

Novel Hydrolyzable and Biodegradable Cationic Gemini Surfactants: 1,3-Bis[(acyloxyalkyl)-dimethylammonio]-2-hydroxypropane Dichloride

Taiga Tatsumi^a, Wanbin Zhang^a, Toshiyuki Kida^a, Yohji Nakatsuji^a,
Daisuke Ono^b, Tokuji Takeda^b, and Isao Ikeda^{a,*}

^aDepartment of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan, and ^bOsaka Municipal Technical Research Institute, Osaka 536-8553, Japan

ABSTRACT: Novel cationic gemini surfactants, 1,3-bis[(acyloxyalkyl)dimethylammonio]-2-hydroxypropane dichloride, which possess hydrolyzable oxycarbonyl moieties in the lipophilic portions, were prepared. These surfactants showed much better micelle-forming ability, ability to lower surface tension, foaming ability, and foam stability than corresponding single-chain surfactants. Their surface properties were largely influenced by changing the position of the oxycarbonyl group in the lipophilic moiety. The critical micelle concentration decreased with a decreasing number of methylene units in the linking moiety between the ammonio and the oxycarbonyl groups within the comparison of lipophilic chains of the same length. These cationic gemini surfactants also showed good biodegradability.

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KEY WORDS: Biodegradable surfactant, bis(ester-ammonium) salt, cationic surfactant, critical micelle concentration, gemini surfactant, hydrophile-lipophile balance, surface-active properties.

Dialkylammonium salts have been widely used in industrial and household products. Increasing usage, however, is causing environmental problems owing to poor biodegradability. Thus, much attention has been paid to the development of novel types of environmentally acceptable cationic surfactants (1). On the other hand, gemini surfactants have been studied because of their excellent surface-active properties in comparison to corresponding single-chain surfactants (2–11). We recently found that bisquaternary ammonium salts II-m (see Scheme 1 for structures) with a linking moiety of the 2-hydroxy-1,3-propylene group are easily prepared and that they possess some good properties as gemini surfactants (12–16). As a candidate for environmentally acceptable cationic surfactants, we prepared a new type of hydrolyzable cationic gemini surfactant, bis(amido-ammonium) salts II-m-n

(amide), by introducing an amido group in the lipophilic part of II-m, as reported in a previous paper (17). Contrary to our expectation, these surfactants showed poor biodegradability, though they had good surface-active properties as gemini surfactants. Here, we report another new type of cationic gemini surfactant, bis(ester-ammonium) salts II-m-n containing oxycarbonyl groups in the lipophile, which may be much easily hydrolyzed.

EXPERIMENTAL PROCEDURE

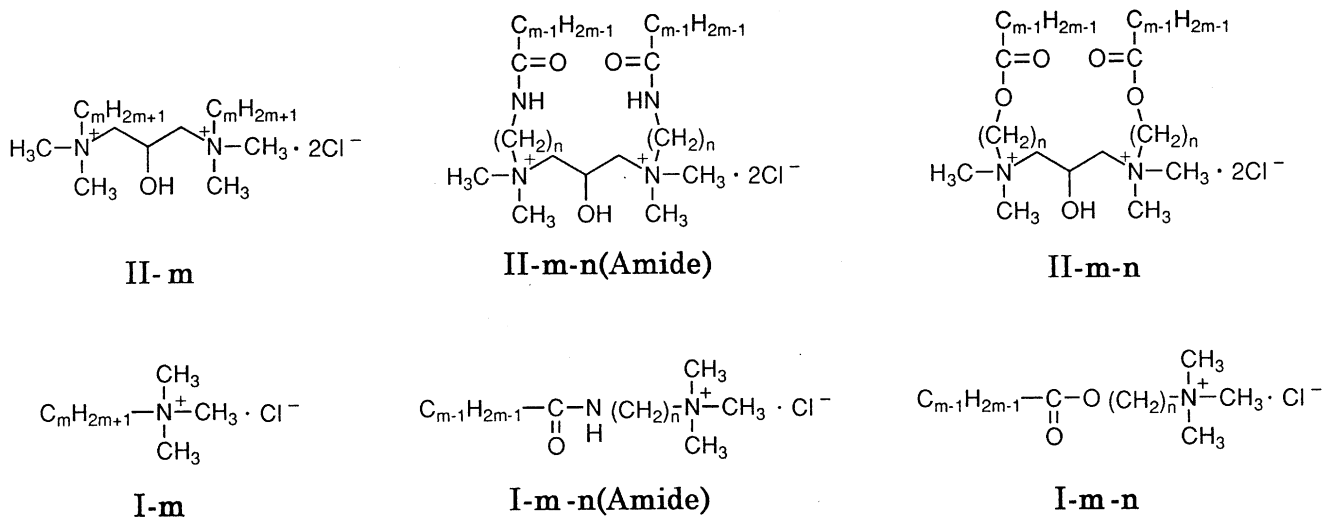
General method. Melting points were measured on a Yanagimoto (Kyoto, Japan) micromelting point apparatus and were not corrected. ¹H nuclear magnetic resonance (NMR) spectra were recorded on a JEOL GSX-400 (Tokyo, Japan) spectrometer and the chemical shifts were referenced to CHCl₃ (δ 7.27) in CDCl₃. Infrared (IR) spectra were obtained on a Hitachi (Tokyo, Japan) 260-10 IR spectrophotometer. Mass spectra were obtained on a JEOL JMS-DX303, and elemental analysis was carried out on a Yanagimoto CHN-Corder.

All chemicals used in synthetic procedures were of reagent grade. Merck, Japan (Tokyo, Japan) 70–230 mesh silica gel was used for column chromatography.

Measurement of surface-active properties. Krafft point was measured by the naked eye for each 1 wt% aqueous solution of the compound. Surface tension of an aqueous solution of quaternary ammonium salt was measured on a Shimadzu Surface Tensometer ST-1 (glass plate; Shimadzu Corp., Kyoto, Japan) at 20°C. Those values that remained constant for a period of 30 min were taken as the surface tension. Critical micelle concentration (CMC) and surface tension at the CMC (γ_{CMC}) were determined as the values at the break point of surface tension vs. concentration plots (semilogarithmic scale). Foaming properties were measured by the semimicro TK method (18) with a 0.1 wt% aqueous solution at 20°C.

Measurement of biodegradability. Biodegradability was evaluated by the oxygen consumption method. The experiment was carried out based on the modified MITI test (19).

*To whom correspondence should be addressed at the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan.
E-mail: ikeda@ap.chem.eng.osaka-u.ac.jp



SCHEME 1

Thus, the sample (30 mg) was added to a dispersion of activated sludge (1 g) in a basic culture solution. The basic culture solution was prepared according to Japan Industrial Standard (JIS) K0102. Activated sludge was obtained from a municipal sewage-treatment plant in Osaka City. The change in biochemical oxygen demand (BOD, mg) of the system was monitored with time at 25°C for 14 d. Biodegradability was estimated using the following equation:

$$\text{biodegradability (\%)} = \frac{(\text{BOD} - \text{blank}) / \text{TOD}}{\text{TOD}} \times 100\% \quad [1]$$

where TOD refers to the theoretical oxygen demand (calculated value, mg).

(2-Decanoyloxyethyl)dimethylamine (EA-10-2). A mixture of decanoic acid (12.1 g, 70 mmol), (2-hydroxyethyl)dimethylamine (12.5 g, 140 mmol), a catalytic amount of *p*-toluenesulfonic acid, and xylene was heated to reflux. The reaction was monitored by measuring the amount of water formed using a Dean-Stark trap and continued for 10 h until the acid had been consumed. After excess (2-hydroxyethyl)dimethylamine and the solvent were evaporated under reduced pressure, compound EA-10-2 was isolated as a colorless liquid (14.1 g, 83%) by fractional distillation. Boiling point (bp), 118°C/0.30 Torr. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 0.88 (*t*, 3H, *J* = 6.6 Hz, CH_3CH_2), 1.28 [*m*, 12H, $\text{CH}_3(\text{CH}_2)_6$], 1.62 (*m*, 2H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.31 [*s*, 6H, $\text{N}(\text{CH}_3)_2$], 2.33 (*t*, 2H, *J* = 7.7 Hz, $\text{CH}_2\text{C}=\text{O}$), 2.61 [*t*, 2H, *J* = 5.9 Hz, $\text{CH}_2\text{N}(\text{CH}_3)_2$], and 4.19 (*t*, 2H, *J* = 5.9 Hz, OCH_2). IR (cm^{-1}): 1739 (C=O). Mass spectrum (MS) [CI(isobutane)] *m/z* 244 [(*M* + 1)⁺, 100].

(2-Dodecanoyloxyethyl)dimethylamine (EA-12-2). Yield = 86%; bp 125°C/0.15 Torr. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 0.88 (*t*, 3H, *J* = 6.6 Hz, CH_3CH_2), 1.27 [*m*, 16H, $\text{CH}_3(\text{CH}_2)_8$], 1.63 (*m*, 2H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.31 [*s*, 6H, $\text{N}(\text{CH}_3)_2$], 2.33 (*t*, 2H, *J* =

7.7 Hz, $\text{CH}_2\text{C}=\text{O}$), 2.60 [*t*, 2H, *J* = 5.9 Hz, $\text{CH}_2\text{N}(\text{CH}_3)_2$], and 4.19 (*t*, 2H, *J* = 5.9 Hz, OCH_2). IR (cm^{-1}): 1739 (C=O). MS [CI(isobutane)] *m/z* 272 [(*M* + 1)⁺, 100].

(2-Tetradecanoyloxyethyl)dimethylamine (EA-14-2). Yield = 91%; bp 132°C/0.15 Torr. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 0.89 (*t*, 3H, *J* = 6.6 Hz, CH_3CH_2), 1.29 [*m*, 20H, $\text{CH}_3(\text{CH}_2)_{10}$], 1.61 (*m*, 2H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.31 [*s*, 6H, $\text{N}(\text{CH}_3)_2$], 2.33 (*t*, 2H, *J* = 7.7 Hz, $\text{CH}_2\text{C}=\text{O}$), 2.61 [*t*, 2H, *J* = 5.9 Hz, $\text{CH}_2\text{N}(\text{CH}_3)_2$], and 4.19 (*t*, 2H, *J* = 5.9 Hz, OCH_2). IR (cm^{-1}): 1739 (C=O). MS [CI(isobutane)] *m/z* 300 [(*M* + 1)⁺, 100].

(2-Hexadecanoyloxyethyl)dimethylamine (EA-16-2). Yield = 86%; bp 136°C/0.10 Torr. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 0.88 (*t*, 3H, *J* = 6.6 Hz, CH_3CH_2), 1.29 [*m*, 24H, $\text{CH}_3(\text{CH}_2)_{12}$], 1.63 (*m*, 2H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.30 [*s*, 6H, $\text{N}(\text{CH}_3)_2$], 2.32 (*t*, 2H, *J* = 7.6 Hz, $\text{CH}_2\text{C}=\text{O}$), 2.59 [*t*, 2H, *J* = 5.9 Hz, $\text{CH}_2\text{N}(\text{CH}_3)_2$], and 4.19 (*t*, 2H, *J* = 5.9 Hz, OCH_2). IR (cm^{-1}): 1739 (C=O). MS [CI(isobutane)] *m/z* 328 [(*M* + 1)⁺, 100].

(4-Decanoyloxybutyl)dimethylamine (EA-10-4). Yield = 82%; bp 51°C/0.06 Torr. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 0.89 (*t*, 3H, *J* = 6.6 Hz, CH_3CH_2), 1.29 [*m*, 12H, $\text{CH}_3(\text{CH}_2)_6$], 1.62 (*m*, 6H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$, OCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{N}$), 2.27 [*s*, 6H, $\text{N}(\text{CH}_3)_2$], 2.30 [*m*, 4H, $\text{CH}_2\text{C}=\text{O}$, $\text{CH}_2\text{N}(\text{CH}_3)_2$], and 4.09 (*t*, 2H, *J* = 6.0 Hz, OCH_2). IR (cm^{-1}): 1729 (C=O). MS [CI(isobutane)] *m/z* 272 [(*M* + 1)⁺, 100].

(6-Octanoyloxyhexyl)dimethylamine (EA-8-6). Yield = 81%; bp 72°C/0.06 Torr. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 0.88 (*t*, 3H, *J* = 6.6 Hz, CH_3CH_2), 1.32 [*m*, 12H, $\text{CH}_3(\text{CH}_2)_4$, $\text{OCH}_2\text{CH}_2\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$], 1.61 (*m*, 6H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$, OCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{N}$), 2.25 [*s*, 6H, $\text{N}(\text{CH}_3)_2$], 2.29 [*m*, 4H, $\text{CH}_2\text{C}=\text{O}$, $\text{CH}_2\text{N}(\text{CH}_3)_2$], and 4.09 (*t*, 2H, *J* = 6.0 Hz, OCH_2). IR (cm^{-1}): 1728 (C=O). MS [CI(isobutane)] *m/z* 272 [(*M* + 1)⁺, 100].

1,3-Bis[(2-decanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride (II-10-2). A mixture of epichlorohydrin (0.19 g, 2.0 mmol), (2-decanoyloxyethyl)dimethylamine

EA-10-2 (1.46 g, 6.0 mmol), and the hydrochloride of EA-10-2 (0.56 g, 2.0 mmol) in 2-propanol (6 mL) was heated to reflux for 72 h. After the solvent was removed under reduced pressure, the waxy product was washed with hexane and purified by silica gel column chromatography with a chloroform/methanol mixture (9:1, vol/vol) to give II-10-2 as a white solid (0.48 g, 39%); mp 126–130°C. ^1H NMR (CDCl_3 , 400 MHz) δ 0.89 (*t*, 6H, $J = 6.6$ Hz, CH_3CH_2), 1.28 [*m*, 24H, $\text{CH}_3(\text{CH}_2)_6$], 1.60 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.36 (*t*, 4H, $J = 7.7$ Hz, $\text{CH}_2\text{C}=\text{O}$), 3.49 (*s*, 6H, N^+CH_3), 3.53 (*s*, 6H, N^+CH_3), 3.80 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 4.05 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{N}^+$), 4.19 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 4.63 (*m*, 4H, OCH_2), 5.19 (*m*, 1H, CHOH), and 7.13 (*br*, 1H, OH). IR (cm^{-1}): 1739 ($\text{C}=\text{O}$). MS (FAB) m/z 579 [$(\text{M} - \text{Cl})^+$, 7]. Anal. calcd. for $\text{C}_{31}\text{H}_{64}\text{O}_5\text{N}_2\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$: C, 59.60; H, 10.49; N, 4.48; Cl, 11.35. Found: C, 59.31; H, 10.23; N, 4.58; Cl, 11.01.

1,3-Bis[(2-dodecanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride (II-12-2). Yield = 53%; mp 158–162°C. ^1H NMR (CDCl_3 , 400 MHz) δ 0.89 (*t*, 6H, $J = 6.6$ Hz, CH_3CH_2), 1.28 [*m*, 32H, $\text{CH}_3(\text{CH}_2)_8$], 1.60 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.36 (*t*, 4H, $J = 7.7$ Hz, $\text{CH}_2\text{C}=\text{O}$), 3.49 (*s*, 6H, N^+CH_3), 3.53 (*s*, 6H, N^+CH_3), 3.80 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 4.05 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{N}^+$), 4.16 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 4.63 (*m*, 4H, OCH_2), 5.20 (*m*, 1H, CHOH), and 7.04 (*br*, 1H, OH). IR (cm^{-1}): 1739 ($\text{C}=\text{O}$). MS (FAB) m/z 635 [$(\text{M} - \text{Cl})^+$, 6]. Anal. calcd. for $\text{C}_{35}\text{H}_{72}\text{O}_5\text{N}_2\text{Cl}_2 \cdot 2.3\text{H}_2\text{O}$: C, 58.93; H, 10.82; N, 3.93; Cl, 9.94. Found C, 58.64; H, 10.44; N, 3.75; Cl, 10.32.

1,3-Bis[(2-tetradecanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride (II-14-2). Yield = 62%; mp 164–166°C. ^1H NMR (CDCl_3 , 400 MHz) δ 0.88 (*t*, 6H, $J = 6.6$ Hz, CH_3CH_2), 1.27 [*m*, 40H, $\text{CH}_3(\text{CH}_2)_{10}$], 1.60 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.36 (*t*, 4H, $J = 7.7$ Hz, $\text{CH}_2\text{C}=\text{O}$), 3.47 (*s*, 6H, N^+CH_3), 3.52 (*s*, 6H, N^+CH_3), 3.79 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 4.05 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{N}^+$), 4.21 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 4.62 (*m*, 4H, OCH_2), 5.19 (*m*, 1H, CHOH), and 7.16 (*br*, 1H, OH). IR (cm^{-1}): 1739 ($\text{C}=\text{O}$). MS (FAB) m/z 691 [$(\text{M} - \text{Cl})^+$, 4]. Anal. calcd. for $\text{C}_{39}\text{H}_{80}\text{O}_5\text{N}_2\text{Cl}_2 \cdot 0.6\text{H}_2\text{O}$: C, 63.40; H, 11.08; N, 3.79; Cl, 9.60. Found: C, 63.06; H, 10.69; N, 3.95; Cl, 9.56.

1,3-Bis[(2-hexadecanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride (II-16-2). Yield = 45%; mp 176–179°C. ^1H NMR (CDCl_3 , 400 MHz) δ 0.88 (*t*, 6H, $J = 6.6$ Hz, CH_3CH_2), 1.28 [*m*, 48H, $\text{CH}_3(\text{CH}_2)_{12}$], 1.60 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.36 (*t*, 4H, $J = 7.7$ Hz, $\text{CH}_2\text{C}=\text{O}$), 3.46 (*s*, 6H, N^+CH_3), 3.53 (*s*, 6H, N^+CH_3), 3.79 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 4.03 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{N}^+$), 4.22 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 4.63 (*m*, 4H, OCH_2), 5.22 (*m*, 1H, CHOH), and 7.42 (*br*, 1H, OH). IR (cm^{-1}): 1739 ($\text{C}=\text{O}$). MS (FAB) m/z 747 [$(\text{M} - \text{Cl})^+$, 3]. Anal. calcd. for $\text{C}_{43}\text{H}_{88}\text{O}_5\text{N}_2\text{Cl}_2 \cdot 1.7\text{H}_2\text{O}$: C, 63.39; H, 11.31; N, 3.44; Cl, 8.70. Found C, 63.25; H, 10.99; N, 3.61; Cl, 9.07.

1,3-Bis[(4-decanoyloxybutyl)dimethylammonio]-2-hydroxypropane dichloride (II-10-4). Yield = 67%; mp 165–167°C. ^1H NMR (CDCl_3 , 400 MHz) δ 0.89 (*t*, 6H, $J = 6.6$ Hz, CH_3CH_2), 1.28 [*m*, 24H, $\text{CH}_3(\text{CH}_2)_6$], 1.60 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 1.91 (*m*, 8H, OCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{N}^+$), 2.34 (*t*, 4H, $J = 7.5$ Hz, $\text{CH}_2\text{C}=\text{O}$), 3.39 (*s*, 6H, N^+CH_3), 3.46 (*s*, 6H, N^+CH_3), 3.63 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{N}^+$), 3.70 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 4.17 (*t*, 4H, J

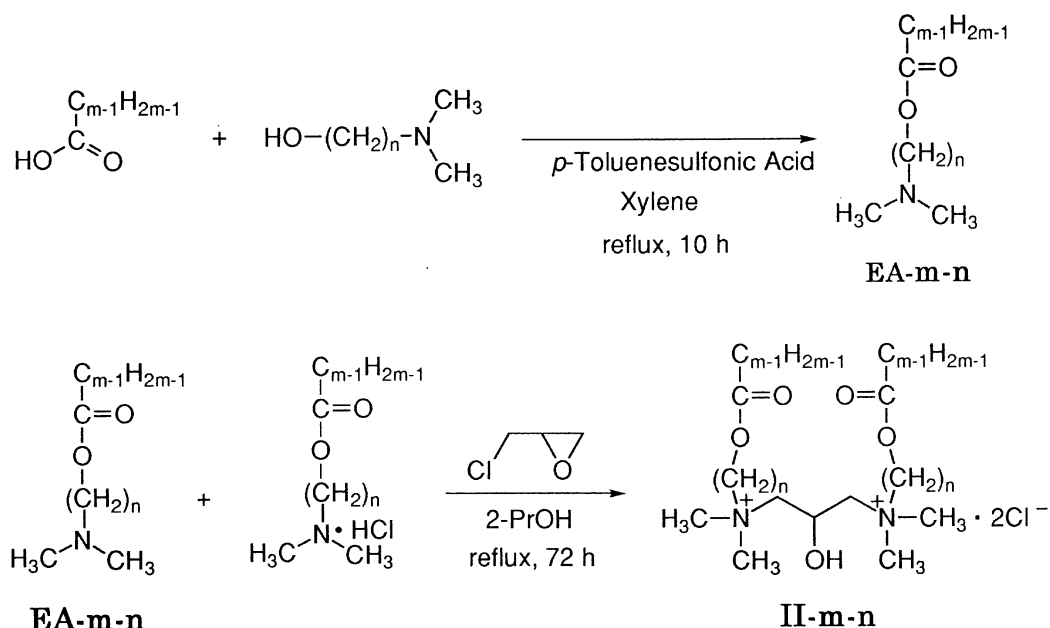
= 6.0 Hz, OCH_2), 4.44 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 5.21 (*m*, 1H, CHOH), and 7.36 (*br*, 1H, OH). IR (cm^{-1}): 1729 ($\text{C}=\text{O}$). MS (FAB) m/z 635 [$(\text{M} - \text{Cl})^+$, 5]. Anal. calcd. for $\text{C}_{35}\text{H}_{72}\text{O}_5\text{N}_2\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$: C, 60.15; H, 10.82; N, 4.01; Cl, 10.15. Found C, 59.78; H, 10.55; N, 4.22; Cl, 10.34.

1,3-Bis[(6-octanoyloxyhexyl)dimethylammonio]-2-hydroxypropane dichloride (II-8-6). Yield = 78%; mp 172–175°C. ^1H NMR (CDCl_3 , 400 MHz) δ 0.89 (*t*, 6H, $J = 6.6$ Hz, CH_3CH_2), 1.28 [*m*, 16H, $\text{CH}_3(\text{CH}_2)_4$], 1.44 (*m*, 8H, $\text{OCH}_2\text{CH}_2\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+$), 1.63 (*m*, 8H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$, $\text{CH}_2\text{CH}_2\text{N}^+$), 1.82 (*m*, 4H, OCH_2CH_2), 2.30 (*t*, 4H, $J = 7.6$ Hz, $\text{CH}_2\text{C}=\text{O}$), 3.29 (*s*, 6H, N^+CH_3), 3.34 (*s*, 6H, N^+CH_3), 3.57 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{N}^+$), 3.64 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 4.06 (*t*, 4H, $J = 6.0$ Hz, OCH_2), 4.26 [*m*, 2H, $\text{CH}(\text{OH})\text{CHN}^+$], 5.17 (*m*, 1H, CHOH), and 7.22 (*br*, 1H, OH). IR (cm^{-1}): 1728 ($\text{C}=\text{O}$). MS (FAB) m/z 635 [$(\text{M} - \text{Cl})^+$, 2]. Anal. Calcd. for $\text{C}_{35}\text{H}_{72}\text{O}_5\text{N}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$: C, 57.91; H, 10.83; N, 3.86; Cl, 9.77. Found C, 57.72; H, 10.58; N, 3.64; Cl, 10.06.

Synthesis of (2-dodecanoyloxyethyl)trimethylammonium chloride (I-12-2). An excess amount of chloromethane was condensed into a solution of (2-dodecanoyloxyethyl)dimethylamine EA-12-2 (1.36 g, 5.0 mmol) in 2-propanol (20 mL) in a sealed glass tube. The mixture was stirred at 50°C for 24 h. After the solvent and unreacted chloromethane were evaporated under reduced pressure, the residue was purified by recrystallization from 20 mL of an acetone/2-propanol mixture (19:1, vol/vol) to afford I-12-2 as a white solid (1.29 g, 80%); mp 63–65°C. ^1H NMR (CDCl_3 , 400 MHz) δ 0.88 (*t*, 3H, $J = 6.6$ Hz, CH_3CH_2), 1.26 [*m*, 16H, $\text{CH}_3(\text{CH}_2)_8$], 1.61 (*m*, 2H, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.36 (*t*, 2H, $J = 7.7$ Hz, $\text{CH}_2\text{C}=\text{O}$), 3.55 [*s*, 9H, $\text{N}^+(\text{CH}_3)_3$], 4.14 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{N}^+$), and 4.56 (*t*, 2H, $J = 5.6$ Hz, OCH_2). IR (cm^{-1}): 1743 ($\text{C}=\text{O}$). MS (FAB) m/z 286 [$(\text{M} - \text{Cl})^+$, 100]. Anal. calcd. for $\text{C}_{17}\text{H}_{36}\text{ClNO}_2 \cdot 0.5\text{H}_2\text{O}$: C, 61.70; H, 11.27; N, 4.23; Cl, 10.71. Found C, 61.50; H, 11.11; N, 4.05; Cl, 10.97.

RESULTS AND DISCUSSION

Preparation of bis(ester-ammonium) salts (II-m-n). The starting amine EA-m-n, (n-acyloxyalkyl)dimethylamine, was prepared by heating a mixture of a fatty acid and two molar amounts of (n-hydroxyalkyl)dimethylamine in the presence of a catalytic amount of *p*-toluenesulfonic acid in xylene. The reaction was monitored by measuring the amount of water produced and thus continued for 10 h. All products were purified by vacuum distillation and used for the next step. Bis(ester-ammonium) salt II-m-n was obtained from the reaction of EA-m-n and the hydrochloride of EA-m-n with epichlorohydrin in 2-propanol at reflux temperature for 72 h (Scheme 2). In this case, an excess of the amine was found to be necessary for completing the reaction within a reasonable time by using different stoichiometries of the starting amine and hydrochloride. Thus, the stoichiometry was established to be 2:1. When ethanol was used as the solvent, formation of the ethyl ester of the corresponding fatty acid caused by the transesterification of



SCHEME 2

EA-m-n was observed. Compounds II-m-n were purified by silica gel column chromatography and all structures were ascertained by ^1H NMR and IR spectroscopy, mass spectrometry, and elemental analysis. To estimate the performance of the novel gemini cationic surfactants, the corresponding mono(ester-ammonium) salt, (2-dodecanoyloxyethyl)dimethylammonium chloride I-12-2, also was

prepared as a reference surfactant by quaternization of EA-12-2 with chloromethane.

Surface-active properties. Values of Krafft point (T_{Kp}), CMC, γ_{CMC} , and foaming properties of bis(ester-ammonium) salts II-m-n are shown in Table 1, along with data for some reference compounds. Krafft points for these surfactants, except II-16-2, were below 0°C , which indicates good

TABLE 1
Surface-Active Properties of Ammonium Salts (at 20°C)^a

Compound	T_{Kp} ($^\circ\text{C}$)	CMC (mM)	γ_{CMC} (mN/m)	Foam (mL) ^b	
				0 min	10 min
II-10-2	<0	1.09	30	260	220
II-12-2	<0	0.082	32	270	260
II-14-2	<0	0.021	30	140	80
II-16-2	28	— ^c	— ^c	— ^c	— ^c
II-10-4	<0	0.17	34	50	0
II-8-6	<0	0.79	34	50	0
I-12-2	<0	0.69	30	20	0
II-12-2(amide) ^d	<0	0.19	33	260	240
I-12-2(amide) ^d	<0	6.1	35	20	0
II-12 ^e	<0	0.14	39	270	270
I-12 ^f	<0	4.5	— ^c	20	0

^a T_{Kp} , Krafft point; CMC, critical micelle concentration; γ_{CMC} , surface tension at CMC. **II-10-2**, 1,3-bis[(2-decanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride; **II-12-2**, 1,3-bis[(2-dodecanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride; **II-14-2**, 1,3-bis[(2-tetradecanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride; **II-16-2**, 1,3-bis[(2-hexadecanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride; **II-10-4**, 1,3-bis[(4-decanoyloxybutyl)dimethylammonio]-2-hydroxypropane dichloride; **II-8-6**, 1,3-bis[(6-octanoyloxyhexyl)dimethylammonio]-2-hydroxypropane dichloride; **I-12-2**, (2-dodecanoyloxyethyl)trimethylammonium chloride; **II-12-2 (amide)**, 1,3-bis[(2-dodecanoylaminoethyl)dimethylammonio]-2-hydroxypropane dichloride; **I-12-2 (amide)**, (2-dodecanoylaminoethyl)trimethylammonium chloride; **II-12**, 1,3-bis(dodecyltrimethylammonio)-2-hydroxypropane dichloride; **I-12**, dodecyltrimethylammonium chloride.

^b0.1 wt% aqueous solution.

^cNot evaluated.

^dSee Reference 17.

^eSee Reference 15.

^fSee Reference 20.

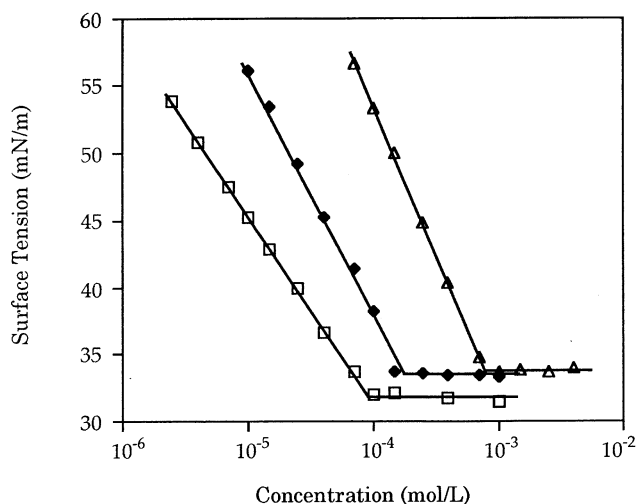


FIG. 1. Plots of surface tension vs. logarithm of concentration of (□) 1,3-bis[(2-dodecanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride (II-12-2), (◆) 1,3-bis[(4-decanoyloxybutyl)dimethylammonio]-2-hydroxypropane dichloride (II-10-4), (△) 1,3-bis[(6-octanoyloxyhexyl)dimethylammonio]-2-hydroxypropane dichloride (II-8-6).

solubility of this type of surfactant in water, enabling them to be used in cold water. The CMC of bis(ester-ammonium) salt II-12-2 was lower than that of the corresponding mono(ester-ammonium) salt I-12-2. This is in accordance with the general tendency observed in a variety of gemini surfactants (2–4), in addition to the cases for II-m and I-m and for II-m-n(amide) and I-m-n(amide), as cited in Table 1, although the extent of the difference in the CMC varied depending on the type surfactant. The ability of bis(ester-ammonium) salt II-12-2 to lower surface tension (γ_{CMC}) was found to be better than that of the bis(amido-ammonium) salt II-m-n(amide) and the bis(alkylammonium) salt II-m. The value of γ_{CMC} of mono(ester-ammonium) salt I-m-n is 30 mN/m, which is much lower than that of I-m-n(amide) (35 mN/m). Accordingly, the ability to lower the surface tension of II-m-n may be ascribed to the introduction of the oxycarbonyl group to the lipophile. A remarkable difference was observed in comparison of the foaming ability and foam stability between bisquaternary ammonium salts [II-m, II-m-n(amide) and II-m-n] and single-chain ammonium salts [I-m, I-m-n(amide), and I-m-n]. Cationic gemini surfactants showed much better foaming ability and foam stability than the conventional ones, and surpass those of anionic surfactants, which generally show good foaming properties. High foaming ability and foam stability are characteristics of bisquaternary ammonium salts.

Effect of the position of the oxycarbonyl group in the lipophile. It was clarified that the oxycarbonyl group position in the lipophile of the bis(ester-ammonium) salts II-m-n has an effect on surface active properties by comparing three isomers (II-12-2, II-10-4, and II-8-6). Plots of molar concentration of homologs vs. surface tension at 20°C are shown in Figure 1.

The CMC value increased as a function of the number

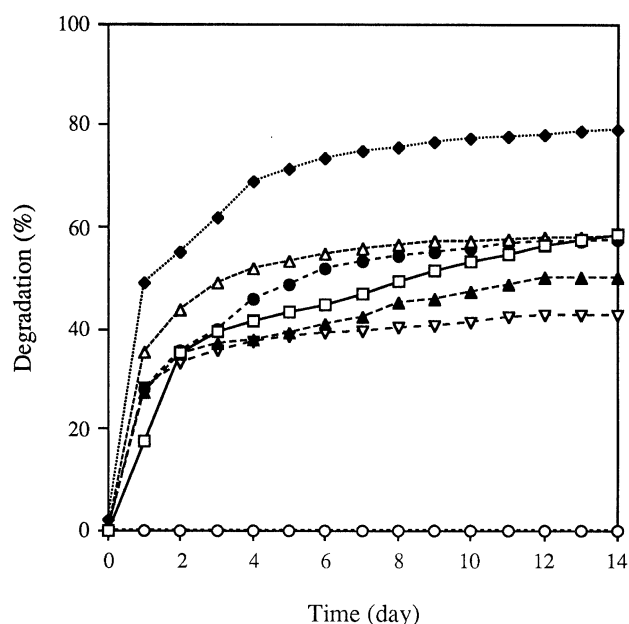


FIG. 2. Biodegradability vs. time for (△) 1,3-bis[(2-decanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride (II-10-2), (□) II-12-2, (●) II-14-2, 1,3-bis[(2-tetradecanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride, (▲) II-10-4, (▽) II-8-6, (○) 1,3-bis[(2-dodecanoyloxyethyl)dimethylammonio]-2-hydroxypropane dichloride, II-12-2(amide), and (◆) (2-dodecanoyloxyethyl)trimethylammonium chloride (I-12-2). See Scheme 1 for other compounds.

of methylene groups (n) between the oxycarbonyl group and the ammonio group when these surfactants possessed the same number of carbon atoms in the lipophile, indicating that II-12-2 has the best micelle-forming ability among the three isomers. In addition, II-12-2 showed much better ability to lower surface tension, better foaming ability, and foam stability than II-10-4 and II-8-6.

Biodegradability. Biodegradability data for bis(ester-ammonium) salt II-10-2, II-12-2, II-14-2, II-10-4, II-8-6, mono(ester-ammonium) salt I-12-2, and bis(amido-ammonium) salt II-12-2(amide) are shown in Figure 2. Contrary to our initial expectation, bis(amido-ammonium) salt II-12-2(amide) did not undergo any biodegradation under these conditions. On the other hand, both mono(ester-ammonium) salt I-12-2 and bis(ester-ammonium) salt II-12-2 showed good biodegradability. For example, the value of biodegradability of II-12-2 after 14 d was 59%, which was comparable to that of sodium dodecanoate reported as 62% (21). Biodegradability values for II-10-2 and II-14-2 were about the same as that of II-12-2. Biodegradability gradually decreased with an increase in the number of methylene groups between the oxycarbonyl group and the ammonio group when these surfactants possess the same number of carbon atoms in the lipophilic part.

In conclusion, bisquaternary ammonium salts II-m-n possessing oxycarbonyl groups in the lipophile are promising, environmentally acceptable cationic surfactants in view of their high performance and good biodegradability.

REFERENCES

- Puchta, R., P. Krings, and P. Sandkühler, A New Generation of Softeners, *Tenside Surfactants Deterg.* 30:186 (1993).
- Nakatsuji, Y., and I. Ikeda, Strategy for Innovation of Surfactant: Combination of Multiple Hydrophobic and Multiple Ionic Hydrophilic Groups, *Chimica Oggi* 15:40 (1997).
- Rosen, M.J., and D.J. Tracy, Gemini Surfactants, *J. Surfact. Deterg.* 1:547 (1998).
- Zana, R., *Dimeric (Gemini) Surfactants in Novel Surfactants*, edited by K. Holmberg, Marcel Dekker, Inc., New York, 1998, pp. 241.
- Menger, F.M., and C.A. Littau, Gemini Surfactants: Synthesis and Properties, *J. Am. Chem. Soc.* 113:1451 (1991).
- Pestman, J.M., K.R. Terpstra, M.C.A. Stuart, H.A. Doren, A. Blisson, R.M. Kellogg, and J.B.F.N. Engberts, Nonionic Bolaamphiphiles and Gemini Surfactants Based on Carbohydrates, *Langmuir* 13:6857 (1997).
- Pérez, L., A. Pinazo, M.J. Rosen, and M.R. Infante, Surface Active Properties at Equilibrium of Novel Gemini Cationic Amphiphilic Compounds from Arginine, Bis(Arg), *Ibid.* 14:2307 (1998).
- Zana, R., and Y. Talmon, Dependence of Aggregate Morphology on Structure of Dimeric Surfactants, *Nature* 362:228 (1993).
- Danino, D., Y. Talmon, and R. Zana, Vesicle-to-Micelle Transformation in Systems Containing Dimeric Surfactants, *J. Colloid Interface Sci.* 185:84 (1997).
- Dreja, M., and B. Tieke, Polymerization of Styrene in Ternary Microemulsion Using Cationic Gemini Surfactants, *Langmuir* 14:800 (1998).
- Oda, R., I. Huc, and S.J. Candau, Gemini Surfactants as New, Low Molecular Weight Gelators of Organic Solvents and Water, *Angew. Chem. Int. Ed.* 37:2689 (1998).
- Login, R.B., *bis-Quaternary Ammonium Compounds*, U.S. Patent 4,734,277 (1988).
- Login, R.B., *bis-Quaternary Ammonium Compounds*, U.S. Patent 4,812,263 (1989).
- Kim, T.-S., T. Hirao, and I. Ikeda, Preparation of bis-Quaternary Ammonium Salts from Epichlorohydrin, *J. Am. Oil Chem. Soc.* 73:67 (1996).
- Kim, T.-S., T. Kida, Y. Nakatsuji, and I. Ikeda, Surface-Active Properties of Novel Cationic Surfactants with Two Alkyl Chains and Two Ammonio Groups, *Ibid.* 73:907 (1996).
- Kim, T.-S., T. Kida, Y. Nakatsuji, and I. Ikeda, Preparation and Properties of Multiple Ammonium Salts Quaternized by Epichlorohydrin, *Langmuir* 12:6304 (1996).
- Kim, T.-S., T. Tatsumi, T. Kida, Y. Nakatsuji, and I. Ikeda, Synthesis and Surface-Active Properties of 1,3-Bis[(2-acylaminoethyl)dimethylammonio]-2-hydroxypropane Dichloride, *J. Jpn. Oil Chem. Soc. (Yukagaku)* 46:747 (1997).
- Yano, W., and W. Kimura, Studies on the Evaluation Methods of Surface Active Agents II. Foam Test: Semimicro Improved TK-Method, *Ibid.* 11:138 (1962).
- Organization for Economic Cooperation and Development, *Guidelines for Testing of Chemicals*, 301C, Modified MITI Test, Paris, 1981.
- Rosen, M.J., *Surfactants and Interfacial Phenomena*, 2nd edn., John Wiley & Sons, New York, 1988, pp. 122.
- Ono, D., S. Yamamura, M. Nakamura, T. Takeda, A. Masuyama, and Y. Nakatsuji, Biodegradation of Different Carboxylate Types of Cleavable Surfactants Bearing a 1,3-Dioxolane Ring, *J. Am. Oil Chem. Soc.* 72:853 (1995).

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Taiga Tatsumi, M.S., is a Ph.D. candidate at Osaka University. His research interest includes synthesis and properties of novel gemini surfactants.

Wanbin Zhang received his Ph.D. at Osaka University under the guidance of Professor Ikeda. He is an assistant professor at Osaka University. His research interests are in the area of industrial organic chemistry and organometallic chemistry.

Toshiyuki Kida received his Ph.D. at Osaka University under the guidance of Professor Ikeda. He is an assistant professor at Osaka University. His research interests are in the area of industrial organic chemistry and supramolecular chemistry.

Yohji Nakatsuji, Ph.D., is an associate professor at Osaka University. His research interests are in the area of industrial organic chemistry and host-guest chemistry.

Daisuke Ono, Ph.D., is a researcher at Osaka Municipal Technical Research Institute. His research interest is synthesis and application of surfactants.

Tokuji Takeda, Ph.D., is a manager of the Technochemistry Department at Osaka Municipal Technical Research Institute. His research interests are in the development and improvement of soaps, detergents, and surfactants.

Isao Ikeda, Ph.D., is a professor at Osaka University. His research interests include synthesis and properties of novel amphiphiles, molecular recognition chemistry, and molecular design of novel chiral ligands for organometallic catalysts.