

# Studies on syntheses and permeabilities of special polymer membranes:

## 30. Ultrafiltration and dialysis characteristics of cellulose nitrate-poly(vinyl pyrrolidone) polymer blend membranes

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The ultrafiltration and dialysis characteristics of the semipermeable polymer blend membranes obtained from cellulose nitrate, poly(vinyl pyrrolidone), and *N,N*-dimethyl formamide were investigated under various conditions. The water content fraction and the ultrafiltration rate were dependent on the poly(vinyl pyrrolidone) content in the membranes, and the strengths were governed by the cellulose nitrate content in the polymer blend. If the pore radius in the membranes, calculated according to the Hagen-Poiseuille equation for capillary model, was identical, the water content in each membrane was not identical. It was found that urea molecules broke very weak hydrogen bonds of the bound water in the membrane, but sodium chloride did not, also, the diffusion of urea through the membrane was more rapid than that of sodium chloride. The ratio of the membrane diffusion coefficient to the ultrafiltration rate was explained qualitatively by the capillary model, however, when the bound water in the water content fraction was considered, this ratio showed better agreement with the model.

### INTRODUCTION

Polymeric membranes are used in such wide fields as desalination by reverse osmosis, concentration by ultrafiltration, and dialysis of blood, etc. Also, theoretical treatments for the transport phenomena through polymeric membranes have been done by many workers<sup>1-4</sup>. However, the relationship between the permeability and the membrane material has not been explained adequately. To make this relationship clear it is necessary to consider the chemical structure of the membrane material and physical structure of the resulting membrane. The simplest method is to prepare the membranes by polymer blending. In this work, cellulose nitrate and poly(vinyl pyrrolidone) are selected as membrane materials, because these two polymers have a good compatibility in solution blending.

This paper deals with the relationship between (1) the chemical and physical nature of the feed and the membrane, and (2) the permeabilities through these membranes. Also the permeation behaviour is analysed according to the capillary model by considering overall water content and bound water content in the membranes.

### EXPERIMENTAL

#### Materials

Daicel Co. best grade cellulose nitrate (CN) which was dried under reduced pressure, and having a degree of

nitration of 11.5%, and BASF Co. best grade poly(vinyl pyrrolidone) (PVP), having average molecular weight of 3500, were employed as membrane materials throughout this study. Commercial *N,N*-dimethyl formamide (DMF) was the solvent for casting solution. Pure commercial sodium chloride (NaCl) and urea were used as the feed solute.

#### Preparation of membranes

The casting solutions were prepared with cellulose nitrate, poly(vinyl pyrrolidone), and *N,N*-dimethyl formamide (DMF) in desired proportions. These casting solutions were mixed for 2 h at room temperature. The membranes were made by pouring the casting solutions onto a rimmed glass plate, allowing complete evaporation of the solvent at a desired temperature. The glass plate with membrane was immersed into water, for 24 h, then removed from the plate. The thickness of the membrane used in this work was 40–60  $\mu\text{m}$ .

#### Apparatus and measurements

The cell for ultrafiltration of pure water consisted of two detachable parts made of stainless steel as reported in earlier papers<sup>5-7</sup>. The effective membrane area in the cell was 11.5 cm<sup>2</sup>. The permeabilities for aqueous solutions of urea and sodium chloride were measured by using the batch type dialyser.

The compositions of feed and permeation solution for aqueous solutions of urea (530nm)<sup>8</sup> were analysed by colourimetric methods. The contents of sodium chloride were determined by means of an atomic absorption spectrophotometer.

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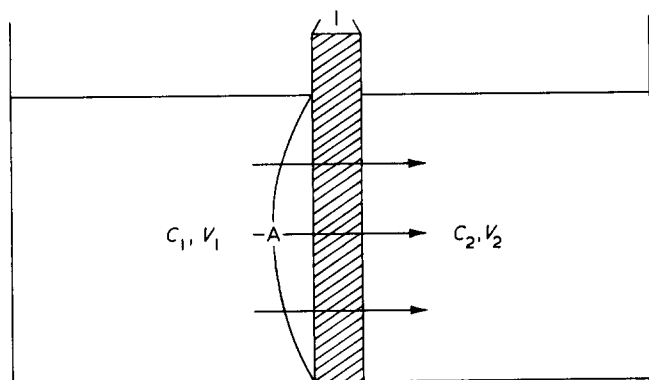


Figure 1 Diagram of a diffusion cell

### Permeability in ultrafiltration

The permeabilities of pure water are defined as:

$$V_{H_2O} = \frac{FRl}{P} \text{ (cm}^2 \text{ s g}^{-1}\text{)} \quad (1)$$

FR: Pure water permeability (cm<sup>3</sup> cm<sup>-2</sup> s<sup>-1</sup>)

l: Membrane thickness (cm)

P: Operating pressure (g cm<sup>-1</sup> s<sup>-2</sup>)

### Water content fraction

The water on the surface and back side of the membrane is wiped with the filter paper. The weight of the weighing bottle in which the membrane is placed is defined as the wet membrane weight. The weighing bottle is dried under reduced pressure with a diffusive pump until the weight is kept constant, and is defined as dry membrane weight.

### Water content fraction(%)

$$= \frac{\text{Wet membrane weight} - \text{Dry membrane weight}}{\text{Wet membrane weight}} \times 100 \quad (2)$$

### Diffusion constant

We assume that the permeation through the polymer membrane as shown in Figure 1 is carried out according to Fick's diffusion theory. The solute flux,  $J_s$  (mol cm<sup>-2</sup> s<sup>-1</sup>), through the membrane is defined as:

$$J_s = P_2 \frac{\Delta C}{l} \quad (3)$$

where  $P_2$  is membrane diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>),  $\Delta C$  is difference of solute concentration between both cells (mol cm<sup>-3</sup>), and  $l$  is membrane thickness (cm). Aqueous solution and water are set into left and right side cell, respectively. When the solute concentrations in both cells after  $t$  h are  $C_1$  and  $C_2$ , respectively and these volumes of solution are  $V_1$  and  $V_2$ , apparent membrane diffusion coefficient,  $P_1$ , is given by <sup>12</sup>:

$$P_1 = \frac{-1}{t(1/V_1 + 1/V_2)} \ln \left[ \frac{1 - (C_2/C_1)}{1 + (V_2/V_1)(C_2/C_1)} \right] \quad (4)$$

If the diffusion coefficient of solute in the membrane is independent of its concentration, and structural change of the membrane does not occur with time, the value of  $P_1$  is independent of the volume and concentration of the solution and diffusion time, and is constant. Furthermore, when the area ( $A$ ) and thickness of membrane are

considered, the membrane diffusion coefficient, ( $P_2$ ) is represented as:

$$P_2 = P_1 \frac{1}{A} \quad (5)$$

$P_2$  is a constant determined by the nature of the membrane, kind of solute, and applied temperature, and is the value indicated as degree of permeability of the solute.

## RESULTS AND DISCUSSION

### Effect of additional amount of poly(vinyl pyrrolidone)

The effect of additional amount of poly(vinyl pyrrolidone) on the value of  $V_{H_2O}$ , the water content fraction, and the membrane strength is shown in Figure 2, where the cellulose nitrate content is kept a constant. The value of  $V_{H_2O}$  and the water content fraction increase, but the membrane strength decreases with the poly(vinyl pyrrolidone) content in the membrane. These results may be attributed to differences in the structure and hydrophilicity of polymer blend membrane. Structural changes of the resulting membranes depend upon differences in the degree of polymer aggregation occurring simultaneously with the evaporation of the casting solvent, and of the micro phase separation based on interaction between cellulose nitrate molecules and poly(vinyl pyrrolidone) molecules.

### Effect of evaporation period and temperature

The relationship between evaporation period and weight of casting mixture at different temperatures is shown in Figure 3. The value of  $W_1$  is the weight of casting mixture at 0 time in evaporation period, and the value of

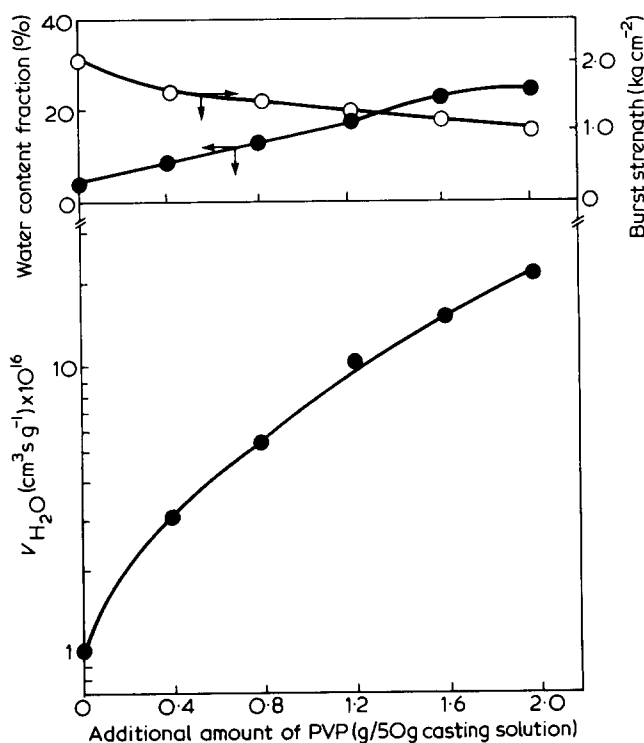


Figure 2 Effect of additional amount of PVP on membrane characteristics. Casting solution; CN/DMF = 4.00/96.00 (wt %); evaporation conditions, 80°C, 1 h; operating conditions, 40°C, 5 kg cm<sup>-2</sup>; feed, pure water

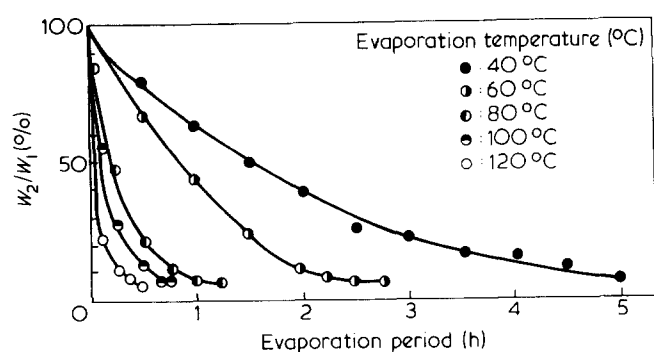


Figure 3 Relationship between evaporation period and  $W_2/W_1$ . Casting solution, PVP/DMF = 4.00/96.00 (wt %); additional amount of CN, 0.8 g/50 g casting solution

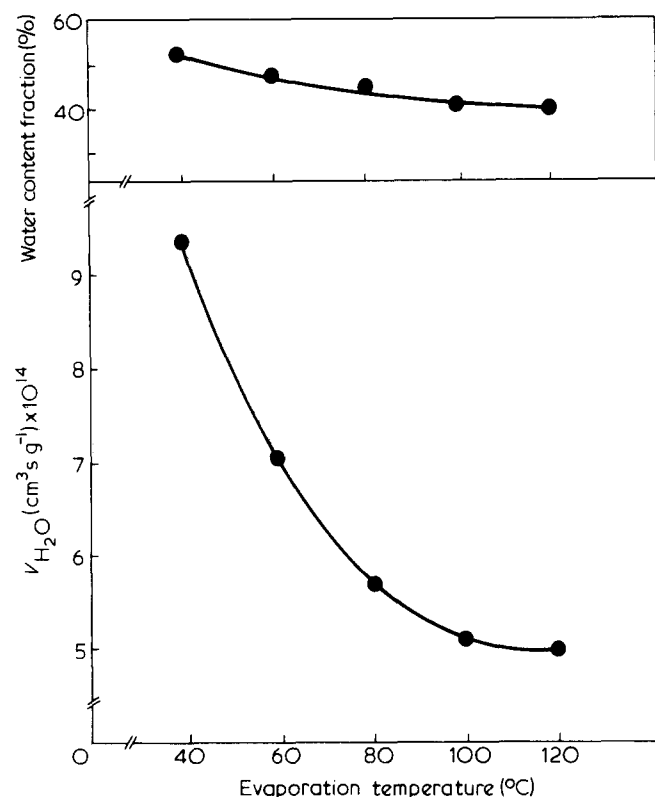


Figure 4 Effect of evaporation temperature on membrane characteristics. Casting solution, PVP/DMF = 4.00/96.00 (wt %); additional amount of CN, 0.8 g/50 g casting solution; operating conditions, 40°C, 5.0 kg cm<sup>-2</sup>; feed, pure water

$W_2$  is the weight of casting mixture after  $t$  h in evaporation period. As seen from Figure 3, the value of  $W_1/W_2$  reaches a constant at 6% after a certain time at each preparation temperature of the membranes. This value corresponds to the polymer content in the casting solution. Therefore, it is implied that the casting solvent is evaporated completely and the resulting membranes are homogeneous and symmetric.

Figure 4 shows the effect of evaporation temperature on the value of  $V_{H_2O}$  and the water content fraction, where the ratio of PVP/CN is 1.0/0.4. The value of  $V_{H_2O}$  and the water content fraction decrease with evaporation temperature. In general, the crystal structure in the polymer membrane is discussed to understand the permeability through the homogeneous membrane; the permeability is

governed significantly by the non-crystalline structure rather than the crystalline structure in the membrane<sup>9</sup>.

When the evaporation temperature is higher, the parts of crystalline structure in the membrane increase because of an increase of conversion to an intermolecular hydrogen bond from an intramolecular hydrogen bond. Therefore, the parts of non-crystalline structure in the resulting membranes decrease and consequently denser membranes are formed. The decrease of value of  $V_{H_2O}$  and water content fraction with an increase in evaporation temperature are dependent on the above factors.

The relationships between the value of  $V_{H_2O}$  and the water content with the changes of evaporation temperature (black circle) and the blend ratio of CN/PVP (white circle) are shown in Figure 5. There is a difference between the values of  $V_{H_2O}$  in the same water content fraction. This result may be attributed to the differences of micro structures of the resulting membranes based on the different preparation condition of the membrane. This presumption will be revealed by investigating in detail the relationship between the permeability and the crystallinity of the dense membrane.

#### Relation among pore radius, $V_{H_2O}$ , and water content fraction in the capillary model

If it is assumed that the permeation through the polymer membrane relates to the capillary model<sup>10</sup>, the pores in the membranes consisting of heterogeneous channels are represented as vertical, cylindrical capillaries as shown in Figure 6. The fluidity of water passing through these pores is determined by Reynolds number.

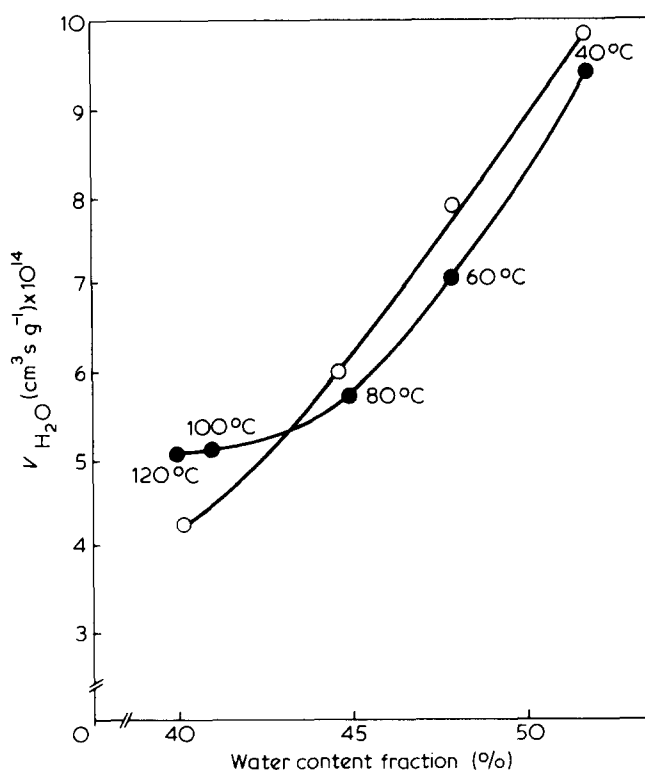


Figure 5 Water content dependence of  $V_{H_2O}$ . Casting solution, PVP/DMF = 4.00/96.00 (wt %); additional amount of CN, 0.8 g/50 g casting solution; operating conditions, 40°C, 5.0 kg cm<sup>-2</sup>; feed, pure water; ●, measurement values obtained with change of evaporation temperature; ○, measurement values obtained with change of ratio of polymer blend

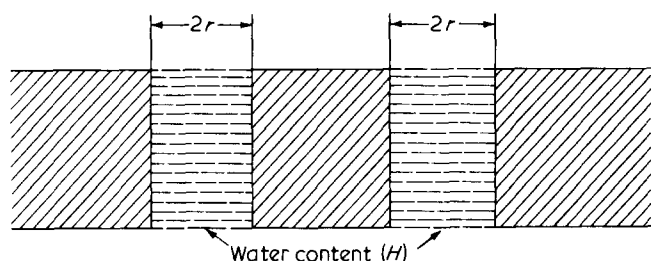


Figure 6 Capillary model

Reynolds number is defined as:

$$\text{Reynolds number } (-) = \frac{2\rho Ur}{\eta} \quad (6)$$

$\eta$ : Viscosity of fluid ( $\text{g cm}^{-1} \text{s}^{-1}$ )  
 $\rho$ : Density of fluid ( $\text{g cm}^{-3}$ )  
 $U$ : Volume flux for one pore ( $\text{cm s}^{-1}$ )  
 $r$ : Pore radius (cm)

$U$  is given in equation (7), and equation (8) is derived from equations (6) and (7):

$$U = \frac{FR}{n} \quad (7)$$

$$\text{Re number} = \frac{2\rho FRr}{n\eta} \quad (8)$$

$FR$ : Pure water permeability ( $\text{cm}^3 \text{cm}^{-2} \text{s}^{-1}$ )  
 $n$ : Density of capillary number  $(-)(n \geq 1)$

In this experiment, if the flow of water in the capillary is laminar flow, Reynolds number becomes  $\leq 2300$ . Also, we assume that  $n$  is unity. The maximum volume flow,  $FR$  at  $40^\circ\text{C}$  is  $2.4 \times 10^{-4} (\text{cm}^3 \text{cm}^{-2} \text{s}^{-1})$ , the viscosity,  $\eta$  and density,  $\rho$  are  $6.565 \times 10^{-3} (\text{g cm}^{-1} \text{s}^{-1})$  and  $0.993 (\text{g cm}^{-3})$ , respectively. By substituting these values into equation (8), the value of  $r$  becomes  $3.17 \times 10^{-4} (\text{cm})$ . The  $r$  value is held in this range. From this result, it is reasonable to assume that the water flows with laminar flow in the capillary. Therefore, the pore radius is given by Hagen-Poiseuille equation (9):

$$V = \frac{\pi nr^4}{8\eta} = \frac{FRI}{P} \quad (9)$$

When the volume in the pore is expressed by water content ( $H$ ), equation (10) is given:

$$H = \pi nr^2 \quad (10)$$

From equations (9) and (10):

$$r = \sqrt{\frac{8\eta V}{H}} \quad (11)$$

Figure 7 shows the relation among the value of  $V_{\text{H}_2\text{O}}$ , the water content fraction, and the value of  $r$ , calculated from equation (11), as the blend ratio of cellulose nitrate and

poly(vinyl pyrrolidone) is changed. As seen in Figure 7, the value of  $V_{\text{H}_2\text{O}}$  and the water content fraction increase with an increase in value of  $r$ . The value of  $r$  is highly dependent on the water content fraction rather than the value of  $V_{\text{H}_2\text{O}}$ .

#### Membrane diffusive constant

The membrane diffusive constants for urea and sodium chloride,  $P_{2(\text{urea})}$  and  $P_{2(\text{NaCl})}$ , are determined by using the batch type dialyser. These constants are obtained from equations (4) and (5) by using the data of dialysis experiments. Figures 8 and 9 show the effect of water content fraction on the constants of  $P_{2(\text{urea})}$  and  $P_{2(\text{NaCl})}$ . However, in general the membrane diffusive constant is given by the following equation<sup>4</sup>:

$$P_2 = \pi nr^2 D = HD \quad (12)$$

The diffusion coefficients for urea and sodium chloride in water,  $D_{\text{urea}}$  and  $D_{\text{NaCl}}$ , are  $1.3812 \times 10^{-5} (\text{cm}^2 \text{s}^{-1})$  for  $0.01 \text{ mol l}^{-1}$  at  $25^\circ\text{C}$ , and  $1.484 \times 10^{-5} (\text{cm}^2 \text{s}^{-1})$  for  $0.1 \text{ mol l}^{-1}$  at  $25^\circ\text{C}$ <sup>12</sup>, respectively. Figures 8 and 9 also include the theoretical curve obtained from these diffusive coefficients and equation (12).

The values of  $P_{2(\text{urea})}$  and  $P_{2(\text{NaCl})}$  increase as the water content fraction increases. Generally the diffusion rate of the solute through the membrane is governed by the membrane surface area, the membrane thickness, the diffusion coefficient of solute in the membrane, and the porosity in the membrane. We assume that the permeability is carried out according to Fick's diffusion theory. The value of  $P_2$  becomes a constant value regardless of the volume and concentration of the solution, and the diffusion time. However, it is dependent on the natures of membrane and solution, and the measurement temperature. Consequently this value expresses the

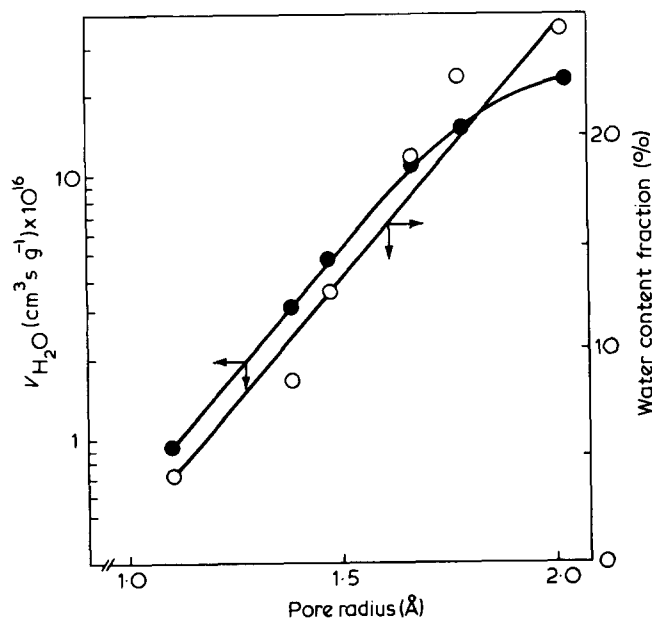


Figure 7 Relation among  $V_{\text{H}_2\text{O}}$ , pore radius, and water content fraction. Casting solution, CN/DMF = 4.00/96.00 (wt %); evaporation conditions,  $80^\circ\text{C}$ , 1 h; operating conditions,  $40^\circ\text{C}$ ,  $5.0 \text{ kg cm}^{-2}$ ; feed, pure water

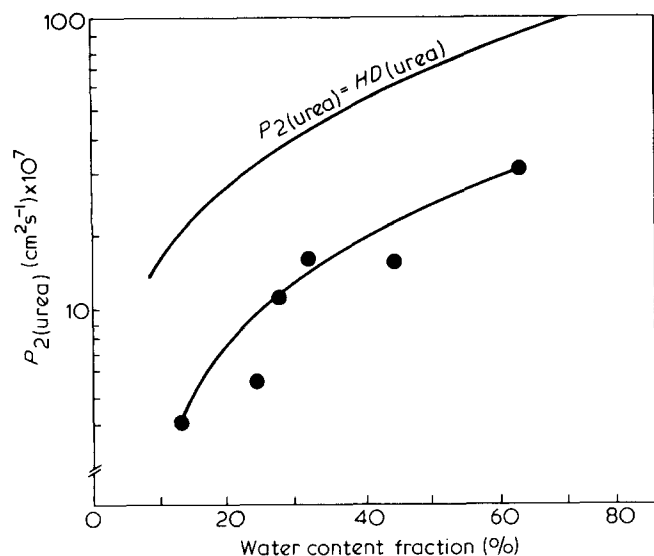


Figure 8 Water content fraction dependence of urea diffusion. Diffusion condition, 25°C; feed, urea aqueous solution (0.01 mol l<sup>-1</sup>)

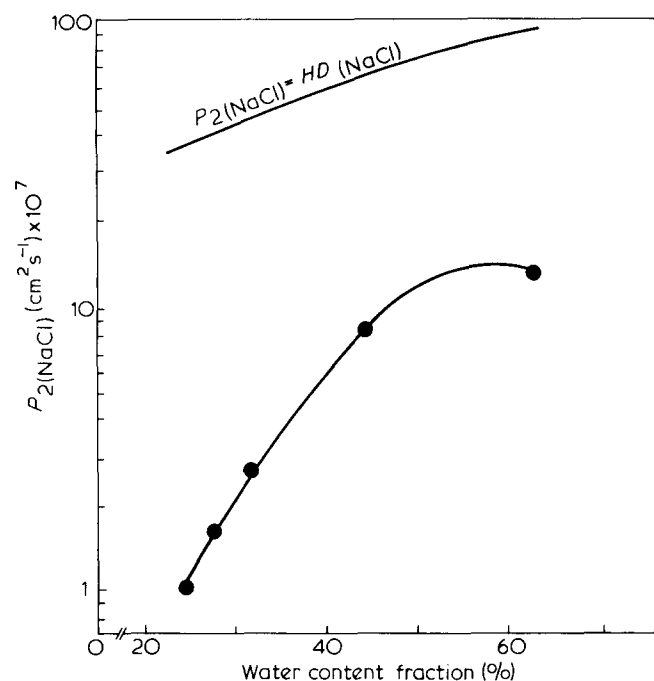


Figure 9 Water content fraction dependence of NaCl diffusion. Diffusion condition, 25°C; feed, NaCl aqueous solution (0.1 mol l<sup>-1</sup>)

degree of permeability. Therefore, the higher water content fraction in the membrane (the more porous membrane), is given the greater value of  $P_2$ . However, there is a considerable difference between the theoretical curve obtained from equation (12) and the experimental values.

#### Correction with bound water

The polymer blend membranes consisting of cellulose nitrate and poly(vinyl pyrrolidone) have higher water content fraction. It is presumed that bound water molecules exist on the wall of capillary in the membrane as shown in Figure 10. In general, the solutes in the permeating molecules do not enter into the bound water layer, therefore, the permeability of solute in aqueous solution is related to free water layer. Here, when the free water fraction in the capillary is represented by  $H_f$ , equation (12) is rewritten:

$$P_{2(\text{exp})} = H_f D \quad (13)$$

where  $P_{2(\text{exp})}$  is the value obtained experimentally.

From equations (12) and (13), the following equation is obtained:

$$\Delta P_2 = D(H - H_f) \quad (14)$$

Figures 11 and 12 show the relationship between the value of  $\Delta P_2$  and the water content fraction. As seen from these Figures, these relationships are the first-order function passing by zero point. Therefore, the value of  $\Delta P_2$  is defined as:

$$\Delta P_2 = KH \quad \begin{array}{l} 0.13 \leq H \leq 0.64 (\text{urea}) \\ 0.25 \leq H \leq 0.64 (\text{NaCl}) \end{array} \quad (15)$$

where  $K$  is the proportionality constant. Free water fraction in the membrane is given by:

$$H_f = -\frac{H(K - D)}{D} \quad (16)$$

The values of  $K$  determined with the least-squares method by using the slopes in Figures 11 and 12 are  $9.77 \times 10^{-6}$

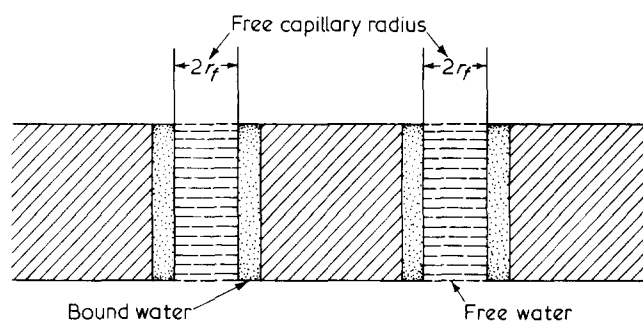


Figure 10 Capillary model contained bound water

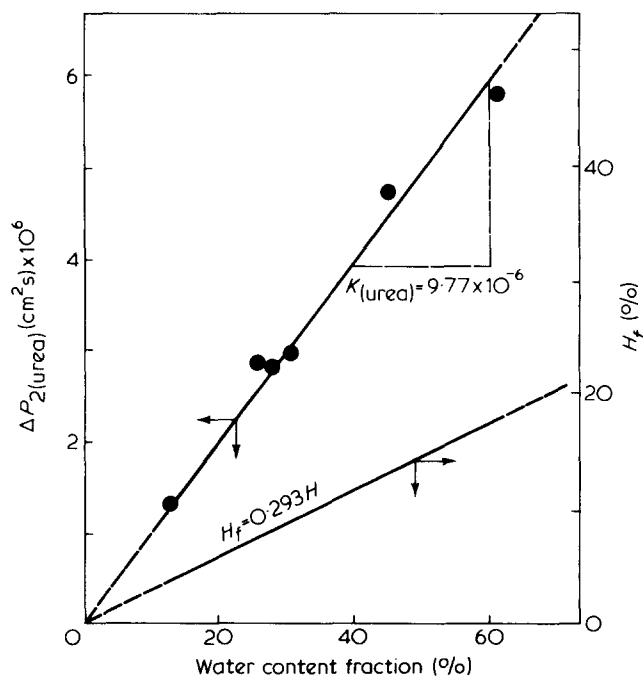


Figure 11 Water content fraction dependence of  $P_2 \Delta(\text{urea})$  and  $H_f$ . Diffusion condition, 25°C; feed, urea aqueous solution (0.01 mol l<sup>-1</sup>)

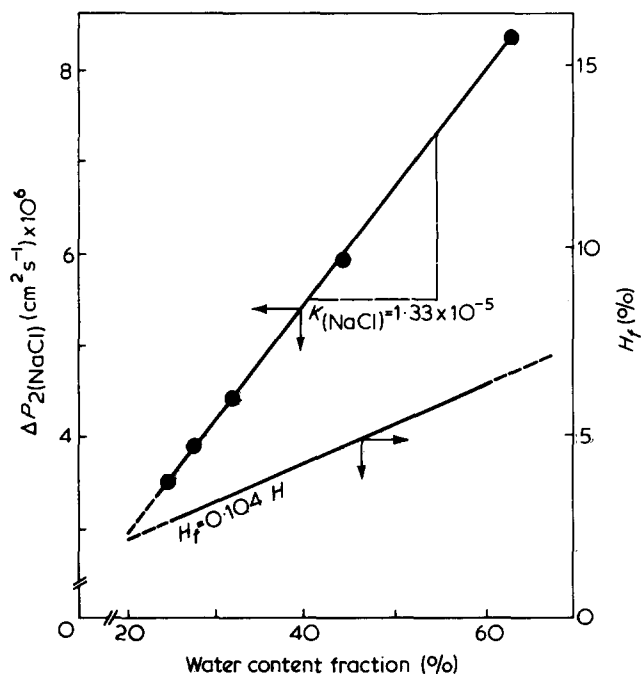


Figure 12 Water content fraction dependence of  $P_2 \Delta(\text{NaCl})$  and  $H_f$ . Diffusion condition, 25°C; feed, NaCl aqueous solution (0.1 mol l<sup>-1</sup>)

(cm<sup>2</sup> s<sup>-1</sup>) for urea and  $1.33 \times 10^{-5}$  (cm<sup>2</sup> s<sup>-1</sup>) for NaCl, respectively. By substituting these values and the diffusion coefficients in water:

$$H_{f(\text{urea})} = 0.293H \quad (17)$$

and  $H_{f(\text{NaCl})} = 0.104H \quad (18)$

These relationships are included in Figures 11 and 12. The equations suggest that even if the water content fraction in the membrane equals the free water fraction,  $H_f$  is changed by the kind of solute in the feed solution. This result may be explained by the fact that the urea molecules break weaker hydrogen bonds in the bound water<sup>12</sup> and consequently, effective pore sizes, which are related to the permeability, become larger. However, such an effect is very small with the sodium chloride molecules. The bound water content in the water content fraction is 70.7% for aqueous solution of urea, and 89.6% for aqueous solution of NaCl. The difference between these bound water contents is 18.9% which indicates that the diffusion of urea molecules is higher than that of sodium chloride molecules.

#### Pore radius

The relationships between the ratios of  $P_{2(\text{urea})}/V_{\text{H}_2\text{O}}$ ,  $P_{2(\text{NaCl})}/V_{\text{H}_2\text{O}}$  and the values of  $r$  determined by equation (11) are given by the straight lines, (C) represented with the black circle plots in Figures 13 and 14. From equations (11) and (12):

$$P_2/V = 8nD/r^2 \quad (19)$$

The model relationships for urea and sodium chloride in equation (19) are shown with lines A in Figures 13 and 14. These lines agree quantitatively with the lines C obtained from experimental values. Therefore, the permeation mechanism through the polymer blend membranes of

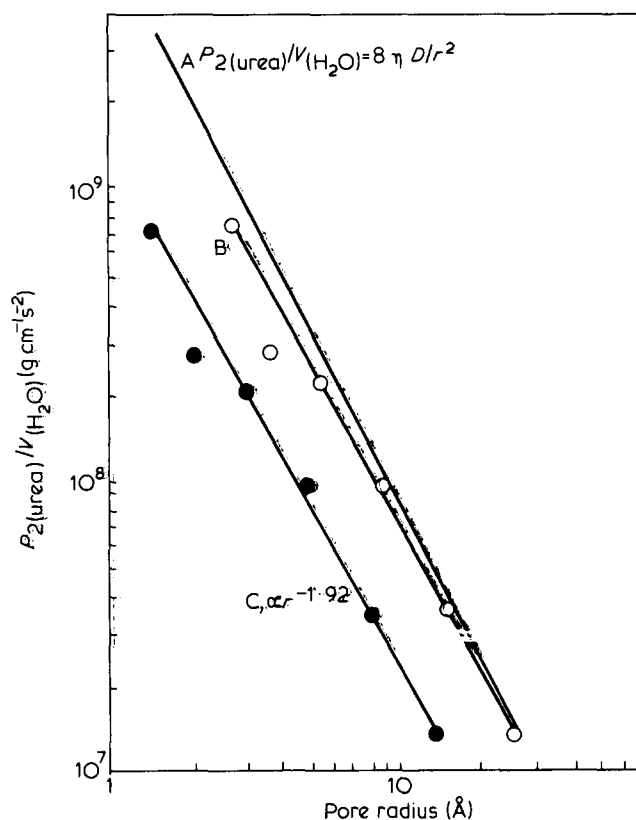


Figure 13 Relationship between  $P_2(\text{NaCl})/V_{\text{H}_2\text{O}}$  and pore radius. Diffusion condition, 25°C; feed, urea aqueous solution (0.01 mol l<sup>-1</sup>)

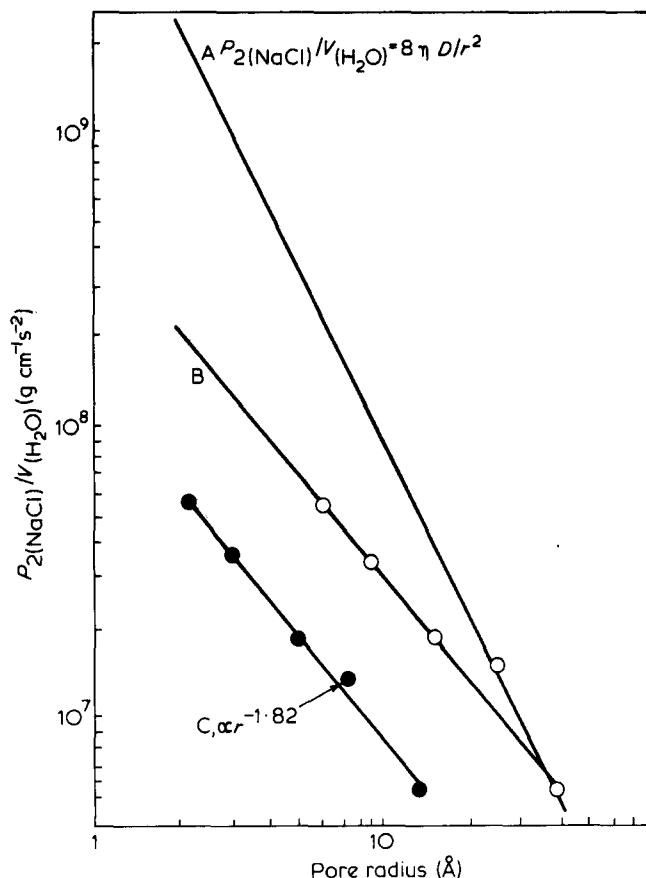


Figure 14 Relationship between  $P_2(\text{NaCl})/V_{\text{H}_2\text{O}}$  and pore radius. Diffusion condition, 25°C; feed, NaCl aqueous solution (0.1 mol l<sup>-1</sup>)

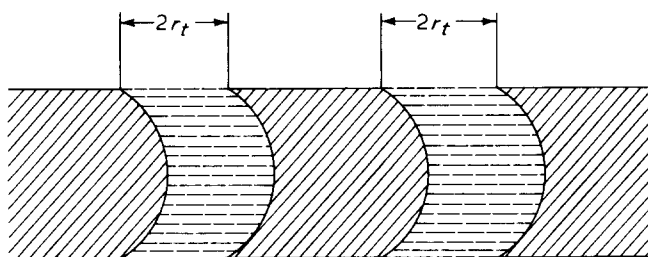


Figure 15 Tortuosity model

cellulose nitrate and poly(vinyl pyrrolidone) used in this work is explained quantitatively with the capillary model. However, there is not sufficient agreement between the model values and the experimental values. Accordingly, when the effect of bound water is considered in the membrane permeation, equations (20) and (21) are given from equations (11), (17) and (18):

$$r_{f(\text{urea})} = \sqrt{\frac{8 V \eta}{0.293 H}} \quad (20)$$

$$r_{f(\text{NaCl})} = \sqrt{\frac{8 V \eta}{0.104 H}} \quad (21)$$

where  $r_f$  is the pore radius that takes into consideration the bound water fraction in the pore. Figures 13 and 14 also include the relationships between  $r_f$  and  $P_{2(\text{urea})}/V_{\text{H}_2\text{O}}$ ,  $P_{2(\text{NaCl})}/V_{\text{H}_2\text{O}}$ , represented with lines B. In the systems of both urea and sodium chloride, the B lines reasonably approach the model lines A, and the system of urea aqueous solution fits better than that of sodium chloride. The discrepancies between the corrected experimental values of the smaller pore radius and the model line in the sodium chloride system may be due to the difficulty in solute diffusion because of the hydrated radius of sodium ions.

#### Tortuosity

Figure 15 shows the tortuosity model. When the pore radius is  $r_t$ , the capillary length is  $l_t$ , and the density of

capillary is  $n_t$ , the tortuosity ( $\epsilon$ ) is defined as:

$$l_t = l \epsilon \quad (22)$$

By considering the tortuosity, equations (11) and (19) are rewritten as follows:

$$r_t = r \epsilon \quad (23)$$

$$(P_2/V)_t = \frac{8 \eta D}{r_t^2} \quad (24)$$

where suffix  $t$  denotes the tortuosity.

In equation (23),  $\epsilon$  is  $\geq 1$ , therefore  $r_t$  is  $\geq r$ . If the values of  $r$  in Figures 13 and 14 are replaced with  $r_t$ , equation (24) is given as the model equation. Since both  $(P_2/V)_t$  and  $r_t$  take into consideration the tortuosity, the relationships between  $(P_2/V)_t$  and  $r_t$  for urea and sodium chloride are identical with those in Figures 13 and 14. But the experimental values on the C lines shift to the right side as understood from equation (23). Consequently, the difference between the experimental values and the corrected values which consider the tortuosity becomes smaller.

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