

Ozone-Cleavable Gemini Surfactants. Their Surface-Active Properties, Ozonolysis, and Biodegradability

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A series of bis(sulfonate) or bis(carboxylate) types of double-chain surfactants (gemini surfactants) containing carbon–carbon double bond(s) in their lipophilic chains and/or the connecting part were prepared with the intention of developing high-performance surfactants having a decomposition character toward ozone. Some profiles with respect to the structural effect of the double bond(s) on the surface-active properties of these gemini types of surfactants were revealed as follows: (1) the displacement of a C–C bond by a C=C bond in the connecting part made a positive contribution both to micellar formation and to the effectiveness and efficiency of adsorption on the surface; (2) in contrast to this, a C=C bond in the lipophilic chains of gemini surfactants made a negative contribution to these properties. Ozonolysis of these gemini surfactants was easily accomplished by passing ozone through their micellar aqueous solutions followed by successive reduction of the resulting mixtures with NaBH₄. A remarkable change in foaming properties was observed before and after the ozonolysis; that is, foam stability of all examined ozonolytic products was extremely low. Finally, biodegradability of some gemini surfactants and their ozonolytic product by activated sludge was estimated. Their degradabilities were much higher than that of sodium dodecylbenzenesulfonate and were comparable to that of sodium 1-dodecanesulfonate under the same conditions.

Introduction

Many filtration plants in which an ozonation process is incorporated to remove or suppress planktons and trihalomethanes in supplied water are operating around the world because ozone is a clean, powerful, and easily available oxidizing agent with sterilizing ability.¹ Use of ozone in wastewater treatment has also come to hold an important position from the standpoint of environmental safeguards. To achieve decolorization, sterilization, or reduction of chemical oxygen demand (COD) in treated water, the ozonation process is now essential in the plant for high-level treatment of wastewater.²

In a previous communication,³ we proposed three ozone-cleavable gemini surfactants bearing carbon–carbon

double bond(s) in their lipophilic chains and/or the connecting part (**4a**, **5a**, and **5b** in Chart 1) that featured “environmentally friendly” characteristics. They were designed on the basis of the following concepts: (i) lowering the quantity of surfactant used would contribute to the reduction of the load on the natural purification system, and (ii) the degradation of the original surfactant molecules into smaller fragments by ozone would assist the treatment process of wastewater. As can be seen from some recent reviews,⁴ double-chain surfactants bearing two hydrophilic ionic headgroups, generally called “gemini surfactants”, have a bright prospect in developing a new class of high-performance surfactants. In connection with the second concept, “chemocleavable” or “destructive” surfactants are also one of the attractive topics in the chemistry of surfactants.⁵ But there is no systematic study on the application of ozone as a trigger for the destruction of cleavable surfactants. Piasecki et al. have reported only the reactivity of amphiphilic acetals toward ozone in water.⁶ Compounds **4a**, **5a**, and **5b** showed excellent surface-active properties, such as a micelle-forming ability at lower concentrations and higher effectiveness and

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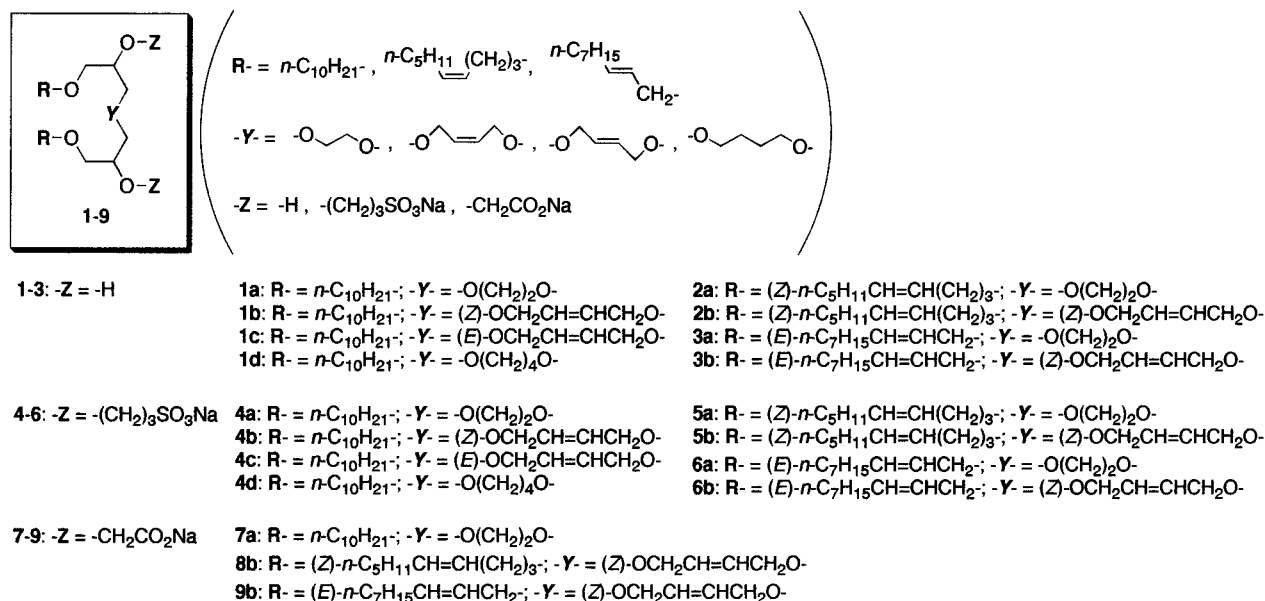
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Chart 1



efficiency of adsorption on the surface,⁷ compared with the conventional single-chain sulfonates, such as [*n*-C₁₀H₂₁O(CH₂)₂SO₃Na],⁸ as expected.

In the present work, first a variety of bis(sulfonate)-type gemini surfactants (**4–6**) listed in Chart 1 were newly prepared. They are regio- and/or geometrical isomers of **4b**, **5a**, or **5b**. Because surface-active properties of a conventional single-chain surfactant bearing carbon-carbon double bond(s) in its lipophilic chain are generally different from those of the corresponding saturated compound,⁹ it is interesting to glance at the structural effects of double bond(s) in these types of gemini amphiphiles on the surface-active properties. The corresponding bis(carboxylate)-type gemini surfactants (**8** and **9**) were also synthesized to compare their surface-active properties with those of saturated bis(carboxylate) compound **7**.¹⁰ Second, ozonolysis of a couple of gemini surfactants was accomplished by passing ozone through their micellar aqueous solutions. The surface tension and foaming ability of the resulting solutions after ozonation and successive reduction of gemini surfactants were measured. Finally, the biodegradability of some gemini surfactants and the fragment material that was obtained after ozonolysis was evaluated by the oxygen consumption method.

Results and Discussion

Preparation of a series of gemini surfactants **4–9** was achieved according to the established method.^{10,11} Synthetic routes to the gemini compounds and their analytical data are mentioned in the Experimental Section and the Supporting Information.

Surface-Active Properties of Gemini Surfactants. The plots of surface tension versus concentration of a series of double-chain bis(sulfonate) surfactants bearing a

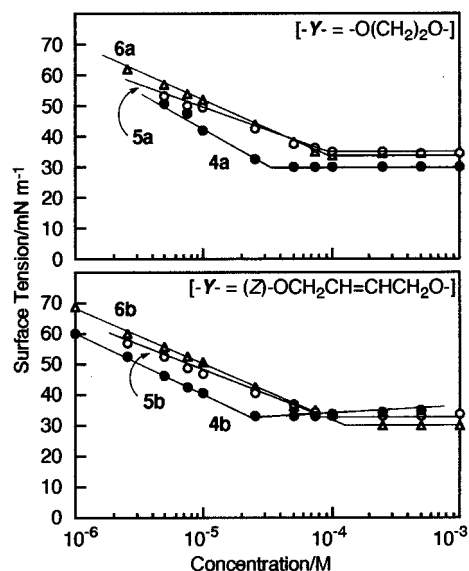


Figure 1. Surface tension (γ)–concentration (C) isotherms for double-chain bis(sulfonate) surfactants bearing a $\text{-O(CH}_2)_2\text{O-}$ connecting group (above) and a $(\text{Z})\text{-OCH}_2\text{CH=CHCH}_2\text{O-}$ connecting group (below) in water at 20 °C.

$\text{-O(CH}_2)_2\text{O-}$ group (above) or a $(\text{Z})\text{-OCH}_2\text{CH=CHCH}_2\text{O-}$ group (below) as a connecting group (-Y-) at 20 °C are illustrated in Figure 1. The values of cmc, γ_{cmc} , $\text{p}C_{20}$ (the negative log of C_{20} , the surfactant molar concentration required to reduce the surface tension by 20 mN m^{−1}), and the cmc/ C_{20} ratios¹² of these compounds are shown in Table 1.

The cmc values of bis(sulfonate) compounds **4–6** vary depending primarily upon whether the lipophilic chains are saturated or unsaturated hydrocarbons. Thus, these values for compounds **5a** and **6a**, bearing a $\text{-O(CH}_2)_2\text{O-}$ connecting group, were larger than that of compound **4a**. Similar to this, compounds **5b** and **6b**, bearing a $(\text{Z})\text{-OCH}_2\text{CH=CHCH}_2\text{O-}$ connecting group, showed higher cmc values than their saturated homologue **4b**. But the effect of the structure of the connecting group on the cmc was not clear: the cmc values of compounds **5b** and **6b**, bearing

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Table 1. Surface-Active Properties of Bis(sulfonate) Types of Gemini Surfactants in Water at 20 °C

surfactant	cmc/mM	$\gamma_{\text{cmc}}/\text{mN m}^{-1}$	$\text{p}C_{20}$	cmc/C_{20}
4a	0.032 ^a	30.0 ^a	5.4	7.3
4b	0.025	33.0	5.6	9.6
4c	0.020	33.0	5.7	10
4d	0.10	36.0	4.8	6.3
5a	0.090	34.0	5.2	16
5b	0.10	33.0	5.3	22
6a	0.088	33.5	5.0	9.2
6b	0.14	30.0	5.1	18

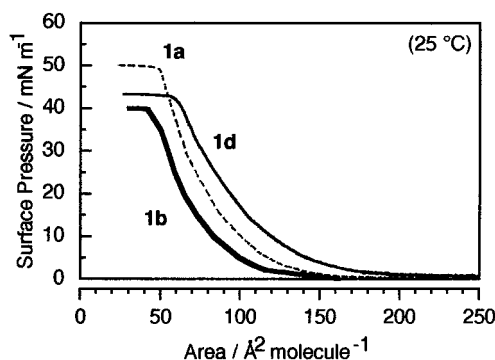
^a Reference 11a.**Table 2. Surface-Active Properties of Bis(sulfonate) Types of Gemini Surfactants in 0.1 M Aqueous NaCl at 20 °C**

surfactant	cmc/mM	$\gamma_{\text{cmc}}/\text{mN m}^{-1}$	$\text{p}C_{20}$	$A/\text{\AA}^2$
4a	0.005	36.0	6.4	69
5a	0.025	38.0	5.9	89
5b	0.025	35.0	6.3	89
6a	0.030	35.0	5.7	67
6b	0.050	31.5	5.6	63

unsaturated lipophilic chains, were larger than those of the corresponding compounds **5a** and **6a**, respectively, whereas compounds **4b** and **4c**, bearing saturated lipophilic chains, showed somewhat smaller cmc values than the corresponding compound **4a**. Additionally, the surface-active properties shown in Table 1 of compounds **4b** and **4c** were almost the same, indicating that geometrical isomerism in the connecting group is of limited significance in these properties.

Concerning the performance of surfactants on the surface, both the effectiveness and the efficiency of adsorption on the surface for these unsaturated gemini surfactants are much higher than those for most of the conventional single-chain anionic surfactants. These can be shown as lower γ_{cmc} and higher $\text{p}C_{20}$ results for compounds **4-6** as compared with $n\text{-C}_{10}\text{H}_{21}\text{O}(\text{CH}_2)_2\text{SO}_3\text{Na}$ ($\gamma_{\text{cmc}} = 41 \text{ mN m}^{-1}$, $\text{p}C_{20} = 2.1$).⁸ The surface tension of various concentrations of compounds **4a**, **5a**, **5b**, **6a**, and **6b** was also measured in 0.1 M aqueous NaCl at 20 °C. In the presence of swamping electrolyte (i.e., NaCl), the coefficient n in the Gibbs adsorption equation, $d\gamma = -nRT \Gamma d \ln C$, is equal to 1, and the values of surface excess concentration (Γ) and area per molecule at the surface (A) can be estimated.⁷ These results are given in Table 2, indicating that compounds **6a** and **6b**, bearing two (*E*)-2-decenyl chains, are more closely packed on the surface than compounds **5a** and **5b**, with two (*Z*)-4-decenyl chains. The addition of electrolyte to an aqueous solution of an ionic surfactant results in increased adsorption on the surface because of the decrease in electrostatic repulsion between the headgroups on the surface.⁷ It generally causes a lowering of the γ_{cmc} value. But this is not necessarily the case for compounds **4a**, **5a**, **5b**, **6a**, and **6b** in this work and for some other gemini surfactants.¹³ The reason for this specific behavior of gemini surfactants has not yet been clarified.

In connection with the adsorptive behavior of these gemini surfactants at the air–water interface, the results of π – A isotherms at 25 °C of double-chain diols **1a**,^{14a} **1b**, and **1d**,^{14b} (Figure 2) that were synthetic precursors of surfactants **4a**, **4b**, and **4d**, respectively, gave useful

**Figure 2.** π – A isotherms for double-chain diol amphiphiles **1a**, **1b**, and **1d** at 25 °C.

information about the effect of the connecting group on the packing manner on the surface. Figure 2 clearly shows that a (*Z*)- $\text{OCH}_2\text{CH}=\text{CHCH}_2\text{O}$ – connecting group, unexpectedly, contributes to tighter packing of the monolayer of these types of diols as compared with not only a $-\text{O}(\text{CH}_2)_4\text{O}-$ group but also a $-\text{O}(\text{CH}_2)_2\text{O}-$ group. We have already clarified the influence of an unsaturated linkage in the lipophilic chains of these types of double-chain diols, bearing a $-\text{O}(\text{CH}_2)_2\text{O}-$ connecting group, on the behavior of π – A isotherms.^{14b} The results showed that an unsaturated bond in the lipophilic chains contributed to loose packing of the monolayer. Of course, the packing manners of these double-chain diols **1** on the surface will not link directly to those for the corresponding gemini surfactants **4** because the compounds **4** have two additional $-\text{O}(\text{CH}_2)_3\text{SO}_3\text{Na}$ parts, which will make a negative contribution to tight packing on the surface by the electrostatic force of repulsion with each other. The γ_{cmc} values of compounds **5b** and **6b**, bearing a (*Z*)- $\text{OCH}_2\text{CH}=\text{CHCH}_2\text{O}$ – connecting group, were smaller than those of compounds **5a** and **6a**, bearing a $-\text{O}(\text{CH}_2)_2\text{O}-$ connecting group, respectively, indicating that the effect of the connecting group on the adsorptive behavior became dominant in the case of these types of gemini surfactants bearing unsaturated lipophilic chains.

The cmc/C_{20} ratios are indices of the relative effects of some molecular structural factor on micellization and on adsorption.^{10,12} For single-chain surfactants, this ratio is generally increased by an increase of bulkiness (branching in the lipophilic group, location of the hydrophilic 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 on the surface. These values for compounds **4b**, **4c**, **5b**, and **6b**, bearing an unsaturated connecting group, are larger than those for the corresponding compounds **4a**, **4d**, **5a**, and **6a** (Table 1). An increase in the cmc/C_{20} ratio as a result of the replacement of the $-\text{O}(\text{CH}_2)_x\text{O}-$ ($x = 2$ or 4) connecting group by the $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{O}-$ group suggests that adsorption is facilitated more than micellization.

Surface-active properties in 0.001 N aq NaOH of newly prepared bis(carboxylate) types of gemini surfactants **8b** and **9b**, bearing a (*Z*)- $\text{OCH}_2\text{CH}=\text{CHCH}_2\text{O}$ – connecting group, were also measured. From the γ – C plots of these two carboxylates **8b** and **9b** (Figure 3; including the result of compound **7a**¹⁰), their properties were: $\text{cmc} = 0.34 \text{ mM}$; $\gamma_{\text{cmc}} = 33 \text{ mN m}^{-1}$; $\text{p}C_{20} = 4.7$; $\text{cmc}/C_{20} = 15$ for compound **8b**, and $\text{cmc} = 0.17 \text{ mM}$; $\gamma_{\text{cmc}} = 32 \text{ mN m}^{-1}$; $\text{p}C_{20} = 5.2$; $\text{cmc}/C_{20} = 19$ for compound **9b**. There was no significant difference in these properties for compounds **7a**, **8b**, and **9b**. With only three examples, we cannot discuss the effect of the unsaturated bond in the lipophilic chains and in

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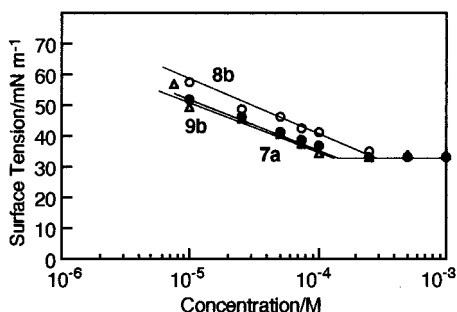


Figure 3. γ -C isotherms for double-chain bis(carboxylate) surfactants in aqueous 0.001 N NaOH at 20 °C.

the connecting group on both micellization and adsorption on the surface of these gemini surfactants having two carboxylate groups in detail. In our previous paper,¹⁰ however, we have already clarified the effect of differences in the charged group of these types of gemini surfactants (i.e., -Z in Chart 1) on their surface-active properties as follows: (1) The cmc value decreases with a change in -Z in the order: $-\text{OCH}_2\text{CO}_2\text{Na} > -\text{OP}(=\text{O})(\text{OH})(\text{ONa}) > -\text{O}(\text{CH}_2)_3\text{SO}_3\text{Na} > -\text{OSO}_3\text{Na}$; (2) Differences in the distance between the ionic charge and the omega oxygen atom in the lipophilic chain have little or no effect on the cmc.

Ozonolyses of Gemini Surfactants. Ozonolyses of alkenes in participating (i.e., protic, nucleophilic) solvents, such as alcohols, generally afford α -oxyalkyl hydroperoxides rather than the corresponding *sec*-ozonides that are normally formed from ozonolyses in nonparticipating solvents.¹ Participation by water in ozonolyses of olefins is also probable, but the expected α -hydroxyalkyl hydroperoxides and their related α,α' -dihydroxydialkyl peroxides have been isolated in only a few cases¹⁵ because these possible products are generally too unstable to be isolated.¹⁶ So, a suitable reductant is required to give stable ozonolytic products (i.e., alcohols) in water (Scheme 1). In this work, NaBH_4 was selected as reductant because it is an inexpensive industrial reductant and can be used in water. Ozonolyses of micellar aqueous solutions (10 mM) of gemini surfactants **4b**, **5a**, and **5b** have already been mentioned in our previous communication.³ An outline of the results is also included in Scheme 1. The structures of degradation products **10**–**12** and hexan-1-ol were confirmed by comparison of their NMR data with those of authentic samples. Because product **10** has a single-chain amphiphilic structure, its surface-active properties in water were investigated. From the γ -C plots of authentic sample **10** (Figure 4), its properties were: cmc = 0.80 mM; $\gamma_{\text{cmc}} = 35 \text{ mN m}^{-1}$; $\text{p}C_{20} = 3.8$; cmc/ $C_{20} = 4.0$. These values are quite different from those of its parent gemini surfactant **4b** (Table 1). Foaming properties also changed remarkably before and after ozonolysis and successive reduction of the aqueous micellar solution of compounds **4b** (Figure 5). Thus, compound **4b** is categorized as a "second generation" type of chemocleavable surfactant,¹⁷ which has different surface-active properties from the original ones after decomposition. In the cases of ozonolyses of gemini surfactants **5a** and **5b**, hexan-1-ol separated out as oil droplets from the reaction medium after reduction with NaBH_4 . It was confirmed that both authentic compounds **11** and **12**³ were freely soluble in

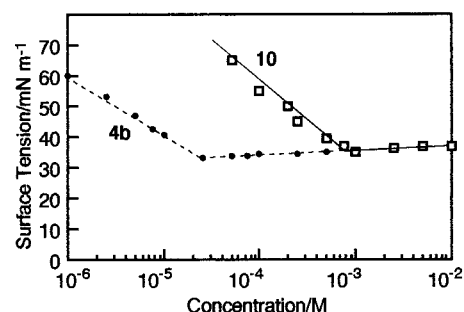


Figure 4. Comparison of γ -C isotherms between parent gemini surfactant **4b** and its ozonolytic fragment compound **10** in water at 20 °C.

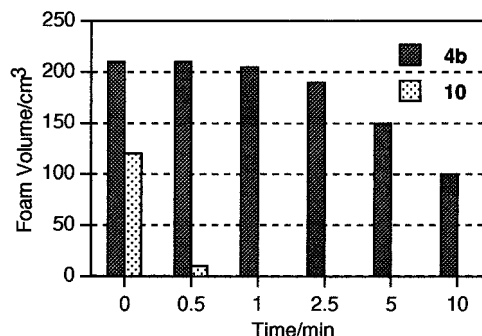


Figure 5. Change of foam volume of 0.1 wt % aqueous solutions of parent gemini surfactant **4b** and its ozonolytic fragment compound **10** with the elapse of time at 20 °C. "Zero minute" means immediately after bubbling of the solution by the semi-micro TK apparatus.¹⁸

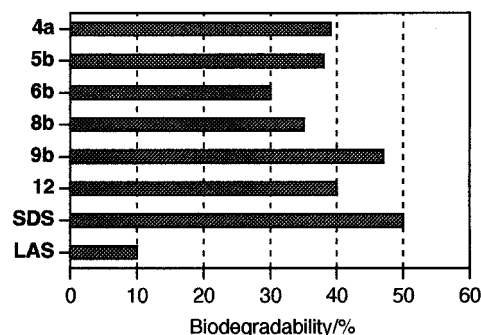


Figure 6. Biodegradability of compounds **4a**, **5b**, **6b**, **8b**, **9b**, and **12** after 14 days, along with the results for sodium 1-dodecanesulfonate (SDS) and sodium dodecylbenzenesulfonate (LAS) measured under the same conditions.

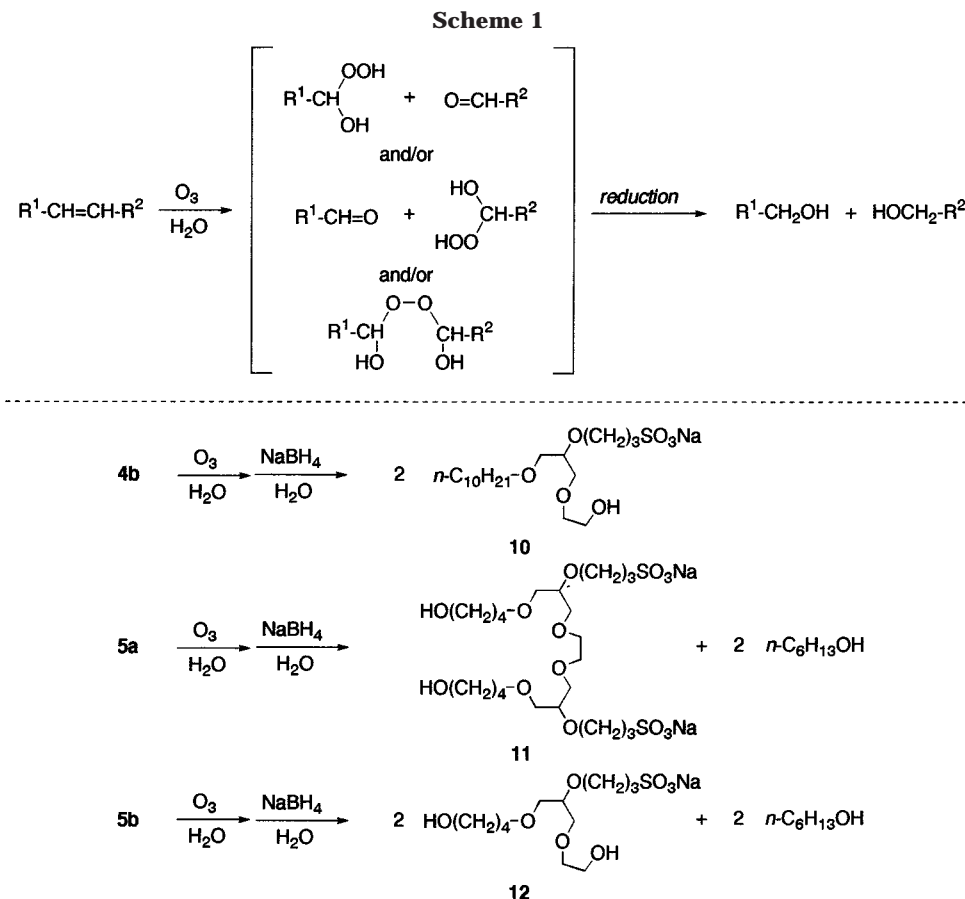
water and showed little ability to lower the surface tension of their aqueous solutions at any concentration less than 20 mM.

Biodegradability. Finally, biodegradability of some gemini surfactants and their ozonolytic products by activated sludge will be briefly mentioned. Procedures for the estimation of biodegradability (%) after 14 days are mentioned in detail in the Experimental Section. Figure 6 illustrates the biodegradability of selected gemini surfactants (**4a**, **5b**, **6b**, **8b**, and **9b**) and the ozonolytic product (**12**) along with the data for sodium 1-dodecanesulfonate (SDS; specially prepared reagent of Nacalai tesque, Co., Kyoto, Japan) and sodium dodecylbenzenesulfonate (LAS; extra-pure reagent of Nacalai tesque, Co.) measured under the same conditions. All inspected compounds prepared in this work showed much better biodegradability than LAS. Unfortunately, a clear relation between the structure of samples and their degradability results was not noticed. Compound **9b**, bearing two

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carboxylate groups, showed the maximum among the inspected gemini surfactants, and its degradability was comparable to that of SDS, which is considered one of the commercially available surfactants with excellent biodegradability. Compound **12**, which is the ozonolytic product of gemini surfactant **5b**, has a slightly higher biodegradability than its parent compound. The biodegradability of other ozonolytic products has not yet been measured.

In summary, an unsaturated bond in the connecting part of bis(sulfonate) types of gemini surfactants makes not negative but positive contributions both to their micellization in water and to their effectiveness and efficiency of adsorption on the surface, whereas a C=C bond in the lipophilic chains seems disadvantageous to their surface-active properties. There is not a distinct difference in biodegradability between the parent gemini surfactant and its ozonolytic product. In the case of gemini surfactants bearing a C=C bond in the connecting part, however, formation of any foam was not observed at all after ozonolysis and successive reduction of their micellar solutions. In conclusion, it is surmised that these types of ozone-cleavable gemini surfactants would have potential promise as new candidates for an environmentally friendly surfactant.

Experimental Section

Materials. Scheme 2 gives an outline of synthetic routes to the gemini surfactants in this work. Ethylene glycol, (*Z*)-2-butene-1,4-diol, 1,4-butanediol, *n*-decanol, and (*Z*)-4-decen-1-ol were commercial products and were used without purification. (*E*)-2-Decen-1-ol was prepared by reference to the reported methods,¹⁸ which were also outlined in Scheme 2. (*E*)-2-Butene-1,4-diol was

synthesized by the reduction of diethyl fumarate by diisobutylaluminum hydride (DIBAL-H; 1.0 M solution in hexane) in benzene.

General procedures for preparation of bis(sulfonate) and bis(carboxylate) types of gemini surfactants in this work have already been reported.^{10,11} The purity of each sample for measurement of interfacial properties was confirmed by TLC, NMR spectral data, and elemental analyses. The purification methods, spectral data, and elemental analytical data for compounds subjected to evaluation of interfacial properties are given in the Supporting Information.

Methods. ¹H and ¹³C NMR spectra were recorded with a JEOL JNM-EX-270 spectrometer. The IR spectra and MS spectra were measured on a Hitachi 260 spectrometer and a JEOL JMS-DX-303 mass spectrometer, respectively.

Surface-active properties were evaluated according to the methods mentioned in previous papers:^{7,8} the surface tension of surfactants was recorded at 20 °C with a Wilhelmy tensiometer (Kyowa CBVP-A3; platinum plate). The cmc was determined from the break point of each surface tension versus concentration curve. The γ_{cmc} is the surface tension at the cmc, with an error of about 1 mN m⁻¹ under our experimental conditions. The pC₂₀ is the negative logarithm of C₂₀, the surfactant molar concentration required to reduce the surface tension by 20 mN m⁻¹. The foaming properties were measured by the semi-micro TK method.¹⁹

The π -A isotherms were recorded with a computer-controlled film balance system (Nippon Laser & Electronics Lab. type NL-LB80S-MTC) at 25 ± 0.5 °C. Concrete procedures for measurement of π -A isotherms have been already mentioned in our previous papers.^{14,20}

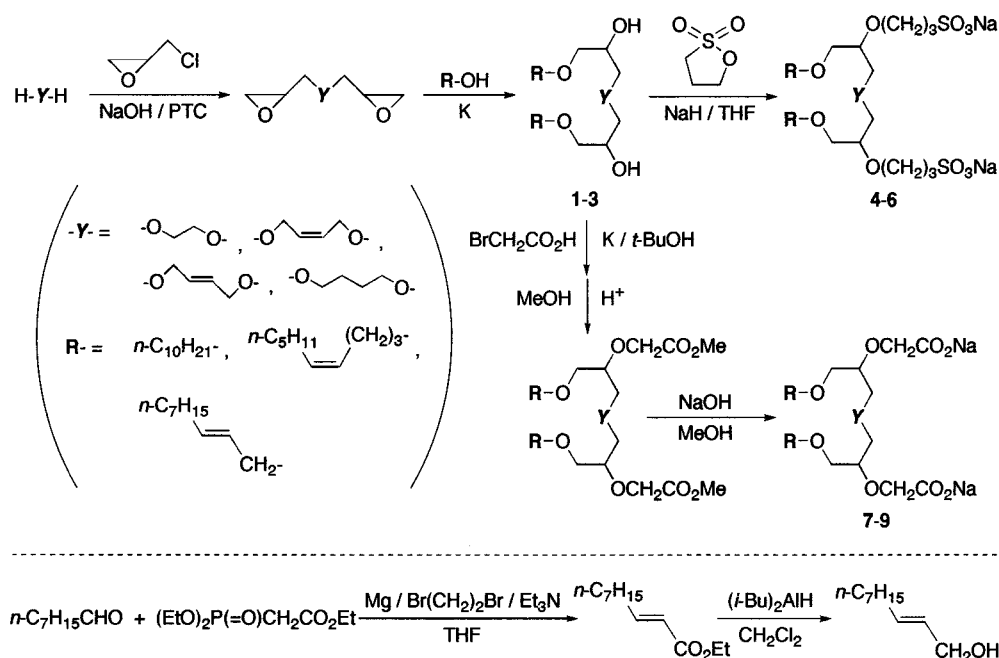
Ozonolysis was carried out with a Nippon Ozone model ON-1-2 ozonator; dry oxygen containing about 2% of ozone was introduced at a speed of 50 L h⁻¹ (1 mmol of ozone per 3 min) in a micellar aqueous solution of surfactant. By use of an excess

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Scheme 2



of ozone (3–5 equiv), every substrate could be completely decomposed. For example, when a 10-mL solution of compound **5b** (10 mM) was used, ozonolysis was continued for 3 min (3.3 equiv).

The biodegradability of some compounds was evaluated by the oxygen consumption method. The procedure was carried out according to the guidelines of the Japanese law for biodegradation of novel chemical compounds (1973, No. 117). It is essentially identical to the Organization for Economic Cooperation and Development (OECD) guidelines for the testing of chemicals [Section 3: 301C "Ready Biodegradability: Modified MITI Test (I)"]. The test sample was added to a dispersion of activated sludge in the basic culture solution (300 mL), which was prepared according to the Japan Industrial Standard (JIS)-K0102. The concentrations of sample and the activated sludge were 100 (w/v) and 30 ppm (w/v), respectively. The activated sludge was obtained from a municipal sewage treatment plant in Osaka City. The suspended solids concentration was about 10 000 ppm after 30 min of standing. A culture dispersion containing only activated sludge (30 ppm) was prepared as a blank (300 mL). A dispersion containing aniline instead of the test sample and activated sludge in the basic culture solution was prepared as a standard (300 mL). The concentration of aniline was the same as that of the test sample. These culture systems were placed in 500-mL culture bottles and were stirred vigorously at 25 °C for at least 14 days. The change in the biochemical oxygen demand (BOD, mg) of the system was monitored with time. The biodegradability was estimated by

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

where "blank" refers to the oxygen consumption (mg) in the blank dispersion and TOD refers to the theoretical oxygen demand (mg). If the biodegradability of aniline after 1 week was not more than 40%, the experiment would be invalidated. The quantity of oxygen consumption was measured with a Coulometer OM-2000 (Ohkura Electronic Co., Tokyo, Japan), which is a BOD meter of closed systems. Oxygen was supplied to the systems by electrolysis of a CuSO_4 solution, and the BOD was evaluated from the quantity of electricity used.

Caution. Since organic peroxides are potentially hazardous compounds, they must be handled with due care; avoid exposure to strong heat or light, mechanical shock, oxidizable organic materials, or transition metal ions. No particular difficulties were experienced in handling any of the new intermediary peroxides with the reaction scales and aqueous media used in these experiments.

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Supporting Information Available: Purification methods and spectral data for all gemini types of compounds **1–9** (except **1a**, **1d**, **4a**, **4b**, **4d**, and **7a**) and ozonolytic products (**10–12**), including elemental analytical results for compounds subjected to evaluation of any interfacial property. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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