

# Pervaporation Separation of Water / Ethanol Mixtures through Polysaccharide Membranes.

## II. The Permselectivity of Chitosan Membrane

AKIRA MOCHIZUKI, YOSHIO SATO, HISASHI OGAWARA, and  
SHUZO YAMASHITA, *Tskuba Research Laboratory,*  
*Kuraray Co. Ltd., Miyukigaoka 41, Tukuba, Ibaragi 305, Japan*

### Synopsis

The separation of water/alcohol mixtures through chitosan membrane was investigated. The degree of the deacetylation of chitosan did not affect the selectivity of the membrane in the separation of the water/ethanol mixture. The selectivity of the chitosan membrane was affected by the specific salts such as  $\text{CoSO}_4$ ,  $\text{ZnSO}_4$ , and  $\text{MnSO}_4$  and it increased when the salts were present in the feed mixture or the membrane was pretreated with the salt solution. This behavior would be explained by the contraction of the "holes" produced by the thermal motion of polymer chains and this contraction would be correlated with the conformation change of chitosan molecule due to the formation of complexes with metal ions.

### INTRODUCTION

In the previous paper,<sup>1</sup> we reported that trace amount of some salts in the feed mixtures increased markedly the selectivity of cuprophane membrane which is one of the regenerated cellulose membranes. This phenomenon was explained by the contraction of the "holes" produced by the thermal motion of the polymer chains due to the conformation change of cellulose molecule. We concluded that the conformation change was caused by the formation of metal complex with the hydroxy group of cellulose. But the salt was indispensable in the feed mixture to maintain the high selectivity because of the low stability of the complex. The presence of the salt in the mixture is not good for practical use; thus we investigated chitosan membrane to improve this problem. As chitosan has the same skeleton as cellulose, it is expected that the permselectivity of chitosan membrane is influenced by the salt in the mixture like cellulose membrane. Moreover, it is also expected that the high selectivity may be kept without the salt in the mixture after the metal complex is formed, because chitosan has an amino group which interacts with the metal ion more strongly than the hydroxy group of cellulose and can form a more stable complex. Indeed, chitosan has been well known as an absorbent of heavy metal ions.<sup>2</sup> Chitosan is the deacetylation product of chitin produced by alkali treatment and the substituent group on the alpha carbon atoms is the amino group as shown in Figure 1. Chitosan is thus a generic name for a complicated product which must be identified in term of the degree of deacetylation and the molecular weight. In this paper, we will report the permselectivity of chitosan membrane and the effect of the salts on it.

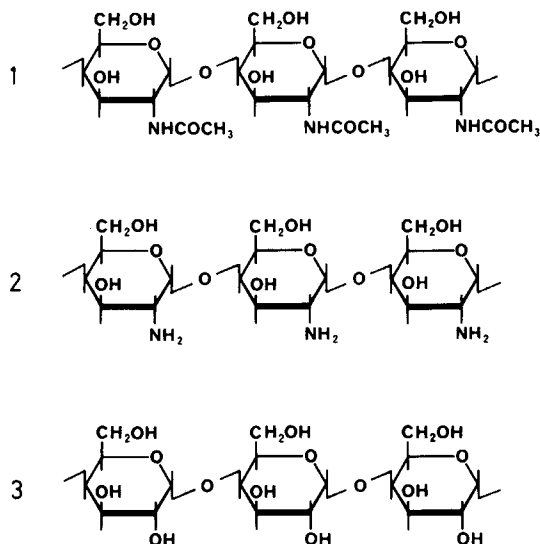


Fig. 1. Chemical structure of polysaccharides: (1) chitin; (2) chitosan; (3) cellulose.

## EXPERIMENTAL

### Chitosan and Its Membrane

Chitosan having various degrees of deacetylation was supplied by Katokichi Co. Ltd. (Japan) and Tokyo Kasei Co. Ltd. (Japan) and the weight-average molecular weight of these chitosan was  $1.0 \times 10^5$  to  $3.0 \times 10^5$  measured by GPC-LALLS (GPC: waters 201D, LALLS: Chromatix CMX-100).

Chitosan membranes were prepared by casting 1 wt % chitosan aqueous solution containing 1 wt % acetic acid on a glass plate, drying at room temperature, and treating in 3 wt % NaOH solution containing 50 wt % ethanol solution. The thickness of the membranes was 20–25  $\mu\text{m}$ .

### Pervaporation Measurement

The pervaporation measurements were conducted in pervaporation mode with a membrane surface of 7.0  $\text{cm}^2$  and a downstream pressure of 0.3 mm Hg (40 Pa). The water/ethanol mixture was recirculated at 120 mL/min and its temperature was kept constant. The permeated vapor was collected in a liquid nitrogen trap. The compositions of the feed mixture and permeate were determined by Shimadzu GC7A gas chromatograph equipped with 1 m long column packed with Porapak Q.

### X-Ray Measurement

Wide angle X-ray diffractograms were obtained with Rigaku Denki model RAD-rA X-ray diffractometer equipped with a scintillation counter. The X-ray source was nickel-filtered Cu K $\alpha$  radiation (40 kV, 20 mA). From the intensity curves, the degree of the crystallinity was evaluated.

### Swelling Degree

The membranes were immersed in water/ethanol mixtures in flasks, and the vessels were placed in a thermostat bath at 25°C. After 2 days, the membranes were removed, pressed between a tissue paper, and weighed with flasks. The membranes were dried under reduced pressure at 60°C for 24 h and weighed again. The swelling degree was expressed as a relative weight increase.

### RESULTS AND DISCUSSION

The crystallinity of four kinds of chitosan membranes having deacetylation degree from 72 to 98 mol % was investigated by X-ray diffraction. The results are shown in Table I. The crystallinity keeps almost constant, 18% in the range of 72–90 mol % deacetylation; and at 98 mol %, it becomes not more than 30%. These results are consistent with the ones of infrared analysis by Mima et al.<sup>3</sup>

The effect of the crystallinity or deacetylation degree of chitosan on the permselectivity was investigated using water/ethanol mixture (50/50 wt/wt).

TABLE I  
Crystallinity of Chitosan Membrane

Deacetylation degree (mol %)	Crystallinity (%)
72	16
82	18
90	18
98	26

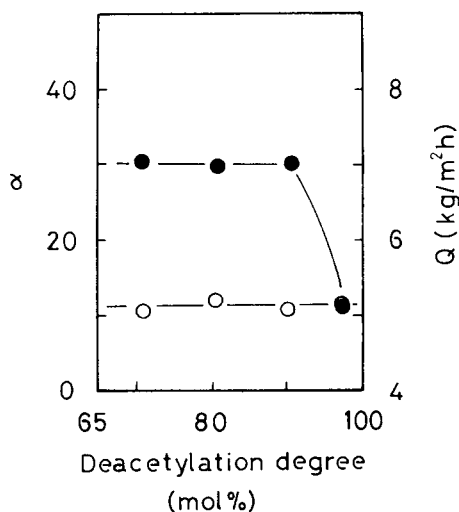


Fig. 2. Effect of crystallinity on permselectivity of chitosan membranes: (○) separation factor; (●)  $Q$ ; water/ethanol = 50/50 wt/wt; 60°C.

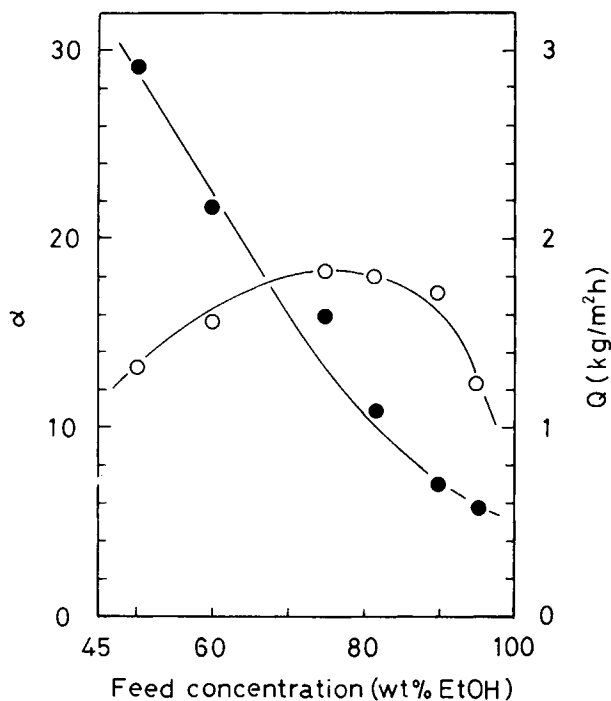


Fig. 3. Effect of ethanol concentration on permselectivity of chitosan membrane: (○) separation factor; (●)  $Q$ ; deacetylation degree = 98 mol %; 60°C.

The results are shown in Figure 2, where the separation factor and permeation rate are plotted as a function of the deacetylation degree. The permeation rate holds nearly a constant value, 7.0 kg/m<sup>2</sup> h in the range of 70–90 mol % deacetylation, and at 98 mol %, it decreases to 5.1 kg/m<sup>2</sup> h, but the separation factor is not affected by the deacetylation degree. The result of the permeation rate corresponds to that of the X-ray diffraction. That is, water and ethanol molecules permeate only the amorphous region of the membrane and they cannot penetrate into the crystalline region, so that the permeation rate of 98 mol % deacetylation membrane is low because of its higher crystallinity. The reason why the separation factor is not affected by the deacetylation degree is that the separation will occur only at the amorphous region.

The effect of ethanol concentration of the feed mixture on the permselectivity of chitosan membrane was investigated using 98 mol % deacetylation chitosan membrane. The results are shown in Figure 3. This figure indicates that the permselectivity is highly influenced by the feed composition. The permeation rate decreases from 2.92 to 0.57 kg/m<sup>2</sup> h with increasing ethanol concentration from 50 to 95 wt %. The curve of the separation factor has a maximum point at about 80 wt % ethanol and its value is 18. The permeation behaviors will be explained by the swelling degree of the membrane. That is, the swelling degree of chitosan membrane decreases with increasing ethanol concentration as shown in Figure 4 and its curve corresponds well to the permeation rate curve of the chitosan membrane.

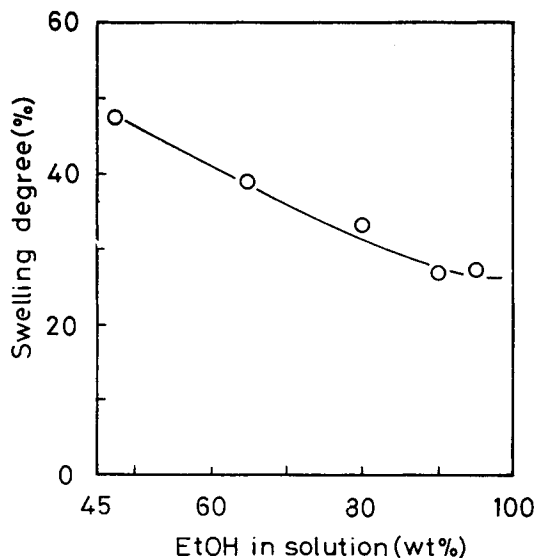


Fig. 4. Swelling degree of chitosan membrane; deacetylation degree = 98 mol %; 25°C.

The effect of the temperature on the permselectivity of chitosan membrane was investigated using 98 mol % deacetylation chitosan membrane. These results are shown in Figure 5, where the total permeation rate at each temperature is divided into permeation rates of water and ethanol. From this Arrhenius plot, the apparent activation energies of each component permeating through the membrane are calculated and its energy for water permeation is 7.27 and 7.02 kcal/mol for ethanol permeation. As the apparent activation energies for each component are thus nearly equal, the separation factor is almost independent on the feed temperature. A similar behavior that the activation energies of both the component are nearly equal was observed with the cuprophan membrane described in the previous paper. The activation energies for water and ethanol permeation through cuprophan membrane were calculated as 7.53 kcal/mol for both the components. There is a similar report by Cabasso et al.<sup>4</sup> They investigated Nafion membrane, which have a rigid molecular structure for a polyelectrolyte, and reported that the apparent activation energies of transport were approximately equal for both permeates, water and *i*-propanol, less than 6 kcal/mol. They concluded that the values were extremely low and within the range of the activation energies that was found for the mobility of small molecules in nonpolymer liquids, and that both permeates were being transported through the same discrete path. This explanation would be applied to the permeation behavior of cuprophan and chitosan membranes.

The decrease of the separation factor with increasing the temperature is generally observed in the conventional membranes, polyvinylalcohol<sup>5</sup> and polyethylene<sup>6</sup> membranes, and these polymer do not have rigid structures. This behavior can be explained by Eyring's hole theory of diffusion. That is, the thermal motion of the polymer chains randomly produces "holes" through which the permeating molecule can diffuse. As temperature is increased, the thermal agitation increases and the diffusive "holes" become larger; therefore,

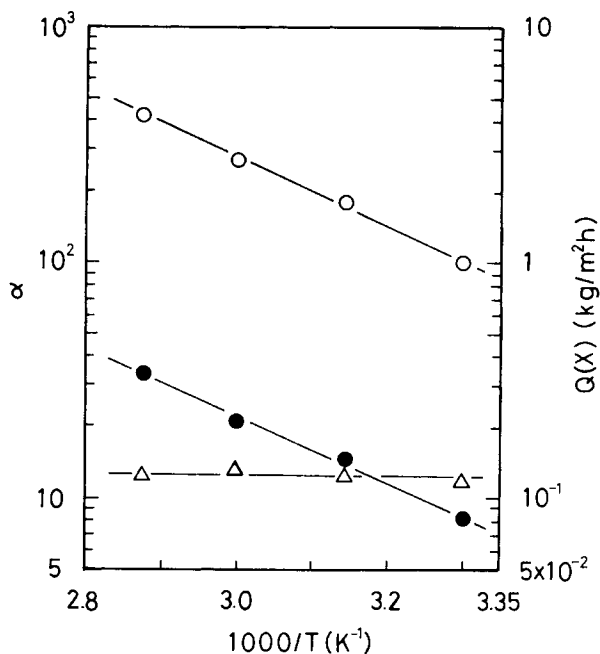


Fig. 5. Effect of temperature on permselectivity of chitosan membrane: (○)  $Q(\text{water})$ ; (●)  $Q(\text{ethanol})$ ; (△) separation factor; deacetylation degree = 98 mol %; water/ethanol = 50/50 wt/wt.

more alcohol molecules can diffuse through the membrane and the separation factor decreases. But in free chitosan and cuprophan membranes, the decreases of the separation factors with increasing the temperature cannot be observed as mentioned above, and the behavior cannot be explained only by Eyring's hole theory. The reason why the separation factors are essentially constant, or the apparent activation factors are essentially constant, or the apparent activation energies are approximately equal for both permeates, water and ethanol, is not still clear, but it is supposed that the structure of the polysaccharides which have a rigid glycosidic skeleton may participate in the effect of temperature on the permselectivity.

Previously, we have discussed the permselectivity of chitosan membrane. Next, we will report the effect of the specific salts on its permselectivity.

The chemical structure of chitosan is identical to that of cellulose except having an amino group at C<sub>2</sub> instead of a hydroxy group. So, it is clear that the interaction between chitosan and the metal ions is stronger than cellulose because Muzzarelli mentioned in his review that the bonds between cellulose molecules and metals ions might not be expected to be strong and that in reality the functional group of cellulose was principally hydroxy.<sup>7</sup> He also reported that there was a correlation between the nitrogen content of substituted polysaccharides and the capacity for collecting transition metal ions, and the nitrogen atom was the main site of attachment.<sup>8</sup> First, the effect of the salt in the feed mixture on the permselectivity of the chitosan membrane was investigated to compare with the cuprophan membrane. The experiments

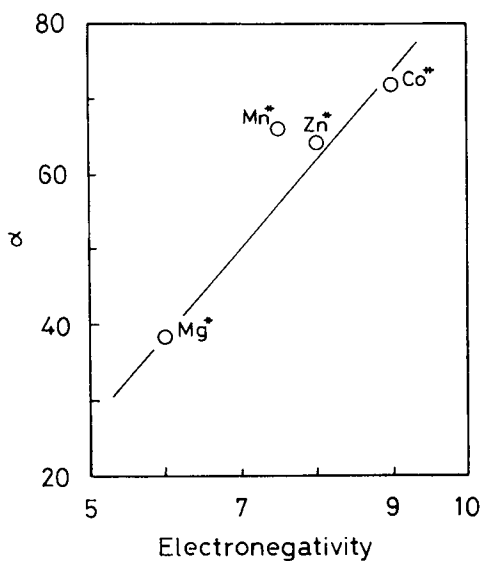


Fig. 6. Relationship between separation factors and electronegativity of metal ions; salt in water/ethanol (= 50/50 wt/wt) mixture;  $1 \times 10^{-2}$  mol/kg sulfate; 60°C; deacetylation degree = 72 mol %.

were carried out using 50 wt % ethanol mixture containing  $1 \times 10^{-2}$  mol/kg metal sulfates.

The results of metal ion species are shown in Figure 6, where the separation factor is plotted against the electronegativity of the metal ion. As can be seen, the separation factor increases with increasing the electronegativity. The effect of counteranion species on the selectivity is summarized in Table II and it indicates that the monovalent anion species are not effective for the increase of the separation factor but divalent ions are effective. These effects of the metal ions and counteranions on the permselectivity of chitosan membrane are similar to that on cuprophan membrane reported in the previous paper.<sup>1</sup> Therefore, the salt will play the same role in chitosan membrane as in cuprophan membrane. That is, first of all, the multivalent metal ion forms a complex with the amino group of chitosan molecule and its conformation is changed by the ionic repulsion and/or the steric hindrance of the complex formed. The new conformation is simultaneously immobilized by the ionic crosslinking of the multivalent anions. But, when the counteranion is monovalent such as  $\text{Cl}^-$ , the new conformation cannot be immobilized because the ionic crosslinking is impossible. The schematic crosslinking of chitosan is

TABLE II  
Effect of Anion Species of Co Salts on Separation Factor<sup>a</sup>

Anion	$\text{SO}_4^{2-}$	$\text{AcO}^-$	$\text{NO}_3^-$	$\text{Cl}^-$	Ion free
$\alpha$	38.3	13.6	18.2	11.5	9.67

<sup>a</sup> $[\text{Co}^{2+}] = 1 \times 10^{-2}$  mol/kg in feed; chitosan: deacetylation degree = 72 mol %; water/ethanol = 50/50 wt/wt; 60°C.

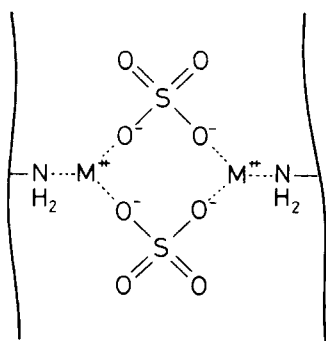


Fig. 7. Schematic crosslinking of chitosan molecule by metal sulfate.

shown in Figure 7. This conformation change will cause the change of the packing state of chitosan molecules, that is, the contraction of the "holes" produced by the thermal motion of polymer chain. Therefore, the permeation of ethanol larger than water through the "holes" is depressed and the separation factor increases. These experiments were carried out using the feed mixture containing metal sulfate as mentioned above, and so these systems are not good for practical use.

As has been described, the complex composed of chitosan and metal salt will be more stable than that of cellulose. Therefore, we assumed that chitosan membrane would show high selectivity even toward ion free water/ethanol mixture when the membrane was pretreated with the salt solution to complex the metal salts.

Then, we investigated the effect of pretreatment on the permselectivity of chitosan membrane. The pretreatment was carried out by soaking chitosan

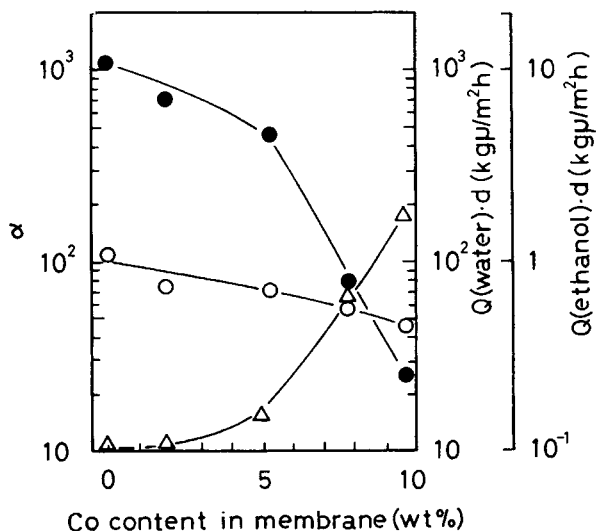


Fig. 8. Permselectivity of chitosan membrane pretreated with  $\text{CoSO}_4$  solution: (○)  $Q(\text{water}) \cdot d$ ; (●)  $Q(\text{ethanol}) \cdot d$ ; (Δ) separation factor; water/ethanol = 50/50 wt/wt; 60°C; deacetylation degree = 72 mol %.



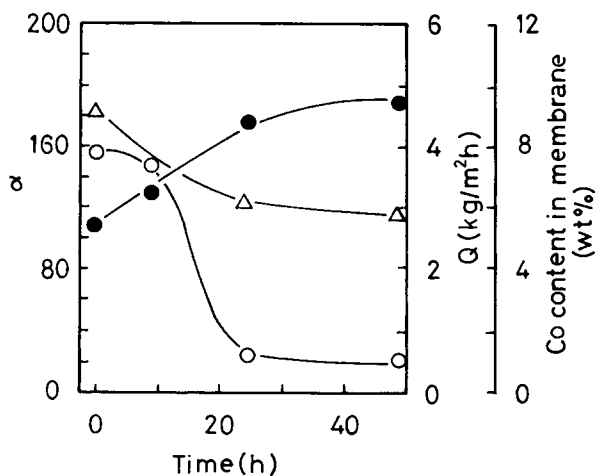


Fig. 9. Time course of permselectivity of pretreated chitosan membrane: (○) separation factor; (●)  $Q$ ; (△)  $\text{Co}^{2+}$  content in membrane; water/ethanol = 50/50 wt/wt (ion free); 60°C; deacetylation degree = 72 mol %.

membranes in water/ethanol (40/60 wt/wt) mixture containing adequate amounts of  $\text{CoSO}_4$  at 60°C for 13 h, and then the separation experiment was carried out using ion free water/ethanol (50/50 wt/wt) mixture. The results are shown in Figure 8, where the total permeation rate is divided into the rates of water and ethanol. The separation factor increases from 10 to 174 with increasing the  $\text{Co}^{2+}$  content in the membrane to 9.8 wt %. These results indicate that the pretreated chitosan membrane shows the high selectivity toward ion free mixture as was expected. The permeation rate of water is not affected by the metal content, but that of ethanol is affected and it decreases from 10.7 to 0.26  $\text{kg}\mu\text{m}/\text{m}^2 \text{ h}$  with increasing the  $\text{Co}^{2+}$  content to 9.8 wt %. Considering these results, the high selectivity is achieved mainly by the marked decrease of the permeation rate of ethanol. These permeation behaviors are similar to those of cuprophane membrane observed when  $\text{CoSO}_4$  concentration in the feed mixture is varied. The marked decrease of the permeation rate of ethanol will support the contraction of the "holes."

As mentioned above, chitosan membranes pretreated with the  $\text{CoSO}_4$  solution showed the high selectivity toward ion-free water/ethanol mixture. But the time course of the pervaporation for ion-free water/ethanol mixture causes the decrease of the selectivity as shown in Figure 9, and it corresponds to the decrease of the content of  $\text{Co}^{2+}$  in the membrane. These results indicate that the release of  $\text{CoSO}_4$  from the membrane occurs, that is, the stability constant of the complex is not so large as to maintain the new conformation of chitosan for a long time in the ion-free mixture.

## CONCLUSION

Chitosan, the chemical structure of which is similar to that of cellulose, was investigated as the pervaporation membrane. The deacetylation degree of chitosan correlated with the crystallinity of its membranes. The selectivity was not affected much but the permeation rate was affected by the crys-

tallinity in ion-free systems. It is because that water and ethanol molecules permeate through the amorphous regions in the membrane.

The specific salts having the multivalent metal ion and anion such as  $\text{CoSO}_4$  increased the selectivity of the chitosan membrane. The reason of this increase would be the contraction of the "holes" produced by the thermal motion of the polymer chain due to the conformation change of chitosan molecule and this conformation change would be caused by the formation of the chitosan metal salt complex like the case of cuprophan membrane.

The gradual decrease of permselectivity in the ion-free system was pointed out to be improved for practical use.

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