

Studies on the Surfactants of the N-Acyl Carboxylic Acid(II)

—Surface-Active Properties of N-Acyl Amidoethyl N-Amido
Carboxylic Acid Derivatives—

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N-아실 카르복시산계 계면활성제에 관한 연구(제2보)

—N-아실 아미도에틸 N-아미도 카르복시산 유도체의 계면성—

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요 약

N-아실 아미도에틸 N-아미도 카르복시산 유도체들의 물리적 특성과 계면성이 연구되었다. 묽은 용액의 표면장력은 22~32dyne/cm의 값을 나타냈으며 이들 *cmc*의 범위는 0.8~6.0mmol/L이었다. 표면장력 저하능은 소수성의 알칼사슬이 길어질수록 그리고 카르복시기와 아미드기 사이의 메틸렌기의 수가 감소할수록 증가하였다. 반응생성물의 구조와 계면성의 관계를 비교·검토한 바 온화한 Krafft point와 뛰어난 습윤성, 낮은 기포력을 나타내었다.

I. INTRODUCTION

Amidoamine derivatives obtained by the reaction of fatty acids or their methyl esters with hydroxyethyl ethylene diamine have softening of textile properties and are recommended as rinsing bath finishes and light-duty detergents.^{1,2)} It was observed that the introduction of an amido group into sulfopropylated amphoteric molecule improved water solubility.^{3,4)} It was also well

known that the introduction of a second amido group into the sulfobetaine molecule, such as the succinimide derivatives, further enhanced water solubility.

Further work⁵⁾ on sulfoquaternary lime soap dispersant showed that water solubility increased as spacing between the cationic and anionic sites was increased from 2 to 3 carbon atoms. Most of simple sulfobetaines, however, limited to water solubility which could be deterrent to their usefulness.⁶⁾

It is therefore of interest to synthesize new water-soluble surfactants based on carboxyl group and amide-solubilizing group and to examine how the spacing between the solubilized carboxyl group and the nearest amido group affects surface activities.

In this study, the nine kinds of N-acyl amidoethyl N-amido carboxylic acid derivatives synthesized by acylation of fatty acid chloride with amidoamine derivatives, resulted from the reaction the monomethyl esters of dicarboxylic acid and ethylene diamine, were compared with respect to their surface active properties. In these cases, surface activities always depends on the length of the solubilizing carboxyl group and the nearest amido group.

II. EXPERIMENTAL METHODS

II - 1. Materials and Experimental Apparatus

The surfactants used in this study were synthesized in our laboratory.⁷⁾ The surface tension, critical micelle concentration(*cmc*), Krafft point, foaming, and wetting ability of N-acyl amidoethyl N-amido carboxylic acid derivatives were measured. Surface tension was determined by the Krüss surface tensiometer(K-8), and the foam heights and their stability were measured by Ross-Miles method.

II - 2. Surface Tension

The du Nouy instrument may generally be used for surface tension of most of liquid systems. In this study, surface tension of the products were measured with a du Nouy tensiometer of the platinum-iridium ring at 0.1~10mmol/L aqueous solution and then the values were corrected to 25°C. The ring was washed with benzene, acetone and then distilled water, heated with oxidizing flame and dried.

The measured values of the synthesized deri-

vatives were revised by the following equation.

$$S=P \times F \dots\dots\dots(1)$$

Where, S(dyne/cm) is a real value of surface tension, P(dyne/cm) is an apparent value, and F is a correction factor given by the following equation.

$$F=0.7250+\sqrt{\frac{0.001452P}{C^2(D-d)}+0.04534}-\frac{0.07Pr}{R} \dots\dots\dots(2)$$

p ; apparent value of surface tension
(dyne/cm),
D ; density of water(g/cm³),
d ; density of solution(g/cm³),
C ; length of ring(mm)

II - 3. Krafft Point

For many ionic materials, it is found that the overall solubility of the material in water increases as the temperature rises. It depends on the crystal lattice energy and heat of hydration of the material being dissolved. The aqueous solubility expressed by the Krafft point was measured by gradually heating a 1.0wt% dispersion of the test compound until a clear solution was obtained.

The experimental method of T_k measurement is as follows.

1. Take a lg of sample in test tube and fill the test tube with distilled water until 100mL.
2. Equip thermometer on the test tube and the test tube was put it into water bath.
3. Heat temperature gradually.
4. Read the temperature that solution is clear suddenly.

II - 4. Foaming Power and Its Stability

The foaming power and its stability of the synthesized surfactants were measured by Ross-Miles method⁸⁾ following JIS K-3362 and the

equipments of foaming power were shown by Fig. 3. The measurements were carried out at the 1.0~3.0mmol/L and 40°C. The reservoir or pipet A is filled with the solution to be examined and then placed on the supporting ring at the head of the receiver B which contains 50mL of the same solution. When the stopcock of reservoir A is opened and then the solution falls, foam is formed in the receiver and is measured in B immediately after the reservoir A is emptied. The orifice of A is so constructed that the turbulence set up causes the stream of solution to break up into droplets just after emerging from the orifice. Foam is produced when these droplets strike the surface of the liquid or foam in the receiver.

When the same method was duplicated three times, foaming heights were recorded immediately(A), and also after 5 minutes(B). The foaming power was represented by foaming height (mm) and its stability(FS) was represented by following equation.

$$FS(\%) = (B/A) \times 100 \dots \dots \dots (3)$$

II -5. Wetting Ability

The wetting ability of all the amphiphiles was determined by using a modified version of the Draves test.⁹⁾ The times in seconds were mea-

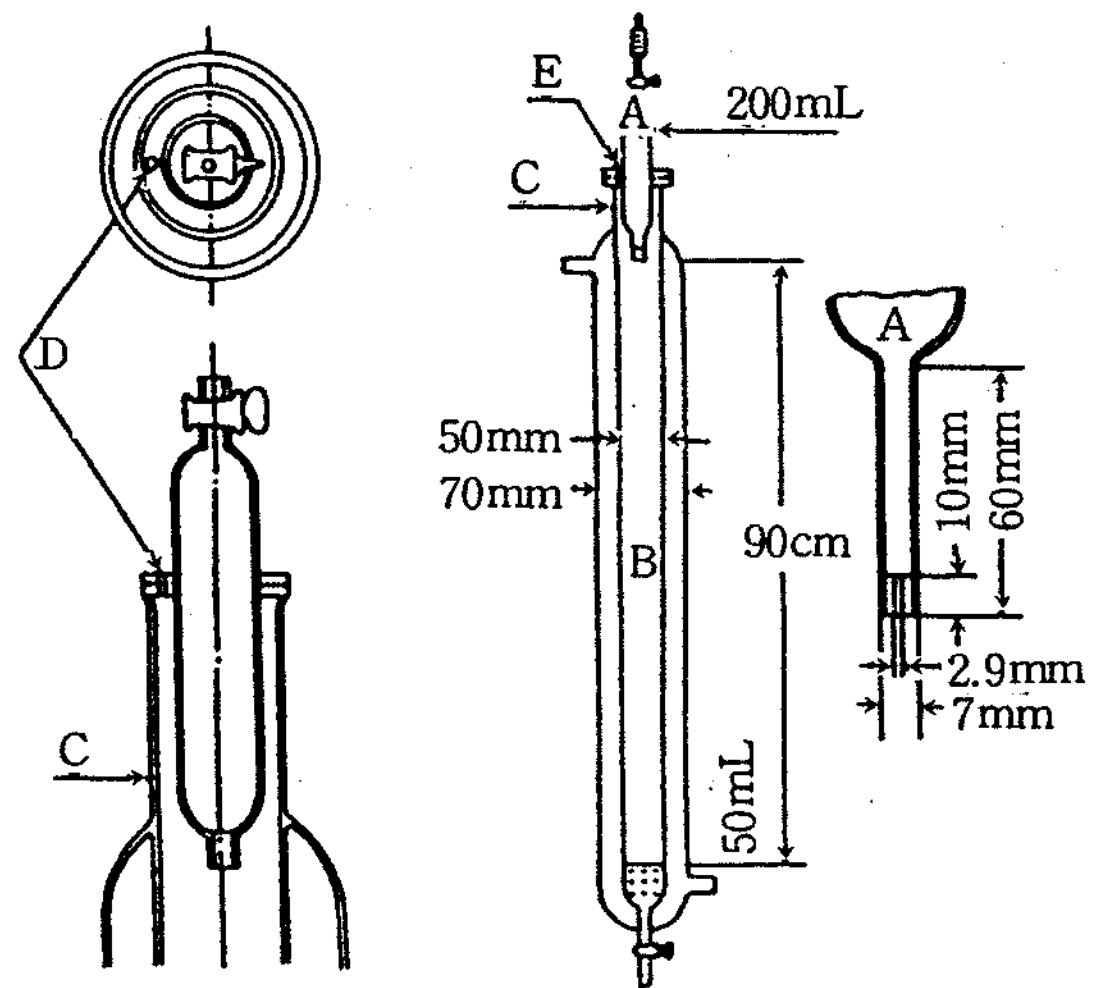


Fig. 1. Apparatus for determination of foaming power.

- A : Foam pipet
- B : Foam receiver
- C : Vertical tube
- D : Hole
- E : Rubber stopper

sured for the standard 5g cotton skein to sink in the solution of the N-acyl amidoethyl N-amido carboxylic acid derivatives at 25°C.

The wetting abilities of nine kinds of N-acyl amidoethyl N-amido carboxylic acid were determined by AATCC Method 17-1960. The measurements of wetting ability were shown in Fig. 2. The skein hanged with a poise(40g) and nylon thread(19mm) was immersed in mass flask that filled with standard concentration solution of the

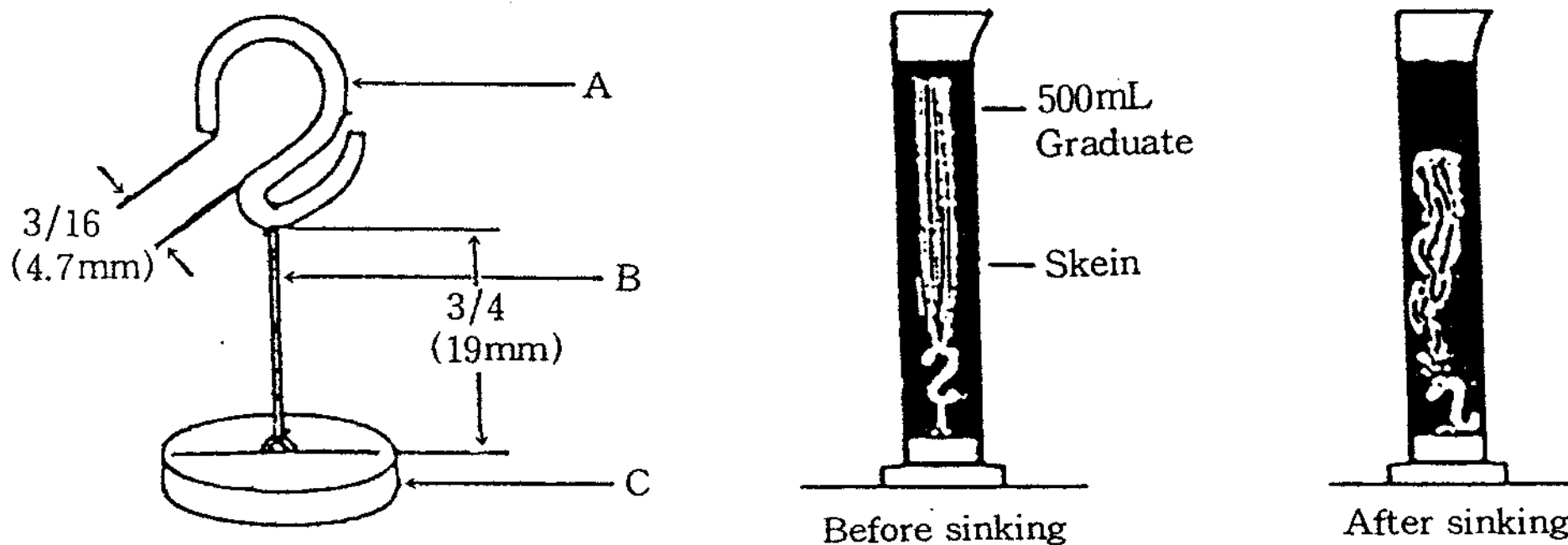


Fig. 2. Apparatus for evaluation of water wetting agents.

- A : Hook(3g)
- B : Nylon thread(19mm)
- C : Lead(40g)

products. The interval time from what poise was reached the bottom of a mass flask to what hook was touched the poise was measured by stop watch. It was repeated the same method three times, and then wetting ability was evaluated with the average of measured time.

III. RESULTS and DISCUSSION

III - 1. Surface Tension

When a surfactant material dissolves in water, the surfactant molecules orient and adsorb on the surface of their solution with their hydrophobic groups facing toward the air. Accordingly the surface of the surfactant solution is covered with the hydrophobic groups of surfactant just as if the surface were covered with an oil film. As the

Table 1. Surface active properties of N-acyl amidoethyl N-amido carboxylic acid derivatives

Comp'd.	Krafft point (°C)	cmc (mol/L × 10 ⁻³)	Γ _{cmc} (dyne/cm)
LAF	71	3.3	27.1
PAF	71	2.5	26.0
SAF	95	0.8	22.0
LAA	72	5.2	29.1
PAA	75	3.9	26.9
SAA	82	2.2	23.0
LAP	64	6.0	31.8
PAP	78	4.5	29.2
SAP	84	3.6	25.3

LAF : N-lauroyl amidoethyl N-amido formic acid
 PAF : N-palmitoyl amidoethyl N-amido formic acid
 SAF : N-stearoyl amidoethyl N-amido formic acid
 LAA : N-lauroyl amidoethyl N-amido acetic acid
 PAA : N-palmitoyl amidoethyl N-amido acetic acid
 SAA : N-stearoyl amidoethyl N-amido acetic acid
 LAP : N-lauroyl amidoethyl N-amido propionic acid
 PAP : N-palmitoyl amidoethyl N-amido propionic acid
 SAP : N-stearoyl amidoethyl N-amido propionic acid

cohesive force of hydrocarbon chain of the surfactant is smaller than that of pure water, the surface tension of the aqueous solution is smaller than that of pure water.

The surface tensions of N-acyl amidoethyl N-amido carboxylic acids were shown in Fig. 3 to 5 and Table 1.

The surface tensions of three kinds of N-lauroyl, palmitoyl, stearoyl amidoethyl N-amido formic acid were shown in Fig. 3. The surface tensions of these surfactants were decreased with the increase in the alkyl chain length. The lowest value (22 dyne/cm) was obtained by N-stearoyl amidoethyl N-amido formic acid.

The surface tensions of N-acyl amidoethyl N-amido acetic acid and those of N-acyl amidoethyl N-amido propionic acid were plotted in Fig. 4 and 5, respectively.

From Fig. 3, 4 and 5, it was found that the number of methylene group between the carboxy group and the nearest acid amide group influenced the surface activities. For the same hydrophobic group, increasing the number of methyl-

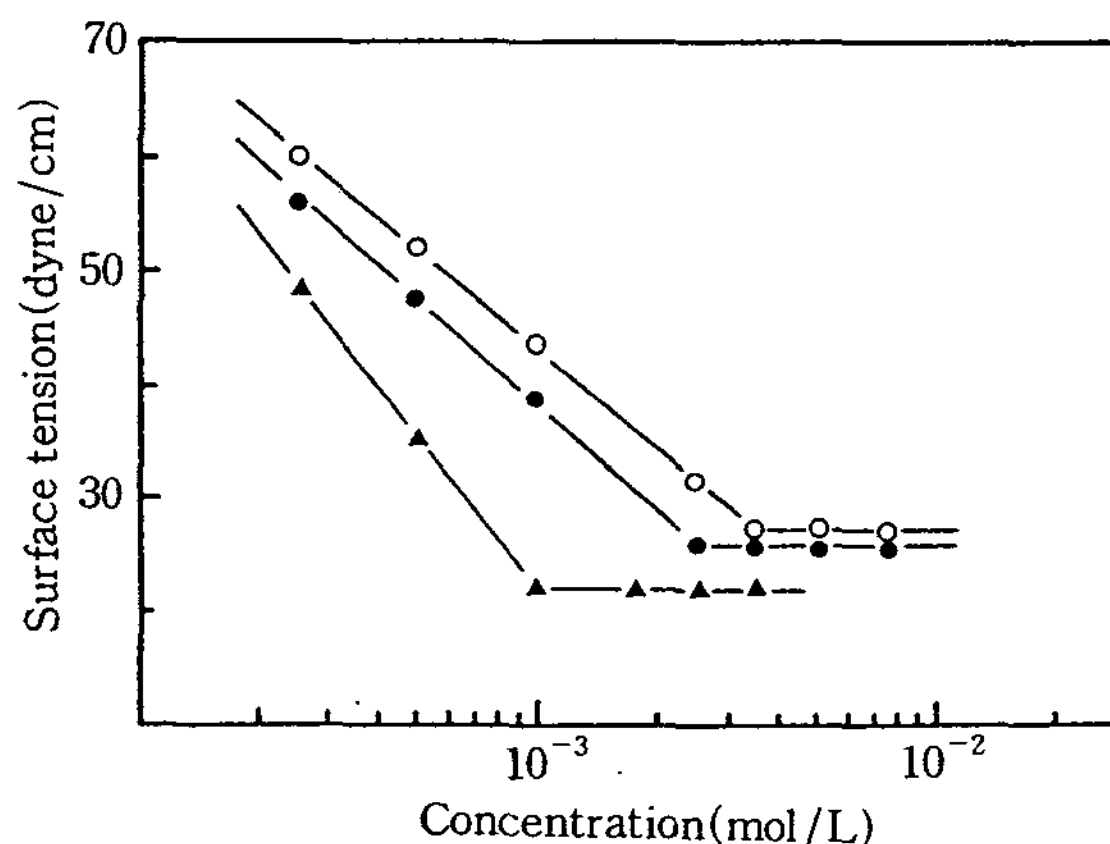


Fig. 3. Surface tension of N-acyl amidoethyl N-amido formic acid.

○ : N-lauroyl amidoethyl N-amido formic acid
 ● : N-palmitoyl amidoethyl N-amido formic acid
 ▲ : N-stearoyl amidoethyl N-amido formic acid

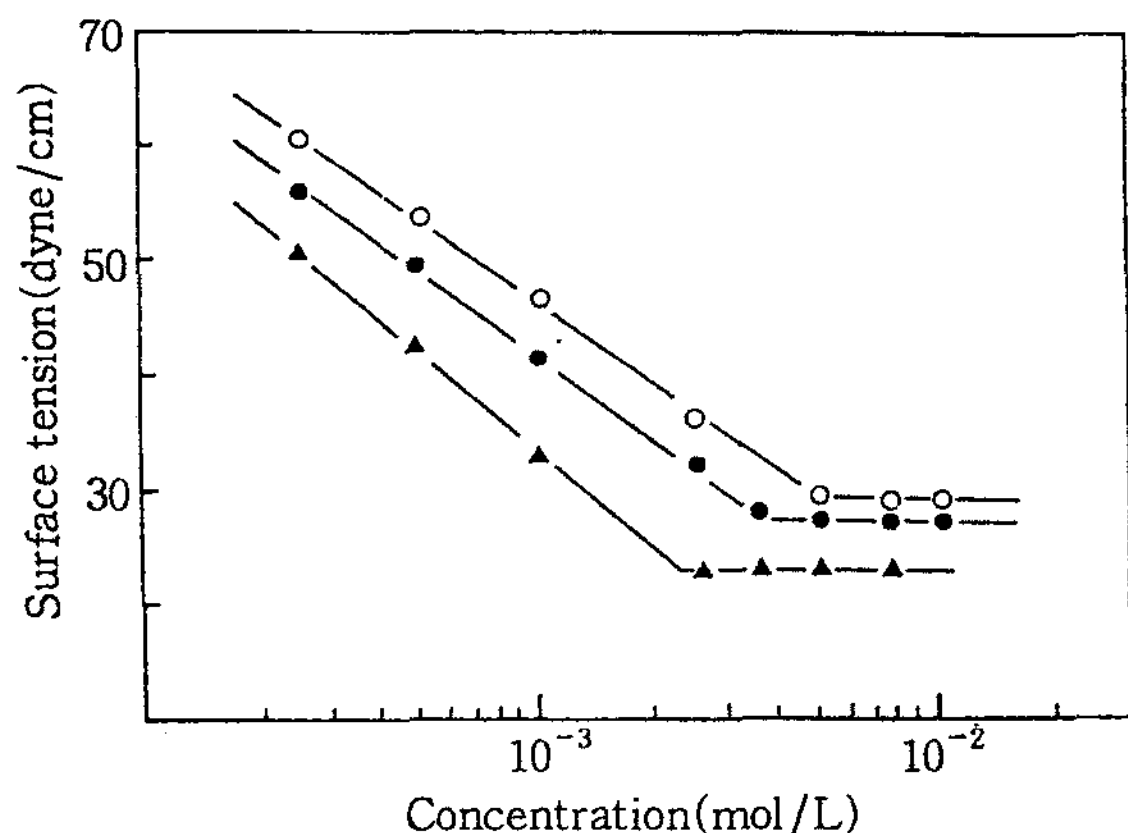


Fig. 4. Surface tension of N-acyl amidoethyl N-amido acetic acid.

- : N-lauroyl amidoethyl N-amido acetic acid
- : N-palmitoyl amidoethyl N-amido acetic acid
- ▲ : N-stearoyl amidoethyl N-amido acetic acid

ene group increased surface tension.

III - 2. Critical Micelle Concentration (*cmc*)

The hydrocarbon groups generally tend to avoid contact with water. Various adsorption phenomena of surfactants depend on this tendency of their hydrophobic groups.

In this study, *cmc* of derivatives was determined from the break point of each surface tension curves in Fig. 3 to 5.

In Fig. 3, the *cmc* of N-acyl amidoethyl N-amido formic acids was 3.3, 2.5, and 0.8 mmol/L respectively. They are decreased according to the decrease of acyl group carbon number, and the lowering ability of surface tension was depended on the carbon number of the hydrophobic group.

In Fig. 4 and 5, the *cmc* of N-acyl amidoethyl N-amido acetic acids and N-acyl amidoethyl N-amido propionic acids were in the range of 5.2~2.2 mmol/L and 6.0~3.6 mmol/L, respectively. It is therefore consistent with the results

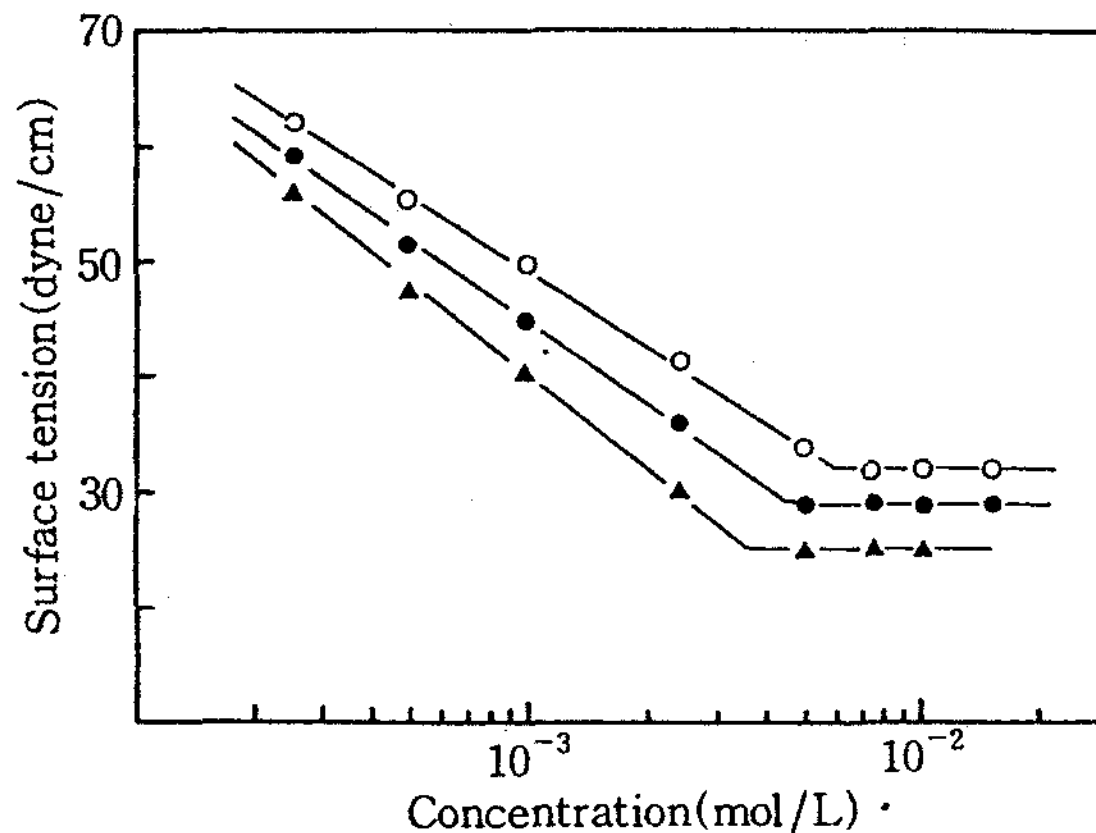


Fig. 5. Surface tension of N-acyl amidoethyl N-amido propionic acid.

- : N-lauroyl amidoethyl N-amido propionic acid
- : N-palmitoyl amidoethyl N-amido propionic acid
- ▲ : N-stearoyl amidoethyl N-amido propionic acid

of surface tension.

III - 3. Krafft Point

When the solubility of an ionic surfactant in water is measured at various temperature, the solubility rapidly increases at a given temperature. Krafft points were listed in Table 1.

It can be seen from the data that Krafft point can vary as a function of the nature of the hydrophobic group. The intimate relationship between the Krafft temperature and solid state of the surfactant is confirmed by the fact that is a good correlation between T_k for a surfactant of a given chain length. In generally, the Krafft temperature of this product were increased with the increase of hydrophobic alkyl chain length.

III - 4. Foaming

Typical foaming power and its stability for the compounds were given is Fig. 6 to 8 and Table 2. The *cmc* of these compounds may be used as a guide in predicting the foaming ability, but not

necessarily the persistence of such a foam.

In Fig. 6, the foaming heights and stabilities of three kinds of N-acyl amidoethyl N-amido formic acids were 45(39), 34(28) and 30(24)mm at 1×10^{-3} mol/L. These of N-acyl amidoethyl N-amido acetic acids and N-acyl amidoethyl N-amido propionic acids were 49(43), 38(33), 32(27) mm and 53(46), 42(38), 35(29)mm, respectively.

In Fig. 6 to 8 and Table 2, it was found that the alkyl chain length and the number of methylene group of these compounds had a large effect on the foaming property. For instance, the synthetic products having an alkyl chain of 12 carbon atoms has the highest foaming property, and increasing the numbers of methylene group enhanced the foaming power.

Table 2. Ross-miles foam height and stability of N-acyl amidoethyl N-amido carboxylic acid derivatives

Comp'd.	Concentration(mol/L)		
	1×10^{-3}	5×10^{-3}	1×10^{-2}
LAF	45(39)	87(79)	92(85)
PAF	34(28)	67(61)	71(66)
SAF	30(24)	55(49)	64(55)
LAA	49(43)	90(82)	96(86)
PAA	38(33)	75(67)	80(72)
SAA	32(27)	65(53)	68(58)
LAP	53(46)	95(85)	99(90)
PAP	42(38)	75(70)	85(78)
SAP	35(29)	63(54)	74(63)

LAF : N-lauroyl amidoethyl N-amido formic acid
PAF : N-palmitoyl amidoethyl N-amido formic acid

SAF : N-stearoyl amidoethyl N-amido formic acid

LAA : N-lauroyl amidoethyl N-amido acetic acid

PAA : N-palmitoyl amidoethyl N-amido acetic acid

SAA : N-stearoyl amidoethyl N-amido acetic acid

LAP : N-lauroyl amidoethyl N-amido propionic acid

PAP : N-palmitoyl amidoethyl N-amido propionic acid

SAP : N-stearoyl amidoethyl N-amido propionic acid

When considering chemical structure, on the other hand, involved in the formation and stabilization of foam, it is necessary to look at differences between foaming and anti-foaming systems as a whole. The foaming property is further influenced by the position of the hydrophilic group within a surfactant molecules. A surfactant which has the hydrophilic group at the center of its molecule produces less foam at lower concentration than one which has the hydrophilic group at the end of its molecule. The products in this study can be used a foam inhibitors.

III-5. Wetting

Fig. 9 and Table 3 showed Draves Wetting ability measured by the method of II-5 for N-acyl amidoethyl amido carboxylic acid deriva-

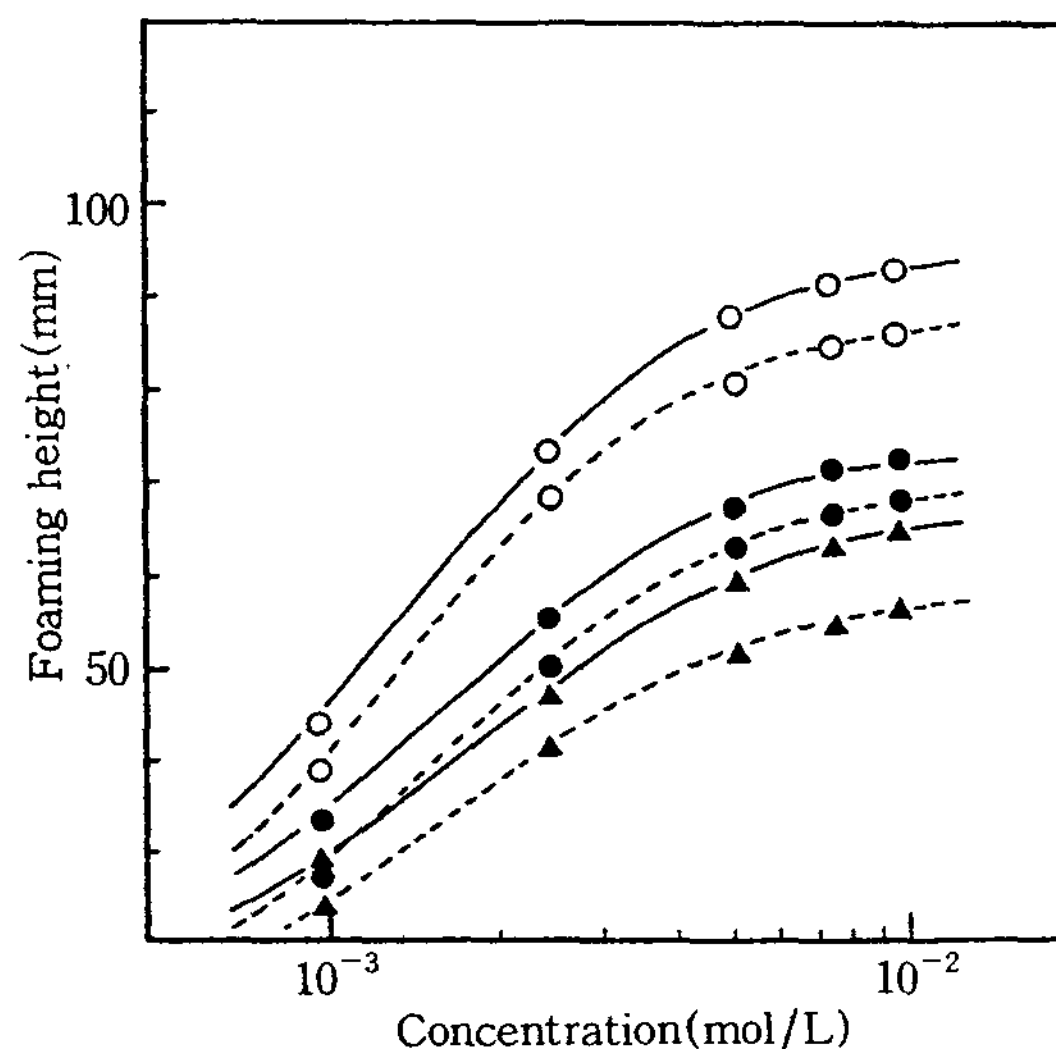


Fig. 6. Ross-Miles foaming power versus concentration curves of N-acyl amidoethyl N-amido formic acids at 40°C.

○ : N-lauroyl amidoethyl N-amido formic acid
● : N-palmitoyl amidoethyl N-amido formic acid
▲ : N-stearoyl amidoethyl N-amido formic acid
— : Foaming power, - - - : Foam stability

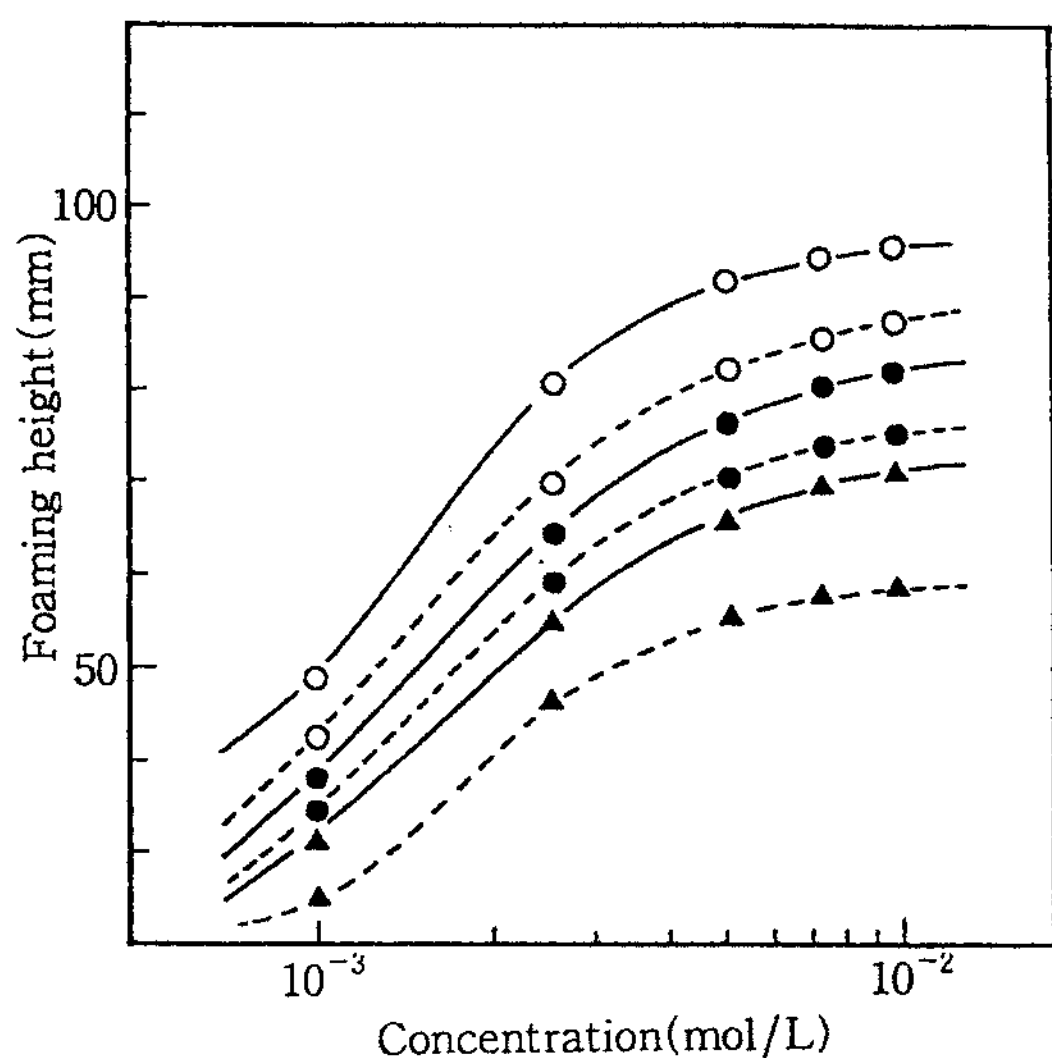


Fig. 7. Ross-Miles foaming power versus concentration curves of N-acyl amidoethyl N-amido acetic acids at 40°C.

- : N-lauroyl amidoethyl N-amido acetic acid
- : N-palmitoyl amidoethyl N-amido acetic acid
- ▲ : N-stearoyl amidoethyl N-amido acetic acid
- : Foaming power, - - - : Foam stability

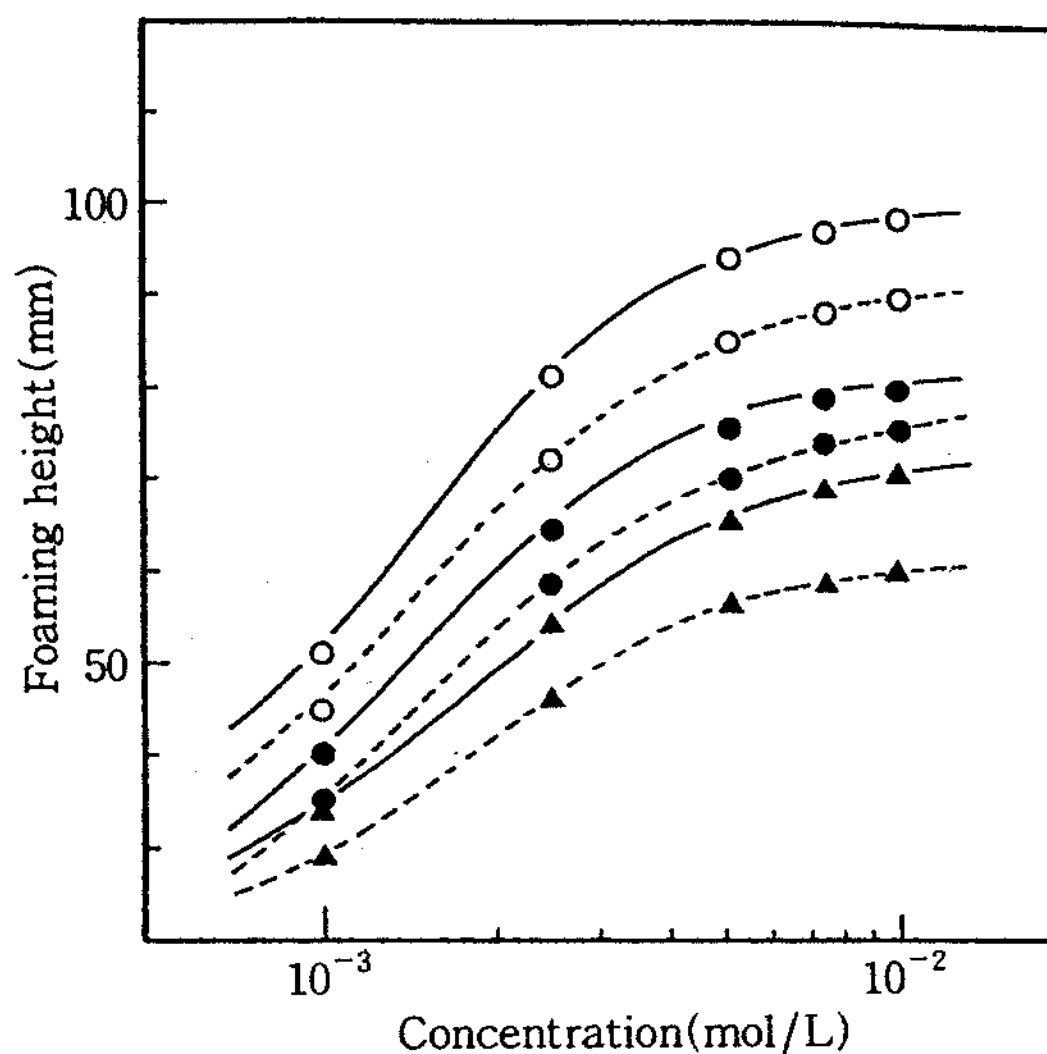


Fig. 8. Ross-Miles foaming power versus concentration curves of N-acyl amidoethyl N-amido propionic acids at 40°C.

- : N-lauroyl amidoethyl N-amido propionic acid
- : N-palmitoyl amidoethyl N-amido propionic acid
- ▲ : N-stearoyl amidoethyl N-amido propionic acid
- : Foaming power, - - - : Foam stability

tives. The sedimentation time in seconds was plotted as a function of the concentration.

As results, wetting ability was enhanced by increasing the length of hydrophobic group. Further, it may be concluded that the spacing between the carboxyl site and the nearest amido group by 0~2 methylene group had influence on sedimentation time. For the same hydrophobic group, increasing the number of methylene group decreased the wetting power.

As one of the methods of making the unwettable surface to be wettable, the hydrophobic groups of surfactants are adsorbed on such a surface and their hydrophilic groups face the water. The products in this study are used for this purpose in such substances as unwettable powder, textile products and so on.

IV. CONCLUSION

The surface active properties of the nine kinds of N-acyl amidoethyl N-amido carboxylic acid derivatives synthesized were investigated. The important results from this study were :

1. The surface tension of the aqueous solution was decreased to 22~34dyne/cm, and showed the tendency that the ability of lowering the surface tension depended on carface tension depended on carbon number of acyl and methylene group. Their *cmc* evaluated by the surface tension method ranged 0.8~6.0 mmol/L.

2. The foaming powers of synthesized surfactants were lower than those of other surfactants, and the lowest value was obtained with

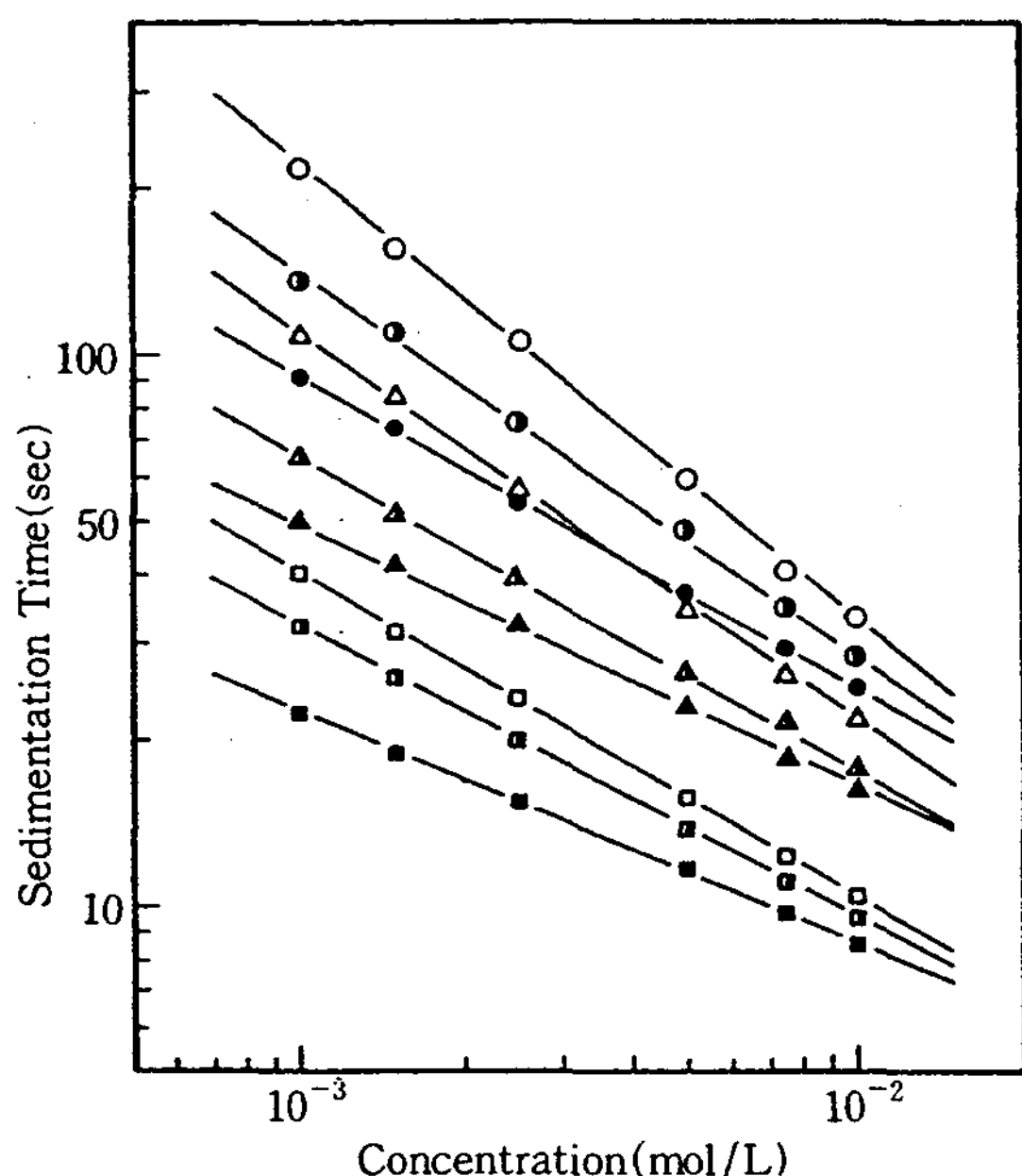


Fig. 9. The effect of wettability for N-acyl amidoethyl N-amido carboxylic acids at 25°C.

- : N-lauroyl amidoethyl N-amido formic acid
- : N-palmitoyl amidoethyl N-amido formic acid
- : N-stearoyl amidoethyl N-amido formic acid
- △ : N-lauroyl amidoethyl N-amido acetic acid
- △ : N-palmitoyl amidoethyl N-amido acetic acid
- ▲ : N-stearoyl amidoethyl N-amido acetic acid
- : N-lauroyl amidoethyl N-amido propionic acid
- : N-palmitoyl amidoethyl N-amido propionic acid
- : N-stearoyl amidoethyl N-amido propionic acid

N-stearoyl amidoethyl N-amido formic acid.

3. The wetting ability was enhanced by increasing the length of hydrophobic groups, and N-lauroyl amidoethyl N-amido carboxylic acid derivatives showed the best wetting property among the synthesized surfactants.

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