Preparation and Properties of Double- or Triple-Chain Surfactants with Two Sulfonate Groups Derived from *N*-Acyldiethanolamines

Yun-peng Zhu, Araki Masuyama, Yoh-ichi Kirito, and Mitsuo Okahara*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Osaka 565, Japan

Bis(sulfonate) types of amphipathic compounds with three long-chain alkyl groups were prepared by the reaction of *N*-(long-chain acyl)diethanolamine diglycidyl ethers with long-chain fatty alcohols, followed by the reaction with propanesultone. The diglycidyl ethers were easily obtained from the corresponding *N*-acyldiethanolamines and epichlorohydrin in the presence of a phase-transfer catalyst. The same types of compounds with two long-chain alkyl groups were also prepared from *N*-acetyldiethanolamine according to similar procedures. All these new double- or triple-chain surfactants were soluble in water and showed much better micelle forming and ability to lower surface tension than general types of single-chain surfactants with one sulfonate group. The critical micelle concentration (CMC) and γ_{CMC} values of the triple-chain compounds were still much smaller than those of the corresponding double-chain compounds with two common alkyl groups. The efficiency of adsorption at the water/air interface (pC_{20}) of these surfactants was very high. Their foaming properties, wetting ability toward a felt chip, and lime-soap dispersing ability were measured.

KEY WORDS: **Double-chain surfactants, triple-chain surfactants, *N*-acyldiethanolamine diglycidyl ethers, *bis*(sulfonate) compounds.**

Many studies have been carried out to clarify the relation between the structure of surfactants and their interfacial properties. However, to our knowledge there has been no systematic study on the amphipathic compounds with multiple lipophilic groups and multiple hydrophilic functional groups, except for a few fragmentary reports (1–3). We have been investigating the design, preparation, and properties of a series of new surfactants with two lipophilic alkyl chains and two ionic head groups (4–7). The molecular structure of these surfactants is apparently shaped as a bundle of two typical surfactant molecules with one lipophilic group and one hydrophilic group each. It was expected from observations of their molecular models that these compounds would possess enough hydrophilicity because of the presence of two ionic head groups and that their inter- or intramolecular hydrophobic interaction would be strengthened as compared to typical surfactants (Fig. 1). We have clarified that the double-chain surfactants with two anionic groups derived from glycol diglycidyl ethers have much better hydrophilicity, micelle formation, and ability to lower surface tension than the corresponding single-chain surfactant with one anionic group (4–7).

In this work, we designed and prepared new types of amphipathic compounds (IV) with two or three lipophilic alkyl chains and two sulfonate groups derived from *N*-acyldiethanolamines (I). Here we report their surface-active properties in water and some interesting results. The synthetic route for these double- or triple-chain surfactants (IVa,d or IVb,c,e,f) is shown in Figure 2.

EXPERIMENTAL PROCEDURES

Materials. *N*-Acyldiethanolamines (I) were synthesized by the reaction of diethanolamine with methyl or ethyl carboxylates in methanol in the presence of a catalytic amount of sodium methoxide (8). A small amount of by-products, mainly the corresponding aminoesters [infrared (IR): ν_{co} 1720 cm^{-1}], could be almost completely removed by silica gel short-column chromatography with a hexane:acetone (9:1–1:1, v/v) eluent. *N*-Acyldiethanolamine diglycidyl ethers (II) were prepared by the reaction of I with epichlorohydrin under phase-transfer catalytic conditions (9). Compound **IIa** was purified by extraction with a water:*n*-butanol solvent system, and others (**IIb,c**) were isolated by Kugelrohr distillation (63–84% yields). Double- or triple-chain dihydroxy compounds (**III**) were obtained by the reaction of II with long-chain fatty alcohols in the presence of potassium (6,10). Purification of **III** was carried out by silica gel column chromatography with a hexane:acetone (1:1, v/v) eluent (40–80% yields). The target compounds (**IV**) were synthesized by sulfonation of the corresponding **III** with propanesultone in dry tetrahydrofuran (THF). They were isolated as a waxy product by silica gel column chromatography with a hexane:ethanol (1:1, v/v) eluent (60–81% yields).

The structures of compounds **I,II,III** were confirmed by their IR (Hitachi 260 spectrometer Hitachi, Tokyo, Japan), mass (JEOL JMS-DX303, JEOL Limited, Tokyo, Japan), and ^{1}H nuclear magnetic resonance (NMR) (JEOL JNM-GSX400, 400 MHz) spectral data. The purity and established structure of compounds **IVa–f** were ascertained by thin-layer chromatography (TLC), IR and ^{1}H NMR spectra, and elemental analyses. It was noted that compounds **IVa–f** were very hygroscopic. The synthetic results of **IVa–f** are summarized in Table 1 with the data from elemental analyses.

Typical procedures for the preparation of **IV** from **I** are as follows:

N,N-Bis*(5,6-epoxy-3-oxahexyl)decanamide* (**IIb**): *N,N-bis-*(hydroxyethyl)decanamide (**Ib**, 10.3 g, 0.070 mol) was dropped into a mixture of epichlorohydrin (129.5 g, 1.4 mol), NaOH (95%) (11.8 g, 0.28 mol), and tetrabutylammonium bisulfate (0.48 g) at 40°C under vigorous stirring. After 5 hr of stirring at 40°C, methylene chloride (250 mL) was added to the reaction mixture, and insoluble solids were filtered off by passage through a Celite 545 short-column. After evaporation of the filtrate, 19.0 g of **IIb** [gas-liquid chromatography (GLC)—pure] was isolated by Kugelrohr

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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.

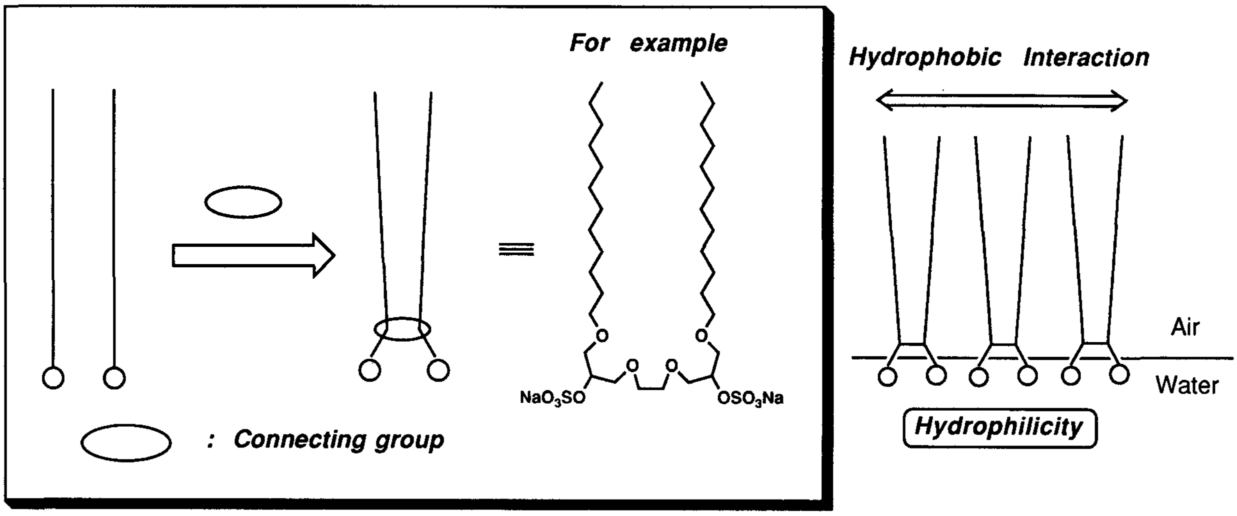
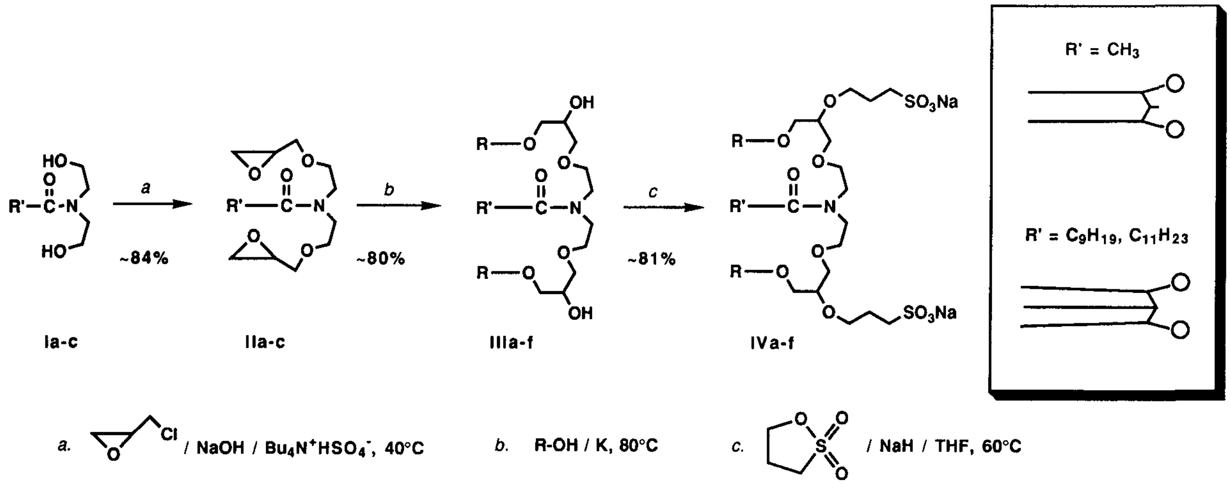


FIG. 1. Stylized illustration of molecular structure of double-chain surfactants with two ionic head groups and their possible adsorptive manners at the water/air interface.



I, II	III, IV	
a R' = CH_3	a R = C_8H_{17}, R' = CH_3	d R = $C_{10}H_{21}$, R' = CH_3
b R' = C_9H_{19}	b R = C_8H_{17}, R' = C_9H_{19}	e R = $C_{10}H_{21}$, R' = C_9H_{19}
c R' = $C_{11}H_{23}$	c R = C_8H_{17}, R' = $C_{11}H_{23}$	f R = $C_{10}H_{21}$, R' = $C_{11}H_{23}$

FIG. 2. Preparation of double- or triple-chain surfactants (IV).

distillation (175°C/0.08 mmHg) as a colorless liquid (73% yield). IR (neat): 2930, 2850, 1640, 1460, and 1105 cm^{-1}.

N,N-Bis*(5-hydroxy-3,7-dioxaheptadecyl)decanamide* (IIIe): Metallic potassium (1.17 g, 0.030 mol) was dissolved into decanol (28.5 g, 0.18 mol) at 70°C. Compound IIb was dropped carefully into the resulting solution. The reaction mixture was then stirred for 12 hr 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 $MgSO_4$, any excess of dodecanol was distilled off under reduced pressure. Compound IIIe was obtained as a colorless liquid by silica gel column chromatography of the residue with a hexane:acetone (1:1, v/v) eluent (10.6 g, 77% yield). IR (neat): 3400, 2930, 2850, 1620, 1460, and 1120 cm^{-1}; mass [*m/e*, relative intensity]: 688 [$(M+1)^+$, 13], 456 [100], and 242 [25]; ^1H NMR ($CDCl_3$): δ 0.88 (*t*, 9H), 1.18-1.67 (*m*, 46H), 2.35 (*t*, 2H), 2.81 (*s*, 2H), and 3.37-3.93 (*m*, 22H).

TABLE 1

Preparation and Properties of Amphipathic Compounds (IVa–f)[a]

Compound	R	R	Yield[b] (%)	^{1}H NMR ($CDCl_3$) (δ)	Anal. found(calc'd)[c]
IVa	C_8H_{17}	CH_3	60	0.88(*t*,6H), 1.05–1.52(*m*,24H), 1.88–2.07(*m*,4H), 2.19(*s*,3H), 2.79–3.04(*m*,4H), 3.21–3.77 (*m*,26H)	H, 8.45 (8.42) C, 49.12(49.44) N, 1.60 (1.70) S, 7.32 (7.76)
IVb	C_8H_{17}	C_9H_{19}	68	0.88(*t*,9H), 1.19–1.67(*m*,38H), 1.96–2.14(*m*,4H), 2.38(*t*,2H), 2.87–3.00(*m*,4H), 3.35–3.70(*m*,26H)	H, 9.37 (9.13) C, 53.70 (53.77) N, 1.58 (1.49) S, 6.85 (6.84)
IVc	C_8H_{17}	$C_{11}H_{23}$	67	0.88(*t*,9H), 1.07–1.66(*m*,42H), 1.93–2.14(*m*,4H), 2.37(*t*,2H), 2.87–3.10(*m*,4H), 3.35–3.94(*m*,26H)	H, 9.07 (9.25) C, 55.57(55.73) N, 1.54 (1.48) S, 6.61 (6.76)
IVd	$C_{10}H_{21}$	CH_3	81	0.88(*t*,6H), 1.10–1.64(*m*,32H), 1.90–2.15(*m*,4H), 2.17(*s*,3H), 2.83–3.20(*m*,4H), 3.35–3.80(*m*,26H)	H, 9.08 (8.75) C, 53.54 (52.82) N, 1.80 (1.62) S, 7.36 (7.42)
IVe	$C_{10}H_{21}$	C_9H_{19}	66	0.88(*t*,9H), 1.19–1.79(*m*,46H), 1.96–2.13(*m*,4H), 2.41(*t*,2H), 2.88–3.12(*m*,4H), 3.33–3.80(*m*,26H)	H, 9.31 (9.40) C, 56.66 (56.59) N, 2.11 (1.59) S, 6.76 (6.57)
IVf	$C_{10}H_{21}$	$C_{11}H_{23}$	62	0.88(*t*,9H), 1.16–1.66(*m*,50H), 1.90–2.03(*m*,4H), 2.34(*t*,2H), 2.85–3.09(*m*,4H), 3.25–3.92(*m*,26H)	H, 9.83 (9.53) C, 57.14 (57.40) N, 1.76 (1.39) S, 6.38 (6.39)

[a] IR spectra: 2920, 2830, 1620, 1460, 1200, 1110 and 1030 cm^{-1}.

[b] Based on **III**.

[c] Calculated values of **IVa** and **b** are based on the assumption that these compounds contain one mole of bound water.

*Disodium 10-decanoyl-5,15-*bis*(2-oxadodecyl)-10-aza-4,7,13,16-tetraoxa-1,19-nonadecanedisulfonate* (IVe): Dry THF (10 mL) solution containing 3.44 g of compound IIIe (5 mmol) and another dry THF (10 mL) solution containing 2.44 g of propanesultone (20 mmol) were dropped in this order into a suspension of sodium hydride (0.80 g net, 20 mmol) and dry THF (10 mL) at 30°C. After 24 hr 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*-butanol (3 × 150 mL):water (150 mL) solvent system, the combined organic extracts were dried with $MgSO_4$. The target compound (IVe) was isolated as a white waxy product by silica gel column chromatography of the crude with a hexane:ethanol (1:1, v/v) eluent (3.22 g, 66% yield).

Methods. Surface-active properties were evaluated according to the methods mentioned in a previous paper (6): Surface tension was measured with a Wilhelmy tensiometer (glass plate) at 20°C. Foaming properties were measured by the semi-micro TK method with a 0.1 wt% aqueous solution. Wetting ability was estimated by the sedimentation time of a piece of felt (JIS-R28W, 15 × 15 mm, 70 mg, stainless hook included) from the surface to the bottom of 50 mL of 0.1 wt% or 0.05 wt% aqueous surfactant solution in a 100-mL glass cylinder (i.d. 30 mm) at 20°C. Lime-soap dispersing ability was determined with a 0.05 wt% aqueous solution in 333 ppm of hard water by the Borghetty-Bergman method (11).

RESULTS AND DISCUSSION

It has been pointed out that the *N*-acyldiethanolamines may rearrange to the corresponding aminoesters upon being heated (12), but in the series of *N*-acyldiethanolamine derivatives (II–IV) studied in this work, it was confirmed by TLC, IR, and ^{1}H NMR spectra that neither isolated product contained the corresponding aminoester derivatives. Especially the diglycidyl ethers (II) were easily purified by distillation under reduced pressure.

Among the prepared *bis*(sulfonate) types of surfactants, double-chain compounds (R' = methyl; **IVa,d**) were freely soluble in water at 1 wt% concentration (*i.e.* Krafft point: $T_{Kp} < 0°C$). Triple-chain compounds (R' = long-chain alkyl; **IVb,c,e,f**) were soluble in water at any temperature at 0.05 wt%. The surface tension-concentration plots of aqueous solutions of **IV** are shown in Figure 3.

The critical micelle concentration (CMC, determined from the break point of each curve in Fig. 3), the ability to lower surface tension above the CMC (γ_{CMC}), the efficiency of adsorption at the water/air interface [pC_{20},C_{20}: the concentration (mol/L) of surfactant in the bulk phase required to produce a 20 mN/m reduction in the surface of water, $pC_{20} = -\log C_{20}$], and the CMC/C_{20} ratio of these surfactants (**IV**) are summarized in Table 2, along with the reference data for sodium dodecylsulfonate measured under the same conditions. The quantitative limit of the Wilhelmy method in this work is about 10^{-6} mol/L, because the error variation in surface tension of a surfactant solution with time becomes very large below this

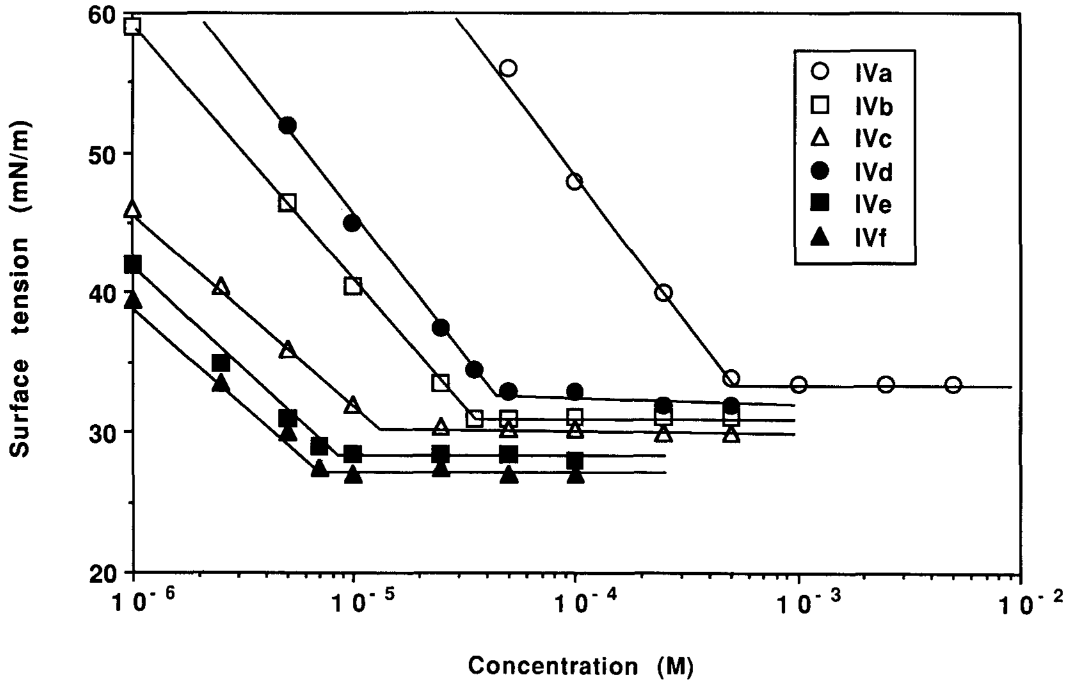


FIG. 3. Surface tension-concentration plots of compounds IVa–f in water at 20°C by the Wilhelmy method.

TABLE 2

The CMC, γ_{CMC}, pC_{20} and CMC/C_{20} Values of IVa–f and Reference Compound (20°C)

Compound	R	R′	CMC (mM)	γ_{CMC} (mN/m)	pC_{20}	CMC/C_{20}
IVa	C_8H_{17}	CH_3	0.52	33.5	4.2	7.5
IVb	C_8H_{17}	C_9H_{19}	0.035	31.0	5.6	14
IVc	C_8H_{17}	$C_{11}H_{23}$	0.012	30.5	6.5[a]	43[a]
IVd	$C_{10}H_{21}$	CH_3	0.043	32.5	5.3	7.9
IVe	$C_{10}H_{21}$	C_9H_{19}	0.0080	28.0	6.7[a]	39[a]
IVf	$C_{10}H_{21}$	$C_{11}H_{23}$	0.0072	27.5	6.9[a]	63[a]
(Ref.)	$C_{12}H_{25}SO_3Na$[b] (45°C)		9.8	39.0	2.5	3.0

[a] Estimated value.
[b] T_{Kp} = 39°C.

concentration. The reduction in surface tension ($\pi = \gamma_0 - \gamma$, γ_0: the surface tension of water) of compounds **IVc**, **e**, and **f** was already beyond 20 mN/m even at 10^{-6} mol/L. Therefore, the C_{20} values of **IVc**, **e**, and **f** were estimated by extrapolation of the lines below the CMC value in Figure 3.

As compared with the single-chain dodecylsulfonate, compounds **IVa–f** showed fairly small CMCs (about 1/20 - 1/150) and γ_{CMC} values. These values for the triple-chain surfactants were much smaller than those of the corresponding double-chain surfactants containing two common alkyl chains (R). A difference in the CMC values of the homologues with two octyl groups (**IVa–c**) between the double-chain compound and triple-chain compounds was larger than that of the homologues with two decyl groups (**IVd–f**). Compounds **IVe**, **f** exhibited a superlative degree of micelle-forming property and ability to lower surface tension among the hitherto known anionic surfactants (13). Along with their good hydrophilicity, these compounds satisfactorily display fundamental surface-active properties. It may be difficult to achieve these properties only by the structural modification of general single-chain surfactants.

It has been mentioned that the pC_{20} value is an index of the efficiency of adsorption of a surfactant at the liquid/gas interface (14). The efficiency of adsorption of compounds **IV** was very high because the pC_{20} values of **IV** were much larger than hitherto reported values of the general single-chain surfactants (14). If the third lipophilic chain (R′) of **IV** is increased by two methylene groups, it is estimated from the difference between **IVa** and **IVb** (or **IVd** and **IVe**) that pC_{20} is increased by about 0.35 for adsorption at the surface.

It has been pointed out that one of the meanings of the CMC/C_{20} ratio is an index of the relative effects of some structural factor of a surfactant on micellization and

TABLE 3

Foaming Properties[a], LSDR and Wetting Ability[a] of IVa–f and Reference Compounds (20°C)

Compound	R	R′	Foam volume (mL)			LSDR	Wetting time (s)
			0′	3′	5′		
IVa	C_8H_{17}	CH_3	260	130	100	11.3	391
IVb	C_8H_{17}	C_9H_{19}	270	250	210	6.2	18
IVc	C_8H_{17}	$C_{11}H_{23}$	260	245	245	8.2	55
IVd	$C_{10}H_{21}$	CH_3	260	90	30	6.9	40
IVe	$C_{10}H_{21}$	C_9H_{19}	180	40	30	5.7	102
IVf	$C_{10}H_{21}$	$C_{11}H_{23}$	270	15	0	6.6	377
(Ref.)	$C_{12}H_{25}SO_3Na$ (45°C)[b]		215	160	130	94	15
	Aerosol-OT		—	—	—	—	5

[a] 0.1 Wt% aq. surfactant solution for **IVa,d**, 0.05 wt% aq. surfactant solution for **IVb,c,e,f.**

[b] 0.5 Wt% aq. surfactant solution (above its CMC).

on adsorption (14). Hitherto reported CMC/C_{20} ratios of general anionic surfactants range from 1.3 to 28 (15). The hydrophilic part of these double- or triple-chain surfactants is apparently bulky and located in a center of the molecule. It has been found that the CMC/C_{20} ratio of general ionic surfactants is increased by the introduction of branching in the lipophilic group or by locating the head group in a central position in the molecule, and by the introduction of a larger hydrophilic group (15). A large increase in these ratios of double- or triple-chain surfactants (**IV**) may indicate that adsorption is facilitated more than micelle formation.

Foaming properties, wetting property, and lime-soap dispersing requirement (LSDR) of compounds **IV** and reference compounds are listed in Table 3. Foaming and wetting properties were measured with a 0.1 wt% solution for double-chain surfactants (**IVa,d**) or a 0.05 wt% solution for triple-chain surfactants (**IVb,c,e,f**). All these properties of sodium dodecylsulfonate were measured at a 0.5 wt% because its CMC is about 0.27 wt%. Foam stability of double-chain compound **IVd** is almost similar to that of the previously reported disodium 1,ω-*bis*(decyloxymethyl)-1,ω-alkanedisulfates (6). Homologues with two octyl chains (**IVa–c**), however, showed higher foam stability than homologues with two decyl chains (**IVd–f**). Although the difference of measured concentration between double-chain compounds and triple-chain compounds must be considered, it is surmised that foaming properties may vary with the combination of the three lipophilic chains.

The lime-soap dispersing ability of compounds **IVa–f** was much better than that of the general single-chain sulfonate but slightly lower than the previously reported double-chain surfactants bearing two sulfate groups (6). Together with the factors mentioned in the previous report (6), the amide group may make a positive contribution to the lime-soap dispersing ability because this group is known to have a strong affinity for calcium ions (16).

Wetting times for surfactants **IVa–f** with a felt chip occur over a wide range and are slower than the wetting time for sodium *di*(2-ethylhexyl) sulfosuccinate (Aerosol-OT, delivered by Nippon Cyanamid Co., Tokyo, Japan) under the same conditions. Although the influence of the structure of these types of compounds on the wetting property is not clear yet, the wetting ability of **IVb** is relatively good.

Triple-chain surfactants in this work may be used in various applications as new types of high-performance surfactants because they can be prepared in good yields from commercially available raw materials and they exhibit excellent surface-active properties at low concentrations. An investigation of other types of triple-chain surfactants with plural ionic head groups is now in progress.

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