11.5.3 Thermodynamics of Dyeing

In essence, the dyeing of PAN fibres with cationic dyes occurs by means of an *ion-exchange mechanism* which has been interpreted using both Langmuir isotherm and Donnan equilibrium models. In the former approach, the anionic dye sites in the fibre are assumed to be identical, and the effects of pH and electrolytes on dyeing are considered in totality. To explain dye adsorption in excess of the number of anionic dye sites in the fibre (i.e. overdyeing), a constant partition (Nernst) mechanism is superimposed on the Langmuir model. The Donnan equilibrium model distinguishes between weakly and strongly anionic dye sites and considers the influence of all dyebath components (protons, inorganic cations, anions, etc.) separately.

Although the dyeing of PAN fibres with basic dyes and other dye classes such as vat dyes, azoic colorants and disperse dyes was discussed soon after the fibre's commercial introduction (e.g. [90–93]), systematic investigations of the mechanism of the interaction of cationic dyes with PAN fibres were undertaken only when dyes of adequate light fastness had been developed [94]. These studies revealed that the cationic dyes associate with anionic (i.e. acidic) sites within the substrate (e.g. [94–97]), and Laucius *et al.* [95] proposed a *saturation value* for such dye sites. In the latter context, Glenz and Beckmann [96] correlated equilibrium cationic dye uptake with anionic site content of the fibre, showing that several basic dyes on PAN fibre displayed *equilibrium saturation values* of $\sim$37 mmol kg^{-1} at 80–100°C. Vogel *et al.* [98] recorded a saturation value of 31–32 mmol kg^{-1} and also found that maximum dye uptake corresponded to the sulfur content (0.09%) of the fibre, proposing that the sites were either sulfonate or sulfate groups located either within the polymer chains or at chain ends. Both the number and nature of the anionic sites within PAN fibres varies between different types of commercial fibre as shown by the data presented in Table 11.1.

The equilibrium adsorption of various cationic dyes on PAN fibres conforms to the Langmuir isotherm model (e.g. [25, 96, 98, 100–104]) such as that presented in Figure 11.3.

The adherence of equilibrium dye sorption to a Langmuir mechanism is demonstrated by plots of the reciprocal of dye concentration in the fibre versus that in the dyebath [25, 100] as illustrated by those shown in Figure 11.4.

Table 11.1 Acidic group content of PAN fibres [99].

	acid group content/ m eq g^{-1}	
fibre	strongly acid	weakly acid
Acrilan 16 (Chemstrand)	31	21
Orlon 42 (Du Pont)	46	17
Dralon (FBy)	48	53
Beslon (Toyo)	70	44
Courtelle E (Courtaulds)	0	154
Acribel (Fabelta)	28	30

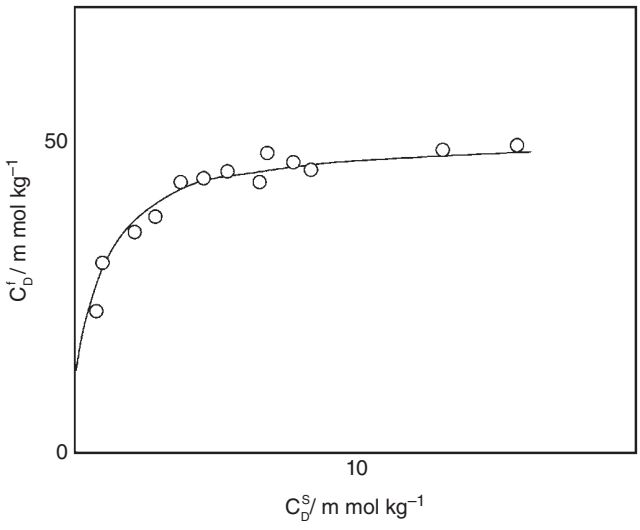

Figure 11.3 Sorption of C.I. Basic Blue 3 on *Dralon X-100* at 98.5°C. Reproduced from [101], with permission from SAGE.

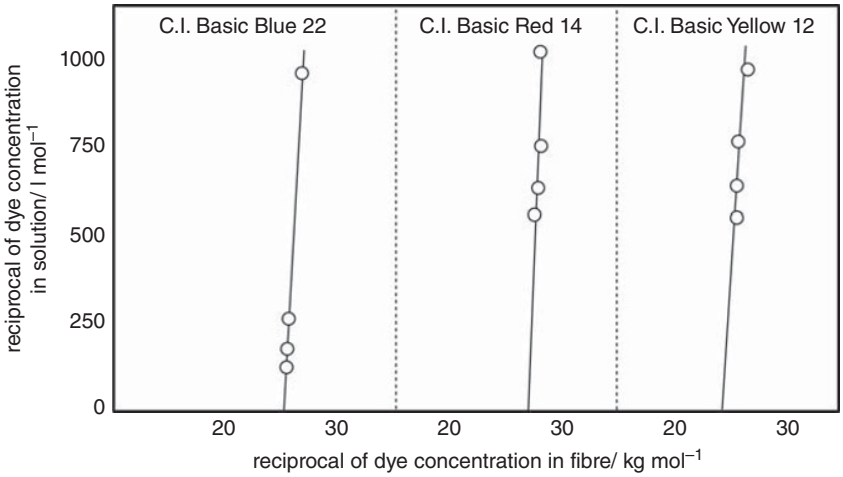

Figure 11.4 Reciprocal plots of Langmuir sorption of basic dyes on PAN. Reproduced from [25], copyright of the Society of Dyers and Colourists.

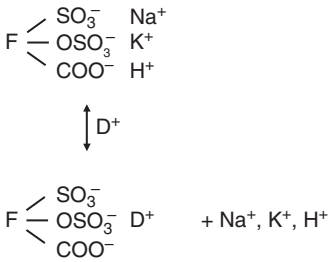

Figure 11.5 Ion-exchange mechanism.

Remington and Schroeder [97] reported that the acidic sites in the PAN fibres were introduced during polymerisation and suggested in the case of undyed PAN fibre, that colourless cations are associated with the anionic sites and, during dyeing, these colourless cations are replaced by coloured cations (i.e. basic dye molecules). According to this theory, the fibre is assumed to act as an *ion-exchange medium*, and dyeing can be described as an *ion-exchange mechanism*, Figure 11.5, wherein the dye cation, D^+, exchanges with colourless cations (H^+, K^+ or Na^+) that are associated with the acidic sites $\left(-SO_3^-, -OSO_3^-, -COO^-\right)$ in the fibre, *F*. This ion-exchange mechanism has been confirmed by several workers (e.g. [23, 25, 100, 105]).

According to Cegarra [23], the dye must be dissociated in order for it to interact with the fibre, the number of dye sites available for ion exchange depending on both the number of acidic groups and the extent of their dissociation and accessibility to dye cations; also, dye uptake will be affected by factors that influence the degree of ionisation of both the dye and fibre. The sorption of cationic dyes by PAN fibres can be interpreted in terms of the previous ion-exchange mechanism (Figure 11.5) on the basis of a Langmuir adsorption model (e.g. [25, 100, 104, 106, 107]; see [108] for a review of the various approaches). The treatment presented in the following text is based on that of Peters [107] and Sumner [106].

The ion-exchange equilibrium can be expressed as Eq. 11.1 [100] since it involves the exchange of the dye cation, D^+, with the cation, C^+, associated with the acidic group, $-SO_3^-$, in the fibre, *F*, which for simplicity, will be taken as a proton, H^+:

$$F{-}SO_3C + D^+ \rightleftarrows F - SO_3D + C^+ \tag{11.1}$$

The corresponding equilibrium *exchange constant*, K_H^D, is given by Eq. 11.2 (in the term K_H^D, the upper symbol depicts that the cation D^+ replaces the proton H^+ in the fibre). $[D^+]_f$ and $[H^+]_f$ are the quantities of dye cations and protons in the fibre (units: mol kg^{-1}) and $[D^+]_s$ and $[H^+]_s$ the corresponding amounts (units: mol l^{-1}) of dye cations and protons, respectively, in solution. For simplicity, activity coefficients are assumed equal to unity in both the fibre and solution phases:

$$K_H^D = \frac{[H^+]_s[D^+]_f}{[D^+]_s[H^+]_f} \tag{11.2}$$

Since the fibre must be electrically neutral, then Eq. 11.3 applies where $[S]_f$ is the number of available acidic sites in the fibre:

$$[S]_f = [H^+]_f + [D^+]_f \tag{11.3}$$

Substituting 11.3 into 11.2 gives the Langmuir isotherm in the form of Eq. 11.4 or in the Scatchard form, Eq. 11.5, assuming that pH remains constant during dyeing:

$$\frac{[D^+]_f}{\left([S]_f - [D^+]_f\right)} = \frac{K_H^D}{[H^+]_s}[D^+]_s \tag{11.4}$$

$$\frac{[D^+]_f}{[D^+]_s} = \frac{K_H^D}{[H^+]_s}\left([S]_f - [D^+]_f\right) \tag{11.5}$$

Assuming that the pH of the dyebath is constant (i.e. $[H^+]_s$ = constant), then Eq. 11.4 can be rearranged to give Eq. 11.6 from which it follows that a plot of $1/[D^+]_f$ versus $1/[D^+]_s$ at constant pH should yield a straight line of intercept $1/[S]_f$ on the abscissa, this having been obtained for several types of PAN fibre [25] (Figure 11.4), the saturation values of the fibres agreeing with the number of acidic groups present in the substrates as determined from titration:

$$\frac{1}{[D^+]_f} = \frac{1}{[S]_f} + \frac{1}{\frac{K_H^D}{[H^+]_s}[S]_f} \cdot \frac{1}{[D^+]_s} \tag{11.6}$$

Rosenbaum extended this analysis to explain the effects of competition between the dye cations and cations such as Na^+ ions, for which, in the case of no other ions exerting an influence, electrical neutrality is given by Eq. 11.7:

$$[S]_f = [H^+]_f + [D^+]_f + [Na^+]_f \tag{11.7}$$

Two ion-exchange constants can be defined (Eqs. 11.8 and 11.9) and the corresponding sorption isotherms described by Eq. 11.10, the exchange constants in Eqs. 11.8 and 11.9 being the reciprocal form of that given in Eq. 11.2:

$$K_D^H = \frac{[H^+]_f[D^+]_s}{[D^+]_f[H^+]_s} \tag{11.8}$$

$$K_D^{Na} = \frac{[Na^+]_f[D^+]_s}{[D^+]_f[Na^+]_s} \tag{11.9}$$

Thus, inserting the values for $[H^+]_f$ and $[Na^+]_f$ from Eq. 11.7 into Eqs. 11.8 and 11.9 gives Eq. 11.10:

$$[S]_f - [D^+]_f = \frac{[D^+]_f}{[D^+]_s}\left(K_D^H[H^+]_s + K_D^{Na}[Na^+]_s\right) \tag{11.10}$$

Rearranging Eq. 11.10 gives Eq. 11.11 which can be rearranged to provide Eq. 11.12 according to which when $1/[D^+]_f$ is plotted against $1/[D^+]_s$ with $[H^+]_s$ and $[Na^+]_s$ constant, a straight line should result, whose slope varies with pH and electrolyte concentration, as has been observed [100]:

$$\frac{1}{K_M} = \left([S]_f - [D^+]_f\right) \cdot \frac{[D^+]_s}{[D^+]_f} = K_D^H[H^+]_s + K_D^{Na}[Na^+]_s \tag{11.11}$$

$$\frac{1}{[D^+]_f} = \frac{1}{[S]_f K_M} \cdot \frac{1}{[D^+]_s} + \frac{1}{[S]_f} \tag{11.12}$$

According to Eq. 11.5, in the absence of Na^+ ions, if the partition coefficient (i.e. $[D^+]_f/[D^+]_s$) is plotted versus $1/[D^+]_f$, then a straight line of slope $K_H^D/[H^+]_s$ should be obtained with an intercept of $[S]_f$ on the abscissa. Such a linear relationship was observed in the cases of five cationic dyes applied to PAN film at pH 3.4 (Figure 11.6).

However, linearity was observed for only ~80% of the dye concentration range employed and, at high dye concentrations, a tail developed which implied that dye was being adsorbed in excess of the number of acidic sites in the PAN film [104]. Although extrapolation of the linear portion of the plots provided a consistent value for $[S]_f$

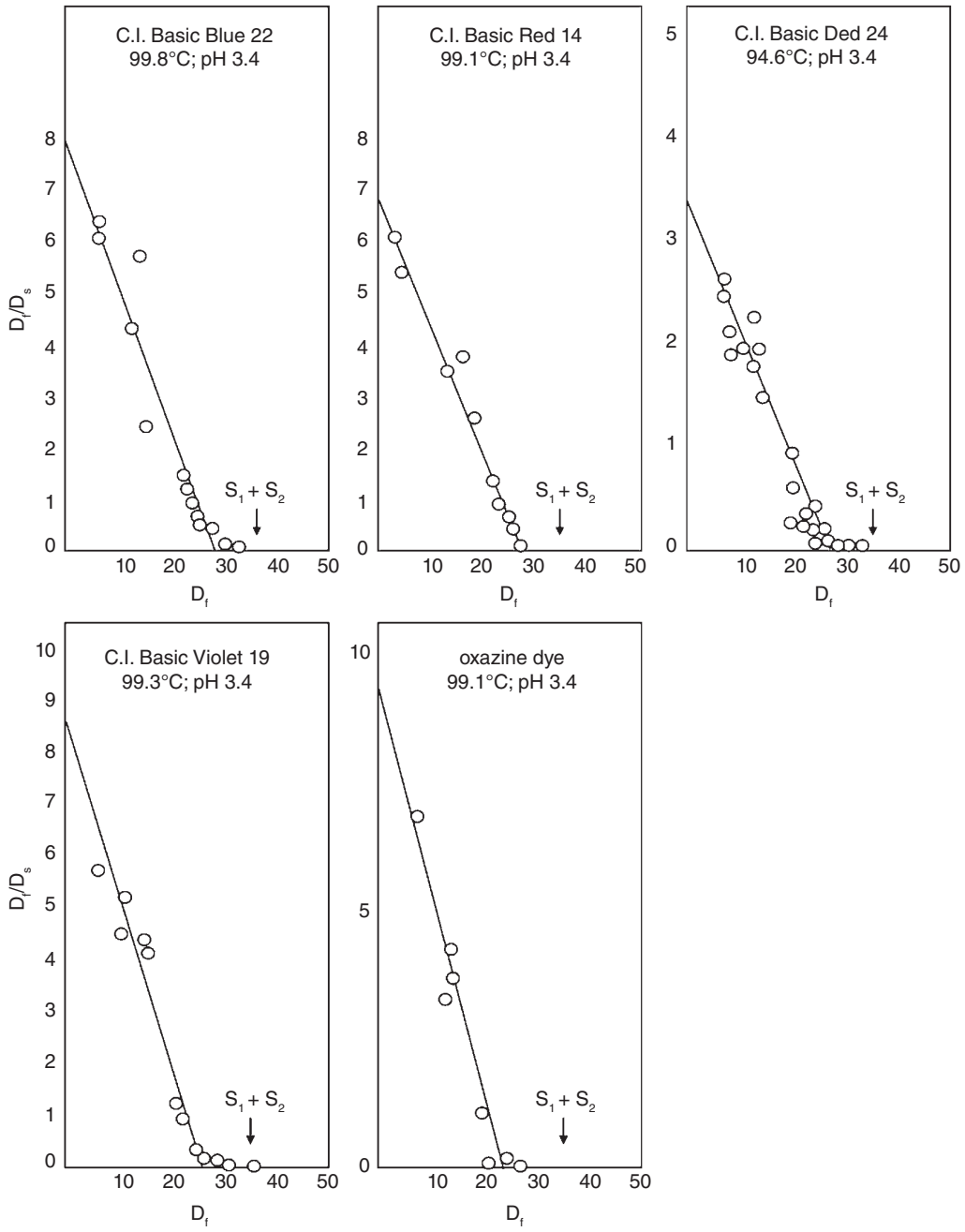

Figure 11.6 Langmuir plots of dye adsorption isotherms. Reproduced from [104], copyright of the Society of Dyers and Colourists.

of 26–28 mmol kg^{-1}, this was lower than the 35.1 mmol kg^{-1} value obtained by titration. Since the amount of sulfonate groups in the PAN film was ~80% of the total strongly acidic group content and corresponded to 28 mmol kg^{-1}, it was proposed that the dyeing may involve two types of acidic group in the substrate, namely, sulfonate groups and sulfate groups, denoted by S_1 and S_2, respectively (Figure 11.6), and that $(S_1 + S_2) = 35.1$ mmol kg^{-1}. An isotherm was defined (Eq. 11.13) to describe this adsorption process which fitted the data of dyes which presented this particular behaviour [104] where $[S]_1$ and $[S]_2$ are the amounts of the two types of acidic group in the substrate and K_1 and K_2 the exchange constants for the two types of group:

$$[D^+]_f = \frac{K_1[S]_1[D^+]_s}{1 + K_1[D^+]_s} + \frac{K_2[S]_2[D^+]_s}{1 + K_2[D^+]_s} \tag{11.13}$$

As not all of the dyes examined conformed to this equation as dye uptake was not always equivalent to the quantity $(S_1 + S_2)$, the authors [104] considered that during the long dyeing times required to achieve dye equilibrium, the sulfate groups may have been hydrolysed, or the acidic groups were incompletely ionised at the pH used (i.e. pH 3.4). Thus,

the value of S_1 was considered to relate to the number of accessible, ionised, acidic groups present at this particular pH. The observed dye uptake in excess of the acidic group content of the PAN film (i.e. *overdyeing*) may be attributed to interactions other than ion–ion operating between the cationic dyes and anionic sites in the fibre, as proposed for the dyeing of PA fibres with some anionic dyes. In this context, Harwood *et al.* [104] proposed that a dual-mode sorption mechanism may be operative that involves both a Langmuir *adsorption at sites* process and a constant partition (Nernst) *solution in the fibre* process, which led to the relationship presented in Eq. 11.14, which was found to provide a good fit to the experimental data:

$$[D^+]_f = \frac{K_1[D^+]_s}{1 + K_1[D^+]_s} \cdot [S]_f + K_3[D^+]_s \tag{11.14}$$

Such a dual-mode sorption mechanism had been proposed earlier by Glenz and Beckmann [94, 96] who reported a Langmuir isotherm on which was superimposed a constant partition (Nernst) solution mechanism:

$$\frac{[D^+]_f}{([S]_f - [D^+]_f)} = K^D_{Na}[D^+]_s \tag{11.15}$$

Guion and McGregor [109] found that Eq. 11.15 did not fit well the equilibrium sorption data obtained for C.I. Basic Blue 22 on PAN filaments, as the exchange constant, K^D_{Na}, varied with increasing $[D^+]_f$, and also, it was observed that at high values of $[Na^+]_s$, Cl^- ions were sorbed by the fibre to a small but nonetheless significant extent. These workers concluded that that the dye cations could exchange not only with strongly acidic groups in the substrate (i.e. $-SO_3^-$ and OSO_3^-) but also that weakly acidic groups were involved in dyeing and that the sorption of dye cations initiated the dissociation of the weakly acidic groups.

Harwood *et al.* [104] applied a Donnan approach, developed by McGregor and Harris [110], to describe equilibrium sorption (Eq. 11.16) according to which, assuming that the fibre is electrically neutral, the concentration of a particular ion, X, of charge z in the fibre is related via a distribution coefficient, K, to the ion's concentration in the internal solution phase, i, which, in turn, is related to the concentration of the ion in the external aqueous phase, s, by a Donnan coefficient, λ:

$$[X]_i = \lambda^z K[X]_s \tag{11.16}$$

The distribution equation, Eq. 11.16, applies to all ions (i.e. D^+, Na^+, H^+, OH^- and Cl^-) as shown in Eqs. 11.17, 11.18, 11.19, 11.20 and 11.21:

$$[D^+]_i = \left(\frac{1}{\lambda}\right) K_D[D^+]_s \tag{11.17}$$

$$[Na^+]_i = \lambda K_{Na}[Na^+]_s \tag{11.18}$$

$$[H^+]_i = \lambda K_H[H^+]_s \tag{11.19}$$

$$[OH^-]_i = \left(\frac{1}{\lambda}\right) K_{OH}[OH^-]_s \tag{11.20}$$

$$[Cl^-]_i = \left(\frac{1}{\lambda}\right) K_{Cl}[Cl^-]_s \tag{11.21}$$

The distribution equations can be combined such as in Eq. 11.22, the resulting exchange coefficient, K^D_H, not requiring the assumption of an ion-exchange mechanism:

$$\frac{K_D}{K_H} = K^D_H = \frac{[D^+]_f [H^+]_s}{[D^+]_s [H^+]_f} \tag{11.22}$$

Since for electrical neutrality Eq. 11.23 applies, where S^- is the concentration of ionised acidic sites in the fibre, then Eq. 11.24 describes the sorption isotherm for proton exchange which shows that the presence of the anions OH^- and Cl^- increases the saturation value and can therefore result in the overdyeing depicted in Figure 11.6 [104, 107]:

$$[D^+]_f + [H^+]_f + [Na^+]_f = [S^-]_f + [OH^-]_f + [Cl^-]_f \tag{11.23}$$

$$\frac{[D]_f}{[S^-]_f + [Cl^-]_f + [OH^-]_f - [Na^+]_f - [D^+]_f} = K_H^D \frac{[D^+]_s}{[H^+]_s} \tag{11.24}$$

McGregor and Harris' general model [110] to describe ion sorption on fibres that contain polarisable groups has been applied to the sorption of cationic dyes on PAN fibres by other workers (e.g. [101, 108, 111–115]). For example, a Donnan approach was found [113] to give a reasonable description of the equilibrium sorption of 10 cationic dyes on the assumption that the fibres contained two types of ionisable acidic group, namely, strongly acidic sulfonic and sulfato as well as weakly acidic carboxylic acid groups. Subsequently, the equilibrium sorption of two cationic dyes by PAN fibres at different values of pH and amounts of NaCl were interpreted using a Donnan approach, again assuming that fibres contained two different types of acidic group [115]. Yang and Ladisch [116] reported that the dye distribution coefficient employed in the Donnan model cannot be treated as a constant, as it changes with the type and concentration of electrolyte used, because it is a function of chemical potential change owing to hydrophobic interaction.