

Preparation and Surface Active Properties of Amphipathic Compounds with Two Sulfate Groups and Two Lipophilic Alkyl Chains

Yun-peng Zhu, Araki Masuyama and Mitsuo Okahara*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan

These compounds with various connecting groups between the two lipophilic groups were prepared by the reaction of glycol diglycidyl ethers with long-chain alcohols, followed by sulfation with chlorosulfonic acid or with a mixture of chlorosulfonic acid and acetic acid. The Krafft point of all these new amphipathic compounds was below 0°C, and they had good water solubility. These compounds were superior in surface active properties to general anionic surfactants with one lipophilic chain and one hydrophilic group, such as sodium dodecylsulfate. The effect of the structure of the connecting group on CMC, γ_{CMC} , foaming properties and wetting ability was investigated. They also showed excellent lime-soap dispersing ability.

Recently, synthetic amphipathic compounds with plural lipophilic chains have been widely applied to biomimetic "functional" materials in artificial bilayer membrane systems (1-2). Like this example, the development of new functions of surfactants or improvement of surface active properties will be achieved by a molecular design free from the classical concept that the surfactant consists of one lipophilic chain and one hydrophilic group.

On the other hand, we have developed a convenient synthetic method for glycol diglycidyl ethers (3), and studied the preparation and properties of many kinds of functional products derived from them (4-7). In our previous communication (8), we have shown that amphipathic compounds with two long-chain alkyl (octyl or decyl) groups and two sulfate or sulfonate groups (Fig. 1), which are derived from ethylene glycol diglycidyl ether, have good water solubility and excellent surface active properties in water.

Linfield *et al.* (9) have also reported that oxyethylated N,N'-dialkyl-N,N'-dihydroxyethyl diamides can be applied to soil wetting agents with excellent ability. However, there are only few reports on the interfacial properties of amphipathic compounds with both plural lipophilic and plural hydrophilic groups (10).

In this work, we prepared a series of title surfactants from glycol diglycidyl ethers and measured their surface active properties in water. Here we compare these surfactants with common anionic surfactants and try to clarify the structural effect of these surfactants on surface active properties. The synthetic route for these new types of compounds (IIIa-j) is shown in Figure 2.

EXPERIMENTAL

Materials. Ethylene glycol-, tri(ethylene glycol)- and butylene glycol diglycidyl ethers were prepared under

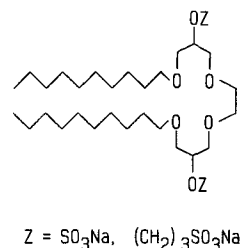


FIG. 1. Amphipathic compounds with two hydrophilic ionic groups and two lipophilic alkyl chains (8).

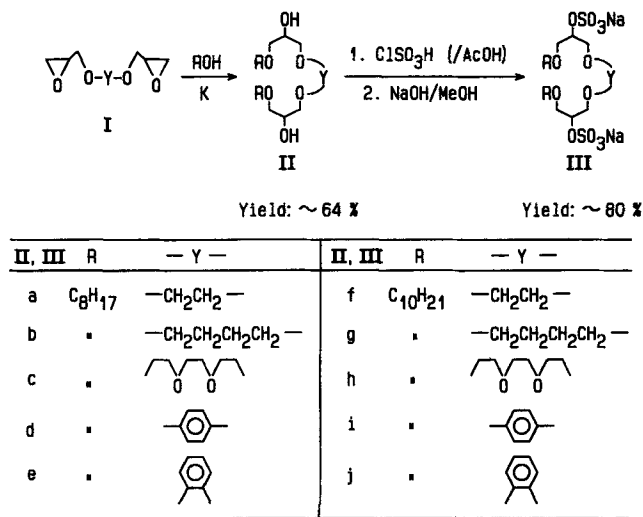


FIG. 2. Preparation of amphipathic compounds (III).

phase-transfer catalytic conditions reported previously (3). Hydroquinone diglycidyl ether and pyrocatechol diglycidyl ether were prepared in a yield of 64-68% by the successive treatment of a mixture of epichlorohydrin and hydroquinone or pyrocatechol (4:1 molar ratio) in 10 N aqueous NaOH solution at 40°C for two days, followed by the addition of saturated 5 N aqueous NaOH solution of sodium carbonate at room temperature for 20 hr. Hydroquinone diglycidyl ether was isolated by recrystallization from a mixed solution of ethanol, acetone and dioxane (m.p., 112-115°C). Pyrocatechol diglycidyl ether was obtained by distillation under reduced pressure (b.p., 142-152°C/0.65 Torr, m.p., 41.8-42.5°C). Preparation of 1,ω-bis(alkyloxymethyl)glycols (IIa-j) was carried out according to the method

*To whom correspondence should be addressed.

mentioned in the previous paper (6). Disodium 1, ω -bis(alkyloxymethyl)-1, ω -disulfates (IIIa-j) were synthesized by sulfation of the corresponding diols (IIa-j) in chloroform at ca. 0°C. Chlorosulfonic acid was used for sulfation of IIa-c,f-h. In the case of glycols with a phenylene group (II d,e,i,j), a mixture of chlorosulfonic acid and acetic acid was used. Purification was done by silica gel column chromatography or recrystallization. Their purity and established structure were ascertained by thin-layer chromatography (TLC), spectral (IR, ^1H NMR, MASS), and elemental analyses. Their purity was also confirmed from the observed sharp break point in surface tension-concentration curves.

Disodium 1, ω -bis(alkyloxymethyl)-1, ω -disulfate (III): Typical procedure. Chlorosulfonic acid (1.40 g, 12 mmol) was dropped carefully into a mixture of 1,14-bis(decyloxymethyl)-3,6,9,12-tetraoxatetradecane-1,14-diol (IIh; 1.73 g, 3 mmol) and sodium carbonate (1.27 g, 12 mmol) in chloroform (25 mL). The reaction was continued until the TLC peak based on IIh disappeared (6 hr) at ca. 0°C. The reaction mixture was neutralized with 10 N alcoholic sodium hydroxide solution to pH 10. After evaporation of the solvent, hot alcohol (45 mL) was

added to the residue to remove inorganic salts by filtration. After evaporation of alcohol in the filtrate, water (45 mL) was added to the residue. This aqueous solution was extracted with n-BuOH (30 mL, four times). After the extracts were combined and distilled, the residue was dissolved in a mixture of water and ethanol (50:50, v/v). This solution was washed with hexane several times and evaporation of the aqueous solution phase gave 2.0 g of crude product as solids. TLC-pure disodium 1,14-bis(decyloxymethyl)-3,6,9,12-tetraoxatetradecane-1,14-disulfate (IIIh) was obtained by silica-gel column chromatography with a chloroform:ethanol (9:1, v/v) eluent as white solids (1.57 g, 67% yield). The synthetic results of IIIa-j are summarized in Table 1 with the data from elemental analyses.

Methods. The Krafft point (T_{Kp}) was determined by the naked eye with a 1% aqueous solution. The surface tension of surfactants was measured with a Wilhelmy tensiometer using a series of aqueous solutions at various concentrations at 20°C. The foaming properties were evaluated by the semi-micro TK method (12) with a 0.1 wt% aqueous solution of surfactant at 20°C. Wetting ability was estimated by the sedimentation time of a piece of felt (JIS-R28W, 15 × 15 mm,

TABLE 1

Preparation and Properties of Amphipathic Compounds (IIIa-j)^a

Compound	Yield ^b (%)	Method ^c	$^1\text{H-NMR}^d$ (δ , ppm)	Anal. found (calcd.)	
IIIa	80	A	0.88(t,6H), 1.20-1.80(m,24H), 3.30-4.35(m,16H), 4.60-4.85(m,2H)	H, 7.62 C, 44.57 S, 9.92	(7.52) (45.14) (10.03)
IIIb	70	A	0.88(t,6H), 1.20-1.80(m,24H), 3.20-4.0(m,24H), 4.60-4.80(m,2H)	H, 7.61 C, 45.87 S, 8.72	(7.71) (46.35) (8.81)
IIIc	35	A	0.88(t,6H), 1.20-1.80(m,28H), 3.36-4.4(m,16H), 4.60-4.80(m,2H),	H, 8.08 C, 47.20 S, 9.44	(7.80) (46.78) (9.60)
IIId	80	B	0.80(t,6H), 1.10-1.62(m,24H), 3.40-3.70(m,8H), 3.70-4.10(m,4H), 4.40-4.50(m,2H), 6.80(s,4H)		^e
IIIe	53	B	0.80(t,6H), 1.20-2.00(m,24H), 3.20-4.50(m,12H), 4.60-5.00(m,2H), 6.80(s,4H)	H, 7.25 C, 48.18 S, 9.23	(7.00) (48.30) (9.32)
III f	72	A	0.80(t,6H), 1.20-1.80(m,32H), 3.30-4.35(m,16H), 4.70(m,2H)	H, 7.98 C, 48.33 S, 9.20	(8.07) (48.42) (9.03)
IIIg	66	A	0.80(t,6H), 1.18-1.80(m,32H), 3.20-4.00(m,24H), 4.60-4.80(m,2H)	H, 7.89 C, 48.35 S, 7.90	(8.28) (49.11) (8.18)
IIIh	40	A	0.80(t,6H), 1.20-1.80(m,36H), 3.30-4.0(m,16H), 4.60(m,2H)	H, 9.03 C, 50.11 S, 8.21	(9.20) (49.84) (8.75)
IIIi	72	B	0.80(t,6H), 1.10-1.62(m,32H), 3.40-4.00(m,8H), 4.00-4.25(m,4H), 4.40-4.50(m,2H), 6.80(s,4H)	H, 7.41 C, 50.08 S, 8.83	(7.54) (51.68) (8.62)
IIIj	70	B	0.80(t,6H), 1.10-1.87(m,32H), 3.20-4.40(m,12H), 4.60-4.80(m,2H) 6.80(s,4H)	H, 7.76 C, 51.14 S, 8.47	(7.54) (51.68) (8.62)

^aIR Spectra (Hitachi 260 Spectrometer): IIIa,b,c,f,g,h.: 3500, 2950, 1640, 1484, 1240, 1100 and 800 cm^{-1} ; III d,e,j,i: 3500, 2950, 1640, 1600, 1500, 1200, 1100 and 800 cm^{-1} .

^bBased on diols (II).

^cA, ClSO_3H was used as sulfating agent; and B, a mixture of ClSO_3H and AcOH was used as sulfating agent.

^d(JEOL JNM-GSX400, 400 MHz) s: singlet, t: triplet, m: multiplet. All compounds, except III d,i, were measured in CDCl_3 . Compounds III d,i were measured in d_6 -DMSO.

^eThis compound was too hygroscopic to determine its elemental analysis.

SURFACTANTS WITH TWO SULFATE GROUPS AND TWO LIPOPHILIC ALKYL CHAINS

70 mg, stainless hook included) from the surface to the bottom of a 50 mL of 0.1 wt% aqueous surfactant solution in a 100 mL glass cylinder (i.d. 30 mm) at 20°C. Lime-soap dispersing ability (LSDR) was determined in 333 ppm of hard water (a hardness composition of 68% Ca^{2+} , 32% Mg^{2+}) by the Borghetty-Bergman method (13).

RESULTS AND DISCUSSION

Preparation of the disodium disulfate (III) products was easy and they could be isolated in good yields. However, when glycols with a phenylene group (II d,e,i,j) were reacted with chlorosulfonic acid, sulfation on the aromatic ring also occurred, so that isolation of the product was very elaborate. It was found that this problem could be avoided by using a mixture of chlorosulfonic acid and acetic acid (1:1.2–1.5 molar ratio) as sulfating agent, and isolation of III with a phenylene group could be carried out in a manner similar to that used for the other disulfates.

All these disodium disulfates (III) were readily soluble in water, and these surfactants have excellent hydrophilicity for practical use because the Krafft point (T_{Kp}) of all compounds was below 0°C. It is considered that the remarkable decrease in T_{Kp} of III is attributed to the cooperative effect of the two sulfate groups, the ether oxygens in the connecting group and the centrally located hydrophilic part mentioned about branched alkyl anionics (14,15). It has been reported that the "dissolving temperature", which is proportional to the Krafft point, decreases as the location of the hydrophilic group changes from the terminal to the center of the molecule in the case of surfactants with one hydrophilic group (14). The surface tension-concentration plots of aqueous solutions of III are shown in Figure 3.

The CMC values and the ability to lower surface tension (γ_{CMC}) of compounds (III) are listed in Table 2, along with the data of reference compounds containing one alkyl chain and one sulfate group (11). The CMC values of a series of surfactants with two lipophilic chains and two sulfate groups were much smaller than these of general anionic surfactants with one longer lipophilic chain and one hydrophilic group such as SDS. Surfactants with two decyl groups (III f,h,i,j) had excellent micelle forming property in addition to good water solubility as ionic surfactants. The CMC values of III b,g with a butylene connecting group were found to be larger than the others, but a reason for this has not been clarified.

It indicates that the γ_{CMC} value depends on the structure of the connecting group. Surfactants with plural lipophilic groups generally show excellent ability to lower surface tension as compared with those having a single lipophilic group (16). The γ_{CMC} values of III a,f with an ethylene connecting group were below 30 $\text{mN}\cdot\text{m}^{-1}$ and they exhibited the maximum ability to lower surface tension among the compounds in this work. It was observed that the γ_{CMC} value increased with increased bulkiness of the connecting group. Phenylene connecting group, which is rigid and bulky as compared with other connecting groups, make a negative contribution to effective adsorption on the surface.

As shown in Table 3, foaming ability and foam stability of these surfactants (except III c,h) are as good as those of common anionic surfactants, such as SDS. Compounds III c,h resulted in low foaming ability, probably because of their high hydrophilicity due to the tri(oxyethylene) connecting group.

Wetting property and lime-soap dispersing requirement (LSDR) are listed in Table 4 with data for some reference compounds. Wetting times for these surfac-

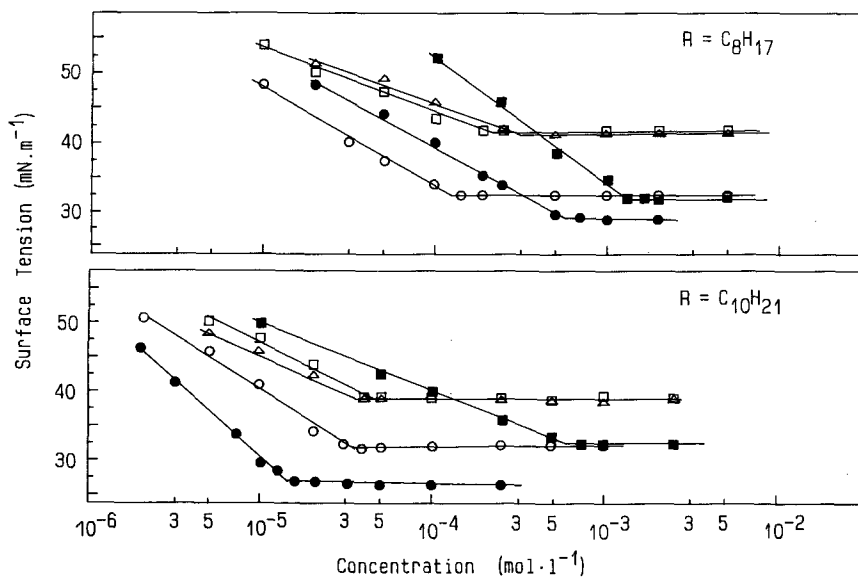


FIG. 3. Surface tension-concentration plots of amphipathic compounds (III) in water at 20°C by Wilhelmy method. Y: ●, $-(\text{CH}_2)_2$; ■, $-(\text{CH}_2)_4$; ○, $-\text{CH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2-$; □, 1,2- C_6H_4 ; and △, 1,4- C_6H_4 .

TABLE 2

The CMC and γ_{CMC} Values of Compounds (IIIa-j) and Reference Compounds (20°C)

Compound	R	-Y-	CMC (M)	γ_{CMC} (mN/m)
IIIa	C ₈ H ₁₇	-(CH ₂) ₂ -	6.0 × 10 ⁻⁴	29.2
IIIb	C ₈ H ₁₇	-(CH ₂) ₄ -	1.5 × 10 ⁻³	32.0
IIIc	C ₈ H ₁₇	-CH ₂ (CH ₂ OCH ₂) ₂ CH ₂ -	1.8 × 10 ⁻⁴	32.5
III d	C ₈ H ₁₇	1,4-phenylene	3.0 × 10 ⁻⁴	41.8
IIIe	C ₈ H ₁₇	1,2-phenylene	1.7 × 10 ⁻⁴	42.0
III f	C ₁₀ H ₂₁	-(CH ₂) ₂ -	1.3 × 10 ⁻⁵	27.0
III g	C ₁₀ H ₂₁	-(CH ₂) ₄ -	6.0 × 10 ⁻⁴	32.5
III h	C ₁₀ H ₂₁	-CH ₂ (CH ₂ OCH ₂) ₂ CH ₂ -	3.2 × 10 ⁻⁵	32.0
III i	C ₁₀ H ₂₁	1,4-phenylene	3.5 × 10 ⁻⁵	38.8
III j	C ₁₀ H ₂₁	1,2-phenylene	3.5 × 10 ⁻⁵	39.5
	C ₁₂ H ₂₅ SO ₄ Na (25°C) ^a		8.2 × 10 ⁻³	39.5
	C ₁₈ H ₃₇ SO ₄ Na (50°C) ^a		2.3 × 10 ⁻⁴	—

^aReference 11.

TABLE 3

Foaming Properties of Compounds (IIIa-j)^a (20°C)

Compound	Foam Volume (ml)	
	0'	5' (min)
IIIa	220	0
IIIb	140	0
IIIc	50	0
III d	240	0
IIIe	240	30
III f	250	0
III g	200	40
III h	50	0
III i	265	30
III j	260	35

^a0.1 wt% aqueous solution.

tants with a felt chip are of very wide range, and the influence of the connecting group on the wetting property is not clear. However, the wetting time of IIIg with two decyl groups and a butylene connecting group compared with that of sodium di(2-ethylhexyl) sulfosuccinate (Aerosol-OT) under the same conditions.

The LSDR of III f-j with two decyl groups was about six, and their lime-soap dispersing ability was greatly improved in comparison with normal surfactants with one lipophilic group and one functional group. The LSDR of III f-j also compared with that of the terminal amide type of alcohol ethoxylates previously reported (17). From Corey-Pauling Koltun (CPK) atomic models, it can be estimated that two sulfate groups and an ether oxygen in the connecting group of III form a bulky hydrophilic part which is one of the required molecular structures for an effective lime-soap dispersing agent (18). It is also thought that the two anionic groups of III are effective for interaction with bivalent calcium or magnesium ions.

New types of amphipathic compounds with two sulfate groups and two lipophilic alkyl chains studied in this work possessed excellent water-solubility, micelle forming property, ability to lower surface tension and lime-soap dispersing ability in comparison with normal anionic surfactants with one lipophilic group and one functional group. It was found that the foaming properties and wetting ability of these compounds depended on the structure of the connecting group. An investiga-

TABLE 4

Wetting Ability^a and Lime-Soap Dispersing Requirement (LSDR) of Compounds (III) at 20°C

Compound	Wetting Time(s)	LSDR
III f	80	5.8
III g	9	6.1
III h	140	5.4
III i	110	5.9
III j	58	5.8
SDS	86	30
Aerosol-OT	5	—

^a0.1 wt% aqueous surfactant solution.

tion of various types of amphipathic compounds with plural functional groups and plural lipophilic chains is now in progress.

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SURFACTANTS WITH TWO SULFATE GROUPS AND TWO LIPOPHILIC ALKYL CHAINS

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