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Synthesis and Properties of Bis (sulfonate) Types of Double-chain Surfactants Bearing a Sulfur Atom in the Connecting Part

Yun-Peng ZHU, Araki MASUYAMA, Yohji NAKATSUJI*,
and Mitsuo OKAHARA

Department of Applied Chemistry, Faculty of Engineering, Osaka University
(2-1, Yamadaoka, Suita-shi, 〒565)

Double-chain diol compounds and double-chain bis(sulfonate) surfactants, each bearing a sulfur atom as a sulfide, sulfoxide, or sulfone in the middle of the connecting part between two alkyl chains, were prepared. The emulsifying properties of the double-chain diols were studied in a mixed system of liquid paraffin and water. The double-chain bis(sulfonate) compounds bearing two decyl groups as the lipophilic part were easily soluble in water. Some surface-active properties of the surfactants bearing a sulfur atom in the connecting part were examined along with a similar type of double-chain surfactant having an oxygen atom in place of a sulfur atom. Displacement of the ether oxygen in the middle of the connecting group by the sulfide sulfur atom caused a slight decrease in cmc. A bulky group such as sulfinyl or sulfonyl in the middle of the connecting part negatively affected the micelle forming properties and the capacity to lessen surface tension. The double-chain bis(sulfonate) surfactants showed much greater lime-soap dispersing ability than sodium 1-dodecanesulfonate.

1 Introduction

We have developed novel types of double-chain surfactants with two hydrophilic head groups, which belong to a new category of surfactant structure^{1)~5)}. We have noticed that the surface-active properties of these double-chain surfactants are dependent on three structural factors: 1, the length of the alkyl chain, 2, the kind of hydrophilic group, and 3, the structure of the connecting part between the two lipophilic chains. The third factor seems to be especially significant for the cmc and γ_{cmc} values. The structure of the connecting part arises from diepoxide compounds as one of the starting materials. The connecting parts that we have studied till now are derived from diepoxide compounds such as bis (2,3-epoxypropyl) ether, ethylene glycol-, di(ethylene glycol)-, tri(ethylene glycol)-, butylene glycol-, pyrocatechol- and hydroquinone diglycidyl

ethers. We chose these diepoxides from the viewpoints of the "length" and "flexibility" of the connecting part (Fig.-1).

In this work, with a view to exploring the structural effect of the connecting part on surface-active properties from another standpoint, we designed new double-chain bis (sulfonate) types of surfactants using a diglycidyl ether containing a sulfur atom as a starting compound. The valence of the sulfur atom can be easily changed by conventional reactions. We first synthesized a diol compound (1) bearing a thio group in the connecting part and then prepared bis (sulfonate) compound (2) from 1. Sulfinyl (5) and sulfonyl (6) derivatives bearing two sulfonate groups were obtained by the selective oxidation of 2. A sulfoxide-type diol (3) and a sulfone-type diol (4) were also afforded by the selective oxidation of 1 (Fig.-2). We measured the surface-active properties of 2, 5, and 6 in water and compared these results with that of the corresponding

* Corresponding author: Yohji NAKATSUJI

Fig.-1 A variety of double-chain surfactants derived from diepoxide compounds.

bis(sulfonate) compound with an oxygen atom in place of the sulfur atom in the connecting part (8, in Fig.-2) to study the structural effect of the connecting group. Additionally, we employed double-chain diol compounds (1, 3, 4, and 7) to run a preliminary experiment on their emulsifying properties. The preparative route for the studies compounds is shown in Fig. -2.

2 Experimental

¹H-NMR spectra were measured in CDCl₃ with a JEOL JNM-GSX 400 (400 MHz) spectrometer using TMS as an internal standard. The IR spectra and Mass spectra (including FAB-Mass) were recorded on a Hitachi 260 spectrometer and a JEOL JMS-DX 303 mass spectrometer, respectively. An O/W emulsion system was prepared by the following recipe : A mixture of diol-type surfactant (0.1 g), liquid paraffin (Nacalai Tesque, Inc., extra pure grade, 4.0 g), and water (15.9 g) was homogenized at 70°C for 3 min using a homogenizer (Polytron^R Model KR, 10,000 rpm). After leaving the mixture at ambient temperature for 5 min, the measurements were started. Stability of the prepared emulsion was evaluated by the ratio of the emulsified-layer volume to the total volume of the mixture. The Krafft point (T_{Kp}) was measured by the naked eye with a 1 wt % aqueous solution of

surfactants. The surface tension of a surfactant solution was measured at 20°C with a Wilhelmy tensiometer (Shimadzu ST-1) using a glass plate. The cmc and γ_{cmc} values were determined from the break point of each surface tension *vs.* concentration (on log scale) curve. The foam properties were measured by the Semi-micro TK method⁶⁾. The lime-soap dispersing requirement (LS-DR) was estimated in hard water with 333 ppm of the total hardness as CaCO₃ by the Borghetty-Bergman method⁷⁾.

2,2'-Thiodiethanol diglycidyl ether was synthesized under phase-transfer catalytic conditions according to the previously reported method of preparing di(ethylene glycol) diglycidyl ether⁸⁾. Sulfide-type diol 1 was prepared by the ring-opening reaction of the diglycidyl ether by potassium *n*-decanoate⁹⁾. It was isolated by Kugelrohr distillation (bp : 160~170°C/0.04 Torr) in 65 % yield (mp : 34.0~35.0°C).

Double-chain bis(sulfonate) compound (2) was synthesized by the reaction of 1 with 1,3-propanesultone in the presence of NaH in THF⁴⁾. The sulfoxide-type diol 3 and sulfone-type diol 4 were prepared by the reaction of 2 with equimolar 30 wt% hydrogen peroxide solution in a mixed solvent of benzene and ethanol below 10°C and with a twice molar amount of 30 wt% hydrogen peroxide solution under reflux conditions,

Fig.-2 Preparation route for double-chain diols (1, 3, 4) and the corresponding bis (sulfonate)s (2, 5, 6) bearing a sulfur atom in the connecting part, along with the structures of reference compounds (7, 8).

respectively¹⁰⁾. Compound 2 was oxidized with 30 wt% hydrogen peroxide solution to give sulfoxide-type bis(sulfonate) compound (5) and sulfone-type bis (sulfonate) compound (6), respectively, under different conditions as described below.

Disodium 5,15-bis(2-oxadodecyl)-4,7,13,16-tetraoxa-10-thia-1,19-nonadecanedisulfonate (2): A solution of 1 (1.10 g, 2 mmol) in THF (10 mL) was added to a stirred dispersion of NaH (60 %) (0.33 g net, 8 mmol) in THF (20 mL) at 60°C. After a solution of 1,3-propanesultone (0.74 g, 6 mmol) in THF (10 mL) was dropped into the mixture at 60°C, the reaction was continued under reflux conditions until the TLC peak based on 1 disappeared (24 h). Any excess of NaH was deactivated by addition of methanol (5 mL) at ambient temperature. This resultant mixture was dissolved in water (60 mL) and the aqueous solution was extracted with *n*-BuOH (3 × 45 mL). The extracts were combined and condensed under reduced pressure. Finally, the TLC-pure product 2 (0.80 g) was isolated as white hygroscopic crystals in 48 % yield by silica gel column chromatography of the obtained residue with a dichloromethane : methanol (100 : 5, vol/vol) eluent. IR (neat) 3500, 2980, 1240, 1100 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.88 (t, 6 H), 1.10~1.65 (m, 32 H), 2.00~2.20 (m, 4 H), 2.70~2.78 (m, 4 H), 2.95~3.15 (m, 4 H), 3.35~3.85 (m, 22 H); Anal. Found : C, 51.00; H, 8.88; S, 11.42 %. Calcd. for C₃₆H₇₂O₁₂S₃Na₂ : C, 51.53; H, 8.65; S, 11.46 %.

1,13-Bis(decyloxy)-7-oxo-4,10-dioxo-7-thia-2,12-tridecanediol (3): Diol 1 (3.30 g, 6 mmol) was dissolved in a mixed solvent of benzene (15 mL) and ethanol (5 mL). Hydrogen peroxide solution (30 wt%) (0.80 g, 7 mmol) was dropped into the mixture below 10°C. The reaction mixture was then stirred below 10°C for 12 h, followed by deactivation of any excess of hydrogen peroxide with 1.1 g of sodium thiosulfate. After evaporation of the mixture under reduced pressure, the residue was purified to give 2.58 g of the desired 3 in 76 % yield by silica gel column chromatography using a hexane :

ethanol (8 : 1, vol/vol) eluent. Mp. 42.5~43.7 °C; IR (neat) 3500, 2980, 1240, 1000, 900 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.88 (t, 6 H), 1.21~1.60 (m, 32 H), 2.77 (s, 2 H), 2.98~3.10 (m, 2 H), 3.10~3.15 (m, 2 H), 3.40~3.80 (m, 12 H), 3.90~4.10 (m, 6 H); FAB-Mass (*m/e*, relative intensity) : 589 [(M+Na)⁺, 15], 567 [(M+1)⁺, 100].

1,13-Bis(decyloxy)-7,7-dioxo-4,10-dioxo-7-thia-2,12-tridecanediol (4): A mixture of 1 (2.20 g, 4 mmol), 30 wt% hydrogen peroxide (0.91 g, 8 mmol), benzene (5 mL), and ethanol (5 mL) was refluxed for 5 h. Evaporation of the reaction mixture gave a 2.50 g crude product, which was chromatographed on silica gel using hexane : acetone (6 : 1, vol/vol) eluent to afford 4 (2.05 g) in 88 % yield. Mp. 47.5~48.5°C; IR (neat) 3500, 2980, 1300, 1120, 900 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.88 (t, 6 H), 1.20~1.56 (m, 32 H), 2.78 (s, 2 H), 3.30~3.70 (m, 16 H), 3.90~4.10 (m, 6 H); FAB-Mass (*m/e*, relative intensity) : 605 [(M+Na)⁺, 30], 583 [(M+1)⁺, 100], 137 [85], 85 [60], 57 [100].

Disodium 10-oxo-5,15-bis(2-oxadodecyl)-4,7,13,16-tetraoxa-10-thia-1,19-nonadecanedisulfonate (5): Compound 2 (2.51 g, 3 mmol) was dissolved in a mixed solvent of ethanol (15 mL) and water (8 mL). Hydrogen peroxide solution (30 wt%) (0.45 g, 4 mmol) was dropped into the mixture below 10°C. The reaction was continued below 10°C for ca. 20 h, followed by deactivation of any excess of hydrogen peroxide with 0.63 g of sodium thiosulfate. Water (50 mL) was added to the resultant mixture and the aqueous solution was extracted with *n*-BuOH (3 × 45 mL). After the extracts were combined and condensed under reduced pressure, the residue was dissolved in a 45 mL of chloroform : methanol (2 : 1, vol/vol). The insoluble solids were filtered off by passage through a Celite 545 short column. After evaporation of the filtrate, TLC-pure target compound 5 (1.58 g) was isolated as white hygroscopic crystals in 62 % yield by silica gel column chromatography of the residue using a chloroform : ethanol (7:1, vol/vol) eluent. IR (neat) 3500, 2980, 1240, 1100 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.88 (t,

6 H), 1.10~1.65 (m, 32 H), 2.05~2.18 (m, 4 H), 2.90~3.20 (m, 8 H), 3.30~4.0 (m, 22 H); Anal. Found: C, 50.21; H, 8.82; S, 11.22%. Calcd. for $C_{36}H_{72}O_{13}S_3Na_2$: C, 50.57; H, 8.49; S, 11.25%.

Disodium 10,10-dioxo-5,15-bis(2-oxadodecyl)-4,7,13,16-tetraoxa-10-thia-1,19-nonadecanedisulfonate (6): Hydrogen peroxide (30 wt%) (0.90 g, 8 mmol) was dropped into the solution of **2** (2.51 g, 3 mmol) in methanol (15 mL) at about 40°C. The reaction mixture was stirred under reflux conditions for 10 h. After evaporation of the resultant mixture, the residue was purified to give **6** (1.55 g) in 59% yield as colorless hygroscopic crystals by silica gel chromatography using a chloroform: ethanol (3:1, vol/vol) eluent. IR (neat) 3500, 2980, 1240, 1100 cm^{-1} ; 1H -NMR ($CDCl_3$) δ 0.88 (t, 6 H), 1.20~1.55 (m, 32 H), 2.04~2.17 (m, 4 H), 3.00~3.10 (m, 4 H), 3.40~4.00 (m, 26 H); Anal. Found: C, 48.27; H, 8.23; S, 11.17%. Calcd. for $C_{36}H_{72}O_{14}S_3Na_2$: C, 49.64; H, 8.33; S, 11.04%.

Double-chain diol (**7**) and bis (sulfonate) compound (**8**) as reference compounds were prepared according to the method reported previously⁴⁾.

3 Results and Discussion

Synthesis. There is another possible route for the preparation of sulfoxide-type bis (sulfonate) (**5**) and sulfone-type bis (sulfonate) (**6**) besides the route illustrated in Fig.-2. That is the reaction of sulfoxide-type diol **3** or sulfone-type diol **4** with 1,3-propanesultone to afford **5** or **6**, respectively. We tried this reaction route using similar procedures to prepare sulfide-type bis(sulfonate) (**2**) from the corresponding diol **1**. When sulfoxide-type diol **3** was treated with NaH in THF, the resulting solution, distinctly different from that of sulfide-type diol **1**, became dark brown. 1,3-Propanesultone was added dropwise to this solution and a tar-like mixture was obtained as a crude product. At least more than 5 spots were observed in its TLC. Purification of the crude product was too difficult to isolate the target compound **5**. It is

surmised that in the presence of a strong base like NaH, deprotonation will occur at the methylene group adjacent to the sulfinyl group¹¹⁾ besides the deprotonation of the hydroxyl groups. The resultant "thioenolate" anion may attack 1,3-propanesultone to give many undesired by-products (Fig.-3).

When sulfone-type diol **4** was reacted with 1,3-propanesultone in THF in the presence of NaH, no tar-like mixture formed. After extraction and condensation according to a procedure similar to the preparation of **2**, a chloroform solution (30 mL) of the resultant reaction mixture was passed through a Celite 545 short column. The filtrate was condensed, but its infrared spectrum showed no adsorption near 1240 cm^{-1} assigned to S=O bond. Hence, the Celite was washed with ethanol and concentrated to afford 1.78 g of crude product as yellow semi-solids. Finally, **6** (0.85 g) was isolated as a pale yellow crystal in 48% yield by silica gel chromatography of the crude product with the following gradient eluent system: $CHCl_3$: EtOH (150:30, vol/vol), subsequent to $CHCl_3$: EtOH: MeOH (150:40:10, vol/vol).

Emulsion stability. Double-chain diol "precursors" (**1**, **3**, **4**, and **7**) are oil-soluble nonionic surfactants themselves. So the emulsifying ability of these diols was evaluated in the O/W emulsion system using liq-

Fig.-3 Results of the reaction of **3** or **4** with 1,3-propanesultone.

Fig.-4 The relation of volume % of O/W emulsified layer and the elapse of time.

uid paraffin as the oil component. Fig.-4 illustrates the stability of the emulsion system along with the result of the commercial emulsifier, Span-40 (Sorbitan monopalmitate, Wako Pure Chemical Industries, Ltd.), under the same conditions. As can be observed from Fig.-4, the structure of the connecting group has a pronounced effect on the stability of the emulsion. It is roughly estimated that the stability of the emulsion decreased in the following order: $4 > \text{Span-40} \gg 3 > 7 = 1$. It is additionally noted that the sulfone-type diol 4 afforded higher stability of the emulsion than Span-40, which is known as a good emulsifier. Since the behavior of emulsion systems constructed by surfactants is affected by various factors, it is hard to evaluate the emulsifying ability of these new diols based on the present experimental results only. We plan to explore the emulsifying properties of these diols in various emulsion systems and to discuss where the HLB of these diols is located among a series of existing nonionic emulsifiers.

Surface-active properties. Since double-chain sulfonate compounds (2, 5, 6, and 8) were readily soluble in water even below 0 °C, their Krafft points are below 0 °C. In comparison with a typical single-chain reference, sodium 1-dodecanesulfonate (Krafft point: 39 °C)⁴⁾, these double-chain sulfonate compounds have higher water solubility. This may be attributed to the cooperative contributions of the two sulfonate groups

and the presence of ether oxygen atoms and thio, sulfinyl or sulfonyl groups in the connecting part to water solubility as previously explained^{1)~4)}

The surface-tension *vs.* concentration (on log scale) curves in deionized water are shown in the upper graph of Fig.-5. The cmc and γ_{cmc} values and the efficiency of adsorption at the surface [pC_{20} , the negative

Fig.-5 Surface tension *vs.* concentration plots of surfactants 2, 5, 6, and 8 in deionized water (above) and in 0.1 M NaCl solution (below) at 20 °C.

Table-1 The results of cmc, γ_{cmc} and pC_{20} of compounds 2, 5, 6, 8, and sodium 1-dodecanesulfonate in deionized water at 20°C.

Compound	cmc (mM)	γ_{cmc} (mN/m)	pC_{20}
2	0.044	33.5	5.7
5	0.11	36.0	4.8
6	0.20	38.5	4.4
8 ^a	0.060	36.0	4.9
$C_{12}H_{25}SO_3Na^b$	9.8	39.0	2.5

a) Ref. 4.

b) Measured at 45°C.

log of C_{20} , the surfactant molar concentration required to reduce the surface tension by 20 mN/m¹²⁾] of these double-chain surfactants are listed in **Table-1**, along with the data for sodium 1-dodecanesulfonate.

The cmc values of all these double-chain sulfonate compounds are lower than that of sodium 1-dodecanesulfonate, suggesting that the double-chain surfactants have higher micelle forming ability. It appears that the difference in the middle group of the connecting part (S, SO, SO₂, or O) greatly influences the cmc values. The increasing order of cmc is : 2 (S) < 8 (O) < 5 (SO) < 6 (SO₂). This result indicates that increasing the bulkiness of the middle group in the connecting part increases the cmc values of these types of double-chain surfactants. In addition, the difference in the polarity of the connecting part must be taken into account for explanation of the difference in their cmc values because the polarity of the molecule is concerned with the hydrophilicity (or lipophilicity) of the molecule, which strongly affects the micelle formation. For example, the dipole moment values of dimethyl sulfoxide and dimethyl sulfone are 2.3 D and 4.5 D, respectively, which are larger than these of dimethyl ether and dimethyl sulfide (1.3 D and 1.5 D, respectively)¹³⁾. So it is surmised that sulfonyl and sulfinyl groups make a stronger contribution to the hydrophilicity of the molecule than sulfide and ether oxygen atoms. Larger cmc values of 5 and 6 compared with 2 and 8 are also reasonable with respect to the difference in the

hydrophilicity of the connecting part.

The plots of surface tension *vs* concentration (on log scale) of compounds 2, 5, 6, and 8 in the presence of a swamping electrolyte¹⁴⁾ (0.1 M NaCl) are also shown in the lower graph of **Fig.-5**. The cmc values of compounds 2, 5, 6, and 8 in 0.1 M NaCl are 0.020 mM, 0.056 mM, 0.060 mM, and 0.024 mM, respectively. All of these cmc values are lower than the values in deionized water. These results are explained by considering that thickness of the ionic atmosphere surrounding the anionic head groups is decreased by the additional electrolyte, and the electrical repulsion between head groups in the micelle consequently decreases¹⁵⁾. From the slope of each plot in the concentrations below its cmc, the area per molecule (*A*) values of 2, 5, 6, and 8 at the surface are estimated at about 112 Å², 116 Å², 132 Å², and 115 Å², respectively, using the Gibbs adsorption equation in the presence of swamping electrolyte¹⁶⁾. The "*A*" value of 6 bearing a sulfonyl group is larger than the values of the others, clearly reflecting the bulkiness of the sulfonyl group. Their "*A*" values are about twice the value for the single-chain sodium 1-dodecanesulfonate (57 Å² in 0.1 M NaCl at 25°C)¹⁷⁾. Therefore, the packing density of these surfactant molecules at the surface is probably similar to that of the corresponding single-chain surfactant.

It appears that the γ_{cmc} values also depend on the structure of the connecting group. The increasing order of γ_{cmc} in water is 2<8=5<6, reflecting the bulkiness of the middle group in the connecting part to a certain degree. In our studies on a series of double-chain surfactants derived from oligo (ethylene glycol) diglycidyl ethers^{2)~4)}, it has been clarified that the γ_{cmc} values increase with an increase in the length of the connecting part. Higher γ_{cmc} values reflect a loosely packed adsorption at the surface. As also expected from the higher value of area per molecule at the surface, the Van der Waals interaction of the lipophilic chain between the adsorbed molecules of 6 at the surface will be weaker than the others. It is

concluded that not only the length but also the steric bulkiness of the connecting group affects the ability to lower surface tension.

The pC_{20} values of double-chain compounds 2, 5, 6, and 8 were much higher than that of the reference single-chain surfactant. This tendency, which has also been observed for other double- or triple-chain compounds^{18),19)}, indicates that the efficiency of adsorption of these types of double-chain surfactants is very high. Among the compounds 2, 5, 6 and 8, compound 2 with a sulfide sulfur atom in the connecting part shows somewhat higher efficiency of adsorption than the others. As a conclusion, insertion of a bulky group into the connecting part makes a negative contribution to the hydrophobic interaction between the alkyl chains of double-chain surfactants, so that it lowers the micelle-forming property, the ability to lower surface tension, and the efficiency of adsorption.

Foaming properties and lime-soap dispersing requirement (LSDR) are summarized in Table-2.

It appears that foam stability rather than foaming ability strongly depends on the structure of the middle group in the connecting part. Compound 6 with a sulfonyl group showed higher foam stability than the others. Though the reason for this has not been clarified, it is noteworthy that the

foam formed by compound 6 was apparently viscous in comparison with other foams. The difference in LSDR values for 2, 5, 6 and 8 is within experimental error, and the lime-soap dispersing ability of these double-chain surfactants is good compared with that of sodium 1-dodecanesulfonate. The hydrophilic part inclusive of the connecting group of these double-chain surfactants is considered to be bulky. It is reported that a bulky hydrophilic part is an important structural factor for an effective lime-soap dispersing agent^{2),4),20)}.

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Table-2 Foaming properties and LSDR of compounds 2, 5, 6, 8, and sodium 1-dodecanesulfonate at 20°C.

Compound	Foam volume (mL) ^a		LSDR ^b
	0'	5' (min)	
2	260	40 ^a	7.7
5	260	50	6.1
6	270	260	7.3
8 ^c	250	0	6.6
C ₁₂ H ₂₅ SO ₃ Na	215	130	94

a) Measured at 0.1 wt % except for sodium 1-dodecanesulfonate (1 wt %, 45°C).

b) Measured at 0.25 wt % aq. surfactant solution at 20°C except for sodium 1-dodecanesulfonate (0.5 wt %).

c) Ref. 4.

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連結部に硫黄原子を含む二鎖ビス（スルホン酸塩）型界面活性剤の合成と物性

朱 云鵬・益山新樹・中辻洋司・岡原光男
大阪大学工学部応用化学科（〒565 吹田市山田丘 2-1）

二つのアルキル鎖をつなぐ連結部の中央に、スルフィド、スルホキシド、あるいはスルホン構造の形で硫黄原子を含む二鎖型ジオール化合物及び二鎖ビス（スルホン酸塩）型界面活性剤を合成した。二鎖型ジオール化合物の乳化特性を流動パラフィン-水混合系で評価した。二本のデシル基を有する二鎖ビス（スルホン酸塩）型化合物は容易に水に溶けた。これらの二鎖型界面活性剤と、硫黄原子の代わりに酸素原子を連結部に有する対応する構造の二鎖型化合物の種々の界面活性能を検討した結果、連結部中央のエーテル酸素原子をスルフィド硫黄原子で置換することにより、臨界ミセル濃度が低下することが認められた。連結基中央部のスルフィニル基やスルホニル基のような立体的にかさ高い構造は、ミセル形成能や表面張力低下能に対して不利な寄与をすることがわかった。これらの二鎖ビス（スルホン酸塩）型界面活性剤は、1-ドデカンスルホン酸ナトリウムよりも良好なカルシウムセッケン分散力を示した。 連絡者：中辻洋司