Preparation and Properties of Sulfonate Salt-Type Cleavable Surfactants with a 1,3-Dioxane Ring

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A series of di-anionic cleavable surfactants were prepared by the condensation of aldehydes with 2,2-*bis*(hydroxymethyl)-1,3-propanediol, followed by reaction with 1,3-propanesultone in the presence of sodium hydride. Surfactant 5a had a different ^{1}H nuclear magnetic resonance spectrum in D_2O than products 5b–d. This was rationalized by its different conformation, which originates from the self-coiling of its alkyl chain. The critical micelle concentrations, Krafft points and hydrolysis properties of these surfactants were determined.

KEY WORDS: Aldehydes, 2,2-*bis*(hydroxymethyl)-1,3-propanediol,1,3-propanesultone, cleavable surfactants, critical micelle concentration, 1,3-dioxane ring, Krafft point, hydrolysis, self-coiling.

Micelles and vesicles derived from surfactants have been widely used as mimetic membrane systems in chemistry and biology. Cleavable surfactants have become of great interest in surfactant chemistry over the past decade as a possible means to overcome the troublesome emulsion formation of conventional surfactants during extraction procedures. There exists a destructible group between the hydrophobic and hydrophilic portions of cleavable surfactants. The destructible groups are labile under mild conditions such as acid (1–12), base (13), salt (14), heat (15) and light (16), and they are reactive to neutral molecules (17). Up to now, the main interest has been focused on surfactants with a 1,3-dioxolane ring (1–11). There are only a few reports on surfactants with a 1,3-dioxane ring (18–20). Of the studied surfactants, di-anionic surfactants have not been investigated as much. We have recently reported the first example of di-anionic cleavable surfactants with a 1,3-dioxane ring (21). However, under acidic conditions, the carboxylate-type surfactants are converted to carboxylic acid before the 1,3-dioxane ring is cleaved. To eliminate the influence of the change of the hydrophilic head group on the hydrolysis of surfactants and to compare these products with other cleavable surfactants, we report the preparation and properties of another series of di-anionic surfactants with a 1,3-dioxane ring.

EXPERIMENTAL PROCEDURES

Materials. *n*-Hexanal (Merck, Darmstadt, Germany), *n*-octanal (Tokyo Kasei, Tokyo, Japan), *n*-decanal (Fluka, Buchs, Switzerland) and *n*-dodecanal (Koch-Light) were used after distillation under reduced pressure. 2,2-*bis*(Hydroxymethyl)-1,3-propanediol was purchased from Shanghai Chemical Plant (Shanghai, China) and was purified by recrystallization from distilled water. Sodium hydride (Fluka) and 1,3-propanesultone (Tokyo Kasei) were used as provided. Pyrene (Sigma Chemical Co., St. Louis, MO) was purified by three recrystallizations from ethanol. All other reagents were of analytical grade and used without further purification.

*Synthesis of 2-alkyl-5,5-*bis*(hydroxymethyl)-1,3-dioxane* (3a–d). The synthetic procedure for 2-undecyl-5,5-*bis*-(hydroxymethyl)-1,3-dioxane (**3a**) was as follows: A mixture of 13.0 g (96 mmol) of 2,2-*bis*(hydroxymethyl)-1,3-propanediol (2) and 100 mL of dimethylformamide (DMF) was heated and stirred until 2 was completely dissolved. Dodecanal (**1a**; 16.3 g, or 89 mmol) and 1 g (5 mmol) of *p*-toluenesulfonic acid monohydrate was added. The solution was heated and stirred at 80–90°C for 10 h. One hundred mL of ethyl acetate was added to dissolve the residue after DMF was evaporated under reduced pressure. The organic solution was washed successively with two 50-mL portions of 5% aqueous sodium bicarbonate and water, and then dried over anhydrous sodium sulfate for 3 h. After filtration, the filtrate was evaporated. The resultant solid was recrystallized from benzene to give 19.1 g (71%) of white solid **3a**. Products **3b–d** were prepared by the same procedure.

Synthesis of sulfonate-type surfactants **5a–d**. Product **5a** was synthesized by the following procedure: A suspension of 1.3 g (54 mmol) of sodium hydride in 200 mL benzene (distilled from $LiAlH_4$) was stirred while 6.8 g (22.5 mmol) of **3a** was added slowly. This suspension was stirred and refluxed for 24 h under nitrogen atmosphere. After cooling, 6.6 g (54 mmol) of 1,3-propanesultone was added dropwise to the benzene suspension. Refluxing with stirring was continued for another 24 h under nitrogen atmosphere. Benzene was evaporated to give 15.0 g of crude product, which was purified by recrystallization from a mixture of ethanol and water, giving 11.4 g (86%) of white powdery solid **5a**. Products **5b–d** were prepared by the same procedure.

Determination of the critical micelle concentrations (CMCs) of surfactants **5a–d**. The CMC was determined by the plot of the intensity ratios of peak III to peak I of pyrene vs. surfactant concentrations, and the midpoint on the sharp break of the plot was taken as the CMC (22).

Krafft point determination of surfactants **5a–d**. The Krafft point was determined by the naked eye with a 1% aqueous solution of surfactant (23).

Hydrolysis of cleavable surfactants **5a–d**. A weighed amount of surfactant and 25 mL of 2N HCl were placed in a 100-mL Erlenmeyer flask equipped with a magnetic stirrer. The mixture was stirred at 50°C for a given time and extracted with three 25-mL portions of diethyl ether. The ether layer was dried over anhydrous sodium sulfate for 3 h. After filtration, the filtrate was evaporated to give the corresponding alkanal.

RESULTS AND DISCUSSION

A series of sulfonate-type cleavable surfactants, **5a–d**, were readily prepared by condensation of aldehydes with 2,2-*bis*(hydroxymethyl)-1,3-propanediol in DMF with *p*-toluenesulfonic acid monohydrate as catalyst, followed by

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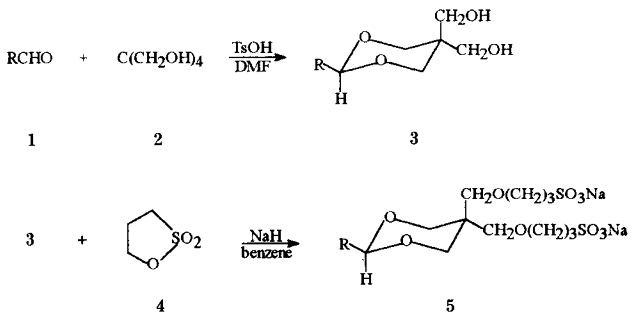

a, R = $C_{11}H_{23}$; b, R = C_9H_{19}; c, R = C_7H_{15}; d, R = C_5H_{11}

SCHEME 1

TABLE 1

Yields and Melting Points of Monoacetals 3a-d

Compound	3a	3b	3c	3d
Yield (%)	71	64	61	56
Melting point (°C)	94-94.5	90-90.5	86-86.5	82-82.5[a]

[a]Conrad *et al.* (24) reported a melting point of 80-82°C for this compound.

reaction with sodium hydride and 1,3-propanesultone in benzene (Scheme 1).

2,2-*bis*(Hydroxymethyl)-1,3-propanediol (2) is quite insoluble in almost all organic solvents, such as benzene. Conrad *et al.* (24) found that the reaction of aldehydes with 2 in benzene gave diacetals as the only products. Although 2 is quite soluble in diethylene glycol diethyl ether at its boiling point, the condensation reaction was slow, and a pure product was not isolated. Conrad *et al.* (24) prepared the monoacetals of 2 in aqueous dioxane. We found that 2 was completely dissolved in hot polar organic solvents such as DMF and dimethylsulfoxide, and we successfully prepared the monoacetals of 2 in the DMF solvent.

The yields and melting points of monoacetals **3a–d** are listed in Table 1. Monoacetals **3a–d** were characterized by ^1H nuclear magnetic resonance (NMR), infrared spectroscopy (IR) and elemental analyses (Table 2). The yields and CMCs at 25°C of surfactants **5a–d** are listed in Table 3. Surfactants **5a–d** were also characterized by ^1H NMR, IR and elemental analyses (Table 4).

Table 3 shows that the ^1H NMR chemical shift pattern of **5a** is different from those of **5b–d**. Most prominently, the acetal hydrogen and the two magnetically equivalent axial hydrogens of **5a** show an upfield shift of 0.19 ppm (76 Hz) and 0.17 ppm (68 Hz), respectively, in relation to the corresponding hydrogens of **5b–d**.

TABLE 2

Analytical and Spectral Data of Monoacetals 3a-d

Compound	Elemental analysis found (calcd) C (%)	Elemental analysis found (calcd) H (%)	^1H NMR (80 MHz, δ)[a]	IR (cm^{-1})
3a	67.52 (67.51)	11.38 (11.33)	0.87 (*t*, J = 6 Hz, 3H, CH_3), 1.24-1.57 (*m*, 20H, $(CH_2)_{10}$), 2.00 (*s*, 2H, CH_2OH), 3.47 (*s*, 2H, CH_2OH), 3.53 (*d*, J = 11.6 Hz, 2H, H_a), 4.01 (*d*, J = 11.6 Hz, 2H, H_e), 4.03 (*s*, 2H, CH_2OH), 4.44 (*t*, J = 5 Hz, 1H, CH)	3269, 2955, 2920, 2851, 1470, 1406, 1155, 1116, 1036, 936, 719, 701
3b	65.69 (65.66)	11.15 (11.02)	0.87 (*t*, J = 6 Hz, 3H, CH_3), 1.25-1.55 (*m*, 16H, $(CH_2)_8$), 2.30 (*s*, 2H, CH_2OH), 3.47 (*s*, 2H, CH_2OH), 3.53 (*d*, J = 11.7 Hz, 2H, H_a), 4.01 (*d*, J = 11.7 Hz, 2H, H_e), 4.04 (*s*, 2H, CH_2OH), 4.45 (*t*, J = 5 Hz, 1H, CH)	3268, 2955, 2922, 2852, 1470, 1406, 1154, 1114, 1037, 938, 720, 699
3c	63.66 (63.38)	10.81 (10.64)	0.87 (*t*, J = 6 Hz, 3H, CH_3), 1.26-1.55 (*m*, 12H, $(CH_2)_6$), 2.30 (*s*, 2H, CH_2OH), 3.47 (*s*, 2H, CH_2OH), 3.53 (*d*, J = 11.6 Hz, 2H, H_a), 4.01 (*d*, J = 11.6 Hz, 2H, H_e), 4.03 (*s*, 2H, CH_2OH), 4.45 (*t*, J = 5 Hz, 1H, CH)	3271, 2955, 2925, 2855, 1471, 1406, 1154, 1113, 1037, 936, 722, 700
3d	60.47 (60.52)	10.20 (10.16)	0.87 (*t*, J = 6 Hz, 3H, CH_3), 1.25-1.55 (*m*, 8H, $(CH_2)_4$), 2.30 (*s*, 2H, CH_2OH), 3.47 (*s*, 2H, CH_2OH), 3.53 (*d*, J = 11.7 Hz, 2H, H_a), 4.01 (*d*, J = 11.7 Hz, 2H, H_e), 4.03 (*s*, 2H, CH_2OH), 4.45 (*t*, J = 5Hz, 1H, CH)	3272, 2949, 2928, 2856, 1470, 1406, 1151, 1108, 1039, 934, 721, 695

[a]$CDCl_3$ was used as solvent and tetramethylsilane as the internal standard; H_a and H_e correspond to the axial and equatorial hydrogen of the 1,3-dioxane ring, respectively. NMR, nuclear magnetic resonance; IR, infrared.

TABLE 3

Yields and Critical Micelle Concentrations (CMC) at 25°C of Surfactants 5a–d

Surfactant	5a	5b	5c	5d
Yield (%)	86	83	92	90
CMC (M)	0.0020	0.0074	0.028	0.10

The coiling/aggregation of neutral organic molecules in aqueous media and aqui-organo binary systems have been widely noticed (25). The self-coiling of the acyl chains of surfactants in aqueous media has been reported (26,27). The different chemical shift pattern of **5a** in D_2O is most probably due to its different conformation. The alkyl chain of **5a** is long enough to coil and reaches the neighborhood of the axial hydrogens of the 1,3-dioxane ring, resulting in the observed upfield shift. Another possible reason is the intermolecular interactions in the micelle of **5a**. The ^1H NMR of **5a** in Table 3 was measured above its CMC because of its low CMC, while those of **5b–d** were recorded below their CMCs. However, the same ^1H NMR spectrum of **5b** was obtained above and below its CMC. So, the effect of intermolecular interactions is not an important factor in our case.

The Krafft point is one of the fundamental properties of ionic surfactants. Surfactants **5a–d** were readily soluble at room temperature. The 1% aqueous dispersions of surfactants **5a–d** were cooled below 0°C, then allowed to thaw, and all became a clear solution at 0°C. Hence, the Krafft points of **5a–d** were below 0°C. The remarkably low Krafft points of **5a–d** are attributed to the introduction of the two hydrophilic sulfonate groups, the acetal oxygens and the ether oxygens (28). The low Krafft points and excellent hydrophilicity make them applicable over a wide range of temperatures.

Surfactants **5a–d** are stable under neutral and alkaline conditions, but they can be decomposed into corresponding aldehydes, and water-soluble compound **6** in acidic media (Scheme 2). The destructible characteristics of surfactants **5a–c** in 2 N HCl at 50°C are shown in Table 5. Under the same conditions, the time needed to decompose completely increases with increasing alkyl chainlength for the series of surfactants **5a–c** (8,9). Surprisingly, surfactant **5d** was resistant to acid. Under the same conditions, even for longer contact time, the percentage of destructibility was less than 10%. The exact reason is not known.

TABLE 4

Analytical and Spectral Data of Surfactants 5a–d

Compound	Elemental analysis found (calcd) C (%)	H (%)	S (%)	^1H NMR (400 MHz, δ)[a]	IR (cm^{-1})
5a	46.91 (46.77)	7.43 (7.51)	10.75 (10.86)	0.91 (*t*, J = 7 Hz, 3H, CH_3), 1.31 (*m*, 18H, $(CH_2)_9$), 1.60 (*m*, 2H, $C\mathit{H}_2CH$), 1.96–2.08 (*m*, 4H, $C\mathit{H}_2CH_2SO_3$), 2.91–2.99 (*m*, 4H, CH_2SO_3), 3.25 (*s*, 2H, CCH_2O), 3.55 (*t*, J = 6 Hz, 2H, $OC\mathit{H}_2CH_2$), 3.60 (*d*, J = 11.6 Hz, 2H, H_a), 3.64 (*t*, J = 6 Hz, 2H, $OC\mathit{H}_2CH_2$), 3.71 (*s*, 2H, CCH_2O), 3.96 (*d*, J = 11.6 Hz, 2H, H_e), 4.49 (*t*, J = 5 Hz, 1H, CH)	2952, 2923, 2852, 1469, 1407, 1373, 1221, 1190, 1115, 1068, 966, 937, 738, 618, 529
5b	45.08 (44.83)	7.20 (7.16)	11.20 (11.40)	0.87 (*t*, J = 7 Hz, 3H, CH_3), 1.29 (*m*, 14H, $(CH_2)_7$), 1.62 (*m*, 2H, $C\mathit{H}_2CH$), 1.96–2.08 (*m*, 4H, $C\mathit{H}_2CH_2SO_3$), 2.94–3.02 (*m*, 4H, CH_2SO_3), 3.32 (*s*, 2H, CCH_2O), 3.57 (*t*, J = 6 Hz, 2H, $OC\mathit{H}_2CH_2$), 3.67 (*t*, J = 6 Hz, 2H, $OC\mathit{H}_2CH_2$), 3.71 (*s*, 2H, CCH_2O), 3.77 (*d*, J = 11.7 Hz, 2H, H_a), 3.96 (*d*, J = 11.7 Hz, 2H, H_e), 4.68 (*t*, J = 5 Hz, 1H, CH)	2953, 2924, 2852, 1468, 1407, 1371, 1221, 1190, 1114, 1069, 968, 938, 739, 620, 529
5c	42.71 (42.69)	6.79 (6.79)	11.73 (11.99)	0.87 (*t*, J = 7 Hz, 3H, CH_3), 1.28 (*m*, 10H, $(CH_2)_5$), 1.62 (*m*, 2H, $C\mathit{H}_2CH$), 1.98–2.08 (*m*, 4H, $C\mathit{H}_2CH_2SO_3$), 2.94–3.01 (*m*, 4H, CH_2SO_3), 3.32 (*s*, 2H, CCH_2O), 3.57 (*t*, J = 6 Hz, 2H, $OC\mathit{H}_2CH_2$), 3.67 (*t*, J = 6 Hz, 2H, $OC\mathit{H}_2CH_2$), 3.71 (*s*, 2H, CCH_2O), 3.77 (*d*, J = 11.7 Hz, 2H, H_a), 3.96 (*d*, J = 11.7 Hz, 2H, H_e), 4.68 (*t*, J = 5 Hz, 1H, CH)	2953, 2927, 2855, 1469, 1407, 1372, 1222, 1190, 1113, 1068, 969, 937, 740, 619, 529
5d	40.14 (40.31)	6.39 (6.37)	12.48 (12.66)	0.87 (*t*, J = 7 Hz, 3H, CH_3), 1.28 [*m*, 4H, $(CH_2)_2$], 1.38 (*m*, 2H, CH_2), 1.62 (*m*, 2H, $C\mathit{H}_2CH$), 1.97–2.08 (*m*, 4H, $C\mathit{H}_2CH_2SO_3$), 2.94–3.01 (*m*, 4H, CH_2SO_3), 3.32 (*s*, 2H, CCH_2O), 3.57 (*t*, J = 6 Hz, 2H, $OC\mathit{H}_2CH_2$), 3.67 (*t*, J = 6 Hz, 2H, $OC\mathit{H}_2CH_2$), 3.71 (*s*, 2H, CCH_2O), 3.77 (*d*, J = 11.8 Hz, 2H, H_a), 3.95 (*d*, J = 11.8 Hz, 2H, H_e), 4.68 (*t*, J = 5 Hz, 1H, CH)	2953, 2929, 2856, 1469, 1410, 1372, 1222, 1190, 1111, 1068, 967, 939, 739, 619, 530

[a] D_2O was used as solvent and sodium 2,2-dimethyl-2-silapentane-5-sulfonate as the internal standard. Abbreviations as in Table 2.

$$5 \xrightarrow[H_2O]{H^+} \underset{\mathbf{1}}{RCHO} + \underset{\mathbf{6}}{(HOCH_2)_2C(CH_2O(CH_2)_3SO_3Na)_2}$$

SCHEME 2

TABLE 5

The Destructibility of Surfactants 5a–c in 2N HCl at 50°C

Compound	5a		5b		5c	
Surfactant concentration (mM)	10	20	10	20	10	20
Time (h)	10	15	4	7	1.5	2
Decomposition (%)	100	100	100	100	100	100

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