6.6.2 Chemical Adsorption (Chemisorption)

Chemical adsorption generally involves an attraction between the adsorbent and the adsorbate that is much stronger than that which exists through the polar and van der Waals type forces that exist in cases of physical adsorption. Certainly, when a reactive dye is applied to a fibre and becomes bound to the fibre by a *covalent bond*, the process can be referred to as chemical adsorption. Before any chemical reaction can take place, the dye has to be adsorbed by the fibre through initially a physical adsorption process. Once this has occurred, the dye and the fibre will then be in close enough proximity to each other so that chemical reaction to form a covalent bond can occur.

In a reactive dyeing process, physical adsorption is a necessary precursor to chemical adsorption, and so all of the factors that affect physical adsorption will have an influence in reactive dyeing.

6.6.3 Adsorption Isotherms

With the exception of reactive dyeing, dye adsorption occurs by physical adsorption, and at the end of the dyeing process, there is a distribution of dye molecules between the fibre phase and the solution phase. Dye adsorption isotherms are obtained by measuring how much dye is in the fibre $[D]_f$ and how much remains in solution $[D]_s$, when the dyeing has been allowed to proceed, at a constant temperature, to equilibrium. The process is repeated for different initial amounts of dye added to the dyebath, that is, for different depths of shade being applied.

Three types of adsorption isotherm can be identified, called the *Nernst*, *Freundlich* and *Langmuir* isotherms, and the various dye/fibre systems correspond to one of these types.

The simplest of the three types is the *Nernst adsorption isotherm* (Figure 6.17) where a graph of $[D]_f$ plotted against $[D]_s$ is a straight line. This isotherm is shown by disperse dyes on hydrophobic fibres such as polyester and nylon and is typical of the behaviour of the dye forming what is effectively a solid solution in the fibre. Both the dye and the fibre are electrically neutral, so there are no charge attraction or repulsion influences on the

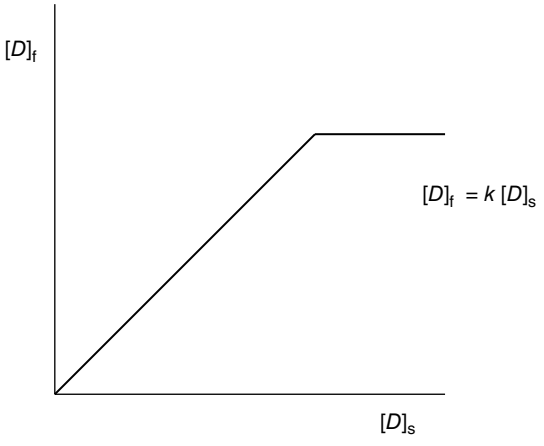

Figure 6.17 The Nernst isotherm.

adsorption of dye. The ratio $[D]_f/[D]_s$ is called the *partition coefficient*, K, and because the graph is linear, K remains constant until the saturation point of the dye in the fibre is reached. At this point, no more dye can be taken up by the fibre, no matter how much more dye is put into the dyebath.

The equation of this isotherm is quite simply stated as

$$\left[D\right]_f = K\left[D\right]_s . \tag{6.7}$$

If the isotherm is determined at a higher temperature, the solubility of the disperse dye in both the fibre and the aqueous phases increases. However the dye solubility increases more in the water, so the slope of the isotherm is lower and the equilibrium exhaustion of the dye is lower.

The second type of adsorption isotherm, the *Freundlich adsorption isotherm*, is shown in Figure 6.18.

Here the graph is not linear, but significantly the line keeps rising, with no apparent saturation being reached.

This type of isotherm is shown by anionic dyes, such as direct dyes, vat dyes (in their reduced form) and reactive dyes (during the exhaustion phase, before fibre reaction) applied to cellulosic fibres.

It appears that there are an infinite number of locations in the cellulosic fibre at which anionic dyes can be adsorbed. Another feature of these systems is that the anionic dyes can build up in multilayers in the fibre, and this feature contributes to the apparently unrestricted uptake of dye.

The equation of this isotherm is

$$\left[D\right]_f = k\left[D\right]_s^x \tag{6.8}$$

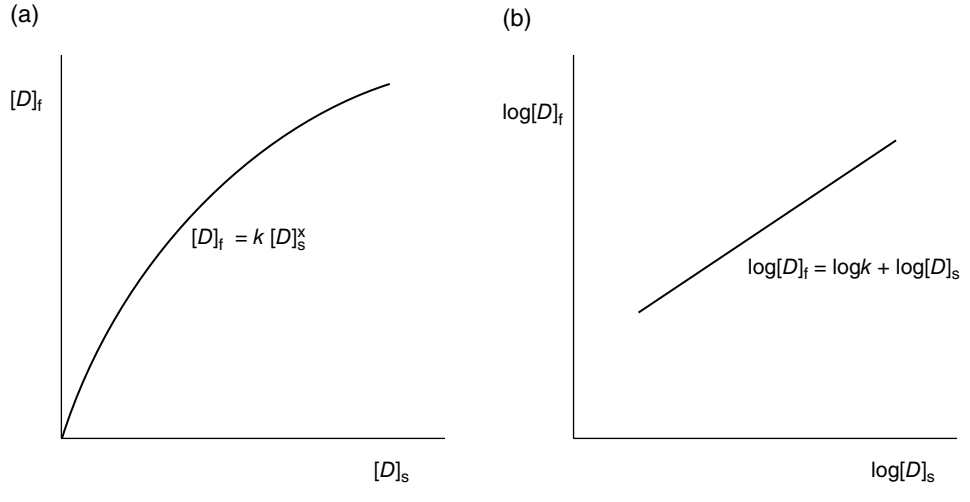

Figure 6.18 The Freundlich isotherm.

where k and x are constants. Taking logarithms of this equation gives

$$\log\left[D\right]_{\mathrm{f}} = \log k + x \log\left[D\right]_{\mathrm{s}} \tag{6.9}$$

which has the form of a simple linear equation, so if, instead of plotting $[D]_{\mathrm{f}}$ against $[D]_{\mathrm{s}}$, as shown in Figure 6.18a, $\log[D]_{\mathrm{f}}$ is plotted against $\log[D]_{\mathrm{s}}$, a straight line is obtained (Figure 6.18b).

When anionic dyes are applied to cellulosic fibres, different processes take place at the fibre–water interface than occur with disperse dye systems. Anionic dyes carry one or more negatively charged sulphonate groups, and the –OH groups in the cellulose molecule can dissociate to a certain extent, creating a negative charge at the fibre surface. This is explained later in Section 6.7.2, but the point to note here is that the adsorption of anionic dyes onto cellulosic fibres is a complex process.

The third type of isotherm is the *Langmuir adsorption isotherm*, which applies to systems in which charged dye ions are taken up at 'sites' with the opposite electrical charge in the fibre. Typical of dye/fibre systems that are adsorbed at specific sites in the fibre are acid dyes on wool and nylon, and basic (cationic) dyes on acrylic fibres (see Figure 6.15).

The shape of the adsorption isotherm exhibited by these dye/fibre systems is illustrated in Figure 6.19a. Dye builds up regularly in the fibre, but because the total number of dye sites is limited, the adsorption tails off as the sites all become occupied.

The equation of the Langmuir isotherm is

$$\left[D\right]_{\mathrm{f}} = \frac{k\left[S\right]_{\mathrm{f}}\left[D\right]_{\mathrm{s}}}{1 + k\left[D\right]_{\mathrm{s}}} \tag{6.10}$$

where $[D]_{\mathrm{f}}$ is the concentration of dye in fibre and $[D]_{\mathrm{s}}$ is the concentration of dye remaining in solution at equilibrium, $[S]_{\mathrm{f}}$ is the concentration of dye in the fibre when all the sites are occupied. As with the Freundlich isotherm, it can be converted to a linear form, this time not by taking logarithms, but by expressing it in the form

$$\frac{1}{\left[D\right]_{\mathrm{f}}} = \frac{1}{k\left[S\right]_{\mathrm{f}}\left[D\right]_{\mathrm{s}}} + \frac{1}{\left[S\right]_{\mathrm{f}}} \tag{6.11}$$

The point where the straight line of the graph of $1/[D]_{\mathrm{f}}$ plotted against $1/[D]_{\mathrm{s}}$ intercepts the $1/[D]_{\mathrm{f}}$ axis gives the reciprocal of the saturation value, $1/[S]_{\mathrm{f}}$, from which $[S]_{\mathrm{f}}$ can be easily obtained (Figure 6.19b).

The equation of the Langmuir isotherm can be derived using the principles of reaction kinetics, explained in Section 1.5.2. The application of these principles involves some assumptions about the dye/fibre system however:

- The fibre has a fixed number of available dye sites and is uniform and homogeneous.
- All sites are equally accessible and have the same affinity for dye molecules – this means there is no preferential adsorption at particular sites.

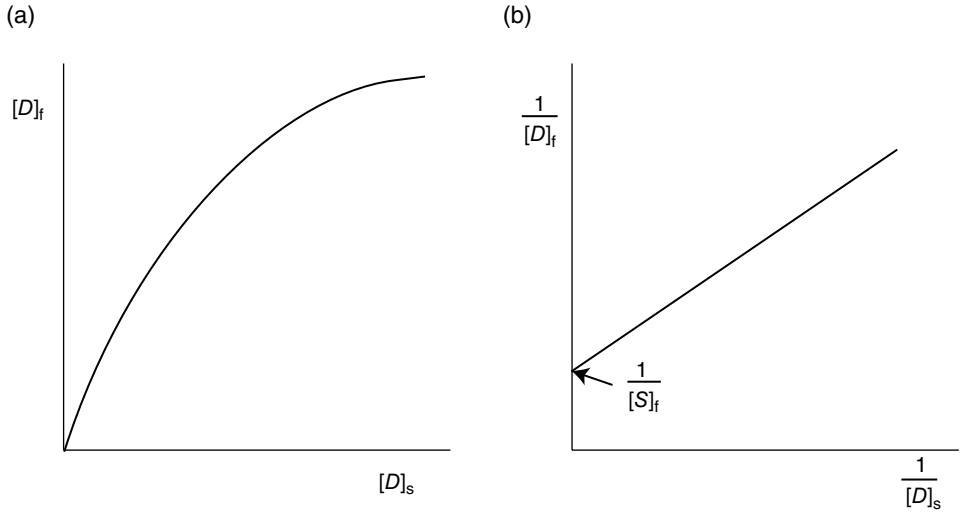

Figure 6.19 The Langmuir isotherm.

- Each site can accommodate only one dye molecule.
- There is no interaction between the adsorbed dye molecules, and the presence of a dye molecule at a site does not hinder the adsorption of another dye molecule at an adjacent site.

When a dyeing has reached equilibrium, dye is continually leaving the fibre and going back into the dye liquor, whilst simultaneously dye is continually arriving at the fibre surface and being adsorbed. By the law of mass action (see Section 1.5.2), the rate at which dye leaves the fibre (desorbs) is proportional to the concentration of dye in the fibre:

$$-\frac{d\left[D\right]_f}{dt} = k_{des}\left[D\right]_f, \tag{6.12}$$

the negative sign indicating that concentration decreases. The rate of adsorption is proportional to both the concentration of dye in solution and the number of dye sites available (given by $[S]_f - [D]_f$), so

$$\frac{d\left[D\right]_f}{dt} = k_{ads}\left[D\right]_s\left(\left[S\right]_f - \left[D\right]_f\right) \tag{6.13}$$

Because the system is at equilibrium, these two rates, the rate of adsorption and the rate of desorption, are equal:

$$k_{des}\left[D\right]_f = k_{ads}\left[D\right]_s\left(\left[S\right]_f - \left[D\right]_f\right) \tag{6.14}$$

Rearranging Equation 6.14 gives

$$\left[D\right]_f = k_{sys}\left[D\right]_s\left(\left[S\right]_f - \left[D\right]_f\right) \tag{6.15}$$

where $k_{sys} = k_{ads}/k_{des}$. Equation 6.15 can be rearranged to give Equations 6.10 and 6.11.

As will be seen later, dyes often show uptake on the fibre to an extent that is greater than the theoretical saturation value $[S]_f$. One reason for this is that in addition to becoming adsorbed at the charged sites in the fibre by ionic bonding, dye molecules can also be adsorbed in other regions, the attraction due to van der Waals type forces – the secondary forces described in Section 6.6.1 and also Section 1.4.3.