## 4.5 IONIC DYES APPLIED TO OPPOSITELY CHARGED SUBSTRATES

The most important dyeing systems to be considered under this heading are the application of

(a) anionic dyes, i.e. acid dyes, to wool and polyamide fibres;
(b) cationic dyes, i.e. basic dyes, to acrylic fibres.

### 4.5.1 Anionic dyes on wool

As a result of its chemical structure wool contains a considerable number of both acidic and basic groups and hence, in contrast to cellulose, it was natural to consider that the adsorption of ions by wool was directly concerned with the presence of these groups; this in turn led to the idea that ions are adsorbed by wool on specific sites in the fibre. It is certain that the ionised groups constituting these sites are the side-chain $—NH_3^+$ and side-chain $—COO^-$ groups of the wool protein. There will be some contribution from other ionised groups, e.g. hydroxyl, but this will be only small. The ionisation of the $—NH_2$ groups to $—NH_3^+$ and of —COOH groups to $—COO^-$ is pH-dependent and hence so are also the respective concentrations of these groups and the overall charge on the protein. This in turn will alter the receptivity of the protein to other ions, including dye anions. This dependence on pH of the charge on the protein is best illustrated by considering a model, water-soluble protein containing (per molecule)

100 aspartic acid residues (Asp) with $pK_{COOH} = 3.86 = pK_{Asp}$
30 lysine residues (Lys) with $pK_{NH^2} = 8.95 = pK_{LysH^+}$
50 arginine residues (Arg) with $pK_{NH_2} = 13.20 = pK_{ArgH^+}$

Assuming that the $pK$ values in the protein are the same as for the free amino acids then the net charge on the protein can be calculated from

$$\text{net charge} = [LysH^+] + [ArgH^+] - [Asp^-]$$
$$= \frac{[H][\text{lysine}]}{K_{LysH^+} + [H]} + \frac{[H][\text{arginine}]}{K_{ArgH^+}[H]} - \frac{K_{Asp}[\text{aspartic}]}{K_{Asp} + [H]} \quad (4.99)$$

where [lysine], [arginine] and [aspartic] represent *total* concentrations, charged and uncharged. The amounts of the various ions and the resultant net charge are shown in Table 4.12 over a range of pH values, and the net charge is shown as a titration curve in Figure 4.13.

Starting at low pH, all the aspartic acid residues will be un-ionised (—COOH), whereas lysine and arginine will be protonated ($—NH_3^+$). The total charge is +80. It can be seen that as the pH increases the protein begins to lose hydrogen ions, due to the ionisation of the carboxylic acid groups,

TABLE 4.12

**Titration of a hypothetical, water-soluble protein** (for details see text)

| | pH: | 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 |

and the negatively charged groups so formed result in a decrease in the net positive charge on the protein. At pH 3.86 the carboxyl groups will be half-ionised, and at a pH between 4 and 5 the number of negative groups will equal the number of positive groups, so that the protein will carry a net charge of zero. This is the *isoelectric point* of the protein. Further increase in pH results in further loss of hydrogen ion until, at about pH 6, the change becomes negligibly small and all the carboxyl groups may be assumed to be ionised. Nothing further happens until approximately pH 7, when loss of hydrogen ion from the positively charged amino groups of lysine becomes significant. This change is half-complete at pH 8.95, and for all practical purposes is complete at approximately pH 11. Eventually the much more basic arginine begins to lose its hydrogen ions.

Several points are worth noting about the titration curve.

(a) The number of molecules of acid or base bound is, at all pH values, numerically equivalent to the net charge on the protein.
(b) The maximum acid-binding capacity is determined by the number of basic groups present in the protein, although the process of acid-binding is in fact the back-titration of ionised carboxylic acid groups.
(c) The maximum base-binding capacity is fixed by the number of carboxylic acid groups and the process is one of titration of basic groups.
(d) The pH ranges over which the various titrations occur is determined by the p$K$ values of the groups concerned.

Included in Figure 4.13 are approximate curves for the titration of gelatine and of wool. The curve for gelatine, a soluble protein, resembles that of the model quite closely, whereas that of wool, an insoluble protein, is rather different in that it shows a region between pH 4 and pH 12 in which only

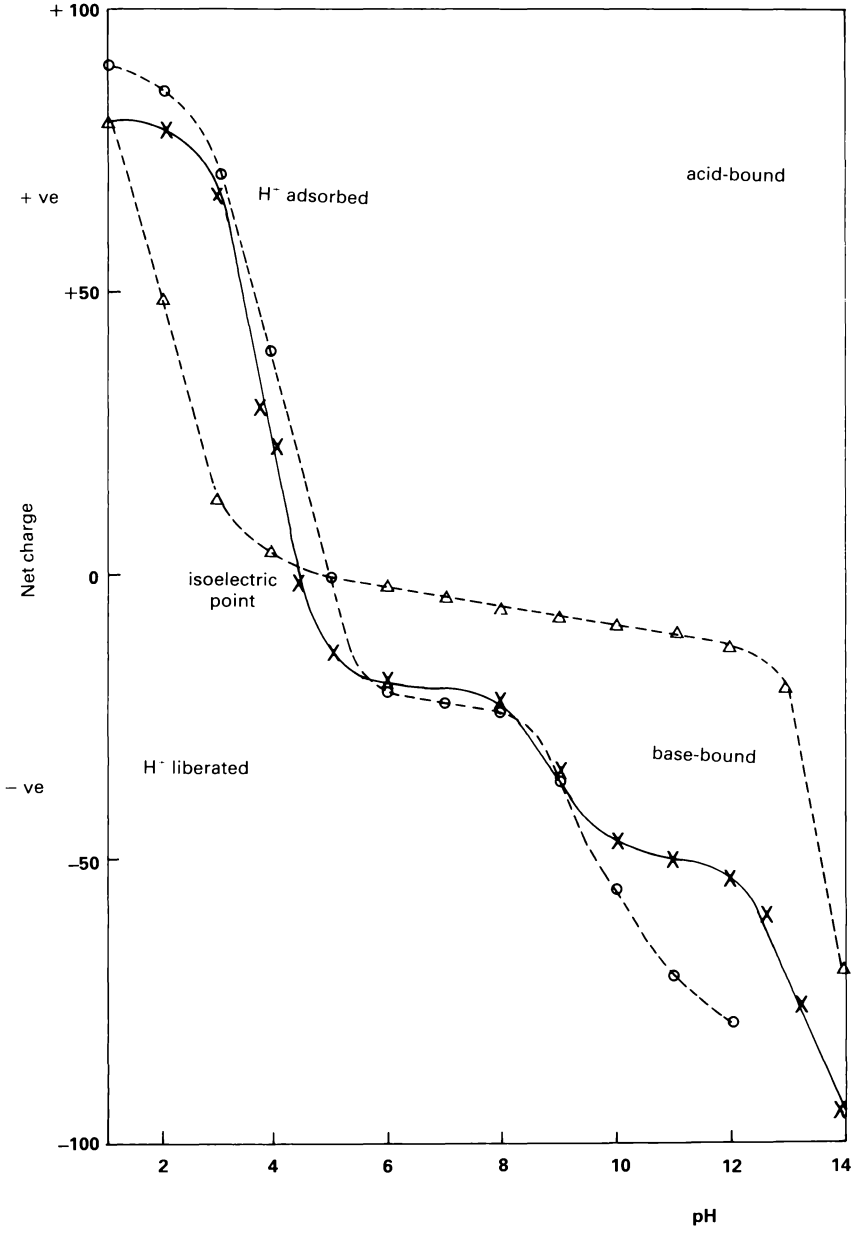


*Figure 4.13 – Titration curve of model soluble protein (—×—×—×—); also included are approximate curves for gelatine (- - - ○ - - - ○ - - - ○ - - -) and wool (- - - △ - - - △ - - - △ - - -)*

small amounts of acid or base are bound. This has been interpreted as being due to the electrical charge carried by the fibre and to the need when dealing with water-swollen, solid proteins to consider the system as being

$$\text{adsorbate in dyebath} \rightleftharpoons \text{adsorbate in internal solution} \rightleftharpoons \text{adsorbate in fibre}$$

with the proviso that each part of the system must be electrically neutral. If a protein is considered at its isoelectric point (i.e. no charge on the fibre) then the adsorption of a hydrogen ion will render the fibre positively charged, making it more difficult for a second proton to be adsorbed. The positive charge on the fibre will attract into the internal phase a counterion, however, so that the adsorption becomes a simultaneous uptake of positive and negative ions. This extra requirement makes it more difficult for the fibre to adsorb protons and results in the titration curve being displaced to lower pH. The converse is true on the other side of the isoelectric point, where the curve is moved to higher pH values. The result is the long, rather flat portion of the curve which is not due to changes in the dissociation constants of the constituent amino acids, but to the charge on the fibre. In spite of this the process of adsorption of acids and bases, outlined above for the model protein, still applies.

### 4.5.2 The reactivity of wool

Before moving to a theoretical study of the adsorption of acids by wool it is useful to consider the reactivity of wool, in particular its reactions with water. Wool fibres, and indeed all protein fibres, are very susceptible to hydrolysis, particularly at elevated temperatures. Many of the acid side-chains are in the form of the amide and these readily lose ammonia to give the carboxylic acid. The peptide links are also susceptible to hydrolysis, particularly under acid or alkaline conditions, producing new carboxylic acid and amino end-groups. In addition the protein can contain some water-soluble, low-r.m.m. material. Hence any aqueous dyeing experiment involving wool may well be carried out in a dyebath that contains a greater or lesser quantity of unknown material as a result of fibre hydrolysis and the dissolution of water-soluble fractions. Thus there is a situation in which both the fibre and the dyebath are changing in some undefined manner which is a function of time, temperature and dyeing conditions. In addition wool has such a relatively large capacity for adsorbing ions that great care is required, and this is not always obvious from experimental reports, to ensure that adventitious ions in unknown amounts are not introduced by the fibre into the dyeing system.

Clearly all of the above makes it very difficult to carry out meaningful experiments to determine the thermodynamics of wool dyeing, and this in turn means that much of the data in the literature must be viewed with a

certain amount of suspicion unless the experimental processes are adequately selected, described and carried out. Such a situation is illustrated in Table 4.16 on p. 331, which gives the results of applying a pure free dye acid to wool. Since the only known addition to the dyebath is the dye acid, and since this is a strong acid and hence will be fully dissociated, the equivalent concentrations of hydrogen ion and dye ion in the dyebath should be the same. The difference, shown in column 3 of the table, is marked and indicates that the dyebath contained other ionic material of unknown composition. It is obvious that this will not be an isolated case and clearly, despite the considerable amount of work that has been carried out to establish a theory which will describe the titration of wool, none of the proposed models has been thoroughly tested because of the difficulties of obtaining accurate experimental data.

### 4.5.3 The theoretical analysis of the titration curve

Taking the general picture of a water-swollen fibre forming an equipotential volume, surrounded by an external bath, then it is possible to define, for each mobile ion in the system, that

$$\mu_f = \mu_f^{\ominus} + RT \ln a_f \tag{4.100}$$

where f indicates the fibre,

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i \tag{4.101}$$

where i indicates the internal solution and

$$\mu_s = \mu_s^{\ominus} + RT \ln a_s \tag{4.102}$$

where s indicates external solution.

At equilibrium, within the equipotential volume, $\mu_i = \mu_f$ and hence

$$-\Delta\mu_{i,f}^{\ominus} = -(\mu_f^{\ominus} - \mu_i^{\ominus}) = RT \ln \frac{a_f}{a_i} \tag{4.103}$$

There will be a difference in potential between this equipotential volume and the external solution and this must be allowed for, so that at equilibrium $\mu_i = \mu_s - \psi F$ and hence

$$-\Delta\mu_{si}^{\ominus} = -(\mu_i^{\ominus} - \mu_s^{\ominus}) = RT \ln \frac{a_i}{a_s} + \psi F \tag{4.104}$$

where $\psi F$ is the electrical work required to move one mole of cation from

the external to the internal solution against this potential. Combining Eqns 4.103 and 4.104, and considering only cations, gives:

$$-\Delta\mu^{\ominus}_{s,f} = -(\Delta\mu^{\ominus}_{s,i} - \Delta\mu^{\ominus}_{i,f}) = RT \ln \frac{a^{+}_{f}}{a^{+}_{s}} + \psi F \qquad (4.105)$$

and a similar equation can be written for anions:

$$-\Delta\mu^{\ominus}_{s,f} = RT \ln \frac{a^{-}_{f}}{a^{-}_{s}} - \psi F \qquad (4.106)$$

By adding Eqns 4.105 and 4.106 the unknown electrical work term is eliminated:

$$-\Delta\mu^{\ominus}_{\pm} = RT \ln a^{+}_{f} a^{-}_{f} - RT \ln a^{+}_{s} a^{-}_{s} \qquad (4.107)$$

where $\Delta\mu^{\ominus}_{\pm}$ is the combined affinities of the cation and anion.

It was at this point, where values had to be assigned to the activities of the ions in the fibre, that a difference of opinion arose and this led to two different approaches being formulated, namely the Langmuir or Gilbert–Rideal method [67] and the Donnan method [68]. The differences between the two are described pictorially in Figure 4.14 for a simple, monobasic strong acid HX.

### 4.5.4 The Langmuir (Gilbert–Rideal) method

In this approach it is assumed that the fibre contains sites for both cations and anions (Figure 4.14(a)). The activities of both in the fibre are therefore equated, in the Langmuir sense, to $\theta/(1-\theta)$ where

$$\theta_{H} = \frac{[H]_{f}}{[S]_{H}} \quad \text{and} \quad \theta_{X} = \frac{[X]_{f}}{[S]_{X}} \qquad (4.108)$$

and $[H]_f$ and $[X]_f$ are the amounts of the two ions adsorbed and $[S]_H$ and $[S]_X$ are the maximum amounts possible, i.e. the saturation values. Eqn 4.107 therefore becomes, for the monobasic acid,

$$-\Delta\mu^{\ominus}_{\pm} = RT \ln \left( \frac{\theta_{H}}{1-\theta_{H}} \cdot \frac{\theta_{X}}{1-\theta_{X}} \right) - RT \ln ([H]_{s}[X]_{s}) \qquad (4.109)$$

and at the standard state $\theta/(1-\theta)$ equals unity, i.e. $\theta = 0.5$, and the situation is one of half-saturation of the available sites.

In the case of wool adsorbing acid from a solution that contains no other

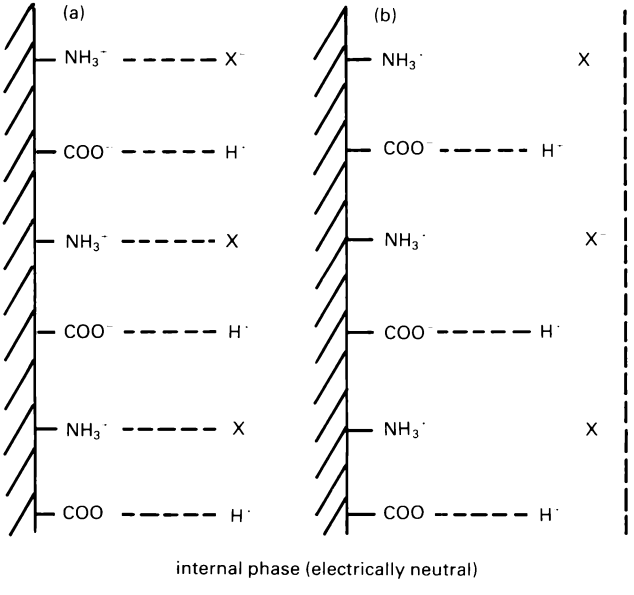


*Figure 4.14 – Pictorial representation of two approaches to wool dyeing theory: (a) Gilbert–Rideal, (b) Donnan*

electrolytes then, for electrical neutrality in the solution, $[H]_s = [X]_s$ and since in wool the numbers of positive and negative sites are very nearly equal, i.e. $[S]_H \approx [S]_X$, then $[H]_f = [X]_f$ and Eqn 4.109 becomes

$$-\Delta\mu_{\pm}^{\ominus} = 2RT \ln\left(\frac{\theta_H}{1-\theta_H}\right) - 2RT \ln [H]_s \qquad (4.110)$$

or

$$\frac{-\Delta\mu_{\pm}^{\ominus}}{4.606RT} = \log\left(\frac{\theta_H}{1-\theta_H}\right) + pH_s = -\log\left[\left(\frac{1}{\theta_H}-1\right)[H]_s\right] \qquad (4.111)$$

This equation makes two points.

(a) If $\log [\theta_H/(1-\theta_H)]$ is plotted against $pH_s$ then a straight line of negative unit slope should be obtained.
(b) The pH at which half-saturation occurs, i.e. at which $\theta_H/(1-\theta_H) = 1$ and $\log [\theta_H/(1-\theta_H)] = 0$, is a measure of the affinity.

### 4.5.5 The Donnan method

In the above treatment the sites for hydrogen ion adsorption are clearly defined, leading to un-ionised —COOH groups, but those concerned with

anion adsorption are not. The Donnan method avoids this difficulty by assuming that, while hydrogen ions are adsorbed on specific sites in the fibre, the anions are merely present in the internal solution in accordance with the Donnan theory of membrane equilibrium at a concentration of $[X]_i$ mol $l^{-1}$ (Figure 4.14(b)). Thus Eqn 4.107 becomes, for an acid HX,

$$-\Delta\mu_+^{\ominus} = RT \ln\left(\frac{\theta_H}{1-\theta_H} \cdot [X]_i\right) - RT \ln ([H]_s[X]_s) \qquad (4.112)$$

It must be noted that this equation now defines the affinity of the cation alone, since the anion affinity has been equated to zero, i.e. no combination takes place. If no other electrolyte is present then, for electrical neutrality in the internal phase,

$$V[X]_i = V[H]_i + [H]_f \qquad (4.113)$$

and assuming that $V[H]_i$ is negligible compared to $[H]_f$

$$[X]_i \approx \frac{[H]_f}{V} \qquad (4.114)$$

so that

$$-\Delta\mu_+^{\ominus} = RT \ln\left(\frac{\theta_H}{1-\theta_H} \cdot \frac{[H]_f}{V}\right) - RT \ln ([H]_s[X]_s) \qquad (4.115)$$

Since $[H]_f = \theta_H[S]_H$,

$$-\Delta\mu_+^{\ominus} - RT \ln [S]_H + RT \ln V =$$

$$RT \ln\left(\frac{\theta_H^2}{1-\theta_H}\right) - RT \ln ([H]_s[X]_s) \qquad (4.116)$$

But in the absence of other electrolyte $[H]_s = [X]_s$, so that

$$\frac{-\Delta\mu_+^{\ominus}}{2.303RT} - \log\left(\frac{[S]_H}{V}\right) = \log\left(\frac{\theta_H^2}{1-\theta_H}\right) + 2pH \qquad (4.117)$$

Thus by this treatment a plot of log $[\theta_H^2/(1-\theta_H)]$ against pH should give a straight line of slope $-2$.

### 4.5.6 Comparison of the two approaches

An analysis [41] of the results of titrating wool with hydrochloric acid [69] revealed that both methods gave a linear relationship, but that the Gilbert–Rideal equation gave a slope of 0.88 instead of 1.0 whilst the Donnan method gave a slope of 1.4 instead of 2.0. Whether these discrepancies are due to assuming that the experimental results are accurate and uninfluenced by fibre decomposition and its attendant problems, or whether they have their source in the theoretical treatment, is impossible to decide. For example, both approaches take the measured adsorption as $[H]_f$ whereas it is in fact $[H]_f + V[H]_i$. The assumption that $V[H]_i$ is negligible is possibly not always valid. It may also be that the chosen values of $[S]_H$ and $V$ are not the best possible. Whatever the reason, the results of this analysis do not indicate that a preference should be given to either approach.

When the effect of added electrolyte (potassium chloride) on the titration curve of hydrochloric acid on wool is considered, the Gilbert–Rideal equation (Eqn 4.110) becomes

$$-\frac{\Delta\mu_{\pm}^{\ominus}}{2.303RT} = 2\log\left(\frac{\theta_H}{1-\theta_H}\right) + \mathrm{pH} - \log[Cl]_s \qquad (4.118)$$

and a plot of $\log[\theta_H/(1-\theta_H)]$ against pH, at constant chloride ion concentration, should give a straight line of slope $-0.5$ which is displaced to higher values of pH with increasing chloride ion by the difference in the value of $\log[Cl]_s$. Analysis of a set of results [41, 69] did indeed give straight lines with the correct displacement of pH with electrolyte concentration, but the slopes varied from approximately 0.4 to 0.5 as chloride ion concentration increased from 0.005 to 0.2 mol $l^{-1}$.

When the effect of added potassium chloride was studied using the Donnan approach [68] attention was concentrated on the internal rather than the external pH. By Donnan membrane theory,

$$[H]_i[Cl]_i = [H]_s[Cl]_s \qquad (4.119)$$

For electrical neutrality

$$[H]_f + V[H]_i = V[Cl]_i = a \qquad (4.120)$$

where $a$ = the total concentration of hydrogen ions taken up by the fibre. Substituting $[Cl]_i = a/V$ from Eqn 4.120 into Eqn 4.119, followed by taking logarithms and substituting $pH_i$ for $-\log[H]_i$ and $pH_s$ for $-\log[H]_s$, leads to

$$pH_i = pH_s + \log\frac{a}{V} - \log[Cl]_s \qquad (4.121)$$

This equation applies when $[H]_s$ and $[Cl]_s$ are not equal (e.g. in the presence of potassium chloride). In the special case where $[H]_s = [Cl]_s$ it simplifies to

$$pH_i = 2pH_s + \log\frac{a}{V} \tag{4.122}$$

When, from the experimental data, the amount of acid adsorbed was plotted against $pH_s$ (the external pH), different curves were obtained for each concentration of added chloride ion present but when plotted against $pH_i$ (the internal pH) the plots resolved to a single curve. These are the results expected from Eqn 4.122.

Thus, bearing in mind the provisos listed above with regard to fibre decomposition and possible wrong assumptions, it would appear that both approaches give a satisfactory interpretation of the effect of electrolyte on the titration curve. Further critical studies have been carried out [70, 71, 72, 73] without establishing which of these approaches and others is to be preferred, but there was some indication [70] that the Gilbert–Rideal (Langmuir) method gave a truer interpretation of the adsorption of acids by wool. For this reason this approach will be adopted for the remainder of this discussion. The application of the Donnan theory is described elsewhere [74].

### 4.5.7 The saturation uptake of wool

Before the Gilbert–Rideal theory can be used to calculate the affinity of a monobasic acid for wool, using Eqns 4.109 or 4.111, it is necessary to determine values of $[S]_H$ and $[S]_X$, the saturation values for cations and anions respectively. The values chosen greatly affect the value of $\theta$ obtained, particularly as $\theta$ approaches unity.

By inspection of the titration curve for hydrochloric acid it is clear that $[S]_H$ must lie between 0.8 and 0.9 mol $kg^{-1}$ of dry fibre, but a better estimate may be obtained if Eqn 4.111, in which it has already been assumed that $[S]_H \approx [S]_X$ for wool, is rearranged to give Eqn 4.111a, since $\theta_H = [H]_f/[S]_H$:

$$\exp\left(\frac{\Delta\mu_{\pm}^{\ominus}}{2RT}\right) = \left(\frac{1}{\theta_H} - 1\right)[H]_s = \left(\frac{[S]_H}{[H]_f} - 1\right)[H]_s = K \tag{4.111a}$$

Rearranging Eqn 4.111a leads to:

$$\frac{1}{[H]_f} = \frac{K}{[S]_H} \cdot \frac{1}{[H]_s} + \frac{1}{[S]_H} \tag{4.123}$$

Thus a graph of $1/[H]_f$ against $1/[H]_s$ should give a straight line of slope

$K/[S]_H$ and intercept $1/[S]_H$. Such a result is found, and the value of $[S]_H$ thus obtained is probably more satisfactory than that given by inspection of the titration curve, although there are problems due to extrapolating lines of poor linearity. By a similar analysis it can be shown that a graph of $1/[X]_f$ against $1/[X]_s$ should also give a straight line with an intercept of $1/[S]_X$. Using this method with the hydrochloric acid titration results gave a saturation value $[S]_H$ of 0.82 mol $kg^{-1}$ [74].

TABLE 4.13

**Affinity of hydrochloric acid for wool at 0°C** [41, 69]

| Acid alone | | | Constant ionic concentration (0.1M) | | |
|---|---|---|---|---|---|
| pH | $\theta$ | $-\Delta\mu_{\pm}^{\ominus}$ /kJ (kcal) $mol^{-1}$ | pH | $\theta$ | $-\Delta\mu_{\pm}^{\ominus}$ /kJ (kcal) $mol^{-1}$ |
| 1.09 | 0.927 | 22.8 (5.43) | 1.09 | 0.929 | 22.6 (5.37) |
| 1.47 | 0.940 | 27.8 (6.62) | 1.38 | 0.935 | 24.5 (5.83) |
| 1.66 | 0.830 | 24.5 (5.83) | 1.68 | 0.908 | 24.3 (5.78) |
| 1.71 | 0.793 | 23.9 (5.68) | 1.99 | 0.858 | 23.7 (5.64) |
| 1.74 | 0.770 | 23.6 (5.63) | 2.27 | 0.810 | 23.6 (5.62) |
| 1.93 | 0.695 | 23.9 (5.68) | 2.54 | 0.735 | 23.0 (5.48) |
| 2.06 | 0.622 | 23.7 (5.65) | 2.81 | 0.655 | 22.76 (5.42) |
| 2.28 | 0.549 | 24.7 (5.88) | 3.21 | 0.544 | 22.8 (5.42) |
| 2.34 | 0.475 | 23.9 (5.70) | 3.65 | 0.435 | 23.1 (5.50) |
| 2.45 | 0.427 | 24.2 (5.75) | 4.21 | 0.305 | 23.4 (5.57) |
| 2.73 | 0.305 | 24.6 (5.86) | 4.62 | 0.214 | 23.4 (5.56) |
| 3.04 | 0.207 | 25.6 (6.10) | 5.03 | 0.149 | 23.5 (5.60) |
| 3.27 | 0.134 | 25.6 (6.10) | 5.47 | 0.092 | 23.3 (5.55) |
| 3.62 | 0.082 | 26.8 (6.38) | – | – | – |
| 3.84 | 0.055 | 27.1 (6.45) | – | – | – |

An alternative method has been proposed [8] which in certain cases produces improved linearity and hence more certain extrapolation. Again it is assumed that for a monobasic acid $[S]_H \approx [S]_X$ and $\theta_H = \theta_X$, so that Eqn 4.109 may be written

$$-\Delta\mu_{\pm}^{\ominus} = RT \ln\left(\frac{\theta_X}{1-\theta_X}\right)^2 - RT \ln [H]_s[X]_s \qquad (4.109a)$$

from which it follows that

$$\left(\frac{\theta_X}{1-\theta_X}\right)^2 = [H]_s[X]_s \exp\left(-\frac{\Delta\mu_{\pm}^{\ominus}}{RT}\right) \qquad (4.124)$$

Substituting $K$ from Eqn 4.111a and rearranging then gives

$$\frac{1}{[X]_f} = \frac{1}{K[S]_X}\left(\frac{1}{([H]_s[X]_s)^{\frac{1}{2}}}\right) + \frac{1}{[S]_X} \qquad (4.125)$$

A graph of $1/[X]_f$ against $[H]_s[X]_s^{-\frac{1}{2}}$ should give a straight line of slope $1/K[S]_X$ and intercept $1/[S]_X$. A value of 0.90 mol $kg^{-1}$ of dry wool was found from measurements of the adsorption of the free acid of Metanil Yellow YK (C.I. Acid Yellow 36) on wool.

Using a saturation value of 0.82 mol $kg^{-1}$ of dry wool the standard affinity of hydrochloric acid for wool has been calculated from the experimental results obtained [41, 69] in the absence and presence of potassium chloride, using Eqns 4.111 and 4.118 respectively. The results are shown in Table 4.13, which shows that the consistency is reasonably satisfactory, although the results with acid alone tend to rise when $\theta$ is less than 0.3. The mean affinities at various ionic concentrations (Table 4.14, column 2) show a drift to lower values as the ionic concentration increases, however. The last column in the table shows that the drift can be eliminated almost completely by using activities for the ions in solution instead of concentrations, that is, by multiplying the latter by the mean activity coefficient $f_{\pm}$. Eqn 4.118 therefore becomes

$$\frac{-\Delta\mu_{\pm}^{\ominus}}{2.303RT} = 2 \log \frac{\theta_H}{1-\theta_H} - RT \log [H]_s - RT \log [Cl]_s - 2RT \log f_{\pm} \qquad (4.126)$$

To extend this correction to other acids is only rarely possible, because the required values of the activity coefficients are seldom available. Hence it is necessary to revert to the usual procedure and equate them to unity.

TABLE 4.14

**Mean affinity of hydrochloric acid for wool at 0 °C at different ionic concentrations** [41]

| Ionic concentration/M | $-\Delta\mu_{\pm}^{\ominus}$ (mean) /kJ (kcal) mol$^{-1}$ | $2RT \ln f_{\pm}$ /kJ (kcal) mol$^{-1}$ | Corrected $-\Delta\mu_{\pm}^{\ominus}$ /kJ (kcal) mol$^{-1}$ |
|---|---|---|---|
| Acid alone | 24.6 (5.86) | 0.46 (0.11) | 25.1 (5.97) |
| 0.01 | 24.4 (5.81) | 0.46 (0.11) | 24.9 (5.92) |
| 0.02 | 23.9 (5.69) | 0.59 (0.14) | 24.5 (5.83) |
| 0.04 | 23.7 (5.64) | 0.80 (0.19) | 24.5 (5.83) |
| 0.10 | 23.6 (5.61) | 1.13 (0.27) | 24.7 (5.88) |
| 0.20 | 23.1 (5.51) | 1.42 (0.34) | 24.5 (5.85) |
| 0.50 | 22.3 (5.32) | 1.97 (0.47) | 24.3 (5.79) |
| 1.00 | 22.0 (5.25) | 2.40 (0.57) | 24.6 (5.82) |
| Mean | 23.43 ±0.84 (5.58 ± 0.20) | | 24.61 ± 0.25 (5.86 ± 0.06) |

In order to compare the affinities of a range of acids it is preferable to use a standard set of experimental conditions for all the acids, and the most obvious choice is when the fibre is half-saturated since then the acid in the fibre is in its standard state. As described earlier, under such conditions Eqn 4.111 becomes

$$-\Delta\mu_{\pm}^{\ominus} = 4.606\ RT.\mathrm{pH_{mid}} \tag{4.127}$$

where $\mathrm{pH_{mid}}$ is the pH in the solution at which the fibre is half-saturated. This treatment can be applied to any titration curve, but again the principal problem remains of assigning a value to $[S]_H$, the maximum acid-binding power of wool. The figures in Table 4.15 have been calculated using a value of 0.90 mol kg$^{-1}$ of dry wool. It must be noted that the affinities obtained in this way are the sums of the affinities of the cation and the anion, i.e. $\Delta\mu_{\pm}^{\ominus}$. Although thermodynamically incorrect, it is possible to separate the affinities of the two ions if $\Delta\mu_{HCl}^{\ominus}$ is taken as a starting point and $\Delta\mu_{Cl}^{\ominus}$ is equated to zero, arbitrarily. The value of $\Delta\mu_{HCl}^{\ominus}$ has been determined by several workers

TABLE 4.15

**Affinity of acids for wool at 0 °C** [41]

| Acid | $pH_{mid}$ | Total affinity /kJ (kcal) $mol^{-1}$ | Anion affinity /kJ (kcal) $mol^{-1}$ | Source ref. |
|---|---|---|---|---|
| Hydrochloric | 2.12 | −22.3 (−5.30) | – | |
| Sulphuric acid monoethyl ester | 2.21 | −23.1 (−5.50) | −0.80 (−0.20) | 74 |
| Sulphuric[a] | 2.96 | −47.7 (−11.36) | −3.2 (−0.76) | 74 |
| Sulphuric[a] (at 22 °C) | 2.90 | −50.8 (−12.10) | −3.4 (−0.80) | 75 |
| Trichloracetic | 2.62 | −27.3 (−6.50) | −5.0 (−1.20) | 74 |
| Benzenesulphonic | 2.50 | −26.0 (−6.20) | −3.8 (−0.90) | 74 |
| 4-Toluenesulphonic | 2.53 | −26.5 (−6.30) | −4.2 (−1.00) | 74 |
| 4-Toluenesulphonic[b] | 2.63 | −27.3 (−6.50) | −5.0 (−1.20) | 76 |
| *o*-Xylenesulphonic | 2.61 | −27.3 (−6.50) | −5.0 (−1.20) | 74 |
| Naphthalene-$\beta$-sulphonic | 3.11 | −32.6 (−7.75) | −10.3 (−2.45) | 74 |
| Naphthalene-$\beta$-sulphonic[b] | 3.18 | −33.2 (−7.90) | −10.9 (−2.60) | 76 |
| Anthraquinone-$\beta$-sulphonic[b] | 3.63 | −38.0 (−9.05) | −15.8 (−3.75) | 76 |
| 2-Nitrobenzenesulphonic | 2.72 | −28.4 (−6.75) | −6.1 (−1.45) | 74 |
| 2,4-Dinitrobenzenesulphonic | 3.03 | −31.7 (−7.55) | −9.5 (−2.25) | 74 |
| 2,5-Dichlorobenzenesulphonic | 2.98 | −31.1 (−7.40) | −8.8 (−2.10) | 74 |
| 1-chloro-4-nitrobenzene-2-sulphonic | 2.98 | −31.1 (−7.40) | −8.8 (−2.10) | 74 |
| Chromic[c] | 3.30 | −34.4 (−8.20) | −12.2 (−2.90) | 77 |
| Picric | 3.72 | −39.9 (−9.25) | −16.6 (−3.95) | 74 |
| 1-Naphthol-2,4-dinitro-7-sulphonic | 4.06 | −42.4 (−10.10) | −20.2 (−4.80) | 74 |
| 2,4,6-Trinitroresorcinol | 3.48 | −36.3 (−8.65) | −14.1 (−3.35) | 74 |

[69, 77], whose results give an average figure of $-22.3$ kJ ($-5.3$ kcal) mol$^{-1}$, a value which is only slightly affected by temperature. This may be taken as the affinity of the hydrogen ion and subtracted from the total affinities of the monobasic acids to obtain the affinities of the various anions (Table 4.15, column 4).

It is obvious that there is a clear tendency for the affinity of the anion to increase with increasing r.m.m. and complexity or with the introduction of polar groups. Hence the affinity cannot be due only to electrostatic effects – otherwise all monobasic acids would have the same value as hydrochloric acid. Clearly there must be a considerable contribution from non-electrostatic forces of attraction.

With regard to the acids listed, three points must be made. Sulphuric acid is treated as dibasic, so that the value of the $\Delta\mu^{\ominus}$ term has been obtained by subtracting $2\Delta\mu^{\ominus}_{H}$ from the total affinity. Chromic acid is considered monobasic under the conditions used (since its second dissociation has a p$K$ of 6.4), but complications arise because of changes in the valency state during the experiment giving trivalent chromium ions [78]. The adsorption of weak acids by wool is quite different from that of strong acids, and their behaviour suggests that they are essentially adsorbed in the undissociated state [75].

### 4.5.8 The adsorption of free dye acids: affinity determination

In this method wool is dyed to equilibrium from solutions containing increasing amounts of pure, free dye acid. The dyebaths therefore contain varying concentrations of hydrogen and dye ions but, because no other ions are present, these two concentrations must be equivalent. Similarly, because wool has approximately equal amounts of negatively and positively charged fibre groups, the concentrations of hydrogen and dye ions in the fibre must also be equivalent. This would be so in the ideal case, but in practice fibre decomposition, the presence of water-soluble fibre fractions and the possibility that adventitious electrolyte may be added with the wool result in this equivalence being destroyed. For the dyebath the presence in the final equilibrium solution of other electrolytes is demonstrated by the lack of agreement between $[H]_s$ and $[D]_s$ in Table 4.16, where the difference between the two is given under the heading $[U]_s$. The fact that part of this effect is due to wool decomposition, and is therefore time-dependent, is demonstrated in Table 4.17 and it has been observed that this effect becomes worse as the affinity of the dye increases. In similar experiments [79] the dyebath was found to contain a sparingly soluble, crystalline deposit which was similar to those found with certain amino acids.

Nevertheless, despite these problems, the method gives consistent results and titration curves have been obtained for several free dye acids [8]. These are shown in Figure 4.15, together with curves for hydrochloric and

TABLE 4.16

**The adsorption of Metanil Yellow free acid by wool** [41]

Assuming the wool contains: 0.6 mol $kg^{-1}$ of a basic group with $pK_A = 12.5$
0.18 mol $kg^{-1}$ of a basic group with $pK_A = 10.3$
0.05 mol $kg^{-1}$ of a basic group with $pK_A = 6.1$
0.79 mol $kg^{-1}$ of an acidic group with $pK_A = 4.1$
0.027 mol $kg^{-1}$ of an acidic group with $pK_A = 10.3$
and using: $V = 0.3$ l $kg^{-1}$, $z = 1$, $[Na]_s = 0$, $[Cl]_s = 0$.

| pH | $[H]_s$ /mol $l^{-1}$ $\times 10^6$ | $[U]_s$ /mol $l^{-1}$ $\times 10^4$ | $[D]_s$ /mol $l^{-1}$ $\times 10^4$ | $[D]_f$ /mol $l^{-1}$ $\times 10$ | $-\Delta\mu^{\ominus}$/kJ (kcal) $mol^{-1}$ Langmuir | New treatment (Eqn 4.167) |
|---|---|---|---|---|---|---|
| 5.77 | 1.70 | 0.491 | 0.508 | 1.23 | 46.6 (11.1) | 21.0 (5.00) |
| 5.83 | 1.48 | 1.39 | 1.40 | 2.23 | 47.9 (11.4) | 22.9 (5.45) |
| 5.77 | 1.70 | 2.34 | 2.36 | 3.10 | 47.9 (11.4) | 23.4 (5.58) |
| 5.58 | 2.63 | 3.34 | 3.37 | 4.27 | 47.9 (11.4) | 23.5 (5.60) |
| 5.48 | 3.31 | 4.02 | 4.05 | 5.63 | 48.3 (11.5) | 24.3 (5.79) |
| 5.27 | 5.37 | 4.36 | 4.41 | 6.50 | 47.9 (11.4) | 23.8 (5.66) |
| 5.30 | 5.01 | 5.49 | 5.54 | 7.97 | 49.1 (11.7) | 24.8 (5.90) |
| 4.92 | 12.0 | 5.43 | 5.55 | 9.33 | 47.9 (11.4) | 23.5 (5.59) |
| 4.63 | 23.4 | 6.11 | 6.34 | 13.2 | 48.7 (11.6) | 24.0 (5.71) |
| 3.98 | 105 | 11.3 | 12.4 | 18.4 | 46.6 (11.1) | 21.1 (5.03) |
| | | | | Mean | 47.9 ± 0.9 (11.4 ± 0.2) | 23.2 ± 1.2 (5.53 ± 0.28) |

naphthalene-$\beta$-sulphonic acids for comparison. It can be seen that the main effect of increasing affinity is to move the curve to higher pH values, just as was found for the simpler acids by the change in $pH_{mid}$ in Table 4.15. On any curve, too high a pH results in minimal adsorption whilst too low a pH produces high exhaustion and a consequently low concentration of dye in the bath, which in turn minimises levelling and migration possibilities. Thus for each dye there is an optimum pH range which produces good exhaustion combined with adequate levelling. This range moves to higher values as the

TABLE 4.17

**pH and dye concentration of a solution of Naphthalene Orange G free acid in contact with wool at 60 °C for varying times** [41]

| Time /days | Dye concentration /(mol $l^{-1}$) × $10^3$ | pH | $[H]_s$ /(mol $l^{-1}$) × $10^3$ | $[U]_s$ /(mol $l^{-1}$) × $10^3$ |
|---|---|---|---|---|
| 0 | 21.0 | 1.70 | 20.0 | 1.0 |
| 1 | 9.80 | 2.13 | 9.40 | 0.40 |
| 2 | 9.66 | 2.25 | 8.75 | 0.91 |
| 3 | 9.62 | 2.37 | 7.99 | 1.62 |
| 5 | 9.62 | 2.55 | 6.53 | 3.09 |
| 7 | 9.62 | 2.72 | 4.47 | 5.15 |

dye anion affinity increases, i.e. in practical terms, from levelling → milling → supermilling dyes.

The total dye affinity $\Delta\mu_{\pm}^{\ominus}$ may be calculated for each point on the titration curve by substituting the measured values in Eqn 4.109 with [X] equated to [D]. The derived Eqn 4.111 cannot be used, because of the lack of equivalence between [H] and [D] in solution. Because of possible fibre decomposition during the prolonged treatment required to reach equilibrium, the method is limited to dyes of low affinity (i.e. fast-diffusing dyes) which can be isolated as the free acid. The method does yield consistent results, however, as shown in Table 4.16, column 6.

With polybasic dyes a further problem arises as to whether the dye is assumed to be occupying only one site or as many sites as it has charges. In the former case, for a dye carrying a charge of $z$ then $z\theta_D = \theta_H$ and Eqn 4.109 becomes

$$-\Delta\mu_{\pm}^{\ominus} = -(z\Delta\mu_H^{\ominus} + \Delta\mu_D^{\ominus}) = RT \ln \left(\frac{\theta_H}{1-\theta_H}\right)^z \left(\frac{\theta}{z-\theta_H}\right) - RT \ln [H]_s^z[D]_s \qquad (4.128)$$

Alternatively, if the dye occupies $z$ sites then $\theta_D = \theta_H$, and

$$-\Delta\mu_{\pm}^{\ominus} = -(z\Delta\mu_H^{\ominus} + \Delta\mu_D^{\ominus}) = (z+1)\,RT \ln \frac{\theta_H}{1-\theta_H} - RT \ln [H]_s^z[D]_s \qquad (4.129)$$

The relative merits of the two approaches are difficult to assess. The steric problem of $z$ sites being in the required position favours the former, but the

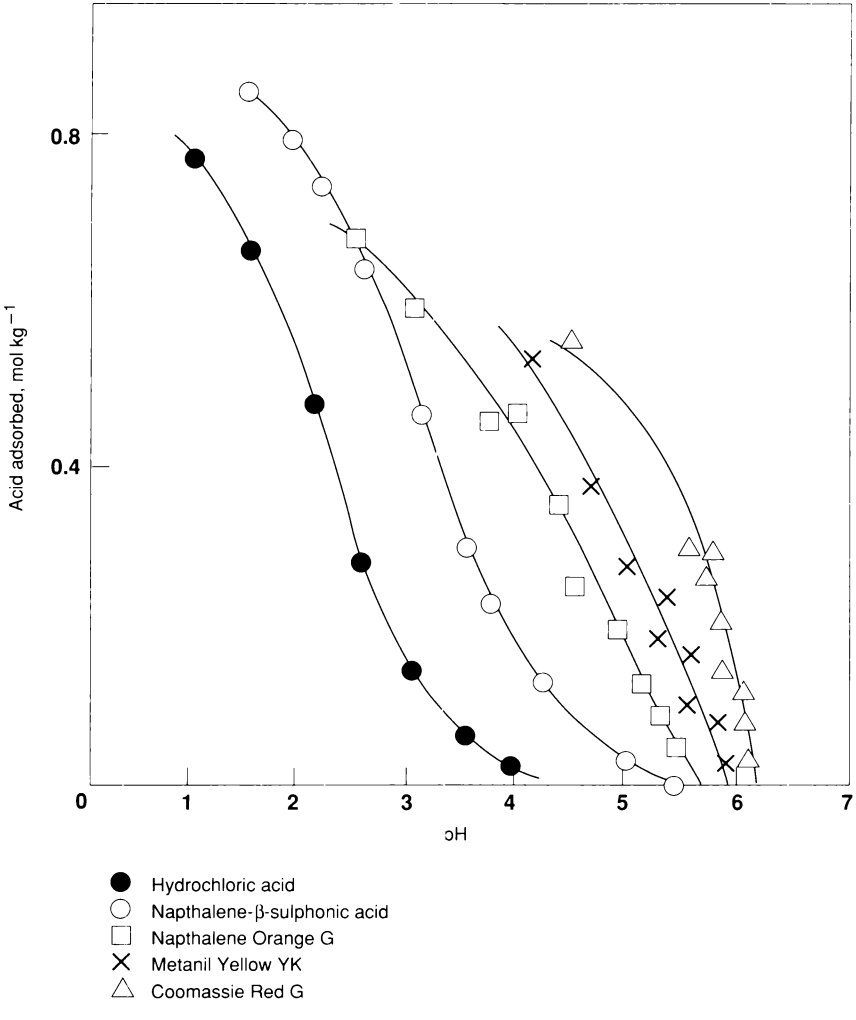


*Figure 4.15 – Titration curves of wool with free acids [8]*

fact that the fibre is saturated when an equivalent amount of dye is adsorbed favours the latter. However, measurements on the trisulphonated dye Naphthalene Scarlet 4R (C.I. Acid Red 18) [41] gave affinities which, in consistency, seemed marginally to favour the idea that three sites are occupied by one dye ion (Table 4.18).

TABLE 4.18

**Affinity of Naphthalene Scarlet 4R (free acid) for wool at 60 °C [41]**

| | $-\Delta\mu^{\ominus}_{\pm}$ kJ (kcal) $mol^{-1}$ for each dye anion occupying | |
|---|---|---|
| $\theta_H$ | one site | three sites |
| 0.080 | 110.0 (26.2) | 113.0 (26.9) |
| 0.166 | 106.3 (25.3) | 108.8 (25.9) |
| 0.523 | 99.1 (23.6) | 102.5 (24.4) |
| 0.855 | 95.3 (22.7) | 102.9 (24.5) |
| 0.945 | 95.3 (22.7) | 105.4 (25.1) |
| Mean | 101.2 ± 5.9 (24.1 ± 1.4) | 106.7 ± 3.9 (25.4 ± 0.9) |

### 4.5.9 Determination of affinity by displacement

It was known empirically that when applying low-affinity, levelling dyes to wool, the addition of neutral electrolyte to an acid dyebath reduces the amount of dye adsorbed, the effect increasing with increasing electrolyte concentration. Because of its overall effect on the quality of the dyeing the electrolyte was said to be acting as a *levelling agent*. This observation indicates that, when more than one type of anion is present in the dyebath, there is competition for sites in the wool, the final distribution of dye and electrolyte anions depending not only on the affinity of each but on their relative concentrations. The effect is observed only with dyes of low affinity, and only in acid solution. In neutral or alkaline solution the addition of electrolyte promotes adsorption in the same way as in the dyeing of cellulose. The pH of the changeover is determined by the isoelectric point of the dyed fibre.

This competition for sites led to the development of a method of comparing the affinities of dye anions with that of an inorganic anion by determining how much dye was displaced by given concentrations of inorganic electrolyte $Na_yX$ [10]. It was assumed that under the experimental conditions the amount of sodium ions taken up by the fibre was negligible in comparison with that of hydrogen ions, in other words that the dyebath contained an acid $H_yX$ and the dye acid $H_zD$. Again assuming that the number of basic and acidic sites in wool are the same, then

$$\theta_H = \theta_X + \theta_D \tag{4.130}$$

where $\theta_X$ is the fraction of positive sites occupied by the non-dye ion and assuming, if both ions are polybasic, that they occupy a number of sites equivalent to their charge. The affinity of the dye anion is given therefore by

$$-\Delta\mu_D^{\ominus} = RT \ln \frac{\theta_D}{1 - \theta_D - \theta_X} - RT \ln [D]_s + z\psi F \tag{4.131}$$

and that of the non-dye anion by

$$-\Delta\mu_X^{\ominus} = RT \ln \frac{\theta_X}{1 - \theta_D - \theta_X} - RT \ln [X]_s + y\psi F \tag{4.132}$$

Multiplying by $y$ and $z$ respectively and subtracting removes the electrical work term, to give

$$-(y\Delta\mu_D^{\ominus} - z\Delta\mu_X^{\ominus}) = RT \ln \left( \frac{\theta_D}{1 - \theta_D - \theta_X} \right)^y \left( \frac{1 - \theta_D - \theta_X}{\theta_X} \right)^z - RT \ln \frac{[D]_s^y}{[X]_s^z} \tag{4.133}$$

If the desorbing electrolyte is chosen so that the basicity of its anion is the same as that of the dye, then $y = z$ and Eqn 4.133 becomes

$$-(\Delta\mu_D^{\ominus} - \Delta\mu_X^{\ominus}) = RT \ln \frac{\theta_D}{\theta_X} \cdot \frac{[X]_s}{[D]_s} \tag{4.134}$$

The problems of estimating $[X]_f$ in order to obtain a value of $\theta_X$ may be overcome by carrying out the experiment at a sufficiently low pH that $\theta_H \rightarrow 1$, so that (from Eqn 4.130) $\theta_X = 1 - \theta_D$. Under these conditions

$$-(\Delta\mu_D^{\ominus} - \Delta\mu_X^{\ominus}) = RT \ln \frac{\theta_D}{1 - \theta_D} \cdot \frac{[X]_s}{[D]_s} \tag{4.135}$$

The results of desorbing Naphthalene Orange G (C.I. Acid Orange 7) from wool using sodium chloride at 60 °C are shown in Table 4.19 [41], where it has been assumed that the affinity of the chloride ion is so small that $\Delta\mu_X^{\ominus} = 0$. It can be seen that results are reasonably consistent over a wide range of salt concentrations.

The displacement method is a quite elegant means of determining affinities,

TABLE 4.19

**Affinity of Naphthalene Orange G by desorption with sodium chloride at 60 °C**

| $\theta_D$ | Dye in solution /(mol $l^{-1}$) × $10^5$ | Chloride ion in solution /mol $l^{-1}$ | $-\Delta\mu^{\ominus}$ /kJ (kcal) $mol^{-1}$ |
|---|---|---|---|
| 0.271 | 0.805 | 0.01 | 17.0 (4.05) |
| 0.271 | 1.02 | 0.02 | 18.0 (4.28) |
| 0.271 | 1.52 | 0.05 | 19.7 (4.69) |
| 0.271 | 3.18 | 0.10 | 19.6 (4.66) |
| 0.271 | 4.18 | 0.15 | 20.0 (4.75) |
| 0.271 | 5.66 | 0.20 | 19.9 (4.73) |
| 0.271 | 6.51 | 0.25 | 18.1 (4.32) |
| 0.271 | 11.9 | 0.50 | 20.4 (4.85) |
| 0.403 | 0.964 | 0.01 | 18.1 (4.32) |
| 0.403 | 1.16 | 0.02 | 19.6 (4.66) |
| 0.403 | 3.01 | 0.05 | 19.4 (4.63) |
| 0.403 | 6.65 | 0.10 | 19.2 (4.56) |
| 0.403 | 8.33 | 0.15 | 23.3 (5.54) |
| 0.403 | 11.1 | 0.20 | 19.7 (4.68) |
| 0.403 | 14.4 | 0.25 | 19.6 (4.67) |
| 0.403 | 29.6 | 0.50 | 19.5 (4.64) |
| 0.403 | 33.0 | 1.00 | 21.1 (5.02) |
| | | Mean | 19.3 ± 0.8 (4.6 ± 0.2) |

particularly if the apparatus shown in Figure 4.2 is used. There is an economy of experimental effort, and the short times of treatment involved are said to minimise decomposition of the wool although this could be offset by the use of very acid solutions to ensure that $\theta_H \rightarrow 1$. The limitation that the method applies only to low-affinity dyes because of the low affinity of the displacing inorganic ions can be overcome by using, as a displacing anion, a dye of contrasting colour. By this method it is possible to measure the amounts of each dye in the fibre and in the equilibrium solution by spectrophotometric means, thereby eliminating the need to keep the fibre saturated with ions, i.e. there is no need to use strongly acid solutions. From the results, the affinities of the two dyes may be calculated; it has however been found empirically that determining the affinity of one dye using a dye of known affinity as displacing agent rather than an inorganic ion gives better results, in that they are more closely comparable with those from other methods.

### 4.5.10 The adsorption of acid dyes by wool from neutral solution

The adsorption on to wool of the monobasic dye Naphthalene Orange G from neutral solutions has been studied at 60 °C in the presence of 0.1 mol $l^{-1}$ of sodium chloride [9]. In order to express the behaviour of the dye quantitatively Eqn 4.109 was modified by the replacement of [H] by [Na] throughout to give, for a dye of basicity $z$,

$$-\Delta\mu_{\pm}^{\ominus} = RT \ln \left( \frac{\theta_{Na}}{1 - \theta_{Na}} \right)^{z} \cdot \frac{\theta_D}{1 - \theta_D} - RT \ln [Na]_s^z [D]_s \qquad (4.136)$$

or, assuming that $\theta_{Na} = \theta_D$,

$$-\Delta\mu_{\pm}^{\ominus} = (z + 1)RT \ln \frac{\theta_D}{1 - \theta_D} - RT \ln [Na]_s^z [D]_s \qquad (4.137)$$

When this equation was used to evaluate the results they were found to be inconsistent, in that affinity decreased markedly with increasing concentration of dye applied and that on average it was much lower than values obtained by other methods, i.e. titration or desorption under acid conditions. In a further study [41] the saturation values of various level-dyeing acid dyes were determined from the adsorption isotherms using the method of reciprocal plotting; this revealed that the saturation value of wool dyed from neutral solution was very much lower in every case than that dyed from acid solution, i.e. *ca* 300 instead of 900 mmol $kg^{-1}$. When dibasic dyes were studied the discrepancy was even greater, with a saturation value of *ca* 100 mmol $kg^{-1}$. In addition, when the sodium chloride concentration was increased it was found that whilst at high applied dye concentrations the isotherm was

displaced to higher values of dye adsorbed, as would be expected, at low concentrations the adsorption was reduced.

It must be concluded that the reversal in the effect of added electrolyte occurs at a pH which is determined by the quantity and basicity of the adsorbed dye. Equally it must be concluded that the understanding of the neutral dyeing of wool is far from satisfactory.

### 4.5.11 The enthalpy of dyeing and the entropy of dyeing of acid dyes on wool

Studies of the effect of temperature on the affinity of acid dyes for wool have produced results that are very difficult to interpret. Few, if any, demonstrate a linear relationship when $-\Delta\mu^{\ominus}/T$ is plotted against $1/T$ as required by Eqn 4.21 [80], and indeed some results produce a parabolic relationship indicating that the enthalpy of dyeing goes from negative, through zero, to positive as the temperature increases [81]. Such results have tended to be over-emphasised – perhaps correctly, but possibly not, in view of the difficulties associated with measuring affinities on wool due to factors such as fibre degradation and dyebath contamination, and to the problems of calculating entropy values discussed previously. It would appear, however, that large values of the enthalpy of dyeing can be observed.

### 4.5.12 The maximum dye-combining power of wool

The theories described for the adsorption of simple acids and dyes by wool demand that the maximum acid-binding power of wool should be an amount equivalent to the number of basic groups in the fibre, although there is some doubt of the precise meaning of this in terms of polybasic anions. Most of the experimental evidence, particularly with low-affinity anions, indicates that an effect which may be considered as fibre saturation occurs when wool has adsorbed 0.8–0.9 moles of monobasic anion per kilogram of dry wool. Certain high-affinity dyes have been studied which show adsorptions in excess of this amount, however [82, 83]. Experiments in which wool was first deaminated with nitrous acid and then acetylated showed a decrease in the maximum amount of hydrochloric acid taken up to a value of 0.008 mol $kg^{-1}$, but this wool still adsorbed dye in excess of this (0.07 mol $kg^{-1}$) indicating that forces other than coulombic interaction between positive sites and negative dye were operating [84]. Thus, although there is much evidence that the dyeing of wool can be explained by the presence in the fibre of positive sites, certain discrepancies must be noted. These are

(a) the residual adsorption of dyes on completely deaminated wool;
(b) the excessive uptake of certain dyes;

(c) the upward trend of the titration curves of strong acids at low pH values;
(d) the fact that weak acids are adsorbed in the undissociated state in amounts far in excess of the number of basic groups in the fibre [85].

Although several suggestions have been advanced to account for the excessive adsorption, e.g. the ionisation of the weakly basic peptide groups to produce new sites at acid pH values, the situation is far from clear.

### 4.5.13 Anionic dyes on nylon

In the dyeing of wool problems arise because of fibre decomposition and dyebath contamination. Although less well realised this also occurs with polyamides, considerable quantities of ammonia being liberated into the dyebath from the decomposition of acid amide groups [86, 66]. That some discrepancy does occur is illustrated in Table 4.21, column $[U]_s$ (p. 344), which is the difference between $[H]_s$ and $[D]_s$. Using a pure, dye-free acid with no other addition these should be the same, and hence the difference must indicate the presence of some unknown cation or anion. Also the imido groups may hydrolyse, in particular under acid or alkaline conditions [87, 66]. Both effects are dependent on the internal pH of the fibre rather than the external pH in the bath, the hydrolysis of imido groups being particularly observed under conditions of 'overdyeing' when very severe acidic conditions can develop inside the fibre phase due to the excess of negative ions present. Measurements of the uptake of HCl by nylon 6, in which the experimental technique minimised the amount of adventitious impurity in the dyebath [88, 66], gave results that were quite different from those obtained by the conventional method. Clearly, as with wool, the problems of obtaining meaningful results are considerable but nevertheless progress has been made in establishing a mechanism of dyeing.

Nylon 6.6 is made by condensing stoichiometric proportions of hexamethylenediamine with adipic (hexane-1,6-dioic) acid. A product thus made should contain equal numbers of amino and carboxyl groups at the ends of the polymer chains but, because the chain length has to be controlled, small amounts of a monocarboxylic acid are added which reacts with some of the amino groups thereby terminating the growing chains with acyl groups. The finished product therefore contains fewer basic than acidic end-groups with, in addition, some terminal acyl groups. A typical nylon 6.6 has, by analysis, the constitution shown in Table 4.20.

The presence of basic and acidic groups in nylon suggested a similarity to wool and indeed, both experimentally and theoretically, the problem of the dyeing of nylon was attacked along similar lines. As with wool the adsorption of simple acids and alkalis was studied as a preliminary to the study of more complex dye ions, and the results were very similar. Typical acid titration

TABLE 4.20

**Constitution of a typical nylon yarn**

| Group | mol $kg^{-1}$ of dry yarn |
|---|---|
| Amine | 0.036 |
| Carboxyl | 0.090 |
| Amide | 8.85 |
| Terminal acyl | 0.063 |

curves produced for hydrochloric acid [41, 74, 89] show evidence of an inflection in the curve at acid pH (*ca* 2–3), at which point the amounts of acid adsorbed corresponded reasonably well with the number of basic end-groups in the fibre. At lower pH further acid is adsorbed, an effect which has been attributed to the ionisation of the amido groups producing more basic sites [90, 91, 92]. Curves taken to pH values higher than 7 show a shallow inflection at pH 6–7 which corresponds to the pH at which the remaining ionised carboxyl groups are equal in amount to the basic groups present, i.e. the isoelectric point of fibre. (See Figure 4.13 for a soluble protein.) The dependence of the amount of acid adsorbed on the number of basic end-groups has been demonstrated by deamination and by acetylation [74, 89] when the amount of acid adsorbed was reduced to a very small value. Additions of neutral electrolyte resulted in the displacement of the hydrochloric acid titration curve to higher pH values [74, 89]. When nylon is titrated with other acids the titration curve moves to higher pH values as the size and complexity of the anion increases [89].

Thus, in all respects related to the adsorption of simple acids, nylon behaves qualitatively in a manner exactly similar to wool and hence it is reasonable to apply the same basic equations. Certain modifications are necessary, however, to take into account the fact that, unlike wool, in most nylons the numbers of basic and acidic groups are not the same, acidic groups being in excess.

Starting from Eqn 4.109, if $[H]_f$ is the concentration of hydrogen ions bound to the nylon and $C$ is the saturation value (which, for normal dyeing conditions, is equal to the total number of carboxyl groups),

$$\theta_H = \frac{[H]_f}{C}$$

Also, if the content of amino groups is $B$, then for adsorption of the acid HX,

$$\theta_X = \frac{[X]_f}{B}$$

and the equation becomes

$$-\Delta\mu_{\pm}^{\ominus} = RT \ln \frac{[H]_f}{C - [H]_f} \cdot \frac{[X]_f}{B - [X]_f} - RT \ln [H]_s[X]_s \quad (4.138)$$

$[H]_f$ is the total concentration of hydrogen ions in the fibre, i.e. the amount adsorbed at any particular point on the titration curve $[H]_{ad}$ plus the amount present at the start of the titration which, if the titration was started at the isoelectric point of the fibre, is equal to the difference between the numbers of acidic and basic end-groups in the fibre:

$$[H]_f = [H]_{ad} + (C - B) \quad (4.139)$$

Clearly if the titration is started at some other point Eqn 4.139 no longer applies and, in this case, when $[H]_{ad}$ is plotted against $pH_s$ the shape of the titration curve will be different.

For a titration that starts at the isoelectric point, substituting in Eqn 4.138 using Eqn 4.139 gives

$$-\Delta\mu_{\pm}^{\ominus} = RT \ln \frac{[H]_{ad} + (C - B)}{B - [H]_{ad}} \cdot \frac{[X]_f}{B - [X]_f} - RT \ln [H]_s[X]_s \quad (4.140)$$

At any point in the titration the fibre must be electrically neutral, and hence the number of unfilled positive sites must equal that of unfilled negative sites. Thus, if the only electrolyte present is the acid HX, then

$$C - [H]_f = B - [X]_f \quad (4.141)$$

Combining Eqns 4.139 and 4.141 $[H]_{ad} = [X]_f$, and also, for electrical neutrality in solution, $[H]_s = [X]_s$. Substituting these equalities in Eqn 4.140 and rearranging gives

$$\frac{-\Delta\mu_{\pm}^{\ominus}}{2.303RT} = \log k \quad (4.142)$$

where

$$k = \frac{[X]_f(C - B + [X]_f)}{(B - [X]_f)^2[H]_s^2} \quad (4.143)$$

and $[X]_f$ is the amount adsorbed as observed in the titration experiment.

Rearranging Eqn 4.143,

$$\frac{[[X]_f([X]_f + C - B)]^{\frac{1}{2}}}{[H]_s} = Bk^{\frac{1}{2}} - [X]_f k^{\frac{1}{2}} = r \qquad (4.144)$$

and a graph of $r$ (calculated from experimental values of $[X]_f$) against $[X]_f$ should be linear with a slope of $-k^{\frac{1}{2}}$ and an intercept of $Bk^{\frac{1}{2}}$ from which the affinity and the maximum dye uptake, i.e. the amino group content, can be calculated.

Using data obtained from the titration of nylon 6.6 with hydrochloric acid [74, 93] straight-line relationships are indeed obtained when $r$ is plotted against $[Cl]_f$, giving values for $-\Delta\mu_{\pm}^{\ominus}$ of 43.7 (10.4), 45 (10.7) and 45.8 (10.9) kJ (kcal) $mol^{-1}$ at 18, 34.8 and 55.5 °C respectively. These must be compared with others obtained by calculating the affinity at the various points along the titration curve using Eqn 4.142 [41]. The average so obtained was 44.5 kJ (10.6 kcal) $mol^{-1}$ at room temperature although there was some variation in the results (±1.7 kJ) with a trend to higher values of $-\Delta\mu_{\pm}^{\ominus}$ as the pH increased.

The alternative approach of applying the Donnan method, as described for wool, is available when affinities may be calculated using the equivalent to Eqn 4.116. Variations in the values obtained are greater than in those using the Langmuir equations, however, which would therefore appear to be preferable.

### 4.5.14 The affinity of dyes for nylon

The simplest practical method would appear to be the direct measurement of the titration curve of the pure dye free acid, but even this is difficult as the experiment must be carried out under conditions in which the fibre is not saturated with dye, i.e. in the pH range 4–7. This in turn requires the application of very dilute, unbuffered solutions of dye and a very precise experimental technique. Work is reported on two dibasic dyes, Naphthalene Red EA (C.I. Acid Red 13) and Solway Blue BN (C.I. Acid Blue 45), using nylon 6.6 [41]. Two approaches have been used for calculating the dye affinity from these results, both assuming a nylon with an amine content of 0.037 and a carboxylic acid content of 0.090 mol $kg^{-1}$. The first uses Eqn 4.109 in the form for a dye of basicity $z$:

$$-\Delta\mu_{\pm}^{\ominus} = RT \ln\left(\frac{\theta_H}{1-\theta_H}\right)^z \cdot \frac{\theta_D}{1-\theta_D} - RT \ln [H]_s^z[D]_s \qquad (4.145)$$

which becomes, assuming that the maximum number of sites available to both hydrogen and dye ions is determined by the number of basic groups in

the fibre and that $[H]_f = z[D]_f$,

$$-\Delta\mu_{\pm}^{\ominus} = (z + 1)RT \ln \frac{\theta_D}{1 - \theta_D} - RT \ln [H]_s^z[D]_s \qquad (4.146)$$

Alternatively Eqn 4.140 may be used in the form for a dye of basicity $z$ [74] which gives, when $[H]_{ad}$ is equated to $z[D]_f$,

$$-\Delta\mu_{\pm}^{\ominus} = RT \ln \left( \frac{C - B + [D]_f}{B - [D]_f} \right)^z \cdot \frac{z[D]_f}{B - z[D]_f} - RT \ln [H]_s^z[D]_s - RT \ln z \qquad (4.147)$$

The affinities obtained for Naphthalene Red EA using the two equations are shown in Table 4.21. Neither set shows a definite trend but there is some variation, most probably due to random experimental error. Unfortunately the results are not the same and this is repeated when other methods of calculation are used, indicating that a problem still remains in deciding on the correct form of equation to use. Providing that the same equation is used, however, then the affinities so obtained may be compared.

In order to avoid the practical problems of measuring acid titration curves, affinities have been determined using a desorption method. Unfortunately, whilst some of the practical problems are overcome, the essential question remains of the form of equation that should be applied to the results. Using the Gilbert–Rideal equations to deduce a formula for calculating the relative affinity of a dye anion by desorption with sodium chloride [94] gave, for a monobasic dye,

$$-(\Delta\mu_D^{\ominus} - \Delta\mu_{Cl}^{\ominus}) = RT \ln \frac{\theta_D}{1 - \theta_D} - RT \ln [D]_s + RT \ln [Cl]_s \qquad (4.148)$$

and, for a dibasic dye,

$$-(\Delta\mu_D^{\ominus} - 2\Delta\mu_{Cl}^{\ominus}) = RT \ln \left( \frac{\theta_D}{1 - \theta_D} \right)^2 \cdot \frac{\theta_D}{2 - \theta_D} - RT \ln [D]_s + 2RT \ln [Cl]_s \qquad (4.149)$$

These were applied to the results of desorptions from nylon during which the fibre was kept as saturated as possible with hydrogen ions, and in this way the affinities of six acid dyes were obtained (Table 4.22). Other workers [95] used Eqn 4.142 in the form for a monobasic dye, which gives Eqn 4.150 as the equivalent of Eqn 4.143:

TABLE 4.21

**The titration of nylon 6.6 with Naphthalene Red EA free acid** [41]

Fibre end-groups: $-NH_2 = 0.037$ mol kg$^{-1}$ $K_{NH_2} = 2.6 \times 10^{-11}$
$-COOH = 0.090$ mol kg$^{-1}$ $K_{COOH} = 1.6 \times 10^{-5}$
Temperature = 60 °C, $V = 0.1$ l kg$^{-1}$, $z = 2$, $[Na]_s = 0$, $[Cl]_s = 0$.

| | | | | | $-\Delta\mu^{\ominus}$/kJ (kcal) mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Langmuir | | New treatment (Eqn 4.167) | |
| | $[H]_s$ | $[U]_s$ | $[D]_s$ | $[D]_f$ | | | $NH_2$ (mol l$^{-1}$) = | |
| pH | /(mol l$^{-1}$) $\times 10^7$ | /(mol l$^{-1}$) $\times 10^5$ | /(mol l$^{-1}$) $\times 10^5$ | /(mol l$^{-1}$) $\times 10$ | Eqn 4.146 | Eqn 4.147 | 0.37 | 0.36 |
| 4.71 | 195.0 | 52.8 | 27.4 | 1.79 | 115.1 (27.4) | 121.0 (28.8) | 40.7 (9.7) | 50.8 (12.1) |
| 5.08 | 83.2 | 10.6 | 5.35 | 1.76 | 114.6 (27.3) | 118.4 (28.2) | 47.5 (11.3) | 52.1 (12.4) |
| 5.15 | 70.8 | 3.83 | 2.27 | 1.72 | 114.6 (27.3) | 119.3 (28.4) | 48.7 (11.6) | 51.7 (12.3) |
| 5.39 | 40.7 | 4.06 | 2.24 | 1.66 | 115.1 (27.4) | 117.6 (28.0) | 49.6 (11.8) | 51.3 (12.2) |
| 5.79 | 16.2 | 3.88 | 2.02 | 1.53 | 115.1 (27.4) | 120.1 (28.6) | 51.7 (12.3) | 52.5 (12.5) |
| 6.10 | 7.94 | 3.61 | 1.85 | 1.40 | 115.5 (27.5) | 119.7 (28.5) | 53.3 (12.7) | 54.2 (12.9) |
| 6.17 | 6.76 | 2.63 | 1.35 | 1.22 | 113.4 (27.0) | 118.0 (28.1) | 53.3 (12.7) | 53.3 (12.7) |
| 6.30 | 5.01 | 2.37 | 1.21 | 1.13 | 113.8 (27.1) | 118.4 (28.2) | 53.8 (12.8) | 54.2 (12.9) |
| 6.37 | 4.27 | 2.03 | 1.04 | 1.07 | 113.0 (26.9) | 118.9 (28.3) | 54.2 (12.9) | 54.6 (13.0) |
| 6.28 | 5.25 | 1.66 | 0.855 | 1.05 | 115.5 (27.5) | 118.0 (28.1) | 53.3 (12.7) | 53.8 (12.8) |
| 6.72 | 1.91 | 1.68 | 0.850 | 0.890 | 116.0 (27.6) | 121.4 (28.9) | 57.5 (13.7) | 57.9 (13.8) |
| 6.54 | 2.88 | 1.45 | 0.740 | 0.780 | 113.8 (27.1) | 118.4 (28.2) | 54.2 (12.9) | 54.6 (13.0) |
| 6.70 | 2.00 | 1.20 | 0.610 | 0.745 | 113.8 (27.1) | 119.7 (28.5) | 56.7 (13.5) | 56.7 (13.5) |
| 6.94 | 1.15 | 0.552 | 0.282 | 0.570 | 114.2 (27.2) | 122.6 (29.2) | 60.1 (14.3) | 60.1 (14.3) |
| 6.83 | 1.48 | 0.669 | 0.342 | 0.460 | 110.9 (26.4) | 119.7 (28.5) | 56.7 (13.5) | 57.9 (13.8) |
| 6.90 | 1.26 | 0.211 | 0.112 | 0.415 | 113.4 (27.0) | 123.1 (29.3) | 60.1 (14.3) | 60.5 (14.4) |
| | | | | Means | 114.2 ± 1.26 (27.2 ± 0.3) | 119.7 ± 1.7 (28.5 ± 0.4) | 53.3 ± 4.6 (12.7 ± 1.1) | 54.6 ± 2.9 (13.0 ± 0.7) |

TABLE 4.22

**Affinity of acid dyes for nylon at 98 °C and pH 3.2** [94]

| Dye | C.I. generic name | $z$ | $-(\Delta\mu^{\ominus}_{B} - z\Delta\mu^{\ominus}_{Cl})$ /kJ (kcal) $mol^{-1}$ |
|---|---|---|---|
| Metanil Yellow YK | Acid Yellow 36 | 1 | 26.0 (6.2) |
| Anthraquinone Blue RXO | | 1 | 25.2 (6.0) |
| Orange RO | | 1 | 24.4 (5.8) |
| Orange 11 | Acid Orange 7 | 1 | 21.0 (5.0) |
| Anthraquinone Green G | | 2 | 20.6 (4.9) |
| Anthraquinone Blue B | | 2 | 9.7 (2.3) |

$$k = \frac{[D]_f(C - B + [D]_f)}{(B - [D]_f)^2.[H]_s[D]_s} \tag{4.150}$$

Rearranging Eqn 4.150 gives the equivalent to Eqn 4.144 but in terms of $[D]_f$:

$$\left[\frac{[D]_f(C - B + [D]_f)}{[H]_s[D]_s}\right]^{\frac{1}{2}} = Bk^{\frac{1}{2}} - [D]_f k^{\frac{1}{2}} = r \tag{4.151}$$

TABLE 4.23

**Affinity of acid dyes for nylon** [95]

| Dye | Temp /°C | Saturation value $B$ /mmol $kg^{-1}$ | $k \times 10^{11}$ | $-\Delta\mu^{\ominus}_{HD}$ /kJ (kcal) $mol^{-1}$ | $-\Delta H^{\ominus}$ /kJ (kcal) $mol^{-1}$ | $\Delta S^{\ominus}$ /J (cal) $K^{-1}\,mol^{-1}$ |
|---|---|---|---|---|---|---|
| Metanil Yellow YK (C.I. Acid Yellow 36) | 21 | 30.3 | 40.0 | 71.2 (16.96) | 38.2 (9.1) | 113.4 (27) |
| | 80 | 29.2 | 3.0 | 78.0 (18.56) | | |
| Quinizarine Blue (C.I. Acid Violet 43) | 21 | 28.0 | 31.0 | 70.6 (16.81) | 38.2 (9.1) | 109.2 (26) |
| | 80 | 28.3 | 2.3 | 77.1 (18.36) | | |

Plotting $r$ against $[D]_f$ for results from both adsorption and desorption experiments gave the same straight line, from which the affinity and the maximum dye uptake could be calculated (Table 4.23).

Another, more comprehensive investigation into the dyeing of nylon with acid dyes [96] used a statistical, thermodynamic argument to derive Eqn 4.152:

$$-(\Delta\mu_D^{\ominus} - \Delta\mu_Y^{\ominus}) = RT \ln \frac{\theta_D}{1 - \theta_D} \cdot \frac{[Y]_s}{[D]_s} - RT \ln \frac{z}{y} \qquad (4.152)$$

where Y is an anion of charge $y$, and applied this to the results from the desorption of three dibasic acid dyes with chloride ions. The results for one of the dyes are shown in Table 4.24, where it can be seen that a reasonable consistency in the value of the affinity is obtained using this equation.

An alternative equation was derived using the principles of the Donnan approach:

$$-\Delta\mu_D^{\ominus} = RT \ln \frac{\theta_D}{(1 - \theta_D)^z} \cdot \frac{[Cl]_s}{[D]_s} - RT \ln zV \qquad (4.153)$$

where $V$ = the volume of the internal phase in $1\ kg^{-1}$ of dry fibre; but this gave results that were far from consistent and must be considered unsatisfactory. In this work some 14 dyes were studied using chloride ion desorption, with the results shown in Table 4.25. In addition certain of the dyes were desorbed using sulphate ions, when it was found that the affinities obtained were very much higher than with chloride. To correct this it was considered that, at the pH of the experiments (3.20), the sulphate would not be present as $SO_4^{2-}$ but as $HSO_4^-$ (the p$K$ for the second dissociation of sulphuric acid being 1.92) and hence an amount of 10.79 kJ (2.87 kcal) $mol^{-1}$ was subtracted from the measured affinities. This tended to overcorrect but did give results which were closer to those from chloride desorption.

The use of desorption techniques does not seem to be the answer to the problems associated with the measurement of titration curves since, once again, the availability of different equations, all purporting to give affinity but in fact giving different values from the same experimental data, leads to uncertainty and consequent lack of confidence that an acceptable equation has been derived.

### 4.5.15 The overdyeing of nylon

Adsorption of anionic dye in excess of the number of basic groups available in the fibre is much more important for nylon than it is for wool, because of the smaller number of basic groups involved, i.e. *ca* 30–50 mmol $kg^{-1}$ for

TABLE 4.24

**Affinity of Solway Blue A (C.I. Acid Blue 69) by desorption from nylon 6.6 using sodium chloride** [74, 96]

Fibre end-groups: $-NH_2 = 0.030$ mol kg$^{-1}$ $K_{NH_2} = 2.6 \times 10^{-11}$
$-COOH = 0.090$ mol kg$^{-1}$ $K_{COOH} = 1.6 \times 10^{-5}$
Temperature = 75 °C, pH = 3.52, $[H]_s = 3.02 \times 10^{-4}$, $z = 2$.

| | | $-\Delta\mu^{\ominus}$/kJ (kcal) mol$^{-1}$ | | | | |
|---|---|---|---|---|---|---|
| | | Sites | | New treatment (Eqn 4.167) | | |
| $\theta_D$ | [NaCl] /mol l$^{-1}$ | Donnan (Eqn 4.153) | Gilbert–Rideal (Eqn 4.152) | $V = 0.05$ | $V = 0.1$ | $V = 0.2$ |
| | 0.051 | 18.0 | 18.4 | 17.6 | 17.2 | 16.8 |
| 0.346 | | (4.29) | (4.38) | (4.19) | (4.10) | (4.01) |
| | 0.101 | 20.2 | 18.6 | | 17.1 | |
| | | (4.82) | (4.44) | | (4.07) | |
| | 0.201 | 23.1 | 19.5 | | 17.3 | |
| | | (5.50) | (4.64) | | (4.13) | |
| | 0.051 | 19.4 | 19.3 | | 18.5 | |
| 0.447 | | (4.61) | (4.59) | | (4.41) | |
| | 0.101 | 21.6 | 19.4 | | 18.1 | |
| | | (5.15) | (4.62) | | (4.32) | |
| | 0.201 | 24.3 | 20.1 | | 17.9 | |
| | | (5.79) | (4.79) | | (4.27) | |
| | 0.051 | 19.4 | 19.4 | | 18.6 | |
| 0.460 | | (4.62) | (4.62) | | (4.42) | |
| | 0.101 | 21.2 | 19.0 | | 17.6 | |
| | | (5.05) | (4.52) | | (4.18) | |
| | 0.201 | 24.3 | 20.2 | | 17.9 | |
| | | (5.78) | (4.80) | | (4.25) | |
| | 0.051 | 20.5 | 19.8 | 20.0 | 19.2 | 18.4 |
| 0.549 | | (4.88) | (4.72) | (4.76) | (4.58) | (4.39) |
| | 0.101 | 24.4 | 20.0 | | 18.6 | |
| | | (5.81) | (4.76) | | (4.42) | |
| | 0.201 | 25.7 | 21.1 | | 18.5 | |
| | | (6.12) | (5.03) | | (4.40) | |
| | Means | 21.8 ± 2.3 | 19.6 ± 0.7 | | 18.1 ± 0.6 | |
| | | (5.20 ± 0.56) | (4.66 ± 0.17) | | (4.30 ± 0.15) | |

nylon compared with 800–900 mmol kg$^{-1}$ for wool. Typical titration curves for three acid dyes on nylon 6.6 are shown in Figure 4.16 and it can be seen that three regions are distinguishable [91]. Region A is typical of anionic titration; its position on the pH axis is defined by the affinity of the anion

TABLE 4.25

**The affinities of acid dyes for nylon by desorption at 75 °C** [96]

| Dye | $z$ | $-(\Delta\mu_D^{\ominus} - \Delta\mu_Y^{\ominus})$/kJ (kcal) mol$^{-1}$ by desorption with | | |
|---|---|---|---|---|
| | | chloride | sulphate | hydrogen-sulphate |
| Naphthalene Red J | 1 | 32.2 (7.66) | – | – |
| Naphthalene Orange 1 | 1 | 25.9 (6.17) | 32.8 (7.80) | 20.7 (4.93) |
| Naphthalene Orange RO | 1 | 25.3 (6.03) | 32.8 (7.80) | 20.7 (4.93) |
| Naphthalene Orange G | 1 | 24.4 (5.82) | 30.8 (7.33) | 18.7 (4.46) |
| Lissamine Fast Red 7BP | 2 | 27.8 (6.62) | 35.9 (8.54) | (5.67) |
| Naphthalene Red EA | 2 | 27.4 (6.52) | – | – |
| Lissamine Fast Red 6B | 2 | 22.6 (5.37) | 31.0 (7.39) | 19.0 (4.52) |
| Lissamine Fast Yellow 2G | 2 | 22.3 (5.31) | 30.7 (7.31) | 18.7 (4.44) |
| Azo Geranine 2G | 2 | 21.5 (5.11) | – | – |
| Solway Blue BN | 2 | 21.2 (5.05) | 30.2 (7.18) | 18.1 (4.31) |
| Naphthalene Fast Orange 2G | 2 | 21.0 (5.00) | 26.9 (6.41) | 14.9 (3.54) |
| Solway Blue A | 2 | 19.6 (4.67) | 28.6 (6.80) | 16.5 (3.93) |
| Naphthalene Scarlet 4R | 3 | 24.7 (5.88) | – | – |
| Tartrazine N | 3 | 21.0 (5.01) | 27.5 (6.54) | 15.4 (3.67) |

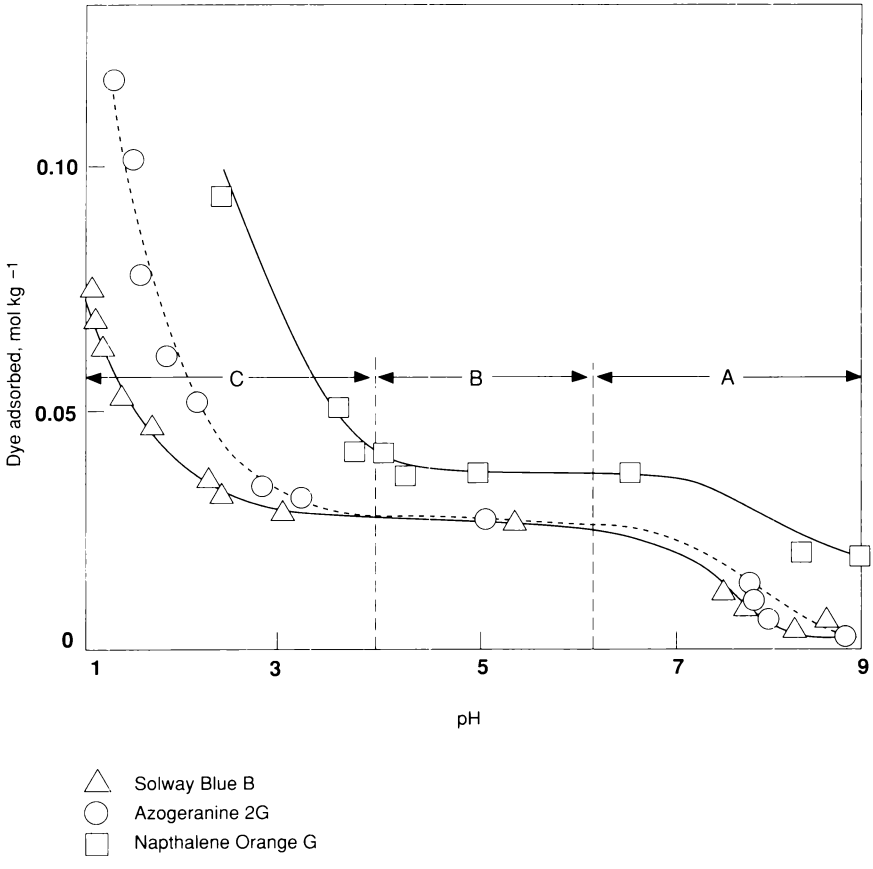


*Figure 4.16 – Adsorption of acid dyes on nylon yarn at different pH values at 60 °C [91]*

used. As the pH decreases this changes to a plateau region B, which extends over several pH units at values again determined by the affinity of the anion. This region is not always well defined but corresponds essentially to the number of amino end-groups present in the nylon, i.e. it is a region of electrostatic saturation; this has been clearly demonstrated with nylons containing different amounts of end-group [41], when the amount of dye adsorbed was in linear relationship to the number of end-groups present

[97]. At lower pH values is region C, where dye is adsorbed in amounts which exceed the normal (so-called) 'saturation value' and adsorption continues to increase with decreasing pH apparently without limit. The change from region B to region C is clearly also dye-dependent and with certain dyes can occur at relatively high pH values. This dyeing in excess of the amount of available amino end-group is referred to as *overdyeing*. It can also occur with certain dyes as the concentration applied is increased at constant pH [96].

Several explanations have been offered to explain this adsorption of dye in excess of the number of available basic sites. One is that in this region of low pH the amido groups of the nylon chain are hydrolysed, thereby producing amino groups for further dye adsorption [95]; the process is favoured by the need for the large amounts of dye taken up to be accompanied by hydrogen ions, thereby making the internal pH of the fibre even lower than that in the external bath. That such hydrolysis occurs is demonstrated by the fall in viscosity of solutions of overdyed nylon. In addition, if overdyed nylon is stripped of dye and then redyed at higher pH values, then in regions A and B the dye uptake is greater than with the untreated fibre showing that more basic sites are now available. An alternative explanation of overdyeing is that, at the high levels of acidity in the fibre, the main-chain amido groups become ionised to give —$OCNH_2^+$—, which then provide extra sites for dye adsorption. This of course would be only a temporary feature, and would not result in increased uptake after stripping and redyeing unless such ionisation was a precursor to hydrolysis.

Such explanations of overdyeing revolve around the presence in the fibre of an increased number of dyeing sites, and as such they are the result of the almost universal adoption of a site theory to explain the dyeing of nylon. The possibility that overdyeing and indeed all dyeing of nylon occurs as a result of attractive forces which are non-electrostatic in nature has only recently been considered [98, 99], an approach described in section 4.6. With such a mechanism, of course, overdyeing would be achieved without the formation of new sites but when it occurs it results in fibre degradation due to the development of highly acidic conditions in the internal fibre phase. The changing electrical environment in the fibre, as a result of degradation, will favour the adsorption of even more dye.

### 4.5.16 Cationic dyes on acrylic fibres

The polymerisation of acrylonitrile and its copolymers is carried out using redox initiators and the residues of these, attached to the chain ends, result in most acrylic fibres containing sulphate or sulphonic acid end-groups. Because of these anionic groups acrylic fibres can be dyed with cationic (basic) dyes as discussed in Chapter 3. The capacity of these fibres to take

up basic dye is increased if the co-monomer also carries an acidic group, for example sulphonic, phosphoric or carboxylic acid. However, whilst the dye uptake of fibres containing only strongly acidic groups is unaffected by pH changes over a wide range, because the anionic groups remain ionised, those containing weakly acidic groups (such as carboxylic acid) show a decrease in dye uptake as the pH is reduced due to the group changing to the un-ionised form.

For acrylic fibres not containing acid co-monomers, the uptake of basic dye is limited by the number of acidic end-groups in the fibre. This was established [100, 101, 102] when reciprocal plots of $1/[D]_f$ against $1/[D]_s$ were found to give saturation values of 31–35 mmol $kg^{-1}$, which agreed very closely to the number of end-groups measured by titration or by sulphur analysis (Figure 4.17).

The fibre carries acidic groups and it has been considered that it should

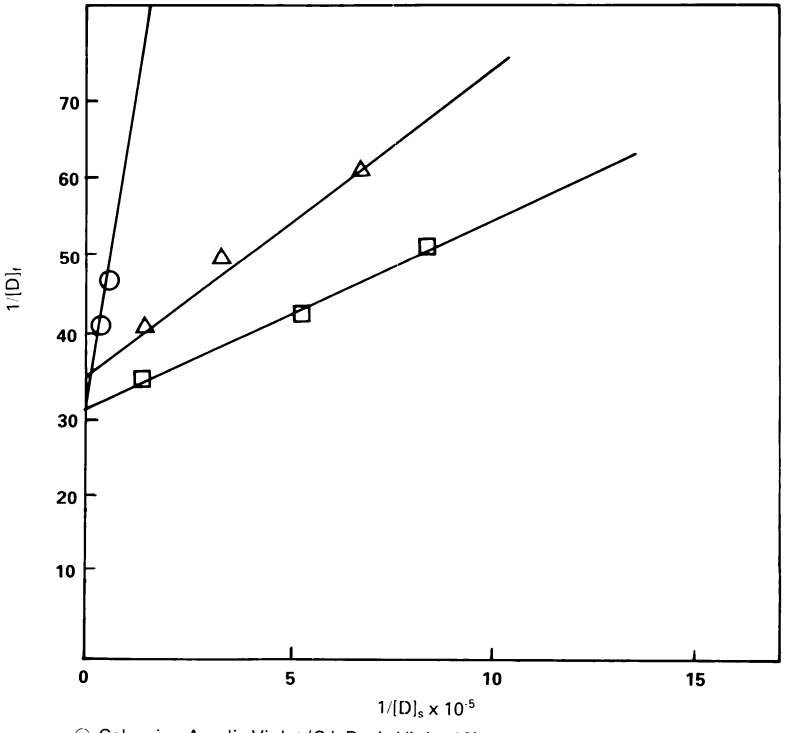


*Figure 4.17 – Reciprocal isotherms for basic dyes on Orlon 42 at 100 °C [100, 101]*

act as an ion-exchange medium in which hydrogen ions associated with the acid groups are exchanged for dye cations [103, 104], thus:

$$\text{Fibre—}SO_3H_f + D_s^+ \rightleftharpoons \text{Fibre–}SO_3D_f + H_s^+$$

which would have an equilibrium constant

$$K_H^D = \frac{[H]_s[D]_f}{[D]_s[H]_f} \tag{4.154}$$

Although the convention adopted throughout is that fibre concentrations are in terms of mol $l^{-1}$ of fibre phase, there is no need to define a $V$ term in the above since it appears at top and bottom and hence cancels out. Since the fibre must be considered to be electrically neutral, then

$$[S]_f = [H]_f + [D]_f$$

where $[S]_f$ = the number of available acidic sites, and hence

$$K_H^D = \frac{[H]_s}{[D]_s} \cdot \frac{[D]_f}{[S]_f - [D]_f} \tag{4.155}$$

Assuming the pH of the bath to remain constant, i.e. $[H]_s$ = constant, then Eqn 4.155 may be rearranged to give

$$\frac{1}{[D]_f} = \frac{1}{[S]_f} + \frac{1}{K'[S]_f} \cdot \frac{1}{[D]_s} \tag{4.156}$$

where

$$K' = K_H^D/[H]_s$$

Thus a plot of $1/[D]_f$ against $1/[D]_s$, measured at constant pH, should give a straight line with an intercept of $1/[S]_f$. This has been done [101] using a variety of fibres, and the values of $[S]_f$ obtained agreed well with the results from the titration of the dissolved fibres. It was also found, however, that this saturation value increased as the pH of application increased, a result that was interpreted as being due to the presence of weakly acidic end-groups in the fibre which only ionised at higher pH.

The action of added sodium ions in reducing the equilibrium uptake of dye confirms the ion-exchange mechanism, demonstrating that ions such as sodium can exchange with either hydrogen ions or dye ions. In order to

account for the action of sodium ions two ion-exchange constants have been defined [103]:

$$K_D^H = \frac{[H]_f}{[D]_f} \cdot \frac{[D]_s}{[H]_s} \tag{4.157}$$

$$K_D^{Na} = \frac{[Na]_f}{[D]_f} \cdot \frac{[D]_s}{[Na]_s} \tag{4.158}$$

(It must be noted that these equations are in the reciprocal form compared to Eqn 4.154.) If no other ions exert any significant influence then, for electrical neutrality,

$$[S]_f = [D]_f + [H]_f + [Na]_f \tag{4.159}$$

Replacing $[H]_f$ and $[Na]_f$, using Eqns 4.157 and 4.158 respectively, gives

$$[S]_f - [D]_f = \frac{[D]_f}{[D]_s}(K_D^H[H]_s + K_D^{Na}[Na]_s) \tag{4.160}$$

If a measured constant $K_M$ is defined such that

$$\frac{1}{K_M} = ([S]_f - [D]_f) \cdot \frac{[D]_s}{[D]_f} = K_D^H[H]_s + K_D^{Na}[Na]_s \tag{4.161}$$

then this can be rearranged to give Eqn 4.161a:

$$\frac{1}{[D]_f} = \frac{1}{[S]_f K_M} \cdot \frac{1}{[D]_s} + \frac{1}{[S]_f} \tag{4.161a}$$

and, at constant $[H]_s$ and $[Na]_s$, a plot of $1/[D]_f$ against $1/[D]_s$ should again be linear but having a slope that varies with pH and salt concentration. This was found to be so. In addition, if $1/K_M$ is plotted against $[H]_s$ with $[Na]_s$ constant or against $[Na]_s$ with $[H]_s$ constant, then a linear relationship should be obtained in both cases. Again this was found [103].

Using various modifications of these equations [103] it was possible to describe how the Langmuir adsorption constant could be affected by sodium and hydrogen ion concentrations and, in addition, how the separate ion-exchange 'constants' were influenced by the amount of dye present.

If Eqn 4.155 is rearranged then, in the absence of sodium ions, it becomes

$$\frac{[D]_f}{[D]_s} = \frac{K_H^D}{[H]_s}([S]_f - [D]_f) \tag{4.162}$$

and hence if $[D]_f/[D]_s$ is plotted against $[D]_f$ a straight line of slope $K_H^D/[H]_s$ should result, with an intercept when $[D]_f/[D]_s = 0$ of $[S]_f$. From the results of experiments using five representative basic dyes on films made from a copolymer of acrylonitrile with *ca* 7 per cent of vinyl acetate [105] it was indeed found that linear relationships were obtained but that with some dyes this obtained only over 80 per cent of the concentration range; at higher values of $[D]_f$ a 'tail' was shown, indicating that under these conditions dye was being adsorbed in excess of the number of acidic end-groups (Figure 4.18(a)). The results obtained from the linear plots and from extrapolation

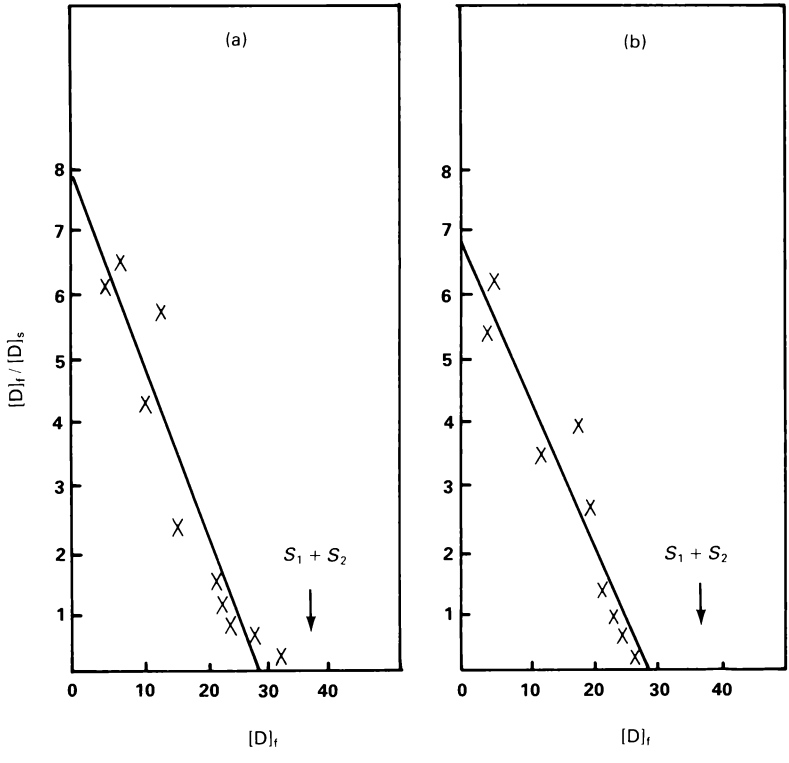


*Figure 4.18 – Langmuir plots of adsorption isotherms ($[D]_f$ in mmol $kg^{-1}$) [104]: (a) C.I. Basic Blue 22, (b) C.I. Basic Red 14*

of the linear part of the curves produced consistent values for the intercept of 26–28 mmol $kg^{-1}$ ($S_1$) shown in Table 4.26. However, the total amount of end-group from titration measurements was 35.1 mmol $kg^{-1}$ ($S_1 + S_2$). Since with certain dyes the amount of dye adsorbed reached values approximat-

TABLE 4.26

**Adsorption of basic dyes by an acrylic copolymer film** [105]

pH = 3.4, $[H]_s = 3.98 \times 10^{-4}$ mol $l^{-1}$, $K_1 = K_H^D/[H]_s$.

| Dye | Temp. /°C | $K_1$ $\times 10^{-6}$ | $K_1S_1$ $\times 10^{-4}$ | $S_1$ /mmol $kg^{-1}$ | $K_H^D$ | $-\Delta\mu^\ominus$ /kJ (kcal) $mol^{-1}$ |
|---|---|---|---|---|---|---|
| C.I. Basic Blue 22 | 99.8 | 0.29 | 0.81 | 28 | 115 | 14.7 (3.50) |
| C.I. Basic Red 14 | 99.1 | 2.50 | 6.90 | 28 | 995 | 21.4 (5.09) |
| C.I. Basic Red 24 | 94.6 | 1.30 | 3.40 | 27 | 518 | 19.1 (4.55) |
| C.I. Basic Violet 19 | 99.3 | 3.30 | 8.50 | 26 | 1312 | 22.2 (5.29) |
| Oxazine dye | 99.1 | 3.70 | 9.50 | 26 | 1472 | 22.6 (5.37) |

ing to $(S_1 + S_2)$ it was considered that two kinds of fibre end-group were operating, which led to the defining of an isotherm based on

$$[D]_f = \frac{K_1[S]_1[D]_s}{1 + K_1[D]_s} + \frac{K_2[S]_2[D]_s}{1 + K_2[D]_s} \tag{4.163}$$

which was shown to fit the data for those dyes which showed this 'tail'. Unfortunately not all dyes conform with this equation, which represents a weakness in the proposition. It has also been suggested [102] that, because at a certain level the amount of dye adsorbed increases linearly with the concentration of dye applied, a constant-partition 'solution' process is superimposed on the Langmuir isotherm. This led to the formulation of the equation

$$[D]_f = \frac{K_1[D]_s}{1 + K_1[D]_s} \cdot [S]_f + K_3[D]_s \tag{4.164}$$

which also gave a good fit to the data.

Just as for nylon, the apparent 'overdyeing' of acrylic fibres is the consequence of the adoption of a site mechanism of dyeing, and again the possibility must be considered that dyeing is the result of attractive forces which are non-electrostatic in nature [98, 99]. This will be dealt with later. However, since Eqn 4.155, based on an ion-exchange mechanism, appears

to give a satisfactory interpretation of the greater part of the dyeing process, the constant $K_H^D$ can be regarded as a measure of affinity, so that $-\Delta\mu_D^\ominus = RT \ln K_H^D$.

Some values of $-\Delta\mu_D^\ominus$ are given in Table 4.26.