

Preparation and Properties of Novel Water-Soluble Surfactants. I. Synthesis and Surface Activity of Polycarboxylated Multihydrophilic Surfactants

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ABSTRACT: A series of novel surfactants containing multianionic and nonionic hydrophilic moieties were prepared by reacting fumaric acid with polyoxyethylenated stearyl ether in the presence of a peroxy-type free radical initiator to form a carboxylic-acid-group-containing addition product. The structure of these surfactants was confirmed by infrared, nuclear magnetic resonance, and elemental analysis. These surfactants exhibit excellent functional properties of self-sequestering. This means that besides good surfactant properties, including surface

tension, foaming, and wetting, they possess autonomous sequestering ability without any help of additional sequestering agent. When used in cotton bleaching procedures, these surfactants increase the penetration of the fibers of gray fabrics and increase the whiteness of bleached cotton. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3559–3564, 2006

Key words: synthesis; surfaces; surfactants; water-soluble polymers; hydrophilic polymers

INTRODUCTION

That water-soluble surfactants containing multihydrophilic and hydrophobic moieties exhibit surface activity similar to traditional surfactants are also reported in our previous studies.^{1–4} Surfactants are characterized by the possession of both polar and nonpolar regions on the same molecule. The polar or hydrophilic region of the molecule may carry a negative charge or nonionic groups, giving rise to anionic or nonionic surfactants.⁵ However, in traditional concept, a surfactant is made of one nonpolar or hydrophobic moiety, and one polar head connected together. For these reasons of single structure, the application of surfactants provides limitation in some cases and the mixture of various surfactants is often used as an end-product in commercial application.⁶

In the last few years, new types of surfactants having more than one hydrophobic and hydrophilic moiety in the molecule have attracted considerable interest, since it became evident that these compounds exhibit extraordinary surface activity. For example, the surfactants containing two hydrophilic groups and two hydrophobic groups, named as Gemini surfactants, are shown to exhibit more surface activity than do traditional surfactants containing lower cmc values, adsorb strongly to

form closely packed monolayers at hydrophobic surfaces, and have greater efficiency in reducing surface tension.^{7–9} In the present study, a series of novel surfactants containing multianionic and nonionic hydrophilic moieties are prepared by reacting fumaric acid with polyoxyethylenated stearyl ether in the presence of a peroxy-type free radical initiator to form a carboxylic-acid-group-containing addition product. The surface-active properties of these surfactants, including surface tension, foaming, wetting, self-sequestering ability, and the application properties in cotton bleaching procedures were evaluated.

EXPERIMENTAL

Materials

The polyoxyethylenated stearyl ether supplied by Sino-Japan Chemical Co. was of commercial grade. The fumaric acid, benzoyl peroxide, and other reagents purchased from Hayash Pure Chemical were of reagent grade and were used without further purification. Sodium dodecylbenzene sulfonate (SDBS) was supplied by Sigma–Aldrich and used to compare the surface activity of multihydrophilic surfactants.

Preparation

The novel surfactants were prepared by two steps, which are shown in Figure 1. In the first step a series of polyoxyethylenated stearyl ether was reacted with

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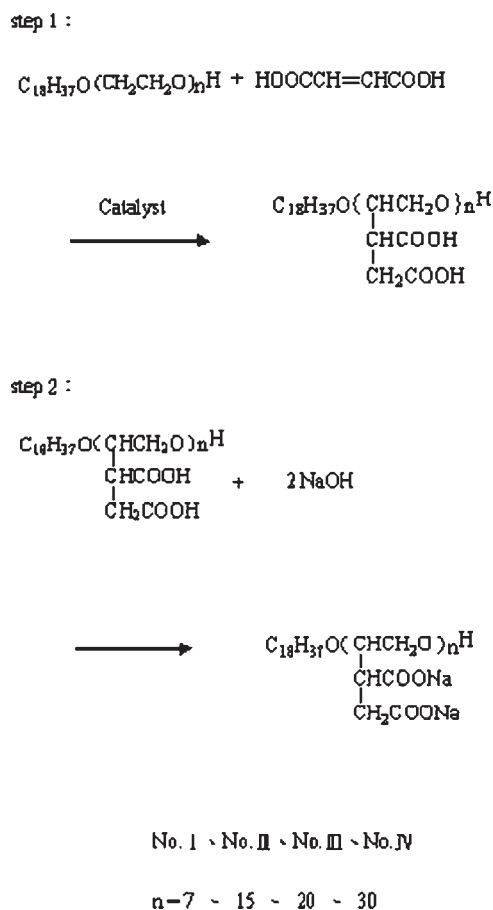


Figure 1 Synthesis of multihydrophilic surfactants.

fumaric acid in the presence a peroxy-type free radical initiator to form a carboxylic acid group containing addition product. The second step involved the neutralization of the products obtained in the first step by

sodium hydroxide solution. The following example shows a typical recipe for preparing an anionic derivative of polyoxyethylenated stearyl ether. A reaction mixture of 1.0 mol polyoxyethylenated stearyl ether, (the weight of ethers used in the reaction mixture varies from 578, 930, 1150, and 1590 g for the ethers containing ethylene oxide units of 7, 15, 20, and 30, respectively), 1.0 mol (116 g) fumaric acid, and 1 g of benzoyl peroxide was stirred mechanically and heated to 100–105°C under a nitrogen atmosphere. The reaction mixture was stirred at this temperature for 8 h. Then the reaction mixture was cooled to about 70°C under nitrogen and neutralized by addition of sodium hydroxide solution.

The sodium salt of the product was purified by removing the impurities with ethanol. The purity of the purified product was determined by TLC, using acetone/benzene (3/2) as an eluant. Compounds I, II, III, and IV, as shown in Table I, have 7, 15, 20, and 30 ethylene oxide units, respectively (as depicted in Fig. 1).

Analysis

The structure of the final products was confirmed by infrared (IR), proton nuclear magnetic resonance (¹H NMR) spectral analysis, and elemental analysis. IR spectra were obtained with a Japanese spectroscopic FT/IR-3 spectrophotometer and ¹H NMR spectra were obtained with a Varian 360 L NMR. The anionic group was determined by the method described in JIS, K3362.¹⁰

Measurement

Surface tension was determined at room temperature with a Japan Kaimenkaguka CBVP-A3 surface tensi-

TABLE I
Analyses of Multihydrophilic Surfactants

Compound	Mol. of EO used	Anionic group content (%)	Elemental analysis			
			C (%)		H (%)	
			Found	Calc.	Found	Calc.
I	7	1.988	61.86	62.79	9.29	9.30
II	15	2.851	62.47	63.56	9.73	8.53
III	20	3.609	59.66	58.77	9.54	8.26
IV	30	3.944	58.68	57.58	9.50	7.93

TABLE II
Analyses of IR Spectrum and ¹H NMR Spectrum

Function group	IR		¹ H NMR	
	Vibration mode	cm ⁻¹	Function group	Chemical Shift δ (ppm)
R-CH ₂	Stretching	2851–2940	-CH ₂ CH ₂ O-	3.2–3.7
R-OH	Stretching	3449–3647	-CH ₃ CH ₂ -	0.5–1.3
R-COO	Stretching	1582–1774	-C-CH-CO-	3.8–4.0

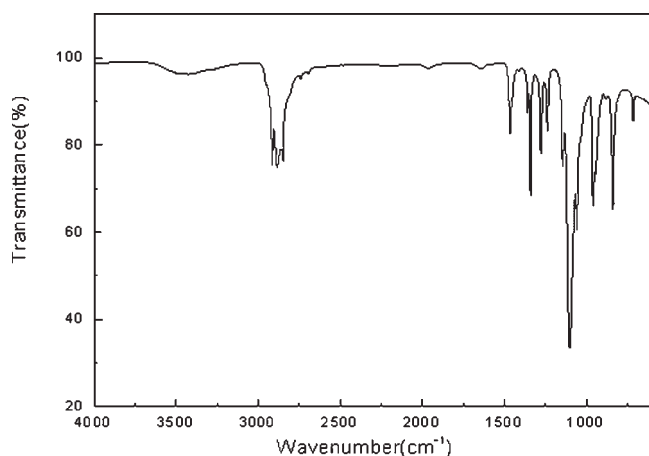


Figure 2 FTIR spectra of compound IV.

ometer. Foaming properties were determined by the Ross-Miles method. Foam production was measured by the height of the foam initially produced, and foam stability was measured by the height after 3 min. The contact angle was measured by a FACE CA-5 contact angle meter. Self-sequestering ability was determined by the sequestering ability of surfactants for calcium ion. A HI 8418 model was used to measure the equilibrium calcium ion concentrations. A gray cotton fabric was used to study the effect of surfactants on hydrogen peroxide bleaching. The bleaching recipe included H_2O_2 (20%, 10 g/L), NaOH (5 g/L), Na_2SiO_3 (5 g/L), surfactant (2 g/L), liquor ratio 30:1, temperature 80°C , time 40 min. After bleaching, the reflectance of the cotton fabric was measured using an ACS spectrophotometer and the results were used to calculate whiteness values. The bleached fabric was also used to evaluate the wetting ability by measuring the height of water penetrating the fabric.

RESULTS AND DISCUSSION

Preparation of multianionic surfactants

The desired novel surfactants are made by reacting fumaric acid with a series of polyoxyethylenated stearyl ethers in the presence of butyl peroxide as a free radical initiator. As can be seen from Figure 1, above, this free radical initiated addition is believed to occur by a three-step mechanism, as reported.¹¹⁻¹³ Fumaric acid is one of the ethylene known unsaturated dicarboxylic acids. It is suitable for this study because it does not homopolymerize. In this reaction the carboxylic acid replaces a hydrogen atom on a carbon adjacent to an oxygen atom in an ether linkage and free radical addition reactions with them are completed by removal of hydrogen from another polyol or from another hydrogen atom source.

The reactions have been monitored by following the disappearance of fumaric acid in the reaction mixture. And the structure of addition products is confirmed by element analysis, and IR and ^1H NMR spectra analyses.

Table I shows the results of an elemental analysis of the final multihydrophilic surfactants containing different lengths of a polyoxyethylene chain. Strictly speaking, calling these new surfactants by the term "oligomeric" would be more appropriate. However, the lengths of polyoxyethylene chain used were below 30 ethylene oxide units because the longer polyoxyethylene chain provided more hydrophilicity and decreased the surface activities in solutions.

Table II lists the results of IR spectrum and ^1H NMR spectrum. A typical IR spectrum of the synthesized multihydrophilic surfactants (Fig. 2) displayed bands at $3449\text{--}3647\text{ cm}^{-1}$ ($-\text{OH}$), $2851\text{--}2940\text{ cm}^{-1}$ ($-\text{CH}_2$), and $1582\text{--}1774\text{ cm}^{-1}$ ($-\text{COO}$). These bands were char-

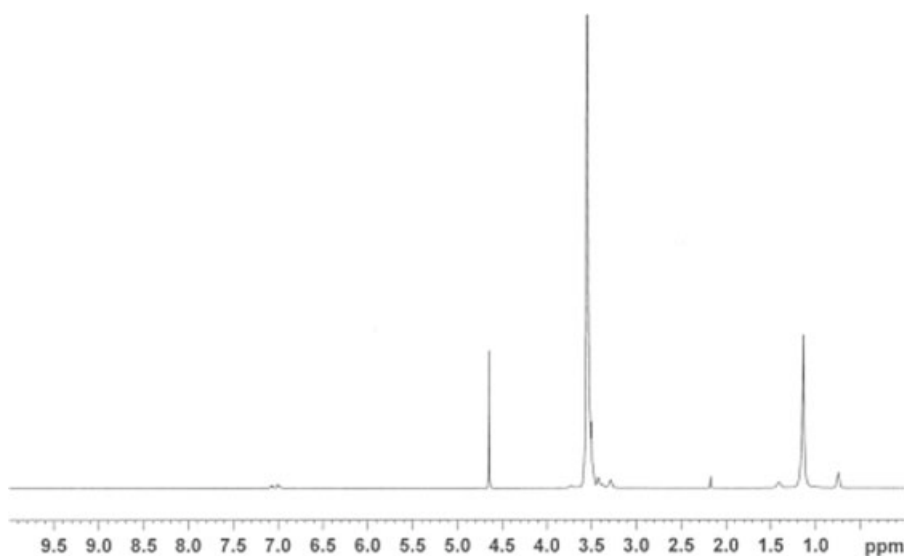


Figure 3 ^1H NMR spectra of Compound IV.

acteristic of the desired compounds. The compound structure was further supported by the ^1H NMR spectrum (Fig. 3). It gave signals at δ 0.5–1.3 ppm ($-\text{CH}_3\text{CH}_2-$), δ = 3.2–3.7 ppm ($-\text{CH}_2\text{CH}_2\text{O}-$), and δ = 3.8–4.0 ppm ($-\text{C}-\text{CH}-\text{CO}-$).

Surface tension

The compositions of surfactants prepared in the present study consist of three components containing an aliphatic group servicing hydrophobic portion, ethylene oxide (block) and neutralized carboxylic acid groups (multianionic) servicing hydrophilic portion of surfactants. And because of the amphiphathic structure in these surfactants, similar to the traditional surfactants, they exhibit excellent surface activity, as shown in Figure 4. Increase in the length of polyoxyethylene chain of nonionic portion results in a decreased surface activity clearly. This phenomenon is due to the increase of hydrophilicity of surfactants. As a result, it decreases the concentration of the surfactants at the surface.¹⁴

Foaming properties

The low-foaming tendency of surfactants is an important property required in some applications, such as using surfactants as dyeing auxiliaries in modern textile industry. The low-foaming properties of surfactants prepared in the present study are shown in Table III. All the compounds exhibited not only low foam production, measured by the height of foam initially produced, but also low-foaming stability, measured by

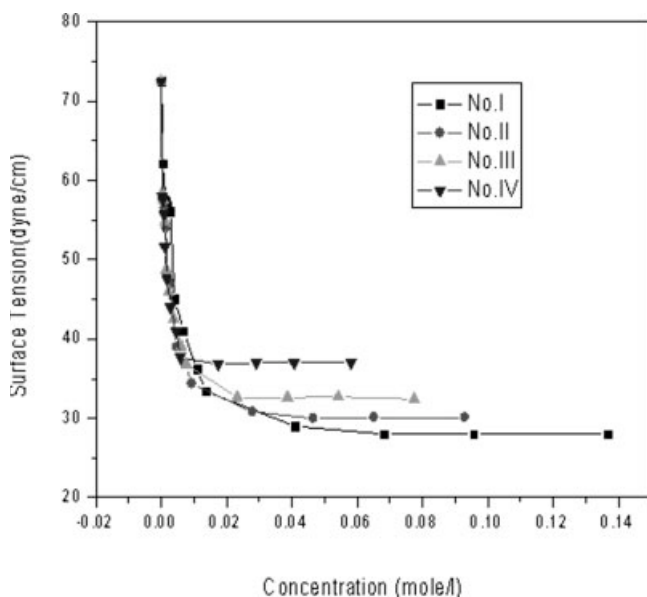


Figure 4 Surface tension against concentration of multihydrophilic surfactants.

TABLE III
Foaming Properties of Multihydrophilic Surfactants

Compound	Foam height (cm)	
	Initial	After 3 min
I	5.8	4.2
II	6.1	4.4
III	9.3	8.2
IV	8.9	8.1
SDBS ^a	15	6.0

^a For sample comparison.

the height after 3 min. They were also compared with that of SDBS and it was found that the compounds possessed the minimal foaming power, and thus may be used as low-foaming agents. These effects show that low foaming property is probably due the presence of multihydrophilic groups, which cause considerable increase in the area per molecule and producing less cohesive forces at the surface.^{2,3}

Wetting power

Wetting power is one of the important properties of surfactants. The outward measure of the degree of wetting is the contact angle. It provides the angle foamed between planes tangential to the surfaces of the solid and the liquid at the wetting perimeter.

Table IV shows the contact angle formed between surfactant solutions and acrylic plastic and cotton fabrics. The smaller contact angles observed for the solutions containing the surfactants, compared with that of water alone, indicate that these compounds show wetting power on both acrylic and cotton substrates.

Self-sequestering properties

It is well known that in a hard water-surfactant system, the surface activities of surfactants are considerably reduced, because of the multivalent ions in water. Certain materials, called sequestering agents, are added to avoid this disadvantage in commercial application of

TABLE IV
Contact Angles of Multihydrophilic Surfactants

Compound	Contact angle (deg)	
	Acrylic plastic	Cotton fabric
H ₂ O	70	124
I	39	69
II	40	73
III	42	79
IV	46	81
SDBS ^a	40	48

^a For sample comparison.

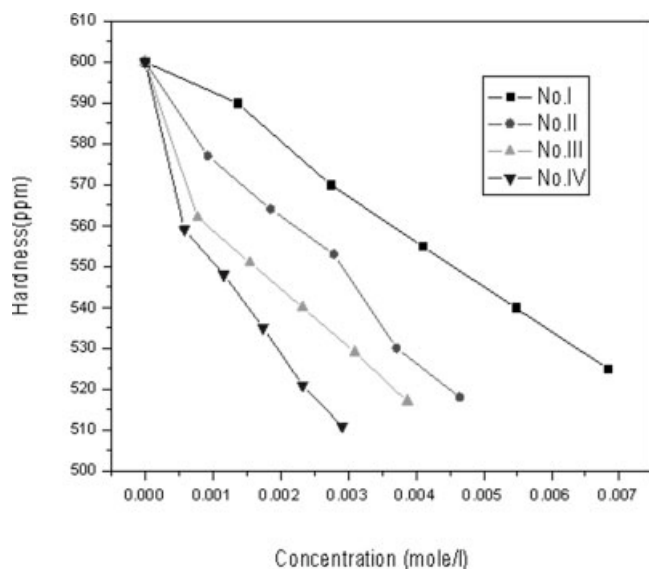


Figure 5 Self-sequestering ability of multi-hydrophilic surfactants.

surfactants. A novel surfactant, namely a self-sequestering surfactant, also has been reported recently for such use.^{15,16} Besides having surfactant characteristics, it also possesses autonomous sequestering characteristics without the help of different complexing compounds. In the present study, the self-sequestering property of surfactants is evaluated by the determining calcium ion sequestering power. The effect of the surfactant level on the free calcium ion concentration is shown in Figure 5. It is obvious that the surfactants prepared in this study have self-sequestering properties. As expected, this is due to the sequestering ability of the multicarboxylic groups of these surfactants. In Figure 6, the surface tension of multi-hydrophilic surfactants including calcium ions possesses excellent surface activity.

Application on cotton bleaching procedures

In textile industry, scouring and bleaching are carried out to prepare the cloth for dyeing. The scouring and bleaching treatments do not rely primarily on the use

TABLE V
The Whiteness and Water Penetrating Height of Bleached Fabric in the presence of Multi-hydrophilic Surfactants

Compound	Whiteness of bleached fabrics (E313)	Height of water adsorption (cm)
I	54.49	5.2
II	53.21	5.6
III	52.94	5.9
IV	53.59	6.0
None	53.44	0
SDBS ^a	58.33	4.6

^a For sample comparison.

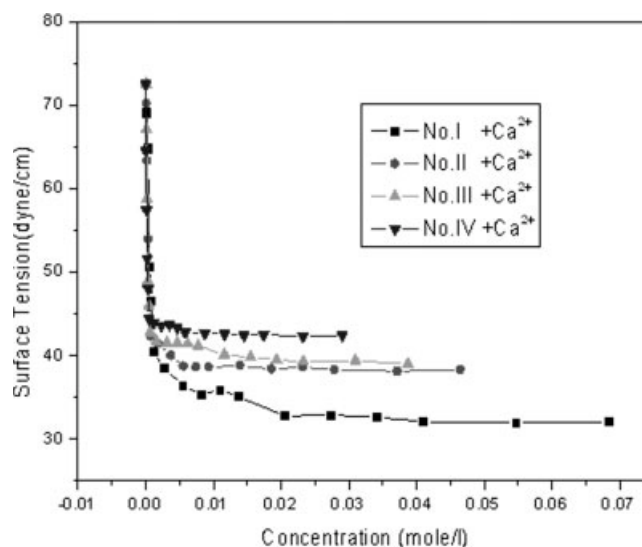


Figure 6 Surface tension against concentration of multi-hydrophilic surfactants including Ca^{2+} .

of traditional surfactants. Nevertheless, rapid and even wetting of the cloth is of major importance, and to assist this, some auxiliaries may be added.

The ability of novel surfactants to improve the whiteness and the wetting power of cotton fabrics in a hydrogen peroxide bleaching system are shown in Table V. Because the novel surfactants exhibit good surface activity and self-sequestering ability, the presence of novel surfactants increased the effects of oxidation on bleaching baths in the process and helped prepare more purified fabrics for the next processes of dyeing or printing.

CONCLUSIONS

A series of novel surfactants, containing multianionic and nonionic hydrophilic moieties, are prepared by reacting fumaric acid with polyoxyethylenated stearyl ether in the presence of a peroxy-type free radical initiator to form a carboxylic acid group containing addition product. These surfactants exhibit excellent properties of self-sequestering. Besides good surfactant properties, including surface tension, foaming, and wetting, they possess autonomous sequestering ability without any help of additional sequestering agent. When used in cotton bleaching procedures, these surfactants increase the penetration of the fibers of gray fabrics and increase the whiteness of bleached cotton.

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