CHAPTER V

SUMMARY AND CONCLUSIONS

The mechanism of dyeing cellulosic fibres with direct dyes has been studied by several workers during the last three decades. However, current theories of the dyeing mechanism are inadequate in many respects and cannot explain all the experimental data. The object of the present work was therefore to study both theoretically and experimentally the physical chemistry and thermodynamics of dyeing cellulose with direct dyes and put forward a clear picture of the dyeing mechanism based on modern physicochemical concepts of surface chemistry, since the adsorption of dyes from aqueous solution on to the fibre phase can be regarded as an interfacial phenomenon. The theoretical explanation given by earlier workers for the equilibrium dyeing of cellulosic fibres with water soluble anionic direct dyes is generally based on the following model for the cellulose-aqueous dye + electrolyte solution system.

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

ii) Electrical neutrality of 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) The activity coefficients of all the ions is 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 fibre at 100% R.H.

In this model, assumptions (i) and (ii) can very reasonably be applied to describe the distribution of dye ions and counterions between the internal cellulose phase and the external solution phase. However, the model is inadequate in many respects. These inadequacies are as follows.

i) The use of an arbitrary constant value for the volume of the internal solution phase i.e. the solution phase inside the cellulose fibre. This is the so-called “Volume Term” used extensively in dyeing theory.

ii) Uncertainty regarding the exact nature of the adsorption isotherm i.e. whether it is Freundlich, Langmuir or a direct partition.

iii) The value to be given for the cellulose surface area available for dye adsorption. Different workers have used different values for the area available for dye adsorption.

iv) The use of concentration terms instead of thermodynamic activities in calculating the Donnan distribution of ions in the system and 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 has been neglected in existing theories.

In order to investigate the factors mentioned above, the following detailed experimental studies were carried out. In all these experiments two highly purified direct dyes, Chlorasol Sky Blue FF (C.I. Direct Blue 1, sodium salt) and Chrysopherine G (C.I. Direct Yellow 12, sodium salt) were used. The cellulosic fibres used in the present investigation were purified cotton, viscose and cuprammonium rayon.

i) Equilibrium dyeing and adsorption isotherms:

Equilibrium adsorption isotherms were measured for the cellulose-aqueous direct dye solution system as a function of temperature and concentration of uni-univalent electrolyte added to the dyebath. The results showed that the adsorption process could be represented by a Langmuir type isotherm. The isotherms showed a characteristic levelling off to form a plateau region at equilibrium dyebath concentrations which correspond to those at which the dye begins to form aggregates.

ii) Specific surface areas of fibres:

In view of the great importance of knowing the surface area of fibre available for the adsorption of polar dye molecules on the fibre surface, detailed experiments were carried out of the
nitrogen and water surface areas for dry and water swollen uncollapsed fibres using the well known Brunauer, Emmett, and Teller (B.E.T.) method. The results showed that the specific nitrogen surface areas of water swollen uncollapsed fibres were very large and the ratio $\frac{1}{g}N_g/\Xi H_2O$ tends to unity for all the three types of cellulose fibres studied. The amount of dye adsorbed by water swollen uncollapsed fibres under any given conditions was found to be identical with the amount adsorbed by the dry fibres when dyed under the same conditions. It was concluded that the nitrogen surface area of water swollen uncollapsed fibres is a measure of the surface area available for dye adsorption. The nitrogen surface areas of water swollen uncollapsed cellulose fibres have therefore been used for calculating the volume of the internal cellulose phase, that is the variable "Volume Term". For this purpose, these areas have been multiplied by the factor $\frac{1}{g}$cm. where $\Xi$ is the thickness of the electrical double layer and varies with temperature and electrolyte concentration. The use of such a variable "Volume Term" in the calculation of the parameters of the Langmuir isotherm, the Donnan ratio $\lambda$ and the thermodynamic quantities $-\Delta H^0$, $-\Delta S^0$ and $-\Delta G^0$ for the adsorption process, gives better agreement between the theory and the experiments than the use of a constant "Volume Term".

iii) Physicochemical properties of aqueous direct dye solutions:

Since it is well known that the physicochemical and thermodynamic properties of aqueous direct dye solutions markedly
influence the adsorption of dye on fibres, a detailed study was made of the following properties of aqueous solutions of Chlorazol Sky Blue FF and Crysophenine G both in the presence and absence of uni-univalent electrolyte (NaCl) added to the dye solutions. The properties studied were (a) The electrical conductivity of dye solutions as a function of temperature, dye concentration and added salt concentration. (b) The solubility of these dyes in aqueous solutions as a function of temperature and salt concentration. Information on the state of aggregation of dye solutions was obtained from a study of both (a) and (b). Definite maxima in the equivalent conductivity versus dye concentration curves occurred at different concentrations depending on the temperature of the solution and the concentration of electrolyte (NaCl) added to the dye solution. The maxima have been interpreted successfully in terms of the formation of ionic aggregates at the concentrations corresponding to the rise in the conductivity curves. The nature of the solubility versus temperature and solubility versus salt concentration curves also gives strong evidence for formation of dye aggregates. In addition, from a study of solubility it was possible to evaluate thermodynamic properties such as mean activity coefficients of dye ions using the solubility product principle and the Debye-Hückel theory. The dyes in dilute solutions were found to behave like strong electrolytes and obeyed one form of the Debye-Hückel expression.

iv) The effect of water structure changes on the dyeing behaviour:

It is well known that in aqueous solutions of electrolytes, the
water structure breaking action of the electrolyte ions affects the thermodynamic properties of the solution and hence can influence the properties of other ions, such as dye ions which are present in the solution. This factor will also influence the adsorption of dyes from such solutions onto the fibre surface. Experiments were therefore carried out to investigate the relation between the extent of dye adsorption and the water structure breaking action of the electrolyte cations for a series of uni-univalent electrolytes, namely, lithium chloride, sodium chloride, potassium chloride, rubidium chloride and cesium chloride which were added to the dyebath. The results showed that there was a marked correlation between the water structure breaking action of the alkali metal cations, the extent of dye adsorption, and the displacement of water molecules on the cellulose surface by the preferentially adsorbed dye molecules.

As a result of all these studies and a detailed theoretical analysis of the parameters which influence the adsorption process, a new model has been proposed for the mechanism of dyeing cellulose with direct dyes from aqueous electrolyte solutions.

The proposed new model is as follows:

1) Donnan equilibria exist between the ions in the internal cellulose phase and the ions in the bulk external solution phase.

2) Electrical neutrality of ions is maintained both in the internal cellulose phase and the external solution phase.
iii) The value $V$ of the internal cellulose phase varies in a well defined manner with temperature and total concentration of the electrolytes present in the external dye solution. The volume $V$ is defined as the product of the thickness of the electrical diffuse double layer at the cellulose-solution interface and the specific surface area of the cellulose.

iv) A Langmuir type adsorption equation can be used to describe the relationship between the adsorbed dye ions and the dye ions present in the internal volume $V$.

v) The surface area available for the adsorption of nitrogen in a close packed monolayer in water swollen uncollapsed fibres is also the total area available for the adsorption of direct dyes.

vi) Use of mean activities in place of concentrations show a significant improvement in the evaluated thermodynamic quantities involved in adsorption.

This model gives a more unified picture of the dyeing mechanism and is able to explain not only the experimental data described in the present work but also those obtained by earlier workers. The thermodynamic parameters evaluated on this model give a self consistent picture of the adsorption process when the data are processed on this model using activities in place of concentration for all ionic species in the system and the variable
"Volume Term" \( V = \frac{A}{n} \times 10^{-3} \) litres/kg of dry fibre to describe the volume of the internal cellulose phase.

Other significant findings of this work are:

1) The close relationship between entropy and orientation of adsorbed dye molecules.

2) The effect of water structure changes at the cellulose-aqueous solution interface on the dyeing behaviour.

3) The relative importance of the possible mechanisms which influence the binding of the dye molecules with the cellulose. These mechanisms are (a) the delocalised \( \pi \) electron system of the dye molecule which forms an intermediate layer between the cellulose surface on one side and the regularly arranged water molecules on the other, (b) the non-polar van der Waals forces operating between the nonsolvated parts of the dye and the cellulose-molecules and (c) the hydrogen bonds formation between hydrogen bonding groups of the dye and the cellulose molecule. The present results suggest that all these three types of binding mechanisms are involved.