Dichroic Study on Polyvinylalcohol Fibre. IV. *A Theoretical Relation between the Intrinsic Double Refraction and the Dichroism*

By Yasuji KOBAYASHI and Saburo OKAJIMA

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The relations between the stretching degree v relative to the isotropic state and the intrinsic double refraction Γ or the dichroism D of a cellulose fibre were already calculated by the authors.[1] Now in this paper the relation between Γ and the dichroic orientation is derived in a more general form.

A. Double Refraction. — The refractive index parallel to the fibre axis z of a refractive indicatrix, whose principal axis points to θ, φ is already calculated as (1), where θ and φ are the latitude and the azimuth.

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[1] S. Okajima, *J. Soc. Chem. Ind. Japan*, **43**, 351 (1940); S. Okajima and Y. Kobayashi, *J. Soc. Textile and Cellulose Ind. Japan*, **3**, 98 (1947).

$$n_z=\left(\frac{1}{n_\alpha{}^2}\sin^2\theta+\frac{1}{n_\gamma{}^2}\cos^2\theta\right)^{-1/2}. \tag{1}$$

Now developing the right-hand side of (1) into a power series and neglecting the higher terms of $\Gamma_\infty=n_\gamma-n_\alpha$, n_z is simplified as (2) or (2′),

$$n_z=n_\gamma-(n_\gamma-n_\alpha)\sin^2\theta, \tag{2}$$

$$=n_\gamma\cos^2\theta+n_\alpha\sin^2\theta, \tag{2′}$$

while the refractive index parallel to the x-axis of the above refractive indicatrix is given by (3) according to the previous calculation:

$$n_x=n_\alpha+(n_\gamma-n_\alpha)\sin^2\theta\cos^2\varphi. \tag{3}$$

Now the refractive indices of the fibre $n_\parallel$ and $n_\perp$, parallel and perpendicular to the fibre axis are generally shown by (4) and (5) respectively:

$$n_\parallel=\int_0^{\pi/2}\int_0^{\pi/2}J_0 n_z\sin\theta\mathrm{d}\theta\mathrm{d}\varphi\Big/\int_0^{\pi/2}\int_0^{\pi/2}J_\theta\sin\theta\mathrm{d}\theta\mathrm{d}\varphi, \tag{4}$$

$$n_\perp=\int_0^{\pi/2}\int_0^{\pi/2}J_0 n_x\sin\theta\mathrm{d}\theta\mathrm{d}\varphi\Big/\int_0^{\pi/2}\int_0^{\pi/2}J_\theta\sin\theta\mathrm{d}\theta\mathrm{d}\varphi, \tag{5}$$

where J_θ is a distribution function of the mers.

Substituting the equations (2) and (3) into the equations (4) and (5) respectively,

$$n_\parallel=n_\gamma-(n_\gamma-n_\alpha)\cdot f(J_\theta), \tag{6}$$

$$n_\perp=n_\alpha+1/2\cdot(n_\gamma-n_\alpha)\cdot f(J_\theta), \tag{7}$$

and $\Gamma=n_\parallel-n_\perp=(n_\gamma-n_\alpha)\cdot\{1-3/2\cdot f(J_\theta)\}$, (8)

where $f(J_\theta)=\int_0^{\pi/2}J_\theta\cdot\sin{}^3\theta d\theta$,

and $\Gamma/\Gamma_\infty=f_o=1-3/2\cdot f(J_\theta)$, (9)

as defined by P. H. Hermans[2].

From (6) and (7)

$$(n_\parallel+2n_\perp)/3=(n_\gamma+2n_\alpha)/3=n_{iso}$$
$$=\text{constant}. \tag{10}$$

The relation (10) was already proved experimentally by the authors[3] in the case of the cellulose fibre.

B. Dichroic Orientation $\mathbf{f_D}$.—When the long axis of a particle of the dye-cellulose complex lies in the direction θ, φ, the coefficients of transparency of the particle, t_z and t_x, for the plane-polarized light vibrating parallel and perpendicular to z are

$$t_z=\beta-(\beta-\alpha)\cos^2\theta, \tag{11}$$

$$t_x=\beta-(\beta-\alpha)\sin^2\theta\cos^2\varphi, \tag{12}$$

where α and β are t_z and t_x at $\theta=0$, respectively, i.e., the principal coefficients of transparency.

The coefficients of light absorption, $K_\parallel$ and $K_\perp$, of a fibre for the plane-polarized light vibrating parallel and perpendicular to the fibre axis are also given by

$$K_\parallel=\frac{\int_0^{\pi/2}\int_0^{\pi/2}J_\theta\cdot k_z\cdot\sin\theta\mathrm{d}\theta\mathrm{d}\varphi}{\int_0^{\pi/2}\int_0^{\pi/2}J_\theta\cdot\sin\theta\mathrm{d}\theta\mathrm{d}\varphi}, \tag{13}$$

and

$$K_\perp=\frac{\int_0^{\pi/2}\int_0^{\pi/2}J_\theta\cdot k_x\cdot\sin\theta\mathrm{d}\theta\mathrm{d}\varphi}{\int_0^{\pi/2}\int_0^{\pi/2}J_\theta\cdot\sin\theta\mathrm{d}\theta\mathrm{d}\varphi}, \tag{14}$$

where

$$t_z=10^{-kz},\ t_x=10^{-kx},\ \alpha=10^{-k_\parallel},\ \beta=10^{-k_\perp}, \tag{15}$$

Now developing the right-hand sides of (15) and neglecting the higher terms of every k (k is very small), we obtain

$$\left.\begin{aligned}k_z&=k_\parallel\cos^2\theta+k_\perp\sin^2\theta\\k_x&=k_\perp+(k_\parallel-k_\perp)\sin^2\theta\cos^2\varphi\end{aligned}\right\}. \tag{16}$$

Then k_z and k_x are of the same forms as these of n_z and n_x respectively and therefore substituting these relations into (13) and (14), $K_\parallel$ and $K_\perp$ can be given in the same forms as $n_\parallel$ and $n_\perp$ respectively, i.e.,

$$K_\parallel=k_\parallel-(k_\parallel-k_\perp)\cdot f(J_\theta), \tag{17}$$

$$K_\perp=k_\perp+1/2\cdot(k_\parallel-k_\perp)\cdot f(J_\theta), \tag{18}$$

and, therefore, the dichronic orientation f_D is

$$\begin{aligned}f_D&=(K_\parallel-K_\perp)/(K_\parallel+2K_\perp)\\&=(k_\parallel-k_\perp)/(k_\parallel+2k_\perp)\cdot\{1-3/2\cdot f(J_\theta)\}\\&=(k_\parallel-k_\perp)/(k_\parallel+2k_\perp)\cdot f_O\end{aligned} \tag{19}$$

and $1/3\cdot(K_\parallel+2K_\perp)=1/3\cdot(k_\parallel+2k_\perp)$
$=$constant. (20)

Therefore f_D is directly proportional to f_O. The same relation is already obtained by J. M. Preston,[4] where he assumed that $k_\perp$ is equal to 0 and the proportional constant $(k_\parallel-k_\perp)/(k_\parallel+2k_\perp)$ is equal to 1. Our observation on the ramie fibre, which is dyed with Kongo red, indicates that $k_\perp$ is not 0, although it is very small and difficult to be determined accurately and our old data give the constant 0.89. The latest data on the polyvinylalcohol fibre indicate that the possibility of still larger values of 0.95–1. The details will be described in the following paper.

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[2] P. H. Hermans "Contribution to the Physics of Cellulose Fibres", 1946.

[3] S. Okajima and T. Iwamoto, *J. Soc. Chem. Ind. Japan*, **43**, 355 (1940).

[4] J. M. Preston and P. C. Tsien, *J. Soc. Dyers and Col.*, **66**, 361 (1950).

As to the constancy of $k_\parallel+2k_\perp$, it holds good only when the fibre is dyed very lightly. The old data show some deviations from this relation as shown in Table I, but the latest ones prove this to be true as seen in Table II. In this case a sample of cellulose filament was dyed very lightly with Kongo red and $K_\parallel$ and $K_\perp$ were measured by using the filtered Hg-line. In order to prove the rule, $K_\parallel+2K_\perp$ are corrected by dividing by the diameter. The new samples were dyed very lightly but they are sufficient to obtain the exact values of $K_\parallel$ and $K_\perp$, when Hg-line is used, because this is absorbed so much by the dye as compared with the case where D-line is used.

TABLE I

THE ABSORBTION COEFFICIENT OF A POLYVINYL-ALCOHOL FIBRE DYED WITH KONGO RED

v	Diam., mm.	$K_\parallel$	$K_\perp$	$\frac{1/3\,(K_\parallel+2K_\perp)}{\text{Diam.}}$
1.00	0.1417	0.170	0.144	1.08
1.43	0.1185	0.174	0.108	1.10
1.69	0.1090	0.182	0.088	1.10
2.07	0.0985	0.196	0.060	1.07
3.08	0.0807	0.214	0.026	1.10
4.11	0.0700	0.224	0.020	1.26
4.99	0.0635	0.228	0.010	1.30

TABLE II

THE ABSORBTION COEFFICIENT OF A CELLULOSE FIBRE DYED VERY LIGHTLY WITH KONGO RED

v	Diam., mm	$K_\parallel$	$K_\perp$	$\frac{1/3\,(K_\parallel+2K_\perp)}{\text{Diam.}}$
1.00	0.1825	0.468	0.559	2.90
1.05	0.1816	0.485	0.551	2.91
1.14	0.1610	0.497	0.445	2.87
1.27	0.1495	0.525	0.394	2.93
1.38	0.1436	0.536	0.361	2.92
1.54	0.1333	0.559	0.300	2.90
1.66	0.1260	0.598	0.266	2.99
1.81	0.1230	0.567	0.215	2.70
1.90	0.1150	0.578	0.201	2.84
2.11	0.1130	0.578	0.183	2.78
2.21	0.1087	0.582	0.149	2.70
2.28	0.1056	0.594	0.132	2.71
2.40	0.1015	0.615	0.124	2.83
2.55	0.1020	0.611	0.124	2.81
2.56	0.1030	0.611	0.124	2.78
2.69	0.0981	0.671	0.108	3.01

Faculty of Engineering,
Tokyo Metropolitan University,
Tokyo