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Chemical Species Produced from Iodine in Stretched PVA Sheets

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A qualitative dichroism analysis has been made on chemical species produced from iodine in stretched sheets of polyvinyl alcohol. The absorption bands at 290 mμ and 360 mμ have been attributed to the bent triiodine ion, and the transition moments of these bands have been found to be parallel to each other. From the optical density ratio (R_d) curve, the presence of a hidden band at about 420 mμ has been pointed out, and the band has been assigned to the absorption by the linear triiodide ion. Three different chemical species are absorbed in the visible region. By comparing the R_d values, the numbers of iodine atoms in the respective species have been estimated.

The absorption spectra of iodine in polyvinyl alcohol (PVA) sheets or aqueous solutions of PVA consist of several bands in the ultraviolet and visible regions. Two bands at 290 mμ and 360 mμ which may be considered to be due to the triiodide ion always appear, whatever the conditions. From the difference in dichroic properties, Tanizaki *et al.*1) suggested that these bands originated with different chemical species. The other bands in the visible region are due to the longer polyiodide ions, and either appear or not depending upon the conditions of preparation.1) Savko and Faerman2) observed that the blue color (maximum absorption at 600 mμ) does not appear in solutions of PVA and iodine dissolved in aqueous solutions containing iodide ions, but that dried sheets prepared from these solutions show a very strong absorption at 600 mμ. They concluded, therefore, that water prevents the formation of a blue complex, by displacing the polarized configuration of iodine atoms bound to triiodide anions in the polymer network.2) In the ioidne-PVA mixture, an excess of potassium iodide intensifies the 600 mμ band by completely binding the iodine to form triiodide ions.3) Mokhnach and Propp4) suggested that the iodine complex with polyvinyl alcohol absorbs at 600 mμ, and that the appearance of the 288 mμ band is due to triiodide ions, while that at 350 mμ is due to hypoiodite ions.4)

Triiodide in various solvents shows two absorption bands, at 290 mμ and 360 mμ, the former being always higher in intensity than the latter.5–7) By the continuous-variation method using mixtures consisting of tetramethylammonium iodide and iodine in ethylene chloride, it is confirmed that the only species which absorbs at 295 mμ and 365 mμ is the triiodide ion.8) Robin found that the high intensity of the I_3^- bands could be explained using the MO theory only if the ion were bent.9)

From the X-ray diffraction pattern of iodine in stretched PVA sheets, West10) concluded that straight chains of polyiodides are formed, all of them parallel to the stretching direction. Rundle11) pointed out that, in the one-dimensional array,

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1) Y. Tanizaki, T. Kobayashi and N. Ando, *Nippon Kagaku Zasshi*, **80**, 455 (1959).

2) S. S. Savko and G. P. Faerman, *Opt. Spektrosk.*, **22**, 912 (1967); *Chem. Abstr.*, **68**, 50501p (1968).

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4) V.O. Mokhnach and L.N. Propp, *Iodinol Med. Vet. Eksp. Klin. Izsled, Akad. Nauk SSSR., Biol. Inst.*, 1967, 21; *Chem. Abstr.*, **68**, 30450t (1968).

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8) R. E. Buckles, J. P. Yuk and A. I. Popov, *ibid.*, **74**, 4379 (1952).

9) M. B. Robin, *J. Chem. Phys.*, **40**, 3369 (1964).

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11) R. F. Rundle, *ibid.*, **15**, 880 (1947).

all of the I-I spacings are identical, and that all are somewhat shorter than the van der Waals separation.

In the present study, the identification of the various species formed from iodine in the stretched PVA sheets was attempted using their linear dichroism. The analysis of the dichroic spectra could not be applied in the present case because the chromophores in the sheet could not be oriented enough to allow the application of the theory.[12] Although quantitative analysis could not be carried out for this reason, useful qualitative information regarding the absorbing species, especially the triiodide ion, could be obtained.

Experimental

The preparation of PVA sheets from polyvinyl alcohol powder has been described elsewhere.[12] In this experiment, sheets about 0.2 mm thick were prepared from commercial PVA powder, whose polymerization degree was 1400. The adsorption of iodine was achieved by hanging the PVA sheet in a bottle with a mouth 500 m*l* wide and containing a few iodine crystals. Under a low humidity, iodine could not be diffused into the dry PVA sheet; therefore, a drop of water was added to the bottle. The sample sheets were prepared as follows:

(1) The iodine was adsorbed on a dry PVA sheet, and its absorption spectrum was measured using unpolarized light. The spectrum is shown as Curve D in Fig. 1.

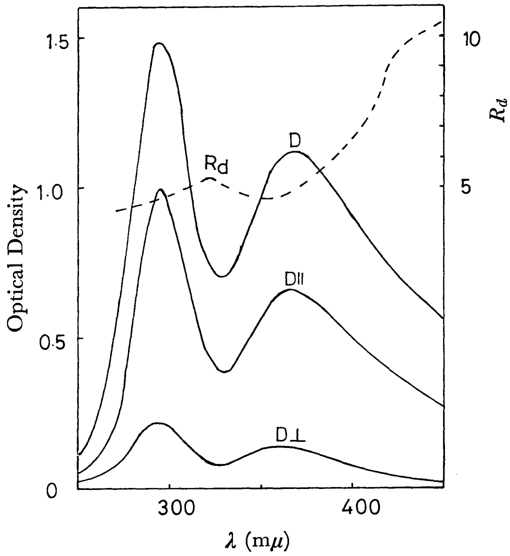

Fig. 1. Absorption spectra of iodine in dry PVA sheet. The D curve is the absorption for the non-stretched state. The $D_{\parallel}$ and $D_{\perp}$ curves (dichroic spectra) are the absorptions of the stretched sheet for light with electric vector parallel and perpendicular, respectively, to the stretching direction. R_d means the ratio of $D_{\parallel}$ and $D_{\perp}$.

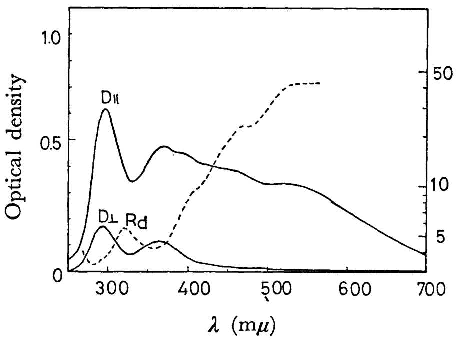

Fig. 2. Dichroic spectra of iodine adsorbed after stretching the dry sheet.

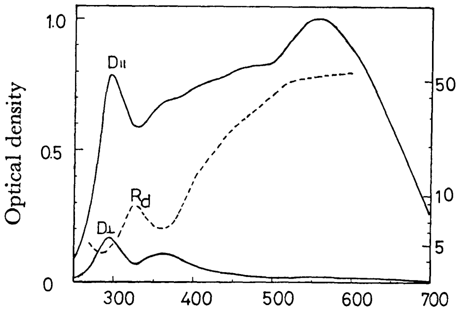

Fig. 3. Dichroic spectra of iodine adsorbed in humid atmosphere after stretching the dry sheet.

(2) After the iodine had been adsorbed, the sheet was stretched. The absorption spectra obtained using plane-polarized light are shown in Fig. 1 ($D_{\parallel}$ and $D_{\perp}$), where $D_{\parallel}$ and $D_{\perp}$ are the absorptions for the light with electric vector respectively parallel and perpendicular to the stretching direction of the sheet.

(3) After stretching, a piece of dry PVA sheet was put in the adsorption bottle. Its dichroic spectra are shown in Fig. 2. Fig. 3 shows the dichroic spectra of a sample sheet prepared in the same way as above, but here more water was added before the iodine adsorption.

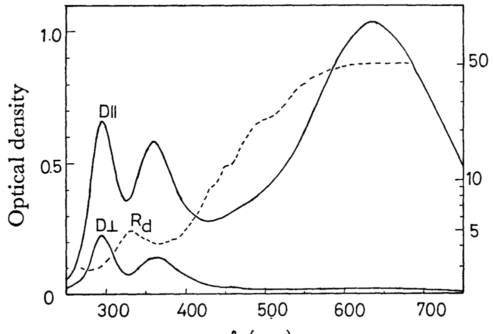

Fig. 4. Dichroic spectra of iodine in the blue-colored state.

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(4) PVA sheet was digested in distilled water for at least two hours, and the wet sheet was put in the bottle and then stretched at room temperature. The sheet was air-dried overnight, and then its dichroic spectra were determined (see Fig. 4).

The adsorption of iodine was done at room temperature (about 20°C) until the iodine concentration was sufficient for spectrophotometric measurements. A dry sheet was stretched at 80°C by a stretching machine. The stretched ratio was 9 for the sheet which was stretched in the dry state, while that for the sheet stretched in the wet state was 8 as determined after the sheet became dry. (The stretch ratio was determined by a procedure described elsewhere,[12] but the deformation of the substrate by stretching did not satisfy the conditions required for the dichroism analysis).

The absorption measurements were made with a Shimadzu QR-50 spectrophotometer, equipped with a Glan-Thomson-type polarizer and a simultaneous rotation apparatus for sample and reference sheets.

Results and Discussion

Figure 1 indicates that the stretching does not induce any change in the absorption pattern. In fact, the absorption curve of an unstretched sample sheet coincided completely with the curve, D, obtained by $D=k(D_{\parallel}+2D_{\perp})$, where k is a constant. Moreover, as can be seen in the other figures, the intensity ratio at 290 mμ and 360 mμ of the $D_{\perp}$ curve is always constant at about 1.6. Therefore, both bands must be attributed to only one species, as has been shown by Buckles *et al.*,[8] this species may be considered to be the triiodide ion.

The triiodide ion can be either linear ($D_{\infty h}$) or bent (C_{2v}) in geometry. From the symmetry, the allowed transitions in the linear ion should have only one kind of polarization (long axis, Z), while the strong transitions in the bent ion can have two kinds of polarization (long axis, Z, and short axis, X).

The R_d curve in Fig. 1 is not flat over the region of the two bands, but rises with a sharp inclination from about 350 mμ to 430 mμ and shows a maximum between the two bands. Such a tendency of the R_d curve is also observed at the corresponding part in all the dichroic spectra shown in other figures. This implies that a different kind of absorption band with a higher R_d value (a smaller orientation angle) is hidden near the 360 mμ band.

According to the empirical facts of the dichroism investigation, a long molecule in a stretched PVA sheet will preferentially orient its long axis parallel to the stretching direction of the sheet. Moreover, if there are two bands orthogonal to each other and if the one has a R_d value larger than about 5, then the other must have a value smaller than 0.5. As for the 290 mμ and the 360 mμ bands, therefore, it can safely be said that their polarizations are parallel to each other; besides, they lie along the Z axis. This conclusion is in agreement with the prediction of Robin.[9]

The hidden band with a higher R_d value can be explained only by considering another species. From the point of view of dichroism, a linear molecule will show a higher R_d value than a bent one. Therefore, the hidden band can be attributed to absorption by a linear species. It seems very probable that a linear triiodide ion is another species which can exist besides the bent ion. The only allowed transition for the linear triiodide ion (calculated as a $a_{1g}\rightarrow a^*_{2u}$ by Robin[9]) will lie somewhere near the band region of 290 mμ and 360 mμ. The behavior of the R_d curve of Fig. 1 can be understood in terms of the existence of the linear triiodide ion.

The polarizations of all the absorptions in the visible region are much more parallel to the stretching direction than that of the triiodide ion. The R_d curve in Fig. 2 is complicated; in it the inflective parts correspond well to the shoulders of the $D_{\parallel}$ curve. Such a correspondence seems to indicate that there are absorptions at 450 mμ and 540 mμ. The long tail in the longer-wavelength side of 540 mμ suggests the presence of a hidden band in this region. Figure 3 shows the dichroic spectra of a sample containing more water than is the case in Fig. 2. The increase in the water content results in an intensifying of the 540 mμ band and shifting it to 570 mμ. The dichroic spectra of the sample (Fig. 4) treated in the wet state show a very intense band at 630 mμ and, at the same time, the disappearance of the 450 mμ and 540 mμ bands, though the R_d curve clearly indicates the existence of these bands.

Thus, taking into account the facts that the iodine atoms in a PVA-iodine complex are arranged in a one-dimensional array[10] and that the R_d value reflecting the orientation of the polarization, which should lie on the long axis of a linear species, is different from band to band, it may be considered that all the absorption bands in the visible region are to be attributed to different species. The only difference among the species is in the geometrical length. The longer the length (the larger the number of atoms) of the species, the longer the wavelength of absorption. This consideration is in agreement with the fact that the longer-wavelength bands have the larger R_d values. With respect to the R_d values, this means that the orientation angle (the angle between the orientation axis and the Z axis) becomes smaller as the length of the species increases.

If the orientation angles of the linear polyiodide ions, including the triiodide ion, have some relation to the lengths of the species, the length can be estimated from a comparison of the R_d values, taking the value of the linear triiodide ion as a standard; therefore, the number of iodine atoms in each species may be determined. The method is illustrated with a model in Fig. 5.

Unfortunately, we could not find the distribution

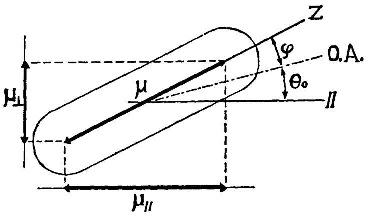

Fig. 5. Schematic illustration of the components ($\mu_\perp$, $\mu_{||}$) of transition moment (μ) of an oriented molecule representative of a species in a distribution state. O.A. represents the orientation axis, and || the stretching direction of the substrate.

function applicable to the present case. Nevertheless, for a stretched state there must be a distribution function which is common to all the species in a stretched sheet. Since the distribution indicates the distribution of an orientation axis (O.A.) of a species, the direction of O.A. must be common to all species. The only difference among species is, therefore, the difference in angle (φ) between O.A. and the transition vectors (μ). The transition vectors of the species are distributed uniformly with the φ around the O.A. axis. If θ_0 is representative of the distribution angle of O.A. to the stretching direction (||), the angle of μ about || can vary from $(\theta_0+\varphi)$ to $(\theta_0-\varphi)$. Allowing θ $(=\langle\theta_0\pm\varphi\rangle)$ to denote an average angle of μ about the direction, we have:

$$R_d = \frac{D_{||}}{D_\perp} = \mu^2 \cos^2\theta/\mu^2 \sin^2\theta \tag{1}$$

As may be seen in Figs. 1—4, the $D_\perp$ of the visible region is very small and is almost constant except for the region affected by the absorption of the bent triiodide ion. Regarding $D_\perp$ as constant for all species under consideration, we can express the ratio of the R_d values for the species A and B as follows:

$$\frac{R_d(B)}{R_d(A)} = \frac{\mu_{||}^2(B)}{\mu_\perp^2(\mathrm{A})} = \frac{\mu_B^2 \cos^2\theta_B}{\mu_A^2 \cos^2\theta_A} \tag{2}$$

If we may assume that μ is proportional to the length (L) of the species, then Eq. (2) becomes:

$$R_d(B)/R_d(A) = L_B^2 \cos^2\theta_B/L_A^2 \cos^2\theta_A \tag{3}$$

Since θ is very small, we can put $\cos^2\theta$ equal to unity for the first approximation. Using the ratio of the observed R_d values and taking the linear triiodide ion (Species A) as a standard, the lengths of the other species can be estimated. If we take 3.1 Å to be the distance between iodine atoms,[10] the number of atoms of the absorbing species can be estimated to be as is shown in Table 1. In the estimation, we use the value of the R_d curve at around 420 mμ, assuming that an absorption band of the linear triiodide ion is hidden in this region.

It is clear from Fig. 5 that the length-ratio obtained here does not mean the actual ratio of the species, but the ratio of the components parallel to the stretching direction. Naturally, the estimated value presented in Table 1 represents the maximum number of iodine atoms for the species in the PVA sheet; that is, the number of atoms of the actual species should not exceed the number shown in Table 1.

Table 1. Estimation of the number of iodine atoms in the species which have the visible absorption bands

Band	$\sqrt{\frac{R_d}{R_d(\mathrm{I_3^-})}} = \frac{L}{L(\mathrm{I_3^-})}$	Number of atoms
420 mμ	1.0	3
450 mμ	1.4—1.5	4
540 mμ	2.0	5
630 mμ	2.8	7

Several workers have estimated the number of iodine atoms in the species formed in the blue colored amylose-iodine system,[13—15] but their results have not always coincided. The reported values are for starch-iodine systems, so that a direct comparison with the PVA-iodine system is not possible. As has been confirmed by the X-ray diffraction analysis of the halogens incorporated within hydrophilic high polymers (including starch and PVA), the characteristic pattern is independent of the polymer in which the halogens are incorporated. The systems depend only on the type of halogens.[10] This fact suggests that a qualitative comparison is possible. According to the estimated values by Ono *et al.*,[13] for instance, a species consisting of more than one hundred iodine atoms is possible only if the iodine atoms in the polymer are helical or are arranged in a manner similar to that of helical. Since it is known that, in all cases, the iodine atoms are linearly arranged,[10] such large polyiodines are very difficult to understand from the point of view of dichroism.

From the results presented in Table 1, the following mechanism of the formation of polyiodide chains can be proposed, though there is no evidence for the mechanism of the formation of the triiodide ion at the present stage:

$\mathrm{I_4}$: $\mathrm{I_2 + I_2 = I_4}$

$\mathrm{I_5^-}$: $\mathrm{I_3^- + I_2 = I_5^-}$

$\mathrm{I_7^-}$: $\mathrm{I_3^- + I_4 = I_7^-}$ and/or $\mathrm{I_5^- + I_2 = I_7^-}$

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