Preparation and Properties of Sodium Alkyl $\beta$-Sulfopropionates

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Abstract

A series of sodium alkyl $\beta$-sulfopropionates containing 11 to 17 carbon atoms was prepared from $\beta$-bromopropionic acid, sodium sulfite and even-numbered straight chain alcohols of 8 to 14 carbon atoms. The Krafft point, critical micelle concentration (cmc), emulsifying power, calcium ion stability and resistance to acid hydrolysis were determined. Sodium alkyl $\beta$-sulfopropionates, in which the ester linkage (hydrophilic group) is moved toward a more central position in the alkyl chain, have higher cmc values and lower Krafft points than the corresponding sodium alkyl sulfonacetates. The sodium alkyl $\beta$-sulfopropionates were less stable toward hydrolysis than the sodium alkyl sulfonacetates because the adjacent sulfo group in the sulfonacetates protects the ester linkage through steric hindrance. The emulsifying power increases, but the calcium ion stability decreases, with increasing alkyl chain length for a series of sodium alkyl $\beta$-sulfopropionates.

Introduction

The sodium sulfoalkyl esters derived from the higher alcohols have interesting surface active properties because of the ester linkage in the molecule. In a previous report (Hikota and Meguro, submitted for publication) it has been shown that sodium alkyl sulfonacetates have higher critical micelle concentration (cmc), lower Krafft point, greater emulsifying power and better calcium ion stability than the corresponding sodium alkyl sulfates. In the present type of surfactant, the surface activities will be altered through change in the length of the methylene group in the hydrophilic portion $\text{OCO(CH}_2\text{)}_n\text{SO}_3\text{Na}$. The present report concerns the preparation of a series of sodium alkyl $\beta$-sulfopropionates $\text{ROCO(CH}_2\text{)}_2\text{SO}_3\text{Na}$ of 11 to 17 carbon atoms and an investigation of surface active properties and stability to hydrolysis.

Materials

The preparation of sodium alkyl $\beta$-sulfopropionate is represented in the following chemical equations.

$$\text{ROH + BrCH}_2\text{COOH }\rightarrow \text{ROCOCH}_2\text{CHBr} \quad [2]$$

Commercially pure octyl, decyl, dodecyl and tetradecyl alcohols used in this experiment were further purified by vacuum distillation. Gas chromatography showed that each of the higher alcohols was more than 98% pure. Carbon tetrachloride, sodium sulfite, 47%

Table I

<table>
<thead>
<tr>
<th>Alkyl</th>
<th>Critical micelle concentration (mmole/1.)</th>
<th>Surface tension</th>
<th>Krafft point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octyl</td>
<td>48.7</td>
<td>48.5</td>
<td>12.5</td>
</tr>
<tr>
<td>Decyl</td>
<td>15.1</td>
<td>9.2</td>
<td>26.8</td>
</tr>
<tr>
<td>Dodecyl</td>
<td>2.8</td>
<td>2.5</td>
<td>30.9</td>
</tr>
<tr>
<td>Tetradecyl</td>
<td>0.7</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Relation between Krafft point and the total number of carbon atoms in the alkyl chain of sodium alkyl $\beta$-sulfopropionates and alkyl sulfonacetates.

Fig. 2. Equivalent conductivity of sodium decyl (O) and dodecyl (●) $\beta$-sulfopropionate.
hydrobromic acid and ethylene cyanohydrin were reagent grade. The reaction steps were carried out as follows.

1. \( \beta \)-Bromopropionic acid: \( \beta \)-bromopropionic acid was prepared by the method of Kendall and McKenzie (1). Ethylene cyanohydrin, 1.5 mole, was brominated in the usual way by 5 moles of 47% hydrobromic acid. The product was extracted with carbon tetrachloride, the removal of which gave 1.2 moles of solid \( \beta \)-bromopropionic acid.

2. Esterification: A mixture of 0.3 mole of higher alcohol, 0.3 mole of \( \beta \)-bromopropionic acid, and 3 ml of concentrated hydrochloric acid in 200 ml of toluene was heated and stirred at reflux temperature for 15 hr with azeotropic removal of water.

3. Sulfonation: The sulfonation procedure was essentially that described previously for the preparation of sodium alkyl sulfoacetates (Hikota and Meguro, submitted for publication). A mixture of 0.3 mole of alkyl \( \beta \)-bromopropionate and 0.5 mole of sodium sulfite in 200 ml of water was stirred and refluxed for 40 hr. After cooling, the reaction mixture was obtained as a cream-colored emulsion. Water was removed under reduced pressure.

The crude material was purified by three recrystallizations from ethyl alcohol followed by extraction with petroleum ether for 100 hr. The product was dried at room temperature under reduced pressure to give the purified sodium alkyl \( \beta \)-sulfopropionate as a white flaky powder.

These compounds showed no definite melting point because of decomposition above 170°C. Purity of the compounds was confirmed by infrared spectrum and elemental analysis. Analyses of these compounds for carbon and hydrogen gave the calculated values for their composition within ±0.3%.

**Methods**

**Kraft Point**

It is well known that the solubility of an ionic surfactant increases rapidly a few degrees above a certain temperature called the Krafft point. Krafft points of the sodium alkyl \( \beta \)-sulfopropionates were determined by a conductivity method (2) using a Leeds and Northrup conductivity bridge No. 4866.

The rapid increase of solubility at the Krafft point accompanied the rapid increase in electrical con-