4.4: Physical Properties of Carboxylic Acids

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 4.4.1). 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 [$CH_3(CH_2)_4COOH$] is barely soluble in water (about 1.0 g/100 g of water). Palmitic acid [$CH_3(CH_2)_{14}COOH$], 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.

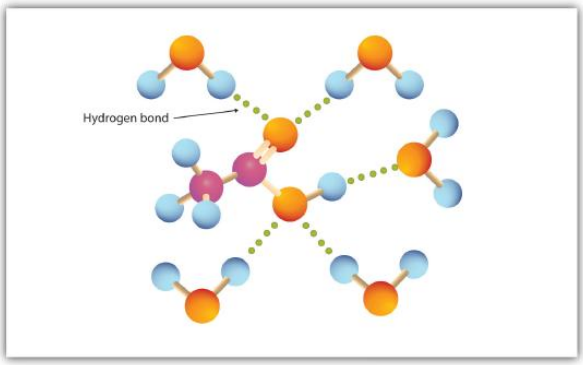

Figure 4.4.1: Hydrogen Bonding between an Acetic Acid Molecule and Water Molecules. Carboxylic acids of low molar mass are quite soluble in water.

Table 4.4.1 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 4.4.1: Physical Constants of Carboxylic Acids

Condensed Structure	Name of Acid	Melting Point (°C)	Boiling Point (°C)	Solubility (g/100 g of Water)
HCOOH	formic acid	8	100	miscible
CH_3COOH	acetic acid	17	118	miscible
CH_3CH_2COOH	propionic acid	–22	141	miscible
$CH_3(CH_2)_2COOH$	butyric acid	–5	163	miscible
$CH_3(CH_2)_3COOH$	valeric acid	–35	187	5
$CH_3(CH_2)_4COOH$	caproic acid	–3	205	1.1
C_6H_5COOH	benzoic acid	122	249	0.29

Example 4.4.1

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

Solution

1. The compounds have comparable molar mass values, 88 g/mol for butanoic acid and 86 g/mol for 2-pentanone. However, only butanoic acids will form hydrogen bonding. Therefore, butanoic acid will have a higher boiling point.
2. Although butyric acid (butanoic acid) and 1-butanol can both form hydrogen bonds, it is expected that butyric acid is more soluble because it forms more extensive hydrogen bonding.

Exercise 4.4.1

1. Which compound has the higher boiling point—$CH_3CH_2CH_2OCH_2CH_3$ or $CH_3CH_2CH_2COOH$? Explain
2. Which compound is more soluble in water—CH_3COOH or $CH_3CH_2CH_2CH_3$? Explain.

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.