8.1.7.1.6 Aqueous Phase Transfer This section considers the mechanism of the interactions that occur between PES fibres and disperse dyes applied from aqueous dispersion. Since, as mentioned, the mechanism of the aqueous phase transfer of disperse dyes is identical for all types of fibre, the following mechanistic discussion is applicable to the other types of fibre on which disperse dyes are commercially used (i.e. CA, CTA and PA) as well as those on which the dye class does not enjoy widespread use (e.g. cellulosic fibres and wool).

8.1.7.1.7 Mechanism of Dye Transfer The historical development of the mechanism by which disperse dyes are adsorbed onto textile fibres with disperse dyes has been well discussed [13, 125, 167–171]. Briefly, in the 1920s, two different views were proposed to explain the mechanism of transfer of the dyes to CA fibres that solid dye was adsorbed on the fibre surface and dye diffusion then occurred within the substrate by means of a *solid solution* process or the dye was adsorbed from a very dilute solution present in the dyebath. The former proposal stemmed from observations made by Kartaschoff [172] which assumed, essentially, that the dyes had no water solubility whilst the latter suggestion was made without experimental evidence by Clavel and Stanisz [173, 174]. The matter was subsequently resolved by the findings of Bird *et al.* [157–175] which demonstrated that disperse dyes possessed low water solubility that was promoted in the presence of dispersing agents and also by the findings of Schuler and Remington [176], which supported Clavel's theory that dyeing takes place from a dilute aqueous solution that is maintained in a saturated state by dissolution of dye particles within the bulk dyebath dispersion.

According to the generally accepted mechanism of the aqueous phase transfer of disperse dyes, as illustrated in Figure 8.10, at the start of dyeing, the greater proportion of dye is present in bulk dispersion within the dyebath, although a small amount of dye dissolves, forming an aqueous solution. Dye molecules from the aqueous solution are adsorbed at the fibre surface and these dye molecules then diffuse from the surface to the interior of the sub-strate. Subsequently, more dye particles from the bulk dye dispersion dissolve, thereby replenishing the aqueous dye solution from which dye molecules are further adsorbed at the fibre surface. This process of dye particles from the bulk dispersion dissolving and forming an aqueous dye solution from which dye adsorption occurs at the fibre surface continues until either the dyebath is exhausted of dye or the fibre is saturated with dye. The mechanism of the disperse dyeing of a hydrophobic fibre such as PES (or PA, CTA, or indeed any type of fibre) can thus be considered to comprise five sequential stages, of which the last is commonly considered as being the rate-determining step:

(1) dissolution of dye molecules from the surface of dispersed dye particles and the establishment of a monomolecular state in the aqueous dyebath;
(2) convective diffusion of the dissolved dye molecules through the bulk dyebath to the fibre surface;
(3) diffusion of the dye molecules through the diffusional boundary layer present at the fibre surface;
(4) adsorption of the dye molecules onto the surface of the substrate;
(5) diffusion of the dye molecules within the fibre interior.

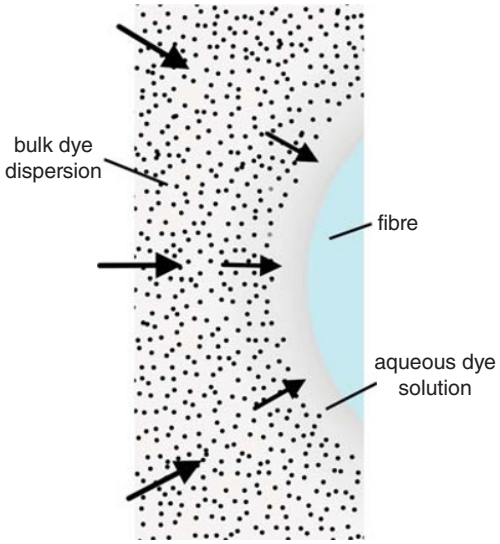

Figure 8.10 Representation of mechanism of the aqueous phase transfer of disperse dyes to hydrophobic fibres.

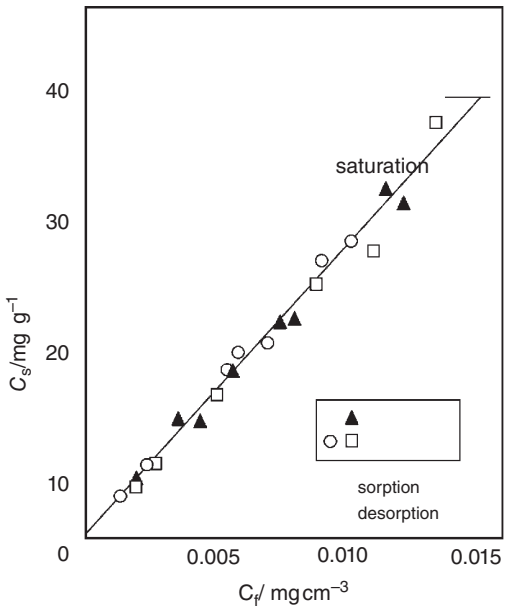

Figure 8.11 Adsorption isotherms for 1-amino-4-hydroxyanthraquinone on PES at 100 C. Reproduced from [176], with permission from the Royal Society of Chemistry.

From the foregoing, it is apparent that, despite the low aqueous solubility of disperse dyes, even under the HT dye-ing conditions employed for PES (130–140 C), the mechanism of their adsorption onto PES, as well as other fibres relies upon their dissolution in water and, therefore, the aqueous dyeing of textile fibres with disperse dyes occurs from aqueous solution, as observed for all other types of dye. However, as discussed below, the nature of the interactions that operate between disperse dyes and textile substrates is under much debate.

8.1.7.1.8 Thermodynamics of Dyeing Rectilinear adsorption isotherms have been obtained for disperse dyes on several types of fibre including PES [158, 176–178], PTT [178], CA [158, 168, 175, 179], PA [180–182], PP [183], wool [184] and CV [185] (Figure 8.11).

In the case of PES, Schuler and Remington obtained Nernst isotherms for the uptake of 1-amino-4-hydroxyanthraquinone (Figure 8.11), 1,4-dihydroxyanthraquinone and *N*,*N*-diphenyl-3-nitrosulphanilide in the absence of dispersing agent [176], which obeyed Eq. 8.1 where K is the partition coefficient, $[D]_f$ and $[D]_s$

represent the amount of dye in the fibre and solution phases and S_f and S_s are the saturation values of the dye in the fibre and solution phases. Clearly, dye adsorption varies in a linear fashion upto saturation of the fibre, S_f.

$$K = \frac{[D]_f}{[D]_s} = \frac{S_f}{S_s} \tag{8.1}$$

Schuler and Remington [176] proposed that the linearity of the Nernst isotherms obtained, such as that shown in Figure 8.11, implies that the dyeing mechanism is best described as dye solution in the fibre, thus supporting Kartaschoff's earlier proposal that the dyes are retained within the fibre by a process of solid solution, this being analogous to the partition of a solute between two immiscible solvents insofar as the dye dissolves in and diffuse within the fibre as it would in an organic solvent. Furthermore, these workers also suggested that the linearity of the isotherms strongly suggests that the dye is similarly dispersed in both the aqueous and fibre phases as single molecules [176].

However, as mentioned above, considerable debate attends the mechanism by which disperse dyes interact with textile fibres (e.g. [170, 186, 187]). Whilst some authors feel that the fibre acts as a solid solvent for the disperse dye which is distributed between the aqueous solution and the fibre on the basis of a simple partition, other researchers consider that disperse dyes are adsorbed onto specific sites within a fibre and therefore adsorption follows a Langmuir type model. Rattee and Breuer [170] make the point that Nernst isotherms are also obtained for disperse dyes on hydrophilic fibres such as PA and wool, for which substrate types, the accepted mechanism of adsorption in the case of other types of polar dye (e.g. acid dyes) is adsorption at sites. Vickerstaff [167] argues that there can be little difference between an adsorption at sites model and a solid solution model insofar as both models require that the dye molecules interact with the fibre by, for instance, H-bonding and dispersion forces, via appropriate groups in the substrate, such interactions being indistinguishable between the fibre acting as a solvent for the dye or the fibre providing adsorption sites for the dye.

More recent studies have proposed a dual-mode sorption model in which Langmuir-type sorption onto specific adsorption sites in the substrate occurs in parallel with Nernst-type dissolution of the dye in the fibre. By way of explanation, in the late 1920s, Burns and Wood [188] proffered that the adsorption of disperse dyes on CA fibre occurred from true solution, similar to that observed for direct dyes on cellulosic fibres, and suggested that the dyes were adsorbed at specific sites within the substrate. Curvilinear adsorption isotherms have been obtained for disperse dyes on various fibre types, a major cause of curvature being attributed to the presence of large dye particles of lower aqueous solubility, with linear isotherms being obtained if the dye is present either in the dissolved or solubilised state [125] (e.g. [168]); curved isotherms are observed for dyes of low aqueous solubility [171]. For example, Burns and Wood [188] obtained curved sorption isotherms in the case of three purified commercial disperse dyes on CA fibres at low temperature (26°C) and Vickerstaff and Waters [171] observed that curved isotherms were obtained for the adsorption of four, purified disperse dyes on CA fibre (Figure 8.12a), the linearity of the ensuing $[D]_s/[D]_f$ versus $[D]_s$ plots (Figure 8.12b) implying that sorption followed a Langmuir model.

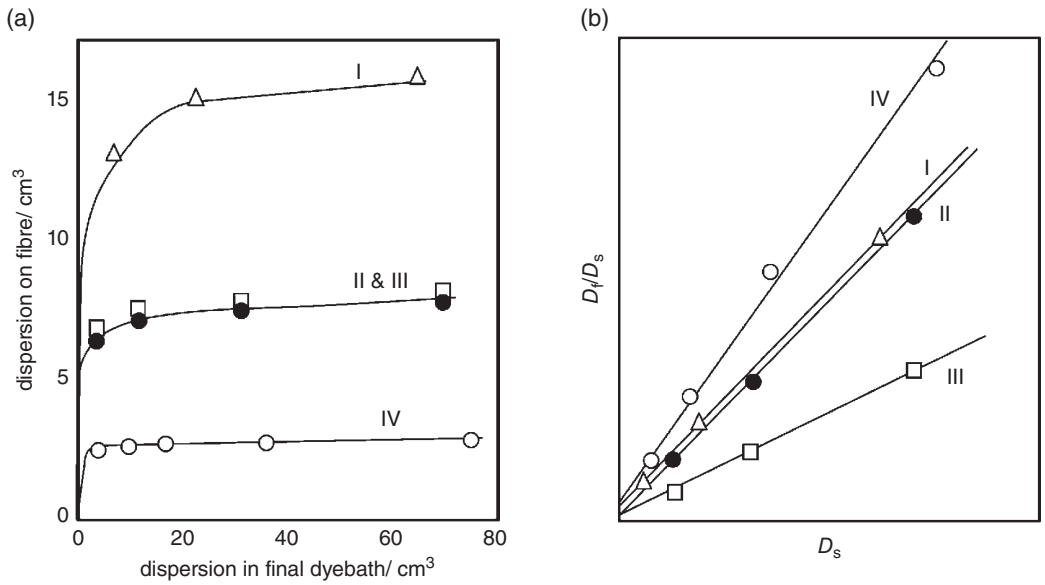

Figure 8.12 (a) Adsorption isotherms of disperse dyes on CA at 85°C. (b) D_s/D_f versus D_s plot of data. Reproduced from [171], copyright of the Society of Dyers and Colourists.

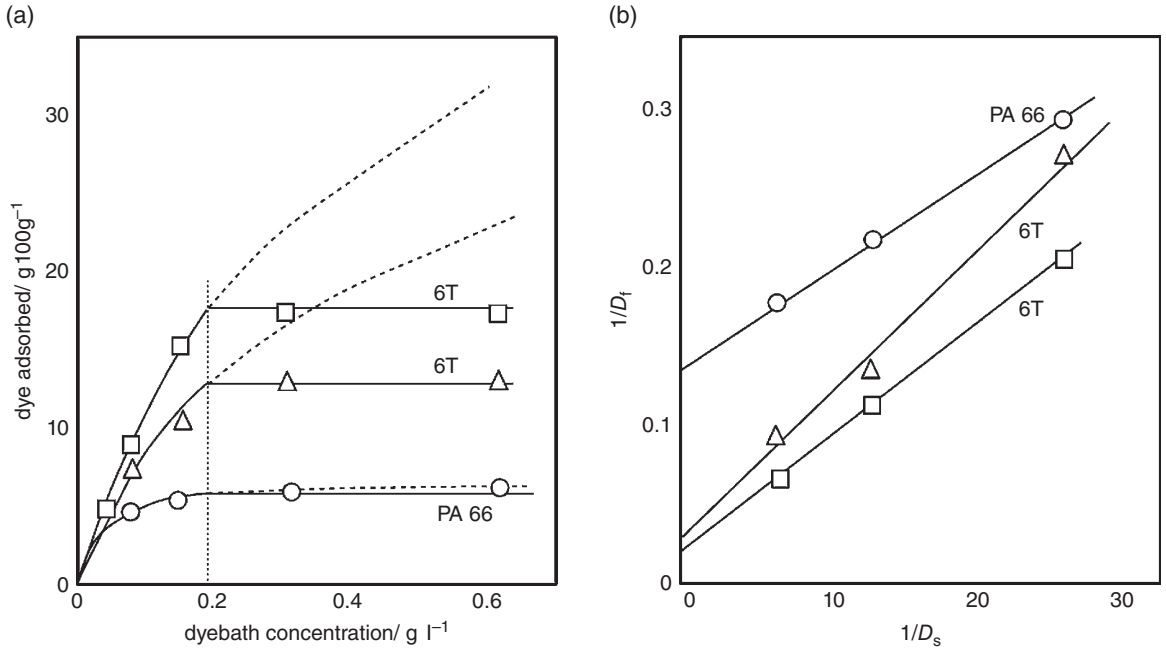

Figure 8.13 Adsorption isotherms for C.I. Disperse Blue 6 on PA 66 and on two different types of PA 6T at 97°C (a); $1/D_f$ versus $1/D_s$ plot of data at three lowest low D_s values (b). Reproduced from [189], SAGE.

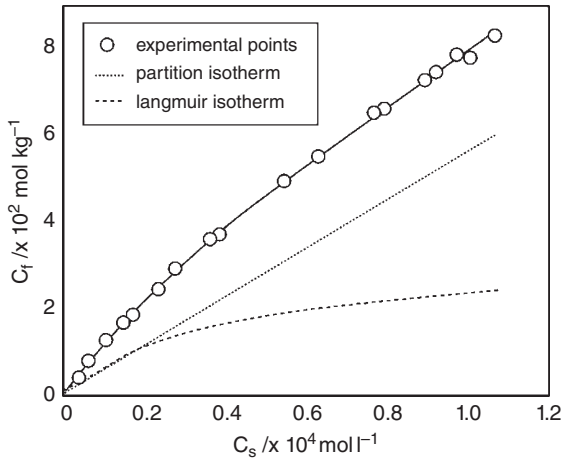

Figure 8.14 Sorption isotherms for C.I. Disperse Red 15 on 0.35 dtex PES microfibre at 95°C. Reproduced from [194], SAGE.

Brody [189] found that the adsorption of the commercial disperse dye *Celliton Blue FFG* on both PA 66 and PA 6 T fibres was curvilinear (Figure 8.13a) but also observed that the reciprocal Langmuir plot (i.e. $1/[D]_f$ vs $1/[D]_s$; Figure 8.13b) was linear for the three lowest experimental values of $[D]_s$ implying Langmuir sorption at sites. This author also observed that the saturation value obtained for each of the three different PA fibres used occurred at the same dyebath concentration, $\sim$0.2 g l^{-1} (Figure 8.13a) which was attributed to the dyebath rather than the fibre being saturated at this particular dyebath concentration. Recent work has shown that curvilinear isotherms are secured for C.I. Disperse Red 86 under HT dyeing conditions (i.e. 110, 120 and 130°C) [190]. These findings were interpreted [189] as supporting Stubbs' [191] views on the sorption of disperse dyes on CA fibres insofar as the linear portion of the adsorption isotherm is not Nernst-type behaviour indicative of solid solution, but rather is the lower part of a Langmuir-type sorption process, with the horizontal segment of the plot signifying that the dyebath rather than the fibre is saturated with dye.

More recently, Shibusawa *et al.* have determined the sorption isotherms of several purified disperse dyes on different polymers (e.g. PA 6 [192, 193], PES [193–195]) and observed that the isotherms of most of the dyes were curved, convex upward, at low amounts of dye (Figure 8.14). A dual-mode sorption model was proposed in which the curvature of isotherm is ascribed to sorption onto specific adsorption sites in the substrate, which accords with simple Langmuir-type adsorption and which occurs in parallel with Nernst-type dissolution of the dye in the fibre, Eq. 8.2, where C_P and

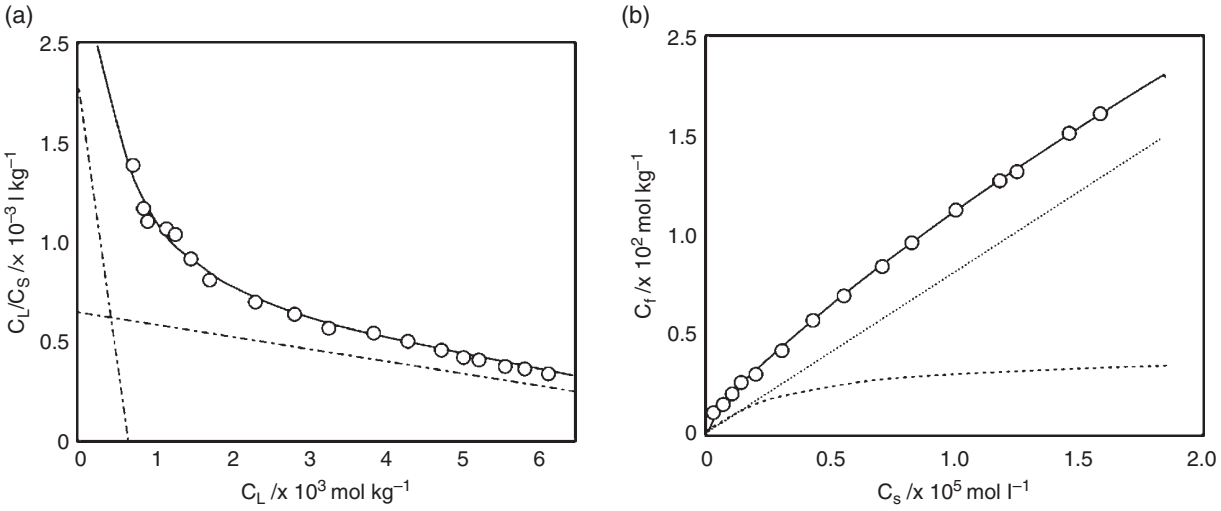

Figure 8.15 (a) Scatchard plot for the Langmuir sorption in the isotherm (b) of C.I. Disperse Violet 1 on PA 6 at 60°C (legend as for Figure 8.14). Reproduced from [193], with permission from John Wiley & Sons, Inc.

C_L are the dye concentrations resulting from Nernst partitioning and Langmuir sorption at sites, respectively, C_f and C_s are the equilibrium dye concentrations in the fibre and solution, S is the saturation value for the Langmuir sorption, with K_P and K_L the Nernst and Langmuir partition coefficients, respectively.

$$C_f = C_P + C_L = K_P C_S + \frac{K_L C_S S}{1 + K_L C_S} \tag{8.2}$$

The dyes are considered to exist in the polymer as two distinct species namely those adsorbed by a Nernst partition mechanism (dissolved species) and those adsorbed by means of a Langmuir sorption (adsorbed species), the former being normally predominant except at low values of C_f, with the ratio C_L/C_P increasing with decreasing C_f [196]. Differences were observed in the nature of the dual-mode sorption model depending on the temperature of dye adsorption [193]. At low temperatures (40–60°C for PA 6 and 95°C for PES) three concurrent modes of sorption were identified namely, Nernst-type partitioning and bimodal Langmuir sorption that involved sorption on to higher affinity sites of small saturation value as well as sorption onto lower affinity sites of large saturation value. This is illustrated by the results obtained for C.I. Disperse Violet 1 on PA 6 at 60°C. The curve obtained in a Scatchard plot[9] (Figure 8.15a) of the experimental isotherm data presented in Figure 8.15b was considered to be indicative of the presence of two types of Langmuir binding sites, one with a very high affinity constant (K_{L1}) and small saturation value (S_1) and another with a low affinity constant (K_{L2}) and large saturation value, S_2. However, at high temperatures (80–90°C), dye sorption onto the high affinity site in PA 6 decreased to such an extent that sorption could be described in terms of a dual-sorption model. Papadokostaki also found in the case of CA fibres that the Nernst sorption isotherm for 4-aminoazobenzene departed increasingly from linearity as the temperature was lowered which was consistent with the presence of strong absorption sites [198].

The dual mode sorption approach has been adopted by other workers in the cases of both conventional dtex and microfibre PA 66 [199]. It has been found that the Langmuir equation best described the sorption isotherms obtained for disperse dyes on PES fibres at 130°C, the correlation being better for microfibres (0.22 and 0.56 dtex) than conventional dtex fibres [200]. However, subsequently, it was observed that the dual mode model described the sorption of disperse dyes onto supermicrofibre PES (0.07 dtex) at both 120 and 130°C and that the Langmuir equation did not adequately describe the supermicrofibre [177].

Clearly, the nature of the interactions between disperse dyes and fibres has not been fully elucidated. Whatever the mechanism(s) involved, Vickerstaff's [167] argument that, in effect, such interactions would be indistinguishable between the fibre acting as a solvent for the dye or the fibre providing adsorption sites for the dye, seems apposite.

[9] a graphical method, based on a transformation of the Langmuir equation, first proposed in 1949 by Scatchard [197], that is commonly used to interpret the nature of ligand–acceptor binding in proteins. A linear plot indicates that sites are equivalent and the Langmuir equation applies whilst deviation from linearity shows that adsorption occurs by more than one type of binding site over the concentration range used.

State of the Dyes in Fibre and Dyebath Although the molecular state of disperse dyes in both the fibre and aqueous phases has received interest, its precise nature remains unresolved. In this context, as Jones [201] points out, since disperse dyes are mostly of very low aqueous solubility, even under HT dyeing temperatures, experimental difficulties arise in determining whether disperse dyes are monomolecularly dispersed or comprise aggregates (e.g. [202]). Nonetheless, Schuler and Remington [176] concluded from the linearity of the Nernst sorption isotherms obtained for disperse dyes on PES fibres that the dye was monomolecularly dispersed in both the solution and fibre phases, a view supported by Hoffman and Lauritzen [203], whilst Merian [204] considered that monomolecular dye is present in the fibre. However, other workers consider that the dyes are adsorbed initially in monomolecular form but, subsequently, partially aggregate [205] or undergo a change in intermolecular interactions with the substrate [206]. McDowell and Weingarten [202] suggest that some dyes may associate in solution whereas Giles [207–209] consider that although a proportion of adsorbed dye in hydrophobic fibres is monodisperse, the remainder is in the form of small aggregates.

From the discussion of dye aggregation in solution and in the fibre in Chapter 3, it seems unlikely that disperse dyes do not aggregate in both solution and fibre phases, although the presence of dispersing agents as well as levelling agents may reduce the propensity for the dyes to aggregate in the aqueous dyebath phase.

Dye–Fibre Substantivity A discussion [13] of the findings of several workers [147, 176, 179, 187, 210, 211] concluded that as with all dye types on all fibre types, the substantivity of disperse dyes towards PES fibres can be attributed to a variety of intermolecular forces and that H-bonding predominates, though van der Waals forces also contribute. As with other classes of dye, relatively small differences in the structure of a disperse dye can have marked effects on dye–fibre substantivity. Several authors have sought to correlate dye structure to dyeing behaviour using solubility parameter concept. As discussed in Chapter 5, the solubility parameters for various disperse dyes have been determined and, whilst the results obtained provide some information on dye–fibre interaction, the subject requires further investigation.

Temperature As mentioned, because of the low rate of diffusion of disperse dyes in PES fibres at temperatures upto 98 C, commercially acceptable rates of dyeing can be achieved either by the use of carriers at the commercial boil or by the use of high temperatures in the region 130–140 C. HT dyeing currently dominates the exhaust application of disperse dyes to PES fibres, the high pressure (1.2–1.3 bar) dyeing process having been developed shortly after the commercial introduction of the fibres [217, 258–266]. Compared to carrier dyeing at the commercial boil, HT dyeing offers advantages such as greater migration, higher depths of shade, superior fastness, shorter dyeing times and better build-up (Figure 8.27).

Both the rate and extent of dye exhaustion increase with increasing temperature above 98 C (Figures 8.28 and 8.29). The observed enhancement of both the rate and extent of dye uptake as well as improved migration secured under HT conditions can be attributed not only to the higher kinetic energy of the dye molecules coupled with the greater segmental mobility of the polymer chains in the substrate but also increased dye solubility, the latter feature having been demonstrated by the finding that the aqueous solubility of several disperse increased markedly, in some cases by a factor of 30, over the range 80–130 C [159].

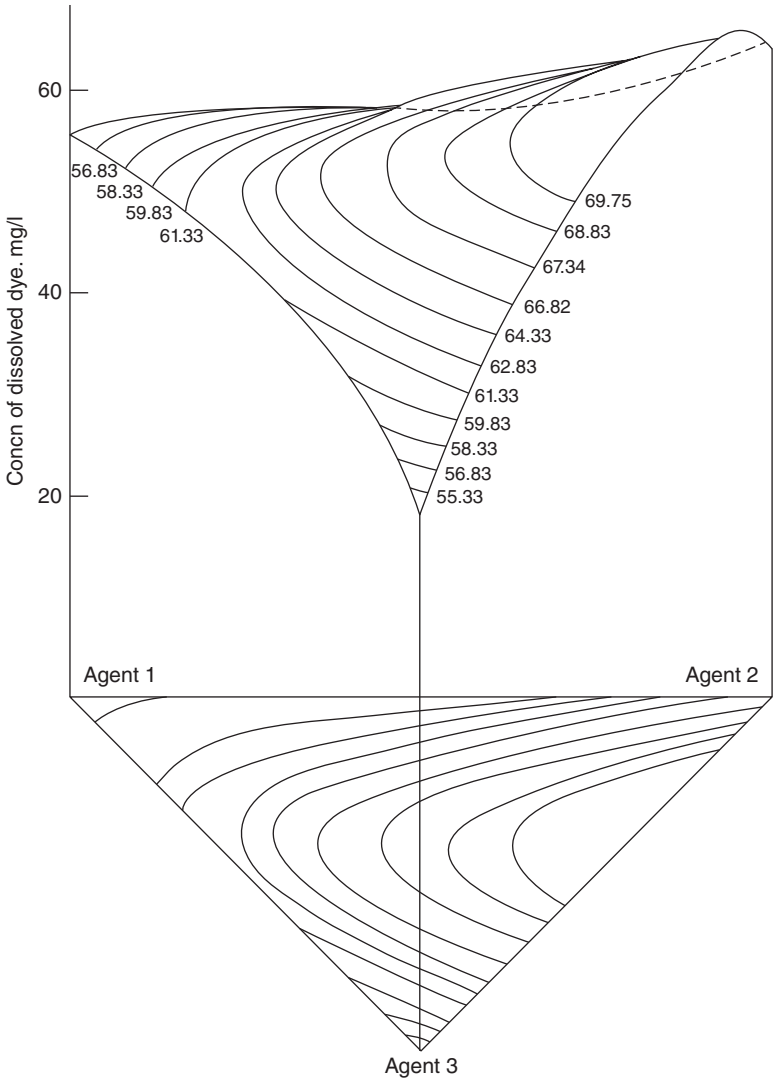

Figure 8.26 Solubilisation of C.I. Disperse Orange 21 in a mixture of three dispersing agents at 130°C. Reproduced from [250], copyright of the Society of Dyers and Colourists.

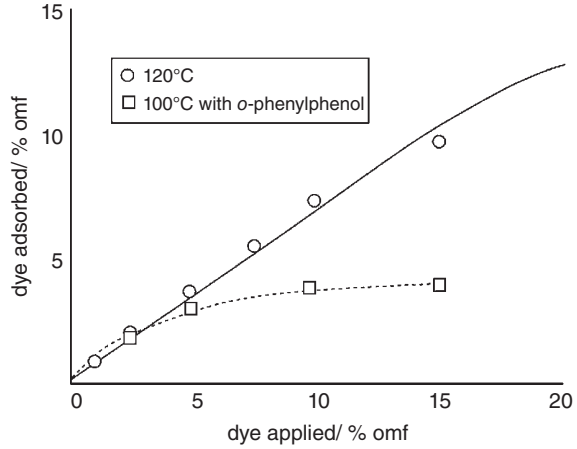

Figure 8.27 Build-up of C.I. Disperse Orange 13 on PES under HT and carrier dyeing conditions. Reproduced from [266], copyright of the Society of Dyers and Colourists.

As such increases often occur over a particular, small range of temperature (~30°C) that is commonly referred to as the *critical temperature range*, a test method has been devised to determine the time-, temperature- and concentration-dependence of disperse dye uptake on PES fibres [164].

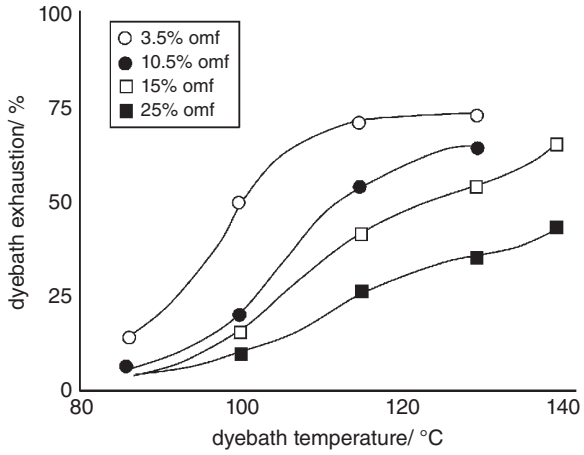

Figure 8.28 Effect of dyebath temperature on exhaustion of C.I. Disperse Orange 3. Reproduced from [267], copyright of the Society of Dyers and Colourists.

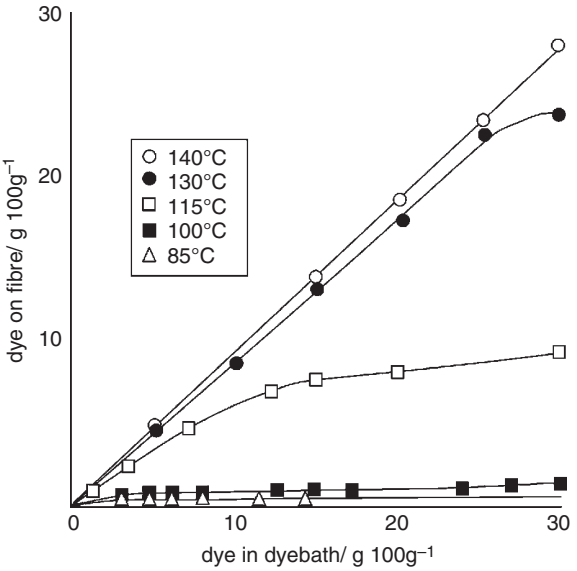

Figure 8.29 Effect of temperature on build-up of C.I. Disperse Orange 13 on PES. Reproduced from [267], copyright of the Society of Dyers and Colourists.

In the case of the adsorption of a disperse dyes onto PES (or other fibre type), the standard affinity of the dye for the substrate at a given temperature, T, is given by Eq. 8.4 where K is the partition coefficient and R the gas constant.

$$-\Delta\mu^{o} = RT\ln K \tag{8.4}$$

Schuler and Remington [176] observed that in the case of purified C.I. Disperse Red 15 on PES fibres, K (the gradient of the linear adsorption isotherm) decreased whilst the saturation value of the dye in the fibre increased with increasing temperature (Figure 8.30). Identical findings have been obtained for the uptake of other disperse dyes on, for example, CA fibres [186, 268].

From Eq. 8.4 it follows that as K increases with increasing temperature then the affinity of the dye decreases with increasing temperature, as with all dye–fibre systems owing to the exothermic nature of dye adsorption. Schuler and Remington found that the heat of dyeing, ΔH^{o}, of C.I. Disperse Red 15 on PES was −61.7 kJ mol^{-1} [176]. As standard affinity involves both the standard entropy (ΔS^{o}) and standard heat (ΔH^{o}) of dyeing (Eq. 8.5), the combination of Eqs. 8.4 and 8.5 gives Eq. 8.6 which simplifies to Eq. 8.7.

$$\Delta\mu^{o} = \Delta H^{o} - T\Delta S^{o} \tag{8.5}$$

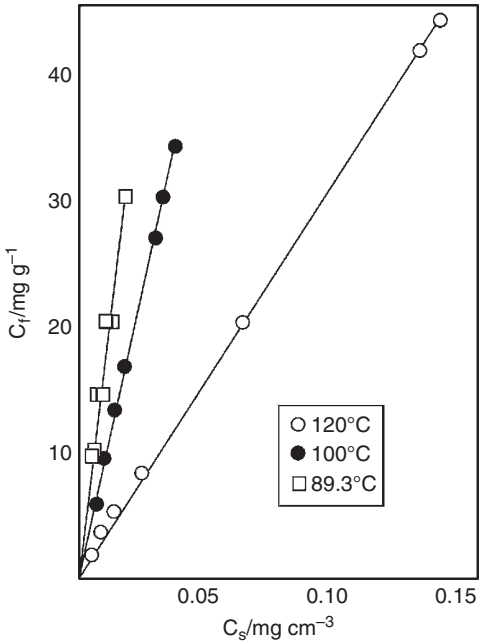

Figure 8.30 Effect of temperature on distribution of purified C.I. Disperse Red 15 on PES. Reproduced from [176], with permission from the Royal Society of Chemistry.

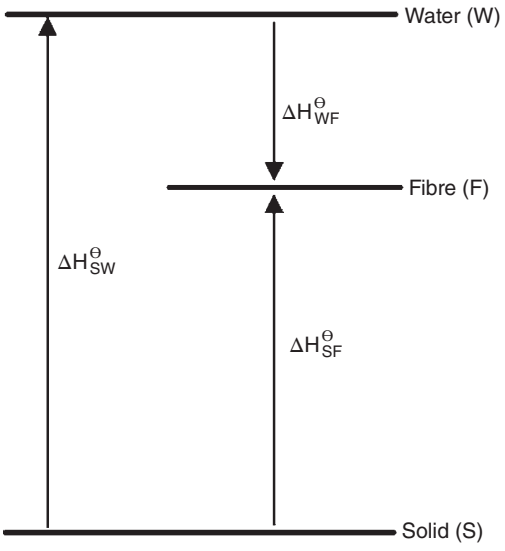

Figure 8.31 Enthalpy diagram after Majury [179].

$$\ln K = -\left(\frac{\Delta H^{o}}{R}\right).\left(\frac{1}{T}\right) + \frac{\Delta S^{o}}{R} \tag{8.6}$$

$$\ln K = -\left(\frac{\Delta H^{o}}{RT}\right) + \frac{\Delta S^{o}}{R} \tag{8.7}$$

Thus, as T increases, the term $(\Delta H^{o}/RT)$ approaches zero and, therefore, K becomes more determined by the entropy change (through the term $\Delta S^{o}/R$) that occurs upon dye adsorption. Since dye adsorption onto the fibre from solution involves a loss in entropy (disorder) for the dye molecule, the adsorption of dye is a less favoured process than is the desorption of dye into solution and, therefore, both the partition coefficient, K, and the standard affinity of the dye, $-\Delta\mu^{o}$, decrease with increasing temperature. The adsorption of disperse dyes has indeed been shown to be accompanied by a negative entropy change (e.g. [184, 269]).

The effect of temperature on dye adsorption has been interpreted in terms of the enthalpies of the various processes involved in dye adsorption, as first proposed by Majury [179] in a study of the dyeing of CA fibres with model disperse compounds. Accordingly, three enthalpic parameters are involved (Figure 8.31) and are as follows:

(1) the standard heat of dissolution of the solid dye in water, $\Delta H_{SW}{}^{o}$;
(2) the standard heat of dyeing, $\Delta H_{WF}{}^{o}$;
(3) the standard heat of dissolution of the solid dye in the fibre, $\Delta H_{SF}{}^{o}$.

In the case of the adsorption of several disperse dyes onto CA fibres, Bird and Harris [269] showed that the dissolution of the dyes in water was an endothermic process (i.e. $\Delta H_{SW}{}^{o}$ was positive) but this heat was regained when the dye was transferred from solution to the fibre (i.e. $\Delta H_{WF}{}^{o}$ was negative) and transfer of the solid dye to the dry fibre was also endothermic (i.e. $\Delta H_{SF}{}^{o}$ was positive). Since $\Delta H_{SW}{}^{o}$ was positive, dissolution of the dye in water increases with increasing temperature, as recorded in other studies of disperse dyeing [156, 157]. Also, as ΔH^{o}_{SF} is positive, then dissolution of the solid dye in the fibre will increase with increasing temperature. The absolute values of these enthalpy changes were observed to follow the order: $\Delta H_{SF}{}^{o} < \Delta H_{WF}{}^{o} < \Delta H_{SW}{}^{o}$ [176, 269]. Since $\Delta H_{SW}{}^{o} > \Delta H_{SF}{}^{o}$, the partition coefficient, K, will decrease with increasing temperature. Furthermore, since the transfer of dye from solution to the fibre, $\Delta H_{WF}{}^{o}$, was negative, this process (i.e. dye adsorption) should also decrease with increasing temperature. Thus, these two latter outcomes explain the observed reduction in partition coefficient, K, that accompany an increase in dyeing temperature (Figure 8.30 and [176, 186, 268]). Bird and Harris [269] further demonstrated the significance of dye solubility on disperse dye adsorption by the correlation that was observed between dye solubility and partition coefficient (Figure 8.32).

The findings (Figure 8.30 and [186, 268]) that the saturation values for disperse dye uptake increase with increasing temperature can be attributed to the endothermic nature of both the $\Delta H_{SW}{}^{o}$ and $\Delta H_{SF}{}^{o}$ processes (i.e. dye dissolution in the water and fibre phases, respectively) which means that both D_s and D_f will increase with increasing temperature.