Syntheses of Anionic Surfactants Having Two Polyfluoroalkyl Chains and Their Flocculation Ability for Dispersed Magnetite Particles in Water

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Four anionic surfactants having two polyfluoroalkyl chains in a molecule, sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate, $CF_3(CF_2)_7(CH_2)_2OCOCH_2CH(SO_3Na)COO(CH_2)_2(CF_2)_7CF_3$, sodium salt of bis(1*H*,1*H*,9*H*-hexadecafluorononyl) 2-sulfosuccinate, $H(CF_2)_8CH_2OCOCH_2CH(SO_3Na)COOCH_2(CF_2)_8H$, sodium salt of bis(1*H*,1*H*,7*H*-dodecafluoroheptyl) 2-sulfosuccinate, $H(CF_2)_6CH_2OCOCH_2CH(SO_3Na)COOCH_2(CF_2)_6H$ and sodium salt of bis(1*H*,1*H*,5*H*-octafluoropentyl) 2-sulfosuccinate, $H(CF_2)_4CH_2OCOCH_2CH(SO_3Na)COOCH_2(CF_2)_4H$, were prepared from maleic anhydride, the corresponding alcohols having a polyfluoroalkyl chain and sodium hydrogensulfite. The flocculation and redispersion abilities of these surfactants against dispersed magnetite particles in water have been examined in comparison with other four anionic surfactants having a single polyfluoroalkyl chain in a molecule; sodium pentadecafluorooctanoate, $CF_3(CF_2)_6COONa$, sodium 9*H*-hexadecafluorononanoate, $H(CF_2)_8COONa$, sodium 7*H*-dodecafluoroheptanoate, $H(CF_2)_6COONa$, and sodium 5*H*-octafluoropentanoate, $H(CF_2)_4COONa$. These abilities were estimated by measurement of the contact angle against water using pelleted surface-modified magnetite. The abilities of the surfactants having two polyfluoroalkyl chains against flocculation-redispersion were superior to those of the surfactants having one polyfluoroalkyl chain. Especially, sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate was the most effective surface active agent for these abilities.

It is well known that fluorocarbon polymers exhibit the properties of water and oil repellency, high lubricity, thermal and chemical stability, and so on. It is expected that new composite materials with high performance are produced by dispersing some inorganics into these fluorocarbon polymers. To disperse inorganics into organic polymers, the surface of the inorganics should be modified. Normally there are two ways, one is the use of coupling agents[1–6)] and the other is the employment of surfactants such as sodium oleate.[7–11)]

In this paper, the results of the syntheses and characterizations of anionic surfactants having two polyfluoroalkyl chains in a molecule and their flocculation and redispersion abilities for dispersed magnetite particles in water are reported. These abilities were compared with those of anionic surfactants having one polyfluoroalkyl chain in a molecule.

Experimental

Materials. 1*H*,1*H*,2*H*,2*H*-Heptadecafluoro-1-decanol, $CF_3(CF_2)_7(CH_2)_2OH$ (bp 88—90 °C/500 Pa), 1*H*,1*H*,9*H*-hexadecafluoro-1-nonanol, $H(CF_2)_8CH_2OH$ (bp 63 °C/53 Pa), 1*H*,1*H*,7*H*-dodecafluoro-1-heptanol, $H(CF_2)_6CH_2OH$ (bp 169—170 °C) and 1*H*,1*H*,5*H*-octafluoro-1-pentanol, $H(CF_2)_4CH_2OH$ (bp 139—140 °C), pentadecafluorooctanoic acid, $CF_3(CF_2)_6COOH$ (bp 95 °C/133 Pa), 9*H*-hexadecafluorononanoic acid, $H(CF_2)_8COOH$ (bp 92—93 °C/53 Pa), 7*H*-dodecafluoroheptanoic acid, $H(CF_2)_6COOH$ (bp 69—70 °C/120 Pa) and 5*H*-octafluoropentanoic acid, $H(CF_2)_4COOH$ (bp 40—42 °C/120 Pa) were donated from Daikin Industries, Ltd. or obtained from PCR Inc. and purified by distillation. The purity of these alcohols and carboxylic acids were checked by the use of ^{1}H NMR, ^{19}F NMR spectra and gas chromatography, and the impurities were not detectable. The reagent grade maleic anhydride (bp 63—65 °C/660 Pa) and solvents (toluene, 1,4-dioxane and tetrahydrofuran(THF)) were commercially obtained and purified by distillation. *p*-Toluenesulfonic acid, sodium hydrogensulfite, sodium carbonate, iron(II) chloride, and iron(III) chloride were used without further purification. Magnetite particles were made by the method of Shimoiizaka et al.[10)] and the average particle size was 109 Å (by light scattering).

Measurements and Instruments. FT-IR spectra were measured in a liquid film or by a KBr method with a JEOL JIR-5300 spectrophotometer. Each spectrum was recorded at a resolution of 4 cm^{-1} with the total of 30 scans. Pulsed Fourier Transform 100-MHz ^{1}H NMR was run in THF-d_8, trifluoroacetic acid, or acetone-d_6 with TMS as an internal standard using a JEOL JNR-PX-100 spectrometer at room temperature. The FT mode 90-MHz ^{19}F NMR was recorded at 27 °C on a JEOL JNM-FX-90Q in THF with fluorobenzene (δ=$-$113.6[12)] from $CFCl_3$ in $CDCl_3$) as an external standard. The assignments of the ^{19}F NMR spectra were referred to in the data book.[12)] Gas chromatography was performed with a Hitachi 063 (PEG-6000 supported Chromosorb A NAW 30—60 mesh 5 m packed column, TCD) or Hitachi G-3000 gas chromatograph (OV-1 25 m Fused capillary column, FID) and the intensities were measured with a Hitachi 834 chromato processor or a Hitachi D-2500 chromato integrator. The centrifuge was used with a Hitachi himac CR20B2 (10000 rpm, 10 min at 20 °C). Light scattering measurements were run with Malvern Co. 4700 Submicron Particle Analyzer (Argon Laser, 5 W, 488 nm). Ultrasonic operations were carried out using a Branson Ultrasonics Corporation Model 250 Sonifier Cell Disruptor System (200 W, 20 kHz). Potential difference was measured using Yokogawa Model PH-82 pH meter. The contact angle θ(°) was measured at 23 °C with an Elma-Kougaku Co. Gonio-type apparatus. ESCA data were taken with a Shimadzu ESCA-750.

Synthesis of Bis(polyfluoroalkyl) Maleate. Synthesis of Bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) Maleate: A mixture of 1*H*,1*H*,2*H*,2*H*-heptadecafluoro-1-decanol 30.12 g (64.9 mmol), maleic anhydride 3.03 g (30.9 mmol) and *p*-toluenesulfonic acid monohydrate 1.18 g (6.2 mmol) as a catalyst in 120 cm^3 toluene was refluxed under stirring at 110 °C for 15 h. During the reaction, the water liberated was removed azeotropically from the reaction system to shift the equilibrium of the esterification reaction. The reaction was finished when 90% or more water being formed, based on the theoretical values. After the reaction, the mixture was cooled at 70 °C and washed sufficiently with 70 °C water to remove *p*-toluenesulfonic acid and excess maleic anhydride. A white solid, bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) maleate, was obtained by fractional distillation (yield 27.1 g, 86.8%): Bp 195—197 °C/400 Pa, mp 62—63 °C; IR 3062, 2980, 2912, 1724, 1641, 1639, 1466, 1464, 1425, 1396, 1375, 1333, 1201, 1146, 1078, 1049, 1016, 1014, 972, 841, 820, 704, 658 cm^{-1}; ^{1}H NMR (in THF-d_8) δ=2.64 (CH_2CF_2, t(t)(triplet(triplet)), J=18.8 (6.7) Hz, 4H), 4.51(OCH_2, t, J=6.7 Hz, 4H), 6.40(CH, s(singlet), 2H).

Syntheses of Bis(1*H*,1*H*,9*H*-hexadecafluorononyl) Maleate, Bis(1*H*,1*H*,7*H*-dodecafluoroheptyl) Maleate, and Bis(1*H*,1*H*,5*H*-octafluoropentyl) Maleate: The procedure and purification techniques were almost the same as those for the preparation of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) maleate.

Bis(1*H*,1*H*,9*H*-hexadecafluorononyl) maleate was obtained by the reaction of 1*H*,1*H*,9*H*-hexadecafluoro-1-nonanol 39.3 g (90.9 mmol), maleic anhydride 4.30 g (43.9 mmol) and *p*-toluenesulfonic acid monohydrate 1.48 g (7.8 mmol) in 200 cm^3 toluene at 110 °C for 20.5 h. A colorless jelly product 15.9 g (yield 38.4%) was obtained: Bp 129—131 °C/27 Pa; IR 3097, 3076, 3022, 2981, 2960, 1747, 1655, 1454, 1412, 1350, 1288, 1201, 1144, 1088, 1039, 1038, 984, 957, 852, 816, 769, 702, 661, 636, 538 cm^{-1}; ^{1}H NMR (THF-d_8) δ=6.64 (CF_2H, t(t), J=51.0 (5.1) Hz, 2H), 4.83 (OCH_2, t, J=13.6 Hz, 4H), 6.55 (=CH, s, 2H).

Bis(1*H*,1*H*,7*H*-dodecafluoroheptyl) maleate was prepared under the following conditions: 1*H*,1*H*,7*H*-dodecafluoro-1-heptanol 37.6 g (113 mmol), maleic anhydride 5.29 g (53.9 mmol), and *p*-toluenesulfonic acid monohydrate 2.05 g (10.8 mmol) in 210 cm^3 toluene at 110 °C for 14 h. A liquid colorless product 14.8 g (yield 36.9%) was obtained: Bp 126—127 °C/13 Pa; IR 3057, 3010, 2980, 2912, 1757, 1753, 1720, 1707, 1639, 1635, 1587, 1566, 1562, 1550, 1546, 1460, 1410, 1382, 1263, 1196, 1140, 984, 949, 862, 831, 744, 715, 671 cm^{-1}; ^{1}H NMR (THF-d_8) δ=6.11 (CF_2H, t(t), J=50.8(5.0) Hz, 2H), 4.76 (OCH_2, t, J=13.6 Hz, 4H), 6.40 (=CH, s, 2H).

Bis(1*H*,1*H*,5*H*-octafluoropentyl) maleate: 1*H*,1*H*,5*H*-octafluoro-1-pentanol 37.7 g (162 mmol), maleic anhydride 7.27 g (74.1 mmol) and *p*-toluenesulfonic acid monohydrate 2.83 g (14.9 mmol) in 300 cm^3 toluene at 110 °C for 21 h. A liquid colorless product 15.4 g (yield 38.2%) was obtained: Bp 109—110 °C/40 Pa; IR 3070, 3012, 2980, 1755, 1701, 1684, 1653, 1646, 1645, 1558, 1538, 1522, 1506, 1456, 1409, 1383, 1288, 1172, 1132, 1085, 1043, 980, 904, 808, 754, 711, 605, 546, 437, 418, 415, 407, 401 cm^{-1}; ^{1}H NMR (THF-d_8) δ=6.13 (CF_2H, t(t), J=51.4 (5.4) Hz, 2H), 4.74 (OCH_2, t, J=14.0 Hz, 4H), 6.41 (=CH, s, 2H).

Synthesis of Surfactant Having Two Polyfluoroalkyl Chains. Synthesis of Sodium Salt of Bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-Sulfosuccinate: Sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate was prepared as follows. To a stirred clear solution of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) maleate 5.00 g (5.0 mmol) in 85 cm^3 1,4-dioxane, aqueous sodium hydrogensulfite (11.9 g (7.0 mmol) of sodium hydrogensulfite in 35 cm^3 water) was added at 50 °C. The mixture was refluxed under stirring until many foams began to appear for about 10—15 h from the start of reaction. Then 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 cm^3 hot (50 °C) 1,4-dioxane on the disk to remove the unreacted bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) maleate. The product was dispersed ultrasonically in 50 cm^3 water. This colloidal dispersion was separated by centrifugation and the upper aqueous layer was decanted off to remove the excess sodium hydrogensulfite. The purification by the water washing/centrifugation was repeated three times or more. The products free from sodium hydrogensulfite were washed with 100 cm^3 THF on a sintered glass disk to remove water. A white powder, sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate, was obtained after vacuum drying (yield 4.74 g, 86.0%): IR 1736, 1726, 1600, 1461, 1369, 1333, 1201, 1147, 1120, 1049, 1012, 870, 836, 739, 702, 656 cm^{-1}; ^{1}H NMR (CF_3COOH) δ=2.51 (a and f, t(m(multiplet)), J=17.7 Hz, 4H), 3.36 (c, broad, 2H), 4.50 (b, d, and e, m, 5H) for $C_8F_{17}CH_2^aCH_2^bOCOCH_2^cCH^d(SO_3Na)COOCH_2^eCH_2^fC_8F_{17}$.

Syntheses of Sodium Salt of Bis(1*H*,1*H*,9*H*-hexadecafluorononyl) 2-Sulfosuccinate, Sodium Salt of Bis(1*H*,1*H*,7*H*-dodecafluoroheptyl) 2-Sulfosuccinate, and Sodium Salt of Bis(1*H*,1*H*,5*H*-octafluoropentyl) 2-Sulfosuccinate: The synthetic method and purification techniques were almost the same as those for the preparation of sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate.

Sodium salt of bis(1*H*,1*H*,9*H*-hexadecafluorononyl) 2-sulfosuccinate was obtained by the reaction of bis(1*H*,1*H*,9*H*-hexadecafluorononyl) maleate 17.8 g (18.9 mmol) in 100 cm^3 1,4-dioxane with aqueous sodium hydrogensulfite (2.54 g (24.4 mmol) in 50 cm^3 water) at 98 °C for 50 h. A white powder 9.54 g (yield 48.3%) was obtained: IR 2983, 2937, 1759, 1730, 1400, 1396, 1351, 1277, 1242, 1201, 1146, 1080, 941, 874, 808, 706, 688, 654 cm^{-1}; ^{1}H NMR (CF_3COOH) δ=3.15 (c, broad, 2H), 3.8—4.9 (b, d, and e, broad, 5H), 5.50 (a and f, t(m), J=51.4 Hz, 2H) for $H^a(CF_2)_8CH_2^bOCOCH_2^cCH^d(SO_3Na)$-$COOCH_2^e(CF_2)_8H^f$.

Sodium salf of bis(1*H*,1*H*,7*H*-dodecafluoroheptyl) 2-sulfosuccinate was prepared by the reaction of bis(1*H*,1*H*,7*H*-dodecafluoroheptyl) maleate 6.63 g (8.9 mmol) in 50 cm^3 1,4-dioxane with aqueous sodium hydrogensulfite (0.93 g (8.96 mmol)/25 cm^3 water) at 98 °C for 50 h. A white powder 4.29 g (yield 56.1%) was obtained: IR 2983, 2939, 1761, 1733, 1441, 1396, 1354, 1350, 1315, 1242, 1194, 1140, 1078, 1014, 972, 928, 862, 829, 798, 739, 735, 687, 665, 655 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ=3.28 (c, d, J=6.8 Hz, 2H), 4.22 (d, t, J=6.8 Hz, 1H), 4.66 (b, t, J=14.4 Hz, 2H), 4.77 (e, t, J=14.4 Hz, 2H), 6.57 (a and f, t(t), J=51.3 (5.7) Hz, 2H) for $H^a(CF_2)_6CH_2^b$-$OCOCH_2^cCH^d(SO_3Na)COOCH_2^e(CF_2)_6H^f$.

Sodium salt of bis(1*H*,1*H*,5*H*-octafluoropentyl) 2-sulfosuccinate 5.39 g (87.9%) was synthesized as a white powder from the reaction of 1,4-dioxane solution of bis(1*H*,1*H*,5*H*-octafluoropentyl) maleate (5.15 g (9.46 mmol) in 50 cm^3 1,4-dioxane) with aqueous sodium hydrogensulfite (1.08 g

(10.4 mmol)/25 cm^3 water) at 98 °C for 50 h: IR 2985, 2939, 1763, 1741, 1483, 1441, 1433, 1405, 1354, 1315, 1263, 1240, 1165, 1132, 1049, 968, 903, 806, 758, 707, 675, 655 cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ=3.30 (c, d, J=6.8 Hz, 2H), 4.53 (d, t, J=6.8 Hz, 1H), 4.80(b and e, t, J=14.4 Hz, 4H), 7.72(a and f, t(t), J=51.3 (5.7) Hz, 2H) for $H^a(CF_2)_4CH_2^bOCOCH_2^cCH^d$-$(SO_3Na)COOCH_2^e(CF_2)_4H^f$.

Synthesis of Surfactant Having One Polyfluoroalkyl Chain. Syntheses of Sodium Pentadecafluorooctanoate, C_7F_{15}-COONa, Sodium 9*H*-Hexadecafluorononanoate, $H(CF_2)_8$-COONa, Sodium 7*H*-Dodecafluoroheptanoate, $H(CF_2)_6$-COONa, and Sodium 5*H*-Octafluoropentanoate, $H(CF_2)_4$-COONa: These surfactants were prepared from the corresponding carboxylic acids with an excess of sodium carbonate in purified THF. After the reaction at 66 °C for 10 h, the excess sodium carbonate was removed by filtration. White powdery surfactants were obtained after vaccum drying. In each case, the yield of the surfactants was higher than 95%. The purity of these surfactants was confirmed on the basis of ^{1}H NMR (measured in THF-d_8) and IR spectra, and the impurities were not detectable.

Sodium pentadecafluorooctanoate: IR 1695, 1425, 1365, 1325, 1234, 1205, 1147, 1105, 1020, 987, 891, 823, 777, 739, 737, 735, 671, 665, 640, 561, 530 cm^{-1}; ^{1}H NMR no proton.

Sodium 9*H*-hexadecafluorononanoate: IR 2933, 1697, 1659, 1425, 1342, 1288, 1196, 1151, 1083, 982, 864, 823, 771, 735, 733, 667, 650, 586, 559, 536, 507 cm^{-1}; ^{1}H NMR δ=6.47 (HCF$_2$, t(t), 50.0 (5.3) Hz), no –COOH proton.

Sodium 7*H*-dodecafluoroheptanoate: IR 2927, 2912, 2872, 1697, 1421, 1327, 1259, 1184, 1138, 1135, 1082, 945, 823, 822, 819, 769, 719, 669 cm^{-1}; ^{1}H NMR δ=6.22 (HCF$_2$, t(t), 51.0 (5.4) Hz), no –COOH proton.

Sodium 5*H*-octafluoropentanoate: IR 2919, 2862, 1696, 1428, 1403, 1303, 1240, 1172, 1126, 1082, 1050, 921, 896, 834, 819, 726, 649 cm^{-1}; ^{1}H NMR δ=6.58 (HCF$_2$, t(t), 51.7 (6.1) Hz), no –COOH proton.

Stability of Dispersed Magnetite in Water: Magnetite powder 1.00 g was put into 50 cm^3 water, and the mixture was dispersed ultrasonically for 15 min. It was confirmed that the dispersion was not sedimented and that the colloidal precipitate did not appear for 3 days or more.

Measurement of Flocculation Ability: The adsorption of the surfactants was achieved by ultrasonic irradiation (200 W, 20 kHz, 15 min) to magnetite particles (0.100 g) in 40 cm^3 aqueous solution of the surfactants at various concentrations. The ultrasonic irradiation was utilized to progress an adsorption reaction and to prevent aggregation of magnetite particles. The flocculation and redispersion abilities of the surfactants against magnetite particles were observed after leaving them standing for 24 h at room temperature.

Measurement of Contact Angles of Water on Surface-Modified Magnetite: The surface wettabilities of the modified magnetite were evaluated by the contact angle θ(°) against water on the pelleted magnetite. The pellets to measure the contact angle were prepared as follows. Pressed cellulose disks were preliminary made by pressing 40 mg cellulose powder in a die for IR pellets at 200 kg cm^{-2} for 10 min; 0.15 g of surface-modified magnetite was then placed on it. The surface-flattened pellets of magnetite were obtained by pressing again at 200 kg cm^{-2} for 15 min in the die. The contact angles were measured using 1.0×10^{-6} dm^3 of water drops. The contact angles were evaluated by extrapolating to time zero from a plot of the advancing contact angle θ(°) vs. time.[13)]

Amount of Adsorbed Surfactant: The amounts of adsorbed surfactant on the surface-modified magnetite just after the beginning of flocculation and just before the beginning of redispersion were quantitated from the measurement of the potential difference of the upper clear solution, using the calibration curve obtained with an aqueous surfactant solution at various concentrations.

ESCA Measurement: The samples for ESCA measurement were obtained from the middle point of the flocculation range; the sample treated with sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate was obtained from the ratio of [Surfactant/Magnetite]=0.07 (see Fig. 1) and another one treated with sodium pentadecafluorooctanoate was prepared from that of 0.90. These samples were washed sufficiently with water, dried in a reduced pressure and powdered with an agate mortar.

Results and Discussion

The yields of several sodium salt of bis(polyfluoroalkyl) 2-sulfosuccinate derivatives were not very high. This is probably because water-soluble surfactants, although the solubility was considerably low, had to be washed with water to remove the unreacted sodium hydrogensulfite.

The surfactants are known to change the surface properties of many substances by adsorption. We examined the surface modification ability of the surfactants having polyfluoroalkyl chain(s) by use of magnetite particles. Figure 1 shows the regions of flocculation and redispersion of magnetite particles obtained by adding the solution of the eight different surfactants at various initial concentrations. In a range of a lower surfactant concentration, the magnetite particles were flocculated with an increase in the surfactant concentration. On the contrary, the flocculated magnetite particles were dispersed again as the surfactant concentration was further increased. The region of flocculation-redispersion depended on the surfactant used. The relationship between the flocculation and the redispersion of magnetite particles is schematically illustrated in Fig. 2. The surface of magnetite particles in water is positively charged, then the surface adsorbs surfactants at a moiety of negatively charged ion (–SO_3^- or –COO^-).[14)] In a lower concentration range of surfactant, the magnetite particles adsorb the surfactants in a monolayer and the particles are surrounded by the surfactants orientating the polyfluoroalkyl chains outside. Thus, the modified magnetite particles are flocculated in water, since the surface of the modified particles have a hydrophobic property. The flocculating magnetite particles were, however, dispersed again when the surfactant concentration increased further. This means that the magnetite particles modified with a surfactant in a monolayer are surrounded by the second surfactants to make a bilayer by an interaction of polyfluoroalkyl chains, in which the second surfactants are orientated

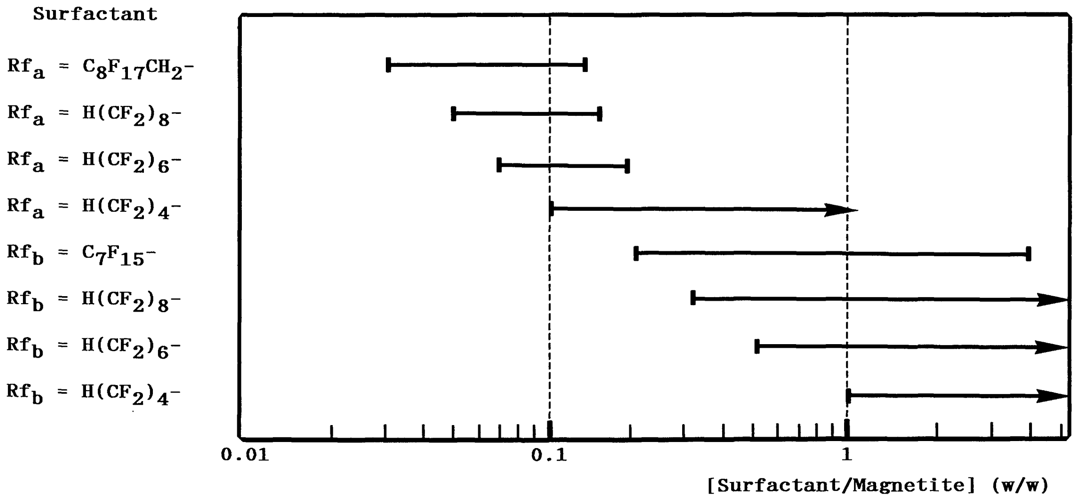

Fig. 1. Comparison of flocculation and redispersion abilities of the surfactants having polyfluoroalkyl chain(s) using magnetite particles. Rf_a and Rf_b groups are for $Rf_aCH_2OCOCH_2CH(SO_3Na)COOCH_2Rf_a$ and Rf_bCOONa, respectively.

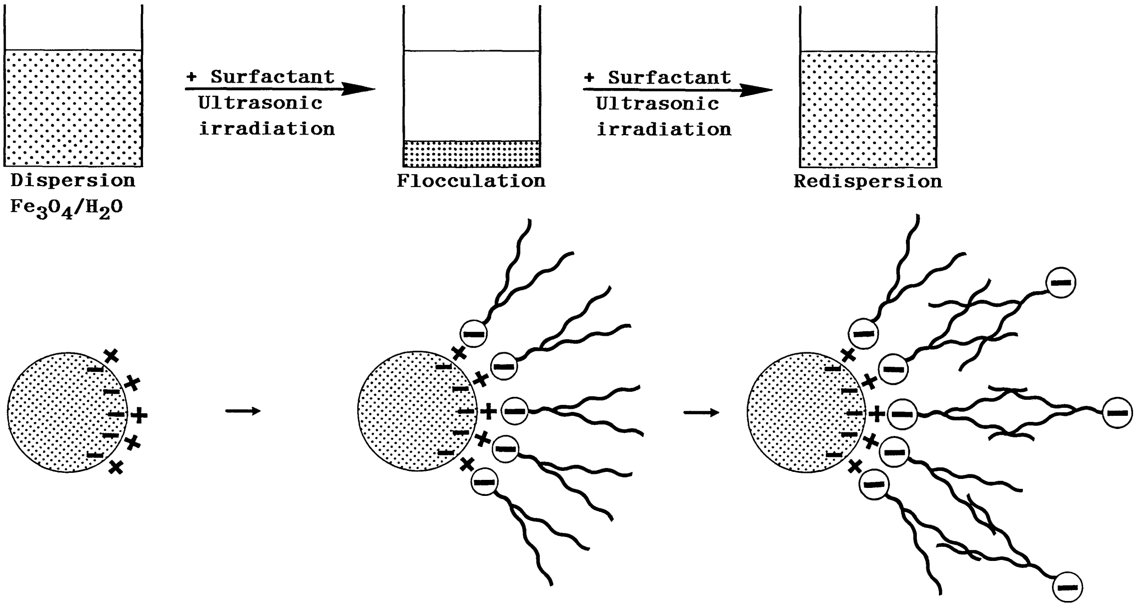

Fig. 2. Schematic illustration for flocculation and redispersion of magnetite particles.

outside at the ion moiety. From the relationship between flocculation and redispersion shown in Fig. 1, it is concluded that the ability of surfactants having two polyfluoroalkyl chains against flocculation-redispersion is superior to that of the surfactants having one polyfluoroalkyl chain. Especially, the surfactants having those two polyfluoroalkyl chains which include a trifluoromethyl group at the end of the chains were the most effective. Some of the beginning points of redispersion were incomplete to measure (drawn by the arrows in Fig. 1), because of the low solubility of these surfactants.

The results of the measurement of the contact angle against water on the modified magnetite, whose samples were obtained from the middle point in each flocculation range and pelleted, are listed in Table 1. Since the untreated magnetite pellet absorbed water drops too rapidly to determine the contact angle, the contact angle was described 0°. The values of the contact angle indicate that the surfactants having a trifluoromethyl group at the end of the chain(s) have higher hydrophobicity than the others. In the case of the surfactants having hydrogen at the end of the chain(s), the value increases with an increase in the chain length. However, these values are independent of the flocculation ability, because the amount of surfactant

Table 1. Contact Angles of Water on the Surface-Modified Magnetite Treated with the Surfactants Having Polyfluoroalkyl Chain(s)

Surfactant[a]	Contact angle θ(°) of water
Untreated	0
$Rf_a=CF_3(CF_2)_7CH_2-$	125
$Rf_a=H(CF_2)_8-$	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

a) $Rf_aCH_2OCOCH_2CH(SO_3Na)COOCH_2Rf_a$, Rf_bCOONa.

Table 2. Amount of Adsorbed Surfactant

Surfactant	Amount of adsorbed surfactant (mg/g magnetite)
$CF_3(CF_2)_7(CH_2)_2OCOCH_2-CH(SO_3Na)COO(CH_2)_2(CF_2)_7CF_3$	
After flocculation	29.5
Before redispersion	109
$CF_3(CF_2)_6COONa$	
After flocculation	176
Before redispersion	440

adsorbed on the magnetite surface in the middle point of the flocculation range should be different from one another.

Some of the results of the amount of adsorbed surfactant on the magnetite surface are listed in Table 2. In the case of sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate, only 29.5 mg of surfactant were needed to flocculate 1 g of magnetite particles, and 109 mg for redispersion. On the other hand, in the case of sodium pentadecafluorooctanoate, much more surfactant was required for the flocculation (176 mg) and redispersion (440 mg). These observations also suggest that the ability of the surfactants having two polyfluoroalkyl chains for the flocculation and redispersion against the magnetite particles in water is superior to that of the surfactants having one polyfluoroalkyl chain in a molecule.

The two surface-modified magnetite samples for the ESCA measurements were obtained from the middle point of the flocculation range given in Fig. 1 ($Rf_a=C_8F_{17}CH_2-$ and $Rf_b=C_7F_{15}-$). It was found that the atomic ratio of Fe : F in the vicinity of the surface modified with sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate was 1 : 7.53, and the ratio 1 : 4.86 was obtained from the surface treated with sodium pentadecafluorooctanoate. From these values, it was calculated that the molar ratio of Fe_3O_4: surfactant was 1 : 0.66 and 1 : 0.85, respectively. Although the initial surfactant concentration ratio (molar ratio) used to make these two samples was [sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate] : [sodium pentadecafluorooctanoate]=1 : 33, the molar ratio obtained from these two samples was [adsorbed sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate] : [adsorbed sodium pentadecafluorooctanoate]=0.66 : 0.85. These data also suggest that the surfactant having two polyfluoroalkyl chains has a relatively high adsorption ability; in these cases, the adsorption ability ratio is [sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate] : [sodium pentadecafluorooctanoate]=(0.66/1) : (0.85/33)=1 : 0.04.

In conclusion, the abilities of the anionic surfactants having two polyfluoroalkyl chains for the flocculation and the redispersion against magnetite particles in water were superior to those of the surfactants having one polyfluoroalkyl chain in a molecule. Especially sodium salt of bis(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) 2-sulfosuccinate possessing a CF_3- group at the end of the polyfluoroalkyl chains, was the most effective surface active agent for these abilities.

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