Theoretical Aspects of the Role of Fibre Structure in Dyeing

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A comparison is made between the pore theory and the free-volume theory as applied to the diffusion of dyes through fibres. The usefulness and the limitations of the theories are discussed, and the use of the free-volume theory for explaining the mechanism of carrier action during dyeing is described.

Introduction

The resistance to the transport of a dye molecule through a fibre arises from two principal causes. One is due to the strong forces of adsorption which exist between the dye molecule and the polymer chains, and the other to the restrictions imposed on the movement of dye by the structure of the polymer.

ADSORPTION OF DYES BY SUBSTRATE

The forces of adsorption are the usual interactions which occur between polar and polarisable molecules (dispersion forces, hydrogen bonds, etc.) but it is difficult to resolve the importance of one type of interaction over another. Because of their influence, a finite fraction of the total amount of dye present in the fibre at any instant is always immobilised and is not free to diffuse. Consequently, it may be expected that the diffusion coefficients of dyes in polymers will be very much smaller than those of dyes in aqueous solution. The adsorption of dye does not apparently modify the characteristics of the diffusion process, since the diffusion coefficient of non-ionic dyes in fibres is constant and independent of dye concentration. Similarly, with ionic systems in which the diffusion coefficients are dependent on concentration, such dependence may be explained in terms of electrical potential gradients arising from the different mobilities of the simultaneously diffusing ions in the system [1]. Furthermore, the concentration dependence of the diffusion coefficients of acid dyes into nylon 6 and 6.6 is independent of the form of the substrate [2]. In such cases, studies of the relationships between polymer structure and dyeing kinetics are best carried out either with non-ionic dyes or with ionic dyes at low dye concentrations where the diffusion process approximates to one with a constant diffusion coefficient.

The role played by the polymer structure is difficult to define. One complication which arises in formulating concepts is that although diffusion into fibres takes place in the radial direction, at right angles to the major axis of the fibre and hence to the polymer molecules, dichroic measurements show that the major axis of the dye is oriented parallel to the fibre axis. Consequently, the orientation of the dye molecules during diffusion must be considered. However, the dye molecule must weave its way through a network of polymer chains or dislocations, loosely termed the 'amorphous' regions of the fibre, irrespective of the orientation of the dye molecules. Although the highly ordered 'crystalline' regions are not penetrated by dye, they may nevertheless supply surfaces for adsorption of dye. However, the exact location of the dye in the polymer has not been established with certainty and adsorption may also take place in the amorphous regions.

MOVEMENT OF DYE THROUGH FIBRE

Dyeing is normally carried out from an aqueous solution, in which hydrophilic fibres such as cotton or wool swell markedly, presumably yielding an open water-filled structure, in which water-filled channels or pores provide a route for the dye to reach its adsorption site. However, in hydrophobic fibres such as poly(ethylene terephthalate), which do not take up large quantities of water, the dye must find a path through the polymer matrix itself.

Various properties of polymers affect the diffusion of compounds into the structure. For example, in isotropic agar gels, the resistance to diffusion of small inorganic ions through the polymer is demonstrated by the decrease in diffusion coefficient which accompanies an increase of the concentration of agar in the gel [3]. Other structural features obviously influence diffusion. Thus, dye will diffuse much more rapidly through films of regenerated cellulose that have been prepared in a 'never dried' form than through the commercially available dried films [4]. The difficulties in investigating the effects of different variations in structure arise because it is impossible to vary one structural parameter at a time. Mechanical treatments, e.g. the stretching or drawing of viscose rayon or nylon filaments, result in changes of both density and orientation, which lead to a dramatic decrease in the rate of adsorption of dye [5]. When polyester is heat set the crystallinity of the fibre and the glass-transition temperature are changed and differences in the rate of penetration of dye result. Sometimes, when such processing has been carried out under conditions which have been accidentally non-uniform, the variations in the structural effects produced are ultimately manifest as unlevel dyeing properties.

It is apparent from the above discussion that the diffusion of dyes into fibres is related to the molecular order and morphology of the fibres and it is very difficult to describe with precision the way in which such structural features affect the dyeing. Attempts to correlate diffusion coefficients with structure have therefore been made by using different models to represent the fibre structure, and the merits of two models are discussed here. Both may present, at best, an over-simplified picture of the real situation, but they are both interpretations arising from the different combinations of many polymer properties, which together show up as an effect on the diffusion of dye through the fibre.

The Pore Model and the Free-volume Model

The first model – the pore model – is mechanical in character and presents the fibre as a network of interconnecting channels or pores, containing water, through which the dye is considered to diffuse.

The second model is based upon the concept of 'free volume', which is the volume associated with molecules which is not occupied by the constituent atoms. It arises from the thermal motions of the atoms and increases with increasing temperature. The concept has been used to explain the variations with temperature of the physical properties of amorphous polymers. Below a certain temperature, the polymer chains are frozen into position and the only motions they can undergo are thermal vibrations, but further increases of temperature eventually provide sufficient energy for bond rotation in the backbone of the polymer chain. At this point, a whole segment of the polymer chain between two simultaneously rotating bonds changes its position by rotation, until it is hindered from moving further by other polymer molecules. The change in position is referred to as a segmental jump. Such motions may occur only when sufficient free volume has been created to provide a space large enough to accommodate the polymer segment, but, once the segment has moved, the space it has vacated is left for another segment to occupy and the process is repeated throughout the whole of the polymer structure. Consequently, there is a sudden marked increase in free volume over a narrow temperature range and an associated increase in the segmental mobility, which can be detected by marked changes in the physical properties. The temperature at which this occurs is referred to as the glass-transition temperature (T_g).

The free-volume model has been used to explain the variations with temperature of the viscosity of liquid systems [6] and the diffusion of organic vapours through polymers [7]. In a dyeing system, the dye molecules are visualised as moving through the fibre in a series of jumps from one location to another, their ability to do so depending upon the development of free volume adjacent to their positions, owing to the segmental movement of intervening polymer chains.

Both models are useful and it was considered worthwhile to examine the ability of each model to describe the diffusion of dyes into fibres.

THE PORE MODEL

It is possible that the route taken by a water-soluble dye into the interior of a hydrophilic fibre is similar to that of the water which causes the swelling of the fibre. The existence of discrete capillary channels in cellulosic films may be inferred from the fact that some liquids of small molecular size permeate the film faster than expected from a process of random diffusion through the structure [8]. Such random diffusion was observed only when penetrant molecules were used which were above a certain size.

In general, the diameter of the pores may be expected to vary with the type of fibre. As an example, the easier sorption of direct dye by cotton as compared with viscose rayon, has been taken as an indication of the larger pore size of the former. In non-swelling media, the uptake of the dye is negligible unless the fibre is pre-swollen [9]. It is to be expected, however, that the morphological differences between different fibres will be more detailed than can be explained in terms of pore size. Cotton, for example, is highly crystalline and composed of fibrils that are impenetrable by dyes, whereas some forms of viscose rayon show a skin and a core, indicating gross heterogeneities in the structure. Unfortunately, simple models cannot take into account structural features of this kind and at most they can only give a guide to the behaviour of dye molecules in fibres. In using the pore model to describe the dyeing process, the dye is considered to diffuse through and be simultaneously adsorbed on the walls of channels or pores.

If α is the fraction of the volume occupied by the channels and τ is the tortuosity (the ratio of the length of channel to the direct path), the flux, J of dye crossing unit area of polymer in the one dimension x may be written as:

$$J = -\frac{\alpha}{\tau} D_i \frac{\partial C_i}{\partial x} \tag{1}$$

where C_i is the concentration of dye in the pore. Since in practice C_i is very much less than the concentration C_A of the dye adsorbed on the walls, and diffusion coefficients are deduced from changes in C_A, i.e.

$$J = -\frac{\alpha}{\tau} D_i \frac{dC_i}{dC_A} \frac{\partial C_A}{\partial x} \tag{2}$$

The internal isotherm for the instantaneous adsorption process, given by dC_i/dC_A, cannot be evaluated directly and its form must be assumed or deduced from the external isotherms. The measured diffusion coefficient, D_M, is given by $(\alpha/\tau)(dC_i/dC_A)D_i$, and hence includes the adsorption properties and the tortuosity of the pores. Since the external isotherm for the non-ionic dyes is linear, it is a reasonable first approximation to use a linear internal isotherm:

$$K = \frac{C_A}{C_i} \tag{3}$$

where K is the partition coefficient.

In effect, Eqn 3 relates the measured diffusion coefficient to the affinity of the dye, i.e.

$$\ln D_M = \ln \frac{\alpha}{\tau} D_i - \frac{\Delta\mu^\circ}{RT} \tag{4}$$

where $\Delta\mu^\circ = RT \ln K$.

From Eqn 4, the calculated energy of activation is related to the heat of dyeing, the heat changes arising from changes in D_i with temperature being small (4 kcal/mole) [22]. Measurements of the energy of activation of three dyes on secondary cellulose acetate and triacetate showed that the heats of activation of the dyes into the crystalline cellulose triacetate were considerably greater than for the secondary acetate, even though the corresponding heats of dyeing were approximately the same [10] (Table 1). Thus the dye encounters a greater resistance to motion from the crystalline or more highly oriented polymer.

However, the model itself is somewhat crude in that it assumes that the dye molecule diffuses without hindrance down the tortuous channels. But when the dimensions of the dye molecule approach the diameter of the pores, the

TABLE 1 [10]

Comparison of Activation Energies of Diffusion in Secondary Acetate and Cellulose Triacetate (kcal/mole)

Dye	Secondary acetate			Triacetate		
	ΔH_{dif}	$-\Delta H$	$\Delta H'$	ΔH_{dif}	$-\Delta H$ (approx.)	$\Delta H'$
p-Nitroaniline	15	7	8	26	7	19
NN-Dimethyl-*p*-nitroaniline	13	8	5	20	8	12
Aminoazobenzene	18	9	9	31	9	22

ΔH = Heat of dyeing (obtained from equilibrium measurement)
ΔH_{dif} = Total heat of activation (derived from the temperature coefficient of diffusion)
$\Delta H' = \Delta H_{dif} - \Delta H$

geometry of the system will impose restrictions on the movement of the dye and no allowance has been made for this effect. That the polymer molecules are oriented in the direction of the fibre axis suggests that the pores should be regarded as having elliptical cross-sections whose major axis is at least equal to the length of the dye molecule. The introduction of a steric effect of this kind is tantamount to introducing an accessibility factor. An estimate of such a factor may be made by assuming that, when an originally isotropic fibre containing channels of circular cross-section, oriented perpendicular to the fibre axis, is stretched or drawn, the cross-sections of the original channels undergo an affine deformation and become elliptical. If the dye molecules are regarded as rods of length l lying in the plane at right angles to the axis of the pore, those dye molecules whose axes make an angle of at most γ with the major axis of the ellipse will be able to enter the pore as indicated in Figure 1. It can be shown using co-ordinate geometry that such a restriction to entry reduces the effective pore volume by a factor, ϵ, given by γ/π. By assuming that the ratio of the length of the dye molecule to the diameter of the cross-section of the isotropic material is L, this factor may be calculated for different stretch ratios λ. These changes are shown in Figure 1a and indicate that a considerable restriction may be imposed on the ability of the dye to enter such a pore. It is of interest to note that, when the length of the dye molecule is greater than the diameter of the hole, stretching increases the accessibility in the early stages of drawing, which is in accordance with the results of Tagaki *et al.* [11]. In a real fibre, however, holes with a range of sizes may be expected, so that the true value of this factor cannot be estimated. The values of ϵ may nevertheless be taken as a guide of the anticipated effect.

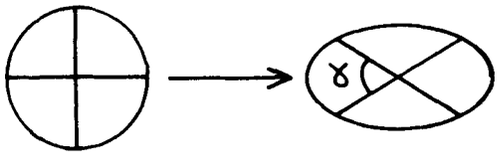


Figure 1 – Change of pore sectional shape on drawing

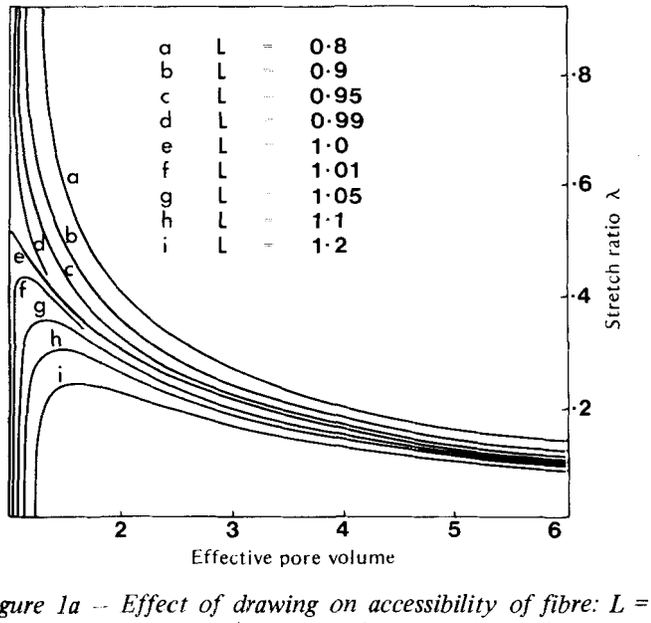


Figure 1a – Effect of drawing on accessibility of fibre: L = [length of dye molecule/diameter of circular channel]

The above discussion reveals that the pore model cannot be accepted in its entirety. The description of the diffusion process which it offers suffers from the main defect that structural parameters of the polymer, namely the size, shape and tortuosity of the pores, cannot be defined with any confidence. Moreover, once the pores are defined, the role played by the polymer structure is treated as a passive one in which it merely supplies surfaces for dye sorption. The correlation suggested between dye affinity and the diffusion coefficient could be accepted only if the dye molecule in the pore were able to be located out of range of the adsorption forces, i.e. in the interior of the pore the solution is supposed to possess normal properties of water. However, the relative size of the dye and the diameter of the pore would make this unlikely; hence, although some correlation between the adsorption properties and diffusion coefficient may be expected, the relevant adsorption properties may not necessarily be equated with those observed in a simple equilibrium experiment.

FREE-VOLUME MODEL

The pore model infers that the dimensions of the pores could be small enough to preclude the entry of the dye into the fibre and this would appear to be the situation that exists with those hydrophobic fibres that do not swell markedly in water. Nevertheless, it is possible to dye such fibres and, intuitively, it seems that a more realistic picture for the transport process in this case is one in which the dye molecule is adsorbed on a polymer chain and is able to move only when the segmental movement of the adjacent chains is such that a hole is formed of a size sufficiently large to accept the dye molecule and polymer segments together. As already noted, this situation exists only when the temperature is greater than the glass-transition temperature of the polymer (T_g). This concept is interesting because it suggests that the dyeing properties and the viscoelastic properties should be related as they are both governed by the segmental mobility.

The importance of the glass-transition temperature in dyeing is emphasised when the dyeing properties of polyester and acrylic fibres are examined. The glass-transition temperatures of these fibres in water falls within the region of 60–90°C and dyeing occurs at a significant rate only when the temperature is raised above this region. Once the T_g has been passed, the rate of dyeing becomes high. Because of this effect, some workers have referred to a transition temperature for

dyeing and have demonstrated that those values obtained are similar to those transition temperatures obtained for changes in physical properties [12].

A semi-empirical equation that describes the variation of viscoelastic properties of amorphous polymers with temperature, with reference to free volume (and hence segmental mobility of the polymer chains), has already been produced by Williams, Landel and Ferry [13], and Fujita [7] has demonstrated that the variation of diffusion coefficients of n-alkyl acetates at different temperatures through poly(methyl methacrylate) can be related to the viscoelastic properties through the equation:

$$\log \frac{D_T}{D_{T_g}} = \log \frac{\eta_{T_g}}{\eta_T} = \log \frac{1}{a_T} \qquad (5)$$

where D_T = the value of the diffusion coefficient at the appropriate temperature, η = the value of any property of the polymer which is dependent upon segmental mobility of the appropriate temperature, T_g = glass-transition temperature or any appropriate reference temperature above the glass transition and a_T = shift factor of Williams, Landel and Ferry equation (WLF Eqn) in which

$$\log a_T = \frac{-A(T-T_g)}{B+(T-T_g)} \qquad (6)$$

where A and B are constants.

In this system, therefore, the variations in the viscoelastic properties, and the diffusion coefficient of n-alkyl acetates, with temperature are both controlled by the segmental mobility of the polymer chains.

The shift factor in the WLF equation represents the fraction by which any property dependent upon the frequency of segmental jumps is changed in going from T_g to the ambient temperature. This could represent a change in the modulus of a fibre or, if the above reasoning is correct, the diffusion coefficients of dye through a fibre. The fractional change depends only upon the difference between T_g and the ambient temperature, and therefore the effect of temperature upon the properties of a whole range of different amorphous polymers of different T_g may be described by this relationship, which reflects the effect of temperature on the frequency of the segmental jumps. Once the correct values for the constants A and B are chosen, the results at one temperature can be superimposed upon those of another by multiplying by the appropriate value of the shift factor ($\log a_T$).

An equation of the same form has been derived mathematically to relate the change in free volume to the change in the viscosity of a polymer with temperature [14]. In the equation the constants A and B appear in terms of the critical free volume needed to permit a segmental jump and the free volume at a given temperature. A large number of polymers have been found to conform with the WLF relationship over the temperature range from T_g to $T_g + 120$. The equations are intended for use with amorphous rubbery polymers in which all the molecules are free to respond to an applied stress and are not intimately bound together in the closely packed, highly organised 'crystalline' regions encountered in fibres.

However, Rosenbaum has successfully used the WLF relationship, in the form of Eqn 6, to express the relationship between the diffusion coefficients of a basic dye in acrylic fibres and the variation in the physical properties with temperature [12]. This provides a real connection between the dyeing behaviour at temperatures above T_g and the segmental ability of the constituent polymer molecules. Similar arguments have been used by Bell [15] to explain the effect of temperature on the diffusion of acid dyes into nylon 6.6, and by Dumbleton *et al.* for the diffusion of disperse dyes into polyester [16].

Carrier Dyeing

The free-volume approach has also provided the basis for a quantitive description of the action of carriers in carrier dyeing. The various theories of carrier action have already been reviewed and the most likely explanation of the mechanism is that plasticisation of the fibre by the carrier leads to an enhanced rate of dyeing. Direct proof of such a mechanism has been obtained recently [17].

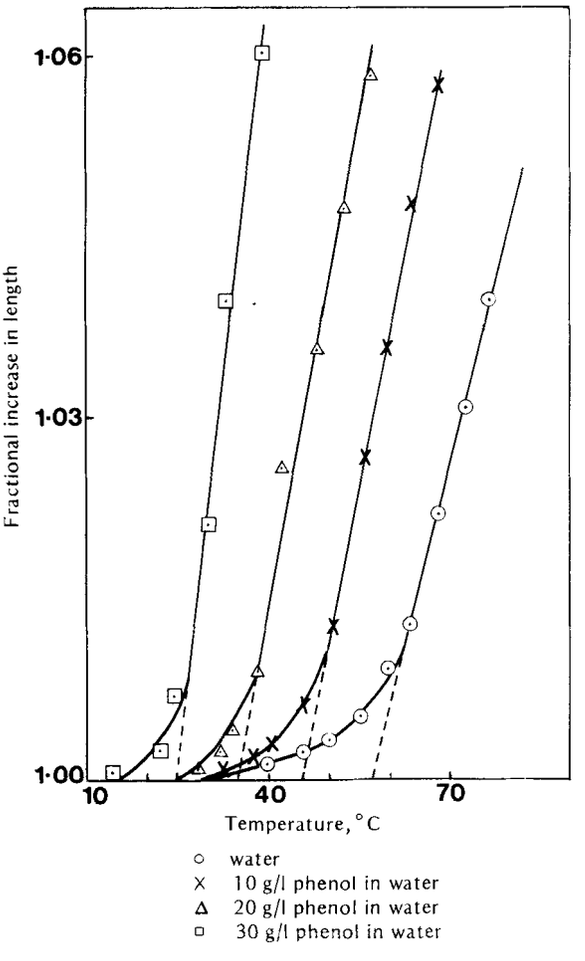


Figure 2 – Effect of temperature on fractional increase in length of Acrilan filaments immersed in aqueous solutions of phenol

Measurements of the elongation of acrylic filaments held taut by a small weight, when immersed in different solutions of carrier at different temperatures, demonstrated that the presence of carriers in the fibre lowered the glass-transition temperature. The glass transition was detected as a sudden increase in elongation at a particular temperature (Figure 2)

and increases in the concentration of carrier cause a proportional decrease in the transition temperature. In these experiments the filaments were first subjected to a conditioning treatment in the appropriate solution at 95°C. If this was not done the change in physical properties caused by the phenol could not be detected until the T_g of the filaments in water was reached. The response then became very marked indeed and subsequent experiments on the same filament enabled the reduction in T_g caused by entry of the phenol into the filament to be estimated. Several water-soluble carriers were examined in this way and, when the diffusion coefficient of a sample dye, *p*-aminoazobenzene, was measured in the presence of different carriers, the values obtained were related to $(T-T_g)$ (Figure 3).

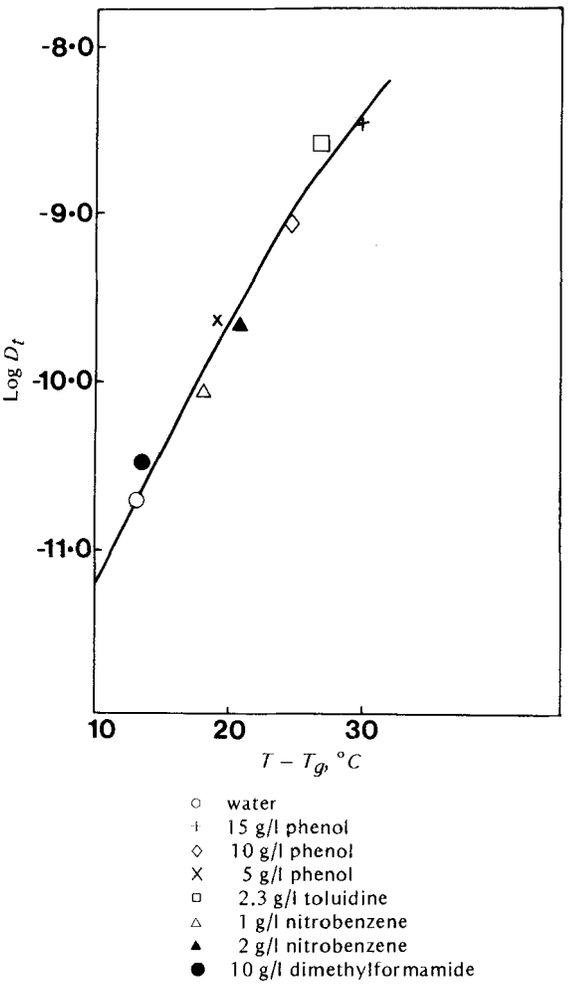


Figure 3 – Effect of aqueous solutions of different carriers on diffusion coefficient of p-aminoazobenzene in Acrilan fibre at 70°C

One of the difficulties in testing the free-volume theory with a dyeing system is the narrow temperature range over which the dyeing experiments may be carried out. The rate of dyeing of synthetic-polymer fibres below the T_g is too low to measure, and, if the temperature is allowed to rise too far above T_g, the rate of dyeing becomes too high to measure accurately. Consequently, it is not easy to obtain results over a wide enough range of temperatures to decide whether the points lie on a curve or a straight line. However, confirmation of the importance of segmental mobility in the dyeing process is given by the variation in activation energy with concentration of phenol (Table 2). Table 2 shows that, when the activation energy of the diffusion process is determined by assuming the results follow an Arrhenius relationship over the temperature range examined, there is a decrease in activation energy as the T_g is decreased by increasing the concentration of phenol.

TABLE 2

Effect of Phenol Concentration on the Activation Energy for Diffusion of *p*-Aminoazobenzene into Acrylic Fibre

Concn of Phenol in dyebath (g/l)	$-\Delta H$ (kcal/mole)
0	72.5
5.0	61.4
10.0	54.4
15.0	46.0
20.0	44.2

The theory, as presented in Eqn 6, shows that the properties that are governed by segmental mobility should conform to the relationship given when calculated values of log aT are plotted against $(T-T_g)$. However, it is difficult to produce absolute values of log aT from diffusion data, because the diffusion coefficient for disperse dyes at $T_g(D_{Tg})$ cannot be measured. Consequently, it is assumed that D_{Tg} does not change when the T_g is changed and the values of log D against $(T-T_g)$ are plotted instead. If the results conform to the theory, it should then be possible to superimpose them on to the calculated curve by a vertical shift of the points. The data for Dispersol Fast Scarlet B (C.I. Disperse Red 1) have been treated in this way and the coincidence of the experimental

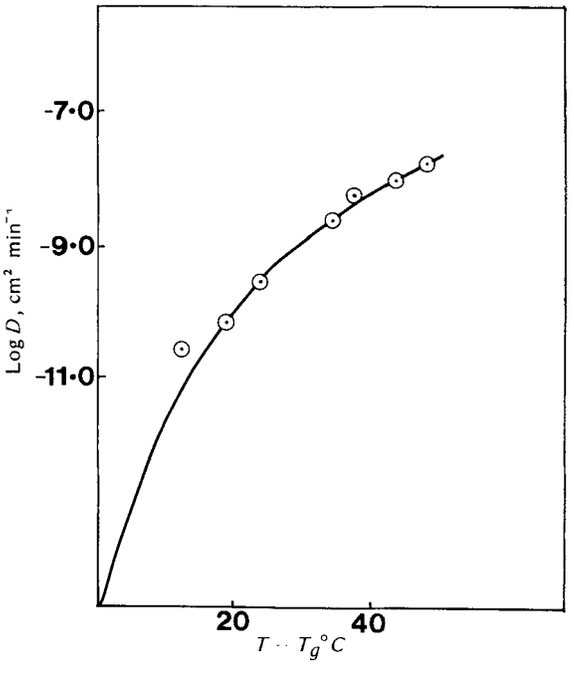


Figure 4 – Matching diffusion data for C.I. Disperse Red 1 to the WLF equation (Eqn 6) using A = 10.8 and Y = 28.5

points and the calculated curve is shown in Figure 4. The fit is very satisfactory and the results are similar to those obtained by Rosenbaum [12] for the diffusion of basic dyes into acrylic fibres. Clearly, therefore, the diffusion of basic dyes and disperse dyes into acrylic fibres is governed by the segmental mobility of the polymer chains. Furthermore, the results confirm that the action of carrier-like compounds may be described in terms of the additional free volume which the carrier introduces into the system and the associated increase in the segmental mobility of the polymer chains.

It is more difficult to fit experimental results for the carrier dyeing of polyester fibres and films to the theory, because it is not easy to locate the T_g. It lies in the region of 80–100°C and measurements are accordingly restricted in the absence of carrier to a narrow range of temperatures above the T_g measurements. However, it is possible to detect a dyeing transition temperature which decreases with increasing carrier concentration and this may be taken as a reference temperature instead of a glass transition (Figure 5). By

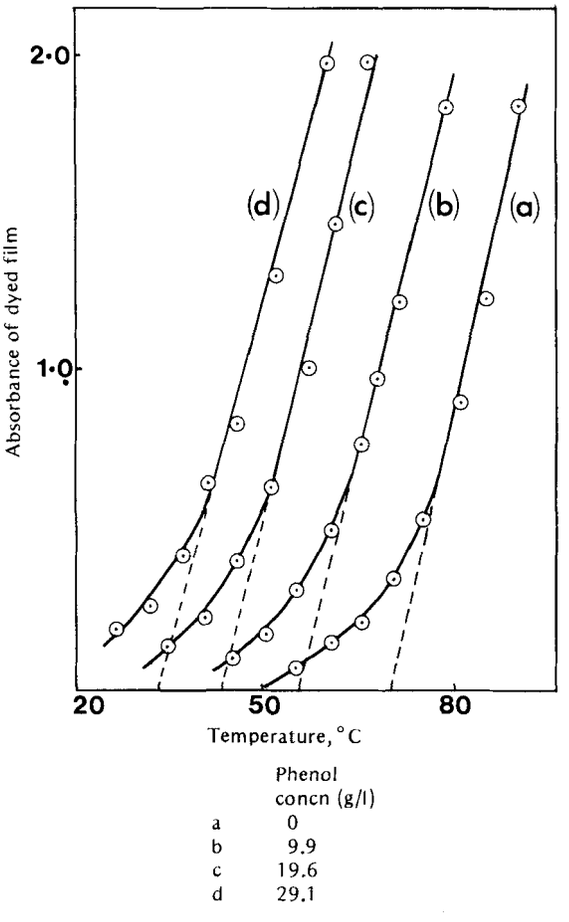
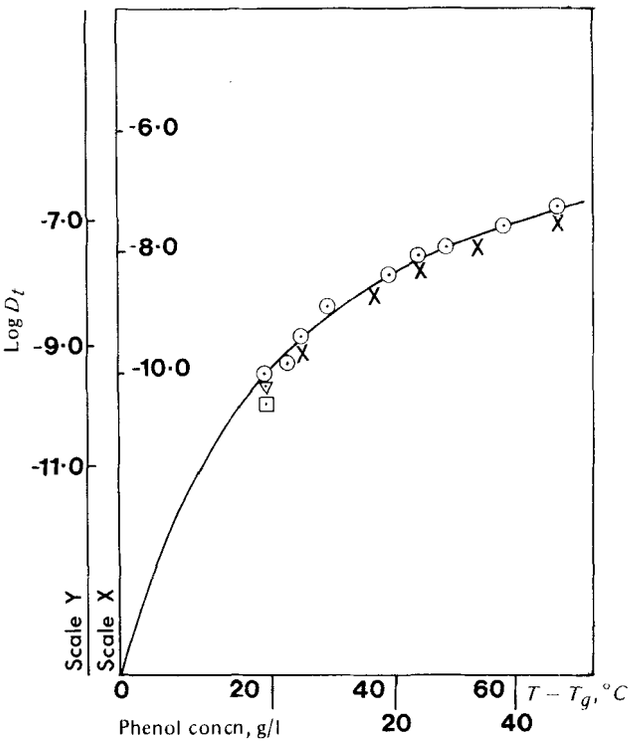


Figure 5 – Uptake of p-aminoazobenzene by polyester film after dyeing for 10 min at different temperatures in presence of phenol

adopting this procedure for the polyester films used in the experiments, it was shown that the variations in the diffusion coefficient with temperature could also be fitted on to the calculated curve (Figure 6). Thus, although the polyester film was highly orientated and highly crystalline, the system still conforms to the theoretical principles outlined above,



○ C.I. Disperse Orange 3 (Scale Y) on films of thickness 11.4 μm
▽ C.I. Disperse Orange 3 (Scale Y) on films of thickness 8.3 μm
× C.I. Disperse Red 1 (Scale X) on films of thickness 11.4 μm
□ C.I. Disperse Red 1 (Scale X) on films of thickness 8.3 μm

Figure 6 – Matching diffusion data for different dyes into poly(ethylene terephthalate) films to WLF equation (Eqn 6) using A = 10.8 and Y = 28.5

reinforcing the view that dyeing is governed by the response of the small amount of amorphous material present in the substrate.

On this argument, the ability of the dye to progress through a fibre depends on the ability of the polymer chains to overcome interchain forces and change their conformations. Thus the dye is pictured as passing through the 'amorphous' or dislocated regions of the polymer again via a tortuous path to avoid the impenetrable crystalline regions; the latter may play a role apart from obstruction in that it may be possible for dye to move across crystalline surfaces. However, for the purposes of defining a model, the fibre may be considered as a two-phase system in which only a fraction θ of amorphous material is available for diffusion. Eqn 1 may now be written as

$$J = -\frac{\theta}{\tau} D \frac{\partial C_A}{\partial x} \qquad (7)$$

The dye may be considered to move essentially by a process in which the molecule moves in jumps from one point to another, corresponding to the movements of the polymer segments.

Equations representing the diffusion of dye may therefore be analogous to equations representing the segmental movements of polymer chains. According to Bueche [14], if the jump distance is δ and the frequency of the occurrence is ϕ,

the pre-exponential term in the usual Arrhenius relationship may be represented by

$$D_o = \frac{\phi_o \delta^2}{6} \tag{8}$$

The fraction of jumps which result in the movement of the dye molecule will depend on the probability that the molecule may be released from its absorption site and the probability of a hole of appropriate size being formed adjacent to the dye molecule.

These probabilities may be written formally in terms of free energy necessary to release the dye molecule, ΔG_D, and that necessary to form a hole ΔG_H, i.e. a hole of a size at least equal to a minimum volume v^*, capable of accommodating the dye. Hence ϕ at any temperature may be written as

$$\phi = \phi_o \exp \frac{-\Delta G_D}{RT} \exp \frac{-\Delta G_H}{RT} \tag{9}$$

Substituting Eqn 9 into Eqn 8 and putting ΔG_D and ΔG_H in terms of their respective heat and entropy terms yields

$$\ln D = \ln \frac{\delta^2 \phi_o}{6} - \frac{\Delta H_D + \Delta H_H}{RT} + \frac{\Delta S_D + \Delta S_H}{R} \tag{10}$$

Thus Eqn 10 stresses the point that the magnitude of the diffusion coefficient is dependent on the polymer properties as given by ΔG_H, as well as on the adsorption forces, as represented by ΔG_D. The equation could lead to the correlation of the diffusion coefficient of the dye, if ΔG_D is equated to the affinity of the dye, as discussed in connection with the pore model.

Eqn 10 is of the same form as that derived on transition-state arguments, but here ($\Delta H_D + \Delta H_H$) has replaced ΔH^*, the transition-state enthalpy change and ($\Delta G_H + \Delta S_H$) has replaced ΔS^*, the transition-state entropy change. The latter has been employed to calculate the activation energies and entropies of diffusion of disperse dyes into polyester fibres [18]. It may be assumed over the normal range of dyeing temperatures that ΔH_D, ΔH_H and ΔS_D are independent of temperature, but for ΔS_H this is not so.

The energy of activation determined from the slope of log D *versus* $1/T$ therefore contains contributions from ΔH_D, ΔH_H, ΔS_D and ΔS_H. On this basis, the very large values of the activation energies of dyeing, for cellulose triacetate as compared with secondary acetate, must be attributed to the contributions made by the segmental movement.

The enthalpy term ΔH_H may be regarded as arising from the energy required to overcome interchain forces forming a hole of a size at least equal to v^*, and $\Delta S_H/R$ is the entropy contribution which arises from the number of ways the chain segments may arrange themselves to form a hole [14]. In terms of free-volume arguments, this is calculated on the assumption that a certain quantity of free volume is ascribed to each segment; the term $\Delta S_H/R$ is then the number of arrangements of these free-volume elements which can on combination yield a volume of size equal to v^*. Such a calculation makes the entropy term approximately equal to $\beta v^*/v_f$, where β is a constant and v_f is the fractional free volume available in the amorphous regions at the ambient temperature.

Inserting these factors into Eqn 10 results in Eqn 11:

$$\ln D = \ln \frac{\delta^2 \phi_o}{6} + \frac{\Delta S_D}{R} - \frac{\Delta H_D + \Delta H_H}{R} - \frac{\beta v}{v_f} \tag{11}$$

Provided the temperature of diffusion is greater than T_g, v_f may be written in terms of the free volume at the glass transition v_g and α_e, where α_e is the expansion coefficient for the polymer above T_g minus the expansion coefficient of the polymer in its glassy state.

$$v_f = v_g + \alpha_e (T - T_g) \tag{12}$$

The term ΔH_H was introduced formally to make possible allowance for any contribution which may arise from the specific polar forces between the polymer chains. However, it may be argued that the term $\beta' v^*/v_f$, which has been equated to the entropy, also contains contributions to the enthalpy, by virtue of the introduction of the expansion coefficient, but unfortunately there is insufficient evidence to establish this point. Substituting Eqn 12 into Eqn 11 and rearranging, ln D may be written as:

$$\ln D = \ln \frac{\delta^2 \phi_o}{6} + \frac{\Delta S_D}{R} - \frac{\Delta H_D + \Delta H_H}{RT} - \frac{AB}{B + T - T_g} \tag{13}$$

where $A = \beta' v^*/v_g$ and $B = v_g/\alpha_e$ which in Beuche's treatment of polymer properties, correspond to the constants A and B in an equation of the same form as that derived by Williams, Landel and Ferry (WLF). Re-arranging Eqn 13 gives

$$\ln D = \ln \frac{\delta^2 \phi_o}{6} + \frac{\Delta S_D}{R} - \frac{1}{T}\left[\frac{\Delta H_D + \Delta H_H}{R} + \frac{AB}{1 - (T_g - B)/T}\right] \tag{14}$$

A plot of log D or the measured diffusion coefficient against $1/T$ should give a curved line whose slope decreases with increases in temperature. Using a value of $\Delta H_D + \Delta H_H$ of 10 kcal, and the normal values attributed to the constants of the WLF equation of $A = 17.5$ and $B = 52$, the graphs shown in Figure 7 indicate how the behaviour for the two values of T_g is influenced by the contribution of $\Delta H_D + \Delta H_H$. The activation energy of diffusion deduced from the practical measurement will vary with the T_g of the polymer and the range of temperatures chosen for the measurements. Curvatures for such plots have been observed for the diffusion of acid dyes into nylon 6 and 6.6 [15] and for the cationic dyes into acrylic fibres [12]. Figure 3 shows that the energy of activation deduced from the slope of a graph of ln D *versus* $1/T$ is dependent on the contribution which the entropy term $-\Delta S_D/R$ makes and hence on the range of temperatures used relative to the glass-transition temperature. The slopes approach the same value of approximately $-[(\Delta H_H + \Delta H_D)/R] - AB$ in the higher temperature ranges.

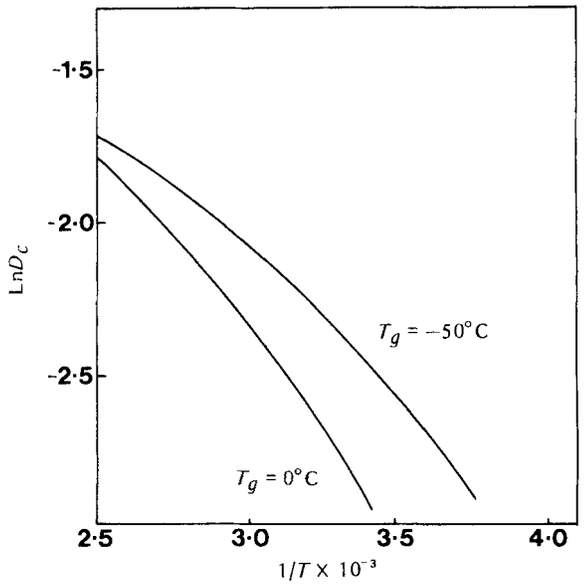


Figure 7 – Plot of log D_C calculated according to Eqn 14 assuming $\Delta H_D + \Delta H_H = 10$ kcal when $T_g = -50°C$ and when $T_g = 0°C$

Equation 13 may be put into the normal WLF form by taking the logarithms of the ratio of the diffusion coefficients at the temperature T and T_g, D_T and D_g, i.e.

$$\ln \frac{D_T}{D_{T_g}} = \ln \frac{T}{T_g} + \frac{\Delta H_D + \Delta H_H}{R} \frac{T - T_g}{TT_g} + \frac{A(T - T_g)}{B+(T-T_g)} \quad (15)$$

$$= \ln \frac{T}{T_g} + \frac{\Delta H_D + \Delta H_H}{R\,T_g} \left[\frac{T - T_g}{T_g + (T-T_g)} \right] + \frac{A\,(T-T_g)}{B+(T-T_g)} \quad (16)$$

Since $\ln T/T_g$ does not vary significantly with temperature and the variation of T_g (measured in °K) is normally small, Eqn 16 shows that the introduction of the enthalpy term still retains, at constant T_g, the dependence of $\ln (D_T/D_{Tg})$ the single variable $T-T_g$ deduced for the usual WLF treatment. Using the same constants as for Figure 7, a plot has been made in Figure 8 showing that the dependence on temperature is greater than that depicted by the WLF equation. However, it is likely that the WLF curve obtained experimentally contains an enthalpy contribution and hence a new curve in which the enthalpy contribution is subtracted could be constructed, as indicated in Figure 8.

In the above, a value of $\Delta H_H + \Delta H_D$ was taken as 10 kcal/mole merely to demonstrate its importance; such a value is arbitrary, but nevertheless may be regarded as feasible for the diffusion process of simple molecules in secondary cellulose acetate (Table 2).

The results shown in Figure 7 stress the difficulties in

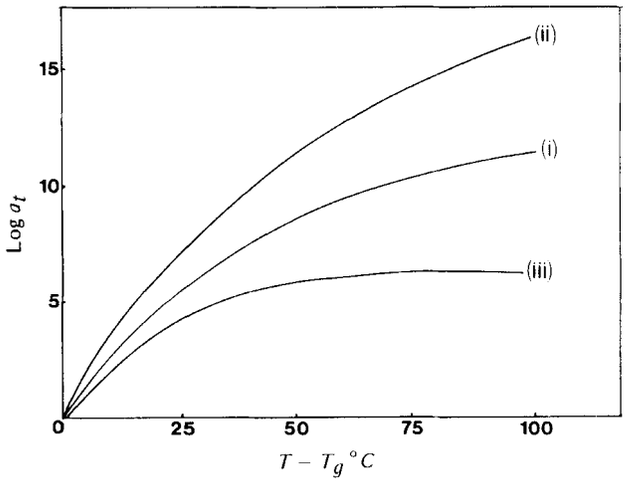


Figure 8 – (i) Relationship between log (D_T/D_{T_g}) calculated using Eqn 6; (ii) Relationship calculated using Eqn 16 which allows for the enthalpy term; (iii) Relationship calculated by subtracting the enthalpy term from (i) ($T_g = 0°C$; $\Delta H_D + \Delta H_H = 10$ kcal)

assigning an exact meaning to the value of the activation energy that is obtained practically, since this contains contributions from ΔH_H, ΔH_D and the entropy term. At the higher temperatures, the contribution from the last of these may be relatively small (e.g. *AB* using WLF constants is 910). To estimatee ΔH_H would require a knowledge of ΔH_D or the value of ΔG_D. The importance of the enthalpy or affinity of activation of the dye is also difficult to assess. In a polymer, the chains may be expected to be located at an average distance of 5–7 Å apart, and, if the width of the dye molecule is that of a benzene ring or more commonly that of a naphthalene (2.5 Å and 5.0 Å respectively), the dye molecule may never be out of the range of adsorption forces. Thus, it is unlikely that the activation energy for diffusion can be equated with the heat of dyeing, but should be smaller. ΔS_H similarly may be expected to be different from that calculated from adsorption experiments, since the dye will assume the orientation of the polymer chains and presumably maintain this orientation when a jump occurs. Hence, the activation energy found from practical experiments, although having a contribution from adsorptive forces, is expected to get its major contribution from the polymer properties.

Effects imposed by stretching the polymer are not explicitly taken into account by such a model. Drawing a fibre preferentially orientates the chains in the stretch direction. The dye molecule has then to penetrate an array of chains whose contacts have been markedly increased and hence the energy for hole formation may be expected to increase. At the same time, the number of possible conformations available for the chains to assume must decrease, thereby reducing the contribution of the entrophy term ΔS_H. Activation energies determined for the diffusion of Orange II (C.I. 15510) into nylon 6.6 steadily increase from 22 to 28 kcal/mole when the material is extented by a factor of 6 [19]. A change of activation energy of this magnitude is more than adequate to account for the reduction in diffusion coefficient on drawing.

Clearly, the free-volume theory has severe limitations and indeed does not allow a calculation *ab initio* of the diffusion

coefficient. However, the dependence of the diffusion coefficient on one structural parameter of the polymer is stressed, namely that of the glass transition, and as already mentioned has been found to be useful in providing a basis of comparison for the diffusion coefficients of a set of acrylic fibres with different T_g values and for the effect of carriers on dyeing [12, 17]. However, the values of A and B in the WLF plot in this work were 10.5 and 28.5 respectively, and hence did not agree with those found for other polymers derived from mechanical data. In view of the above discussion on orientated polymers, it would seem, at this stage, that the observed constants in such a plot should be regarded as arbitrary. Nevertheless, the free-volume arguments provide a more realistic framework in which to work than the pore model.

Finally, it must be pointed out that the dyeing properties of the polymer are modified by heat treatments. As an example, dry treatments cause a reduction in the rate of diffusion of dyes into nylon, whereas steam treatments increase the rate [20]. In a set of experiments in which nylon 6 was dyed with dyes of different sizes, increase in molecular size decreased the diffusion coefficient of the dry set material, but not the wet [21]. Again the activation energy of Orange II into nylon 6.6 decreased when the samples had been treated in boiling water [19]. Such observations suggest that the increased segmental mobility brought about by the presence of moisture leads to increased crystalline perfection and the rejection of chain ends from the ordered regions. Such chain ends could in fact be surrounded by void space. In such void spaces in the polymer, the diffusion of the dye molecule could be enhanced and hence the magnitude of the resulting diffusion coefficient may be expected to be determined by the passage of the dye not only through the dye network of tie molecules but also through the void spaces.

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