

# Preparation, Surface-Active Properties and Acid Decomposition Profiles of a New "Soap" Bearing a 1,3-Dioxolane Ring

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New soap-type surfactants bearing a 1,3-dioxolane ring were prepared in good yields by the acid-catalyzed condensation of 1-*O*-alkylglycerols (alkyl: decyl, dodecyl, tetradecyl, heptadecyl, octadecyl, or *cis*-9-octadecenyl) with oxocarboxylic acid esters, followed by alkaline hydrolysis without any expensive reagent and special equipment. These surfactants were soluble in alkaline water at room temperature. Their critical micelle concentrations were much smaller than that of sodium dodecanoate. An alkaline solution of the octadecyl homologue was non-foaming, but the other homologues, including the *cis*-9-octadecenyl derivative, showed high foaming ability in alkaline solutions. The structural effect of these compounds on the area per molecule at the surface is also discussed. Because these surfactants contain a 1,3-dioxolane ring, they can be utilized as a new acid-decomposable type of cleavable surfactant. At pH 1, they decompose almost completely into nonsurface-active species after 80 min.

**KEY WORDS:** Acid decomposition, cleavable surfactants, soap-type surfactants, 1-*O*-alkylglycerols, 1,3-dioxolane.

Soap should be considered again as an active component of detergents from an ecological standpoint on a global scale because it possesses better biodegradability than commercial surfactants derived from petroleum chemicals. On the negative side, soap has several problems such as lower surface-active properties, little solubility in cold water and formation of insoluble calcium soap in hard water. These drawbacks have hampered the substitution of soap for synthetic surfactants, which are predominantly used in detergents.

We have found that novel carboxylates, sodium 2-[carboxylato(alkyl)]-2-methyl-4-alkyloxymethyl-1,3-dioxolanes (IV), can be prepared easily in good yields by the acid-catalyzed condensation of 1-*O*-alkylglycerols with oxocarboxylic acid derivatives and subsequent alkaline hydrolysis without any expensive reagents and special equipment. These sodium carboxylates bearing a long-chain alkyl group can be utilized as a useful new soap-type surfactant because a 1,3-dioxolane ring is easily hydrolyzed under acidic conditions. In this work, we will clarify both surface-active properties and acid-decomposition profiles in an aqueous solution of the carboxylate surfactants derived from 1-*O*-(long-chain alkyl)glycerols and oxocarboxylates. Various types of the former starting materials are available as oleochemicals (1-4) and are formulated in many cosmetic products (5-7). Some of them are naturally occurring. Of the oxocarboxylic acid esters, ethyl pyruvinate, ethyl acetoacetate and ethyl levulinate are commercially available. The levulinic acid is a saccharide

derivative that is industrially made from starch or cellulose. So, it is reasonable to say that these new compounds bearing a 1,3-dioxolane ring are also prepared from naturally occurring products. Several cleavable surfactants bearing a 1,3-dioxolane ring have been reported (8-21); however, the structure of the compounds in this work is different. Additionally, we will report to what degree these new compounds solve conventional problems related to the use of a typical soap as described above.

Figure 1 shows the synthetic route for the target sodium carboxylates (IV) studied in this work.

## EXPERIMENTAL PROCEDURES

**Materials.** 1-*O*-Hexadecylglycerol (Id) and 1-*O*-octadecylglycerol (Ie) were commercial products (Nikko Chemicals Co., Tokyo, Japan) of which the purity was confirmed by gas-liquid chromatography. The other alkylglycerols (Ia, Ib, Ic and If) were prepared from the corresponding fatty alcohols and epichlorohydrin according to the reported method (22-26). The target sodium carboxylates (IVa-n) were synthesized by the acid-catalyzed condensation of 1-*O*-alkylglycerols (Ia-f) with oxocarboxylic acid esters (IIa-c) and subsequent alkaline hydrolysis (Fig. 1). The sodium carboxylates (IV) were isolated by recrystallization from ethanol (IVh-m) or by reversed-phase column chromatography (ODS40 Ultra Pack column purchased from Yamazen Corp., Osaka, Japan) with methanol as an eluent (IVa-g and IVn). Their structure and purity were confirmed by infrared (Hitachi 260 spectrometer; Hitachi Limited, Tokyo, Japan) spectral data, <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H-NMR; JEOL JNM-GSX 400; JEOL Limited, Tokyo, Japan) spectral data and elemental analysis. Typical synthetic procedures are as follows:

*2-Ethoxycarbonylmethyl-2-methyl-4-hexadecyloxymethyl-1,3-dioxolane (IIIi).* In a round-bottom flask fitted with stirrer and Dean-Stark receiver, 1-*O*-hexadecylglycerol (Id; 3.80 g, 12 mmol), ethyl acetoacetate (IIb; 1.30 g, 10 mmol), and *p*-toluenesulfonic acid (0.10 g, 0.5 mmol) were dissolved in toluene (40 mL). The solution was refluxed for 2 h. The solvent was evaporated at reduced pressure, and the residue was partitioned between CHCl<sub>3</sub> (50 mL) and 5% NaHCO<sub>3</sub> aqueous solution (30 mL). The organic layer was washed with H<sub>2</sub>O (30 mL) and saturated NaCl (30 mL) in that order and dried (MgSO<sub>4</sub>). The solvent was evaporated, and the oily product (IIIi) was isolated by Kugelrohr distillation of the residue; yield: 4.11 g (96%); bp 160°C/0.05 Torr.

*Sodium 2-(carboxylatomethyl)-2-methyl-4-hexadecyloxymethyl-1,3-dioxolane (IVi).* In a round-bottom flask fitted with stirrer, IIIi (4.07 g, 9 mmol) and NaOH (0.38 g, 9 mmol) were dissolved in MeOH (15 mL). The solution was stirred at 60°C for 20 min. The solvent was evaporated, and the product was recrystallized from EtOH; yield: 3.32 g (83%); m.p. 60-62°C.

The synthetic results and physical properties of the compounds in this work are summarized in Tables 1 (for

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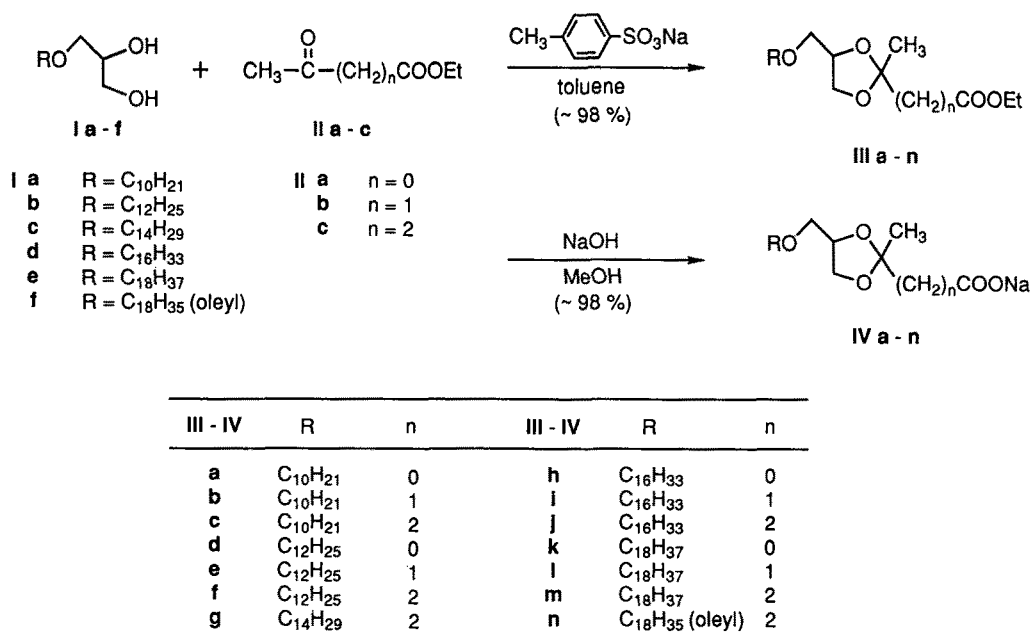


FIG. 1. New "soap" bearing a 1,3-dioxolane ring prepared in this work.

compounds III) and 2 (for compounds IV). Sodium dodecanoate as a conventional soap was purchased from Nakalai Tesque, Inc. (Kyoto, Japan).

**Methods.** The Krafft point ( $T_{Kp}$ ) was determined by the naked eye with a 1-wt% aqueous solution. The surface tension of a surfactant solution was measured with a Wilhelmy tensiometer (Shimadzu ST1; Shimadzu Limited, Kyoto, Japan; glass plate) at 20°C. Foaming properties were evaluated by the semi-micro TK method with a 0.1-wt% aqueous solution at 20°C (27). These properties were measured in sodium hydroxide solutions at pH 12.

The detergency of compounds IV was evaluated according to JIS (the Japan Industrial Standard) K 3303 as follows: A mixture of compound IV (0.5 g), sodium carbonate (0.2 g) and sodium sulfate (0.3 g) was used as the soap for the measurement of detergency. The reference soap (1.0 g) consisted of sodium oleate (0.3 g), sodium stearate (0.1 g), sodium palmitate (0.1 g), sodium carbonate (0.2 g) and sodium sulfate (0.3 g). The examined soap (1.0 g) was dissolved in distilled water (500 mL) at 50°C, and the solution was diluted to 1 L by addition of hard water, which was prepared with CaCl<sub>2</sub>·2H<sub>2</sub>O and MgCl<sub>2</sub>·6H<sub>2</sub>O (a hardness composition of 70% Ca<sup>2+</sup>, 30% Mg<sup>2+</sup>). Detergency was measured in two kinds of solutions of which the total hardness as CaCO<sub>3</sub> was 50 ppm and 100 ppm, respectively. The artificially soiled cloth was prepared by immersing a white cotton cloth (satisfying JIS L 0803; 10 cm × 40 m) in a soil mixture composed of myristic acid (6.64 g), oleic acid (6.64 g), tristearin (6.64 g), triolein (6.64 g), cholesterol stearate (0.88 g), paraffin wax (m.p. 48–50°C; 4.40 g), squalene (4.40 g), cholesterol (3.52 g), carbon black (0.48 g), clay (*Kantoh Loam*, Tokyo, Japan; 39.76 g) and tetrachloromethane (2.5 L) with a continuous soiling machine (Toyo Seiki Manufacture Co., Tokyo, Japan), and subsequently drying the cloth at 25°C for three weeks. Five sheets of the soiled cloth and five sheets of the unsoiled white cloth (10 cm × 10 cm each)

were washed with the solution of the examined soap in the bath of a mechanically stirred washing machine named "Abstergent Tester" (Ueshima Manufacture Co., Tokyo, Japan), which is a familiar type of Terg-O-Tometer<sup>R</sup>, at 120 rpm at 25°C for 10 min. The contents were then rinsed twice with water in the Abstergent Tester at 120 rpm for 3 min. Each washed cloth was dried in air and successively with an electric iron. The detergency of the examined soap was estimated by

$$\text{detergency (\%)} = 100 (R_w - R_s)/(R_0 - R_s) \quad [1]$$

where  $R_s$  and  $R_w$  refer to the initial and final surface reflectivity of the soiled cloth as measured by a reflectance meter (1001DP Type, Nippon Densyoku Kogyo Co., Tokyo, Japan), and  $R_0$  refers to the initial surface reflectivity of the unsoiled cloth.

The decomposition properties of surfactants in D<sub>2</sub>O with the addition of DCl were measured by <sup>1</sup>H-nuclear magnetic resonance (NMR) spectroscopy according to a similar method described in our previous report (28).

## RESULTS AND DISCUSSION

The sodium carboxylates (IV) were prepared from 1-O-alkylglycerols (I) by the following two steps: acid-catalyzed condensation with ethyl oxocarboxylates (II) in the presence of *p*-toluenesulfonic acid in toluene, then alkaline hydrolysis of the resulting ester compounds (III) bearing a 1,3-dioxolane ring in an equivalent of sodium hydroxide in methanol to afford IV in good yields. When ethyl levulinate (IIc) was reacted with I, a crude intermediate ester was obtained directly from the toluene solution containing the reaction mixture after washing it with weak alkaline water. In the other cases, chloroform was used as an extracting solvent after evaporating off the toluene because washing the toluene solution with

## NEW SOAP BEARING A 1,3-DIOXOLANE RING

TABLE 1

Preparation and Properties of Intermediate Esters (III)<sup>a,b</sup>

Compound	Yield <sup>c</sup> (%)	Boiling point <sup>d</sup> (°C/Torr)	<sup>1</sup> H-NMR <sup>e</sup> ( <i>d</i> )	Anal. found (calc'd)
IIIa	79	120/0.05	0.88 ( <i>t</i> , 3H), 1.16–1.32 ( <i>m</i> , 17H), 1.54–1.63 ( <i>m</i> , 5H), 3.37–3.66 ( <i>m</i> , 4H), 3.85 ( <i>m</i> , 1H), 4.15–4.25 ( <i>m</i> , 3H), 4.30–4.46 ( <i>m</i> , 1H)	C, 65.64 (65.42) H, 10.95 (10.37)
IIIb	94	120/0.05	0.88 ( <i>t</i> , 3H), 1.20–1.40 ( <i>m</i> , 17H), 1.45–1.65 ( <i>m</i> , 5H), 2.63 ( <i>s</i> , 1.2H), 2.75 ( <i>s</i> , 0.8H), 2.63 ( <i>s</i> , 1.2H), 2.75 ( <i>s</i> , 0.8H), 3.00–3.60 ( <i>m</i> , 4H), 3.80 ( <i>m</i> , 1H), 4.00–4.20 ( <i>m</i> , 3H), 4.30 ( <i>m</i> , 1H)	C, 66.29 (66.25) H, 10.69 (10.53)
IIIc	97	125/0.05	0.88 ( <i>t</i> , 3H), 1.15–1.40 ( <i>m</i> , 20H), 1.50–1.65 ( <i>m</i> , 2H), 2.00 ( <i>m</i> , 2H), 2.40 ( <i>m</i> , 2H), 3.40–3.60 ( <i>m</i> , 4H), 3.65–3.80 ( <i>m</i> , 1H), 4.00–4.15 ( <i>m</i> , 3H), 4.25 ( <i>m</i> , 1H)	C, 66.90 (67.00) H, 10.78 (10.69)
IIId	78	140/0.05	0.88 ( <i>t</i> , 3H), 1.16–1.32 ( <i>m</i> , 21H), 1.48–1.66 ( <i>m</i> , 5H), 3.37–3.66 ( <i>m</i> , 4H), 3.85 ( <i>m</i> , 1H), 4.15–4.25 ( <i>m</i> , 3H), 4.30–4.46 ( <i>m</i> , 1H)	C, 67.54 (67.00) H, 11.15 (10.69)
IIIe	97	140/0.05	0.88 ( <i>t</i> , 3H), 1.20–1.40 ( <i>m</i> , 21H), 1.45–1.65 ( <i>m</i> , 5H), 2.66 ( <i>s</i> , 1.2H), 2.75 ( <i>s</i> , 0.8H), 3.40–3.60 ( <i>m</i> , 4H), 3.80 ( <i>m</i> , 1H), 4.05–4.25 ( <i>m</i> , 3H), 4.30 ( <i>m</i> , 1H)	C, 67.81 (67.71) H, 10.99 (10.82)
IIIf	96	140/0.05	0.88 ( <i>t</i> , 3H), 1.15–1.40 ( <i>m</i> , 24H), 1.50–1.65 ( <i>m</i> , 2H), 2.00 ( <i>m</i> , 2H), 2.40 ( <i>m</i> , 2H), 3.40–3.60 ( <i>m</i> , 4H), 3.65–3.80 ( <i>m</i> , 1H), 4.00–4.12 ( <i>m</i> , 3H), 4.25 ( <i>m</i> , 1H)	C, 68.46 (68.36) H, 11.09 (10.95)
IIIg	92	155/0.05	0.88 ( <i>t</i> , 3H), 1.20–1.39 ( <i>m</i> , 28H), 1.50–1.60 ( <i>m</i> , 2H), 2.00 ( <i>m</i> , 2H), 2.40 ( <i>m</i> , 2H), 3.40–3.54 ( <i>m</i> , 4H), 3.63–3.75 ( <i>m</i> , 1H), 4.00–4.15 ( <i>m</i> , 3H), 4.25 ( <i>m</i> , 1H)	C, 69.41 (69.53) H, 11.27 (11.18)
IIIh	77	165/0.05	0.88 ( <i>t</i> , 3H), 1.16–1.32 ( <i>m</i> , 29H), 1.53–1.66 ( <i>m</i> , 5H), 3.37–3.66 ( <i>m</i> , 4H), 3.85 ( <i>m</i> , 1H), 4.15–4.25 ( <i>m</i> , 3H), 4.30–4.46 ( <i>m</i> , 1H)	C, 69.27 (69.53) H, 11.17 (11.18)
IIIi	96	160/0.05	0.85 ( <i>t</i> , 3H), 1.15–1.35 ( <i>m</i> , 29H), 1.45–1.65 ( <i>m</i> , 5H), 2.67 ( <i>s</i> , 1.2H), 2.72 ( <i>s</i> , 0.8H), 3.40–3.60 ( <i>m</i> , 4H), 3.80 ( <i>m</i> , 1H), 4.05–4.22 ( <i>m</i> , 3H), 4.30 ( <i>m</i> , 1H)	C, 70.33 (70.05) H, 11.60 (11.29)
IIIj	97	160/0.05	0.88 ( <i>t</i> , 6H), 1.15–1.40 ( <i>m</i> , 32H), 1.50–1.65 ( <i>m</i> , 2H), 2.00 ( <i>m</i> , 2H), 2.40 ( <i>m</i> , 2H), 3.40–3.60 ( <i>m</i> , 4H), 3.65–3.80 ( <i>m</i> , 1H), 4.00–4.15 ( <i>m</i> , 3H), 4.25 ( <i>m</i> , 1H)	C, 70.53 (70.54) H, 11.40 (11.39)
IIIk	76	175/0.05	0.88 ( <i>t</i> , 3H), 1.16–1.32 ( <i>m</i> , 33H), 1.53–1.66 ( <i>m</i> , 5H), 3.37–3.66 ( <i>m</i> , 4H), 3.85 ( <i>m</i> , 1H), 4.15–4.25 ( <i>m</i> , 3H), 4.30–4.46 ( <i>m</i> , 1H)	C, 70.94 (70.54) H, 11.26 (11.39)
IIIl	94	175/0.05	0.85 ( <i>t</i> , 3H), 1.15–1.35 ( <i>m</i> , 33H), 1.45–1.65 ( <i>m</i> , 5H), 2.66 ( <i>s</i> , 1.2H), 2.72 ( <i>s</i> , 0.8H), 3.40–3.56 ( <i>m</i> , 4H), 3.80 ( <i>m</i> , 1H), 4.10–4.20 ( <i>m</i> , 3H), 4.30 ( <i>m</i> , 1H)	C, 70.87 (71.01) H, 11.28 (11.48)
IIIm	98	175/0.05	0.88 ( <i>t</i> , 3H), 1.15–1.40 ( <i>m</i> , 36H), 1.50–1.65 ( <i>m</i> , 2H), 2.00 ( <i>m</i> , 2H), 2.40 ( <i>m</i> , 2H), 3.40–3.60 ( <i>m</i> , 4H), 3.65–3.80 ( <i>m</i> , 1H), 4.00–4.15 ( <i>m</i> , 3H), 4.25 ( <i>m</i> , 1H)	C, 71.61 (71.44) H, 11.78 (11.56)
III n	90	180/0.05	0.88 ( <i>t</i> , 3H), 1.20–1.40 ( <i>m</i> , 28H), 1.57 ( <i>m</i> , 2H), 1.90–2.10 ( <i>m</i> , 6H), 2.40 ( <i>m</i> , 2H), 3.38–3.70 ( <i>m</i> , 4H), 3.90 ( <i>m</i> , 1H), 4.05–4.29 ( <i>m</i> , 4H), 5.35 ( <i>m</i> , 2H)	C, 71.87 (71.75) H, 11.33 (11.18)

<sup>a</sup>Infrared (IR) spectra (neat): 2900, 1740 and 1110 cm<sup>-1</sup>.<sup>b</sup>Mass or fast atom bombardment mass spectra (70 eV, JEOL JMS-DX303, JEOL Limited), *m/z* (rel. intens.): IIIa: 331[(M + 1)<sup>+</sup>, 35], 257(100) and 57(83); IIIb: 344(M<sup>+</sup>, 2), 257(100) and 131(85); IIIc: 358(M<sup>+</sup>, 5), 257(100) and 99(45); IIId: 359[(M + 1)<sup>+</sup>, 100], 285(15) and 173(5); IIIe: 373[(M + 1)<sup>+</sup>, 100], 357(4) and 285(40); IIIf: 387[(M + 1)<sup>+</sup>, 100], 299(10) and 285(15); IIIg: 415[(M + 1)<sup>+</sup>, 100], 313(10) and 99(5); IIIh: 415[(M + 1)<sup>+</sup>, 30], 314(100) and 57(80); IIIi: 428(M<sup>+</sup>, 3), 341(100) and 131(87); IIIj: 442(M<sup>+</sup>, 0.3), 341(100) and 57(50); IIIk: 443[(M + 1)<sup>+</sup>, 80], 371(15) and 345(100); IIIl: 456(M<sup>+</sup>, 6), 367(100) and 131(64); IIIm: 471[(M + 1)<sup>+</sup>, 6], 99(100) and 57(60); III n: 469[(M + 1)<sup>+</sup>, 100], 367(7) and 145(12).<sup>c</sup>Based on II.<sup>d</sup>Kugelrohr distillation.<sup>e</sup>In CDCl<sub>3</sub>, tetramethylsilane as an internal standard. Abbreviation: NMR, nuclear magnetic resonance.

weak alkaline water caused the formation of a troublesome emulsion. All the intermediate esters (III) were isolated by Kugelrohr distillation. Sodium carboxylates with a hexadecyloxymethyl or octadecyloxymethyl group (IVh–m)

were isolated by recrystallization from ethanol. Other compounds were waxy products, so they were purified by reversed-phase column chromatography with methanol as an eluent. In the range of this study, the difference in

TABLE 2

Preparation and Properties of Final Carboxylates (IV)<sup>a</sup>

Compound	Yield <sup>b</sup> (%)	Melting point (°C)	<sup>1</sup> H-NMR <sup>c</sup> (d)	Anal. found (calc'd)
IVa	95	waxy	0.88 (t, 3H), 1.20–1.40 (m, 14H), 1.45–1.65 (m, 5H), 3.40–3.65 (m, 4.5H), 3.77 (m, 0.5H), 3.96 (m, 0.5H), 4.20 (m, 0.5H), 4.33 (m, 1H)	C, 59.15 (59.24) H, 9.25 (9.01)
IVb	98	waxy	0.88 (t, 3H), 1.20–1.40 (m, 14H), 1.45–1.65 (m, 5H), 2.46 (s, 1.2H), 2.63 (s, 0.8H), 3.40–3.60 (m, 4H), 3.70 (m, 1H), 4.15 (m, 1H), 4.35 (m, 1H)	C, 60.83 (60.34) H, 9.67 (9.23)
IVc	92	waxy	0.88 (t, 3H), 1.20–1.40 (m, 17H), 1.57 (m, 2H), 1.95 (m, 2H), 2.23 (m, 2H), 3.45–3.80 (m, 5H), 4.05 (m, 1H), 4.30 (m, 1H)	C, 60.98 (61.34) H, 9.34 (9.44)
IVd	95	waxy	0.88 (t, 3H), 1.20–1.40 (m, 18H), 1.47–1.60 (m, 5H), 3.40–3.65 (m, 4.5H), 3.80 (m, 0.5H), 4.00 (m, 0.5H), 4.13 (m, 0.5H), 4.30 (m, 1H)	C, 60.75 (61.34) H, 9.48 (9.44)
IVe	97	waxy	0.88 (t, 3H), 1.20–1.40 (m, 18H), 1.45–1.65 (m, 5H), 2.48 (s, 1.2H), 2.64 (s, 0.8H), 3.40–3.65 (m, 4H), 3.75 (m, 1H), 4.10 (m, 1H), 4.30 (m, 1H)	C, 61.80 (62.27) H, 9.98 (9.63)
IVf	97	waxy	0.88 (t, 3H), 1.20–1.40 (m, 21H), 1.57 (m, 2H), 1.95 (m, 2H), 2.25 (m, 2H), 3.45–3.80 (m, 5H), 4.05 (m, 1H), 4.30 (m, 1H)	C, 63.12 (63.13) H, 10.04 (9.80)
IVg	90	waxy	0.90 (t, 3H), 1.23–1.40 (m, 25H), 1.55 (m, 2H), 1.95 (m, 2H), 2.25 (m, 2H), 3.41–3.73 (m, 5H), 4.05 (m, 1H), 4.25 (m, 1H)	C, 63.63 (64.68) H, 10.09 (10.11)
IVh	85	54–56	0.88 (t, 3H), 1.20–1.40 (m, 26H), 1.42–1.63 (m, 5H), 3.38–3.65 (m, 4.5H), 3.75 (m, 0.5H), 4.00 (m, 0.5H), 4.10 (m, 0.5H), 4.25 (m, 1H)	C, 64.58 (64.68) H, 10.11 (10.11)
IVi	83	60–62	0.88 (t, 3H), 1.20–1.40 (m, 26H), 1.45–1.65 (m, 5H), 2.49 (s, 1.2H), 2.53 (s, 0.8H), 3.40–3.63 (m, 4H), 3.75 (m, 1H), 4.07 (m, 1H), 4.25 (m, 1H)	C, 65.19 (65.37) H, 10.45 (10.26)
IVj	87	145–148	0.88 (t, 3H), 1.20–1.40 (m, 29H), 1.57 (m, 2H), 1.95 (m, 2H), 2.25 (m, 2H), 3.45–3.80 (m, 5H), 4.05 (m, 1H), 4.30 (m, 1H)	C, 65.93 (66.02) H, 10.19 (10.39)
IVk	89	62–64	0.88 (t, 3H), 1.20–1.40 (m, 30H), 1.42–1.63 (m, 5H), 3.36–3.65 (m, 4.5H), 3.75 (m, 0.5H), 4.00 (m, 0.5H), 4.10 (m, 0.5H), 4.25 (m, 1H)	C, 65.36 (66.02) H, 10.73 (10.39)
IVl	91	65–67	0.85 (t, 3H), 1.20–1.40 (m, 30H), 1.45–1.65 (m, 5H), 2.45 (s, 1.2H), 2.59 (s, 0.8H), 3.45–3.60 (m, 4H), 3.70 (m, 1H), 4.10 (m, 1H), 4.30 (m, 1H)	C, 66.85 (66.63) H, 10.80 (10.52)
IVm	86	147–150	0.88 (t, 3H), 1.20–1.40 (m, 33H), 1.58 (m, 2H), 1.95 (m, 2H), 2.25 (m, 2H), 3.45–3.80 (m, 5H), 4.05 (m, 1H), 4.30 (m, 1H)	C, 67.25 (67.21) H, 10.32 (10.63)
IVn	90	waxy	0.88 (t, 3H), 1.20–1.40 (m, 25H), 1.55 (m, 2H), 1.90–2.10 (m, 6H), 2.20 (m, 2H), 3.40–3.80 (m, 5H), 4.07 (m, 1H), 4.23 (m, 1H), 5.34 (m, 2H)	C, 63.69 (64.97) <sup>d</sup> H, 10.75 (10.28) <sup>d</sup>

<sup>a</sup> Infrared (IR) spectra (IVa–g,n: neat; IVl–m: KBr pellet): IVa,d,h,k: 2900, 1610 and 1120 cm<sup>-1</sup>; IVb,c,e,f,g,i,j,l,m: 2900, 1580 and 1120 cm<sup>-1</sup>; IVn: 2900, 1600 and 1060 cm<sup>-1</sup>.

<sup>b</sup> Based on III.

<sup>c</sup> Compounds IVa–f: in D<sub>2</sub>O, DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as an internal standard and IVg–l in CD<sub>3</sub>OD, tetramethylsilane. Abbreviation: NMR, nuclear magnetic resonance.

<sup>d</sup> Calculated values of IVn are based on the assumption that this contains one mole of water. This compound is highly hygroscopic.

kinds of oxocarboxylates (II) and the alkyl group of I did not affect the yield of III or IV. Each of the compounds, III and IV, consisted of a mixture of diastereoisomers. For IIIb, e, i, l and IVb, e, i, l derived from acetoacetate (IIb), two singlet peaks assigned to the methylene protons between the ring and the carbonyl group were detected. But, the apparent information about the diastereoisomers of other compounds was not obtained because the <sup>1</sup>H-NMR signals assigned to these protons overlapped other peaks.

The plots of surface tension *vs.* concentration for a series of compounds IV and sodium dodecanoate are shown in Figure 2. The T<sub>Kp</sub>, the critical micelle concentration (CMC), the ability to lower surface tension (γ<sub>CMC</sub>) and the area per molecule at the surface calculated from the Gibbs adsorption equation (29) of compounds IV are summarized in Table 3, along with the reference data for sodium dodecanoate measured under the same conditions.

Compounds IVa–j and IVn are freely soluble in water

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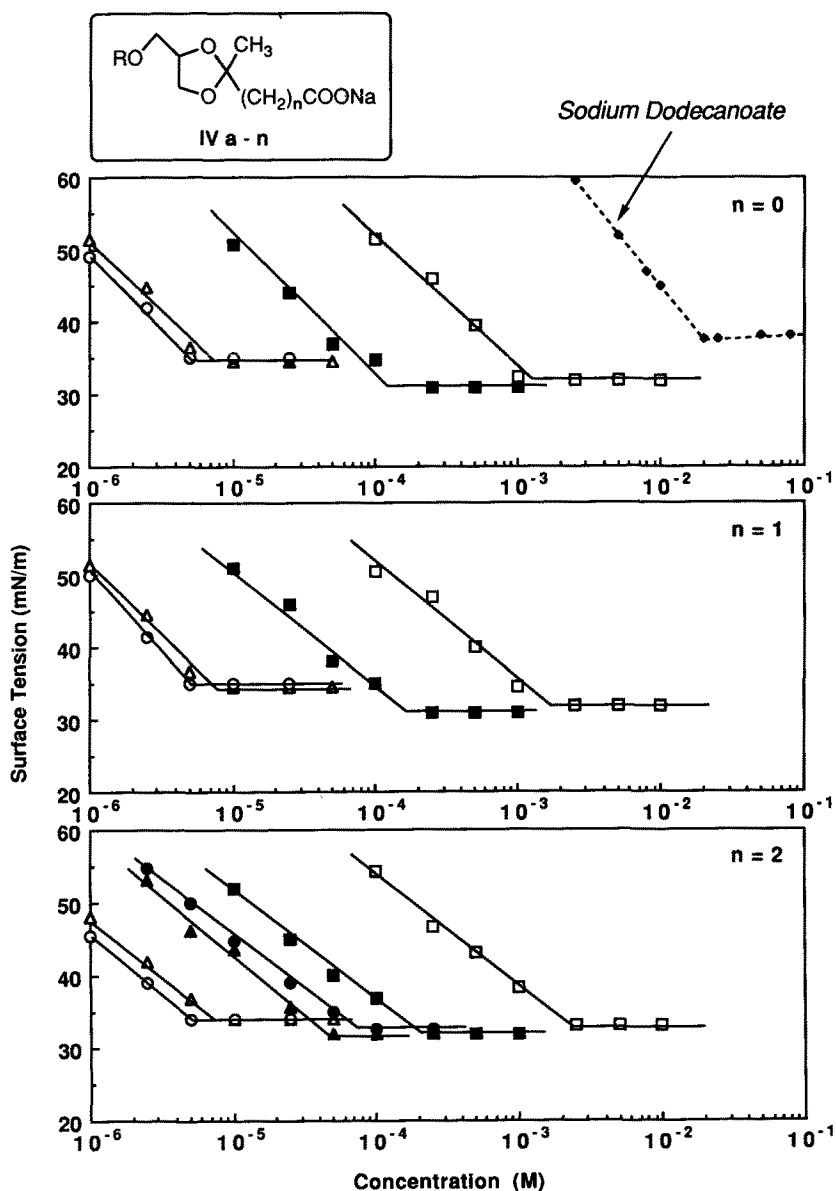


FIG. 2. Surface tension-concentration plots of aqueous surfactant solutions of compounds IV at pH 12.  $\square$ : R =  $C_{10}H_{21}$ ,  $\blacksquare$ :  $C_{12}H_{25}$ ,  $\blacktriangle$ :  $C_{14}H_{29}$ ,  $\triangle$ :  $C_{16}H_{33}$ ,  $\circ$ :  $C_{18}H_{37}$ ,  $\bullet$ :  $C_{18}H_{35}$ .

at 1 wt% concentration (i.e.  $T_{Kp} < 0^\circ C$ ). The other compounds IVk-m, which have an octadecyl group, are soluble in water at any temperature at 0.1 wt%. Compounds IV have higher water solubility than sodium dodecanoate, which has relatively good water solubility among the conventional soaps. It is surmised that the 1,3-dioxolane ring and the ether oxygen in the side chain contribute to the increase in hydrophilicity of the molecules.

The CMC values of these compounds IV are surprisingly smaller than that of sodium dodecanoate. The CMC value of sodium dodecanoate is about ten times as high as those of compounds IVa-c, which show higher CMC's than other compounds IV. Among IVa-m, the CMC values of the compounds with the same "n" value decrease with an increase in the length of the alkyl chain (R). However, among IVh-m, which have a hexadecyl or an octadecyl

chain, the difference in the CMC values between these compounds becomes small. The change in the "n" value seems to hardly affect the CMC. Especially the CMC values of compounds IVk (n = 0), IVl (n = 1) and IVm (n = 2), each of which has an octadecyl group, which are almost the same. The CMC of IVn bearing an octadecenyl (oleyl) group is one order of magnitude larger than that of the corresponding IVm bearing a saturated octadecyl chain.

The  $\gamma_{CMC}$  values of these compounds IV are smaller than that of sodium dodecanoate. Clear correlation between the  $\gamma_{CMC}$  and the length of the alkyl chain (R) or the number of "n" is not observed. The area per molecule at the surface (A) of the compounds IV is larger than that of sodium dodecanoate, probably because of the existence of the bulky 1,3-dioxolane ring in the molecule. Their A values gradually decrease with an increase in the length

TABLE 3

Surface-Active Properties of Sodium Carboxylates (IV)<sup>a</sup>

Compound	R	n	T <sub>Kp</sub> <sup>b</sup> (°C)	10 <sup>3</sup> CMC (mol/L)	γ <sub>CMC</sub> (mN/m)	10 <sup>2</sup> A (nm <sup>2</sup> )
IVa	C <sub>10</sub> H <sub>21</sub>	0	<0	1.2	32.0	106
IVb	C <sub>10</sub> H <sub>21</sub>	1	<0	1.7	32.0	116
IVc	C <sub>10</sub> H <sub>21</sub>	2	<0	2.3	33.0	124
IVd	C <sub>12</sub> H <sub>25</sub>	0	<0	0.12	31.0	98
IVe	C <sub>12</sub> H <sub>25</sub>	1	<0	0.16	31.0	113
IVf	C <sub>12</sub> H <sub>25</sub>	2	<0	0.20	32.0	124
IVg	C <sub>14</sub> H <sub>29</sub>	2	<0	0.046	32.0	120
IVh	C <sub>16</sub> H <sub>33</sub>	0	<0	0.0070	35.0	96
IVi	C <sub>16</sub> H <sub>33</sub>	1	<0	0.0076	34.5	98
IVj	C <sub>16</sub> H <sub>33</sub>	2	<0	0.0080	34.0	120
IVk	C <sub>18</sub> H <sub>37</sub>	0	<0 <sup>c</sup>	0.0050	35.0	93
IVl	C <sub>18</sub> H <sub>37</sub>	1	<0 <sup>c</sup>	0.0050	35.0	93
IVm	C <sub>18</sub> H <sub>37</sub>	2	<0 <sup>c</sup>	0.0050	34.0	116
IVn	C <sub>18</sub> H <sub>35</sub>	2	<0	0.070	32.5	120
(Reference: typical soap)						
C <sub>11</sub> H <sub>23</sub> COONa			19	20	37.5	69

<sup>a</sup> At 20°C, pH 12. Abbreviations: T<sub>Kp</sub>, Krafft point; CMC, critical micelle concentration.

<sup>b</sup> At 1 wt%.

<sup>c</sup> At 0.1 wt%. These compounds were insoluble in alkaline water at 1 wt% at any temperature.

of the alkyl chain, as do typical surfactants, because the hydrophobic interaction between the adsorbed surfactant molecules on the surface may increase (29). The A values of the compounds IV derived from levulinate (n = 2) are larger than the compounds IV with the corresponding alkyl chain derived from the other oxocarboxylates (n = 0 or 1).

The foaming ability and foam stability of compounds IV are summarized in Table 4 along with the data for sodium dodecanoate.

The foam stability of compounds derived from levulinate (n = 2) is somewhat lower than that of the compounds bearing the corresponding alkyl chain derived from the other oxocarboxylates (n = 0 or 1) in the range from IVa to IVj. Interestingly, all compounds bearing an octadecyl group (IVk–m) are nonfoaming. It has also been reported that for sodium alkyl carboxylate homologues the foaming ability of sodium tetradecanoate is the maximum and that of sodium hexadecanoate falls drastically (30). The compound IVn bearing an unsaturated oleyl group is placed between IVf and IVg with the same "n" number among the homologues of IV bearing a saturated alkyl group with respect to the CMC, γ<sub>CMC</sub> and foaming properties.

The detergency of several compounds IV and the reference soap for the artificially soiled cloth is summarized in Table 5.

The detergency of these compounds IV in 50-ppm hard water is almost the same as that of the reference soap. In 100-ppm hard water, however, all compounds except IVl showed higher detergency than the reference soap. In the range of this work, it is recognized that the compounds IV bearing a shorter alkyl chain have excellent detergency in 100-ppm hard water. The solubility in hard water

TABLE 4

Foaming Properties of Sodium Carboxylates (IV)<sup>a</sup>

Compound	R	n	Foam volume (mL) per min			
			0	3	5	10
IVa	C <sub>10</sub> H <sub>21</sub>	0	250	240	200	200
IVb	C <sub>10</sub> H <sub>21</sub>	1	240	200	200	150
IVc	C <sub>10</sub> H <sub>21</sub>	2	270	120	100	100
IVd	C <sub>12</sub> H <sub>25</sub>	0	270	270	270	270
IVe	C <sub>12</sub> H <sub>25</sub>	1	260	260	260	260
IVf	C <sub>12</sub> H <sub>25</sub>	2	280	200	130	120
IVg	C <sub>14</sub> H <sub>29</sub>	2	260	260	200	160
IVh	C <sub>16</sub> H <sub>33</sub>	0	270	270	270	270
IVi	C <sub>16</sub> H <sub>33</sub>	1	260	260	260	260
IVj	C <sub>16</sub> H <sub>33</sub>	2	240	210	210	180
IVk	C <sub>18</sub> H <sub>37</sub>	0	0	—	—	—
IVl	C <sub>18</sub> H <sub>37</sub>	1	0	—	—	—
IVm	C <sub>18</sub> H <sub>37</sub>	2	0	—	—	—
IVn	C <sub>18</sub> H <sub>35</sub>	2	270	180	120	80
(Reference: typical soap)						
C <sub>11</sub> H <sub>23</sub> COONa <sup>b</sup>			200	200	190	100

<sup>a</sup> At 20°C, pH 12, 0.1 wt%.

<sup>b</sup> At 1 wt%. This compound was nonfoaming at 0.1 wt%.

TABLE 5

## Detergency of Sodium Carboxylates

Compound	R	n	Detergency (%)	
			at 50 ppm <sup>a</sup>	at 100 ppm <sup>a</sup>
IVf	C <sub>12</sub> H <sub>25</sub>	2	76.3	75.3
IVh	C <sub>16</sub> H <sub>33</sub>	0	74.8	70.0
IVi	C <sub>16</sub> H <sub>33</sub>	1	78.8	71.4
IVj	C <sub>16</sub> H <sub>33</sub>	2	78.0	68.4
IVl	C <sub>18</sub> H <sub>37</sub>	1	76.7	59.4
IVm	C <sub>18</sub> H <sub>37</sub>	2	76.2	66.4
Reference soap			77.2	63.1

<sup>a</sup> Total hardness of the examined solution as CaCO<sub>3</sub>.

for some compounds IV was evaluated by the modified Hart method (31,32). For conventional sodium carboxylates, insoluble calcium soap began to precipitate at 250 ppm (for sodium dodecanoate) and 340 ppm (for sodium oleate) of total hardness as CaCO<sub>3</sub>. Compared to these results, compound IVf bearing a dodecyl group remained soluble in hard water up to 500 ppm of total hardness. It is predicted that the 1,3-dioxolane ring may make a positive contribution to the solubility in hard water.

Finally, the decomposition property of three compounds IVa,b,c bearing a decyl group in D<sub>2</sub>O by the addition of DCl was measured by <sup>1</sup>H-NMR. Figure 3 shows selected <sup>1</sup>H-NMR spectral changes of IVc at pH 1 as an example. The peaks assigned to the three kinds of protons (H<sub>4</sub>, H<sub>5A</sub>, H<sub>5B</sub>) in the dioxolane ring of compound IVc gradually disappeared with time. Also, the original peak at δ 2.22 assigned to the methylene protons at the α-position to the carboxylate group immediately shifted to δ 2.35 after the addition of DCl. This result indicates that protonation to the carboxylate group occurred. Similar spectral changes

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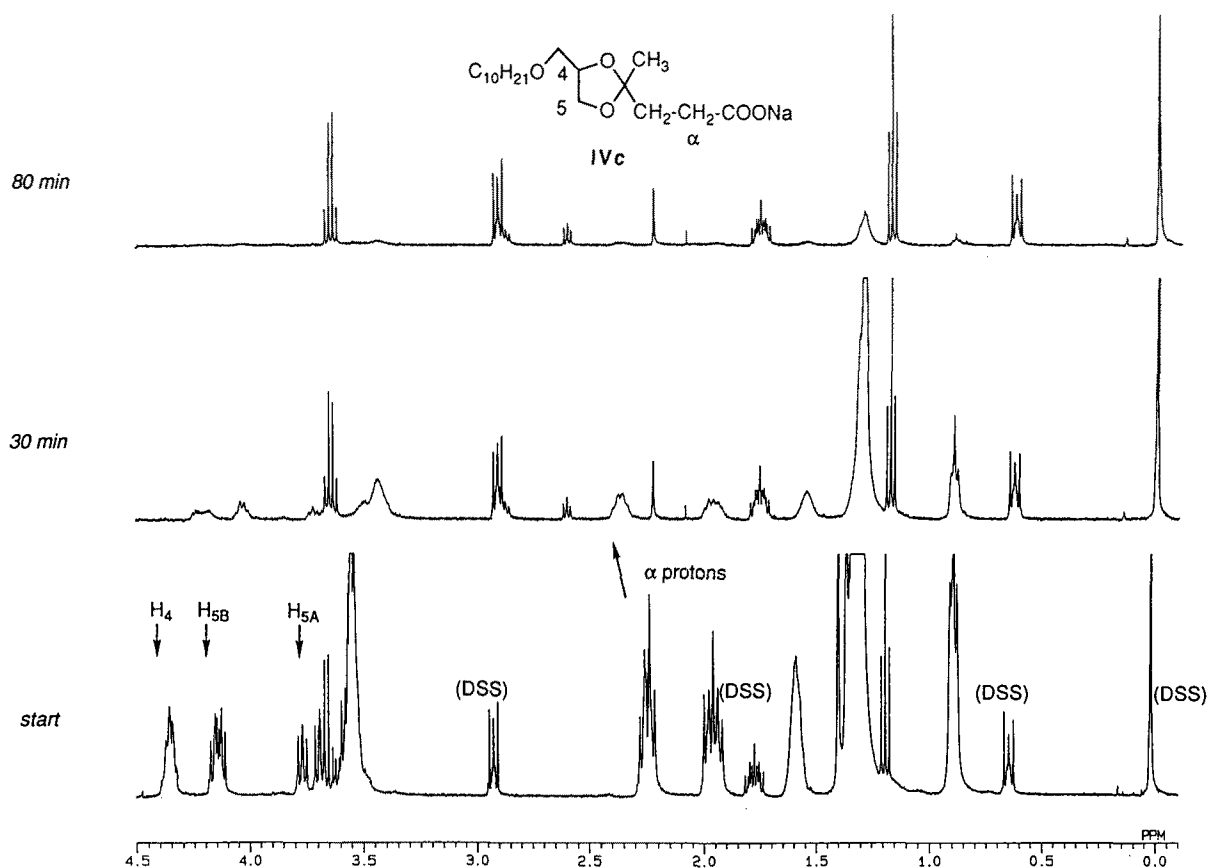


FIG. 3.  $^1\text{H}$ -nuclear magnetic resonance (NMR) spectral changes in a 20-mM  $\text{D}_2\text{O}$  solution of IVc by the addition of DCl (pD 1) at  $25^\circ\text{C}$ .

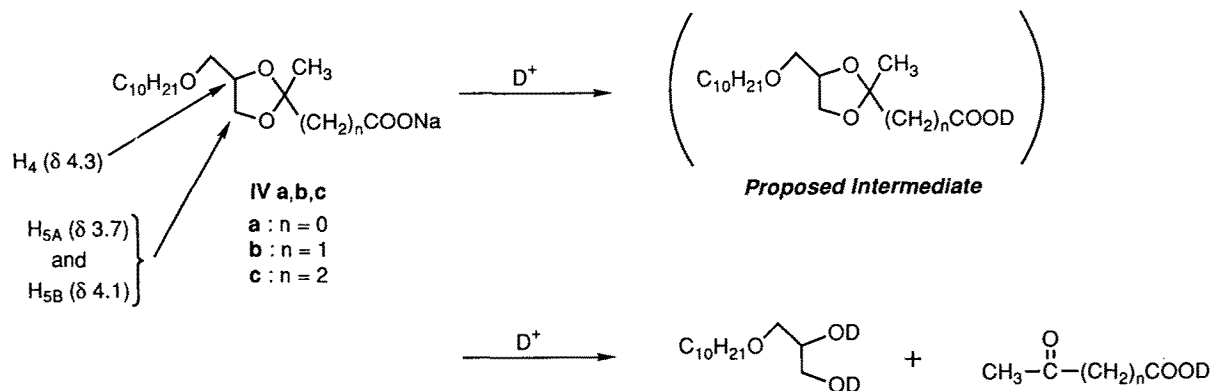


FIG. 4. A probable course of the decomposition of IVa-c.

are also observed in the case of IVa and IVb. A probable course of the decomposition based on these results is illustrated in Figure 4. First, a carboxylate group may be protonated. The decomposition of a 1,3-dioxolane group may then take place to afford 1-O-alkylglycerol and oxocarboxylic acid.

The decomposition percentage was calculated from the integrated intensity ratio of the protons on the 1,3-dioxolane ring to the methylene protons of DSS (sodium

2,2-dimethyl-2-silapentane-5-sulfonate) as an internal standard. About 90% of IVa-c decomposed after 30 min, and they were almost completely decomposed after 80 min at pD 1. At pD 3, however, these compounds IVa-c were stable in the form of free acid (in the style of the proposed intermediate in Fig. 4), and hydrolysis of the 1,3-dioxolane ring was not observed for a week. Finally, it has been confirmed that these compounds IV are stable at ambient temperature for at least five months.

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