

〈總 說〉

Modern Trend in Development of Surfactants —from Their Molecular Structure and Novel Function—

Isao Ikeda and Tae-Seong Kim

Department of Molecular Chemistry
Graduate School of Engineering
Osaka University

(Received Oct., 31, 1997)



I. Introduction

Many kinds of surfactants are used in very large amount in our daily life. In industry, many more kinds of surfactants are utilized in large quantities. Food, fabrics, plastics, engineering, architecture, mechanical engineering, mining, paper industry, electronics, drugs, agriculture, and so on can be listed as users. Thus, as a key technology, surfactants have been playing a quite important role in almost all industries as well as in our daily life. Actually, new technology or new process almost could not be developed without the contribution of surfactants. For a certain period in the past, however, the surfactant chemistry and industry had been considered to be fully matured, and the required performances in those industries were usually obtained by blending the established surfactant components.

However, nowadays, the circumstances surrounding surfactant industry are changing.

Especially, surfactants are particular chemicals since they are usually discharged into effluent after use in various industries or our daily life. The amount of these surfactants has reached considerable level affecting the hydrosphere environment. They should also be hygi-

enically safe since they are often directly applied to human body or hair.

From the points of environment(atmosphere, hydrosphere, safety for human body, and so on) and the necessary replacement of raw material of surfactants, from petro-chemical material to oleochemical material, investigations on the development of environmentally acceptable surfactants and also those having higher performance are becoming active. For these purposes, studies on the correlation between molecular structure and surface activity are also brisk. And studies to develop high performance surfactants as well as novel surfactants which have new functions by introduction of new concept are activated. Moreover, the possibility of establishing new high technology itself besides the traditional auxiliary key technology have come into existence.

The surfactant industry is plunged into a new era and is one of the busiest fields among chemical industries, possessing an actively developing mind.

II. Development of high performance and new functional surfactants

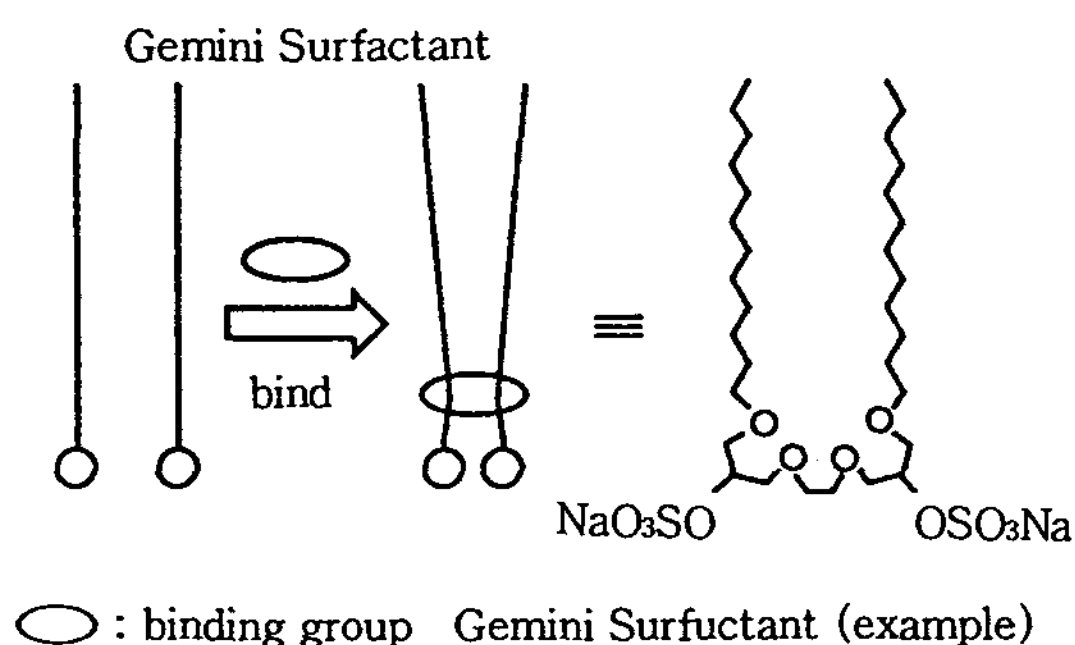
Generally, the kind of hydrophilic group, the kind and the shape of hydrophobic group, and

hydrophile-lipophile balance (HLB) can be enumerated as factors affecting the physical properties of surfactants. Recently, some efforts to prepare novel amphiphilic compounds with new functions by adding some molecular modifications, besides adjustment of the fundamental factors, have been reported.

1. Amphiphilic compounds with multi-chain and multi-hydrophilic group

1) Gemini Surfactants

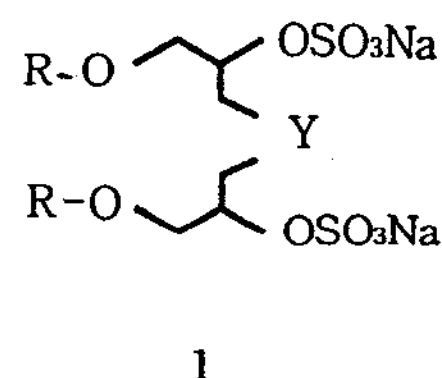
High performance surfactants which display superior activity by a smaller quantity in use are important from the point of improvement of productivity in industries where surfactants are used, as well as the points of resources and environment¹⁾. Recently, many works worthy of notice on these high performance surfactants are reported.



Scheme 1.

Multi-chain and multi-hydrophilic group surfactants (double chain and double hydrophilic group surfactant : Gemini Surfactant, Scheme 1), which are formally synthesized by binding two single-chain and single-hydrophilic group surfactant with a proper linking unit, display a superior performance which can not be expected from the correlation of the structure and property of single-chain and single-hydrophilic group surfactants²⁾. Double-chain and double-

hydrophilic group surfactants prepared from diepoxide form micelles at an extremely low concentration in aqueous solution, show superior surface-tension lowering ability, and have good water solubility compared to the conventional single-chain and single-hydrophilic group surfactants (Table 1, compound 1)³⁾. By analysis of the behavior of insoluble monolayer film on water concerning a series of double-chain and double-hydrophilic group surfactants, it was known that the structure of linking unit affects the surface properties of these compounds⁴⁾. Triple-chain and double-hydrophilic group surfactants derived from N-acyldiethanolamine and 1-O-alkyl glycerol surpass double-chain and double-hydrophilic group surfactants in surface activity.



Meanwhile triple-chain and triple-hydrophilic group compound derived from 1,1,1-tris(hydroxymethyl)ethane shows characteristic aggregation and adsorption behavior, which is converse to the relation of hydrophobic chain length and critical micelle concentration recognized in the case of conventional surfactants⁵⁾. From the comparison of the π -A isotherms of insoluble monolayer film of the triol derived from tris(hydroxymethyl)ethane and epichlorohydrin and those of the triol derived from 1-O-alkyl glycerol and epichlorohydrin, it was disclosed that in the former compound, a small difference in the structure of the linking unit (additional one methylene group) forces the hydrophobic chain to adsorb onto the water sur-

Table 1. Fundamental properties of gemini surfactants

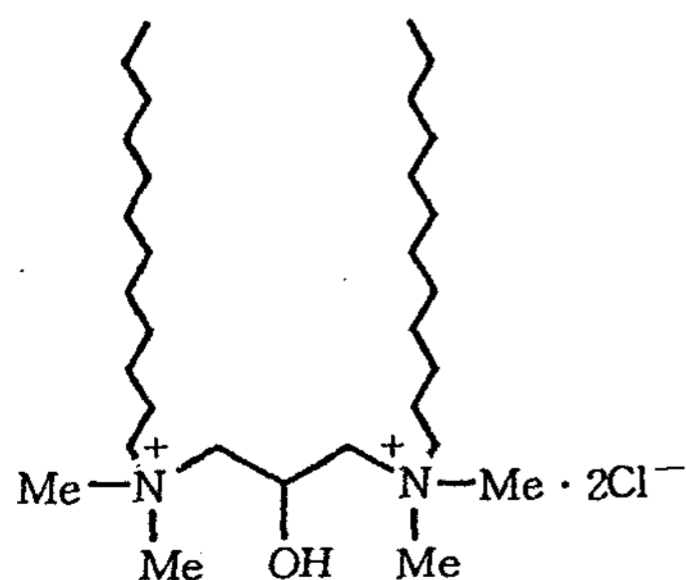
Compound	T_{kp} ($^{\circ}C$)	CMC (mM)	pC_{20}	γ_{CMC} (mM/m)	Foam(mL)		
					0'	5'	30'
1 R=C ₁₀ H ₂₁ Y=OC ₂ H ₄ O	<0	0.013	—	27	—	—	—
1 R=C ₁₀ H ₂₁ Y=p-OC ₆ H ₄ O	<0	0.035	—	39	—	—	—
n-C ₁₂ H ₂₅ OSO ₃ Na	<0	16	—	39	—	—	—
2 R=C ₁₂ H ₂₅	<0	1.07	3.2	35	280	—	270
2 R=C ₁₆ H ₃₃	<0	0.014	5.3	37	100	—	10
RN(CH ₃) ₃ Cl	<0	12	2.6	39	20	—	0
13 R=C ₁₁ H ₂₃	<0	0.090	—	27.5	270	270	—
C ₁₁ H ₂₃ CO ₂ Na	19	20	0	37.5	200	190	—

T_{cp} : Krafft point, CMC : critical micell concentration, γ_{CMC} : surface tension at CMC

face less easily.

2) Oligomeric ammonium compounds with multi-chain and multi-hydrophilic group

Two moles of alkyldimethylamine or dialkylmethylamine, one mole of hydrogen chloride, and one mole of epichlorohydrin react under mild conditions to give bis-ammonium salt 2 almost quantitatively. This compound is also a gemini surfactant and has high solubility in water, extremely low CMC, and good γ_{CMC} . Interestingly, some of this kind of surfactants show very high foaming ability and very high foam stability, while usual cationic surfactants show quite low foaming ability (Table 2)⁶⁾. This



2

property is sensitive to the HLB or the chain length of compound 2⁷⁾.

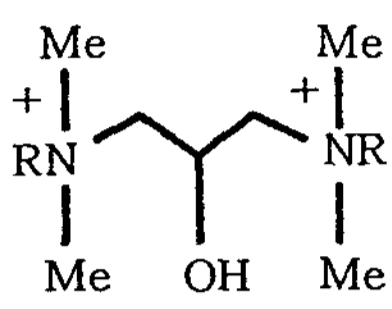

Tris- and tetrakis-ammonium salts (Compounds II and IV) and the corresponding amine-ammonium salts were synthesized rather easily by multi-step process. Their surface active properties and adsorption behavior on solid surface are shown in Table 3 and Figure 1⁸⁾.

The oligomeric amines corresponding to ammonium salts I, II, and III showed interesting π -A isotherms. Although dodecyldimethylamine showed no pressure on compression of the film, all the oligomeric dodecylamines formed liquid expansion films. And the collapse pressure of the films was higher than that of stearyldimethylamine, showing that the interaction between lipophilic groups became very large by connecting monomeric amine molecules⁹⁾.

The CMC lowered with the increase of the linking number, tetrakis-ammonium salts showed quite low CMC (Table 3). The amount of salt adsorbed on felt increased with the linking number up to 3, while that of the tetrakis-ammonium salt is lower than the tris-homologue (Figure 1).

Table 2. Surface-active properties of bis-alkyldimethylammonium salts

at 20°C

Compound	R	Krafft ^a point(°C)	γ_{CMC}^b (mN/m)	CMC(M) ^b	pC ₂₀	Foam(mL) ^c	
						0'	30'
	C ₁₀ H ₂₁	<0	36.5	3.2×10 ⁻³	2.9	40	0
	C ₁₂ H ₂₅	<0	37.0	7.8×10 ⁻⁴	3.2	280	270
	C ₁₄ H ₂₉	<0	39.0	1.4×10 ⁻⁴	4.4	270	270
	C ₁₆ H ₃₃	<0	42.2	1.9×10 ⁻⁵	5.3	100	10
	C ₁₈ H ₃₇	- ^e	- ^e	- ^e	- ^e	- ^e	0
	C ₁₀ H ₂₁ ^f			6.1×10 ⁻²			
	C ₁₂ H ₂₅ ^f	<0	39.0	1.2×10 ⁻²	2.6	20	0
	C ₁₆ H ₃₃ ^f				1.3×10 ⁻³		

a : Krafft point : by the naked eye, 1 wt% aq. solution

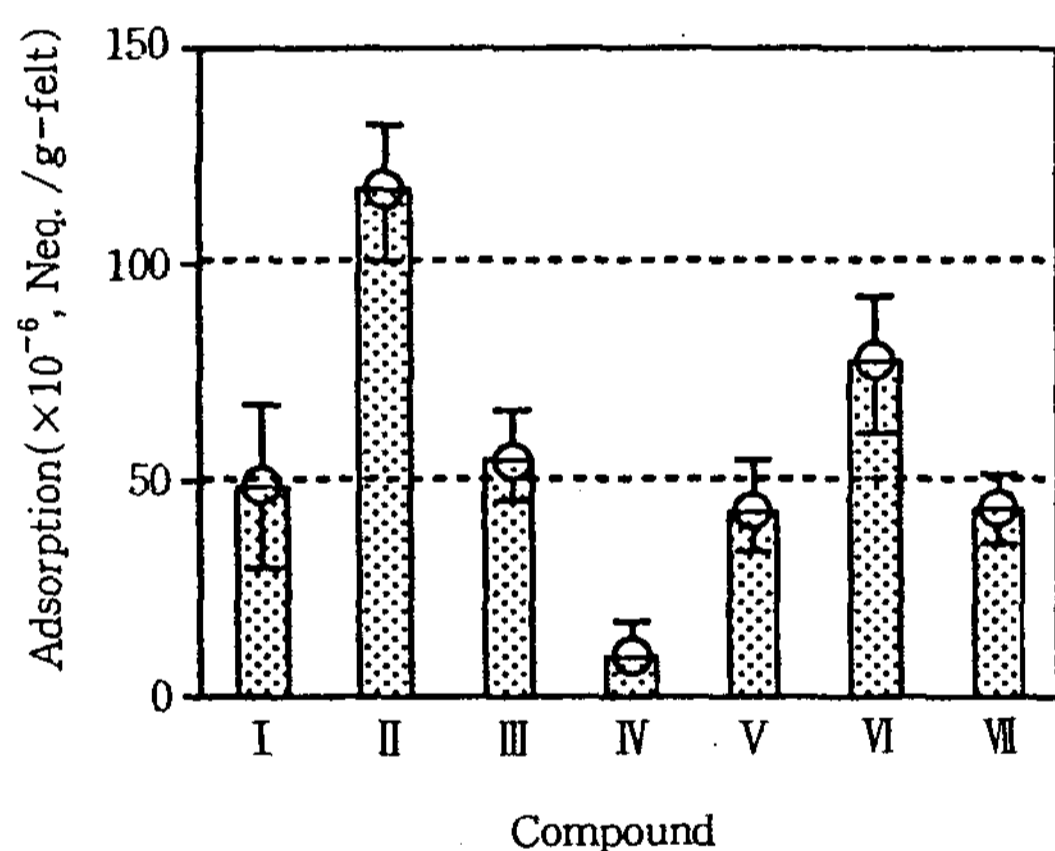
b : Surface tension : Wilhelmy tensiometer

c : Foam property : semi-micro TK method, 0.1 wt% aq. solution

d : at 1 wt% aq. solution

e : not evaluated.

f : reported values.



Experimental conditions

- conc. of surfactant : 1×10⁻³ M
- felt : JIS-R28W
- adsorption : at 50°C for 12h
- No. of experiment : 5

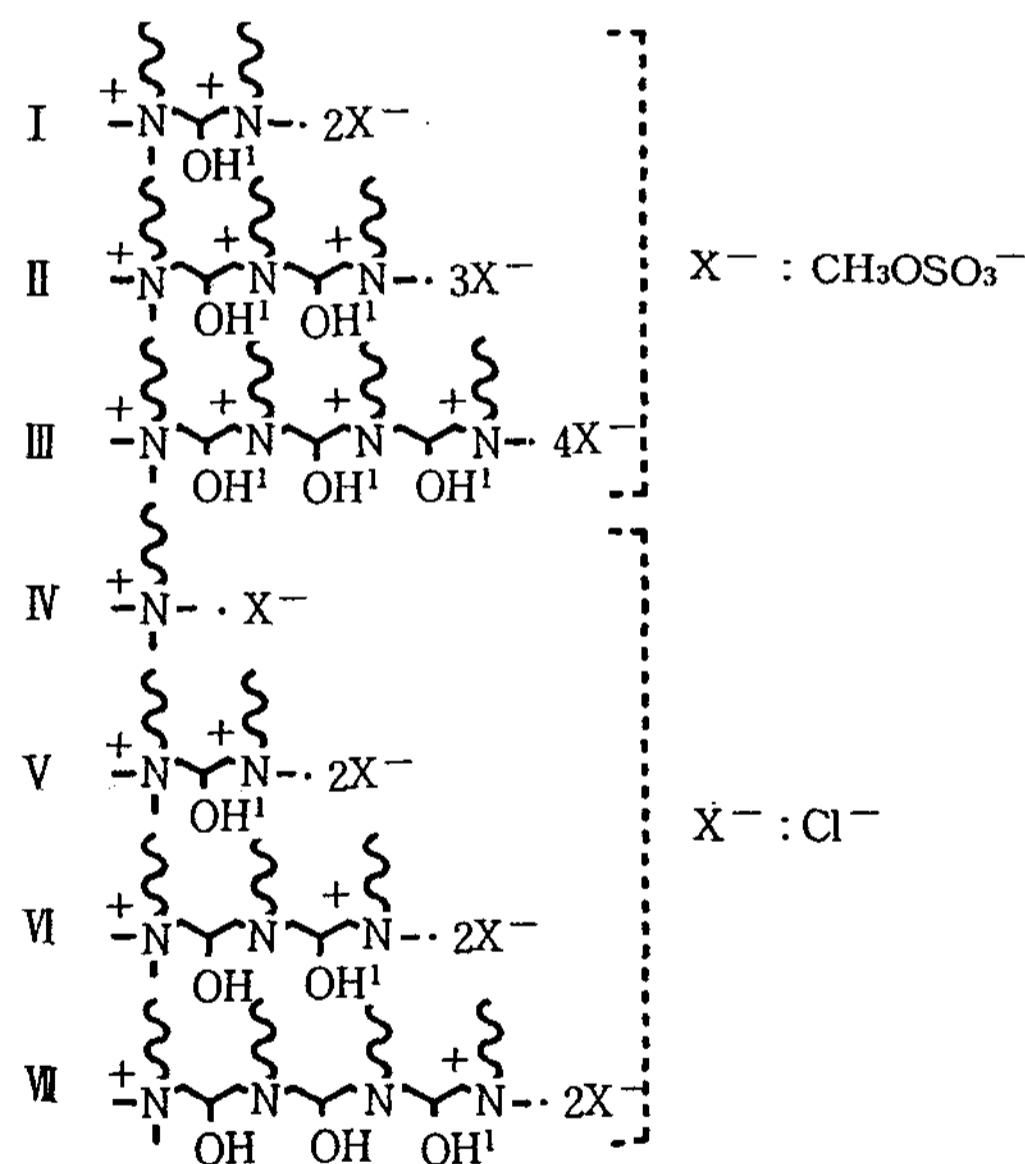


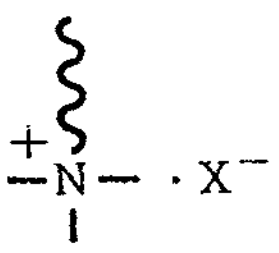
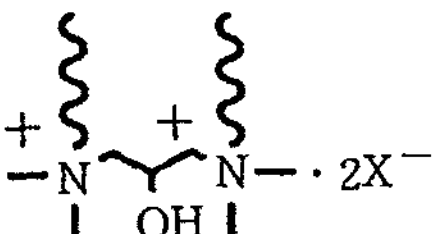
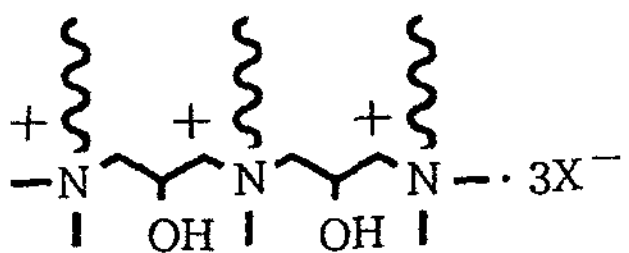
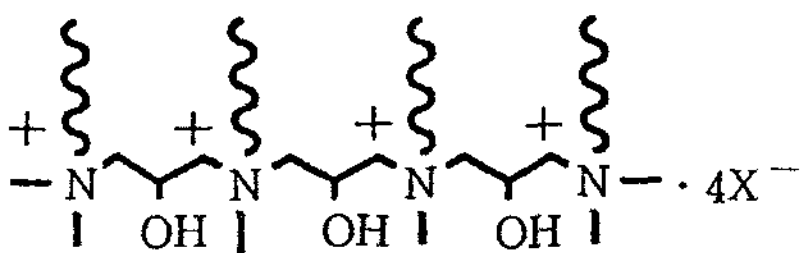
Fig. 1. Adsorption of oligomeric ammonium and amine-ammonium salts on solid surface(dodecyl derivatives)

Cationic gemini surfactant containing amide moiety in its lipophilic chain³⁾ can be considered to be gentle to the environment. This kind of surfactants also have good water solubility,

very low CMC, very good surface tension lowering ability, and quite high foaming ability and foam stability depending on the length of lipophilic chain compared with single-chain

Table 3. Surface-active properties of oligomeric ammonium salts

at 20°C

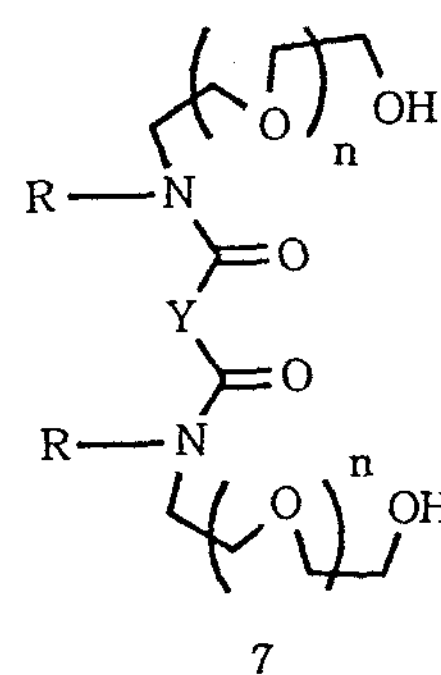
Compound (dodecyl derivative)	Krafft ^a point(°C)	γ_{CMC}^b (mN/m)	CMC(M) ^b	pC ₂₀
	- ^c	- ^c	1.3×10^{-2d}	2.3 ^d
	<0	29.1	9.8×10^{-5}	4.6
	- ^e	32.0 ^e	9.7×10^{-6e}	5.4
	- ^e	34.0 ^e	4.5×10^{-6e}	5.8

 $X^- : CH_3OSO_3^-$ *a* : Krafft point : by the naked eye, 1 wt% aq. solution*b* : Surface tension : Wilhelmy tensiometer*c* : not reported.*d* : reported values, at 25°C*e* : The solution was clouded at 1 wt% aq., but the surface tension was measured in the range of concentration in which the solution was clear by dilution.single-hydrophilic surfactant 4 (Table 4)¹⁰⁾.

More environmentally friendly cationic gemini surfactants are those which contain an ester group in each lipophilic chain (Compounds 5, 6). Those shown in Table 5 have the same lipophilic chain length but contain an ester group in the different position in the chain. Quite interestingly, the position of the ester group in the chain has very large effect on CMC and γ_{CMC} ⁹⁾.

Linfield synthesized a series of double-chain nonionic surfactants 7, and reported that nonionic surfactants 7 have good water solubility and strong wettability, and are effective as soil wetting agent¹¹⁾. As can be seen in the case of surfinol (2,5-dialkylhex-3-yne-2,5-diol and its ethoxylate), it has been known that double-chain and double-hydrophilic group surfactants

display good wettability. These compounds, however, are usually composed of shorter hydrophobic chains and smaller hydrophilic groups than gemini surfactant.



(R : 3-heptyl, octyl, 2-ethylhexyl
 -Y- : -(CH₂)_n-, -CH=CH-, -N(CH₂)₂N-)

Table 4. Surface active properties of bis-amido-ammonium surfactants

^a0.1 wt% aqueous solution, at 20°C

Compound	R	Krafft point (°C)	CMC (mM)	γ_{CMC} (mN/m)	Foam(mL) ^a	
					0'	10'
3a	C ₉ H ₁₉	<0	1.2	33	40	0
3b	C ₁₁ H ₂₃	<0	0.19	33	260	240
3c	C ₁₃ H ₂₇	<0	0.010	33	270	260
3d	C ₁₅ H ₃₁	17	0.0048	33	80	10
4	C ₁₁ H ₂₃	<0	6.1	35	20	0

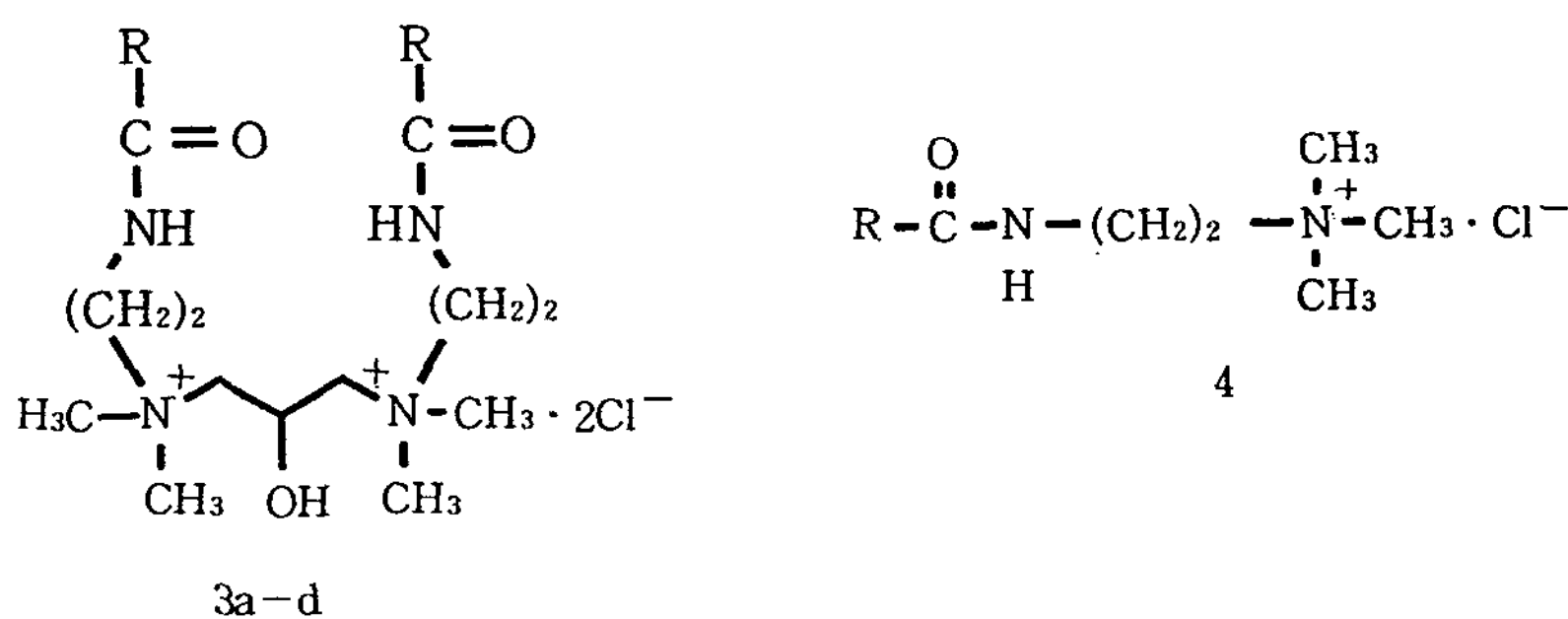
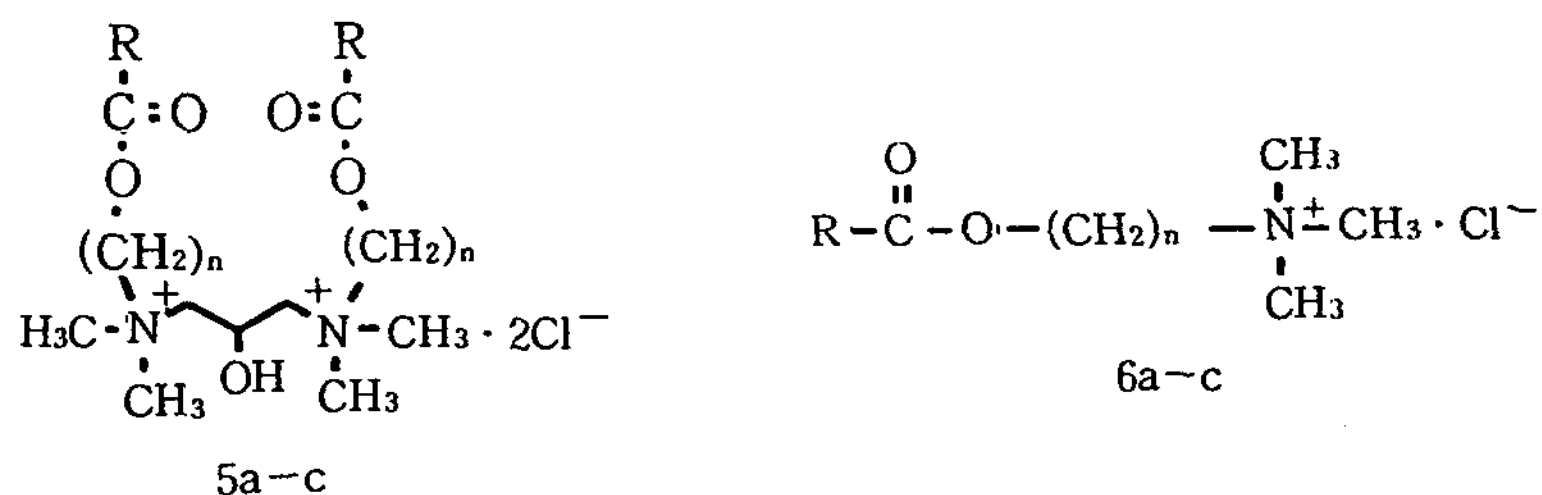


Table 5. Surface active properties of bis-ester-ammonium surfactants

^aMeasured by Wilhelmy method, at 20°C

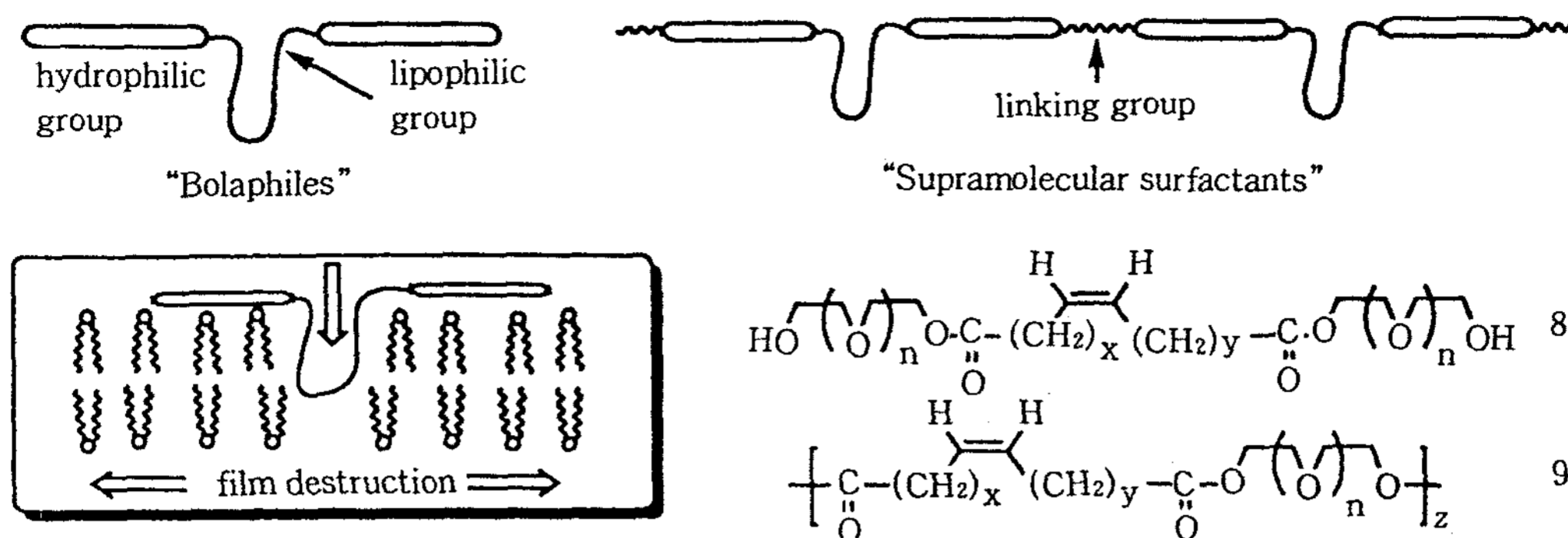
Compound	R	n	Krafft point (°C)	CMC ^a (mM)	γ_{CMC}^a (mN/m)	Foam(mL)	
						0'	10'
5a	C ₁₁ H ₂₃	2	<0	0.082	28	270	260
5b	C ₉ H ₁₉	4	<0	0.17	34	50	0
5c	C ₇ H ₁₅	6	<0	0.79	34	50	0
6a	C ₁₁ H ₂₃	2	<0	0.60	24	60	30
6b	C ₉ H ₁₉	4	<0	7.1	28	20	0
6c	C ₇ H ₁₅	6	<0	14.4	27	10	0



Menger also synthesized another kind of gemini surfactants, and reported an unusual surface active properties where the CMC increases with the longer hydrophobic chain due to re-

straint of adsorption alignment depending on the structure of the linking group¹²⁾.

3) Lipid bilayer-interfering amphiphilic compound "Bolaphiles"



Scheme 2.

Since lipid bilayer membrane has a potential as a molecular material, it is necessary from the viewpoint of industrial importance to develop a process to regulate its physical property as well as to develop its function. Regulation of lipid bilayer membrane is also important from the viewpoint of medical science, since units of living thing tissue are wrapped by lipid bilayer membrane.

Lipophilic part of compound 8, which penetrates into a lipid bilayer membrane in a shape of loop, destroys the alignment of chains of phospholipid, resulting in the breakdown of the tissue unit (Scheme 2). Thus, an application to chemical remedy for HIV (human immunodeficiency virus) by breakdown of its cell membrane, for example, can be expected. Polymerized "Supramolecular Surfactants" 9 show higher activity for this purpose. Proper modification of molecular structure may bring about improvement of performance and membrane selectivity¹³⁾. Since cholesterol makes the lipid membrane closer, it is difficult for compounds 8 and 9 to penetrate effectively into those containing a large amount of cholesterol. Thus, membrane-breakdown ability decreases in inverse proportion of cholesterol content of the membrane. Compound 9 shows weak solubilizing power to human blood cell membrane which

contains 50% of cholesterol. On the contrary, it solubilizes the cell membrane of human bacterium (*Proteus Mirabilis*) which contains no cholesterol¹⁴⁾.

2. Reactive surfactants

Depending on the use of a surfactant, there are cases in which surface activity is required only during an objective process, and after the completion of the process the surface active material should be removed to afford the final product or to prevent deterioration of product. For example, the quality of emulsion polymerization product may be deteriorated by remaining emulsifier. In these cases, the emulsifier is removed by utilizing the clouding phenomenon in the case of nonionic surfactant or by adding polyelectrolyte in the case of anionic surfactant. These processes, however, may be inadequate or may cause secondary defects in some cases. From these reasons, development of a destructible surfactant, which can be decomposed under specific conditions to extinguish its activity after attaining its purpose have gathered attentions.

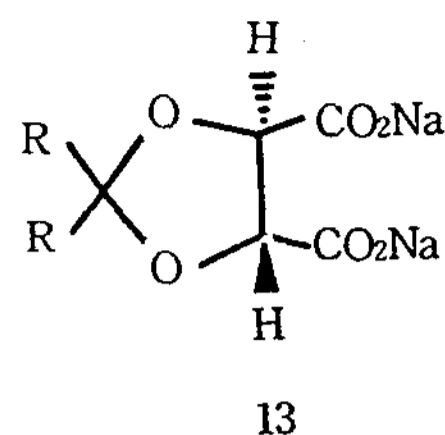
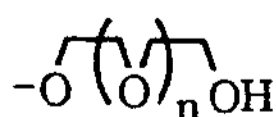
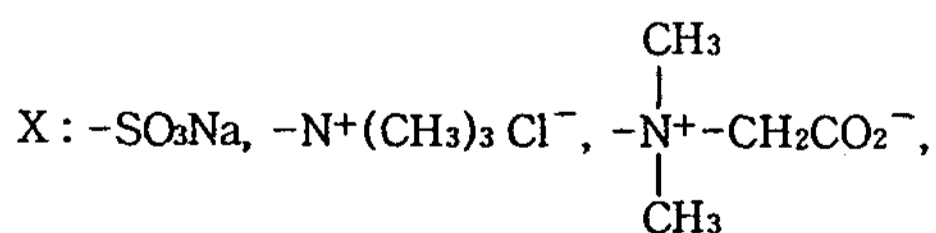
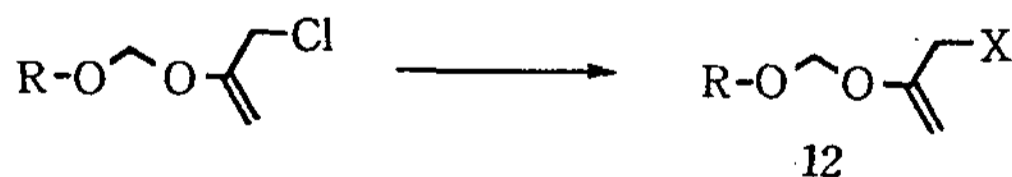
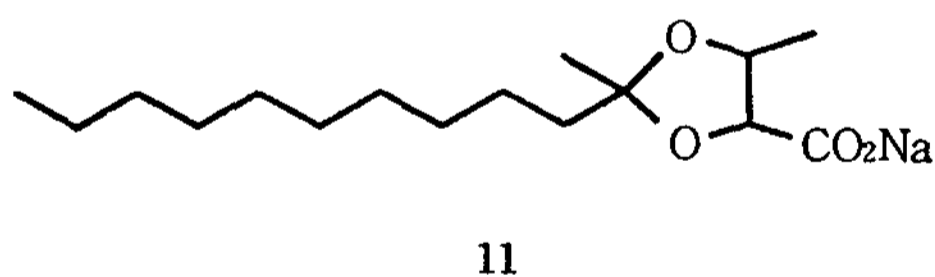
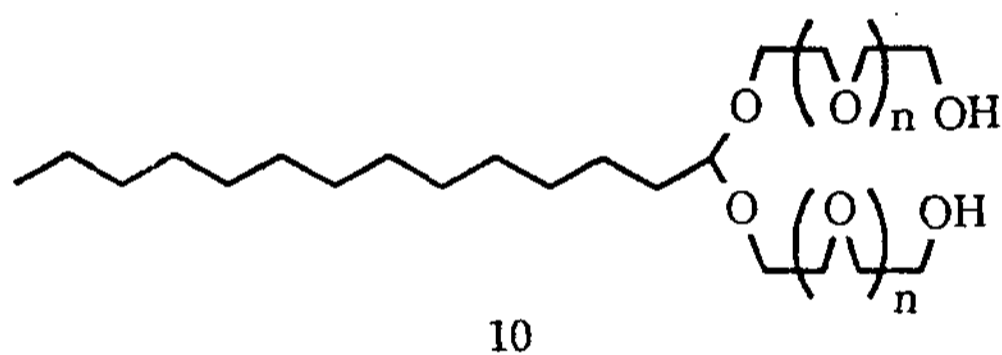
1) Acetal-type surfactants¹⁵⁾

Ionic surfactants and nonionic surfactants containing acetal moiety in linking group between the lipophilic and hydrophilic groups

have been synthesized by some research teams (compound 10, 11)¹⁶⁻²¹. In this kind of surfactants, the instability of acetal linkage under acidic conditions is utilized. The rate of acidic hydrolysis depends on the structure and the ionic character. It is disclosed that in the case of cationic surfactants the rate is considerably small, reflecting the difficulty of protonation on the acetal linkage affected by an adjacent cationic atmosphere²¹.

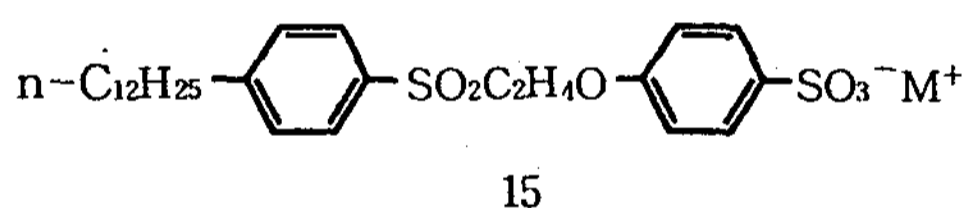
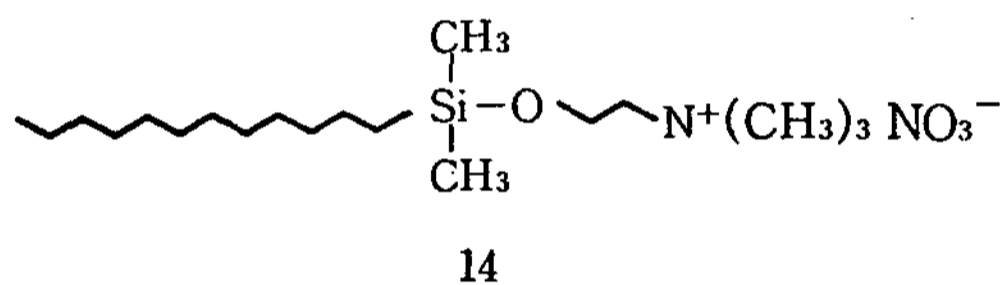
A series of acetal compounds 12 can be prepared with ease from allyl chloride which is derived from epichlorohydrin and fatty alcohol.

The acetal compound 13 derived from tartaric acid is a very interesting surfactant. It has low Krafft point (below 0°C), extremely low CMC, good surface tension-lowering ability, and good foaming ability and foam stability, even when it has two long lipophilic chains of heptadecyl groups²².



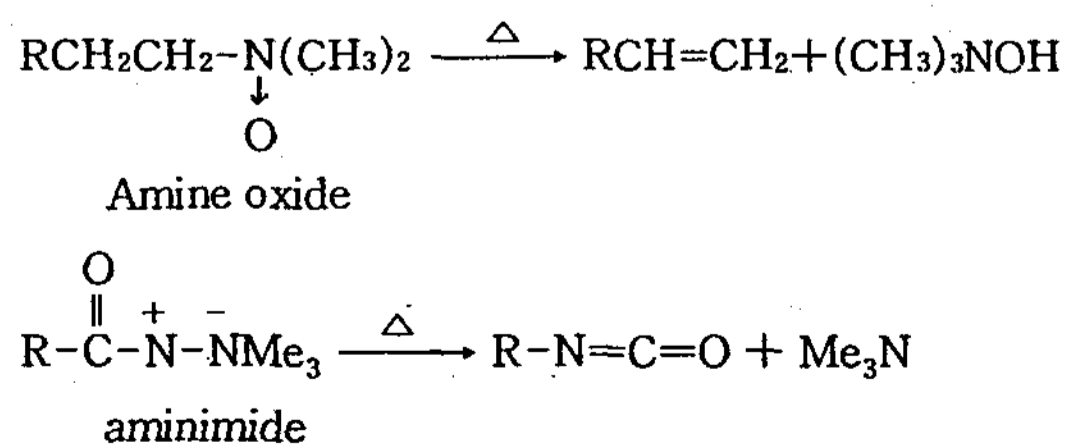
2) Surfactants destructible under alkaline condition

Examples of surfactants hydrolyzable under high pH conditions are rare: Siloxy derivative 14 is one of them. This compound contains a silicon-oxygen-carbon linkage, which is hydrolyzed with ease to silanol and alcohol under alkaline conditions²³. Compound 15 containing aryloxyethylenesulfonyl moiety is also hydrolyzed in alkaline solution²⁴.

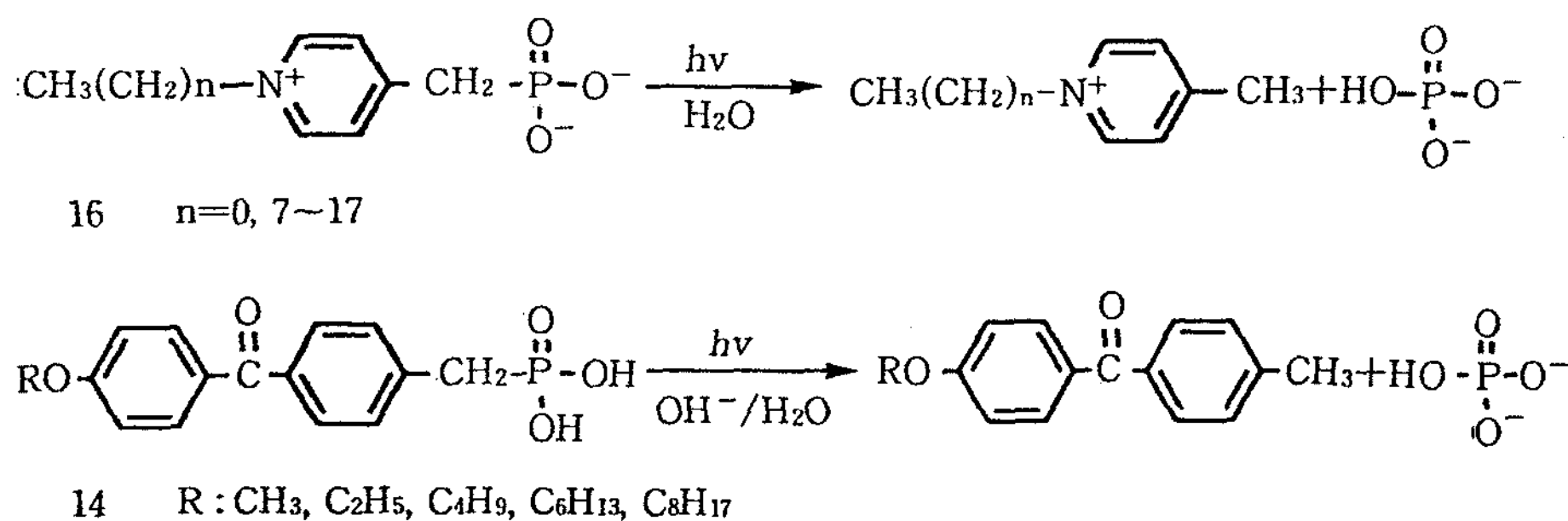


3) Pylorizable surfactant

Amine oxide-type surfactant decomposes over 150°C to afford olefin and a hydroxyamine derivative (Scheme 3)²⁵. Aminimide-type surfactant containing a cationic nitrogen-anionic nitrogen linkage and the blocked isocyanate-type surfactant are also reported to belong to pylorizable surfactants.



Scheme 3.



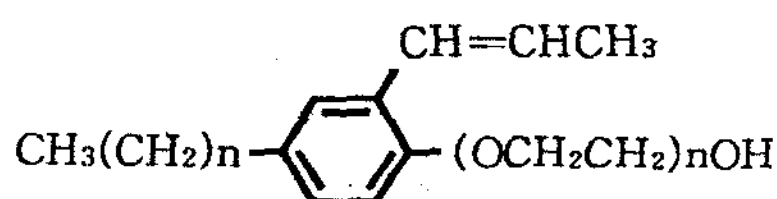
Scheme 4.

4) Photo-denaturalizable and photo-destructible surfactant

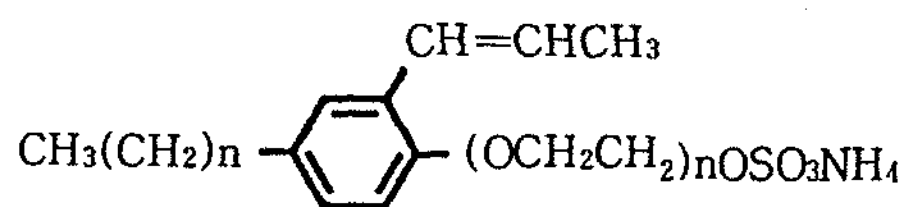
Although the phosphonic group does not absorb light, the compound bearing benzophenone²⁶⁾ or pyridinium moiety²⁷⁾ linked to this group by a methylene group absorbs UV light to decompose and loses, or changes, its surface activity (Scheme 4). This shows a possibility to develop a new use of surfactant, though there are many factors yet to be solved, such as surface activity, efficiency of destructibility, or production.

5) Copolymerizable surfactant

Copolymerizable surfactants 18 and 19 are already commercially available. Emulsifier molecule (or unit) remaining in the polymer product produced by emulsion polymerization using copolymerizable emulsifier does not display its surface activity. On kneading these surfactant molecules copolymerize with monomer molecules and disperse into the polymer bulk and no more aggregate. By using this kind of surfactants, moreover, the waste water from production plant is not contaminated with the emulsifier, which forces environmental loads to hydro-sphere.



18



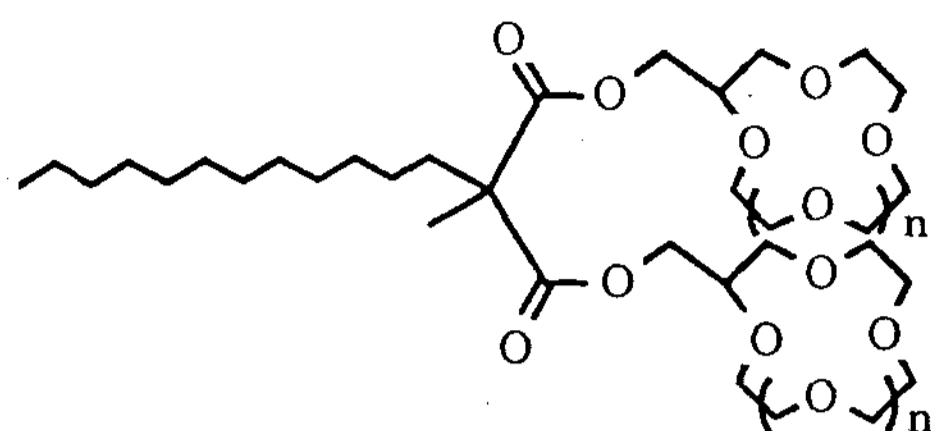
19

3. Amphiphilic compound having recognition ability

Amphiphilic compounds having recognition ability or discrimination ability can be exemplified as one of those which have a possibility to construct a new high technology (industry). For example, if it is possible to equip them with a recognition ability or a discrimination ability toward specific cells such as germs, "Bolaphiles" and "Supramolecular Surfactants" described above may function as high performance drugs.

1) Amphiphilic bis-crown ethers as a neutral ion carrier

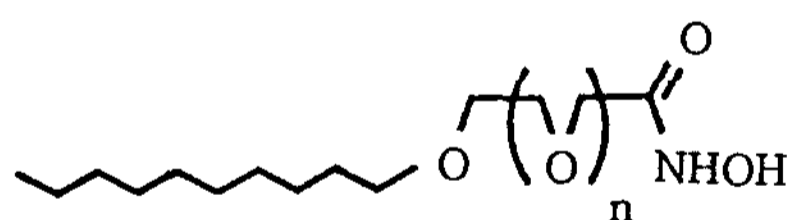
When amphiphilic bis-crown ether 20 is mixed to polyvinyl chloride together with plasticizer, it adsorbs on the liquid-liquid interface of plasticizer and water to function as a neutral ion-sensor. Though the character of bis-crown ether may change depending on the structure of linking moiety of the two crown ether rings, bis-12-crown-4-ether and bis-15-crown-5-ether display superior selectivities toward sodium cation and potassium cation in water, respectively²⁸⁾, and have been practically utilized in the field of medical science.



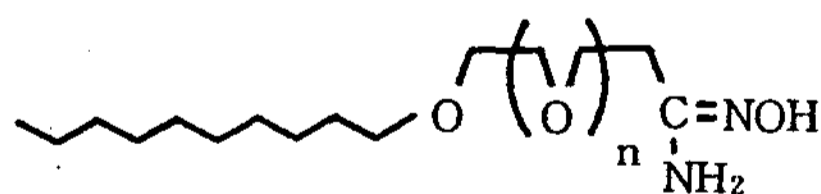
20 (n=1, 2)

2) Modified alkylethoxylate surfactant

By modifying the end hydroxy group of alkylethoxylate with a functional group bearing coordination ability toward a specific metal cation, the resulting compound forms micells in a selectively coordinated structure with the metal ion, and may be utilized as a carrier in selective transport of metal ion or in extraction of metal ion. For example, amphiphilic compound 21 can remove contaminative ferric ion from a ferrous ion aqueous solution, since this compound has a larger selectivity toward Fe^{3+} than with Fe^{2+} ²⁹⁾. Compound 22 can be also utilized in extraction of valuable Ga^{3+} from Bayer solution which is contaminated with Al^{3+} , since compound 22 has a large selectivity toward Ga^{3+} in the solution containing Al^{3+} ³⁰⁾.



21

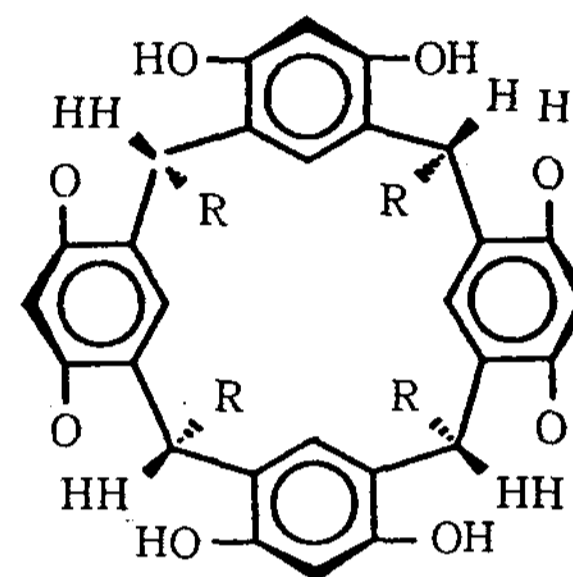


22

3) Multi-hydrogen bonding surfactant

Cyclic tetramer of resolsinol having long hydrophobic chains 23 displays affinity selectively toward sugar of specific steric structure through multi-hydrogen bonding³¹⁾. If a proper

molecular design is provided, this compound may be utilized as a sensor toward sugar dissolved in aqueous solution, since this compound forms a stable molecular membrane and an electrode containing this compound shows an electric response toward sugar dissolved in aqueous solution.

23 R : C₁₁H₂₃

III. Conclusion

In various industries, surface chemistry concerns the industrial processes and plays an important role so often. Thus, the selection of surfactant or surface-modifier decides the issue of the process. Meanwhile, it is quite difficult to discuss the phenomena on interface which is a very complicated field by means of the molecular structure of amphiphilic compound or the interaction between surfactant molecules or between the substrate and surfactant molecule. Therefore, it is almost impossible at present to design a molecular structure and to develop a new surfactant having the required performance, even though lots of informations concerning the correlation between molecular structure and the properties have been accumulated. It is easy to speculate that reform in technology becomes harder, and required performance of surfactant becomes more intricate and more delicate. In order to respond to these circum-

stances which may happen in the future, it is necessary to develop seeds concerning the surfactant as many as possible prior to occurrence of the requirement.

Because of the complicated function of amphiphilic compound and the complicated circumstances where the compounds are used, many unexpected discoveries concerning interfacial phenomena or functions of amphiphilic compound will be brought about in the process of developing these seeds, and the surfactant chemistry and industry will become wider and more important.

References

1. M. J. Rosen, *CHEMTECH*, **23**, 30(1993).
2. a) M. Okahara, A. Masuyama, Y. Sumida, and Y.-P. Zhu, *J. Jpn. Oil Chem. Soc.(YUKAGAKU)*, **37**, 746(1988). b) A. Masuyama, Y. Nakatsuji, *Hyoumen*, **32**, 536(1994).
3. a) Y.-P. Zhu, A. Masuyama, and M. Okahara, *J. Am. Oil Chem. Soc.*, **67**, 459(1990). b) Y.-P. Zhu, A. Masuyama, T. Nagata, and M. Okahara, *J. Jpn. Oil Chem. Soc.(YUKAGAKU)*, **40**, 473(1991).
4. a) Y.-P. Zhu, A. Masuyama, Y. Kobata, Y. Nakatsuji, M. Okahara, and M. J. Rosen, *J. Colloid Interface Sci.*, **158**, 40(1993). b) A. Masuyama, T. Kawano, Y.-P. Zhu, T. Kida, and Y. Nakatsuji, *Chem. Lett.*, 2053(1993).
5. a) Y.-P. Zhu, A. Masuyama, Y. Kirito, and M. Okahara, *J. Am. Oil Chem. Soc.*, **68**, 539(1991). b) Y.-P. Zhu, A. Masuyama, Y. Kirito, M. Okahara, and M. J. Rosen, *J. Am. Oil Chem. Soc.*, **69**, 626(1992). c) A. Masuyama, M. Yokota, Y.-P. Zhu, T. Kida, and Y. Nakatsuji, *J. Chem. Soc., Chem. Commun.*, 1435(1994).
6. T.-S. Kim, T. Hirao, and I. Ikeda, *J. Amer. Oil Chem. Soc.*, **73**, 67(1996).
7. T.-S. Kim, T. Kida, Y. Nakatsuji, T. Hirao, and I. Ikeda, *J. Amer. Oil Chem. Soc.*, **73**, 907(1996).
8. T.-S. Kim, T. Kida, Y. Nakatsuji, and I. Ikeda, *Langmuir*, 1996, 6304.
9. I. Ikeda and T.-S Kim, unpublished data.
10. T.-S. Kim, T. Tatsumi, T. Kida, Y. Nakatsuji, and I. Ikeda, *J. Jpn. Oil Chem. Soc.*, **46**, 747(1997).
11. T. J. Micich and W. M. Linfield, *J. Am. Oil Chem. Soc.*, **65**, 820(1998).
12. F. M. Menger and C. A. Littau, *J. Am. Chem. Soc.*, **115**, 10083(1993).
13. a) S. L. Regen, N. Jayasuriya, and W. Fabianowski, *Biochem. Biophys. Res. Commun.*, **159**, 566(1989). b) N. Jayasuriya, S. Bosak, and S. L. Regen, *J. Am. Chem. Soc.*, **112**, 5844(1990). c) N. Jayasuriya, S. Bosak, and S. L. Regen, *J. Am. Chem. Soc.*, **112**, 5851(1990).
14. Y. Nagawa and S. L. Regen, *J. Am. Chem. Soc.*, **113**, 7237(1991).
15. T. Takeda, *Hyoumen*, **32**, 109(1994).
16. T. Kuwamura and H. Takahashi, *Bull. Chem. Soc. Jpn.*, **45**, 617(1972).
17. B. Burczyk and A. Sokolowski, *Tenside, Surfactants, Deterg.*, **15**, 68(1978).
18. D. A. Jaeger and M. R. Frey, *J. Org. Chem.*, **47**, 311(1982).
19. T. Takeda, S. Yasuhara, and S. Watanabe, *J. Jpn. Oil Chem. Soc.(YUKAGAKU)*, **30**, 486(1981).
20. S. Yamamura, M. Nakamura, K. Tanaka, and T. Takeda, *J. Jpn. Oil Chem. Soc.(YUKAGAKU)*, **40**, 104(1991).
21. D. Ono, A. Masuyama, and M. Okahara, *J. Org. Chem.*, **55**, 4461(1990).
22. D. Ono, T. Tanaka, A. Masuyama, Y. Nakatsuji, and M. Okahara, *J. Jpn. Oil Chem. Soc. (YUKAGAKU)*, **42**, 10(1993).

23. D. A. Jaeger and M. D. Ward, *J. Org. Chem.*, **47**, 2223(1982).
24. D. A. Jaeger, C. T. Finley, M. R. Walter, and C. A. Martin, *J. Org. Chem.*, **51**, 3956 (1986).
25. Y. Hayashi, F. Shirai, T. Shimizu, Y. Nagano, and K. Teramura, *J. Am. Oil Chem. Soc.*, **62**, 555(1985).
26. Y. Okamoto, H. Yoshida, and S. Takamuku, *Chem. Lett.*, 569(1988).
27. Y. Okamoto, A. Hosoda, and S. Takamuku, *Bull. Chem. Soc. Jpn.*, **63**, 3053(1990).
28. a) I. Ikeda, T. Katayama, M. Okhara, and T. Shono, *Tetrahedron Lett.*, **22**, 3615(1981).
b) T. Shono, M. Okahara, I. Ikeda, K. Kimura, and H. Tamura, *J. Electroanal. Chem.*, **132**, 99(1982).
29. A. Masuyama, T. Okano, M. Okahara, *Abstract of Japan Chem. Soc. 58th Annual Meeting*, **4 III H40**(1989).
30. M. Araki, T. Okano, and M. Okahara, *Ind. Eng. Chem. Res.*, **29**, 290(1990).
31. a) Y. Aoyama, *Kagakutokougyou*, **43**, 896 (1990). b) K. Kurihara, K. Ohto, Y. Tanaka, Y. Aoyama, and T. Kunitake, *J. Am. Chem. Soc.*, **113**, 444(1991).