Preparation and Properties of Cleavable Dianionic Surfactants with a 1,3-Dioxane Ring

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Some cleavable dianionic surfactants were prepared by the reaction of aldehydes with diethyl *bis*(hydroxymethyl)-malonate, followed by saponification with sodium hydroxide. The critical micelle concentrations of the surfactants were determined.

KEY WORDS: Aldehydes, cleavable dianionic surfactants, critical micelle concentration, diethyl *bis*(hydroxymethyl)malonate, 1,3-dioxane ring.

Surfactants are widely used for catalytic reactions and product isolation in chemistry and biology. To overcome troublesome emulsions and to facilitate extraction procedures after various applications of surfactants, cleavable surfactants have been introduced (1) and have become a focus of investigation in recent years (2–4). They are stable under certain conditions but can be decomposed to nonsurfactant compounds under other, mild conditions (*e.g.*, acid, base, salt, heat or light). Most of the reported destructible surfactants are based on a 1,3-dioxolane ring or a silicon-oxygen bond. To our knowledge, there are only two reports (5,6) on cleavable surfactants with a 1,3-dioxane ring and no studies on cleavable dianionic surfactants in the literature. We report the preparation and properties of some cleavable dianionic surfactants with a 1,3-dioxane ring, which can be easily prepared by the reaction of a series of aldehydes with diethyl *bis*(hydroxymethyl)malonate, followed by saponification with sodium hydroxide in ethanol.

EXPERIMENTAL PROCEDURES

Materials. All aldehydes were commercially available and were distilled before use. Diethyl *bis*(hydroxymethyl)-malonate (**2**) was prepared according to Block's method (7). ^{1}H nuclear magnetic resonance (NMR) (80 MHz, $CDCl_3$): δ 1.25 (6H, *t*, J = 7 Hz, CH_3), 2.89 (2H, *s*, OH), 4.08 (4H, *s*, CH_2), 4.22 (4H, *q*, J = 7 Hz, CH_2).

Synthesis of 1,3-dioxane ester compounds (**3a–g**). **3a** was synthesized as follows: 13.0 g dodecanal (**1a**; 71 mmol), 15.5 g of **2** (70 mmol), 0.2 g *p*-toluenesulfonic monohydrate (TsOH; 1 mmol), and 150 mL benzene were stirred and refluxed under a Dean-Stark trap until no more water was collected (*ca.* 3 h). Sodium acetate (0.3 g) was added to the cooled reaction mixture and the mixture was stirred for 30 min, filtered and washed twice with 50 mL water. The benzene layer was dried over 15 g anhydrous sodium sulfate for 2 h. After filtration, benzene was evaporated. The residue was fractionated by distillation under reduced pressure to give 20.9 g of **3a** (yield, 77%) as colorless liquid, b.p. 187°C/2 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87 (3H, *t*, J = 7 Hz, CH_3), 1.22–1.36 (24 H, *m*, $(CH_2)_9$, CH_3), 1.58 (2H, *m*, CH_2CH), 3.92 (2H, *d*, J = 11.5 Hz, H_a), 4.16 (2H, *q*, J = 7 Hz, $COOCH_2$), 4.31 (2H, *q*, J = 7 Hz, $COOCH_2$), 4.49 (1H, *t*, J = 5 Hz, CH), 4.69 (2H, *d*, J = 11.5 Hz, H_e). Infrared (IR) (KBr): 2926, 2855, 1736, 1465, 1383, 1369, 1256, 1224, 1153, 1117, 1094, 1048 cm^{-1}. Anal: calcd. for $C_{21}H_{38}O_6$: C, 65.26%; H, 9.91%. Found: C, 65.68%; H, 10.14%. The other esters **3b–g** were synthesized by the same procedure and also characterized by ^{1}H NMR, infrared spectroscopy and elemental analysis.

Synthesis of cleavable dianionic surfactants (**4a–g**). The synthetic procedure of **4a** was as follows: 20.9 g of **3a** (54 mmol) and 5.0 g sodium hydroxide (125 mmol) in 100 mL ethanol were stirred and refluxed for 8 h. The cooled mixture was filtered and the solid was washed with cold water and ethanol, and then dried at 70°C under vacuum. 19.3 g of **4a** (yield, 95%) was obtained as white powdery solid. ^{1}H NMR (400 MHz, D_2O, DSS): δ 0.86 (3H, *t*, J = Hz, CH_3), 1.27–1.35 (18H, *m*, $(CH_2)_9$, 1.55 (2H, *m*, CH_2), 3.84 (2H, *d*, J = 11.5 Hz, H_a), 4.58 (2H, *d*, J = 11.5 Hz, H_e), 4.61 (1H, *t*, J = 5 Hz, CH). IR (KBr): 2925, 2855, 1614, 1468, 1440, 1404, 1375, 1332, 1302, 1159, 1117, 1084 cm^{-1}. The other surfactants **4b–g** were synthesized by the same procedure and also characterized by their spectral data.

Measurements of critical micelle concentrations (CMCs). The CMCs of **4a–g** were determined by variations of the pyrene peak III/I ratio as a function of surfactant concentration (8).

Hydrolysis of surfactants **4a–g**. Two hundred thirty-one mg of **4a**, 25 mL 0.1 N HCl and 25 mL diethyl ether were added to a separatory funnel. The mixture was separated immediately without foaming into ethereal and aqueous layers after vigorous shaking. The surfactants **4b–g** have similar property.

RESULTS AND DISCUSSION

A new type of cleavable surfactant can be easily prepared in high yields by only two steps, as shown in Scheme 1. The yields and boiling points of **3a–g** are listed in Table 1. The yields and CMCs at 25°C of **4a–g** are listed in Table 2.

Because surfactants **4** are slightly hygroscopic, their elemental analysis data were not shown. However, after correction for the absorbed water, determined by thermogravimetric analysis (TGA), the elemental analysis data coincide well with the calculated data. For example, the elemental analysis of **4a** were C, 52.82%; H, 7.71%, and the absorbed water was 3.03%. So, the corrected data were C, 54.47%; H, 7.60%, which were close to the calculated data, C, 54.54%; H, 7.54%.

From ^{1}H NMR data, it is evident that both **3** and **4** exist in only one conformation, *i.e.*, the chair conformation with equatorial alkyl chain (see Scheme 1). Axial protons at carbon-4 and carbon-6 of the 1,3-dioxane ring are magnetically equivalent, and so are equatorial protons. The former absorb at a higher field than the latter.

Owing to two hydrophilic carboxylates, **4** show good solubility in water and have much higher CMCs than cleavable surfactants with comparable alkyl chain reported previously (3,5).

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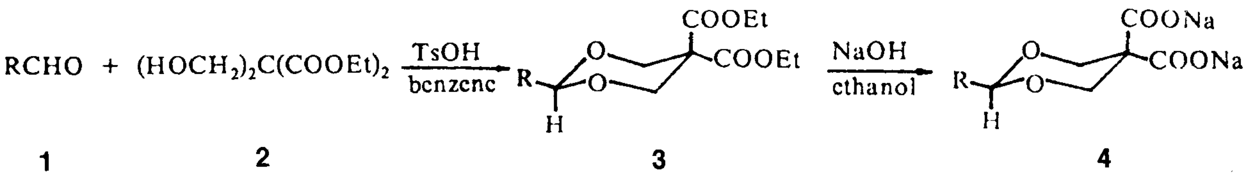

a, $R = C_{11}H_{23}$; **b**, $R = C_{10}H_{21}$; **c**, $R = C_9H_{19}$; **d**, $R = C_8H_{17}$; **e**, $R = C_7H_{15}$; **f**, $R = C_6H_{13}$; **g**, $R = C_5H_{11}$

SCHEME 1

TABLE 1

Yields and Boiling Points of 3a–g[a]

Compound	3a	3b	3c	3d	3e	3f	3g
Yield (%)	77	80	81	81	82	83	83
b.p. (°C/2 mm Hg)	187	177	168	159	150	141	132

[a]The yields and critical micelle concentrations at 25°C of 4a–g are listed in Table 2.

Surfactants 4a–g are stable under neutral and basic conditions, but labile in acidic medium. Aqueous solutions of 4a–g were defoamed immediately after addition of dilute hydrochloric acid. Further studies on the hydrolysis of 4a–g are in progress.

TABLE 2

Yields and CMCs[a] of 4a–g

Compound	4a	4b	4c	4d	4e	4f	4g
Yield (%)	95	94	94	96	94	95	93
CMC (M)	0.026	0.044	0.072	0.12	0.20	0.33	0.55

[a]CMC, critical micelle concentration.

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REFERENCES

1. Cuomo, J., J.H. Merrifield and J.F.W. Keana, *J. Org. Chem. 45*:4216 (1980).
2. Jaeger, D.A., J. Jamrozik, T.G. Golich, M.W. Clennan and J. Mohebalian, *J. Am. Chem. Soc. 111*:3001 (1989).
3. Yamamura, S., M. Nakamura and T. Takeda, *J. Am. Oil Chem. Soc. 66*:1165 (1989).
4. Jaeger, D.A., M.D. Ward and A.K. Dutta, *J. Org. Chem. 53*:1577 (1988).
5. Kida, T., A. Masuyama and M. Okahara, *Tetrahed. Lett. 31*:5939 (1990).
6. Burczyk, B., M. Banaszczyk, A. Sokolowski and A. Piasecki, *J. Am. Oil Chem. Soc. 65*:1204 (1988).
7. Block, P. Jr., *Org. Synth. Coll. 5*:381 (1973).
8. Kalyanasundaram, K., and J.K. Thomas, *J. Am. Chem. Soc. 99*:2039 (1977).

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