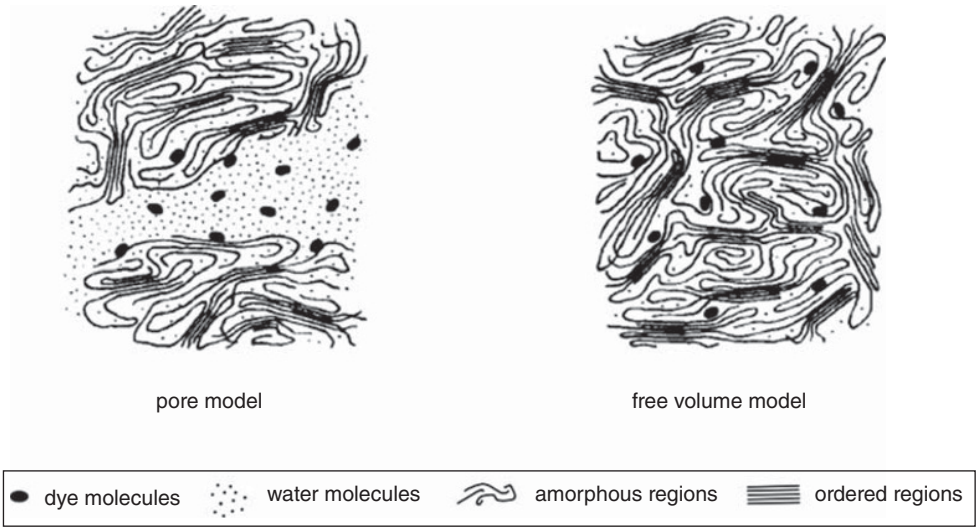

Figure 6.27 Schematic representation of pore model and free volume model of dye diffusion. Reproduced from [186], copyright of the Society of Dyers and Colourists.

6.3.11.1 Diffusion Models

There are two different models that have been used to interpret the aqueous diffusion of dyes within polymers, namely a *pore model* (aka *porous matrix model*) in which dye diffusion is considered to occur through water-filled pores and a *free volume model* in which such pores are neglected (Figure 6.27).

The former model was devised in the 1930s to describe the diffusional characteristics of anionic dyes within cellulosic fibres whilst the free volume concept was developed to describe the diffusion of dyes within hydrophobic fibres such as PES and PAN.

Essentially, whilst each model represents an attempt to correlate dye diffusion coefficient with fibre structure, because of the highly complex physical structure of textile fibres, each model may be considered to present, at best, an oversimplification of the real situation [187]. Indeed, the two models can be regarded as reflecting the two extremes of fibre hydrophilicity/hydrophobicity insofar as the pore model may best describe the diffusional character of dyes

within markedly hydrophilic fibres such as cotton, CV and CLY, whilst the free volume may more adequately describe dye diffusion within markedly hydrophobic substrates such as PES, with the various other types of fibre positioned in between these two extremes of fibre/water interaction [188–190]. However, it seems likely that, in the aqueous dyeing of the common types of textile fibre, both models operate simultaneously, but to different extents depending on structural aspects of both the polymer and diffusing molecules [190].

6.3.11.1.1 Pore Model (Aka Porous Matrix Model) of Dye Diffusion within Fibres The fundamental principle of the porous matrix model of dye diffusion is that the fibre contains void space or *pores* that enable it to absorb water and that dye molecules can dissolve in this water and diffuse through the water-swollen fibre. As discussed previously, both the sorption and transport of water in fibres is a (complex) function of both the capillarity of the fibres and the water permeability of the fibrous medium; capillarity reflects the driving force for water transport within fibres whilst permeability describes the ease and uniformity of water movement through the fibrous assembly.

According to the essentially mechanical pore model of dye diffusion, which was devised in the 1930s to describe the diffusion of anionic dyes in cellulosic fibres [191–193] and subsequently developed by various workers [125, 153, 194–198], dissolved dye molecules in the aqueous dyebath are able to enter a water-swollen fibre and subsequently diffuse within the water-filled pores of the substrate. When a diffusing dye molecule collides with a *binding site* located on the surface of a pore wall, it becomes adsorbed and immobilised, although, depending on the dye–fibre forces of interaction, the adsorbed dye molecule may desorb from the site, re-dissolve in the water within the pore and diffuse further into the substrate through the water-filled pore network. This model is based on three assumptions [47]:

(1) dye migration occurs only in the water-filled pores;
(2) the diffusing dye molecules are in equilibrium with dye sites on the pore walls;
(3) the adsorbed dye molecules are immobile.

Several forms of diffusion equation have been proposed for this model[21] (e.g. [138, 153]) in which the pores are considered as being *tortuous* and occupy a volume of the substrate, α, the flux in one dimension being given by Eq. 6.62 [49], where C_i and C_a are the amounts of dye in the pore and adsorbed on the pore walls, respectively, τ is the tortuosity (pore length:direct path ratio) and D_m the measured diffusion coefficient.

$$J = -\frac{\alpha}{\tau} D_i \frac{dC_i}{dC_a}\frac{dC_a}{dx} = -D_m \frac{dC_a}{dx} \tag{6.62}$$

The pore model assumes that the diameter of the pores is greater than the dimensions of the diffusing dye molecules, which, in many cases, seems unrealistic because the pore diameter of water swollen is of the order 2–10 nm [13] whilst the minimum dimensions of dye molecules are 1–2 nm long and 0.6–0.8 nm wide [199].

The basic principle of the pore model, which represents capillary theory as applied to fibres, is that the water-absorbent fibre contains *pores* in which water absorption occurs as a result of capillary forces. Fibrous materials, such as cotton and CV, are believed to comprise networks of interconnected pores of different sizes that develop different *capillary pressures*. As previously discussed in Chapter 3, in simple terms, capillary pressure is the difference in pressure that develops across an air/water interface because of the curved meniscus in a capillary. In the case of a wetting liquid such as water, capillary pressure corresponds to a negative pressure above the meniscus relative to atmospheric pressure. Water moves through the porous material because of the capillary pressure developed within the pores. Essentially, the modelling of liquid flow through porous media employs derivatives of the Laplace equation and utilises various parameters, such as porosity and permeability, of which the two most important are *pore volume* that influences the volume of water absorbed and *pore size* that influences the rate of water sorption and transport [200]. Although evidence suggests that pores appear to be present in natural fibres, the extent of the involvement of such pores in dye diffusional processes is difficult to resolve in reality owing to the highly complex, unresolved fine structure of such substrates.

In more recent years, the literature relating to dye removal from wastewater has grown significantly and aspects of this concern the diffusional behaviour of dyes within various types of porous networks (e.g. [201–204]).

6.3.11.1.2 Free Volume Model Some workers consider that the pore model of diffusion implies that dye uptake will not occur if the pores are of insufficient size, a situation that seems applicable to hydrophobic fibres that display low swelling in water, such as PES.

[21] which sometimes is referred to as the diffusion/adsorption model.

The free volume model of dye diffusion was therefore proposed, in which the diffusion of a dye molecule, which has been initially adsorbed onto a polymer chain, through a polymeric material such as a fibre can only occur when the segmental mobility of the composite molecular chains is such that sufficient free volume is formed that can accommodate both the dye molecule and chain segment [187]. As recounted earlier in Chapter 1, such a situation exists only at temperatures $>T_g$.

An increase in temperature will result in a corresponding increase in the mobility of the molecular chains within the fibre, which will lead to both thermal expansion and reduced density. Thus, the free volume of the substrate will increase, leading to increased diffusivity. That free volume model and dye diffusion are related is highlighted by Rosenbaum's observations on the kinetics of basic dye diffusion within PAN fibres [175, 205–207].

It is well accepted that the segmental mobility of the polymer chains within fibres greatly influences the rate of dye diffusion, since the onset of dyeing and the T_g of the fibre often coincide. This was clearly demonstrated in the cases of basic dyes within PAN fibres [206] and disperse dyes within PES fibres [208], for which significant dye diffusion was found to not occur until the dyeing temperature was ~70–80°C, at which point the rate of dye uptake increased markedly. As discussed, Eqs. 6.52 and 6.53 imply that a plot of log D or ln D versus $1/T$ should produce a straight line relationship, this having been observed for several dyeing systems, as exemplified by Figure 6.23, which shows the results obtained for the diffusion of azobenzene vapour into CA film [169]. However, Figure 6.28 reveals, for example, that in the case of the Arrhenius plot obtained for C.I. Basic Blue 4 within PAN fibre, a sigmoid curve was obtained. The activation energy was found to increase exponentially as temperature was reduced. Below the break in the curve in Figure 6.28, which coincided with the T_g (57°C) of the fibre as determined by physical measurement, the rate of dye diffusion reduced and the activation energy of diffusion was constant, as shown by the inset within Figure 6.28, in which the activation energy of diffusion is denoted by the symbol $E*$.

The dependence of the observed dye diffusion on segmental chain mobility within the PAN fibre was confirmed by the adherence of the results to a WLF relationship of the form given by Eq. 6.63 [206] (see Section 1.4.2.3.6).

$$\log\frac{D_T}{D_g} = -\log a_T = \frac{A\left(T-T_g\right)}{B+\left(T-T_g\right)} \tag{6.63}$$

The coincidence of experimental points with the relationship calculated from Eq. 6.63 is shown in Figure 6.29 and, therefore, clearly demonstrates that dye diffusion is governed by the activation energy of the molecular processes taking place in the polymer structure and, in the absence of other complicating factors, this should be the same for all dyes studied. Further evidence in support of the notion that segmental chain mobility and, thus, free volume govern dye diffusion has been secured in the cases of disperse dyes on PAN [209, 210] and PES [211, 212], as well as acid dyes on PA 66 [213].

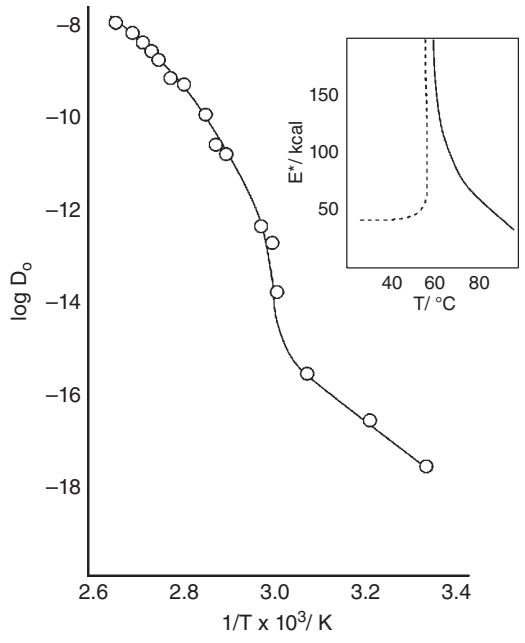

Figure 6.28 Arrhenius plot of apparent diffusion coefficient of C.I. Basic Blue 4 within PAN fibre. Reproduced from [206], with permission from John Wiley & Sons, Inc.

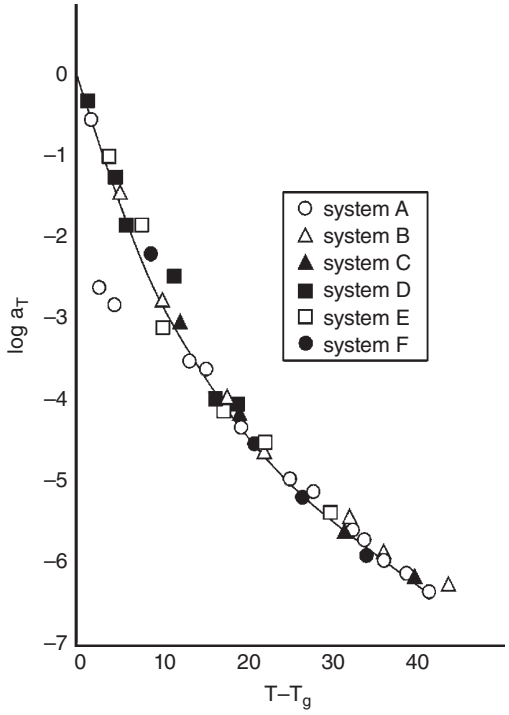

Figure 6.29 Effect of experimental data to the curve of log a_T versus ($T - T_g$) calculated using Eq. 6.63. Reproduced from [206], with permission from John Wiley & Sons, Inc.

Whilst the above discussion of dye diffusional behaviour is observed at temperatures $>T_g$, the diffusion of dyes and other low molar mass compounds in both fibres and polymers at temperatures $<T_g$ is more complicated owing to the non-equilibrium nature of polymers in their glassy state, which results in marked non-Fickian behaviour.