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SURFACE ACTIVE SUBSTANCES CONTAINING AN OLIGO(HEXAFLUOROPROPENE OXIDE) CHAIN AS A HYDROPHOBIC AND OLEOPHOBIC MOIETY

Nobuo ISHIKAWA* and Mikio SASABE

Department of Chemical Technology, Tokyo Institute of Technology, Ookayama,
Meguro-ku, Tokyo 152 (Japan)

SUMMARY

Oil soluble surface active substances, $(HFPO)_n$-Ar, where Ar is an aryl group and $(HFPO)_n$ is an oligo(hexafluoropropene oxide) group, n = 2 - 5, were prepared and tested for their surface activities in toluene or m-xylene. Addition of a small amount of $(HFPO)_{4-6}$-Ar (0.2 - 0.5 wt%) was found to decrease remarkably the surface tension of these solvents (down to 12 - 14 $dyn \cdot cm^{-1}$ at 20 ^oC). Water soluble surfactants $(HFPO)_n$-Ar'SO_3Na, where Ar' is an arylene group, were also prepared by sulfonation of $(HFPO)_n$-Ar. Some of these substances (n = 4 - 6) decreased the surface tension of water down to 16 $dyn \cdot cm^{-1}$ at 20 ^oC in the concentration of 10^{-4} - 10^{-5} $mole \cdot l^{-1}$.

INTRODUCTION

Surface active compounds bearing perfluorinated carbon chains as a hydrophobic and oleophobic moiety are well known to give a much lower surface energy in their solutions than those bearing hydrocarbon chains [1-3].
As perfluorinated carbon chains for this purpose, straight perfluoroalkanoic or perfluoroalkanesulfonic acids such as perfluorooctanoic acid or perfluorooctanesulfonic acid derived by electrofluorination or telomerization processes, or branched perfluoroalkenes such as oligomers of tetrafluoroethene or hexafluoropropene are usually used. The molecular structures of these perfluorinated carbon chains, particularly the straight ones, are known to be hard and inflexible, which usually give a surface active substance having a high melting point, a high Kraft point, and low solubility in solvents.

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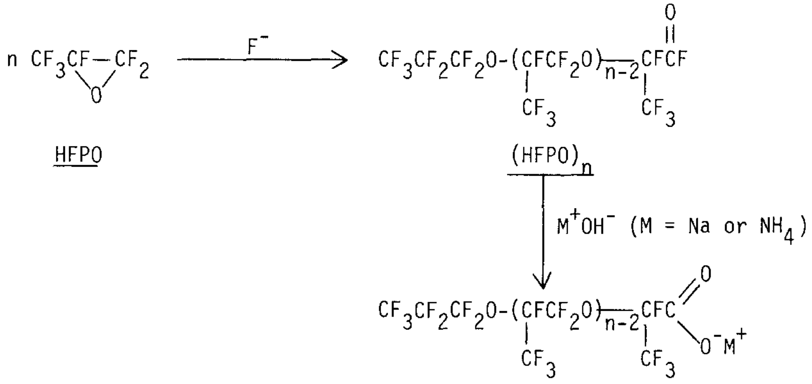
The molecular structure of polyethers, either hydrocarbon or fluorocarbon, are known to be much more flexible and they have lower melting points and higher solubilities. In the fluorocarbon series, the most readily available polyethers so far are the oligomers of hexafluoropropene oxide, $(HFPO)_n$ [4,5]. Sodium or ammonium salts of the carboxylic acid derived by hydrolysis of the trimer, tetramer, or pentamer of hexafluoropropene oxide, $(HFPO)_{3-5}$, were reported by Ponomarenko *et al.* to be quite effective in lowering the surface tension of water [6].



The oligo(hexafluoropropene oxide) chains were thus expected to be suitable as the hydro- and oleophobic part of surface active molecules. We now wish to report the preparation and surface active properties of oil soluble molecules which contain an aromatic ring as an oleophilic moiety and of water soluble molecules which contain an arenesulfonic acid group as a hydrophilic group on one side of the molecule and an oligo(hexafluoropropene oxide) group as an oleo- and hydro-phobic group on the other side.

RESULTS AND DISCUSSION

Preparation of arenes carrying an oligo(hexafluoropropene oxide) chain and their sulfonic acids

From the synthetic point of view, arenes and arenesulfonic acids carrying an oligo(hexafluoropropene oxide) group are prepared most easily by the Friedel-Crafts condensation between an arene and an oligomer of hexafluoropropene oxide followed by sulfonation.

$$\begin{tikzcd}
\mathrm{HFPO} \arrow[r, "F^-"] & (\mathrm{HFPO})_n \arrow[r, "\mathrm{ArH/AlCl_3}"] & (\mathrm{HFPO})_n\text{-}\mathrm{Ar} \arrow[d, "\mathrm{SO_3/H_2SO_4}"] \\
 & & (\mathrm{HFPO})_n\text{-}\mathrm{Ar'SO_3H}
\end{tikzcd}$$

Anionic oligomerization of hexafluoropropene oxide is well known and several procedures have been reported [7-9]. We conducted the oligomerization, n = 2 - 6, by the method using potassium fluoride as the anion source in diglyme solvent.

The resulting oligomers of HFPO are acid fluorides and are capable of acylating a benzene ring by means of a Friedel-Crafts catalyst such as $AlCl_3$ as reported by Tamborski et al. [10]. Various benzenes and toluenes carrying an oligo(hexafluoropropene oxide) group were prepared by using the dimer to hexamer of hexafluoropropene oxide, $(HFPO)_n$ where n = 2 - 6. The results of acylation and the ^{19}F and ^1H nmr data for these acylated products are given in Table 1 and 2 respectively. The acylated toluenes were shown to be para-disubstituted by inspection of their ^1H nmr spectra.

Sulfonation of these acylated benzenes and toluenes was achieved by heating them with 30% fuming sulfuric acid at 50 - 60 ^oC. The resulting sulfonic acids were purified by salting out the respective sodium sulfonate followed by crystallization of the salt from ethanol.

The structure of the pure sodium sulfonates were obvious from their ^{19}F and ^1H nmr spectra (Table 3). The sulfonic acid group in the aromatic ring was proved to be meta to the acyl group by close analysis of the chemical shifts for the four aromatic hydrogens.

Surface activities of $(HFPO)_n$-Ar in aromatic solvents

All of the $(HFPO)_n$-Ar compounds described above dissolved readily in aromatic solvents such as toluene or xylene, revealing remarkable effects on lowering the surface tensions of these solvents.

TABLE 1

Acylation of benzene and toluene with $(HFPO)_n$

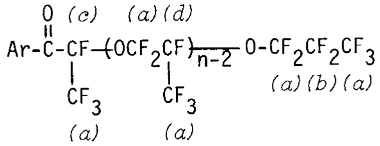
Starting materials		$AlCl_3$/HFPO	Reaction		Product Ar-$(HFPO)_n$	
ArH	n in $(HFPO)_n$	(mole)	Temp (°C)	Time (h)	B.p. (°C/mmHg)	Yield (%)
C_6H_6	2	2.4	70 - 80	2.5	100/40 (80/18)[a]	69
"	3	3.3	70 - 80	1	119/25 (112/20)[a]	71
"	4	2.1	70 - 80	1	113/5 (114/5)[a]	74
"	5	2.4	70 - 80	2	116-117/1	63
"	6	2.4	70 - 80	2	144-146/2	69
PhMe	2	2.4	50 - 75	2	119/45	78
"	3	2.5	80 - 90	1.5	120/25	79
"	4	2.1	80 - 90	1.5	122-123/4	71
"	5	2.4	70 - 80	1.5	135-136/2	65
"	6	2.4	70 - 80	2	150-151/2	60

[a] Values given in lit [10].

TABLE 2

The ^{19}F and ^{1}H nmr chemical shifts for $(HFPO)_n$-Ar

a) The ^{19}F chemical shifts for

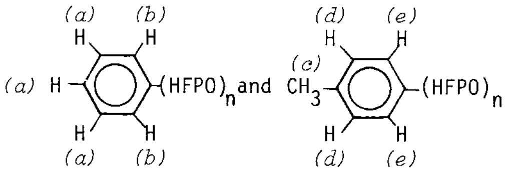


$$Ar\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{(a)}{CF_3}}{\overset{(c)}{CF}}\text{-}(\overset{(a)}{OCF_2}\underset{\underset{(a)}{CF_3}}{\overset{(d)}{CF}})_{n-2}\text{-}O\text{-}\underset{(a)}{CF_2}\underset{(b)}{CF_2}\underset{(a)}{CF_3}$$

F	δ*	no. of F
(a)	0.3 - 0.5	(5n-2)F
(b)	51.2	2F
(c)	49.7	1F
(d)	66.7	(n-2)F

* δ ppm upfield from ext. CF_3CO_2H (CCl_4).

b) The ^{1}H chemical shifts for



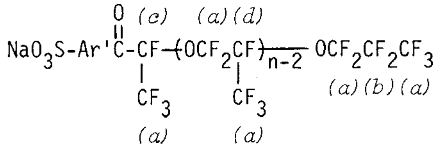
H	δ**	no. of H
(a)	7.4 - 7.8 (m)	3H
(b)	7.9 - 8.2 (m)	2H
(c)	2.45 (s)	3H
(d)	7.3	2H $\rbrace\ J_{(d)-(e)}=9$ Hz
(e)	7.9	2H

** δ ppm downfield from int. TMS (CCl_4).

TABLE 3

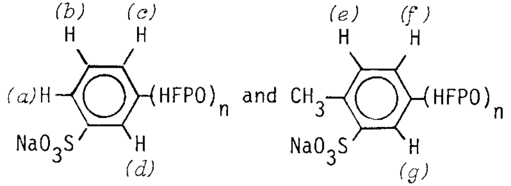
^{19}F and ^{1}H chemical shifts for $(HFPO)_n\text{-}Ar'SO_3Na$

a) The ^{19}F chemical shifts for



$$NaO_3S\text{-}Ar'\overset{\overset{(c)}{O}}{\overset{\|}{C}}\text{-}\underset{\underset{(a)}{CF_3}}{CF}\text{-}\!\left(OCF_2\overset{(a)(d)}{\underset{\underset{(a)}{CF_3}}{CF}}\right)_{n-2}\text{-}\underset{(a)(b)(a)}{OCF_2CF_2CF_3}$$

b) The ^{1}H chemical shifts for



F	δ*	no. of F	H	δ**	no. of H
(a)	2.7 - 5.3	(5n-2)F	*(a)*	7.97 (d)	1H
(b)	52.2	2F	*(b)*	7.40 (t)	1H
(c)	50.5	1F	*(c)*	7.79 (d)	1H
(d)	67.2	(n-2)F	*(d)*	8.27 (s)	1H
			(e)	7.19 (d)	1H
			(f)	7.65 (d)	1H
			(g)	8.40 (s)	1H

δ* ppm upfield from ext. CF_3CO_2H (EtOH).

δ** ppm downfield from int. TMS (EtOH).

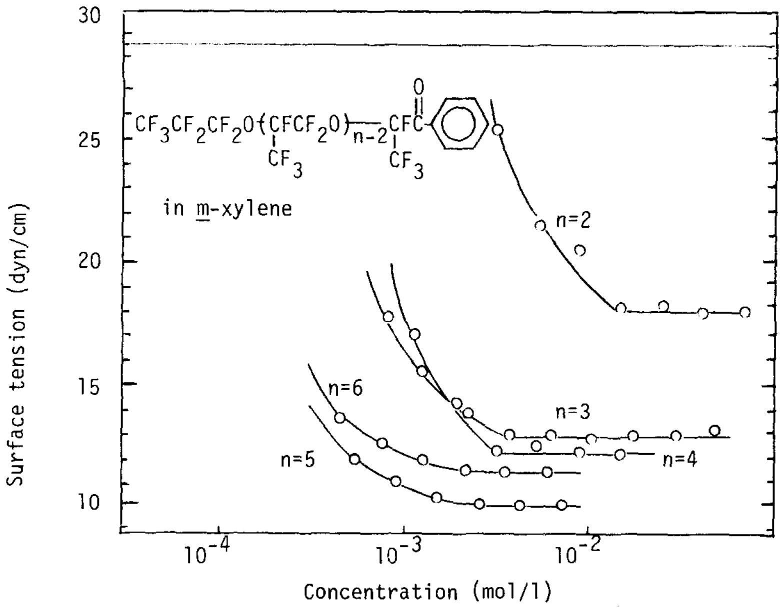


Fig 1. Surface tension vs. concentration for $(HFPO)_n$-Ph/m-xylene solutions (20°C)

TABLE 4

Surface tensions for $(HFPO)_n$-Ph/m-xylene solutions (20 °C)

n	γ_{min} (dyn·cm^{-1})	C_{min} (wt%)	C.M.C. (mol·l^{-1})
2	17.8	0.58	1.48×10^{-2}
3	12.8	0.21	3.75×10^{-3}
4	12.1	0.23	3.19×10^{-3}
5	9.9	0.23	2.58×10^{-3}
6	11.3	0.29	2.18×10^{-3}

For example, the surface tensions of m-xylene solutions with various concentrations of $(HFPO)_{2-6}$-Ph at 20 °C are shown in Fig. 1. The lowest surface tensions, γ_{min}, the concentrations of $(HFPO)_n$-Ph at this point, C_{min}, and the critical micelle concentrations, C.M.C. ($mol \cdot l^{-1}$) estimated from the bending point of the curves are given in Table 4. From these figures it was observed that the surface tension of xylene (28.6 $dyn \cdot cm^{-1}$) is generally lowered even at a very low concentration of $(HFPO)_n$-Ph, and the extent of this lowering effect depended on the length of the perfluorinated oligoether chains. Thus the effect increased from $(HFPO)_2$-Ph to $(HFPO)_5$-Ph, which lowered the surface tension to less than 10 $dyn \cdot cm^{-1}$. However, $(HFPO)_6$-Ph showed a weaker effect than $(HFPO)_5$-Ph, revealing that there is a balance between the oleophobic group, $(HFPO)_n$, and the oleophilic group, Ph, in the molecules. Each curve showed a clear bending point, from which the C.M.C. was determined.

Activity was also given in toluene (Table 5), and in this case too, $(HFPO)_5$-Ph showed the strongest effect.

In the $(HFPO)_n$-$C_6H_4CH_3$ series, however, it was found that $(HFPO)_6$-$C_6H_4CH_3$ was the most effective for lowering the surface tension of toluene and xylene (Table 5). Presumably this is caused by the well balanced oleophobic group, $(HFPO)_6$, and the oleophilic p-tolyl group in this molecule. Thus in comparison with the $(HFPO)_5$-Ph molecule the oleophilic methyl group in the para-position of the aromatic ring needed one more oleophobic unit of HFPO to achieve a balance.

Surface activities of $(HFPO)_n$-Ar'-SO_3Na in water

The surface tensions of aqueous solutions containing sodium salts of the sulfonic acids, $(HFPO)_n$-Ar'-SO_3Na, were measured at 20 °C and the results are shown in Fig. 2 and Fig. 3. The values of γ_{min} and the C.M.C. are given in Table 6. From these figures, it was found that in both the benzene- and toluenesulfonic acid series, those carrying a $(HFPO)_4$ group showed the highest effect for lowering the surface tension, down to 16 $dyn \cdot cm^{-1}$, at very low concentration, 0.001 wt%. These facts show that the oxygen atoms in the perfluorinated oligoether chains have no hydrophilic properties, presumably because electron density of the unshared electron pairs of the oxygen atoms is lowered considerably due to the neighbouring perfluoroalkyl groups (strong -I effect). Furthermore, the most hydrophobic trifluoromethyl groups might be aligned on the surface of the water as the oligoether structure is sufficiently flexible to make this kind of conformation feasible

TABLE 5

γ_{min} and C_{min} for Ar-$(HFPO)_n$/toluene and /xylene (20 °C)

Ar-$(HFPO)_n$		Solvent	γ min	C min
Ar	n		(dyn·cm^{-1})	(wt%)
Ph	2	toluene	21.0	2.3
"	3	"	12.8	2.3
"	4	"	13.5	2.3
"	5	"	12.2	0.46
"	6	"	12.7	0.46
_p_-MeC_6H_4	2	"	21.4	2.3
"	3	"	13.7	2.3
"	4	"	14.8	0.46
"	5	"	12.7	0.46
"	6	"	12.0	0.46
_p_-MeC_6H_4	2	_m_-xylene	21.5	2.3
"	3	"	14.3	2.3
"	4	"	13.8	2.3
"	5	"	12.8	0.46
"	6	"	11.9	0.46

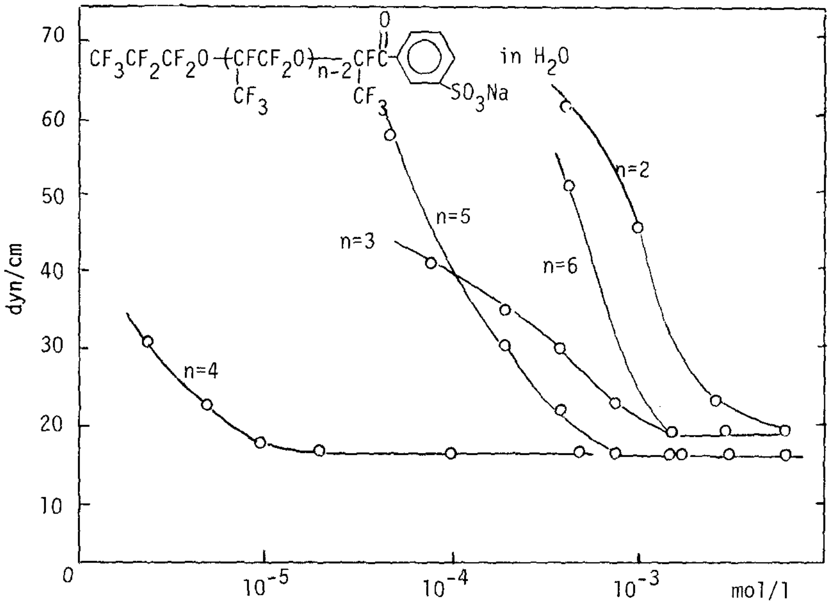


Fig 2. Surface tension vs concentration for $(HFPO)_n$-$C_6H_4SO_3Na/H_2O$ solutions (20 °C)

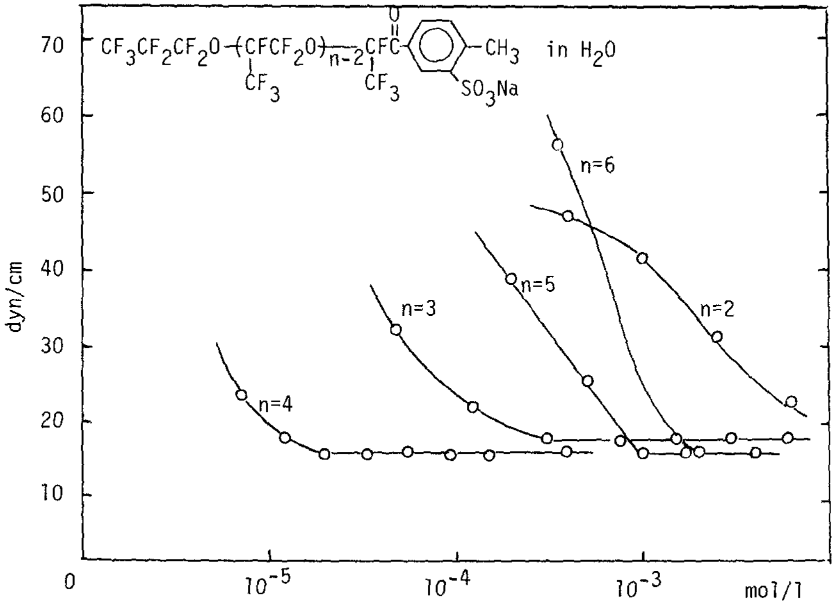
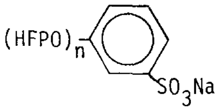
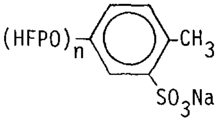


Fig 3. Surface tension vs concentration for $(HFPO)_n$-$C_6H_3(CH_3)SO_3Na/H_2O$ solution (20 °C)

TABLE 6

Surface tensions for $(HFPO)_n$-Ar'-SO_3Na/H_2O solutions (20 ^{0}C)

Sodium sulfonate	n	γ_{min} (dyn·cm^{-1})	C_{min} (wt%)	C.M.C. (mol·l^{-1})
	2	19.0	~0.30	———
	3	19.0	0.078	1.2×10^{-3}
	4	16.4	0.0012	1.5×10^{-5}
	5	16.0	0.074	7.5×10^{-4}
	6	15.9	~0.20	1.7×10^{-3}
	2	22.4	~0.30	———
	3	17.9	0.020	3.0×10^{-4}
	4	16.3	0.0013	1.5×10^{-5}
	5	16.2	0.10	1.0×10^{-3}
	6	15.9	0.20	1.7×10^{-3}

EXPERIMENTAL

Anionic oligomerization of HFPO

In a glass pressure vessel (300 ml) were placed calcined and finely ground potassium fluoride (3 g) and diglyme (40 ml). The mixture was cooled in a dry ice-acetone bath and liquefied HFPO (72 g, 43 ml) was introduced into the vessel. The whole was brought up to room temperature and was magnetically stirred for 24 h. The lower layer of the reaction mixture was separated and was subjected to fractional distillation. The yield and boiling point of each oligomer are shown on the next page. The identification of each oligomer could be readily achieved using glc and ^{19}F nmr.

n in $(HFPO)_n$	Yield (%)	B.p. (°C/mmHg)
2	3	52-56/760
3	10	112-115/760
4	27	93-96/80
5	30	126-131/80
6	9	110-114/10

Friedel-Crafts acylation

A typical run was as follows. Into a mixture of benzene (15 ml) and finely ground aluminum chloride (1.28 g, 9.6 mmol) was added hexafluoropropene hexamer (4 g, 4 mmol) dropwise at 60 °C. After vigorous stirring for 2 h at this temperature, the reaction mixture was poured onto ice (50 g) containing conc. hydrochloric acid (5 ml). An oily material was extracted with diethyl ether (~120 ml) and the extract was washed with 5% sodium bicarbonate solution then with water and dried over magnesium sulfate. The solvent was removed and the residue was subjected to vacuum distillation, yielding the acylated compound, $(HFPO)_6$-Ph (2.89 g, 69%), b.p. 144 - 146 °C/ 12 mmHg. Analysis: Found: C, 27.42; H, 0.50%. $C_{24}H_5O_6F_{35}$ requires C, 27.34; H, 0.48%.

Sulfonation

Into 30% fuming sulfuric acid (28 g) was added $(HFPO)_4$-$C_6H_4CH_3$ (14 g, 19 mmol) portionwise at 50 °C. After stirring for 1 h at 50 - 60 °C the reaction mixture was poured onto ice (200 g), warmed with further addition of water to produce a clear solution, and neutralized by the additon of 5N aqueous sodium hydroxide solution (125 ml). Addition of sodium chloride (70 g) with vigorous stirring caused crystals of the sodium sulfonate to separate. These were collected and dissolved in hot water (550 ml) and the salting out repeated (NaCl 100 g). The crystals were dissolved in dry ethanol (~50 ml) and an insoluble inorganic material was removed by filtration. The filtrate was evaporated, giving the pure sodium salt of the sulfonic acid (10.1 g, 64%).

The other members of the $(HFPO)_n$-Ph and $(HFPO)_n$-$C_6H_4CH_3$ series were sulfonated similarly, the yields of pure sodium salts being in the range 55 - 88%.

Determination of surface tension

Solutions of oil soluble compounds, $(HFPO)_n$-Ar, in purified *m*-xylene and toluene with various concentrations (0.0005 - 0.05 $mol \cdot l^{-1}$) were prepared. The surface tensions were determined on an automatically balanced electro-surface tension meter (Kyōwa Kagaku Co.) at 20 °C. Pure *m*-xylene gave 28.9 $dyn \cdot cm^{-1}$ at 20 °C, in agreement with the literature value [11]. Sodium sulfonate type water soluble compounds, $(HFPO)_n$-Ar'-SO_3Na, were dissolved in deionized and distilled water to produce solutions with various concentrations (0.5×10^{-5} - 1×10^{-2} $mol \cdot l^{-1}$) and the surface tensions were determined on the same apparatus also at 20 °C.

The surface tensions of aqueous solutions of the sulfonic acids were measured in a similar manner.

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