

Permeability of Water and Water Vapor Through Cellulosic Membranes

M. KAWAGUCHI, T. TANIGUCHI, K. TOCHIGI, and A. TAKIZAWA,
*Department of Fiber and Polymer Technology, Nagoya Institute of
Technology, Gokiso-cho, Showa-ku, Nagoya, 466, Japan*

Synopsis

To elucidate the water transport mechanism through homogeneous membranes, water and water vapor permeation through crosslinked cellulose membranes, cellulose diacetate, and cellulose triacetate membranes are studied. It is found that the water flux increases with the degree of hydration; and as for cellulose membranes, the degree of hydration is an increasing function of the degree of crosslinking. Activation energy of hydraulic permeability (K_w) is not equal to that of purely viscous flow, and is smaller than that of the water vapor diffusion coefficient (D) for all membranes. The free-volume concept relating the molar frictional coefficient to temperature and to degree of hydration explains reasonably the temperature dependence of hydraulic permeability and of water vapor diffusion coefficient and gives adequate values for the fractional free volume of the system. The critical volume V^* , appearing in the Cohen-Turnbull expression between friction coefficient and free volume fraction, may be considered as the size of the cluster of water molecules. The value of V^* in the case of hydraulic permeability is larger than that for water vapor diffusion by several times. Furthermore, the value V^* increases with increase of degree of hydration for water permeation and water vapor diffusion.

INTRODUCTION

Elucidation of the water transport mechanism through homogeneous water-swollen membranes is the first necessity for the proper understanding of transport phenomena of aqueous solution through the membranes and of the permselectivity of the membranes. The relation between the water flux and the applied pressure has been studied by Yasuda et al.¹ using membranes of various hydration, and it has been noted that the water flux under the applied pressure exceeds the flux calculated by the diffusion coefficient of tritiated water in highly hydrated membranes. It has been assumed that both bulk flow and molecular diffusional flow could occur in the membrane.

In the present paper, for the purpose of clarifying the above relation in more detail, water permeation through the crosslinked cellulose membranes of various crosslinking density, cellulose diacetate membrane and cellulose triacetate membrane, is studied. Furthermore, the water vapor permeation through the dry membranes of the same kind is examined. By comparison of these two results, the permeation mechanism of both types of experiments and the relation between them will be discussed.

EXPERIMENTAL

Materials

Crosslinked cellulose membranes are prepared by formalization of cellulose membranes which were supplied by Hutamura Kagaku Kogyo Corporation (Oogaki, Japan). The reaction is performed in a reaction bath (100 cc/g cellulose) containing 7.6% HCHO, 12.2% HCl, and 80.2% H₂O by weight at 29°C.² After a specified period of reaction, the membranes are removed and washed for two days in water. These membranes are transparent before and after they are crosslinked.

The characteristics of cellulose membranes used in this study are described in Table I; C-1, C-2, and C-3 denote a reaction time of 45, 30, and 0 times, respectively; C-1 and C-2 are heat treated in evacuated atmosphere at 80°C for 24 hr; C-3 is treated under the same condition for 50 min. The densities of these membranes obtained by the floatation method xylene-tetrachloroethane system at 25°C show almost the same values (Table I). The density of crosslinking in Table I is calculated according to the Flory-Rehner theory³ using the stress-strain curve of heat-treated swollen membrane in water at 25°C observed by Tensilon (Toyo Sokki Corporation, Japan). Figure 1 shows the relation between τ (the force per unit area of the swollen, stretched sample) and $(RT\nu_e/V_0)v_2^{1/3}(\alpha - 1/\alpha^2)$, where R is the gas constant, T is absolute temperature, ν_e is density of crosslinking, V_0 is volume of the unswollen sample, v_2 is volume fraction of polymer in swollen sample, and α is the ratio of length in the swollen, stretched state relative to the swollen, unstretched state.

Cellulose diacetate membrane (CDA) is prepared from 3% cellulose diacetate (Mistubishi Acetate Corporation, Toyama, Japan, acetyl content 39.3%) solution in dioxane; and cellulose triacetate membrane (CTA) is prepared from 3% cellulose triacetate (Mistubishi Acetate Corporation, Toyama, Japan, acetyl content 44.1%) solution in chloroform by the evaporation method. Both membranes are cast on a glass plate, allowed to dry completely in open air, and then annealed at 85°C for 24 hr in evacuated atmosphere. The density of both membranes is obtained by the floatation method using a toluene-tetrachloroethane system at 25°C (Table I). Both membranes are transparent and show no leaks with ethyl violet dye solution supported by the membranes.

TABLE I
Membrane Characteristics

	C-1	C-2	C-3	CDA	CTA
Reaction time, min	45	30	0	—	—
Density of crosslinking, mole/cc	4.4×10^{-3}	4.2×10^{-3}	3.1×10^{-3}	—	—
Density, g/cc	1.523	1.522	1.523	1.032	1.302
Thickness in wet state, cm	3.2×10^{-3}	3.2×10^{-3}	3.2×10^{-3}	3.7×10^{-4}	3.1×10^{-4}
Thickness in dry state, cm	1.3×10^{-3}	—	1.3×10^{-3}	5.35×10^{-3}	4.54×10^{-3}
Degree of hydration	0.72	0.69	0.62	0.17	0.09

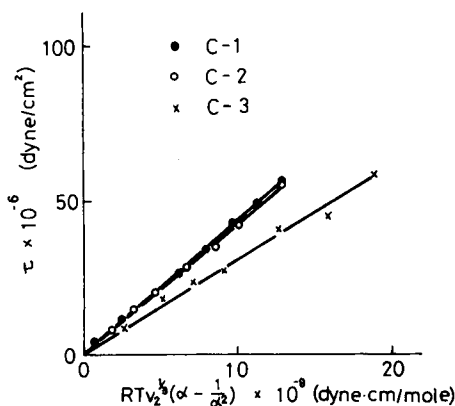


Fig. 1. Stress-strain curve for swollen cellulose membranes in water at 25°C. For notation, see text.

The degree of hydration H in Table I is the volume fraction of water of the water-swollen membrane, and is determined as follows: the membrane is swelled, blotted, and weighed repeatedly several times until a constant weight of the swollen membrane can be obtained to within 1%. The membrane is then dried in evacuated atmosphere at 100°C for 24 hr to constant weight. It was found that the degree of hydration is temperature independent between 25° and 50°C within experimental error for all membranes. Though the value of H is expected to decrease with the density of crosslinking, an inverse trend was observed. The latter tendency has been observed in the case of formalization of rayon fiber.⁴ The thickness of each membrane is listed in Table I.

Measurements

The measurement of hydraulic permeability of the membranes under pressure is carried out by using a Nihon Sinku batch cell (MC4 type) with a volume of about 400 cc and an effective membrane area of 36.3 cm². The cell contains an internal magnetic stirrer. The schematic diagram of the apparatus is shown in Figure 2. The cell is immersed in a water bath in which the temperature is controlled to within 0.05°C. The water flux is measured for the time necessary to collect a given volume (5 cc) of water for cellulose membranes, and the water flux for CDA and CTA was determined by collecting a volume of water for 4 hr. The measurement is made at temperatures between 25° and 50°C (at 5°C intervals) and pressures between 1 and 5 atm (at 1 atm intervals) using compressed nitrogen gas. The pressure is adjusted to 0.05 atm by means of a mercury manometer.

The measurement of water vapor permeation of dry membranes is carried out by using Rouse's apparatus⁵ at 25°C. Accordingly, the pressure of the lower-pressure side of the membrane is always zero. The amount permeated, $Q(t)$, is expressed by the volume at standard state per unit area of the membrane (cc S.T.P./cm²). The example of the permeation curve, $Q(t)$ versus time t , is shown Figure 3 for the CDA-water system. The linear portion of the permeation curve corresponds to the stationary state of permeation, from whose slope the permeation coefficient \bar{P} (cc S.T.P./cm-sec-cm Hg) is deter-

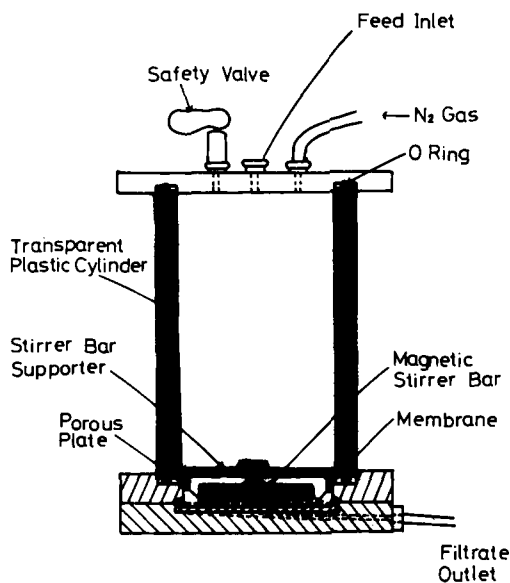


Fig. 2. Schematic diagram of the water permeation cell.

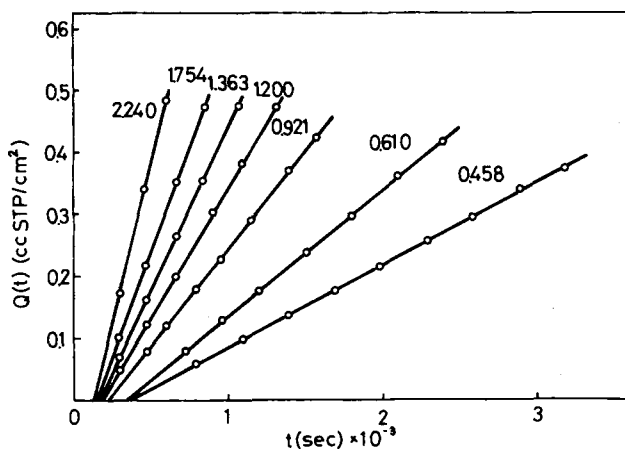


Fig. 3. Permeation curves (amount permeated, $Q(t)$ vs. time t) of CDA-water vapor system. Numbers on curves show applied pressure in cm Hg.

mined. Dividing \bar{P} by the solubility coefficient S (cc S.T.P./cm³·cm Hg) of water to the polymer, the stationary state diffusion coefficient \bar{D} is obtained; S is determined by the sorption isotherms. The pressure of the higher-pressure side of the membrane is set up by controlling the temperature of the water-filled flask, which is connected to the higher-pressure side of the membrane in the vacuum system. The sorption measurement for water vapor is performed by the gravimetric method using the usual quartz spiral balance at 25°C. The solubility coefficient is determined by the ratio of sorbed amount to pressure from the sorption isotherm.

Furthermore, the diffusion coefficient-versus-temperature relationships on these membranes are measured at temperatures between 25° and 50°C (at 5°C intervals) under constant relative pressure p/p_s 0.19. For the same sam-

ple, the solubility coefficient is assumed to be constant between 25° and 50°C.⁶

RESULTS AND DISCUSSION

The relation between the water flux J_{wH} (mole/cm²-sec) and the applied pressure Δp (atm) is shown in Figures 4 and 5. In the pressure range examined, the relation is entirely reversible. The water flux increases with increase in temperature, applied pressure, and degree of hydration systematically.

Figure 6 shows the equilibrium sorption isotherms of water vapor on C-1, C-3, CDA, and CTA; C-1 is more sorptive than C-3, especially at high relative pressure. This trend agrees with the degree of hydration in water. This is explained by the fact that the wet crosslinking process results in a membrane structure that is more accessible to water through intermolecular or intramolecular crosslinks which inhibit recrystallization during the drying process.⁴ In any case, the crosslinking process would yield a more open structure, into

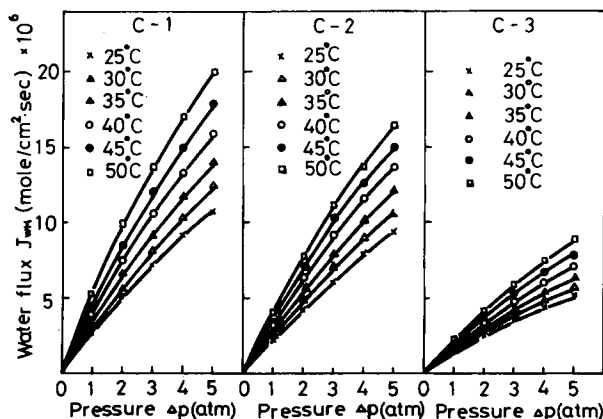


Fig. 4. Water flux J_{wH} vs. applied pressure at various temperatures for cellulose membranes (C-1, C-2, and C-3).

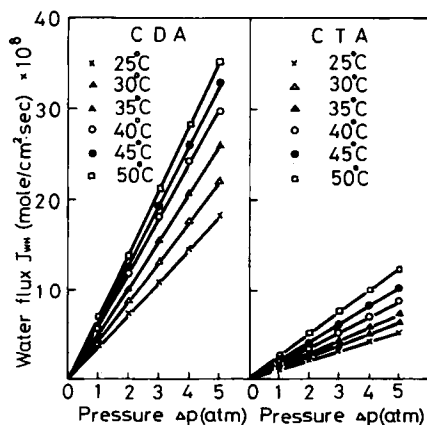


Fig. 5. Water flux J_{wH} vs. applied pressure at various temperatures for cellulose diacetate (CDA) and cellulose triacetate (CTA) membranes.

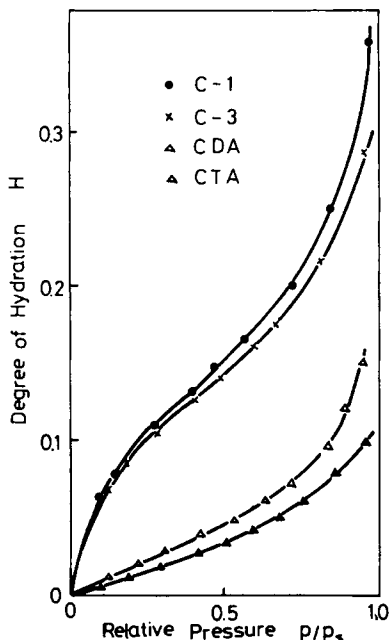


Fig. 6. Sorption isotherms (degree of hydration H vs. relative vapor pressure of water) of C-1, C-3, CDA, and CTA at 25°C.

which water can penetrate more easily. The difference of sorption isotherm between CDA and CTA is assumed to reflect the number of hydroxyl groups.

The permeability coefficient \bar{P} of water vapor increases with increase in the relative vapor pressure or water concentration in the system, as is shown Figure 7. Dividing \bar{P} by S (calculated from Fig. 6), the stationary state diffusion coefficient \bar{D} is obtained (Fig. 8). The diffusion coefficients for both C-1 and C-3 show remarkable concentration dependence, though the tendency slows down in the higher concentration range. This behavior is typical for hydrophilic polymer.^{7,8} In the low concentration range, the interaction between hydroxyl groups of polymer restricts sufficient segmental motion for diffusion of water, and gives a low diffusion coefficient. With increase of water concentration in the membrane, the interaction is disrupted gradually, and the diffusion coefficient increases as a result of segmental mobility. The \bar{D} value for C-1 is larger than that for C-3, which also reflects the influence of hydration (Fig. 6).

On the other hand, the diffusion coefficients for CDA and CTA show little concentration dependence. This behavior is typical for more hydrophobic polymer.⁹ The difference between the \bar{D} for CDA and CTA is a result of the difference of interaction between the hydroxyl groups of the polymer.

According to the frictional model of Spiegel¹⁰ and Kedem et al.^{11,12} the hydraulic water flux J_{wH} under the pressure gradient $\Delta p/\Delta x$ is expressed as follows:

$$J_{wH} = \frac{S_w C_w V_w}{f_{wm}} \frac{\Delta p}{\Delta x} = \frac{S_w}{f_{wm}} \frac{\Delta p}{\Delta x} \equiv K_w \frac{\Delta p}{\Delta x} \quad (1)$$

where S_w is a partition coefficient of water between membrane and solution,

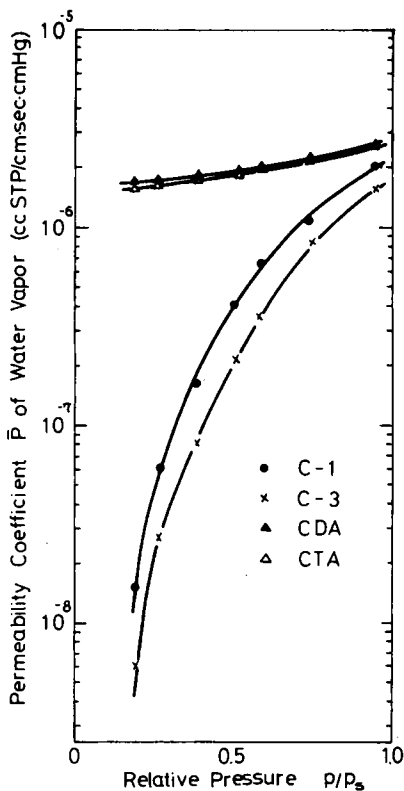


Fig. 7. Permeability coefficient \bar{P} vs. relative vapor pressure of water at 25°C for C-1, C-3, CDA, and CTA.

C_w is molar concentration of water in the adjacent solution, and \bar{V}_w is the molar volume of water. In the present case, $C_w \bar{V}_w = 1$, because the adjacent solution is pure water. The f_{wm} is the molar frictional coefficient between water and membrane and K_w is the hydraulic permeability.

If the frictional coefficient f_{wm} is referred to the friction between water "molecule" and polymer "segment," eq. (1) is only valid when the water content is small and no bulk flow takes place. Otherwise, f_{wm} should have a form like $[f_{wm}(1 - H) + f_{ww}H]$, where H is the volume fraction of water in the membrane. If this expression is adequate, the same value of f_{wm} or f_{ww} could be applied to both water permeation and water vapor permeation. Using this assumption, the calculated f_{ww} value is obtained to be negative for C-1. The fact indicates that the value f_{wm} or f_{ww} does not correspond to the "molecular" interaction and also that the above additivity of f_{wm} and f_{ww} is not satisfied.

Accordingly, we should consider that the value f_{wm} is the frictional coefficient of a permeating cluster of water molecules through the "swollen" membrane.

On the other hand, diffusional flux J_{wD} of heavy water or tritiated water under the concentration gradient $\Delta C_D/\Delta x$ is expressed as follows^{11,13}:

$$J_{wD} = \frac{S_w RT}{f_{Dw} + f_{Dm}} \frac{\Delta C_D}{\Delta x} \equiv P_w \frac{\Delta C_D}{\Delta x} \quad (2)$$

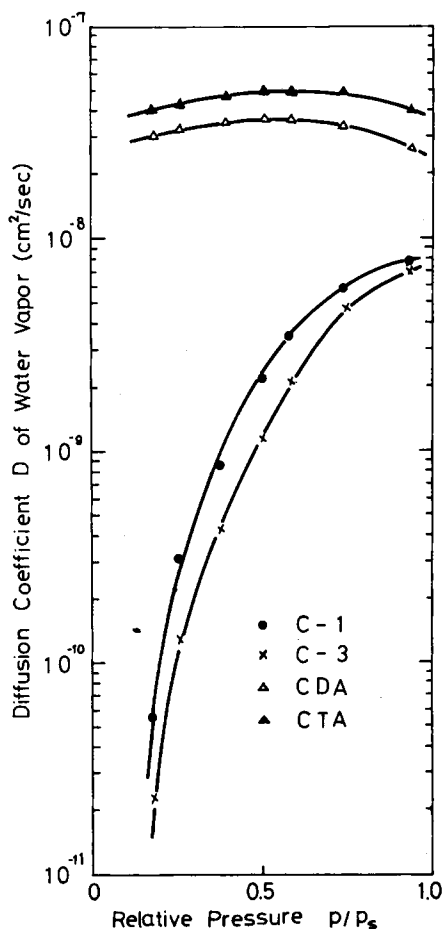


Fig. 8. Stationary state diffusion coefficient \bar{D} vs. relative vapor pressure of water at 25°C for C-1, C-3, CDA, and CTA.

where R is the gas constant, T is absolute temperature, f_{Dw} is the molar frictional coefficient between heavy water and water, f_{Dm} is that between heavy water and membrane, and P_w is the diffusional permeability. By the same reason as in the case of eq. (1), we denote f'_{wm} ($= f_{Dw} + f_{Dm}$) as the frictional coefficient of heavy water molecules permeating through the swollen membrane. Then,

$$J_{wD} = \frac{S_w RT}{f'_{wm}} \frac{\Delta C_D}{\Delta x} \equiv P_w \frac{\Delta C_D}{\Delta x} \quad (3)$$

In the present case, S_w in eqs. (1), (2), and (3) is equal to the degree of hydration H . If it is assumed that $f_{wm} = f'_{wm}$, the ratio of hydraulic permeability to diffusional permeability $\omega = K_w RT/P_w$ under the same motive force is equal to unity. However, ω is generally higher than unity and increases with the degree of hydration.^{1,14} This indicates that the value f_{wm} is lower than f'_{wm} .

Because the relation between water flux and applied pressure is nonlinear for cellulose membranes (Fig. 4), hydraulic permeability K_w is calculated

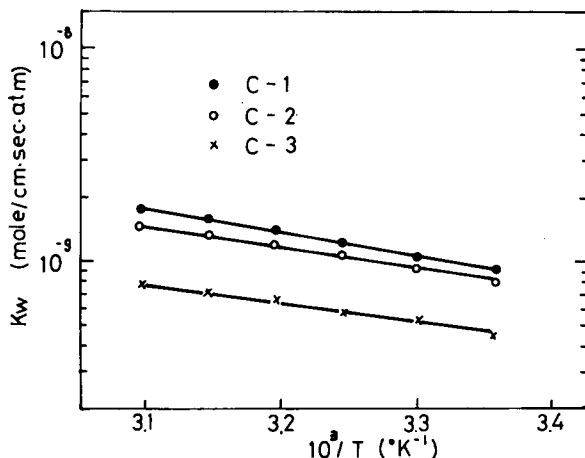


Fig. 9. Temperature dependence of hydraulic permeability K_w for cellulose membranes (C-1, C-2, and C-3).

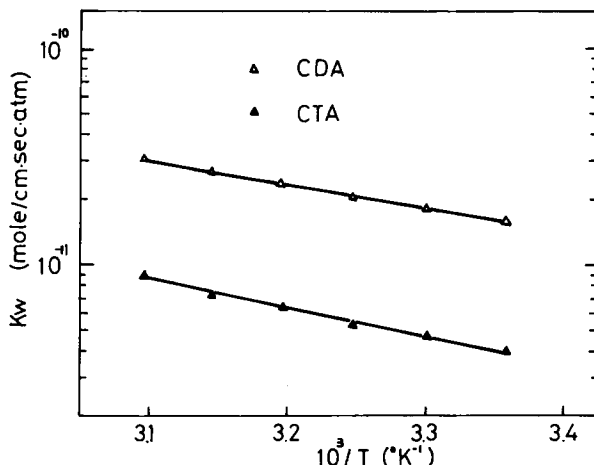


Fig. 10. Temperature dependence of hydraulic permeability K_w for CDA and CTA.

from the initial slope. The values of ω are of the order of 20 for cellulose membranes, and are of the order of 2 for CDA and CTA, referring the Yasuda's¹ and Gary-Bobo's¹⁴ results for P_w 's. This result shows that the flow through the highly hydrated membrane deviates from the purely diffusional flow.

To make clear this problem, the apparent activation energy is calculated from the Arrhenius plot of K_w , which is equivalent to that of $1/f_{wm}$ because H is independent of temperature (25–50°C), and is shown in Figure 9 for C-1, C-2, and C-3. The activation energy is 4.8, 4.5, and 3.9 kcal/mole, respectively. The value increases with increase in H , and does not approach to the apparent activation energy (about 4 kcal/mole at 25°C) obtained from the viscosity coefficient of water.¹⁵ Therefore, the water flow in this study is considered to be different from the purely viscous flow through a rigid capillary. For CDA and CTA, the apparent activation energy obtained from the Arrhenius plot of K_w (Fig. 10) is 5.2 and 6.4 kcal/mole, respectively.

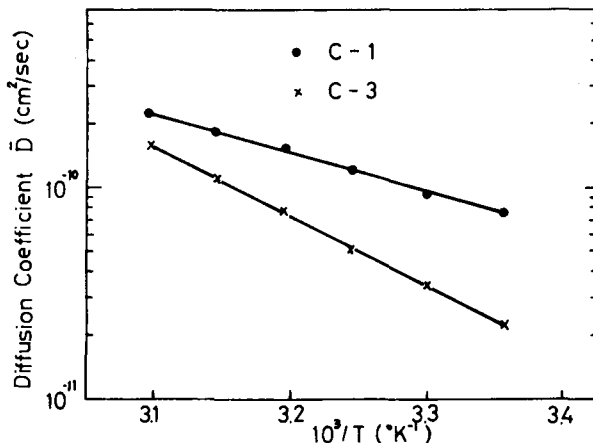


Fig. 11. Temperature dependence of stationary-state diffusion coefficient \bar{D} of water vapor for C-1 and C-3.

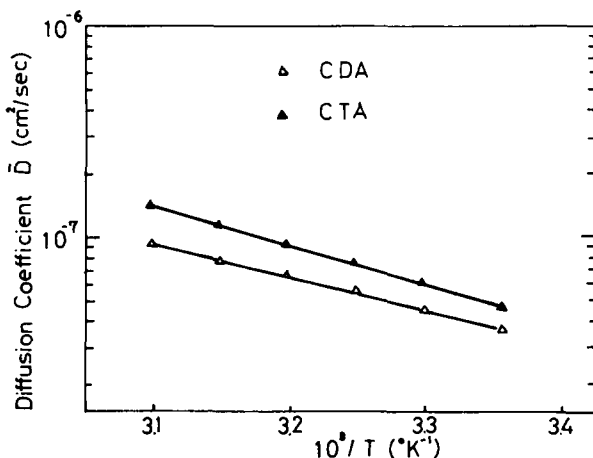


Fig. 12. Temperature dependence of stationary-state diffusion coefficient \bar{D} of water vapor for CDA and CTA.

As for the explanation of the activation energy of hydraulic permeability, Gary-Bobo et al.¹⁴ tried to separate the pressure-induced flow into a diffusive and a bulk flow. The same concept was used by Peterlin et al.¹⁶ However, we are treating homogeneous membranes, which have no rigid pores and are not in the state of phase separation. Furthermore, we can not separate the whole frictional coefficient f_{wm} into f_{wm} and f_{ww} , as is discussed in the deviation of eq. (1). Therefore, we will treat f_{wm} as the whole nature of swollen membrane.

On the other hand, the activation energy of water vapor diffusion calculated from the diffusion coefficient-versus-temperature relationship (Figs. 11 and 12) is 8.4, 14.7, 7.9, and 8.4 kcal/mole for C-1, C-3, CDA, and CTA, respectively. These are larger than that of water permeation for the respective membranes.

In the following, activation energies of hydraulic permeation of water and water vapor diffusion will be analyzed according to the free-volume concept.

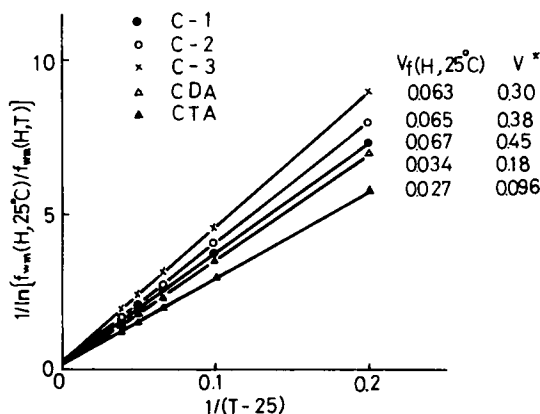


Fig. 13. Relationships between $1/\ln[f_{wm}(H, T_r)/f_{wm}(H, T)]$ and $1/(T - 25)$, eq. (8), for water permeation through five membranes.

In hydraulic permeation, it may be assumed that a cluster of water molecules permeates pushing the polymer matrix away for its passage. The free-volume concept was applied to the viscosity or the deformation of polymer by Doolittle¹⁷ and by Williams et al.¹⁸ as well as to the diffusion phenomena by Fujita.¹⁹ Therefore, it seems reasonable to assume that the frictional coefficient f_{wm} may also depend on the free-volume fraction of the system. Using the free-volume expression developed by Cohen and Turnbull,²⁰ f_{wm} is expressed

$$f_{wm} = A \cdot \exp[V^*/V_f(H, T)] \tag{4}$$

where A is constant, V^* is a characteristic parameter describing a factor of critical volume of permeating cluster, and $V_f(H, T)$ is the fractional free volume of the system whose degree of hydration is H at temperature T . $V_f(H, T)$ is given by

$$V_f(H, T) = H \cdot V_{fw}(T) + (1 - H) \cdot V_{fm}(T) \tag{5}$$

where $V_{fw}(T)$ and $V_{fm}(T)$ are the fractional free volumes of water and membrane, respectively, at a given temperature T . Dependence of the fractional free volume on temperature is expressed as

$$V_{fw}(H, T) = V_{fw}(H, T_r) + \alpha(T - T_r) \tag{6}$$

and

$$V_{fm}(H, T) = V_{fm}(H, T_r) + \beta(T - T_r) \tag{7}$$

where T_r is the reference temperature, α and β are the expansion coefficients of water and membrane, respectively. Substituting eqs. (5)–(7) into eq. (4), the dependence of $f_{wm}(H, T)$ on temperature under constant H is given by

$$\frac{1}{\ln[f_{wm}(H, T_r)/f_{wm}(H, T)]} = \frac{1}{V^*} \left[V_f(H, T_r) + \frac{V_f^2(H, T_r)}{\alpha \cdot H + \beta(1 - H)} \cdot \frac{1}{T - T_r} \right] \tag{8}$$

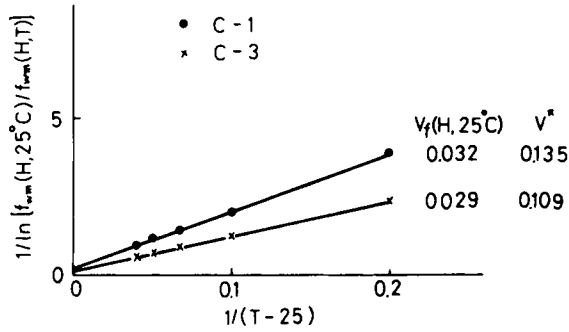


Fig. 14. Relationships between $1/\ln[f_{wm}(H, T_r)/f_{wm}(H, T)]$ and $1/(T - 25)$, eq. (8), for water vapor permeation through C-1 and C-3.

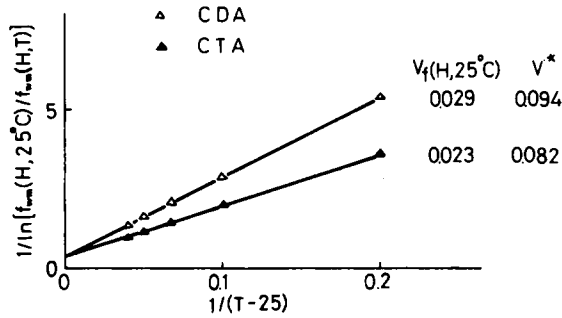


Fig. 15. Relationships between $1/\ln[f_{wm}(H, T_r)/f_{wm}(H, T)]$ and $1/(T - 25)$, eq. (8), for water vapor permeation through CDA and CTA.

Equation (8) shows that the relation between $1/\ln[f_{wm}(H, T_r)/f_{wm}(H, T)]$ and $1/(T - T_r)$ should be linear. Application of this relation to C-1 ($H = 0.72$), C-2 ($H = 0.69$), C-3 ($H = 0.62$), CDA ($H = 0.17$), and CTA ($H = 0.09$) is demonstrated in Figure 13, where the reference temperature T_r is 25°C . As is expected, the relation is linear for all membranes. Calculating the ratio of the slope to the intercept of the straight line and substituting the values of α ($2.4 \times 10^{-4}/\text{deg}$)²¹ and β ($4.0 \times 10^{-4}/\text{deg}$ for cellulose membranes²² and $1.7 \times 10^{-4}/\text{deg}$ for CDA and CTA),²³ the fractional free volumes $V_f(H, 25^\circ\text{C})$ are obtained as 0.067, 0.065, 0.063, 0.034, and 0.027, respectively, for C-1, C-2, C-3, CDA, and CTA. It seems that these values are reasonable, because the fractional free volume of water may be larger than that of the membrane by several times. The critical volumes V^* are calculated from the ratio of the value $V_f(H, 25^\circ\text{C})$ to the intercept of the line, as 0.45, 0.38, 0.30, 0.18, and 0.096 for C-1, C-2, C-3, CDA, and CTA, respectively. The value V^* increases with increase in hydration H . This result shows that the size of the cluster of water permeated through the membrane matrix by applied pressure becomes gradually large with increase in hydration H .

For comparison, this free-volume concept is applied to the stationary-state diffusion coefficient \bar{D} of water vapor-versus-temperature relationships for C-1 ($H = 0.092$), C-3 ($H = 0.088$), CDA ($H = 0.019$), and CTA ($H = 0.014$). As is expected, the relation is linear for all membranes, as shown in Figures 14 and 15. In this case, too, the values $V_f(H, 25^\circ\text{C})$ and V^* are calculated

using eq. (8). The values of the $V_f(H, 25^\circ\text{C})$ are 0.032, 0.029, 0.029, and 0.023 for C-1, C-3, CDA, and CTA, respectively, and the values of the V^* are 0.135, 0.109, 0.094, and 0.082, respectively. The value V^* obtained from water permeation under applied pressure is about 1.2 times of that for water vapor permeation for CTA and 3.3 times for C-1. However, the size of the cluster in hydraulic water permeation may be extremely small compared with that in bulk viscous flow, and the result shows that the determining factor for water permeation is the frictional coefficient between the cluster and membrane.

The authors gratefully acknowledge the support of the Japanese Ministry of Education for Science Research Grant (Coordinated Research (A) in 1973-1974). They also express their thanks to Hutamura Kagaku Kogyo Corporation and Mitsubishi Acetate Corporation for supplying the samples.

References

1. H. Yasuda, C. E. Lamaze, and A. Peterlin, *J. Polym. Sci. A-2*, **9**, 1117 (1971).
2. W. A. Reeve, R. M. Perkins, and L. H. Chance, *Amer. Dyestuff Rep.*, **49**, 639 (1960).
3. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 492.
4. R. A. Gill and R. Steele, *Text. Res. J.*, **32**, 338 (1962).
5. R. E. Rouse, *J. Amer. Chem. Soc.*, **60**, 1068 (1947).
6. V. Stannett and J. L. Williams, *J. Polym. Sci. C*, **10**, 45 (1965).
7. A. Takizawa and A. Tanioka, *Kobunshi Kagaku*, **28**, 24 (1971).
8. J. L. Bert, I. Fatt, and D. N. Saraf, *Appl. Polym. Symp.*, **13** 105 (1970).
9. J. D. Wellons, J. L. Williams, and V. Stannett, *J. Polym. Sci. A-1*, **5**, 1341 (1967).
10. K. S. Spiegler, *Trans. Faraday Soc.*, **54**, 1508 (1958).
11. O. Kedem and A. Katchalsky, *J. Gen. Physiol.*, **45**, 143 (1960).
12. K. S. Spiegler and O. Kedem, *Desalination*, **1**, 311 (1966).
13. B. Z. Ginzburg and A. Katchalsky, *J. Gen. Physiol.*, **47**, 403 (1963).
14. G. M. Gary-Bobo and A. K. Solomon, *J. Gen. Physiol.*, **57**, 610 (1971).
15. R. A. Horne, *Water and Aqueous Solutions*, Wiley, New York, 1972, p. 704.
16. A. Peterlin, H. Yasuda, and H. G. Olf, *J. Appl. Polym. Sci.*, **16**, 865 (1972).
17. A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).
18. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701 (1955).
19. H. Fujita, *Fortschr. Hochpolym. Forsch.*, **3**, 1 (1961).
20. M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).
21. C. D. Hodgman, R. C. Weast, and S. M. Selby, Eds., *Handbook of Chemistry and Physics*, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p. 2134.
22. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, 1967, p. VI-8.
23. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, 1967, p. IX-4.

Received July 30, 1974

Revised January 28, 1975