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An Explanation of Dyeing Mechanisms in Terms of Non-polar Bonding

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Inadequacies are demonstrated in previous attempts to explain dyeing mechanisms on the assumption of polar forces between dye and fibre. The important part played by non-polar forces in adsorption phenomena generally is illustrated by examples. It is postulated that such forces are mainly responsible for dye–fibre attachment and that in aqueous solution they occur between hydrophobic surfaces.

The relative importance of hydrophobic and hydrophilic properties in fibres is deduced from their moisture regain figures and is discussed in relation to fibre structure. The properties of dyes are then similarly considered. Thence the dyeing behaviour of each type of fibre is predicted from the postulate that dye substantivity is due to non-polar forces. It is concluded that this assumption is sufficient to explain the methods adopted for dyeing different fibres and that it eliminates anomalies incapable of explanation on the assumption that dye–fibre attachment is due to polar forces.

Introduction

A knowledge of the forces which bind dyes to fibres is of obvious importance in the development of a theory of dyeing. In this paper the attractive forces which operate in adsorption processes will be considered in their relation to the structure and properties of different fibres. Thus it may be possible to present a unified picture of dyeing mechanisms from existing knowledge on dye substantivity.

Of all dyeing procedures, the dyeing of cellulosic fibres with direct cotton dyes has in the past been the most extensively studied [1]. This work has shown that substantive dyes of this class have linear and planar molecules containing hydrogen-bond-forming groups. It was believed that substantivity could be improved if these groups were separated by a distance which approximated to the repeat spacing of the cellobiose unit in the cellulose chain. The use of benzidine, which gives rise to this spacing, as an intermediate in the manufacture of many direct dyes was quoted as evidence in support of this assumption. However, it has recently been demonstrated [2] by construction of accurate molecular models of cellulose and of direct dyes that polar groups are so distributed along the cellulose chain that this distance has very little significance.

The dyeing of wool with acid dyes has also been investigated thoroughly [3]. Here the maximum uptake of inorganic acids such as hydrochloric acid corresponds closely with that of level-dyeing acid dyes, which shows that combination with hydrogen ions is important. It has been suggested that electrostatic forces between the dye anions and NH_3^+ groups, liberated from salt-links in the fibre by combination with hydrogen ions, make a large contribution to the binding energy. Hydrogen bonding between polar groups in the dye anion and amide groups in the wool has been postulated to account for differences in dye affinity. It has also been suggested [4] that formation of hydrogen bonds is responsible for the uptake of phenol by cellulose acetate.

Thus polar forces have been assumed almost exclusively in order to explain dyeing mechanisms. Some of the difficulties to which this assumption leads may now be considered. It must first be remembered that dyeing normally takes place from water, that is from a highly polar medium which contains both electron-donating and electron-accepting groups. In this environment polar groups in both dye and fibre will initially be strongly attached to water molecules. The formation of a dye–fibre linkage by hydrogen bonding will require a dye–water bond and a fibre–water bond both to be broken, and the freed water

molecules to be taken back into the water structure. The heat of dyeing will then be the net heat change due to all these processes, and attempts to assign it to the heat of formation of dye–fibre bonds alone can have little meaning. Recent work [5] with a number of disperse dyes has shown that their heats of dyeing on to cellulose di- and tri-acetate are similar in magnitude and opposite in sign to their heats of solution. It has also been shown [6] by direct calorimetry that the heat content of solid Naphthalene Orange G is equal to that of the same dye when adsorbed by wool. These results suggest that the forces between dye molecule and fibre in a dyeing are the same as those between dye molecules in the solid form of the dye. They are not easy to reconcile with the suggestion that hydrogen bonding takes place at specific groups in the fibre, since this cannot occur in the solid dye.

Carbolan dyes, which have a much higher affinity for wool than levelling dyes, differ from them in possessing a long aliphatic chain, to which the increase in affinity must be attributed. The formation of polar bonds cannot explain this increased substantivity conferred by a non-polar grouping. Certain vat dyes have high affinity for cellulose in the reduced form and yet contain only two O^- groups which are capable of forming polar bonds. One would expect that these solubilising groups would be predominantly attracted to the aqueous phase. Here, then, is an example of dyes which are substantive and yet contain no groups likely to form polar bonds with the fibre. The view that the O^- groups are inadequate is justified by the negligible affinity for cellulose of smaller molecules of the same type, such as anthraquinone [7]. Finally, Terylene polyester fibre will adsorb a number of organic substances such as diphenyl, which are used as carriers in the dyeing of this fibre and which contain no groups capable of hydrogen bond formation.

These deficiencies in the hydrogen-bonding theory suggest that a consideration of other bonding forces is essential and that non-polar rather than polar forces may predominate in dye–fibre attachment. Recently this point of view has received increasing support. Meggy [8], when considering the affinities of acid dyes for wool, made the following interesting suggestion as to the source of the free energy change. He postulated that, in forming an aqueous solution, the large hydrophobic surface of the dye molecule caused a separation of water molecules against their mutual attraction and so required an uptake of energy. The removal of dye through adsorption by wool will lead to the recovery of this energy by recombination of water molecules, and it will then appear as the free energy of dyeing. Calculation showed the energy available to be of the right order of magnitude to account for the measured affinities. Work has recently been done [9] on the change of molecular area of monolayers of surface-active compounds containing hydrogen-bonding groups on solutions of sucrose, glucose, and cellobiose. From the results it was concluded that the hydroxyl groups of these latter compounds, when in an aqueous environment, are too strongly attached to water molecules to be available for forming hydrogen bonds with other compounds. For this reason it was suggested that bonding of direct dyes to cellulose was due largely to non-polar van der Waals forces.

The importance of non-polar forces in the field of adsorption phenomena generally is fully recognised, and calculation shows that they are responsible for a large proportion of the heat of adsorption. Therefore, it is worth considering at greater length the rôles of all types of bonding forces which are known to take part in adsorption processes.

Possible Adsorption Forces

Consideration of various adsorption phenomena has led to the following classification of attractive forces [10]—

(1) Electrostatic attraction between charged sites in the substrate and ionic substances
(2) Attraction by induction between ionic substances and a non-conducting substrate
(3) Polar van der Waals forces (e.g. hydrogen bonds)
(4) Non-polar van der Waals forces
(5) Chemical forces.

In most adsorption phenomena some or all of these forces will contribute to the total attraction, but the classification is of value since in simple cases it is possible to calculate theoretically the contribution from each type to the total heat of adsorption. Reasonable agreement with the measured value is then found. The results [10] of two such calculations may be quoted—

(1) ADSORPTION ENERGY OF CARBON DIOXIDE ON POTASSIUM IODIDE

	kcal./mole
Non-polar van der Waals forces	3·30
Electrostatic polarisation	1·14
Dipole forces	3·25
Total	7·69
The measured adsorption energy is	7·45

(2) ADSORPTION OF PHENOL ON SODIUM CHLORIDE

Non-polar van der Waals forces of C_6H_5 group	3·4
Dipole forces of OH group	5·3
Non-polar van der Waals forces of OH group	0·60
Electrostatic polarisation of OH group	0·06
Total	9·36

In both these examples non-polar van der Waals forces contribute a considerable proportion of the total heat of adsorption. This is particularly striking, since the ionic nature of the substrates would be expected to favour the formation of polar bonds.

The part played in dyeing processes by each of the forces listed above may now be considered. The first can operate only with protein and polyamide fibres which contain charged groups. The negligible adsorption of simple inorganic ionic substances such as sodium chloride shows that

such forces and also induction forces of the second type are very small and may be ignored. This must be attributed to the fact that there will be strong interaction between the ions and the highly polarisable water molecules, leading to heavy hydration, which will shield the ions from interaction with the fibre. The formation of a chemical bond occurs only in the acid dyeing of protein and polyamide fibres, where the hydrogen ion is combined with ionised carboxyl groups in the substrate. Thus polar and non-polar van der Waals forces must be the main factor in dye adsorption. It has been shown that the assumption that the former type are alone responsible for dye uptake is incapable of explaining certain dyeing phenomena. We shall now postulate that non-polar forces are the principal source of the affinity of dyes for fibres and see how well this assumption explains the facts.

Non-polar van der Waals forces (dispersion forces) are due to interaction between atoms of the adsorbent and the adsorbed molecules and are additive over all the atoms that are sufficiently close together. They are of short range, since the force varies approximately as the inverse sixth power of the distance between interacting atoms, whereas polar forces vary approximately as the inverse third power of this distance. Therefore, for maximum attraction, a close fit is necessary between large areas of the substrate and the adsorbed molecule. In an aqueous environment non-polar bonding will occur predominantly between hydrophobic surfaces, since the presence of polar groups, rendering one surface hydrophilic, will attract water molecules to the surface and prevent the necessary close approach. These are precisely the conditions for maximum bonding due to the forces postulated by Meggy [8], and in aqueous environment it is not possible to distinguish between the two effects. Therefore, in what follows, references to bonding by non-polar van der Waals forces will be taken as including the contribution from the recombination of water molecules by removal of hydrophobic surfaces.

On this hypothesis the affinity of a dye for a fibre will depend on—

(*a*) The hydrophobic–hydrophilic nature of the fibre

(*b*) The hydrophobic–hydrophilic nature of the dye

(*c*) The possibility of close packing between dye and surfaces in the fibre

(*d*) The accessibility of the fibre to dyes.

NATURE OF FIBRES

Adsorption of water by fibres is believed to occur in two ways— some of the water is strongly bound to polar groups in the fibre, and some is much less strongly attached to form so-called "capillary water". The amount of strongly bound water should give an indication of the extent to which the fibre is hydrophilic, while the amount of capillary water should be a guide in deciding to what extent the fibre will be accessible to different types of dye. The shape of moisture adsorption isotherms, and the results of attempts to analyse these into the two components mentioned above, lead to the belief that much of the bound water is adsorbed at lower humidities, and that the increase in absorption at humidities approaching saturation is largely due to capillary water. We shall therefore take the regain at 70% R.H. as an indication of the hydrophilic nature of the fibre, and that at 100% R.H., when compared with that at 70% R.H., as an indication of the relative accessibility of the fibre to dyes. These quantities are tabulated below (Table I) [11, 12] with the fibres arranged by this criterion in order of increasingly hydrophilic nature.

TABLE I [11, 12]

Fibre	Moisture Regain at 70% R.H. (%)	Moisture Regain at 100% R.H. (%)
Vinyl fibres ...	Negligible	
Terylene ...	0·4	0·6
Nylon ...	4·6	7
Cellulose acetate	7·6	8
Silk	11·0	33
Wool ...	16·0	33
Viscose rayon	16·0	33

The newer synthetic fibres of the vinyl type are extremely hydrophobic with negligible water uptake, as also is Terylene, which again has a very small moisture regain. Neither fibre has polar groups likely to combine with water by hydrogen bonding. The good tensile properties of Terylene are attributed to non-polar attraction between the benzene rings of the fibre [13]. This will lead to a close-packed structure which will be very resistant to swelling in water. Nylon is the next most hydrophobic fibre, in spite of its high content of polar amide groups. This must be attributed to the high degree of order and absence of bulky side-chains, which allow close packing and formation of interchain polar bonds, so that most of the polar groups are internally satisfied in this way. Cellulose acetate is almost as hydrophobic as nylon and very much more so than cellulose. This must be due to substitution of two-thirds of the hydroxyl (OH) groups in cellulose by acetoxyl (CH_3COO) groups. This fibre also shows a very small uptake of capillary water. In a recent thesis Rossett [14], who worked on a series of progressively acetylated celluloses, concluded that, at the degree of acetylation corresponding to the commercial product, interchain cohesion is due to non-polar van der Waals forces between glucose ring structures, which leads to a very close-packed structure.

The two natural protein fibres, silk and wool, are both more hydrophilic than the previous fibres, and wool is the more hydrophilic of the two. Both contain a large number of polar groups in the peptide linkages, and since the presence of side-chains prevents the close packing that occurs in nylon, fewer interchain bonds will be formed and consequently more polar groups will be available for water adsorption. Wool also contains a large number of polar side-chains, while the majority of the silk side-chains are non-polar, and the more

hydrophilic nature of wool may be attributable to this fact. Both fibres undergo a large swelling in water, so that they should be easily accessible to dye.

Cellulose is a relatively hydrophilic fibre with a large swelling in water. It is, however, doubtful whether water is adsorbed appreciably in the more crystalline regions, and recent work on cellulose sols [15] suggests that the micelles are hydrophobic. Cellulose sols were prepared from native and mercerised wood cellulose and viscose rayon by peptisation with distilled water after hydrolytic depolymerisation. The sols contained cellulose micelles whose crystalline structure had the same lattice as the crystalline regions of cellulose fibres, and whose dimensions agreed with estimates of the dimensions of such crystallites. The sols were coagulated by addition of small amounts of electrolyte, from which it was deduced that the micelles were hydrophobic. This may be due to internal bonding of the hydrophilic groups in the ordered crystallites, which will prevent their combination with water molecules. In the more disordered, amorphous regions, internal bonding will be less complete and the free groups will render these regions hydrophilic.

NATURE OF DYES

All dyes have a conjugated ring structure that produces colour by selective absorption of light in the visible region of the spectrum and is hydrophobic, with strong non-polar bond-forming capabilities. In disperse dyes and the oxidised form of vat dyes this structure predominates, and the dyes are consequently almost completely insoluble in water. In those classes of dyes which are water-soluble the hydrophobic nature of the ring structure is overcome by the introduction of solubilising groups, usually sulphonic acid groups.

Thus all dyes contain large hydrophobic surfaces which are capable of forming non-polar bonds if they can be sufficiently well fitted to hydrophobic regions in the fibre. Since all fibres are linear polymers, this fit would be most complete for linear dye molecules. Planarity will also be essential to obtain a close fit of the whole area of the dye molecule. Thus the observation that linearity and planarity are essential to substantivity of direct dyes is in agreement with the postulate that attachment to the fibre is due to non-polar forces. Since such forces are additive, increase in the size of the molecule and hence of the molecular weight will lead to an increase of binding energy. This explains the correlation between affinity and molecular weight, examples of which are quoted by Vickerstaff [16] in a recent review. One would expect that a small molecule would have adequate affinity for a hydrophobic fibre, while large molecules would be required for a hydrophilic fibre. This is in agreement with the fact that small, disperse dyes give full depths on Terylene, cellulose acetate, and nylon, while they will dye cellulosic fibres only to very pale colours. The relatively hydrophilic cellulose is dyed with direct or vat dyes which have larger molecules. The failure of the large dye molecules to dye the more hydrophobic fibres must be attributed to inaccessibility, the activation energy for penetration of large molecules into the close-packed fibre structure being prohibitively large.

The observed similarity between heats of formation of solid dye and the dye–fibre complex from dye in solution is explicable on the assumption that non-polar forces are the source of energy in each case. The additivity of such forces over the whole molecule means that the heat of combination per molecule of dye will be determined only by properties of the dye molecule, provided that the fit between dye and fibre is as close as that between dye molecules in the solid dye.

Further evidence of the importance of non-polar forces is provided by work [7] on the affinity of vat dyes of the anthraquinone and carbocyclic types. For series of related compounds a close correlation was found between the affinity of the dyes for cellulose and the extinction coefficient of the dyes in solution. The latter quantity will be a function of the conjugation structure of the dye, on which its non-polar bond-forming capabilities will depend. Thus the correlation with affinity illustrates the importance of these bonds in dye–fibre attachment.

DYEING MECHANISMS

We will now consider the dyeing of each type of fibre to see how well the hypothesis that non-polar bonding is the principal source of affinity explains differences in the dyes used for different fibres.

(a) *Vinyl Fibres*

These fibres are extremely hydrophobic, to such an extent that they have negligible moisture regain. They are not penetrated appreciably by water molecules, and dyeing from aqueous medium is consequently difficult. For consideration of dyeing properties they may be conveniently divided into polyacrylonitrile and polyvinyl chloride types.

(i) Polyacrylonitrile

A representative of this type of fibre is Orlon, which is most commonly dyed with disperse dyes. These small, hydrophobic molecules should have adequate affinity for the very hydrophobic fibre, and dyeing difficulties seem to be largely due to low rates of dyeing. Thus, while pale colours may be dyed at conventional dyeing temperatures below 100°C., it has been shown [17] that heavier dyeings are obtainable by pressure dyeing above 100°C. Alternatively, much deeper colours may be obtained at the lower temperatures by the use of swelling agents such as *m*-cresol and aniline.

(ii) Polyvinyl Chloride

An example of this type of fibre is Vinyon, which, again, is an extremely hydrophobic substance. The dyeing of this fibre has been reviewed by Woodruffe [18], who divides the dyeing methods into three classes—

I Dyes soluble in Vinyon

II Dyes soluble in assistant—assistant soluble in Vinyon

III Dyes having surface affinity for fibre due to polar structure.

The first method is applicable only to certain azoic dyes, whose components are coupled on the fibre to yield the coloured substance. All these substances are strongly hydrophobic, and their solubility in the substrate allows complete penetration. The third method is used only with basic dyes, which on application from an aqueous bath give heavy surface adsorption but no penetration into the fibre.

Method II may be used with dyes of the disperse, direct, and basic types by proper choice of assistant. The essential characteristics of the assistant used are that it shall be soluble in the fibre and act as a solvent for the dye. Its solubility in the fibre permits it to penetrate, while water will not, and it then provides a diffusing medium in the substrate for penetration of dye. Disperse dyes may be applied from aqueous dispersion with addition of an assistant, which may be either water-soluble (e.g. *iso*butyl methyl ketone) or water-insoluble (e.g. dibutyl phthalate). Alternatively, they may be dyed by the solvent-dyeing technique, in which the assistant acts as the dyebath with the disperse dye dissolved in it. This latter technique appears to be essential for dyeing with direct dyes, where the presence of more than about 5% of water in the dyebath inhibits dyeing, presumably because direct dyes are much more hydrophilic than disperse dyes. Basic dyes also may be dyed with assistants or by the solvent technique, when they penetrate the fibre, in contrast to their surface adsorption when dyed alone.

(*b*) *Terylene*

The experimental fact that this fibre is difficult to dye would be expected from the structure that has been outlined. The close-packed structure of benzene rings which suffers negligible swelling in water is analogous to that of graphite, in which sheets of covalently linked carbon atoms are bonded by non-polar van der Waals forces. Adsorption on graphite, other than on the exposed surfaces, is an activated phenomenon in which energy of activation is required to force apart the sheets of carbon atoms to allow adsorbed molecules to penetrate. It is likely that the dyeing of Terylene is similarly an activated process, and one important aspect of "carrier action" is to open up the fibre structure to allow dye to penetrate.

Carriers used are normally fairly small organic molecules containing aromatic rings (e.g. phenol, naphthalene, diphenyl). Their adsorption will be due to non-polar bonding of this ring to the benzene rings of the fibre, and their small size will permit penetration of the Terylene structure. In those carriers such as phenol which contain a polar group, non-polar forces must still be the main attractive force, although the hydroxyl group may form a weak polar bond with the ester linkage adjacent to the benzene ring. It is interesting that Peters and Sumner (quoted by Vickerstaff[19]) have found from direct comparison measurements with phenol and diphenyl that the uptake of the polar compound is much less than that of the non-polar compound. This indicates that the mechanism of combination is essentially non-polar, and that the polar group in the carrier, with much greater affinity for water than for the fibre, decreases the uptake of carrier.

Since the fibre is so hydrophobic, one would expect hydrophobic dyes of small size to have an adequate affinity for it, and disperse dyes having these characteristics are in fact used. Their small size is additionally advantageous in minimising penetration difficulties.

The picture of the dyeing mechanism, then, is of an initially close-packed fibre structure opened up by adsorption of carrier, whose affinity is sufficient to provide the activation energy to swell the fibre. The hydrophobic disperse dye has a high affinity for the very hydrophobic fibre and can penetrate to all parts after swelling. It will be attached mainly by non-polar forces to the aromatic rings of the fibre, in which position polar groups in the dye may also form weak polar bonds with the ester groups.

(*c*) *Cellulose Acetate*

This fibre also is hydrophobic and shows small swelling in water, but neither characteristic is so extreme as in Terylene. Residual hydroxyl groups will make the fibre slightly hydrophilic, and non-polar forces between the glucose rings will not be so strong as between the aromatic rings in Terylene, so that activation energies for penetration of dye molecules will be less. Because it is largely hydrophobic, this fibre also may be dyed with the small hydrophobic molecules of disperse dyes. Since the interchain cohesion is lower than in Terylene, the dyes can be used without carrier, their affinity providing sufficient activation energy to permit penetration. Carriers may be used to increase the rates of dyeing of disperse dyes (unpublished results obtained by Sumner), when their action must be similar to that on Terylene. Because of the residual hydroxyl groups in the fibre, polar groups in the carrier may be advantageous to bond to the hydroxyl groups with elimination of water to permit a closer fit of the hydrophobic surfaces. Phenol is particularly effective in swelling cellulose acetate, and substances of similar constitution to the fibre (e.g. esters) have been found to be effective as carriers.

Cellulose acetate fibres may also be dyed with water-soluble dyes of the Solacet type. These compounds have small molecules, so that penetration of the fibre is not difficult, and are solubilised by SO_3Na or SO_4Na groups. In the ionised form they may be attached to the fibre with their hydrophobic part bonded to the fibre and their charged groups in the hydrophilic environment provided by the residual hydroxyl groups in the substrate. It is also possible that they are not fully ionised in aqueous solution, and unionised dye, since it is more hydrophobic than the ionised form, will have a higher affinity for the fibre. This incomplete dissociation is suggested by

experiments in which dyes of this type were partitioned between water and organic solvent (e.g. amyl acetate), when substantial amounts of dye were found in the organic phase. It is notable that the solubilising group of these dyes is frequently very close to a basic group, which may modify their strengths as electrolytes.

(*d*) *Nylon*

Moisture regain figures for nylon are similar to those for cellulose acetate. The fibres have therefore similar hydrophobic–hydrophilic natures. It is significant that both fibres may be dyed with disperse dyes and Solacet dyes. The mechanism of dyeing with disperse dyes must be postulated as similar to that for cellulose acetate. Since nylon contains free amino and carboxyl groups, dyeing with Solacet dyes will be sensitive to pH, since, under acid conditions, the affinity of the hydrogen ion will contribute to the overall affinity.

The presence of amino and carboxyl groups makes it possible to dye nylon with acid dyes in a similar manner to the dyeing of wool. The free amino groups liberated by combination with acid are undoubtedly hydrated, and probably supply a suitable hydrophilic environment for the sulphonic acid groups in the dye. There are, however, significant differences between the two fibres. Nylon may be much more readily "overdyed"; i.e. the fibre will absorb dye at lower pH values in amounts far in excess of the number of free charged sites. This occurs to a much greater extent, and at higher pH values, than the analogous behaviour with wool. Nylon will adsorb level-dyeing acid dyes under neutral conditions much more readily than wool, and the affinity of such dyes is higher for nylon than for wool. Thus Metanil Yellow has an affinity for nylon of −18·5 kcal. per mole [20], while its affinity for wool is −11·4 kcal. per mole [3(a)]. These points of difference would be expected on the present hypothesis, since nylon is much more hydrophobic than wool. Consequently the hydrophobic part of the dye anion will have a greater affinity for nylon than for wool, and substantivity will be less dependent on the affinity of the hydrogen ion. However, the hydrophilic sulphonic acid group decreases the affinity of the dye anion, and dyes with more than one such group require very large affinities from the rest of the molecule to dye nylon under neutral conditions. Such dyes are to be found on the Carbolan range.

(*e*) *Wool and Silk*

These fibres are fairly hydrophilic, but they must still contain hydrophobic regions in the non-polar side-chains. Their high content of acid and basic groups makes them suitable for dyeing with acid dyes, as the number of such groups is well in excess of that necessary to give depths of colour normally required. Equilibrium studies of acid uptake as a function of pH have shown that adsorption of dye is generally similar to that of inorganic acids such as hydrochloric acid, with the difference that a given quantity of dye is adsorbed at higher pH values than the same quantity of hydrochloric acid. Adsorption of hydrogen ion by virtue of its affinity for carboxyl groups in the wool must be accompanied by adsorption of anions in equal quantity to maintain electrical neutrality. When chloride ion, with negligible affinity for the fibre, is adsorbed it will add nothing to the total affinity. But the dye anion has a large hydrophobic surface, which may be attached by non-polar forces to a hydrophobic surface in the wool, and the resulting decrease of free energy will contribute to the total affinity. The importance of this contribution is emphasised by the behaviour of Carbolan dyes, which have much higher affinities [21] than level-dyeing acid dyes. This must be due to the large increase in hydrophobic dye surface conferred by the long hydrocarbon chain. This will greatly enhance the non-polar bond-forming capabilities of the dye and so increase the total affinity. It should also be noted that Carbolan dyes have adequate affinity under neutral conditions, while corresponding levelling dyes do not readily dye neutral.

The effect of the free NH_3^+ groups produced by adsorption of hydrogen ions on to carboxyl groups is not certain. An interesting observation [22] is that wool dyed to fairly heavy depths with Carbolan dyes under acid conditions is hydrophobic, whereas uptake of the same dye from a neutral bath produces a dyeing which is hydrophilic. It seems, therefore, that the presence of free NH_3^+ groups under acid dyeing conditions produces a charged environment to which the solubilising group of the dye is attracted, while its hydrophobic part is attached to the fibre by non-polar bonding. In the absence of free NH_3^+ groups under neutral conditions such a charged environment does not exist and, while the hydrophobic portion of the dye is still attached by non-polar forces, the solubilising group remains attracted to the aqueous phase and so produces a hydrophilic dyeing.

(*f*) *Cellulose*

This fibre may be dyed with direct and vat dyes, which are similar in that both have large hydrophobic surfaces. Direct dyes are rendered water-soluble by their ionisable groups and they frequently contain a number of polar substituents. On the other hand, certain vat dyes contain no polar groups except two O^- groups in the reduced form of the dye. Thus in direct dyes the hydrophobic surface may be masked by hydrophilic groups while in some vat dyes it is not. Since both classes of dye have affinity for cellulose, it would seem that this affinity must again be due predominantly to non-polar van der Waals forces. Cellulose is a hydrophilic fibre, and one would therefore expect that large molecules would be necessary for adequate substantivity by this mechanism. Both types of dye fulfil this requirement, while the smaller disperse dyes will dye cellulose only to very pale colours. The large swelling which the fibres undergo in water permits adequate penetration of the dye molecules.

We have shown that the importance of linearity and planarity for substantive direct dyes is in agreement with the postulate of non-polar bonding. The presence of polar groups in direct dyes may

be essential to form bonds with the polar groups in the substrate, with elimination of bound water, to allow the necessary close approach of the non-polar bonding surfaces. With a hydrophilic fibre it may be necessary for the dye to have sufficient hydrophilic character to penetrate the water-swollen region of the fibre to achieve the close approach necessary for attachment by non-polar forces. Thus vat dyes in the unionised, insoluble state are not substantive, since in this hydrophobic form they are not able to pass through the hydrophilic cellulose environment and achieve this close approach. Solubilisation by reduction to form ionised groups will allow this penetration, when bonding will occur in a similar manner to that for direct dyes. In those vat dyes (e.g. pyranthrone) which have no polar bond-forming groups but high affinity for cellulose, the very large hydrophobic surfaces must have sufficient non-polar bond-forming powers to attach themselves in this way in spite of the presence of hydrated polar groups on the fibre.

Conclusions

The postulate that the principal contribution to the free energy of dyeing is from non-polar van der Waals forces, which occur in aqueous solution between hydrophobic surfaces of the dye and the fibre, explains the methods of dyeing different fibres. It predicts that small hydrophobic dye molecules will have adequate affinity for a hydrophobic fibre, while larger molecules will be required to dye a hydrophilic fibre. The additive and short-range nature of non-polar forces, with the consequent requirement of close fit of large areas of dye and substrate, explains the chemical criteria of linearity and planarity in substantive direct dyes and the general correlation between affinity and molecular weight in dyes of a particular class. Neither the increased affinity of Carbolan dyes due to a hydrocarbon chain nor the dyeing of Terylene can be interpreted in terms of polar forces, but both are readily explained on the assumption of non-polar bonds.

Formation of polar bonds is probably of importance only to eliminate water molecules bound to polar groups in the fibre, which would otherwise prevent the necessary close approach of dye and fibre surfaces. In the attachment of direct dyes to the hydrophilic regions of cellulose, formation of such polar bonds may be essential. The affinity of certain vat dyes having no polar groups may also be explained by non-polar forces if the very large area of hydrophobic surface in such molecules is adequate to bind to the fibre by this mechanism in spite of the presence of hydrated polar groups in the substrate.

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(*Received 15th February 1955*)

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