Diffusive Permeability of Solutes in Poly(vinyl Alcohol) Membranes as a Function of the Degree of Hydration

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Synopsis

Sorption and permeation of sodium chloride, Congo Red (a direct dye), and Sunset Yellow (an acid dye) in PVA membranes were measured to discuss the relation among the degree of hydration H, permeability P, and diffusion coefficient D. Above H of 0.9, the permeability and diffusion coefficient of various solutes could be described by free volume theory provided that the value of V_s^*/V_{fw} is estimated properly, where V_s^* is the ratio of critical volume of permeating molecule to van der Waals volume of water and V_{fw} is the free volume fraction of water. Below H of 0.9, however, Ogston's relation which predicts a linear relation between $(1 - H)$ and the logarithm of P or D fits better than the free volume relation. It seemed to indicate that the polymer networks simply had a geometrical obstruction effect in the diffusion of solutes. The diffusion coefficient extrapolated at $H = 1$ in Ogston's plot decreased with the increase in the interaction between solute and polymer as suggested by the partition coefficient. The hydration dependence of the partition coefficient K changed at $H = 0.8$ corresponding to the maximum amount of the bound water.

INTRODUCTION

The hydraulic permeability of water[1–10] and diffusive permeability of solutes[10–17] in various hydrogel membranes have been studied by many authors. For example, Yasuda et al.[1,11–13] showed that the permeability was well described by the contribution of the free volume of water contained in the membrane. In the previous paper,[18] hydraulic permeability of water in poly(vinyl alcohol) (PVA) membranes was studied in the region of high degree of hydration. It was shown that the permeability could not exactly be explained by means of the free volume theory. We found that a linear relation between the degree of hydration and logarithm of K_w/H (hydraulic permeability/degree of hydration) holds in PVA and many other hydrogel membranes with H from 0.4 to 0.9, and this was expected from Ogston's relation.[19] In this paper, the diffusive permeability of sodium chloride, Congo Red (a direct dye), and Sunset Yellow (an acid dye) in PVA membranes with the high degrees of hydration is studied to find experimentally the relation between the permeability and the degree of hydration.

EXPERIMENTAL

Materials. PVA and the method of membrane preparation were the same as those described in the previous paper.[18] Sodium chloride (GR grade) was used without further purification. Dyes were purified by the salting out method reported by Robinson and Mills.[20]

Sorption Experiments. Sorption experiments were made to obtain the partition coefficients of NaCl and dyes in water-swollen PVA membranes. In preliminary experiments, the partition coefficient of NaCl was found to be independent of salt concentration in the range from 10^{-3} to 10^{-5} mol/mL. Sorption experiments of the salt in the membranes were carried out by the following procedures. The membranes equilibrated in a 10^{-4} mol/mL NaCl aqueous solution were quickly blotted between sheets of paper to remove the excess solution on the surfaces. They were then dissolved in hot deionized water, and the concentration was measured by Mohr's titration method. Since the partition coefficient of Congo Red depended on the concentration, the sorption experiments of Congo Red were carried out at different concentrations ranging from 7.17×10^{-9} to 2.87×10^{-8} mol/ml. These very low concentrations were chosen to avoid the clustering[21] in PVA membranes. The amount sorbed was calculated from the decrease of the concentration of the solution measured by the optical absorption at 507 nm. Sunset Yellow had an affinity to PVA much smaller than Congo Red. After the membranes had reached the equilibrium, they were dissolved in hot deionized water to measure the concentration from the optical absorption at 484 nm. All the sorption experiments were carried out at 25°C.

Permeation Experiments. In the permeation experiments, PVA membranes were clamped between two cells without any supporting equipment. The effective area for permeation was 7.07 cm². The high concentration side was filled with 285 mL of NaCl (10^{-4} mol/mL), Congo Red (2.87×10^{-8} mol/mL), or Sunset Yellow (4.42×10^{-8} mol/mL) solution, 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 to reduce boundary layer effect. The change in solute concentration in the low concentration side was monitored as a function of time. The permeability was calculated at the steady state using the following equation:

$$P = J\Delta X/(C_1 - C_2) \tag{1}$$

where J is the flux of solute, ΔX is the thickness of the membrane, and C_1 and C_2 are the solute concentrations in high and low concentration sides, respectively. The diffusion coefficients were calculated from P and the partition coefficient K. The diffusion coefficient of Congo Red was also estimated by the time lag θ, using $D = (\Delta X)^2/6\theta$. All the permeation experiments were carried out at 25°C. In addition to the permeation experiments, the diffusion coefficient of NaCl was measured by the desorption method. In the desorption experiments, the membranes (0.1–0.2g) equilibrated in a 10^{-4} mol/mL solution were put into 50-mL deionized water, and the NaCl concentration was measured as a function of time using a chlorine ion electrode.

RESULTS AND DISCUSSION

Sorption and Permeation of NaCl

The partition coefficient K, defined by the amount of NaCl contained in a unit volume of membrane over that in the unit volume of the solution, is plotted against the degree of hydration in Figure 1. It indicates that K is much less than unity, and increases with the degree of hydration, approaching unity at infinite
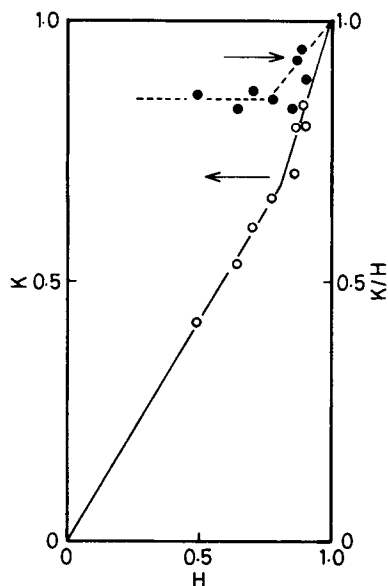
Fig. 1. The partition coefficient of NaCl, K, and K/H as a function of the degree of hydration H: (- - -) relations given by eqs. (6) and (7).

swelling ($H = 1.0$), and that the hydration dependence of K changes at H of about 0.8. As a rough approximation, we may assume a simple additivity of contribution of PVA and water sorbed to use

$$K = K_p(1 - H) + K_s H \qquad (2)$$

where K_p and K_s are partition coefficients in PVA and water, respectively. Then the result in Figure 1 implies that K_p is much less than K_s and

$$K = K_s H \qquad (3)$$

The value of $K_s = K/H$ is also shown in Figure 1. The value of K/H remains at a constant value of 0.85 below H of 0.8, and then it increases to approach unity. Hatakeyama et al.[22,23] studied the melting behavior of water in PVA hydrogels to show that one repeating unit of PVA has six water molecules of so-called bound water, which gives H of 0.76. This implies that the increase in the slope of $K–H$ plot above $H = 0.8$ in Figure 1 is related to the increase of the amount of free water in the membranes. If their conclusion is correct, the value of 0.85 for K_s below $H = 0.8$ must correspond to the value for bound water. Then we may assume the following relation for the partition coefficient for water sorbed in the membrane:

$$K_s = (1/H)(0.85 \cdot v_{bw} + 1.0 \cdot v_{fw}) \quad \text{for } H \geq 0.8 \qquad (4)$$

with

$$v_{bw} = (1 - H) \times 3.19, \quad v_{fw} = H - v_{bw} \qquad (5)$$

where 0.85 and 1.0 are the partition coefficients for bound water and free water, v_{bw} and v_{fw} are the volumes of the bound water and free water in a swollen membrane of a unit volume, and 3.19 is the maximum ratio of bound water to
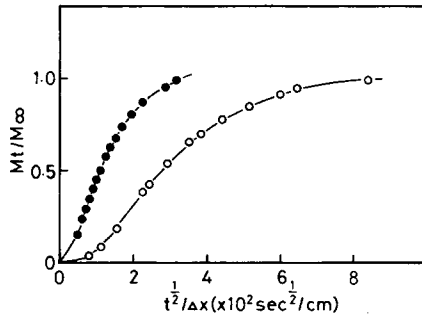
Fig. 2. Desorption curves of NaCl from PVA membranes: (●) $H = 0.899$; (○) $H = 0.624$.

that of polymer, given by (volume of six water molecules/volume of a repeating unit of PVA). Substituting eq. (5) into eq. (4),

$$K_s = 1.48 - 0.48/H, \quad H \geq 0.8 \tag{6}$$

$$K_s = 0.85, \quad H \leq 0.8 \tag{7}$$

The relations given by eqs. (6) and (7) are shown by dotted lines in Figure 1. It should be noted that the difference of the partition coefficients between bound and free waters is as small as 15%. Figure 2 shows some typical desorption curves of NaCl from water swollen PVA membranes. The curves are not linear but sigmoidal, which makes it difficult to obtain the diffusion coefficient D by use of

$$M_t/M_\infty = (4/\sqrt{\pi})(1/\Delta X)(Dt)^{1/2} \tag{8}$$

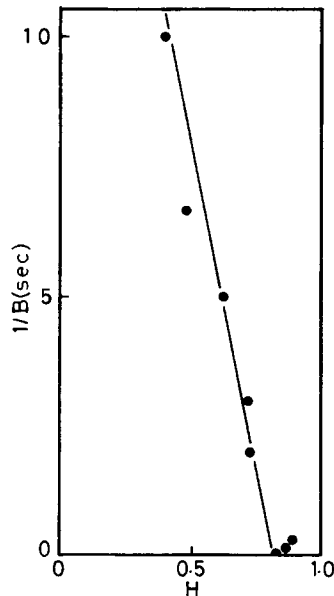where ΔX is the thickness. We assume that the nonlinearity is due to an ob-

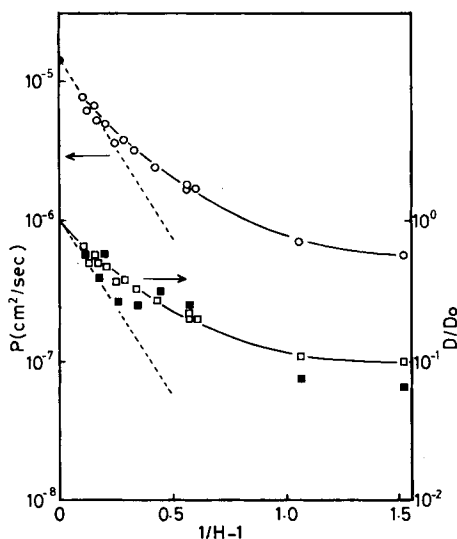Fig. 3. The relaxation time of surface concentration change $1/B$ (s) as a function of the degree of hydration H.

Fig. 4. The relation between the permeability P (cm²/s) and the diffusion coefficient reduced by the value in pure water D/D_0 of NaCl and $1/H - 1$: ($\square$) D/D_0 from permeation experiment; ($\blacksquare$) D/D_0 from desorption experiment; ($\bullet$) diffusion coefficient of NaCl in pure water; (- - -) relations given by eqs. (10) and (11).

struction effect of osmotic pressure which causes a delay in equilibration of NaCl concentration on the membrane surfaces. Under this assumption, Crank's equation[24] [eq. (9)] was used to estimate the diffusion coefficient:

$$M_t/M_\infty = 1 - \exp(-Bt)(4D/B\Delta X^2)^{1/2} \tan(B\Delta X^2/4D)^{1/2}$$
$$- \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp[-(2n+1)^2\pi^2Dt/\Delta X^2]}{(2n+1)^2\{1-(2n+1)^2[D\pi^2/(B\Delta X^2)]\}} \tag{9}$$

The relaxation time for equilibration $1/B$ and the diffusion coefficient D obtained by curve fitting of eq. (9) are shown in Figures 3 and 4. The relaxation time is almost zero for H above 0.8 and increases remarkably at the degree of hydration below 0.8. It should be noted that in this case the property of the membrane is also different above and below $H = 0.8$. According to Yasuda et al.,[11-13] the permeability P and the diffusion coefficient D have the following relations with H:

$$\ln P = A - B/V_{fw}(1/H - 1) \tag{10}$$

$$\ln (D/D_0) = -V_s^*/V_{fw}(1/H - 1) \tag{11}$$

where A and B are constants, V_{fw} is the free volume fraction of water. D_0 is the diffusion coefficient in pure water, and V_s^* is defined as the ratio of critical volume of permeating molecule to van der Waals volume of water. B becomes equal to V_s^* at high degrees of hydration. In Figure 4, the permeability from the permeation experiments is plotted as a function of $1/H - 1$, according to eq. (10). We find an approximately linear relation, expected from eq. (10), only in the region of H above 0.9 ($1/H - 1 = 0.11$). The slope of the dotted line gives 6 to the value of V_s^*/V_{fw}, which is much larger than 0.986 expected by Yasuda et al.[11] In the Appendix, the value of V_s^*/V_{fw} is estimated as 5.88 from the temperature

dependence of the self-diffusion coefficient of water[25] and diffusion coefficient of NaCl in pure water.[25]   In the same figure, the diffusion coefficient, standardized by the diffusion coefficient of NaCl in pure water, is plotted according to eq. (11).   The values of the diffusion coefficients obtained from the desorption experiments agree well with those from the permeation experiments, which shows the legitimacy of the use of Crank's equation.   The H dependence of the diffusion coefficient is quite similar to that of the permeability.   In the range of the degree of hydration lower than ca. 0.9, the H dependences of P and D are much better described by eqs. (12) and (13) than by eqs. (10) and (11),

$$\ln P = \ln D_0 + A(1 - H) \qquad (12)$$

$$\ln (D/D_0) = B(1 - H) \qquad (13)$$

with constants A and B.   The relations of eqs. (12) and (13) are well satisfied for the hydraulic permeability of PVA membrane as was shown in a previous paper.[18]   It should be noticed that relations (12) and (13) seem to satisfy not only our experimental data on PVA but also other cases; such as the diffusion of oligosaccharides, polyhydric alcohols, and poly(ethylene oxide)s in polyacrylamide gel determined by Brown and Johnson,[16] and the permeability of NaCl and urea in poly(methyl methacrylate) (PMMA) gel determined by Tanzawa.[10]   As discussed in the previous paper, eqs. (12) and (13) may be related to eqs. (14) and (15) given by Ogston[19]:

$$\ln P = \ln D_0 + [\ln K/(1 - H) - (1 + r/R)^2](1 - H) \qquad (14)$$

$$\ln (D/D_0) = -(1 + r/R)^2(1 - H) \qquad (15)$$

where r is the radius of the solute which can be calculated from the diffusion coefficient and R is the radius of a fibril in the membrane.   For our PVA, r/R is calculated to be 1.09.   These results indicate that in the diffusion of NaCl in PVA membrane, the polymer network simply has a geometrical obstruction effect.

Sorption and Permeation of Dyes

Congo Red

Figure 5 shows sorption curves of Congo Red by swollen PVA membranes. The shapes of curves indicate that the mode of dye sorption changes during the course of sorption, i.e., monomolecular sorption at the early stage and subsequent clustering of dye in the membrane.   Fujino and Fujimoto,[21] from their optical absorption experiments, showed that clustering of Congo Red occurred in PVA membranes with increase in dye concentration.   It is reasonable to discuss the partition coefficient K only in the first stage where the mode of monomolecular sorption prevails over that of clustering.   The amount of dye at the step on each sorption curve was taken as the equilibrium sorption in the first stage.   Thus such an estimated partition coefficient is plotted against the degree of hydration in Figure 6(a) to show (1) that K depends remarkably on the concentration of dye in the sorption bath and (2) that it increases with the increase in H below $H = 0.8$ and then decreases to approach unity at $H = 1.0$.   If we use again eq. (2),
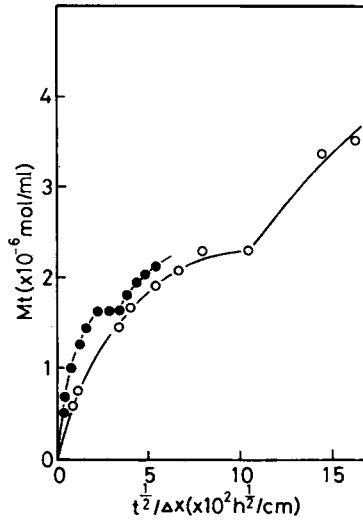
Fig. 5. Sorption curves of Congo Red in PVA membranes: (●) $H = 0.840$; (○) $H = 0.423$.

then

$$K_p = (K - H)/(1 - H) \tag{16}$$

because K_s, the partition coefficient of water in the membrane, is assumed to be unity. Because the value of K is large, the assumption that $K_s = 1.0$ causes no serious error in the estimation of K_p. Thus the calculated K_p plotted against
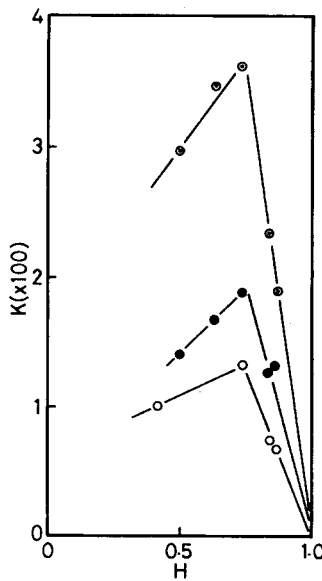

Fig. 6(a). The partition coefficient of Congo Red, K, as a function of the degree of hydration H. Initial dye concentration, (○) 2.87×10^{-8} mol/mL; (●) 1.43×10^{-8} mol/mL; (◉) 7.17×10^{-9} mol/ml.
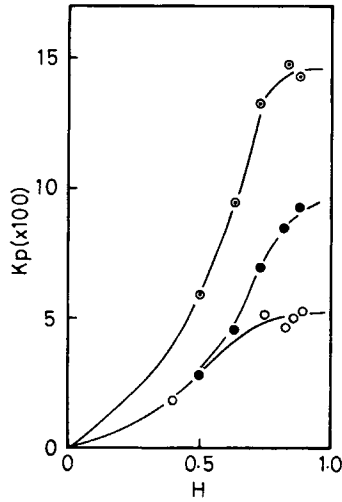
Fig.6(b). The partition coefficient in polymer, K_p, as a function of the degree of hydration H. Symbols in this figure are the same as those in Figure 6(a).

H in Figure 6(b) increases with H to reach constant values depending on H. It is interesting to note that the remarkable increase in K_p is caused by the increase in the amount of bound water. According to Hatakeyama and Yamauchi,[22,23] the maximum amount of bound water in PVA is at about 0.75 in H. This implies
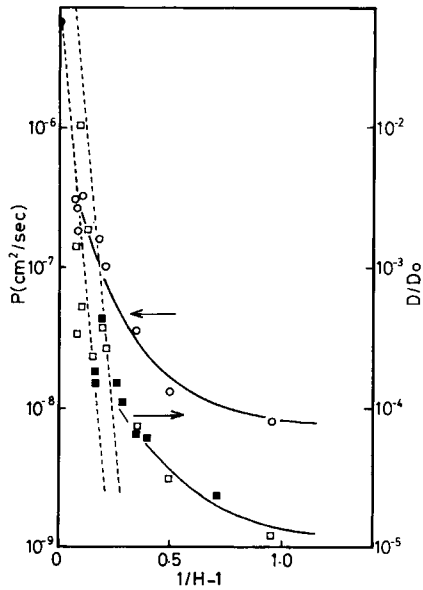

Fig. 7. The dependence of the permeability $P(cm^2/s)$ and the diffusion coefficient reduced by the value in pure water D/D_0 of Congo Red on $1/H - 1$: (■) D/D_0 from sorption experiment; (□) D/D_0 from time lag method; (●) diffusion coefficient of Congo Red in pure water; (- - -) relations given by eqs. (10) and (11).

that the bound water interconnects the Congo Red to the PVA molecules, increasing the affinity between them. Thus no further increase in K_p' is caused above $H = 0.8$, where the increase in H is mainly due to the increase in the free water. The diffusion coefficient was determined from the sorption curves at the first stage, using a relation for the diffusion coefficient in finite dye bath system.[24] It is confirmed that the coefficient is independent of the dye bath concentration. The diffusion coefficient thus obtained, standardized by the value in pure water ($D_0 = 5.68 \times 10^{-6}$ cm²/s at 25°C)[26] is plotted as a function of $1/H - 1$ in Figure 7. Figure 7 also shows the diffusion coefficient obtained from the "time lag method" in the permeation experiment. It should be noted that both values of the diffusion coefficient agree well with each other, forming a curve together. The shape of the curve is similar to that for NaCl shown in Figure 4; it has a gradual increase with increasing H, being followed by a steep increase in the vicinity of $H = 1.0$. We observed that the linear relation expected from eq. (11) is satisfied in the high range of hydration above $H = 0.9$. Then the slope of the line, given by the dotted line, gives 40 for the value of V_s^*/V_{fw} in eq. (11). It is interesting to note that this value is very close to that calculated in the Appendix. In the permeation experiment, even after the apparent steady state of permeation has been reached, the sorption of Congo Red in the membrane still continues, corresponding to the second step in the sorption curve. The permeability of the dye from the permeation experiments is also shown in Figure 7, to indicate that it has a similar shape to that of the diffusion coefficient.

Sunset Yellow

In this case only the equilibrium sorption was measured; hence it was difficult to obtain the sorption curves because of the small extent of sorption. Figure 8 shows the partition coefficient K of Sunset Yellow against the degree of hydration H. This is quite different from that in Figure 6; K is about 2 orders of magnitude lower than that for Congo Red and increases monotonously with the degree of hydration, and does not approach unity at infinite swelling ($H = 1.0$). However, the H dependence of K changes at $H = 0.8$, as seen for Congo Red. We assume again eq. (16) to obtain K_p, as shown in Figure 8. This indicates that water enhances the interconnection of Sunset Yellow molecules to PVA, increasing the affinity between them. It is interesting to note that the remarkable increase in K_p above $H = 0.8$ is caused by the increase in the amount of free water. The diffusion coefficient is so large that the time lag could not be observed in the permeation experiments. The diffusion coefficient was determined from P/K. The diffusion coefficient thus obtained, standardized by the value in pure water ($D_0 = 6.56 \times 10^{-6}$ cm²/s; see the Appendix) is plotted as a function of $(1/H - 1)$ in Figure 9. The shape of the plot is similar to those for NaCl and Congo Red shown in Figures 4 and 8. It should be remarked that the diffusion coefficients of two dyes are quite different in spite of the small difference in the molecular weights. We may consider that a linear relation expected from eq. (11) is satisfied in the high range of hydration above $H = 0.9$. Then the slope of the dotted line gives 30 for the value of V_s^*/V_{fw} in eq. (11). It is interesting to note that this value is very close to that calculated in the Appendix. The permeability of the dye from the permeation experiments is also shown in Figure 9 to indicate that it has a similar shape to that of diffusion coefficient.
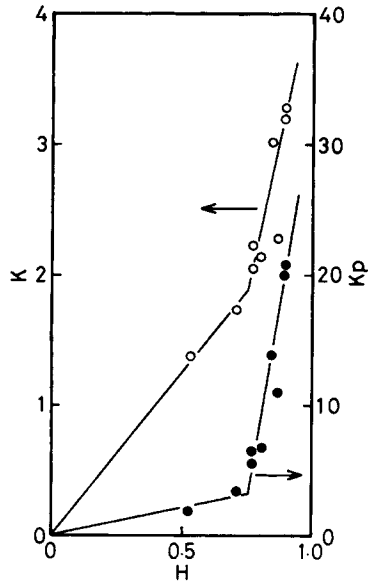
Fig. 8. The partition coefficient of Sunset Yellow, K, and the partition coefficient in polymer, K_p, as a function of the degree of hydration H.

It is confirmed that the plots of $\ln P$ and $\ln(D/D_0)$ against $1 - H$ for Congo Red and Sunset Yellow are approximately linear, similar to the case of NaCl. The plot of $\ln(D/D_0)$ against $1 - H$ for Congo Red deviates from a linear line in a range of H above 0.9. This behavior is similar to the $\ln(K_w/H)$ vs. $(1 - H)$ plot shown
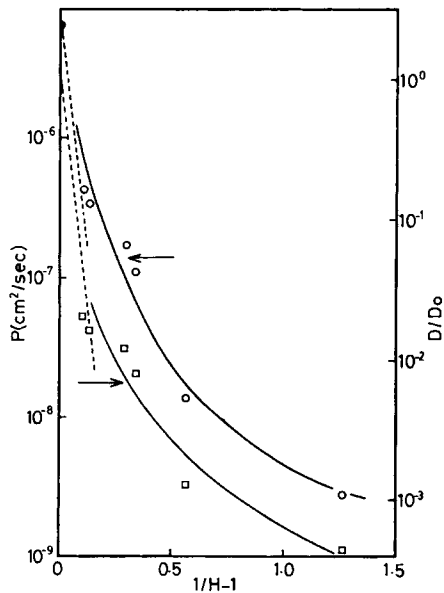

Fig. 9. The dependence of the permeability $P(\text{cm}^2/\text{s})$ and the diffusion coefficient reduced by the value in pure water D/D_0 of Sunset Yellow on $1/H - 1$: (●) diffusion coefficient of Sunset Yellow in pure water; (- - -) relations given by eqs. (10) and (11).
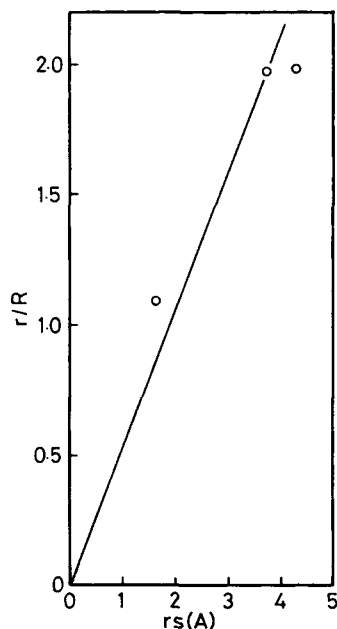
Fig. 10. The values of r/R as a function of the Stokes' radii of solutes.

in the previous paper[18] (K_w = hydraulic permeability). The amount of free water increases with the increase in H above 0.9. Thus the deviation in $\ln(D/D_0)$ vs. $(1 - H)$ plot may be attributed to the difference of the properties of bound and free waters. Equation (15) makes us expect that the intercept at $(1 - H) = 0$ gives the diffusion coefficient in pure water. However, this expectation was not satisfied for the dyes, but it was satisfied for NaCl. The value of r/R calculated by eq. (15) is 2 for the two dyes, although the partition coefficients are quite different between them. Also, Stokes' radius of Sunset Yellow (3.74A) is about
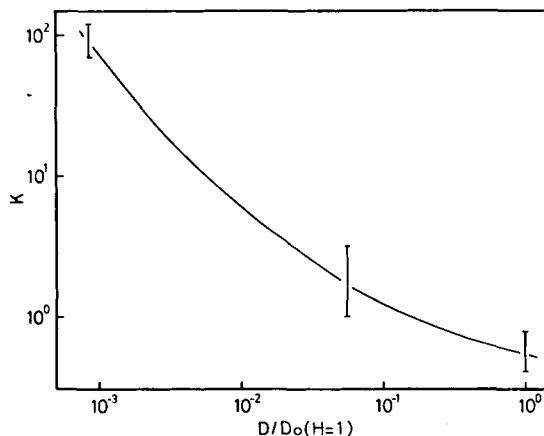

Fig. 11. The values of partition coefficients as a function of the D/D_0 extrapolated to $H = 1.0$ in eq. (15).
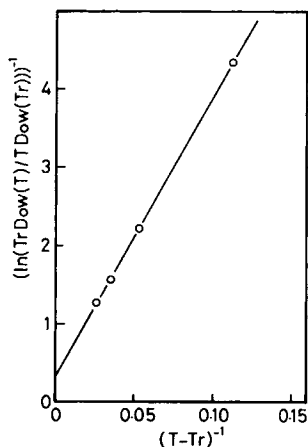
Fig. 12. The relation between $\{\ln[T_r\,D_{0w}(T)/TD_{0w}(T_r)]\}^{-1}$ and $(T - T_r)^{-1}$, $T_r = 289.3K$.

15% smaller than that of Congo Red. Figure 10 shows the values of r/R as a function of the Stokes' radii of the solutes. The value of R is estimated as $2A$ from the slope of the line. This value is so small that it implies that the solutes may diffuse in the water between the polymer chains. The value of D/D_0 extrapolated to $H = 1.0$ in eq. (15) decreases with the increase in the partition coefficient, as shown in Figure 11. It suggests that the diffusion coefficient of a solute through the water in the membrane decreases with the increase in the interaction between the solute and the membrane.

So far we have shown that eqs. (14) and (15) are better than eqs. (10) and (11) to describe the experimental relation between the permeability and the diffusion coefficient and the hydration of membranes. Above $H = 0.9$, the permeability and the diffusion coefficients of solutes can be described by eqs. (10) and (11) provided that the values of V_s^*/V_{fw} are estimated properly.

APPENDIX

Determination of V_{fw} (25°C)

Using the free volume expression developed by Cohen and Turnbull[27] and Einstein's relation, the self-diffusion coefficient of water D_{0w} is described as

$$D_{0w} = A_d RT \exp[-V_w^*/V_{fw}(T)] \tag{17}$$

where A_d is a constant, R is the gas constant, T is the absolute temperature, and V_w^* is a parameter characteristic of the critical volume of water. The fractional free volume of water at temperature T, $V_{fw}(T)$, is given by

$$V_{fw}(T) = V_{fw}(T_r) + E_w(T - T_r) \tag{18}$$

where T_r is the reference temperature and E_w is the expansion coefficient of the free volume of water. Substituting eq. (18) into eq. (17), the following equation is obtained:

$$\{\ln[\text{Tr}\,D_{0w}(T)/TD_{0w}(T_r)]\}^{-1} = V_{fw}(T_r)/V_w^* + [V_{fw}(T_r)]^2/V_w^*E_w(T - T_r) \tag{19}$$

Equation (19) shows that the relation between $\{\ln[T_rD_{0w}(T)/TD_{0w}(T_r)]\}^{-1}$ and $(T - T_r)^{-1}$ should be linear, and this relation is demonstrated in Figure 12. In this case, the reference temperature T_r is 289.8K.[25] Since V_w^* is nearly equal to 1, from the slope and the intercept, $V_{fw}(25°C)$ and E_w

are calculated to be 0.354 and 2.98×10^{-3}, respectively. These values are in accord with those obtained by Miller[28] [$V_{fw}(25°C) = 0.290$, $E_w = 1.96 \times 10^{-3}$], who adopted the free volume theory to the temperature dependence of the viscosity coefficient of water.

Determination of V_s^*

From Einstein's relation and Stokes' law, the following relation is obtained:

$$D_{0w}/D_{0s} = R_s/R_w \tag{20}$$

where R_s and R_w are Stokes' radii of solute and water, respectively. V_s^* is proportional to the cross sectional area of the diffusing molecule, because it represents the conformational entropy for the formation of a hole of cross section A and length L through which the diffusing molecule jumps to a new position. The dependence of the diffusion coefficient D on A was shown by Brandt,[29] Wisniewski et al.,[30] and Yasuda et al.[12] Therefore V_s^* may be replaced by BA, where B is a proportionality factor, and the next relation is obtained:

$$V_w^*/V_s^* = A_w/A_s = (R_w/R_s)^2 \tag{21}$$

where A_s and A_w are cross-sectional areas of solute and water, respectively. From eqs. (20) and (21), we obtain

$$D_{0w}/D_{0s} = (V_s^*/V_w^*)^{1/2} \tag{22}$$

Using the self-diffusion coefficient of water and diffusion coefficients of NaCl and Congo Red in pure water at 25°C, and assuming that V_w^* is equal to 1, the following values are obtained: V_s^* (NaCl, 25°C) = 2.08, V_s^* (Congo Red, 25°C) = 14.2. Using these values, V_s^*/V_{fw} (NaCl, 25°C) = 5.88; V_s^*/V_{fw} (Congo Red, 25°C) = 40.1 are obtained. Since the diffusion coefficient of Sunset Yellow in pure water is not reported in the literature, it was estimated as follows. On the assumption that dye molecules are spherical and the densities of Congo Red and Sunset Yellow are equal, the following equation[31] is obtained according to Einstein's relation and Stokes' law:

$$D_{0su}/D_{0co} = R_{co}/R_{su} = (M_{co}/M_{su})^{1/3} \tag{23}$$

where D_0 is the diffusion coefficient in pure water, R is Stokes' radius, M is molecular weight, and su and co denote Sunset Yellow and Congo Red, respectively. From eq. (23), D_{0su} is calculated to be 6.56×10^{-6} cm²/s. From this value, V_s^* and V_s^*/V_{fw} are found to be 10.6 and 29.9, respectively.

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