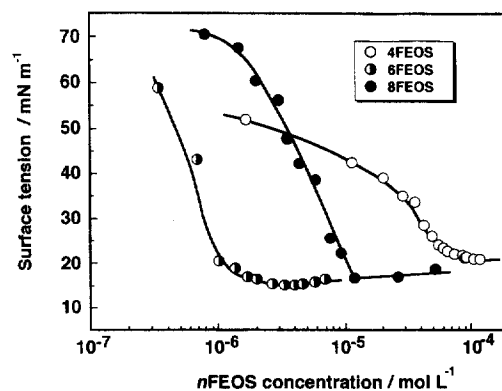


Fig. 1. Surface tension of *n*FEOS aqueous solutions at 30°C.

$n = 6$. This phenomenon is an unusual behavior. In general, the cmc decreases monotonically with an increase in hydrophobic chain length of surfactants. Further studies on the n dependence of the cmc are now in progress by the micellar structure analysis using the light-scattering method.

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