# Pervaporation Separation of Water/Ethanol Mixtures through Polysaccharide Membranes. IV. The Relationships between the Permselectivity of Alginic Acid Membrane and Its Solid State Structure

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## Synopsis

Membranes composed of alginic acid, which is one of the anionic polysaccharides, were investigated as pervaporation membranes for the separation of water/alcohol mixtures. The selectivity of the alginic acid membrane increased markedly by more than 10,000 when the carboxyl group of alginic acid was neutralized by bases. The counter cation ($Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$) influenced the permeation rate for the alginate membranes, which varied from 0.1 kg/m$^2$ h for the Li version to 1.0 kg/m$^2$ h for the Cs version, but the counterion had hardly any effect on the selectivity. The behavior could not be explained simply by the affinity of the alginate membranes toward water, but could be explained well by the conformation change and mobility of alginate molecules investigated by CP/MAS $^{13}$C-NMR, water mobility within the alginate membrane, and crystallinity of the membrane.

## INTRODUCTION

We reported the separation of water/alcohol mixtures through polysaccharide membranes.[1-3] Among the polysaccharide membranes, the regenerated cellulose membrane showed high selectivity when trace amounts of some specific metal salts were added to the feed mixture. Chitosan membrane, one of the cationic polysaccharide membranes, also showed high selectivity when its amino group was neutralized by polybasic acids. It was clarified that the high selectivity of these membranes was brought about by the marked decrease of the permeation rate of alcohol, and the behavior could not be explained well only by the increase of the membrane's affinity toward water due to the formation of the complex between the metal salt and cellulose or due to the neutralization of chitosan. We concluded the reason of the high selectivity of these polysaccharide membranes as follows. The formation of the complex in cellulose or the neutralization of chitosan changed the conformation of the polysaccharide molecules, which caused the change of the packing state of polysaccharide molecules. Thus, the "holes" produced by the thermal motion of the polymer molecule were contracted and the permeation of alcohol molecule larger than water mol-

ecule were depressed. Here, the "hole" means an effective hole through which small molecules (water) can permeate. The "hole" size is always fluctuated by a particular local motion of polymer molecules such as conformational transition which will contribute to the permeation strongly. Higher fluctuation of the size induced by more rapid motion will cause higher permeation, sometimes with a decrease of selectivity. The driving force of the conformation change was the ionic repulsion and/or steric hindrance by the formation of the complex or the neutralization of the polysaccharide molecules.

Considering these results mentioned above, a similar separation behavior is expected with an anionic polysaccharide membrane because it can be neutralized and its skeleton is similar to those of cellulose or chitosan. Herein, the membrane obtained from alginic acid which is a natural polysaccharide and has carboxyl group as shown in Figure 1 was investigated. We would like to report here the permselectivity of alginic acid and its neutralized membranes in the separation of water/alcohol mixtures, and the correlation of the permselectivity with the conformation change and mobility of alginic acid molecules.

## EXPERIMENTAL

### Alginic Acid and Alginate Membranes

Alginic acid was prepared from sodium alginate (Nakarai Chemical Co.) by washing with $0.6N$ hydrochloric acid. The weight-average molecular weight of this alginic acid measured by GPC-LALLS was $1.92 \times 10^5$ (GPC: Waters 201D, LALLS: Chromatix CMX-100). And, then, alginates were obtained by the neutralization of alginic acid thus obtained with alkali hydroxides (LiOH, NaOH, KOH, RbOH, and CsOH). Each alginate membrane was prepared by casting 1 wt % aqueous solution of the alginate onto a glass plate and evaporating water at room temperature. Alginic acid membrane was prepared from sodium
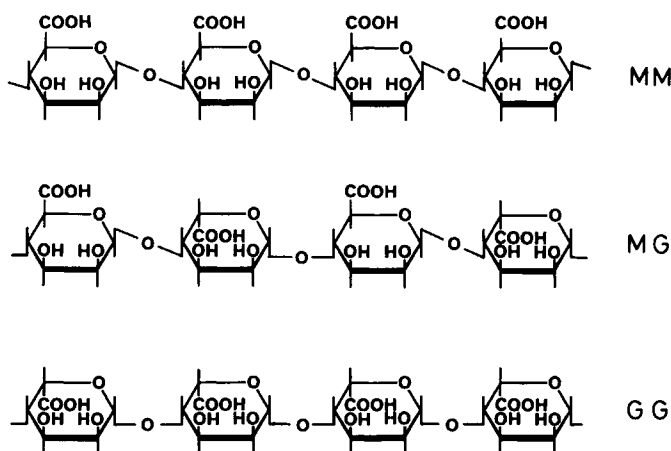


Fig. 1. Chemical structure of alginic acid. Alginic acid is considered as a block copolymer of D-mannuronic and L-guluronic acids, and consists of three types of block: homopolymeric blocks of mannuronic acid (MM) and of guluronic acid (GG), and blocks with an alternating sequence (MG).

alginate membrane by immersing in $0.6N$ hydrochloric acid solution (water/ethanol = 50/50 wt/wt). The thickness of these membranes was 10–12 $\mu$m.

## Neutralization Degree

The neutralization degree of sodium alginate was determined by atomic absorption analysis.

## Pervaporation Measurement

Pervaporation measurements were conducted in pervaporation mode with a membrane surface of 7.0 cm$^2$ and a downstream pressure of 0.3 mm Hg (40 Pa). Water/alcohol 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 using Shimazu GC7A gas chromatograph equipped with 1 m long column packed with Porapack Q and thermal conducivity detectors (TCD).

## X-Ray Measurement

Wide angle X-ray diffractograms were obtained with Rigaku Denki model RAD-rA X-ray diffractometer equipped with a sintillation counter. The X-ray source was nickel-filtered Cu K$\alpha$ radiation (40 kV, 20 mA).

## Swelling Degree

The membranes were immersed in water/alcohol 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.
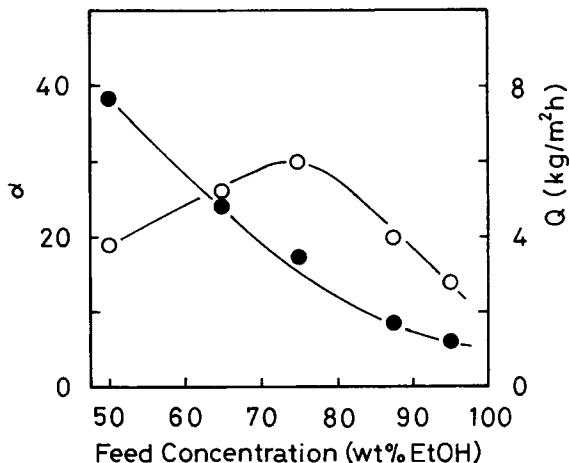


Fig. 2.   Effect of ethanol concentration on permselectivity of alginic acid membrane: (O) separation factor $\alpha$; (●) permeation rate $Q$; 60°C.
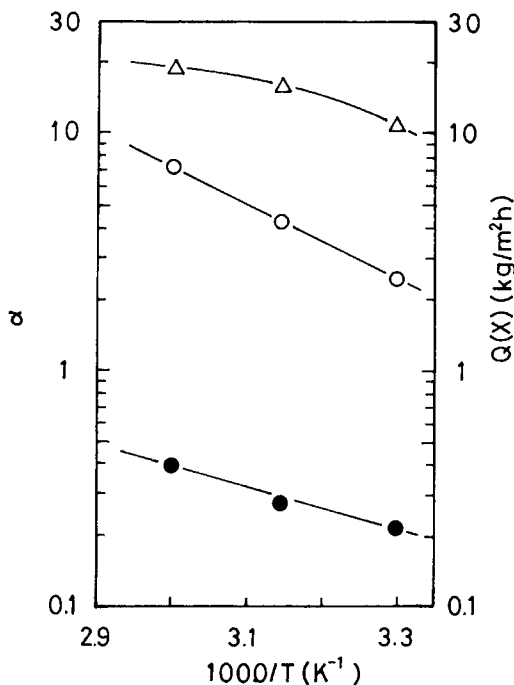
Fig. 3. Effect of temperature on permselectivity of alginic acid membrane: ($\triangle$) separation factor $\alpha$; ($\bigcirc$) permeation rate of water $Q$ (water); ($\bullet$) permeation rate of ethanol $Q$ (ethanol); water/ethanol = 50/50 wt/wt.

## Equilibrium Moisture Regain

The equilibrium moisture regains of alginic acid and alginates were achieved in a vessel where the relative humidity was kept 43% at 25°C by the saturated $K_2CO_3$ solution. The regain was expressed as a relative weight increase.

## Analysis of Solid State Structure

High resolution solid state $^{13}$C-NMR spectra were recorded at 67.5 MHz with a JEOL GX-270 spectrometer with a CP/MAS accessory. The sample ($\sim$ 300 mg) was put in a bullet-type rotor and spun at 3500–3700 rps. Contact time was 1 ms and repetition time was 10 s. Spectral width and data points were 20 and 8 kHz, respectively. $^1$H field strength was 12 mT for both CP and decoupling process. The number accumulated was 1000. $^{13}$C-chemical shifts relative to TMS were determined from the CH lines (29.5 ppm) of solid adamantane. $^{13}$C spin–lattice relaxation time $T_1$ was measured by the Tochia method and $T_{1\rho}$ by standard procedure.

## RESULTS AND DISCUSSION

The effect of ethanol concentration of the feed mixture on the permselectivity of alginic acid membrane is shown in Figure 2. It indicates that the permeation rate decreases from 7.65 to 1.27 kg/m$^2$ h with increasing ethanol concentration
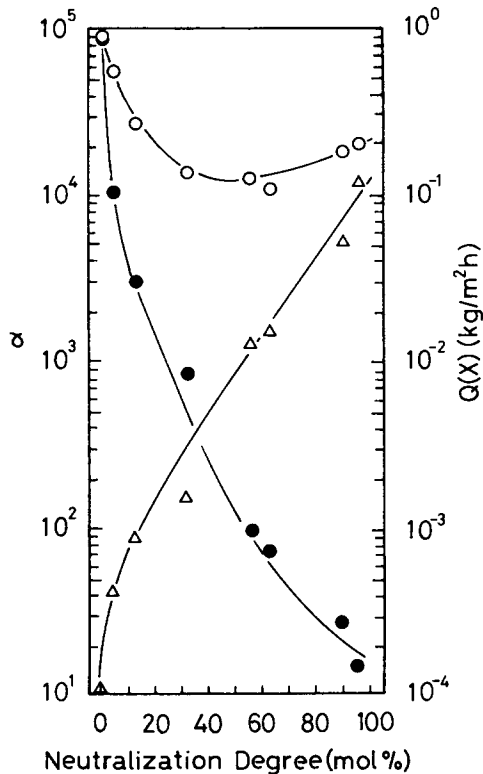
Fig. 4.  Effect of neutralization by sodium hydroxide on permselectivity of alginic acid membrane: ($\triangle$) separation factor $\alpha$; ($\bigcirc$) permeation rate of water $Q$(water); ($\bullet$) permeation rate of ethanol $Q$(ethanol); water/ethanol = 10/90 wt/wt, 60°C.

from 50 to 95 wt %. The curve of the separation factor has a maximum point at about 75 wt % ethanol and its value is 30.0. These behaviors are similar to those of chitosan membrane reported in the previous paper,[2] and the decrease of the permeation rate will be explained by the decrease of the swelling degree of the membrane.

The effect of temperature on the permselectivity of alginic acid membrane was investigated using 50 wt % ethanol mixture. The results are shown in Figure 3 where the total permeation rate at each temperature is divided into the permeation rates of water and ethanol. The increase of the separation factor with increasing temperature is caused by the larger increase of the permeation rate of water than that of ethanol. From the Arrhenius plot, the apparent activation energies of each component permeating through the membrane are calculated and its value for water permeation is 7.21 kcal/mol and for ethanol 3.87 kcal/mol. The activation energy 7.21 kcal/mol for water permeation is very close to those in cuprophan and chitosan membranes, 7.27 and 7.53 kcal/mol, respectively.[1,2] These results indicate that the permeation mechanism of water is all the same for these polysaccharide membranes, although polar groups of the polysaccharides are quite different from one another. The activation energy 3.87 kcal/mol for ethanol permeation is smaller than those in cuprophan and chitosan membranes, 7.53 and 7.02 kcal/mol, respectively.
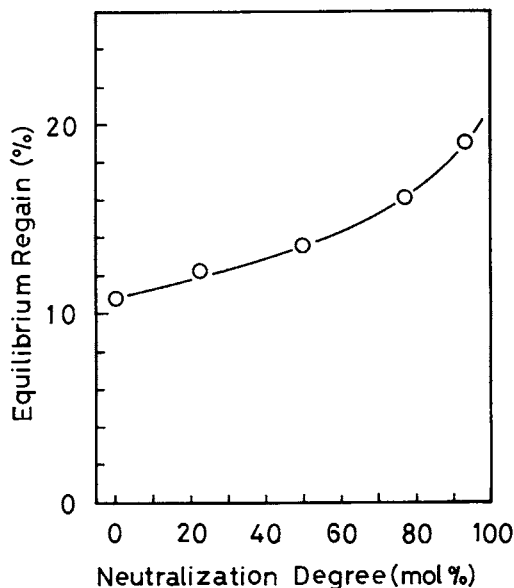
Fig. 5. Effect of neutralization on equilibrium moisture regain of alginic acid: 43% relative humidity, 25°C.

Herein, we report the permselectivity of alginic acid membrane neutralized by sodium hydroxide. As reported in the previous paper,[3] the increase of the neutralization of chitosan membrane by acids caused the marked increase of the selectivity toward the water/ethanol mixture, which was correlated with the solid state structure of chitosan molecule, analyzed by CP/MAS $^{13}$C-NMR. Alginic acid membrane neutralized by bases was expected to show high membrane performance in the same manner as the chitosan membrane neutralized by acids. The correlation of the permselectivity toward the water/alcohol mixture with the neutralization degree was investigated. The experiment was carried out using 90 wt % ethanol mixture because neutralized alginic acid membrane was not strong enough to operate in the lower ethanol concentration mixture (50 wt %). The results are shown in Figure 4, where the total permeation rate is divided into the permeation rates of water and ethanol. The separation factor

TABLE I
Swelling Degree of Ionic Polysaccharide Membrane

| Membrane | Swelling degree (%) |
| --- | --- |
| Alginic acid | 29.4[a] |
| Sodium alginate | 22.5[a] |
| Chitosan | 58.9[b] |
| Chitosan sulfate[c] | 33.7[b] |

[a] Water/ethanol = 10/90 wt/wt, 25°C.
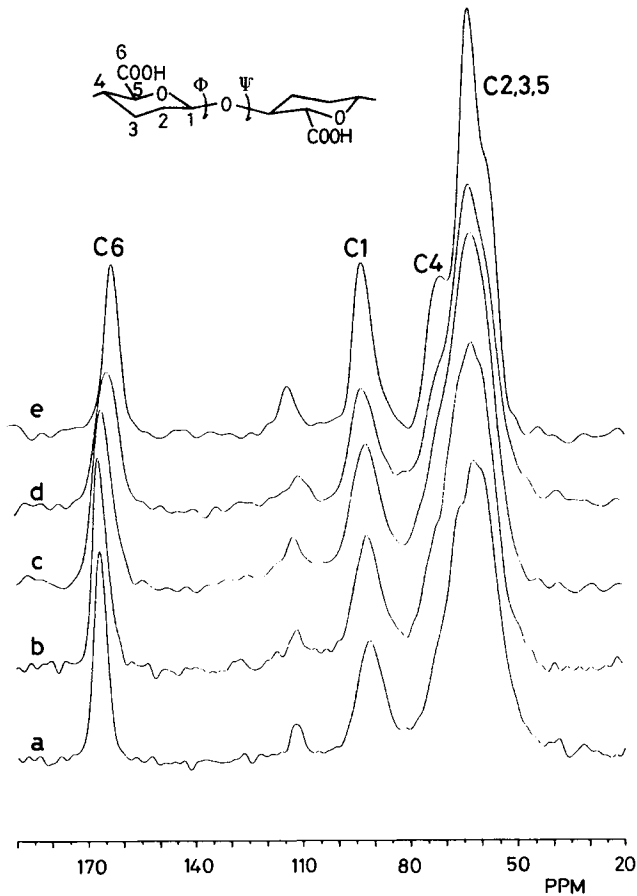[b] Water/ethanol = 50/50 wt/wt.
[c] Neutralization degree = 72 mol %.

Fig. 6.   CP/MAS ^{13}C-NMR spectra of alginic acid neutralized by sodium hydroxide. Neutralization degree: (a) 92.8 mol %; (b) 77.0 mol %; (c) 50.0 mol %; (d) 22.5 mol %; (e) 0 mol %.

increases to over 10,000 with increasing the neutralization degree to 95 mol %. The results indicate that such high selectivity is due to the marked decrease of the permeation rate of ethanol with increasing the neutralization degree. One of the reasons of the increase in the selectivity will be due to the increase of the affinity of the membrane caused by the neutralization. When pervaporation separation mechanism is considered, the active layer of the membrane will not be wet or will not contact with the feed mixture, but will contain some water molecules because the downstream side of the membrane is kept dry by reduced pressure. Hence, the swelling degree of the membrane may not correspond to the permeation behavior. To predict the affinity of the polymer toward water and the mobility of it at the active layer, the polymers having adequate equilibrium moisture regains were investigated. The equilibrium moisture regain of the neutralized alginic acid increases from 10.8 to 21.8 wt % with increasing the neutralization degree from 0 to 95 mol % as shown in Figure 5. However, the marked decrease of the permeation rate of ethanol cannot be explained only by the increase of the affinity. The behavior of neutralized alginic acid membrane in the separation of the water/alcohol mixtures,

TABLE II
Effect of Alcohol Molecular Size on Permselectivity of Sodium Alginate Membrane

| Alcohol | Separation factor $\alpha$[a] | Permeation rate $(kg/m^2 \ h)$[a] | Swelling degree $(\%)$[b] |
|---|---|---|---|
| Methanol | 144 | 0.078 | 15.8 |
| Ethanol | 20,000 | 0.20 | 22.5 |
| n-Propanol | $\infty$[c] | 0.41 | 27.0 |
| i-Propanol | $\infty$[c] | 0.51 | 24.8 |

[a] Alcohol concentration = 77.9 mol % (methanol = 86 wt %, ethanol = 90 wt %, and propanol = 93 wt %), 60°C, 40 Pa.
[b] 77.9 mol % alcohol, 25°C.
[c] Alcohols were not detected by TCD.

which is similar to that of neutralized chitosan membrane, may be also explained by the contraction of the "holes," which is caused by the conformation change of polysaccharide molecules on neutralization. The swelling degree of alginic acid and sodium alginate membranes shown in Table I indicates that the former has a larger swelling degree than the latter and this sequence is reversed for the equilibrium moisture regain. This disagreement is also observed for chitosan and chitosan sulfate membrane as shown in Table I. The results of the swelling degree imply that the free volume of the acid form is larger than that of the
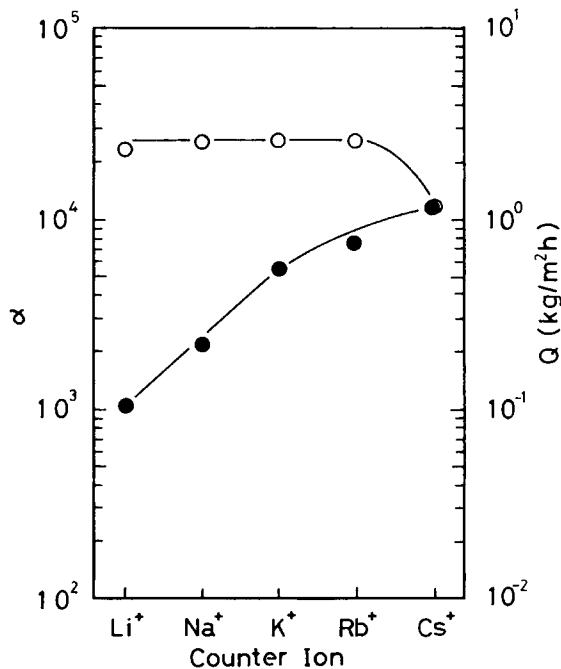


Fig. 7. Effect of counterion on permselectivity of alginate membranes: (O) separation factor $\alpha$; ($\bullet$) permeation rate $Q$; water/ethanol = 10/90 wt/wt, 60°C.

salt form, which coincides with the permeation rates for them (Fig. 4). Consequently, our explanation that the contraction of the "holes" will not conflict with free volume theory.

The conformation change of alginic acid molecule due to the neutralization was investigated using CP/MAS $^{13}$C-NMR. The NMR spectra of sodium alginate having various neutralization degree are shown in Figure 6. The $^{13}$C-NMR signals are assigned on the basis of the previous paper.[3] The broad peaks at 60–80 ppm are assigned to C2, C3, and C5 carbon atoms, but cannot be analyzed in detail owing to unresolved peak. The peak resonanced at about 120 ppm is a spinning side band of carbonyl carbon. With increasing the neutralization degree of alginic acid [Fig. 6(e) → 6(a)], C1 and C4 peak are shifted upfield and C4 peak gradually overlaps with C2, C3, and C5 peaks. For sodium alginate, the peaks overlap each other as shown in Figure 6(a). On the other hand, C2, C3, and C5 peaks are not almost shifted. The carbonyl, C6 carbon, peak is shifted downfield. The upfield shift of C1 and C4 carbons in the 1,4-glycosidic linkage of the neutralized alginic acid will be caused by the different conformation of this linkage. Namely, the values of the tortion angles $\Psi$ and $\Phi$ which are defined as shown in Figure 6 will affect the $^{13}$C chemical shift of C1 and C4 carbon, and a simple linear relationship exists mutually, as pointed out for cellulose by Horii et al.[4]

From the viewpoint of the "holes" conception, the effect of the size of alcohol molecules (methanol, ethanol, $n$-propanol, and $i$-propanol) on the permeation rate and separation factor of sodium alginate membrane were investigated. The results are shown in Table II, where the pervaporation experiment was carried out using 77.9 mol % alcohol mixture (in the case of ethanol, alcohol concentration corresponds to 90 wt %). In addition, the swelling degrees of the membranes in water/alcohol mixtures are also shown in Table II. The separation
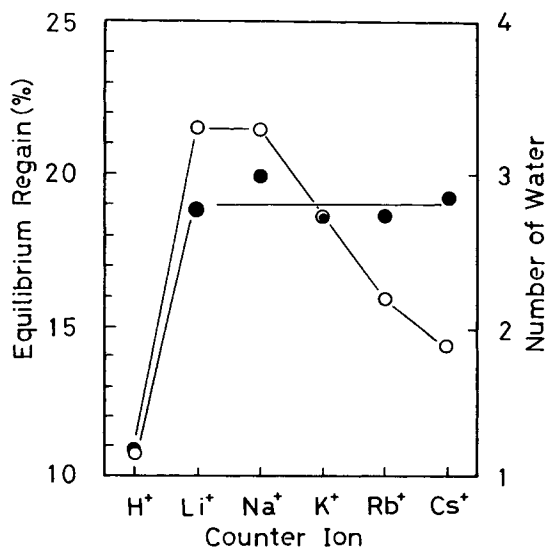


Fig. 8.    Effect of counterion on equilibrium moisture regain and number of water in alginate: (○) regain at 43% relative humidity, 25°C; (●) number of water molecules per counterion or ulonic acid unit calculated from the regain.
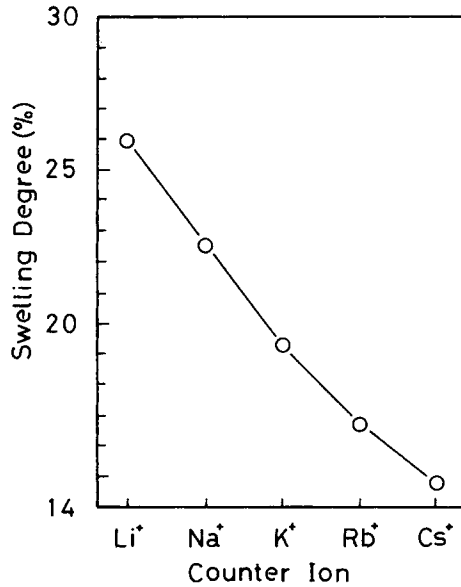
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Fig. 9. Effect of counterion on swelling degree of alginate: water/ethanol = 10/90 wt/wt, 25°C.

factor increases from 144 for methanol mixture to $\infty$ for $n$- and $i$-propanol mixtures with increasing the volume of alcohol molecule from 67.3 Å$^3$ for methanol to 127.3 Å$^3$ for $i$-propanol. These results indicate that larger alcohol molecules, ethanol and propanol, can hardly permeate through the membrane, that is, the "hole" is too small for the alcohol molecules to permeate through, in spite of the increase of the swelling degree in each alcohol mixture. The expansion of the "hole" by the increase of the swelling degree will not be large enough to decrease the selectivity, but it will be enough to increase the permeation rate of water. Table II shows that the permeation rate increases from 0.078 kg/m$^2$ h for methanol mixture to 0.51 kg/m$^2$ h for $i$-propanol mixture with increasing the volume of alcohol molecule. The increase of the permeation rate almost corresponds to the swelling degree of the membrane. The behavior of the swelling degree of the alginate membrane is similar to that of chitosan sulfate membrane reported in the previous paper.[3] The increase of the swelling degree of the alginate membrane in larger alcohol systems may be due to the interaction between water molecule in the mixture and carboxyl group of alginic acid, which increases relatively with increasing the hydrophobicity of alcohols, namely, increasing the number of carbon atoms from 1 to 3.

The effect of countercation species of alginate on the permselectivity was investigated using Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ version membranes. The results are shown in Figure 7. The high separation factor over 10,000 is observed for each membrane irrespective of the counter ion species. But the permeation rate increases markedly in the following order: Li$^+$ (0.1 kg/m$^2$ h) < Na$^+$ < K$^+$ < Rb$^+$ < Cs$^+$ (1.0 kg/m$^2$ h).

Concerning the effects of the counterion, the difference of affinity of each alginate toward water was first examined. The equilibrium moisture regains at 43% relative humidity are shown in Figure 8. The regain decreases in the fol-
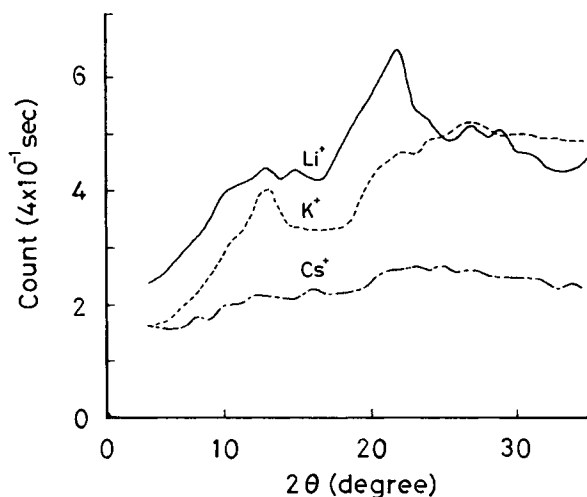
Fig. 10.   Intensity curve of X-ray diffraction of alginates: (a) Li version; (b) K version; (c) Cs version.

lowing order: $Li^+ \geq Na^+ > K^+ > Rb^+ > Cs^+$. The number of water molecules per counterion or ulonic acid unit (glucosidic ring) in the polymer calculated with the equilibrium regain is almost equal in each version, about 2.8 (Fig. 8). This indicates that it is difficult to judge whether the affinity of the salt toward water changes when the counterion varies from $Li^+$ to $Cs^+$. Moreover, the decrease of the swelling degree of the alginate membrane with varying the counterion from $Li^+$ to $Cs^+$ will not indicate the increase of the free volume in the Cs version, as shown in Figure 9. These results indicate that the higher permeation for the Cs version membrane will not be explained by the affinity or the free volume.

Recently, Cabasso et al.[5] and Reineke et al.[6] reported the separation of water/alcohol mixtures through polyelectrolyte membranes. They obtained the different effects of counter cation ($H^+$, $Li^+$, $Na^+$, $K^+$, and $Cs^+$) on the permselectivity of the membranes. Cabasso et al. investigated the Nafion membrane and reported that the permeation rate decreased in the following order: $H^+ > Li^+ > Na^+ > K^+ > Cs^+$ but the separation factor increased: $H^+ < Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Cabasso explained these results as follows. The higher permeation rate for the Li version membrane was attributed to the fact that the free volume fraction of water in the membrane was much higher than in the K or Cs versions. The "free water" in the Cs version was intrinsically more mobile than water molecules in the Li version and, therefore, contributed significantly to the selectivity of the $Cs^+$ version membrane. Reineke et al.[6] investigated the carboxymethylcellulose/poly(acrylic acid) blended membranes and showed that the permeation rate increased in the order $Na^+ < K^+ < Cs^+$; but the separation factors were almost the same irrespective of the counterion species. Reineke explained these results as follows. The permeation rate of various alkali metal membranes correlated well with the energies of hydration of the ions. Although reasons for the higher permeation rates in the K or Cs version membranes must be speculative, it appeared possible that higher water mobility within the Cs version membrane would result from the more facile
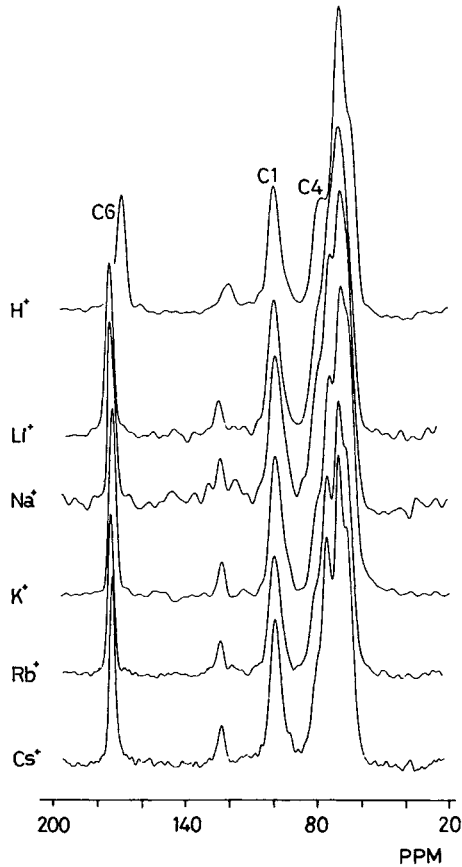
Fig. 11.   CP/MAS $^{13}$C-NMR spectra of alginates.

displacement of water from the Cs$^+$ ion hydration shell. The high selectivity in the membranes was due to the selective solubility of water and a salting-out of the organic component.

Considering these two reports and our results, the higher permeation rate for Cs alginate membrane may be brought about by the facility of water displacement from the Cs$^+$ ion hydration shell.

The relationship between permeation rates for alginate membranes and the crystallinity degree of them was investigated with X-ray diffraction because the low molecules can permeate only through the amorphous region in polymers as described in a previous paper.[2] The intensity curve of X-ray diffraction of alginates (Li, K, and Cs versions) is shown in Figure 10. It is proved that the crystallinity of the alginates is very low at most 10% for Li version, which get difficult to quantify their crystallinity, but it decreases in the following order: Li$^+$ > K$^+$ > Cs$^+$. The Cs version does not seem to have crystalline region. From this result, it will be predicted that the degree of the crystallinity decreases in the following order: Li$^+$ > Na$^+$ > K$^+$ > Rb$^+$ > Cs$^+$. This order coincides with the effect of the countercation with respect to the permeation rate. Consequently, the permeation behavior may be also explained qualitatively by the difference of the crystallinity. However, the fact that in chitosan membranes
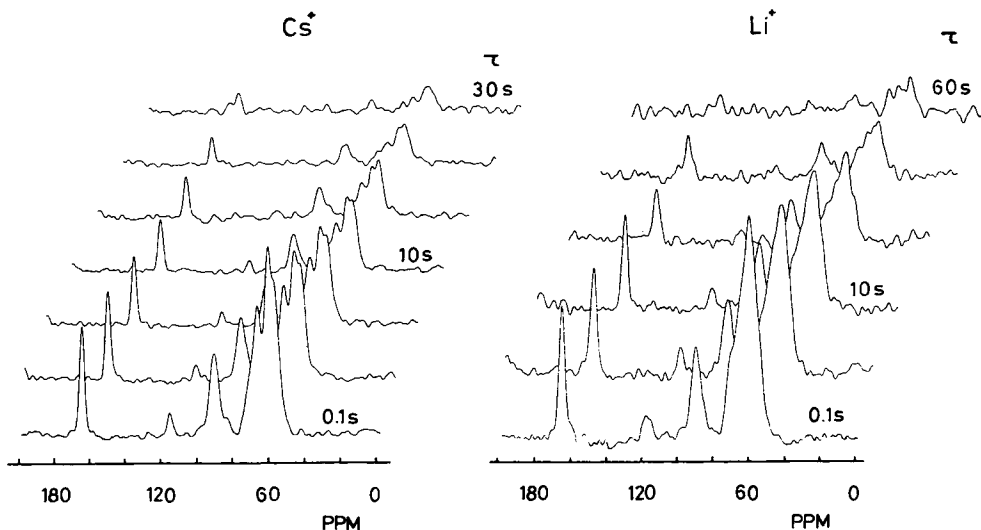
Fig. 12. CP/MAS $^{13}$C-NMR spectra of spin–lattice relaxation time $T_1$ of alginates: (a) Li version; (b) Cs version.

the crystallinity varied from 18 to 26% did not have a tremendous effect on the permeation rate, smaller than two times,[2] as in the alginate membranes, more than 10 times, will suggest that the large difference of the permeation rate between the Li version membrane and the Cs one (0.1 and 1.0 kg/m$^2$ h, respectively) cannot be explained only by the crystallinity of alginates.

It has made clear in the previous papers[3,7] that the permselectivity of the neutralized chitosan membrane was much affected by the conformation and mobility of chitosan molecules. First, the conformation of each alginate was investigated using CP/MAS $^{13}$C-NMR. The results are shown in Figure 11. The resonances for C6, C1, C4, and C2, 3, 5 carbons of each alginate are all the same, which suggests that the conformation of each alginate will be almost the same. It is apparent that the contraction of the "holes" occurs in Li, K, Rb, and Cs alginates as deduced from the result of Na alginate, and so the high separation factor over 10,000 of all the membranes can be explained by the

TABLE III
Spin–Lattice Relaxation Time $T_1$ of Alginate[a]

| Alginate (counterion) | Relaxation time $T_1$ (s) | | | |
|---|---|---|---|---|
| | C6 | C1 | C4 | C2, 3, 5 |
| Li$^+$ | 32.8 | 44.4 | — | 28.4 |
| Na$^+$ | 22.2 | 22.8 | — | 21.5 |
| K$^+$ | 17.3 | 19.3 | 16.2 | 16.8 |
| Rb$^+$ | 15.6 | 15.9 | 12.5 | 14.2 |
| Cs$^+$ | 14.7 | 14.9 | 10.8 | 12.7 |

[a] All alginates had equilibrium moisture regains at 43% RH (25°C).

TABLE IV
Spin–Lattice Relaxation Time $T_{1\rho}$ of Alginate[a]

| Alginate (counterion) | Relaxation time $T_{1\rho}$ (ms) | | | |
|---|---|---|---|---|
| | C6 | C1 | C4 | C2, 3, 5 |
| Li^{+} | 39.3 | 17.7 | — | 11.5 |
| Na^{+} | — | 17.2 | — | 11.8 |
| K^{+} | 92.8 | 13.7 | 14.2 | 13.0 |
| Rb^{+} | — | 12.6 | 13.0 | 12.7 |
| Cs^{+} | 12.9 | 12.9 | 13.7 | 11.8 |

[a] All alginates had equilibrium moisture regains at 43% RH (25°C).

contraction of the "holes." But the increase of the permeation rate in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ cannot be explained.

All investigations to explain the unique permselectivity of alginate membranes above described gave some useful information with respect to static states of the polymer such as equilibrium regain, crystallinity, and conformation. Now that the separation is performed at a dynamic state of the alginate, it will be very difficult to explain the permselectivity only from the static state. The dynamic states of the alginate were investigated by $^{13}C$ spin–lattice relaxation time $T_1$ and the spin–lattice relaxation time in the rotational frame $T_{1\rho}$ of alginate molecules to discuss the mobility of the polymer molecules. $T_1$ depends on the motion with the correlation time in order of $10^8$ Hz and will be related with the local motion of the polymer molecules such as confomational transition, whereas $T_{1\rho}$ depends on the order of $10^5$ Hz and will be related with the segmental motion. Typical CP/MAS $^{13}C$-NMR spectra of spin–lattice relaxation time measured are shown in Figure 12. The observed $^{13}C$ $T_1$ and $T_{1\rho}$ values for each alginate are listed in Tables III and IV. The $T_1$ values decrease in the following order: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. In general, the motion of polymer molecules in the solid state increases with decreasing the values of $T_1$. Therefore, the mobility of each alginate molecule decreases in the following order: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. Figure 13 shows a simple linear relationship between the permeation rates for alginate membranes and the reciprocal of $T_1$ values of C6 carbon. Namely, Figure 13 indicates that the spin–lattice relaxation time $T_1$ correlates strongly with the permeation rates for the alginate membranes. The increase of the mobility of the alginate molecules with varying from $Li^+$ to $Cs^+$ will cause larger fluctuation of the "hole" size, which will bring about more efficient permeation of a relatively smaller molecule such as water through the "holes," and the permeation rate increases. The fluctuation will be small enough to inhibit the permeation of larger alcohol molecules, and so the high selectivity can be almost maintained irrespective of the counterion species. But, larger fluctuation in the Cs version than in other versions causes a slight decrease of the separation factor to 10,000 as shown in Figure 7. On the other hand, Table IV indicates that $T_{1\rho}$ is not correlated with the permeation rates.
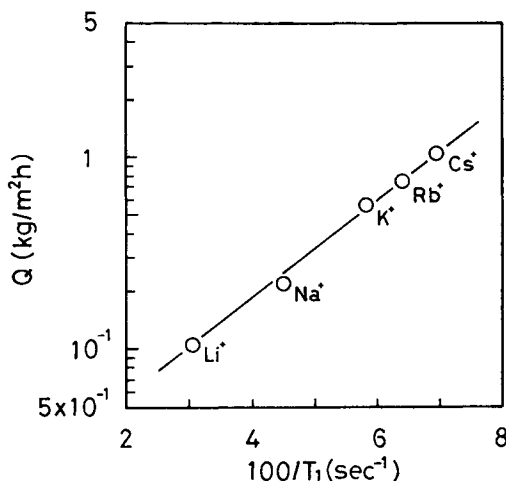
Fig. 13.    Relationship between permeation rate for alginate membranes and reciprocal of spin-lattice relaxation time $T_1$ of C6 carbon. Pervaporation: water/ethanol = 10/90 wt/wt, 60°C.

## CONCLUSION

The separation of water/alcohol mixtures through alginic acid and alginate membranes was investigated.

The selectivity of alginic acid membrane increased markedly to over 10,000 with increasing the neutralization degree of alginic acid by sodium hydroxide. The countercation ($Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$) influenced the permeation rate of the alginate membrane, which increased in the following order: $Li^+$ (0.1 kg/$m^2$ h) < $Na^+$ < $K^+$ < $Rb^+$ < $Cs^+$ (1.0 kg/$m^2$ h), but hardly had any effect on the selectivity. It was very difficult to explain these behaviors only by the affinity of the counterion toward water, but a possible explanation was given by the "hole" theory. The increase of the selectivity by the neutralization would be caused by the contraction of the "holes" due to the change of the packing state of the alginate molecule which would be correlated with the conformation change of the alginate molecule. The conformation change was confirmed by CP/MAS $^{13}$C-NMR. The effect of the counterion on the permeation rate for the alginate membranes could be explained by the mobility of the alginate molecule, the water mobility of the ion hydration shell, and the crystallinity of the polymer. The mobility of the polymer molecules was estimated by the $^{13}$C spin–lattice relaxation time of alginates. It was proved that a local motion of the polymer molecules such as conformational transition was correlated strongly with the permeation rate for the alginate membrane and the mobility of alginate molecule increased in the following order: $Li^+$ < $Na^+$ < $K^+$ < $Rb^+$ < $Cs^+$.

## References

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