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

From Equation 3–4:

$$[\mathrm{B}^-] = K_a \frac{[\mathrm{HB}]}{[\mathrm{H}^+]} \tag{3–8}$$

From Equation 3–5:

$$[\mathrm{HB{\cdot}HB}] = K_d[\mathrm{HB}]^2 \tag{3–9}$$

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

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

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

Table 3–1 Some Useful Solvents

Solvent	*Boiling Point, °C*	*Freezing Point, °C*	*Dielectric Constant, Debye units*
Diethyl ether	35	− 116	4.3
Carbon disulfide	46	− 111	2.6
Acetone	56	− 95	20.7
Chloroform	61	− 64	4.8
Methanol	65	− 98	32.6
Tetrahydrofuran	66	− 65	7.6
Di-isopropyl ether	68	− 60	3.9
Carbon tetrachloride	76	− 23	2.2
Ethyl acetate	77	− 84	6.0
Ethanol	78	− 117	24.3
Benzene	80	5.5	2.3
Cyclohexane	81	6.5	2.0
Isopropanol	82	− 89	18.3
Water	100	0	78.5
Dioxane	102	12	2.2
Toluene	111	− 95	2.4
Acetic acid (glacial)	118	17	6.2
N,N-Dimethylformamide	154	− 61	34.8
Diethylene glycol	245	− 10	37.7

25°C. If the ether is used in a single batch:

$$K_D = C_{et}/C_{aq} = 3.0 = \frac{(4-x)/0.5}{x/0.5}$$

where x is the weight of butyric acid remaining in the water layer. Thus $x = 1$, and 3 g is extracted into the ether layer, as shown in Figure 3–2. However, if the ether is used in two successive 250-ml portions, for the first extraction:

$$K_D = 3.0 = \frac{(4-x_1)/0.25}{x_1/0.50}$$

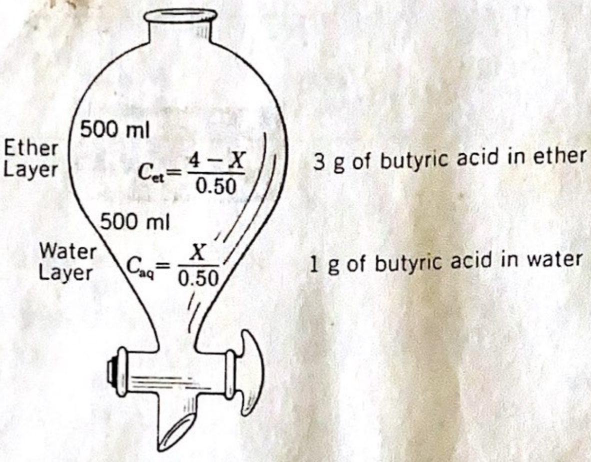
In this case, $x_1 = 1.60$ g remains in the water layer, and 2.40 g is found in the ether layer, which is then removed. In the second extraction with the remaining 250-ml portion of ether:

$$K_D = 3 = \frac{(1.6-x_2)/0.25}{x_2/0.50}$$

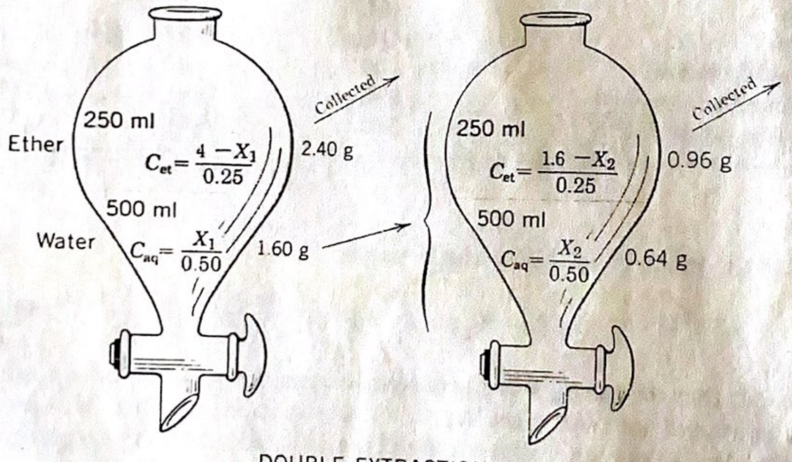
After the second extraction, $x_2 = 0.64$ g remains in the water layer, and an additional 0.96 g is extracted by the ether. Thus a total of $2.40 + 0.96 = 3.36$ g has been extracted, a significant improvement.

A similar calculation shows that had the ether been divided into five 100-ml portions, only 0.23 g of the original 4 g of butyric acid would remain in the aqueous phase after the fifth extraction, and the combined ether extracts would contain 3.77 g.

For the general case, assume that W_0 g of a solute originally present in V_A ml of solvent A is to be extracted with successive portions of V_B ml of solvent B, as



SINGLE EXTRACTION



DOUBLE EXTRACTION

Figure 3–2 Comparison of extraction procedures for butyric acid: 4 g of acid originally in 500 ml of water extracted with one 500-ml portion of ether (top), or two 250-ml portions of ether (bottom).

shown in Figure 3–3.

$$K_D = C_B/C_A; \qquad W_0 = W_A + W_B$$
$$W_A = C_A V_A; \qquad W_B = C_B V_B$$

After the first equilibration:

$$\text{fraction in } A = \frac{W_{A,1}}{W_0} = \frac{C_{A,1} V_A}{C_{A,1} V_A + C_{B,1} V_B} = \frac{V_A}{V_A + \dfrac{C_{B,1}}{C_{A,1}} V_B} = \frac{V_A}{V_A + K_D V_B}$$

or

$$W_{A,1} = W_0 \left(\frac{V_A}{V_A + K_D V_B} \right)$$

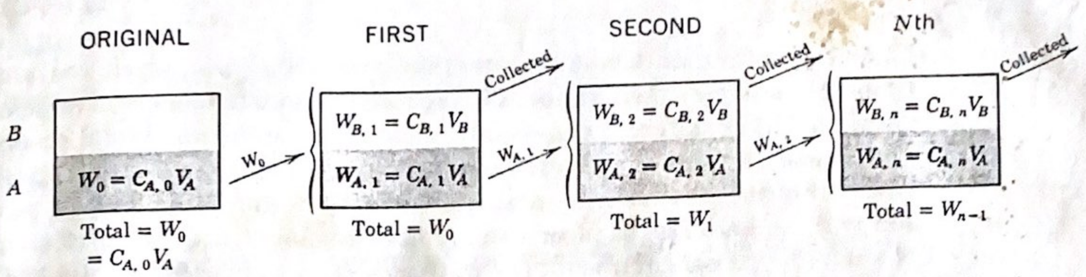


Figure 3–3 Successive extractions of sample of W_0 g originally in V_A-ml of water with V_B-ml portions of ether.

The second extraction is the same as the first, except that $W_{A,1}$ g of solute is present instead of W_0 g. Thus, by analogy (repeating the steps above):

$$W_{A,2} = W_{A,1}\left(\frac{V_A}{V_A + K_D V_B}\right) = W_0\left(\frac{V_A}{V_A + K_D V_B}\right)^2$$

Repeating the procedure through n equilibrations (collecting and combining the B layers) gives:

$$W_{A,n} = W_0\left(\frac{V_A}{V_A + K_D V_B}\right)^n \tag{3–11}$$

where $W_{A,n}/W_0$ is the fraction of the solute remaining in the A layer after n extractions with n equal portions of solvent B. As n increases, $W_{A,n}$ decreases, but the relationship is exponential and diminishing returns soon set in, as shown in Figure 3–4.

More than five successive extractions are seldom worthwhile. If this number has not resulted in an adequate extraction, it is more practical to look for a better extractant (more favorable K_D). It should be noted that in deriving Equation 3–11, it was tacitly assumed that the two phases are completely separated after each equilibration. In practice, this is not always easy to do.

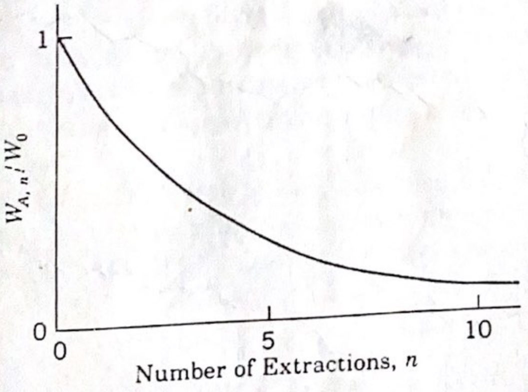


Figure 3–4 Fraction of solute remaining in water layer after a number of successive extractions with fresh portions of ether.

3–4 SEPARATION OF MIXTURES BY EXTRACTION

The extraction of a single substance from one solvent to another is of little interest. The great value of extraction is the possibility of separating two or more substances based upon a difference in their distribution coefficients. If one solute