3

EXTRACTION

3–1 INTRODUCTION

Extraction methods have much in common with distillation methods. In fractional distillation, a separation of components is possible because of the difference in vapor pressure or volatility of the components. At a given temperature and pressure, the equilibrium concentrations of a component in the liquid phase, C_L, and vapor phase, C_G, are expressed by the equation:

$$K = \frac{C_L}{C_G} \tag{3–1}$$

where K is an equilibrium constant. For a two-component system, K is greater for the less volatile component than for the more volatile. Therefore, in the process of vaporization we have achieved a partial separation of the original mixture.

Extraction is an analogous separation process in which a solute is distributed between two immiscible solvents. A similar law defines the ratio of the concentrations of the solute in the two solvents, 1 and 2:

$$K_D = \frac{C_1}{C_2} \tag{3–2}$$

where K_D is the *distribution coefficient* or *partition coefficient*—a special type of equilibrium constant which is related to the relative solubilities of the solute in the two solvents. Often one solvent is water and the other is an organic solvent, so that inorganic ionic species as well as polar organic compounds are found largely in the aqueous phase while nonpolar organic compounds are largely in the organic phase. This is another way of saying "like dissolves like." In dilute solution, to a first approximation, the distribution coefficient is independent of concentration. More precisely, activities should be used in Equation 3–2.

Example. Suppose that we wish to separate the excess fatty acids from a sample of toilet soap. A pair of solvents such as ether and water would be very effective because fatty acids are far more soluble in ether than in water, while the opposite is true for soap. If ether is arbitrarily defined as "solvent 1" in Equation 3–2, then K_D is very large for fatty acids and very small for soap.

In Equation 3–2, phase 1 appears in the numerator and phase 2 in the denominator. Often the organic phase is placed in the numerator, but just as often, the lighter phase (which may or may not be organic) is placed in the numerator. Thus, the assignment of phase numbers is arbitrary and must be explicitly stated to avoid ambiguity in quoting values of the distribution coefficients.

3-2 DISTRIBUTION LAW

The distribution coefficient pertains only to a single species and does not include possible products of side reactions. For example, let us consider the extraction of benzoic acid, HB, from water (acidified with HCl to suppress dissociation of the benzoic acid) into an organic solvent such as ether. Figure 3-1a illustrates the equilibrium situation, for which

$$K_D = \frac{[\mathrm{HB}]_{et}}{[\mathrm{HB}]_{aq}} \tag{3-3}$$

Complications arise however, if the aqueous layer is not acidified and the benzoic acid dissociates

$$\mathrm{HB} \rightleftharpoons \mathrm{H}^+ + \mathrm{B}^-$$

$$K_a = \frac{[\mathrm{H}^+][\mathrm{B}^-]}{[\mathrm{HB}]} \tag{3-4}$$

Now there are two independent equilibria as illustrated in Figure 3-1b. Note that the partition equilibrium pertains only the one undissociated benzoic acid molecules in the two phases and that the dissociation equilibrium pertains only to the species in the aqueous phase (benzoic acid does not dissociate in an ether solution). A second complication arises if benzene is used as the organic solvent in place of ether, as shown in Figure 3-1c. Benzoic acid is partially dimerized in benzene

$$2\mathrm{HB} \rightleftharpoons \mathrm{HB \cdot HB}$$

$$K_d = \frac{[\mathrm{HB \cdot HB}]}{[\mathrm{HB}]^2} \tag{3-5}$$

In extracting benzoic acid, we may want to know how much benzoic acid, regardless of its form, is in each phase. The expression which takes all forms into account is called the *distribution ratio*, *D*

$$D = \frac{\text{total concentration of benzoic acid in organic phase}}{\text{total concentration of benzoic acid in aqueous phase}} \tag{3-6}$$

or

$$D = \frac{[\mathrm{HB}]_{org} + 2[\mathrm{HB \cdot HB}]_{org}}{[\mathrm{HB}]_{aq} + [\mathrm{B}^-]_{aq}} \tag{3-7}$$

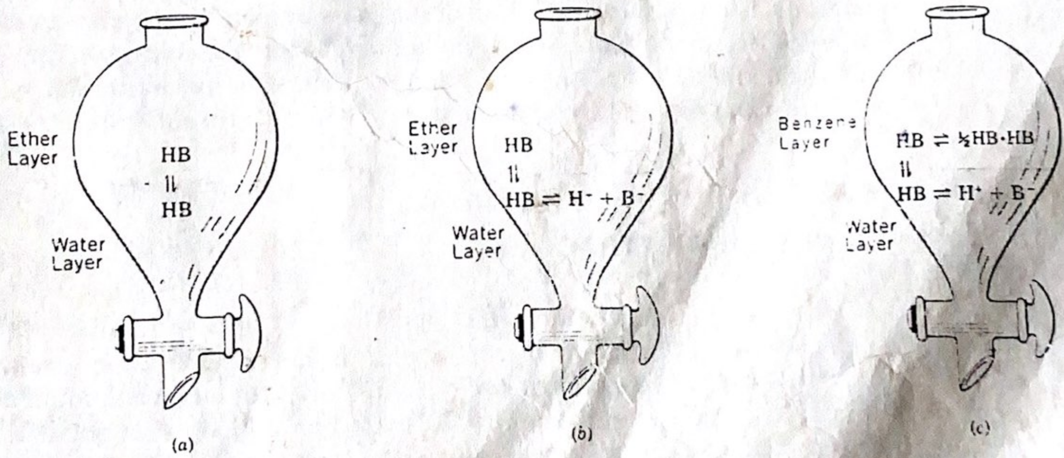

Figure 3-1 Distribution of benzoic acid, HB, between ether and water (a and b) and between benzene and water (c) in an extraction.

In this particular case, we can make substitutions as follows.

From Equation 3–4:

$$[\mathrm{B}^-] = K_a \frac{[\mathrm{HB}]}{[\mathrm{H}^+]} \qquad (3\text{–}8)$$

From Equation 3–5:

$$[\mathrm{HB}\cdot\mathrm{HB}] = K_d[\mathrm{HB}]^2 \qquad (3\text{–}9)$$

Substituting from Equations 3–8 and 3–9 into Equation 3–7, we obtain

$$D = \frac{[\mathrm{HB}]_{\mathrm{org}} + 2K_d[\mathrm{HB}]^2_{\mathrm{org}}}{[\mathrm{HB}]_{\mathrm{aq}} + K_a \dfrac{[\mathrm{HB}]_{\mathrm{aq}}}{[\mathrm{H}^+]_{\mathrm{aq}}}} = \frac{[\mathrm{HB}]_{\mathrm{org}}(1 + 2K_d[\mathrm{HB}])}{[\mathrm{HB}]_{\mathrm{aq}}(1 + K_a/[\mathrm{H}^+])} = \frac{K_D(1 + 2K_d[\mathrm{HB}])}{1 + K_a/[\mathrm{H}^+]} \qquad (3\text{–}10)$$

Equation 3–10 shows that the distribution ratio can be changed by the simple expedient of changing the pH of the aqueous solution. In acid solution (high $[\mathrm{H}^+]$, low pH), D will be large and benzoic acid will be found largely in the organic layer. In alkaline solution (low $[\mathrm{H}^+]$, high pH), D will be small and benzoic acid will be found in the aqueous layer (almost entirely as benzoate ions).

Example / Problem 3–1. One gram of benzoic acid originally dissolved in 100 ml of water is to be equilibrated with 100 ml of ether. The distribution coefficient, K_D is 100 and the dissociation constant, K_a, is 6.5×10^{-5}. Calculate the distribution ratio, D, if the aqueous layer is at pH 3, pH 5 and pH 7. Calculate D at several other pH values and plot D versus pH for this system.

$$D = \frac{K_D}{1 + K_a/[\mathrm{H}^+]}$$

At pH 3: $$D = \frac{100}{1 + 6.5 \times 10^{-5}/10^{-3}} = \frac{100}{1.065} = 93.9$$

At pH 5: $$D = \frac{100}{1 + 6.5 \times 10^{-5}/10^{-5}} = \frac{100}{7.5} = 13.3$$

At pH 7: $$D = \frac{100}{1 + 6.5 \times 10^{-5}/10^{-7}} = \frac{100}{651} = 0.15$$

Expressions similar to Equation 3–10 can be derived for other types of side reactions, for example, formation of ion pairs or metal complexes in either or both phases. If the side reactions involve ionic (charged) species, one can assume that ions exist only in the aqueous layer, or in a very polar organic solvent (high dielectric constant). The characteristics of some useful solvents are listed in Table 3–1.

3–3 SUCCESSIVE EXTRACTIONS

If the distribution coefficient is very large (> 1000), a single extraction in a simple separatory funnel will probably remove essentially all of a solute from one phase to another. However, it can be shown that for a given amount of extracting solvent, it is more effective to divide it into several small portions and use each portion successively rather than to make a single extraction with all of the solvent at one time.

For example, assume that 4 g of butyric acid is to be extracted from 500 ml of water with 500 ml of ether. The distribution coefficient for this system is 3.0 at