9.3.1.1 Thermodynamics of Dyeing

As mentioned, owing to the presence of amino end groups within the substrate, acid dyes, direct dyes, mordant dyes and reactive dyes are substantive towards PA fibres. In terms of the mechanism by which such dyes are adsorbed onto PA fibres, as the application conditions used for these four types of anionic dye on PA fibres are generally similar insofar as exhaustion is undertaken under acidic or slightly alkaline pH conditions, to a first approximation, the following account of the thermodynamics of the adsorption of non-metallised acid dyes on PA fibres can be assumed to apply to the other three classes of anionic dye.

The adsorption of dye anions onto PA substrates has been interpreted in terms of the adsorption of simple acids and alkalis, obtained in the form of *titration curves*. This approach is analogous to that employed for wool fibres (Chapter 10), which is not surprising in view of the chemical resemblance between PA fibres and protein fibres, notably the presence of both amino and carboxyl groups. Two approaches have been used to analyse the data obtained from titration curves, namely a *specific site* (Langmuir) model first proposed by Gilbert and Rideal in 1944 and various *ion-exchange* models based on modifications of a Donnan membrane theory originally proposed by Peters and Speakman in 1949, again in a manner analogous to that of wool, although the approach adopted for the two types of fibre are slightly different because PA fibres contain an excess of carboxyl groups whereas wool contains an equal amount of amino and carboxyl groups. The principles involved in both the Langmuir and Donnan models are discussed in Chapter 10.

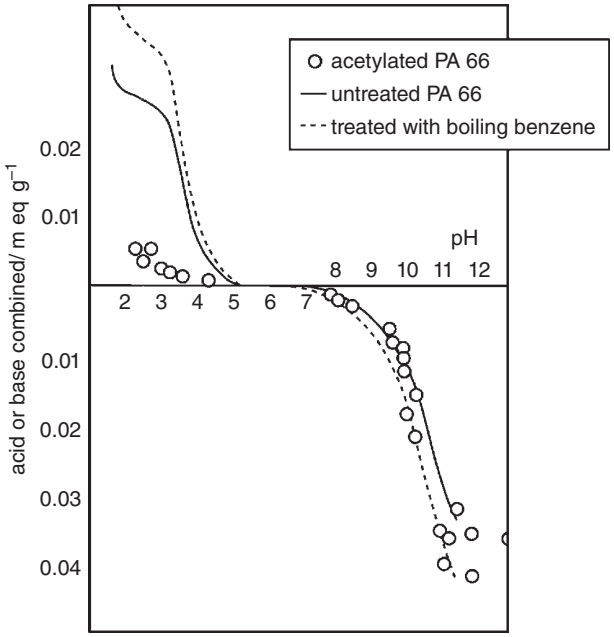

Figure 9.19 Titration curve of PA 66 with HCl and NaOH at 21.5°C (figure 10 on page 2023 of reference [219]). Reproduced from [219], with permission from John Wiley & Sons, Inc.

9.3.1.1.1 Titration Curves The interaction of PA fibres with acids and bases has been a subject of extensive study, the first qualitative investigation having been made by Elod and Schachowsky [216] in 1942. Subsequently, several workers studied the adsorption of various simple acids (e.g. HCl and H_2SO_4 [216–221]) as well as that of more complex acids [219, 220] and NaOH [219, 222]. In the case of HCl and NaOH, the work of Mathieson *et al.* [219] in the case of PA 66 fibre is especially illustrative.

These workers showed that the titration curve of PA 66 with HCl and NaOH (Figure 9.19) comprises two distinct regions, namely one below pH 6 that corresponds to acid adsorption and one above pH 7 that corresponds to the adsorption of alkali, the inflection at pH 6–7 corresponding to the *isoelectric point*[16] of the fibre. Within the acidic region, the titration curve displays an inflection at low pH values (around pH 2–3) that corresponds, approximately, to the AEG content of the fibre. Below pH 2, acid uptake increases, without limit, which has been attributed to adsorption of the acid onto chain amide groups (i.e. ─CONH─) [217–220, 223]. Within the alkaline region, the titration curve exhibits an inflection at ∼pH 12–13, which can be attributed to maximum alkali combination with the carboxyl groups in the fibre.

In terms of the mechanism of acid and alkali adsorption by PA fibres, it is generally considered that at its isoelectric point, PA fibres exist in the zwitterion[17] form (**X**), although because PA fibres typically contain more ─COOH groups than ─NH_2 groups (Table 9.1), the excess carboxyl groups will be undissociated at the isoelectric point and therefore the number of ─COO^- groups present is determined by the number of ─NH_2 groups in the fibre. As acid is added to the isoelectric fibre, (**X**), protons are adsorbed onto the ionised carboxyl groups and the fibre develops a positive charge (**XI**) owing to the protonated amino end groups. Such a process will continue until all the ionised carboxyl groups have been 'back titrated'. The amount of acid adsorbed should therefore be equal to the number of amino end groups in the substrate, and thus acid adsorption should reach a limit. However, as Figure 9.19 clearly shows, at low pH values, acid adsorption does not reach a finite level, but rather continues to increase with decreasing pH [216–219, 224], this having been ascribed to adsorption of protons onto chain amide groups (**XII**) that results in protonation of the amide group (**XIII**).

$$\underset{\textbf{X}}{H_3N^+\text{-nylon-}COO^-} \overset{H^+}{\rightleftharpoons} \underset{\textbf{XI}}{H_3N^+\text{-nylon-COOH}}$$

$$\underset{\textbf{XII}}{\text{-NHCO-}} \overset{H^+}{\rightleftharpoons} \underset{\textbf{XIII}}{\text{-}NH_2{}^+CO\text{-}}$$

[16] the isoelectric point is sometimes abbreviated as *IEP* and the pH at which the parameter occurs is denoted by *pH(I)*, although *pI* is also employed.
[17] see Chapter 5 for a definition.

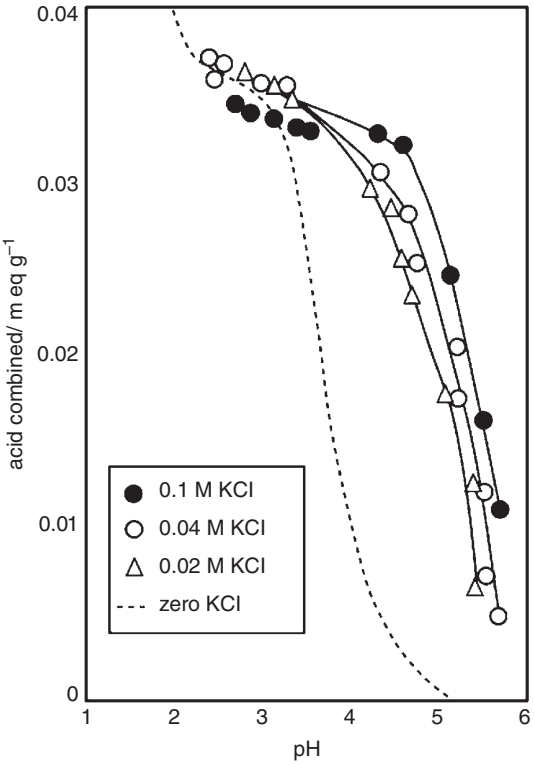

Figure 9.20 Titration curve of PA 66 with HCl at 21.5°C in the presence of KCl. Reproduced from [219], with permission from John Wiley & Sons, Inc.

In the case of the titration of PA fibre with alkali, protons can be removed from the undissociated carboxyl groups (**XIV**) [178, 219, 222]. When all such undissociated carboxyl groups have been ionised, protons are then removed from the protonated AEG in the zwitterion (**XV**) with the result that the fibre carries an overall negative charge (**XVI**). The amount of alkali adsorbed corresponds to the total —COOH group content of the fibre.

$$\underset{\textbf{XIV}}{H_3N^+\text{-nylon-COOH}} \overset{OH^-}{\rightleftharpoons} \underset{\textbf{XV}}{H_3N^+\text{-nylon-COO}^-} + H_2O \overset{OH^-}{\rightleftharpoons} \underset{\textbf{XVI}}{H_2N\text{-nylon-COO}^-} + H_2O$$

The dependence of acid adsorption on the amino end groups was demonstrated by the finding that PA 66 fibres in which most of the —NH_2 end groups had been acetylated displayed much reduced acid uptake (Figure 9.19).

Mathieson *et al.* [219] demonstrated that the addition of electrolyte (KCl) shifted the titration curve to higher pH values (i.e. HCl adsorption at a given pH increased) (Figure 9.20) whilst an increase in temperature slightly reduced the amount of acid adsorbed.

In the case of the titration of PA 66 with more complex acids (Figure 9.21), the curves shift to higher pH values as the size of the anion increases.

The affinity of three such acids (calculated at the pH corresponding to 50% acid adsorption) relative to that of HCl is shown in Table 9.6; as the affinities of the three acids are higher on PA 66, adsorption occurs at higher pH values in the case of the polyamide substrate.

9.3.1.1.2 Analysis of Titration Curves As mentioned, the data obtained from titration curves such as those shown earlier have been interpreted using both a specific site (Langmuir) model (Gilbert–Rideal) as well as various models based on ion exchange (Donnan membrane equilibrium). The principles underlying these two approaches are discussed in Chapter 10. Excellent accounts of the analysis of the titration curves of PA fibres are available (e.g. [178, 217, 225–228]).

As previously recounted, the analysis of the acid titration curves obtained for PA fibres using the Gilbert–Rideal and Donnan approaches is analogous to that employed for wool fibres and reflects the similar chemical nature of PA fibres and protein fibres, notably the presence of both amino and carboxyl groups. However, PA contains far fewer amino groups than wool (Table 9.7), and also PA fibres contain an excess of carboxyl groups whereas wool contains an equal amount of amino and carboxyl groups.

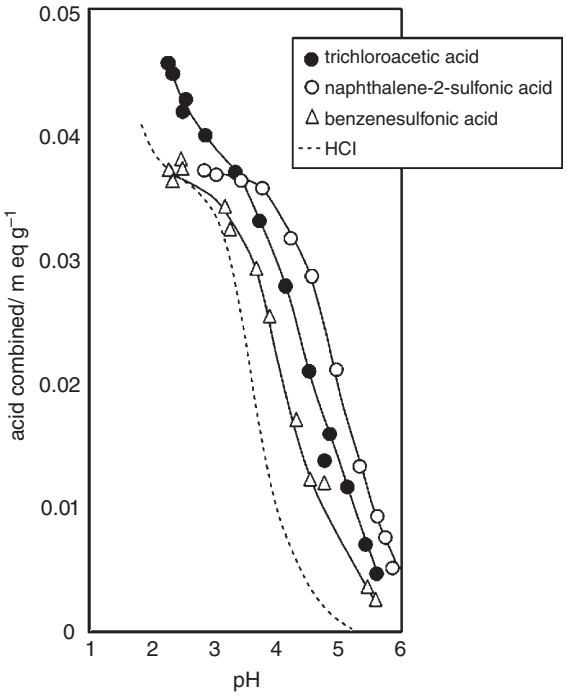

Figure 9.21 Titration curve of PA 66 with various strong acids at 21.5°C. Reproduced from [219], with permission from John Wiley & Sons, Inc.

Table 9.6 Affinity/kJ mol^{-1} at 20°C of various acids relative to HCl [178].

acid	PA 66	wool
Benzenesulfonic acid	9.6	3.4
Trichloroacetic acid	14.2	5.1
Naphthalene-2-sulfonic acid	17.9	10.3

Table 9.7 Amino end groups content of different fibres [229].

fibre	AEG/m eq kg^{-1}
Wool	800–900
Silk	120–200
PA	30–50

The similar behaviour of wool and PA fibres in terms of the dependency of anion affinity on relative anionic mass is shown in Figure 9.22 by the shift in pH required for half-saturation [230].

Gilbert and Rideal (Langmuir) and Peters and Speakman (Donnan) Models Because the adsorption of simple inorganic acids onto PA fibres is analogous, qualitatively, to that of their adsorption on wool, the equations relating to both the Gilbert and Rideal (Langmuir) and Peters and Speakman (Donnan) models discussed in Chapter 10 are applicable, although modifications are required because, as discussed earlier, unlike wool, PA fibres contain more ─COOH groups than ─NH_2 groups. Also, in a manner analogous to wool, discrepancies are observed between experimentally observed findings and theoretical predictions, which, as in the case of wool fibres, can be attributed both to the fibre not being ideally stable, as is assumed in the models and also, perhaps more importantly, to discrepancies that stem from the theoretical treatments themselves.

Excellent detailed accounts of this area are available [178, 217, 228]. Briefly, starting from Eq. 10.7, which was derived for the analysis of the acid titration curves obtained for wool (Chapter 10), in the case of the titration of PA with a monobasic acid, HX, following the approach adopted in Eq. 10.6, values for θ_H and θ_X are given by

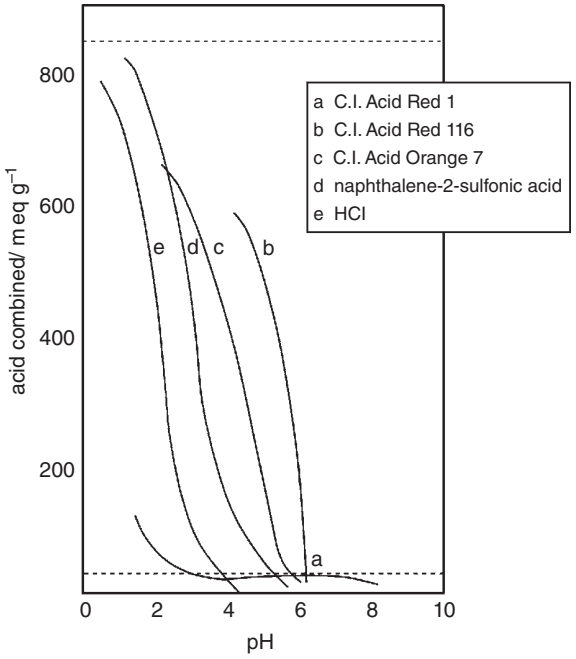

Figure 9.22 Acid titration curves for PA and wool fibres; dotted lines: respective free AEG content of wool (top) and PA (bottom). Reproduced from [230], copyright of the Society of Dyers and Colourists.

Eq. 9.1, where θ is the fractional occupation of sites in the substrate and C is the number of carboxyl groups in the fibre that for regular polyamides exceeds that of amino groups, A.

$$-\Delta\mu^{o} = RT\ln\left(\frac{\theta_{\mathrm{H}}}{1-\theta_{\mathrm{H}}}.\frac{\theta_{\mathrm{X}}}{1-\theta_{\mathrm{X}}}\right) - RT\ln\left([\mathrm{H}^{+}]_{\mathrm{s}}[\mathrm{X}^{-}]_{\mathrm{s}}\right) \tag{10.7}$$

$$\theta_{\mathrm{H}} = \frac{[\mathrm{H}^{+}]_{\mathrm{f}}}{\mathrm{C}} \quad \text{and} \quad \theta_{\mathrm{X}} = \frac{[\mathrm{X}^{-}]_{\mathrm{f}}}{\mathrm{A}} \tag{9.1}$$

Substituting the appropriate terms for θ_{H} and θ_{X} from Eq. 9.1 into Eq. 10.7 results in Eq. 9.2, which can be rewritten in the form of Eq. 9.3.

$$-\Delta\mu^{o} = RT\ln\frac{[\mathrm{H}^{+}]_{\mathrm{f}}}{\mathrm{C}-[\mathrm{H}^{+}]_{\mathrm{f}}}.\frac{[\mathrm{X}^{-}]_{\mathrm{f}}}{\mathrm{A}-[\mathrm{X}^{-}]_{\mathrm{f}}} - RT\ln\left([\mathrm{H}^{+}]_{\mathrm{s}}[\mathrm{X}^{-}]_{\mathrm{s}}\right) \tag{9.2}$$

$$K = \exp\,-\frac{\Delta\mu^{o}_{\mathrm{HX}}}{2.303RT} = \frac{[\mathrm{H}^{+}]_{\mathrm{f}}}{\mathrm{C}-[\mathrm{H}^{+}]_{\mathrm{f}}}.\frac{[\mathrm{X}^{-}]_{\mathrm{f}}}{\mathrm{A}-[\mathrm{X}^{-}]_{\mathrm{f}}}.\frac{1}{[\mathrm{H}^{+}]_{\mathrm{s}}[\mathrm{X}^{-}]_{\mathrm{s}}} \tag{9.3}$$

$[\mathrm{H}^{+}]_{\mathrm{f}}$ is the total amount of protons in the fibre. In the case of a titration curve started at the isoelectric point (i.e. when [C] = [A]), Eq. 9.4 applies in which $[\mathrm{H}^{+}]_{\mathrm{iso}}$ represents the amount of protons adsorbed by the fibre in its isoelectric state (i.e. $[\mathrm{H}^{+}]_{\mathrm{iso}}$ depends on the difference between the number of carboxylic groups, C and amino groups, A, in the substrate).

$$[\mathrm{H}^{+}]_{\mathrm{iso}} = \left([\mathrm{H}^{+}]_{\mathrm{f}} - (\mathrm{C}-\mathrm{A})\right) \tag{9.4}$$

Since, for electrical neutrality, $[\mathrm{H}^{+}]_{\mathrm{iso}} = [\mathrm{X}^{-}]_{\mathrm{f}}$, the latter being equivalent to $[\mathrm{X}^{-}]_{\mathrm{iso}}$. If HX is the only electrolyte present, when Eq. 9.4 is rewritten in the form of Eq. 9.5, it follows that, assuming $[\mathrm{H}^{+}]_{\mathrm{iso}} = [\mathrm{X}^{-}]_{\mathrm{f}}$, Eq. 9.6 applies.

$$[\mathrm{H}^{+}]_{\mathrm{f}} = \left([\mathrm{H}^{+}]_{\mathrm{iso}} + (\mathrm{C}-\mathrm{A})\right) \tag{9.5}$$

$$[\mathrm{H}^{+}]_{\mathrm{f}} = \left([\mathrm{X}^{-}]_{\mathrm{f}} + (\mathrm{C}-\mathrm{A})\right) \tag{9.6}$$

Since for electrical neutrality $[H^+]_s = [X^-]_s$ then Eq. 9.3 can be written in the form of Eq. 9.7 [178]:

$$\frac{-\Delta\mu^{o}_{HX}}{2.303\,RT} = 2\ \mathrm{pH} + \log K \tag{9.7}$$

where

$$K = \frac{\left([X^-]_f + C - A\right)\,[X^-]_f}{\left(A - [X^-]_f\right)^2} \tag{9.8}$$

Thus, a plot of log K as a function of pH should yield a straight line of slope 2, which has been obtained [178]. Taking antilogs, Eq. 9.9 results from which a plot of β versus $[X^-]_f$ provides a straight line of slope $-K^{0.5}$ and intercept A, such plots having been secured [218].

$$\beta = \frac{\left[\left([X^-]_f + C - A\right)[X^-]_f\right]^{0.5}}{[H^+]_s} = K^{0.5}\left(A - [X^-]_f\right) \tag{9.9}$$

Using this approach, values for the affinity of HCl on PA have been determined that ranged from –43.7, –45 and –45.8 kJ mol^{-1} at 18°C, 34.8°C and 55.5°C, respectively [218]. These values compare well with the average value of affinity (–44.5 kJ mol^{-1}) obtained at various points on the HCl titration curve [217].

The alternative Donnan approach described in Chapter 10 can be used to calculate the affinity of acids adsorbed by PA fibres, although greater variation in the affinity values are secured compared with those obtained assuming a Langmuir (Gilbert–Rideal) model [178, 228].

Other Models As discussed in Chapter 10, much debate has attended the applicability of the Gilbert and Rideal and Donnan models. In the case of PA fibres, several alternative models have been developed, including Peters' generalised extension [231] of his earlier Donnan model [232], Mathieson and Whewell's [233] *polyelectrolyte theory* that considered the energy required to remove adsorbed protons from the fibre and transfer these ions to the external solution against osmotic, electrostatic and affinity forces, as well as Myagkov and Paksher's *ion-exchange theory* that involved the use of appropriate dissociation constants. Iijima *et al.* [234] interpreted the titration curves of several weak acids as well as HCl on PA 6 films at 50°C in terms of a dual sorption model that involved ionised and unionised species, which were adsorbed according to a Langmuir and partition (Nernst) mechanism, respectively. The adsorption of strong acids, such as HCl and CF_3COOH, is considered to occur only by a Langmuir mechanism, the greatest contribution from a Nernst mechanism being observed for the weakest acid investigated, namely CH_3COOH [234].

9.3.1.1.3 Adsorption of Dye Anions Curves of the type shown in Figure 9.23 are typically obtained for the equilibrium adsorption of acid dyes on PA fibres as a function of pH. As the sigmoidal-shaped curves resemble those secured

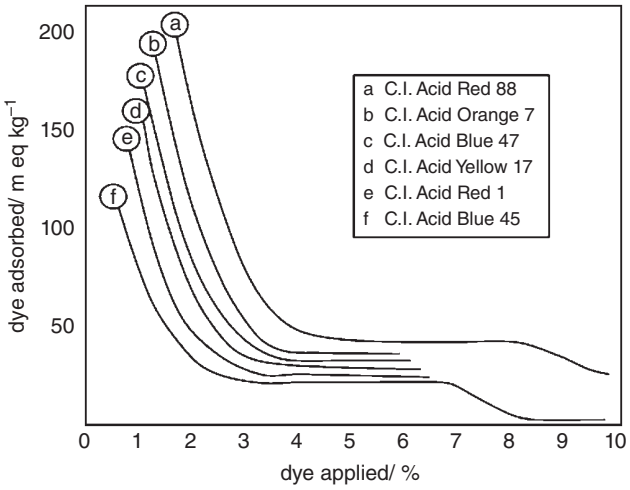

Figure 9.23 Equilibrium uptake of several non-metallised acid dyes on PA 66 as a function of pH. Reproduced from [235], copyright of the Society of Dyers and Colourists.

for the adsorption of simple inorganic acids by the substrate, they are sometimes referred to *as titration curves* of PA fibres with acid dyes.

The findings of Peters [223] and Peters *et al.* [235, 236] (Figure 9.23) for the adsorption of several mono- and di-basic, commercial and purified, non-metallised acid dyes on PA 66 reveal that the titration curves obtained for acid dyes differ from those secured for inorganic acids insofar as in the 'plateau' region of the curve in Figure 9.23, which begins at around pH 3 and corresponds to the AEG content of the fibre, extends over a wide range of pH values, whereas in the case of simple acids, this region is very narrow (Figure 9.21).

The curves shown in Figure 9.23 can be divided into three regions [223], A, B and C (Figure 9.24). In region C, at high pH values (e.g. pH 9), the carboxyl groups will be ionised and the protonated amino end groups may be non-protonated (**XVI**). In this region, it follows that adsorption of dye anions will be low. As pH decreases, dye adsorption increases as the ionisation of the carboxyl groups decreases and the amino end groups become protonated. Further dye uptake occurs with decreasing pH until it reaches a plateau region (B in Figure 9.24) that extends over several units of pH (e.g. pH 3–7) when the carboxyl groups are undissociated and the amino groups are protonated (**XIV**); in this region, dye anion adsorption attains a value that corresponds to the stoichiometric AEG content of the fibre. As pH is lowered further, in region A, a marked increase in dye uptake occurs that continues to increase with decreasing pH, apparently without limit. In this region, dye adsorption occurs in excess of the AEG content of the fibre and has been attributed to dye uptake onto protonated chain amide groups (**XIII**) and is referred to as *overdyeing*.

Thus, within the pH range ~3–7, in which dye adsorption is insensitive to pH, the equilibrium uptake of non-metallised acid dyes on PA fibres conforms to a Langmuir isotherm model [237–239] as illustrated by the results shown in Figure 9.25.

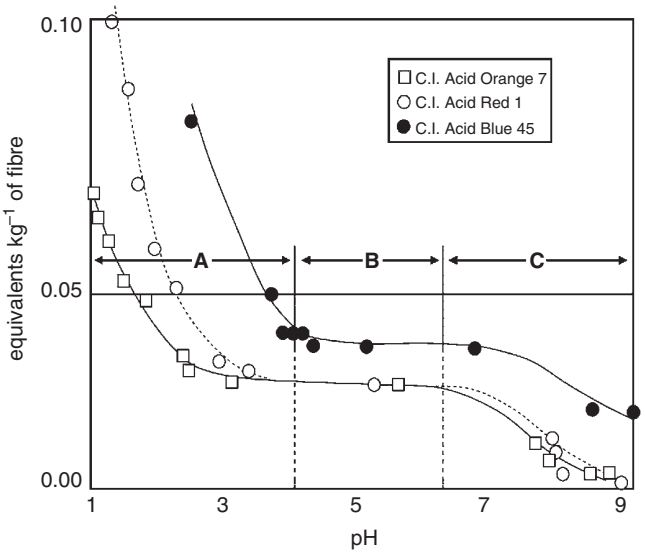

Figure 9.24 Representation of adsorption of acid dyes on PA fibres. Reproduced from [217].

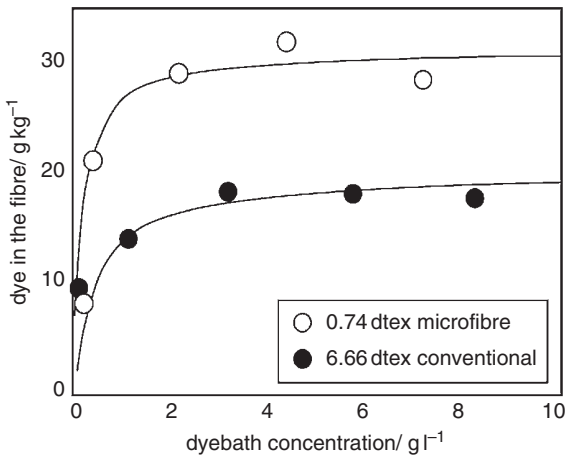

Figure 9.25 Adsorption isotherm for C.I. Acid Yellow 262 on microfibre and conventional PA 66 at 100°C and pH 5.0. Reproduced from [239], copyright of the Society of Dyers and Colourists.

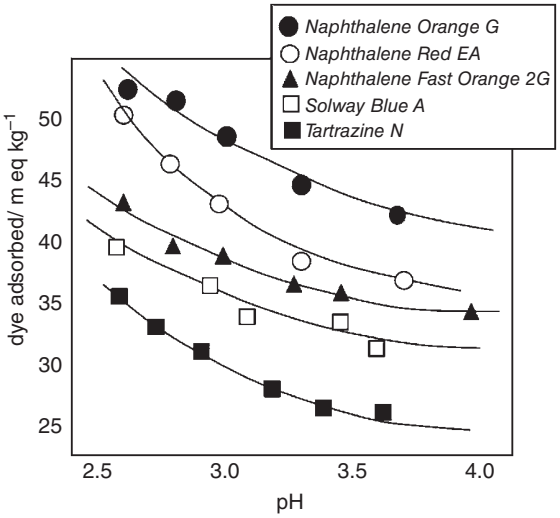

Figure 9.26 Equilibrium dye uptake as a function of pH at 75°C. Reproduced from [236], with permission from SAGE.

However, several workers [216, 240, 241] have observed deviation from the stoichiometric relationship between AEG content and equilibrium anionic dye uptake within the plateau region of the titration curves insofar as dye adsorption values were either lower or higher than the AEG content. Such findings have been attributed to the degree of sulfonation of the dye, as illustrated by the results in Figure 9.26 wherein uptake in excess of AEG was observed for the monosulfonated C.I. Acid Red 88 whilst uptake below AEG was observed in the case of the disulfonated C.I. Acid Blue 45. Atherton *et al.* [236] found that the curves for the adsorption of several dyes on PA 66 fibres within the pH range ~2.5–4.0 were not horizontal but, rather, dye uptake gradually decreased with increasing pH (Figure 9.26).

Overdyeing The adsorption of anionic dye in excess of the AEG content of the fibre, or *overdyeing*, is more important in the case of PA fibres than it is for wool because the latter fibre type contains far greater number of basic groups (Table 9.7). As discussed, three regions are discernible in the typical titration curves obtained for acid dyes on PA 66 (Figure 9.24). The positions of all three regions are clearly dye-dependent, the plateau region, B, which extends over several units of pH and corresponds to the number of amino end groups in the fibre, is often referred to as *electrostatic saturation* and dye uptake in this region is commonly assumed to corresponding to the *saturation value* of the fibre. At lower pH, in region A, dye adsorption exceeds the saturation value of the fibre and dye uptake continues to increase with decreasing pH, apparently without limit; such dye uptake greater than the AEG content of the fibre is referred to as overdyeing.

The phenomenon of overdyeing has been attributed to several causes (e.g. [9]). For example, it was suggested that overdyeing at low pH values could be attributed to dye adsorption onto new amino end groups that were created by hydrolysis of chain amide groups [240]. O'Briain and Peters [242] proposed that overdyeing occurred in two stages, namely an initial rapid uptake of dye in excess of the AEG content, followed by gradual hydrolysis resulting in an increased number of amine groups. Peters [223] suggested that the dyes combined with the amide groups, either by protonation, and subsequent adsorption of the dye anion; the absence of a maximum in dye adsorption at low pH values is thus explained by the large number of amide groups present in PA fibres. However, because overdyeing was observed at pH 4.5, where amide group protonation may not occur, Peters [178] concluded that the dyes were adsorbed in their undissociated form, a view supported by other workers [237]. Holfeld and Shepard [190] consider that, under acidic conditions, acid dyes are converted to their unionised, low aqueous solubility forms that display high solubility in PA fibre. The extent of overdyeing has been shown to be proportional to the affinity of the dye and also is related to the number of sulfonate groups in the dye, because the degree of overdyeing decreases in the order: monosulfonate > disulfonate > trisulfonate over the pH range 2–6, with tetrasulfonated dyes overdyeing only at a pH of <3 [243]. In this context, Atherton *et al.* [236] observed that in the case of PA 66 that had been acetylated to reduce its AEG content from 35 to 2.9 meq. kg^{-1}, the extent to which dye uptake was reduced followed the order: monosulfonated << disulfonated < trisulfonated [236]. It has been proposed [225], in the case of the adsorption of dye in excess of the AEG content, that the driving force for dye adsorption, $-\Delta\mu^{*o}$, can be expressed in terms of Eq. 9.10, where the gain in free energy, $-\Delta\mu^{o}$, promotes dye uptake and the gain in potential energy of the fibre surface, Π, resists dye adsorption; when $-\Delta\mu^{o} = \Pi$, then no adsorption occurs.

$$-\Delta\mu^{*o} = -\Delta\mu^{o} + \Pi \tag{9.10}$$

The generalised approach devised by Sumner [244–246], as discussed in Chapter 10, to describe the affinity of anionic dyes on PA fibres based on Donnan equilibrium theory, predicts that overdyeing can occur without invoking the formation of new sites in the fibre either as a result of ionisation of amide groups or due to fibre hydrolysis.

Measurement of Dye Affinity Relatively few attempts have been made to determine the affinity of dye anions for PA fibres directly from acid dye titration curves owing to experiment challenges that accrue from the high levels of dye exhaustion achieved [178, 217, 228]. For example, the affinity of the dibasic dyes C.I. Acid Red 13 and C.I. Acid Blue 45 was calculated using two equations based on Eq. 10.7 (see [178, 217, 228]) (i.e. assuming a Langmuir equation). Unfortunately, different values of affinity were obtained using the two approaches. In an attempt to avoid the experimental difficulties inherent in acid dye titration, desorption methods have also been used to determine affinity values. However, once again, the use of either the Gilbert–Rideal or Donnan analyses furnishes different values of affinity [178, 228].

Models of Dye Anion Adsorption on PA Fibres Both unimodal and multimodal mechanisms have been employed to describe the mechanism of adsorption of acid dyes on PA fibres, the latter approach tending to be used in the case of dye adsorption at low pH values when overdyeing can arise.

Models that describe the dyeing of PA fibres with acid dyes have been developed based on a generalised Donnan equilibrium approach, such models being applicable to other dye/fibre systems, as exemplified by the approach of Sumner [244–246] that sought to determine the affinity of anionic dyes on PA fibres (and protein fibres). The model devised by McGregor and Harris [247] assumed that no specific interactions occurred between dye anions and charged amino end groups and identified two parameters that determine ion adsorption, namely the partition coefficient, K_i and valency, z_i, of the ions, via Eq. 9.11, where λ_i is the Donnan coefficient and C^f and C^s are the concentrations of dye in the fibre and dyebath, respectively.

$$C_i^f = (\lambda_i)^z K_i C_i^s \tag{9.11}$$

Early studies revealed that the adsorption of non-metallised acid dyes (e.g. [236, 237, 248–252]) and also pre-metallised acid dyes (e.g. [251, 252]) on PA fibres could be explained in terms of a dual-mode mechanism that comprised both a Langmuir or ion-exchange mechanism and a Nernst-type mechanism. From the shape of the adsorption isotherm obtained for the monosulfonated AQ dye, C.I. Acid Blue 78 (Figure 9.27) on PA 66 fibres, Brody [237] concluded that two simultaneous and independent processes occurred, namely Langmuir adsorption via ion–ion forces and Nernst-type adsorption.

Support for this proposal was assumed from the finding that the intercept of the extrapolated linear portion of the isotherm (between 0.4 and 2.0 g l^{-1} applied dye) corresponded to dye uptake of 21 g kg^{-1}, which was close to the amount required to saturate the amino end groups. The linear portion of the isotherm was deemed to arise because of saturation of the amino end groups and was assumed to accord with the Nernst adsorption isotherm observed for disperse dyes [237]. It was proposed [253, 254] that the adsorption isotherm obtained for purified C.I. Acid Blue 182 on PA 6 film could be explained on the basis of surface diffusion incorporating three kinds of Langmuir adsorption mode, namely normal Langmuir-type adsorption, irreversible adsorption and Nernst-type adsorption. A line that fitted the experimental data well was calculated using Eq. 9.12 for this particular trimodal Langmuir adsorption approach, where

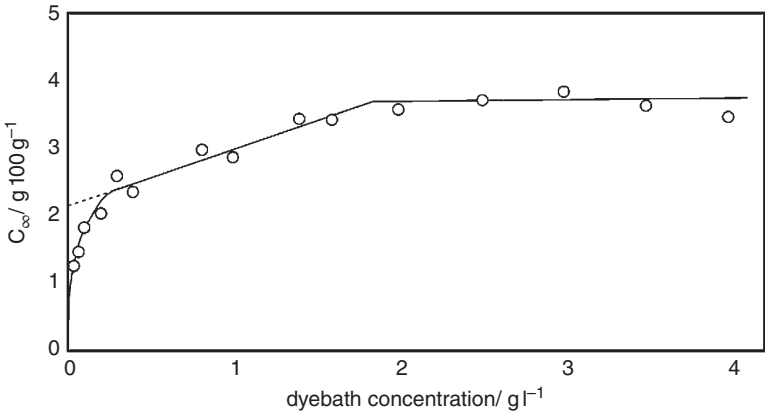

Figure 9.27 Adsorption isotherm for C.I. Acid Blue 78 on PA 66 fibres at 97°C, pH 6.0. Reproduced from [237], with permission from SAGE.

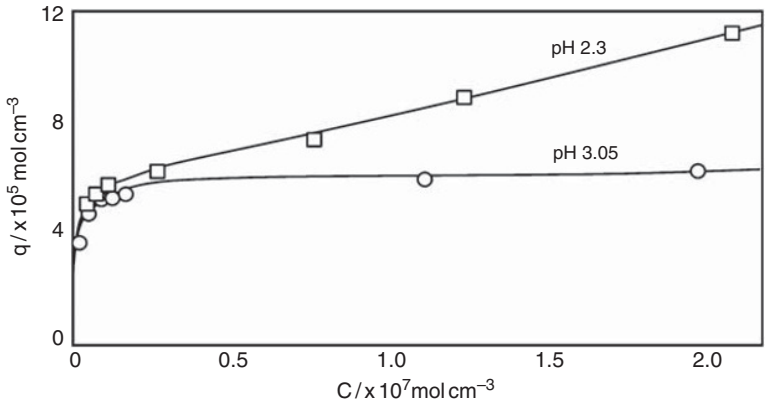

Figure 9.28 Sorption isotherm of C.I. Acid Blue 182 on PA 6 film at 80°C. Reproduced from [255], with permission from John Wiley & Sons, Inc.

q is the concentration of adsorbed dye, K_L the Langmuir-type adsorption constant, K_N the Nernst-type adsorption constant, C the concentration of dye in the pores and S the saturated concentration of adsorbed dye.

$$q = \frac{K_{L1} S_1 C}{1 + K_{L1} C} + S_2 + K_N C \tag{9.12}$$

In a subsequent study [255] of the sorption of C.I. Acid Blue 182 on PA 6 film at different pH values at 80°C, it was observed that the adsorption isotherm (Figure 9.28) could be interpreted in terms of dual-mode adsorption involving Nernst and bimodal Langmuir types (Eq. 9.13).

$$q = \frac{K_L S C}{1 + K_L C} + K_N C \tag{9.13}$$

The population of dye molecules sorbed via the former mechanism increased with decreasing pH and also, as the concentration of dye increased, dye transport within the PA film was dominated by diffusion within pores as well as surface diffusion of the adsorbed Nernst population of dye molecules. The contribution of pore and surface diffusion of the Nernst population of dye molecules increased at lower pH values.

In a study of the adsorption of purified dibasic non-metallised acid dyes coefficient in PA 6 film at 60, 70 and 80°C at pH 2.2 [256], the results were described in terms of a bimodal mechanism consisting of Nernst adsorption and ion exchange, via Eq. 9.14, where K_1 is a constant for the partition mechanism and θ_D the fractional occupation of the charged sites in the substrate.

$$C_D = K_1 C_{DS} + \frac{S\theta_D}{2} \tag{9.14}$$

The ion-exchange process is represented by Eq. 9.15, where A^- and D^{2-} are the monovalent counterion and the dye anion, respectively, K being the equilibrium constant for the ion-exchange process, which is related to θ_D by Eq. 9.16, where S is the amount of the charged sites and C_{DS} and C_{AS} are, respectively, the amounts of dye and counterion in solution.

$$2\left(-NH_3^+ \; A^-\right) + D^{2-} \rightleftharpoons \left(-NH_3^+\right)D^{2-} + 2A^- \tag{9.15}$$

$$K = \frac{C_{AS}^2}{2SC_{DS}} \frac{\theta_D}{(1-\theta_D)^2} \tag{9.16}$$

Clearly, the mechanism of the adsorption of non-metallised acid dyes on PA fibres has attracted much attention and, as the above, brief excursion into the relevant published work implies, the subject has not been entirely resolved.

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10.3.1 Thermodynamics of Dyeing

From the discussion of the electric double layer (Chapter 5), it is apparent that the application of the Donnan theory of membrane equilibrium to the treatment of the electric double layer that is established at a solid surface results in a volume of liquid adjacent to the charged surface. Within this volume, the electrical potential remains constant as a function of distance from the charged surface and then becomes zero at some distance from the surface. According to the Donnan theory, the outer boundary of this volume (depicted by the line NO in Figure 5.12) constitutes a *semi-permeable membrane* that separates the *internal aqueous solution*, *i*, from the bulk or *external aqueous solution*, *s*, the fixed charges on the surface being considered to reside within the internal aqueous solution. In the case of a negatively charged fibre immersed in a solution of, for example, NaCl solution, the equilibrium distribution of Na^+ and Cl^- ions can be described in terms of the Donnan coefficient, λ. The chemical potential of the sodium and chloride ions in the external solution can be expressed as Eqs. 10.2 and 10.3, respectively, and their interrelationship by Eq. 10.4.

$$\frac{[Na^+]_s}{[Na^+]_i} = \exp\left(\frac{F\Psi_{Donnan}}{RT}\right) = \lambda \tag{10.2}$$

[14] an aqueous treatment (aka *fulling*) undertaken to consolidate or compact wool fabrics.

$$\frac{[Cl^-]_s}{[Cl^-]_i} = \exp\left(\frac{-F\Psi_{Donnan}}{RT}\right) = \frac{1}{\lambda} \tag{10.3}$$

$$\frac{[Na^+]_s}{[Na^+]_i} = \frac{[Cl^-]_i}{[Cl^-]_s} = \exp\left(\frac{F\Psi_{Donnan}}{RT}\right) \tag{10.4}$$

or

$$[Na^+]_s[Cl^-]s_1 = [Na^+]_i[Cl^-]_i \tag{10.5}$$

Relationships such as that depicted in Eq. 10.5 have been employed to describe the mechanism of dyeing ionised fibres with ionised dyes, as exemplified by acid dyes on wool and polyamide (PA) fibres and direct dyes on cotton. Such an approach requires knowledge of the volume of the internal solution that is present with the wool, PA or cotton fibres. This quantity is commonly referred to as the *internal volume of the fibre*, *V*, which is typically expressed in $l\,kg^{-1}$. However, much debate attends both the nature and value of *V* (see Section 10.3.1.2.3 and also Chapter 9).

10.3.1.1 Titration Curves

Protein fibres (wool and silk) as well as PA fibres are solid, amphoteric, insoluble materials that swell in water. The adsorption of dye anions onto these types of substrate has been interpreted in terms of the adsorption of simple inorganic acids, obtained in the form of *titration curves*, because the titration curves secured for the interaction between protein fibres and PA fibres with acid dyes are similar to those obtained between the fibres and inorganic acids such as HCl. This similarity is illustrated by the titration curves of wool with HCl and with various acids including dye acids (Figure 10.10).

The applicability of this particular approach to both protein fibres and PA fibres is not surprising in view of their similar chemical nature, namely the presence of both amino and carboxyl groups. The use of this particular approach in the case of PA fibres is discussed in Chapter 9.

In the case of wool, the two types of ionised groups are the side-chain $-NH_3^+$ and side-chain $-COO^-$ groups, whilst other ionised groups, such as —OH, can be expected to contribute, such interactions are considered minor. As protonation of the $-NH_2$ groups to $-NH_3^+$ and ionisation of the —COOH groups to $-COO^-$ are both pH-dependent processes, the relative amounts of the different types of group vary as a function of pH, from which it follows that the overall charge on the protein macromolecule will also vary as a function of pH. In turn, this means that the substantivity of the protein substrate towards ions in solution (e.g. dye anions) also varies with pH.

In essence, the particular charge that a protein material, such as wool, carries at a given pH value depends not only on the number of side chains that bear $-NH_2$ and —COOH groups but also on the pK_a values of the side chains. To illustrate this, the pH dependency of a theoretical, water-soluble protein will be employed, as described by Peters [53] and Sumner [55]. Consider that this model protein contains 100 aspartic acid residues (pK_a of the COOH groups = 3.86), 30 lysine residues (pK_a of the NH_2 groups = 8.95) and 50 arginine residues (pK_a of the NH_2 groups = 13.2). The amounts of the various ionic species present in the theoretical protein material and the resultant net charge of the macromolecule are shown in Table 10.2 over the pH range 2.0–14.0 and depicted in Figure 10.11.

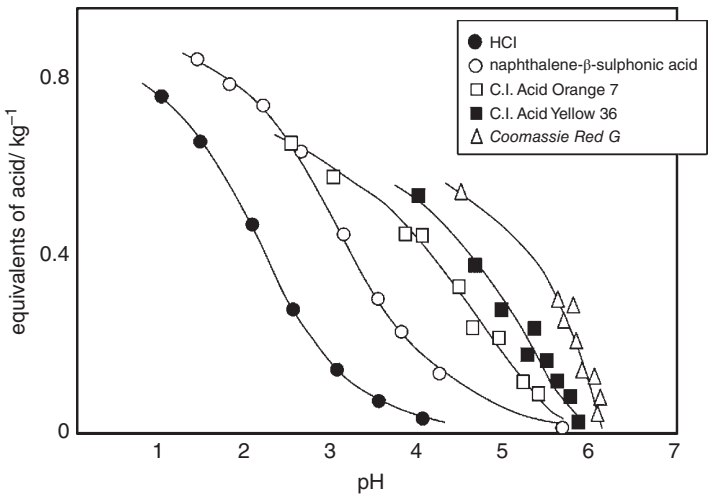

Figure 10.10 Titration curves of wool with free acids. Reproduced from [68].

Table 10.2 Titration of a hypothetical, water-soluble protein [55].

		pH								
amino acid residue		2.0	3.86	4.0	5.0	7.0	8.95	11.0	13.2	14.0
Aspartic acid	COOH	93.6	50	42	6.8	0.1	0	0	0	0
	$-COO^-$	1.4	50	58	93.2	99.9	100	100	100	100
Lysine	$-NH_3^+$	30	30	30	30	29.7	15	0.26	0	0
	$-NH_2$	0	0	0	0	0.3	15	29.7	30	30
Arginine	$-NH_3^+$	50	50	50	50	50	50	49.7	25	6.8
	$-NH_2$	0	0	0	0	0	0	0.3	25	43.2
Net charge		+78.6	+30	+22	−13.2	−20.2	−35	−50	−75	−93.2

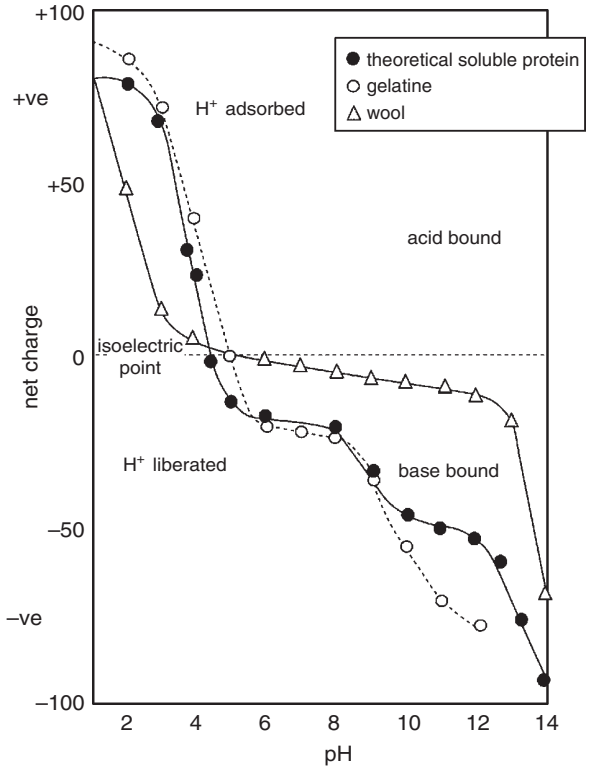

Figure 10.11 Titration curve for theoretical soluble protein, gelatine and wool. Reproduced from [55], copyright of the Society of Dyers and Colourists.

At low pH, although all the aspartic acid residues will be unionised (i.e. —COOH), both lysine and arginine will be protonated (i.e. $-NH_3^-$), resulting in a total charge of +80. With increasing pH, the protein begins to lose protons, owing to ionisation of the carboxyl groups, and the ensuing anionic groups reduce the net positive charge on the protein. At pH 3.86 (the pK_a of the —COOH groups in the aspartic acid residues), the carboxyl groups will be 50% ionised and, at pH 4.0–5.0, the number of positive and negative groups will be equal. Thus, the protein will carry a zero net charge, this being the *isoelectric point*[15] of the macromolecule. With further increase in pH, more protons are lost until, at ~pH 6.0, all the carboxyl groups can be assumed to be ionised. No further changes occur until ~pH 7.0 when loss of protons from the $-NH_3^+$ groups of lysine becomes significant, this being 50% complete at pH 8.95 (the pK_a of the $-NH_2$ groups in the lysine residues) and, in essence, is 100% complete at ~pH 11.0; the more basic arginine residues begin to lose protons at higher pH values.

[15] the isoelectric point is sometimes abbreviated to *IEP* and the pH at which the parameter occurs is denoted by *pH*(*I*), although *pI* is also employed.

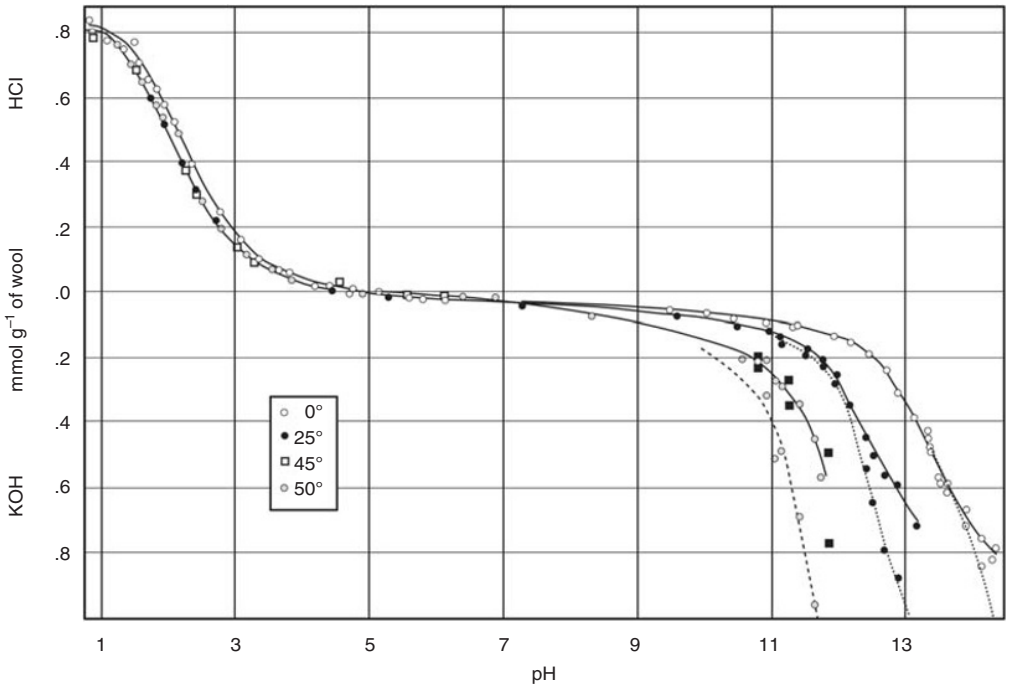

Figure 10.12 Combination of wool with HCl and KOH as a function of pH and temperature in the absence of added electrolyte. Reproduced from [69], The National Institute of Standards and Technology.

Figure 10.12 shows the titration curve for wool as a function of pH and temperature, obtained by Steinhardt *et al.* [69]. Regarding such titration curves:

- the number of molecules of acid or alkali adsorbed is numerically equivalent to the net charge on the protein at all pH values;
- although the maximum amount of acid adsorbed by the protein depends on the number of basic groups (i.e. $-NH_2$) present, the process of acid adsorption is considered to occur via the *back-titration* of the ionised carboxyl groups (i.e. $-COO^- \rightarrow -COOH$);
- the maximum amount of alkali adsorbed by the protein depends on the number of $-COOH$ groups present and the process of alkali adsorption occurs via titration of these basic groups;
- the particular pH range over which acid and alkali are adsorbed is determined by the pK_a values of the $-NH_2$ and $-COOH$ groups concerned.

From Figure 10.12, it is apparent that whilst the approximate titration curve for the soluble protein gelatine is similar to that of the theoretical protein, that for the insoluble protein wool is dissimilar insofar as, between pH 4.0 and 12.0, only small amounts of acid or alkali are adsorbed, this being attributable to the electrical charge carried by the fibre. As previously discussed, adsorption from solution onto fibres is usually considered to operate via a single-phase system namely:

$$\text{adsorbate (e.g. dye and acid) in solution} \rightleftharpoons \text{adsorbate in fibre}$$

However, in the case of adsorption from solution onto water-swollen, solid, amphoteric solid materials such as wool (or PA fibres), it is considered [54, 55] that a two-phase system operates that involves the intermediate stage of adsorption via the internal solution within the substrate, with the condition that each of the three parts of this system must be electrically neutral:

$$\text{adsorbate (e.g. dye and acid) in solution} \rightleftharpoons \text{adsorbate in } \textit{internal solution} \rightleftharpoons \text{adsorbate in fibre}$$

The broad isoelectric point or rather *isoelectric region* that is typically observed for wool (i.e. the pH range over which the fibre remains electrically neutral) (Figures 10.11 and 10.12) has been explained [54, 55] by assuming that the adsorption of a proton will generate a positive charge within the fibre that presents a repulsive potential that reduces the likelihood of the adsorption of a second proton. However, the positive charge created in the fibre attracts a counterion into the internal aqueous solution within the fibre, and therefore the net charge on the wool does not change. Thus, in effect, the system is electrically buffered [54] resulting in the broad portion of the titration curve that is not caused by changes in the dissociation constants of the constituent amino acids but, rather, by changes in the charge carried by the fibre.

10.3.1.2 Analysis of the Titration Curves

Two approaches have been employed to analyse the data obtained from titration curves such as that displayed in Figure 10.12, namely a *specific site* (Langmuir) model first proposed by Gilbert and Rideal in 1944 [70] and various *ion exchange models* based on modifications of a Donnan membrane theory originally proposed by Peters and Speakman in 1949 [71]. These two types of model have been used to analyse the acid/alkali titration curves secured for both wool and PA fibres, although the methodology adopted for the two types of fibre is slightly different, because PA fibres contain an excess of carboxyl groups whereas wool contains an equal amount of amino and carboxyl groups. The use of the two approaches in the case of PA fibres is discussed in Chapter 9.

Extensive accounts of the principles underlying these two treatments of the titration curves of both protein and PA fibres are available (e.g. [53–55, 68, 72, 73]). In essence, the two models differ insofar as the Gilbert–Rideal model assumes that the fibre contains sites for both adsorbing anions and cations (Figure 10.13) whereas, in the Donnan model, only protons are adsorbed onto sites within the fibre, the adsorbing anions being merely present within the internal solution in the fibre.

10.3.1.2.1 Gilbert–Rideal (Langmuir) Model This model was proposed [70] to interpret the titration curves of fibrous proteins such as wool and makes several assumptions:

- the substrate is ideally stable, insofar as only protons and anions from the acid are present in aqueous solution;
- the substrate contains an equal number of positive and negative charges, these being the $-NH_3^+$ and $-COO^-$ groups;
- all anionic sites in the substrate behave identically in terms of their interactions with cations and the behaviour of the cationic sites in the substrate is also assumed to be identical towards anions;
- protons and anions are adsorbed on specific sites namely $-NH_3^+$ and $-COO^-$ groups in the substrate;
- there is no interaction between the sites insofar as the adsorption of one ion does not affect that of another ion.

According to this model, no separate internal aqueous solution phase is present, as is the case with the Donnan model (Figure 10.13). The fibre phase is considered as homogeneous and contains only adsorbed ions, which are adsorbed according to the Langmuir mechanism (i.e. upon specific sites in the fibre).

The activities of the anionic and cationic sites in the fibre are equated to $\theta/(1-\theta)$, where θ is the fractional occupation of sites in the substrate. In the case of a monobasic acid, H*X*, Eq. 10.6 applies, where $[H^+]_f$ and $[X^-]_f$ are the amounts of the cation (i.e. H^+) and anion (i.e. X^-) adsorbed by the substrate, and $[S]_H$ and $[S]_X$ are the maximum amounts possible (i.e. the saturation values of the cation and anion, respectively).

$$\theta_H = \frac{[H^+]_f}{[S]_H} \quad \text{and} \quad \theta_X = \frac{[X^-]_f}{[S]_X} \tag{10.6}$$

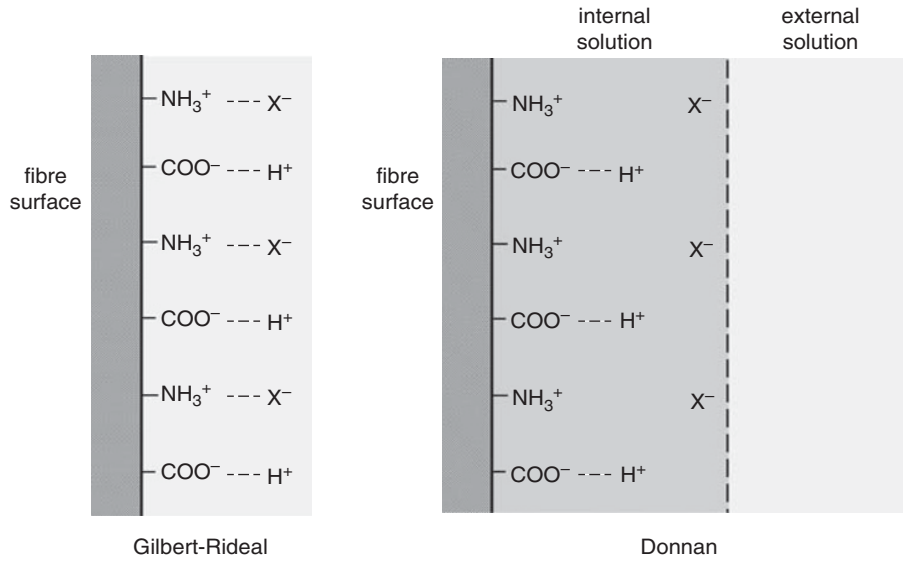

Figure 10.13 Representation of Gilbert–Rideal and Donnan models of wool and PA fibre acid dyeing mechanism.

Thus, Eq. 10.7 applies and, at the standard state, $\theta/(1-\theta)$ is unity when $\theta = 0.5$ (i.e. at half-saturation of the sites in the substrate).

$$-\Delta\mu^{o} = RT\ln\left(\frac{\theta_H}{1-\theta_H}\cdot\frac{\theta_X}{1-\theta_X}\right) - RT\ln\left([H^+]_s[X^-]_s\right) \tag{10.7}$$

Since, for a simple acid solution comprising $[H^+]$ and $[X^-]$, then $\theta_H = \theta_X$ so that Eq. 10.8 applies, where pH_s is the pH of the external aqueous solution (i.e. dyebath) phase:

$$\frac{-\Delta\mu^{o}_{\pm}}{4.606\ RT} = \frac{\log\theta}{1-\theta} + pH_s \tag{10.8}$$

Thus, for acid only (i.e. in the absence of added electrolyte), a plot of $\log\theta/(1-\theta)$ versus pH of the external solution (i.e. pH_s) should yield a straight line of negative unit slope (i.e. −1). However, in the case of the titration of wool with HCl, a plot of $\log\theta_H/(1-\theta_H)$ versus pH_s was found to yield a slope of −0.88 [68] (Figure 10.14) and the plot was slightly sigmoidal rather than rectilinear [54, 71].

To calculate the affinity of a series of acids, standard experimental conditions are preferably employed, for which the chosen standard state $\theta = 0.5$ is commonly used (i.e. at half-saturation of the sites in the substrate) since when $\theta = 0.5$ then $(\theta/1-\theta) = 1$. As such, affinity is given by Eq. 10.9 and, therefore, is related to the pH at which the fibre is half-saturated (i.e. $\theta = 0.5$), namely pH_{mid} [55].

$$-\Delta\mu^{o} = 4.606\ RT\,pH_{mid} \tag{10.9}$$

In the presence of added electrolyte (e.g. KCl), Eq. 10.10 applies, showing that a plot of $\log\theta/(1-\theta)$ versus pH_s at constant $[Cl^-]$ should give a straight line of slope −0.5, which, with increasing $[Cl^-]$, will be shifted to higher pH values.

$$\frac{-\Delta\mu^{o}_{\pm}}{2.303\ RT} = 2\log\left(\frac{\theta}{1-\theta}\right) + pH_s - \log[Cl^-]_s \tag{10.10}$$

Although Vickerstaff [68] found that a plot of $\log\theta_H/(1-\theta_H)$ versus pH_s provided straight lines that shifted to higher pH values as a function of added electrolyte, the slopes varied between −0.4 and −0.5 (Figure 10.15). The discrepancy between the experimentally observed findings and theory can be attributed to the fibre not being ideally stable, as was assumed by the model; in addition, such discrepancies may result from the theoretical treatment itself [55].

Rattee and Breuer [54] point out that whilst the value of affinity determined using Eq. 10.8 reflects experimental data at that particular point, the calculated value of $-\Delta\,\mu^{o}$ will bear little resemblance to experimental values determined at θ values >0.5 or <0.5.

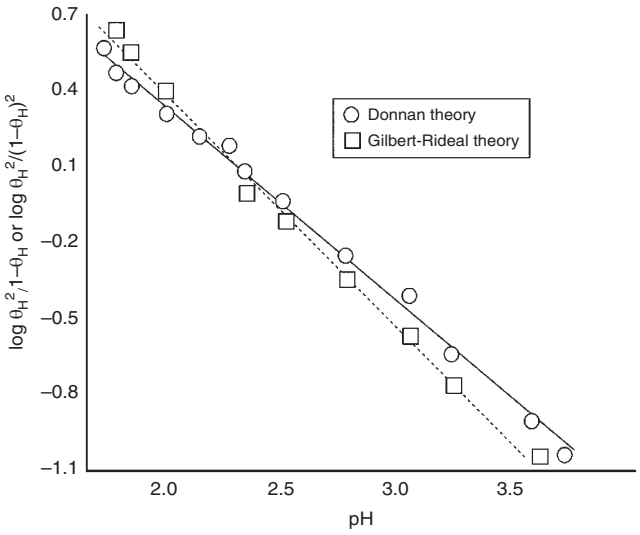

Figure 10.14 Adsorption of HCl by wool at 0°C in the absence of added electrolyte according to the Gilbert–Rideal and Donnan theory. Slope: ○, 0.7 and □, 0.88 (of theoretical value). Reproduced from [68].

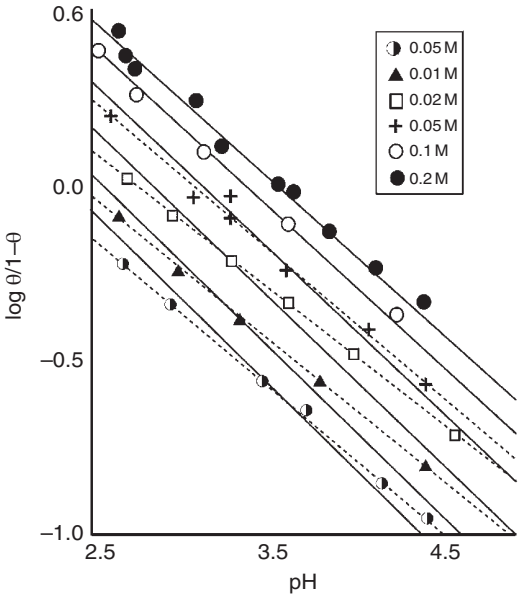

Figure 10.15 Adsorption of HCl on wool at 0°C and different ionic concentrations. Reproduced from [68].

10.3.1.2.2 Donnan Model and the Concept of Internal pH The quantitative analysis of the adsorption of inorganic acids first proposed by Peters and Speakman [71] assumed the Donnan equilibrium distribution of ions between an internal solution phase in the wool fibre and an external (bulk) solution. The swollen substrate containing the internal solution (the latter being assumed to possess the properties of a normal aqueous solution) was considered to constitute an *equipotential volume*. In the case of PA fibres, several variations of this original model have been proposed, each constituting a mechanism based on ion exchange.

According to this approach (Figure 10.13), when an acid, such as HCl, is sorbed by the fibre, whilst the adsorbing cations (i.e. H^+ ions) are adsorbed onto ionised anionic sites in the fibre (i.e. $-COO^-$ groups), the adsorbing anions (i.e. Cl^- ions) are not adsorbed but, rather, are present only in the internal solution of volume, $V\,1\,kg^{-1}$, within the fibre and are not able to directly interact with the cationic sites in the fibre. As such, the anions are assumed to have no affinity for the fibre. This model also invokes the concept of *internal pH*, pH_i, within the swollen fibre, this being different from the *external pH*, pH_s (i.e. the pH of the bulk dyebath solution).

$$\frac{-\Delta\mu_{\pm}^{o}}{2.303\,RT}-\log\frac{[S]_H}{V}=\log\left(\frac{\theta^2}{1-\theta}\right)+2pH_s \tag{10.11}$$

In essence, Eq. 10.11 applies [53, 54, 68] in the case of the adsorption of a simple acid in the absence of added electrolyte where pH_s is the pH of the external solution, from which a plot of $\log \theta^2/(1-\theta)$ versus pH_s should provide a straight line of slope −2. However, in the case of wool, using the titration data obtained by Steinhardt and Harris [74], a line of slope −1.4 was secured [68] (Figure 10.14), the discrepancy between theoretical and experimental values being attributable to fibre degradation as well as incorrect theoretical assumptions, as was the case with the Gilbert–Rideal model discussed earlier.

The internal pH, pH_i, is given by Eqs. 10.12 and 10.13 in the absence and presence, respectively, of added electrolyte, where a is the total concentration of H^+ ions adsorbed by the substrate:

$$pH_i = 2pH_s + \log\frac{a}{V} \tag{10.12}$$

$$pH_i = pH_s + \log\frac{a}{V} - \log[Cl^-]_s \tag{10.13}$$

According to Eq. 10.12, $pH_i > pH_s$, this being illustrated in Figure 10.16 in the case of H_2SO_4.

Steinhardt and Harris had found that in the case of the adsorption of HCl on wool, in the presence of added electrolyte (KCl), the titration curves shifted to higher pH values (Figure 10.17).

Eq. 10.13 shows that for a given value of pH_s (i.e. external pH), pH_i (internal pH) decreases with increasing concentration of chloride ions, which will result in greater acid adsorption. When the experimental data of Steinhardt and

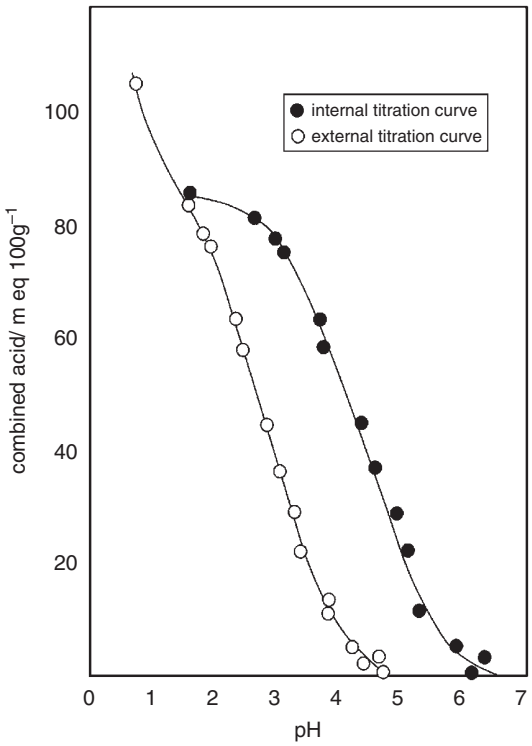

Figure 10.16 Internal and external pH titration curves for H_2SO_4. Reproduced from [71], copyright of the Society of Dyers and Colourists.

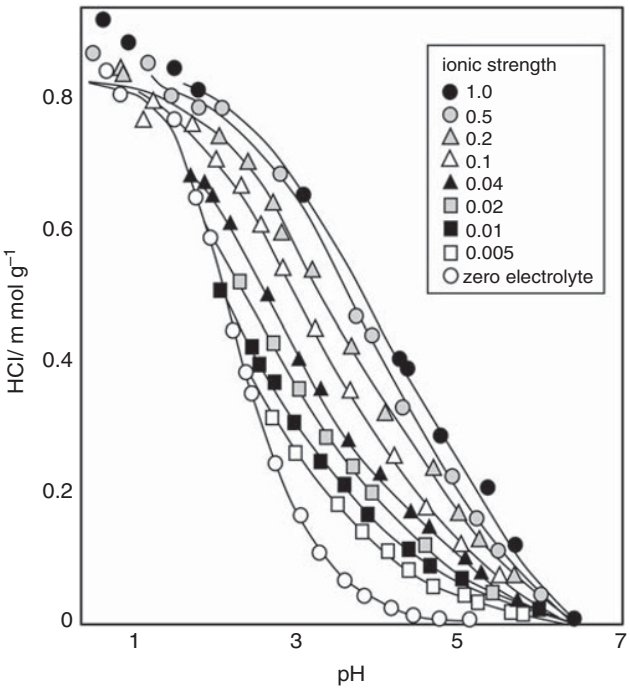

Figure 10.17 Adsorption of HCl in the presence of added KCl at 0°C. Reproduced from [74], The National Institute of Standards and Technology.

Harris [74] were plotted as a function of pH_i, the different titration curves obtained for each value of $[Cl^-]$ resolved to a single line (Figure 10.18).

***10.3.1.2.3 Nature of* V** According to the Donnan treatment discussed earlier, the fibre is assumed to contain an internal solution that resides within an internal volume of the fibre, V (l kg^{-1}). The nature and magnitude of this internal

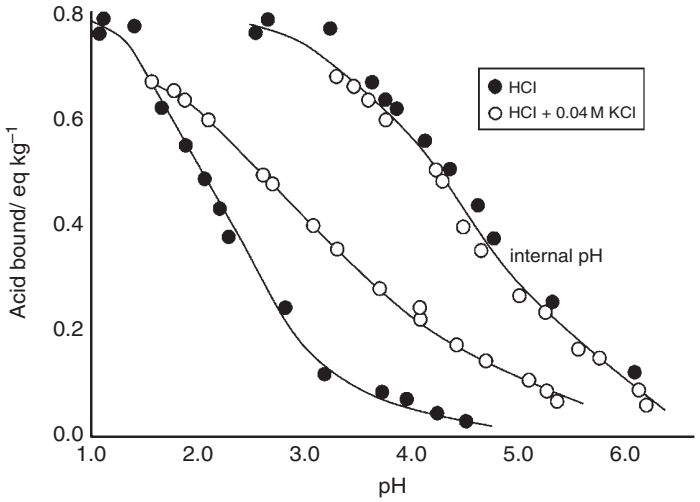

Figure 10.18 Effect of KCl on titration curves of HCl on wool. Left-hand curves: acid adsorbed as a function of pH_s; right-hand curve: acid adsorbed as a function of pH_i. Reproduced from [68].

volume has attended much attention. Some authors consider that V can be described as the volume that is occupied by water at 100% RH [71, 75], although this particular volume within a fibre would be expected to change as a function of, for example, temperature, the amount of water sorbed, degree of fibre swelling and so on; however, values of V are usually assumed to be constant. In the case of wool, Peters and Speakman [71] assumed a value of 0.29 l kg^{-1} whereas Delmenico and Peters [76] proposed values ranging from 0.24 to 0.30 l kg^{-1}, the latter being close to the value of 0.33 l kg^{-1} secured for the equilibrium moisture uptake of the fibre at 100% RH [36]; in the case of cotton, a value of 0.22 kg l^{-1} is usually employed [68]. Other workers [77, 78] treat V as an empirical factor that varies according to the best fit provided for a particular equation. Peters [53] discusses the concept that V can be considered as constituting the liquor within the fibre together with the volume that makes up the electric double layer, the thickness of the latter varying as a function of electrolyte concentration. Debate also surrounds the assumption that the water within the internal volume displays the same properties as bulk water (see also Chapters 7 and 9).

10.3.1.2.4 Applicability of the Two Models Much debate has attended the applicability of the Gilbert–Rideal and Donnan models (e.g. [75, 79–83]), Olofsson [79, 80] suggesting that the Gilbert–Rideal (Langmuir) method provided a more accurate interpretation of acid adsorption by wool. As discussed earlier, Vickerstaff's analysis [68] of Steinhardt and Harris' results [74] for the titration of wool with HCl revealed that whilst both methods gave a linear relationship, the Gilbert–Rideal equation furnished a slope of 0.88 rather than 1.0 whilst the Donnan model provided a slope of 1.4 instead of 2.0. Whether these discrepancies are attributable to the assumption made in the models that the experimental results are unaffected by fibre decomposition and/or the fact that they are an inherent feature of the theoretical treatments themselves has not been resolved. In addition, the wool fibre is considered to comprise a homogenous cylinder of uniform composition. However, evidence garnered from studies of the kinetics of dye adsorption within wool (see Section 10.3.4) reveals that this is not the case and the complex morphology of the wool fibre is of marked significance.

10.3.2 Effect of Electrolyte on Dye Adsorption

Despite the debate that surrounds the applicability of the Gilbert–Rideal and Donnan models, both models provide a satisfactory interpretation of the effect of electrolytes on acid adsorption. In this context, the effect of added electrolyte on anionic dye adsorption varies according to dyebath pH and dye concentration. Under acidic conditions, electrolytes such as Na_2SO_4 reduce anionic dye adsorption, causing dye displacement that promotes dye migration. However, under neutral/slightly alkaline pH conditions, added electrolyte can increase anionic dye uptake slightly.

The particular pH at which these two effects operate depends on fibre charge and dye affinity. Delmenico and Peters [84] reported that, in the case of the adsorption of C.I. Acid Red 88 on wool in the presence of added NaCl, the uptake of Na^+ ions increased markedly with increasing pH (Figure 10.19). Marshall [85] observed that, under weakly acidic dyebath conditions, the effect of added NaCl on the uptake of the monobasic dye C.I. Acid Orange 7 depended on dye concentration: at high amounts of applied dye, added electrolyte increased dye uptake whereas, at low dye concentrations, the opposite effect was observed (Figure 10.20). It was found that, at high dye concentrations, the amount of dye anions adsorbed was greater than that of H^+ ions, the reverse being observed at low dye concentrations [85].

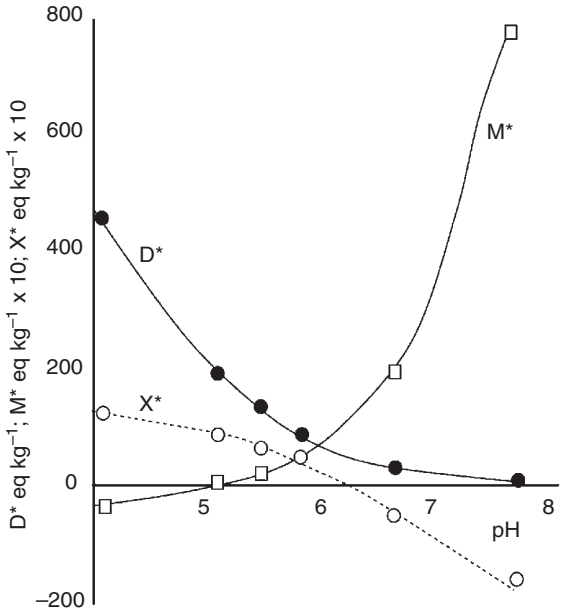

Figure 10.19 Sorption of C.I. Acid Red 88 on wool in the presence of 0.05 M NaCl at 90°C. *indicates measured amounts of ions; $M^* = Na^+$; $X^* = Cl^-$. Reproduced from [84], with permission from SAGE.

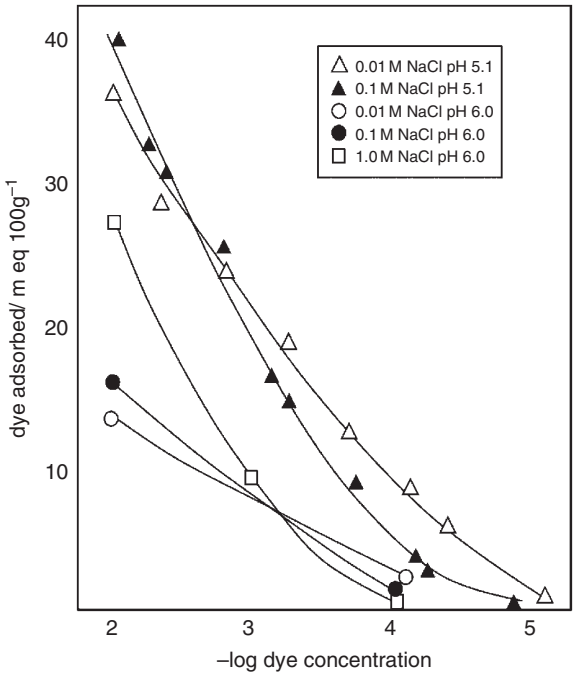

Figure 10.20 Sorption of C.I. Acid Orange 7 on wool in the presence of added NaCl at 60°C. Reproduced from [86], copyright of the Society of Dyers and Colourists.

It was proposed that, at high dye concentrations, Na^+ ions are adsorbed to preserve electrical neutrality within the fibre; when protons are in excess, so Cl^- ions are adsorbed.

At high dye concentrations, the driving force for dye adsorption can be considered to be the affinity of the dye anion, and the fibre carries a negative charge; at low dye concentrations, because the H^+ ions control fibre potential, the fibre carries a positive charge. Added electrolyte increases dye uptake when the fibre is negatively charged and dye desorption occurs when the fibre is positively charged. The particular pH value at which the added electrolyte reverts from promoting dye adsorption to causing dye displacement depends on the affinity and concentration of the dye anion [85]. The situation in the case of polybasic dye anions is more complex, although equivalence of dye uptake with fibre amino group content is observed (e.g. [53]).

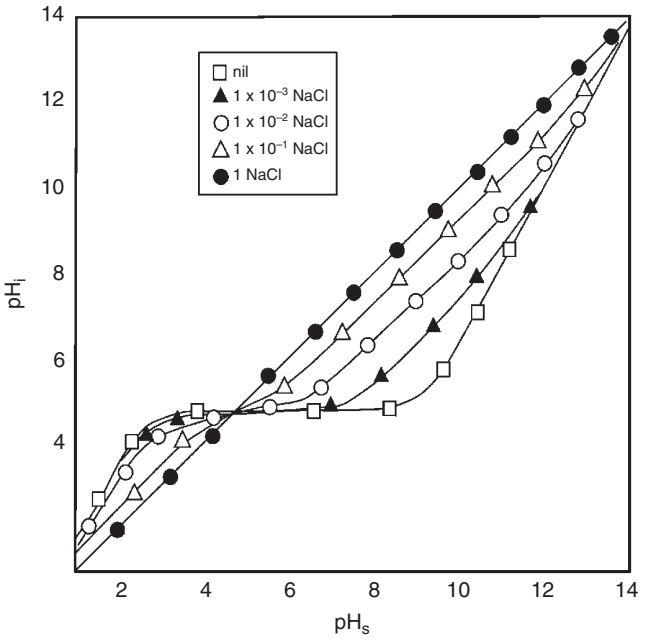

Figure 10.21 Internal pH versus external pH for PA-type fibre in the presence of added NaCl. Substrate contains 4×10^{-1} mol l^{-1} $-NH_2$ groups: $pK = 2.6 \times 10^{-11}$; 8×10^{-1} mol l^{-1} –COOH groups; $pK = 1.6 \times 10^{-5}$. Reproduced from [55], copyright of the Society of Dyers and Colourists.

As discussed in Chapter 7, the internal pH can be calculated using the concept of Donnan membrane equilibrium. Figure 10.21 shows that, in the case of a PA-type fibre, the calculated internal pH over a range of external pH values in the presence of various concentrations of added electrolyte (NaCl) intersects at the isoelectric point of the fibre. At values of external pH lower than the isoelectric point, when the fibre carries a positive charge, $pH_i > pH_s$, and although added electrolyte lowers pH_i, its value is never lower than that of pH_s. At pH values >pH(I) where the fibre carries a negative charge, the situation is reversed and is similar to that recounted for cellulosic fibres.

If the PA-type substrate is immersed in 1×10^{-4} mol l^{-1} aq HCl (i.e. pH = 4), then in the absence of added electrolyte the internal pH decreases (i.e. becomes more acidic) with increasing dye adsorption (Figure 10.20) [55]. Although such an effect is small at pH values below the isoelectric point of the dyed fibre, thereafter more dramatic changes are predicted, with the internal pH attaining a value that is equivalent to 1 M HCl. The presence of added electrolyte progressively reduces this effect.

Figures 10.21 and 10.22 reveal that $pH_i = pH_s$ at the isoelectric point, whereas Figure 10.22 shows that the saturation point for the substrate occurs when the total negative charge on the fibre is balanced by the positive charge (i.e. $[D^-]_f + [COO^-]_f = [NH_3^+]_f$) rather than $[D^-]_f = [NH_3^+]_f$ [55].

The reduction in anionic dye uptake on wool fibres (and PA fibres) imparted by the addition of electrolyte at pH values below the isoelectric point (when the fibre carries a positive charge) has been explained in terms of the concept of internal pH (i.e. in terms of the plot shown in Figure 10.21) [55]. Figure 10.21 shows that at pH values below the isoelectric point, for a given value of $[H^+]_s$, as the concentration of NaCl increases, $[H^+]_f$ increases. Thus, from Eq. 10.14, the ratio $[H^+]_f/[H^+]_s$ will also increase, and therefore in order to achieve a given value of $[D^-]_f/[D^-]_s$, the amount of dye on the fibre, $[D^-]_f$, must decrease for a given value of $[D^-]_s$. Thus, added electrolyte increases the uptake of dye anions. However, at pH values >pH(*I*) (i.e. when the fibre carries a negative charge), the opposite situation applies and the fibre behaves as a cellulosic fibre insofar as electrolyte promotes anionic dye adsorption.

$$\left(\frac{[H^+]_f}{[H^+]_s}\right)^z \cdot \frac{[D^-]_f}{[D^-]_s} = \text{constant} \tag{10.14}$$

10.3.3 Affinities of Acids and Dye Anions

Although both the Gilbert–Rideal and Donnan models can be used to determine the thermodynamic standard affinity (standard free energy change), $-\Delta\mu^o$, for the adsorption of acids or acid dyes on wool (see [53] for such calculations employing the Donnan model), some form of the Gilbert–Rideal equation, namely Eqs. 10.7 or 10.8, is mostly used,

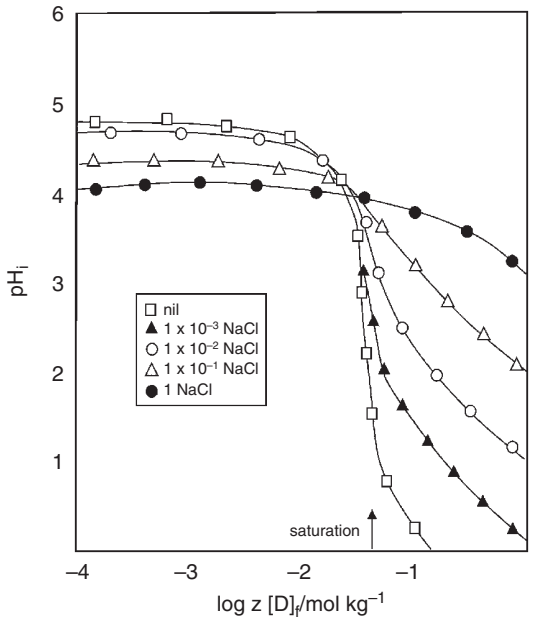

Figure 10.22 Effect of monobasic dye anions on internal pH in the presence of added NaCl. Substrate and [NaCl] (legend as for Figure 10.21); $pH_s = 4$; equivalent % depth of shade for dye of Mr = 1000 and 50% purity: $Z = 1$: 0.2%; 2%; 20%; $Z = 2$: 0.2; 1%; 10%; $Z = 4$: 0.5%; 0.05%; 5%. Reproduced from [55], copyright of the Society of Dyers and Colourists.

which, therefore, assumes that adsorption occurs via a Langmuir-type isotherm. For this calculation, values for the saturation values of the cations and anions, $[S]_H$ and $[S]_X$, respectively, are required; these values affect that of the fractional occupation of sites in the substrate, θ, as θ approaches unity. Sumner [55] provides a comprehensive account of both the approaches that can be employed to determine $[S]_H$ and $[S]_X$, and the use of these parameters in determining the affinity of HCl and other acids, including dye anions, for wool. Whilst the values of affinity for HCl determined using the data of Steinhardt and Harris [74] are constant at ~25.0 kJ mol^{-1} over a very wide range of ionic concentration [55, 68], Lemin and Vickerstaff [85] observed that the values of affinity of a series of inorganic acids and monobasic acid dyes ranged from ~20 to 34 kJ mol^{-1}.

The observation [86] that the value of affinity increased with increasing size of the respective anions implies that forces of interaction other than ion–ion contribute to adsorption. Meggy [87] proposed that the principal contribution to the affinity of a dye anion for wool arises from hydrophobic interactions whilst Derbyshire and Peters [88] suggested that non-polar van der Waals forces constitute the greatest contribution to the standard affinity of dyeing. The increase in entropy that accompanies dye adsorption was also considered a major contributor to the affinity of a dye for the fibre, such positive changes in entropy when combined with small enthalpy changes being indicative of hydrophobic interactions [73]. However, as Peters [53] points out, although, to a first approximation, dye uptake on wool accords to the amine group content of the fibre, dye adsorption in excess of the number of amine groups in wool observed in the case of dye anions of high affinity will be accompanied by protons to maintain electrical neutrality; such adsorption is likely to result in fibre hydrolysis.

10.3.3.1 Other Models for Interpreting the Adsorption of Acids and Dye Anions

Several alternatives to the Gilbert–Rideal and Donnan models have been developed (e.g. [53]) such as Peters' generalised extension [75] of his earlier Donnan model [71] that was applicable to adsorption within the isoelectric region, as well as the Donnan equilibrium approach adopted by Delmenico and Peters [76, 84]. Sumner [89–91] devised a generalised approach for the adsorption of anionic dyes on wool and PA fibres which assumed that the full development of Donnan equilibrium theory could resolve the problems experienced in applying both the Gilbert–Rideal [70] and Peters and Speakman [71] models to practical dyeing systems, namely, that neither model predicts nor considers *overdyeing* (i.e. dye or acid adsorption in excess of the saturation value of the fibre) and that with both models there is uncertainty as to whether polybasic ions occupy a single site or a stoichiometric number of sites within the substrate. According to this approach [55], in the case of protein and PA fibres, electrical neutrality is expressed as follows:

$$\sum \left[NH_3^+\right]_f + [H^+]_f + [Cat^+]_f = [OH^-]_f + [An^-]_f + 2\left[An^{2-}\right]_f + 3\left[An^{3-}\right]_f + \sum z_i [D^-]_{f,i} + \sum y_j [D^-]_{fixed,j} + \sum [COO^-]_f + \sum [O^-]_f \quad (10.15)$$

Eq. 10.16 describes the various Donnan relationships, where $Q_{NH_2} = Q_B$ = the amount of each available cationic group in the fibre with a dissociation constant of K_B.

$$[NH_3{}^+] = \frac{Q_{NH_2}[H^+]_f}{K_{NH_2} + [H^+]_f} = \frac{Q_B\,[H^+]_f}{K_B + [H^+]_f} \tag{10.16}$$

$$\sum \frac{Q_B[H^+]_f}{K_B + [H^+]_f} + [H^+]_f + \frac{[H^+]_f[Cat^+]_s}{[H^+]_s} = \frac{K_W}{[H^+]_f} + \frac{[An^-]_s[H^+]_s}{[H^+]_f} + 2\frac{[An^{2-}]_s[H^+]_s^2}{[H^+]_f^2} + 3\frac{[An^{3-}]_s[H^+]_s^3}{[H^+]_f^3} + \sum z_i[D^-]_{f,i} + \sum y_j[D^-]_{fixed,j} + \sum \frac{K_A Q_A}{K_A + [H^+]_f} \tag{10.17}$$

Knowing the equilibrium dyebath conditions, Eq. 10.17, in which the two terms for acidic groups in Eq. 10.15 are grouped together employing K_A and Q_A, can be solved for the only unknown, $[H^+]_f$, the value of which can then be used in Eq. 10.18 to calculate affinity.

$$-\Delta\mu^o = -RT\ln\frac{[H^+]_f^z[D^-]_f}{[H^+]_s^z[D^-]_s} \tag{10.18}$$

In essence, the fact that various models and theories have been proposed to describe the adsorption of acids and alkalis on wool (and PA) fibres reflects the situation that both the Gilbert–Rideal and Donnan models, as well as the alternative models mentioned earlier, assume the fibre to be a homogenous cylinder of uniform composition. As the foregoing brief discussion of wool fibre structure implies, whilst such an assumption is far from reality, as Sivaraja Iyer points [73], it is perhaps surprising that either theory provides a reasonably satisfactory explanation of the titration data of wool.