Table 2.3 The effects of additives on critical solution temperature (CST)

Type of CST	Solubility of additive in each component	Effect on CST	Effect on miscibility
Upper	Approx. equally soluble in both components	Lowered	Increased
Upper	Readily soluble in one component but not in other	Raised	Decreased
Lower	Approx. equally soluble in both components	Raised	Increased
Lower	Readily soluble in one component but not in other	Lowered	Decreased

proportions of the three components at constant temperature and pressure and it presents a good example of the interpretation and use of such phase diagrams.

Distribution of solutes between immiscible liquids

Partition coefficients

When a substance, which is soluble in both components of a mixture of immiscible liquids, is dissolved in such a mixture, when equilibrium is attained at constant temperature, it is found that the solute is distributed between the two liquids in such a way that the ratio of the activities of the substance in each liquid is a constant. This is known as the Nernst Distribution Law and may be expressed by Equation 2.18:

$$\frac{a_A}{a_B} = \text{constant} \qquad (2.18)$$

where a_A and a_B are the activities of the solute in solvents A and B, respectively. When the solutions are dilute or when the solute behaves ideally, the activities may be replaced by concentrations (C_A and C_B):

$$\frac{C_A}{C_B} = K \qquad (2.19)$$

The constant K is known as the *distribution coefficient* or *partition coefficient*. In the case of sparingly soluble substances, K is approximately equal to the ratio of the solubility (S_A and S_B) of the solute in each liquid. Thus:

$$\frac{S_A}{S_B} = K \qquad (2.20)$$

In most other systems, however, deviation from ideal behaviour invalidates Equation 2.20. For example, if the solute exists as monomers in solvent A and as dimers in solvent B, the distribution coefficient is given by Equation 2.21, in which the square root of the concentration of the dimeric form is used:

$$K = \frac{C_A}{\sqrt{C_B}} \qquad (2.21)$$

If the dissociation into ions occurs in the aqueous layer, B, of a mixture of immiscible liquids, then the degree of dissociation (α) should be taken into account, as indicated by Equation 2.22:

$$K = \frac{C_A}{C_B(1-\alpha)} \qquad (2.22)$$

The solvents in which the concentrations of the solute are expressed should be indicated when partition coefficients are quoted. For example, a partition coefficient of 2 for a solute distributed between oil and water may also be expressed as a partition coefficient between water and oil of 0.5. This can be represented as $K_{\text{water}}^{\text{oil}} = 2$ and $K_{\text{oil}}^{\text{water}} = 0.5$. The abbreviation K_w^o is often used for the former and this notation has become the most commonly used.

Solubility of solids in solids

If two solids are either melted together and then cooled or dissolved in a suitable solvent that is then removed by evaporation, the solid that is redeposited from the melt or the solution will either be a one-phase solid solution or a two-phase eutectic mixture.