Long Chain Alkanesulfonates and 1-Hydroxy-2-Alkanesulfonates: Structure and Property Relations

J. K. WEIL, F. D. SMITH, A. J. STIRTON, and R. G. BISTLINE, JR.,
Eastern Regional Research Laboratory, Philadelphia, Pennsylvania

Abstract

Even chain sodium alkanesulfonates from the Streeker reaction, odd chain sodium alkanesulfonates from the alkaline decarboxylation of \( \alpha \)-sulfo acids, and sodium 1-hydroxy-2-alkanesulfonates from the reduction of esters of \( \alpha \)-sulfo acids were compared with respect to Krafft point, critical micelle concentration, detergency and foam height. Sodium alkanesulfonates and crude fusion products from the \( \alpha \)-sulfo acids (mixtures of alkanesulfonates of one less carbon atom with a lesser amount of a soap of two less carbon atoms) are more soluble and have better detergent and foaming properties. Sodium 1-hydroxy-2-alkanesulfonates resemble monosodium salts of \( \alpha \)-sulfo acids.

Alkanesulfonic acids and 1-hydroxy-2-alkanesulfonic acids obtained from the sodium salts by ion exchange have lower Krafft points and are more readily soluble. The critical micelle concentrations of 1-hydroxy-2-alkanesulfonic acids and \( \alpha \)-sulfo acids are nearly the same and about equal to those of alkanesulfonic acids of one less carbon atom.

Discussion

Sodium Alkanesulfonates and 1-Hydroxy-2-Alkanesulfonates

Properties of aqueous solutions of sodium alkanesulfonates, sodium 1-hydroxy-2-alkanesulfonates, and related compounds of 12-18 carbon atoms are shown in Tables I and II.

Krafft Point. The Krafft point, a convenient indication of relative solubility was measured as the temperature at which a 1% aqueous dispersion becomes clear on gradual heating (4). Sodium alkanesulfonates show a decrease in Krafft point from even to odd members, with increasing chain length (15) similar to alternation in melting points in the fatty acid series (10).

Decarboxylation reduces the Krafft point and improves solubility. The monosodium salts of the \( \alpha \)-sulfo acids and sodium 1-hydroxy-2-alkanesulfonates have the highest Krafft points. Low solubility in both cases may be due to hydrogen bonding of the type

\[
\begin{align*}
\text{RCH}_2\text{CH}(\text{SO}_3\text{Na})\text{CO}_2\text{Na} + \text{NaOH} & \rightarrow \text{RCH}_2\text{CH}(\text{CO}_2\text{Na})\text{CO}_2\text{Na} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \\
\text{RCH}_2\text{CH}_2\text{SO}_2\text{Na} + \text{Na}_2\text{CO}_3 & \rightarrow \text{RCH}_2\text{CH}_2\text{CO}_2\text{Na} + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \\
\text{RCH}_2\text{CH}(\text{SO}_3\text{Na})\text{CO}_2\text{H} \rightarrow \text{NaBH}_4 & \rightarrow \text{RCH}_2\text{CH}(\text{SO}_3\text{Na})\text{CH}_2\text{OH}
\end{align*}
\]

The crude fusion product from disodium \( \alpha \)-sulfo-palmitate was found to consist of 60% sodium pentadecanesulfonate, 25% sodium myristate, and 5% inorganic salts; from disodium \( \alpha \)-sulfostearate, 45% sodium heptadecanesulfonate, 17% sodium palmitate, and 38% inorganic salts. The ratio of alkanesulfonate to soap was 18:1. Removal of soap and inorganic salts and final crystallization from aqueous ethanol gave the sodium alkanesulfonates of 13, 15 and 17 carbon atoms in a pure state. Sodium alkanesulfonates of 12, 14, 16 and 18 carbon atoms were made by the Streeker reaction (11). Alkanesulfonic acids were prepared from the sodium salts by ion exchange.

Reduction

Sodium or lithium salts of methyl \( \alpha \)-sulfolaurate, myristate, palmitate or stearate were reduced to the corresponding primary alcohol in yields of 60-75% by means of sodium or lithium borohydride in isopropyl alcohol, as shown by equation II. With correction for unreduced ester recovered as the hydrolysis product (the neutral salt of the \( \alpha \)-sulfo acid) the yield was nearly 100%. By ion exchange the reduction product was isolated as the 1-hydroxy-2-alkanesulfonic acid or the sodium salt.

\[
\begin{align*}
\text{RCH}_2\text{CH}(\text{SO}_3\text{Na})\text{CO}_2\text{Na} + \text{NaOH} & \rightarrow \text{RCH}_2\text{CH}(\text{CO}_2\text{Na})\text{CO}_2\text{Na} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \\
\text{RCH}_2\text{CH}_2\text{SO}_2\text{Na} + \text{Na}_2\text{CO}_3 & \rightarrow \text{RCH}_2\text{CH}_2\text{CO}_2\text{Na} + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \\
\text{RCH}_2\text{CH}(\text{SO}_3\text{Na})\text{CO}_2\text{H} \rightarrow \text{NaBH}_4 & \rightarrow \text{RCH}_2\text{CH}(\text{SO}_3\text{Na})\text{CH}_2\text{OH}
\end{align*}
\]
or the similar intramolecular compound. Either structure would facilitate the separation of an insoluble crystalline phase.

The sodium alkyl sulfates (17), isomeric with sodium 1-hydroxy-2-alkanesulfonates, and with one more oxygen atom than the sodium alkanesulfonates, have the lowest Krafft points.

Critical Micelle Concentration. Because of the limited solubility of the higher members the cmc of the sodium alkanesulfonates of 12-15 carbon atoms, could be made on the sodium salts they were converted to the more soluble free acids by ion exchange with Dowex 50W-X8 in the acid form (15).

A solution of the sodium salt in 50% ethanol was heated with a portion of the ion exchange resin to facilitate solution and passed through a one foot column of the resin with a bed volume of 300 ml. The aqueous ethanol solution after ion exchange was evaporated to dryness and twice crystallized from dry chloroform to give the alkanesulfonic and 1-hydroxy-2-alkanesulfonic acids in a pure state, as listed in Table I.

TABLE I

Properties of Sodium Alkanesulfonates, Fusion Products, and Sodium 1-Hydroxy-2-Alkanesulfonates

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dist. water</th>
<th>60°C ΔR</th>
<th>Dist. water</th>
<th>60°C ΔR</th>
<th>0.25% Detergency</th>
<th>0.25% Foam height</th>
<th>0.25% Foam height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium alkanesulfonates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dodecane</td>
<td>36</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td>20</td>
<td>1.3</td>
<td>200</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>34.5</td>
<td>109</td>
<td>109</td>
<td>109</td>
<td>18</td>
<td>1.1</td>
<td>180</td>
</tr>
<tr>
<td>Octadecane</td>
<td>32</td>
<td>108</td>
<td>108</td>
<td>108</td>
<td>16</td>
<td>0.9</td>
<td>160</td>
</tr>
</tbody>
</table>

Fusion products

From disodium a-sulfopalmi-late! | | | | | | | |
From disodium a-sulfopalmi-late | | | | | | | |
From disodium a-sulfostearate | | | | | | | |
From disodium a-sulfostearate | | | | | | | |
Sodium 1-hydroxy-2-alkanesulfonates | | | | | | | |
Dodecane | 59 | 14.8 | 14.8 | 14.8 | 14.8 | 14.8 | 14.8 |
Tetradecane | 73 | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 |
Hexadecane | 84 | 26.2 | 26.2 | 26.2 | 26.2 | 26.2 | 26.2 |
Octadecane | 93 | 24.8 | 24.8 | 24.8 | 24.8 | 24.8 | 24.8 |

Detergency and Foam. Detergency was measured as the increase in reflectance after washing GDC No. 26 standard soiled cotton (5), Terg-O-Tometer, 10 swatches/1., 29 min. 110 cycles/min. For comparison ΔR values for sodium dodecyl sulfate are 25.7, 21.5, and for sodium octadecyl sulfate 32.6, 31.0 resp. For comparison ΔR values for sodium dodecyl sulfate are 28.5, 24.0, 21.0, and for sodium octadecyl sulfate 32.6, 28.5, 22.0, 65 resp.

The sodium alkanesulfonates of 12-15 carbon atoms and the fusion product from disodium a-sulfopalmi-Late formed turbid solutions in hard water with excellent foaming properties (12), recorded in Table I.

Alkanesulfonic and 1-Hydroxy-2-Alkanesulfonic Acids

Since solubility limited the measurements which could be made on the sodium salts they were converted to the more soluble free acids by ion exchange with Dowex 50W-X8 in the acid form (15).

A solution of the sodium salt in 50% ethanol was heated with a portion of the ion exchange resin to facilitate solution and passed through a one foot column of the resin with a bed volume of 300 ml. The aqueous ethanol solution after ion exchange was evaporated to dryness and twice crystallized from dry chloroform to give the alkanesulfonic and 1-hydroxy-2-alkanesulfonic acids in a pure state, as listed in Table I.

Melting Point and Krafft Point. Because of the relation of the Krafft point of soaps to the melting point of the fatty acids (4), alternation in the Krafft point of sodium alkanesulfonates would suggest an alternation in the melting point of corresponding alkanesulfonic acids. Although alternation in the melting point of alkanesulfonic acids by decrease from odd to even, has been demonstrated for alkanesulfonic acids of 1-6 carbon atoms (13,14), the data of Table III shows there is neither alternation in melting point nor in Krafft point for alkanesulfonic acids of 12-18 carbon atoms. The melting points are higher than previous literature values (9,13).

The alkanesulfonic acids, and the 1-hydroxy-2-alkanesulfonic acids in particular, have low Krafft points and are easily soluble, in marked contrast to the corresponding sodium salts. Like the a-sulfol fatty

TABLE II

Krafft Point and Critical Micelle Concentration of Sodium Alkanesulfonates, Sodium 1-Hydroxy-2-Alkanesulfonates and Related Compounds

<table>
<thead>
<tr>
<th>C atoms</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>Total number of C atoms</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>Total number of C atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CH₂SO₃Na</td>
<td>38C</td>
<td>48C</td>
<td>57C</td>
<td>66C</td>
<td>6.9</td>
<td>2.03</td>
<td>0.45</td>
<td>0.06</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>CH₃(CO₂H)₂SO₃Na</td>
<td>32C</td>
<td>42C</td>
<td>52C</td>
<td>62C</td>
<td>5.9</td>
<td>1.93</td>
<td>0.38</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>CH₃(CH₂CO₂H)SO₃Na</td>
<td>30C</td>
<td>40C</td>
<td>50C</td>
<td>60C</td>
<td>5.7</td>
<td>1.86</td>
<td>0.35</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>CH₃(CH₂CO₂Na)SO₃Na</td>
<td>38C</td>
<td>48C</td>
<td>58C</td>
<td>68C</td>
<td>6.6</td>
<td>1.92</td>
<td>0.43</td>
<td>0.06</td>
<td>0.06</td>
<td></td>
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