

Pervaporation Separation of Water / Ethanol Mixtures through Polysaccharide Membranes. I. The Effects of Salts on the Permselectivity of Cellulose Membrane in Pervaporation

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Synopsis

In the separation of water/alcohol mixtures through cellulose membranes, the addition of trace amounts of specific salts to the feed mixture (10^{-5} – 5×10^{-3} mol/kg) caused the marked increase of the separation factor and only the salts composed of a multivalent metal ion and a multivalent counteranion were effective for the increase of the selectivity. For example, when 1.5×10^{-3} mol/kg CoSO_4 was added to water/ethanol mixture (35/65 wt/wt), the separation factor was 194 and the permeation rate was $5.14 \text{ kg/m}^2 \text{ h}$. But, in the absence of the salt, the separation factor was only 6.7 and the permeation rate was $5.63 \text{ kg/m}^2 \text{ h}$. We presumed that the increase of the selectivity by the addition of specific salts would be attributed to the contraction of the "holes" produced by the thermal motion of polymer chains and this contraction would be correlated with the conformation change of cellulose molecule.

INTRODUCTION

Pervaporation is a desirable method to separate the liquid mixture whose separation by distillation is difficult. Especially, the separation of binary mixtures of water and lower alcohols by this method has attracted special interest recently. Among the membranes prepared from synthetic polymers, *N*-vinylpyrrolidone grafted onto the polytetrafluoroethylene membrane studied by Aptel et al. showed the best properties.¹ They indicated that the permeation behaviors of this membrane depended on the affinity derived from the basicity of polyvinylpyrrolidone. Poly(vinyl alcohol) membranes were investigated by Huang et al.^{2,3} and they showed remarkable good separation.

With respect to the membranes obtained from natural high polymers, there is considerable research in the literature dealing with the separation of alcohol/water mixtures through cellulose membranes. For example, Huang reported the permeation and separation characteristics of four different water/alcohol systems through cellophane membrane.³ Nagy et al. reported that the permselectivity of cellulose membrane could be modified considerably by its preswelling in water or water/alcohol mixtures.⁴ Heisler et al. investigated the selective permeation of water/alcohol mixtures through cellophane membrane⁵ and they reported that the separation factor increased remarkably when water-soluble, ethanol-insoluble additives (organic salts) were added

to the mixtures. Misra et al. also discussed the effect of the addition of sodium formate to the water/methanol mixture on the selective permeation through cellophane membrane.⁶ The addition of the salts increased the separation factor, but decreased the permeation rate. The reason of this phenomenon was that the addition of the salts to the mixture decreased the activity of water and therefore decreased the plasticization of the membrane. To realize this salt effect, 1–3 wt % salt must have been added to the mixtures.

In spite of the considerable research mentioned above, the separation factors of the membranes were not enough for practical use.

We investigated in detail the permselectivity of cuprophan membrane, which is one of cellulose membranes, and found that the trace amounts of some specific metal salts in the feed mixture increased significantly the selectivity of cuprophan membrane. We report here its behaviors of the selective permeation for both the cases of salt present and no salt present, and discuss the reason of the marked increase of the selectivity in the former case.

EXPERIMENTAL

Apparatus

The schematic pervaporation apparatus we used is shown in Figure 1. The permeation cell was made of stainless steel. The membrane was supported on a sintered stainless disc. The effective membrane area was 7 cm². The water/ethanol mixtures were recirculated at 120 mL/min and the temperature was kept constant by the heat exchanger and the water bath. The pressure on the downstream side was maintained constant at 40 Pa (0.3 mm Hg). 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.

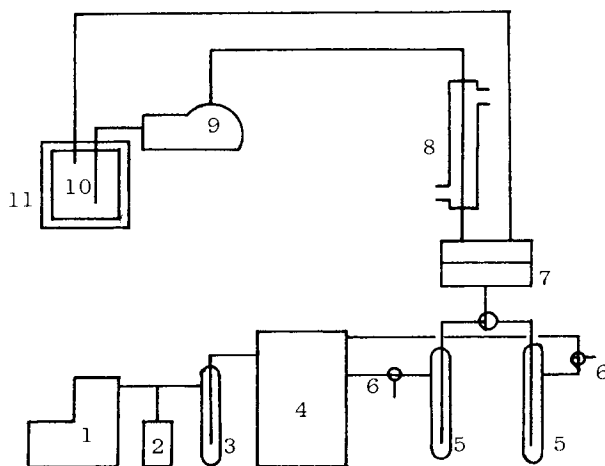


Fig. 1. Schematic presentation of pervaporation apparatus: (1) vacuum pump; (2) McLeod vacuum gage; (3) cold trap; (4) buffer tank; (5) collection trap; (6) vent to atmosphere; (7) permeation cell; (8) heat exchanger; (9) feed pump; (10) feed reservoir; (11) water jacket.

Membrane

The cellulose membrane (Cuprophane membrane, 150PM) was supplied by Enka Company (West Germany) and its thickness was 12 μm . This membrane was used without pretreatment.

The cellulose acetate membrane was obtained by casting dioxane solution containing 10 wt % cellulose acetate, supplied by Kodak, onto a glass plate and allowing the dioxane to evaporate.

Elongation

The elongation of the membrane was determined for different compositions of water/ethanol mixtures at 60°C. Elongation L is defined as $L(\%) = (l_1 - l_0)/l_0 \times 100$, where l_0 designates the length of the wet membrane in ion free water and l_1 the length of the swollen membrane in water/ethanol mixtures.

RESULTS AND DISCUSSION

First of all, six typical experimental results of cuprophane membrane obtained by the addition of trace amounts of salt to the feed mixture are described prior to the detailed results and discussion.

Effect of Metal Salts on Permselectivity

The effect of various metal sulfates added to water/ethanol feed mixture (50/50 wt/wt) on the separation factor was investigated. The results are shown in Figure 2 where the separation factor are plotted against the electronegativity of metal ions. All the values of the separation factors are the ones measured after 6 h from the start of the experiment. When the di- or trivalent metal salt is added to the feed mixture, the separation factors increase with increasing the electronegativity of the metal ion. But in the case

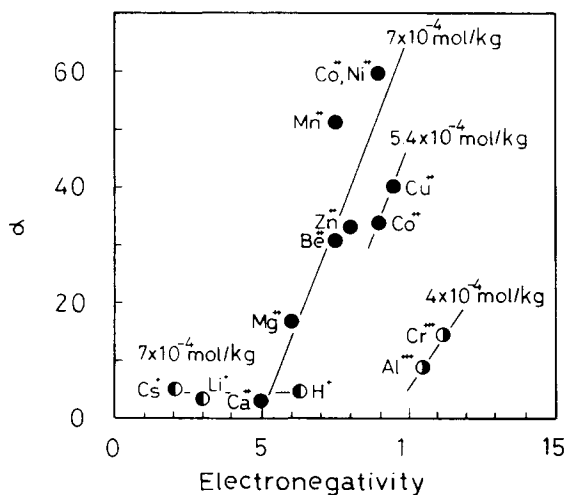


Fig. 2. Relationship between separation factor and electronegativity of metal ions: salt; sulfate, water/ethanol = 50/50 wt/wt, 60°C.

TABLE I
Effect of Anion Species of Mg Salts on Permselectivity^a

Anion	α	Q (kg/m ² h)	Anion	α	Q (kg/m ² h)
(COO ⁻) ₂ ^b	27.7	6.27	Cl	3.51	8.96
Citrate ³⁻	12.9	6.55	Br ⁻	2.94	9.37
H ₂ PO ₄ ^{-c}	40.5	6.96	I ⁻	4.09	9.53
SO ₄ ²⁻	16.4	8.70	ClO ₄ ⁻	3.10	9.92
AcO ⁻	7.81	8.65	ion free	4.33	9.02

^a[Mg²⁺] = 7.0×10^{-4} mol/kg.

^b 1.9×10^{-5} mol/kg.

^c 5.5×10^{-5} mol/kg; water/ethanol = 50/50 wt/wt, 60°C.

of the monovalent metal salts (alkali metal salts), the increase of the separation factor is not found at all.

Effect of Counteranion Species on Permselectivity

The effect of the counteranion species added to the water/ethanol feed mixture (50/50 wt/wt) on the permselectivity was investigated using various Mg salts. The concentration of Mg²⁺ is 7×10^{-4} mol/kg, except magnesium dihydrophosphate, 4.0×10^{-4} mol/kg and magnesium oxalate, 6.2×10^{-5} mol/kg. The results are shown in Table I. The multivalent anions such as sulfate, oxalate, phosphate, and citrate are effective but the monovalent anions are hardly effective for the increase of the separation factor. This tendency is also found in the case of cobaltous salts (Table II).

Dependence of Permselectivity on Concentration of Cobaltous Salt

The dependence of the permselectivity on the concentration of cobaltous sulfate or chloride in water/ethanol feed mixture (50/50 wt/wt) was investigated. The results are shown in Figure 3. When the sulfate is added to the feed mixture, the separation factor increases to 168 and the permeation rate decreases with increasing the concentration of the salt. On the other hand, when the chloride is added to the feed mixture, both the separation factor and permeation rate hold the constant values which are nearly equal to that in ion-free system regardless of the concentration of the salt.

TABLE II
Effect of Cobaltous Salts on Permselectivity^a

Salt	Conc (mol/kg)	α	Q (kg/m ² h)
CoSO ₄	7×10^{-4}	59.7	7.73
Co(NO ₃) ₂	1.5×10^{-3}	5.83	7.95
CoCl ₂	1.5×10^{-3}	4.37	8.34

^aWater/ethanol = 50/50 wt/wt, 60°C.

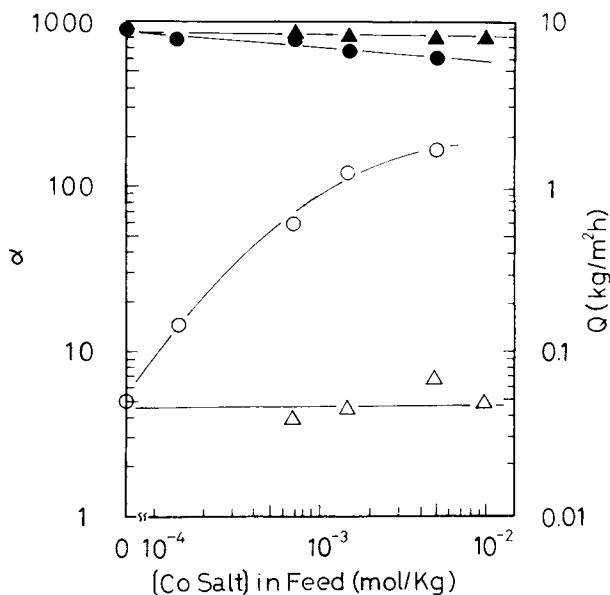


Fig. 3. Dependence of permselectivity on cobaltous salt concentration: (○, ●) CoSO₄; (△, ▲) CoCl₂; water/ethanol = 50/50 wt/wt, 60°C.

Dependence of Permselectivity on Ethanol Concentration

The dependence of the permselectivity on the ethanol concentration in the feed mixture was investigated for both the cases: CoSO₄ present, and no salt present. The results are shown in Figure 4. When the salt is not present in the feed mixture, the curve of the separation factor has a maximum point at 85 wt % ethanol, but the value is not more than 12, and the permeation rate decreases from 18.8 to 0.45 kg/m² h, with increasing the concentration of ethanol. On the other hand, in the presence of the salt, the behavior of the separation factor is quite different from the one without the salt. The separation factor increases and yields values 1 order of magnitude higher than the former in the range of 40–85 wt % ethanol. The curve has a maximum point at about 65 wt % ethanol and its value is no less than 195.

Effect of Molecular Size and Shape of Alcohol on Permselectivity

The relationships between the permselectivity and the size of alcohol molecules having 1–3 carbon atoms were investigated with 28 mol % alcohol feed mixtures for both cases: 1.5×10^{-3} mol/kg CoSO₄ present, and no salt present. The results are shown in Figure 5. In the absence of the salt, the separation factor increases gradually up to 18 with increasing the number of carbon atoms in alcohol molecules and the permeation rate decreases from 14.3 to 5.53 kg/m² h. In the presence of CoSO₄, the separation factor increases sharply when the size of alcohol molecules is larger than methanol. In the case of water/*i*-propanol mixture, the separation factor is 575, but in the case of water/methanol mixture, the separation factor is in the same range as that without salts.

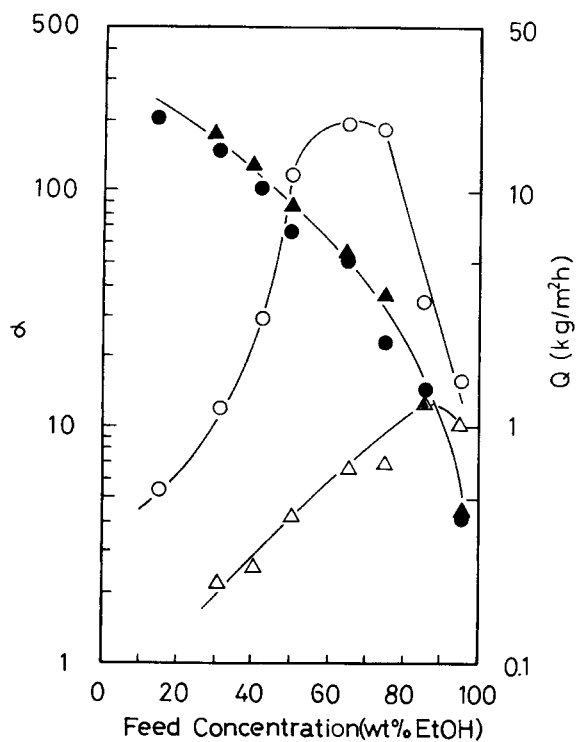


Fig. 4. Dependence of permselectivity on ethanol concentration: (○, ●) with 1.5×10^{-3} mol/kg CoSO_4 present; (△, ▲) without salt present; 60°C .

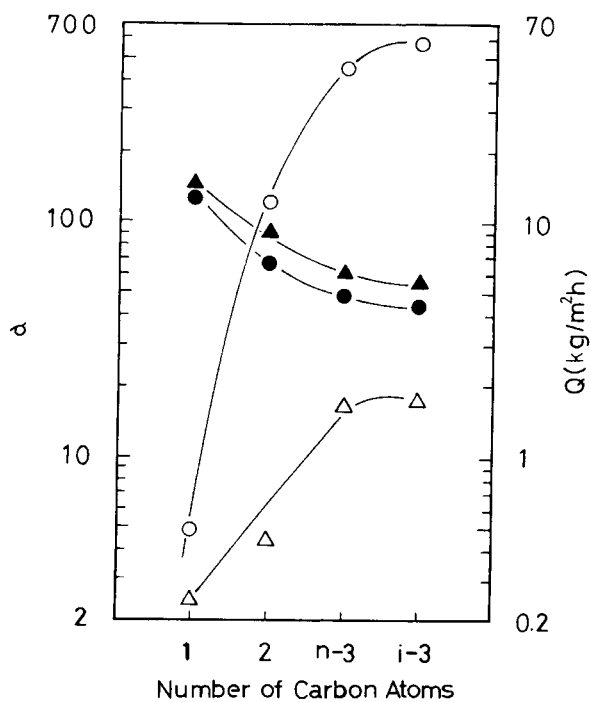


Fig. 5. Effect of molecular length and shape on permselectivity: (○, ●) with 1.5×10^{-3} mol/kg CoSO_4 present; (△, ▲) without salt present. Number of carbon atoms: 1 = methanol, 2 = ethanol, *n*-3 = *n*-propanol, *i*-3 = *i*-propanol. Alcohol concentration = 28 mol % (28 mol % ethanol = 50 wt % ethanol); 60°C .

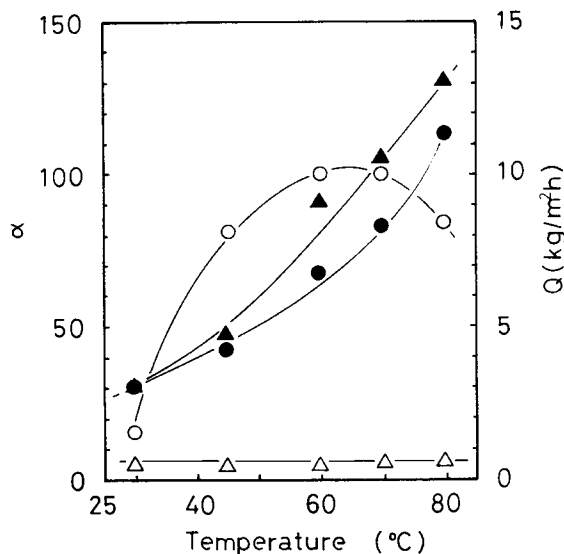


Fig. 6. Effect of temperature on permselectivity: (O, ●) with 1.5×10^{-3} mol/kg CoSO_4 present; (Δ , \blacktriangle) without salt present; water/ethanol = 50/50 wt/wt.

Effect of Temperature on Permselectivity

The permselectivity at various temperatures in the range of 30–80°C was investigated with water/ethanol (50/50 wt/wt) mixture. The results are shown in Figure 6, where the permeation rate and separation factor are plotted against the temperature. In the absence of salt, the rise of the feed temperature results in the increase of the permeation rate from 3.1 to 13.0 $\text{kg/m}^2 \text{ h}$ without the significant decrease in the separation factor, about 5.5. On the other hand, in the presence of 1.5×10^{-3} mol/kg CoSO_4 , the curve of the separation factor has a maximum point at 60°C and its value is 104 and the permeation rate increases from 3.11 to 11.3 $\text{kg/m}^2 \text{ h}$ with increasing the temperature.

As have been described, the permselectivity of cuprophane membrane in the presence of the specific salts proves to be quite different from that in the absence of the salts. The reasons of the unusual behaviors will be discussed in detail hereinafter.

The marked increase of the separation factor is observed only when the specific multivalent metal salts such as CoSO_4 are added as shown in Figure 2. It is also found that the increase of the electronegativity of the metal ions causes the increase of the separation factor. These results indicate that the increase of the separation factor can be correlated with the formation of a complex ion composed of cellulose molecule and the metal ion. The larger the electronegativity of the metal ion which is the same valence becomes, the larger the separation factor becomes, because the increase of the electronegativity causes more strong interaction between the metal ion and the oxygen atom of the hydroxy group in cellulose molecule.

It is not clear, however, why the divalent metal sulfates are more effective than the trivalent ones. In the case of the monovalent metal sulfates (alkali

TABLE III
Effect of CoSO_4 on Permselectivity of Cellulose
Acetate Membrane^a

$[\text{CoSO}_4]$ (mol/kg)	α	$Q \cdot d^b$ (kg/m ² h)
Ion free	6.62	7.34×10^{-5}
1.5×10^{-3}	4.67	6.66×10^{-5}
2.8×10^{-3}	5.78	7.25×10^{-5}

^a Water/ethanol = 50/50 wt/wt, 60°C.

^b d = membrane thickness.

metal salts), the increase of the separation factor cannot be found at all because alkali metal ion hardly complexes cellulose. This postulate is supported by the results of cellulose acetate membrane described as follows. The effect of CoSO_4 on the permselectivity of the acetate membrane was investigated with water/ethanol feed mixture (50/50 wt/wt). The results are shown in Table III. CoSO_4 does not affect the permselectivity of the membrane at all, though it is one of the most effective salts for the increase of the selectivity of cuprophan membrane. The reason is that cobaltous ion cannot complex cellulose acetate because it has no hydroxy group which can coordinate to metal ion. Hence, it is necessary for the membrane to have coordinating ability to metal ion to show the marked increase of the selectivity. Moreover, this result indicates that the change of the solution structure by the addition of the salt does not cause the increase of the selectivity obtained in this research.

The increase of the selectivity in the presence of the specific salts may be explained by the increase of the affinity of cellulose toward water due to the formation of the complex. However, considering those results of the dependence of the permselectivity on ethanol concentration, Co^{2+} concentration, temperature, and alcohol species mentioned above, the unique permselectivity of cuprophan membrane in the presence of the specific salts cannot be explained only by the increase of the affinity of cellulose toward water, which is a conventional reason.

In addition, we also found that the effects of the anion species on the permselectivity are different from one another as shown in Tables I and II. These results indicate that the increase of the separation factor is observed only when the salt of the multivalent anion is used and is not observed at all in the case of the monovalent anions.

In order to interpret these unique behaviors, we propose a new concept that, together with affinity, the contraction of the "holes" produced by the thermal motion of cellulose also influences the permselectivity of cuprophan membrane, and this contraction is caused by the conformation change of cellulose molecule. The effect of the salts on the conformation change of cellulose molecule is supposed as follows. First of all, the multivalent metal ion forms a complex with the hydroxy group of cellulose molecule and the conformation of cellulose molecule is changed by ion repulsion and/or the steric hindrance of the complex. The new conformation is simultaneously immobilized by the ionic crosslinking with the multivalent anions. But, when the counteranion is monovalent, the new conformation cannot be immobilized

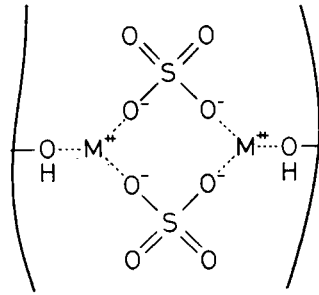


Fig. 7. Schematic cross-linking of cellulose molecule by metal sulfate.

because the ionic crosslinking is impossible. This assumption correlates with the effects of the anion species of magnesium and cobaltous salts on the permselectivity above mentioned. The schematic ionic cross-linking of cellulose is shown in Figure 7.

To assure the conformation change of cellulose molecule, the solid state structures of cellulose molecule were investigated with CP/MAS ¹³C-NMR for both the cases: CoSO₄ present and no salt present. The spectra are shown in Figure 8. Each peak of spectrum (a) is assigned according to the method of Horii et al.⁷ The chemical shifts of C₁, C₄, and CH₂OH carbons were determined to be 105.5, 87.8, and 63.7 ppm, respectively. C₂, C₃, and C₅ carbon lines

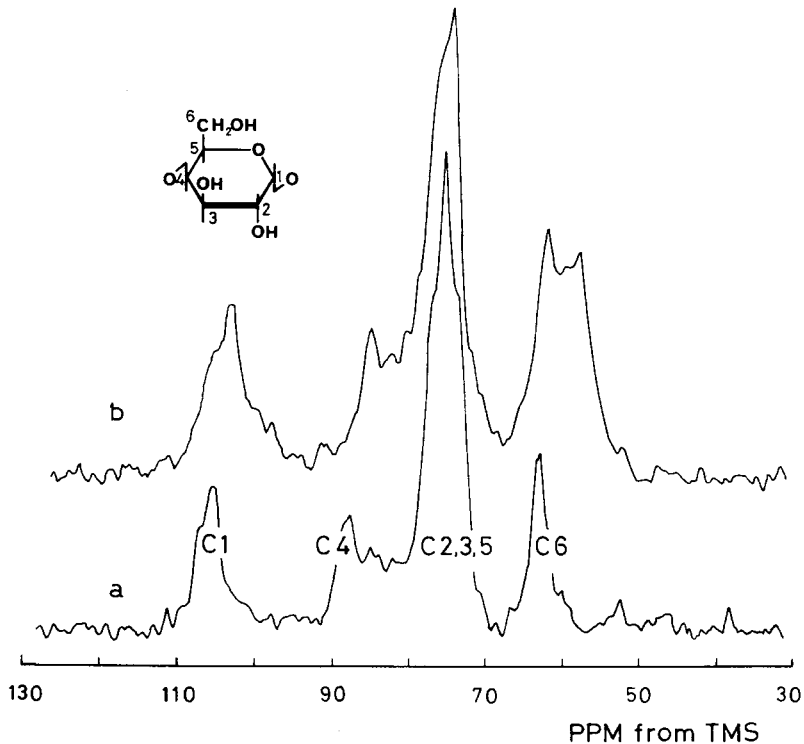


Fig. 8. CP/MAS ¹³C-NMR spectra of cuprophan membrane: (a) without salt present, $\alpha = 5.2$; (b) with 1.5×10^{-3} mol/kg CoSO₄ present, $\alpha = 96.5$; water/ethanol = 50/50 wt/wt, 60°C.

were assigned to 74.7 ppm. Horii et al. reported that there were simple relationships between ^{13}C chemical shifts of C_1 and C_4 and the dihedral angle about β -1,4-glycosidic linkage, and between the shift of C_6 and the torsion angle about the exocyclic C—C bond. Thus, it can be concluded that the chemical shifts of each carbon correlates with the conformation of cellulose molecule. Comparing the spectrum (a) in the absence of CoSO_4 with the spectrum (b) in the presence of the salt, the large highfield shifts about 2 ppm appear for the C_1 , C_4 , and C_6 lines of the glucose. Therefore, it is apparent that the conformation change of cellulose molecule does take place when the specific salts are added to the feed mixture.

The conformation change of cellulose molecule will be correlated with the permselectivity of the membrane. According to Eyring's hole theory of diffusion, there are "holes" produced by the thermal motion of polymer chains in the membrane and the permeating molecules can diffuse through the "holes." When the conformation of cellulose molecule is changed, the "holes" are assumed to become smaller. This contraction of the "holes" hardly has an effect on the diffusivity of water molecule but affects that of alcohol molecule larger than water molecule. So, only the diffusivity of alcohol decreases and the separation factor increases when the salt is added to the feed mixture.

The experimental results mentioned above also support our new concept of the separation mechanism in pervaporation.

We discuss the effects of the salts on the permselectivity of cuprophan membrane in detail from a viewpoint of the contraction of the "holes" due to the conformation change of cellulose molecules. Figure 3 shows that, in the presence of CoSO_4 , the separation factor increases and the permeation rate decreases with increasing the salt concentration and that, in the presence of CoCl_2 , the separation factor and the permeation rate are almost constant irrespective of the salt concentration. The permeation rates in Figure 3 are divided into the permeation rates of water and ethanol in order to discuss the separation mechanism. The results are shown in Figure 9. In the presence of CoSO_4 , the permeation rate of water, Q (water), is nearly constant irrespective of the salts concentration, but the permeation rate of ethanol, Q (ethanol), decreases sharply as the salt concentration increases. The results indicate that the increase of the separation factor is caused by the decrease of the permeation rate of ethanol.

On the other hand, the addition of CoCl_2 to the feed mixture in the range of $0-1 \times 10^{-2}$ mol/kg (0.125 wt %) does not affect the permeation rates of each component at all, so that it is indicated that the swelling degree of the membrane will not reduce in this range. This explanation is supported, moreover, by the fact that the salt concentration is 1-2 orders of magnitude lower than that investigated by Heisler et al.⁵ and Misra and Kroesser.⁶ Our results show that the solubility and diffusivity of water into the membrane are almost unchanged by the addition of the salts in the range of $0-1 \times 10^{-2}$ mol/kg, as the permeation rates of water are nearly constant in three cases: CoSO_4 present, CoCl_2 present, and no salt present. With respect to the solubility and diffusivity of ethanol into the membrane, they will be also unchanged by the similar reason in the case of CoCl_2 . But, in the presence of CoSO_4 , the permeation rate of ethanol decreases markedly with increasing the salt concentration. These permeation behaviors will not be explained well by

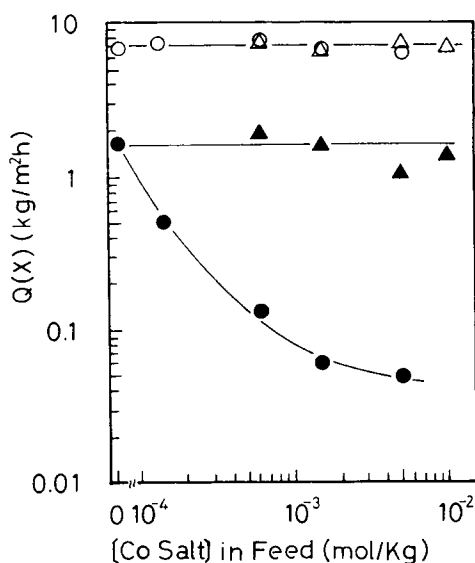


Fig. 9. Dependence of permeation rates of water and ethanol on salt concentration: (○) $Q(\text{water})$ and (●) $Q(\text{ethanol})$, with CoSO_4 present; (△) $Q(\text{water})$ and (▲) $Q(\text{ethanol})$, with CoCl_2 present; water/ethanol = 50/50 wt/wt, 60°C.

the conventional explanation, solubility and diffusivity, but can be explained as follows by the contraction of the "holes" due to the conformation change.

When CoSO_4 concentration increases, the amounts of the complex in the membrane will increase and the ratio of cellulose molecule having the new conformation will increase. This new conformation will contract the "holes" produced by the motion of cellulose molecule as mentioned above. The increase of the parts having the new conformation will cause the decrease of the number of the "holes" through which ethanol can permeate, but hardly affect the permeation of water because water molecule is small enough to permeate through the contracted "holes." So, only the permeation rate of ethanol decreases and the marked increases of the separation factor is obtained with increasing the concentration of CoSO_4 . In the case of CoCl_2 , the new conformation cannot be stabilized because the Cl^- ion cannot crosslink the complexes. Therefore, the contraction of the "holes" does not occur and the permeation rates of water and ethanol are almost constant irrespective of the salt concentration.

Secondly, the dependence of the permselectivity on the ethanol concentration shown in Figure 4 is discussed in detail, where the pervaporation measurements were carried out using a certain ethanol concentration mixture. The total permeation rate is divided into the permeation rates of water and ethanol and the results are shown in Figure 10. These results indicate that the permeation rates of water both in the presence of CoSO_4 and in the absence of it are nearly equal and they decrease with increasing ethanol concentration, but the behaviors of the permeation rates of ethanol quite differ from each other. Namely, in the case of no salt present, the permeation rate of ethanol decreases mildly with increasing ethanol concentration, and this decrease brings about the slight increase of the separation factor, not more than 15.

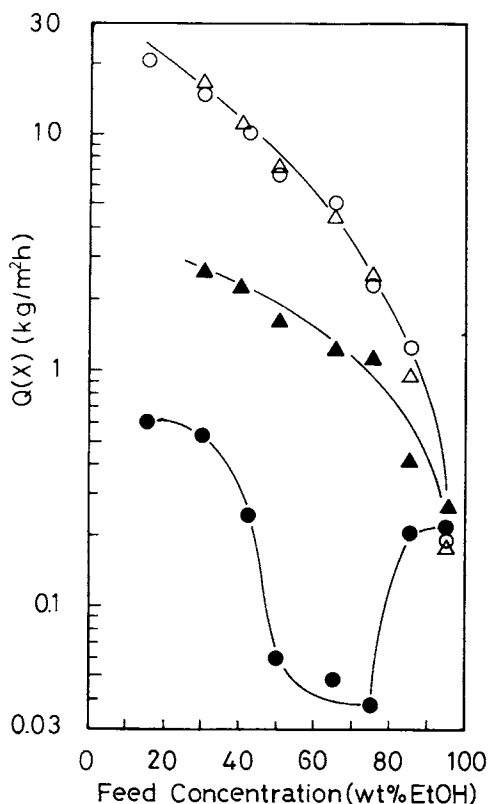


Fig. 10. Dependence of permeation rates of water and ethanol on ethanol concentration: (○) $Q(\text{water})$ and (●) $Q(\text{ethanol})$, with 1.5×10^{-3} mol/kg CoSO_4 present; (△) $Q(\text{water})$ and (▲) $Q(\text{ethanol})$, without salt present; 60°C .

The behaviors of the permeation rate of water and ethanol in the absence of salt will be explained by the decrease of the swelling degree of the membrane with increasing the ethanol concentration in the feed. This explanation is consistent with the result of the swelling degree represented by the elongation of the membrane shown in Figure 11.

In the case of CoSO_4 present, the permeation rate of ethanol decreases simply in the range of 15–45 wt % ethanol and is 1 order of magnitude lower than that in the absence of the salt. Beyond this limit, 45 wt %, it decreases markedly with increasing ethanol concentration to 75 wt % and, in this range, it is 2 orders magnitude lower. But, over 75 wt % ethanol, the permeation rate of ethanol increases sharply and nearly equals the one in the absence of the salt. With respect to the permeation rate of water in the presence of CoSO_4 , it is almost equal to the one in the absence of the salt throughout all the range. Therefore, the marked decrease of the permeation rate of ethanol in the range of 45–75 wt % ethanol in the feed brings about the increase of the separation factor in this range. The decrease of the permeation rate of water in the presence of CoSO_4 can be explained by the decrease of the swelling degree of the membrane in the same manner as in the absence of the salt. However, the permeation behavior of ethanol cannot be explained well only by the swelling

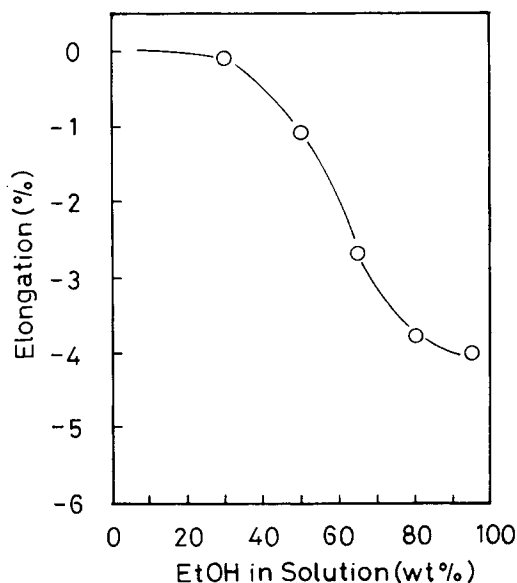


Fig. 11. Effect of ethanol concentration on elongation of cuprophane membrane; 60°C.

degree, but can be explained as follows by the contraction of the "holes" due to the conformation change of cellulose molecule. Below 45 wt % ethanol, the motion of cellulose molecule is so vigorous that the new conformation formed cannot be retained well enough because water acts as a plasticizer for cellulose molecules, and consequently only the moderate decrease of the permeation rate of ethanol is observed with increasing ethanol concentration. So, the high selectivity cannot be obtained. But the motion of cellulose molecule becomes less vigorous with increasing ethanol concentration from 45 wt %, so that the retention of the new conformation becomes easier, and the contraction of the "holes" is accelerated. Thus, the permeation rate of ethanol decreases sharply. This results in the marked increase of the selectivity in this range.

When ethanol concentration becomes higher, over 75 wt %, the motion of cellulose molecule becomes too moderate to change the conformation of cellulose molecule to the new one even when the complex with CoSO₄ forms, because the concentration of water which acts as a plasticizer decreases. In addition, the salt concentration decreases due to the decrease of the salt solubility to the mixture, and hence the probability of forming the complex decreases. For these reasons, the "holes" are not contracted well. So, the permeation rate of ethanol increases and the separation factor decreases above 75 wt % ethanol. This assumption that the mobility of cellulose molecule decreases with increasing ethanol concentration is supported by the dependence of the swelling degree of the membrane on ethanol concentration shown in Figure 11.

Summarizing the above-mentioned is as follows.

It is necessary for the contraction of the "holes" to change the conformation of cellulose molecules by the formation of a complex with CoSO₄. The mobility of cellulose molecule will decrease with decreasing the water content in the feed mixture because water acts as a plasticizer for cellulose molecules.

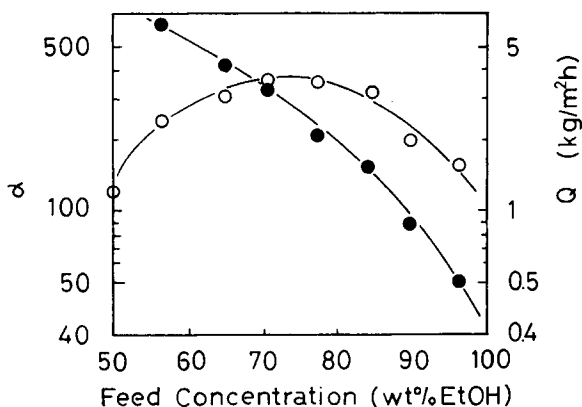


Fig. 12. Dependence of permselectivity on ethanol concentration, with 1.5×10^{-3} mol/kg CoSO_4 present at 50 wt % ethanol; 60°C .

The magnitude of the mobility of cellulose molecule will be correlated with the change and retention of its conformation. Therefore, it is difficult to retain the new conformation in lower ethanol concentration for the vigorous motion of cellulose molecule and difficult to change the conformation in higher ethanol concentration for the poor motion, so that there is an appropriate ethanol concentration range to contract the "holes," which causes the high selectivity.

Judging from the result mentioned above, the membrane cannot be expected to show the high selectivity in the high ethanol concentration range (over 80 wt %), for cellulose molecules are hardly converted into the new conformation favorable for separation because of the low mobility of them in this range. But even in this range, the remarkable high separation factor can be obtained if an appropriate experimental method is adopted. Namely, ethanol concentration in the feed is increased gradually and continuously after the separation factor becomes high enough at 50 wt % ethanol in the presence of CoSO_4 . The result is shown in Figure 12 and proves to be quite different from the result shown in Figure 4. The behavior of the permselectivity obtained from this method is explained as follows. The contraction of the "holes" in 50 wt % ethanol causes the increase of the separation factor to 120. Once the conformation is changed to the new one, it is retained irrespective of the increase of ethanol concentration because of the decrease of the mobility of cellulose molecule due to the decrease of water concentration. Thus, the new conformation can be maintained even in the range over 80 wt % ethanol. Therefore, the permeation of ethanol is settled down in this range and the separation factor keeps high value.

We also investigated the separation of various alcohol mixtures and found that the size of alcohol molecules (methanol, ethanol, *n*-propanol, and *i*-propanol) had a significant effect on the permselectivity for both cases: CoSO_4 present and no salt present. As shown in Figure 5, the permeation rates in both cases decrease exponentially when the number of carbon atoms of the aliphatic alcohol is increased from 1 to 3 (C_1 to C_3). Ticknor⁸ reported a similar decrease in the magnitude of diffusion coefficient with increasing the

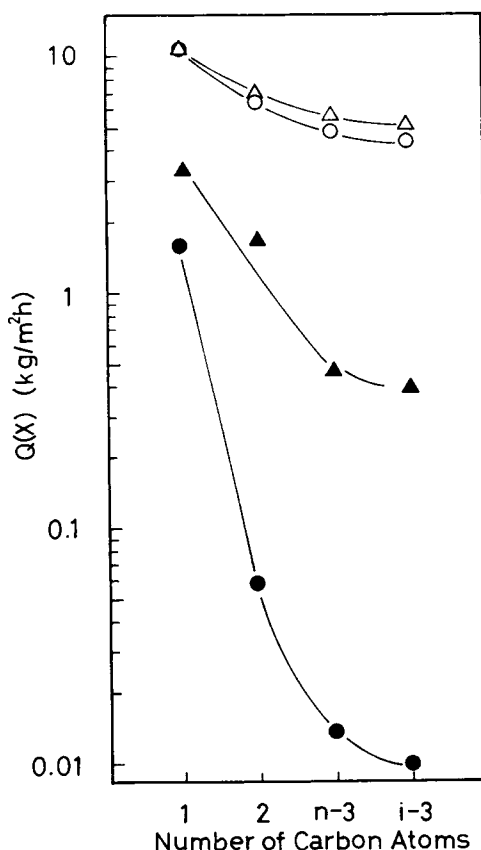


Fig. 13. Effect of chain length of alcohol molecule on permeation rates of water and alcohol: (○) $Q(\text{water})$ and (●) $Q(\text{alcohol})$, with 1.5×10^{-3} mol/kg CoSO_4 present; (△) $Q(\text{water})$ and (▲) $Q(\text{alcohol})$, without salt present; water/alcohol = 72/28 mol/mol; 60°C.

carbon number of penetrant alcohol. The separation factors in both cases are also found to depend on the molecular length with respect to linear alcohols, but the effects of the molecular length on the separation factors are quite different from one another. The separation factor increases in higher ratio in the presence of CoSO_4 (92.9-fold) than in the absence of the salt (6.8-fold) with increasing the carbon number, C_1 to $n\text{-}C_3$. To analyze these behaviors of the separation, the total permeation rates are divided into the permeation rates of water, $Q(\text{water})$, and alcohol, $Q(\text{alcohol})$. These results are shown in Figure 13. The permeation rates of water are nearly equal for each alcohol mixtures irrespective of the presence of CoSO_4 or not, and they decrease in the low ratio (about 1/2-fold) with increasing the carbon number of alcohol, C_1 to $n\text{-}C_3$. This result shows the addition of CoSO_4 hardly affects the permeation of water.

However, the permeation rates of alcohols are quite different in each case. In the absence of the salt, the permeation rates of alcohols decrease in the lower ratio (1/5.8-fold) than those in the presence of CoSO_4 (1/114-fold) with increasing the carbon number, C_1 to $n\text{-}C_3$. Comparing the permeation rates of alcohols in the presence of CoSO_4 with those in the absence of the salt, the

former ones are significantly smaller except that of methanol, that is, the ratios of the rate with CoSO_4 present to the rate without salt present are 1/27.3-fold for ethanol, 1/32.9-fold for *n*-propanol, 1/40-fold for *i*-propanol, and 1/2.0-fold for methanol. These results show that the remarkable increase of the separation factors with increasing the carbon number of alcohols observed in the presence of CoSO_4 is caused only by the decrease of the permeation rate of each alcohol.

The relationship between the permselectivity and the molecular size (diffusive cross section) of alcohols is investigated using *n*-propanol and *i*-propanol of which the cross sections are 23.0 and 29.6 Å², respectively. The diffusive cross section is defined as the ratio of the molecular volume V and molecular length L (V/L). As shown in Figures 5 and 13, *i*-propanol having larger cross section than that of *n*-propanol permeates slowly, so that the separation factor for *i*-propanol/water mixture is larger than that for *n*-propanol/water mixture. Considering these results, the relationship between the molecular shapes of alcohols (length and diffusive cross section) and the permselectivity will be also explained by the contraction of the "holes" due to the conformation change of cellulose molecule. Namely, in the presence of CoSO_4 , the contracted "holes" are small enough to hinder the diffusion of the larger alcohol molecule such as ethanol, *n*-propanol, and *i*-propanol, and thus, the permeation rate of the alcohol decreases markedly with increasing the bulkiness of the alcohol molecule. But, this contraction is not small enough to hinder the diffusion of methanol molecule which is much smaller than other alcohols and the permeation rate of it does not decrease so much, even when CoSO_4 is added to the feed mixture.

The temperature dependence of the permselectivity will also support the contraction of the "holes." As shown in Figure 6, the curve of the separation factor with CoSO_4 present has a maximum point at 70°C. This behavior is different from that of the conventional membrane in which the separation factor decreases with increasing the temperature, but the permeation rate behaves like the conventional membrane of which the permeation rate increases with increasing the temperature. According to Eyring's hole theory of diffusion, the thermal motion of polymer chain randomly produces the "holes" through which the permeation molecules can diffuse. As the temperature rises, the thermal agitation increases and the diffusive "holes" become larger. Therefore, more alcohol molecules can diffuse through the membrane, and the separation factor is decreased.

However, in the presence of CoSO_4 the permselectivity of cuprophane membrane does not follow Eyring's theory as mentioned above. In order to interpret the behavior in detail, the total permeation rate at each temperature is divided into the permeation rates of water and ethanol and apparent activation energies of each component permeating through the membrane are calculated from an Arrhenius plot in Figure 14. This figure shows clearly that the permeation rate of water in the presence of CoSO_4 is equal to that in the absence of the salt and that the apparent activation energy for water permeation is 7.53 kcal/mol in both cases. The activation energy for ethanol in the absence of the salt is also the same value, 7.53 kcal/mol. However, in the presence of CoSO_4 the Arrhenius plot for ethanol permeation has a minimum point at about 50°C. It is not clear yet why the minimum point appears, but

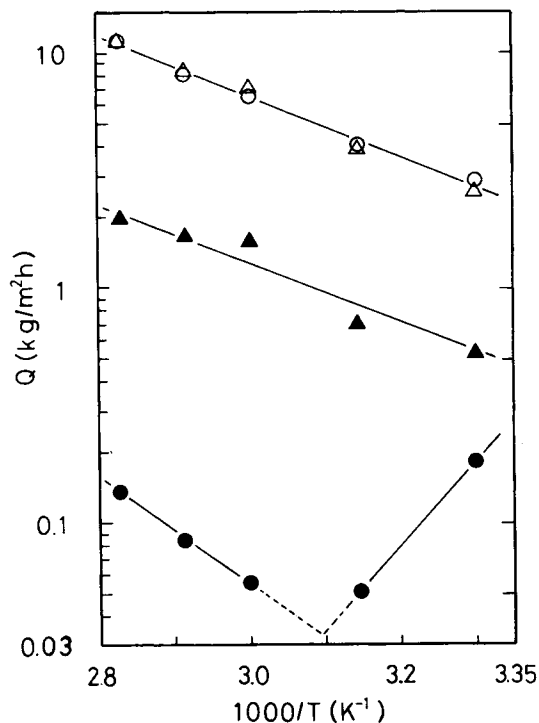


Fig. 14. Semilog plots of permeation rates of water and ethanol vs. absolute temperature: (○) $Q(\text{water})$ and (●) $Q(\text{ethanol})$, with 1.5×10^{-3} mol/kg CoSO_4 present; (△) $Q(\text{water})$ and (▲) $Q(\text{ethanol})$, without salt present; water/ethanol = 50/50 wt/wt.

in the range of 50–80°C, the apparent activation energy for ethanol permeation is calculated to be 10.63 kcal/mol. This result shows that only the activation energy for ethanol permeation is increased by the presence of CoSO_4 in the feed mixture, though the activation energy for water permeation is equal for both cases. Namely, this will indicate that only ethanol molecule is prevented from permeating through the diffusive “holes” in the case of CoSO_4 present. In other words, the “holes” becomes small enough to prevent the ethanol permeation but the contraction of the “holes” is not so small as to influence the permeation of water. Therefore, the permeation rate and activation energy for water permeation are equal to those in the absence of the salt.

CONCLUSIONS

The unique permselectivity of cuprophan membrane mentioned above is observed only when the specific salts are added to the feed mixture, and, in order to keep the high selectivity, the presence of the salt in the mixture is always necessary.

All the results indicate that the unique behaviors of the permselectivity will be related with the contraction of the “holes” due to the conformation change of cellulose molecule. We are now working farther using CP/MAS ¹³C-NMR in order to clarify the relationship between the unique separation behaviors and the conformation change of cellulose molecule.

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References

1. P. Aptel, J. Cuny, J. Jozefonvicz, G. Morel, and J. Neel, *J. Appl. Polym. Sci.*, **16**, 1061 (1972); **18**, 351, 365 (1974).
2. V. Shantora and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **26**, 3223 (1981).
3. R. Y. M. Huang and N. R. Jarvis, *J. Appl. Polym. Sci.*, **14**, 2341 (1970).
4. E. Nagy, O. Borlai, and A. Ujhidy, *J. Memb. Sci.*, **7**, 109 (1980).
5. E. G. Heisler, A. S. Hunter, J. Siciliano, and R. H. Tradway, *Science*, **124**, 77 (1956).
6. A. Misra and W. Kroesser, *J. Polym. Sci.*, **41**, 145 (1973).
7. F. Horii, A. Hirai, and R. Kitamaru, *Polym. Bull.*, **10**, 357 (1983); *Polymers for Fibers and Elastomers*, ACS Symposium Series, C. Arthur, Jr., Ed., Am. Chem. Soc., Washington, DC, (1984), p. 27.
8. L. B. Ticknor, *J. Phys. Chem.*, **62**, 1483 (1958).

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