Chapter - 5

SUMMARY AND CONCLUSIONS
The physicochemical properties of cellulose-aqueous electrolyte solution systems are markedly influenced by the surface charge density on the cellulose and the ionic charges in solution. The surface charge on cellulose arises due to the presence of intrinsic ionised carboxyls. It is further enhanced by the adsorption of dyes or other ionic solutes on the cellulose surface. Dyeing cellulose with water soluble ionised substantive dyes, or in general, ionic equilibria in cellulose-aqueous solution systems, therefore, depend on electrochemical phenomena such as the Donnan equilibrium, and the electrokinetic potential.

From direct measurements of Donnan potential in dyed and undyed cellophane-aqueous electrolyte solution systems, it was shown, by previous workers, that a Donnan equilibrium exists in cellulose-aqueous solution systems, over a wide range of salt and dye concentration. For this purpose, cellulose with its imbibed solution was regarded as an equipotential volume phase. From studies of distribution of electrolyte ions, in cellophane-aqueous electrolyte solutions, it was shown, that such systems were governed by Donnan equilibrium conditions. Studies on the measurement of zeta potential of undyed cellulose in aqueous electrolyte solutions and in dye solutions, have given information on the surface charge densities of these fibre surfaces and their variation with electrolyte concentration.

However, from all the abovementioned studies, it was
not possible to obtain specific information on the following points.

a. The actual volume of the internal Donnan phase, i.e., the so-called "volume term" $V$,

b. the true area of the charged cellulose surface available for dye adsorption,

c. the degree of dissociation of the charged groups present on cellulose surface, and

d. the quantitative influence of these electrochemical phenomena on adsorption of solutes on the cellulose surface from aqueous solutions.

In the theory of dyeing of cellulose with direct dyes, the volume $V$ of the internal cellulose phase is a very important parameter, since its value determines quantitatively, the Donnan distribution of the dye and electrolyte ions in the system. The adsorption of dyes on cellulose occurs from this internal Donnan phase. In the generally accepted electrochemical theory of dyeing put forward by several workers in the past, this volume was assumed to be constant and equal to the amount of moisture taken up by cellulose at 100% R.H. However, in many cases it was found, that arbitrarily chosen values for $V$ ranging from 0.2 to 0.9 litres per kilogram of dry fibre had to be used to correlate theoretical and experimental results of dye adsorption on cellulose. In a recent modified theory of dyeing cellulose with direct dyes, a clearer picture of the volume term has been given, by defining it
as the product of the internal surface area of cellulose and
the thickness of the electrical double layer present at the
cellulose-aqueous solution interface. Since the thickness
of the electrical double layer is a function of the electro­
lyte concentration and temperature, it is evident, that the
internal volume cannot be constant but should vary in a
definite manner with the electrolyte concentration and temper­
ature. This theory adequately explains the experimental dye
adsorption isotherms, and the thermodynamics of dyeing cellulose
with direct dyes in the presence of electrolytes.

Several workers have studied the zeta potentials
at the cellulose-aqueous solution interface. The streaming
potential technique has been widely used to calculate the zeta
potential. These workers have been mainly concerned with the
explanation of the abnormal increase in zeta potential of
cellulose in dilute electrolyte solutions, followed by a
linear decrease with increasing electrolyte concentration.
The increase in zeta potential in dilute solutions was attri­
buted to surface conductivity effects. Subsequent workers
have attempted to eliminate the surface conductivity effects,
by suitable experimentation or by modifying the equation
to calculate the true zeta potential. The apparent increase
in surface charge density with increasing electrolyte concentra­
tion, although the zeta potential decreases, has been explained
by some workers in terms of anion adsorption on cellulose.
Such an hypothesis, of anion adsorption on a negatively charged
cellulose surface has not been supported by clear cut experimental evidence. On the contrary, it has been shown, that the anions are repelled from the cellulose surface and only cations are diffusely adsorbed. The results obtained by many workers on the measurements of zeta potential of oxy­celluloses in aqueous electrolyte solutions, have indicated a decrease in the zeta potential, instead of an increase, with increasing carboxyl group content of cellulose introduced through oxidation. Such a decrease in zeta potential has not been explained so far.

The surface charge density calculated from the experimentally measured zeta potential has not been correlated with the specific BET nitrogen surface areas of water-swollen un­collapsed fibres, or with changes in the number of dissociable charged groups and changes in swelling and internal surface area, due to chemical modifications. These modifications may be oxidation or, for example, crosslinking of cellulose with form­aldehyde from slightly aqueous reaction baths. It has been reported, that the internal surface area is affected by cross­linking from such a reaction bath. Measurements of zeta potential in cellulose-dye solution systems, has not led to any clear conclusion about the amount of dye adsorbed in relation to the potential barrier that influences adsorption. This is because the dye solutions were streamed under non­equilibrium conditions of experiment.

No attempt has so far been made, to measure directly,
the surface potential of spread cellulose films over aqueous electrolyte and dye solutions. Such measurements could be used to explain the orientation of dye and other solute molecules at the cellulose surface.

In order to investigate the factors mentioned above, the following extensive experimental studies have been made.

Detailed experimental measurements of the Donnan potentials were carried out in undyed and dyed cellophane-aqueous KCl solution systems. This measured Donnan potential is not the true Donnan potential, since, in this type of measurement, there is a considerable uncertainty regarding the diffusion potential and liquid junction potential. The factors which influence such potentials, are the concentration of sorbed electrolyte ions, the ionic mobilities of these sorbed ions in the membrane, and the variation of these factors with electrolyte concentration.

Hence, these measurements have been supplemented by an experimental study of membrane potentials and membrane conductivities of cellophane-aqueous KCl solution systems and direct analytical measurements of sorption of the potassium and chloride ions.

The following studies of zeta potential have been made using the streaming potential method. The area of the charged cellulose surface that is available for solute adsorption, has been determined from the calculated surface charge
density using the zeta potential measurements in undyed cotton and viscose-aqueous KCl solution systems. These areas have been correlated with the BET nitrogen adsorption surface areas of the swollen, uncollapsed fibres. The influence of the degree of dissociation of the charged groups present on cellulose and the extent of swelling on zeta potentials, have been studied for oxycellulose containing different amounts of carboxyl groups. The effect of changes in area due to cross linking of cellulose with formaldehyde, under aqueous and slightly aqueous conditions, have been studied by measurements of zeta potential in cross linked cellulose-aqueous NaCl solutions. Zeta potential measurements have also been carried out, on cotton fibres dyed with Chlorazol Sky Blue FF as a function of varying adsorbed dye concentration at a fixed concentration of NaCl. These results have been correlated with the equilibrium adsorption of the dye on cotton fibres under identical conditions of NaCl concentration and temperature.

Since cotton fibres spread from the solvent "Cadoxen" did not give reproducible values of surface potentials, preliminary experiments were carried out on the surface potentials of films of cellulose acetate spread on aqueous direct dye solution containing NaCl.

From all the abovementioned studies the following important conclusions have been drawn.

1. a. The measured Donnan potential depends solely on the
value of the total surface charge and is independent of the structure of the different direct dyes used. The contribution to the surface charge due to the intrinsic ionised carboxyl and the sulphonic acid groups (of the adsorbed dye) is dependent only on the total number of such groups present and not on whether the adsorbed dye is a mono- or poly-sulphonated dye. This also means, that these dyes, with their sulphonic acid groups, are all oriented on the cellulose surface in the same manner, irrespective of the dye structure.

1. b. Direct experimental evidence has been obtained from Donnan potential measurements, for the use of a variable volume term V, instead of a constant volume term to describe the volume of the internal charged cellulose phase. The nature of this variation indicates that the total volume of the internal Donnan phase is a function of the thickness of the electrical double layer as suggested in the more recent theory of dyeing.

1. c. The total ionisable surface groups due to carboxyl groups and/or the sulphonic acid groups from adsorbed dye, are dissociated only to an extent of approximately 27 per cent.

2. a. From direct chemical analysis, it has been shown that the distribution of the sorbed electrolyte ions can be expressed in terms of a Donnan equilibrium in cellophane-KCl solution system.

2. b. From measurements of transport numbers, concentration
of Donnan sorbed electrolyte ions, and the membrane specific conductivity, it is concluded that the mobilities of the potassium and chloride ions in the membrane, though they are much less than in free solution, are both reduced to the same extent. This reduction in individual ionic mobilities is approximately one-third as compared to mobility values in free aqueous solutions.

2. c. Using the measured concentration values for the sorbed ions in the modified equation of the Teorell-Meyer-Sievers theory, it is shown that the contribution to the Donnan potential, of the diffusion potential due to differences in sorbed ion concentrations, is negligible. Likewise, the contribution of the diffusion potential due to changes in ionic mobilities, has also been found to be negligible.

2. d. Thus, the measured potential may be regarded, to a close approximation, as the true Donnan boundary potential.

3. a. The zeta potential varies linearly with logarithm salt concentration. This behaviour has been commonly observed for many systems.

3. b. The Eversole and Boardman equation which relates the measured zeta potential with the thickness of the electrical double layer has been found to be valid for viscose and cotton in aqueous NaCl and KCl solutions. Using the surface potential values calculated from this equation, estimates of the surface charge densities in these fibres have been obtained. These
values of the surface charge density are in good agreement with the theoretical surface charge densities.

3. c. The theoretical surface charge densities have been calculated assuming that the total charge due to dissociated carboxyl groups is only 27 per cent of the total number of such groups in the case of viscose (see Conclusion 1 c). In the case of cotton however, the total charge is assumed to be the same as the total carboxyl group content. Evidence for this assumption has been obtained from the dyeing data on oxycellulose of other workers. These results therefore show, that the area available for solute adsorption from aqueous solutions is very large and is equal to the BET nitrogen areas for the water swollen uncollapsed fibres.

3. d. The apparent increase in surface charge density with increasing electrolyte concentration is explained mathematically in terms of the relative manner in which the thickness of the electrical double layer and the zeta potential vary with the logarithm of the electrolyte concentration. It is not necessary to postulate anion adsorption to explain the results.

3. e. The decrease in zeta potential of the oxidised cotton, with increasing carboxyl group content is satisfactorily explained in terms of an increased swelling of these fibres as a result of oxidation, (resulting in an increase in surface area) and also due to the proportionate decrease in the dissociation of the carboxyl group content of oxycellulose.
3. f. The zeta potential was found to increase with increasing per cent bound formaldehyde (i.e., increasing cross linking) in the case of Form D treated cottons (slightly aqueous cross linking), and remain unaffected in the case of Form W treated cotton (aqueous cross linking). It has been shown recently, that there is a decrease in surface area of Form D treated cottons with increasing per cent bound formaldehyde content and almost no change in area in the case of Form W treated cottons. The increase in zeta potential, in Form D cottons is attributed to an increase in charge density with increasing per cent bound formaldehyde. The zeta potential is unaffected in the case of Form W treated cottons, since there is no change in area and hence, the surface charge density remains the same as for untreated cottons.

3. g. Zeta potential measurements in dyed cottons have been correlated with the amount of dye adsorbed at equilibrium by cellulose. The curve of zeta potential versus the charge on cellulose is similar to equilibrium dye adsorption isotherm.

4. a. Preliminary studies on the surface potential of cellulose acetate films spread over aqueous NaCl + dye solution, indicate, that up to a concentration of 0.1M NaCl the dipolar orientation of molecules at the surface of the spread film results in a positive surface potential. But at concentrations greater than 0.1M NaCl, there is a reversal in the sign of the surface potential. This has been attributed to the formation of a strong negative double layer potential, which over weighs the positive dipolar surface potential.