Equilibrium Absorption of Direct Dyes by Cellulose

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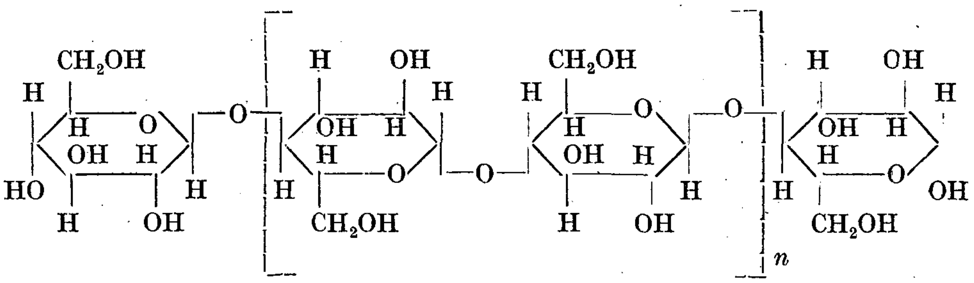
IN studying the mechanism of dyeing, the chemical constitution and fine structure of the fibre to be dyed, the chemical constitution of the dye, the state of the aqueous solutions of dyes, the influence of added substances and the dyeing conditions have all to be taken into account. The nature of the phenomenon of dye absorption by fibres is of interest and of technical importance. Because of the various physical and chemical differences between the different fibres such as cotton, viscose, cellulose acetate, wool, silk, nylon, etc. and the wide variations in the constitution and properties of the numerous dyes which are now available, it is to be expected that no single theory of dyeing can cover all dyeing processes.

Considerable progress has been achieved in the elucidation of the mechanism of dyeing. Thus, the chemical constitution and the physical structure of cellulose have been investigated and considerable success has been achieved by theoretical considerations as well as by physical, chemical and physico-chemical methods. Various methods have been evolved for the accurate estimation of dye absorbed by cellulose fibres, even to the extent of 1/10 of a mg present in about 10 mg of cellulose, by colorimetric method using photo-electric spectrophotometer. Standard materials have been prepared for the reproducibility of experimental results and better methods of purification of dyestuffs have been found out. The influence of various factors such as the concentrations of the dye and foreign electrolyte in the dyebath, the temperature of dyeing, the carboxyl content of cellulose, etc. on the absorption of dye by cellulose at equilibrium have been investigated thoroughly and important conclusions are arrived at and thermodynamic explanations have been given to the observed facts so as to lay the facts on a sound scientific footing. Finally, different theories have been propounded in order to explain the mechanism of dyeing and curiously enough, similarities between the different treatments have been observed.

Cotton[2] contains a group of linear polymers and has a polycondensate of β-glucose, viz. cellulose, as its principal constituent. The usually accepted molecular constitution of cellulose, as proposed by Haworth, is shown below, where n has a value varying from about 600 to 10,000 :



In the above structure anhydro β-glucose units are shown to be bound by 1:4-oxygen bridges. Various theories concerning the structure of cellulose

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*Second Year Student, Textile Chemistry Section, have been put forward, e.g. particle theory, miscellar theory, continuous structure theory, etc., the last of which has been fairly widely accepted. According to the continuous structure theory, cellulose is supposed to contain crystalline, mesomorphous and amorphous phases, all consisting of the same chemical material but the chain molecules are arranged in different ways in the different phases. In the crystalline region, the chain molecules are supposed to be placed in a strictly parallel order, in the mesomorphous state, they are less parallel while in the amorphous region, they are not arranged in any orderly manner. If the chains are long, they extend from the crystalline region to the amorphous through the mesomorphous region. In reality, it is supposed that there is no sharply defined borderline between the crystalline and mesomorphous or between the mesomorphous and amorphous phases of the macromolecule. The crystalline part of the fibre is not formed of a large single crystal, but of aggregations of submicroscopically small crystals called "crystallites." The length of the cellulose crystallite in viscose rayon is found to be 300° A.U. and its width 40°A.U. Cellulose also possesses properties of an anisotropic crystal, which behaves towards X-rays as a three dimensional grating and thus indicates a certain regularity of internal structure.

The mechanism of the process by which direct dyes become permanently fixed on cellulosic materials has caused much controversy. The foundations of the fundamental work on direct dyeing of cellulose were laid in 1933 by two groups of workers, Neale and Stringfellow on one hand and Boulton, Delph, Fothergill and Morton on the other. Prior to their work, the problem of direct dyeing, from the point of view of a technician or that of a theoretical physical chemist, hab been handicapped by the lack of adequate quantitative data due to the difficulty of purifying the dyes, of estimating accurately small amounts of dyestuffs absorbed by cellulosic materials, etc. The workers, prior to 1933, did not maintain concentrations of dyestuffs in the dyebaths the same when other factors such as time were being investigated and also they did not try to separate the effects of the kinetics of dyeing and of equilibrium dyeing. Further, they laid much emphasis on the colloidal behaviour of dyeing process, while the newer theories stress on the molecular solutions of dyestuffs in the dyebath.

Hanson, Neale and Stringfellow,[4] working on the absorption of direct dyes by cellulose, had found a technique to determine accurately the amounts of dyestuffs of the order of 1/10 of a mg. present in as small an amount of cellulose as 10 mg. In 1933, Boulton[1] and his co-workers attempted "to study the process of dyestuff absorption by viscose in a strictly quantitative manner." The results so obtained showed that if sufficiently long time is given for dyeing, an equilibrium will be established between the dye in the cellulose and that in the dyebath. The mass of dye absorbed per unit mass of cellulose at equilibrium or, in other words, the equilibrium absorption, according to Boulton *et al.*, depends on the temperature of dyeing concentrations of dye and foreign electrolyte in the dyebath and on the nature of the substrate dyed. Based on this work, Boulton and his co-workers were able to propound a tentative theory trying to explain the mechanism of dyeing. According to the theory, when cellulose is entered into a dye solution, a part of the dye is adsorbed by the cellulose surface which subsequently attains an equilibrium with the dye in solution. To maintain this equilibrium, which is disturbed by the diffusion of the adsorbed dyestuff in the sub-microscopic channels of cellulose structure, more and more dye is adsorbed on the surface till all the accessible parts of cellulose are dyed. At this stage, the thin elongated molecular structure of the dyes (this is so in the case of most of the dyes) is supposed to lie along the cellulose chain when co-ordinated and *this is in harmony with the dichroic* behaviour of dyed cellulosic fibres. Thus, ramie dyed with Congo Red is colourless under polarised light with the fibre axis parallel to the plane of polarisation and is deeply coloured when it is perpendicular.

Since 1933,[6] four dyeing theories have been put forward. All the theories make the same fundamental assumptions. The direct dye may be written as Na_xD ionising in solution as

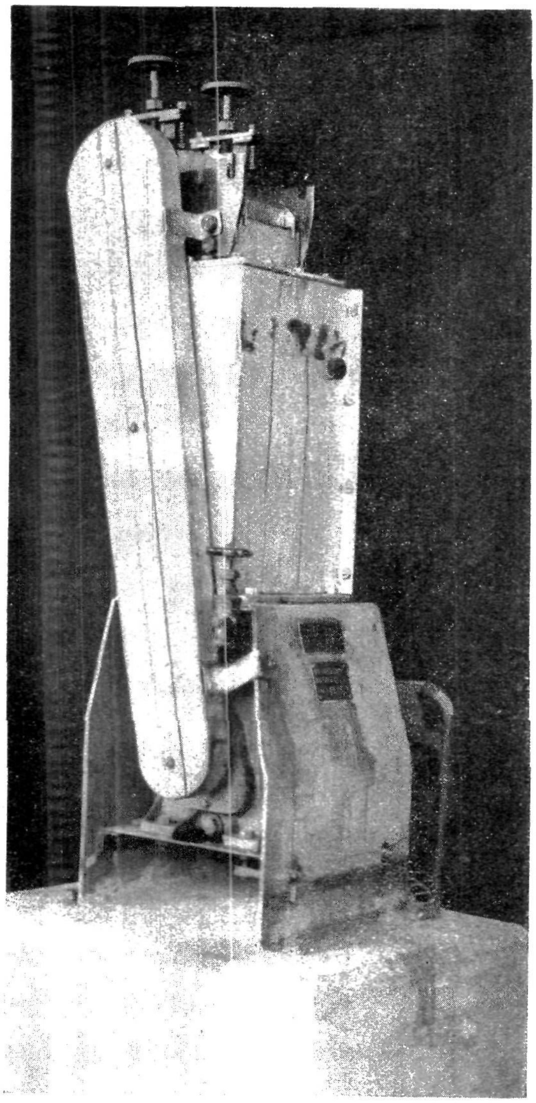
$$Na_xD \underset{}{\overset{(H_2O)}{\rightleftarrows}} x\,Na^+ + D^{x-}$$

where, D^{x-} is the large organic anion. All the theories assumed that the dye anions are preferentially adsorbed by cellulose and it is thought that the dye anions are held to hydroxy group (primary hydroxy) of cellulose by hydrogen bonding. When cellulose adsorbs dye anions preferentially, it becomes negatively charged and to preserve electrical neutrality, sodium cations are held by electro-static attraction in the vicinity of the adsorbed dye anions. The ultimate aim of all the theories is to relate the concentration of adsorbed dye anions to such variables as temperature of dyeing and concentrations of dye and foreign electrolyte in the dyebath. To solve the problem, the theories use thermodynamic treatments and they differ in the approximations they make and in the choice of variables they attempt to relate.

The first theory of Hanson, Neale and Stringfellow[4] treats the problem as one of the distribution of dye anions in two phases—the dyebath and the cellulose phase—and assumes the applicability of Donnan equilibrium to the system. An arbitrary value for the volume of water associated with unit mass of cellulose phase was assumed and the theoretical variations of the equilibrium absorption with the concentrations of dye and salt *in the dyebath were in reasonable agreement* with the experimental results. The theory demands that the presence of carboxy groups of cellulose (after chemical degradation during the processing of cellulose, some of the primary alcoholic groups of cellulose get oxidised to carboxy groups) should lower the equilibrium absorption, which has been, in practice, found to be true.

Willis, Warwicker, Standing and Urquhart[8], in order "to contribute towards the attainment of a real understanding of the dyeing process," examined the absorption of Chrysophenine G by cellulose sheet over a wide range of temperatures and salt concentrations and presented a theory of dyeing process, which in most respects agrees well with the experimental results. The heat of dyeing of Chrysophenine G was found to be 14 k. cal. per mole of the dye absorbed, a value that is not inconsistent with the assumption that each dye molecule is held to cellulose chain molecule by two hydrogen bonds (energy required for one hydrogen bond formation is 7 k. cal.). In their experiments, estimations of aqueous dye solutions were done colorimetrically using a photo-electric spectrophotometer. The adsorbed dye on the cellulose sheet was determined by direct colorimetric examinations of the dyed sheet itself.

The next theory is that of Crank.[3] His treatment was "to modify the linear form of Langmuir equation so as to take into account the fact that ions and not neutral molecules are adsorbed during dyeing." Non-aggregation and complete dissociation of the dye molecules were assumed. When the cellulose structure —a three dimensional network of more or less parallel molecular chains, so



STANDFAST MOLTEN METAL DYEING MACHINE
(TEXTILE CHEMISTRY SECTION)

Photo by : C. B. WADIKAR

arranged as to form crystalline and amorphous regions— is swollen in water, the molecular chains in the amorphous regions move apart forming capillaries, along which the dye molecules diffuse, as dyeing proceeds. The walls of the capillaries are considered as presenting an adsorbing surface containing a large number of active sites, each of which can accommodate not more than one dye anion. It was also assumed that no other ions are adsorbed at the sites. The active sites are randomly distributed throughout the mass of cellulose. The final equilibrium absorption of dye is pictured as that involving a balance between the number of dye anions held by the cellulose active sites and the number of dye anions escaping from the sites as they attain sufficient energy to break whatever bonds exist between the cellulose molecule and the dye anions. The dye anions held on the capillary walls attract an excess of cations to preserve electrical neutrality and the adsorbed dye anion is thus surrounded by positively charged ionic atmosphere. The cations tend to return to the region of lower concentration, i.e. the dyebath and exert a desorbing tendency on the dye anions held in cellulose. This escaping tendency decreases effectively the energy required by a dye anion to leave the active site; this decrease is a function of dye adsorbed and external dye and salt concentrations.

The last theory is that of Peters and Vickerstaff, who made the same fundamental assumptions that dye anions are preferentially adsorbed by cellulose and they considered the system as two distinct phases, the cellulose phase and the solution phase. Their treatment is essentially thermodynamic and to calculate the ionic product of the dye in the cellulose, they assumed a value for the volume of water associated with unit mass of cellulose. By this theory, affinity of direct dyes for cellulose was footed on a rigid thermodynamic definition and enabled the affinity to be calculated from equilibrium absorption data. The work of Peters and Vickerstaff has been extended by Marshall and Peters[5] who concluded that the mode of attachment of direct dye to different cellulosis fibres, in particular cuprammonium rayon, viscose rayon and cotton, is the same, as indicated by heats of reaction and affinities of a number of dyes. They also arrived at the conclusion that dyeing with such dyes consists in a molecular attraction between the dye molecules and the cellulose chain molecules, the energy changes on adsorption being thus independent of the molecular structure of the dye. The differences in the dyeing behaviour of various cellulosic fibres must arrive solely from differences in their physical structure, particularly as it affects the effective volume of the cellulose phase for adsorbed ions. They have also outlined a simple thermodynamic treatment of equilibrium dyeing and this is quite adequate to describe quantitatively the behaviour of direct dyes on cellulose provided that the dyes are not aggregated. Deviations from this behaviour to be expected on this theory may be regarded as an indication of the presence of aggregates.

All the four theories[6] stated above are quantitative and though the agreement between the theories as a whole and experimental results is fairly good, it is not exact. The divergences, according to Standing,[6] may be due to one or more of the following reasons: (1) all the theories make the simplifying assumption that the activity cœfficient of the dye in cellulose is equal to that of the dye in the dyebath, which is probably not justified, (2) the volume associated with unit mass of cellulose should be known, since the theoretical calculations depend on the value assumed for this volume and it is not possible to obtain this value accurately and (3) the carboxyl content of cellulose affects equilibrium absorption especially when the inorganic salt concentration is low; many dye-absorptions have been carried out on regenerated cellulose and the effect of carboxyl groups in cellulose has not always been taken into account while interpreting the results.

Summarising, it may be said that[7] "many attempts have been made in recent years at mathematical and thermodynamic analysis of direct dyeing of cellulose. Dyeing equilibrium and dyeing kinetics are problems of utmost complexity, but by arbitrary simplifications of the system, mathematical treatment has been possible and considerable progress has been made in deriving quantitative relationships between the various factors involved in the absorption of direct dyes by cellulose."

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