4.3 CLASSIFICATION OF DYEING SYSTEMS

Earlier it was said that in order to use Eqn 4.16 to calculate the affinity of a dye for a particular fibre it was necessary to choose a suitable function to represent the activity of the dye in the fibre phase, and that the function chosen depended on the model or mechanism of dyeing appropriate to the system under consideration. A study of the various dyeing systems of interest to which the equation would apply, i.e. reversible systems, reveals that they can be classified as follows:

1. *Non-ionic dyes* The only major class of dyes under this heading is that of the disperse dyes, and they may be considered
   (a) on essentially non-ionic substrates, such as the hydrophobic fibres produced from polyester, secondary cellulose acetate and cellulose triacetate, and
   (b) on ionic substrates such as nylon, wool and cellulose.
2. *Ionic dyes* applied to substrates which themselves carry a charge. These may be sub-divided into two classes:
   (a) where the substrate carries the same charge as the dye, as exemplified by anionic dyes on cellulose, and
   (b) where the substrate carries an opposite charge to that on the dye, under the normal conditions of application, such as anionic dyes on wool and nylon and cationic dyes on acrylic fibres.

This sub-division of ionic dyes describes the original thinking on the mechanisms of dyeing. It has more recently been suggested that such a separation of ideas is superfluous and that there need be only one system, i.e. ionic dyes on ionic substrates. Despite this suggestion, however, the various methods of applying the theory will be discussed, initially, according to this classification.

4.3.1 Non-ionic dyes on essentially non-ionic substrates

The introduction of secondary cellulose acetate in the 1920s produced an immediate problem, in that this fibre could not be dyed with the available water-soluble dyes. It was found, however, that coloration of the fibre was achieved using weakly polar dyes of relatively small molecular size. Such dyes, because of their lack of solubilising groups, are almost insoluble in water and this meant that they had to be applied as an aqueous dispersion of essentially solid dye particles in the dyebath in order to produce acceptable strengths of dyeing. Such a method of application led naturally to the adoption of the name *disperse dyes*.

In attempting to explain the mechanism of transfer of dye molecules from the solid dye particles to the substrate, two views were expressed. One

suggested that solid dye was adsorbed on the surface of the material, from where it penetrated the fibre by a process of dissolution or solid-state diffusion; in support of this it had been observed microscopically that particles of dye adhered to the surface of the fibre and then slowly disappeared as adsorption took place [22]. Support for this view came from the further observation that if secondary cellulose acetate was shaken with solid dye powder for several days at 60 °C it became dyed. When such evidence was combined with the general belief held at the time that disperse dyes were insoluble in water, it is not surprising that this view of the mechanism of dyeing was preferred to the alternative. This was that disperse dyes were transferred to the fibre from a dilute solution surrounding the particles, by the same processes as ionic dyes [23], i.e. an aqueous solution theory. Later it was found that surface adhesion of particles did not always occur, and that when it did it was not of importance. The most convincing evidence against the solid-state diffusion theory came from an experiment in which a solid dye dispersion was retained in a Cellophane bag which was, in turn, immersed in the dyebath [24]. A fibre placed in the external solution became dyed even though there was no contact with the solid dye. Such an observation demands that the dye dissolves in the dyebath, and this possibility was demonstrated unequivocally when it was shown that disperse dyes had a measurable solubility in water [25, 4, 6]. This solubility is increased significantly by the presence of surface-active agents [25].

As a result of the above observations, the currently accepted mechanism of dyeing with disperse dyes is that the dye exists in two forms in the dyebath: solid dye and dye in solution. In the presence of fibre the following equilibrium situation is set up:

$$\text{dye}_{\text{solid}} \overset{\text{solubility}}{\rightleftharpoons} \text{dye}_{\text{dissolved}} \overset{\text{affinity}}{\rightleftharpoons} \text{dye}_{\text{fibre}} \tag{4.30}$$

where the overall position of equilibrium is determined by the solubility and the affinity obtaining at the temperature of the dyeing. In the presence of surface-active agents the situation could be complicated by the presence of dye in micelles of agent, i.e.

$$\text{dye}_{\text{solid}} \rightleftharpoons \text{dye}_{\text{micelles}} \rightleftharpoons \text{dye}_{\text{dissolved}} \rightleftharpoons \text{dye}_{\text{fibre}} \tag{4.31}$$

By taking due precautions to ensure that the dyebaths contained no particulate dye, and by achieving equilibrium by both adsorption and desorption techniques, it was established that the dyeing system was truly reversible and that the results conformed to a rectilinear isotherm. Typical results are shown in Figures 4.1 and 4.5, and there are many more instances in the

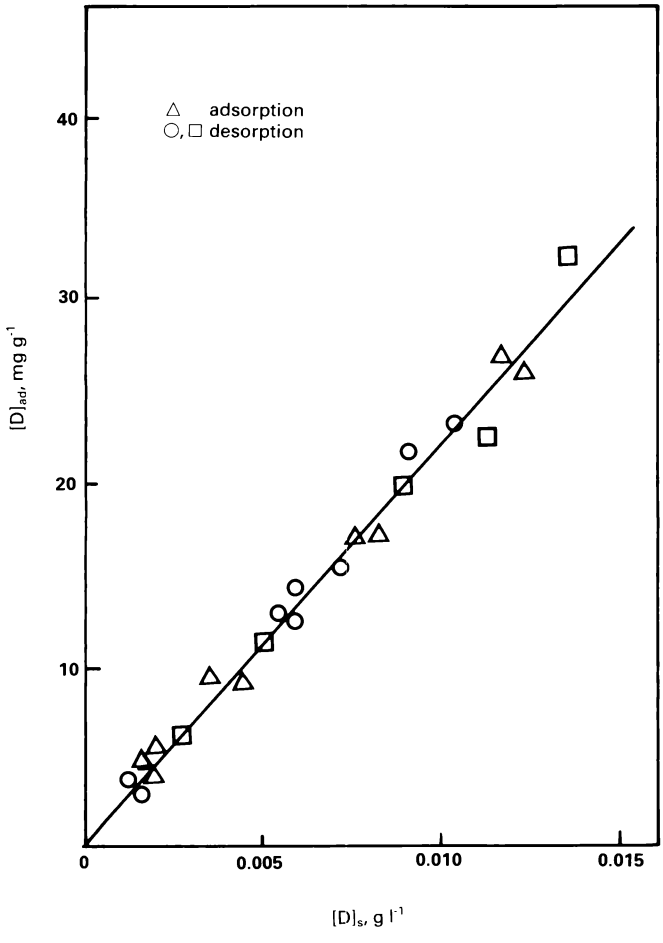

Figure 4.5 – Distribution of 1,4-dihydroxyanthraquinone between polyester fibre and water at 100 °C [6]

results of other workers using aqueous dyebaths. In all these cases the only equilibrium in the system at the end of dyeing is that between dye in true solution and dye on the fibre. Other workers using non-aqueous dyebaths have produced similar results [26, 27]. It is therefore well established that dyeing with disperse dyes is the transfer of dye molecules from a molecular dispersion (i.e. solution) into the fibre and because of the linearity of the isotherms obtained, the amount of dye adsorbed $[D]_{ad}$ relative to the concentration in the bath $[D]_s$ can be expressed by a partition coefficient K, i.e.

$$\frac{[D]_{ad}}{[D]_s} = K \tag{4.32}$$

As more dye is introduced into the system a point will be reached at which the amount of dye in the dyebath at equilibrium exceeds the solubility of the dye. In the ideal case further additions of dye will produce no further change in the concentration of dye in solution, and hence no change in the concentration of dye on the fibre. At this point, therefore, if the abscissa denotes total dye in the bath rather than dye in solution, then the isotherm will become horizontal (Figure 4.1).

It would appear that the system of disperse dyes on hydrophobic fibres is one that is explained by the simplest of dyeing mechanisms, simple partition. There are certain complicating factors, however, which if not taken into account can lead – and indeed have led – to misleading results and consequently erroneous interpretations.

The first of these is the effects of added surface-active agent. Such agents increase the 'solubility' of the dye [25], an effect that occurs at concentrations of agent in excess of its critical micelle concentration due to adsorption of dye molecules into the micelles of the surfactant. There is no evidence available to suggest that the presence of surfactant actually increases the concentration of dye in true molecular solution. Whether or not any such change occurs, the concentration of dye in 'solution' measured in the presence of surfactant does not represent the concentration of dye in true molecular solution which is capable of taking part in the equilibrium partition between solution and fibre but some value in excess of this. Hence, even in the absence of particulate dye, the experimentally measured value of $[D]_s$ is too large for the corresponding value of $[D]_{ad}$, with the result that the calculated value of the partition coefficient K is reduced.

When the isotherm is considered it is found that the presence of surfactant does not affect the linearity but merely reduces the slope, again because the measured concentration of dye in solution is possibly in excess of that available for dyeing. As a result of such experimental observations, surface-active agents are said to reduce the affinity of a disperse dye for a particular fibre because they increase the dye's solubility in the aqueous phase. Such a statement is experimentally and for all practical purposes correct, but in mechanistic terms it is not an established truth. It is possible that it arises due to not measuring, or indeed being able to measure, the concentration of dye in true molecular solution rather than the total dye in both the solution and the micelles of surface-active agent. Some support for the view that the concentration of dye in true solution and the affinity are really unaffected by the presence of surfactant has come from the demonstration that surfactant does not change the amount of dye adsorbed at saturation [5]. This means

either that the affinity and the concentration of dye available for dyeing are unaffected by surfactant, or that any reduction in the value of the affinity has been exactly compensated for by an increase in dye available for dyeing as a result of increased solubility. The latter would appear to be the more unlikely combination of effects.

The second complicating factor to be considered is that of the particle size of the dispersion being applied. In a dispersion the solubility of the particles depends on their surface energy, which in turn depends inversely on the radius of the particle, i.e. its size: hence small particles are more soluble than large ones. Thus in a heterogeneous dispersion (one in which there is a mixture of particle sizes) the solution may be in equilibrium with the smaller particles but supersaturated with respect to the larger ones. In such a case dye will crystallise on the surfaces of the larger particles, making them larger, and the smaller ones will disappear. The mean particle size will therefore increase with the result that the solubility will decrease, the concentration of dye in solution will decrease and, because of the constant partition coefficient, the amount of dye adsorbed by the fibre will decrease. This 'ageing' of a dispersion with time has been clearly demonstrated [24]. If the dispersion were homogeneous (i.e. if all the particles were the same size), this would not occur and the dispersion would be stable. Unfortunately all practical systems are heterogeneous.

Consider now the shape of the isotherm obtained, for the moment ignoring the effects of 'ageing'. On that part of the isotherm where dye is applied in excess of the saturation level, i.e. the horizontal part, more and more solid dye is being added and, at the same time, a smaller and smaller fraction is being dissolved. The mean particle size of the excess solid dye will therefore change and its solubility will change, resulting in a change in the amount of dye adsorbed. This part of the isotherm therefore need not be flat, but may rise or fall depending on how the mean particle size changes. If 'ageing' of the dispersion also occurs, then it is more than probable that the mean particle size will increase as more solid dye becomes available and the isotherm will fall.

The linear, rising part of the isotherm could also be affected by changes in particle size. In more fundamental studies carried out at long liquor-to-goods ratios, it is possible to ensure that the starting dyebath is free of particulate dye, the dye having sufficient solubility to permit the required mass of dye to be dissolved in the large volume of dyebath available. Under other more practical conditions, the demands of achieving the required depth of shade could mean that the amount of dye initially present in the aqueous phase is in excess of the solubility, and hence at the start of dyeing (and possibly for a considerable part of the dyeing time) particles of dye will be present. Complete solution will be achieved only as the dyebath becomes

exhausted. The effects of crystal growth, with the resulting changes in solubility, could therefore be in evidence in this part of the isotherm.

Two extreme cases may be described. Firstly, if the rate of adsorption of dye by the fibre is greater than the rate of crystal growth, then dye in solution will be adsorbed before it can produce increased particle size. Hence particle size in the dyebath will decrease with increasing time, and the ultimate equilibrium will be achieved with a solution of dye which contains no particles. Secondly, if the rate of crystal growth is greater than the rate of dyeing, then crystals will grow resulting in a lower solubility, i.e. a lower $[D]_s$ and hence a lower $[D]_{ad}$. Such a drop in $[D]_{ad}$ will result in an even lower rate of dyeing, thereby increasing the effect. Under these circumstances, as the applied concentration is increased, the possibility of large particles forming is greater and the potential size of such particles is also increased. This will produce a decrease in $[D]_s$ and hence in $[D]_{ad}$. The normal methods of estimating the dye in the equilibrium dyebath would include the dye particles as well as the dye in molecular solution. Thus the values of $[D]_s$ used in preparing the isotherm would be too large by an amount which increased as the applied concentration increased, resulting in a curved rather than a linear isotherm.

A further effect which can occur with many disperse dyes, particularly under high-temperature dyeing conditions, is that at a certain critical temperature the crystal habit of the dye changes, generally to a more stable form which is markedly less soluble. It has been demonstrated [28] that an approximately six-fold reduction in solubility is possible by the physical modification of the particular dye studied. Such alteration would obviously produce marked changes in the concentration of dye in solution and hence in the amount on the fibre. Also, when the physical change takes place, crystals of the new modification would be surrounded by a solution of dye far in excess of their solubility and hence would grow, with all the expected consequences.

Most of the fundamental studies have been carried out using purified dyes. If commercial dyes are used a further complication is possible because, as supplied, they contain dispersing agent which is present as an aid to milling, to produce a redispersible product and to promote dispersion stability in the dyebath. Thus the greater the concentration of dye in the initial bath, the greater is the concentration of surfactant. This results in two effects: the greater the concentration of dye, the higher is the observed solubility and the lower the calculated partition coefficient, as discussed above. Both effects could markedly influence the shape of the isotherm and its linearity. Fortunately the full effects of this situation are not realised in most instances, since the initial dyebath is prepared using a swamping amount of extra surfactant.

4.3.2 The energetics of dyeing with non-ionic dyes

As described earlier and in Chapter 1, the standard affinity of a dye at temperature T K is defined by Eqn 4.16, and a value of the affinity can be calculated once the correct model for the dyeing system is decided and suitable values are ascribed to the activities of the dye in the fibre phase a_f and in the solution a_s. With non-ionic disperse dyes the linearity of the isotherms has resulted in their adsorption being regarded as a process of 'solid' solution defined by a partition coefficient (Eqn 4.32). The constancy of the partition coefficient implies that the dye is behaving ideally in both phases, so that the activities in Eqn 4.16 may be replaced by concentrations, i.e.

$$-\Delta\mu^{\ominus} = RT \ln \frac{[D]_{ad}}{[D]_s} = RT \ln K \tag{4.33}$$

where $[D]_{ad}$ = the concentration of dye in the fibre (mol kg^{-1}), $[D]_s$ = the concentration of dye in the bath (mol l^{-1}) and the standard state in both phases is unit concentration. Using this equation the standard affinities of disperse dyes on cellulose diacetate, cellulose triacetate and polyester substrates have been calculated by many workers.

The significance of the affinities obtained is somewhat uncertain, in view of the different possible ways of expressing the concentrations of dye in either or both phases. The experimental methods give results in which $[D]_{ad}$ is in grams or moles of dye per unit mass of fibre and $[D]_s$ in grams or moles of dye per litre of solution. Whether grams or moles of dye are used as units is unimportant, as long as the same units are used for both quantities, but the measurement of fibre in terms of mass and that of solution in terms of volume result in K having the dimensions of $[\text{mass}]^{-1}$ when, in fact, it should have no dimensions. Such a situation has no serious disadvantages for many applications, e.g. the comparison of a range of dyes on a single fibre, and it might be assumed that workers who adopt this approach have equated litres to kilograms of dyebath, thereby removing the problem of dimensions with only a small resulting error. The alternative approach is to postulate that a volume of water V (1 kg^{-1}) is associated with the fibre and that the dye in the fibre is contained in this volume. Hence $[D]_{ad}/V$, where $[D]_{ad}$ is in mol kg^{-1}, gives a concentration $[D]_f$ in mol l^{-1} and K_V become dimensionless. Eqn 4.33 therefore becomes

$$-\Delta\mu_V^{\ominus} = RT \ln \frac{[D]_{ad}}{V[D]_s} = RT \ln \frac{[D]_f}{[D]_s} = RT \ln K_V \tag{4.34}$$

This concept of a volume term for fibres will be further discussed in relation

to anionic dyes on cellulose. It has the advantage that the affinities of dyes on different fibres may be compared and, more particularly, that the affinities of dyes on different physical modifications of the same initial polymer may be equated by a suitable choice of V. For any given set of experimental results changing the value of V in Eqn 4.34 will alter the values of K_V and $\Delta\mu^{\ominus}_V$, and these values will be different from those of K and $\Delta\mu^{\ominus}$ obtained using Eqn 4.33 except, of course, for the case where $V = 1$, i.e. when $K = VK_V$. Obviously, therefore, it must be made absolutely clear which equation is being used.

The dyeing of cellulose diacetate, cellulose triacetate and poly(ethylene terephthalate) fibres from dyebaths containing aqueous solutions of disperse dyes has produced a lot of experimental data [6, 29, 30, 31, 32], from which affinities have been calculated. For all three fibres the isotherms were linear, reaching a saturation value as in Figure 4.3, curve A. From determinations of affinity at different temperatures values of the standard enthalpy (heat) of dyeing $\Delta H^{\ominus}$ have also been obtained for the different dyes on the various fibres using the methods associated with Eqns 4.20, 4.21 and 4.23. This in turn permitted calculation of the standard entropy changes involved, using Eqn 4.28. In all cases it was found that there was a decrease in entropy when the dye was adsorbed, suggesting an increase of order of the dye in the system. (Of course, the entropy of the total system – which includes fibre and water as well as dye – must increase, see section 1.2.5.)

In an effort to describe the energetics of the process, the solid dye has been used as the baseline for computation. Thus

$$\Delta H^{\ominus}_{SF} = \Delta H^{\ominus}_{SW} + \Delta H^{\ominus}_{WF} \tag{4.35}$$

where the enthalpy changes concerned are $\Delta H^{\ominus}_{SF}$ when dye moves from the crystal to the fibre (the enthalpy of solution in the fibre), $\Delta H^{\ominus}_{SW}$ when dye moves from crystal to water (the enthalpy of solution), $\Delta H^{\ominus}_{WF}$ when dye moves from water to fibre (the enthalpy of dyeing). The general picture that emerges from a study of a range of dyes on cellulose acetate is shown in Figure 4.6 [74]. The enthalpy of solution calculated from the effect of temperature on solubility using the equation

$$\Delta H^{\ominus}_{SW} = R\frac{\mathrm{d}(\ln \text{ solubility})}{\mathrm{d}(1/T)} \tag{4.36}$$

is positive and large in value, i.e. a rise in temperature markedly increases the solubility. The enthalpy of dyeing $\Delta H^{\ominus}_{WF}$ is negative and numerically smaller than $\Delta H^{\ominus}_{SW}$, so that the enthalpy of solution in the fibre $\Delta H^{\ominus}_{SF}$ is also positive. Whilst interesting, this approach does little to clarify the situation.

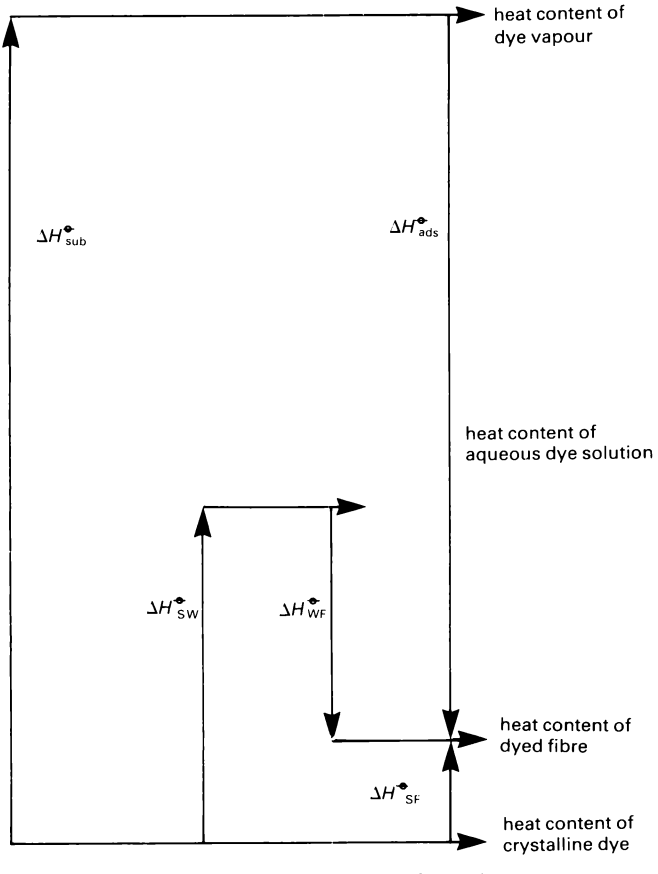

Figure 4.6 – Energy level diagram for dyeing processes

In a further attempt to resolve the energetics of the process, the vapour-phase dyeing of cellulose acetate was studied [33, 34]. Again the isotherms were linear, but the partition coefficients and hence the affinities were found to be extremely high when compared with those of the same dyes applied from aqueous solution. The enthalpies of adsorption of dye from the vapour phase are also high and found to be very close in value to the enthalpies of sublimation of the dyes when they are calculated using the equation

$$\Delta H^{\ominus}_{\text{adsorption}} = -\Delta H^{\ominus}_{\text{sublimation}} + \Delta H^{\ominus}_{SW} - \Delta H^{\ominus}_{WF} \qquad (4.37)$$

A general type of result is included in Figure 4.6. Clearly the results are very interesting and this approach is worthy of further study, particularly in view of the 'Thermosol' process, in which disperse dye is transferred from the

solid or adsorbed state on one fibre to the adsorbed state on another through the vapour phase [35], and of the transfer-printing process with disperse dyes.

For many years workers have tried to establish whether the adsorption of disperse dyes by hydrophobic fibres is a process of 'solid solution' or one involving a 'site' mechanism. The idea of 'sites' being available in the fibre appears to have arisen because certain dyes on certain fibres do not produce rectilinear isotherms, and in such cases the results can be fitted using a Langmuir type of isotherm. This in turn led to the postulate that where linear isotherms are obtained they are merely the earlier part of a Langmuir isotherm, as discussed previously. Rightly or wrongly, such ideas would appear to ignore the possibility that the results are affected by such variables as particle size, solubility, the presence of dispersing agents and perhaps also modification of the fibre structure by the presence of dye. To date it must be said that the situation is not totally resolved and the understanding of disperse dye systems is still not complete, but that the weight of evidence would appear to favour the mechanism of 'solid solution', particularly the results of the vapour-phase studies [33]. This situation is discussed more fully in Chapter 2.

4.3.3 Non-ionic dyes on ionic substrates

Disperse dyes on nylon

This system is of considerable commercial importance, because of the good level-dyeing characteristics of the dyes and their ability to cover up fibre irregularities. The adsorption isotherms obtained are the same shape as those on the essentially non-ionic fibres, i.e. they are rectilinear and show a clear saturation value [36]. As a result it is again generally assumed that a 'solid solution' mechanism is operating and that affinities may be calculated using Eqns 4.33 or 4.34. The results are little affected by the pH of application unless, of course, the pH chosen results in the ionisation of the dye, in which case the system has changed to one in which both dye and fibre are ionic.

Because nylon is known to contain 'sites' on which it can be assumed that dyeing may take place, the problem of 'solid solution' *versus* 'site' adsorption has been raised with respect to this fibre. Again the situation has not been resolved, although the general tendency is to use the former model.

Disperse dyes on acrylic fibres

Although acrylic fibres are usually dyed with basic dyes, disperse dyes are used for pale to medium depths of shade. In fundamental studies linear isotherms are again obtained and affinities, enthalpies of dyeing and entropy changes have been determined for disperse dyes on this fibre [37].

Disperse dyes on cellulose and wool

These fibres are not usually dyed with disperse dyes, because of the very low affinities and saturation values which are observed. In the dyeing of blends, however, there is a problem of the staining of the wool or cellulose part of the blend by the disperse dye used for the other component. It is of interest to know the affinities of certain disperse dyes for these two fibres, and as a result adsorption studies have been carried out on cellulose [38] and on wool [31, 29]. In both cases it was found that adsorption followed the 'solid solution' model in that linear isotherms were obtained from which affinities, enthalpies of dyeing and entropy changes were obtained using the appropriate equations.

4.3.4 Affinity and partition coefficient

It is useful, in the context of disperse dyes whose adsorption on all fibres can be described by a relatively simple equation, to consider the implications of the magnitude of the affinity, and hence of the partition coefficient, on the properties of the dyes in practical applications.

The percentage exhaustion of a dyebath when dyeing is carried out to equilibrium is related to the partition coefficient (or ratio) by the equation

$$\% \text{ exhaustion} = \frac{K}{K + L} \times 100 \tag{4.38}$$

where K = the partition coefficient as defined in Eqn 4.33 and L = the liquor-to-goods ratio.

If the partition coefficient is defined as in Eqn 4.34, then

$$\% \text{ exhaustion} = \frac{VK_V}{VK_V + L} \times 100 \tag{4.39}$$

The results of carrying out this calculation for various values of the partition coefficient, at a selection of liquor-to-goods ratios, are given in Table 4.3.

It is also possible to illustrate how wet-fastness is related to affinity and partition coefficient by calculating how much water would be required, in a single treatment, to reduce the amount of dye on the fibre by a given percentage. If one kilogram of fibre containing D_0 g kg^{-1} of dye is treated with W litres of water and the system is allowed to come to equilibrium, then,

$$[D]_0 = [D]_{ad} + W[D]_s$$

where $[D]_{ad}$ = the concentration of dye on fibre (g kg^{-1}) and $[D]_s$ = the

TABLE 4.3

The practical meaning of the partition coefficient

$-\Delta\mu^{\ominus}$ /kJ (kcal) mol^{-1}		Partition coefficient	% exhaustion at a liquor ratio (LR) of			Volume of water required to remove 5% of dye /l	Number of washes at 25:1 LR to remove 95% of dye
at 80 °C	at 100 °C	K	5	25	100		
(0)	(0)	1	16.7	3.8	1.0	0.0526	1
6.8 (1.61)	7.2 (1.71)	10	66.7	28.6	9.1	0.526	3
13.5 (3.22)	14.3 (3.41)	100	95.2	80.0	50.0	5.26	14
20.3 (4.83)	21.5 (5.12)	1 000	99.5	97.6	90.9	52.6	122
27.0 (6.44)	28.7 (6.83)	10 000	100	99.8	99.0	526	1 183
33.8 (8.05)	35.8 (8.53)	100 000	100	100	99.9	5260	13 010

concentration of dye in solution (g l^{-1}). If, at the temperature of the treatment,

$$\frac{[D]_{ad}}{[D]_s} = K \tag{4.32}$$

then it can be shown that

$$K\left(\frac{[D]_0}{[D]_{ad}} - 1\right) = W \tag{4.40}$$

If the value of W is that required for the removal of 5 per cent of the original dye present then $[D]_0 = 1$ and $[D]_{ad} = 0.95$. The results of carrying out this calculation for various values of K are shown in Table 4.3, column 7 and illustrate the dependence of wet-fastness on affinity.

Another common problem is that of removing unwanted disperse dye from a fibre in situations where reduction clearing is not possible. The final column of Table 4.3 lists the number of washes required at a liquor-to-goods ratio of 25:1, to reduce the residual adsorbed disperse dye to less than 5 per cent of that on the fibre at the start of washing.

Because the isotherm is linear and hence the partition coefficient is a constant independent of dye concentration, each wash will remove the same fraction of adsorbed dye. If after the first wash

$$\frac{[D]_{ad(1)}}{[D]_0} = \frac{K}{K + L} \tag{4.41}$$

then after x washes

$$\frac{[D]_{ad(x)}}{[D]_0} = \left(\frac{K}{K + L}\right)^x \tag{4.42}$$

where $[D]_{ad(x)}$ = concentration of dye on fibre after x washes and $[D]_0$ = concentration of dye on fibre before washing.

If $[D]_{ad(x)}$ is required to be at most 5 per cent of the dye that was on the fibre at the start of washing, then $[D]_{ad(x)}/[D]_0 \leqslant 0.05$. Taking logarithms of both sides of Eqn 4.42 allows the calculation of a value of x, rounded up to the next whole number, that will fulfil this requirement for chosen values of K and L, that is, the number of washes required. The figures, although ridiculous from the point of view of practical application, do illustrate the difficulty of removing unwanted dye of medium to high affinity. Fortunately the need to remove dye of such a high degree of fastness does not arise in most applications.

It must be remembered that if the partition coefficient is defined as in Eqn 4.34, then K in Eqns 4.40 and 4.42 should be replaced by VK_V.

4.4 IONIC DYES

4.4.1 Electrical effects

In dyeing systems involving ionic dyes it is useful to consider the possible electrical effects.

When a solid containing charged groups is immersed in water it acquires an electrical potential. Even if the solid possesses no intrinsic charge of its own, the adsorption of ions from the water, or from the surrounding aqueous solution, will result in an electrical potential being generated. The presence of such a potential will result in oppositely charged ions (counterions) being attracted to the surface whilst similarly charged ions (co-ions) will be repelled. Because of this there will be an imbalance of ions near the surface under consideration, there being a layer adjacent to the surface where counterions predominate (Figure 4.7(a)). Helmholz [39], who assumed that the boundaries of this electrical double layer were sharp, treated it mathematically as a parallel-plate condenser. Since the effect of the electrical potential falls as distance from the surface increases, however, so will the concentration of counterions decrease and that of co-ions increase with increasing distance into the surrounding liquid (Figure 4.7(b)). This led Goy [39] to develop a treatment based on the concept of a diffuse electrical double layer.

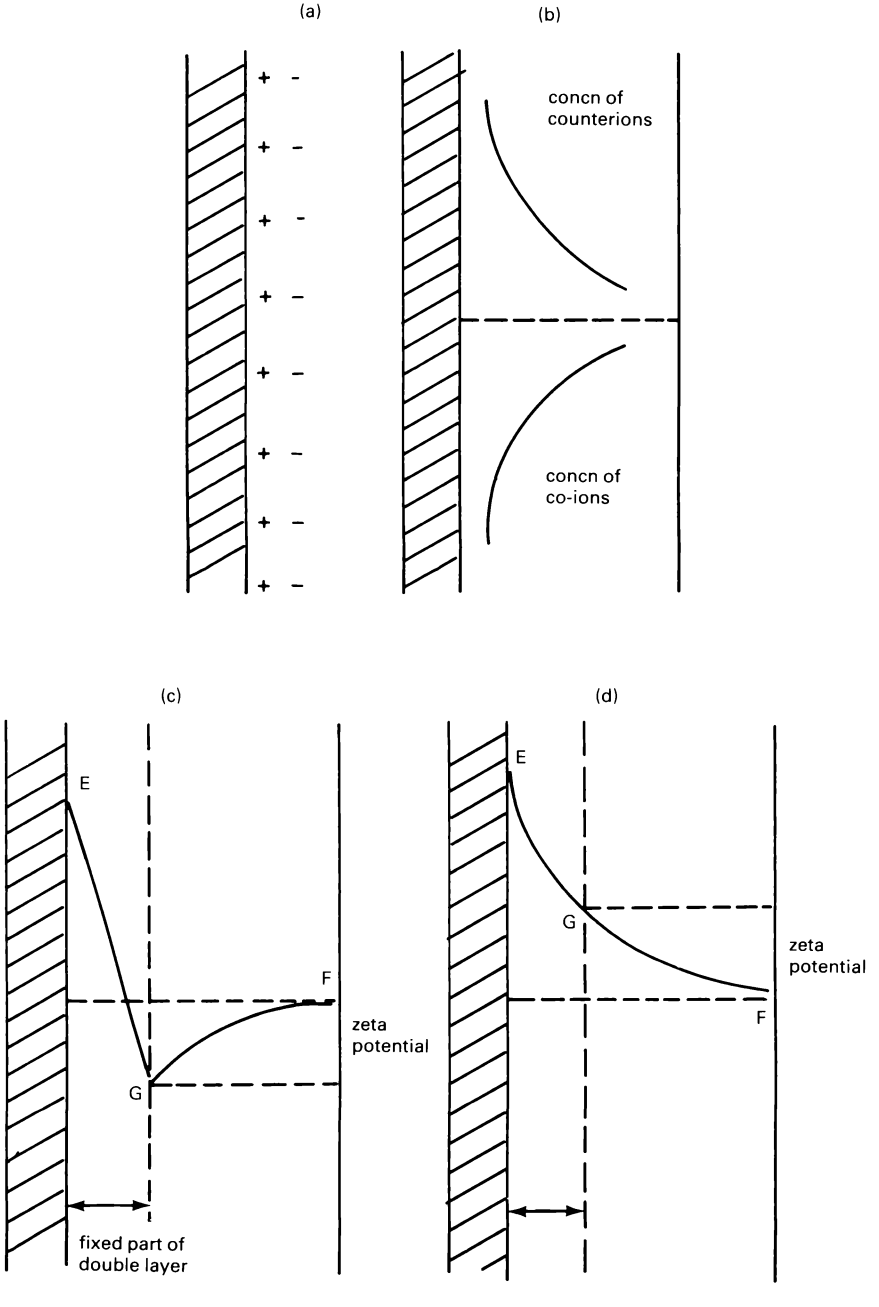

Figure 4.7 – The electrical double layer

More recently Stern [39] has shown that neither the sharp nor the diffuse theory is alone adequate and hence developed a view combining the essential features of both. Accordingly he postulated that the double layer is in two parts, one that is approximately a single solvent molecule in thickness, which remains fixed to the surface, and a second layer that extends some distance into the aqueous phase and is diffuse due to the opposing forces of thermal agitation and electrostatic attraction. The result is a sharp fall in potential in the first layer followed by a gradual fall in the second, until the bulk of the liquid is reached where the charge distribution becomes uniform. The potentials at a solid–liquid boundary may be represented in two ways, depending on the properties of the ions present in the solution. Thus Figure 4.7(c) would apply to ions with the same charge as the solid but which possess forces of attraction for the solid that exceed the electrical forces of repulsion over short but not over longer distances. Figure 4.7(d) would represent the distribution of ions with a charge opposite to that of the solid or ions for which the forces of attraction are greater than those of repulsion at all distances.

Figures 4.7(c) and (d) permit the illustration of two other quantities. The potential difference between E and F is the thermodynamic or reversible potential between the solid and the bulk of the solution, whilst that between G and F (that is, between the fixed and freely mobile portions) is the zeta or streaming potential.

The situations presented in Figures 4.7(c) and (d) would be representative of the distribution of dyes near the fibre surface. Such large ions would produce short-range forces of attraction and long-range forces of either attraction or repulsion depending on the nature of the charges on the dye and fibre. Figure 4.7(c) shows a dyeing system where the fibre and dye possess the same charge, the dye being attracted only over short distances from the fibre. This would result in a single layer of dye ions on the fibre surface, a condition which is called *unimolecular adsorption*. On the other hand Figure 4.7(d) shows a system where the attraction of the dye increases at all distances towards the fibre, resulting in the possibility of *multilayer* or *diffuse adsorption*. Both types are possible in dyeing, although in fact they are best described as extremes of the same behaviour since a dyeing system may change from one to the other during the course of a dyeing, or may be of one kind or the other depending on the presence or absence of neutral electrolytes in the dyebath.

4.4.2 The internal volume of fibres

The Donnan theory of membrane equilibrium considers the distribution of ions on the two sides of a semi-permeable membrane (see section 1.5). When this theory was applied to the treatment of the electrical double layer on a

solid surface it was necessary to define a volume of liquid V l kg^{-1} adjacent to the surface, in which the potential is a constant with distance but falls to zero at the outer boundary of this layer. The potential so described is called the *Donnan potential*, ψ_{Donnan}. The thickness of this layer can be defined so that its volume equates to the volume of the diffuse layer as visualised in the double-layer theory. The outer boundary can then be regarded as a membrane separating the internal solution (i) from the external solution (s), the fixed charges on the surface being considered to be in the internal solution. Using this approach the equilibrium distribution of ions at the interface between a solution of sodium chloride and a negatively charged fibre can be described. The chemical potential of the sodium and chloride ions in the external solution can be written

$$\mu_{\text{Na,s}} = \mu^{\ominus}_{\text{Na,s}} + RT \ln [\text{Na}]_{\text{s}} \tag{4.43}$$

$$\mu_{\text{Cl,s}} = \mu^{\ominus}_{\text{Cl,s}} + RT \ln [\text{Cl}]_{\text{s}} \tag{4.44}$$

(omitting, for simplicity's sake, to write in the electrical charges) and in the internal solution

$$\mu_{\text{Na,i}} = \mu^{\ominus}_{\text{Na,i}} + RT \ln [\text{Na}]_{\text{i}} + F\psi_{\text{Donnan}} \tag{4.45}$$

$$\mu_{\text{Cl,i}} = \mu^{\ominus}_{\text{Cl,i}} + RT \ln [\text{Cl}]_{\text{i}} - F\psi_{\text{Donnan}} \tag{4.46}$$

where F is the Faraday constant and ideal behaviour is assumed, i.e. activities have been equated to concentrations. Because both solutions are ideal and of the same kind, then $\mu^{\ominus}_{\text{Na,s}} = \mu^{\ominus}_{\text{Na,i}}$ and $\mu^{\ominus}_{\text{Cl,s}} = \mu^{\ominus}_{\text{Cl,i}}$. Also, because the two phases are in equilibrium, $\mu_{\text{Na,s}} = \mu_{\text{Na,i}}$ and $\mu_{\text{Cl,s}} = \mu_{\text{Cl,i}}$, so that from Eqns 4.43 and 4.45

$$\frac{[\text{Na}]_{\text{s}}}{[\text{Na}]_{\text{i}}} = \exp(F\psi_{\text{Donnan}}/RT) = \lambda \tag{4.47}$$

and from Eqns 4.44 and 4.46

$$\frac{[\text{Cl}]_{\text{s}}}{[\text{Cl}]_{\text{i}}} = \exp(-F\psi_{\text{Donnan}}/RT) = 1/\lambda \tag{4.48}$$

where λ is the *Donnan distribution coefficient*. Hence

$$\frac{[\text{Na}]_{\text{s}}}{[\text{Na}]_{\text{i}}} = \frac{[\text{Cl}]_{\text{i}}}{[\text{Cl}]_{\text{s}}} = \exp(F\psi_{\text{Donnan}}/RT) \tag{4.49}$$

or $$[Na]_s\,[Cl]_s = [Na]_i\,[Cl]_i \qquad (4.50)$$

Since many dyeing systems are influenced by ionic equilibria, the use of equations such as Eqn 4.50 provides an invaluable method of evaluating the energetics of the system. In addition, the treatment invoking an internal phase offers a means of overcoming the problem that concentrations of adsorbed or fixed ions in the fibre are measured in amounts per kilogram. By assuming that all such ions are present in the internal solution, division by V (1 kg^{-1}) gives concentrations in terms of amounts per litre of internal phase. Of course, an acceptable method for evaluating V must be available.

4.4.3 Ionic dyes applied to substrates that carry the same charge as the dye

The most common and the most important dyeing system to be considered under this heading is the application of anionic dyes to cellulose, both natural and regenerated, and this section therefore includes discussions of direct dyes, vat dyes in the reduced leuco form and reactive dyes when applied under non-reacting conditions on these substrates.

A very comprehensive study of the adsorption of the direct dye Chrysophenine G (C.I. Direct Yellow 12) on Cellophane sheet has been carried out [40], in which complete adsorption isotherms were obtained over a wide range of dye and salt concentrations at various temperatures. A typical example of the results obtained is shown by the continuous curves in Figure 4.8 for measurements at 40 °C [41], where the general shape of the curves resembles that illustrated in Figure 4.3, curve B, i.e. the dye is being adsorbed according to a Freundlich isotherm. This is apparently confirmed when the results are plotted on logarithmic scales (Figure 4.9), when it can be seen that the points lie essentially on straight lines. Such a result can be misleading, however, due to the insensitivity implicit in a log–log plot. Thus, if values of x and K in the Freundlich equation (Eqn 4.4) are calculated from the lines in Figure 4.9 (Table 4.4) and then used to calculate values of $[D]_{ad}$ for a range of values of $[D]_s$, the broken curves in Figure 4.8 result. At the higher salt concentrations, the good agreement shown in the log–log presentation is not so obvious when the experimentally obtained and the calculated isotherms are compared. Even if the fit to such an isotherm had been perfect, however, it is not easy to see how the resulting values of x and K could be used to define the properties of the dye under all conditions of application, in terms of one or two constant parameters.

Several theories have been advanced to interpret the adsorption of anionic dyes by cellulosic materials, all of them invoking the presence of an electrical

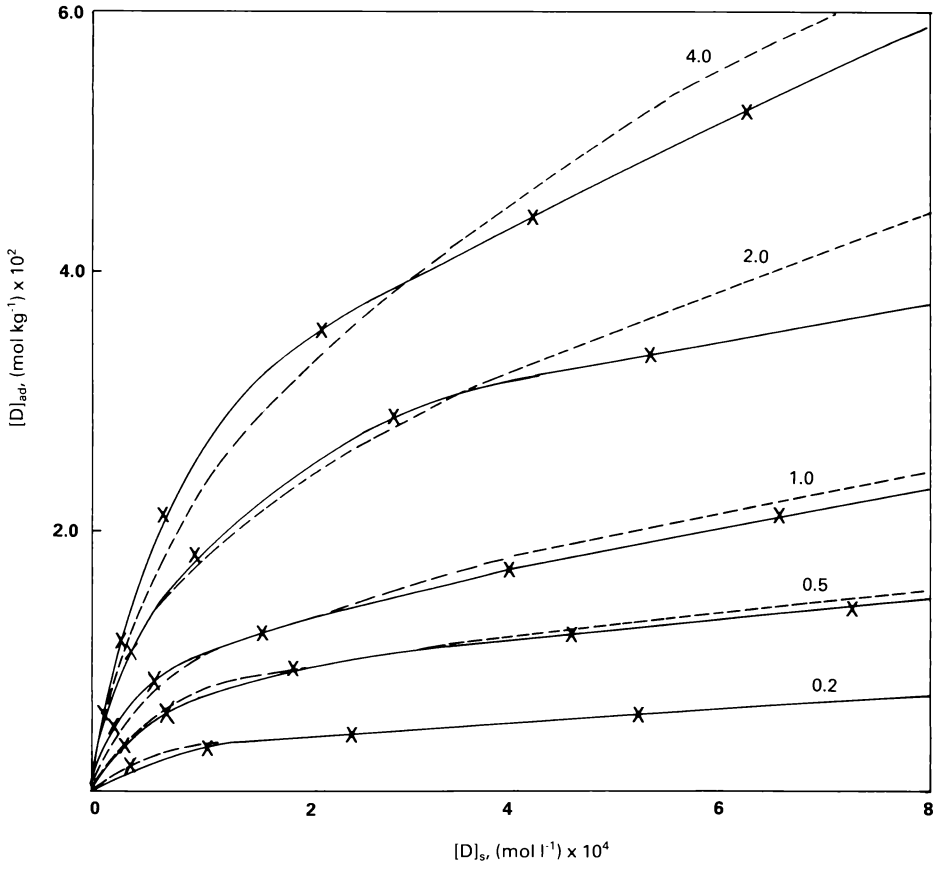

Figure 4.8 – Adsorption isotherms of Chrysophenine G on cellulose sheet at 40 °C [40]; the numbers on the curves represent concentrations (g l^{-1}) of sodium chloride in the dyebath

charge at the fibre–water interface due to the adsorption of dye ions and, indeed, assuming that it is only the dye ions that are adsorbed by the cellulose. Also inherent in these theories is that the dye is completely ionised in both phases, and that oppositely charged ions cannot move far apart so that any volume in the system must be electrically neutral. One of these theories [40], a kinetic thermodynamic approach to the problem, resulted in the development of some very complex mathematical expressions to describe the adsorption of dye. It was necessary to make a simplifying assumption to reduce the equations to experimentally manageable proportions, in that the system was reduced to a surface layer and an external solution, i.e. a system very similar to those described below. For this reason further discussion of

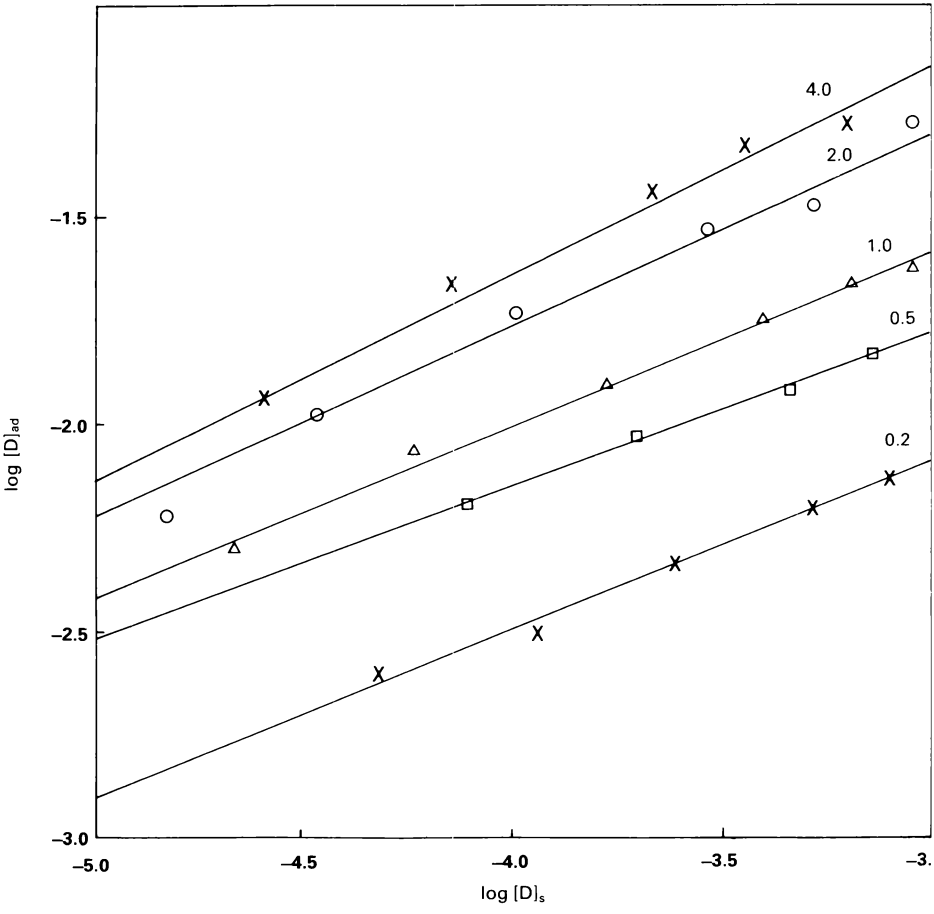

Figure 4.9 – Adsorption of Chrysophenine G on Cellophane sheet at 45 °C [40, 41]: log–log curves; the numbers on the lines represent concentrations (g l^{-1}) of sodium chloride in the dyebath

this theory is not included here; the reader is referred to the original paper for greater detail.

Probably the earliest attempt to produce an equation that would describe the situation divided the system into three parts – the fibre, a volume V of internal aqueous solution and the external solution – and applied the Donnan theory of membrane equilibrium across the boundary between the internal and external solutions [42]. Such a system involves unimolecular adsorption with the various ions distributed as shown in Figure 4.10, which assumes that the system contains only a dye (Na_zD) and sodium chloride. If it is

TABLE 4.4

Freundlich constants for the adsorption of Chrysophenine G on Cellophane sheet at 40 °C [40, 41]

Sodium chloride concentration /g l^{-1}	x	k
0.2	0.409	0.138
0.5	0.367	0.208
1.0	0.415	0.454
2.0	0.456	1.126
4.0	0.497	2.213

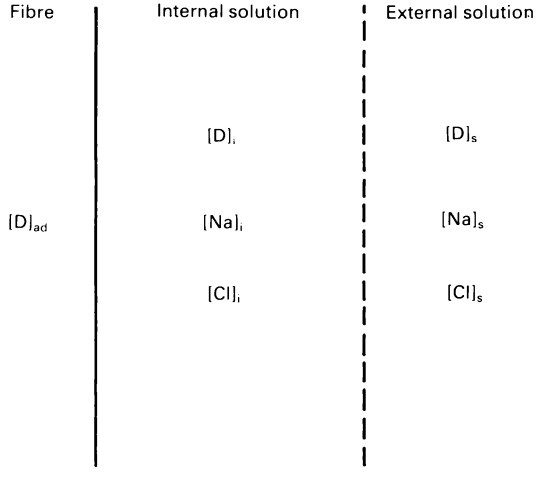

Figure 4.10 – Distribution of ions in a three-phase system

assumed that the concentration of adsorbed dye $[D]_{ad}$ (mol kg^{-1}) is in equilibrium with the concentration of dye in the internal solution $[D]_i$ (mol l^{-1}) according to a simple partition isotherm, then from Eqn 4.34

$$K_V = \frac{[D]_{ad}}{V[D]_i} = \exp\left(-\Delta\mu^{\ominus}/RT\right) \tag{4.51}$$

or

$$K_V = \frac{[D]_f}{[D]_i} \tag{4.52}$$

As discussed earlier, V (l kg^{-1}) must be included to make the equation dimensionally correct. Applying the Donnan equilibrium of Eqn 4.50 to the dye Na_zD,

$$\frac{[D]_i}{[D]_s} = \left(\frac{[Na]_s}{[Na]_i}\right)^z \tag{4.53}$$

Hence from Eqns 4.51 and 4.53 the affinity of the dye may be defined:

$$-\Delta\mu^\ominus = RT \ln K_V = RT \ln\left(\frac{[Na]_i^z[D]_{ad}}{V[Na]_s^z[D]_s}\right) \tag{4.54}$$

or, using Eqns 4.52 and 4.53,

$$-\Delta\mu^\ominus = RT \ln K_V = RT \ln\left(\frac{[Na]_i^z[D]_f}{[Na]_s^z[D]_s}\right) \tag{4.55}$$

All the concentrations in Eqns 4.54 and 4.55 are experimentally measurable with the exception of $[Na]_i$, and this requires to be calculated as follows. If it is assumed that the surface phase includes the surface of the fibre and that a state of electrical neutrality must exist, then

$$[Na]_i = [Cl]_i + \frac{z[D]_{ad}}{V} + z[D]_i \tag{4.56}$$

However, since the quantity of dye on the fibre which is measured at the end of dyeing will include the dye in the internal phase, then for practical purposes this equation must be written

$$[Na]_i = [Cl]_i + \frac{z[D]_{ad}}{V} \tag{4.57}$$

and substituting from Eqn 4.50 gives

$$[Na]_i = \frac{[Na]_s[Cl]_s}{[Na]_i} + \frac{z[D]_{ad}}{V} \tag{4.58}$$

This is a quadratic equation in $[Na]_i$, which can be solved using

$$[Na]_i = \frac{[D]_{ad}}{V}\left[\frac{z}{2} + \left(\frac{z^2}{4} + \frac{[Na]_s[Cl]_sV^2}{[D]_{ad}^2}\right)^{\frac{1}{2}}\right] \tag{4.59}$$

Again, if $[D]_{ad}/V$ is replaced by $[D]_f$, the equation becomes

$$[Na]_i = [D]_f \left[\frac{z}{2} + \left(\frac{z^2}{4} + \frac{[Na]_s[Cl]_s}{[D]_f^2} \right)^{\frac{1}{2}} \right] \tag{4.60}$$

Whilst the differences between Eqns 4.54 and 4.55 and between Eqns 4.59 and 4.60 may appear to be trivial, and indeed they are in this case, the opportunity has been taken to introduce the idea of evaluating concentrations in the fibre in the units of mol l^{-1} of internal phase, e.g.$[D]_f$, by dividing experimentally determined values in mol kg^{-1}, e.g. $[D]_{ad}$, by V at the outset. This removes the necessity of including V in the equations, which in the more complicated derivations to be discussed later will be to considerable advantage.

Another treatment based on the assumption of three phases in the system has been made [43]. This started by presuming a Langmuir distribution of dye, but when modified to the practical situation and also to include the Donnan distribution, it produced equations identical to those above.

The most widely used treatment of this dyeing system, and one which is frequently used by current workers in the field, is that of using the concept of diffuse adsorption [41, 44]. Here the system is divided into two parts, a surface layer (f) and the external solution, and any adsorbed or fixed ions on the fibre are considered to be dissolved in the surface layer. For a dye Na_zD and sodium chloride the assumed distribution is as in Figure 4.11, where all the concentrations in the internal phase have already been converted from mol kg^{-1} to mol l^{-1} of phase by dividing by V.

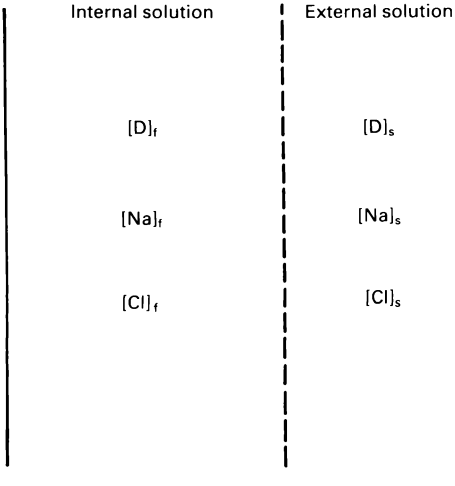

Figure 4.11 – Distribution of ions in a two-phase system

When these two phases are in equilibrium and assuming that the system is reversible, then the equation developed in Chapter 1 and discussed earlier (Eqn 4.16) may be used. If the activity of the dye is taken as $[Na]^z[D]$ in each phase, this equation becomes

$$-\Delta\mu^{\ominus} = -(\mu_f^{\ominus} - \mu_s^{\ominus}) = RT \ln \frac{[Na]_f^z[D]_f}{[Na]_s^z[D]_s} \tag{4.61}$$

The only quantity in this equation which is not experimentally measurable is $[Na]_f$, and this can be calculated using the condition of electrical neutrality

$$[Na]_f = [Cl]_f + z[D]_f \tag{4.62}$$

by applying the Donnan equality

$$[Cl]_f = \frac{[Na]_s[Cl]_s}{[Na]_f} \tag{4.63}$$

to give the result

$$[Na]_f = [D]_f\left[\frac{z}{2} + \left(\frac{z^2}{4} + \frac{[Na]_s[Cl]_s}{[D]_f^2}\right)^{\frac{1}{2}}\right] \tag{4.64}$$

The similarity between Eqns 4.55 and 4.61, and between Eqns 4.60 and 4.64, is obvious.

Throughout the above discussion it is clear that the standard state, i.e. when $a_f = 1$, is when the ionic product $[Na]_f^z[D]_f = 1$, and that $a_s = 1$ when $[Na]_s^z[D]_s = 1$.

4.4.4 The value of V

One problem remaining to be discussed is the choice of a value for V, the volume of the internal phase per kilogram of fibre. Inspection of Eqn 4.61 reveals that when the correct values are used in the equation not only should a constant value of $\Delta\mu^{\ominus}$ be obtained for all points on the isotherm, but a graph of log $[Na]_f^z[D]_f$ against log $[Na]_s^z[D]_s$ should be a straight line of unit slope. This method was used to establish a value of V for cotton using the results on Chlorazol Sky Blue FF (C.I. Direct Blue 1) [44]. By way of illustration a few of these results are included in Table 4.5, where values of $[D]_f$, $[Na]_f$ and $\Delta\mu^{\ominus}$ have been calculated for different assumed values of V. From these results the required log–log graphs have been drawn (Figure 4.12), and it can be seen that a value of V of 0.2 l kg^{-1} produces a line which is very close to the required slope of unity. A volume of 0.1 l kg^{-1} gives a

TABLE 4.5

Chlorazol Sky Blue FF on cotton at 90 °C [44]: calculation of affinity using different values of V

$[D]_s$ /mol l^{-1} $\times 10^4$	$[Na]_s$ /mol l^{-1} $\times 10^2$	$[D]_{ad}$ /mol kg^{-1} $\times 10^3$	*	$V = 0.1$	$V = 0.2$	$V = 0.22$	$V = 0.3$
0.0958	8.55	2.58	$[D]_f$	2.58	1.29	1.17	0.86
			$[Na]_f$	1.51	1.15	1.12	1.04
			$-\Delta\mu^\ominus$	30.7 (7.32)	25.3 (6.03)	24.7 (5.88)	22.9 (5.45)
0.252	8.56	3.79	$[D]_f$	3.79	1.90	1.72	1.26
			$[Na]_f$	1.90	1.32	1.27	1.14
			$-\Delta\mu^\ominus$	31.7 (7.55)	25.2 (6.01)	24.4 (5.82)	22.2 (5.29)
0.504	8.57	4.95	$[D]_f$	4.95	2.48	2.25	1.65
			$[Na]_f$	2.30	1.49	1.42	1.25
			$-\Delta\mu^\ominus$	32.7 (7.79)	25.4 (6.05)	24.5 (5.84)	22.0 (5.25)
1.01	8.59	6.19	$[D]_f$	6.19	3.09	2.81	2.06
			$[Na]_f$	2.74	1.66	1.59	1.36
			$-\Delta\mu^\ominus$	33.4 (7.95)	25.2 (6.00)	24.4 (5.82)	21.6 (5.15)
2.02	8.63	7.60	$[D]_f$	7.60	3.80	3.45	2.53
			$[Na]_f$	3.27	1.91	1.79	1.50
			$-\Delta\mu^\ominus$	33.9 (8.09)	25.4 (6.05)	24.3 (5.79)	21.2 (5.06)
4.04	8.71	8.84	$[D[_f$	8.84	4.42	4.02	2.95
			$[Na]_f$	3.74	2.12	1.98	1.64
			$-\Delta\mu^\ominus$	33.8 (8.06)	24.9 (5.93)	23.8 (5.67)	20.6 (4.91)
	Average		$-\Delta\mu^\ominus$	32.8 ± 1.2 (7.80 ± .28)	25.2 ± 0.17 (6.01 ± .04)	24.4 ± 0.17 (5.80 ± .04)	21.8 ± 0.59 (5.18 ± .14)

* $[D]_f$ values are given in (mol l^{-1}) × 10^2, $[Na]_f$ in (mol l^{-1}) × 10, and $-\Delta\mu^\ominus$ in kJ (kcal) mol^{-1}. $[NaCl]_s = 8.55 \times 10^{-2}$ mol l^{-1}.

line of greater slope and values of $\Delta\mu^\ominus$ that increase with increasing applied dye concentration, whereas a volume of 0.3 l kg^{-1} gives the reverse effects. The volume of 0.2 l kg^{-1} gives values of $\Delta\mu^\ominus$ which show no trend, merely the expected experimental variations. Previous workers have selected a V of 0.22 l kg^{-1}, which the figures in Table 4.5 show to be slightly inferior in achieving the right slope with no trend in $\Delta\mu^\ominus$. Their value was chosen using all the dyeing results available as opposed to the few considered in the table, however, and hence must be accepted as the more suitable.

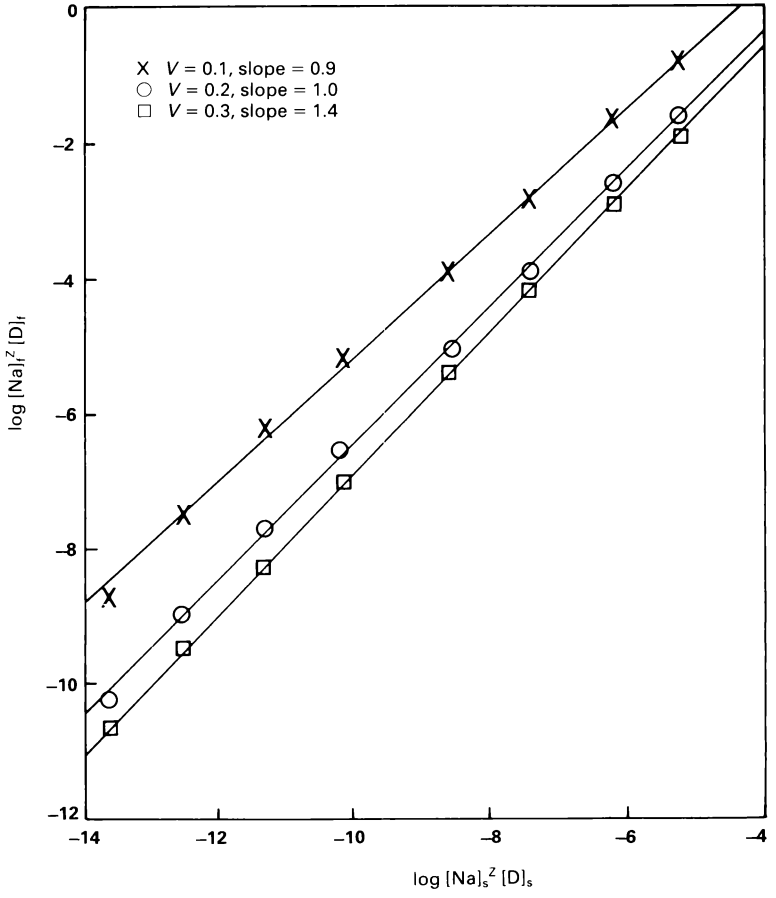

Figure 4.12 – Ionic product plot for Chlorazol Sky Blue FF on cotton at 90 °C [42]: $[D]_s = 5.04 \times 10^{-5}$ mol l^{-1}, salt variable

Another approach to determining the volume of the surface phase was based on the idea that it should correspond to the amount of water adsorbed by the fibre at 100 per cent relative humidity [42]. This was supported by the fact that the value of 0.22 l kg^{-1}, determined as above, corresponded to the value obtained for the adsorption of water by cotton at 90 °C [45]. Unfortunately, data for the other fibres were only available for 25 °C and the application of these figures (Table 4.6, column 2) to the dyeing of Chlorazol Sky Blue FF on cotton, Cellophane sheet and cuprammonium rayon gave affinities of −24.4 (−5.82), −29.5 (−7.03) and −31.4 (−7.48) kJ (k cal) mol^{-1} respectively. Such a variation is greater than might have

TABLE 4.6

Values of the volume of the internal phase in cellulosic fibres [41]

Fibre	By moisture regain /l kg^{-1}	By dye adsorption/l kg^{-1}	
		Chlorazol Sky Blue FF	Chrysophenine G
Cotton	0.22	0.22	0.30
Mercerised cotton	0.26	–	0.50
Viscose rayon	0.46	0.45	0.45
Cellophane sheet	0.33	0.45	0.45
Cuprammonium rayon	0.37	0.60	0.65

been anticipated, but is not surprising because there is no reason to assume that the surfaces available for the adsorption of the small water molecules will be the same as for the much larger dye ions [41].

If it is assumed that the volume of the internal phase is solely a function of the accessibility of the surface to the large dye molecules and that, once the correct values of V are used, the affinity of a given dye will be the same for a variety of cellulosic materials, then an alternative method of determining relative values of V for different substrates is available. This was done using the dyeing data for Chlorazol Sky Blue FF [44] on different cellulosic materials taking the volume term of 0.22 l kg^{-1} and a $\Delta\mu^{\ominus}$ of 24.4 (5.82) kJ (k cal) mol^{-1} as the base point and then calculating the necessary values of V for the other materials so as to produce the same affinity. The results are shown in Table 4.6, column 3.

Marshall and Peters made a further extensive study of the problem using measured data on Chrysophenine G (C.I. Direct Yellow 12) [46]. They used the method already described, of plotting the logarithms of the ionic product in the fibre against that in solution calculated using a series of values of V and selecting the one which gave the best straight line of unit slope. The results are given in Table 4.6, column 4. Although the log–log graphical method is not very sensitive to small changes in V (and hence the results should be regarded as approximate), the similarity between the values in columns 3 and 4 of Table 4.6 is very satisfying and would appear to confirm that, to a reasonable approximation, it is acceptable to assume that the affinity of a dye is a constant for all cellulosic fibres.

4.4.5 Determination of dye affinities

A great many affinity determinations have been made over the years and, in fact, are still being carried out, using the methods described above. The

TABLE 4.7

The effect of temperature on the affinity of direct dyes for cellulose [46, 41]

Dye	C.I. Direct	z	Fibre[a]	$-\Delta\mu^{\ominus}$ (kJ(kcal) mol^{-1}) at temperature of 60 °C	70 °C	80 °C	90 °C	100 °C
1. Those dyes which gave unit slope at 60 °C and 90 °C:								
Chrysophenine G	Yellow 12	2	B	16.0 (3.8)	14.3 (3.4)	13.4 (3.2)	11.8 (2.8)	–
			V	16.4 (3.9)	–	–	13.0 (3.1)	10.9 (2.6)
			C	16.4 (3.9)	15.1 (3.6)	13.4 (3.2)	12.6 (3.0)	–
Durazol Fast Yellow 6G	Yellow 46	2	B	25.2 (6.0)	22.3 (5.3)	17.6 (4.2)	16.0 (3.8)	–
			V	24.4 (5.8)	–	–	13.4 (3.2)	–
Chlorazol Brown M	Brown 2	2	B	26.0 (6.2)	25.2 (6.0)	24.8 (5.9)	24.8 (5.9)	–
			V	27.3 (6.5)	–	–	25.6 (6.1)	23.5 (5.6)
Durazol Grey RG	Black 61	2	B	18.9 (4.5)	18.0 (4.3)	16.8 (4.0)	16.0 (3.8)	–
			V	20.2 (4.8)	–	–	16.0 (3.8)	14.7 (3.5)
Chlorazol Fast Scarlet 8B	Red 26	3	B	24.0 (5.7)	22.7 (5.4)	20.2 (4.8)	18.0 (4.3)	–
			V	24.0 (5.7)	22.3 (5.3)	20.6 (4.9)	19.3 (4.6)	–
			C	24.0 (5.7)	22.7 (5.4)	22.3 (5.3)	20.6 (4.9)	–
Chlorazol Sky Blue FF	Blue 1	4	B	30.2 (7.2)	27.7 (6.6)	26.5 (6.3)	25.2 (6.0)	–
			V	32.3 (7.7)	–	–	26.5 (6.3)	24.8 (5.9)

continued overleaf

[a] Fibre: B = cuprammonium rayon (V = 0.65), V = viscose rayon (V = 0.45), C = bleached cotton (V = 0.30).

Dye	C.I. Direct	z	Fibre[a]	$-\Delta\mu^{\ominus}$ (kJ(kcal) mol^{-1}) at temperature of 60 °C	70 °C	80 °C	90 °C	100 °C
2. Those dyes which gave unit slope at 90 °C but not at 60 °C:								
Chlorazol Fast Orange G	Orange 23	1	B	15.5 (3.7)	–	13.9 (3.3)	12.6 (3.0)	–
			V	14.3 (3.4)	–	–	13.4 (3.2)	11.3 (2.7)
Chlorazol Violet N	Violet 3	2	B	20.6 (4.9)	19.3 (4.6)	18.0 (4.3)	18.0 (4.3)	–
			V	19.3 (4.6)	–	–	18.0 (4.3)	16.0 (3.8)
Chlorazol Fast Orange R	Orange 26	2	B	21.8 (5.2)	20.6 (4.9)	18.5 (4.4)	17.2 (4.1)	–
			V	20.2 (4.8)	–	–	17.2 (4.1)	14.7 (3.5)
Chlorazol Orange Brown X	Brown 12	2	B	20.2 (4.8)	23.1 (5.5)	–	24.0 (5.7)	–
			V	–	–	–	25.2 (6.0)	23.1 (5.5)
Chlorazol Fast Scarlet 4BA	Red 24	3	B	19.7 (4.7)	17.6 (4.2)	17.6 (4.2)	16.8 (4.0)	–
			V	18.5 (4.4)	–	–	16.0 (3.8)	12.6 (3.0)
3. Those dyes which did not give unit slope at any temperature:								
Durazol Red 2B	Red 81	2	B	16.0 (3.8)	15.1 (3.6)	14.3 (3.4)	13.4 (3.2)	--
			V	16.4 (3.9)	–	–	13.4 (3.2)	12.6 (3.0)
			C	16.0 (3.8)	14.7 (3.5)	13.9 (3.3)	13.0 (3.1)	–
Chlorazol Fast Scarlet 4B	Red 23	2	B	22.3 (5.3)	21.8 (5.2)	21.4 (5.1)	20.2 (4.8)	–
			V	21.4 (5.1)	–	–	20.6 (4.9)	17.6 (4.2)
Durazol Fast Scarlet 2G	Red 76	3	B	24.4 (5.8)	22.7 (5.4)	21.4 (5.1)	21.0 (5.0)	–
			V	–	–	–	19.7 (4.7)	–

results of a typical series of experiments are given in Table 4.7 [46] covering a number of dyes and fibres using the values of V listed in Table 4.6, column 4. The experiments were carried out in the presence of 0.01M or 0.02M sodium chloride over a range of applied concentrations for each dye. The affinities quoted in the table are the averages of the results so obtained. When the log–log plots of the ionic products were made it was found that the theoretical unit slope was not always obtained, but that the deviation from unity decreases as the temperature increased. A slope less than unity suggested that all the dye in solution was not available for dyeing, assuming the correct

V term was being applied, which in turn the authors interpreted as being possibly due to the aggregation of dye in solution, an effect which would be greatest at the lower temperatures. In Table 4.7 the dyes are classified relative to this behaviour, according to the sub-headings in the table. The consistency of the affinities on the different fibres, extending as it does over a range of dyes varying in basicity from one to four, led the authors to conclude that the measured affinities are indeed those of the dyes for 'cellulose' in whatever form it is presented, and that the volume term is a useful means of specifying the difference in dyeing behaviour of the different fibres.

4.4.6 The effect of temperature on affinity

As described earlier, the effect of temperature on dye uptake can be expressed using the standard enthalpy (heat) of dyeing $\Delta H^{\ominus}$, which can be determined by measuring the affinity at different temperatures and plotting $\Delta\mu^{\ominus}/T$ against $1/T$. The slope of the line obtained gives $\Delta H^{\ominus}$. This has been done [46] for the dyes listed in Table 4.7, when it was found that the dyes in group 1 produced straight lines from which $\Delta H^{\ominus}$ could be readily obtained giving the results shown in Table 4.8. It can be seen immediately that the

TABLE 4.8

Heats of dyeing of direct dyes on cellulosic fibres/kJ (kcal) mol^{-1} [46]

Dye	Cuprammonium rayon	Viscose rayon	Cotton	Mean
Chrysophenine G	−59(−14)	−59(−14)	−59(−14)	−59(−14)
Durazol Fast Yellow 6G	−130(−31)	–	–	−130(−31)
Chlorazol Brown M	−42(−10)	−50(−12)	–	−46(−11)
Durazol Grey RG	−59(−14)	−67(−16)	–	−63(−15)
Chlorazol Fast Scarlet 8B	−88(−21)	−80(−19)	−80(−19)	−84(−20)
Chlorazol Sky Blue FF	−84(−20)	−97(−23)	–	−92(−22)

enthalpy of dyeing for a given dye on different fibres is the same to a reasonable approximation, thereby confirming that the energetics of the system are those between dye and cellulose irrespective of the form in which the fibre is presented. As a piece of corroborative evidence this is even more valuable, since in the calculation of $\Delta H^{\ominus}$ by subtracting affinities at two temperatures the volume term is eliminated from the equation, so that the constancy of the results does not rely on a suitable choice for the value of V.

When the remaining dyes in Table 4.7 were considered, it was found that the graph of $\Delta\mu^{\ominus}/T$ against $1/T$ did not always produce straight lines thereby suggesting that $\Delta H^{\ominus}$ was changing with temperature, possibly due to

aggregation effects; sufficient dyes did, however, produce a linear relationship on one or other of the fibres studied to discourage too much speculation relating to their positions in groups 2 and 3.