J. of Korean Oil Chemists' Soc.,
Vol. 12. No. 1, May, 1995. 101~107

분해성계면활성제에 관한 연구(제2보)

-1, 3-Dioxlane고리를 갖는 분해성계면활성제의 합성-

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Studies on the Destructible Surfactants(2)

-Surface-Active Properties of Cleavable Surfactant with 1, 3-Dioxolane Ring-

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(Received March 30, 1995)

요 약

케탈이나 아세탈반응에 의하여 이루어진 1, 3-디옥솔란 고리가 산수용액 중에서 불안정해 쉽게 가수분해되는 성질을 이용하여 소수부로는 지방산의 탄화수소사슬을 친수부로는 소디움 카르복시산(Soap)을 도입하여 분해 후 계면활성을 띠지 않는 분해성 계면활성제이다. 이 화합물의 수용액에 대한 표면장력은 31dyne/cm였고, 임계미셀농도는 1.0×10^{-5}mol/L이었다. 기포력은 비교적 좋지 않았으며, 유화력은 콩기름보다 벤젠에서 양호하였다. 또한 이 화합물의 산분해 특성을 1wt% 수용액과 벤젠 사이의 계면장력 변화에 의하여 측정한 결과 pH 1~4범위에서 약 300분 안에 모두 가수분해됨을 확인하였다.

I. INTRODUCTION

Surfactants are useful for micellar reaction, emulsion polymerization, phase-transfer reaction and other organic synthesis.[1~8] Because of troublesome emulsion formed by surfactants, however, we have frequently been confronted with the difficulty of separating desired products from the emulsions.[1~5] So the isolation of the desired products has traditionally been carried out by the addition of an appropriate metal salts.[1~3] For example, in polymerization process in the presence of surfactants, for the purpose of breaking the emulsion, metal salt such as calcium or magnesium salt has been added after the completion of the polymerization.[2~5] But this procedure often debases the water-resistance and electrical insulation of the resultant polymer.[1~5]

An alternative approch involves the use of cleavable surfactants that can be converted to surface-inactive products at the end of the reaction.[1~6] And these cleavable surfactants have come to interest about 15 years ago. The types of cleavable surfactants are disulfide link compounds, silicon-oxygen bonding compounds and 1, 3-dioxolane ring compounds which are studied in recent years in advanced nations. Their 3-type

cleavable surfactants are degraded in respectively conditions.[1~11]

Silicon-oxygen bond compounds[9] and disulfide link compounds[10] have been synthesized and found to be effective as catalysts, emulsifiers, or solubilizers, but these were obtained only by the use of the complicated synthesis paths and the special reagents.[2, 3] These problems limit the use of the surfactants. But without special apparatuses and reagents, cleavable surfactant having 1, 3-dioxolane ring was expected the solution of the problems.

In this study, the surface active properties of the surfactant have been measured in repectively conditions, which are emulsifing power and stability, surface-tension decreasing power and foaming power and stability. And the hydroylsis property of the surfactant was analyzed by the variation of the interface tensions between benzene and aqueous solution depending on variation of time and pH.

Ⅱ. EXPERIMENTAL METHODS

1. Surface Active Properties

In this study, Krafft point[12] and HLB[13] value of sodium 2-amido-2-carboxylate-4-methyl dodecanate-1, 3-dioxolane were measured as basic surface active properties and other surface active properties are followed.

$$\text{HLB value} = 7 + \Sigma(\text{Group number of hydrophilic}) - \Sigma(\text{Group number of lipophilic}) \quad \cdots\cdots(1)$$

1) Surface Tension

The measurement of the surface tension was preformed in aqueous solution(0.01~10mmol/l) by using ring method at 30°C. After washed with benzene, acetone and distilled water in order, and oxidized in flame, the platinum-irridium alloy ring was used in tests. The measured values were revised by the following equation.

$$S = P \times S \quad \cdots\cdots(2)$$

In equation, S(dyne/cm) is a real value of surface tension, P(dyne/cm) is an apparent value and F is a correction factor obtained by follwing equation.

$$F = \sqrt{0.11452P(D-d)/C^2 + 0.04534 - 0.07Pr/R} \quad \cdots\cdots(3)$$

where, R; a radius of ring(mm), r; a radius of ring line(mm), P; apparent value of surface tension(dyne/cm), density of water (g/cm^3), d; density of solution(g/cm^3), c; length of ring(mm).

2) Foarming Power and Stability

Foaming power and stability was measured by Ross-Miles method[14] according to JIS K-3362 at 30°C used a equipment of Foaming power. The measurement was carried out at the concentration of 10 mmol/L.

With method the same this, Foaming height were recorded immediataly, and after 5 min. The foaming power was represented to initial Foaming height and the foaming stability (FS) was represented to Foaming height after 5min.

And Foaming properties were evaluated by the semi-micro TK method with 1wt% aqueous solution at 30°C.[15]

3) Emulsifying Power

Rosano,[16] Kimura[17] and Meguro et al.[18] had been reported the method of measurements for emulsifying power. In this study, used an improvement on that of Meguro[18] method. That is, 30mL of liquid paraffin and 30mL of a 10 mmol/L aqueous test solution were stirred with magnetic bar for 10 minutes. Emulsion phase was put in a 100mL glass-stoppered test tube, and the test tube was standed in water bath at 30°C, and the volume of the aqueous solution separted from the emulsion layer was measured after 15 min. It was represented emulsifying power.

4) Hydrolysis of Surfactant

This experiment was operated by the study of David a. Jager.[19, 20] First of all, the interface tension between 0.1wt% surfactant aqueous solution(20mL) and benzene(20mL) was obtained in 30℃ by ring method. The 2N HCI was added in aqueous phase to pH 1, 2, 3 and 4 respectively and as time goes by, the interface tensions were recored. So the property of hydrolysis for surfactant was analyzed by the variation of the interface tensions.

Ⅲ. RESULTS AND DISCUSSION

1. Surface Active Properties

The ionic surfactants have a generally low solubility at low temperatures in aqueous solution and micelles are not formed. As the temperature is raised, the solubility slowly rises, and at a temperature known as the krafft point the solubility does rapidly increase. In present study, the measurement result of krafft point for sodium 2-amido-2-carboxylate-4-methyl dodecanate-1, 3-dioxolane was 27±0.5°.

And acoording to David's equation, the HLB (hydrophilic-lipophilic balance) value of sodium 2-amido-2-carboxylate-4-methyl dodecanate-1, 3-dioxolane is 13 and this could be applied as O/W type emulsifier.

1) Surface Tesion, Critical Micelle Concentration(*cmc*) and Interface Adsorption Properties

The plot of surface tension vs. concentration for sodium 2-amido-2-carboxylate-4-methyl dodecanate-1, 3-dioxolane are shown in Fig. 1. From the Fig. 1, *cmc*, the ability to lower surface

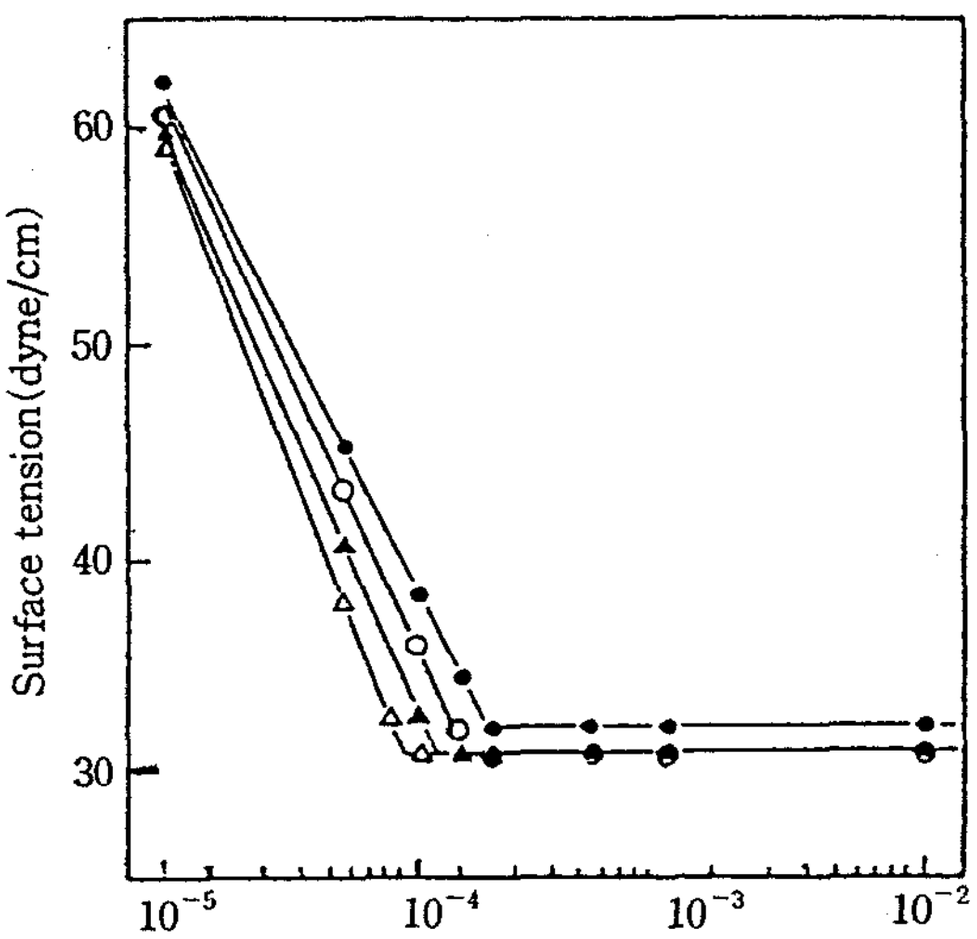

Fig. 1. Surface tention of cleavable surfactants at 30℃.

● Sodium 2-(carboxylato)-2-methyl-4-dodecyloxymethyl-1, 3-dioxolane
○ Sodium 2-(carboxylatomethyl)-2-methyl-4-dodecyloxymethyl-1, 3-dioxolane
▲ Sodium 2-(carboxylatoethyl)-2-methyl-4-dodecyloxymethyl-1, 3-dioxolane
△ Sodium 2-amido-2-carboxylate-4-methyldodecanate-1, 3-dioxolane

Table 1. Surface active properties of sodium carboxylates

Comp'd	T_{kp}(℃)	$10^4 cmc$(mol/L)	γ_{cmc}(dyne/cm)	Γ_{max}(mol/cm^2×10^{10})	A(nm^2/molecule)
A	<0	1.23	31	1.70	98
B	<0	1.62	31	1.47	113
C	<0	2.01	32	1.34	124
D	27	0.97	31	1.00	166
E	19	200	37.5	2.41	69

A : Sodium 2-(carboxylato)-2-methyl-4-dodecyloxymethyl-1, 3-dioxolane
B : Sodium 2-(carboxylatomethyl)-2-methyl-4-dodecyloxymethyl1, 3-dioxolane
C : Sodium 2-(carboxylatoethyl)-2-methyl-4-dodecyloxymethyl-1, 3-dioxolane
D : Sodium 2-amideo-2-carboxylate-4-methyldodecanate-1, 3-dioxolane
E : Sodium dodecanate

tension(γ_{cmc}) and the area per molecule[21] at the surface were obtained. And the values were noted in Table 1 with the comparative reference.[22] The results were compared with other cleavable surfactants[22] that have the same alkyl group carbon number(11).

As the result, the *cmc* value of sodium 2-amido-2-carboxylate-4-methyl dodecanate-1, 3-dioxolane relatively is lower than others[22] and the ability to lower surface tension(γ_{cmc}) differs little. But the adsorption area per a molecular at interface is relatively larger than other.[22]

2) Foaming Power and Stability

Foaming power and stability were measured by the method of 1-2) and the result was shown in Fig. 2, 3, and Table 2 with reference.[22, 23]

The presence of foam in a product or process may or may not be desirable. Foams have widely technical importance, as such, in the fields of fire fighting polymeric foamed insulation, foam rubbers, and foamed structural materials such as concrete. But foams may cause to many problem in emulsion process.[23]

The foaming power and stability for sodium 2-amido-2-carboxylate-4-methyl dodecanate-1, 3-dioxolane are relatived inferior to other surfactants.[22, 23]

3) Emulsifying Power

Emulsifying power and stability were obtained by 1-3) method. As guessed from HLB value, this product is O/W emulsifier. From results of the emulsifying power and stability of the product for liquid paraffin and soybean oil, the emulsion properies for liquid paraffin are better than soybean oil. The result was ploted in Fig. 4.

4) Hydrolysis of Surfactant

The interface tensions of 1wt% surfactant solution and benzene from pH 1 to pH 4 at 30°C were monitored over time respectively. Within 1 minute after the solution was prepared, γ=0.31 dyne/cm, which is indicative of the presence of

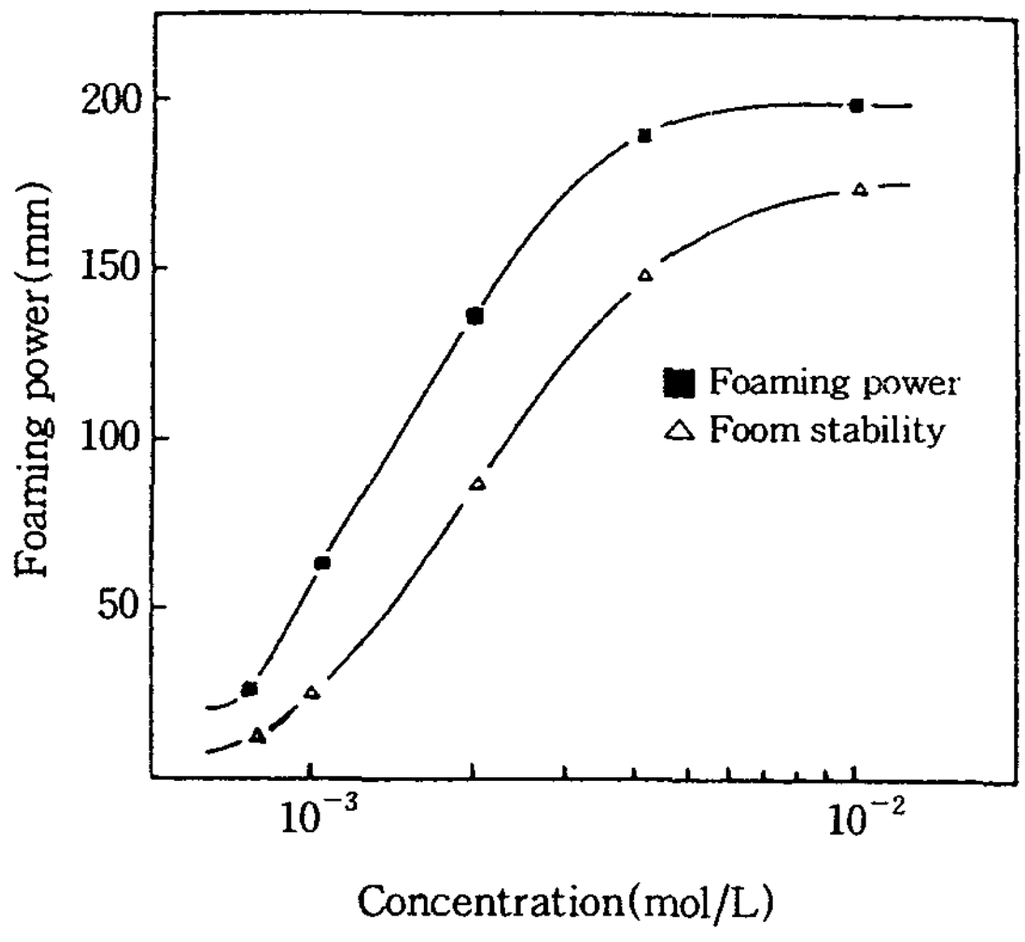

Fig. 2. Ross-Miles foam hieghts vs. concentration curves of surfactant at 30°C.

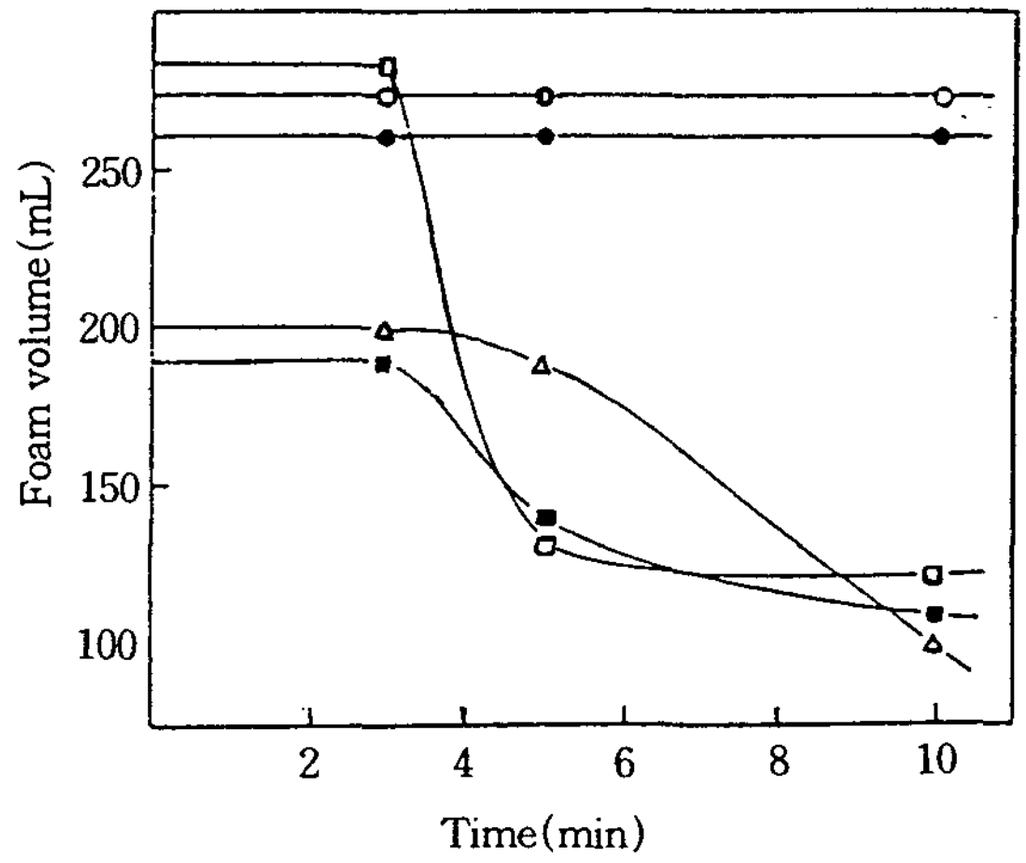

Fig. 3. Foaming power and stability of sodium carboxylates by TK-method.

○ Sodium 2-(carboxylato)-2-methyl-4-dodecyloxymethyl-1, 3-dioxolane[a)]
● Sodium 2-(carboxylatomethyl)-2-methyl-4-dodecyloxymethyl-1, 3-dioxolane[a)]
□ Sodium 2-(carboxylatoethyl)-2-methyl-4-dodecyloxymethyl-1, 3-dioxolane[a)]
■ Sodium 2-amide-2-carboxylate-4-methyldodecanate-1, 3-dioxolane[b)]
△ Sodium dodecanate[c)]
** Foaming test by TK-Method **
a) At 20°C, pH 12, 0.1 wt%
b) At 30°C, 1wt%, this compound was nonfoaming at 0.1wt%
c) At 1wt%

aggregated surfactant. After 100 minutes, γ increased to 3.62~1.84 dyne/cm as pH order. After 150 minutes, γ increased to 5.47 dyne/cm but after that time γ was not changed at pH 1.

Table 2. Foaming properties of sodium carboxylates

Compound	Foam volume(mL)per min.			
	0	3	5	10
A[a)]	270	270	270	270
B[a)]	260	260	260	260
C[a)]	280	280	130	120
D[b)]	190	190	140	110
E[c)]	200	200	190	100

A : Sodium 2-(carboxylato)-2-methyl-4-dodecyloxymethyl-1, 3-dioxolane[a)]
B : Sodium 2-(carboxylatomethyl)-2-methyl-4-dodecyloxymethyl-1, 3-dioxolane[a)]
C : Sodium 2-(carboxylatoethyl)-2-methyl-4-dodecyloxymethyl-1, 3-dioxolane[a)]
E : Sodium 2-amideo-2-carboxylate-4-methyldodecanate-1, 3-dioxolane[b)]
D : Sodium dodecanate[c)]
** Foaming test by TK-Method **
a) At 20°C, pH 12, 0.1 wt%
b) At 30°C, 1wt%, this compound was nonfoaming at 0.1wt%
c) At 1wt%

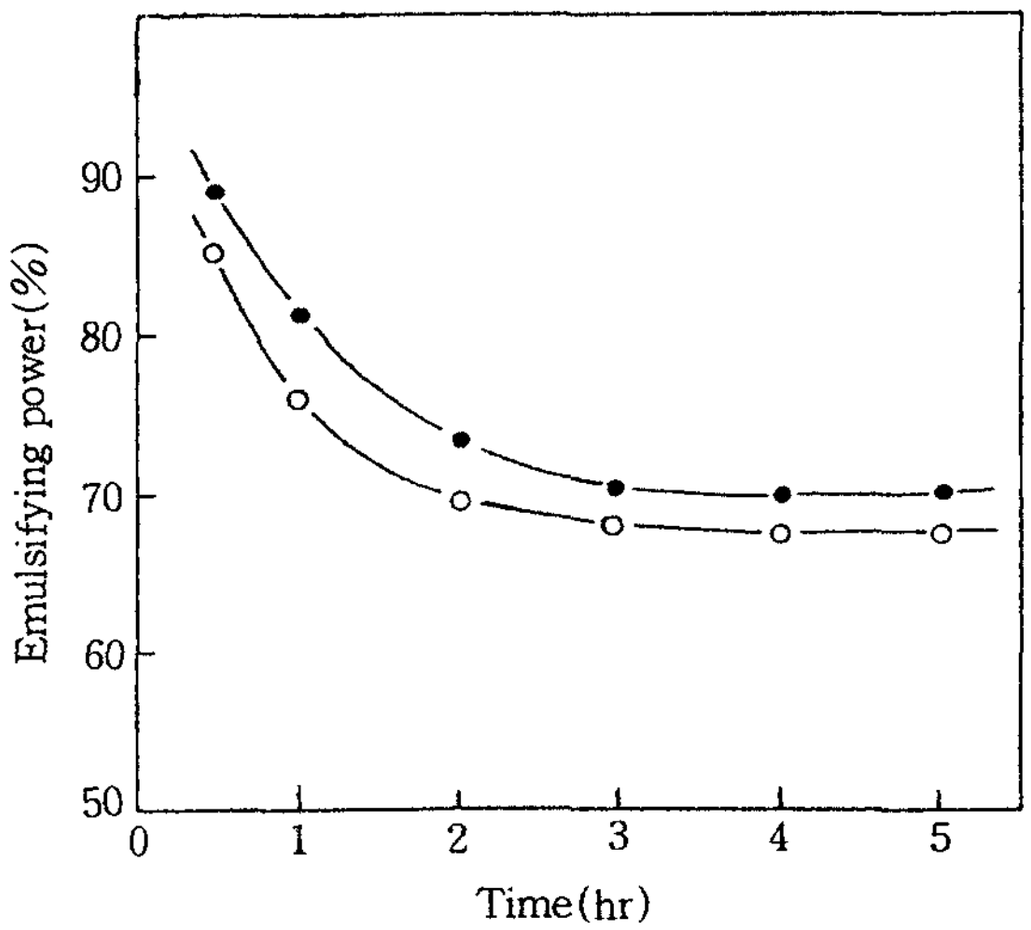

Fig. 4. Emulsifying power of sodium 2-amido-2-carboxylate-4-methyl dodecante-1, 3-dioxolane for benzed and soybean oil at 30°C
● : Liquid paraffin,　○ : Soybean Oil

Thus we known that acid decomposition was completed. But at pH 2~4, the acid decomposition was not completed in this time. At pH 4, decomposition was completed after about 300 minutes. At pH 2 and 3, decomposition time were between 150 and 300minutes. And the order of the decomposition times was pH 1, 2, 3 and 4.

But it is at above pH 5 that the decomposition was not well taken place. And the results were ploted in Fig. 5.

Ⅳ. CONCLUSION

In this study, sodium 2-amido-2-carboxylate-4-methyl dodecanate-1, 3-dioxolane of the cleavable sufactant, synthesized in Ⅰ, it's surface activities were better than other surfactants.[22] So the important results of this study is followed as.

1. The *cmc* value(9.73×10^{-5}mol/L) of sodium 2-amido-2-carboxylate-4-methyl dodecanate-1, 3-dioxolane relatively is lower than other cleavable surfactants and the ability to lower surface tension(γ_{cmc}, 31 dyne/cm) differ little. And adsorption area per a molecular for this product

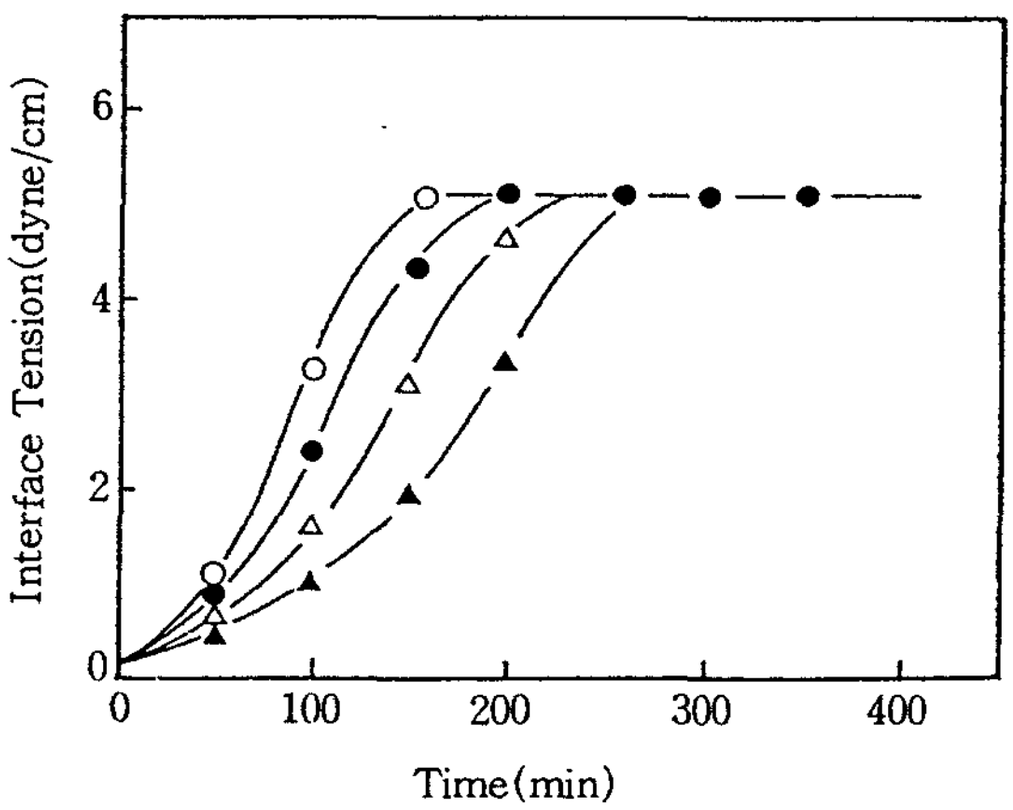

Fig. 5. Interface tension between 1wt% aqueous solution(10mL) and benzene(10mL) for acid hydrolysis at pH 1, 2, 3 and 4, 30°C.
○ : pH 1, ● : pH 2, △ : pH 3, ▲ : pH 4

is larger than other surfactants.

2. From the experimental results, emulsifying power and stability were relatively excellent. And emulsion for liquid paraffin was better than soybean oil.

3. Foaming power for this product was lower than other sunfactants, but in its stability, this product was lower than other cleavable surfactants but higher than sodium dodecanate.

4. According to the result of hydrolysis of surfactant in pH 1, 2, 3 and 4, sodium 2-amido-2-carboxylate-4-methyl dodecanate-1, 3-dioxolane is completely decomposed in about 150~300 minutes. And the order of decomposition was pH 1, 2, 3 and 4.

From the results, sodium 2-amido-2-carboxylate-4-methyl dodecanate-1, 3-dioxolane is expected good O/W emulsifier that has decomposibility in acid.

V. ABSTRACT

As the surfactants that were used in micellar reaction, emulsion polymerization and phase-transfer reaction etc. have the problems, the cleavable surfactant was converted to inactive compound after such as the reaction in the condition.

Because 1, 3-dioxolane ring by ketal or acetal reactioc is lack of stability in acid condition, it is easily made to acid-hydrolysis. And cmc value of the surfactant is assumed 1.0×10^{-5} mol/L and surface tension in cmc is 31 dyne/cm.

Compared with other surfactant, this surfactant foam property is not better. But emulsion property was relatively good. According as acid-hydrolysis property was observed the interface tension change between aqueous solution and benzene by the variation of pH and time, this surfactant was made to hydrolysis within about 300minutes in pH 1~4.

Therefore this surfactant is expected to be a good emulsifier that has the bad foam property and the acid-hydrolysis property in acid condition.

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