報 文

Preparation and Surface Active Properties of Alkali Salts
of *N*-Perfluorooctanoylamino AcidsChikai KIMURA, Kageaki KASHIWAYA, Mitsunobu KOBAYASHI,
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Ethyl perfluorooctanoate was reacted at 30°C for 2 h in ethanol with ethyl ester of amino acid (glycine, α - and β -alanine) to prepare *N*-perfluorooctanoylamino acid ester. The esters thus prepared were saponified to form the desired surface active agents by acidification with hydrochloric acid and successive neutralization with alkali hydroxides. The aqueous solution of these surfactants were subjected to the determination of surface tension, critical micelle concentration, Krafft point, wettability and oil repellency according to the conventional methods. Generally, the glycine derivatives were only slightly soluble in water showing higher Krafft points and poor surface activities. The α -alanine derivatives showed lower Krafft point due to the presence of methyl side chain and superior wettability to other amino acid derivatives. The β -alanine derivatives exhibited significant surface tension depression and in the case of K salt the surface tension was depressed to 15 dyn/cm.

1 Introduction

It has long been known that the *N*-acylated amino acids¹⁾ type surfactants have been prepared by the condensation of fatty acid derivative with amino acid or hydrolysate of natural protein, and marketed under the name such as Medialan (Höchst) or Lamepon. As has been described in the recent review²⁾, (Chem, Fabrik Grünau) these materials are now gaining more interest and commercial use because of their good detergency and lime soap dispersant properties. In addition, they are nonirritating to skin and thus useful for cosmetic and toiletries³⁾.

On the other hand, the recent development of organic fluorine-containing compounds has included the preparation and application of fluorinated surfactant⁴⁾. However, little information has been reported about the surfactants derived from perfluoro carboxylic acid and amino acid.

As part of the investigation of the preparation and properties of perfluoroamide-linked surfactants^{5)~7)}, an attempt has been made at

this time to obtain the *N*-acylated amino acid salt using ethyl perfluorooctanoate and typical amino acids such as glycine, DL- α -alanine and β -alanine according to the following reaction sequence.

Thus, nine kinds of surfactants have been prepared with a good yield in each step and their surface active properties were determined and compared with each other.

2 Experimental

2.1 Materials

Amino acids employed in the experiment were obtained commercially and used without further purification. Ethyl perfluorooctanoate was prepared according to the known procedure described in the previous publication⁷⁾ and characterized regarding bp 172~174°C, n_D^{20} 1.3124; IR (cm⁻¹), 1780 (C=O), 1100~1300

(CF).

2.2 Method of preparation

2.2.1 Ethyl ester of amino acid

Amino acid was esterified by ethyl alcohol according to the method adopted in the preparation of benzyl ester⁹⁾.

Thionyl chloride (26.2 g, 0.22 mol) was added with stirring to an ethanol solution (200 ml) of amino acid (0.22 mol) at (200 ml) 0~5°C. After the addition, stirring was continued for further 2 h at 40°C. The reaction mixture was cooled to room temperature, diluted with ethyl ether until turbidity appeared and then refrigerated for about 3 h. The solid material was filtered off and recrystallized from ether-ethanol mixed solvent.

The amino acid ester hydrochloride (0.1 mol) thus obtained was dissolved in 100 ml of chloroform and a large excess amount of triethylamine was added to the solution dropwise over a period of 10 min and stirring was continued for about 3 h. Chloroform was evaporated in reduced pressure and the product was distilled off *in vacuo*.

2.2.2 *N*-Perfluorooctanoylamino acid ethyl ester

Ethyl perfluorooctanoate (13.2 g, 0.03 mol) was dissolved in 20 ml of ethanol and the solution was added to the amino acid ethyl ester (0.03 mol) in ethanol (10 ml). The reaction mixture was stirred at 30°C for about 2 h. Then, the solvent was evaporated in reduced pressure and the residue distilled in *vacuo*.

2.2.3 *N*-Perfluorooctanoylamino acid

The above ester (0.04 mol) was mixed with sodium hydroxide (1 g, 0.004 mol) dissolved in 50 ml of water and stirred at 80°C for 1 h. Aqueous hydrochloric acid (9%) was added to the mixture cooled in the ice-water bath until the solution became acidic. The product separated was filtered off, washed with water and recrystallized from acetone-trile.

2.2.4 Alkali metal salt of *N*-perfluorooctanoylamino acid

N-Perfluorooctanoylamino acid was

neutralized with aqueous alkali hydroxide and the solution was evaporated to dryness to obtain the corresponding alkali salt.

2.3 Measurement of surface active properties

Surface tension was measured at 30°C using the Wilhelmy type tensiometer and the values obtained were plotted against the concentration of surfactant. The critical micelle concentration (cmc) was determined by the conductivity method and the Krafft point was shown by the temperature at which 1% suspension became clear solution. Wettability was estimated by the sinking time determined by the canvas disk test. Oil repellency was determined according to the 3 M Oil Repellency Test⁹⁾.

3 Results and Discussion

3.1 Preparation of intermediates

The amino acid ethyl ester was prepared in 55~78% yield, though a part of the product was polymerized, from the corresponding hydrochloride obtained in excellent yield (83~93%) by esterification of the amino acid with ethyl alcohol in the presence of thionyl chloride. The properties of the amino acid ethyl esters and

Table-1 Properties of amino acid derivatives.

R	HCINH ₂ RCOOC ₂ H ₅	NH ₂ RCOOC ₂ H ₅	
	mp (°C)	bp (°C/mmHg)	n_D^{20}
CH ₂	143~144	41~42/7	1.4237
CH(CH ₃)	85~86	40~42/9	1.4185
CH ₂ CH ₂	55~56	51~52/9	1.4267

Table-2 Properties of *N*-perfluorooctanoylamino acids and their ethyl esters.

R	C ₇ F ₁₅ CONHRCOOC ₂ H ₅		
	bp (°C/mmHg)	mp (°C)	IR (cm ⁻¹)
CH ₂	118~121/3	29~30	3330, 1740
CH(CH ₃)	116~117/3	32~33	1700, 1550
CH ₂ CH ₂	120~123/2	31~32	1300~1100
R	C ₇ F ₁₅ CONHRCOOH		
	mp (°C)	NV (Calcd)	RI (cm ⁻¹)
CH ₂	134~135	121.2 (119.0)	3300~3290 1720~1710
CH(CH ₃)	168~169	115.5 (115.6)	1690 1550~1530
CH ₂ CH ₂	121~122	114.0 (115.6)	1300~1100

their hydrochlorides were shown in **Table-1**.

The amino acid ethyl ester was reacted with ethyl perfluorooctanoate to obtain *N*-perfluorooctanoylamino acid ester in 64~91% yield. The ester thus obtained was converted to the corresponding acid as a white crystal in 66~99% yield. The properties of these *N*-perfluorooctanoyl compounds were shown in **Table-2**.

3.2 Surface tension

The surfactants prepared at this time showed great ability of surface tension reduction in accordance with the general feature of the fluorine-containing surfactant. Among the three kinds of amino acid derivatives, the glycine derivatives were found to be generally poorly soluble in water and inferior to other amino acid derivatives in surface tension reduction (**Figs.-1, 2**), although the lithium-containing derivative exhibited a greater efficiency as shown in **Fig.-3**. On the contrary, α - and β -

Fig.-1 Surface tension curves of sodium salts of *N*-perfluorooctanoylamino acids at 30°C.

Fig.-2 Surface tension curves of potassium salts of *N*-perfluorooctanoylamino acid.

Table-3 Critical micelle concentration (cmc) and Krafft point of *N*-perfluorooctanoylamino acid salt ($C_7F_{15}CO-NHRCOOM$)

Surfactant		cmc $\times 10^3$ (M)	Krafft point (°C) (1%)
R	M		
CH ₂	Na	—	60
	K	10.9	26
	Li	—	93
CH(CH ₃)	Na	10.51	<0
	K	8.73	<0
	Li	9.67	68
CH ₂ CH ₂	Na	10.88	40
	K	10.18	<0
	Li	—	76

alanine derivatives, especially the latter, showed much better properties in surface tension reduction suggesting the significant chain effect in the hydrophobic group.

3.3 cmc

The values of cmc determined at 30°C are presented in **Table-3**. The cmc decreased in the order of Na>Li>K for the α -alanine derivatives.

3.4 Krafft point

Krafft point (**Table-3**) was also affected by the kind of metal. Thus, the lithium salt showed the highest Krafft point as anticipated from the poor solubility in water. The lowest Krafft point of α -alanine is considered to be caused by the branched hydrophobic group.

Table-4 Wettability of *N*-perfluorooctanoylamino acid salts ($C_7F_{15}CONHRCOOM$) at 30°C (Sinking time, s)

Surfactant		Concentration (g/100 ml)							
R	M	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0
CH ₂	Na	>300	>300	>300	>300	—	—	—	—
	K	>300	>300	>300	>300	>300	>300	>300	>300
	Li	>300	—	—	—	—	—	—	—
CH(CH ₃)	Na	>300	24	12	5	3	2	2	1
	K	>300	26	11	4	3	3	2	1
	Li	>300	>300	28	9	4	3	2	2
CH ₂ CH ₂	Na	>300	>300	60	45	15	6	6	5
	K	>300	>300	>300	>300	26	15	13	9
	Li	>300	>300	73	33	20	—	—	—

Fig.-3 Surface tension curves of lithium salts of *N*-perfluorooctanoylamino acids at 30°C.

Table-5 Oil repellency of *N*-perfluorooctanoyl-
amino acid salt ($C_7F_{15}CONHRCOOM$)

Surfactant		Oil repellency	
R	M	Adhesion (%)	Rating
CH ₂	Na	1.83	100
		0.34	60
		0.21	50
	K	9.49	100
		2.22	100
		0.48	0
	Li	1.88	60
		0.90	50
		0.26	0
CH(CH ₃)	Na	2.21	100
		1.59	100
		0.22	100
	K	2.22	100
		1.59	100
		0.95	100
	Li	3.16	100
		1.57	100
		1.30	90
CH ₂ CH ₂	Na	3.34	100
		1.65	100
		0.75	100
	K	2.81	100
		1.96	100
		0.52	100
	Li	2.41	100
		1.25	100
		0.40	70

3.5 Wettability

A similar feature was observed with regard to the wettability as shown in **Table-4**. The glycine derivatives showed poor wettability, while α -alanine derivative exhibited excellent wettability.

3.6 Oil repellency

Oil repellency is another characteristic property of fluorine-containing surfactant and good property was demonstrated by all surfactant, although, among them, the alanine derivatives were slightly superior to the glycine derivatives as shown in **Table-5**.

In conclusion, the present results suggest that the β -alanine derivative is the most excellent surfactant among the three kinds of amino acid derivative.

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