Bottiger\textsuperscript{1} made the important discovery in 1884 that Congo Red, a red dye derived from benzidine, dyed unmordanted cotton by an extremely simple process of merely boiling the cotton in a solution of the dye. There was a great incentive to follow up Bottigers' work and it was not long before an adequate range of analogous dyes for cotton textiles became available and were widely used in industry. Since then many empirical studies of the effect of temperature, electrolyte concentration etc. upon the dyeing of cellulosic fibres with various direct dyes have been made because of the immediate technical value of such studies. Studies of the dyeing mechanism of a more fundamental nature have also been made, but the greater part of the earlier investigations were made using impure dyes.\textsuperscript{2} The results of those investigations have therefore lost most of their significance. Important work using specimens of dyes of analytical purity was started only after the discovery of the method of purification of direct dyes by Robinson and Mills\textsuperscript{3} in 1931. As a result of various studies carried out since then, many theories have been advanced over the past three decades to explain the phenomenon of dyeing cellulosic fibres with direct dyes.\textsuperscript{4-11} It may be mentioned here that in order to obtain a clear picture of the mechanism of the equilibrium dyeing of cellulose with direct dyes, it is essential to collect information about (a) the chemical constitution and fine structure of the fibre, (b) the specific surface area of the fibre, (c) the chemical constitution of the dye,
(d) physicochemical properties of the aqueous dye solution, (e) the influence of added electrolytes on dyeing, and other conditions of the dyeing process such as temperature, dye concentration etc., (f) the mode of fixation of the dye on the fibre surface, (g) the manner of the transference of the dye from the solution to the interior of the fibre, (h) electrical properties of the dye solution-fibre interface and (i) the dynamic interactions of these factors.

Cellulose itself is a polymer of $\beta$-1-4-anhydroglucopyranose (fig.1) occurring as a fibrous material in plants.$^{12}$

The fibres showing satisfactory tensile properties, are composed of a large number of chains made up with an average of at least 500 glucose units.$^{13,14}$ These chains are held together essentially linearly by hydrogen bonding as shown in fig.2.$^{14,15,16}$

The X-ray diffraction diagrams for cellulose indicate that cellulosic fibres have crystalline or micellar regions where the chain-like molecules are arranged in an orderly and regular manner and amorphous regions where bending or twisting of chains give rise to regions of disorder or openness.$^{17}$ Now, the most generally accepted view, excepting in points of finer detail is that a single chain molecule may be a component of several crystallites separated by amorphous regions (see fig.3).

The X-ray diffraction diagram indicates the presence of unit cells of the dimensions shown in fig.4 in the crystalline region of the cellulose.$^{18}$

The amorphous regions or pores show an average diameter of about 5 Å.$^{19}$
Fig. 1 The Cellulose chain

Fig. 2 Probable intra molecular hydrogen bonds indicated by broken lines

Fig. 3 Sketch of cellulose chains which belong partly to crystallites and partly to disordered areas

Fig. 4 Diagram of the positions of the atoms in the elementary cell of native cellulose

Fig. 5 Cross-sections of viscose fibre after equilibrium dyeing
Cellulose is a hygroscopic material which is insoluble in water but swells due to an opening up to a certain limit of the internal regions of the fibre by movements of the chain molecules which tend to move apart from each other due to imbibition of water and a forcing apart of the cellulose chains. An analysis of water-swollen fibres indicates that the crystalline orientation of the chain molecules in the micelles remain unaltered. This suggest therefore that the water mainly enters the amorphous intermicellar regions of the cellulose.\textsuperscript{20,21,22} Pores and channels of diameters ranging from about 15 to 100 Å are formed in the amorphous region by swelling fibres with water.\textsuperscript{25}

In dyeing cellulosic fibres with direct dyes from an aqueous dyebath, the penetration of the dye molecules to the interior of the fibre is brought about by the diffusion of dye molecules along the water filled swollen capillary channels.\textsuperscript{4} The extent of swelling is therefore one of the important factors controlling the process of adsorption of dye. Since crystallites are very closely packed entities of cellulose chain molecules, dye molecules cannot penetrate into the crystallites which are unaffected by water. The adsorption therefore takes place on the more or less individual molecular chains in the amorphous regions of the cellulose. The greater equilibrium adsorption of direct dyes on viscose fibre than on cotton fibre is explained as due to higher fraction of amorphous region present in the viscose fibre than in the cotton fibre.\textsuperscript{22}

The rate of dyeing cellulose with direct dyes increases
enormously with increase of temperature. This cannot be explained as due to a change in cellulose fine structure, because the ultra-filtration rate of water-swollen viscose sheet and hence the mean diameter of the capillary pores does not vary measurably between 20°C and 80°C, when corrected for changes in the viscosity of water. Furthermore, the rate of dyeing experiments have shown that aqueous dye solutions contain particles of all sizes from single molecules or ions up to large micelles all in a state of dynamic equilibrium. The structure of aqueous dye solutions studied by a variety of experiments strongly indicate the formation of aggregates of dye molecules in aqueous solutions of the dyes. It has however, not been possible from the experiments to estimate with accuracy the degree of association. In the 1920s it was assumed that direct dyes in aqueous solutions are dispersed to colloidal micelles of uniform size and only those particles of just the right dimensions are allowed to diffuse within the fibre pores and be adsorbed — "the optimum degree of dispersion theory." Recently Bach, Pfeil, Philippin and Reich have also suggested on the basis of spectroscopic analysis of the dyed cellulose sheets that the dyes are taken up by the fibre as aggregates and are retained in the pores as aggregated particles.

Several experimental studies have shown that these theories are not valid. Thus for example, Boulton and Morton with the help of a widely accepted demonstration of the optical dicroic behaviour of adsorbed molecules of direct dyes proved that cellulose is dyed only by single molecules or by the smallest aggregates and that they are
replaced very quickly by similar particles in an amount sufficient to restore the disturbed equilibrium between single ions and the aggregates ions in the solution. Morton\textsuperscript{25} has also shown that ramie dyed with an alcoholic solution of a direct dye, in which aggregation is very improbable, is optically indistinguishable from ramie dyed from the usual aqueous direct dye + electrolyte solution. The mean particle size of these dyes increases with increasing amount of electrolyte added to the dye solution and decreases with increasing temperature. The aggregates of direct dyes are probably formed by coordinate bonds such as hydrogen bonds between such polar groups as hydroxyl, amino etc. of the aggregating dye molecules. The adsorption of direct dyes from aqueous solutions on cellulosic fibres is truly reversible\textsuperscript{4,10,56-59} and at equilibrium the tendency of dye molecules to be adsorbed become equal to the opposing tendency of the adsorbed dye molecules to be dissolved in the water phase. The comparative lack of affinity of direct dyes for the water phase results in their invariable tendency to aggregate in solution. It is therefore suggested that the dyes are adsorbed by cellulose from aqueous solutions only if, amongst other conditions, it behaves as a colloidal electrolyte. Furthermore, the direct dyes of greater aggregating tendency show greater affinity for the adsorption by the cellulosic fibres. As Valko\textsuperscript{6} has pointed out, it is most likely that the nature of intermolecular forces which are responsible for the association of dye molecules to form colloidal aggregates are also responsible for the adsorption of these dye molecules on the cellulosic surface.
Cellulose acquires a negative surface charge on immersion in water due to the ionization of the small amounts of carboxylic groups of the oxycellulose present in cellulosic fibres. Direct dyes are salts of sulphonic acids. Dye anions are therefore repelled by the negative surface charge of the fibre. In fact, absolutely pure Chlorazol Sky Blue FF in distilled water does not stain viscose. However, Benzopurpurine 4B is appreciably adsorbed from solutions in distilled water. When electrolytes such as sodium chloride are added to the dyebath, the positively charged sodium ions neutralize the effect of the fibre surface charge, so that the negatively charged dye anions diffuse into the pores and are finally adsorbed on the fibre surface until equilibrium is reached. The adsorbed dye anions are directly bound to the cellulose chain and the sodium ions are held by the sulphonic acid groups so that the entire complex is electrically neutral. The sodium ions of the added electrolyte restrain the tendency of the sodium ions in the dye molecules adsorbed by cellulose to escape into the surrounding water. Another important function of salt is to lower the solubility of the dye in water, since increase in solubility tends to increase the adsorption of the dye. The magnitude of the salt effect varies from dye to dye. At equilibrium, the adsorbed dye is distributed uniformly throughout the fibre and is not confined to the superficial layer of cellulosic yarn or fibre (see fig.5). The amount of dye adsorbed at equilibrium increases with increasing amounts of electrolyte added to the dyebath. An exceptionally important quantitative analysis of the effect of salt on the equilibrium adsorption of direct dyes by
was given by Hanson, Neale and Stringfellow in terms of anionic equilibria of the Donnan membrane type. The electrical nature of dyeing celluloses with direct dyes has been considered in the theories of dyeing put forward by Crank, Standing and Warwicker and Peters and Vickerstaff. In general, there are three main postulates employed in these theories. They are:

1) Electrical neutrality of the cellulose phase and the dyebath.

2) Donnan equilibrium between the concentration of free ions in the aqueous phase and the cellulose phase.

3) A direct proportionality between the concentration of dye adsorbed and the concentration of the dye in solution.

The kinetic thermodynamic theory of dyeing put forward by Willis, Warwicker, Standing and Urquhart essentially gives rise to the same picture of the dye adsorption process. However, in all these theories and the associated thermodynamic treatment, in order to relate dye concentrations in the fibre phase to those in the equilibrium solution, arbitrarily selected volume terms have been used by most workers in calculating the thermodynamic affinity for the adsorbed dye molecules on the cellulose substrate. The physical meaning of this volume term is not defined although it appears to have some relationship to the amount of moisture adsorbed by cellulose at 100% R.H. Values used by earlier workers range from 0.2 litres/kilogram to 0.9 litres/kilogram of dry cellulose. All these values have been selected by trial and error.
so as to fit in the theory used for calculating the thermodynamic quantities. Furthermore, in all thermodynamic calculations activities have been replaced by concentration terms, since activities of dye ions were not known.

The amount of equilibrium adsorption of direct dyes decreases with increase of temperature. This indicates that the adsorption of direct dyes by cellulose, like the aggregation of dyes in aqueous solutions is an exothermic process.\textsuperscript{4,10,39,43-45} The energies of adsorption computed from simple thermodynamic treatment of the experimental data on the equilibrium adsorption isotherms of direct dyes on celluloses at different temperatures, suggest clearly that there is an intermolecular attraction force between the dye and the cellulose which is greater than the electrical force at the interface of the cellulose-aqueous solution which opposes the adsorption of dye. The differential heat of dyeing calculated from affinities at different temperatures represents the energy of bond formation between dye and cellulose. The reported values of the differential heat of dyeing for different dyes are not the same.\textsuperscript{10,45-47} The values were, however, used until 1954 to postulate that the union between dye molecules and cellulose is by means of hydrogen bonding, although there were no evidences for assuming that the postulated hydrogen bonds are the only possible binding forces between the dye and the cellulose. In 1954, Vickerstaff\textsuperscript{48} summarized the requirements for good affinity of dyes for cellulose as follows.

1) The molecule should be capable of assuming a linear configuration.
2) The aromatic nuclei should be capable of assuming a coplanar arrangement.

3) The molecule should contain groups capable of forming hydrogen bonds.

4) The presence of a conjugated system of double bonds, which by resonance promotes coplanarity of the molecule and probably favours hydrogen bonding formation by the groups at the end of the conjugated chain. Favourable, but not essential conditions are:

5) Hydrogen bonding groups should preferably be spaced at about 10.3 Å to correspond with the repeat distance in the cellulose chain.

6) The molecule should contain minimum number of solubilizing groups necessary for solubility.

7) The solubilizing groups should be distributed along one side of the molecule and the hydrogen bonding groups on the other side.

In formulating these conditions, hydrogen bonding between the hydroxyl groups on cellulose and amino, azo, and other groups on dye molecule was considered to be the primary force attracting and holding the dye molecules to the cellulose. In the same year, Robinson demonstrated by use of molecular models that there are so many available hydroxyl groups on a cellulose chain that the repeat distance of 10.3 Å is of no importance. Dyes with hydrogen
bondable groups can easily find conveniently located hydroxyl groups somewhere in the cellulosic fibre. While Venkataraman and Vickerstaff have pointed out several nonlinear direct dyes which have good affinity for cellulose, Zollinger and Nurstein and Lead have pointed out many direct dyes which do not contain hydrogen bondable groups and yet showing good affinity for cellulose. Giles and coworkers on the basis of refractive index measurements and surface film experiments demonstrated that when cellulose is immersed in water, the hydroxyl groups are so firmly solvated that hydrogen bonding with dye could not possibly take place and therefore suggested that the main, if not the only source of affinity of dyes is van der Waal's attraction exerted between the dye molecules and the cellulose chain. Furthermore, using Peters and Sumners data on the affinity of vat dyes he pointed out a close relationship between the affinities and molecular weights of the dyes. Gill has argued against hydrogen bonding on the grounds that since water forms hydrogen bonds with cellulose and with the hydrogen bonding groups of the dye, for any single hydrogen bonding to form between dye and cellulose, two hydrogen bonds would have to be broken down, which he considered improbable. He therefore concluded that van der Waal's forces are the principal cause of attachment of direct dyes to cellulose. Derbyshire and Peters have suggested that since cellulose is highly solvated, only molecules with large hydrophobic surfaces, which can displace solvated water from cellulose and therefore exert large van der Waal's attraction can have adequate affinity for cellulose. Furthermore, they have stated that the hydrophilic groups on a dye molecule are necessary
to enable it to penetrate the water swollen regions of the fibre and achieve the close approach necessary for attachment by non-polar forces. The planarity and shape of the dye molecule are important factors for van der Waal forces to be operative.

Lead\(^5^4\),\(^6^0\) put forward the same phenomenon of solvation of cellulose as an argument against the van der Waal force theory. Thus, he stated that since these forces fall off very rapidly with distance, if the surfaces of dye and fibre are separated by even a single layer of water molecules, the van der Waal forces would be reduced to a negligible value. Since these forces are inversely proportional to the seventh power of the distance, an increase in separation from say 1.5 Å to 5 Å would reduce the force to approximately 1% of its former value. He postulated that the extended π electron system of the dye molecule is an ideal arrangement to form an intermediate layer between the cellulose on one side and the regularly arranged water molecules on the other, since interactions can take place between the delocalized π electrons and the hydrogen atoms of the hydroxyl groups on either side, without restriction as to spacing. The same arrangement is possible even if the cellulose hydroxyl groups are solvated. It is thus apparent in view of the above mentioned work on the nature of dye fibre interaction, that the nature of the forces is not clear.

Entropy changes also occur during dyeing owing to restriction in the mobility of the dye molecule as a result of its attachment to the cellulose molecule. The entropy change should increase with an
increase in the points of attachment and therefore with an increase in the heat of adsorption. Affinity is related to heat of dyeing and entropy of dyeing by the well known equation,

$$\Delta f^o = \Delta H^o - T \Delta S^o$$

Thus, the affinity depends not merely on the strength of the bond formed during dyeing, but also on the entropy changes which occur simultaneously. It is only when we resolve affinity into its components - heat of dyeing and entropy of dyeing, that we begin to obtain a true picture of the energetics of the dyeing process. Vickerstaff has said "The investigation of entropy change in dyeing is still in a very elementary stage, and it may be that more far-reaching conclusions can be arrived at by further study."

The above summary of the work which has been carried out on the equilibrium dyeing shows that there are many points which need examination. Thus for example, experimental work on specific surface areas of the cellulose fibres under the conditions used in dyeing has not been carried out so far. Detailed studies on the thermodynamic properties such as mean ionic activities of dye ions in aqueous solution have not been carried out so far. In addition, as pointed out earlier, the nature of the adsorption isotherm, that is, whether the isotherm belong to the Langmuir, Freundlich or direct partition type is not known. The so called "Volume Term" does not have a clear physical meaning and still remains an arbitrary factor. Very little attempts have been made to use thermodynamic activities instead of concentration terms for evaluating heats, affinities and entropies of dyeing. The influence of changes in the structure of water in
cellulose-aqueous dye + electrolyte solution systems has not been considered in any of the work reported so far in the literature. The present thesis embodies the results of work which has been mentioned above. For this purpose, the picture of the dyeing mechanism has been based on the modern physicochemical concepts of surface chemistry, the equilibrium adsorption of direct dyes from aqueous solutions on to the fibre phase being regarded as an interfacial phenomenon.
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