13.3. EQUILIBRIUM DATA

The equilibrium condition for the distribution of one solute between two liquid phases is conveniently considered in terms of the distribution law. Thus, at equilibrium, the ratio of the concentrations of the solute in the two phases is given by $C_E/C_R = K'$, where K' is the distribution constant. This relation will apply accurately only if both solvents are immiscible, and if there is no association or dissociation of the solute. If the solute forms molecules of different molecular weights, then the distribution law holds for each molecular species. Where the concentrations are small, the distribution law usually holds provided no chemical reaction occurs.

The addition of a new solvent to a binary mixture of a solute in a solvent may lead to the formation of several types of mixture:

(a) A homogeneous solution may be formed and the selected solvent is then unsuitable.
(b) The solvent may be completely immiscible with the initial solvent.
(c) The solvent may be partially miscible with the original solvent resulting in the formation of one pair of partially miscible liquids.
(d) The new solvent may lead to the formation of two or three partially miscible liquids.

Of these possibilities, types (b), (c), and (d) all give rise to systems that may be used, although those of types (b) and (c) are the most promising. With conditions of type (b), the equilibrium relation is conveniently shown by a plot of the concentration of solute in one

phase against the concentration in the second phase. Conditions given by (c) and (d) are usually represented by triangular diagrams. Equilateral triangles are used, although it is also possible to use right-angled isosceles triangles, which are discussed in Chapter 10.

The system, acetone (**A**)–Water (**B**)–methyl isobutyl ketone (**C**), as shown in Figure 13.5, is of type (c). Here the solute **A** is completely miscible with the two solvents **B** and **C**, although the two solvents are only partially miscible with each other. A mixture indicated by point H consists of the three components **A**, **B** and **C** in the ratio of the perpendiculars HL, HJ, HK. The distance BN represents the solubility of solvent **C** in **B**, and MC that of **B** in **C**. The area under the curved line NPFQM, the binodal solubility curve, represents a two-phase region which will split up into two layers in equilibrium with each other. These layers have compositions represented by points P and Q, and PQ is known as a "tie line". Such lines, two of which are shown in the diagram, connect the compositions of two phases in equilibrium with each other, and these compositions must be found by practical measurement. There is one point on the binodal curve at F which represents a single phase that does not split into two phases. F is known as a *plait* point, and this must also be found by experimental measurement. The plait point is fixed if either the temperature or the pressure is fixed. Within the area under the curve, the temperature and composition of one phase will fix the composition of the other. Applying the phase rule to the three-components system at constant temperature and pressure, the number of degrees of freedom is equal to 3 minus the number of phases. In the area where there is only one liquid phase, there are two degrees of freedom and two compositions must be stated. In a system where there are two liquid phases, there is only one degree of freedom.
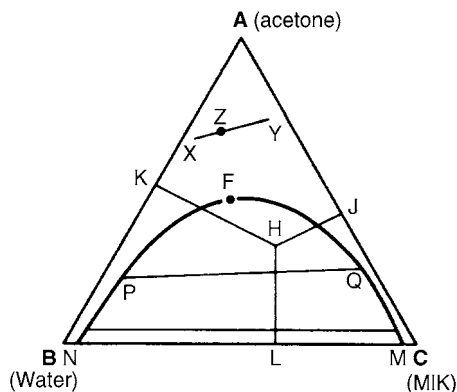

Figure 13.5.   Equilibrium relationship for acetone distributed between water and methyl isobutyl ketone

One of the most useful features of this method of representation is that, if a solution of composition X is mixed with one of composition Y, then the resulting mixture will have a composition shown by Z on a line XY, such that:

$$XZ/ZY = (\text{amount of Y})/(\text{amount of X}).$$

Similarly, if an extract Y is removed, from a mixture Z the remaining liquor will have composition X.

In Figure 13.6 two separate two-phase regions are formed, whilst in Figure 13.7 the two-phase regions merge on varying the temperature. Aniline (**A**), water (**B**), and phenol (**C**) represent a system of the latter type. Under the conditions shown in Figures 13.6 and 13.7, **A** and **C** are miscible in all proportions, although **B** and **A**, and **B** and **C** are only partially miscible.
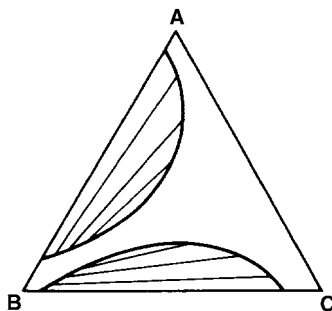

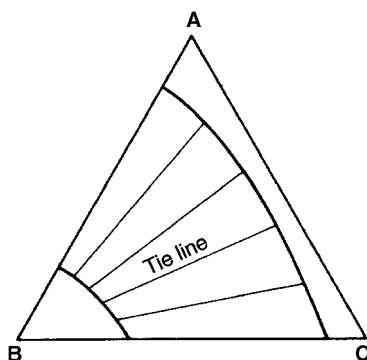Figure 13.6.   Equilibrium relationship for the aniline–water–phenol system

Figure 13.7.   Equilibrium relationship for the aniline–water–phenol system at a higher temperature

Whilst these diagrams are of considerable use in presenting equilibrium data, Figure 13.8 is in many ways more useful for determining the selectivity of a solvent, and the number of stages that are likely to be required. In Figure 13.8 the percentage of solute in one phase is plotted against the percentage in the second phase in equilibrium with it. This is equivalent to plotting the compositions at either end of a tie line. The important factor in assessing the value of a solvent is the ratio of the concentrations of the desired component in the two phases, rather than the actual concentrations. A selectivity ratio may be defined in terms of either mass or mole fractions as:

$$\beta = \left[\frac{x_A}{x_B}\right]_E \bigg/ \left[\frac{x_A}{x_B}\right]_R \tag{13.2}$$

where x_A and x_B are the mass or mole fractions of **A** and **B** in the two phases E and R.
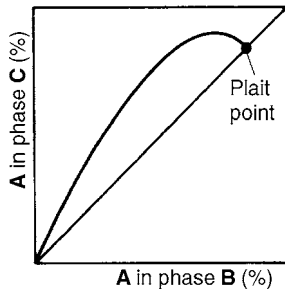
Figure 13.8.   Equilibrium distribution of solute **A** in phases **B** and **C**

For a few systems β tends to be substantially constant, although it more usually varies with concentration. The selectivity ratio has the same significance in extraction as relative volatility has in distillation, so that the ease of separation is directly related to the numerical value of β. As β approaches unity, a larger number of stages is necessary for a given degree of separation and the capital and operating costs increase correspondingly. When $\beta = 1$ any separation is impossible.