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## Properties and Applications of Sodium 2-Alkyl-5-(Ethoxycarbonyl)-1,3-Dioxane-5-Carboxylate Synthesized with Nano-Sulfonated Carbon

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A series of novel sodium 2-alkyl-5-(ethoxycarbonyl)-1,3-dioxane-5-carboxylate surfactants were synthesized in high yield using nanosolid superacid sulfonated carbon as a catalyst and characterized by <sup>1</sup>H NMR, IR and elemental analysis. Critical micelle concentration (CMC) of the surfactants was determined and the results showed that the CMC values were less than  $1.0 \times 10^{-3}$  mol/L. Other relevant surface properties were also evaluated, such as emulsion stability, foam ability and degradability. In relation to emulsion formation, foam stability and the range of application of temperature, the new surfactants showed better properties than traditional surfactants when used as an emulsifier in emulsion polymerization. Moreover, the surfactants were stable under alkaline and neutral conditions, and degraded into raw materials under acid condition. Convenient synthesis process with high yield and superior properties promisingly make the title compounds to be a type of 'environmentally friendly' surfactants.

Keywords: Nanosolid Superacid, Synthesis, Acetal, 1,3-Dioxane, Surfactant.

#### **1. INTRODUCTION**

Toothpaste, shampoo, detergent and washing powder like old friends to meet every day in our lives, and they have a common point, that is all of their active constituents are surfactants. Classical surfactants consist of two obvious parts, one polar and the other nonpolar, incompatible with each other. Because of this amphiphilicity, surfactant molecules tend to self-aggregate into micelles, which form the basis of many biochemical processes. Surfactants were widely used in different industrial areas, such as cleaning, paint, emulision, catalysis, microreactor, pharmaceuticals and so on.<sup>1-3</sup> Long-chain acetal, which could be synthesized by fatty aldehyde and polyhydric alcohols using acid as a catalyst, is an important type of materials to make segregative and degradable surfactants.<sup>4,5</sup> Compared with traditional surfactants, this type of acetal compounds possess unusual physicochemical properties and can be used in the emulsion polymerization and emulsion of organic reactions with higher efficiency.<sup>6-8</sup> After the reaction, microemulsion could be decomposed under

acid condition, and the products could be separated easily from two phases.<sup>9-11</sup> In recent years, nanomaterials such as nanosolid superacids have attracted so much attention by their better chemical properties.<sup>12-20</sup> Sulfonated carbon was usually used as a kind of nanosolid superacid in organic catalytic synthesis and worked very well.<sup>21-28</sup> In this paper, a new type of segregative and degradable surfactants containing 1,3-dioxane were synthesized by diethyl 2,2-bis(hydroxymethyl)malonate with long-chain fatty aldehyde, using nanosolid superacid sulfonated carbon as a catalyst (Scheme 1). It was showed that these new surfactants were stable under alkaline and neutral conditions, and would degrade into the raw materials in acid environment. From the above, these surfactants are promising to be a novel type of competitive and eco-friendly ones.29-33

#### 2. EXPERIMENTAL SECTION

# **2.1. Instrumentation and Materials** *2.1.1. Instruments*

according to the literature.<sup>28</sup> SEM image of the sulfonated

The nanosolid catalyst sulfonated carbon was prepared

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Scheme 1. Synthesis of surfactants 3a~3d.

carbon is shown in Figure 1. Melting point data were recorded on a XRC-1 microscopic melting point meter with the thermometer without correction. Element analysis was recorded on PE2400 instrument. The IR spectra were recorded in the 4000–400 cm<sup>-1</sup> region using KBr pellets and a Niconet AVATAR-360 spectrometer. <sup>1</sup>H NMR spectra were recorded in a DMSO solution with a VARAN UNTTY INOV-400 spectrometer. 2,2-Bis(hydroxymethyl) malonate (98%, Aladdin) and all of the aldehyde (Aladdin) were purified by distillation before use. Other materials and solvents were commercially available and were used without further purification.

#### 2.1.2. General Procedure for the Synthesis of Diethyl 2-Alkyl-1,3-Dioxane-5,5-Dicarboxylate (2a-2d)

A solution of diethyl 2,2-bis(hydroxymethyl) malonate (12 mmol), **1** (10 mmol) and sulfonated carbon (1.0 g) were heated to reflux in a mixture of N,N-dimethylformamide (10 mL) and cyclohexane (6 mL) under stirring for 3 h. After cooling to room temperature, the solution was filtered and the solvent was removed in vacuo, the residue was dissolved in EtOAc (15 mL), washed with saturated brine (10 mL × 2) and water (10 mL × 2), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was filtered and concentrated to give **2a–2d** as colorless oil.

**2a**: A colorless oil; yield 78.1%; b.p. 124 °C (0.1 Mpa); <sup>1</sup>H NMR (DMSO, 400 MHz)  $\delta$  (ppm): 0.85 (*t*, 3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 1.21 (*t*, 6H, O–CH<sub>2</sub>–<u>CH<sub>3</sub></u>); 1.28–1.29 (*m*, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 1.48





(q, 2H, <u>CH</u><sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 4.14 (q, 4H, O-<u>CH</u><sub>2</sub>-CH<sub>3</sub>); 4.19–4.21 (d, J = 11.2 Hz, 2H, Hax); 4.379 (t, 1H, -<u>CH</u>); 4.452–4.593 (d, J = 11.2 Hz, 2H, Heq); IR (KBr) v: 2961.3, 2873.7, 1725.6, 1465.7, 1446.2, 1368.1, 1242.9, 1185.1, 1151.8, 1109.1, 857.1, 756.1 cm<sup>-1</sup>; Anal. Calcd for C<sub>14</sub>H<sub>24</sub>O<sub>6</sub>: C 58.33%, H 8.33%, Found C 58.28%, H 8.37%.

**2b**: A colorless oil; yield 75.6%, b.p. 182 °C (0.1 Mpa); <sup>1</sup>H NMR (DMSO, 400 MHz)  $\delta$  (ppm): 0.89 (*t*, 3H, C<sub>5</sub>H<sub>10</sub><u>CH</u><sub>3</sub>); 1.152 (*t*, 6H, O–CH<sub>2</sub><u>CH</u><sub>3</sub>); 1.21–1.29 (*m*, 8H, CH<sub>2</sub><u>C</u><sub>4</sub>H<sub>8</sub>CH<sub>3</sub>); 1.456 (*q*, 2H, <u>CH</u><sub>2</sub>C<sub>4</sub>H<sub>8</sub>CH<sub>3</sub>); 3.925–3.953 (*d*, *J* = 11.2 Hz, 2H, Hax); 4.12–4.23 (*q*, 4H, O-<u>CH</u><sub>2</sub>–CH<sub>3</sub>); 4.481–4.509 (*d*, *J* = 11.2 Hz, 2H, Heq); 4.560–4.568 (*t*, 1H, –CH); IR (KBr) *v*: 2929.4, 2858.4, 1731.1, 1465.0, 1381.5, 1367.1, 1250.8, 1218.4, 1149.3, 1110.9, 1043.7, 937.6, 861.4 cm<sup>-1</sup>; Anal. Calcd for C<sub>16</sub>H<sub>28</sub>O<sub>6</sub>: C 60.76%, H 8.86%, Found C 60.66%, H 8.78%.

**2c:** A colorless oil; yield 71.26%, b.p. 198 °C (0.1 Mpa); <sup>1</sup>H NMR (DMSO, 400 MHz)  $\delta$  (ppm): 0.87 (*t*, 3H, C<sub>6</sub>H<sub>12</sub><u>CH</u><sub>3</sub>); 1.17 (*t*, 6H, O–CH<sub>2</sub><u>CH</u><sub>3</sub>); 1.19–1.22 (*m*, 10H, CH<sub>2</sub><u>C<sub>5</sub>H<sub>10</sub></u>CH<sub>3</sub>); 1.45 (*q*, 2H, <u>CH</u><sub>2</sub>C<sub>5</sub>H<sub>10</sub>CH<sub>3</sub>); 3.93–3.95 (*d*, *J* = 11.2 Hz, 2H, Hax); 4.12–4.27 (*m*, 4H, O–<u>CH</u><sub>2</sub>–CH<sub>3</sub>); 4.49–4.52 (*d*, *J* = 11.2 Hz, 2H, Heq); 4.57 (*s*, 1H, –CH); IR (KBr) *v*: 2927.3, 2856.7, 1737.1, 1465.1, 1367.3, 1252.1, 1222.9, 1149.6, 1112.3, 1095.0, 1041.8, 940.8, 863.4 cm<sup>-1</sup>; Anal. Calcd for C<sub>17</sub>H<sub>30</sub>O<sub>6</sub>: C 61.82%, H 9.09%, Found C 61.75%, H 9.12%.

**2d**: A colorless oil; yield 68.09%, b.p. 222 °C (0.1 Mpa); <sup>1</sup>H NMR (DMSO, 400 MHz)  $\delta$  (ppm): 0.86 (*t*, 3H, C<sub>7</sub>H<sub>14</sub><u>CH</u><sub>3</sub>); 1.16 (*t*, 6H, O-CH<sub>2</sub><u>CH</u><sub>3</sub>); 1.21–1.26 (*m*, 12H, CH<sub>2</sub><u>C</u><sub>6</sub><u>H</u><sub>12</sub>CH<sub>3</sub>); 1.44 (*q*, 2H, <u>CH</u><sub>2</sub>C<sub>6</sub>H<sub>12</sub>CH<sub>3</sub>); 3.93–3.95 (*d*, *J* = 11.2 Hz, 2H, Hax); 4.12–4.23 (*s*, 4H, O–<u>CH</u><sub>2</sub>–CH<sub>3</sub>); 4.48–4.51 (*d*, *J* = 11.2 Hz, 2H, Heq); 4.57 (*s*, 1H, –CH); IR (KBr) *v*: 2929.0, 28558.2, 1737.3, 1465.1, 1367.2, 1251.4, 1218.5, 1149.5, 1111.0, 1043.6, 937.5, 861.1 cm<sup>-1</sup>; Anal. Calcd for C<sub>19</sub>H<sub>34</sub>O<sub>6</sub>: C 63.69%, H 9.50%, Found C 63.71%, H 9.47%.

#### 2.1.3. General Procedure for the Synthesis of Sodium 2-Alkyl-5-(ethoxycarbonyl)-1,3-Dioxane-5-Carboxylate (3a-3d)

A solution of **2** (50 mmol) and NaOH (49 mmol) were heated to reflux in ethanol (12 mL) with stirring for 12 h. After cooling to room temperature, the reaction mixture was filtered and the crude product was purified by

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Scheme 2. Degradation process of surfactants 3a~3d.

recrystallization from isopropyl alcohol to afford a white powdery solid.

**3a**: A white powdery solid, yield 59.42%; <sup>1</sup>H NMR (DMSO, 400 MHz)  $\delta$  (ppm): 0.85 (*t*, 3H, C<sub>3</sub>H<sub>6</sub><u>CH</u><sub>3</sub>); 1.07–1.18 (*m*, 10H, CH<sub>2</sub><u>C</u><sub>4</sub><u>H</u><sub>8</sub>CH<sub>3</sub>); 1.21 (*t*, 3H, O–CH<sub>2</sub><u>CH</u><sub>3</sub>); 4.07–4.09 (*q*, 2H, O–CH<sub>2</sub>-CH<sub>3</sub>); 4.10–4.12 (*d*, *J* = 11.2 Hz, 2H, Heq); 4.21 (*t*, 1H, –CH); 4.39–4.40 (*d*, *J* = 11.2 Hz, 2H, Hax); IR (KBr) *v*: 2949.9, 1733.5, 1574.6, 1420.5, 1236.1, 1096.7, 1030.9 cm<sup>-1</sup>; Anal. Calcd for C<sub>12</sub>H<sub>19</sub>O<sub>6</sub>Na: C 51.06%, H 6.74%, Found C 51.03%, H 6.79%.

**3b**: A white powdery solid, yield 60.96 %; <sup>1</sup>H NMR (DMSO, 400 MHz)  $\delta$  (ppm): 0.86 (t, 3H, C<sub>5</sub>H<sub>10</sub><u>CH</u><sub>3</sub>); 1.21 (t, 3H, O–CH<sub>2</sub><u>CH</u><sub>3</sub>); 1.24–1.29 (m, 10H, CH<sub>2</sub><u>C</u><sub>4</sub>H<sub>8</sub>CH<sub>3</sub>); 1.42–1.43 (q, 2H, <u>CH</u><sub>2</sub>C<sub>4</sub>H<sub>8</sub>CH<sub>3</sub>); 3.84–3.96 (q, 2H, O–CH<sub>2</sub>–CH<sub>3</sub>); 4.14–4.15 (d, J = 10.8 Hz, 2H, Hax); 4.33–4.35 (t, 1H, –CH); 4.46–4.58 (d, J = 10.8 Hz, 2H, Heq); IR (KBr) v: 2939.3, 2867.6, 1736.1, 1613.6, 1459.9, 1249.6, 1156.5, 1043.3, 862.9, 588.0 cm<sup>-1</sup>; Anal. Calcd for C<sub>14</sub>H<sub>23</sub>O<sub>6</sub>Na: C 54.19%, H 7.42%, Found 54.d2%, H 7.47%.

**3c**: A white powdery solid, yield 60.34%; <sup>1</sup>H NMR (DMSO, 400 MHz)  $\delta$  (ppm): 0.87 (t, 3H, C<sub>6</sub>H<sub>12</sub><u>CH<sub>3</sub></u>); 1.17 (t, 3H, O–CH<sub>2</sub><u>CH<sub>3</sub></u>); 1.25–1.29 (m, 10H, CH<sub>2</sub><u>C<sub>5</sub>H<sub>10</sub>CH<sub>3</sub>); 1.44–1.45 (q, 2H, <u>CH<sub>2</sub>C<sub>5</sub>H<sub>10</sub>CH<sub>3</sub>); 3.84–3.97 (q, 2H, O–CH<sub>2</sub>–CH<sub>3</sub>); 4.14–4.23 (d, J = 11.2 Hz, 2H, Hax); 4.33–4.36 (t, 1H, –CH); 4.47–4.59 (d, J = 11.2 Hz, 2H, Hax); 2H, Heq); IR (KBr) v: 2934.4, 2864.6, 1737.4, 1612.8, 1458.2, 1250.0, 1155.4, 1046.4, 867.9 cm<sup>-1</sup>; Anal. Calcd for C<sub>15</sub>H<sub>25</sub>O<sub>6</sub>Na: C 55.56%, H 7.72%, Found C 55.50%, H 7.69%.</u></u>

**3d**: A white powdery solid, yield 52.63%; <sup>1</sup>H NMR (DMSO, 400 MHz)  $\delta$  (ppm): 0.88 (t, 3H, C<sub>7</sub>H<sub>14</sub><u>CH</u><sub>3</sub>); 1.18 (t, 3H, O–CH<sub>2</sub><u>CH</u><sub>3</sub>); 1.26–1.29 (m, 12H, CH<sub>2</sub>C<sub>6</sub><u>H</u><sub>12</sub>CH<sub>3</sub>); 1.47 (q, 2H, <u>CH</u><sub>2</sub>C<sub>6</sub>H<sub>12</sub>CH<sub>3</sub>); 3.73–3.96 (q, 2H, O–CH<sub>2</sub>– CH<sub>3</sub>); 4.18–4.21 (d, J = 11.2 Hz, 2H, Hax); 4.34–4.35 (t, 1H, –CH); 4.50–4.52 (d, J = 11.2 Hz, 2H, Heq) IR (KBr) v: 2930.6, 2861.3, 1736.8, 1616.6, 1461.3, 1337.5, 1250.0, 1155.0, 1049.3, 868.6, 785.8, 579.6 cm<sup>-1</sup>; Anal. Calcd for C<sub>17</sub>H<sub>29</sub>O<sub>6</sub>Na: C 57.95%, H 8.24%, Found C 57.91%, H 8.25%.

#### 2.2. Methods

#### 2.2.1. Critical Micelle Concentration (CMC)

The CMCs of surfactants were determined by conductivity measurements. A series of concentration of surfactants  $3a \sim 3d$  solution were prepared from 0.00005 mol/L

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to 0.0100 mol/L with water in 50 mL volumetric flasks, then were kept in thermostated water bath at 25 °C for 10 min. The conductivity of the solution was measured using a conductivity cell (type DDS-11A). Each solution was measured three times and the final averaged values were used to draw a  $\kappa$ -C curve. The concentration corresponding to the breakpoint of the specific conductivity versus concentration was taken as the CMC.

#### 2.2.2. Emulsion Stability

The emulsion stability of surfactants was measured as the time of separation of the aqueous phase from the emulsion layer. Emulsions were prepared by mixing 20 mL of aqueous surfactant solutions (2 wt%) and 20 mL of benzene at room temperature.

#### 2.2.3. Foaming Ability

The foaming ability was obtained under vigorous shaking of aqueous surfactant solutions (0.1 wt%) contained in a 50 mL glass-stopper graduated cylinder at room temperature for 5 s, and the height of foam at the moment and the height of foam 30 s later were recorded timely. The ratio between them (the rest height of foam vs. the initial height) was taken as the foaming ability of the surfactant.

#### 2.2.4. Degradability

Surfactants  $3a \sim 3d$  can be degraded into biodegradable raw material molecules, aldehydes and 3-ethoxy-2,2bis(hydroxymethyl)-3-oxopropanoic acid, through adding dilute HCl with heating. The degradation process is given in Scheme 2.



Figure 2. Plot of specific conductance of aqueous  $3a \sim 3d$  surfactant solutions as a function of the concentration (C) at 298 K.

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Table I. Emulsifiability and foam ability of surfactants 3a~3d.

#### 3d Surfactant 3a 3b 3c $CMC \times 10^3$ (mol/L) 0.9 0.8 0.8 0.7 Emulsifiability (min) 4.2 17.5 40.0 57.7 Foam stability (%) 38.57 47.05 72.48 90.38

### 3. RESULTS AND DISCUSSION

### 3.1. CMC

All the four studied surfactants showed sharp breaks in the concentration isotherms (Fig. 2) which were used to determine the CMC (Table I). It is clear that the values of CMCs of surfactants  $3a \sim 3d$ , given in Table I, are all less than  $9.0 \times 10^{-4}$  mol/L.

#### 3.2. Emulsion Stability

The stability of benzene-in-water emulsion in the presence of these four surfactants was investigated. The emulsions were stabilized by adding an emulsifier or surfactant. Here, in the present case, the stability of the emulsion increases with the increase in length of the hydrophobic tail of the surfactant (Table I). In the presence of **3a**, it takes 4.2 min for separation of the aqueous layer from the emulsion whereas for 3b, 3c and 3d the times taken were 17.5 min, 40.0 min and 57.7 min, respectively. Thus, the emulsion stability increases with the increase in the hydrophobic tail length.

#### **3.3. Foaming Ability**

The foam ability data for the four surfactants are list in Table I. It is clear that the initial height of foam produced by surfactants, emulsifiability and foam stability increase with the increase in the tail length.

#### 3.4. Degradability

Surfactants  $3a \sim 3d$  are a type of single carboxylic acid sodium salt with 1,3-dioxane ring, and are water-soluble and stable under neutral and alkaline conditions, and turn into segregative solid precipitation under acid condition so that the system can eliminate the undesirable bubbles and emulsifying phenomenon. The precipitation can be processed with alkali to generate the original surfactants to reuse and can also be easily degraded into biodegradable raw material molecules through adding dilute acid with heating. The degradability of **3a-3d** in 0.1 N HCl at 25 °C was examined and the results are shown in Table II. From Table II, it is clear that 3a-3d are all degraded within 2 hours.

Table II. Degradation of surfactants 3a-3d in 0.1 N HCl at 25 °C.

Surfactants	3a	3b	3c	3d
Surfactant quality (g) Time $(h)$	0.5	0.5	0.5	0.5
Decomposition (%)	100	100	100	100

#### 4. CONCLUSIONS

The sodium 2-alkyl-5-(ethoxycarbonyl)-1,3-dioxane-5carboxylate containing 1,3-dioxane ring is a new type of surfactant synthesized using nanosolid superacid sulfonated carbon as a catalyst. CMC, emulsion stability, foam ability and degradability of surfactants were determined and the results showed that the new surfactants give better results and show better properties than traditional surfactants in relation to emulsion formation, foam stability and the range of application temperature as well as the CMC values less than  $1.0 \times 10^{-3}$  mol/L. In addition, the tests showed that these new surfactants were stable under alkaline and neutral conditions, and would degrade into the raw materials in acid environment. From the above, these surfactants are promising to be a novel type of competitive and eco-friendly ones. Moreover, with rapid advances in nanotechnology,36-60 we believe more efficient nanocatalysis system will be developed and more eco-friendly surfactants with more satisfactory properties will be developed.

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