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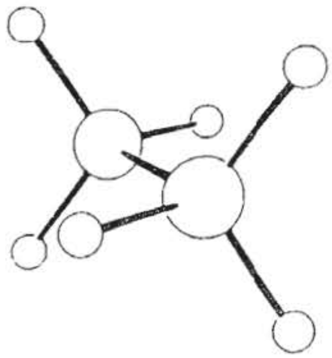
INTRODUCTION TO ORGANIC CHEMISTRY

THIRD EDITION



THIRD EDITION

Introduction to Organic Chemistry

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becomes less important than the nonpolar hydrocarbon tail (R). Consider the reaction of a carboxylic acid such as dodecanoic acid with hydroxide ion.

$$CH_3(CH_2)_{10}COOH + OH^- \overset{K}{\rightleftharpoons} H_2O + CH_3(CH_2)_{10}CO_2^- \qquad (17\text{-}3)$$

The equilibrium constant for reaction (17-3) may be derived as follows.

$$K_a = \frac{[CH_3(CH_2)_{10}CO_2^-][H^+]}{[CH_3(CH_2)_{10}COOH]} = 1.3 \times 10^{-5}\ M \qquad (17\text{-}4)$$

$$K_w = [H^+][OH^-] = 10^{-14}\ M^2 \qquad (17\text{-}5)$$

Rearranging (17-5), we have

$$[H^+] = \frac{10^{-14}}{[OH^-]}\ M \qquad (17\text{-}6)$$

Substituting (17-6) into (17-4) and expanding, we have

$$K = \frac{[CH_3(CH_2)_{10}CO_2^-]}{[CH_3(CH_2)_{10}COOH][OH^-]} = 1.3 \times 10^{9}\ M^{-1} \qquad (17\text{-}7)$$

Equation (17-7) is merely the equilibrium expression for reaction (17-3). The large value of K shows that the reaction proceeds to completion; dodecanoic acid is converted by aqueous sodium hydroxide completely into the salt, sodium dodecanoate. Note that the anions of carboxylic acids are named by dropping **-ic** from the name of the parent acid and adding the suffix **-ate**. Although dodecanoic acid is a neutral molecule, sodium dodecanoate is a salt. Dissolution of this salt gives an anion and a cation, which can be solvated by water. It is not surprising that the solubility of sodium dodecanoate (1.2 g per 100 mL) is much greater than that of dodecanoic acid itself (0.0055 g per 100 mL).

EXERCISE 17.5 Equation (17-7) can be used to calculate the ratio of ionized and nonionized dodecanoic acid at a given pH, by inserting the proper value for $[OH^-]$. Calculate this ratio for pH = 2, 4, 6, and 8.

D. Soaps

The sodium and potassium salts of long-chain carboxylic acids ("fatty acids") are obtained by the reaction of natural fats with sodium or potassium hydroxide. These salts, referred to as soaps, have the interesting and useful ability to solubilize nonpolar organic substances. This phenomenon can easily be understood if one considers the structure of such a salt.

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CO_2^-\ K^+$$

The molecule has a polar ionic region and a large nonpolar hydrocarbon region. In aqueous solution a number of carboxylate ions tend to cluster together so that the hydrocarbon tails are close to each other, thus reducing their energy by the attractive van der Waals forces enjoyed by normal hydrocarbons. The surface of the sphere-like cluster is then occupied by the highly polar CO_2^- groups. These polar groups face the medium, where they may be solvated by H_2O or paired with a cation. The resulting spherical structure, called a **micelle**, is depicted in cross section in Figure 17.3. The wavy lines in the figure represent the long hydrocarbon chains of the salt molecules.

Organic material such as butter or motor oil that is not normally soluble in water may "dissolve" in the hydrocarbon interior of a micelle. The overall process of soap

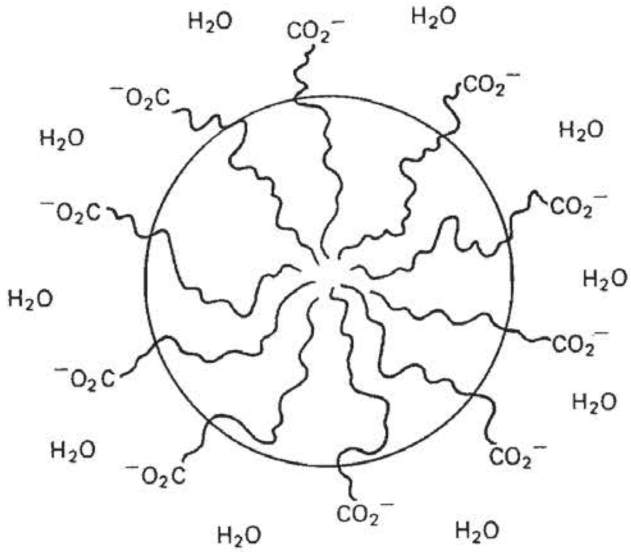


FIGURE 17.3 Cross section of a micelle.

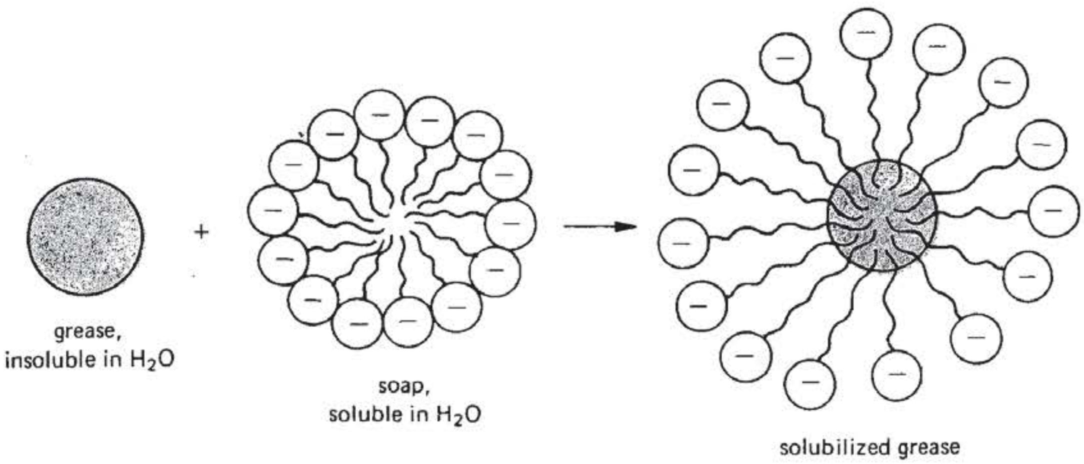
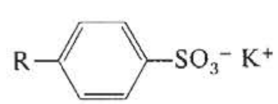


FIGURE 17.4 Schematic diagram of soap solubilization.

Certain bacteria can metabolize soaps. This degradation is most rapid when there are no branches in the hydrocarbon chain of the soap molecule. Since the naturally occurring fatty acids are all unbranched compounds, soaps derived from natural fats are said to be **biodegradable**. Before 1933 all cleaning materials were soaps. In that year the first synthetic detergents were marketed. Detergents have the useful property of not forming the hard "scum" that often results from the use of a soap with hard water. This scum is actually the insoluble magnesium and calcium salts of the fatty acid. The first detergents were alkylbenzenesulfonates. Like soaps, they had a large nonpolar hydrocarbon tail and a polar end.



R = branched alkyl chain

However, being branched compounds, these early detergents were not rapidly biodegradable. Since the materials could not be completely metabolized by the bacteria that operate in sewage treatment plants, they were passed into natural waterways with the treated

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