The Chemistry of Dyeing

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1 Introduction

Fermentation, cooking, and dyeing are probably the most venerable of man's ventures into applied chemistry. All three may well have originated at the same point in man's activities, the cooking pot. Each involves processes of considerable complexity and, in the modern context, provides the basis for academic and industrial research frequently crossing classical interdisciplinary boundaries. In each case, also, the development of scientific attitudes has involved clearing away centuries of entrenched empiricism, although it. must be agreed that previous experience has often provided the clues for scientific explanation of particular phenomena.

In modern terms dyeing involves the synthesis of complex, coloured organic compounds with solubility in appropriate solvents (almost universally water), which are capable of becoming adsorbed on to molecular 'surfaces' of appropriate substrates in a controllable manner, and of diffusing within those substrates. Thus the chemistry of dyeing covers aspects of the organic chemistry of aromatic compounds, the nature of solutions of complex molecules, polymer chemistry, adsorption and related interfacial phenomena, diffusion, and polymer physics. Since the interaction of complex aromatic molecules with substrates extends beyond the obvious topic of textile colouration into histology and biochemistry, the chemistry of dyeing provides a meeting point for investigators with apparently disparate interests. This is further emphasized by the fact that in textile dyeing the concern of the chemist does not end with the colouration process, since the consumer demands that the dyed material be fast to wet treatments, *e.g.* washing, and to light. Thus photochemical degradation of dyes is a relevant topic in dyestuff and dye application research.

The year 1856 saw the chance discovery of mauveine by W. H. Perkin and the beginning of the synthetic dyestuff industry, for many years the major part of the organic chemicals industry in Britain and Germany. Its inevitable concern with the many aspects of dyes and dyeing created within the industry a favourable environment, particularly in Britain, for the development of other branches of industrial chemistry, *e.g.* pharmaceuticals. Important contributions were also made to the industrial chemistry of fibrous polymers and surfactant compounds. It is clear that a comprehensive review of activities in the sphere of the chemistry of dyeing could run to considerable length, or discuss matters so briefly as to provide little useful information. Therefore, for the purposes of the present treatment, attention will be confined as closely as

possible to the chemistry of the dyeing process itself, and other aspects will be left for other occasions.

2 Natural Colouring Matters

Until the second half of the last century dyers universally used materials extracted from roots, leaves, insects, *etc.* for the colouration of materials. These were not always obtained in their directly usable coloured form: frequently the colouring matters had to be released from their glucosides by fermentation. One of the oldest dyes, indigo, is obtained from the woad plant *Isatis tinctoria* as its glucoside indican, which interacts with plant yeasts in water to give the water-soluble leuco indigo. Air oxidation then yields the blue indigo pigment. Two other ancient natural dyes, (1) and (2), have the structures shown. Of these two, Kermesic acid (2) is possibly the oldest dye so far identified, being known in the time of Moses.
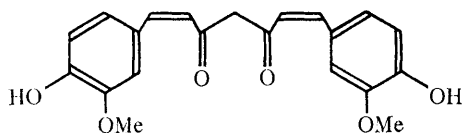
Curcumin *(the colouring matter
from turmeric root)*

(1)
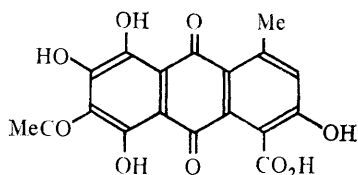
Kermesic acid *(the colouring matter from
the insect Quercus coccifera)*

(2)

Dyers showed great initiative in devising means of obtaining and applying colouring matters to textiles, and over the centuries experience was accumulated and passed on through traditional means such as guilds. In addition, manuals came to be written which often contain early publications of general interest in applied chemistry. For example, the *Plictho* of Gioanventura Rosetti, published

in 1548, contains the first known reference to a method for manufacturing hydrochloric acid. Despite the limitations of natural colouring matters dyers produced a wide range of shades. The *Plictho* contains some hundred recipes for colouring different textiles. Another important contribution to early chemistry was the technique of mordanting which anticipated organometallic-complex chemistry. The discovery arose from the fact that the dyes which gave a desired colour often exhibited no affinity for the material to be dyed. It was found that pretreatment of the material with either a tannin or a solution of certain mineral salts, *e.g.* alum or iron salts, conferred upon it affinity ('teeth') for the dye. The use of different mordanting compounds gave different shades with the same dye and led to a further extension of the available shade choice.

In practice, the exact shade produced using natural dyes depended on the contribution of traces of secondary colouring matters, as well as other factors. The composition of the coloured extract of a plant depends upon climatic, seasonal, and regional factors, as might be expected. In addition, the ease with which mordants may be used is accompanied by an inevitable sensitivity of the shade towards trace metals present in the water used for dyeing. This is also a factor subject to regional and seasonal variations. As a consequence the shades produced by ancient dyers were highly individual, and the emergence of dyeing as a 'mystery' is not surprising. The methods used by early dyers were not capable of producing results of the highest quality, and while this might often be a disadvantage astute business men were able to turn it to advantage, as in the case of Persian carpets. Here much of the unique character of the carpets depends upon the lack of penetration of the wool fibres by natural colouring matters, which gives a special interest to the appearance of the pile. This effect is extremely difficult, if not impossible, to achieve with synthetic dyes available.

3 The Appearance of Synthetic Dyes

Affairs remained virtually unchanged over centuries until synthetic dyes were produced in quantity during the second half of the last century. Thus were provided standardized products covering a wider range of shades than was accessible previously, and generally at a lower price. The major natural dyes of high quality, indigo and madder (alizarin) were rapidly replaced by their synthetic equivalents. The discoveries of Griess in diazo chemistry in 1861 were soon put to good use to develop the azo colouring matters virtually unknown in nature and generally superior to natural dyes in almost every way. The early discovery of sulphonation opened the way to producing dyes of any desired solubility. The first developments occurred at a time when structural organic chemistry was in its infancy, and bulk manufacture of organic chemicals like aniline, or simple substances like sodium nitrite, had to be specially developed. The rapid development of structural organic chemistry, stimulated at least in part by interest in dye chemistry, provided the basis for a systematic explanation of some of the factors determining dyeing behaviour, and the observation of correlations between chemical structure and properties. The first manifestation of this new approach was the work of Böttiger, who achieved the objective of

producing sulphonated azo dyes applicable to cellulose fibres directly, without a mordant. This was not possible prior to Böttiger's work in the 1880's, although the direct application of dyes to wool and silk were well known. Böttiger showed that linear bis- and tris-azo dyes bearing sulphonic acid groups were suitable for direct cotton dyeing in the presence of salt, and the first 'direct dye', Congo Red (3), was marketed in 1888.
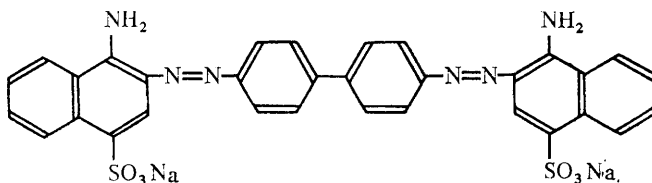
Congo Red (Böttiger, 1884)

(3)

Further systematic studies were encouraged by this progress and led to the classification of dyes according to their behaviour as acid dyes (sulphonated dye anions), basic dyes (dye cations), direct dyes (selected acid dyes for cotton dyeing), acid milling dyes (selected acid dyes giving high fastness on wool), *etc.* It was from this time that the chemistry of the dyeing process began to be regarded as a matter for investigation, albeit in a crude way. Further investigations were directed towards finding improved dyes giving fastness to light and washing, and also improved ease of application. As a consequence of these efforts further dye classes came to be developed, and also an understanding of the processes involved in their adsorption and retention by the fibre.

4 The Search for Washing Fastness

The need to produce dyeings which resisted washing processes and did not fade in sunlight has always been accepted. The dyers of France were organized from the early sixteenth century into two guilds: the *teinturier du grand teint* and the *teinturier du petit teint*, the former producing relatively fast dyeings. From the early eighteenth century onwards the post of Inspector General of the Dyeing Industry was held by a succession of eminent French chemists, whose responsibility it was to devise and improve chemical methods of distinguishing between fast and fugitive dyes. In the progress of their work the concepts of the affinity of dyes for fibres and their diffusion into fibres came to be developed in a rudimentary way. In addition, concepts of physical entrapment came to be developed to explain the fastness of some dyes. Progress was naturally limited because these efforts predated chemistry in the modern sense. Nevertheless, the necessary approaches towards the achievement of fast dyeing were tentatively indicated by the eighteenth century, although little could be done until synthetic dyes became available and the beginning of systematic structural organic chemistry.

The lack of fastness in dyeing arises from the essential reversibility of the dyeing process. In short, the washing process is a desorption procedure which reverses the adsorption process of the dyeing. The production of a fast dyeing thus becomes a problem of making the dyeing process either fully irreversible or at least not reversible during washing procedures.

This objective is achieved to some extent during the application of dyes on to mordanted materials. On wool a chrome mordant provides a basis for dyeings of very high fastness. The shades produced by mordanting are in all cases dull, however, owing to the electronic interaction of the metal atom with the main chromogenic system. An alternative approach is based on the fact that it is possible to dye wool at 100 °C while washing is normally carried out at 40 °C. The rate of diffusion of dyes is much greater at the higher temperature so that high molecular weight dyes may be adsorbed rapidly in dyeing but desorbed slowly in washing. Neither of these lines of attack was fruitful in cotton dyeing, partly because the chemical differences between proteins and cellulose make fast mordanting impossible in the latter case, and partly because cotton goods are washed very much more severely than wool goods. The most successful approach was based on the dyeing behaviour of indigo, which is applied as a substantive leuco dye from solution and then oxidized to the pigment form within the fibre. Mechanical entrapment provides the fastness in this case. René Bohn discovered in 1902 that anthraquinonoid compounds could be prepared which were not only better dyes than indigo but also more stable, thus giving rise to the modern vat dyes which remain the fastest class of dyes for cellulose. The approach taken in developing fast-to-washing acid dyes was applied to dyes for the man-made fibres, although in this case very high temperature dyeing methods had to be developed. The most recent approach has been with the fibre-reactive dyes which achieve a non-reversible dyeing process by chemical reaction with the fibre. The concept of chemically reacting dyes and substrates originated in the same period as Bohn's discoveries, but its translation into practice took many years.

The production of fast-to-washing dyes produced many problems in dye application. Consequently, some thirty years ago serious attempts began to be made to explain the dyeing process in physico-chemical terms. The objective was partly to obtain a clearer idea of what kinds of dye would be fast, and partly to provide a means of developing better dyeing methods. The effort made took place almost entirely in industrial laboratories and was directed very largely by industrial attitudes. Although great progress was made and indeed a new academic subject established, the theoretical developments reflect their origins.[1] In the recent period, a unifying approach to the somewhat diverse body of information has become possible, and it is on this basis, rather than chronological development, that the topic will be considered here.

[1] T. Vickerstaff, 'The Physical Chemistry of Dyeing', Oliver and Boyd, London, 2nd edn., 1954.

5 Binding Forces in Dyeing

The process of dyeing involves adsorption of dye molecules by a substrate, normally a textile polymer, from an external phase which initially contains all the dye. An equilibrium is eventually established whereby a new external phase concentration and a dyed material result. This differs from imbibition of the initial dye solution by the material by virtue of the concentration changes. The loss of dye by the external solution is normally termed *exhaustion* and this reflects the *affinity* or *substantivity* of the dye for the substrate. The existence of the affinity factor was clear to Berthollet and is described in his work 'Elément de l'art de la teinture' of 1791. However, chemical knowledge of that time, or indeed for many years after, was not able to deal usefully with such concepts. Today such effects are considered in energetic terms and the concentration changes are seen as gains in free energy. The desorption of the dye from the substrate in these terms requires the input of energy, so that the free energy change measures the constraint upon desorption or the *binding force* between the dye and the substrate.

The binding forces between interacting molecular systems are now extensively studied in a much wider area of interest than colouration, and current ideas are reviewed in detail elsewhere.[2] Nevertheless, for the present purpose some brief description is valuable. It should be stated at the outset that the dyeing process, reflecting as it does a competition between substrate and external phases, may be considered in terms of negative as well as positive effects in the dye–substrate interaction.

Five general kinds of binding forces are believed to influence dye adsorption. The simplest forces which require consideration are the coulombic interactions between ionic charge centres in dye ions and in substrates. Clearly they may be attractive or repulsive according to circumstances. Their mode of action is simply electrostatic, and consequently they should not be affected by environmental factors of a non-ionic character. Coulombic interactions have been very extensively studied in relation to the adsorption of dye ions and their role will be considered at a later stage.

Both dyes and substrates are frequently of a significantly polar character, quite apart from their propensities for ionization. Dipolar effects are present, and direct or induced dipolar interactions are to be expected. These will be subject to slightly different influences compared with ionic (coulombic) interactions and can be more generally effective.

By reason of their necessary structural features dye molecules have low-lying electronically-excited states which interact with visible light, and also may participate readily in adsorption interactions through dispersion forces. These forces, according to classical theory, fall off very rapidly with distance and it would be expected that with large molecules interacting thermal effects would readily lead to bond rupture. However, McLachlan has shown recently that in the 'three body' situation, *e.g.* dye–solvent–substrate susceptibility factors en-

[2] H. C. Longuet-Higgins, *Discuss. Faraday Soc.* No. 40 'Intermolecular Forces', 1965, 7.

able the perturbational effects giving rise to dispersion forces to be transmitted through the solvent.[3]

An important and common induced binding force is the hydrogen bond. Care must be taken in proposing hydrogen-bond mechanisms in dye binding owing to the often forgotten presence of water, which can act as a competing species for binding positions in the dye or the substrate. On purely energetic grounds hydrogen-bond–dye binding is improbable in aqueous systems unless special statistical factors are operating.

The last form of binding force which needs to be considered is the so-called hydrophobic interaction, which arises from the disturbance caused by non-polar solutes or residues of the water structure. Such solutes or residues promote water structuring in their vicinity, and there is a consequent entropic driving force for association to limit the ordering effect on the water.[4]

All of the above kinds of binding force can be expected in the consideration of dye binding, but this is no less true in relation to the properties of the polymeric substrates with which the dye is to interact. The physical structure of the polymer into which it is proposed the dye will enter and become adsorbed, depends upon the cohesive forces between polymer molecules. Cellulose is insoluble, for example, entirely because of the cohesive effect of multiple hydrogen bonding. When cellulose is immersed in water, the water can compete for some of the hydrogen bonding centres, leading to some swelling of the cellulose, but solution cannot be achieved without special methods. Polyamide fibres such as Nylon 66, acrylic fibres such as Orlon, and polyester fibres are all dependent entirely upon internal cohesive forces for their solution and melting properties. Special chemically cross-linked polyamides and wool keratin supplement regular cohesive forces with covalent bonding between polymer chains, providing additional stabilization. The centres for the action of cohesive forces in polymers are not essentially different from those involved in dye binding. Thus wool keratin exhibits coulombic cross-links between $-NH_3^+$ and $-COO^-$ groups as well as the general forces discussed. In acrylic fibres the presence of $-SO_3^-$, in some cases $-COO^-$, and other ionic groups, has an anti-cohesive effect offset by general forces. As a consequence, in these and in all other cases it must be expected that dye binding by the substrate is not a simple case of adsorption on to an active surface.

The above considerations are well exemplified by the behaviour of small molecules such as phenols. Phenolic compounds are readily taken up by proteins and polyamides from aqueous solution. Where phenol itself is used, it possesses sufficiently high aqueous solubility and affinity for considerable amounts to become adsorbed. Binding is thought to be due to a combination of induced dipole effects and hydrophobic interaction, together with dispersion forces. In the case of polyamides, the extent to which phenol molecules can compete with the internal cohesive forces in the polymer is sufficient to lead to disruption

[3] A. D. McLachlan, *Discuss. Faraday Soc.* No. 40 'Intermolecular Forces', 1965, 239.
[4] A. K. Covington and P. Jones, 'Hydrogen Bonded Solvent Systems', Taylor and Francis, London, 1968.

of the polymer structure, swelling of the fibres, and eventually dissolution. The affinity of the adsorbate can be increased by substituting the phenol with alkyl groups. However, these reduce the aqueous solubility because of their water structuring influence and limit the external concentration. The swelling per mole adsorbed remains the same but the adsorption is reduced. If *o*-phenyl phenol is used, the limitation upon uptake imposed by low aqueous solubility is considerable, and all that occurs is some swelling and a lowering of the glass transition temperature. These observations are quite general so that the physical structure of all textile polymers is readily modified by appropriate simple compounds with adequate solubility. Thus cellulose acetate is swollen by phenols or aniline, cotton cellulose by morpholine, acrylic fibres by furfural, nylon by phenols, pyridine, or aromatic amines, polyester fibres by aryl phenols, *etc*.

None of the above adsorbates are dyes of course, and in order for compounds to be made which absorb visible electronic energy, their population of delocalized electrons must be greatly increased by extending the resonance system. Dyes have inevitably larger molecular size and weight, compared with the compounds already discussed, but no other new principle is involved. For example, aniline and the dye *p*-phenylazoaniline behave in the same way with only quantitative differences. The subject of dye binding requires a consideration of the participation of both the dye and the substrate in the interaction. In the same way as cohesive forces operate in polymers, dye molecules designed to show ready adsorption on to polymers frequently exhibit dye–dye interactions, either in the external solution phase or on the adsorbing surface itself. Such interactions may favour or disfavour adsorption according to circumstances. In addition, the dye–substrate interaction involving large and frequently flexible molecules can lead to configurational changes in either or both components. These may favour or disfavour further adsorption. They may also lead to metastable molecular configurations of a different colour from that expected. Every instance of dye–substrate interactions involves a complex balance of these several effects. The outcome of the resolution has sometimes apparently unrelated consequences. Some particular examples provide a basis for a consideration of how the various factors may operate.

A useful example of the interplay of effects is provided by the dyeing of polyester fibre with disperse dyes.[5] This substrate cannot be dyed from aqueous solvents with dye ions, owing to coulombic repulsion effects and the hydrophobic nature of the polymer. On the other hand, it cannot be dyed with insoluble non-polar materials owing to the need for a molecular dispersion in order to permit diffusion through the polymer matrix. Consequently, disperse dyes which are weakly polar and sparingly soluble in water are used. If the dyes are too polar they are fairly water soluble but have low affinity. Dyeing is most readily carried out using fairly low molecular weight dyes of low solubility and which diffuse rapidly within the fibre. However, such dyes possess a signi-

[5] T. Vickerstaff, ref. 1, p. 484; I. M. S. Walls, *J. Textile Inst.*, 1954, **45**, 258; E. Merian, J. Carbonell, U. Lerch, and V. Sanahuja, *J. Soc. Dyers and Colourists*, 1963, **79**, 505; J. Thompson, Ph.D. Thesis, University of Leeds, 1970.

ficant vapour pressure due to their relative lack of cohesive energy in the solid state; when the polymer is heat-treated some dye volatilizes. The vapour pressure may be reduced either by making the dye more polar or by increasing the cohesive energy in the solid state through an increase in molecular size. The first solution leads to a lower affinity for the fibre while the second leads to slower diffusion. Since the problems arising from the second solution are the more readily overcome, this is the one adopted by dyestuff chemists. To solve the diffusion problem a quantity of a second compound with affinity but which is not coloured, *e.g.* a phenol, may be added to the dyebath. When this is adsorbed it disrupts the cohesive forces in the polymer and leads to swelling and consequently a more ready diffusion of the dye. Alternatively, the polymer may be rendered more permeable by heat alone. As a consequence, dyeing at temperatures above 100 °C under pressure has become commonplace.

It is found that disperse dyes are displaced by water even from hydrophobic fibres. Thus the maximum adsorption observed when the system is saturated with water may be as little as one third of the value observed when the dye is taken up from the dry vapour.[5] Whether the competition is isosteric, *i.e.* competition of water and dye molecules for the same adsorption sites, or allosteric, *i.e.* water adsorption leading to configurational changes in the polymer unfavourable to dye adsorption, is not known. The effect of water is so marked as to suggest that the latter explanation may prove the correct one. However, the competitive effect explains why uptake of disperse dyes by relatively hydrophilic substrates such as wool keratin or cotton cellulose is small. In order to achieve a satisfactory level of uptake it is necessary in these cases to use larger molecules of higher intrinsic affinity, and at the same time make them soluble enough by the introduction of polar groups such as $-SO_2NH_2$ or SO_3^-. This introduces the factor of coulombic forces in the latter case.

In wool keratin both carboxy and ammonium groups are present, so that in the presence of increasing amounts of acid the fibre develops an increasingly positive potential, owing to the back-titration of the carboxy-groups. The uptake of dye anions does not lead to any unfavourable coulombic effects until the adsorbed ion concentration exceeds the concentration of ammonium groups. Since this is a very large value, greatly exceeding any practical requirement, no real limitation is experienced. However, with polyamide fibres, *e.g.* Nylon 66, the concentration of fixed positive and negative charges is quite small, and unfavourable coulombic effects manifest themselves at depths of shade of practical interest.[6] With very small ions such as chloride, or even small dye ions, the coulombic repulsion effect is sufficient to produce a 'saturation' effect when the adsorbed ion concentration is equal to the fixed charge concentration of opposite sign. However, when dye ions of higher affinity are used the saturation value may exceed the fixed charge value. With very high affinity ions it is difficult to detect any significant electrostatic saturation level. This coulombic effect is an example of dye–dye interaction on the adsorbing surface. At the point of

[6] T. Vickerstaff, ref. 1, p. 439; H. Brody, *Textile Res. J.*, 1965, **35**, 844.

electrostatic saturation the fibre surface has zero charge, and any further adsorption will lead, in the case of dye anions, to a negative potential and consequently an increasing potential energy in the surface. On the other hand, adsorption occurs because free energy is gained. The two effects are in opposition and adsorption stops when the two are equal. This will only happen when the potential energy exceeds zero in the case where the free energy gain is very small.

The situation of electrostatic saturation observed with polyamides is found *ab initio* when cellulose is dyed with anions. Cellulose contains few fixed positive charges with the consequence that the adsorption of ions leads immediately to coulombic repulsion effects. This effect can be offset by increasing the ionic strength of the external solution to lower the surface potential, but for simple anionic dyes the effect is not great enough for practical interest. Dyes of high affinity must be built up by extending conjugation so as to provide a balancing free energy gain. This is precisely what was done by Böttiger in developing the direct cotton dyes. However, one undesirable consequence is that the extended conjugation systems which are necessary contain many interacting centres for the absorption of electronic energy, leading to dull shades. This problem is overcome and the level of fastness raised to a quite new level with fibre reactive dyes.[7] The dyes in this case are generally of lower affinity than direct cotton dyes and hence of brighter shade. The exhaustion equilibrium is, however, continually displaced by virtue of the chemical reaction between the dye and the fibre. This results in a satisfactory level of dyebath exhaustion despite the lower affinity, and provides very high fastness to washing since affinity factors are no longer determinate in this respect.

Coulombic effects may be generally regarded as disfavouring dye adsorption more than favouring it. Other interaction effects between adsorbed dyes may, however, assist adsorption. An extensively studied example of this is provided by Acridine Orange adsorbed by soluble protein molecules. In solution Acridine Orange tends to form dimers, and the electronic interaction of the two chromogens causes a marked colour change. In very dilute solution (10^{-5} mol l^{-1}) the dye exists in the monomer form, but if a small amount of a soluble protein is added to such a solution there is an immediate colour change consistent with dimerization. In fact what has occurred is the adsorption of the Acridine Orange on to the protein with a simultaneous interaction between the adsorbed dye molecules. This phenomenon is termed *stacking* of the adsorbed dye.[8] The free energy gain of dimerization of Acridine Orange is considerable ($-5·7$ kcal mol^{-1}) and the stacking effect adds a free energy gain comparable to that of the actual dye–substrate interaction. The formation of stacks appears to be very dependent upon steric factors and it is likely that the dye–dye interactions can produce new configurational forms of flexible proteins. Thus rigid proteins give rise to low

[7] W. F. Beech, 'Fibre Reactive Dyes', Logos Press, London, 1970; I. D. Rattee, *J. Soc. Dyers and Colourists*, 1969, **85**, 23.
[8] D. F. Bradley and M. K. Wolf, *Proc. Nat. Acad. Sci. U.S.A.*, 1959, **45**, 944; R. F. Beers, *J. Bacteriol.*, 1964, **88**, 1249; R. F. Beers and G. Armilei, *Nature*, 1965, **208**, 466

probabilities of stacking, whereas with flexible systems the probability is high. If the probability is defined as

$$K = \frac{\text{probability of dye existing in stacks}}{\text{probability of dye adsorbed as monomer}}$$

then the correlations shown (Table) are obtained.

Table

Protein	General description of configuration	K
DNA	Rigid two-stranded configuration	1·96
Polyadenylic acid	pH > 7, single-stranded flexible coil	~100
	pH < 5, rigid two-stranded helix	~ 5
Heparin	Flexible single-stranded coil	600

The steric factor is not likely to be the only one determining the stacking probability, but it is undoubtedly of considerable importance. Stacking or adsorption in aggregates is by no means uncommon, although on insoluble substrates it has been little studied.

Since a protein in solution will normally adopt a configuration of lowest energy, interaction with a dye molecule can produce new configurations which may be more or less stable to hydrolytic attack. Glazer has shown that α-chymotrypsin is rendered unstable by the dye Evan's Blue.[9a] This dye was able to produce some 70% autolysis in 3 h at ambient temperatures. Just how sterically dependent the effect is can be seen from the fact that the isomeric dye Trypan Blue produces very little autolysis under otherwise identical conditions. The two dye structures are shown [(4) and (5)]. Evan's Blue brings about no autolysis with other proteins. Glazer believes that the dye–protein interaction stabilises least folded conforms of the protein in such a manner as to increase the probability of hydrolysis. The opposite effect, *i.e.* stabilization, has also been observed. Bound methyl orange ions have been observed to stabilize serum albument.[9b]

Another interesting example of a conformational effect is provided by the work of Merian *et al.*[10] who applied an azo dye in the *trans*-configuration to polyester fibres. Irradiation with u.v. light converted the dye into the *cis*-configuration with shrinkage of the polymer fibres. The effect was reversible and did not occur in the absence of dye. The effect serves to demonstrate the closeness of the conformation of the adsorbate and adsorbant in this case.

6 Adsorption Isotherms and the Application of Thermodynamics to Dye Binding
Thus far, discussion has been concerned with the molecular mechanisms involved in dye-binding interactions. Much of our theorising in this regard is based on the study of the energetics of adsorption and the pursuit of clues provided by
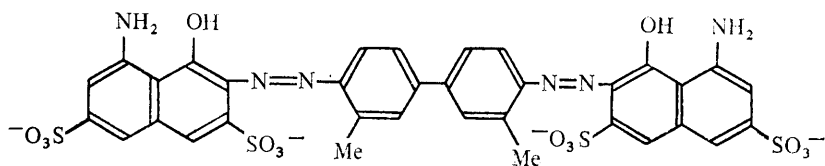
[9] (a) A. N. Glazer, *Proc. Nat. Acad. Sci. U.S.A.*, 1969, **64**, 235; (b) G. Markus, *ibid.*, 1965, **54**, 253.
[10] H. Husy, E. Merian, and G. Schetty, *Textile Res. J.*, 1966, **36**, 615; 1969, **39**, 94.
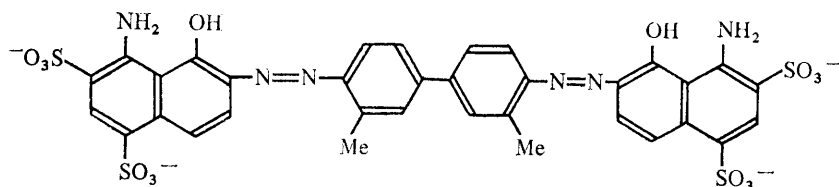
Evan's Blue (C.I. Direct Blue 53)

(4)

Trypan Blue (C.I. Direct Blue 14)

(5)

general thermodynamic considerations. The general description of adsorption phenomena, *i.e.* the generalization of experimental data, takes the form of isotherms, isobars, and isosteres. These are derived from the postulate for the adsorption of an ideal gas on to a homogeneous adsorbing surface when no interaction occurs between adsorbed molecules:

$$\Gamma = \frac{kp}{\sqrt{T}} \exp(Q/RT) \tag{1}$$

where Γ represents the surface concentration, p the external pressure, T the temperature, Q the activation energy of the adsorption interaction, R the gas constant, and k a constant relating to the gas itself. By creating conditions in which T, p, and Γ respectively are kept constant, isotherms, isobars, and isosteres relating to the adsorption can be derived. The isotherm expressed in equation 1 is a simple proportionality between Γ and p; it is known as the *partition isotherm*. It is not necessarily the case that the manifestation of a partition isotherm demonstrates the ideality of the adsorbate or the homogeneity of the adsorbing surface. It can be shown that this kind of isotherm is observed in ideal mixing situations, *i.e.* where the interactions between non-adsorbed molecules away from the surface are comparable with that between the adsorbed molecules and the surface. This can be shown as follows: the adsorption interaction may be represented as the transformation of two interacting pairs of dissimilar molecules

into two similar pairs. Designating the adsorbate as 1 and the adsorbant molecules as 2 this gives

$$1 \text{——} 1 \qquad 1 \text{——} 2$$
$$\text{————→}$$
$$2 \text{——} 2 \qquad 1 \text{——} 2$$
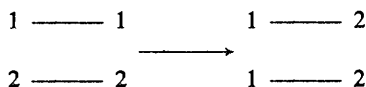
The change in potential energy (ΔU^0) will be, as a consequence,

$$2\Pi_{12} - (\Pi_{11} + \Pi_{22}) = \Delta U^0 \tag{2}$$

For ideal mixing to occur ΔU^0 must be zero so that

$$\Pi_{12} = (\Pi_{11} + \Pi_{22})/2 \tag{3}$$

and it is not necessary to postulate ideality (*i.e.* $\Pi_{11} = 0$) for the non-adsorbed molecules.

Partition isotherms are exhibited by disperse dyes on all textile substrates. The measurement of isosteric heats of adsorption at different values of Γ has shown that the adsorbing surfaces act homogeneously.[11] The values of the isosteric heats compare closely with the heat of solution of the dyes when dyeing is carried out in the presence of water, or with the heat of sublimation for dyeings from the vapour phase. There is some evidence, however, which suggests that these effects may be fortuitous.

It is clear that if an adsorbed molecule occupies some particular binding site on a surface, then an unadsorbed molecule arriving at that site cannot be adsorbed. In other words, a probability factor needs to be considered when there is a limited number of adsorption sites. This is the problem considered by Langmuir in producing his classical isotherm equation

$$\Gamma = \frac{KSp}{1 + Kp} \tag{4}$$

in which Γ and p have their earlier significance, S is the concentration of adsorption sites, and K is the equilibrium constant for the interaction. When $S \gg \Gamma$, equation 4 revers to a partition isotherm equation. This condition can arise when S is so large that convenient experimental concentrations keep $\Gamma \ll S$, or when the saturated vapour pressure or solubility of the adsorbate is very low, imposing an upper limit on Γ consistent with a given value of K. Thus the partition isotherm shown with disperse dyes on substrates may be more due to the solubility characteristics of the dye than any property of the adsorbing surface. This example serves to show the shortcoming of isothermal or isosteric generalizations in explaining molecular mechanisms. It is rare that they provide just a single explanation for any phenomenon.

The adsorption of dye ions on surfaces (inevitably charged) tends to follow the Langmuir isotherm equation except where stacking may occur or extensive

[11] F. Jones and R. Seddon, *Textile Res. J.*, 1964, **34**, 373; 1965, **35**, 334.

configurational changes, such as fibre swelling, take place. Again the obedience of the equation by the adsorption equilibrium does not mean that the adsorbing fibre bears a relatively limited number of sites, although this is not precluded. The surface potential energy effect previously discussed in relation to the adsorption of ions can equally well provide an explanation, with each adsorbed dye molecule treated as an 'anti-site' repelling approaching molecules. This approach has been shown to apply in dye-ion adsorption by cellulose[12] and to be theoretically quite general.[13]

Nevertheless, much useful information is provided by isothermal or isosteric generalizations from the point of view of demonstrating likely molecular factors. These arise from consideration of the energy factors in dye adsorption and the application of thermodynamic concepts. Assuming a stable polymeric substrate and a stable dye, then at equilibrium the chemical potentials of the dye in the solution and fibre phases, μ_s and μ_f respectively, must be equal. Since

$$\mu_s = \mu^0_s + RT \ln A_s \text{ and } \mu_f = \mu^0_f + RT \ln A_f \tag{5}$$

in which $\mu^0_{s,f}$ represent standard state chemical potentials and A_s, A_f are activities in the solution and fibre phases respectively, then the standard affinity, $\Delta\mu^0$ (or $\mu^0_f - \mu^0_s$) is given by

$$\Delta\mu^0 = RT \ln A_f/A_s \tag{6}$$

In dilute solution, neglecting aggregation effects, A_s may be equated with the dye concentration. The value of A_f is more difficult to define and much discussion has raged among dyeing theoreticians on this point. This renders absolute affinity values doubtful, although they nevertheless are useful numerical generalizations of isothermal data. However, useful information can be drawn from the isosteric data. If for a given dye experimental conditions ensure that at different temperatures the concentration of bound dye is a constant, then since $A_f = f(D_f)$ where (D_f) is the bound dye concentration in appropriate units, A_f will be constant if $f(D_f)$ is temperature independent. This enables the activation energy of adsorption to be calculated from equation 6 and the classical relationship between affinity, enthalpy, and entropy. Thus

$$\ln A_s = \frac{-\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R} + \ln f(D_f) \tag{7}$$

Several assumptions have to be made if equation 7 is to be used to calculate the isosteric heat of adsorption. Firstly, it must be assumed that the temperature change affects only the state of the dye adsorption equilibrium directly so that no other changes, *e.g.* transitions, in the polymer due to temperature, indirectly

[12] S. R. Sivarajan, G. Srinivasan, G. T. Baddi, and M. R. Ravidrishnan, *Textile Res. J.*, 1964, 34, 807; S. R. Sivaraja Iyer and N. T. Baddi, 'Contributions to the Chemistry of Synthetic Dyes and the Mechanism of Dyeing', Symposium Proceeding, 36, Centre of Advanced Study, U.D.C.T., University of Bombay, 1968.
[13] M. A. V. Devanathan, *Proc. Roy. Soc.*, 1962, **267**, 256.

cause a change in the equilibrium adsorption situation through entropic or other effects. Secondly, in the absence of direct knowledge of the activity coefficient of the dye at the different temperatures, molar concentrations are employed. This is not a problem providing the change, if any, in the activity coefficient of the dye in solution is small enough over the temperature range. An additional problem arises because several substrates of interest, such as wool keratin, polyamides, and polyesters, are unstable to dyebath conditions especially where achievement of adsorption equilibrium is required. The reactions involved are various but naturally enough all are temperature dependent and the desorbed decomposition products can affect 'equilibria' considerably. From the point of view of 'absolute' measurements the situation is clearly impossible. Nevertheless, progress can be made provided the many aspects of non-ideality are borne in mind. Cellulose is a very stable substrate from the point of view of dye adsorption studies, and very useful data have been obtained[14] which show that the isosteric heat of adsorption of direct cotton dyes on cellulose is concentration dependent and shows a sharp break at a surface concentration equivalent to saturation. Adsorption continues beyond this point due to multilayer formation. In protein investigations heat of adsorption studies have suggested the contribution of hydrophobic interaction to dye binding. This is possible because unlike other dye-binding interactions, hydrophobic interactions are endothermic.

Some of the problems presented by the properties of dye-substrate systems, in attempted applications of thermodynamic analysis, will not be unfamiliar to chemists working in comparably complex fields such as polymer, surface, or biological chemistry. In all these fields experience is being gained increasingly in the use of flexible theoretical models which provide greater insight in relation to molecular mechanisms. At the same time in dye-adsorption work, attempts to gain information about the adsorption system which are thermodynamically meaningful are beginning to reveal new problems as well as solutions. Some of these will be discussed at a later stage. However, at a more practical level the cautious application of classical theoretical concepts to dye adsorption has proved, and is proving, fruitful.

7 The Dyeing Process

Thus far, discussion has been directed towards the dye-binding equilibrium in so far as such a term may be employed with metastable and complex polymeric substrates. However, in practice even an apparent equilibrium is rarely attained, and the concern of those whose business is to dye materials rather than physical chemistry is generally with the kinetics of the dyeing process. These are subject to many variable factors relating particularly to diffusion, and in dyeing machines to mass-transfer factors.

Diffusion may occur owing solely to a simple entropic driving force leading to an equalization of distribution of some species in a system, or this may be combined with a free-energy-gain factor. Broadly speaking, the uniform dis-

[14] E. H. Daruwalla and A. D'Silva, *Textile Res. J.*, 1963, **33**, 40.

tribution of a soluble dye in solution arises from the first factor. The proviso is necessary because dye solutions are frequently non-ideal but any errors that are made due to such approximations are small. In an adsorption process, however, free-energy-gain effects provide the driving force and are involved in the diffusion process. The substrates in which there is any interest are less permeable than water to a moving dye molecule or ion, and consequently diffusional processes in substrates are slower and generally rate determining. However, they are subject to diffusion in the external phase because of mass-transfer effects.

The dye adsorption process consists initially of the adsorption on to the surface of the polymer of dye from adjacent solution. This sets up a concentration gradient within the polymer leading to diffusion. This process in turn depletes the polymer surface of dye and disturbs the surface equilibrium. Provided that dye replenishes the adjacent solution rapidly, the diffusion rate within the fibre determines the rate of uptake of dye. However, the replenishment of the surface solution depends upon the admittedly rapid diffusional properties of the dye in the water, and in the absence of enforced circulation this can be slow enough in practice to make the rate of dye uptake dependent upon the concentration gradient in the liquor near the surface. Circulation of the liquor introduces a new parameter and the rate of dyeing may be seen to be dependent upon stirring rates. The dyebath is most conveniently considered, as a consequence, in terms of three components:

    (i) the general solution
    (ii) the hydrodynamic boundary layer
    (iii) the adsorbing substrate

The thinner the hydrodynamic boundary layer the less effect it can have on the diffusional processes, and this is achieved by increasing the rate of liquor flow past the surface. In the following discussion of diffusional factors, attention will be confined to a situation of optimum flow so that only the effect of dye–substrate interaction need to be considered. The chemical engineering aspects of dye adsorption are extensively reviewed elsewhere.[15]

The initial adsorption at the surface of a polymer substrate phase involves a free-energy gain, and if no diffusion occurred then an equilibrium would be very rapidly established. However, minimization of the free energy of the system is achieved by diffusion of the adsorbed dye into the polymer to find unoccupied adsorption sites and creating unoccupied sites at the polymer solution interface. Since the adsorption interaction on a molecular scale is specific rather than general, the moving dye molecules must negotiate a path through the polymer system from one interaction point to the next. The diffusional process is consequently subject to two constraints: firstly, the general physical constraint provided by the probability of 'diffusional space' being created in front of the molecule as a consequence of the thermal motion of polymer chains; secondly, there is the specific constraint presented by unoccupied adsorption sites which will tend to hold the diffusing molecule in one place.

[15] R. McGregor and R. H. Peters, *J. Soc. Dyers and Colourists*, 1965, **81**, 393; R. McGregor, *ibid.*, 1965, **81**, 429.

The constraint offered in the first of the above instances will depend upon the size and shape of the diffusing molecule and the polymer structure. For small ions, *e.g.* chloride, diffusing through a polyamide, it has been shown that this kind of constraint is not an important consideration.[16] However, as the population of diffusing ions or molecules increases crowding effects become significant.[16] An increase in the size of the molecules may have the same effect. General physical constraints of this kind are of great importance in dyeing kinetics. They are responsible for many of the problems of dyeing polyester fibres, wool keratin, and polyamides. An increase in the thermal agitation of the polymer chains by raising the temperature of the system, or the addition of swelling agents which disrupt cohesive bonds in the polymer by competitive action, are the means normally adopted to achieve adequately rapid dyeing in such cases.

The constraint presented by the adsorption interaction is frequently difficult to distinguish from the general physical constraint offered by the molecular network of the polymer. This is because larger dye molecules generally exhibit higher affinity, so that both constraints increase with size. However, with small ions only adsorption constraints occur and the diffusional behaviour can be described satisfactorily in terms of the probability of a diffusing ion becoming trapped by an adsorption site. With dye molecules and ions complications arise since adsorption itself involves probability factors due to size. The relationship between probability of site trapping and concentration may be rendered more complicated as a consequence. Constraints on diffusion due to adsorption effects are normally dependent upon the concentrations of adsorption sites and the adsorbed dye because of the probability factor involved in adsorption. The diffusional behaviour of the dye is consequently described by Ficks equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D\,\frac{\partial c}{\partial x}\right] \tag{8}$$

in which the rate of change of adsorbed concentration ($\partial c/\partial t$) is related to the concentration gradient ($\partial c/\partial x$) by the diffusion coefficient (D). It has been shown that the nature of the concentration dependence of D relates to the adsorption, so that if the concentration gradient is replaced by the chemical potential gradient it more closely approaches a constant.[17] If various values of D are determined so that a limiting value D_0 is calculated for $c \rightarrow 0$, then this represents a measure of the physical constraint and the maximum adsorption constraint. It is not possible to arrive at any meaningful value by extrapolation to a maximum value of D which should equal the physical constraint factor alone because of crowding effects at high concentration.

Diffusional studies of dyes in polymers have attracted much detailed attention and many difficult technical situations have been explained.[17] Recent attempts

[16] G. Chantrey and I. D. Rattee, *J. Soc. Dyers and Colourists*, 1969, **85**, 618; G. Chantrey, Ph.D. Thesis, University of Leeds, 1971.

[17] R. H. Peters, J. H. Petropoulos, and R. McGregor, *J. Soc. Dyers and Colourists*, 1961, **77**, 704; R. H. Peters in 'Diffusion in Polymers', ed. J. Crank and G. S. Park, Academic Press, London, 1968.

to combine concepts of dyeing kinetics with theories of the equilibrium have been made through the application of the theory of the thermodynamics of irreversible processes. An idealized model can be constructed[18] which has some limited applicability. As with other refined quantitative theoretical approaches, further progress is held up by relative lack of knowledge with regard to all the factors operating in the system.

8 Possible Future Trends

As in many other complex fields, attempts to determine scientific explanations of the dyeing process create more questions than they answer. Nevertheless, this process is paradoxically accompanied by a clearer understanding. The introduction of fibre-reactive dyes in 1956 and their rapid development was greatly facilitated by the state of knowledge of dyeing chemistry. To a large extent, developments in this field have resulted more from scientific analysis of the dyeing situation than chance (the traditional method).

In the recent period it has begun to be appreciated that, like polymers, dyes exhibit an interesting physical chemistry of their own. This affects important parameters such as ease and extent of solution, precipitation in manufacture, drying, and bulk handling properties. As man-made substrates become increasingly important, the disperse dyes which are used to dye them will dominate the dyestuff scene. It is in this connection that solid-state studies are important and in the coming period are likely to provide a growth point in the study of the chemistry of dyes and dyeing. Much remains to be done, however, in further elucidating molecular mechanisms of adsorption, particularly in relation to the chemical structure of the dye since the accuracy with which the behaviour of a dye structure can be predicted leaves much to be desired.

[18] B. Milicevic and R. McGregor, *Helv. Chim. Acta*, 1966, **49**, 1302; *ibid.*, p. 1319; *ibid.*, p. 2098.