The Relation between the Deformation of Substrate of PVA Sheet by Stretching and the Stretch Ratio R_s

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In the hope of analyzing relative directions of transition moments of dyes by their dichroism in stretched polyvinyl alcohol (PVA) sheets, the following equation has been derived previously in reference to the relation between the observed optical density ratio R_d and the stretch ratio R_s[1],

$$R_d=\frac{2+2(2r^2-1)T(R_s)}{(2r^2+1)-(2r^2-1)T(R_s)} \tag{1}$$

where

$$\left.\begin{aligned} T(R_s)&=\frac{R_s^2}{R_s^2-1}\\ &\times\left\{1-\frac{N(R_s)}{\sqrt{R_s^2-1}}\ln(R_s+\sqrt{R_s^2+1})\right\}\\ N(R_s)&=2\\ &\times\left\{\frac{1}{\sqrt{R_s^2-1}}\ln(R_s+\sqrt{R_s^2-1})+R_s\right\}^{-1}\\ R_s&>1 \end{aligned}\right\} \tag{2}$$

and the angle between the orientation axis of a molecule and the direction of its transition moment is given by $\cot^{-1}r$. When Eq. 1 was derived, it was assumed that an imaginary sphere in substrate of PVA sheet changes into a spheroid, keeping its volume constant, with the stretching of the PVA sheet. The relation between R_d and R_s expressed by Eq. 1, which was derived on the basis of such an assumption, coincided well with the experimental results of the dyes which the authors used. However, it has become necessary to ascertain whether the assumption is practically correct or not. This inspection was carried out by a very simple check measurement. Therefore, the method and the results obtained will be reported.

The object of this paper is to confirm the following subjects: 1) whether the width and the thickness of a PVA sheet decrease in the same ratio, when the sheet is stretched; 2) whether the relation between two quantities used when R_s was defined—namely the lengths of both long and short axes of an ellipse deformed from a circle drawn on the sheet by stretching it—coincides with the theoretical relation derived by assuming an ellipsoid of constant volume as just mentioned; 3) and whether if the two facts are just as expected, the relation between R_d and R_s of poly-iodine ions in PVA sheet[2], which seem to have both their transition moment and orientation axis in the same direction, must have the same behavior both experimentally and theoretically.

The Change in Width and Thickness of PVA Sheet When It Is Stretched.—The width and the thickness of PVA sheet were measured with a caliper and a micrometer. Let w_0 be the initial length of PVA sheet perpendicular to the stretching direction (the width), t_0 be the initial thickness, and w and t be their respective values corresponding to any R_s. Values of $(w/w_0)/(t/t_0)$ are plotted in Fig. 1, in which the white circles mean values when the ratio of the initial lengths of sheet parallel and perpendicular to the stretching direction is about 1 : 1, and the black circles those corresponding to the ratio of about 1 : 3. The figure shows clearly that the width and the thickness decrease in the same ratio at least in the former case (which has the same condition as the others which the authors have reported).

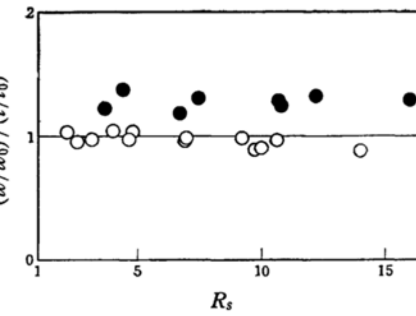

Fig. 1

1) Y. Tanizaki, This Bulletin, **32**, 75 (1959).

2) Y. Tanizaki, T. Kobayashi and N. Ando, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 445 (1959).

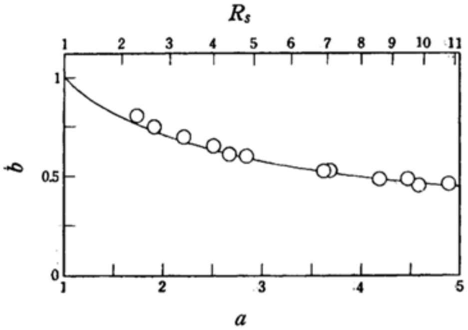

Fig. 2

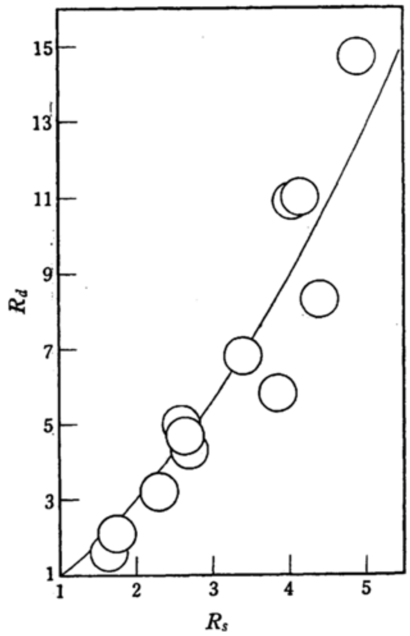

Fig. 3

The Relation between Lengths of Long and Short Axes. — Let a be the length of the long axis and b that of the short one of an ellipsoid, and then its volume is proportional to ab^2 and R_s is defined by a/b, with $a=b$ before stretching. Now, taking up a case in which the width decreases in proportion to the thickness as shown in Fig. 1, the authors searched for the following relation, to see whether the values of R_s actually used were correct. If an assumed sphere in a PVA sheet changes into ellipsoids, keeping its volume constant, when it is stretched, then the theoretical relation of $b-a$ or $b-R_s$ will be expressed by the curve shown in Fig. 2. Observed values corresponding to the curve are also shown in the figure, and they fit it satisfactorily.

The Relation between R_d and R_s of Poly-iodine Ions in PVA Sheet. — The absorption at about 600 mμ of iodine in PVA is due to linear poly-iodine ions constituted by many iodine atoms[3]. Therefore, in such a polyatomic molecule, its orientation axis coincides with the direction of its transition moment, and then the value of r mentioned above becomes infinity and Eq. 1 has the simple form of

$$R_d=[2T(R_s)]/[1-T(R_s)] \quad (3)$$

In Fig. 3 a curve drawn by Eq. 3 is shown, and corresponding observed values are also shown by white circles. This experiment was performed as follows.

Iodine was adsorbed by PVA sheets in solutions containing boric acid ~5 g.%, potassium iodide 1~2 g.%, ammonium iodide 1~2 g.% and iodine 0.2~0.5 g.%. The sheets, which were swollen beforehand in water, were dehydrated in alcohol to be put back in a hard state, in order to prevent adsorbed iodine from fleeing from the sheets. However, even by this method, iodine could not be adsorbed in a satisfactorily uniform manner. The PVA sheets which adsorbed iodine were stretched after they were dried well at room temperature. The absorption spectra by polarized light of any stretched iodine-PVA sheet did not always show the same values at corresponding angles, when the sample sheet was rotated (0° to 360°); that is, $D_{\parallel}$ (or $D_{\perp}$) of a sample was measured at two angles, but the two observed values did not always coincide with each other. Therefore, it is their average values that are shown in Fig. 3.

The agreement between the curve drawn by Eq. 3 and the observed values is a direct verification of the propriety of distribution function which was used when Eq. 1 was derived. Therefore, if only samples which are sufficiently long as compared with their width are used, when PVA sheets are stretched, it may be considered that the deformation of their substrate occurs with a constant volume (at least when $R_s<15$). This shows that the fundamental assumption employed for the derivation of the equation was proper.

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3) See Ref. 2 and those cited in it.