

# Ozone-cleavable gemini surfactants, a new candidate for an environmentally friendly surfactant

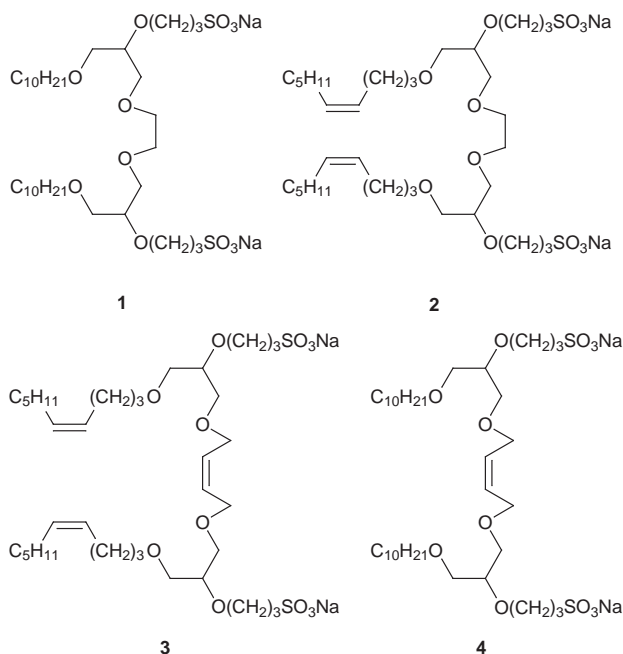
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Three types of gemini surfactants bearing carbon–carbon double bond(s) showed excellent surface-active properties, and readily decomposed into non-surface-active fragments and/or single-chain surfactants with different surface-active properties upon exposure to ozone in water.

Surfactants are one of the representative chemical products which are consumed in large quantities every day on a world-wide scale. Special regard concerning environmental safeguards should be paid to the development of the next generation of new surfactants. Application of ozone in waste water treatment is noted as a modern key technology for the environmental protection of rivers and lakes.<sup>1</sup> Many sewage treatment plants in which an ozonation process is incorporated are operating around the world.

We herein propose a new design of novel surfactant featuring ‘environmentally-friendly’ characteristics. The concept is based on the following two points: (i) lowering the quantity of surfactant used will contribute greatly to reducing the load on the natural purification system, and (ii) breaking down the original surfactant molecules into smaller fragments after they have fulfilled their original applications will assist the waste water treatment process. Concerning the first point, double-chain surfactants bearing two hydrophilic ionic head groups, generally called ‘gemini surfactants’,<sup>2</sup> are an attractive motif



because many types of gemini surfactants, such as **1**,<sup>3</sup> have very small CMC (critical micelle concentration) values and have the ability to significantly lower surface tension, both of which properties cannot be achieved *via* simple modification of the structure of conventional single-chain monoionic surfactants.<sup>4</sup>

The second point is connected with ‘chemocleavable’ or ‘destructive’ surfactants, which are one of the stimulating targets of research in the chemistry of amphiphilic compounds.<sup>5</sup> Taking into account these backgrounds, we have recently designed and prepared three types of gemini surfactants bearing carbon–carbon double bond(s) in their lipophilic chains and/or the connecting part (**2–4**). Ozonation is applied as a trigger for the destruction of these unsaturated gemini surfactants in water. In connection with our latter approach, Piasecki and co-workers have investigated the reactivity of long-chain alkyl-substituted cyclic acetals toward ozone in water.<sup>6</sup>

Preparation of the target compounds **2–4** was achieved according to the established method.<sup>3</sup> Thus they were synthesised by the reaction of 1,2:9,10-diepoxy-4,7-dioxadecane (for preparation of **2**) or (Z)-1,2:11,12-diepoxy-4,9-dioxadodec-6-ene (for **3** and **4**) with (Z)-dec-4-en-1-ol (for **2** and **3**) or decan-1-ol (for **4**) in the presence of base, followed by sulfopropylation of the resulting double-chain diols with propane-1,3-sultone.‡ Table 1 summarises the data for their CMC,  $\gamma_{\text{CMC}}$  (the surface tension at CMC, as an indication of the effectiveness of adsorption at the air/water interface)<sup>7</sup> and  $pC_{20}$  (the efficiency of adsorption)<sup>7</sup> values, which were obtained from respective surface tension *vs.* concentration (on a log scale) curves measured by the Wilhelmy method. The corresponding data for the gemini surfactant **1**<sup>3</sup> and the single-chain sulfonate [C<sub>10</sub>H<sub>21</sub>O(CH<sub>2</sub>)<sub>2</sub>SO<sub>3</sub>Na] **5**<sup>7</sup> are also included in Table 1 as reference amphiphiles.

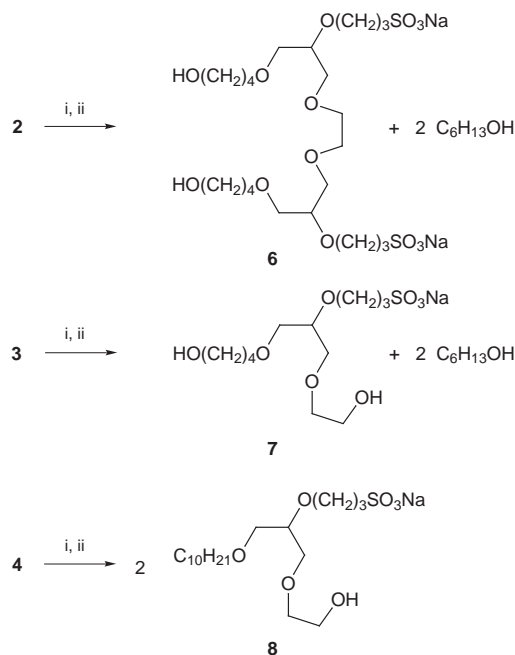
The CMC of a surfactant bearing carbon–carbon double bond(s) in its lipophilic chain is generally higher than that of the corresponding saturated compound.<sup>7</sup> This is also the case for the CMC of gemini surfactants **1–3**. It should be noted, however, that the CMC values of **2** and **3** are two orders lower than that of the conventional single-chain analogue **5**. Interestingly, the CMC of the gemini surfactant **4** is very similar to that of the corresponding saturated gemini surfactant **1**, indicating that the CMC is not affected by an unsaturated bond in the connecting part of these gemini surfactants. In summary, both effectiveness and efficiency of adsorption on the surface for a series of gemini surfactants **1–4**, regardless of the presence or the absence of double bond(s) in the molecule, are much higher than those for the single-chain surfactant **5**.

Ozonolysis of gemini surfactants **2–4** was easily accomplished by passing ozone through their micellar aqueous solutions ( $1 \times 10^{-2}$  mol dm<sup>-3</sup>) at room temperature. Subsequent treatment of the reaction mixture with NaBH<sub>4</sub> afforded

**Table 1** Interfacial properties of surfactants **1–5** measured by the Wilhelmy method at 20 °C in water

Surfactant	CMC/mol dm <sup>-3</sup>	$\gamma_{\text{CMC}}$ /mN m <sup>-1</sup>	$pC_{20}$
<b>1</b> <sup>a</sup>	$3.2 \times 10^{-5}$	30.0	5.2
<b>2</b>	$9.0 \times 10^{-5}$	34.0	5.1
<b>3</b>	$1.0 \times 10^{-4}$	33.5	5.2
<b>4</b>	$2.5 \times 10^{-5}$	33.0	5.7
<b>5</b> <sup>b</sup>	$1.6 \times 10^{-2}$	41.0	2.1

<sup>a</sup> Ref. 3. <sup>b</sup> Ref. 7.



**Scheme 1** Reagents and conditions: i, **2**, **3** or **4** in water ( $1 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ),  $\text{O}_3$  (10 equiv.), room temp.; ii,  $\text{NaBH}_4$  (1.5 equiv.), 5 min., room temp.

the corresponding degradation products, as shown in Scheme 1. These products could be extracted as a mixture in each case with  $\text{CHCl}_3$ -MeOH (3:1, v/v). Their structures were confirmed by comparison of their  $^1\text{H}$  and  $^{13}\text{C}$  NMR data with those of hexan-1-ol and authentic samples of **6–8**. Judging from the TLC results of the extracted mixtures and their  $^1\text{H}$  NMR spectra in  $\text{D}_2\text{O}$ , other degradation products were not observed and compounds **6–8** were found to be produced almost quantitatively.

After ozonolysis and successive reduction of micellar solutions of gemini surfactants **2** and **3**, oil droplets (*i.e.* hexan-1-ol) appeared in the solutions; stable foams were not observed, even immediately after shaking the solutions. Stable foams were generated, however, by shaking solutions containing ozonolysis product **8**. Compound **8** was still surface-active and its surface-active properties were:  $\text{CMC} = 8.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ;  $\gamma_{\text{CMC}} = 35$  mN  $\text{m}^{-1}$ ;  $pC_{20} = 3.8$ . Thus the interfacial properties of the parent gemini surfactant **4** and the single-chain surfactant **8** are quite different. Thus, surfactant **4** is categorised as a second generation type of cleavable surfactant.<sup>8</sup>

In summary, the readily accessible gemini surfactants **2–4** possess considerable potential as high-performance surfactants. Fragmentation of **2–4** in water smoothly takes place on exposure to ozone, followed by reduction with  $\text{NaBH}_4$  under

mild conditions. Studies on various surface-active properties of a homologous series of gemini surfactants and their biodegradability are now in progress.

This work was supported in part by the Fund for Environmental Protection Research from the Nihon-Seimei Foundation.

## Note and References

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‡ All new compounds gave satisfactory spectroscopic and microanalytical data.

§ A suitable reductant is required to give stable degradation products in water because the corresponding unstable  $\alpha,\alpha'$ -dihydroxy peroxides are formed by ozonolysis of the substrates.  $\text{NaBH}_4$  was chosen because it is an inexpensive industrial reductant and can be used in water.

¶ Authentic compound **6** was prepared by the reaction of  $\text{THPO}(\text{CH}_2)_4\text{OH}$  (THP = tetrahydropyranyl) with ethylene glycol diglycidyl ether, followed by sulfopropylation with propane-1,3-sultone and successive deprotection of the THP group by treatment with sulfuric acid. The reaction of  $\text{THPO}(\text{CH}_2)_4\text{OH}$  with mono-THP-protected ethylene glycidyl ether, or the reaction of decyl glycidyl ether with mono-THP-protected ethylene glycol, followed by sulfopropylation and successive deprotection afforded authentic compounds **7** and **8**, respectively.

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Received in Cambridge, UK, 27th July 1998; 8/05825C