Preparation and Properties of Glycerol-Based Double- or Triple-Chain Surfactants with Two Hydrophilic Ionic Groups

Yun-peng Zhu[a], **Araki Masuyama**[a,*], **Yoh-ichi Kirito**[a], **Mitsuo Okahara**[a] and **Milton J. Rosen**[b]

[a]Department of Applied Chemistry, Faculty of Engineering, Osaka University, Osaka 565, Japan and [b]Surfactant Research Institute, Brooklyn College, City University of New York, Brooklyn, New York 11210

A novel series of glycerol-based double- or triple-chain surfactants with two sulfonate, two sulfate or two carboxylate groups was conveniently prepared by reactions of 1-O-alkylglycerol diglycidyl ethers with long-chain fatty alcohols, and followed by reactions with propanesultone, chlorosulfonic acid or bromoacetic acid, respectively. The sulfate and carboxylate types of compounds have higher water solubilities than the corresponding sulfonate type of compound bearing the same lipophilic group. The triple-chain surfactants show excellent surface-active properties, such as micelle forming and ability to lower surface tension, compared not only with the corresponding single-chain anionic surfactants, but also with the corresponding double-chain surfactants. The effect of the difference in head groups of these compounds on surface-active properties is described. Foaming properties, wetting ability and lime-soap dispersing requirement are also discussed.

KEY WORDS: 1-O-Alkylglyceroldiglycidyl ethers, double-chain surfactants, glycerol-based surfactants, surfactants with 2–3 lipophilic groups and 2 ionic head groups, triple-chain surfactants.

Intense interest has recently been generated in the development of new amphipathic compounds derived from natural products. Glycerol is one of the major oleochemical products and a useful compound for this purpose. It is predicted that natural glycerol production will increase substantially in the 1990s with the growth of oleochemistry in place of petrochemistry (1). Among industrial surfactants, mono- or dialkylglycerides and lecithins are currently the representative chemicals derived from glycerol (2).

In previous work, we designed and prepared a series of novel amphipathic compounds bearing two lipophilic alkyl chains and two hydrophilic groups. We have shown that these "double-chain with double-ionic group" compounds show greater ability to lower surface tension and to form micelles than comparable single-chain surfactants bearing one ionic head group (3–6). Those results suggested that two alkyl chains in one molecule can make a positive contribution to the surface and micellar properties because the inter- or intramolecular lipophilic interaction may be strengthened, compared to corresponding single-chain surfactants. This speculation prompted us to prepare "triple-chain" surfactants, which would be expected to have still better properties than the double-chain surfactants. In our last paper (7), we reported the preparation and properties of new triple-chain surfactants derived from N-acyldiethanolamines, which showed the expected excellent surface-active properties.

In this work, we prepared new types of surfactants bearing two or three alkyl chains and two sulfonate, two sulfate or two carboxylate groups from 1-*O*-alkylglycerols in good yields. Here we report the synthetic method for the novel surfactants and their surface-active properties in water.

Figure 1 shows the synthetic route for the double- or triple-chain compounds with two sulfonate groups (**5a–f**), a triple-chain compound with two sulfate groups (**6f**) and a triple-chain compound with two carboxylate groups (**8f**).

EXPERIMENTAL PROCEDURES

Methods. ^{1}H nuclear magnetic resonance (NMR) spectra were measured in $CDCl_3$ with a JEOL JNM-GSX400 (400 MHz; JEOL Ltd., Tokyo, Japan) spectrometer and tetramethylsilane (TMS) as an internal standard. The infrared (IR) spectra and mass spectra [including fast atom bombardment (FAB)-mass] were recorded on a Hitachi 260 spectrometer (Hitachi Co., Tokyo, Japan) and a JEOL JMS-DX303 mass spectrometer, respectively. Surface-active properties were evaluated according to the methods mentioned in the previous papers (4–7): the surface tension of surfactant solutions was measured at 20°C with a Wilhelmy tensiometer (Shimadzu ST-1; Shimadzu Ltd., Kyoto, Japan; glass plate). The critical micelle concentration (CMC) was determined from the break point of each surface tension *vs.* concentration (on log scale) curve. The γ_{CMC} is the surface tension at the CMC. Wetting ability was estimated by the sedimentation time of a piece of felt at 20°C (4). Foaming properties were measured by the semi-micro TK method (8). The lime-soap dispersing requirement (LSDR) was evaluated in hard water with 333 ppm of total hardness as $CaCO_3$ by the Borghetty-Bergman method (9). Surface-active properties of compounds **5** and **6** were measured under neutral conditions, while those for carboxylate **8** were measured at pH 11.

Materials. 1-*O*-Alkylglycerols (**2**) with any alkyl group can be easily prepared by some established methods (10–14). In this work, **2b** and **2c** were prepared by reaction of commercially available 2,2-dimethyl-1,3-dioxolane-4-methanol (**1**) with *n*-alkyl bromide, followed by deprotection of the acetal group. Compound **2a** was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan).

1-*O*-Alkylglycerol diglycidyl ethers (**3a–c**) were prepared by reaction of compounds **2a–c** with epichlorohydrin under phase-transfer catalytic conditions (4,15). 1,8-*Bis*(alkyloxymethyl)-4-alkyloxymethyl-3,6-dioxa-1,8-octanediols (**4a–f**) were also prepared from the corresponding **3a–c** according to the previously reported method (4,16).

Disodium 5,12-*bis*(alkyloxymethyl)-8-alkyloxymethyl-4,7,10,13-tetraoxa-1,16-hexadecanedisulfonates (**5a–f**) were prepared by reaction of compounds **4a–f** with propanesultone in the presence of NaH in tetrahydrofuran (THF). They were isolated as a white waxy product by silica gel column chromatography with a hexane:ethanol (1:1, vol/vol) eluent (60–70% yield). Typical procedures for the preparation of **5**, **6** and **8** from **1** are as follows:

1-O-Decylglycerol (2c): After metallic sodium (2.76 g, 0.12 mol) was dissolved in *tert*-butanol (100 mL), racemic 2,2-dimethyl-1,3-dioxolane-4-methanol (**1**, 13.2 g, 0.10 mol) was slowly added and the mixture was stirred under reflux

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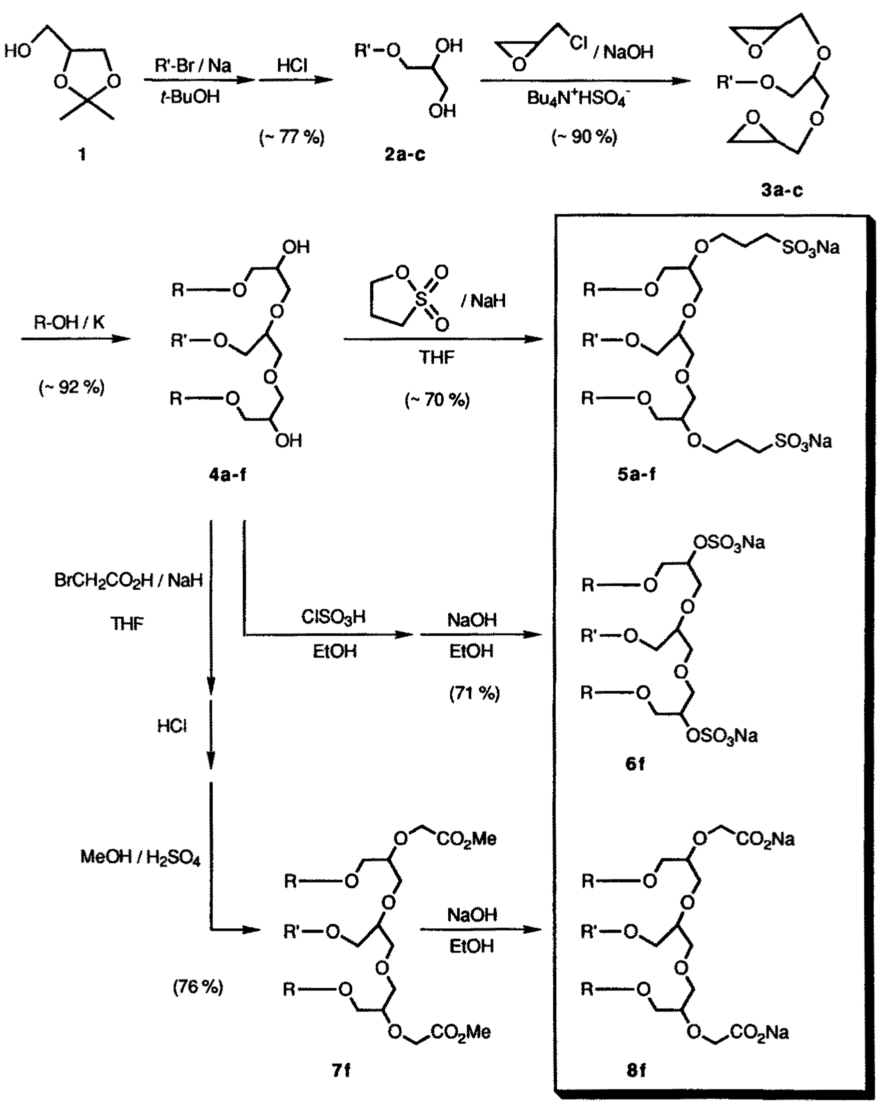
[*] To whom correspondence should be addressed at Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan.



2, 3	
a	$R' = CH_3$
b	$R' = C_8H_{17}$
c	$R' = C_{10}H_{21}$

4 - 8		
a	$R = C_8H_{17}$,	$R' = CH_3$
b	$R = C_{10}H_{21}$,	$R' = CH_3$
c	$R = C_8H_{17}$,	$R' = C_8H_{17}$
d	$R = C_{10}H_{21}$,	$R' = C_8H_{17}$
e	$R = C_8H_{17}$,	$R' = C_{10}H_{21}$
f	$R = C_{10}H_{21}$,	$R' = C_{10}H_{21}$

FIG. 1. Preparation of double- or triple-chain surfactants derived from 1-*O*-alkylglycerols.

conditions for 1 h. After decyl bromide (24.3 g, 0.11 mol) was dropped carefully into the mixture at 60°C, the reaction was continued under reflux conditions until the thin-layer chromatography (TLC) peak based on 1 disappeared (12 h). After evaporation of the solvent, the reaction mixture was dissolved in diethyl ether (200 mL) and washed with 18% hydrochloric acid (100 mL) and water (3 × 100 mL). The oily residue obtained by evaporation of the ether layer was dissolved in a mixed solution of ethanol (150 mL) and 1N hydrochloric acid (30 mL). After *ca.* 6 h of stirring at reflux temperature, the mixture was cooled and 150 mL of water was added. The resultant solution was extracted with ether (3 × 150 mL), and the combined ether extracts were dried over magnesium sulfate and condensed. The residue was distilled at 110–115°C/0.05 Torr to give 15.4 g of the gas-liquid chromatography (GLC)-pure **2b** (77% yield). IR (neat): 3500, 2980, 1100 cm^{-1}.

*1-O-Decylglyceryldiglycidyl ether (**3c**):* 1-*O*-Decylglycerol (**2c**, 15.8 g, 0.068 mol) was dropped into a mixture of epichlorohydrin (37.8 g, 0.41 mol), sodium hydroxide (pellets, 95%) (11.4 g, 0.27 mol) and tetrabutylammonium hydrogen sulfate (4.0 g) at 40°C under vigorous stirring. After 4 h of stirring at 40°C, methylene chloride (100 mL) was added to the reaction mixture, and the insoluble solids were filtered off by passage through a Celite 545 short column. After evaporation of the filtrate, 21.0 g of **3c** (GLC-pure) was isolated by Kugelrohr distillation (140°C/0.05 Torr) as a colorless liquid (90% yield). IR (neat): 2980, 1460, 1100 cm^{-1}; FAB-mass [*m/e*, relative intensity]: 367 [(M + Na)$^+$, 10], 345 [(M + 1)$^+$, 20], 197 [15], 85 [50], 57 [100]; ^{1}H NMR (CDCl$_3$): δ 0.88 (*t*, 3H), 1.20–1.60 (*m*, 28H), 2.60–2.65 (*m*, 2H), 2.79–2.80 (*m*, 2H) and 3.10–3.92 (*m*, 13H).

1,4,8-Tris(decyloxymethyl)-3,6-dioxa-1,8-octanediol (4f): Metallic potassium (1.56 g, 0.04 mol) was dissolved into *n*-decanol (38.0 g, 0.24 mol) at 60°C. Compound **3c** (10.3 g, 0.03 mol) was dropped carefully into the resulting alkoxide solution. The reaction mixture was then stirred for 12 h at 80°C. After neutralization with 10% hydrochloric acid at ambient temperature, the reaction mixture was extracted with a methylene chloride (3 × 150 mL):water (150 mL) solvent system. After the organic extracts were combined and dried with magnesium sulfate, any excess of *n*-decanol was distilled off under reduced pressure. Compound **4f** was obtained by silica gel chromatography of the residue with a hexane:acetone (3:1, vol/vol) eluent (18.6 g, 92% yield). IR (neat): 3500, 2980, 1100 cm^{-1}; mass [*m/e*, relative intensity]: 661 [(M + 1)$^+$, 20], 197 [20], 85 [75], 57 [100]; ^{1}H NMR (CDCl$_3$): δ 0.88 (*t*, 9H), 1.26–1.60 (*m*, 48H), 2.65 (*s*, 2H, -O$\underline{\text{H}}$), 3.30–4.0 (*m*, 21H).

Disodium 5,8,12-tris(decyloxymethyl)-4,7,10,13-tetraoxa-1,16-hexadecanedisulfonate (5f): Dry THF (10 mL) solution containing compound **4f** (3.31 g, 5 mmol) and another dry THF solution (10 mL) containing propanesultone (2.44 g, 20 mmol) were dropped in this order into a suspension of sodium hydride (0.60 g net, 15 mmol) at 60°C. After 24 h of stirring under reflux conditions, 20 mL of methanol was added at ambient temperature to deactivate any excess of sodium hydride. After evaporation and subsequent extraction of the reaction mixture with a n-BuOH (3 × 150 mL):water (150 mL) solvent system, the combined organic extracts were dried with magnesium sulfate. The target compound **5f** was isolated by silica gel chromatography of the crude product with a hexane:ethanol (1:1, vol/vol) eluent (3.32 g, 70% yield).

Disodium 1,4,8-tris(decyloxymethyl)-3,6-dioxa-1,8-octanedisulfate (6f): Chlorosulfonic acid (1.40 g, 12 mmol) in dichloromethane (10 mL) was dropped carefully into a stirred solution of **4f** (1.98 g, 3 mmol) in dichloromethane (15 mL) below 0°C. The reaction was continued until the TLC peak based on **4f** disappeared (4 h) at *ca.* 0°C. The reaction mixture was changed to pH 10 with alcoholic sodium hydroxide solution. After evaporation and subsequent extraction of the reaction mixture with a n-BuOH (3 × 45 mL):water (150 mL) solvent system, 3.32 g of the crude product was obtained by condensation of the combined organic extracts. The crude product was dissolved in dichloromethane and dried with magnesium sulfate, and then the insoluble solids were filtered off by passage through a Celite 545 short column. After evaporation of the filtrate, 1.86 g of **6f** was isolated as a white waxy product by silica gel chromatography of the residue with the following gradient elution system: dichloromethane: ethanol (10:1, vol/vol) subsequent to hexane:dichloromethane (1:1, vol/vol).

Disodium 4,7,11-tris(decyloxymethyl)-3,6,9,12-tetraoxa-1,14-tetradecanedioate (8f): Bromoacetic acid (1.24 g, 9 mmol) in THF (15 mL) was dropped into a stirred suspension of 1.98 g of **4f** (3 mmol) and 0.43 g of sodium hydride (18 mmol) at 60°C in an atmosphere of nitrogen. The reaction mixture was stirred under reflux conditions for 20 h. Methanol was then added to the mixture to deactivate any excess sodium hydride. The residue obtained by evaporation of the reaction mixture was dissolved in 100 mL of ether and washed with 18% hydrochloric acid and water until the aqueous phase became neutral. After the organic extracts were dried with magnesium sulfate, 2.30 g of the crude carboxylic acid was obtained by evaporation of the dried solution. Next, the crude carboxylic acid was esterified with methanol in the presence of concentrated sulfuric acid according to the usual procedures. Pure **7f** (1.85 g) was isolated by silica gel chromatography with a hexane:acetone (3:1, vol/vol) eluent (76% yield). The target compound **8f** was prepared by hydrolysis of **7f** with sodium hydroxide in ethanol at 60°C for 3 h, followed by evaporation of the solution. The IR spectrum of the obtained product clearly showed the absence of unhydrolyzed ester **7f**.

The purity and established structure of compounds **5a–f** and **6f** were confirmed by thin-layer chromatography (TLC), spectra (IR and ^{1}H NMR) and elemental analyses. Because the disodium *bis*(carboxylate) compound (**8f**) was hygroscopic, the structure of the intermediate *bis*(methyl ester) (**7f**) was ascertained by the similar techniques instead of **8f**. The purity of surfactants **5a–f**, **6f** and **8f** was also checked from the observed clear break point in their surface tension *vs.* concentration curves. The synthetic results, ^{1}H NMR spectra and elemental analyses data of **5a–f**, **6f** and **7f** are summarized in Table 1.

RESULTS AND DISCUSSION

Although double- (long-chain) compounds bearing two sulfonate groups (R′ = methyl; **5a,b**) were freely soluble in water at 1 wt% concentration, the solubility of triple-chain compounds bearing two sulfonate groups (R = C_8H_{17} or $C_{10}H_{21}$; **5c–f**) was slightly lower than that of **5a,b**, and compounds **5c–f** were soluble in water at any temperature only at 0.1 wt% concentration. On the other hand, triple-chain compounds **6f** and **8f** were freely soluble in water, even at 1 wt% concentration. These results appear to indicate that sulfate and carboxylate types of triple-chain compounds have higher water solubility than the corresponding sulfonate types. On the other hand, compound **5f** has 6 more carbon atoms than **6f**, and 4 more carbon atoms than **8f** in the neighborhood of the head groups. These additional carbon atoms could account for the lower solubility of **5f**. However, there is evidence from other sources that an essential difference in the degree of hydration of the ionic head groups may be one of the reasons for the difference in water solubility. In the case of typical single-chain surfactants, the Krafft point of sodium 1-alkanesulfonate is higher than that of either the sodium alkyl sulfate or the sodium carboxylate with a corresponding alkyl group. For example, the T_{Kp} values of sodium 1-dodecanesulfonate, sodium dodecylsulfate, sodium dodecanoate and sodium tridecanoate are 38°C, 16°C, 19°C and 27°C, respectively (17).

The plots of surface tension *vs.* concentration (on log scale) in water are illustrated in Figure 2. The critical micelle concentration (CMC), the ability to lower surface tension (γ_{CMC}), the efficiency of adsorption at the surface [pC_{20}, the negative log of C_{20}, the surfactant molar concentration required to reduce the surface tension by 20

TABLE 1

Preparation and Properties of Compounds 5a–f, 6f and 7f[a]

Compound	R	R′	Yield[b] (%)	^{1}H NMR ($CDCl_3$) (γ)	Anal. found (calc'd)[c]
5a	C_8H_{17}	CH_3	70	0.88 (*t*, 6H), 1.18–1.61 (*m*, 24H) 1.94–2.14 (*m*, 4H), 2.77–3.15 (*m*, 4H) 3.16–4.11 (*m*, 26H)	H, 8.84 (8.41) C, 49.89 (50.11) S, 8.18 (8.36)
5b	$C_{10}H_{21}$	CH_3	67	0.88 (*t*, 6H), 1.17–1.62 (*m*, 32H), 1.93–2.18 (*m*, 4H), 2.93–3.14 (*m*, 4H). 3.26–3.93 (*m*, 26H)	H, 8.87 (8.87) C, 51.63 (51.41) S, 7.97 (7.62)
5c	C_8H_{17}	C_8H_{17}	60	0.88 (*t*, 9H), 1.11–1.61 (*m*, 36H), 1.88–2.19 (*m*, 4H), 2.86–3.13 (*m*, 4H) 3.16–3.92 (*m*, 25H)	H, 9.63 (9.09) C, 54.25 (54.14) S, 7.09 (7.41)
5d	$C_{10}H_{21}$	C_8H_{17}	67	0.88 (*t*, 9H), 1.11–1.61 (*m*, 44H), 1.99–2.13 (*m*, 4H), 2.92–3.15 (*m*, 4H), 3.33–3.81 (*m*, 25H)	H, 10.05 (9.41) C, 56.00 (56.06) S, 7.28 (6.96)
5e	C_8H_{17}	$C_{10}H_{21}$	62	0.88 (*t*, 9H), 1.15–1.61 (*m*, 40H), 1.95–2.18 (*m*, 4H), 2.90–3.14 (*m*, 4H), 3.35–3.95 (*m*, 25H)	H, 9.33 (9.25) C, 54.93 (55.13) S, 6.61 (7.18)
5f	$C_{10}H_{21}$	$C_{10}H_{21}$	70	0.88 (*t*, 9H), 1.08–1.57 (*m*, 48H), 1.95–2.11 (*m*, 4H), 2.84–3.00 (*m*, 4H), 3.30–3.85 (*m*, 25H)	H, 8.93 (9.58) C, 54.31 (55.88) S, 6.41 (6.63)
6f	$C_{10}H_{21}$	$C_{10}H_{21}$	71	0.88(*t*, 9H), 1.10–1.60 (*m*, 48H), 3.43–4.10 (*m*, 19H), 4.71 (*m*, 2H)	H, 9.39 (9.13) C, 52.36 (53.04) S, 6.82 (7.26)
7f	$C_{10}H_{21}$	$C_{10}H_{21}$	76	0.88 (*t*, 9H), 1.26–1.70 (*m*, 48H), 3.30–3.90 (*m*, 27H), 4.31 (*s*, 2H), 4.33 (*s*, 2H)	H, 11.09 (11.01) C, 66.97 (67.13)

[a] IR spectra, compounds **5a–f**: 3450, 2980, 1200 and 1100 cm^{-1}; compound **6f**: 3500, 2980, 1200 and 1120 cm^{-1}; compound **7f**: 2980, 1750 and 1100 cm^{-1}.

[b] Based on compounds **4a–f**.

[c] Calculated values of **5f** and **6f** are based on the assumption that they contain one mole of water.

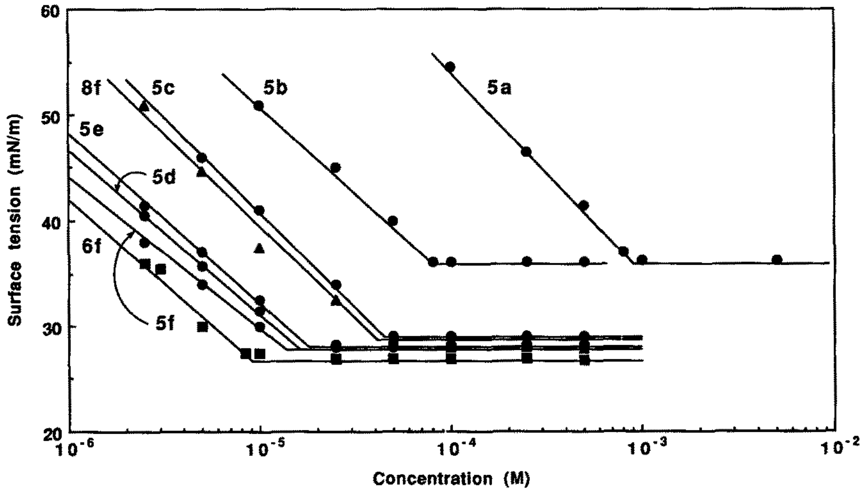


FIG. 2. Surface tension-concentration plots of amphipathic compounds (5a–f, 6f and 8f) in water at 20°C.

mN/m (18)], and the CMC/C_{20} ratio of these surfactants **5a–f**, **6f** and **8f** are listed in Table 2, along with the data on corresponding reference single-chain compounds. Because values of the surface tension were obtained only above *ca.* 10^{-6} mol/L concentration of surfactant, the C_{20} values of compounds **5d–f** and **6f** were estimated in Figure 2 by extrapolation of the lines below the CMC values.

All of the double- and triple-chain compounds **5a–f**, **6f** and **8f** have much smaller CMC values, and all of the triple-chain compounds have much smaller γ_{CMC} values than the corresponding single-chain surfactants. It appears, from a comparison of the CMC values of com-

TABLE 2

CMC, γ_{CMC}, pC_{20} and CMC/C_{20} Values of Compounds 5a–f, 6f, 8f and Reference Compounds at 20°C

Compound	R	R′	CMC (mM)	γ_{CMC} (mN/m)	pC_{20}	CMC/C_{20}
5a	C_8H_{17}	CH_3	0.85	36.5	3.9	6.7
5b	$C_{10}H_{21}$	CH_3	0.081	36.0	5.0	8.1
5c	C_8H_{17}	C_8H_{17}	0.046	29.0	5.6	18
5d	$C_{10}H_{21}$	C_8H_{21}	0.016	28.0	6.3[a]	32[a]
5e	C_8H_{17}	$C_{10}H_{21}$	0.019	28.0	6.4[a]	48[a]
5f	$C_{10}H_{21}$	$C_{10}H_{21}$	0.014	28.0	6.6[a]	56[a]
6f	$C_{10}H_{21}$	$C_{10}H_{21}$	0.009	27.0	6.7[a]	45[a]
8f[b]	$C_{10}H_{21}$	$C_{10}H_{21}$	0.040	29.0	5.7[a]	20[a]
$C_{12}H_{25}SO_3Na$[c]			12.4	39.0	2.4	3.1
$C_{12}H_{25}OSO_3Na$			8.2	38.0	2.4	2.1
$C_{11}H_{23}COONa$[d]			20	37.5	2.3	4.0

[a] Estimated values.

[b] At pH 11.

[c] Cited from reference 22. Measured at 25°C.

[d] At pH 10.

pounds **5a–f**, that the effect of increased chainlength in the alkyl group (R) of double-chain compounds (R′ = CH_3; **5a,b**) on the CMC is larger than in triple-chain compounds (R′ = $C_{10}H_{21}$; **5c–f**). This means that the choice of alkyl groups to regulate the CMC value is a more important factor in double-chain compounds than in triple-chain compounds. A similar effect of alkyl chainlength on the CMC value was found also for the previously reported double- or triple-chain surfactants derived from N-acyldiethanolamines (7). The CMC values of **5f**, **6f** and **8f**, which consist of the same structure except for the hydrophilic group, show that the decreasing order of CMC is: carboxylate (**8f**) > sulfonate (**5f**) > sulfate (**6f**), which is the same order as for the single-chain surfactants. The γ_{CMC} values of the triple-chain compounds **5c–f**, **6f** and **8f** are all below 30 mN/m, and below those of the double-chain compounds.

The pC_{20} values of the triple-chain surfactants **5c–f**, **6f** and **8f** are larger than the values for not only the corresponding single-chain surfactants but also for the double-chain surfactants **5a,b**. Because a similar tendency has been observed with the triple-chain surfactants derived from N-acyldiethanolamine (7), it is suggested that increasing the number of alkyl chains in the molecule increases the efficiency of adsorption, even when the number of hydrophilic groups increases. Among the triple-chain compounds containing similar alkyl chains (**5f**, **6f**, **8f**), the pC_{20} value of the carboxylate **8f** is considerably lower than others. This is especially noteworthy because **8f** has two more CH_2 groups than **6f**.

The CMC/C_{20} ratios are indices of the relative effects of some molecular structural factor on micellization and on adsorption (19). The values (18–56) for the triple-chain surfactants are much larger than those (6.7–8.1) for the double-chain materials, which in turn are greater than those (2.1–4.0) for the corresponding single-chain compounds. These data indicate that adsorption is favored more and more, relative to micellization, as the number of long alkyl chains in the molecule is increased. The CMC/C_{20} ratio has been found in previous work (19) to be increased by structures in the molecule that increase its bulkiness (branching in the lipophilic group, location of the head group in a central position in the molecule, introduction of a larger hydrophilic group) because of the greater inhibiting effect of bulkiness on micellization than on adsorption at the planar aqueous solution/air interface (19). Our results are consistent with those previous observations. Since the value of the surface tension at the CMC, γ_{CMC}, has been shown to be decreased by an increase in the value of the CMC/C_{20} ratio (20), this may account for the observed lower γ_{CMC} values of the triple-chain compounds, compared to those of the double- or single-chain materials.

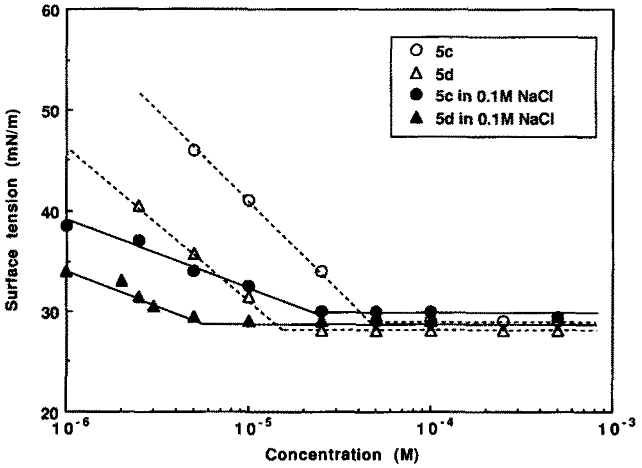


FIG. 3. Surface tension-concentration plots of compounds 5c and 5d in aqueous solution (----) and in 0.1 M NaCl solution (——).

The surface tension of various concentrations of **5c** and **5d** was also measured in the presence of swamping electrolyte (0.1 M NaCl). The plots of surface tension *vs.* concentration on log scale (solid line) are shown in Figure 3 along with the results in the absence of NaCl (dashed line).

The CMC values of **5c** and **5d** in the presence of 0.1 M NaCl are about 0.023 nM (γ_{CMC}: 30 mN/m) and 0.005 mN (29 mN/m), respectively, which are smaller than the values in water (Table 2). In the presence of swamping electrolyte, the coefficient n in the Gibbs adsorption equation, $d\gamma = -nRT\Gamma d\ln C$, is equal to 1, and the values of the surface ex-

TABLE 3

Foaming Properties, Wetting Ability and LSDR of Compounds 5a–f, 6f and 8f and Reference Compounds (20°C)

Compound	R	R′	Foam volume (mL)[a]		Wetting time[a] (s)	LSDR[b]
			0	5 (min)		
5a	C_8H_{17}	CH_3	260	140	91	14
5b	$C_{10}H_{21}$	CH_3	260	20	81	6
5c	C_8H_{17}	C_8H_{17}	270	270	11	7
5d	$C_{10}H_{21}$	C_8H_{17}	270	250	176	11
5e	C_8H_{17}	$C_{10}H_{21}$	270	265	34	12
5f	$C_{10}H_{21}$	$C_{10}H_{21}$	260	20	317	8
6f	$C_{10}H_{21}$	$C_{10}H_{21}$	265	260	220	18
8f[c]	$C_{10}H_{21}$	$C_{10}H_{21}$	240	80	905	33
$C_{12}H_{25}SO_3Na$[d]			—	—	—	94
$C_{12}H_{25}OSO_3Na$			240	240	65	30
$C_{11}H_{23}COONa$[e]			200	170	—	—

[a] Measured concentrations of the solutions are mentioned in the text.

[b] Measured at 0.05 wt% aq surfactant solution for **5a–f**, 0.25 wt% for **6f**, **8f** and sodium dodecylsulfate, and 0.05 wt% for sodium 1-dodecanesulfonate.

[c] At pH 11.

[d] Cited from reference 7; measured at 45°C.

[e] At pH 10.

cess concentration (Γ) and the area per molecule at the surface (A) can be calculated (21). The A values of **5c** and **5d** are estimated at about 120 Å^2 and 135 Å^2, respectively. These are both less than three times the values for $C_{10}H_{21}SO_3Na$ (43 Å^2) and for $C_{12}H_{25}SO_3Na$ (57 Å^2) in 0.1 M NaCl at 25°C (22), indicating that these triple-chain compounds are somewhat more closely packed at the aqueous solution/air interface than these single-chain reference compounds.

Foaming properties, wetting ability and lime-soap dispersing requirement (LSDR) of compounds **5a–f**, **6f 8f** and reference compounds are listed in Table 3. Foaming properties and wetting ability were measured with a 0.1 wt% aqueous solution for **5a**, **6f** and **8f**, 0.5 wt% for sodium 1-dodecanesulfonate and sodium dodecylsulfate, 1 wt% for sodium dodecanoate, and 0.05 wt% for **5b–f** because of their respective solubilities at 20°C. All concentrations, however, were above the CMCs of the compounds, where foaming should be at its maximum.

Among the sulfonate surfactants, triple-chain compounds **5c–e** showed good foaming ability and excellent foam stability. The foam stabilities of the double-chain compounds, **5a** and especially **5b**, and of triple-chain compound **5f** were low. These results are similar to the foaming properties of the triple-chain surfactants derived from N-acyldiethanolamines (7). Although the difference in the experimental conditions has to be considered, foaming ability of **5f**, **6f** and **8f** with the common lipophilic groups was good as compared with the reference single-chain surfactants. It is to be expected that the triple-chain surfactants, with their greater chain-chain cohesiveness, would show greater foam stability than double-chain materials. On the other hand, triple-chain compound **5f**, having the lowest water solubility of all the triple-chain compounds investigated, may not have sufficient solubility for foam stability. Evidence for this is the good foam stability of surfactant **6f**, which has greater water solubility than **5f** or **8f**. It was additionally observed that closely packed small-bubble foam was formed in the case of **6f**, while loosely packed large-bubble foam was produced in the case of **5f** or **8f**.

Wetting times of these double- or triple-chain compounds covered a wide range. Wetting times of **5f**, **6f** and **8f** with three decyl chains were not as good as those for the triple-chain compounds from N-acyldiethanolamines (7). It appears that too bulky a structure in these types of triple-chain surfactants decreases wetting ability. The poor wetting times of the double-chain compounds probably reflect their relatively high γ_{CMC} values, while the poor wetting times of the triple-chain compounds probably reflect their bulkiness, with only the smallest compound, **5c**, showing good wetting power.

The lime-soap dispersing ability of the *bis*(sulfonate) compounds **5a–f** was better than that of sodium 1-dodecanesulfonate, but lower than that of the previously reported double-chain *bis*(sulfonate) types of surfactants derived from oligo(ethylene glycol) diglycidyl ethers (6). Compounds **5a–f** showed lime-soap dispersing ability similar to that of the triple-chain sulfonate types of surfactants derived from N-acyldiethanolamines (7). Parris *et al.* (23) and Linfield (24) have reported that single-chain potassium 4-oxa-1-hexadecanesulfonate, which is prepared by the reaction of dodecanol with propanesultone, exhibits much higher lime-soap dispersing ability than sodium dodecyl sulfate; the LSDR value of the former is 9 and the latter is 30. In the case of our triple-chain surfactants, the positive effects of the sulfopropyloxy group on the lime-soap dispersing ability was also observed because the LSDR value of **5f** was smaller than that of **6f**. It is noteworthy that the triple-chain *bis*(carboxylate) surfactant **8f** has medium lime-soap dispersing ability, comparable to that of sodium dodecyl sulfate. This suggests that these types of carboxylates may be useful in hard water. It is well-known that a bulky hydrophilic part is one of the required structures for an effective lime-soap dispersing agent (4,24).

ACKNOWLEDGMENT

A part of this work was supported by a Grant-in-Aid for Scientific Research (No. 02453086) from the Ministry of Education of Japan, which is gratefully acknowledged.

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[Received September 20, 1991; accepted March 17, 1992]