

# Sorption and Permeation of Iodine in Water-Swollen Poly(vinyl Alcohol) Membranes and Iodine Complex Formation

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## Synopsis

The sorption and the permeation of iodine in water-swollen poly(vinyl alcohol) (PVA) membranes and the formation of PVA-iodine complexes were studied. The logarithms of the permeability and the diffusion coefficient decreased approximately linearly with the increase in polymer volume fraction. When the membrane was soaked in an aqueous  $I_2$ -KI solution, it contracted and Young's modulus increased. These findings were explained in terms of the formation of extra junction points due to the PVA-iodine complexes. These changes were reversible and could be recovered by replacing the solution with water. The length of the polyiodine chain increased with the increase in the degree of hydration of the membrane. At a fixed degree of hydration, Young's modulus of an iodine-sorbed membrane was much greater than that of a membrane soaked in pure water. This finding was explained on the basis of a double-network structure. The extension of the membrane promoted the complex formation, and the complex disappeared when the tension was released. The critical strain necessary for the complex formation was independent of the degree of hydration. The length of polyiodine chain increased with strain and became constant at higher strains.

## INTRODUCTION

It is well known that an aqueous solution of poly(vinyl alcohol) (PVA) gels when it is kept at a comparatively low temperature for a long time.<sup>1</sup> In the gel networks, crystallites were considered to act as junction points.<sup>2</sup> The addition of an  $I_2$ -KI solution accelerated the gelation.<sup>3</sup> This result may be explained in terms of the formation of extra junction points due to PVA-iodine complexes. The complex develops a characteristic blue color as the amylose-iodine complex. X-ray studies on the stretched PVA films containing iodine showed the presence of polyiodine chains (PVA-iodine complex),<sup>4,5</sup> which was supported by the spectroscopic studies in a visible region.<sup>6,7</sup> The stretched PVA films with iodine are important for polarizing devices.

Zwick proposed a model for the PVA-iodine complex in which a polyiodine chain is surrounded by helical PVA molecules,<sup>8</sup> analogous to the structure of the amylose-iodine complex.<sup>9,10</sup> Rundle and co-workers proposed another model in which a polyiodine is arranged parallel to an extended PVA chain.<sup>11</sup> Tebelev and co-workers proposed a similar model in which polyiodine chains are surrounded by several extended PVA chains.<sup>12</sup> This model is analogous to that of the fringed-micellar structure, and seems to be more

suitable than Zwick's model for the explanation of the acceleration of the gelation caused by the addition of iodine.

The sorption of iodine in a water-swollen PVA membrane is necessary for the formation of PVA-iodine complexes. The network structure in the membrane will be changed by the extra junction points due to iodine complexes. The complex formation depends on the concentration of iodine in the PVA membrane<sup>8</sup> and on the reaction temperature.<sup>7,13</sup> In general, the higher the concentration and the lower the temperature, the easier to form complexes. When the concentration decreases at a fixed temperature, it finally becomes impossible for PVA to form complexes with iodine. It was shown that the extension of PVA membranes promoted the formation of complexes at a fixed concentration of iodine.<sup>7</sup>

In this article, the sorption and permeation of iodine in water-swollen PVA membranes and the formation of PVA-iodine complexes were studied. The logarithms of the permeation and diffusion coefficients changed almost linearly with the volume fraction of PVA in the membrane. Young's modulus and the volume of the membrane changed due to the sorption of iodine. The formation and the structure of the complex were studied spectroscopically. The effect of the extension of the membrane, soaked in a dilute I<sub>2</sub>-KI solution, on the formation of the complex was also studied.

## EXPERIMENTAL

### Materials

A PVA sample of DP = 2000 (Koso Chemical Co., degree of hydrolysis = 0.992) was used in this study. Membranes, 200  $\mu\text{m}$  thick, were cast on PMMA plates from 7% aqueous solutions at 25°C. In order to obtain membranes with various degrees of hydration (volume fraction of water in the membrane at equilibrium), they were annealed at various temperatures for 10–15 min under vacuum. They were then dipped in water at 25°C until the swelling equilibrium was reached (for 5 days), during which water was repeatedly renewed. Iodine and potassium iodide (Yanagishima Pharmaceutical Co., GR grade) were used without further purification.

### Sorption Experiment

In I<sub>2</sub>-KI solutions with an excess of KI, most of the iodine molecules are in the form of I<sub>3</sub><sup>-</sup>, and therefore KI<sub>3</sub> was considered to be sorbed and permeate in the water-swollen PVA membranes. Sorption experiments were carried out at 25°C in order to obtain the partition coefficient, *K*, defined as the ratio of the concentration of KI<sub>3</sub> in the membrane to that in the solution. The concentration of iodine in the solution changed only slightly during the sorption experiment. In a typical experiment, a water-swollen PVA membrane (0.1g) was kept in an I<sub>2</sub>-KI solution (50 mL, [I<sub>2</sub>] = 5 × 10<sup>-5</sup> mol/mL, [KI] = 10<sup>-4</sup> mol/mL) for a fixed time. It was then blotted quickly between sheets of paper to remove the excess solution on the surfaces, and was dissolved in hot deionized water. The concentration of KI<sub>3</sub> was determined by iodometry.

### Permeation Experiment

Permeation experiments were carried out at 25°C, using the same apparatus as in a previous study.<sup>14</sup> A water-swollen membrane was clamped between two cells without any supporting equipment. The effective area of the membrane for permeation was 7.07 cm<sup>2</sup>. The high-concentration side was filled with 285 mL of an I<sub>2</sub>-KI solution ([I<sub>2</sub>] = 5 × 10<sup>-5</sup> mol/mL, [KI] = 10<sup>-4</sup> mol/mL), while the low-concentration side was filled with 75 mL of deionized water at the start of the experiment. The solutions in both sides were stirred by stirrers in order to reduce the boundary-layer effect. The change in the solute concentration in the low-concentration side was monitored as a function of time by means of the optical absorption at 500 nm. The permeability  $P$  of KI<sub>3</sub> was calculated at the steady state. The diffusion coefficient  $D$  was calculated from  $P$  and  $K$ ,  $D = P/K$ .

### Extension Experiment

PVA membranes, 1–2 cm long and 4 mm wide, soaked in an I<sub>2</sub>-KI solution ([I<sub>2</sub>] = 5 × 10<sup>-5</sup> mol/mL, [KI] = 10<sup>-4</sup> mol/mL) were stretched at a rate of 2.3 mm/min at 25°C, and the force was measured by the use of a strain gauge with a maximum capacity of 80 g. The stress was calculated from the force and the cross-sectional area of the membrane. Young's modulus was calculated from the initial slope.

### Visible Absorption Spectra

The visible absorption spectra of PVA membranes which had been soaked in an I<sub>2</sub>-KI solution ([I<sub>2</sub>] = 5 × 10<sup>-5</sup> mol/mL, [KI] = 10<sup>-4</sup> mol/mL) at 25°C were recorded on a Hitachi 124 UV-VL Spectrophotometer. The absorption spectra of the membranes which has been stretched to various degrees in a more dilute I<sub>2</sub>-KI solution ([I<sub>2</sub>] = 5 × 10<sup>-7</sup> mol/mL, [KI] = 10<sup>-6</sup> mol/mL) were also measured.

## RESULTS AND DISCUSSION

### Sorption and Permeation of Iodine

In Figure 1, the permeability and the diffusion coefficient of KI<sub>3</sub> obtained from the permeation experiments are plotted against  $1-H_0$ , the volume fraction of PVA ( $H_0$  is the degree of hydration in pure water). The diffusion coefficients were also estimated from sorption data at the early stage using<sup>15</sup>

$$M(t)/M(\infty) = (4/\sqrt{\pi})(Dt)^{1/2}/\Delta X \quad (1)$$

where  $\Delta X$  is the thickness of the membrane and  $M(t)$  and  $M(\infty)$  are the amounts of KI<sub>3</sub> sorbed in the membrane at time  $t$  and after infinite time, respectively. Although the volume of the membrane decreased due to the sorption of iodine, as described below, the diffusion of iodine into the membrane took place much faster than the contraction of the membrane. Therefore, the volume was assumed to be constant until the sorption equilibrium was reached. The diffusion coefficients thus obtained are also shown in

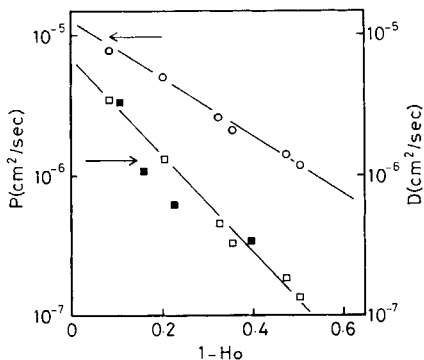


Fig. 1. The dependence of the permeability  $P$  and the diffusion coefficient  $D$  of iodine on the volume fraction of PVA,  $1-H_0$ : ( $\square$ )  $D$  from permeation experiment; ( $\blacksquare$ )  $D$  from sorption experiment.

Figure 1, and seem to agree with those calculated from the permeation data. As the figure shows, the plots of  $\log P$  and  $\log D$  against  $1-H_0$  are almost linear, implying the following relation between  $D$  and  $H_0$ <sup>14</sup>:

$$\ln D = \ln D_0 - (1 + r/R)^2(1 - H_0) \quad (2)$$

where  $D_0$  is the diffusion coefficient in pure water and  $r$  and  $R$  are the radii of a solute and of a fibril, respectively. From the slope, the value of  $r/R$ , was calculated to be about 2. This was very close to those obtained for Congo Red and Sunset Yellow.<sup>14</sup> Further, the value of  $D_0$  estimated from the intercept was close to those of two dyes in pure water ( $5.7 \times 10^{-6}$  cm<sup>2</sup>/s<sup>16</sup> and  $6.6 \times 10^{-6}$  cm<sup>2</sup>/s<sup>14</sup> for the dyes and  $6.1 \times 10^{-6}$  cm<sup>2</sup>/s in this case). Stokes' radius calculated from  $D_0$  using the Stokes-Einstein equation was 4A and this was probably close to  $r$ . The partition coefficient of KI<sub>3</sub> calculated according to

$$K = M(\infty)/C(s) \cdot V \quad (3)$$

where  $C(s)$  is the concentration of KI<sub>3</sub> in the solution and  $V$  is the volume of the membrane, is plotted against  $H_0$  in Figure 2. It was larger than unity and decreased with the increase in  $H_0$ , approaching to unity at infinite swelling ( $H_0 = 1.0$ ). In this case, the  $H_0$ - $K$  plot showed no inflection such as observed at  $H_0 = 0.75$  for some solutes.<sup>14</sup> As a rough approximation,  $K$  is given by a simple additivity of contribution of PVA and the water in the membrane,

$$K = K_p(1 - H_0) + K_s H_0 \quad (4)$$

where  $K_p$  and  $K_s$  are partition coefficients in PVA and in the water, respectively. If  $K_s$  is assumed to be unity, eq. (4) becomes

$$K_p = (K - H_0)/(1 - H_0) \quad (5)$$

As the value of  $K$  was large, this assumption caused no serious error in the estimation of  $K_p$ . Thus calculated  $K_p$  was 15 and was independent of  $H_0$ ,

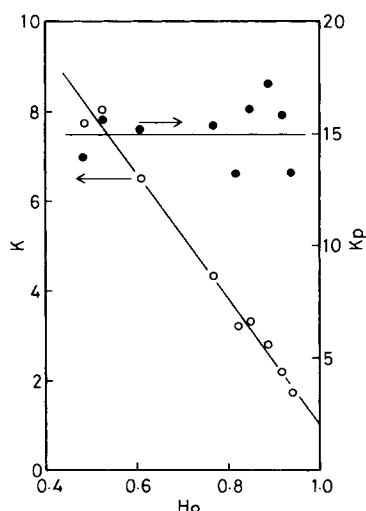


Fig. 2. The partition coefficient of iodine in the PVA membrane,  $K$ , and that in the polymer,  $K_p$ , against  $H_0$ .

corresponding to 13 vinyl alcohol residues per an iodine atom. This value is close to that reported by Zwick (12 repeating units per an iodine atom in the presence of borate).<sup>8</sup> However, it should be remarked that thus estimated value is not unequivocal because PVA consists of crystalline and amorphous phases, and the former does not take part in the iodine sorption.

### Changes in Volume and Modulus Due to Iodine Sorption

When water-swollen PVA membranes were soaked in an  $I_2$ -KI solution, they contracted and Young's modulus increased. Figure 3(a) shows the changes in length and Young's modulus during soaking cycles in the  $I_2$ -KI solution and in water. These changes were reversible, as those in the well-known mechanochemical systems.<sup>17,18</sup> The increase in Young's modulus and the contraction of PVA membranes in  $I_2$ -KI solutions are related to the formation of extra junction points due to PVA-iodine complexes. The contraction of the membrane soaked in the  $I_2$ -KI solution was anisotropic; it took place mainly in the plane direction of the membrane and scarcely in the thickness direction. The contraction in the plane direction was uniform and isotropic. This anisotropic contraction may be explained in terms of the preferable molecular orientation parallel to the plane of the membrane. It should be remarked that the changes in modulus and in length caused by the soaking in the  $I_2$ -KI solution were much slower than those due to the subsequent soaking in pure water. In Figure 3(b), the volume, Young's modulus, and the amount of iodine sorbed in the membrane are plotted against the soaking time. The membrane used had  $H_0$  of 0.9. This figure shows that the iodine sorption ended in a short time and that the changes in volume and in Young's modulus took place mainly after the completion of the sorption. The same trend was observed for other membranes. These results show that the rate of the formation of the PVA-iodine complex was smaller than that of the iodine sorption.

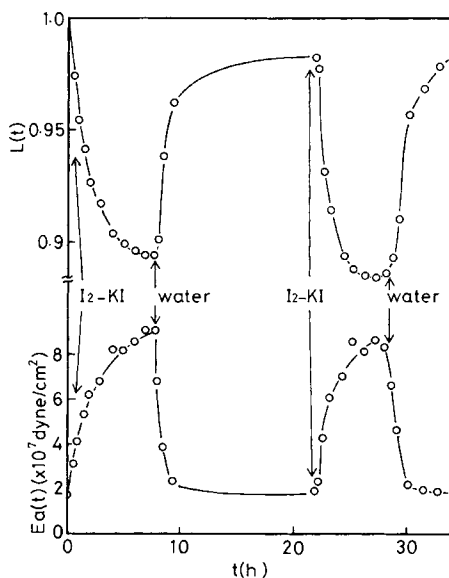


Fig. 3(a). The changes in length,  $L(t)$ , and in Young's modulus,  $E_a(t)$ , during soaking cycle in an  $I_2$ -KI solution and in water.  $H_0 = 0.647$ .

It is well known that Young's modulus of a polymer gel,  $E$ , is expressed as a function of the volume fraction of the polymer,  $V_p$ , as follows<sup>19-22</sup>:

$$\log E = \log A + B \log V_p \quad (6)$$

where  $A$  and  $B$  are constants. Young's moduli of water-swollen PVA membranes are plotted against the volume fraction of polymer,  $V_p = 1 - H_0$ , in Figure 4, to show that eq. (6) is satisfied in this case; the logarithm of modulus increased linearly with the logarithm of  $V_p$  with an inflection at  $H_0 = 0.75$ , giving following relations:

$$\log E_0 = \log (7 \times 10^7) + 2 \times \log (1 - H_0) \text{ for } H_0 \geq 0.75 \quad (7)$$

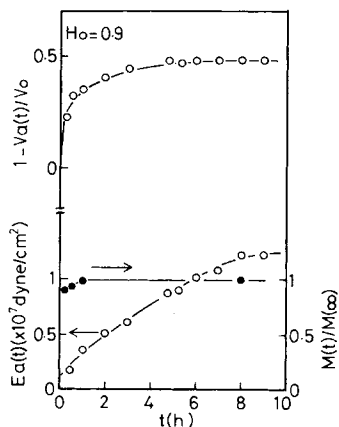


Fig. 3(b).  $E_a(t)$ , the decrease in volume,  $1 - V_a(t)/V_0$  ( $V_0$  is the initial volume) and  $M(t)/M(\infty)$  against soaking time.  $H_0 = 0.9$ .

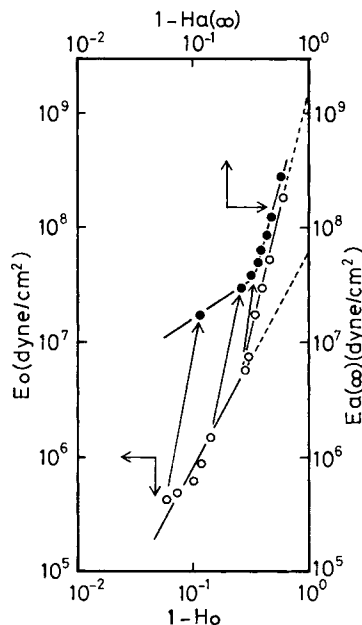


Fig. 4. The relations between  $E_0$  and  $1-H_0$  and between  $E_a(\infty)$  and  $1-H_a(\infty)$ .

$$\log E_0 = \log (2 \times 10^9) + 5 \times \log (1 - H_0) \text{ for } H_0 \leq 0.75 \quad (8)$$

It is interesting to note that  $H_0$  of 0.75 corresponds to the maximum amount of bound water. Hatakeyama et al.<sup>23,24</sup> studied the melting behavior of water in PVA hydrogels and showed that one repeating unit of PVA fixed six water molecules to make bound water. This value corresponds to  $H_0$  of 0.76. When a water-swollen PVA membrane was soaked in an  $I_2$ -KI solution, the volume fraction of PVA and Young's modulus increased along the arrows shown in the figure. The same figure shows the relation between Young's modulus,  $E_a(\infty)$ , and the volume fraction of PVA,  $1-H_a(\infty)$ , at the equilibrium state in the  $I_2$ -KI solution. Young's modulus of the iodine-sorbed membrane depended on the degree of hydration in the same manner as that of the membrane in pure water. An inflection point also appeared at  $H_a(\infty)$  of 0.7, which corresponds approximately to the maximum amount of bound water. It should be noted that  $E_a(\infty)$  was always larger than  $E_0$  at a fixed degree of hydration, and this tendency became more pronounced at higher degrees of hydration. This fact cannot be explained on the basis of a homogeneous network structure,<sup>25</sup> but may be explained in terms of a double-network structure,<sup>26</sup> which is shown schematically in Figure 5. In the water-swollen PVA membrane, water molecules are mixed with amorphous chains in each fibril (amorphous chain network) and also with fibrillar (fibrillar network). Distances between fibrillar network chains are larger than those between amorphous network chains. Thus the extra junction points due to the iodine complexes are mainly formed from amorphous network chains, causing a slight decrease in hydration, while increasing remarkably Young's modulus.

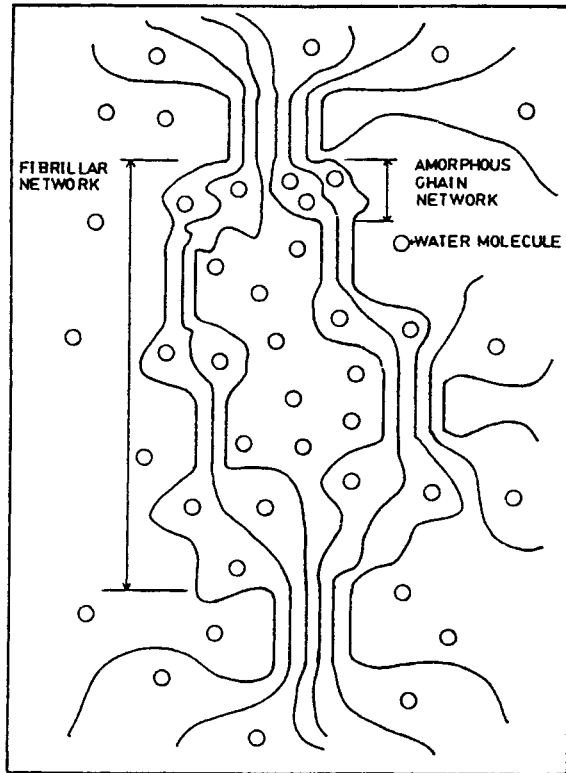


Fig. 5. A schematic representation of the double-network structure.

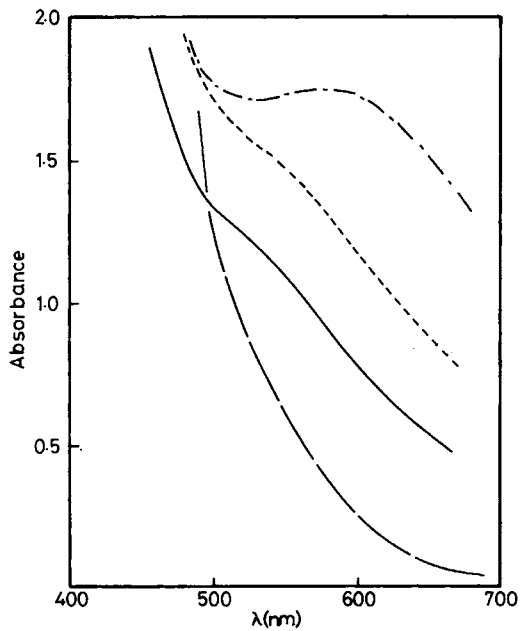


Fig. 6. The absorption spectra of iodine-sorbed PVA membranes together with that of an  $I_2$ -KI solution.  $H_0$ : (— · —) 0.867; (---) 0.738; (—) 0.388; (— —)  $I_2$ -KI.



### Visible Absorption Spectra

Figure 6 shows absorption spectra of PVA membranes which had been soaked in an  $I_2$ -KI solution ( $[I_2] = 5 \times 10^{-5}$  mol/mL,  $[KI] = 10^{-4}$  mol/mL), together with that of the solution. On account of the strong extinction, meaningful spectra could only be obtained at the initial stage of sorption. An absorption maximum due to the PVA-iodine complex<sup>8</sup> appeared in a visible region for all membranes, while it could not be observed in the spectrum of the  $I_2$ -KI solution. The absorption maximum,  $\lambda_{\max}$ , remained constant during the iodine sorption, that is, it was independent of the amount of iodine sorbed in the membrane. Figure 7 shows the relation between  $\lambda_{\max}$  and  $H_0$ . The  $\lambda_{\max}$  increased linearly with the increase in  $H_0$ , approaching 620 nm, which corresponds to that of the PVA-iodine complex in aqueous solutions.<sup>7,27</sup> The  $\lambda_{\max}$  remained constant after the membrane had been dried. The number of iodine atoms in the polyiodine chain in the PVA-iodine complex has been estimated by several methods,<sup>28-30</sup> indicating that the longer polyiodine absorbs at longer wavelength. Therefore, it is concluded that the length of the polyiodine chain increased with the increase in  $H_0$ , the volume fraction of water in the PVA membrane.

### Effect of Extension on Complex Formation

As described above, PVA membranes soaked in an  $I_2$ -KI solution ( $[I_2] = 5 \times 10^{-5}$  mol/mL,  $[KI] = 10^{-4}$  mol/mL) formed iodine complexes at 25°C, but it was impossible to form the complex when the membranes were soaked in a dilute  $I_2$ -KI solution ( $[I_2] = 5 \times 10^{-7}$  mol/mL,  $[KI] = 10^{-6}$  mol/mL). The extension of PVA membranes promoted the formation of the PVA-iodine complexes. Figure 8 shows the absorption spectra of PVA membranes

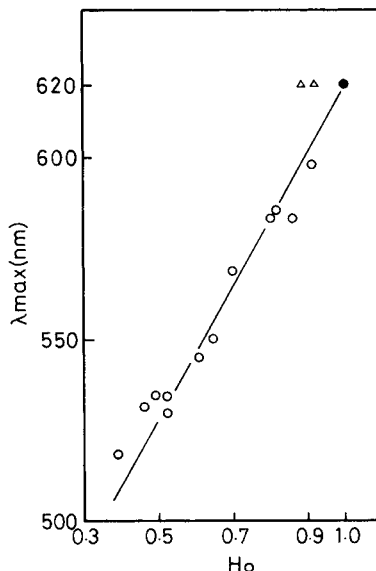


Fig. 7. The wavelength at the absorption maximum,  $\lambda_{\max}$ , as a function of  $H_0$ : (△) Ref. 7; (●) Ref. 27.

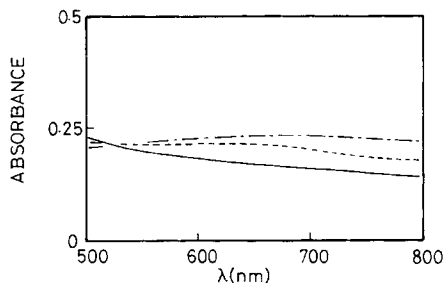


Fig. 8. The change in absorption spectrum of an iodine-sorbed PVA membrane during extension.  $H_0 = 0.867$ . Strain: (—) 0; (---) 0.87; (- · -) 2.69.

which had been stretched in the dilute solution at 25°C. Without strain, the absorbance decreased monotonously with increasing wavelength, which shows that no complexes were formed at this stage. A broad absorption peak appeared under extension and the membrane turned to blue. The  $\lambda_{\max}$  due to the PVA-iodine complex increased with extension. These changes were reversible and the original pale brown membrane could be recovered by releasing the tension.

It is interesting to recall that the extension of polymer chains increases the melting point of polymer crystals, as discussed quantitatively by some authors for ideal rubber chains<sup>31</sup> and for the crystalline polymer chains in drawn specimens.<sup>32</sup> The shift of the melting point is explained in terms of the excess free energy of the amorphous phase. The formation of the PVA-iodine complex under tension is considered to be due to the excess free energy stored in PVA chains. A more detailed analysis of the effect of extension on the complex formation will be discussed in a separate paper.

The critical strain  $S_c$  necessary for the complex formation at 25°C (the strain at which the peak maximum could first be observed in a visible region) is plotted against  $H_0$  in Figure 9. The value of  $S_c$  was approximately 0.9 and was independent of  $H_0$ . In the same figure, the  $\lambda_{\max c}$  ( $\lambda_{\max}$  at  $S_c$ ) is shown. The  $\lambda_{\max c}$  increased with  $H_0$  below 0.7 and became constant (650

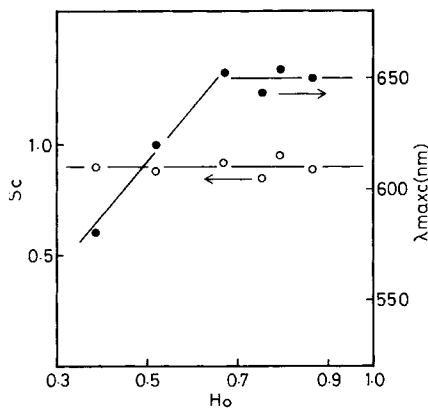


Fig. 9. The critical tension  $S_c$  and  $\lambda_{\max c}$  as a function of  $H_0$ .

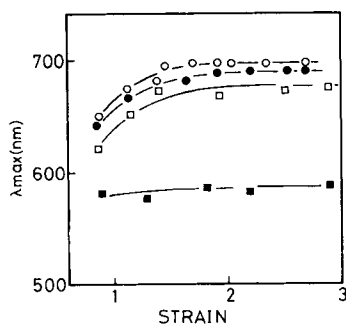


Fig. 10. The  $\lambda_{\max}$  as a function of strain,  $S(S \geq S_c)$ .  $H_0$ : (○) 0.867; (●) 0.754; (□) 0.517; (■) 0.388.

nm) at higher  $H_0$ 's. Therefore, the critical length of the polyiodine chains ascertained by  $\lambda_{\max c}$  increased below  $H_0$  of 0.7 and over that it became constant. It is interesting to note that  $H_0$  of 0.7 is close to the maximum amount of bound water in water-swollen PVA membranes.<sup>23,24</sup> Figure 10 shows  $\lambda_{\max}$  as a function of strain,  $S(S \geq S_c)$ . The  $\lambda_{\max}$  or the length of the polyiodine chain increased with strain and approached to a constant value. The length of the polyiodine chain may be related to those of the oriented PVA chains in the membrane.

## CONCLUSION

Linear relations between the logarithms of the permeability and the diffusion coefficient of iodine and the polymer volume fraction were observed. When water-swollen PVA membranes were soaked in an  $I_2$ -KI solution ( $[I_2] = 5 \times 10^{-5}$  mol/mL,  $[KI] = 10^{-4}$  mol/mL), the contraction occurred and Young's moduli increased. These changes were reversible and could be recovered when the solution was replaced with water, and were shown to be related to the development of extra junction points due to the formation of the PVA-iodine complexes. It was indicated that the complexes were formed by the extension of PVA membranes soaked in a dilute  $I_2$ -KI solution ( $[I_2] = 5 \times 10^{-7}$  mol/mL,  $[KI] = 10^{-6}$  mol/mL), and that they were dissociated when the tension was released. The critical strain necessary for the complex formation was independent of the degree of hydration of the membrane.

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