Journal of the American Oil Chemists' Society **Surfactants & Detergents**

Volume 61 **January 1984** **Number 1**

TECHNICAL

NEWS

Technical

♣ Preparation and Surface-Active Properties of Sulfopropylated N-Alkylperfluorooctanamides

CHIKAI KIMURA, KAGEAKI KASHIWAYA, MITSUNOBU KOBAYASHI, Department of Chemical Engineering for Resources, Mining College, Akita University, Tegata, Akita-shi 010, Japan, and **TATSUO NISHIYAMA,** New Akita Chemical Company, Barajima, Akita-shi 010, Japan

ABSTRACT

Sulfopropylation of perfluorooctanamide or its N-alkyl substituted derivatives gave products which were valuable as anionic surfactants. The amides were prepared by the reaction of ethyl perfluorooctanoate with ammonia or *n*-alkyl amines (C_1-C_{12}), and then treated with 1,3-propanesultone to obtain the desired products. The surface-active properties of these compounds were investigated to elucidate the correlation with the chain length of the N-alkyl group. Thus, generally speaking, the N-butyl derivative was found to exhibit properties superior to the others.

INTRODUCTION

Perfluorocarboxylic acid (1) has been recognized as a useful starting material (2) for the preparation of fluorine-containing surfactants (3) which have found ever increasing commercial use. The ester-type derivatives, however, are supposed to be impractical as surfactants because of the ease of hydrolysis in aqueious solution. On the contrary, the amide-type derivatives are more resistant to hydrolysis and thought to have great potential for practical applications Taking this point of view, some of the amide-type derivatives of perfluorooctanoic acid have been prepared and their surface-active properties investigated in previous publications (4,5).

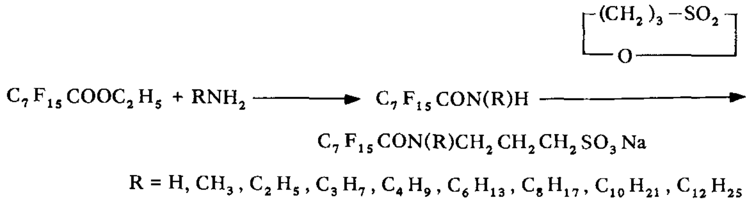
At this time, perfluorooctanamide and its N-alkyl substituted compounds were prepared by the reaction of ethyl perfluorooctanoate with ammonia or *n*-alkyl amines, and then subjected to sulfopropylation by 1,3-propanesultone to obtain anionic surfactants, as shown in Scheme 1.

Efforts have been made to elucidate the effect of the alkyl group (R) on the surface-active properties with respect to surface tension depression, critical micelle concentration (CMC), Krafft point, wettability and oil repellency. Thus it has been found that the compound containing the N-butyl group generally exhibits surface activities superior to those of ther compounds.

EXPERIMENTAL PROCEDURES

Materials

The primary alkyl amines (Tokyo Chemical Industry Co., Tokyo, Japan) were purified by distillation and their purity (>98%) was determined by gas liquid chromatography (GLC). 1,3-Propanesultone (Tokyo Chemical



$$C_7F_{15}COOC_2H_5 + RNH_2 \longrightarrow C_7F_{15}CON(R)H \xrightarrow{\boxed{-(CH_2)_3-SO_2-O-}} C_7F_{15}CON(R)CH_2CH_2CH_2SO_3Na$$

$R = H, CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_8H_{17}, C_{10}H_{21}, C_{12}H_{25}$

SCHEME 1

Industry Co., Tokyo, Japan) was fractionated to give a center cup, bp 124-125 C/1.5 mm Hg. Perfluorooctanoic acid (bp 185-186 C) was made avialable through the courtesy of New Akita Chemical Co., Akita, Japan. The corresponding ethyl ester (bp 171-174 C, n_D^{20} 1.3124) was prepared by heating for 6 hr the solution of the acid (0.3 mol), ethyl alcohol (0.9 mol) and *p*-toluenesulfonic acid (3 g) in benzene (150 mL) and separating the generated water as the benzene azeotrope.

Amidation

Perfluorooctanamide ($C_7F_{15}CONH_2$) was prepared according to the known method (6). Ammonia gas was bubbled through the solution of ethyl perfluorooctanoate (0.05 mol, 22.1 g) in ether (50 mL) for 6 hr with stirring at room temperature. The solvent was distilled off and the residue was recrystallized from benzene. The N-alkylperfluorooctanamides were prepared according to the following procedure. Ethyl perfluorooctanoate (0.07 mol, 30.9 g) was dissolved in 20 mL of ethyl alcohol and added to the solution of *n*-alkyl amine (0.077 mol) in ethyl alcohol (10 mL) with stirring at temperatures below 5 C. Stirring was continued for a further 2 hr and the solvent and excess amine were distilled off under reduced pressure. The residue was purified by distillation of recrystallization from benzene. The yields and properties of these amides are shown in Table I.

Sulfopropylation

The amide (0.05 mol) and toluene (80 mL) were added to the solution of metallic sodium (0.05 mol, 1.15 g) in methyl alcohol (30 mL). This solution was heated with stirring in an atmosphere of nitrogen for 3 hr and the methyl alcohol was separated by azeotropic distillation with toluene. The reaction mixture, cooled to below 60 C, was added to 1,3-propanesultone (0.006 mol, 6.72 g) and then refluxed with stirring for 4 hr. Then the mixture was cooled to 40 C and poured into 300 mL of acetone to precipitate the desired product, which was allowed to stand overnight, filtered off and washed with ether. The yields and melting points (dec) of the products are presented in Table I.

Surface-Active Properties

Surface tension was measured at 30 C using the Wilhelmy type tensiometer and the values of surface tension thus obtained at each concentration are shown in Table II. In Table III are presented the values of CMC which were determined by the conductivity method. Krafft points in Table III are the temperatures at which 1% suspensions of surfactants became clear solutions. Wettability was estimated by the sinking time obtained by the canvas disk test (7) and oil repellency was determined according to the 3M oil repellency test (8). These results are shown in Tables IV and V, respectively.

RESULTS AND DISCUSSION

It has been found that perfluoroalkylamides and their sulfopropylated compounds as anionic surfactants have been prepared readily. N-alkylperfluorooctanamides were obtained as white solids and their melting points were found to vary with the size of the N-alkyl group (R). Thus, the melting points of the amides dropped with increasing carbon number (n) of the alkyl group, but this tendency was reversed at n=3, after which the melting point increased with increasing n. The sulfopropylated compounds, however, did not show a regular change with n and decomposed with melting (Table I).

As a characteristic property of the fluorine-containing surfactant, the sulfopropylated compound showed generally good reducing power of surface tension. But a change in the size of the alkyl group (R) was found to produce a significant effect on the surface tension reduction. Thus, the introduction of small (n<6) or large (n=12) R resulted in a great decrease in the efficency although the change in effectiveness was small. When n was in the range of 6-10, the surfactants exhibited superior surface tension reduc-

TABLE I

Yields and Properties of $C_7F_{15}CONHR$ and $C_7F_{15}CON(R)CH_2CH_2CH_2SO_3Na$

	$C_7F_{15}CONHR^a$			$C_7F_{15}CON(R)CH_2CH_2CH_2SO_3Na^b$	
R	mp (C)	bp (C/mm Hg)	Yield (%)	mp (C) (dec)	Yield (%)
H	142-143	–	56	234	55
CH_3	71-72	–	65	220	69
C_2H_5	26-27	78-79/2	61	201	63
C_3H_7	28-29	90-91/1.5	77	195	60
C_4H_9	32-33	97-98/3	86	197	58
C_6H_{13}	47-48	110-111/2	66	283	40
C_8H_{17}	68-69	–	60	203	40
$C_{10}H_{21}$	70-71	–	67	199	46
$C_{12}H_{25}$	72-73	–	65	203	40

[a] IR (cm^{-1}) ν = 3400-3200 (NH_2), 3340-3320 (NH), 1700 (C=O), 1300-1100 (CF); δ = 1550 (NH).

[b] IR (cm^{-1}) ν =3400 (NH), 1690-1660 (C=O), 1300-1100 (CF), 1060-1040 (SO); δ = 1550 (NH).

TABLE II

Surface Tension of Aqueous Solution of $C_7F_{15}CON(R)CH_2CH_2CH_2CH_2SO_3Na$ at 30 C

R	Surface tension (dyne/cm) at each concentration (g/100 mL)							
	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
H	59.6	54.0	32.8	29.8	23.2	16.4	–	–
CH_3	54.4	50.0	41.0	31.4	22.4	23.8	23.2	22.8
C_2H_5	54.8	44.9	38.2	29.6	23.5	22.7	22.2	21.7
C_3H_7	53.7	47.0	36.8	29.2	21.8	20.9	20.0	19.1
C_4H_9	51.2	44.2	32.0	23.8	21.0	20.0	19.6	19.1
C_6H_{13}	28.0	21.5	18.4	18.0	17.7	17.5	17.4	17.3
C_8H_{17}	22.0	20.3	19.6	19.6	19.4	19.1	18.6	18.6
$C_{10}H_{21}$	28.2	26.8	24.6	24.6	23.0	21.8	20.6	19.6
$C_{12}H_{25}$	53.2	48.2	33.6	33.6	26.6	25.6	23.8	22.2

TABLE III

Critical Micelle Concentration (CMC) and Krafft Point of $C_7F_{15}CON(R)CH_2CH_2CH_2SO_3Na$

R	CMC X 10^3 (mol/L)	Krafft point (C) 1%
H	–	45
CH_3	4.03	10
C_2H_5	3.59	< 0
C_3H_7	2.84	< 0
C_4H_9	2.28	< 0
C_6H_{13}	1.75	> 100
C_8H_{17}	1.15	> 100
$C_{10}H_{21}$	2.44	> 100
$C_{12}H_{25}$	3.27	> 100

TABLE IV

Wettability of $C_7F_{15}CON(R)CH_2CH_2CH_2SO_3Na$ at 30 C

R	Sinking time (sec) at each concentration (g/100 mL)					
	0.05	0.1	0.2	0.3	0.4	0.5
H	>300	>300	>300	120	–	–
CH_3	>300	57	10	7	6	5
C_2H_5	>300	30	11	6	4	3
C_3H_7	>300	83	7	5	5	4
C_4H_9	>300	22	9	7	6	5
C_6H_{13}	80	33	11	10	9	7
C_8H_{17}	240	170	150	55	40	25
$C_{10}H_{21}$	>300	>300	120	35	20	11
$C_{12}H_{25}$	>300	>300	63	30	20	17

TABLE V

Oil Repellency Test of $C_7F_{15}CON(R)CH_2CH_2CH_2SO_3Na$

R	Adhesion (%)	Oil rating
H	4.61	100
	1.38	78
	0.43	60
CH_3	3.69	90
	1.83	80
	0.32	0
C_2H_5	3.11	80
	1.77	60
	0.24	0
C_3H_7	3.33	90
	1.62	90
	0.23	80
C_4H_9	3.31	80
	1.75	80
	0.35	70
C_6H_{13}	3.32	50
	1.47	0
	0.19	0
C_8H_{17}	4.04	50
	1.73	0
	0.34	0
$C_{10}H_{21}$	2.62	0
	0.96	0
	0.37	0
$C_{12}H_{25}$	3.86	0
	1.04	0
	0.42	0

tion to the others in both efficiency and effectiveness.

It has been well known the the CMC decreases generally as the hydrophobic character of the surfactant increases. In accordance with the above general rule, the effect of R was manifested by the decrease in CMC as n increased to 8. When n exceeded 8, on the contrary, the CMC began to increase with increase in n. This feature is considered to be dur to the longer chain induced inhibition to the micelle formation.

As shown in Table III, the Krafft point decreased as n increased to 4, and began to rise significantly when n exceeded 6.

Wettability was found to be good when the surfactant has a relatively small R and it may be seen that the surfactant should have a moderately large alkyl group (R with n=2-4) in order to exhibit good wettability.

Oil repellency, on the other hand, decreased as the length of R increased, as shown in Table V. This result might be expected from the progressive decrease in fluorine content of the surfactant. Thus it can be seen that the surfactant should have on alkyl group smaller than hexyl in order to have excellent oil repellency.

REFERENCES

1. Kauck, E.A., and A.R. Diesslin, Ind. Eng. Chem. 43:2332 (1951).
2. Guenhner, R.A., and M.L. Vietor, Ind. Eng. Chem. Prod. Res. Dev. 1:165 (1962).
3. Schierer, E., Tenside 13:1 (1976).
4. Kimura, C., K. Murai, K. Kashiwaya, T. Kanno and T. Nishiyama, Uukagaku 31:464 (1982) (in Japanese).
5. Kimura, C., K. Kashiwaya, K. Murai, N. Sato and T. Nishiyama, Yukagaku 32:258 (1983) (in Japanese).
6. Husted, D.R., and A.H. Ahlbrecht, J. Am. Chem. Soc. 75:1605 (1955).
7. Seyferth, H., and O.M. Morgan, Am. Dyest. Rep. 27:525 (1938).
8. Crajeck, E.J., and W.H. Petersen, Text. Res. J. 32:320 (1962).

[Received July 13, 1983]