During the last three decades, adsorption of ionic dyes at the cellulose-aqueous electrolyte + dye solution interface has been widely studied. Several workers in this field have contributed to increase the basic understanding of various aspects of such adsorption processes. However, when results obtained by one school were analysed using the theory proposed by another, large discrepancies were shown to occur. Nevertheless, some clear ideas have emerged of the mechanism of dyeing cellulose with water soluble direct dyes in the presence of electrolytes.

The mechanism of adsorption at the charged cellulose-aqueous solution interface, whether it is of an ionised dye, surfactant molecule or any electrolyte, involves the study of important electrochemical phenomena. These are, the Donnan equilibrium and Donnan potential, the zeta potential and the surface potential. However, not much attention has been paid to a study of these electrical charge effects during dyeing in a systematic way. In fact, detailed work in this field is lacking.

In this thesis, therefore, these electrochemical phenomena have been studied in a systematic way and an attempt made to emphasise the importance of these electrochemical factors in dye adsorption processes. The influence of other physicochemical factors such as surface area, swelling, degree of dissociation of the charged groups and
changes in the internal volume of the cellulose phase on these electrochemical phenomena, have also been discussed.

The results of these experimental and theoretical studies have been presented in five chapters, in this thesis. The contents of each chapter are briefly outlined below.

The general introduction provides a critical review of the work done so far on the abovementioned electrochemical parameters, and the needs and objectives of the present studies.

In Chapter 1, the occurrence of a Donnan potential in the cellulose-aqueous electrolyte + direct dye solution, is explained, and the relation between this measured Donnan potential and the so-called "volume term" $V$, of the internal cellulose phase is discussed. The influence of electrolytes on the Donnan potential and the volume term $V$ have also been studied. The evaluation of the true Donnan potentials from the measured potentials and the effect of the dissociation of charges groups (due to intrinsic carboxyl groups and adsorbed dye anions), on the measured Donnan potential is clearly indicated. The experimental study of such Donnan potentials has been carried out in dyed cellophane-aqueous KCl solution systems. Several purified direct dyes were used.

In the evaluation of the true Donnan potential from the measured potential, the variation of the mobilities,
and the concentrations of sorbed electrolyte ions play an important role. These factors mainly affect the diffusion potential in membranes. Studies on membrane potential, Donnan sorption of electrolyte ions and membrane specific conductivity have been carried out for blank cellophane-aqueous KCl solution systems. The results are discussed in Chapter 2.

Though there is no experimental method available to directly evaluate the true surface potential at the cellulose-aqueous dye + electrolyte solution interface, the electrokinetic (zeta) potential measurements have been widely used to obtain qualitative and sometimes semi-quantitative information regarding this potential. Chapter 3, deals with experimental studies of the zeta potential in aqueous NaCl and KCl solutions for cotton, viscose, oxidised cellulose and cotton crosslinked with formaldehyde by the well known Form D and Form W processes. In addition, zeta potentials have also been measured for dyed cotton fibres in aqueous NaCl solutions. Surface charge densities calculated from the measured zeta potentials are analysed in terms of the existing theories of zeta potentials. Suitable explanations for the variation of surface charge densities with other physicochemical parameters such as dissociation of ionisable surface groups and changes in surface areas and swelling due to chemical modifications of the fibre are discussed.

It was mentioned above that the direct measurement
of surface potentials in such system is difficult. This is due to the non-availability of a suitable solvent for cellulose from which spread films can be obtained. The recent formulation of "Cadoxen", a true solvent for cellulose, resulted in an attempt to study the surface potential by spreading a film of cotton cellulose from this solvent on an aqueous electrolyte + dye solution. The ionising polonium-air electrode technique was used to measure the surface potential. Large variations in potential and irreproducibility of results in such a system were observed. A study was therefore undertaken of similar potentials developed at cellulose acetate film-electrolyte + dye solution system, since consistent and reproducible values of the potential were obtained. It is for the first time, that such measurements have been made at a cellulose-solution interface. Some preliminary investigations of these surface potentials have been carried out and discussed in Chapter 4.

In Chapter 5, the summary of all the work contained in Chapters 1 through 4, is given. The salient conclusions arrived at from these studies are also given.

All the Chapters in this thesis have been divided according to the decimal classification, in order to present the work in a concise and lucid manner. Equations, figures, tables and references have been numbered separately for each Chapter. Wherever possible, the abbreviations used in the "Chemical Abstracts" of the American Chemical Society have
been followed.

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