

# Preparation and Properties of Bis(sodium sulfate) Types of Cleavable Surfactants Derived from Diethyl Tartrate

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Edited by T. Oida, Kyoto Inst. Tec., and accepted August 27, 2004 (received for review June 2, 2004)

**Abstract:** Bis(sodium sulfate) surfactants each bearing two alkyl groups were easily prepared by the acid-catalyzed transesterification of diethyl tartrate with fatty alcohols (octyl, decyl, or dodecyl) and subsequent sulfation with sulfamic acid without any expensive reagents and special equipment. These surfactants had better water-solubility, smaller critical micelle concentration (cmc) and lower surface tension at cmc compared to sodium dodecylsulfate and sodium tetradecylsulfate. These surfactants bearing octyl or decyl chains had low-foaming properties and good solubility in hard water. They decomposed easily into nonsurface-active species under acidic or alkaline conditions. Their biodegradabilities were almost the same as that of sodium dodecanoate.

**Key words:** cleavable surfactant, anionic surfactant, gemini surfactant, ester group, biodegradation

## 1 Introduction

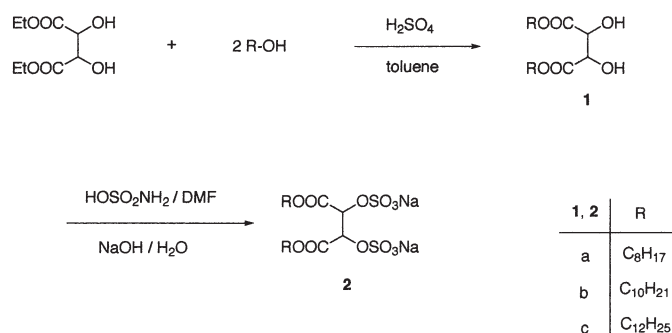
Recently, cleavable surfactants have become a focus of great interest in the field of surfactant chemistry. Such compounds are designed so as to decompose into non-surface active species on exposure to acid, alkali, light, or heat after accomplished their original functions. The various types of known cleavable surfactants have been developed in which the decomposition property can be controlled through adjustment of the solution pH. In particular, there are many reports concerning acetal and 1,3-dioxolane types of amphiphilic compounds (1-10).

We have been investigating the preparation and properties of a series of acid- and alkali-cleavable surfactants (11-23). We have mentioned some considerations about the order of the decomposition rate of the cleavable surfactants with different types of hydrophilic groups and clarified that the cleavable moiety (non-cyclic acetal group, 1,3-dioxolane ring or ester) has a good effect on the various surface-active properties.

Biodegradability of these surfactants was higher or almost the same as that of the corresponding conventional surfactants. On the other hand, it is known that gemini surfactants have much higher solubility in water, smaller cmc and lower surface tension at cmc than the corresponding surfactants having one lipophilic part and one hydrophilic group in the molecule.

In this work, we found that chemocleavable gemini surfactants were easily synthesized by the acid-catalyzed transesterification of diethyl tartrate with fatty alcohols and subsequent sulfation without any expensive reagents and special equipment (**Scheme 1**). Tartaric acid is available as a natural product derived from plant tissues such as fruits. We clarified their surface-active properties and the decomposition profiles in water upon exposure to alkali or acid, and compared with those of the conventional surfactants with one alkyl chain and one sulfate group.

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**Scheme 1** Preparation of Bis(sodium sulfate) Types of Cleavable Surfactants.

## 2 Experimental

### 2.1 Materials and Synthesis of Ester Derivatives

Fatty alcohols and diethyl tartrate were obtained commercially (Nacalai Tesque, Inc.). The target chemocleavable gemini surfactants were synthesized by the acid-catalyzed transesterification of diethyl tartrate with fatty alcohols and subsequent sulfation.

Infrared spectra were recorded on a Shimadzu FT-IR DR-8100. <sup>1</sup>H-NMR spectra were measured in CDCl<sub>3</sub> or CD<sub>3</sub>OD with a JEOL JNM-EX270 (270 MHz) spectrometer using TMS as an internal standard.

#### 2.1.1 Dialkyl tartrate (**1a**), as a typical procedure

In a round-bottomed flask equipped with a stirrer and Dean-Stark receiver, diethyl tartrate (2.06 g, 10 mmol), octyl alcohol (3.13 g, 24 mmol), and sulfuric acid (0.05 g, 0.5 mmol) were dissolved in toluene (40 mL). The solution was refluxed for 4 h. The toluene solution was washed with aqueous NaHCO<sub>3</sub> solution (5%, 30 mL) and saturated NaCl (30 mL). The organic layer was dried over MgSO<sub>4</sub> and the solvent was evaporated. The residue was distilled with Kugelrohr equipment to remove the unreacted octyl alcohol (120°C/0.1 Torr) to give the product, **1a**; 3.37 g, 90% yield.

All the other compounds **1** were also isolated by distillation with Kugelrohr equipment. The conditions of distillation were as follows: **1b**; 140°C/0.1 Torr, **2c**; 160°C/0.1 Torr.

#### 2.1.2 Bis(sodium sulfate) (**2a**), as a typical procedure

A solution of the dioctyl tartrate, **1a** (3.74 g, 10 mmol) and sulfamic acid (2.14 g, 22 mmol) in DMF (10 mL) was stirred at 50°C for 3 h. After cooling to room temperature, NaOH (0.88 g, 22 mmol) aqueous

solution (5 mL) was added to the reaction mixture. To a reaction mixture was added ethanol (30 mL), then a white precipitate was filtered and washed with hexane to give sulfate Gemini, **2a**; 1.83 g, 32% yield.

The yields, special date, and so on were summarized in **Table 1**.

### 2.2 Physical Properties of **2**

Krafft point ( $T_{kp}$ ) of the surfactants was determined by the naked eye using a 1 wt% aqueous solution. The surface tension of a surfactant solution was measured with a Wilhelmy tensiometer (surface tensiometer CBVP-A3; Kyowa Kaimenkagaku Co., Ltd.; platinum plate) at 25°C. Foaming properties were evaluated by the semi-micro TK method with a 0.1 wt% aqueous solution at 25°C (24). The hard water solubility of these compounds (0.5 wt%) was evaluated by the modified Hart method (25,26). The decomposition tests were carried out as follows; a mixture of **2** (0.02 M), dodecane or tetradecane (30 mg, internal standard), and aqueous NaOH or aqueous HCl were placed in water (20 mL) and hexane (10 mL) into a sealed Erlenmeyer flask. A fatty alcohol generated was monitored by GLC analysis (Shimadzu, GC-14B; column: CBP1-W12-500; **2a**: 120°C, **2b**: 140°C, **2c**: 160°C) (13). The hydrodynamic diameter of surfactants was measured by dynamic light scattering (DLS) method (90° scattering angle) at 25°C. The DLS apparatus was model DLS-6000HL with a He-Ne ion laser manufactured by Otsuka Electronics Co., Ltd. The sample (0.02 M) was filtered through a 0.2 μm filter (Millipore). Biodegradability of the surfactants was evaluated by an oxygen consumption method according to the guidelines which was based upon the Order prescribing the items of test, relating to new chemical substances of the Chemical

Substance Control Law (Japanese Law No. 117, 1973) with activated sludge (21). The activated sludge was obtained from a municipal sewage treatment plant in Osaka City. Biochemical oxygen demand (BOD) after 2 wk was determined by the quantity of oxygen consumed. The biodegradability was estimated by:

$$\text{Biodegradability (\%)} = \text{BOD/TOD} \times 100$$

where TOD refers to the theoretical oxygen demand. The quantity of oxygen consumption was measured with a Coulometer OM-3100 (Ohkura Electronic Co.), which is a BOD meter for closed systems.

### 3 Results and Discussion

Preparation of new types of the sulfate gemini surfactants (**2a-c**) from tartrate is shown in **Scheme 1**. The intermediates, dialkylesters (**1**), were synthesized

almost quantitatively by the transesterification of fatty alcohols with diethyl tartrate in the presence of H<sub>2</sub>SO<sub>4</sub> as a catalyst in toluene. A mixture of toluene and ethanol in the Dean-Stark receiver were taken out once to remove ethanol from the reaction system completely. The unreacted fatty alcohols were removed by distillation with Kugelrohr equipment. The target chemo-cleavable gemini surfactants (**2**) were prepared through reaction of compounds **1** with sulfamic acid. The reaction mixture was stirred keeping the temperature below 50°C. They were washed with hexane to purify.

Plots of surface tension vs. concentration for compounds **2a-c** are shown in **Fig. 1**. The Krafft point ( $T_{Kp}$ ), the cmc, and the ability to lower surface tension ( $\gamma_{cmc}$ ) of these surfactants are summarized in **Table 2**, along with reference data for the conventional surfactants containing one alkyl chain and one sulfate group measured under the same conditions.

All these compounds **2** prepared in this work were

**Table 1** Preparation and Properties of Double-Chain Ester Compounds (**1, 2**)<sup>a</sup>.

Compound	Yield (%)	mp (°C)	<sup>1</sup> H-NMR <sup>b</sup> ( $\delta$ )	Anal. <sup>c</sup> Found (Calc'd)
<b>1a</b>	90 <sup>d</sup>	40.0-41.5	0.88 (t, 6H, J=6.6), 1.20-1.40 (m, 20H), 1.60-1.80 (m, 4H), 3.15 (s, 2H), 4.26 (t, 4H, J=6.6), 4.53 (s, 2H)	C, 63.95 (64.14) H, 10.06 (10.23)
<b>1b</b>	94 <sup>d</sup>	49.0-51.0	0.88 (t, 6H, J=6.4), 1.20-1.40 (m, 28H), 1.60-1.80 (m, 4H), 2.82 (s, 2H), 4.26 (t, 4H, J=6.4), 4.52 (s, 2H)	C, 67.09 (66.94) H, 10.82 (10.77)
<b>1c</b>	94 <sup>d</sup>	61.0-63.0	0.88 (t, 6H, J=6.6), 1.20-1.40 (m, 36H), 1.60-1.80 (m, 4H), 2.95 (s, 2H), 4.26 (t, 4H, J=6.6), 4.52 (s, 2H)	C, 68.69 (69.09) H, 11.34 (11.18)
<b>2a</b>	32 <sup>e</sup>	143.0-145.0	0.88 (t, 6H, J=6.8), 1.25-1.45 (m, 20H), 1.65-1.80 (m, 4H), 4.10-4.30 (m, 4H), 5.14 (s, 2H)	C, 36.86 (36.92) H, 6.78 (6.82) S, 9.71 (9.85)
<b>2b</b>	33 <sup>e</sup>	155.0-157.0	0.88 (t, 6H, J=6.8), 1.25-1.45 (m, 28H), 1.65-1.80 (m, 4H), 4.10-4.30 (m, 4H), 5.15 (s, 2H)	C, 40.80 (40.79) H, 7.22 (7.42) S, 8.99 (9.07)
<b>2c</b>	45 <sup>e</sup>	165.0-167.0	0.87 (t, 6H, J=6.9), 1.25-1.45 (m, 36H), 1.65-1.80 (m, 4H), 4.10-4.30 (m, 4H), 5.14 (s, 2H)	C, 44.38 (44.08) H, 7.58 (7.93) S, 8.26 (8.46)

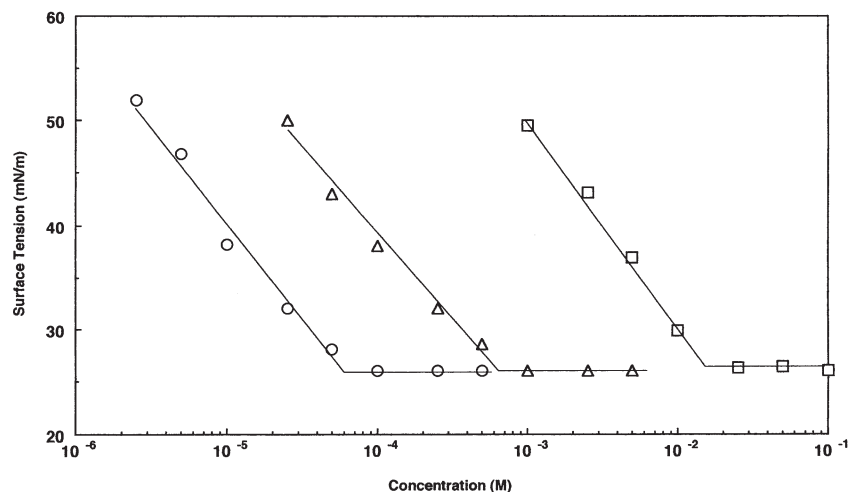
a) IR spectra (neat): **1a,b,c**: 3380, 2920, 1740 and 1470 cm<sup>-1</sup>; **2a,b,c**: 2920, 1750, 1240 and 1060 cm<sup>-1</sup>.

b) In CDCl<sub>3</sub> (**1**) and CD<sub>3</sub>OD (**2**), TMS as an internal standard.

c) Calculation values of **2** are based on the assumption that these compounds contain bound water.

d) Based on ethyl tartrate.

e) Based on **1**.



**Fig. 1** Surface Tension-Concentration Plots of Aqueous Surfactant Solutions of Compounds **2** at 25°C: □, **2a**; △, **2b**; ○, **2c**.

readily soluble in water which is significant for practical use. Though the  $T_{Kp}$  values of compounds **2** were below 0°C, the  $T_{Kp}$  of dodecyl sulfate (SDS) was 16.3 °C and that of tetradecyl sulfate was 21.0°C. This result clearly shows that the solubility in water of compounds **2** is higher than that of the conventional surfactants.

The cmc value of **2b** was about one order of magnitude larger than that of **2c**. However, the difference in the cmc values between **2a** and **2b** became more than one order of magnitude. The cmc values of the compounds **2b**, **c** were much smaller than those of the conventional surfactants with one longer lipophilic chain such as tetradecyl sulfate. The cmc of SDS was about two order of magnitude larger than that of **2c**, which

had the same alkyl chain length. The  $\gamma_{cmc}$  values of **2** were all below 30 mN/m. Though a clear correlation between the  $\gamma_{cmc}$  and the length of the R is not observed, these surfactants have much better ability to lower surface tension than the conventional surfactants. That results imply that compounds **2** are more tightly packed at the surface than the single-chain surfactants. In the range of this work, a series of cleavable surfactants **2** have much higher water-solubility, smaller cmc and lower surface tension at cmc compared with the corresponding conventional surfactants.

Foaming properties and solubility in hard water for compounds **2** are summarized in **Table 3**, along with reference data for SDS.

Compounds **2a**, **b** showed both low foaming ability and low foam stability. On the other hand, compound **2c** had good foaming ability. Foaming properties of compound **2** were lower than those of SDS.

The solubility in hard water for compounds **2** in this work decreased with an increase in the length of the lipophilic group. Compound **2a** was still soluble in hard water above 2000 ppm of total hardness as CaCO<sub>3</sub>. These values for compounds **2a**, **b** were larger than that of SDS. The value for compound **2c** was smaller than that of SDS bearing the same alkyl chain length. Compound **2c** was easier crystallized out of hard water compared with SDS.

The decomposition properties of compound **2b** bearing decyl groups by the addition of NaOH or HCl were measured using GLC.

**Table 2** Surface-Active Properties of Bis(sodium sulfate) (**2**) and the Reference Compounds<sup>a)</sup>.

Compound	R	$T_{Kp}$ <sup>b)</sup> (°C)	cmc (mM)	$\gamma_{cmc}$ (mN/m)
<b>2a</b>	C <sub>8</sub> H <sub>17</sub>	< 0	16.0	26.5
<b>2b</b>	C <sub>10</sub> H <sub>21</sub>	< 0	0.65	26.0
<b>2c</b>	C <sub>12</sub> H <sub>25</sub>	< 0	0.060	26.0
<i>(reference compounds)</i>				
	C <sub>12</sub> H <sub>25</sub> SO <sub>4</sub> Na	16.3	8.2	32.5
	C <sub>14</sub> H <sub>29</sub> SO <sub>4</sub> Na <sup>c)</sup>	21.0	2.2	34.8

a) At 25°C.

b) At 1 wt%.

c) Cited in reference 27.

**Table 3** Foaming Properties and Solubility in Hard Water of Bis(sodium sulfate) (**2**) and the Reference Compound<sup>a)</sup>.

Compound	R	Foam volume (mL) <sup>b)</sup>			Solubility in hard water <sup>c)</sup> (ppm)
		0	1	5 (min)	
<b>2a</b>	C <sub>8</sub> H <sub>17</sub>	60	15	5	> 2000
<b>2b</b>	C <sub>10</sub> H <sub>21</sub>	60	15	5	1340
<b>2c</b>	C <sub>12</sub> H <sub>25</sub>	200	70	50	340
(reference compound)					
	C <sub>12</sub> H <sub>25</sub> SO <sub>4</sub> Na	215	190	130	610

a) At 25°C.

b) At 0.1 wt%.

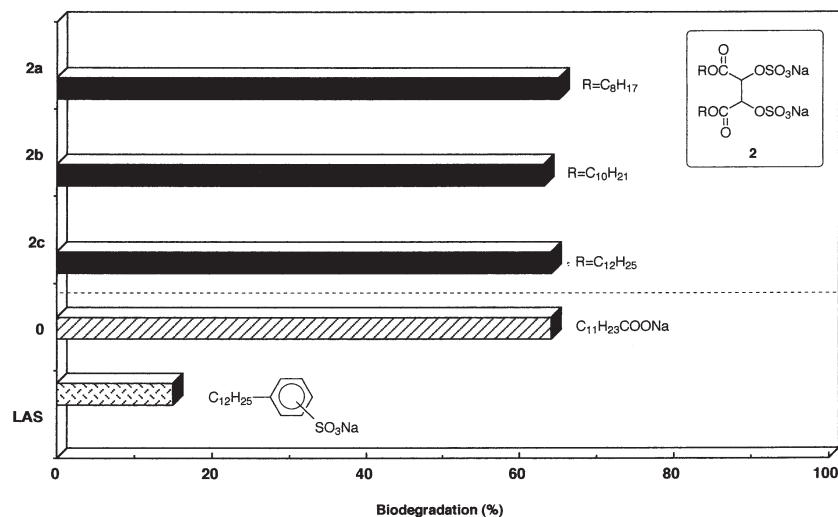
c) These values are the maximal total hardness as CaCO<sub>3</sub> of hard water in which a 0.5 wt% of the compound can dissolve.

Decomposition profiles of **2b** are summarized in **Table 4**. Under alkaline conditions, compound **2b** decomposed immediately at 1 M NaOH, and 85 min at 0.1 M NaOH. Under acidic conditions, **2b** required about 12 h at 5 M HCl, and 1.5 day at 1 M HCl to decompose almost completely. Acid decomposition was slower than alkali decomposition. The decomposition properties of **2a, c** were almost the same as that of **2b**. The rate of decomposition of surfactants was usually measured using <sup>1</sup>H-NMR spectroscopy previously. The <sup>1</sup>H-NMR spectrum of compounds **2** in D<sub>2</sub>O contained no discernible signals for **2**, probably because the lack of signals, due to line width broadening, is consistent with the absence of micelles and with the presence

**Table 4** Decomposition Profiles for Bis(sodium sulfate) (**2b**) at 25°C<sup>a)</sup>.

Compound	Time for complete decomposition			
	NaOH		HCl	
	1 M	0.1 M	5 M	1 M
<b>2b</b>	Immediately	85 min	12 h	1.5 day

a) Determined by the GLC analysis.

**Fig. 2** Biodegradability of Compounds **2a**, **2b** and **2c** after 2 wk, along with the Data for Sodium Dodecanoate and Sodium *n*-Dodecylbenzenesulfonate.

of vesicles or other large aggregates (28). The presence of aggregates with a hydrodynamic diameter of about 140 nm (**2a**) was observed by DLS analysis. It has been also confirmed that these compounds are stable at ambient temperature for at least 1 yr.

Finally, the biodegradability of compounds **2** was measured by the BOD method in the presence of activated sludge. Biodegradability data for compounds after 2 wk are shown in **Fig. 2**, along with the data for sodium dodecanoate and sodium *n*-dodecylbenzenesulfonate (LAS) measured under the same conditions.

The test chemicals going a result of greater than 60% BOD (within 28 days) should be regarded as readily biodegradable. The biodegradabilities of these cleavable surfactants **2a-c** after 14 days are more than 60%. The biodegradability of **2** was almost the same compared with that of sodium dodecanoate, which is known to be a good biodegradable compound. The biodegradability of sodium *n*-dodecylbenzenesulfonate (LAS), which is popular component in commercial detergents, was 15% under same conditions. These surfactants have much higher biodegradation than LAS.

The chemocleavable gemini surfactants were easily prepared by relatively simple methods from easily accessible commercial reagents. These surfactants had better water-solubility, smaller critical micelle concentration (cmc) and lower surface tension at cmc compared to the conventional surfactants. They have acid- and alkali-decomposition property and good biodegradability.

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