PART II

PHYSICAL CHEMISTRY OF DYING OF CELLULOSIC FIBRES WITH REACTIVE DYE: EFFECT OF ELECTROLYTES ON ADSORPTION.
### Chapter V

**Physical chemistry of dyeing of cellulosic fibres with reactive dyes**

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Chapter V

Physical Chemistry of Dyeing of Cellulosic Fibres with Reactive Dyes.

5.1 Introduction.

It was considered at one time (1,2) that if the dye could be attached with cellulose by the covalent linkage then the dyed goods will have high degree of wash fastness. This search led to the discovery of reactive dyes (3). These dyes are exhausted from their aqueous solution onto the cellulose at pH 7 and are fixed at pH 10.5 - 11. This range of pH is obtained by adding alkali to the exhausted dyebath. The addition of alkali causes cellulose to ionise to cell-0\(^{-}\) ions. The cell-0\(^{-}\) ions can then attack an electron-deficient carbon atom of, for example a halogeno-heterocyclic dye to form a covalent linkage. The addition of alkali to the dyebath also produces simultaneously the ionisation of water. The OH\(^{-}\) ions thus produced hydrolyse the dye and make it incapable of fixation. The hydrolysed dye formed exerts a very powerful de-activating action on the remaining chlorine atom of the dichloro-triazine type of dye (4). The hydrolysed form of the reactive dye is usually very similar
to the reactive form of the dye in diffusion and sorption properties. As a result of this, the hydrolysed dye is also exhausted equally well along with the reactive form on the cellulose during the course of dyeing. At the end of the dyeing cycle the hydrolysed dye is held on the fibre by physical forces. During subsequent washing and soaping this hydrolysed dye which does have appreciable affinity for the fibre is not removed from the fibres easily, thereby making the washfastness of the fibres concerned quite poor. Hence this hydrolysed and unfixed dye must be removed from the fibre surface in order to obtain desired washfastness properties.

The dyeing of cellulosic fibres with reactive dyes can be considered to occur in the following steps:

1) Diffusion of dye molecules from the solution phase to the cellulose/solution interface.

2) Adsorption of dye molecules from the interface on to the cellulose surface.

3) Diffusion of dye molecules into the microstructure of cellulose.
iv) Reaction between dye molecules and cellulose hydroxyls in the alkaline medium.

v) Reaction between dye molecules and water in the alkaline medium.

vi) Adsorption of hydrolysed dye from solution.

vii) Hydrolysis of adsorbed dye on the cellulose surface.

Generally, it is observed that only 30-70% of the dye becomes chemically bound (step iv) and rest of the dye is hydrolysed (step v and vii). As a result, the dye is not fully utilised, and the removal of unfixed dye from the fabric phase consumes chemicals, water, time and manpower.

An improvement in exhaustion and fixation of these dyes, may not only lead to better utilization of dye, but also reduce the amount of dye available for hydrolysis. This aim can be achieved by the following possible ways.

a) modifying the structure of cellulose either by opening up of the structure or introducing more active groups and/or

b) modifying the interface between dye solution and cellulose and/or
c) modifying the technique of application.

All the three approaches have potentialities to yield valuable results and require extensive experimental investigations.

The addition of alkali to the dyebath causes hydrolysis of the dye in the solution phase as well as on the fibre phase. However, it can be assumed as a first working hypothesis that the hydrolysis takes place mainly in the solution phase and is negligible at the fibre phase. This indirectly leads to the assumption that the exhausted (adsorbed) dye almost quantitatively takes part in the bond formation with cellulose. Therefore, one simple method to improve the efficiency of fixation would be to increase exhaustion.

The adsorption of a dye from its aqueous solution depends upon (i) state of dye molecules in the solution (ii) nature of the interface between cellulose and dye solution (iii) and (iv) the potential barrier to the transfer of dye from solution phase to the fibre phase. Generally, reactive dyes have low substantivity and therefore salt is added to get appreciable adsorption of the dye (6). In the neutral
solution, the reactive dyes behave just like direct dyes. It is known that the exhaustion of direct dyes increases with the increase in electrolyte concentration (7). This has been attributed to the action of electrolyte cation, which decreases the potential barrier, preventing the dye anion (co-ion) from reaching the negatively charged cotton surface. Besides this electrolyte may also change polar characteristics of the media which would facilitate the formation of transition state or of an intermediate of the Meisenheimer complex type (8). In the work presented in this chapter the role of electrolytes in the adsorption of hydrolysed form of reactive dyes has been investigated.

5.2 Review of the work done in the field.

The very marked effect of the additions of electrolytes on the dyeing equilibrium was realized long back. Hanson, Meale and Stringfellow (9) appear to be the first to assess quantitatively the effect of electrolyte concentration on dye uptake while developing the theory of dyeing. Willis, Warwick, Standing and Urquhart (10) in 1935 studied extensively the effect of common salt concentration on the equilibrium adsorption of direct dye.
Chrysophanine G and proved that the dye uptake of cellulose is proportional to common salt concentration in the dye bath.

Subsequently a number of workers have studied the effect of electrolytes on the adsorption of direct dyes. When the importance of salt addition in the dye bath was realized, a question of considerable interest that came up was whether direct dyes in the complete absence of electrolytes will dye cellulose at all. Boulton et al (11) found that electrolyte free chlorazol sky blue FF did not colour cuprammonium rayon in absence of electrolyte. A similar observation was made by Hanson and Neale (12), and by Schramek and Gotte (13). These results led to the generalization that direct dyes will not dye cellulose in the complete absence of electrolytes. On the basis that adsorption of dye is due to the existence of hydrogen bonding forces between fibre and dye opposed by the electrical surface charge, there is no reason to believe that the attractive forces will be destroyed by the mere removal of electrolyte. The surface charge density on the fibre is however very greatly increased by the removal of electrolyte.
and it is conceivable that the electrical repulsion forces so developed might overtake the attractive forces at all distances from the fibre surface and thus lead to a complete lack of adsorption or even negative adsorption (this has in fact been observed in case of Chlorazol Sky Blue FF).

According to this explanation the effect should be more pronounced with polysulphonated dyes which carry large negative charges, whereas with dyes having lower number of sulphonic acid groups and high affinity for cotton fibres, some dyeing might possibly occur even in the absence of electrolyte. This view seems to be closer to the facts as the most studied dye in this connection is tetrasulphonated Chlorazol Sky Blue FF. With the disulphonated Benzoquinoline 4 B, Neale and Boulton et al (11) observed that adsorption in absence of salt, although small, still persisted, while Schramek and Gotte (13) were able to obtain an adsorption isotherm of oxamine violet (disulphonated) in absence of salt. Willis et al (10) have also studied complete isotherms of chrysophenine G. in absence of electrolyte.

The isotherm in absence of electrolyte is interesting and simple. In this particular case the sodium ions in the fibre and in the bath can come only from the ionisation
of the dye, so that electrical neutrality requires,

\[
\left[\text{Na}_\sigma\right] = Z \left[D_\sigma\right] \quad \text{and} \quad \left[\text{Na}_\delta\right] = Z \left[D_\delta\right]
\]

And the general equation assumes the form,

\[
\frac{\left[D_\delta\right]}{\left[D_\sigma\right]} = \text{constant} \quad \ldots \ldots \ldots \ldots (5.1)
\]

(here the symbols have their usual meaning)

Hence in this case a plot of the concentration of dye in the dye bath ( \([D_\sigma]\) ) against the concentration of dye on the fibre ( \([D_\delta]\) ) should be a straight line passing through the origin. However, experimentally only the results of Millis et al (10) were somewhat closer to straight line, whereas Schramek and Cotte’s (13) and Peters and Vickerstaff’s (14) results give straight lines which do not pass through origin. From their results Peters and Vickerstaff concluded that cotton contains a limited and small number of sites for which the dye has a very high affinity. These sites absorb dye strongly from dilute aqueous solutions even in the absence of electrolyte, but when all of these are saturated dyeing on the less active but more plentiful sites occurs. This behaviour is in agreement with the observation of Gnahn and Keuffler (15)
who observed that the last traces of direct dye cannot be removed from cotton by water only.

Boulton (16) determined the amount of salt needed to produce 50% exhaustion for a number of dyes to indicate salt sensitivity of dyes. Afterwards a number of workers studied salt sensitivity of direct dyes.

The effect of different electrolytes:

The effect of electrolytes other than sodium chloride and sodium sulphate has not been studied intensively, as the use of these electrolytes is very economical and their replacement by other electrolytes is not likely. Whatever little amount of work has been done in this direction is mostly of academic interest. It is a well established fact that the nature of the anion of the added electrolyte has very little effect on the adsorption. Heale and Patel (17) observed identical results with sodium chloride and sodium sulphate, but disodium hydrogen phosphate produced significantly less adsorption of chlorazol sky blue FF. This may be due to the difference of pH of the solutions or the fact that the ionic concentration of sodium ions is less. Willis et al (10) studied the
adsorption of Chrysophenine G. in presence of sodium chloride, sodium bromide, potassium chloride, potassium bromide and sodium sulphate. The interchange of chloride and bromide ions produced no detectable difference in adsorption, while the replacement of sodium chloride by the equivalent quantity of sodium sulphate produced only very small reduction in adsorption. The nature of the cation and particularly its valency has a much greater effect. The subject was first studied by Victoroff (18) who measured the amount of dye adsorbed by cellulose in an arbitrarily fixed time from solutions containing various electrolytes. The results have little quantitative significance as no attempt was made to establish equilibrium, but using sulphates he found that the order of cations producing increasing adsorption of Benzo pure Blue was

\[ \text{NH}_4^+ < \text{Na} < \text{K} < \text{Mg} < \text{Ni} < \text{Mn} < \text{Zn} < \text{Cd} < \text{Al} \]

Similar experiments for three hours at 20°C (quite inadequate for equilibrium) were made by Schrenkel and Goret (13) who using Dianil Blue R, arrived at the series:

\[ \text{NaOH} < \text{Na}_2\text{CO}_3 < \text{Na}_2\text{SO}_4 < \text{NaCl} < \text{MgSO}_4 \]
The series contains simultaneous variations of anions, cations and pH.

Boulton et al. (11) found that adsorption is approximately the same from dyebaths containing equivalent quantities of different inorganic electrolytes having a univalent cation, but is increased if the cation is divalent.

Seale and Patel (17) examined the effect of several cations on the rate and equilibrium adsorption of Benzopurpurine 43 and Chloranil Sky Blue FF. The order of effectiveness varied somewhat with concentration but in N/10 solutions of electrolytes using Chloranil Sky Blue FF, the order was

\[
\text{Na}_2\text{HPO}_4 < \text{KH}_2\text{PO}_4 < \text{NaCl} < \text{NH}_4\text{Cl} < \text{MgCl}_2 < \text{ZnSO}_4 < \text{CaCl}_2 < \text{BaCl}_2
\]

In these experiments aluminium was also used but produced only low adsorption which Seale and Patel attributed to the formation of the insoluble aluminium salt of the dye. Insoluble salts were also formed with cerium, copper and thorium ions. The results being expressed mainly in graphical form, are not available for quantitative treatment. The observations indicate that the nature of the
cation of a salt and particularly its valency is of great importance in promoting adsorption of direct dyes on cellulose. The nature of the anion appears to be of secondary importance.

Iyer, Srinivasan and Baddi (7) and Baddi (19) studied the effect of different uni-univalent alkali metal chlorides on the adsorption of chlorazol Sky Blue FF on cotton fibres. It was found that the dye uptake increased markedly with increasing size of the alkali metal cation. It was pointed out that apart from the usual well known effects of electrolyte cations, an important contributory factor to the adsorption process arises from the disturbance caused by the cations to the structure of water hydrogen bonded to the cellulose surface and "Iceberg" water around the hydrophobic parts of dye molecules. This effect, which will increase with the size of the alkali metal cation explained the results (Li < Na < K < Rb < Cs) adequately.

In a recent publication Shanai and Mahra (20) found that the presence of sodium chloride suppresses the ionisation of carboxyl group of chemically modified celluloses
and thus increases the dye uptake of direct dyes.

5.3 Experimental.

5.3.1 Materials.

Cotton fibres used were of ISC-67 variety. These were purified by a method described in literature (9) and discussed in detail in Section 2.2.1e. All the electrolytes used in the adsorption studies were of Analar grade. All the solutions were prepared in distilled water and stored in thoroughly cleaned and steamed Pyrex flasks.

The dyes used were Procion Brilliant Navy Blue MK, Procion Blue RS, Procion Red Brown MR, and Procion Brilliant Blue MR. These dyes were hydrolysed by heating at boil with 0.1 N sodium hydroxide solution for half an hour and allowed to stand overnight. The dyes were purified by the method suggested by Mehta andcoworkers (10) which involves the treatment of the dye sample with dimethylformamide. The soluble portion was separated and the dye was precipitated with acetone and petroleum ether (B.P. 40-60). The separated dye was dried at room temperature. This procedure was repeated until the optical density of a solution of given concentration remained constant.
5.3.2 Effect of Electrolytes on the adsorption of dyes.

In all the experiments 0.25 g of conditioned cotton fibres (25°C and 65% R.H.) and 25 c.c. of dye solutions containing 0.050/l dye and known amounts of electrolytes ranging from 0.1 N to 1.0 N solutions were taken in the flasks. The flasks were immersed in a thermostatically controlled water bath maintained at 40°C and mechanically shaken continuously for 48 hours. The period was found to be adequate to reach equilibrium. The concentration of the dye molecules adsorbed by the cotton fibres were calculated from the difference in concentration of the dye in the initial and equilibrium solutions.

5.3.3 Equilibrium Adsorption Isotherms of Dyes.

0.25 g of cotton and 25 c.c. of dye solutions containing known amounts of the dye ranging from 0.025 to 5 C/l and 0.5 N of different electrolytes were taken in conical flasks. The conical flasks were then immersed in a thermostatically controlled water-bath maintained at the desired temperature to ± 0.1°C and mechanically shaken for 48 hours. The amount of dye adsorbed by the cotton fibres
was calculated from the difference in concentration of the dye in the initial and equilibrium solutions. The experiments were carried out at 30°, 40° and 50°C.

5.4 Results and Discussion.

5.4.1 Influence of electrolytes on the adsorption process.

Figure 54-56 show the effect of different electrolytes on the adsorption of Procion Brilliant Navy Blue H3B (C.I. Reactive Blue 9), Procion Rubine H3 (C.I. Reactive Red 6), Procion Fast Brown 34RL (C.I. Reactive Brown 10) and Procion Brilliant Blue H6R (C.I. Reactive Blue 4) at 40°C.

The general trend of dye uptake in the presence of different electrolytes at equivalent concentration is in the order:

ammonium chloride > ammonium sulphate > sodium chloride > magnesium chloride > lithium chloride. The observed increase in dye sorption in the presence of different electrolytes may be explained in terms of the following different possibilities:

In general the increase in adsorption with increase in concentration of electrolytes can be accounted for, in terms of partial screening of the surface charge on cellulose by the crowding of the cation at the cellulose
Fig. 5.1: Effect of electrolytes on the sorption of the hydrolysed form of C.I. Reactive Blue 9 (Procion Navy Blue M3R) at 40°C.
Fig. 9.2: Effect of electrolytes on the sorption of the hydrolysed form of C.I. Reactive Red 6 (Procion Rubine LB) at 40°C.
Fig. 9.3: Effect of electrolytes on the sorption of the hydrolysed form of C.I. Reactive Brown 10 (Procion Red Brown MN) at 40°C.
Fig. 5.4: Effect of electrolytes on the sorption of the hydrolysed form of C.I. Reactive Blue 4 (Procion Brill. Blue MR) at 40°C.

- Ammonium Chloride
- Ammonium Sulphate
- Sodium Chloride
- Magnesium Chloride
- Lithium Chloride

Dye adsorbed in grams/kg of dry cotton

Concentration of Electrolyte in gram equivalents/litre
water interface. It is well known that the adsorption of
dye anion is influenced by the Donnan potential. The
addition of electrolytes reduces the Donnan potential and
increases the chemical potential of dye anions. Both these
factors usually favour adsorption of dye be cellulose. Thus,
it is possible to explain an increase in dye sorption with
increase in concentration of added electrolytes, irrespective
of the nature of the electrolytes. However, this does not
explain the relative effectiveness of different electrolytes
(7).

Another factor, which can result in a large
variation in dye adsorption is a marked reduction in the
solubility of the dyes in the presence of these electrolytes,
the dye in solution possess higher degree of aggregation
leading to higher adsorption. However this factor also
cannot account quantitatively the observed results, as the
relative changes in solubilities of the dyes in presence of
these electrolytes do not necessarily follow the expected
pattern. Iyer and coworkers (7) have shown that in the case
of alkali metal chlorides there is a marginal increase in
solubility at equivalent concentrations as the molecular
weight is increased in the series, but even then the sorption of direct dyes also shows an increasing trend from Li to Cs.

Cotton is known to have a negatively charged surface in water and in electrolyte solutions. The origin of the negative charge has been reported to be due to (a) ionisation of surface polar groups (21, 22) and/or (b) interaction of surface polar groups with the solvent molecules (23). This leads to the formation of oriented layers of water molecules, which apparently attract ions giving rise to an adsorption potential. The over-crowding of such ions, which are potential determining ions, may change the polarity of the surface. In most of the cases H⁺ and OH⁻ ion concentrations in the system determine the polarity of the surface. It is reported that cotton assumes a zero charge at pH 2.7. It is negative above this pH and positive at pH lower than 2.7 (5). In a system containing cotton fibre, dye and electrolyte solutions, the fibre and the dye both are negatively charged, and thus a barrier is created, hindering the sorption of the dye co-ion on the cellulose surface. The pH of the system is lowered to a greater extent in the presence of acidic salts like magnesium chloride, ammonium
chloride and ammonium sulphate than in the presence of neutral salts like lithium chloride, sodium chloride etc.

The lowering of pH of the dye solution in the presence of magnesium chloride and ammonium salts makes the cotton surface less negative, and therefore, more approachable by negatively charged dye ions, thus resulting in an increased adsorption.

Another factor which could affect the adsorption of dye is the modification of water structure (24) caused by added electrolyte. This concept was earlier utilized by Iyer et al. (7) in explaining the effect of electrolytes on the adsorption of Chlorazol Sky Blue FF. The introduction of ionic species into water is known to modify the structure of water. The modification depends upon the size and charge on the cation. Generally solutes are divided into three main groups based on the nature of the modification brought about in the structure of water. (i) structure breakers (ii) electro-restrictive structure makers and (iii) hydrophobic structure makers.

From a consideration of the thermodynamic behaviour of aqueous solutions of organic molecules, Frank and Evans (25)
postulated the presence of structural regions of low entropy, called "icebergs" around hydrophobic portions of the organic molecules in water. It is therefore, reasonable to expect that a similar orientation of water molecules occurs around dye molecules dissolved in water (27). Katayama et al (28) investigated the partition of several disperse dyes between benzene and water and found that the transfer of disperse dyes from benzene to water is always accompanied by large negative enthalpy and entropy changes, indicating the presence of "icebergs" around the dye molecules in water.

The dyes used in the present investigations contain ionizable sulphonate groups. According to Hamaty and Schoraga (26) these ionized groups strongly affect the structure of water around them over a distance of a few molecular diameters by electrostatic interaction and interfere with the establishment of the "iceberg" around the hydrophobic part of the solute. Therefore, it can be easily visualized for the dye anions dissolved in water that those hydrophobic parts of the ion which are further away from the influence of $SO_3^-$ ions are surrounded by "iceberg" in which the orientational disorder of water in less than in bulk water. When these dye
anions aggregate or interact with solid surfaces, the
structure of "icabergs" around the hydrophobic portions
must break down and reform, contributing towards the
heat and entropy changes of the system.

Likewise, when cellulose is immersed in water, the
water itself is initially sorbed onto the cellulose
surface, forming a monolayer of strongly bound water
molecules. The energy of interaction of water with diffe-
rent kinds of cellulosic materials lies within 5 to 6 K,
cals., as measured by heat of wetting. This heat is of the
same order of magnitude as for hydrogen bonding. Stamm (29)
on the basis of the analysis of the results of several
worker concluded that initially adsorbed water has the
reduced energy level and reduced mobility similar to that
of water in ice. Hence the disruption of aqueous monolayer
and the removal of adsorbed water molecules from the
cellulose surface is a essential condition for the dye
adsorption to occur.

Considering all the factors which influence the
structure of water in aqueous solution, it may be expected
that in a system containing cellulose, electrolyte, and dye
solution, the charged cations probably disrupt the monolayer of water molecules sorbed on the cellulose surface. It is quite reasonable that cations, which can break the water-water hydrogen bonds in bulk water, can also break the hydrogen bonds between water and cellulose hydroxyls. This disturbance in the sorbed water molecules will increase with increasing concentration of electrolytes, and in effect will bring the dye anions into closer contact with the surface. Since the structure-breaking effect of the electrolyte increases with increasing radius of the cation, it can be expected that at equivalent concentration of electrolytes, the disruption of the monolayer of water sorbed on cellulose and the icebergs on the hydrophobic portion of the dye will also increase in the order

$$\text{Li}^+ < \text{Mg}^{++} < \text{Na}^+ < \text{NH}_4^+$$

These interactions operate at high concentrations of electrolytes, whereas at low concentration of electrolytes, the disruption of the monolayer of adsorbed water molecules on cellulose and the icebergs on the hydrophobic portion of the dye may not be enough to have any observable effect on the dye adsorption. In this range of concentrations of
electrolytes the effectiveness of different electrolytes in increasing the dye sorption is observed to be in the order of

\[ \text{Li}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{Mg}^{++} \]

which may probably be due to their ability to change the pH of the solution, whereas at higher concentrations the effectiveness of different electrolytes is in the order of

\[ \text{Li}^+ \approx \text{Mg}^{++} \approx \text{Na}^+ < \text{NH}_4^+ \]

This may be attributed to their ability to modify the cellulose-water interface and the icebergs on the hydrophobic part of the dye.

It can therefore be concluded that there are three different possible roles—namely, partial screening of the surface charge on cellulose by the crowding of the cations at the cellulose water interface, pH of the bath and the ability of electrolytes to modify the structure of water by which an increase in sorption could be explained. Of the possible roles, the ability of the electrolytes to modify the pH of the solution plays a dominant role at lower concentrations of electrolytes whereas at higher concentration the ability of the electrolyte to modify the
cellulosic-water interface plays decisive role. Thus it is possible to explain the observed increase in sorption of dyes in presence of electrolytes.

5.4.2 Thermodynamics of the Adsorption Process.

There are very few examples of adsorption isotherms which can adequately be described by the equation.

\[ n = K'P \]  
(5.1)

where \( n \) is the concentration of adsorbate on the surface of adsorbent, \( K' \) is a constant and \( P \) is pressure.

Normally there are departures from this equation due to (a) heterogeneity of adsorption surface, (b) modification of adsorbent by adsorbate, (c) variation of the probability of adsorption with \( n \) and (d) interaction of adsorbate molecules on the surface or in the external phase.

The isotherms obtained experimentally are generally described in terms of empirical equations or equations based on theoretical models, namely partition isotherm, Langmuir isotherm, Freundlich isotherm, Temkin isotherm and BET isotherm.

Adsorption of dyes by textile fibres are often described in terms of Freundlich Partition isotherm (solid solution) and/or Langmuir model of adsorption. The theoretical shapes
of the adsorption isotherms derived from different models are shown in fig. 5.5.

It can be seen from the figure that adsorption from dilute solutions can be expressed successfully in terms of any one of the models. However, the shape of the isotherm differs markedly at higher concentrations. Langmuir treated adsorption and desorption as reversible chemical reactions and arrived at the following equation

$$\frac{1}{[D_0]} = \frac{e^{-\Delta H^0/R T}}{[D_e]} \frac{1}{[D_g]} + \frac{1}{[D_g]} \ldots \ldots \ldots (5.2)$$

Where $[D_0]$ = concentration of dye adsorbed on cellulose in gram ions/kg of dry fibres.

$[D_e]$ = concentration of dye in external equilibrium solution in moles/litre.

$-\Delta H^0$ = affinity of dye molecules for adsorption on cellulose surface in K. cal/mole.

and $[D_g]$ = total number of sites for the dye adsorption and is termed as saturation value of the adsorbed dye in moles/kg.

However, Hanson, Neale, and Stringfellow (9) treated the system at equilibrium consisting of dye in the
Fig. 5.5: The theoretical shapes of the adsorption isotherms derived from different models.
external and internal phases and dye adsorbed on the fibre.
The ionic distribution between the internal and external phase was calculated from the Donnan equation and the authors arrived at the expression which is analogous to the equation of Peter and Vickerstaff (30) at low salt concentrations,

\[
\frac{[D_\gamma]}{[D_i]} = \left( \frac{W}{2 [Na_\sigma]} \right) + \left( \frac{W}{2 [Na_\sigma]} \right)^2 + \left( \frac{[Cl_\gamma]}{[Na_\sigma]} \right)^{1/2} \left( \frac{Z}{2} \right) \] ........................ (5.3)

where the subscripts i and σ stand for internal and external phase (solution phase) respectively and W is surface charge on cotton per unit volume of internal cellulose phase.

In arriving at the above equation the contribution of electrical forces to the total surface charge was neglected. However, Daruwalla et al. (21) stressed the importance of the electrical forces due to ionisation of carboxylic groups. Hence, \( Z \left[ D_\theta \right] + \left[ COO^- \right] \) was substituted for W in equation (5.3), which resulted,
\[
\frac{[D_\sigma^-]}{[D_1]} = \left[ \frac{Z [D_\sigma] + [\text{COO}^-]}{2 \left[ Na_\sigma^- \right] V} \right]^Z \left[ \frac{Z [D_\sigma] + [\text{COO}^-]}{2 \left[ Na_\sigma^- \right] V} \right]^2 + \left[ \frac{Cl^-}{Na_\sigma^-} \right]^{1/z} \right]^{2/z} \ldots (5.4)
\]

where \( Z \) is the valency of the dye anion and \( V \) is the volume of internal cellulose phase.

The equation (5.4) takes the following form when an excess of sodium chloride is added to the dyebath,

\[
\frac{1}{[D_1]} = \frac{1}{[D_\sigma^-]} \exp \left[ \sinh^{-1} \left( \frac{Z [D_\sigma] + [\text{COO}^-]}{2 \left[ Na_\sigma^- \right] V} \right) \right] \ldots \ldots (5.5)
\]

From the dye concentration in the dyebath, \([D_\sigma^-]\), the dye concentration in the internal phase of cellulose \([D_1]\) was computed by equation (5.5), however, this is possible only with the knowledge of volume term \( V \). Arbitrary values for \( V \) (21, 30-34) have been assigned ranging from 0.02 to 0.9 litres/kg to get reasonable agreement between the experimental data and the model. It has been reported that the volume term \( V \) appeared to have some relationship with the amount of moisture adsorbed by the cellulose at 100% R.H. Iyer and coworkers (35) attempted to correlate the volume term with surface area which is available for
the adsorption of polar molecules and the thickness of the electrical double layer. Megregor (36) in another attempt expressed V in terms of measurable parameters.

Adsorption isotherms of hydrolysed form of Procion Brilliant Navy Blue M3R (C.I. Reactive Blue 9) Procion Rubine MB (C.I. Reactive Red 6) Procion Brilliant Blue MR (C.I. Reactive Blue 4) and Procion Red Brown M3R (C.I. Reactive Brown 10) at 40°C in presence of sodium chloride on cotton are shown in fig.56. Isotherms obtained at 30°, 40° and 50°C in the case of Procion Brilliant Navy Blue M3R are shown in fig.57. The effect of different electrolytes on the adsorption of Procion Brilliant Navy Blue M3R are shown in fig.58.

All the isotherms are characterised by an initial smooth rising portion followed by a plateau where the adsorption remains practically constant over a wide range of equilibrium dyebath concentrations. Similar isotherms have been reported earlier in the case of adsorption of chlorazol sky blue FF (7) and of ethylene urea type of crosslinking agents (37) on cotton. The start of the plateau region has been attributed to the tendency of the
Fig. 5, 6: Adsorption isotherms of different dyes in presence of sodium chloride at 40°C.

- **Procion Navy Blue M3R** (C.I. Reactive Blue 9)
- **Procion Brill Blue MR.** (C.I. Reactive Blue 4)
- **Procion Rubine X** (C.I. Reactive Red 6)
- **Procion Red Brown M4R** (C.I. Reactive Brown 10)

Amount of dye in equilibrium dyebath in moles / litre

$[D_0]$
Fig. 5.7: Adsorption isotherms of C.I. Reactive Blue 9 at different temperatures.

Amount of dye in equilibrium dyebath in moles/litre

Moles/kg of dry cotton

Amount of dye adsorbed in

250 x 10^3

200

150

100

60

20
Fig. 5.8: Adsorption isotherm of C.I. Reactive Blue 9 in presence of different electrolytes.
dye molecules to aggregate and the completion of monolayer.
The isotherm upto the beginning of the plateau region has
been analysed on the basis of the following equation.

\[
\frac{1}{[D_2]} = e^{-\frac{\Delta H^0/RT}{D_1}} + \frac{1}{[D_2]} \quad \ldots \ldots \ldots \ldots (5.6)
\]

The limiting saturation values \([D_2]\) and the
affinity values which have been calculated from the
intercept and the slope of the linear plot, \(\frac{1}{[D_2]}\) \(\wedge\) \(\frac{1}{[D_2]}\)
are given in table I.

The effect of temperature on the adsorption of
dyes is conveniently expressed in terms of the exothermic
heat of adsorption which has been determined from the
isotherm data at two different temperatures using following
equation,

\[
\Delta H^0 = \left( \frac{\Delta H_1^0}{T_1} - \frac{\Delta H_2^0}{T_2} \right)
\left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \ldots \ldots \ldots (5.7)
\]

The values thus calculated are shown in table I.

It can be seen from the table I that the limit-
ing saturation values obtained in the presence of ammonium
chloride are higher than in the presence of sodium chloride.
<table>
<thead>
<tr>
<th>System</th>
<th>Temp. (°C)</th>
<th>Limiting Saturation Value (D) x 10^3 Mols/kg</th>
<th>Affinity Values Kcal/mole</th>
<th>Enthalpy Value H^0 Kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Procion Rubyine MB</td>
<td>30°</td>
<td>33.0</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>40°</td>
<td>21.0</td>
<td>4.83</td>
<td>2.37</td>
</tr>
<tr>
<td></td>
<td>50°</td>
<td>12.5</td>
<td>4.92</td>
<td></td>
</tr>
<tr>
<td>Procion Red Brown M3R</td>
<td>30°</td>
<td>22.0</td>
<td>4.23</td>
<td></td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>40°</td>
<td>16.5</td>
<td>5.25</td>
<td>2.19</td>
</tr>
<tr>
<td></td>
<td>50°</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Procion Brilliant Blue</td>
<td>30°</td>
<td>172.8</td>
<td>5.26</td>
<td></td>
</tr>
<tr>
<td>Navy Blue M3R</td>
<td>40°</td>
<td>133.1</td>
<td>5.26</td>
<td>3.87</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>50°</td>
<td>112.8</td>
<td>5.31</td>
<td></td>
</tr>
<tr>
<td>Procion Brilliant Blue</td>
<td>30°</td>
<td>200.0</td>
<td>5.67</td>
<td></td>
</tr>
<tr>
<td>Navy Blue M3R</td>
<td>40°</td>
<td>188.0</td>
<td>5.74</td>
<td>2.68</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>50°</td>
<td>173.0</td>
<td>5.84</td>
<td></td>
</tr>
<tr>
<td>Procion Brilliant Blue</td>
<td>30°</td>
<td>182.0</td>
<td>5.60</td>
<td></td>
</tr>
<tr>
<td>Navy Blue M3R</td>
<td>40°</td>
<td>165.00</td>
<td>5.73</td>
<td>2.76</td>
</tr>
<tr>
<td>Ammonium sulphate</td>
<td>50°</td>
<td>154.0</td>
<td>5.83</td>
<td></td>
</tr>
</tbody>
</table>
This has been discussed earlier (Section 5.4:1) in terms of (i) lowering of Donnan potential in presence of added electrolytes (ii) dissociation characteristics of electrolytes and their influence on the ionisation of intrinsic carboxyl groups of cellulose and (iii) the ability of ions of the electrolytes to modify the structure of water. Here it is again confirmed that out of above mentioned causes to account for the increase in the adsorption of dyes in presence of electrolytes, the ability of the ions to modify the structure of water is very important.

The affinity values shown in table I for dye Procion Brilliant Navy Blue NGR, show very little variation in presence of sodium chloride, ammonium chloride and ammonium sulphate. Similar fairly constant values of affinity have been reported by Iyer and coworkers (7) who concluded from their results that the nature of the adsorption process and the driving force involved there in are independent of the nature of the cation used. These constant affinity values support the modification introduced by them in the theory of dyeing of cellulosic fibres by direct dyes.
(Viz- the use of variable volume term in calculating the concentration of dye in internal cellulose phase during adsorption).

As is evident from table 1 the enthalpy values (i.e., $\Delta H^\circ$) for the adsorption process are lower in case of both the ammonium salts compared to sodium chloride. The present results may be satisfactorily explained as follows:

During the process of dye adsorption cations of the added electrolytes break the hydrogen bondings between the cellulose surface and the water monolayer adsorbed on it. Thus desorption of water takes place making a way for dye adsorption. The desorption of water is expected to be more in case of $\text{NH}_4^+$ ions compared to $\text{Na}^+$ ions, as the size of $\text{NH}_4^+$ ions will be bigger. Since the desorption of water is an endothermic process, more heat will be consumed in the presence of ammonium salts. As is evident from fig. 7 adsorption of dyes is an exothermic process. A part of heat liberated in the adsorption of dyes is consumed in the desorption of water from the cellulose surface. In case of ammonium salts, where more desorption of water takes place consumption of heat will be higher. This will lead to a
smaller enthalpy change for adsorption of dyes in the presence of sodium chloride.

Thus it can be inferred from this study, that the modification of structure of water by electrolytes plays an important role in the adsorption and hence fixation of reactive dyes on cellulosic fibres.
REFERENCES


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Chapter VI

Summary and conclusions.

6.1 Zeta potential at cellulose and crosslinked cellulose-aqueous electrolyte interface.

The streaming potentials have been measured at the interface between chemisorbed cotton (with different crosslinking agents: dimethylolethylene urea (DMEU), dimethylol-propylene urea (DMFU) and dimethylol dihydroxy ethylene urea (DMDHEU)) and different electrolyte solutions (NaCl, KCl, NaI, NaBr, and MgCl₂·6H₂O). Data were obtained as a function of concentration of electrolytes.

The streaming potentials were found to increase with increasing concentration of chemisorbed resins. In the case of DMEU and DMDHEU this trend was observed throughout the concentration range studied. However in the case of DMEU the increase in streaming potential was significant only up to the concentration of 6x10⁻³ moles/Kg of cotton, above which concentration it was almost constant.

The zeta potentials were found to be inversely proportional to the electrolyte concentration. The rate of change of zeta potential was much smaller than the theoretical
values calculated from the different models of double layer. The discrepancy between the observed and theoretical values have been discussed.

The surface charge density \( \rho^- \) on cotton at the interface has been calculated and found to increase with electrolyte concentration. This functional relationship between \( \rho^- \) and \( c \) has been explained from the consideration of the modification of the structure of water in the vicinity of the ion. The increase in surface charge density with the increase in electrolyte concentration was in the order

\[ \text{KCl} > \text{NaI} > \text{NaBr} > \text{NaCl}, \]

which is in the structure breaking capacity of these electrolytes.

The contribution of surface conductivity to the conductivity of the cotton plug at different concentrations of electrolytes was also calculated. The experimental values for surface conductivities are several orders of magnitude higher than the theoretical values calculated from the diffused part of the double layer. The discrepancy between the experimental and theoretical data was explained on the basis of a concept based on the modification of structure of water by electrolytes.
6.2 Electrokinetic and adsorption studies on cellulose, modified celluloses and modified reactive dyed celluloses.

The zeta potentials of untreated and different chemically modified fibres in the blank as well as reactive dyed forms have been studied by streaming potential methods. An attempt has been made to correlate the values of $d\zeta$ in case of all the fibres with their equilibrium $d\log_{10} C$ adsorption behaviour for reactive dyes. It has been observed, in general that all the modifications under study give higher values of zeta potentials and the values of $d\zeta$ and $d\log_{10} C$ give a good qualitative idea about the adsorption capacity of modified fibres.

(a) Untreated fibres.

The values of zeta potentials as well as of $d\zeta$ for untreated fibres increase after dyeing.

(b) Cyanoethylated fibres.

The values of $d\zeta$ and saturation equilibrium $d\log_{10} C$ adsorption for the modified fibres are higher compared to untreated fibres. This has been explained on the basis of hydrolysis of $-CN$ groups to $-COH_2$ groups.
(c) Carbamoylthylated fibres.

Carbamoylthylated fibres give higher adsorption and higher values of $d \frac{C}{S}$. This has been attributed to the complex formation between the free sulphonic groups of already reacted dye and carbamoylthyl groups of fibres.

(d) Dimethylaminoethylchloride-treated fibres.

The values of $d \frac{C}{S}$ and saturation equilibrium adsorption were observed to be lower for dimethylaminoethylchloride-treated fibres. This behaviour has been explained on the basis of the reduction in hydrophilic nature of the fibre, and the inertness of tertiary amino groups towards reactive dyes.

(e) Nitrated cellulose.

These modified fibres have been found to show lower $d \frac{C}{S}$ and lower dye uptake compared to untreated fibres. This has been attributed to the hydrophobic nature, and inertness of nitro groups towards reactive dyes.

(f) Dimethylaminoacetamide-treated (crosslinked) fibre.

The tertiary amino group is not likely to dissociate in aqueous medium, even then the values of $d \frac{C}{S}$ and $d \log_{10}C$
dye uptake have been found to be higher in case of dimethy-laminocetanide-treated fibres. The observed results have been explained on the basis of opening up of the cellulose structure, which is preserved in the modification due to the establishment of crosslinks.

(g) Acetylated fibres.

The introduction of acetyl group is known to introduce hydrophobic and nonionic nature in the fibres; even then higher values of $\log^{\frac{5}{d}}$ and dye uptake were observed possibly due to the opening-up of the cellulose structure. Increasing the degree of substitution after a limit was found to have a reverse effect on dye uptake.

(h) Carboxymethylated fibres.

Carboxymethyl group was observed to have a negative effect on dye uptake and $\log^{\frac{5}{d}}$. These characteristics have been attributed to the increased negative surface charge on these fibres.

(i) 2-Aminoethylsulphuric acid-treated fibres.

The electrokinetic data of 2-Aminoethyl sulphuric acid treated fibres give the indication that the primary
amino group enters into the complex formation and reaction with reactive dye giving higher dye uptake.

6.3 Surface potential at the interface between cellulose and solution of crosslinking agents.

Films of cellulose from cellulose dissolved in cadoxen and of cellulose acetate in acetone were spread on the solution of crosslinking agents. Surface potentials were measured at the interfaces of cellulose/cellulose acetate and the solutions of crosslinking agents. Data were obtained as a function of concentration of dimethylolethylene urea, dimethylolpropylene urea and MgCl$_2$·6H$_2$O and at different pH.

The surface potential was found to increase with the increase of pH from 1 to 3; beyond this pH no significant change was noticed.

The surface potentials decrease with the increase in the concentration of DMEU and DMFU in the solution phase. This was probably due to the accumulation of charges of resin molecules i.e., methylol hydroxyls and carbonyl groups.

An increase in the surface potential with the increase in concentration of MgCl$_2$·6H$_2$O has been explained
on the basis of increased ionization of carbonyl groups of cellulose/cellulose acetate and due to the modification of water structure in the presence of magnesium chloride. The results are in agreement with the thermodynamics of chemisorption of these crosslinking agents on cellulose.

6.4 Physical chemistry of dyeing of cellulosic fibres with reactive dyes.

The effect of different electrolytes on the sorption of the hydrolysed form of four different reactive dyes has been investigated. The electrolytes studied were sodium, ammonium, lithium and magnesium chlorides, and ammonium sulphate, which differ widely in their ability to increase the sorption of hydrolysed reactive dyes by cellulose. Their relative efficiencies were in the order: ammonium chloride > ammonium sulphate > sodium chloride > lithium chloride > magnesium chloride.

The effect of the electrolytes has been discussed in terms of partial screening of the surface charge on cellulose by the crowding of the cations at the cellulose-water interface, pH of the bath, and the ability to modify the structure of water. The ability of the electrolytes to
modify the pH of the solution plays a dominant role in sorption increase at lower concentrations of electrolytes whereas at higher concentrations the ability of the electrolytes to modify the cellulose-water interface plays a decisive role.

The thermodynamics of adsorption of reactive dyes in the presence of sodium chloride, ammonium chloride, and ammonium sulphate has been studied. It was observed that the enthalpy changes in presence of ammonium salts were lower compared to the changes in presence of sodium chloride. These lower values of enthalpy changes in case of ammonium salts have been attributed to the higher desorptions of aqueous monolayer adsorbed on cellulose prior to the dye adsorption.