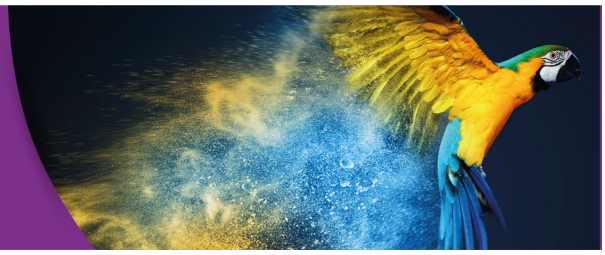


ASDC Dyeing Theory

4.2. Kinetics of Dyeing

4.2.3. Dye Diffusion Models

Learning Objectives for this section

- What is the role of boundary conditions in relation to dye/fibre systems?
- What are the fundamentals of the Porous Matrix Model?
- What are the fundamentals of the Free Volume Model?

Boundary layers in dye diffusion

The effects of textile fibre geometry and dyebath solution/fibre interchange on the rate and extent of dye uptake has received attention [e.g. (2, 75, 121, 122); see (11) for a summary], such studies being based on the assumption that a *diffusional boundary layer* will be present at the fibre surface that will influence the rate of dyeing. In essence, during an aqueous dyeing process, the dye liquor and fibre undergo *relative motion*, in which the dye molecules are carried to the fibre surface by the process of *convective diffusion* which involves both:

(i) *molecular diffusion*: that results from a difference in dye concentration between different regions of the dyebath liquor and;

(ii) *convective mass transport*: which is responsible for the essentially *mechanical transfer* of dye molecules within the moving dyebath liquor.

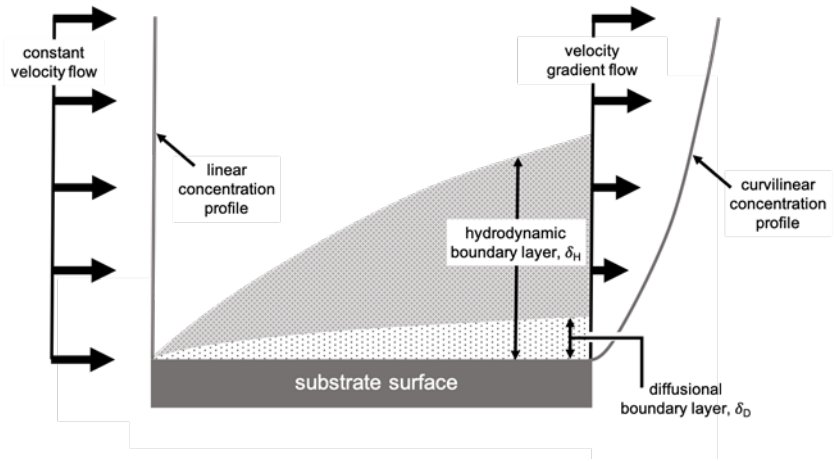
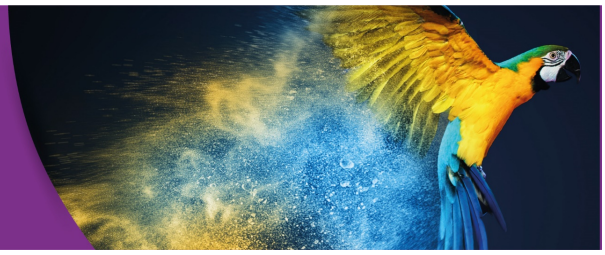


Figure 21 simplified representation of effect of hydrodynamic boundary layer, of thickness δ_H and diffusional boundary layer of thickness δ_D, on liquid velocity flow and solution concentration (assuming initial steady-state, constant laminar liquid flow)

As the velocity of the moving dyebath liquor will decrease as the textile fibre surface is approached, a *velocity gradient* is developed within the dyebath that varies as a function of distance from the fibre surface (Figure 21). This situation results in the formation of a *hydrodynamic boundary layer* of liquid at the surface in which the velocity of the liquid changes from 99% of that of the bulk dyebath flow velocity to zero at the surface. Within this hydrodynamic boundary layer, at a particular point away from the surface, the liquid velocity will be so small that molecular diffusion will dominate the transfer of dye molecules to the surface, so that a *diffusional boundary layer* is formed that consists of a layer of liquid adjacent to the surface in which the dye concentration increases from its value at the surface to ~99 % of that within the bulk aqueous dyebath liquor (Figure 21).

Adopting the approach depicted by Figure 21, a *quasi-steady-state diffusional model* was derived (122, 123) which revealed that the thickness of the diffusional boundary layer, δ_D, present at the surface of a plane sheet of polymer of uniform thickness, was ~10% of that of the hydrodynamic boundary layer, δ_H (4). As the diffusional boundary layer was assumed to offer the main barrier to dye transport, to which steady-state conditions applied (122, 123), the rate of dye transfer could be described by the use of Fick's first equation, which predicted



that the rate of dye uptake onto a polymer sheet could be expressed in terms of a dimensionless parameter *L*, Equation 24, where *l* is the half thickness of the polymer sheet, D_f the (assumed constant) diffusion coefficient of the dye in the substrate and D_s that within the dyebath, *K* being the equilibrium partition coefficient for sorption of dye.

$$L = \frac{D_s l}{K D_s \delta_D} \qquad 24$$

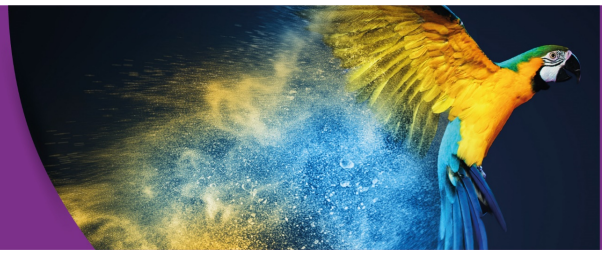
According to Equation 24, because δ_D decreases as dyebath liquor flow increases, the value of *L* approaches infinity; using experimental rate of uptake data obtained for C.I. Acid Red 18 on PA 66 at 75°C, the validity of *L* was demonstrated (133).

However, the relevance to real dyeing systems of such theoretical studies, which by necessity employ conditions that bear little semblance to those likely to be encountered in typical (especially commercial) dyeing processes, and which, for simplicity of mathematical modelling employ idealised substrates (films, slabs, etc.) that do not reflect the anisotropic, hierarchical, multicomponent nature of real textile fibres, is debateable.

Kinetics-based adsorption equations

In recent years, the adsorption of dyes from wastewater onto a variety of potential adsorbent materials has attracted considerable attention and various *kinetics-based adsorption equations* have been employed to analyse experimentally obtained adsorption data. In essence, such equations seek to describe the mechanism of adsorption in terms of the *order of reaction*[1] between the adsorbate and adsorbent [see for example (125-127)]. As equations

[1] If the macroscopic (observed, empirical or phenomenological) rate of reaction for any reaction can be expressed by an empirical differential rate equation (or rate law) which contains a factor of the form $k[A]^{\alpha}[B]^{\beta}$ ... (expressing in full the dependence of the rate of reaction on the concentrations [A], [B] ...) where α, β are constant exponents (independent of concentration and time) and k is independent of [A] and [B] etc. (rate constant, rate coefficient), then the reaction is said to be of order α with respect to A, of order β with respect to B, ... , and of (total or overall) order n = α + β + ... The exponents α, β, ... can be positive or negative integral or rational nonintegral numbers. They are the reaction orders with respect to A, B, ... and are sometimes called 'partial orders of reaction'. Orders of reaction deduced from the dependence of initial rates of reaction on concentration are called 'orders of reaction with respect to concentration'; orders of reaction deduced from the dependence of the rate of reaction on time of reaction are called 'orders of reaction with respect to time'. The concept of order of reaction is also applicable to chemical rate processes occurring in systems for which concentration changes (and hence the rate of reaction) are not themselves measurable, provided it is possible to measure a chemical flux: 124. IUPAC. Compendium of Chemical Terminology: Gold Book (http://goldbook.iupac.org/) accessed 12-02-2013. International Union of Pure and Applied Chemistry; 2013.



of this type have been used to describe the kinetics of adsorption of various types of dye on different types of textile fibre, a brief discussion of the fundamental principles involved seems appropriate.

Pseudo-first order reaction rate law, k1

The most widely used equation to depict pseudo-first order kinetics is that proposed by Lagergren (1898) (128) to describe the kinetics of the adsorption of oxalic acid and malonic acid onto charcoal, which is based on the *adsorption capacity* of the adsorbent material, Equation 25, where *k1* is the *pseudo-first rate constant* (unit: min^{-1}) and q_e and q_t the amounts of adsorbate adsorbed per gram of adsorbent at equilibrium, *e*, and time *t*, respectively.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad 25$$

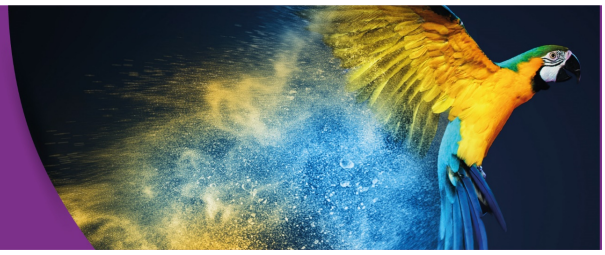
Upon integration, employing boundary conditions of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, as described by Ho and McKay (1998) (129), Equation 26 is realised from which it follows that a plot of log (q_e-q_t) versus *t* should yield a straight line of slope $-k_1$ and intercept of log q_e. Should the intercept not equal q_e then the reaction is not likely to be of first order rate even if the plot displays a high correlation with the experimental data. Equation 27 is the natural log form of the equation often is employed in the literature.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad 26$$

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad 27$$

Pseudo-second order reaction rate law, k2

In order to describe the kinetic adsorption process as a function of *adsorbate concentration*, Lagergren's second-order rate equation, Equation 28, is utilised where *k2* is the *pseudo-second order rate constant* (unit: min^{-1}). Integration, employing boundary conditions of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ (129), yields the most commonly employed form of the equation, Equation 29, from which a plot of t/q_t versus *t* should yield a straight line.



$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad 28$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad 29$$

Effect of temperature on dye diffusion

The rate of dye diffusion increases with increasing temperature due to the greater kinetic energy of the dye molecules; in addition, factors related to fibre structure (e.g. increased swelling, increased porosity, etc.) are also likely to contribute towards the observed thermally-induced rise in dye diffusion rate. However, the amount of dye adsorbed at equilibrium will *decrease* with increasing temperature (Figure 22) owing to the *exothermic nature* of dyeing processes discussed above.

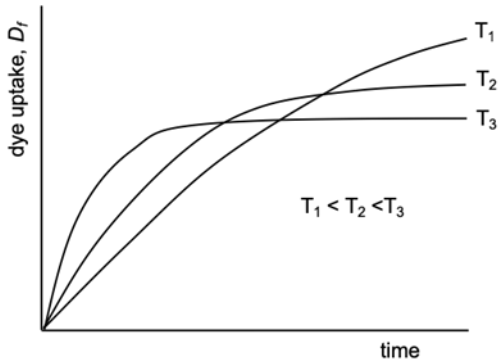
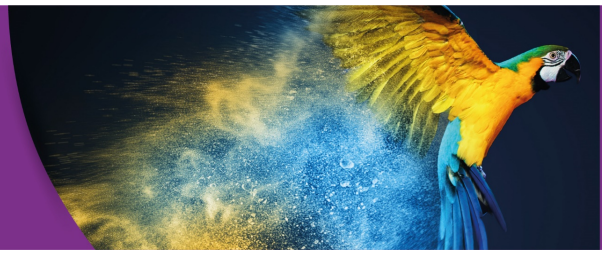


Figure 12 representation of the effect of temperature on rate of dyeing and equilibrium dye uptake

The temperature-dependence of diffusion coefficient follows an *Arrhenius relationship2* and is expressed as Eq 30 where D_T is the diffusion coefficient at temperature T, D_o a *pre-exponential constant* and E_D the *activation energy of diffusion.*

$$D_T = D_0 \exp(-E_D/RT) \qquad 30$$

[2] the Arrhenius equation is a mathematical expression that describes the effect of temperature on the rate (velocity) of a chemical reaction



$$\ln D_T = \ln D_0 - \frac{E_D}{RT} \quad (31)$$

$$\log D_T = \log D_0 - \frac{E_D}{2.303RT} \quad (32)$$

The activation energy E_D and constant D_o can be estimated from a *ln D* versus *1/T* plot via Eq 31 (or a log *D* versus *1/T* plot via Eq 32), the ensuing linear *Arrhenius plot* (Figure 23) being of slope $-E_D$, with an intercept on the *1/T* axis of D_o. Such linear relationships between *ln* D_T and *1/T* have been observed for several dyeing systems [see (11)], as exemplified by that secured for the apparent diffusion coefficient of aminoazobenzene in CA film over the temperature range 130–150°C at constant vapour concentration, the apparent activation energy of diffusion being 96.1 kJ mol^{-1} (130)

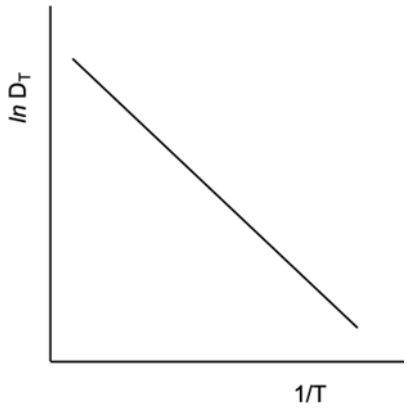
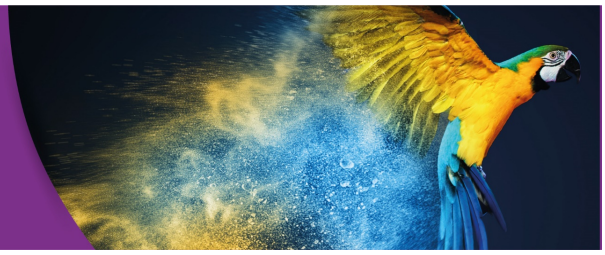


Figure 23 representation of the Arrhenius plot of dye diffusion coefficient as function of 1/T

Models of dye diffusion in textile fibres

Two different models have been used to interpret the aqueous diffusion of dyes within textile fibres and polymers namely the *porous matrix model* that assumes diffusion proceeds within water-filled pores and the *free volume model* which disregards the notion of water-filled pores and instead assumes that dye diffusion occurs within the space that exists between the composite polymer chains in textile fibres.



Porous matrix model

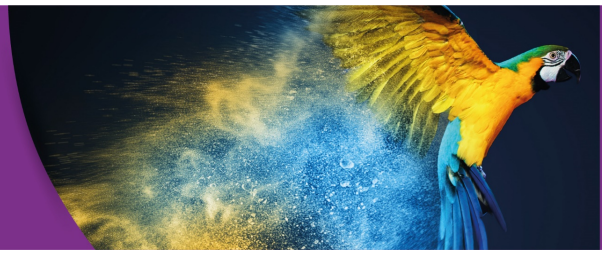
This essentially *mechanical model* was devised in the 1930's to interpret the diffusional behaviour of anionic dyes in cellulosic fibres (131-133) and has been subsequently developed by several workers [e.g. (112, 134-139)]. It is assumed that the substrate consists of networks of *interconnected pores* of different sizes, with the result that different *capillary pressures*[3] are developed that provide the *driving force* for water transport within the fibre; dyes that are dissolved in this capillarity-driven water are able to therefore move through the water-swollen substrate. When diffusing dye molecules collide with a *binding site* located on the surface of a pore wall, they can become *immobilised* and *adsorbed*; if, however, forces of interaction operating between the dye and pore wall site are so disposed, the adsorbed dye molecule may vacate the site, re-dissolve in pore water and diffuse further within the water-swollen substrate.

Several diffusion equations have been proposed based on the porous matrix model [e.g. (112, 140)], such as that expressed by Equation 33 (7), which assumes the pores display a certain level of *tortuousity*, τ, (pore length:direct path ratio) and occupy a particular volume of the substrate, α, the one-dimensional flux (rate of flow of dye per unit area), J, being related to the amount of dye in the pore, C_i, and the amount of dye adsorbed on the pore walls C_a, where D_m is the measured dye diffusion coefficient.

$$J = -\frac{\alpha}{\tau} D_i \frac{dC_i}{dC_a} \frac{dC_a}{dx} = -D_m \frac{dC_a}{dx} \qquad 33$$

However, although pores may well be present in several types of natural fibre, as exemplified by cotton and wool, which are *hygroscopic* and display characteristically high moisture regain (e.g. moisture regain/% cotton: 8.5 @ 65% RH, 20°C (11); 22.6 @ 100%RH, 25°C (142); wool: 17 @ 65% RH, 20°C (11), 32.9-35.3 @ 100% RH, 25°C (143)), the precise size, shape and tortuosity of these pores has not been confidently defined. Furthermore, the model assumes

[3] capillary pressure, pc, is the pressure difference that develops across an air/water interface because of the curved meniscus that forms within the capillary; water can accumulate and move through the fibre because of the capillary pressure developed within the pores: 11. Burkinshaw SM. Physico-chemical aspects of textile coloration. Chichester: Wiley; 2016.



that aqueous dye solution which resides in the pores displays the same properties of normal water (e.g. solvency, mobility, diffusivity, etc.), an assumption which has not been verified and seems somewhat unlikely, bearing in mind the influence of charged fibre surfaces on the distribution of sorbed dye ions/molecules in an aqueous dye solution, as predicted by both *electric double-layer* and *Donnan equilibrium* theories [see (11)].

Furthermore, because the porous matrix model was devised for cellulosic fibres that are characteristically hydrophilic, adsorb meaningful amounts of water and swell substantially in water, the relevance of the model to substrates that do not display such characteristics, notably PET, CTA, PAN, etc., persuaded researchers to consider an alternative dye diffusion model based on the concept of *free volume.*

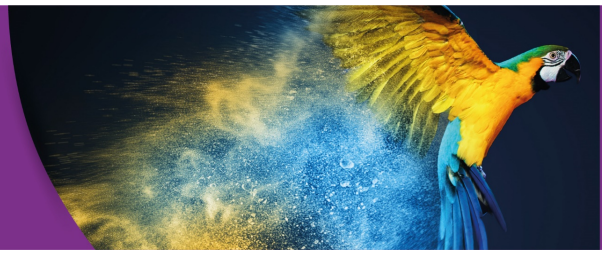
Free volume model

In essence, *free volume* is the *three-dimensional space* that exists between polymer chains. The concept of free volume is used to explain chain mobility and relaxation processes in polymers in relation to *glass transition temperature*, T_g, the diffusion of low molar mass materials in polymers and, as discussed below, the diffusion of dye molecules in semi-crystalline polymers and fibres.

By way of brief explanation, all common textile fibres can be considered as being *assemblages of semi-crystalline, partially oriented, linear*[4] *organic polymers*[5] (11). In essence, the polymers that comprise textile fibres are *semi-crystalline* because they contain both *crystalline regions* in which order extends over long distances, resulting in regular structure, as well as *amorphous domains* in which the polymer chains are randomly arranged; thus, within a textile fibre, the *degree of order* typically ranges from *fully ordered* to *fully disordered*. Because of the presence of amorphous and crystalline domains, semi-crystalline polymers and, therefore, semi-crystalline textile fibres which are derived from such polymers, display different, but interrelated, *thermal behaviour*, namely:

[4] there are two types of linear polymer namely *homochain polymers* (eg polyethylene, PE) that contain only C atoms in the main chain and *heterochain polymers* (eg PA) that contain atoms other than C in the main chain: 11. Burkinshaw SM. Physico-chemical aspects of textile coloration. Chichester: Wiley; 2016.

[5] *although some fibres fall outside these simple strictures, as exemplified by glass fibre, GF fibres which are completely amorphous*



(i) a *melting* transition (aka *crystalline melting temperature*), T_m, that is a characteristic feature of the crystalline domains;

(ii) a *glass transition*, T_g [6], (aka *glass transition temperature, glass-liquid transition*) that relates to the amorphous domains.

Both T_m and T_g are important because marked conformational changes in polymer (and fibre) structure occur at these two particular thermal parameters which impart pronounced changes in several physical properties (e.g. specific volume, modulus (stiffness), plasticity, etc.); from the viewpoint of dyeing, T_m and T_g define the upper and lower temperature limits for aqueous dyeing processes7. Whereas the melting transition, T_m, denotes the temperature range over which the crystal structure within crystallites is destroyed and changes into a disordered, amorphous liquid, the glass transition, T_g, denotes the range of temperatures over which the amorphous material (or the amorphous regions within a semi-crystalline polymer such as those utilised in textile fibres) changes from a hard, relatively *brittle glassy state* into a *viscous, rubbery state*8.

According to free volume theory, the amorphous domains in semi-crystalline polymers contain holes or cavities that arise from imperfect/irregular packing of the constituent polymer chains: these holes constitute the space within the polymer that is not occupied by the component macromolecules; this unoccupied space or volume is referred to as *free volume*. Free volume constitutes the available space in which the polymer molecules can undergo *rotational* and *translational motion*9, and thereby alter their *conformation*. Briefly, in the amorphous regions within a semi-crystalline polymer or fibre, the constituent polymer

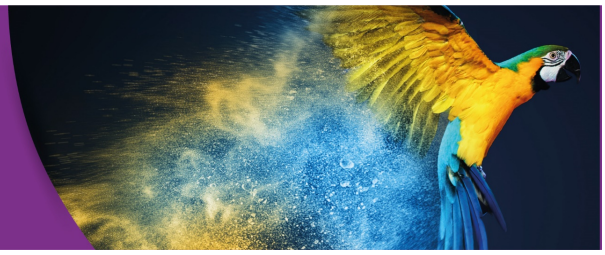
---

[6] T_g is defined as *a temperature-, time- (or frequency-) and composition-dependent, material-specific change in physical state, from a glassy mechanical solid to a rubbery viscous liquid capable of flow in real time*: 144. Slade L, Levine H. Glass Transitions and Water-Food Structure Interactions. In: Kinsella JE, Taylor SL, editors. Advances in Food and Nutrition Research. New York: Academic press; 1995.

[7] and that of other wet processes

[8] $T_m > T_g$ because stronger intermolecular forces operate between crystallites than between the essentially randomly arranged molecular chains within the non-crystalline regions

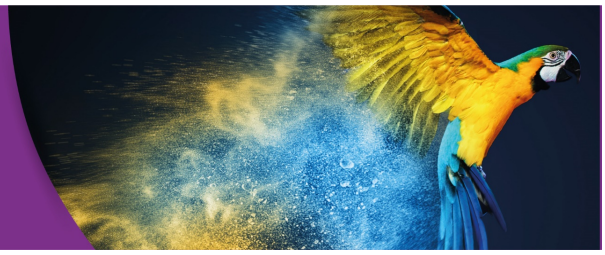
[9] a rigid body undergoes rotational motion in which the body retains its overall shape; translational motion is that by which a body is able to shift position from one point in space to another



chains are unable to move at temperatures $<T_g$ because of the confining influence of neighbouring polymer chains; consequently, the macromolecules are able to undergo only *vibrational motion*. When temperature is increased, the amplitude of these vibrations increase, until, at a particular temperature, sufficient energy will have been absorbed that allows the polymer chains to undergo *bond rotation*, with the result that small amounts of free volume coalesce and larger regions of free volume form. Eventually, *polymer segments* that reside between two rotating bonds in the same chain are able to change position and undertake a *segmental jump*, which creates a *vacated space* into which an adjacent polymer segment can jump; this cooperative *segmental movement* continues throughout the polymer until it is sterically hindered by adjacent polymer molecules. The thermal energy required to facilitate segmental mobility occurs over the very narrow temperature range of the glass transition temperature, T_g, at which point, free volume increases significantly and the polymer undergoes a dramatic change in physical state, from a *glassy mechanical solid* to a *rubbery viscous liquid.*

According to free volume theory, the diffusion of a dye molecule that has been adsorbed onto a polymer chain within a fibre, can only occur within the substrate when *sufficient free volume* is available to accommodate *both* the *diffusing dye molecule* and the *polymer chain segment* that has undertaken a *segmental jump* to generate *vacated space* which the dye molecule can occupy. This situation exists only at temperatures $>T_g$ when an increase in temperature of a polymer will be accompanied by a corresponding increase in the mobility of the macromolecular chains within the fibre, resulting in increased free volume and enhanced diffusivity of the dye molecules.

The connection between segmental mobility of polymer chains within fibres and the rate of dye diffusion was recognised in early studies of the disperse dye/PET and basic dye/PAN dyeing systems (145, 146), insofar as significant dye uptake occurred only when the dyeing temperature had reached ~70-80°C, which coincided with the approximate region of the fibre's T_g. Tangible proof that dye diffusion was linked to fibre T_g was obtained (146) in the case of the application of C.I. Basic Blue 4 to PAN fibre at different temperatures, for which the ensuing Arrhenius plot (Figure 24) was not linear, as predicted by Equation 32 and displayed in Figure 23, but, instead, was sigmoidal in shape. Furthermore, the activation energy of diffusion was initially constant as a function of increasing temperature up to 57°C, which coincided with the T_g of the PAN fibre, at which point it increased markedly and



thereafter, decreased, as shown by the inset of Figure 24, in which the activation energy of diffusion is denoted by the symbol *E**.

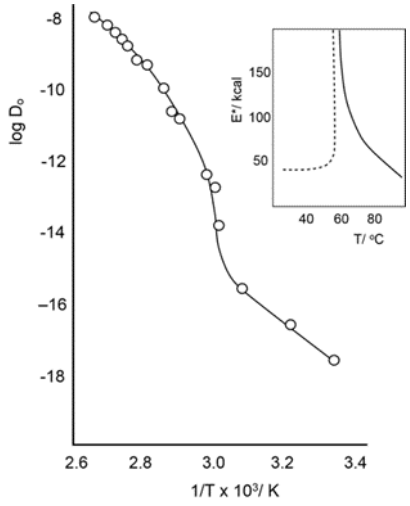
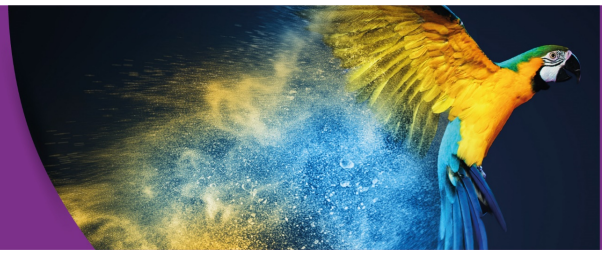


Figure 24 Arrhenius plot of apparent diffusion coefficient of C.I. Basic Blue 4 within PAN fibre (146)

The adherence of the diffusional behaviour observed for C.I. Basic Blue 4 within the PAN fibre to a *WLF relationship*[10] of the form given by Equation 34 confirmed that dye diffusion coincided with the segmental chain mobility within the substrate (146).

[10] the *Williams, Landel and Ferry*, *WLF*, equation describes the *temperature-dependency* of several electrical and mechanical properties of polymers, including *viscoelastic response*, which is of relevance to aqueous dyeing processes. The WLF equation is a consequence of the *time-temperature superposition principle* (aka *time-temperature equivalence*) by means of which, the temperature-dependent mechanical properties of viscoelastic polymers, such as textile fibres, can be predicted at a (selected) reference temperature based on the mechanical property observed (measured) at another temperature



$$\log \frac{D_T}{D_T} = -\log a_T = \frac{A(T-T_g)}{B+(T-T_g)} \qquad 34$$

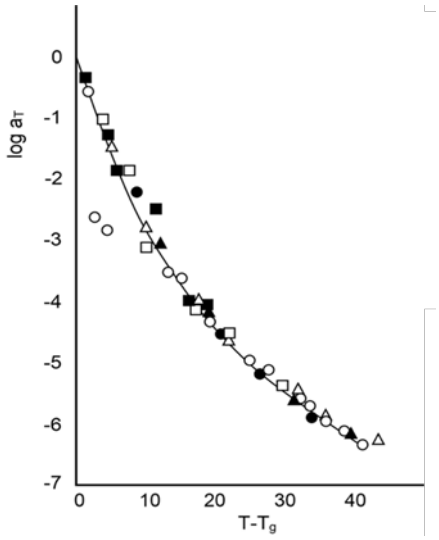


Figure 25 adherence of experimental data to the curve of log a_T versus (T-Tg) (146)

This is clearly demonstrated by the coincidence of experimental points and the values of shift factor calculated using Equation 34 displayed in Figure 25, from which is it is apparent that dye diffusion within the PAN polymer is governed by the activation energy of the relaxation processes and chain mobility in the polymer, and, thus, free volume. Evidence in support of the connection between dye diffusion and free volume has been obtained for various dye/fibre systems, such as disperse dyes/PAN (147, 148), disperse dyes/PET (149, 150) and acid dyes/PA 66 (151).

Summary

The theory of dyeing has been the subject of considerable attention over many centuries [see (11)] and continues to attract much research interest. However, despite the astonishing volume of information relating to dyeing theory that has been generated in the form of books, papers, reports and review articles over this sizeable period of time, our knowledge of the precise nature of dye-fibre substantivity and the mechanisms that are involved in dye-fibre interactions is still far from complete.