CHAPTER I: CURRENT THEORIES OF THE EQUILIBRIUM DYEING OF CELLULOSE WITH DIRECT DYES AND THE PROPOSED NEW MODEL FOR THE CELLULOSE-AQUEOUS DIRECT DYE + ELECTROLYTE SOLUTION SYSTEMS
CHAPTER I

CURRENT THEORIES OF THE EQUILIBRIUM DYEING OF CELLULOSE WITH DIRECT DYES AND THE PROPOSED NEW THEORETICAL MODEL FOR THE CELLULOSE-AQUEOUS DIRECT DYE + ELECTROLYTE SOLUTION SYSTEMS.

1. Current Theories of Equilibrium Dyeing:

When cellulose is immersed in a solution of a direct dye, the dye is adsorbed by the cellulose at a decreasing rate until an equilibrium is reached between the concentration of the dye adsorbed on the cellulose and the concentration of the dye present in the dyebath. At this stage, the adsorbed dye is distributed uniformly throughout the fibre and is not confined to the superficial layer of the fibre. Furthermore, the adsorption of direct dyes is completely reversible. The amount of dye adsorbed at equilibrium increases with increasing amounts of salt added to the dyebath. Therefore, addition of salt to the dyebath is an important factor in dyeing cellulose with direct dyes. In early theories, the effect of added electrolytes was attributed to the formation of dye aggregates of just the right dimension, so that they are taken up by the cellulose and are retained in the fibre pores - "the optimum degree of dispersion theory". As Valko points out the presence of aggregates in direct dye solutions is of no importance in itself but merely indicates the associating tendency of the dye molecules. He further states that the intermolecular forces which lead to aggregations in solution are the same as those which attract the dye to the fibre. This idea has received considerable support from the work of Boulton and Morton and Kruger and Rudow on the optical behaviour of dyed fibres and dye solutions. However, as mentioned earlier, recently Bach, Pfeil, Philippar and Reich from optical
absorption studies of dyed cellulose fibres have concluded that
the dye molecules penetrate the cellulose singly and then coagulate
after being deprived of their water of solvation. Thus, according
to Bach et al\textsuperscript{12} the dye molecules are present in the aggregated form
inside the cellulose phase.

Harrison\textsuperscript{13} demonstrated that the negative zeta potential of
cotton with respect to water is considerably reduced by the addition
of inorganic salts. He suggested that this negative zeta potential
was responsible for the increase of equilibrium adsorption with
increasing amounts of salts added to the dyebath. Although the
hypothesis is qualitative, it was the first attempt to explain the
action of the added salt in terms of the electrochemical nature of
dyeing rather than in terms of the then popular "optimum degree of
dispersion theory". The first quantitative relationship between the
amount of dye adsorbed at equilibrium and the concentration of the
electrolytes present in the equilibrium dyebath was developed by
Hanson, Neale and Stringfellow\textsuperscript{14} in terms of an ionic equilibrium of
the Donnan membrane type. They postulated that the dye anions are
first adsorbed by the cellulose and attract the sodium ions near
them in order to maintain electrical neutrality in the cellulose
phase. As a result of this, the concentration of sodium ions in the
cellulose phase becomes greater than in the dyebath. The negative
surface charge on the cellulose surface, which increases with
adsorption of dye anions tends to oppose further adsorption of dye
anions. The effect of adding sodium chloride to the dyebath is
threelfold. (a) It increases the activity of the dye in solution,
(b) It reduces the concentration gradient of gegenions between the surface layer of cellulose and the external solution and thus reduces the osmotic work which must be done in bringing gegenions into the fibre during the adsorption and (c) the negative electrical charge on the surface is screened by the Na\textsuperscript{+} ions, so that dye ions can approach more closely before any electrical repulsion becomes operative. All these effects of the addition of salt reduce the activation energy for the dyeing process. The theory also accounts quantitatively for the decrease in the amount of equilibrium dye adsorption as the carboxyl content of the cellulose is increased.\textsuperscript{15} The kinetic thermodynamic theory of dyeing put forward by Willis, Warwicker, Standing and Urquhart\textsuperscript{6} gives rise essentially to the same Donnan equilibrium picture of the dye adsorption process, but it does not lend itself to the evaluation of the energetics of dyeing. In the development of this theory an assumption is made for simplicity that the forces of attraction between dye and cellulose are constant over a small volume near the active centres in the fibre and are elsewhere zero. This simplifying assumption is equivalent to the division of the solution into an internal cellulose phase and an external aqueous solution phase. Peters and Vickerstaff\textsuperscript{16} have shown that the theories put forward by both Willis et al and Neale et al can be derived using a conventional thermodynamic method. In this method, for the dye and electrolyte ions in the fibre phase, an assumption is made that the activity of an electrolyte may be represented as the product of the ionic activities and that these are proportional...
to the ionic concentrations, the proportionality constant having
the dimensions of a reciprocal volume. The introduction of this
arbitrary constant is equivalent to the division of the solution
phase into an internal cellulose phase and an external aqueous
solution phase. Marshall and Peters\textsuperscript{17} employed the method of
Peters and Vickerstaff for calculating the affinities of fourteen
direct dyes on various fibres. In these calculations the following
simplifying assumptions were made.

(a) The direct dyes are completely dissociated both in solution
and on the fibre.

(b) The dye anions alone are specifically adsorbed by the cellulose,
although other ions may be carried into the fibre for
maintaining electrical neutrality.

(c) The activity terms for the electrolytes present in the external
solution are replaced by concentration terms.

(d) The volume $V$ in litres/kg. of dry fibre is termed the effective
volume of the cellulose phase. This is the so-called "Volume
Term" extensively used in the current theories of dyeing for
calculating internal isotherms, affinities and heats of dyeing.\textsuperscript{2,6,17,18}

Another theory essentially similar to that of Hanson, Neale and
Stringfellow has been suggested by Crank\textsuperscript{19} on the bases of a diffusion
adsorption model. In this theory, direct dyeing is regarded as a
process of activated diffusion with adsorption, the energy of
activation arising from the fact that the diffusing ions have to penetrate a surface potential barrier due to the combined electric charge of the cellulose itself and the dye ions adsorbed on its surface.

In the development of these theories mentioned above no serious account was taken of the effect of carboxyl groups present in the cellulose on the equilibrium adsorption. Standing and Warwicker by applying the Dorman theory of membrane equilibrium for the adsorption of Chrysophenine G taking into account the carboxyl groups in viscose sheet, suggested that the number of carboxyl ions which directly affect the equilibrium adsorption may be less than the total number of carboxyl groups in the viscose sheet.

The main postulates employed in all these current theories of dyeing may be summarized as follows.

i) Dorman equilibria exist between the ions in the internal cellulose phase and the ions in the bulk external solution phase.

ii) Electrical neutrality is maintained in the internal cellulose phase and the bulk external solution phase.

iii) The adsorption of dye on the fibre is directly proportional to the concentration of the free dye ions in the internal solution phase.

iv) Since activities of dye ions are not known, the activity
coefficients of all ions involved in the dyeing equilibrium are considered to be equal to unity.

v) The volume used for the internal cellulose phase is generally constant for a given fibre and is related to the percentage of water vapor taken up by the fibres at 100 percent relative humidity. Values of 0.22, 0.37 and 0.44 litre/kg. of dry fibres have been used extensively for cotton, cuprammonium rayon and viscose fibres respectively.

Of all the assumptions listed above only assumptions (i) and (ii) can very reasonably be applied to describe the distribution of dye ions and counter ions between the internal cellulose phase and the external solution phase. The other assumptions are inadequate in many respects, although the deviations of the experimental data from the theories are attributed by most workers to lack of knowledge regarding the activity of dye ions and aggregating behaviour of direct dyes. The main inadequacies are as follows.

i) The use of an arbitrary constant value for the volume V of the internal cellulose phase.

ii) Uncertainty regarding the exact nature of the adsorption isotherm.

iii) The value to be given for the cellulose surface area available for dye adsorption. The values estimated by different workers vary widely from one another.21-32

iv) The use of concentration terms in place of thermodynamic
activities in calculating the Donnan distribution of ions in the system and the thermodynamic quantities such as affinity, heats and entropies of dyeing.

v) The contribution of ionized cellulose carboxyl groups to the total electrical charge on the cellulose surface and hence its influence on the Donnan distribution of mobile ions. This factor has so far not been considered by most workers in calculating the Donnan distribution of ions.


In view of the above mentioned deficiencies in the existing theories, the following model for the cellulose-aqueous direct dye + electrolyte solution system is presented. This model is based on the following analysis of the system. The cellulose with its internal volume of solution is regarded as an equipotential volume phase i. Between the free dye ions in the internal solution and the dye ions adsorbed on the cellulose surface there exists a Langmuir relation, i.e. the dye ions are adsorbed on the fibre in a monomolecular layer with limiting saturation values for adsorption in this monomolecular layer. The equilibrium between the dye in the internal solution phase i and the dye in the bulk external solution phase ε is governed by the conditions for a Donnan membrane equilibrium. The volume V of the internal cellulose phase is a variable function of the temperature and the electrolyte concentrations of the dyebath and is defined by the product of the surface area of the fibre available for dye adsorption
and the thickness of the electrical double layer present at the 
cellulose-aqueous solution interface. The present method of 
analysis of equilibrium adsorption data on the basis of this 
proposed new model is as follows.

3. The Present Method of Analysis of Equilibrium Adsorption Data.

3.1 List of symbols used:

The following symbols will be used in the development of this 
theoretical analysis.

\[ D_{dp} \] Concentration of dye adsorbed on cellulose in gram 
ions/kg. of dry fibre.

\[ D_{dph} \] Concentration of adsorbed dye in ions/sq.cm. of cellulose.

\[ D_{di} \] Concentration of dye in internal cellulose phase in 
moles/litre.

\[ D_{do} \] Concentration of dye in external equilibrium solution in 
moles/litre.

\{ Na and Cl \} Sodium and chloride ion concentrations respectively in the 
\{ Cl \} external equilibrium solution in moles/litre.

\{ Na and Cl \} Sodium and chloride ion concentrations respectively in the 
\{ Cl \} internal cellulose phase in moles/litre.

\[ z \] Valency of dye anion.

\[ \lambda \] The Donnan distribution coefficient.

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The Donnan potential in millivolts.

\[ \Psi_D \]

Reciprocal thickness of the electrical double layer, which is given by

\[ T^{-1}_{\text{cm}} = 26 \sqrt{\frac{2N\pi e^2}{\varepsilon_0 k T}} \times N \times 10^5 \]

... (1.1)

where \( N \) is Avogadro's number, \( \varepsilon_0 \) is dielectric constant of water, \( k \) the Boltzmann constant, \( T \) the absolute temperature, and \( e \) the electronic charge in electrostatic units.

\( V \)

The volume of the internal cellulose phase in litres/kg. of dry fibre.

\( A \)

The surface area of cellulose available for dye adsorption.

\[ 10^{16} \frac{\text{ions/sq.cm.}}{D^7^s^*} \]

The limiting co-area. It is defined as the area in \( \AA \) per adsorbed dye molecule when the available surface area of adsorbent is covered with a monolayer of dye = \( \sqrt{D^7^s^*} \) ions/sq.cm. under the given experimental conditions.

\[ \frac{A}{D} \times 10^5 \]

The volume of the internal cellulose phase in litres per kg. of dry cellulose. ... (1.2)

\( \Delta \mu^O \)

The affinity of dye molecules in k.cal./mole.

\( \Delta H^O \)

The differential heat of adsorption in k.cal./mole.

\( \Delta S^O \)

The entropy of adsorption in cal.deg.\(^{-1}\)mole\(^{-1}\).
\[ W = \text{Cellulose surface charge per unit volume of internal cellulose phase} = \frac{C_{\text{COO}^-} + z \sqrt{\frac{d}{q}}}{V} \text{ gram equivalents per litre.} \]

where \( C_{\text{COO}^-} \) = concentration of cellulose carboxyl groups in gram ions/kg. of dry cellulose.

\[ W^* = C_{\text{COO}^-} + z \sqrt{\frac{d}{q}} \text{ gram equivalents per kg. of dry cellulose.} \]

3.2 Calculation of the Volume of the Internal Cellulose Phase:

In the current theories of dyeing, \( V \) which is the volume of the internal cellulose phase in litres/kg. of dry fibre is generally used as an arbitrary and indeterminate parameter. Hanson, Neale and Stringfellow\(^{14}\) ascribed a value of 0.22 litres per kg. of dry fibre to the volume of the cellulose phase on the ground that this gave the most satisfactory agreement between the calculated and observed dye adsorption. They also noted, that this figure agrees with the amount of water adsorbed by cotton at 90\(^\circ\)C and 100\% R.H. according to the results of Urquhart and Williams.\(^{25}\) Accordingly several workers have used the volumes of 0.22, 0.37 and 0.44 litres/kg. of dry cotton, cuprammonium rayon and viscose fibres respectively, based on the moisture sorption data of Urquhart and Eckersall\(^{54}\) at 90\(^\circ\)C for cotton and 22\(^\circ\)C for the other fibres (data at 90\(^\circ\)C not being available), the relative humidity being 100\% in all cases. Thus, the value of \( V \) was regarded as a constant for a particular type of cellulose independent of temperature, salt and dye concentration in the dyebath. However, it was soon realised that it was a very arbitrary value which could be varied to get agreement between the experimental results and the
Schofield and Talibuddin in an attempt to measure the internal surface of jute fibres considered the Gouy theory of the ionic distribution in the diffuse component of the electrical double layer at the fibre-solution interface and extended the treatment to obtain an expression for the small increase in concentration that occurs when a salt solution is shaken up with a sample of dry fibre. In this expression, the major contribution to the volume of the internal phase in jute fibres comes from a term, which is proportional to the product of the surface area of the fibre and the thickness of the electrical diffuse double layer at the jute-electrolyte solution interface. Alexander and Kitchner on the basis of the assumptions that (a) the important factor in the sorption of acids and dyes by wool is the effective range of the interionic forces, and (b) this range is modified by the concentration of mobile ions in the solution, have considered the effective range on the solution side to be of the same order as the thickness of a diffuse double layer under the given conditions of adsorption. Recently Ikeda and Isemura in an attempt to explain the surface pressures of ionized monolayers assumed that the boundary between the surface and the bulk phases behaves as a semipermeable membrane and that, the distribution of diffusible counter and co-ions between these phases is governed by a Donnan membrane type equilibrium. The surface phase thickness is shown to be equivalent to twice the thickness of the electrical diffuse double layer if the potential of the membrane is considered equal to half of that due to the ionized groups in the Gouy theory.
Fig. 1 Plots of $\sinh \frac{e^{\psi D}}{kT} \text{ vs.} \frac{1}{K_w}$ and $\sinh \frac{e^{\psi D}}{kT} \text{ vs.} \frac{1}{\sqrt{K_w}}$

Figs. 2 & 3 Adsorption Isotherms for Chlorazol Sky Blue FF on Cuprammonium rayon fibre. NaCl = 10.0 g./litre Temperature = 50°C
reciprocal of the square root of the concentration of sodium chloride added to the dyebath. They have not given any theoretical explanation for the use of such a variable volume term. However, from equations 1.1 and 1.2 which are given above, according to the proposed model, it can easily be seen that since $T$ varies directly with $\sqrt{NaCl}$, $V$ will vary inversely as $\sqrt{NaCl}$. Neale and Saha and Sivarajan and Jayaram have measured the Donnan e.m.f. in cellophane sheet-aqueous alkali metal chloride solution systems. An analysis as explained below of their results also support the use of a variable volume term. Thus, if we assume that the measured e.m.f. $\psi_D$ is equal to the Donnan potential which exists in the charged cellulose-aqueous electrolyte solution system, then $\psi_D$ can be expressed by the following equation.

\[ \psi_D = \frac{kT}{e} \sinh^{-1} \frac{w^*}{2 \sqrt{\pi} V} \]

i.e. \[ \sinh \frac{e\psi_D}{kT} = \frac{w^*}{2 \sqrt{\pi} V} \] ... 1.3

where \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( e \) is the electronic charge, \( w^* \) is the total surface charge, \( \sqrt{\pi} \) is the concentration of electrolyte and \( V \) is the internal volume of the cellulose phase.

If the "Volume Term" \( V \) used in this equation is constant and has the value of 0.44 litre/kg. of dry cellulose, which is the value used in earlier theories of dyeing\(^2,14,16\) a plot of $\sinh \frac{e\psi_D}{kT}$ versus $\sqrt{\pi}NaCl$ would be linear. On the other hand, if the variable volume term \( V = \frac{A}{T} \times 10^{-3} \) litres/kg. of dry fibre which is proposed in
the present thesis, is substituted in equation 1.3 above, \( \tau \) also
being substituted from the equation 1.1, the following equation
is obtained

\[
\sinh \frac{e \psi_D}{kT} = \frac{W^*}{2^B \sqrt{m_7}}
\]

where \( B \) is a constant for the solvent at the given temperature.

According to this equation 1.4, a plot of \( \sinh \frac{e \psi_D}{kT} \) versus \( \frac{1}{\sqrt{m_7}} \)
would give a straight line. An examination of the figure 1 (see p.41),
which is obtained from the analysis of the results of Sivarajan and
Jayaraman shows that the plots of \( \sinh \frac{e \psi_D}{kT} \) versus \( \frac{1}{\sqrt{m_7}} \) are
linear in agreement with equation 1.4. These results of the measured
Donnan e.m.f. therefore support the hypothesis that the "Volume Term"
\( V \) is not constant but varies with electrolyte concentration. Further
justification for the use of variable "Volume Term" is provided from
a comparison of the thermodynamic quantities which are discussed
later.

3.3 Calculation of Internal Dye Concentration:

In a model based on a Donnan distribution since the two Donnan
phases have each to be electrically neutral, for electrical
neutrality in the internal cellulose phase,

\[
W + C_1 \lambda_1 + z D_1 \lambda_1 = N_{Na} \lambda_1
\]

and for electrical neutrality in the external bulk solution phase,

\[
C_1 \lambda_1 + z D_1 \lambda_1 = N_{Na} \lambda_1
\]
The Donnan distribution of mobile ions leads to the following equation.

\[
\frac{\sqrt{N_{Na}^7}}{\sqrt{N_{Na}^1}} = \frac{\sqrt{C_{Na}^7}}{\sqrt{C_{Na}^1}} = \left[ \frac{\sqrt{D_{Na}^7}}{\sqrt{D_{Na}^1}} \right]^{1/2} = \lambda \quad \ldots \quad 1.7
\]

\[
\therefore \frac{\sqrt{C_{Na}^7}}{\sqrt{N_{Na}^1}} \quad \ldots \quad 1.8
\]

Substituting this value of \( \frac{\sqrt{C_{Na}^7}}{\sqrt{N_{Na}^1}} \) in equation 1.5,

\[
W + \frac{\sqrt{N_{Na}^7} - \sqrt{C_{Na}^7}}{\sqrt{N_{Na}^1}} + 2 \sqrt{D_{Na}^7} = \sqrt{N_{Na}^1} \quad \ldots \quad 1.9
\]

i.e. \( \sqrt{N_{Na}^1} - \sqrt{N_{Na}^7} (z \sqrt{D_{Na}^7} + w) - \sqrt{N_{Na}^7} \sqrt{C_{Na}^7} = 0 \)

\[
\therefore \sqrt{N_{Na}^1} = \frac{(z \sqrt{D_{Na}^7} + w) \pm \sqrt{(z \sqrt{D_{Na}^7} + w)^2 + 4 \sqrt{N_{Na}^7} \sqrt{C_{Na}^7}}}{2} \quad \ldots \quad 1.10
\]

Neglecting the term \( 2 \sqrt{D_{Na}^7} \) being negligible in comparison with \( W \), and also since the equation with the negative sign is inadmissible,

\[
\sqrt{N_{Na}^1} = \frac{W + \left( W^2 + 4 \sqrt{N_{Na}^7} \sqrt{C_{Na}^7} \right)^{1/2}}{2} \quad \ldots \quad 1.11
\]

Dividing throughout by \( \sqrt{N_{Na}^7} \),

\[
\frac{\sqrt{N_{Na}^1}}{\sqrt{N_{Na}^7}} = \frac{W}{2 \sqrt{N_{Na}^7}} + \left[ \frac{W}{2 \sqrt{N_{Na}^7}} \right]^2 + \frac{\sqrt{C_{Na}^7}}{\sqrt{N_{Na}^7}} \quad \ldots \quad 1.12
\]

The above equation is analogous to equation 14 of Peters and Vickerstaff. However, in equation 14 of Peters and Vickerstaff the contribution of carboxyl groups to the total charge of the
surface has not been considered. It is evident from the quantitative explanation given below that it is important to consider the influence of the ionized carboxyl groups of the cellulose on the dye adsorption. Therefore, substituting

\[ \frac{Z \sqrt{D_{D_1}^2 + \sqrt{C00-7}^2}}{V} \]

for \( W \) the following equation is obtained.

\[ \frac{N_{Na_1}}{N_{Na_2}} = \frac{Z \sqrt{D_{D_1}^2 + \sqrt{C00-7}^2}}{2 \sqrt{N_{Na_2} V}} \left[ \left( \frac{Z \sqrt{D_{D_1}^2 + \sqrt{C00-7}^2}}{2 \sqrt{N_{Na_2} V}} + \frac{C_{L_4}^2}{N_{Na_2}} \right) \right]^{\frac{1}{2}} \quad \ldots \quad 1.13 \]

Now substituting in equation 1.13 the value of \( \frac{N_{Na_1}}{N_{Na_2}} \) from equation 1.7,

\[ \frac{\sqrt{D_{D_1}}}{\sqrt{D_{D_1}}} = \left\{ \frac{Z \sqrt{D_{D_1}^2 + \sqrt{C00-7}^2}}{2 \sqrt{N_{Na_2} V}} + \left[ \frac{Z \sqrt{D_{D_1}^2 + \sqrt{C00-7}^2}}{2 \sqrt{N_{Na_2} V}} + \frac{C_{L_4}^2}{N_{Na_2}} \right] \right\} \quad \ldots \quad 1.14 \]

In the presence of excess of sodium chloride added to the dyebath,

\[ \sqrt{C_{L_4}^2} \approx \sqrt{N_{Na_2}} \]

\[ \therefore \frac{\sqrt{D_{D_1}}}{\sqrt{D_{D_1}}} = \left\{ \frac{Z \sqrt{D_{D_1}^2 + \sqrt{C00-7}^2}}{2 \sqrt{N_{Na_2} V}} + \left[ \frac{Z \sqrt{D_{D_1}^2 + \sqrt{C00-7}^2}}{2 \sqrt{N_{Na_2} V}} + 1 \right] \right\} \quad \ldots \quad 1.15 \]

\[ \therefore \ln \left( \frac{\sqrt{D_{D_1}}}{\sqrt{D_{D_1}}} \right) = Z \sinh^{-1} \frac{Z \sqrt{D_{D_1}^2 + \sqrt{C00-7}^2}}{2 \sqrt{N_{Na_2} V}} \]

\[ \therefore \frac{1}{\sqrt{D_{D_1}}} = \frac{1}{\sqrt{D_{D_1}}} \times \frac{Z \sinh^{-1} \frac{Z \sqrt{D_{D_1}^2 + \sqrt{C00-7}^2}}{2 \sqrt{N_{Na_2} V}}}{2 \sqrt{N_{Na_2} V}} \quad \ldots \quad 1.16 \]

The introduction of the concentration of ionized carboxyl groups \( \sqrt{C00-7} \) of the cellulose into these equations is necessary, since it contributes significantly to the negative charge of the cellulose
surface. The Donnan distribution and hence the value of $J_{i}$ is markedly influenced by the presence of the carboxyl groups $COO^{-}$ in the cellulose. Particularly, in the case of lower values of $D_{q}$, the neglect of the carboxyl group $COO^{-}$ contribution to the total charge of the cellulose surface will introduce serious errors in the calculated values of $D_{1}$. For example, in the case of the adsorption of Chlorazol Sky Blue FF on viscose at 50°C and in the presence of 2 g./litre of NaCl added to the dyebath, when $D_{q} = 17.5 \times 10^{3}$ moles/kg. of dry fibre and $D_{w} = 35.50 \times 10^{6}$ moles per litre, the calculated value of $D_{1}$ taking into account the contribution of the carboxyl groups which is equal to $54.0 \times 10^{5}$ moles/kg. of dry viscose, is equal to $0.237 \times 10^{6}$ moles/litre. The calculated value of $D_{1}$ without taking into account the contribution of the carboxyl groups is equal to $2.179 \times 10^{6}$ moles/litre. Thus in this case, the neglect of the contribution of carboxyl groups to the total charge of the cellulose surface introduces in this case an error of 89.12 percent. However, in most of the current theories of dyeing $^{2,6,14,16}$ this factor has not been considered. In the present study, the total contribution $D_{q} + COO^{-}$ to the cellulose surface charge has been taken into account in all the calculations of the values of $D_{1}$ and $a_{w}$.  

3.4 Calculation of Mean Ionic Activities.

In order to assess the influence on the calculated thermodynamic quantities, of using mean ionic activities in place of concentration terms, mean ionic activities of all ions have been calculated as follows.
From equation 1.7 and equation 1.16,
\[
\left[ \frac{1}{\lambda} \right]^2 = e^{3 \sinh^{-1} \frac{\sqrt{D_{\lambda}} + \sqrt{D_{\sigma}}}{2 N_{\sigma}^{-}}} \frac{1}{V} \quad \ldots \quad 1.17
\]

Equation 1.17 gives the values of $\lambda$. These values of $\lambda$ are substituted in equation 1.7, viz. $\frac{N_{\sigma}}{N_{\sigma}} = \lambda$ and $\frac{N_{\sigma}}{N_{\lambda}}$ is calculated for the corresponding value of $\frac{N_{\sigma}}{N_{\lambda}}$. The mean ionic activities corresponding to these concentrations of $\frac{N_{\sigma}}{N_{\sigma}}$ and $\frac{N_{\sigma}}{N_{\lambda}}$ are calculated by interpolation of the published mean activity coefficients $f_+^+$ of the sodium chloride. Then the refined value of the Donnan distribution coefficient is given by
\[
\lambda_{\text{refined}} = \frac{f_+^+ \sqrt{N_{\sigma}}}{f_{\lambda}^+ \sqrt{N_{\lambda}}^1} \quad \ldots \quad 1.18
\]

Since these $\lambda_{\text{refined}}$ values are thermodynamically more correct than $\lambda$ values calculated from concentration terms, all adsorption isotherm data are recalculated for $\lambda_{\text{refined}}$ using equation 1.18.

These $\lambda_{\text{refined}}$ values are then used to calculate the internal mean ionic activity $\sqrt{a_+^1}$ of the dye using the following equation, which follows from equation 1.18 and equation 1.18.
\[
\frac{1}{\sqrt{a_+^1}} = \frac{1}{\sqrt{a_+^0}} \left( \frac{1}{\lambda_{\text{refined}}} \right)^2 \quad \ldots \quad 1.19
\]

where $\sqrt{a_+^0}$ is the mean ionic activity of the dye in the bulk external solution. Values of $\sqrt{a_+^0}$ are calculated from the mean activity coefficients of the dye corresponding to the various bulk external solution concentrations $\sqrt{D_{\sigma}}$ as given below.
From the studies on thermodynamic properties of direct dye solutions (see Chapter II) the following form of the Debye-Hückel expression appeared to represent more closely the mean activity coefficients of direct dyes dissociated completely in aqueous solutions.

\[ -\log f_+ = \frac{AZ_+ Z_- \sqrt{\mu}}{1 + \sqrt{\mu}} \]

In this equation, \( f_+ \) is the mean ionic activity coefficient of the dye anion and \( Z_+ \), \( Z_- \) are the valencies of the cation and anion respectively of the dye. \( \mu \) the ionic strength of the solution is given by the equation,

\[ \mu = \frac{1}{2} \sum C_i Z_i^2 \]

where \( C \) is the concentration in gram ions per litre of the ion \( i \) of valence \( Z_i \). \( A \) is a constant for the solvent and is given by the equation,

\[ A = \frac{N^2 \varepsilon^3}{2.505 \varepsilon^3/\gamma} \left( \frac{2 \pi}{1000} \right)^\frac{1}{2} \frac{1}{(\varepsilon T)^3/2} \]

where \( N \) is the Avogadro's number, \( \varepsilon \) the electronic charge in e.s.u., \( \varepsilon \) the dielectric constant at the absolute temperature \( T \) and \( R \) is the gas constant.

Thus using equation 1.20, the mean ionic activity coefficients \( f_+ \) of dye anions have been calculated.

These mean ionic activity coefficients are then used to calculate the mean ionic activities \( f_+ \) of the dye anions corresponding to the various equilibrium dyebath concentrations.
3.5 Nature of the Adsorption Isotherm.

In most of the current theories of dyeing it has generally been assumed that \( \frac{D}{Q} = K \frac{D}{A} \). That is, there is a direct proportionality between the amount of dye present in the internal cellulose phase and the amount of dye adsorbed at equilibrium. However, a plot of \( \frac{D}{Q} \) versus \( \frac{1}{D} \) or \( \frac{1}{Q} \) is never linear except in the initial portions and the isotherms resemble much more closely a Langmuir type adsorption isotherm. This is clearly brought out in figures 2 and 3. Furthermore, in the thermodynamic reasoning put forward by Peters and Vickerstaff to explain the theories of Willis, Warwick, Standing and Urquhart and Hanson, Neale and Stringfellow an assumption is made that the activity of the adsorbed dye may be represented as the product of the ionic activities of the dye and that these are proportional to the ionic concentrations, the proportionality constant having the dimensions of a reciprocal volume \( \left( \frac{1}{V} \right) \). Here the volume \( V \) is nothing but the empirical constant volume of the internal cellulose phase. However, simple calculations show that the molar concentrations of the dye in the fibre phase using this argument exceed in many cases the solubility limit of the dye in aqueous solutions containing added electrolytes. For instance, in the case of the equilibrium adsorption of Chlorazol Sky Blue FF on viscose at 50°C temperature and in the presence of 10 g./litre of NaCl, when the equilibrium dyebath concentration \( \frac{D}{Q} = 561.5 \times 10^6 \) moles/litre, the amount of dye adsorbed \( \frac{D}{Q} = 78.68 \times 10^5 \) moles/kg. of dry viscose. Since \( V = 0.44 \) litre/kg. of dry viscose, the concentration \( \frac{D}{Q} = 174.3 \times 10^5 \) mole/litre to be adsorbed.
Adsorption Isotherms for Chlorazol Sky Blue FF on Cuprammonium rayon fibre. NaCl = 10.0 g./litre  Temperature = 50°C

Figs. 2 & 3  Adsorption Isotherms for Chlorazol Sky Blue FF on Cuprammonium rayon fibre. NaCl = 10.0 g./litre  Temperature = 50°C
moles/litre. This figure exceeds, by a factor of 90, solubility of Chlorazol Sky Blue FF under the same condition of temperature and sodium chloride concentration, the solubility being $1.895 \times 10^3$ moles/litre. Therefore, it is apparent that the definition of the activity of the dye in the fibre phase in terms of the concentration $\frac{\text{D}}{\text{V}}$ is incorrect. It was therefore thought in the present work that a more reasonable approach to the evaluation of the activity of adsorbed dye on the cellulose would be to use the factor $\frac{\theta}{1-\theta}$ for the activity of the adsorbed dye anions, where $\theta = \frac{\text{D}}{\text{N}}$. The use of the factor $\frac{\theta}{1-\theta}$ to describe the activities of adsorbed dye ions is based on the work of Fowler, Kar, Sexl, and Miller. They have translated the kinetic ideas, which Langmuir used, into the idiom of statistical mechanics to arrive at the Langmuir adsorption isotherm and have shown that the activity of adsorbed molecules may be represented by the term $\frac{\theta}{1-\theta}$, where $\theta$ is the fraction of the sites occupied by the adsorbed molecules. Furthermore, Darwalla and D'Silva have shown that the adsorbed dye reaches a saturation value corresponding to the formation of a monolayer and have used with reasonable success the expression $\frac{\theta}{1-\theta}$ to describe the activity of adsorbed dye ions on cellulose fibres. Using the factor $\frac{\theta}{1-\theta}$ for the activity of adsorbed dye ions it has been shown in the present work that on the basis of the same thermodynamic reasoning as Peters and Vickerstaff the adsorption isotherms for direct dyes on cellulose can be described by a Langmuir type equation.
3.6 The Langmuir Type Equation for the Adsorption of Direct Dyes on Cellulose.

The Langmuir type equation for the adsorption of direct dyes on cellulose can be derived as follows.

In the internal cellulose phase, the chemical potential $\mu_i$ of the mobile dye ion is,

$$\mu_i = \mu_1 + RT \ln \frac{\theta}{1-\theta}$$  \hspace{1cm} (1.25)

where $\mu_1$ is the standard chemical potential of the dye ion in the internal cellulose phase and $\frac{\theta}{1-\theta}$ is the mean activity of dye ions present in the internal cellulose phase.

If the dye is adsorbed on specific sites on the surface, the chemical potential $\mu_\phi$ of the adsorbed dye anion is

$$\mu_\phi = \mu_\phi + RT \ln \frac{\theta}{1-\theta}$$  \hspace{1cm} (1.24)

where $\mu_\phi$ is the standard chemical potential of the adsorbed dye ions and $\theta = \frac{\theta}{1-\theta}$, $\frac{\theta}{1-\theta}$ being the amount of dye adsorbed on the cellulose surface, when it is saturated. The activity of the adsorbed dye ions as explained above is given by the factor $\frac{\theta}{1-\theta}$. When the system reaches equilibrium

$$\mu_i = \mu_\phi$$  \hspace{1cm} (1.25)

Therefore equating equation 1.23 and equation 1.24,

$$\mu_1 + RT \ln \frac{\theta}{1-\theta} = \mu_\phi + RT \ln \frac{\theta}{1-\theta}$$  \hspace{1cm} (1.26)

$$\therefore \Delta \mu = \mu_1 - \mu_\phi = RT \ln \frac{\theta}{1-\theta} - RT \ln \frac{\theta}{1-\theta}$$  \hspace{1cm} (1.27)
where $\Delta \mu^o$ the difference between the standard chemical potential of the dye in the two phases is a quantitative measure of the thermodynamic affinity of the dye for the fibre.

Substituting, $\theta = \frac{\Delta \mu^p}{\Delta \mu^o}$ in equation 1.27 and rearranging the terms,

$$
-\Delta \mu^o = RT \ln \left( \frac{\Delta \mu^p}{\Delta \mu^o} \right) = RT \ln \left( \frac{\Delta \mu^p}{\Delta \mu^o} \right)
$$

Substituting, $\theta = \frac{\Delta \mu^p}{\Delta \mu^o}$ in equation 1.27 and rearranging the terms,

$$
\theta = \frac{\Delta \mu^p}{\Delta \mu^o} = \frac{\Delta \mu^p}{\Delta \mu^o} = \frac{\Delta \mu^p}{\Delta \mu^o}
$$

Taking logarithms on both sides

$$
\log \frac{\Delta \mu^p}{\Delta \mu^o} = \log \left( \frac{\Delta \mu^p}{\Delta \mu^o} \right) + \log \frac{\Delta \mu^p}{\Delta \mu^o}
$$

or

$$
\log \left( \frac{\Delta \mu^p}{\Delta \mu^o} \right) = \log \left( \frac{\Delta \mu^p}{\Delta \mu^o} \right) + \log \frac{\Delta \mu^p}{\Delta \mu^o}
$$

Since equation 1.29 corresponds to one form of the Langmuir type adsorption isotherm, the term $\log \frac{\Delta \mu^p}{\Delta \mu^o}$ should be constant, being the affinity value. Therefore an important test of the equation 1.29 for the validity of a Langmuir type relation, is that a plot of $\log \left( \frac{\theta}{1-\theta} \right)$ versus $\log \left( \frac{\Delta \mu^p}{\Delta \mu^o} \right)$ should give a straight line of unit slope, if the proposed model for the mechanism of dyeing were correct.

Equation 1.28 can be rearranged to get the following equation 1.30, which is the more familiar form of the Langmuir equation.
According to this equation a plot of $\frac{1}{\Delta H_1}$ versus $\frac{1}{T}$ should give a straight line, the slope being equal to

$$-\frac{\Delta \mu^o / RT}{\Delta H_1}$$

and the intercept being equal to $\frac{1}{\Delta H_s}$.

If activities are replaced by concentration terms for dye ions in the solution phase equations 1.29 and 1.30 can be written as follows.

$$\log \frac{\phi}{1-\phi} = \log \Delta H_1 + \log e$$

$$\frac{1}{\Delta H_q} = \frac{-\Delta \mu^o / RT}{\Delta H_1} + \frac{1}{\Delta H_s}$$

3.7 Affinity of Dyeing.

The thermodynamic affinity of the dye is defined as the difference between the standard chemical potential of the dye in solution in the internal cellulose phase and the standard chemical potential of the dye adsorbed on the surface of the cellulose. It is a measure of the tendency of a dye molecule to move from its standard state in solution to its standard state when adsorbed on the cellulose and gives a quantitative expression for the affinity of the adsorbed dye for cellulose. It is clear from the Langmuir type equation 1.29 explained above that the intercept of the straight line on the $\log \frac{\phi}{1-\phi}$ axis in the graph of $\log \frac{\phi}{1-\phi}$ versus $\log \Delta H_1$ gives the value of $\Delta \mu^o / RT$, which can be used to
calculate the affinity $\Delta \mu^\circ$ of the dye for the fibre at the
temperature $T$. By this method, the thermodynamic affinities of
the dye for the cellulose were calculated. Since no attempt has been
made by earlier workers to use mean ionic activities corresponding
to the concentrations of dye ions and other ionic species present
in the equilibrium dyebath in order to estimate the thermodynamic
quantities such as affinities, enthalpy and entropy of dyeing,
this has also been done in the present study. Mean ionic activities
of dye ions have been calculated as explained above under section
3.4 of this chapter. Furthermore, for comparison, the affinities
have been calculated using the constant arbitrary values of the
volume term $V$ used by earlier workers and the variable volume term
$V = \frac{A}{n} \times 10^{-3}$ litre/kg. of dry fibre, which has been proposed
in the present thesis. All these affinity values have been used
to calculate heat of dyeing and entropy of dyeing as explained
in the following sections.

3.8 Heat of Dyeing.

The standard differential heat of dyeing, $-\Delta H^\circ$, may be
defined as the heat adsorbed when one mole of dye is adsorbed
by an undyed fibre from an infinitely dilute solution. Assuming
that $-\Delta H^\circ$ remains constant over a small range of temperature,
heat of dyeing is most conveniently determined by measurements
of the affinities of the dye for the cellulose at different
temperatures and using the following well known equation.
where $\Delta \mu^0_1$ and $\Delta \mu^0_2$ are affinities at the two absolute temperatures $T_1$ and $T_2$ respectively.

3.9 Entropy of Dyeing.

Entropy of dyeing is defined as the difference between the standard entropies of dye in the solution of the internal cellulose phase and when adsorbed on the surface of the cellulose. The entropy of dyeing may be regarded as a measure of the degree of orientation and restraint achieved on the fibre as compared with the solution. From the affinity and heat of dyeing the standard entropy of dyeing $\Delta S^0$ may be calculated using the following equation.

$$\Delta H^0 = \Delta S^0 - T \Delta S^0$$

All these thermodynamic parameters, namely, $-\Delta \mu^0$, $-\Delta H^0$ and $-\Delta S^0$ the derivations of which are explained in this chapter, are discussed in detail in Chapter IV which deals with the comparative analysis of the experimental data in terms of the modified theory of dyeing put forward in the present thesis and the other current theories of dyeing.
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