Studies on the Magnetic Dichroism of Dye-Gelatin Films. IV. Confirmation of Photomagnetism by means of Magnetic Dichroism in Dye-Gelatin Films Excited by Light

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In the last paper⑴ the author reported the changes of magnetic dichroism of dye-gelatin films by excitation of light. As to the cause of this effect, the author briefly pointed out elsewhere that this effect would be due to photomagnetism of dye molecules in solid gelatin.⑵ But its treatment did not include the saturation effect of excited molecules, and the ground conception of the mechanism of magnetic dichroism was not so correct. The author⑶ made phenomenologically a theoretical consideration on the magnetic dichroism of dye-gelatin films as visco-elastic properties of gelatin, taking phosphorescence and photo-dichroism into consideration. In the visco-elastic model entropy-elasticity of chains in net-work structure of gelatin was assumed. This conception would not be so correct. But the results obtained by such a conception could explain the relaxation phenomena well, and the dichroism--time relations accorded with experimental results very well. In an ordinary way, magnetic dichroism is due to diamagnetic orientation, but in the case of paramagnetic molecules, the orientation may differ from diamagnetic ones, and dichroism-time relations are also different. The author obtained a distribution function for paramagnetic orientation and combined it with a diamagnetic one, and then obtained dichroism-time relations in co-existent state of dia- and paramagnetism. These relations can well explain qualitatively the experimental results, reported in the preceding paper. So the author supposes that the differences which appeared in magnetic dichroism-time relations by the excitation of light would be due to the photomagnetism effect, discovered by G. N. Lewis, M. Calvin and M. Kasha⑷.

⑴ D. Yamamoto, This Bulletin, **24**, 211 (1951).

⑵ D. Yamamoto, *Kagaku* (*in Japanese*), **20**, 574 (1950).

⑶ D. Yamamoto, *J. Chem. Soc. Japan*, **72**. 782 (1951).

⑷ G. N. Lewis, M. Calvin and M. Kasha, *J. Chem. Phys.*, **17**, 804 (1949).

Theoretical

Distribution Function in Paramagnetic Orientation.—As in the previous case, the author took the following four assumptions in dye-gelatin systems:

(1) Gelatin has a net-work structure and elements of a chain are allowed of micro-brownian motion to some extent. In this, entropy-elasticity is assumed.

(2) One of dye molecules attaches to one element, and its combination is fairly strong, but weaker than valence combination.

(3) Paramagnetic action of dye molecules in magnetic field is stronger than diamagnetic action of chain, so we neglect the diamagnetic orientation of chains.

(4) By the orientation of dyes, combined elements are set in rotation, and then the elongation or compression in neighboring chains of those elements appears. But in that case knots of network do not slide.

According to those assumptions, the following phenomenological equations were taken for the rotation of dye molecules;

$$\left.\begin{aligned} \frac{\mathrm{d}\vartheta}{\mathrm{d}t} &= \frac{2}{a\cdot G}\cdot\frac{\mathrm{d}F_1}{\mathrm{d}t} \\ \frac{\mathrm{d}\vartheta}{\mathrm{d}t} &= \frac{2}{a\cdot\eta}\cdot F_2 \\ F_1+F_2 &= M/a \ \times\gamma \end{aligned}\right\} \qquad (1)$$

where a is the diameter of a sphere, regarding a molecule with a combined element as a sphere, ϑ is the angle of rotation of a sphere, G is the mean elastic constant, η is the viscosity for inner flow, M is the moment of rotation, γ is a correction term which has the value of $0<\gamma<1$, presumably it is proper to take about $1/3$, and F_1 and F_2 are components for elastic and viscous action. This relation is Voigt's parallel model for visco-elastic system.

Distribution function f is represented by the following differential equation with time, as mentioned in the previous treatment.

$$\frac{\partial f}{\partial t} = -\left\{\frac{2\gamma\cdot M}{a^2\eta}\cdot\exp(-\mathrm{G}/\eta\cdot t)\right\} \times\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}(\sin\theta\cdot M\cdot f) \qquad (2)$$

where θ is the angle between direction of paramagnetic dipole moment and magnetic field. We can obtain a distribution function by solving this equation under given moment of rotation M. Moment M is given by the following relation for paramagnetic dipole

$$M = d\cdot H\cdot\sin\theta$$

where d is a constant proportional to the magnitude of paramagnetic dipolemoment of dye molecule and H is the strength of magnetic field in gauss.

Distribution function is usually represented by the following expanded series:

$$f=\frac{1}{4\pi}\{1+A_1P_1(\cos\theta)+A_2P_2(\cos\theta)+\ldots\} \qquad (3)$$

where P_1, P_2, ... are Legendre's spherical functions and A_1, A_2, ... are constants without θ. By the second order approximation, we can write a distribution function f_{para} for paramagnetic orientation as follows

$$f_{para}=\frac{1}{4\pi}\{1+R(t)P_1(\cos\theta)+S(t)P_2(\cos\theta)\} \qquad (4)$$

where $R(t)$ and $S(t)$ are functions with time. They are obtained approximately by the following method. At first $R(t)$ is obtained by the first order approximation;

$$f_{para}=\frac{1}{4\pi}\{1+R(t)P_1(\cos\theta)\} \qquad (5)$$

Combining Eqs. (2), (5) and relation $P_1(\cos\theta)=\cos\theta$, we obtained $R(t)$ as follows.

$$R(t)=-\frac{2\gamma\cdot d\cdot H}{a^2G}\{1-\exp(-G/\eta\cdot t)\} \qquad (6)$$

Next, we take the second order approximation as

$$f_{para}=\frac{1}{4\pi}\{1+R(t)P_1(\cos\theta)+S(t)P_2(\cos\theta)\} \qquad (7)$$

and by (2), (6), (7) and use $P_2(\cos\theta)=1/2\times(3\cos^2\theta-1)$, we obtain the following equation;

$$\frac{\mathrm{d}S(t)}{\mathrm{d}t}=-\frac{2\gamma\cdot d\cdot H}{a^2\eta}\cdot\exp(-G/\eta\cdot t)\cdot R(t). \qquad (8)$$

By introducing (6) in (8), we obtain the following equation for $S(t)$

$$S(t)=\frac{4\gamma^2d^2H^2}{a^4G\cdot\eta}\{1-\exp(-G/\eta\cdot t)\}^2. \qquad (9)$$

So we obtain the distribution function for paramagnetic orientation as follows:

$$f_{para}=\frac{1}{4\pi}\left\{1-\frac{2\gamma dH}{a^2G}[1-\exp(-G/\eta\cdot t)]\times P_1(\cos\theta)+\frac{4\gamma^2d^2H^2}{a^4G\eta}[1-\exp(-G/\eta\cdot t)]^2P_2(\cos\theta)\right\}.\quad(10)$$

On the other hand, the distribution function for diamagnetic orientation f_{dia} is as follows, as mentioned in a previous paper;

$$f_{dia}=\frac{1}{4\pi}\left\{1+\frac{2\gamma bH^2}{a^2G}[1-\exp(-G/\eta\cdot t)]\cdot P_2(\cos\theta)\right\},\quad(11)$$

where b is a diamagnetic constant depending on the diamagnetic susceptibility of a dye molecule.

Magnetic Dichroism—Time Relations for Paramagnetic Molecules.—Prior to the consideration for magnetic dichroism in coexsistent state of dia- and paramagnetic molecules, magnetic dichroism owing merely to paramagnetic molecules are treated. If paramagnetic molecules have molecular dichroism $(\alpha_1'-\alpha_2')$ in voluntary measuring wave length, in which α_1' is the molecular extinction coefficient parallel to the dipole moment and α_2' is one perpendicular to the α_1' direction. This conception is the same as used by W. Kuhn *et al.*,⁽⁵⁾ for exposition of electric dichroism of dye molecules.

Let α_p' be parallel component along to the direction of magnetic field H_z, directions perpedicular to H_z are H_y and H_x, and component α_s' be along the direction H_y, direction of observation is parallel to H_x, and φ be the angle between α_2' and H_y as shown in Fig. 1, the following equations are obtained.

$$\alpha_p'=(\alpha_1'-\alpha_2')\cos^2\theta+\alpha_2'$$
$$\alpha_s'=(\alpha_1'-\alpha_2')\sin^2\theta\cos^2\varphi+\alpha_2'.$$

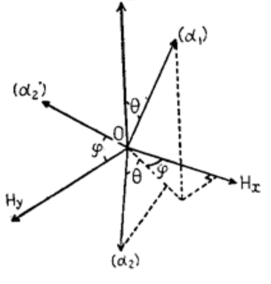

Fig. 1.

So, the factor of dichroism for a molecule $\alpha_p'-\alpha_s'$ is as follows:

$$\alpha_p'-\alpha_s'=(\alpha_1'-\alpha_2')(\cos^2\theta-\sin^2\theta\cdot\cos^2\varphi).\quad(12)$$

Dichroism of a film is represented by the following relations for N-molecules (in the material used $N=c\cdot l$, where c is mol concentration per cm²., and l is thickness of film in cm.)

$$\begin{aligned}D&=N\int(\alpha_p'-\alpha_s')f\,\mathrm{d}\Omega\\&=\frac{N}{4\pi}\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}(\alpha_1'-\alpha_2')(\cos^2\theta-\sin^2\theta\cdot\cos^2\varphi)\\&\quad\times\{1+R(t)P_1(\cos\theta)+S(t)P_2(\cos\theta)\}\sin\theta\cdot\mathrm{d}\theta\cdot\mathrm{d}\varphi,\end{aligned}\quad(13)$$

where Ω is solid angle involving θ. While

$$\iint(\cos^2\theta-\sin^2\theta\cdot\cos^2\varphi)\sin\theta\cdot\mathrm{d}\theta\cdot\mathrm{d}\varphi=0$$

$$\iint P_1(\cos\theta)(\cos^2\theta-\sin^2\theta\cdot\cos^2\varphi)\sin\theta\cdot\mathrm{d}\theta\cdot\mathrm{d}\varphi=0$$

$$\iint P_2(\cos\theta)(\cos^2\theta-\sin^2\theta\cdot\cos^2\varphi)\sin\theta\cdot\mathrm{d}\theta\cdot\mathrm{d}\varphi=\frac{4}{5}\pi.$$

so we obtain for dichroism D the following formulas

$$\begin{aligned}D&=\frac{1}{5}N(\alpha_1'-\alpha_2')S(t)\\&=\frac{4}{5}N(\alpha_1'-\alpha_2')\cdot\frac{\gamma^2d^2H^2}{a^4G\eta}\times\{1-\exp(-G/\eta\cdot t)\}^2\quad(14)\\&=D_{\infty\cdot para}\{1-\exp(-t/\tau)\}^2,\quad(15)\end{aligned}$$

where $D_{\infty\cdot para}$ is the value of dichroism for $t=\infty$.

Magnetic Dichroism—Time Relations in the Case of Co-existence of Dia- and Paramagnetic Molecules.—In the case of diamagnetic orientation D is given by the following equation after distribution function f_{dia}, as mentioned in the previous paper,

$$D_{dia}=D_\infty\{1-\exp(-t/\tau)\}\quad(16)$$

where $1/\tau=G/\eta$.

On the other hand, in the case of co-existence of both states, two factors should be considered. One of them is the degree of

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(5) W. Kuhn, H. Dürkop and H. Martin, *Z. physik. Chem.*, (B) **45**, 121 (1939).

saturation, *i. e.*, paramagnetic molecules/total molecules, and the other is molecular dichroism of paramagnetic state. If the saturation factor is put ξ, the number of paramagnetic molecules is $N\xi$, and the number of diamagnetic molecules is $N(1-\xi)$, and they are in equilibrium. As the life time of excited state τ' is shorter than relaxation time of magnetic dichroism, *i. e.*, $\tau' \ll \tau$, orientation is governed by $(1-\xi)N$'s diamagnetic molecules and $N\xi$ paramagnetic molecules statistically, so dichroism observed is as follows;

$$D_{dia}=(1-\xi)^2 D_{\infty\cdot dia}\{1-\exp(-t/\tau)\} + (1-\xi)\xi\cdot D'_{\infty\cdot dia}\{1-\exp(-t/\tau)\} \qquad (17)$$

for molecules in diamagnetic part, and

$$D_{para}=(1-\xi)\cdot\xi\cdot D_{\infty\cdot para}\{1-\exp(-t/\tau)\}^2 + \xi^2 D'_{\infty\cdot para}\{1-\exp(-t/\tau)\}^2 \qquad (18)$$

for paramagnetic part, after Eqs. (15) and (16), where

$$D_{\infty\cdot dia}=\frac{4}{5}N(\alpha_1-\alpha_2)\cdot\frac{\gamma b H^2}{a_2 G}, \qquad (19)$$

$$D_{\infty\cdot para}=\frac{4}{5}N(\alpha_1-\alpha_2)\cdot\frac{\gamma^2 d^2 H^2}{a^4 G\cdot\eta}, \qquad (20)$$

$$D'_{\infty\cdot dia}=\frac{4}{5}N(\alpha_1'-\alpha_2')\frac{\gamma b H^2}{a^2 G} \qquad (21)$$

$$D'_{\infty\cdot para}=\frac{4}{5}N(\alpha_1'-\alpha_2')\frac{\gamma^2 d^2 H^2}{a^4 G}, \qquad (22)$$

and $(\alpha_1-\alpha_2)$ is molecular dichroism for a diamagnetic molecule, and $(\alpha_1'-\alpha_2')$ is for paramagnetic molecules. In dye-gelatin phosphors, ξ is not so large that we are able to neglect ξ^2 for ξ. So we can neglect the second term of Eq. (18). By combining the two cases, we obtain the following relation in the case of co-existence of both states.

$$D=(1-\xi)[(1-\xi)D_{\infty\cdot dia}\{1-\exp(-t/\tau)\} + \xi\cdot D_{\infty\cdot para}\{1-\exp(-t/\tau)\}^2 + \xi\cdot D'_{\infty\cdot dia}\{1-\exp(-t/\tau)\}]. \qquad (23)$$

Comparison with Experimental Results

On Eq. (23), we consider two processes to compare theoretical works with experimental results.

(1) **In the Case of $(\alpha_1'-\alpha_2')=0$.**—At first we consider the case of $D'_{\infty\cdot dia}=0$, *i. e.*, $(\alpha_1'-\alpha_2')=0$. In this case, Eq. (23) is taken as follows :

$$D=(1-\xi)\cdot D_{\infty\cdot dia}[(1-\xi)\{1-\exp(-t/\tau)\} + \xi\cdot D_{\infty\cdot para}/D_{\infty\cdot dia}\times\{1-\exp(-t/\tau)\}^2] \qquad (24)$$

In the dye-gelatin phosphors, ξ is very small in comparison with dye-boric acid glass phosphor, so we are able to put it down as follows, for $(1-\xi)\doteqdot 1$:

$$D=D_{\infty\cdot dia}[\{1-\exp(-t/\tau)\} + \xi\cdot D_{\infty\cdot para}/D_{\infty\cdot dia}\times\{1-\exp(-t/\tau)\}^2]. \qquad (25)$$

For various values of $\xi\cdot D_{\infty\cdot para}/D_{\infty\cdot dia}$, curves of (25) are shown in Fig. 2. As $b<0$, and $(d^2)>0$, so the sign of $D_{\infty\cdot para}/D_{\infty dia}$ is negative.

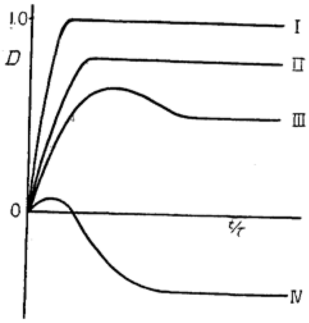

Fig. 2.—$\xi D_{\infty\cdot para}/D_{\infty\cdot dia}=$: I, 0; II, −1/5; III, −1/2; IV, −7/5.

(2) **In the case of $(\alpha_1'-\alpha_2')\neq 0$.** — If $\xi D'_{\infty\cdot dia}$ is fairly large, the term $\xi D'_{\infty\cdot dia}/D_{\infty\cdot dia}\cdot\{1-\exp(-t/\tau)\}$ is added into Eq. (25):

$$D=D_{\infty\cdot dia}[\{1-\exp(-t/\tau)\} + \xi\cdot D'_{\infty\cdot dia}/D_{\infty\cdot dia}\cdot\{1-\exp(-t/\tau)\} + \xi\cdot D'_{\infty\cdot para}/D_{\infty\cdot dia}\{1-\exp(-t/\tau)\}^2] \qquad (26)$$

and its curves are changed into what is shown in Fig. 3, for some cases.

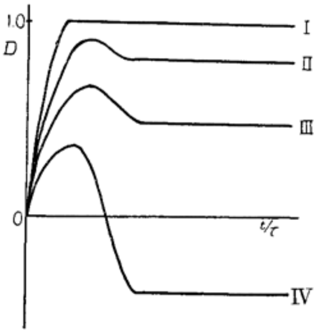

Fig. 3.—The case of $D'_{\infty\cdot dia}/D_{\infty}=1/10\sim 1/2$; I, II, III and IV correspond to I, II, III and IV in Fig. 2 respectively.

Experimental results as mentioned in the preceding paper on the malachite green-, fuchsine and fluorecein-gelatin films are in good accordance with curve IV in Fig. 3, and results on the other dyes-gelatin films with curve III in Fig. 2 or curve III in Fig. 3, in the range of measuring errors. In the former there may be molecular dichroism in paramagnetic molecules, in the measuring wave length.

Behavior in the Case of Shutting off the Excitation of Light

By shutting off the excitation of light, the value of dichroism returns rapidiy to that of mere magnetic dichroism. Its behavior is represented by the following equation, after Eq (25) or (26).

$$D=D_{\infty\cdot dia}[1+\xi\cdot D_{\infty\cdot para}/D_{\infty\cdot dia}\cdot\exp(-t/\tau')] \qquad (27)$$

or

$$D=D_{\infty\cdot dia}[1+\xi\cdot D_{\infty\cdot para}/D_{\infty\cdot dia}\cdot\exp(-t/\tau') + \xi\cdot D'_{\infty\cdot dia}/D_{\infty\cdot dia}\cdot\exp(-t/\tau')] \qquad (28)$$

where τ' is the mean life time of paramagnetic molecules. So, in this effect, relaxation time is equal to the life time of paramagnetic molecules. Experimental results mentioned before are in good accordance with this consideration, in the range of measuring errors.

Quantitative Considerations

It is very difficult to compare theoretical calculations with experimental results, and to get an accurate value of d, the important value for paramagnetic dipole moment. Because in the case of mere magnetic dichroism, G and η were not such suitable values for the materials used.

Summary

The Differences which appeared in the magnetic dichroism-time relations of dye-gelatin films by excitation of light were discussed under assumption of photomagnetism effect. Results obtained are to some extent in good accordance with experimental results qualitatively. The author, however, can not decide that this effect is entirely due to the photomagnetism. It will be valid, to some extent, to regard the effect to be due to photomagnetism.

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