## 6.2 Kinetic Aspects of Dyeing

The transfer of dye molecules from the bulk dyebath solution into the fibre involves three stages:

(A) Transfer of the dye molecules from the bulk aqueous solution to the surface of the fibre. This stage is influenced by the solubility of the dye and the flow rates of the dye liquor through the fibre, yarn or fabric in the dyeing machine.
(B) Adsorption of the dye molecules onto the fibre surface. The word 'adsorption', rather than 'absorption', is used here because this stage is concerned with the dye becoming attached to the surface of the fibres. The factors of importance governing adsorption are the nature of the surface and the dye/fibre interactions occurring, temperature, pH, the presence of auxiliary chemicals and dye concentration.
(C) Diffusion of the dye molecules from the fibre surface into the interior of the fibre. The rate at which this process occurs depends on factors such as the molecular size and shape of the dye, the structure of the fibre (e.g. how crystalline it is) and temperature.

Of these three stages, stage (B) is very rapid in comparison with the other two stages, and stage (A) is only fast if there is efficient movement of the dye liquor around the individual fibres. These stages are represented diagrammatically in Figure 6.1.

For the transfer of dye molecules to the fibre surface in stage (A), it is important that the dye liquor moves efficiently, relative to the fibres, in a process known as *convective diffusion*. Dyeing machines vary in their operation in that some circulate the dye liquor around the stationary fibres, others move the fibres in the stationary dye liquor, whilst others move both dye liquor and fibres at the same time. Convective diffusion is made up of the *macroscopic motion* of the dye liquor and *molecular diffusion*. If there is no movement of the dye

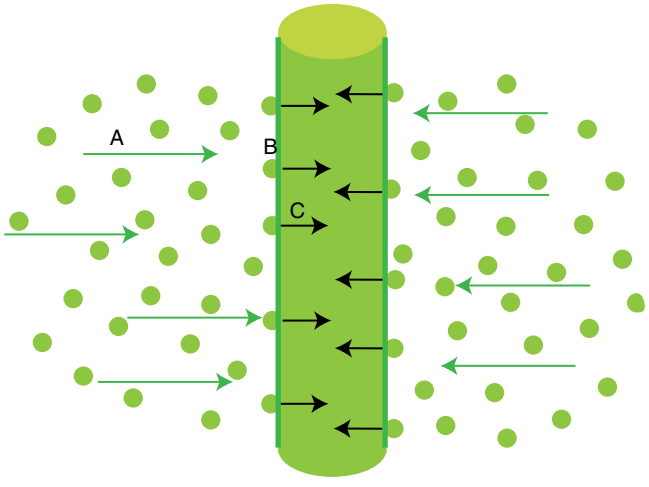



**Figure 6.1** Transfer of dye molecules from dye solution into a fibre. A: Transfer of molecules to the fibre surface. B: Adsorption of dye molecules at the fibre surface. C: Diffusion of dye molecules into the fibre matrix.

liquor relative to the fibres at all, then transfer of the dye molecules to the fibre surface will rely totally on molecular diffusion, which is a slow process. However, whatever the speed of movement of the dye liquor, there is always a layer of liquid adjacent to the fibre surface that is stationary through which the dye must pass by molecular diffusion. This layer is called the *diffusional boundary layer* (see Figure 6.2). Because it is necessary for dye molecules to diffuse across this layer, stage (A) can influence the rate of dyeing. It is necessary therefore that this layer of stationary liquor is as thin as possible, which is achieved by effective stirring of the dye liquor (or movement of the fibres in the dye liquor).

As the dye molecules reach the fibre surface and are adsorbed onto it, the concentration of dye at the surface builds up. All naturally occurring processes involve levelling out differences in concentration between regions, so diffusion from the fibre surface into its interior occurs. Initially dye builds up at the fibre surface and the fibre is 'ring-dyed' ('A' in Figure 6.3). Gradually, as the dyeing operation proceeds, the concentration of dye increases towards the centre of the fibre ('B' in Figure 6.3) so that in an ideal situation, at the end of the process, there is a uniform distribution of dye throughout the polymer matrix of the fibre ('C' in Figure 6.3).

The diffusion of dye molecules from the surface of a fibre to its interior is a slow process and is influenced by the fact that the polymer structure is very non-uniform in terms of its ease of access. Some parts are highly crystalline, whilst other regions are more amorphous with voids through which dye molecules can pass more easily (see Section 2.2). There are

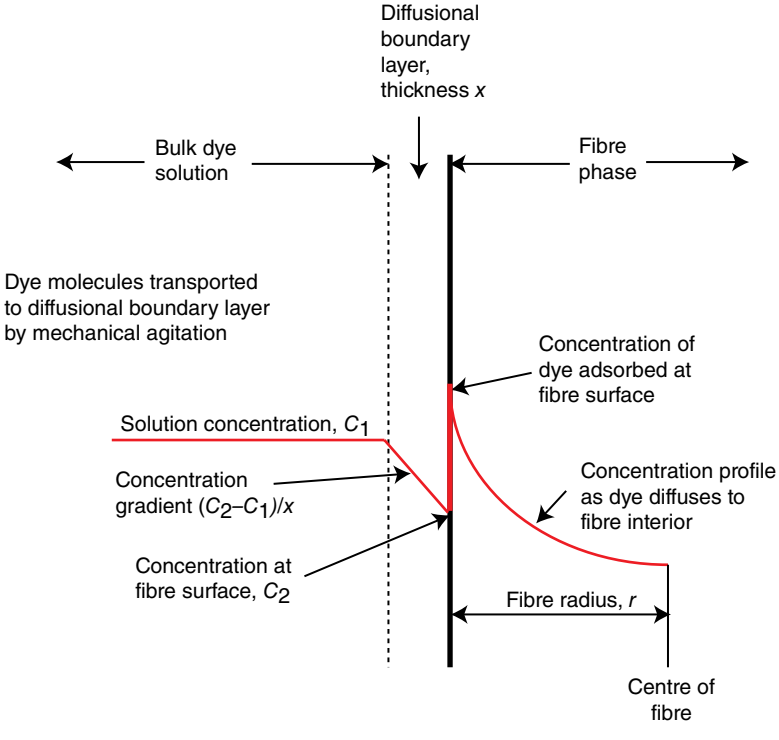



**Figure 6.2** Transport of dye from bulk solution to interior of a fibre.

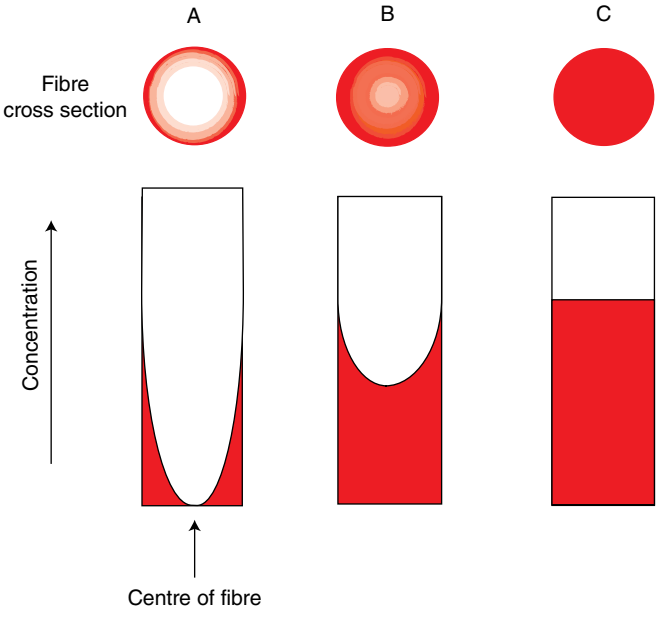



**Figure 6.3** Diffusion of dye into a fibre from an infinite dyebath.

two models of the mode by which dye molecules diffuse into fibres – the pore model and the segmental-mobility model. The pore model visualises tortuous channels of water-filled pores in the amorphous regions of the fibre matrix through which dye molecules can pass. This model is particularly relevant to the dyeing of natural cellulosic fibres such as cotton and flax, which are highly crystalline in their structures but between the crystalline regions exist the amorphous regions. It is necessary for the dye molecules to be long and flat (planar) in shape so they can move along these narrow channels (Figure 6.4a and b). The segmental-mobility model envisages the displacement of the polymer molecules by the dye molecules as they enter the fibre (Figure 6.4c and d), this model applying to the diffusion of disperse dyes by hydrophobic fibres.

For some dye/fibre systems, such as anionic dyes applied to regenerated cellulosic fibres such as viscose and lyocell fibres, it is highly likely that a combination of the two processes takes place.

Another complicating issue is the fact that the dye molecules must diffuse through a medium to which they are attracted by various intermolecular forces (see Section 1.4.3). Dye molecules that are small in size are able to diffuse more quickly than large molecules, but the shape of the molecules also has an influence, with long linear-shaped molecules being able to diffuse more quickly than bulky molecules. Temperature is an important factor in governing the rate of diffusion: at higher temperatures all processes occur faster, so the rate of diffusion is higher at higher temperatures. Because diffusion, especially diffusion of the dye molecules through a solid substrate, is a relatively slow process, stage (C) of Figure 6.1 is usually the rate-determining step of the overall dyeing process. Studies of the diffusion properties of dyes in the fibre substrate are therefore important in understanding the kinetics of dyeing processes.

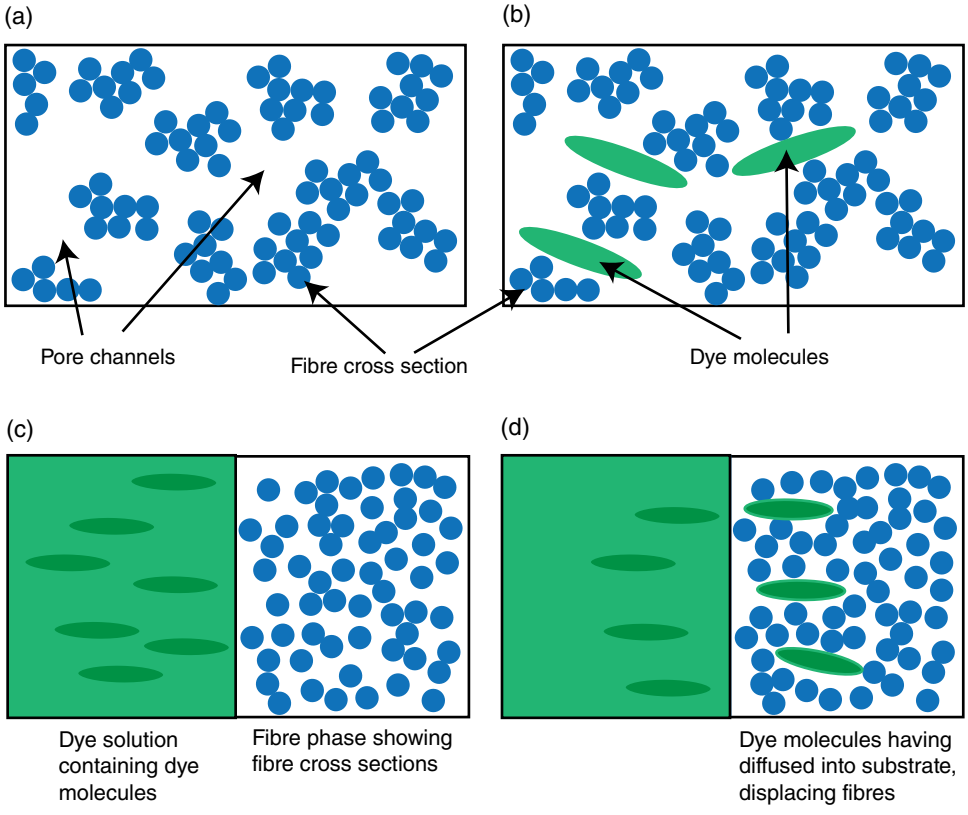



**Figure 6.4** Diffusion of dye molecules into fibrous substrates. (a) and (b): pore model, (c) and (d): segmental-mobility model.

Before considering diffusion in more detail, it is useful to consider the behaviour of dye molecules in solution in water. It is well known that the molecules of many dye types aggregate in water, and this property markedly influences the ability of dyes to diffuse, both in water and in the fibre. The next section therefore considers dye aggregation in more detail.

## 6.3 Dye Aggregation

The ability of dye molecules to aggregate in solution is not always visually obvious, yet some dye types aggregate to such an extent that they form dispersions. The aggregation of dyes in solution leads to lower rates of diffusion of the molecules from the bulk solution to the fibre surface. Additionally, once adsorbed at the fibre surface, diffusion within the fibre is hindered, resulting in ring dyeing, as illustrated in Figure 6.3A. A lower colour yield is then obtained. Conversely, there are some advantages to aggregation of dye molecules in the fibre, as long as uniform distribution of dye throughout the fibre can be achieved. The light-fastness and wet fastness of dyes that aggregate in the fibre are very good. The improvement varies with the dye application class and the type of fibre being dyed. Table 6.1 shows the general aggregation properties of the various dye application classes.

**Table 6.1** Aggregation behaviour of dye application classes.

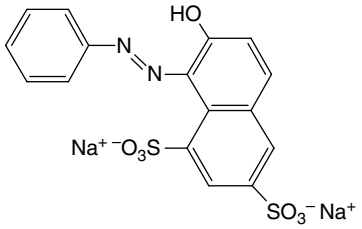
| application class | aggregation |
|---|---|
| Acid levelling | Low |
| Acid milling | High |
| Direct | High |
| Vat | High |
| Sulphur | High |
| Azoic | High |
| Reactive | Low |
| Disperse | High |

Aggregates may form gradually over time, with the result that what was originally an optically clear solution becomes cloudy as it ages, and it is possible that the dye then precipitates out of solution. The formation of dye aggregates involves dye molecules aligning themselves closely in a regular way with, in some cases, well over 100 molecules closely bound in one aggregate. The aggregation number of a dye, which is the average number of dye molecules in an aggregate, can be determined experimentally, and it is found that different dyes all have their own individual behaviour. A number of different experimental techniques have been used to determine the aggregation number of dyes in solution. Such techniques include conductivity, light scattering, osmotic pressure and diffusion methods. Whilst the results of the various methods do not always agree with each other in absolute terms, they agree in the trends they show as the solution conditions change.

In general, the larger the size of a dye molecule, the greater is the tendency for it to form aggregates in solution. Attractive forces occur between the planar hydrophobic parts of dye molecules, and the larger the molecule, the greater the opportunity for aggregation to occur. However, two aspects of the structure of the molecule hinder aggregation:

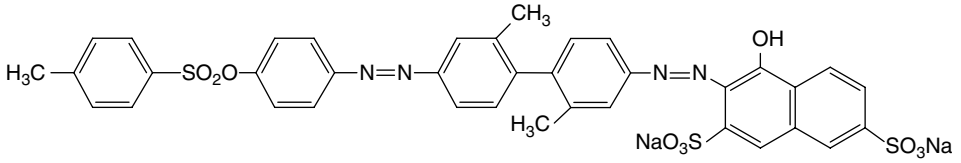
(1) Charge repulsion
(2) Steric hindrance

Hydrophilic charged groups, such as sulphonate groups ($-SO_3^-$) present in molecules to confer water solubility, act to repel neighbouring molecules. The simple acid dye C.I. Acid Orange 10 (**6.1**) does not aggregate at all because its molecules have two negative $-SO_3^-$ (sulphonate) groups in the molecule, causing charge repulsion with nearby molecules, and this repulsion dominates over any attractive forces acting between the –OH groups or between the hydrophobic aromatic rings, because the molecules are so small.

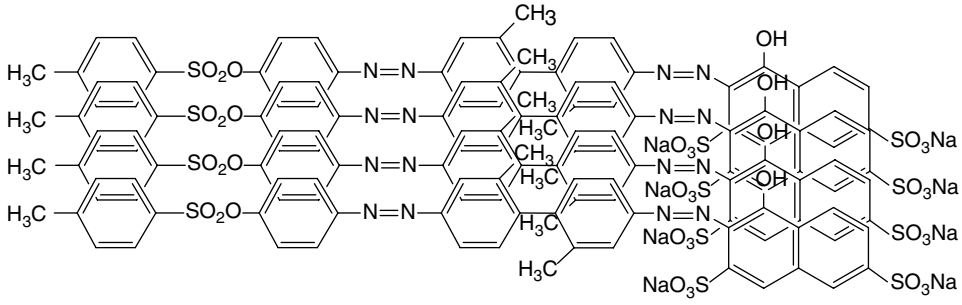



**6.1**

In larger dye molecules, the aggregation number is smaller if there are more $-SO_3^-$ groups and especially if they are spread apart in the molecule. The molecules of the dye C.I. Acid Red 111 (**6.2**) contain two $-SO_3^-$ groups, but they are close together at one end of the molecule, so this dye aggregates readily (**6.3**):




**6.2**



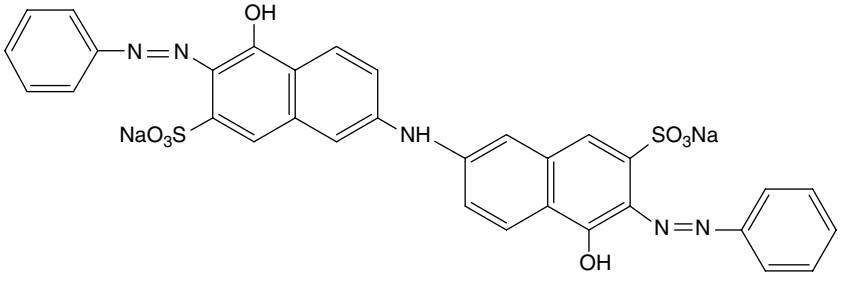

**6.3**

The size of a dye molecule is not the overriding factor in determining the aggregation behaviour of dye molecules; the ratio of molecular size to ionic group content is the most important factor. In comparing this ratio for the two dyes, Acid Orange 10 and Acid Red 111 (Table 6.2), it is easy to see why Acid Red 111, with its much greater ratio, aggregates so readily.

Another feature of the molecular structure of dyes that influences their aggregation behaviour is the shape of the molecule and the presence of any functional side groups in the molecule that may cause *steric hindrance*. Dyes whose molecules have flat planar structures show strong tendencies to aggregate, and typical of these types of dyes are those of the direct dye application class. A typical direct dye is C.I. Direct Red 31 (**6.4**), the molecule of which is long, thin and flat planar in shape:

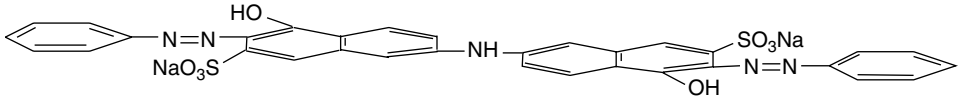
**Table 6.2** Size/charge ratios of dyes showing different aggregation behaviour.

| dye | degree of aggregation | molecular weight | number of $-SO_3^-$ groups | ratio M.Wt/$-SO_3^-$ |
|---|---|---|---|---|
| Acid Orange 10 | Low | 406 | 2 | 203 |
| Acid Red 111 | High | 752 | 2 | 376 |




**6.4**

If the molecule is turned on its side, it is flat (**6.5**), and this planarity enables neighbouring molecules to align:




**6.5**

However, if bulky side groups are present, they can prevent the close alignment of dye molecules and so hinder the stacking of the molecules.

The sulphonate ($-SO_3^-$) group is bulky, having a tetrahedral shape, and if these groups are distributed across a dye molecule, they can reduce the extent to which the molecules are able to aggregate, as illustrated in Figure 6.5. In dye molecules containing even more sulphonate groups, such as tri- and tetra-sulphonated dyes, aggregation is suppressed even more.

Aggregation tends not to occur when sulphonate groups are spread evenly across the molecule, as is the case with many reactive dyes. C.I. Reactive Red 1 (**6.6**) is a typical example of a dichlorotriazinyl reactive dye with sulphonate groups spread across the molecule:

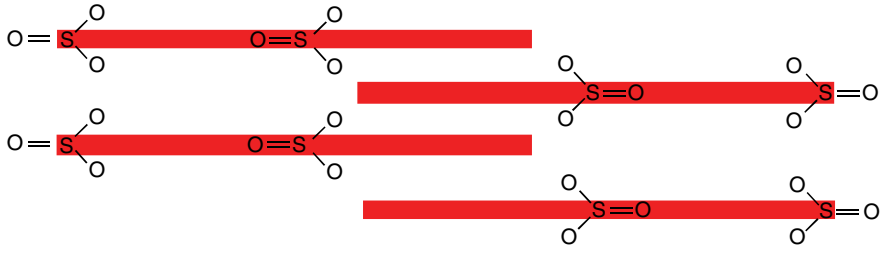
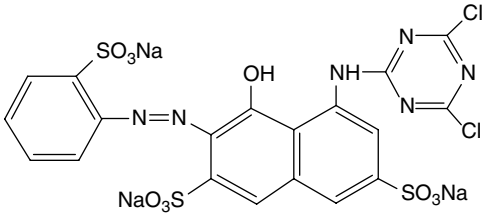
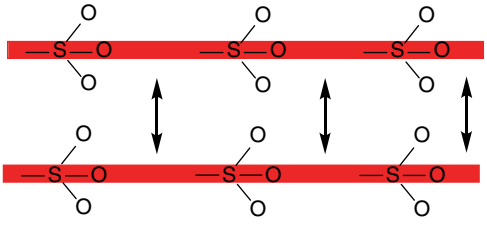


**Figure 6.5** Disruption of molecular stacking due to steric hindrance by bulky sulphonate groups.




**6.6**




For aggregation to occur, it is not necessary for dye molecules to overlap completely, and aggregate structures such as those shown in Figure 6.6 are possible. Indeed overlapping of the type (d) has been confirmed [1] for the dye C.I. Direct Blue 1 (**6.7**). The molecules stack over each other at the central biphenyl group:

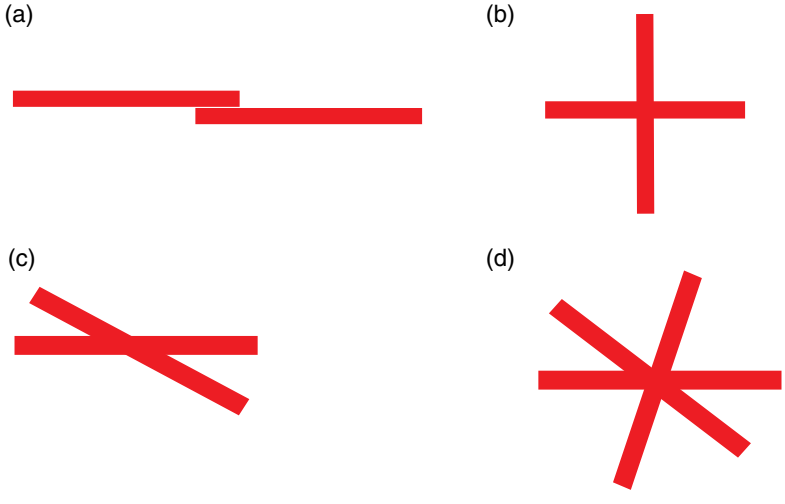
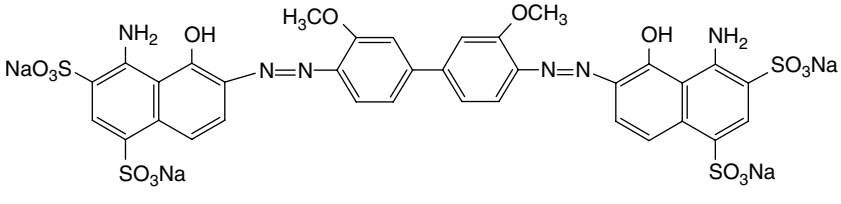



**Figure 6.6** Overlapping structures of dye molecules in aggregates.




**6.7**

In addition to molecular size, shape and the ratio M.Wt:No. of $-SO_3^-$ groups, a number of other factors influence the extent to which a given dye aggregates in solution. These factors are:

- Concentration
- Presence of electrolyte
- Temperature
- Presence of organic solvent

# Concentration

In the case of dyes that are prone to aggregation, the extent of aggregation increases with increase in concentration. This is because at higher concentrations, the repulsive forces are overcome, the influence of the charged groups being reduced by oppositely charged counter-ions. Usually at low concentrations, aggregation is minimal, and when the absorbances of dye solutions are measured, Beer's law applies (see Section 7.8). However at higher concentrations, when aggregates form, not all molecules in an aggregate are able to absorb light, so the absorbance is less than it should be. When a Beer's law graph is drawn, of absorbance versus concentration, the line deviates from linearity at higher concentrations (Figure 6.7):

Further evidence of aggregation occurring can be seen when the absorbance spectra of dye solutions at different concentrations are plotted. For example, in Figure 6.8, only one absorbance peak is observed for the dye at low concentration when the dye molecules exist as individual entities, but at a higher concentration when perhaps a dimer is formed, a second absorbance peak at a different wavelength is formed. The formation of the dimer reduces the

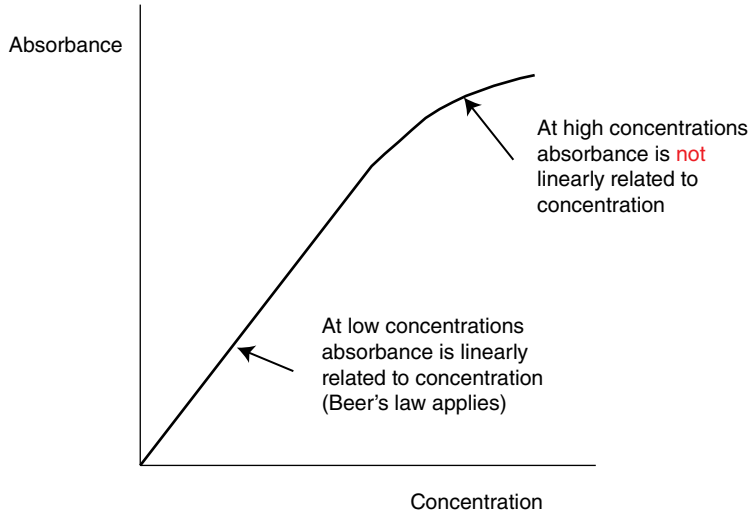



**Figure 6.7** Effect of dye aggregation on Beer's law plots.

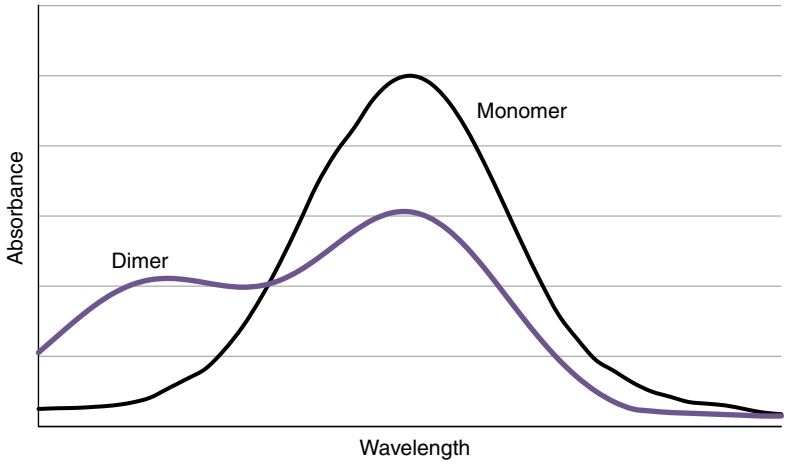



**Figure 6.8** Absorbance spectrum of a dye forming a dimer at high concentrations.

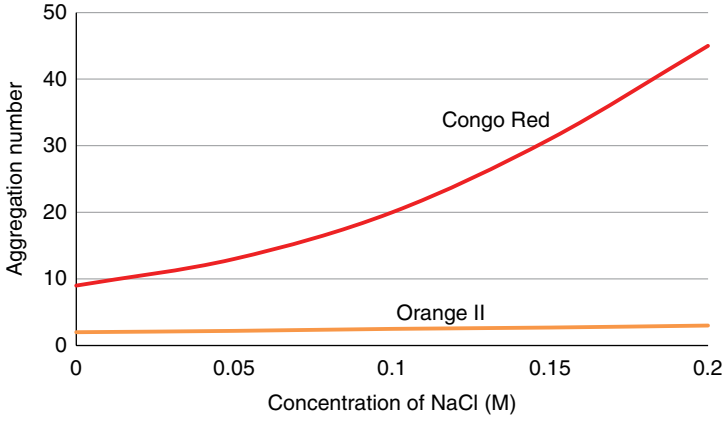



**Figure 6.9** Effect of salt concentration on dye aggregation.

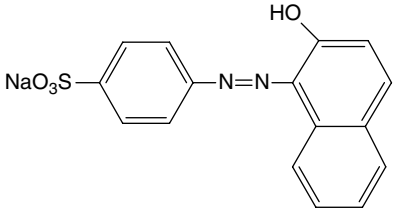
number of individual dye molecules in the solution, so the absorbance at the $\lambda_{max}$ for the individual dye molecules decreases.

## Presence of Electrolyte

In the presence of electrolyte, dyes in solution aggregate to a greater extent, because the repulsive forces are overcome, or suppressed, by the charged counter-ions. The mode of action is similar to that which occurs at the electrical double layer, and negatively charged dye ions are able to diffuse into negatively charged fibre surfaces (see Section 6.7.2). A good example of the effect of electrolyte is its significant effect on the dye C.I. Direct Red 28, known as Congo Red (Figure 6.9).

The molecules of the dye Congo Red are large and it only possesses two sulphonate groups so is prone to aggregation. The presence of electrolyte only serves to suppress charge

repulsion between sulphonate groups, thereby facilitating further aggregation. In contrast, the dye C.I. Acid Orange 7 (known as Orange II) has a very simple structure (**6.8**) and does not tend to aggregate and so the salt has very little effect:




**6.8**

In general, dyes that have an inherent tendency to aggregate are more susceptible to the presence of electrolytes. Aggregation can cause considerable difficulties in dyeing processes by slowing both the rate of adsorption and the rate of diffusion of dye through the fibre.

# Temperature

An increase in temperature causes dye aggregates to break down, so the aggregation number decreases as temperature increases. This trend is exemplified by the dyestuff C.I. Direct Blue 1 (**6.7**) as shown in Figure 6.10.

The aggregation of water-soluble dyes has consequences for the uptake of dyes by fibres during a dyeing process. Large aggregates of dye molecules diffuse more slowly through water to the fibre surface than the individual molecules, and so the rate of dyebath exhaustion is lower. As the temperature of the dyebath is raised and the aggregates break down, the rate of exhaustion gradually increases.

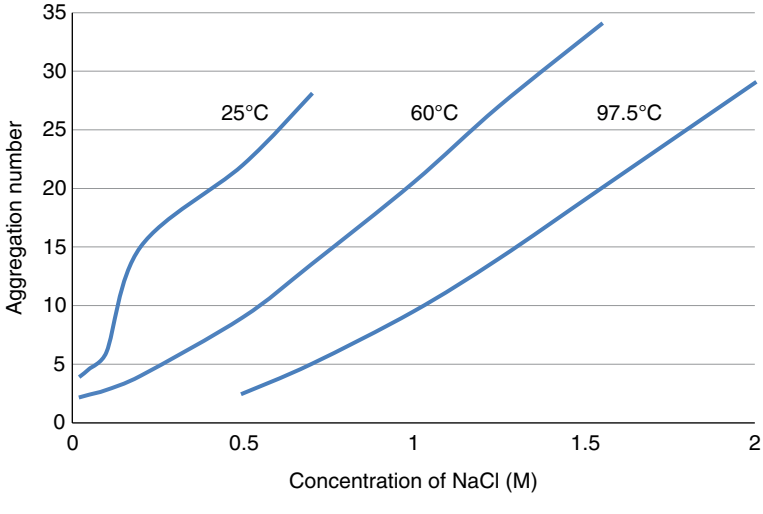



**Figure 6.10** Effect of temperature on the aggregation of C.I. Direct Blue 1 (Source: Valko [3]. Reproduced with permission of John Wiley & Sons).

# Solvent

If certain organic solvents or compounds such as urea are added to dye solutions, then the degree of aggregation (the aggregation number) reduces. The presence of a dye molecule in water, especially a dye molecule containing hydrophobic components, causes the water molecules around it to assume a more ordered structure than those further away. These water molecules therefore lose entropy. If the dye molecules aggregate, there will be fewer dye molecules to cause increased order of the water molecules, so there is greater disorder over-all and the entropy of the system increases. Addition of a solvent, especially one that can preferentially form hydrogen bonds with water, such as ethanol, disturbs the water structure around dye molecules and enables dye molecules to exist more easily as individual entities. The compound urea has an especially strong action in this respect and greatly increases the solubility of dyes in water. For this reason it is often added to print pastes where the volume of water available to dissolve the dye and other print paste components is limited.