Dichroism of dyed cellulose fibres

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higher than calculated on the basis of Beer's law, also demonstrate that dichroism of shape may play a part. For idealized models we have calculated that a specimen whose real orientation corresponds to \( f_D = 0.50 \) might yield a value higher by about 15 percent after swelling. Actually the effect is smaller (some units in the second decimal place).

It is not possible to discriminate between the possibilities a) and b). Anyhow it seems to be necessary not to interpret the differences in \( f_D \) between swollen and dry specimen in terms of orientation.

Summary.

In this research, concerned with cellulose fibres, the relationship between fibre orientation and the anisotropic light absorption of the fibres, when dyed with certain direct dyestuff, has been studied theoretically as well as experimentally.

Starting from the electromagnetic theory of light and from known geometrical considerations on particle orientation in fibres, equations were derived giving the relation between the extinction for polarized light in the two principal directions and the orientation factor \( f_D \) (\( D = \text{dichroism} \)) (Ch. III-2). The assumptions and simplifications introduced in order to arrive at equations which can be practically used have been set forth and their justifications analyzed (Ch. III-4). It has been shown that in these equations a constant factor \( C \) remains undetermined.

From a comparison of experimental data on dichroism with those from birefringence and X-ray investigation it has been concluded that the magnitude of the constant \( C \) must lie between the limits 1 and about 1.12 for the dyestuffs employed (Ch. III-4 and Ch. VI-3).

The relation between \( C \) and the optical character of the dye molecules as well as the geometry of their absorption on the cellulose chain segments has been discussed (Ch. III-3 and 4). From observations on dyed optically biaxial films it seems likely that the dyestuffs used in this work possess only one absorption vector, lying at an undetermined angle relative to the axis of the cellulose chain and whose geometrical locus is independent of \( \lambda \) (Ch. III-3). The possible occurrence of the Wiener-effect (dichroism of shape) in swollen fibres has been analyzed and its sign and magnitude estimated (Ch. III-5).
Two dyestuffs whose purity was tested (Ch. IV-1) where used, Congo Red and Chlorazol Sky Blue FF. The fibres investigated comprised several types of rayons and series of model filaments of various orientations. Optical and X-ray orientation factors $f_o$ and $f_x$ of most of these objects where known from previous research (Ch. IV-2).

All objects where dyed homogeneously and to an equilibrium state (Ch. IV-3). Two methods of light absorption measurements with polarized light were employed, an objective photocell method for model filaments (Ch. V-1) and a visual method, using a Leitz-microscope-photometer for fibres with a very small diameter, which required high microscopic magnifications (Ch. V-2).

It has been found, in conformity with previous workers, that the dichroism of dyed cellulose fibres is a function of the concentration of the dyestuff in the fibre. It decreases with increasing concentration of the dye (Ch. VI-1).

This concentration dependence can be explained, either on the basis of deviations from the simplifying assumptions introduced in the derivation of the theoretical relation between the orientation and the measured extinctions which may become significant at higher concentrations, or in terms of a particular distribution of absorption sites of different energy, characterized by the fact that sites with the highest energy have, on the average, better orientation than those with lower energy. The better oriented absorption sites with the highest energy would then be localized near or on the crystallites (Ch. VI-3).

In order to find a quantity which can suitably be correlated with the orientation of the fibre, the measurements should either be extrapolated to zero-concentration (as was done in the case of rayons) or measured at a sufficiently low concentration of the dye (this was applied in the case of model filaments).

In rayons, the orientation factor $f_{D'}$ when evaluated by setting $C=1$, remains below $f_x$ and $f_o$. A general difference between the rayons with and without skin-core differentiation is revealed by the fact that, in case of the skin-free fibres, the values of $f_{D'}$, $f_o$ and $f_x$ become practically equal if $f_o$ is evaluated using the maximum possible value of $C$ (1.12). In the other rayons no such simple relation holds (Ch. VI-3).
In model filaments, the values of $f_D$, when evaluated in setting C either 1 or 1.12, remain well below $f_x$ as well as below $f_0$ indicating a difference in intrinsic structure between these objects and rayon (Ch. VI-4).

It was clearly established that fibres dyed with CR give a higher $f_D$ than the same objects dyed with CSB, which shows that the value of $f_D$ depends on the dyestuff used. It seems that the CR molecule is capable of penetrating into regions which are blocked for the more bulky CSB molecule, and arguments were given why these regions belong to the better orientated ones (Ch. VI-4).

Differences in dichroism between filaments dyed before and after the first drying operation (and also spun-dyed fibres) were found and discussed (Ch. VI-4).

Filaments measured in the swollen state yield values of $f_D$ which, in general, are slightly higher than those of the same objects measured in the air-dry state. Furthermore, the overall extinctions of swollen and dried fibres cannot be calculated from each other by merely accounting for the difference in concentration of the dye and the usual corrections for the refractive indices (Ch. III-6). The possible reasons for these effects are discussed and it is shown that, among other things, dichroism of shape may play a role (Ch. III-5, VI-4).

In series of model filaments spun from viscoses of various cellulose concentration, the curves giving the dichroic orientation factor as a function of the stretch applied in the preparation of the filaments are steeper the higher the cellulose concentration. This confirms the results of previous optical and X-ray measurements (Ch. VI-4).

It remains undetermined to what extent the crystalline and non-crystalline portions of the fiber substance each contribute to the dichroic orientation factor.