their concentrations exceed certain values. In aqueous solution the centre of these aggregates resembles a separate organic phase and organic solutes may be taken up by the aggregates, thus producing an apparent increase in their solubility in water. This phenomenon is known as solubilization. A similar phenomenon occurs in organic solvents containing dissolved solubilizing agents because the centre of the aggregates in these systems constitutes a more polar region than the bulk of the organic solvent. If polar solutes are taken up into these regions, their apparent solubility in the organic solvents is increased.

Solubility of gases in liquids

The amount of gas that will dissolve in a liquid is determined by the nature of the two components and by temperature and pressure.

Provided that no reaction occurs between the gas and liquid then the effect of pressure is indicated by Henry's Law which states that at constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas above the liquid. The law may be expressed by Equation 2.16:

$$w = kp \tag{2.16}$$

where w is the mass of gas dissolved by unit volume of solvent at an equilibrium pressure p and k is a proportionality constant. Although Henry's Law is most applicable at high temperatures and low pressures, when solubility is low, it provides a satisfactory description of the behaviour of most systems at normal temperatures and reasonable pressures, unless solubility is very high or reaction occurs. Equation 2.16 also applies to the solubility of each gas in a solution of several gases in the same liquid provided that p represents the partial pressure of a particular gas.

The solubility of most gases in liquids decreases as the temperature rises. This provides a means of removing dissolved gases. For example, water for injections free from either carbon dioxide or air may be prepared by boiling water with minimum exposure to air and prevention of access of air during cooling. The presence of electrolytes may also decrease the solubility of a gas in water by a 'salting out' process, which is caused by the marked attraction exerted between electrolyte and water.

Solubility of liquids in liquids

The components of an ideal solution are miscible in all proportions. Such complete miscibility is also observed in some real binary systems, e.g. ethanol and water, under normal conditions. However, if one of the components tends to self-associate because the attractions between its own molecules are greater than those between its molecules and those of the other component, i.e. if a positive deviation from Raoult's Law occurs, the miscibility of the components may be reduced (Raoult's Law is discussed more fully in Chapter 3). The extent of the reduction in miscibility depends on the strength of the self-association and, therefore, on the degree of deviation from Raoult's Law. Thus, partial miscibility may be observed in some systems whereas virtual immiscibility may be exhibited when the self-association is very strong and the positive deviation from Raoult's Law is large.

In those cases where partial miscibility occurs under normal conditions, the degree of miscibility is usually dependent on the temperature. This dependency is indicated by the *phase rule*, introduced by J. Willard Gibbs, which is expressed quantitatively by Equation 2.17:

$$F = C - P + 2 \tag{2.17}$$

where P and C are the numbers of phases and components in the system, respectively, and F is the number of degrees of freedom, i.e. the number of variable conditions such as temperature, pressure and composition, that must be stated in order to define completely the state of the system at equilibrium.

The overall effect of temperature variation on the degree of miscibility in these systems is usually described by means of phase diagrams, which are graphs of temperature versus composition at constant pressure. For convenience of discussion of their phase diagrams, the partially miscible systems may be divided into the following types.

Systems showing an increase in miscibility with rise in temperature

A positive deviation from Raoult's Law arises from a difference in the cohesive forces that exist between the molecules of each component in a liquid mixture. This difference becomes more marked as the