FIBRE MODELS AND DYE DIFFUSION

The dyeing of synthetic fibres has been described using theories based on polymer structure. These same theories have been applied to the dyeing of natural fibres. All fibres have been considered to consist of radially iso-tropic bundles of polymer molecules, and microstructural aspects have been largely ignored.

Not only does water act as a solvent for dyes but all the natural fibres also absorb significant quantities of water. The maximum water uptake of wool is 32–38%, silk takes up 30–41%, cotton absorbs about 45% and viscose absorbs about 50% by weight [106]. Theories concerning the physical state of water molecules inside wool and cotton have been reviewed by Morton and Hearle [107].

The presence of water inside the fibres seems to be crucial to dye diffusion mechanisms. Hori and Zollinger have recently summarised theories on the role that water plays in diffusion within textile polymers [108]. Swelling is generally considered to open up the fibre structure and thereby make it more accessible to water-soluble dyes. Two types of interaction between water and polymers have been postulated. In one case the water is considered to be interstitial and provides an internal aqueous phase and an internal water–polymer interface. In the other case the water is assumed to dissolve in the polymer. Two corresponding theoretical models have been advanced

to describe the types of dyeing behaviour that may be encountered. These are the porous matrix model and the polymeric chain model respectively.

Porous matrix (pore) model

This model was put forward in 1935 [109–111] and has been modified subsequently by a number of workers. The most modern form of this theory has been given by Weisz and Zollinger [112–114]. The textile fibre is considered to be composed of a solid polymer matrix that contains a myriad of interconnected channels or pores. Under dyeing conditions the channels are filled with 'free' water that is not associated intimately with the polymer. The water acts principally as a solvent for dye, which enters the fibre by diffusing through the water-filled channels connected to the fibre surface. The polymer chains lining the channel walls provide adsorption sites for the dye molecules. Dye that is free to diffuse is considered to be in equilibrium with adsorbed dye. Thus individual dye molecules are assumed to progress towards the centre of the fibre by a series of stop–go events. The model does not distinguish between situations in which adsorbed dye molecules remain at the interface between the pore and the polymer, or in which dye molecules may penetrate between the polymer chains.

An expression based on pore theory has been obtained that relates the intrinsic diffusion coefficients of dyes in the water phase inside fibres (D) to the diffusion coefficients measured in dye exhaustion experiments (D_{app}) according to Eqn 12:

$$D_{app} = \gamma \frac{P}{b} \frac{C_o}{C_f} nD \qquad (12)$$

where γ is a constant that varies from 1.0 to 1.6 depending on the form of the immobilisation isotherm, P is the fraction of the fibre accessible to diffusion, b is a tortuosity constant that is rarely greater than $3^{1/2}$ (except with strongly anisotropic fibre structures), C_f is the total concentration of dye per unit volume of fibre that is in equilibrium with the concentration C_o in the solution external to the fibre, and n is the partition coefficient of the dye between the mobile portion of the internal and external aqueous phases.

Using pore theory, Weisz and Zollinger have obtained intrinsic diffusion coefficients of direct dyes in cellulose, levelling acid dyes in nylon, disperse dyes in nylon and polyester, and disperse dyes in cellulose acetate. They have shown that, by appropriate selection of values for the parameters in Eqn 12, all the calculated intrinsic diffusion coefficients can be made to approach the magnitude of the free volume diffusivities of the dyes in water [115]. For example, values of D were obtained from data reported by Neale from exhaustion studies of direct dyes on cotton. The values of D_{app} ranged from 3×10^{-12} m^2/s to 1.2×10^{-14} m^2/s at 90°C [12] and the variables in Eqn 12 were assigned the values $n = 1$, $b = 1.7$, $\gamma = 1.6$ and $P = 0.25$. The optimised values of D were typically more than 1000 times greater than the corresponding values of D_{app} and none was greater than $2\text{–}5 \times 10^{-10}$ m^2/s, which is of the same order as the diffusivities of the dyes in water.

Polymeric chain (free volume) model

This model was first proposed in 1960 to account for diffusion processes in polymers [116]. The polymer chains that form the structural components of fibres are conceived as forming structures referred to as 'matrix' and 'crystallites'. In the matrix the polymer chains are randomly arranged while in crystallites chains are closely aligned in regular packed structures. At ambient temperature, because of the rigidity of the structure and the close contact of the chains, it is assumed that it is difficult for dyes to penetrate between the polymer chains, even in the matrix. However, at temperatures above their glass transition temperatures, polymers are known to 'melt' and behave as though they are highly viscous liquids. Under these conditions it should be possible for dyes to penetrate the fibres relatively easily. Dyes are thought to penetrate by moving through small voids between the polymer chains, especially in the matrix. The voids are assumed to open randomly and close due to thermal motion. The ease with which a molecule can penetrate through this type of dynamic polymer jungle depends on the proportion of 'free volume' occupied by the voids relative to the total volume of the polymer. In this type of polymer, water is considered to be strongly bound to hydrophilic residues and its presence causes a decrease in the glass transition temperature and an increase in the 'free volume'. When fully swollen with water, wool and cotton have glass transition temperatures below ambient temperature. The relevant values are about –10°C [117] and 0°C [118] respectively. This means that, in principle, the polymer model could apply to proteinaceous and cellulosic fibres under all practical dyeing conditions.

Applicability of models to natural fibres

Physical measurements have shown that pores appear to be present in all natural fibres [119]. The involvement of pores in diffusion processes appears to depend on the type of fibre involved [120].

It is thought that about half of the water absorbed by cotton under dyeing conditions is intimately associated with the cellulose fibrils and the rest is present as free water in pores within the fibres [121]. The total pore volume and pore size distribution in cotton fibres can be measured by exclusion methods [122] and has been shown to vary depending on the pretreatment of the cotton [123]. From these data it has been deduced that for uptake of direct dyes by cotton the most important pores are those with diameters between 1 and 6 nm. The total amount of dye absorbed appears to be proportional to the volume of pores in this diameter range relative to the total fibre volume. Stone and Scallan have shown that pores less than 3 nm in diameter in wet cellulose have a total surface area of 260 m^2/g [124]. It appears that the dyes are taken up as a monomolecular layer in these pores, at least in concentrations corresponding to the

plateau region of the Langmuir type dye absorption isotherm [125]. Arguments in favour of aggregation of dyes within the pores by multilayer absorption at high dye concentrations have been summarised by Giles [31].

Diffusion in cellulose is now commonly described in terms of the free volume theory. For example, the diffusion coefficient of CI Direct Yellow 12 in cellophane has been measured by the multiple membrane method at pressures up to 250 MPa by Seta and Ito, who have concluded that the diffusion behaviour could be explained provided that the dye molecules diffused into the fibre 'end-on' [126]. 'End-on' diffusion is now believed to be the normal mode of entry of direct dyes into cellulose [127].

Because the diffusion coefficients of CI Direct Blue 15 and Yellow 12 in cellulose have been found to vary with dye concentration, it has been suggested that the pore model requires further refinement [128]. A number of modifications to the theory have been proposed that include variable-sized pores [129] and the possibility of dual surface and pore diffusion [130].

Jovanovic and co-workers have examined a number of different wools by a variety of methods and found pores ranging mostly in diameter from 4 to 1000 nm [131]. Generally the specific internal surface area of the pores was about ten times greater than the external surface area. BET studies using nitrogen suggest a pore structure that becomes more extensive with chemical modification of the wool fibre surface [27]. Work on the uptake of water vapour indicates that only 6 or 7% of water absorbed at saturation can be accommodated in a monolayer on the accessible surface [29]. In the light of recent discoveries concerning wool structure, the most likely source of pores within wool fibres would appear to be the cell membrane complex, the structure and function of which will be discussed later. There is always the possibility that cracks may be created in wool and cotton fibres when surface areas are measured by adsorption methods that include a vacuum drying step, because the fibres contract as they lose water. This would lead to the estimates of surface areas being too high.

The Donnan membrane theory of dyeing provides some support for the existence of free water in pores inside cotton and wool fibres. Vickerstaff has reviewed the way in which it has been used to calculate adsorption isotherms and affinity of dyes [16]. According to this theory, the mobile ionic species are distributed in aqueous solutions both inside and outside a dyeable substrate, and the internal and external phases are separated by a semipermeable membrane at the solid surface. The theory requires the internal solution to have a definite volume which contains the diffusing ions. A value of 0.29 l/kg was assumed by Speakman and Peters for wool [132], and subsequent work by Delmenico and Peters gave experimental values varying from 0.24 to 0.30 l/kg [133]. This is only slightly less than the value of 0.34 l/kg obtained for the equilibrium water content of wool at saturation. In the case of cotton the internal volume of water has been usually taken as 0.22 l/kg, also very close to the moisture content at saturation [16]. No attempt appears to have been made to reconcile Donnan theory with more modern ideas about the role of water inside fibres during dyeing.

The most telling piece of evidence in favour of the polymeric chain model in wool is the variation in glass transition temperature that can be predicted by the Fox equation. This equation was developed from the polymeric chain model as it applies to simple polymers [134]. The fact that it describes the behaviour of a complex polymer is something of a surprise and seems to imply that there is little free water associated with pores in wool [117].

After studying the dyeing kinetics of two types of polyacrylonitrile fibres with different degrees of porosity, Rohner and Zollinger have concluded that the pore model and the polymeric chain model mechanisms are not mutually exclusive and can be considered to operate simultaneously [135].

Zollinger and Hori have recently summarised discussions on the two models in relation to dyeing wool and cellulosic fibres [119,127,136]. The dyeing of cellulosics is claimed to be best understood in terms of the porous matrix model, while the behaviour of wool and silk most nearly approximates to the polymeric chain model. Mitsuishi, Yagi and Ishiwatari have recently claimed that the dyeing behaviour of silk can best be explained in terms of the polymeric chain model [69].

LOW-TEMPERATURE AND ACCELERATED DYEING PROCESSES FOR WOOL

Studies of conventional aqueous methods for dyeing of wool have revealed that diffusion coefficients of dyes used in commercial processes are generally small. This is consistent with the methods being relatively prolonged and energy intensive. Consequently there has been keen interest in the development of low-temperature and accelerated dyeing methods that may offer savings in both time and energy. The term 'low temperature' has been applied to processes conducted at 90°C or below. More recently it has been discovered that wool dyed at low temperature can be processed with less fibre breakage, giving products with superior strength and durability compared with conventionally dyed wool. This has been attributed to reduced chemical and physical damage incurred by the fibre. Dyeing processes carried out at low temperature have usually been assumed to operate by increasing the rates of dye diffusion inside fibres. Few workers have acknowledged the possibility that rapid disappearance of dye from solution may be due to other causes.

Generally three types of low-temperature process have been developed based on the use of:

(a) Surfactant type dyeing assistants
(b) Fibre pretreatments
(c) Solvents or carriers.

These dyeing methods have been reviewed by Lewis and Bahn [30,137].

Surfactant-type dyeing assistants

The most common approach to low-temperature dyeing has been to use special surfactants as dyeing assistants. These auxiliaries enable exhaustion to be achieved at temperatures below the boil so that the final maximum temperature of the dyeing process can be limited to between 80 and 90°C, depending on the dye. Assistants that have been found effective include nonionic surfactants (such as Lissapol N (ICI) [138]), amphoteric surfactants (such as Albegal B (CGY) [139]), fatty diethanolamides [140] and a host of products such as Aminogen 270 (ACO) [141], Baylan NT (BAY), Coloron A (ATL) [142], Intratex W (CKC) [143], Keriolan A (CHT) [144], Lanasan LT (S), Solvafol 910 [145], Syntegal V7 [146], Unisol BT (ICI) [147], Unisol MFD (ICI) and Verilan 80 (FW) [148]. These assistants have usually been recommended for use with selected milling, chrome and 1:2 metal-complex dyes.

Diffusion coefficients and activation energies for diffusion have been calculated from exhaustion experiments, on the assumption that the rate of dyeing is determined only by diffusion processes. Several workers have suggested that the surfactants interact with the dyes and the fibre to increase the rates of diffusion inside the fibre [138]. No convincing evidence to support this assumption has been produced. Facilitated exhaustion of dye could be due to interactions between the surfactant and dye, particularly at the interface between the fibre and the solution [149]. It is possible that a micellar layer containing a relatively high concentration of dye is formed on the fibre surface and that this acts as a reservoir from which dye diffuses into the fibre. Experimental evidence appears to support this view.

A study of fibre cross-sections has shown that the fibres are rapidly 'ring dyed' but subsequently the speed with which an levelling acid dye can penetrate the fibres depends on the r.m.m. of the dye [23]. The suitability of levelling acid, milling and metal-complex dyes for use in this type of low-temperature dyeing process seems to depend on the ability of the dye to achieve at least minimal fastness requirements. Certainly with high r.m.m. dyes (such as 1:2 metal-complex dyes) the average degree of penetration into the fibres is less than occurs at the boil in a comparable dyeing time, but in many cases complete penetration of the fibres does not appear to be required for adequate fastness properties to develop. In the Concept AFD (ICI) approach to low-temperature dyeing the relationship between the maximum dyeing temperature, depth of dyeing and fastness properties has been determined for combinations of metal-complex dyes and auxiliaries such as Unisol MFD. Recommendations have been made concerning the minimum dyeing temperature that may be used to achieve desired levels of fastness. In fact, many wool dyes can be applied at temperatures 10–20 degC degrees below the boil and still diffuse into the fibres within realistic dyeing times.

It is noteworthy that surfactant-assisted processes have been used extensively with chrome dyes. As already pointed out, these dyes have low r.m.m. and achieve high levels of fastness by complex formation in a subsequent chroming step after diffusion of the complexing chromophores into the interior of the fibre.

Chemical treatments

Certain chemical treatments carried out in a separate step before dyeing may be used to confer low-temperature dyeability upon wool. Chemicals that have been used for this purpose include a mixture of common salt, nonionic detergent and ammonia [150] and a special surfactant at pH 8 [151,152]. These treatments have been followed by dyeing processes in which the maximum temperature has been limited to between 80 and 90°C. It seems likely that the fibres are modified during the pretreatments, presumably by alteration to the structure of the cell membrane complex, which facilitates uptake and entry of dye into the fibre cortex [152]. However, the presence of substantive surfactants in these treatments could lead to formation of transient dye–surfactant complexes on the fibre surface and in the intercellular cement in the cuticle regions; this could facilitate exhaustion of dye without promoting diffusion.

Solvents and carriers

Several different solvents and carrier type substances have been used to increase wool dyeing rates [142]. Research has been carried out with compounds such as butanol, amyl alcohol, benzyl alcohol [153], formic acid, urea, phenolic materials [154] and solvents such as Irgasolvent CLW (CGY). Commercial processes based on these studies have been developed but none has been widely used owing to cost and pollution problems. These include the butanol-assisted method of Peters and Stevens [155], the Irgasolvent CLW process [156], the CSIRO formic acid [157,158] and concentrated urea pad–steam [159] processes, and the concentrated urea cold-pad–batch process of Ciba-Geigy [160] and IWS [161].

In early work it was noted that the effective alcohols had limited solubility in water. This led to the suggestion that the increased dyeing rates were due to the formation of an alcohol phase on the fibre surface in which the dyes were highly soluble [162]. Subsequently, when it was shown that all the alcohols were absorbed by wool, the alcohols were then postulated to be acting as carriers that increased the rates of dye diffusion [163,164].

Using the same theoretical approach as Medley and Andrews, Al-Hariri, Coates and Rattee showed that, when wool was dyed in the presence of 20 g/l benzyl alcohol, the diffusion coefficient of CI Food Yellow 3 increased by a factor of three, and the surface admittance increased nearly twelve-fold [63]. They also found that *m*-cresol and *p*-methoxyphenol had a major effect on diffusion rates inside the fibres without changing the surface admittance to any great extent.

The role of concentrated aqueous solutions of urea (30–35%) in increasing the rate of dyeing has been much discussed. The use of urea has made it possible to develop padding and printing processes in which dye diffusion into the fibres is complete after approximately 10 min at 100°C or within 24 h at room temperature. This corresponds to reductions in dyeing times by at least a factor of three. Much of the work on the action of urea in dyeing wool has been reviewed by Burdett and Galek [165]. Urea is not preferentially taken up by wool fibres. Mechanisms proposed have included disaggregation of dye, formation of complexes with dyes, swelling of the fibre and a change in the hydrogen-bonded network of water molecules inside the fibre. However, none of these explanations seems truly convincing. As already pointed out, dyes appear to diffuse in a monomeric state; complexes would have higher r.m.m. than the uncomplexed dyes and therefore would be expected to diffuse more slowly. Changes in the structure of the hydrogen-bonded network would undoubtedly occur but they may be relatively minor, and this argument has not yet been supported by thermodynamic calculations. Urea-induced swelling of the fibre diameter appears to be too slight under industrial dyeing conditions to produce a large effect on dyeing rate [166,167]. For comparison, swelling with concentrated formic acid produces an increase of about 180% in volume and this would be expected to greatly increase the accessibility of the fibre to dye. Wool is actually dyeable in a few minutes at room temperature in concentrated formic acid [158]. Under these conditions diffusion coefficients must be increased by a factor of at least 1000.

More information about the effect of solvents and related compounds was provided by the discovery that fibres that had been extracted with certain solvents were more easily dyed than normal wool. For example, Medley and Andrews showed that the diffusion coefficient of CI Acid Orange 7 was significantly increased if wool was first extracted with aqueous n-butanol, but there was only a small increase in surface admittance [168,169]. Subsequent work in which wool was extracted with butanol–heptane, formic acid, chloroform–methanol or aqueous propanol, and then dyed with CI Acid Orange 7 and Red 73 has shown that dyeing rates were increased to varying extents, but the activation energy for diffusion was unchanged [170,171]. These results seemed to indicate that material that normally hinders diffusion within the fibres had been removed or modified by extraction with the solvent [169,172]. It has been found that formic acid and aqueous propanol are able to extract lipid and nonkeratinous protein from within wool fibres [173], and this may also be true of other polar solvents. It has been suggested that the most likely locations from which any such material could be removed are the cell membrane complex and the matrix of the cortex. Even concentrated urea solutions have been found to extract soluble protein from wool [174]. The significance of these observations will be discussed in more detail in the section on diffusion pathways.

FIBRE MORPHOLOGY

Study of the actual structures of fibres can provide information about the likely penetration pathways of dyes. Indications also can be obtained of ways in which fibres are likely to deviate from the theoretically assumed models used to describe dyeing behaviour [175,176]. Work carried out to determine structural features relevant to dye penetration and the eventual adsorption sites for dye molecules will be discussed in some detail.

Structure of wool

Merino wool has been the model for wool fibres in general and the complex histological structure of these fibres has been extensively studied and reviewed [177–182]. In Figure 1 an idealised representation of a wool fibre is shown [183]. A fibre consists of a core of spindle-

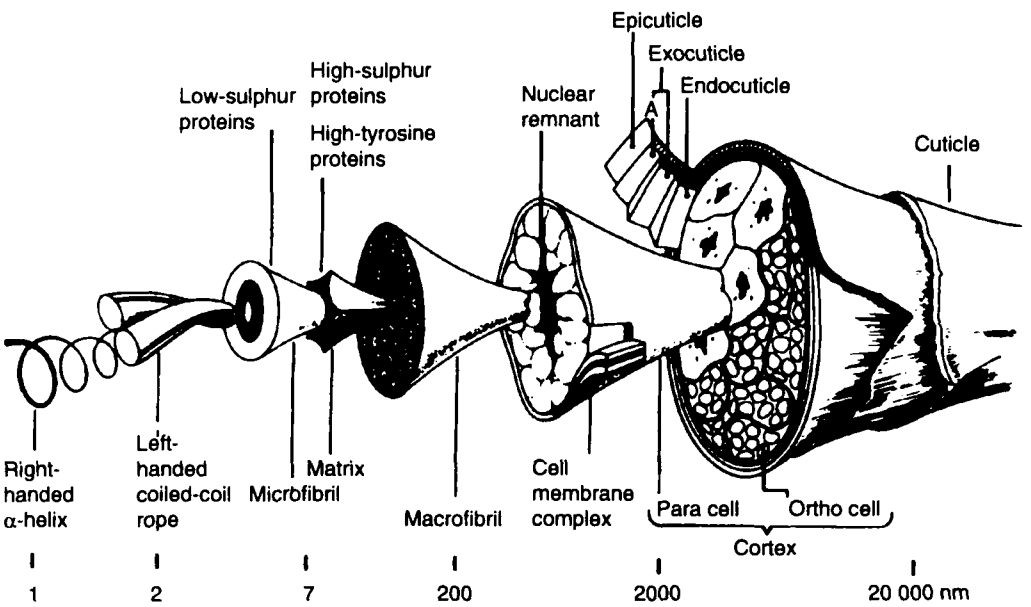

Figure 1 Structure of a merino wool fibre (CSIRO Division of Wool Technology)

shaped cortical cells, each about 100 μm long and 3–7 μm wide. Surrounding the core of cortical cells is a sheath of flattened overlapping cuticle cells.

Cuticle cells are tilted with respect to the longitudinal fibre axis, and their free edges point towards the tip of the fibre. Generally the orthocortical cells are covered by only one layer of slightly overlapping cuticle cells. On the other side of the fibre the region occupied by the paracortical cells is covered by layers of overlapped scales which may be up to three cells thick [184]. Some of the scale edges on the surfaces of merino fibres do not coincide with true cuticle cell boundaries. These are called false scale edges and are thought to be formed by a moulding process during growth of the fibre [179].

Individual cuticle cells are about 300–700 nm thick. Internally they consist of two main layers. The outermost layer, the exocuticle, takes up about half to two-thirds of the cell volume and is composed of highly crosslinked keratinous protein, which contains about 20 mol % half cystine. Along the outer margin of the exocuticle is the A-layer, the most heavily crosslinked region in the fibre, containing about 33 mol % half cystine. The exocuticle extends right around the edges of each scale cell but it does not appear to be present (or is very thin) along the underside of each cuticle cell [185]. The other major component of a cuticle cell is the endocuticle; it has a low cystine content and originates largely from nonkeratinous material.

On the outer surface of each cuticle cell is the epicuticle. This is a very thin semipermeable membrane, about 3 nm thick. The epicuticle is most likely derived from the plasma membrane that originally surrounded each cell. Suggestions that the membrane is composed mainly of protein have been advanced [186], but the outer so-called F-layer of the epicuticle is believed to be hydrophobic and to contain fatty acid residues [187]. Recent (as yet unpublished) work using surface microanalytical methods, such as electron spectroscopy chemical analysis (ESCA) and secondary ion mass spectroscopy (SIMS), has confirmed that the outer surface of the epicuticle is almost exclusively composed of saturated hydrocarbon residues. The 'β-layers' that surround the cuticle and cortical cells are thought to be remnants of lipid components associated with the internal cell membranes. These appear to be of similar thickness to the epicuticle and may be closely related to it. Between the β-layers is the δ-layer or 'intercellular cement'. This layer is irregular and averages about 18 nm in thickness. Its composition appears to consist of proteinaceous material with unusually high proportions of glycine, tyrosine and phenylalanine, and to contain very little cystine. The cellular components of the fibre are strongly bound together by this material. Because it contains little cystine, the intercellular cement has been presumed to be very lightly crosslinked and to be relatively permeable to dye molecules. The β- and δ-layers and the resistant membrane constitute the 'cell membrane complex'. Many aspects of the structure and function of the cell membrane complex have been discussed by Leeder [186] and Zahn [188].

Depending on the breed of sheep, three types of cortical cell may be present. These have been designated as orthocortical, mesocortical and paracortical cells. Merino fibres contain mostly orthocortical and paracortical cells. The two types of cells are grouped together on opposite sides of a fibre. A few scattered mesocortical cells are sometimes found near the boundaries of the ortho- and para-cortical regions [189].

Nonkeratinous structures derived from cytoplasmic components also are present in cortical cells. The most prominent of these are the nuclear remnants in paracortical cells.

Cortical cells are composed of macrofibrillar bundles of α-keratin microfibrils aligned approximately parallel with the fibre axis and embedded in a matrix of amorphous protein. The basic unit of α-keratin is a polypeptide in the form of a helix. Two right-handed α-helices are arranged into a left-handed coil to make an intermediate filament 2 nm in diameter. Groups of intermediate filaments are bundled together to form rod-like microfibrils with an apparently annular structure. The microfibrils are closely packed in an amorphous polypeptide matrix. Groups of several hundred microfibrils form macrofibrils that are about 200 nm in diameter. In a cross-section, twenty or so macrofibrils are contained within one cortical cell. Although the structures of wool proteins are very complicated, it is possible to provide a number of simplifications. Three main types of keratinous protein make up the major part of cortical cells. One contains relatively little sulphur and is the main constituent of the microfibrils while there are two types of matrix proteins; one is rich in sulphur and one is low in sulphur but rich in glycine and tyrosine [190]. About one-sixth of the protein in cortical cells is nonkeratinous and this consists of material derived from the original living cells, such as nuclear remnants and intermacrofibrilar cytoplasmic residues [188].

Ortho-, para- and meso-cortical cells are distinguished by their different arrangements of microfibrils and macrofibrils. In orthocortical cells the microfibrils are closely packed in a whorl pattern, which is believed to derive from twisting of bundles of microfibrils within the cell, and the macrofibrils are quite discrete. On the other hand, in paracortical cells the microfibrils are more or less randomly arranged in relatively large amounts of matrix and the macrofibrils tend to be fused together. Mesocortical cells show approximate hexagonal close packing of the microfibrils [189]. Paracortical cells have been found to be rich in high-sulphur proteins while the orthocortex is composed of a high proportion of low-sulphur proteins [17].

In preparation for textile use, residual contaminants, such as grease, dirt and suint, are usually removed from the fibres by scouring. No other preparation for coloration is required, except when the goods are to be printed.

Structure of silk

Information on the production and structure of silk can

be found in many standard texts on the chemical technology of textile fibres [1,2,191].

Silk is a unique natural fibre because it is produced by insects, which perform spinning and drawing processes analogous to the methods now used to produce synthetic fibres [192]. Silk moth larvae secrete a viscous aqueous polypeptide solution from two sets of large compound glands inside their bodies. The posterior silk glands synthesise only fibroin. These are connected to the middle glands in which the fibroin is stored, and these glands also produce sericin [193]. The two sets of glands are connected by ducts to a spinneret in the head of the silkworm. A single strand is secreted from the spinneret. The strand, which contains about 30% solids, is drawn or stretched by the motion of the silkworm's head and the protein present coagulates as the fibre dries in air [194]. Each fibre is typically 1 to 1.5 km in length and is continuously coiled by the silkworm into a cocoon.

A primary strand of native silk is called a bave. Because of the manner in which it is secreted, a bave is a bicomponent fibre that consists of two more-or-less triangular filaments of fibroin, called brins, which are cemented together and coated by the water-soluble protein gum sericin. Each of the two fibroin filaments was originally secreted by separate silk glands in the silkworm. The thickness of the filaments may vary from 2 to 15 μm.

Fibroin fibres are believed to be composed of a single polypeptide. This protein is rich in glycine, alanine, serine and tyrosine and has an r.m.m. of about 300 000 [192]. Thirteen other amino acids are present but they make up only 13% of the fibre. About 60% of the protein is crystalline in the β-helical form. Single molecules appear to merge with ordered crystalline and disordered amorphous regions alternately throughout their lengths. In the crystalline regions the amino acid sequence glycine–serine–glycine–alanine–glycine–alanine is continually repeated in the polypeptide chains. The chains are oriented in the direction of the fibre axis and are formed into antiparallel β-pleated sheets [195]. Neighbouring chains in the sheets run in opposite directions and are interlocked by hydrogen bonds. The sheets are hydrogen bonded together to form microfibrils which have diameters of 10–15 nm, and these microfibrils clump together in bundles of about 1000 to form fibrils [196]. A schematic diagram of a silk fibre is shown in Figure 2. The polypeptide chains in the amorphous regions of the fibre appear to contain a high proportion of bulky amino acid residues which prevent the polypeptide chains from interlocking together and forming crystals.

Silk differs from wool in that it contains very little cystine and there is no significant degree of crosslinking either within or between the polypeptide chains [192].

In order to produce high-quality silk for textile use the cocoons are first softened in water and then unwound in a process called reeling. Then the sericin in the baves is dissolved to liberate the twin strands of fibroin. Dissolution of sericin is achieved by a degumming process in which raw silk is treated in an alkaline soap bath for several hours. Methods of preparation of silk for dyeing and printing have been reviewed by Chu and Provost [197].

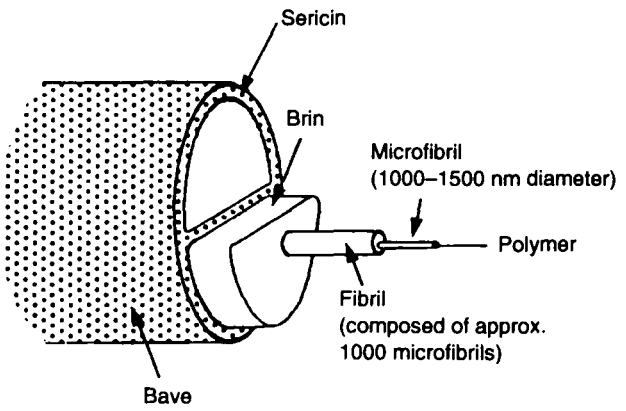

Figure 2 Structure of a silk fibre

Structure of cotton

The structure of cotton is well known [9,11,107,198,199], and only the most salient features will be mentioned here. Cotton fibres are essentially composed of cellulose, which is a polymer consisting of glucose rings joined together by β-glycosidic ether linkages. The actual chemical structure is poly(1,4-β-D-anhydroglucopyranose), with approximately 5000 repeat units [9]. About 70–80% of the cellulose in cotton is in the form of crystallites of the cellulose I type.

Each cotton fibre is derived from a single plant cell. Within a fibre there are several distinctly different structural features. A typical diagram of the structure of a growing cotton fibre is shown in Figure 3; a detailed summary of work on fibre structure has been published recently [200]. On the outside of the fibre is a cuticle layer of pectin, fats and waxes. This surrounds a primary wall about 100 nm thick, which is a network of cellulose microfibrils randomly interlaced and interspersed with pectin (10% by weight), fatty material (10% by weight) and proteinaceous material (15% by weight). Inside this is a winding, transition lamella or S-1 layer of a similar thickness in which the microfibrils are bundled together to form a 'weave' pattern oriented at between 45° and 70° to the fibre axis.

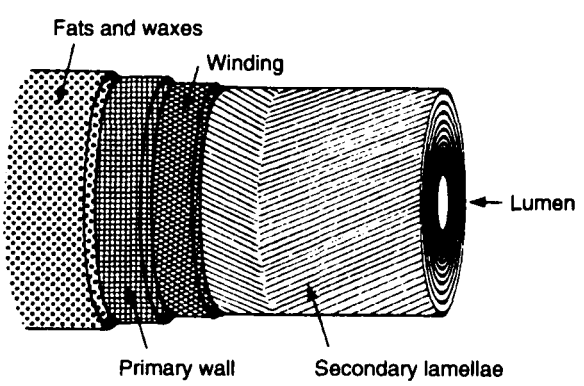

Figure 3 Structure of a cotton fibre

The bulk of the fibre is composed of a multilayer secondary S-2 cell wall. In growth the layers of the secondary wall are laid down, one each day, each layer inside the other, so that the layers resemble the rings of a tree. It takes typically 24 days for a fibre to grow to full maturity. Each daily growth ring is between 200 and 400 nm thick and consists of two sublayers, one of which is solid and compact and the other porous. Parallel cellulose elementary crystallites about 3.5 nm in diameter are bundled together into microfibrils 10–30 nm in diameter in each layer of the secondary wall. These in turn are fused together into flattened, tape-like macrofibrils which contain some 1000 or more elementary crystallites. The macrofibrils composing the layers in the secondary wall are arranged in spirals which change direction at random intervals along the length of a fibre. The innermost layer of the secondary wall (sometimes called the S-3 layer or tertiary wall) encloses a lumen in the centre of each fibre; this is mostly empty except for a small amount of proteinaceous material.

Cotton fibres grow inside a seed pod or boll. When this opens, moisture evaporates from the fibres and they are no longer able to maintain their circular cross-sections. They collapse to form ribbon-like false-twisted fibres with rather variable, kidney bean shaped cross-sections [1,11,201].

It is clear from electron micrographs that the interior of dry cotton fibres consists of a rather open network of cellulose fibrils [200]. It has been estimated that elongated cavities, about 3 nm in diameter, between the fibrils occupy about 30–35% of the fibre volume. However, in wet cotton the structure is scarcely any less open than in the dry fibres. An extensive filamentary network of natural cleavage planes appears to be present. This has been revealed by electron micrographs of fibre cross-sections in which butylmethacrylate polymer had been deposited from solution in the interstices of the fibres [200,202]. Complementary work using fixation techniques and metal-ion staining has provided electron micrographs showing that crystallites in the secondary wall are about 6 nm in diameter with an average separation of about 4 nm in fully water-swollen fibres [203].

Cotton is usually prepared for textile use by caustic soda scouring to remove oils, fats and waxes, and often is then bleached. In some cases mercerising is also carried out. Various pretreatment methods have been summarised by Bille [21] and Dickinson [204] and discussed at length by Campbell [205].

Mercerisation of cotton (i.e. treatment with 20% sodium hydroxide at room temperature) changes the unit cell of the cotton crystallites from cellulose I to cellulose II [199]. Cellulose II has a slightly more angular monoclinic unit cell than cellulose I [107]. The degree of crystallinity and the average size of the crystallites are both reduced by mercerisation [203,206]. This has the effect of making the fibre cross-sections more circular, and of increasing the moisture absorption, maximum dye absorption, rate of dyeing and cross-sectional area of the fibres [200]. Treatment with liquid ammonia is also now used as an alternative to caustic soda mercerising. This treatment confers some of the changes produced by caustic soda.

Structure of regenerated cellulose fibres and films

Cellulose fibres and films have been made by two main types of processes: the most commonly used is the viscose process and the other is the cuprammonium process [207,208]. A certain amount of fibre has also been produced by modified viscose processes, which yield high-tenacity polynosic, modal and high wet modulus fibres. Diffusion studies have mostly been carried out on conventional viscose media. Chemically modified forms of cellulose, such as cellulose acetate and cellulose triacetate, have been studied. Strictly speaking, these forms of cellulose are not natural polymers and have not been discussed in this review.

The conventional process for making viscose is by extruding an aqueous alkaline solution of sodium cellulose xanthate into a solution containing sodium sulphate, sulphuric acid and a zinc salt. The degree of crystallinity in the regenerated cellulose is typically about 40–45%. This depends on the exact conditions used for coagulation, and on the amount of stretch imparted during the process. As in native cotton, some of the cellulose polymer chains are oriented to form crystalline fibrils within an amorphous matrix.

Viscose fibre has a skin–core structure [209]. The surface of each fibre is irregular and serrated, and the cellulose crystals in the outer regions of the fibre are rather smaller than those in the interior of the fibre [210]. Whereas the crystalline form found in nature is cellulose I, regenerated crystalline cellulose is always in the cellulose II form.

FIBRE STRUCTURE AND DYE DIFFUSION

Diffusion mechanisms will now be discussed in relation to the insights provided by knowledge of the physical structures of the fibres.

Wool and hair fibres

In the foregoing section on the use of Fick's laws to study diffusion in wool it was indicated that there are theoretically based reasons for believing that wool fibres may have a barrier to the entry of dye at their surfaces. Physical evidence for the existence of a barrier has been obtained by microscopic examination of fibres at low magnification. During the early stages of dyeing, dye was seen to penetrate more rapidly into tips and cut ends than into intact middle portions of fibres [211,212]. In addition, damage caused by cutting, abrasion or bruising, or distortion of the scales by bending and knotting of fibres, produced sites at which dye penetrated rapidly [213–215]. Chemical modification of cuticle cells by treatment with chlorine or potassium hydroxide was also found to permit rapid uptake of dye, presumably by increasing the permeability of the surface barrier [61,212,216].

Initially the surface barrier was thought to be the epicuticle [217,218]. This structure was assumed to form a continuous sleeve over the surface of the fibre. Subsequently the epicuticle was found to be confined to individual cuticle cells [219,220] and is now considered to be too permeable and thin to retard the penetration of dyes significantly. The exocuticle on the outer surface of each scale cell, with its highly crosslinked A-layer, has been suggested as the most likely barrier to dye penetration [221].

Intercellular diffusion of dyes as a pathway for the entry of dyes has been proposed in a number of different studies dating back to that of Hall in 1937 [6]. These studies have included work on fibre structure [178,188, 222,223], the mechanism of dyeing wool from formic acid solutions [214], the modification of fibres to remove specific areas of the fibre prior to dyeing [224], and the isolation of morphological fibre components from wool dyed with reactive dyes [225].

Direct evidence for intercellular penetration of materials into wool fibres has also been obtained. Micrographic examination of cross-sections of Lincoln fibres, which had been treated with potassium permanganate in concentrated sodium chloride solutions, showed that manganese dioxide had been deposited in the cortex adjacent to junctions between overlapping scale cells [226]. This seemed to indicate that permanganate ions had entered the cortex by diffusion between the cuticle cells. The susceptibility of processed wools to dye staining, compared with unprocessed wool, has been linked to raising of the outer edges of the scales from the fibre surface during processing [219].

Other evidence for intercellular diffusion paths has come from studies of the uptake of an anionic polymer. It has been found that the relatively large molecules of the polymer Synthappret BAP (BAY), which have an average r.m.m. of approximately 3000, can slowly diffuse into wool fibres at very low pH to give add-ons of 60% by weight [227,228]. Micrographic evidence indicates that substantial amounts of the polymer become located in the intercellular regions between the cortical cells. The polymer could presumably only reach this location by diffusion between, rather than through, the cells.

In more recent work the diffusion of platinum and uranium metal complexes into wool fibres has been followed by transmission electron microscopy of fibre cross-sections [229]. The heavy metal complexes had structures similar to those of chromium-containing metal-complex dyes. It seems reasonable to assume that the diffusion of these complexes should occur by the same pathway as followed by conventional metal-complex dyes. Fibres were dyed under isothermal conditions at 90°C. The complexes were observed exclusively in the intercuticular regions during the early stages of dyeing. Subsequently the complexes were found to be present in the nonkeratinous regions of the endocuticle and the intercellular cement of the cortex. The complexes penetrated the whole nonkeratinous network of the cell membrane complex as dyeing proceeded and transferred from the endocuticle to the exocuticle. Eventually the complexes became incorporated into the macrofibrillar matrix.

Direct observation of the penetration pathways of conventional dyes did not become possible until a technique had been developed for enabling the dyes to be detected at very low concentrations.

Direct observation of dye penetration

Relatively thick sections viewed by optical transmission microscopy have been used to provide limited information on the extent of dye penetration. While much thinner cross-sections could yield information about the fine detail of penetration pathways, too little dye is usually present to be readily seen. However, dark-field fluorescence microscopy provides a system for visualising dyes that fluoresce in the presence of u.v. radiation. The sensitivity of this type of system is considerably greater than that of conventional transmission microscopy.

The first use of a commercially available, fluorescent levelling acid dye (CI Acid Red 52) to study dye uptake and diffusion in wool fibres was in 1985 [23]. Distinctly different patterns of dye uptake at the fibre surface were observed when wool was dyed by different methods. In conventional dyeing the dye was taken up first at locations on the outer edges of those scales that appeared to have been damaged. In the presence of certain dyeing assistants, including some used for low-temperature dyeing, the initial uptake of dye was found to be very even. All the scale edges were coloured, so that the pattern of scale edges was highlighted in considerable detail. It was suggested that this could have resulted from preferential dye uptake directly into the cell membrane complex underneath the scale cells or to the formation of a concentrated dye–surfactant micellar layer at the fibre surface from which dye migrated through the intercellular cement. Different breeds of sheep and mohair have been found to show similar initial patterns of dye uptake [7]. This behaviour also has been reported with two other dyes, CI Acid Yellow 73 [22] and CI Basic Violet 10 [230], neither of which are normally used for wool dyeing. It is noteworthy that certain chemical treatments carried out before dyeing, such as chlorination, completely obliterate the scale edge uptake pattern, and penetration of dye seems to occur rapidly through the cuticle cells into the fibre cortex [23].

In the case of Angora rabbit fibres, the pattern of dye uptake revealed a hitherto unknown and rather unique cuticle cell structure [7]. Firstly the cuticle cells appear to be relatively large so that only one or two cells envelop the circumference of each fibre. Secondly the fine scale patterns on angora fibres consist mostly of 'false' scale edges that do not correspond with cuticle cell boundaries.

The pathways for the diffusion of the basic dyes CI Basic Violet 10 and its octadecyl ester (octadecylrhodamine B) into merino wool fibres under aqueous and nonaqueous conditions have been investigated by Sideris, Holt and

Leaver [231]. The results showed that the dyes entered the fibres through the cell membrane complex between the cuticle and cortical cells of the fibre. Only the intercellular network of the fibre was dyed when the dyes were applied from an anhydrous solvent. However, when aqueous solvents were used, initially only the cell membrane complex in the orthocortex was dyed. This suggests that there may be a difference in the swelling of the intercellular material in the orthocortex and paracortex. As the proportion of water in the dyeing solution increased, a greater degree of penetration of CI Basic Violet 10 was observed within the cortex, with the orthocortex being dyed more deeply than the paracortex. The greater staining of the orthocortex by basic dyes also has been attributed by other workers to a difference between the network structure of the intercellular cement in the orthocortex and the paracortex [232]. Application of octadecylrhodamine B from water resulted in the cell membrane complex only being dyed. The high r.m.m. of this dye, or a strong tendency to absorb in the cell membrane complex, may have prevented it from penetrating the cortical cells.

Brady has used the fluorescent wool dye CI Acid Red 52 to show in considerable detail how dye penetrates merino wool fibres during dyeing processes [233]. This has been the only work to date that has been performed with a commercial anionic wool dye. Intercellular diffusion was confirmed as the principal means for entry of dye into fibres. The pathway of penetration was found to be the same both in conventional dyeing, in which the temperature is ramped to the boil, and in pad–batch dyeing, which is carried out at ambient temperature.

Fluorescence microscopy has been used to follow the penetration of fluorescent, nonionic pyrazolines into wool fibres swollen with perchloroethylene/methanol mixtures [234]. The path of initial access of the compounds could not be determined, but once inside the fibre they did not penetrate the cortical cells and were confined to the intercellular regions.

Other evidence for the penetration of dyes via the cell membrane complex has been obtained from various studies. Joko and Koga have investigated the dyeing of extended wool fibres and have interpreted an increase in the initial rate of dye uptake in terms of preferential absorption in the intercellular cement, which had been made more accessible by stretching of the fibres [235]. Removal of small amounts of nonkeratinous protein by enzymatic digestion under mild conditions has been found to increase the rate of dyeing [236]. Severe enzyme treatments, which caused substantial weight losses (14–20%), have been found to reduce dyeing rates, but this may have been due to the loss of amino groups and digestion of material in addition to the nonkeratins [237].

Brief reviews of some of the above chemical and physical evidence for intercellular diffusion in wool dyeing have been provided by Finnimore [238] and Koga [239].

Diffusion pathways in wool fibres

The sequence of events involved in the uptake of dye by unmodified wool and hair fibres is illustrated in Figure 4; it appears to be as follows. Dye enters the fibres most readily by diffusion through the intercellular cement between the scale cells. The barrier to rapid entry of dye seems to be located at or near the outer surface of the cuticle cells. The most likely structure to constitute this barrier is the exocuticle. The surface barrier does not appear to be completely impermeable but constitutes a structure through which dyes diffuse much more slowly than through other regions of the fibre. Starting at the outermost ends of the cuticle cells, the endocuticle and then the exocuticle become coloured as dye travels through the intercellular cement and penetrates the cells from their undersides.

Because of the anisotropic structure of merino fibres, the diffusion paths under the scales on the orthocortex side of a fibre are shorter than on the paracortex side; thus dye enters the orthocortex before the paracortex. Within the cortex, dye diffuses through the intercellular cement to reach the cortical cells. Dye enters the nuclear remnants of paracortical cells of merino fibres soon after it begins to move into the cortex. The orthocortical cells are penetrated at about the same rate as dye diffuses through the cell membrane complex between the cells, but paracortical cells are penetrated rather more slowly. At

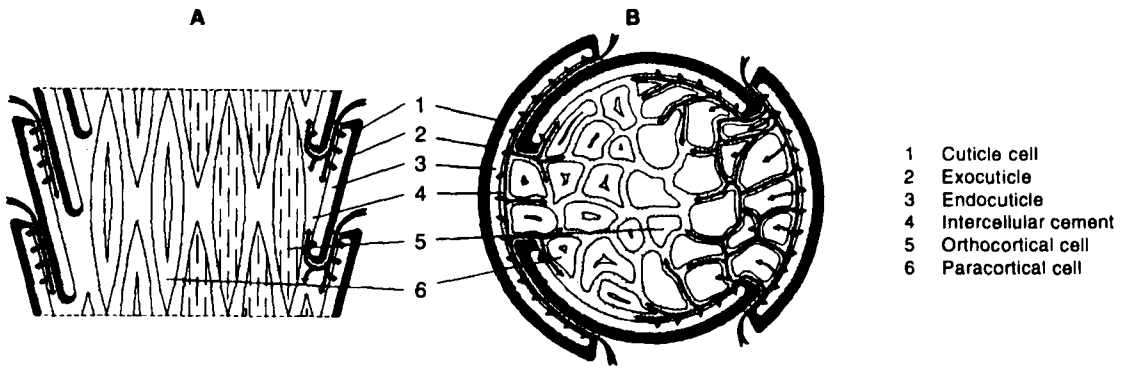

Figure 4 Diffusion pathways in a merino wool fibre; A is a longitudinal-section in the early stages of dyeing, B is a cross-section illustrating entry of dye into the cortex

equilibrium dye is located mainly in the macrofibrils of the cortex and in the exocuticle, and is not retained by the intercellular cement, the nuclear remnants or the endocuticle. With some modified wools, in which the cuticle has been oxidised or physically removed, dye enters the cortex much more rapidly than when the cuticle cells are intact, apparently by direct penetration of the exocuticle rather than by diffusion between the cuticle cells.

The principal absorption sites for dyes, except possibly for reactive dyes, appear to be within the high-sulphur matrix proteins. It is in these regions that the fibre provides locations with a mixture of polar and nonpolar interactions for which wool dyes have high affinity.

Results obtained by Baumann seem to suggest that reactive dyes may become immobilised in the nonkeratinous proteins [240]. This may reflect the fact that, at least under some conditions, reaction may take place while the dyes are entering the fibre. Similar results were obtained by Lewis and Smith, who used a highly reactive vinylsulphone fluorescent dye analogue; they found that it reacted in the endocuticular and cuticular intercellular regions and did not completely penetrate the interior of the fibre [241]. However, by selection of dyes with appropriately moderate reactivity, in combination with suitable dyeing conditions of temperature and pH, it may be possible to obtain dyeings in which there is appreciable reaction with the keratinous proteins.

A general picture is beginning to emerge concerning the low-temperature dyeability of wool in the presence of certain solvents and carriers. Leeder and Rippon have used an empirical formula developed by Zahn to predict the swelling of proteins from their amino acid composition. They showed that the potential of the intercellular cement to swell is much greater than for any other component of a wool fibre [214]. In concentrated formic acid the intercellular cement may swell by as much as 1000%, and this could account for the extremely high rate of dyeing observed. It also seems possible that compounds which can selectively swell or extract material from the intercellular cement may influence dye penetration behaviour without producing any marked changes in fibre dimensions. In this way it may be possible for solvents such as aqueous propanol and chemicals such as urea to facilitate penetration of dye between the cuticle and cortical cells, making the interior structures of the fibre accessible to dye in shorter times and at lower temperatures than would otherwise be achievable. That these dyeing assistants can extract proteins from wool may simply be an indication of their ability to swell the unkeratinised protein of the cell membrane complex.

From the foregoing discussion on diffusion pathways, the most appropriate theoretical model for an intact wool fibre would be of a permeable but crosslinked (high-sulphur) polypeptide polymer into which dyes could diffuse, interspersed with impervious crystalline helical (low-sulphur) regions, and connected to the external solution by a variable network of swellable channels with limited capacity to absorb dye.

Silk

It is to be expected that dyes would diffuse more rapidly through the amorphous regions of silk fibres than through the crystalline regions. The fibres do not appear to have a morphologically distinct surface layer, and surface barrier effects in dyeing would not be anticipated.

A fluorescent dye has been used to observe the uptake of dye by silk in the early stages of dyeing [7]. The fibres take up dye very rapidly, but somewhat unevenly at low temperature. The uneven dye uptake is most likely related to short-term variations both in fibre shape and in the proportion of crystalline-to-amorphous fibroin protein. These variations are probably caused by uneven drawing of the filaments by the silk moth larvae. There is no evidence for a surface barrier that resists dye penetration. Preferential diffusion of dye around the fibrils has not been demonstrated.

Cotton and viscose

The dyeing properties of both native and regenerated cellulose depend on structure at the molecular, fibrillar and morphological levels. It is generally accepted that dyes cannot readily penetrate inside cellulose fibrils [208]. The diffusion of a dye appears to depend on its ability to penetrate cellulose via disordered regions of the structure. These disordered structural features are principally physical voids or pores between the fibrils, and may also include regions of amorphous polymer. As the degree of orientation of the cellulose chains is decreased, the dye uptake, fibre volume swelling and average size of the internal pores all have been observed to increase [242]. Evidence indicates that the dye diffusion rate in noncrystalline cellulose acetate is sensitive to structural differences between samples [243].

If fibres or films are not allowed to dry after coagulation of the cellulose, the diffusion of dyes is more rapid, and the equilibrium dye uptake is higher [201]. Work has been carried out on so-called 'never dried' cotton and viscose [128,244]. Cellulose becomes more compact after it has been dried, and swelling is less on subsequent wetting. This is believed to occur because the aggregation state of the crystalline fibrils increases on the first occasion that cellulose is dried, and the volume fraction of the voids decreases. The equilibrium absorption of CI Direct Green 26 (r.m.m. 1350) is believed to be dependent on the available internal surface area [245]. When cotton fibres are dried for the first time the uptake of this dye decreases by a factor of ten. The effect of drying can be reversed to some extent by mercerisation. This process produces a two-fold increase in dye uptake as well as enhanced dyeing rates [70,201,206]. At least some of the effects of mercerisation may be associated with a decrease in the degree of crystallinity of the fibre, in addition to an opening up of the fibre structure. Similar effects to mercerisation have also been found by treatment with phosphorus compounds and liquid ammonia [246].

Diffusion along the axis of extrusion in viscose fibres and films takes place more readily than in the direction

normal to the surface [247,248]. This is believed to be due to orientation of cellulose chain molecules parallel to the fibre axis during extrusion [249]. Viscose with a thick skin has been observed to dye at a slower rate than normal viscose, and the skin has been found to contain less dye than the core [250]. There has been no evidence for either surface effects or for rapid axial diffusion that could be attributed to fibre structure in the dyeing of cotton.

In summary, the most plausible general mechanism for dye migration within cellulose is that dyes move into the fibres, via pores containing water, at similar rates to those at which they diffuse in the bulk solvent. Dyes with low affinity for cellulose, such as reactive dyes and the leuco forms of vat dyes, are only weakly adsorbed on the internal surfaces of the pores, and quickly penetrate the structure at relatively low temperatures. On the other hand, the higher r.m.m. dyes, such as direct dyes, which generally have high affinity for cellulose, are more strongly adsorbed from the aqueous phase. In the first instance, uptake of dye probably occurs by interaction with hydrated cellulose microfibrils which line the surfaces of the pores. Migration of some dyes on the pore surfaces seems likely. Multilayer adsorption (or aggregation) probably occurs at high concentrations of nonreactive dyes.

No direct observations of dye migration pathways within cotton fibres have been made. However, there is potential for such studies along similar lines already being used with wool, in which fluorescence and electron micrographic techniques are employed.

CONCLUSION

Basic information from the measurement of diffusion has provided useful insights into the mechanisms of dyeing and the properties of dyed material. However, because of the complicated structures of natural fibres, detailed theoretical treatments to describe the uptake of dyes have been difficult to develop. Dye diffusion has been observed and described in phenomenological terms, but is not yet completely understood at the molecular level. The best fit between theory and experiment has been obtained with viscose, which is the natural polymer that most closely resembles synthetic polymers. New methods are being developed for the direct determination of diffusion pathways, particularly in keratin fibres, that have the potential to provide further explicit information on how colouring materials actually enter natural fibres and where they are finally located within the fibres.

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