Dichroism

V. A. SHENAI*

LIGHT, according to the electromagnetic theory, which tries to explain most of the optical phenomena and to a great extent succeeds, can be understood as transverse electromagnetic waves transmitted with a velocity of about 3.0 x 10^{10} cm/sec., though it can also be understood as discontinuous particles of energy (quanta of photons), a postulation of the corpuscular theory of light. In ordinary light, the vibrations occur at various angles (or axes of vibration) around the principle direction of the beam (while perpendicular to the direction of the beam) so that the resultant wave motion occurs in all different planes along the principle line of propagation. In *plane polarised* or *linear polarised* light, the electrical vibration is limited to only one axis of vibration. Therefore, the wave is limited to one plane, the plane of vibration.

One of the phenomena, best explained by the electromagnetic theory of light is *Dichroism,* also called *Pleochroism,* a property of optically anisotropic substances and consists in light absorption by such substances being greater when it vibrates in one direction from when it vibrates in another direction.[3] In fibres, for example, the greatest difference in absorption is generally found between light vibrating along the length of fibre axis and at right angles to this direction. Hence, the fibre exhibits different brightnesses when oriented with its long axis in the vibration direction of the light than when at right angles to it. When polychromatic polarised light is used, different colours may occur in different positions.

The earliest known examples of this effect were found in certain coloured crystals, e.g., tourmaline. Similar behaviour has been noted by Ambronn for fibres of natural cellulose dyed with direct cotton dyes.[6] He observed that in polarised light, the fibre appeared fully coloured in one position and completely colourless in a perpendicular position. Similarly dye crystals, flowing dye solutions and streaks of the solid dye on glass show dichroic behaviour. In dichroism, we come across (a) *complete positive dichroism,* which is said to be possessed by a coloured substance, if it appears colourless when its longitudinal axis is parallel to the plane of polarisation and fully coloured when that axis and the plane of polarisation are at right angles and (b) *complete negative dichroism* which is similarly defined as the case where the body is coloured when its longitudinal axis is parallel and colourless when that axis is perpendicular to the plane of polarisation. In general, a complete dichroism in either sense is seldom possessed by dyes or dyed systems so that only partial dichroism, where the change in light absorption is from weaker to stronger as the plane of polarisation is rotated, is more frequently encountered.

The dichroic effect can be explained on the basis of wave mechanical considerations.[9] The original Bohr theory of electrons rotating round atoms in orbits is modified by wave mechanics. The *stationery states* of the Bohr theory are replaced by three dimensional stationery waves in which the negative charge of the electron is smeared out and represented by the square of the wave amplitude of different points round the atom. The *fundamental* of a three dimensional wave around a point is a wave with a high amplitude at the centre rapidly decreasing outwards in all directions to a spherical node at infinity. In a normal hydrogen atom, for example, the electron is represented as a spherical cloud of negative electricity, dense near

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*Research student, Textile Chemistry Section.

the nucleus, and rapidly falling of in density outwards.

When light passes through a transparent substance, it merely causes a temporary oscillation of the charge clouds of the molecules in unison with the wave, giving rise to the phenomena of *refraction* and *dispersion.* A more radical effect occurs when light is absorbed. Here the energy of the light wave is taken up by the molecule and an electron is caused to change its pattern to a higher orbital. Thus the absorption of light by the hydrogen molecule raises one electron from theσg orbital to either the σg or the πu orbital (Fig. 1). The energy required is high so that the hydrogen molecule absorbs only at very short wave-lengths (E = hν The first transition occurs at about 1050A.

Directional light absorption by a diatomic molecule :—

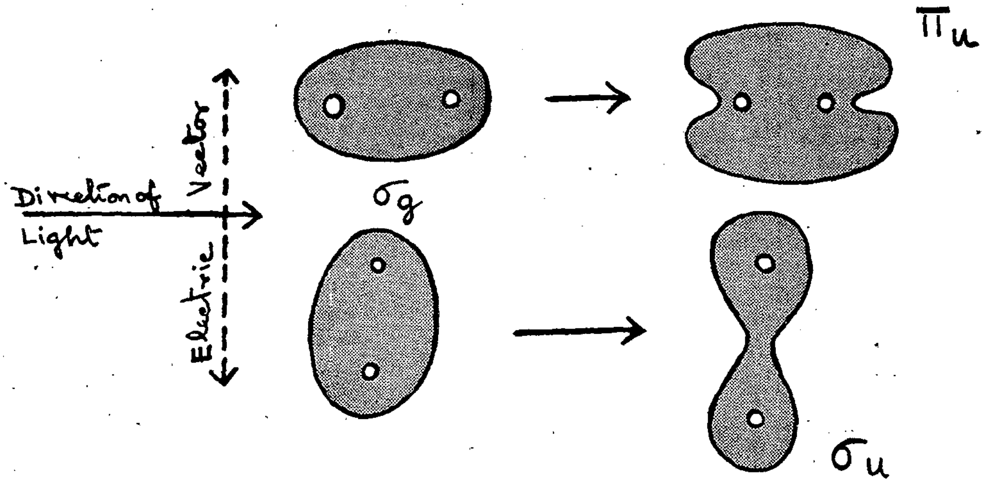


Fig. 1

The light absorption is highly directional as illustrated in Fig. 1. When the pattern of the electron changes on absorption, a new node is developed, and this is always at right angles to the electric vector of the absorbed light. Light of wave-length 1050A would not be absorbed by the H_2molecule at the top left of Fig. 1, but would be strongly absorbed by the bottom left molecule which is correctly oriented to facilitate $\sigma_g \longrightarrow \sigma_u$ transition. At 950A, the reverse is true, and the top left molecule absorbs to give $\sigma_g \longrightarrow \pi_u$ transition. This effect is shown by all systems of oriented non-spherical molecules.

It was shown by Weigert [14], [2] that exposure of very thin layers of silver chloride (when sensitized by free silver produced by a previous exposure to ordinary light) to plane polarised light, renderes the layer colour-adapted and dichroic, i.e. causes it to exhibit different extinction coefficients in polarised light according to the direction of plane of polarisation. This is a sign of definite anisotropy in the layer. The optical axis of the photo-anisotropic system is always parallel to the plane of the electric vector. After a preliminary exposure to polarised light, the orientation set up determines or orients a subsequent decomposition effect by non-polarised light. This, Weigert termed, *induced photoanisotropy.* Zocher and Coper[17], [2] have obtained the effect by the use of circularly polarised light. Weigert regarded the effect as due to definite alterations in the shape of complex silver micelles. It has, however, been shown by Cameron and Taylor[1], [2] that the effect can be produced in single crystals of silver chloride, previously rendered blue by exposure. Both silver and a silver halide lattice are necessary, but gelatin, or other components of photographic emulsions or the gel state are not essential. It is suggested that suitably dimensioned and oriented silver particles can respond to polarised light by ejecting electrons in a definite direction. These reform silver from silver ions in the lattice, the chlorine being assumed to migrate.

Dichroic method has been used by Smirnov and Shoshina[11] for the investigation of molecular anisotropy of complicated dyestuffs like Congo Red, Trypaflavine, Alizarine Red, Acridine Orange, Rhodamine etc. The dyestuffs are adsorbed on cellophane foils and the light absorption and transmittance are measured in different directions and for varying wavelengths by the Konig-Martens spectrophotometer and dichroism values are calculated.

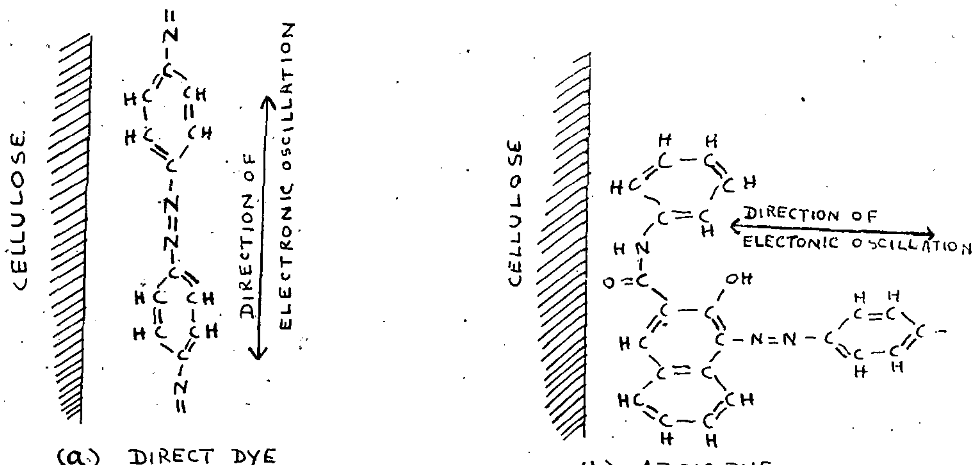
Using polarised infra-red radiation, the structure of oriented Terylene film has been determined recently by Miller and Willis.[4] The infra-red absorption spectrum of Terylene from $5\mu - 15\mu$ has been interpreted in detail by assignment of the absorption bands to atomic groups in the molecule. From the data thus obtained, they concluded that not only is the chain direction parallel to the direction of drawing, but also the plane of the molecules is approximately perpendicular to the plane of the film. This study has been extended by Weston[15] to cover the spectral region $2.5\mu - 4.0\mu$, using the high dispersion of a lithium fluoride film. Using polarised radiation and oriented film at 90° to the beam direction, the following results have been obtained—(a) the bands at 3080 cm^{-1} appear to show little or no dichroism, (b) the bands at 2980 cm^{-1} and 2920 cm^{-1} both show parallel dichroism and (c) the band at 2850 cm^{-1} shows perpendicular dichroism.

The colour of a dye is due to the electronic oscillations along the conjugated chain of bonds running through the molecule.[13] These electrons can be excited by plane polarised light as explained earlier. In other words, parallel oriented dye molecules will display different absorption coefficients towards plane polarised light according to whether the plane of polarisation is parallel or at right angles to the length of the molecules, the absorption being greater in the latter case. The dichroism of dyed fibres has been studied in detail by J. M. Preston, who has measured the dichroic constants of a number of cellulose fibres dyed with various direct dyes. The dichroic constant is defined as K_1/K_2 where K_1 is the absorption coefficient for light polarised at right angles and K_2 that for light polarised parallel to the fibre length. In a fibre containing dye molecules perfectly oriented parallel to the fibre axis, this fraction would have a value of infinity, while in a fibre where the dye molecules were randomly distributed, the value would be 1.0. Values between these two limits can be attributed either to the imperfect orientation of the dye on a perfectly ordered substrate, or to an imperfectly oriented substrate, the arrangement of which is completely reproduced by the dye. The results obtained by Preston are shown in the following table :—

Table I. Dichroism of cellulosic fibres

	Fibre	Dichroic constant	Orientation (%)
1.	Complete orientation	Infinity	100
2.	Ramie	9	82
3.	Viscose Rayon	1·4 - 3·3	41 - 62
4.	Cellophane	1·5	43
5.	Unoriented	1·0	33

Morton[6] has observed that highly stretched viscose fibres display a dichroic effect when dyed, especially when examined through a ploarising device.[13] For example, if a bundle of parallel threads of highly stretched viscose rayon dyed with direct dyes is examined through a piece of *Polaroid,* the fibres appear to absorb more or less light as the *Polaroid* is rotated. A specially interesting observation is that in fibres dyed with azoic dyes, the plane of maximum absorption of light is rotated through 90° as compared with dyeings with direct dyes. Hence the azoic dyes must be arranged with their conjugated chains at right angles to the cellulose micelles, which agrees with the view that in these dyes the amide group is the only substantivating group so that the complete dye is attached to the fibre at one end only, as is shown in Fig. 2.



(a) DIRECT DYE

(b) AZOIC DYE

FIG. 2

ELECTRONIC VIBRATIONS OF DIRECT AND AZOIC DYES RELATIVE TO CELLULOSE SURFACE

A study of cellulose-dyestuff complex, started as early as 1931 by Preston, in terms of dichroic measurements has led to a better understanding of the structure of cellulose fibres.[8] The degree of orientation of cellulose chain molecules in various cellulosic fibres has been quantitively related to dichroic constant (Table I). He also studied the effect of tension during the dyeing and drying of cellulose and found that if a sheet of cellophane was dyed in a solution of Congo Red under a tension applied in axial direction of 10 gm/cm. of width, a value of dichroic constant of 1.64 was obtained, while if the tension was increased to 250 gm./cm. of width, the dichroic constant increased to 2.13. Another aspect studied was the effect of depth of dyeing. The results of experiments carried out on cellophane indicate that there is a slight but significant decrease in the dichroic constant with darker dyeings, the change in the case of Paramine Green GG being 0.08, when the density was increased from 0.53 to 2.08 at 6400A. This, it is reported, is probably due to the interior of the cellophane not being quite so well oriented as the surface, and that more dyestuff penetrates into the interior with the darker dyeings.

Dye molecules in dyed fibres take up a definite orientation with respect to the oriented polymer molecules, depending on the availability of suitable bonds to do so and on this account, the absorption of light in the fibre, as in the dye molecules themselves or in crystals of dyes varies with the vibration direction of light.[9] Often, the dichroism is observed in different depths of the same colour. Cellulose dyed with Congo Red or stained with iodine exhibits partial positive dichroism, while cellulose dyed with Magdala Red shows partial negative dichroism. From this it can be concluded that the dichroic effect also depends on the absorption characteristics of the dye molecules and orientation in the fibre. However, the absorptions for parallel and perpendicular vibration directions are not necessarily very different; for, cellulose dyed with Prussian Blue is not dichroic at all.

Morton[6] has developed a molecular theory of dyeing of cellulose, basing on an extensive study on dichroic behaviour of substantive dyes. He concluded from the study that direct dyes are absorbed and fixed on the cellulose as single molecules, not as micelles, and that the long axis of the dye molecules are parallel to the long axis of the cellulose molecules. This view has been confirmed by a comparison of dyeings on ramie dyed from alcholic and aqueous salt solutions respectively. It is generally held that direct dyes are in molecular solution in the former and in the miscellar solution in the latter medium. No difference in fastness and optical properties has been noted between the two sets of dyeings. Morton also found that fibres dyed with vat dyes showed no dichroism or at the most a very slight positive dichroism. The vat dyes, therefore, are either not inherently dichroic or else the molecules or molecular aggregates are not oriented by the fibre molecules. However, leuco-vat dyes on cotton showed positive dichroism. Therefore, it is probable that the molecule of a vat dye possesses intrinsic dichroism. It is also probable that while the substantive leuco form is oriented by the cellulose molecules, the oxidized form is not and that as a rule, the oxidized dye is retained within the cellulose not by virtue of any special *affinity*, or type of molecular combination, but merely because of its extreme insolubility in water. Very recently Sumner, Vickerstaff and Waters[12] have studied the effects of soaping after-treatment on vat dyeings. They examined the colour changes produced in vat-dyed cellulose fibres by the normal soaping after—treatment by spectro-photometric methods using dyed viscose film. From the increase in the orientation of the dye as shown by the measurements of dichroism, it was concluded that the changes are associated with crystallization of the dye. Vat dyes in the reduced condition are oriented along the long axis of the fibre. But, when once the leuco-vat dye is oxidized, the dye molecules are no longer attached to the cellulose chains through hydrogen bonding. Sumner and co-workers have suggested that immediately on oxidation of the leuco form the change over from the crystallised parallel orientation to crystallised perpendicular orientation begins. In this perpendicular orientation, it is no difficult to see as to why vat dyes on cotton do not show appreciable dichroism. Morton[6] further found that acid dyes, usually applied to wool and other protein fibres, though have negligible affinity, as a class, for cellulose fibres when applied from an aqueous medium, dye ramie from a 0.5% solution in 95% alcohol. Ramie dyed with, for example, Azo Geranine 2GS, Eriofast Cyanine S, Naphthalene Orange GS and Solvay Blue BS exhibited partial or almost complete positive dichroism.

Preston and Su[10] studied the relation between the degree of orientation of regenerated cellulose fibres and the degree of polarisation of their fluorescence under various conditions. The principle used is that fluorescent light from crystals is highly polarised, its plane of polarisation being related to the orientation of the fluorescing molecules. Further if the molecule is so oriented that the direction of electronic oscillations in the chromophoric group is parallel to the electric vector of the exciting light, the emitted fluorescence will have the same vector direction. Molecules, whose chromophoric groups lie at angles to the electric vector, are also capable of absorbing, though with efficiencies diminishing to zero at the angle of 90°. Therefore, the fluorescence emitted from these molecules has its electric vector determined by the chromophoric group direction. For a similar reason, the light from oriented fibres dyed with suitable fluorescent dyes should also be highly polarised. It must be expected that the anisotropies of the polarisation of the fluorescent light and the dichroic absorpion would be similar. With dichroism, as already mentioned, the anisotropy is conveniently expressed as the ratio of the optical densities for light plane polarised parallel and perpendicular to the fibre axis, while with fluorescence the appropriate ratio is that of the intensities of emitted light plane polarised parallel and perpendicular to the fibre axes.

By measuring the dichroism of ramie and cotton fibres dyed with Congo Red, Okajima and Kobayashi[7] have confirmed the theory that the molecules of dye are directly adsorbed by cellulose in definite positions in the micelle surface parallel to the axis of the micelle. They have also ascertained the micelle orientation by determining dichroism. They, further used dichroic measurements as a means of studying micro-structure side by side with X-ray and other optical methods.

Wiley[16] tried to find out a relation between dyed fibre dichroism and the adsorption of dyestuffs on pulps and consequently developed an instrument for the measurement of the dichroism of dyed wood pulp and used it in studying the factors which affect the orientation of dyestuff particles on fibres with the object of obtaining new information concerning the fundamental nature of the pulp—dyestuff bond. The instrument has been designed to measure the transmittances of dyed pulp fibres for light polarised at any desired angle with the fibre axis. The validity of choosing a relation between the transmittances obtained for the two cases, where the plane of polarisation is parallel and perpendicular to the fibre axis, as a means of expressing the degree of dichroism of the fibre was proved. The relation selected was the ratio of absorption coefficients for parallel and perpendicular polarisation. For a given wavelength and depth of dyeing Wiley observed that (a) the dichroism increased with increasing amounts of lignin in pulp, (b) short fibred fractions of pulp exhibited less dichroism than long fibred ones, (c) the dichroism decreased when pulps were treated with chemical swelling agents, (d) a very marked increase in the dichroism was observed as a pulp was beaten, (e) the dichroism increased as a salt was added to the dyebath, (f) the dichroism increased as the concentration of dye in the dyebath was increased and (g) variation of the temperature of the dyebath over a given range had no effect on the dichroism.

Dichroic behaviour of dyed fibres has in many cases, led to the understanding of the position of the dye in the fibre. This is particularly so in the case of cellulose acetate. From the observation of the phototropic behaviour of the dyeings of amino-azobenzene on cellulose acetate, Mechel and Stauffer[13] conclude that the dye has much greater freedom of movement in cellulose acetate, or in other words, it is dissolved in this fibre. The phototropic effect, the property of the system to change colour on exposure to light but to return to its original colour in the dark, can equally well be attributed to the fact that the dye is adsorbed on cellulose acetate by hydrogen bonding at the terminal amino group so that the rest of the molecule is free to move. Further evidence on the position of the dye molecules in the fibre is obtained from dichroic observations. X-ray examination shows that the cellulose chains in cellulose acetate are not very highly oriented with respect to the fibre axis, but if the fibre is hydrolysed, and then dyed with a direct dye, it shows appreciable dichroism, thus indicating an ordered arrangement of the cellulose chains along the fibre axis. When dyed with dispersed dyes, cellulose acetate rayon shows no signs of dichroism, so that the dye molecules cannot be attached directly to the glucose residues of the main chain. Dispersed dyes can also be used to dye nylon fibre, which is very highly oriented and in which the only groups likely to attract the dye are the amide-groups forming part of the nylon chain. Such fibres display a very high degree of dichroism when dyed with dispersed dyes. The lack of dichroism in cellulose acetate can be explained if the dyes are attached to the side chain carbonyl groups. These groups are connected to the main cellulose chain by a single-bond system, leaving them capable of rotating over a wide range of positions, so that there will be no definite orientation of the attached dye molecules.

A study of the technique of making dichroism a quantitative tool in investigations of orientation in cellulose acetate fibres has been carried on intermittently in the laboratories of the Eastmen Kodak Co. (New York) and Tennessee Eastman Co. (Tennessee) since 1944 by Morey and Martin[5] and their collaborators. In determining the orientation by means of dichroic dyes, three basic assumptions were made as follows : (a) that the dye molecule itself is essentially dichroic ; its absorption mechanism is essentially that of a linear oscillator, (b) that the deposition of the dye within the fibre takes place under the influence of adsorptive forces which align the dye spatially in a direction having a direct correspondence to some structural direction of the polymer substrate and (c) that within the dye molecule, the axis corresponding to the linear oscillator is essentially parallel or perpendicuar to the axis defining its attachment or adsorption to the polymer substrate.

The observed dichroism therefore is a function, first, of the dye chosen, and second of the fibre structure which is accessible to the dye. The most accessible surface is, of course, the skin. Next are the walls of capillaries and finally the internal adsorbing surfaces, which with proper swelling, may serve as adsorbing surfaces. Thus the state of dispersion of the dye and the swelling power of the dyebath are also variables.

The study of dichroism of fibres dyed or stained, is therefore found to be of very great importance in so far as it enables us to get an almost clear picture of the microstructure of textile fibres and also the position of the dye molecules in the fibre material.

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