Learning Objectives

• Compare the boiling points of carboxylic acids with alcohols of similar molar mass.
• Compare the solubilities of carboxylic acids in water with the solubilities of comparable alkanes and alcohols in water.

Many carboxylic acids are colorless liquids with disagreeable odors. The carboxylic acids with 5 to 10 carbon atoms all have “goaty” odors (explaining the odor of Limburger cheese). These acids are also produced by the action of skin bacteria on human sebum (skin oils), which accounts for the odor of poorly ventilated locker rooms. The acids with more than 10 carbon atoms are waxlike solids, and their odor diminishes with increasing molar mass and resultant decreasing volatility.

Carboxylic acids exhibit strong hydrogen bonding between molecules. They therefore have high boiling points compared to other substances of comparable molar mass.

The carboxyl group readily engages in hydrogen bonding with water molecules (Figure \(\PageIndex{1}\)). The acids with one to four carbon atoms are completely miscible with water. Solubility decreases as the carbon chain length increases because dipole forces become less important and dispersion forces become more predominant. Hexanoic acid \([\text{CH}_3(\text{CH}_2)_4\text{COOH}]\) is barely soluble in water (about 1.0 g/100 g of water). Palmitic acid \([\text{CH}_3(\text{CH}_2)_{14}\text{COOH}]\), with its large nonpolar hydrocarbon component, is essentially insoluble in water. The carboxylic acids generally are soluble in such organic solvents as ethanol, toluene, and diethyl ether.

\[\text{HCOOH}\]

\text{formic acid}

8

100

miscible

Table 15.4.1 lists some physical properties for selected carboxylic acids. The first six are homologs. Notice that the boiling points increase with increasing molar mass, but the melting points show no regular pattern.

Table \(\PageIndex{1}\): Physical Constants of Carboxylic Acids

<table>
<thead>
<tr>
<th>Condensed Structural Formula</th>
<th>Name of Acid</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
<th>Solubility (g/100 g of Water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOOH</td>
<td>formic acid</td>
<td>8</td>
<td>100</td>
<td>miscible</td>
</tr>
<tr>
<td>Condensed Structural Formula</td>
<td>Name of Acid</td>
<td>Melting Point (°C)</td>
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<td>-----------------------------</td>
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<tr>
<td>CH₃COOH</td>
<td>acetic acid</td>
<td>17</td>
<td>118</td>
<td>miscible</td>
</tr>
<tr>
<td>CH₃CH₂COOH</td>
<td>propionic acid</td>
<td>−22</td>
<td>141</td>
<td>miscible</td>
</tr>
<tr>
<td>CH₃(CH₂)₂COOH</td>
<td>butyric acid</td>
<td>−5</td>
<td>163</td>
<td>miscible</td>
</tr>
<tr>
<td>CH₃(CH₂)₃COOH</td>
<td>valeric acid</td>
<td>−35</td>
<td>187</td>
<td>5</td>
</tr>
<tr>
<td>CH₃(CH₂)₄COOH</td>
<td>caproic acid</td>
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<td>205</td>
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<tr>
<td>C₆H₅COOH</td>
<td>benzoic acid</td>
<td>122</td>
<td>249</td>
<td>0.29</td>
</tr>
</tbody>
</table>

### Concept Review Exercises

1. Which compound has the higher boiling point— butanoic acid (molar mass 88) or 2-pentanone (molar mass 86)? Explain.
2. Would you expect butyric acid (butanoic acid) to be more or less soluble than 1-butanol in water? Explain.

### Answers

1. butyric acid because of hydrogen bonding (There is no intermolecular hydrogen bonding in 2-pentanone.)
2. more soluble because there is more extensive hydrogen bonding

### Key Takeaways

- Carboxylic acids have high boiling points compared to other substances of comparable molar mass. Boiling points increase with molar mass.
- Carboxylic acids having one to four carbon atoms are completely miscible with water. Solubility decreases with molar mass.

### Exercises

1. Which compound has the higher boiling point—CH₃CH₂CH₂OCH₂CH₃ or CH₃CH₂CH₂COOH? Explain.
2. Which compound has the higher boiling point—CH₃CH₂CH₂CH₂CH₂OH or CH₃CH₂CH₂COOH? Explain.
3. Which compound is more soluble in water—CH₃COOH or CH₃CH₂CH₂CH₃? Explain.
4. Which compound is more soluble in water—CH₃CH₂COOH or CH₃CH₂CH₂CH₂CH₂COOH? Explain.
Answers

1. CH₃CH₂CH₂COOH because of hydrogen bonding (There is no intermolecular hydrogen bonding with CH₃CH₂CH₂OCH₂CH₃.)

3. CH₃COOH because it engages in hydrogen bonding with water (There is no intermolecular hydrogen bonding with CH₃CH₂CH₂CH₃.)