CHAPTER 4

Thermodynamics of dye sorption

HARRY H SUMNER

4.1 INTRODUCTION

When a textile fibre is immersed in a solution of dye under suitable conditions, the fibre becomes coloured, the colour of the solution decreases and dyeing has occurred. This process must not be confused with that of imbibition, in which the fibre merely becomes saturated with coloured liquid, and hence stained, whilst the concentration of dye in the solution remains unchanged. In the former case there is obviously some driving force which causes the transfer of dye from the solution to the fibre, and solutes which behave in this manner are said to be *substantive* to the fibre in question. In *Colour terms and definitions* [1] it is suggested that substantivity be defined as 'the attraction between a substrate and a dye or other substance under the conditions of test whereby the latter is selectively extracted from the application medium by the substrate'.

It became obvious from the start that different dyes show marked differences in substantivity for the same fibre, and also that the same dye shows differences on different fibres. Whilst it was (and still is) possible for the dyer to become familiar with these differences on the basis of experience and to adjust dyeing recipes accordingly, it was quickly appreciated that some numerical method of defining substantivity was required. In this way it was hoped to tabulate dyes according to their dyeing behaviour, and subsequently to use the information to select dyes of similar properties for use in mixtures or to select dyes for use under given dyeing conditions. From the point of view of the organic chemist it was thought that such information would help in the designing of new dyes by relating dyeing properties to the chemical constitution of the dye. Many attempts were made to formulate such a classification of dyes but, while useful in a limited sense, they failed to produce a completely satisfactory system because they were dependent upon arbitrary conditions of measurement, including the purity of the dye studied, and any change in these conditions could – and often did – produce

a change in the classification. An example will serve to illustrate the problem. The degree of exhaustion would seem to be an obvious measure of the substantivity of a dye for the textile material concerned. This is usually quoted as a percentage, i.e.

$$\% \text{ exhaustion} = \frac{\text{amount of dye on fibre at end of dyeing}}{\text{amount of dye applied at start of dyeing}} \times 100 \quad (4.1)$$

Unfortunately the exhaustion achieved in a particular dyeing is dependent on many factors, such as the presence and concentration of other substances in the dyebath (including other dyes), the concentration of dye applied, the pH, the temperature, the time of dyeing and the liquor-to-goods ratio. The problems associated with exhaustion are somewhat alleviated by using the so-called substantivity ratio:

$$\text{substantivity ratio} = \frac{\text{concentration of dye on fibre}}{\text{concentration of dye in solution}} \quad (4.2)$$

Because concentrations are used instead of quantities the problem of the liquor-to-goods ratio is removed and, because such ratios are invariably obtained from measurements made when the system has reached an equilibrium position, so is the problem of dyeing time. All the other factors still remain, however. Of course either parameter could be used if it were feasible to spend a prodigious amount of time and effort in accumulating data for every possible set of dyeing conditions and storing this information in some large and efficient data retrieval system.

Clearly any such solution to the problem is unrealistic and any parameter or set of parameters which is to be used to define dyeing properties must be of a sufficiently fundamental nature as to be uninfluenced by variations in the dyeing conditions. Dyeing thermodynamics would appear to provide such a measure of dye and fibre properties.

4.2 BASIC CONCEPTS

4.2.1 Reversible equilibrium systems

Thermodynamic treatments of the dyeing process are almost invariably applied to truly reversible systems at equilibrium. Many dyeing processes are essentially irreversible, at least on a molecular scale, in that they can only be reversed by another drastic chemical reaction. Examples of such systems include the various forms of mordant dyeing, the oxidation of leuco vat and sulphur dyes, the azoic coupling of naphthols within the fibre and the formation of covalent bonds between dye and fibre in reactive dyeing. This chapter is not concerned with any such systems, and will consider only those

which are truly reversible: disperse dyes on various fibres, direct and leuco vat dyes on cellulosic fibres, acid dyes on wool and nylon, and basic dyes on acrylic fibres.

The other essential requirement for the application of thermodynamics is that all measurements of the distribution of dye or other adsorbate must be made when the system is in equilibrium. When an undyed piece of material is placed in a suitable dyebath, uptake of dye is relatively rapid at first; this initial rate decreases, however, until eventually no further dye is adsorbed. It would be wrong to assume that the system is in a static condition at this point, and that dye molecules no longer move between the bath and the fibre. In fact interchange is still occurring, but at this point the rate of adsorption of dye by the fibre is equal to the rate of desorption from the fibre, that is, a state of equilibrium has been achieved. When the system has reached this point it is said that the concentration of dye in the fibre is *in equilibrium* with the concentration of dye in the solution. Before any measured quantities are used in the thermodynamic treatment, it is essential to ensure that true equilibrium has been reached. This is normally considered to be the stage at which dyeings for longer periods of time produce no further increase in the amount of dye taken up by the fibre. An alternative approach to that of dyeing is desorption, in which a dyed piece of material is immersed in a bath containing no dye and desorption allowed to take place until increasing time produces no change in the concentrations reached. The ideal would be to combine the two approaches for each dye–fibre system under consideration. If the system is truly reversible the two methods should give the same equilibrium position. Because of the time and effort required for such a proceeding, however, only a few such experiments have been described, most workers being content to assume reversibility. Neale [2] demonstrated that the dyeing of Cellophane sheet with Chlorazol Sky Blue FF (C.I. Direct Blue 1) was completely reversible (Table 4.1) and Boulton,

TABLE 4.1

Equilibrium of Chlorazol Sky Blue FF on Cellophane sheet [2]

Dye concentration in solution /g l^{-1}	Dye on Cellophane	
	adsorption	desorption
0.2	1.64	1.58
0.1	1.26	1.26
0.05	1.04	1.00

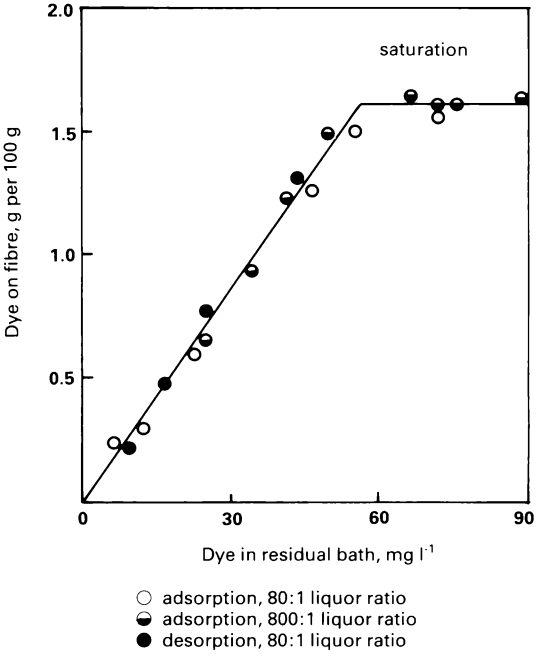

Figure 4.1 – Adsorption and desorption of C.I. Disperse Red 19 on secondary cellulose acetate at 80 °C [5]

Delph, Fothergill and Morton [3] found that the dyeing of cuprammonium rayon with Chrysophenine G (C.I Direct Yellow 12), Chlorazol Sky Blue FF and Benzopurpurine 4B (C.I. Direct Red 2) was also reversible. Studies of the dyeing of secondary cellulose acetate with a disperse dye [4, 5] and of poly(ethylene terephthalate) with 1,4-dihydroxyanthraquinone [6] demonstrated that both dyeing systems were truly reversible, in that the values obtained in both desorption and adsorption experiments lay on the same straight line (Figure 4.1).

4.2.2 Dyebath contents

In addition to ensuring that equilibrium has been achieved, other important precautions must be taken. The contents of the initial dyebath must be known precisely, and these include the adventitious additions that may have been made as a result of impurities in the dye or dyes in question and in the fibre to be dyed. Such impurities could produce significant variations in the results obtained, a fact that has not always been fully appreciated with the result that much of the earlier work on dyeing is of doubtful value. Fortunately

the importance of this is now fully realised. One way of overcoming the problem is to submit the dyes and fibres to be used to a full analysis, so that the nature and amount of any impurity is known and can be included accurately in the dyebath contents. The most usual way of overcoming the problem, however, is to use pure dyes and carefully washed fibre. Such a solution is perfectly acceptable for theoretical studies, but in practice commercial dyes, with all their attendant impurities, have to be used and the method of analysis is the only one available.

Another point to be considered is that the precise contents of the final equilibrium dyebath must also be known. Whilst always of importance, such a precise knowledge was not as vital when using the earlier methods for the mathematical treatment of the results, but the modern treatments are more comprehensive and require a full knowledge of the concentrations of all the ions in the equilibrium dyebath. Again, for theoretical studies carried out in long or very long liquor-to-goods ratios concentrations in the final bath can be equated to those in the initial bath, assuming that the exhaustion of any of the ions present is experimentally insignificant. In shorter liquor ratios, such as are used in practical dyeing, this assumption can be made neither for the dye nor for any of the other ions present; either analysis of the final dyebath must be carried out or the final bath concentrations must be related in some way to those in the initial bath. The question is discussed later in the chapter.

4.2.3 Experimental methods

As described above, any experimental work must be carried out in such a way that the establishment of equilibrium is assured. There is always the danger of a false equilibrium – where the outer surfaces of the material are in equilibrium with the dye solution but the inside of the fibre is not – being mistaken for the true one. The occurrence of such ring-dyeing is well established, and if dyeing is terminated when such a state exists then any conclusions based on the result will be seriously in error. Adequate precautions must be taken to avoid such errors by carrying out preliminary experiments to establish the time required for the system to reach true equilibrium, that is, by carrying out the experiment for increasing lengths of time until increased time produces no change in the situation. Alternatively, where both adsorption and desorption methods are used, equilibrium is assured when both give the same distribution of dye.

Because of the long treatment times required with many systems to ensure that equilibrium has been reached, there is always the danger of decomposition of either the dye or the fibre, or both. This is clearly undesirable, since neither the dye–fibre system nor the application conditions are those intended, and checks are therefore essential. The simplest are to treat the dyebath, in

the absence of fibre, under the conditions required and then compare the treated bath (either chromatographically or spectroscopically) with an untreated one. Similarly, the fibre is treated in a bath containing no dye and then its dyeing properties of this fibre are compared with an untreated one. Unfortunately, neither test gives a completely unambiguous result. If decomposition is observed then it is a positive finding and some action must be taken. If no decomposition is detected, however, this may be meaningful or it may not, since in some cases degradation of the fibre is 'catalysed' by dye [7, 8, 9], and also the rate of decomposition of the dye may be different when the dye is adsorbed into the fibre phase.

In view of the possibilities of degradation and decomposition it is essential to keep the dyeing time to the minimum necessary. In this context efficient agitation of the fibre in the bath or circulation of the bath over the fibre can result in a marked reduction in the time required. Even greater savings may be obtained by choosing the most suitable form of the material to be dyed, where such a choice is possible. This means selecting the material in a form which has the greatest surface area per unit mass and, in particular, avoiding closely packed systems or tightly woven materials. The surest way of reducing the time required is to increase the temperature of dyeing but this is not always possible since the results may be required at a certain temperature. In any case, increasing the temperature could be a two-edged sword: whilst increasing the rate of dyeing it could also increase the rates of decomposition of fibre and dye. Hence the effects of any changes should be checked.

4.2.4 The direct approach: adsorption

The most obvious way of carrying out the necessary dyeings is to immerse the undyed fibre in a dyebath at the chosen liquor-to-goods ratio and continue the dyeing for the required length of time, i.e. the direct approach. This essentially requires no special apparatus, except for adequate means of controlling temperature, supplying sufficient agitation and avoiding the effects of evaporation. At the end of dyeing it is then necessary to determine the concentrations of dye in the fibre and dyebath phases. Some workers have reduced the work required by determining just one concentration and obtaining the other by difference. In general they chose to measure the phase that showed the greatest change in concentration during dyeing. Thus at liquor-to-goods ratios less than *ca* 100:1 and high levels of exhaustion the bath shows the greatest change, and hence the bath is the phase to be measured. When the exhaustion is low the concentration of dye in the bath does not change very much; the percentage experimental error could be relatively large, and in turn will result in a large error when the small concentration of dye on fibre is determined by difference. In such a case it is better to measure the dye concentration on the fibre and obtain that in the

bath by difference. Either method requires an accurate knowledge, not only of the total amount of dye present, but also the mass of fibre and the volume of the dyebath. At longer liquor ratios (greater than *ca* 100:1) the concentration of dye in the bath will, in general, change very little and so the fibre must be the phase to be measured. In general, however, it is undoubtedly better to measure both phases so that the mass balance can be checked to ensure that no losses have occurred either by decomposition or in the experimentation.

Measurement of the concentration of dye in the bath is relatively straightforward. The absorbance (formerly called the optical density) of the solution is measured, possibly after dilution and probably with the addition of a suitable solvent to ensure that the Beer–Lambert Law is obeyed (see Chapter 2), and converted to concentration using an appropriate calibration curve or constant. Determining the concentration of dye on the fibre is more complex, and the following is probably the best method to use. After dyeing the fibre is removed from the dyebath, squeezed to remove as much dye liquor as possible (but not rinsed) and then weighed. It is dried and then conditioned at a known ambient humidity to constant mass. The difference gives the mass of entrained liquor remaining on the fibre after squeezing and the amount of dye in this liquor can be determined from the known concentration of dye in the dyebath. Then either the whole of the fibre sample, including the dye, is dissolved in a suitable solvent, or the dye is extracted from the fibre by repeated treatments in an appropriate solvent. The absorbance of the resulting solution, diluted if required, is measured and the dye concentration obtained using a suitable calibration curve or constant. The total amount of dye on the fibre can thus be determined and corrected for the dye in the entrained liquor to give the amount of dye on a known mass of fibre. In certain cases it may be necessary to correct the dry, conditioned mass of the dyed fibre for the now known mass of dye which it contained.

4.2.5 Desorption

Since the dyeing systems under consideration are assumed to be reversible, the alternatives to the adsorption methods described are those involving desorption of dye from a previously dyed fibre. A sample of the material is first dyed with the required concentration of dye and then it is thoroughly rinsed and dried. It may then be treated in various ways, for example:

1. A quantity of the dyed fibre is immersed in a volume of blank dyebath (i.e. a bath containing all the required ingredients except the dye) at the required temperature, and dye is allowed to desorb until equilibrium is reached. Concentrations of dye in the fibre and solution phases are then determined by standard techniques.

2. The dyed material and a sample of undyed material are placed in the same blank dyebath at the required temperature and are treated until the dye concentration is the same on each. Both pieces and the solution are then analysed for dye concentration. This method not only establishes that equilibrium has been reached but also that the dyeing system is reversible.

3. For the multiple desorption method devised by Gilbert [10], a large sample of material is required which has been dyed to the required depth of shade at a temperature high enough and for a time long enough to ensure uniform distribution of the dye not only through the bulk of the material but also through the cross-section of each individual filament. (In other words, the sample is dyed to equilibrium.) The dyed material is then thoroughly rinsed, dried, conditioned and analysed for dye content. A known mass of this dyed material is introduced into bulb A of the apparatus (Figure 4.2) and a small volume of blank dyebath is added into tube B. The whole

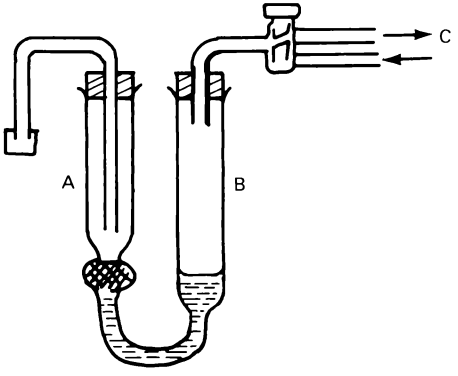

Figure 4.2 – Desorption apparatus [10]

apparatus is immersed in a thermostatted bath at the required temperature. By alternating the application and release of vacuum at C, the liquor is drawn back and forth through the dyed plug. When an adequate quantity of dye has been desorbed, as judged by the colour of the solution, the experiment is stopped and the dyed material is replaced by a fresh sample from the same original dyeing and the experiment restarted. This process is repeated using the same liquor, until the introduction of a fresh, dyed sample produces no change in the concentration of dye in the solution. The concentration of dye in the fibre is now in equilibrium with that in the solution. The concentration in solution is then measured, and that in the fibre is known from the initial analysis. Because each treatment is merely an equilibration between the solution and the outer surfaces of the fibre it requires the transfer of only very small quantities of dye, and hence the time required is quite short (15–

30 minutes per treatment) and the number of equilibrations necessary is generally small. It is claimed that the short treatment times make this a desirable method for use with substrates and dyes which are prone to degradation and decomposition. This is undoubtedly true of the equilibration part of the method, but it must be remembered that the material used had to be dyed at the start under less advantageous conditions.

4.2.6 Adsorption isotherms

The results obtained from dyeing experiments carried out to equilibrium are usually presented in the form of an adsorption isotherm (cf. section 1.5.4), in which the change in the concentration of dye on the fibre with that in the solution is followed under conditions where all the other variables, including temperature, are kept constant. The effects of changes in these other variables are described by the displacement of this concentration isotherm. Experimentally it has been found that most dyeing isotherms approximate in shape to one of three classical forms.

The partition isotherm

This is the simplest possible model. Just as a non-ionic dye dissolves in organic solvents and can be said to have affinity for them, so in dyeing the

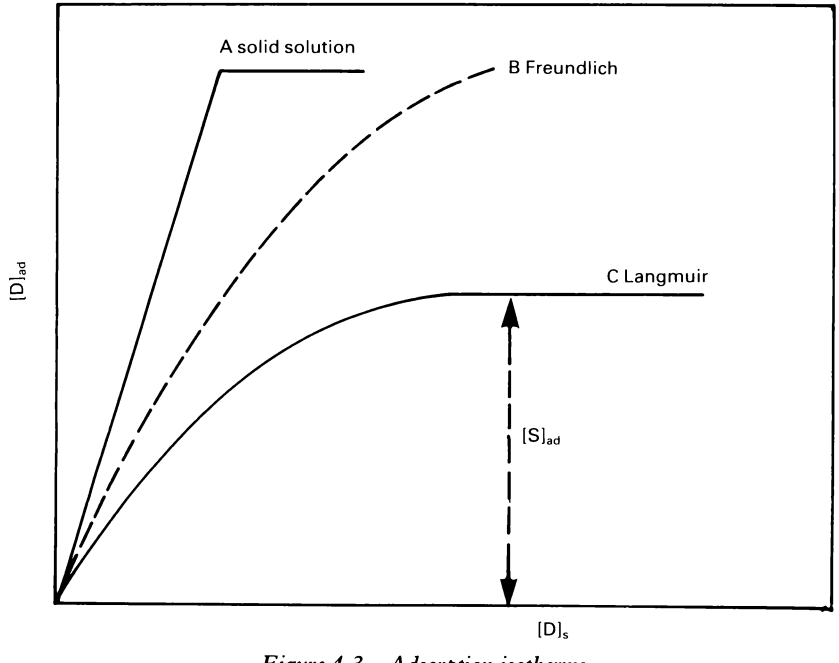

Figure 4.3 – Adsorption isotherms

dye can be considered as dissolving in the fibre because of its affinity for the latter. For this reason the process is often described as conforming to a solid solution model. When the concentration of dye in the fibre $[D]_{ad}$ (g kg^{-1} or mol kg^{-1}) is plotted against the concentration of dye in the dyebath $[D]_s$ (g l^{-1} or mol l^{-1}) a linear relationship is found which abruptly changes to a horizontal plateau (curve A in Figure 4.3). The rising, linear part is defined by the equation

$$[D]_{ad} = K[D]_s \tag{4.3}$$

and the constant K is termed the *distribution coefficient* or the *partition ratio*. The sharp break in the curve marks the saturation of the dye in the solution. Adding dye to the bath in excess of this amount does not change the concentration in solution, which remains at a value equal to the solubility of the dye under the particular experimental conditions, and hence the value of $[D]_{ad}$ remains constant (Eqn 4.3).

The Freundlich isotherm

The classical work of Freundlich on adsorption by animal charcoal led to the purely empirical conclusion that the adsorption isotherms could be defined by the equation, written in terms of dye,

$$[D]_{ad} = K[D]_s^x \tag{4.4}$$

where K is a constant and x is a fraction.

Curve B in Figure 4.3 is a typical isotherm that may be described by this relationship, and such isotherms are widely observed in practice. Eqn 4.4 is such that if logarithms of both sides are taken, a linear equation is obtained:

$$\log [D]_{ad} = \log K + x \log [D]_s \tag{4.5}$$

Thus the obedience of any set of results to the Freundlich isotherm can be confirmed by plotting $\log [D]_{ad}$ against $\log [D]_s$, when a linear relationship should be obtained.

The Langmuir isotherm

This was originally defined to account for the adsorption of gases on metal surfaces, and was derived by Langmuir on kinetic grounds. It has proved to be reasonably well suited to describe dye adsorption by certain textile fibres. Considered in terms of dyeing, the basic postulate is that adsorption of dye takes place on specific sites in the fibre and that when a dye molecule occupies a site that site is saturated and incapable of further adsorption. All the sites

are assumed to be identical, and there is no interaction between them or between dye molecules occupying sites. Assume that a fibre contains $[D]_{ad}$ mol kg^{-1} of dye in equilibrium with a dyebath containing $[D]_s$ mol l^{-1}, and the fibre contains $[S]_{ad}$ potential dye sites per kg. Under these conditions dye will be leaving the fibre with a rate of desorption proportional to the concentration of dye in the fibre, i.e.

$$-\frac{d[D]_{ad}}{dt} = k_1[D]_{ad} \tag{4.6}$$

At the same time dye will be entering the fibre at a rate that depends on the concentration of dye in solution and the number of unoccupied sites in the fibre, which is equal to $([S]_{ad}-[D]_{ad})$. Thus the rate of adsorption will be

$$\frac{d[D]_{ad}}{dt} = k_2[D]_s([S]_{ad}-[D]_{ad}) \tag{4.7}$$

At equilibrium the rate of adsorption equals that of desorption, so that

$$k_1[D]_{ad} = k_2[D]_s([S]_{ad}-[D]_{ad}) \tag{4.8}$$

If this is rearranged and k_2/k_1 equated to k, then

$$[D]_{ad} = \frac{k[S]_{ad}[D]_s}{1 + k[D]_s} \tag{4.9}$$

This is the equation of a Langmuir isotherm, and such isotherms have the form illustrated in Figure 4.3, curve C. It is worthy of note that the horizontal portion of curve C is defined by the number of available sites in the fibre, i.e. it occurs when the fibre is saturated. This is in contrast to the horizontal part of curve A, where the limiting factor can be considered as being the solubility of the dye in the bath.

If Eqn 4.9 is inverted,

$$\frac{1}{[D]_{ad}} = \frac{1}{k[S]_{ad}[D]_s} + \frac{1}{[S]_{ad}} \tag{4.10}$$

it can be seen that if the reciprocal of the concentration of dye adsorbed $1/[D]_{ad}$ is plotted against the reciprocal of the concentration in solution $1/[D]_s$, then a straight line should be obtained with a slope of $1/k[S]_{ad}$ and an intercept on the $1/[D]_s$ axis of $1/[S]_{ad}$. This graphical method has been widely used to obtain the saturation value, that is the number of available sites $[S]_{ad}$ for use in the equation.

A further point which must be made regarding the Langmuir isotherm is that dividing Eqn 4.8 by $[D]_s$ and again equating k_2/k_1 to k gives

$$\frac{[D]_{ad}}{[D]_s} = k([S]_{ad} - [D]_{ad}) \tag{4.11}$$

which when $[D]_{ad}$ is very much smaller than $[S]_{ad}$ leads to the result that

$$\frac{[D]_{ad}}{[D]_s} \approx k[S]_{ad} \tag{4.12}$$

With any particular fibre under a given set of dyeing conditions both k and $[S]_{ad}$ should be constants, so that Eqn 4.12 then becomes a linear relationship which can easily be confused with a simple partition isotherm.

Each of the three classical isotherms described above is based on a postulated model of the adsorption process, and it has been found experimentally that most dyeing isotherms approximate in shape to one or other of them. This in turn led to the assumption that if a set of experimental dyeing results conformed to one of these classical isotherms, then the theoretical model for the particular dyeing process was defined. Whilst such an assumption (whether true or false) produced a workable model to interpret many dyeing processes, in certain cases it also resulted in problems and complications which resulted in further assumptions being necessary to make the model fit the experimental data. Care is therefore necessary when making any decision regarding the most appropriate model based on the observed shape of the experimental isotherm.

4.2.7 Activity coefficients of dyes

As indicated in Chapter 1, thermodynamic equations are based on activities of the species involved (rather than their concentrations) in the two phases, fibre and solution. The experimental methods described above produce results in terms of the concentrations of dye in the two phases, however. If the dye in both cases behaved ideally there would be no problem, because activity could then be equated to concentration. It is unlikely that dyes will behave ideally, particularly in solution, and therefore this simple equality cannot be used and some form of correction factor should be included. Lewis [11] used the relationship

$$a = cf \tag{4.13}$$

where a = the activity, c = the concentration and f = the *activity coefficient*, a factor which describes the degree of departure from ideality.

In general, as $c \rightarrow 0$, $f \rightarrow 1$ so that in very dilute solutions the situation approximates to being ideal and activity can be equated to concentration. In more concentrated solutions, however, a knowledge of the value of the activity coefficient is desirable if the thermodynamic equations are to be applied rigorously.

There is a comprehensive literature describing the available methods of measuring activity coefficients, and attempts have been made to apply certain of these techniques to the study of dye solutions. Unfortunately very little success has been achieved because of the many special problems that are encountered with dyes, principally the low concentrations of dye in solution and the presence in solutions which relate to practical dyeing of swamping concentrations of other solutes.

The alternative to direct measurement is computation. The activities of strong electrolytes in aqueous solutions have been studied by Debye and Hückel [12] who reached and demonstrated the validity of the conclusion that

$$-\ln f = Az^2 I^{\frac{1}{2}} \tag{4.14}$$

where f = the activity coefficient of the ion in question, z = the charge on the ion, A = a constant, approximately equal to 0.5, and I = the ionic strength of the solution as defined by the equation

$$I = \tfrac{1}{2}\Sigma cz^2 \tag{4.15}$$

i.e. half the sum of the concentration of each ion in the solution multiplied by the square of its valency. Although many types of dye are ionised, the theory in this simple form applies only to small spherical ions in solutions of low total ionic strength. While it has been extended to take account of the radii of the ions it is extremely doubtful whether, even then, it would be applicable to dye ions, which are far from being simple spherical ions. In addition, many dyebaths would not be considered to be of low ionic strength.

Because of the lack of experimental results and because the use of the Debye–Hückel equations is not justifiable, it is the usual practice to equate the activity coefficient of the dye ions to unity and simply to substitute concentration for activity in the thermodynamic equations. The only justification for this decision is that it seems to work in a reasonably satisfactory manner; moreover, at the moment no alternative is available.

4.2.8 Aggregation of dyes

The problems associated with the non-ideal behaviour discussed above are accompanied by other problems, which have their origin in the aggregation

of dye molecules or ions in the solution and possibly in the fibre. Determinations of activity coefficients in solution for certain dyes, e.g. Chlorazol Sky Blue FF (C.I. Direct Blue 1) [13] and two acid dyes [14], gave values that would be expected from a strong electrolyte, and hence the assumption must be that they dissolve to give monomolecular solutions under the conditions of measurement. In contrast there is a considerable amount of evidence in the literature that many ionic dyes readily form aggregates in solution. In general the results show that the degree of aggregation increases as the r.m.m. of the dye increases, but that this effect can be counteracted to some extent by increasing the number of solubilising groups in the molecule. Aggregation is promoted by increasing the concentration of dye in solution and also by the presence of added electrolyte; it is reduced by increasing the temperature, however, in many cases to an extent that justifies the suggestion that the dye will not be aggregated at the usual dyeing temperatures in a normal dyebath. In other instances where the usual dyeing temperature is low and large concentrations of electrolyte are present, or where the usual temperature has been reduced for experimental reasons, such an assumption could be in error.

Many methods for studying the aggregation of dyes in solution have been used by various workers [for example, 15–20] and it would have been of considerable value if their results had provided a means of determining what proportion of dye in the solution was capable of being adsorbed by the fibre. For example if, in any particular dyeing system, the fibre is able to adsorb dye in the monomolecular form only, then the concentration of dye in solution which is in equilibrium with that on the fibre is the concentration of single molecules. Most of the methods used produce a result in the form of an aggregation number which expresses the average number of molecules in the aggregates, and this figure is generally arrived at by way of several assumptions. Such a number is useful to demonstrate that changes in the degree of aggregation do occur with changes in dyebath conditions but, except in the case of a simple monomer–dimer equilibrium, they do not permit the calculation of the concentration of the effective form in the equilibrium mixture, assuming it is already known which that form is in terms of dye adsorption.

As a result workers studying the adsorption of dyes by textile materials have had to assume that the dye solutions used are always molecularly dispersed systems and the possibility of aggregation is generally reserved to explain, in a qualitative fashion, why certain sets of results do not conform to the expected pattern. Such interpretations could possibly be correct, but quantitatively they are unsatisfactory.