Pervaporation Separation of Water/Ethanol Mixtures through Polysaccharide Membranes. III. The Permselectivity of the Neutralized Chitosan Membrane and the Relationships between Its Permselectivity and Solid State Structure

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Synopsis

The separation of water/alcohol mixtures through chitosan membrane neutralized by various acids was investigated. The permselectivity of the neutralized chitosan membrane was affected by the species of acids and, only when neutralized by polybasic acids, was a marked increase of the selectivity observed and a high selectivity maintained for ion free mixtures. The marked increase of the selectivity could be explained by the contraction of the "holes" produced by the thermal motion of polymer chains due to the conformation change of chitosan molecule caused by the neutralization. The conformation change was confirmed by the analysis of the solid state structure of the neutralized chitosan using CP/MAS ^{13}C-NMR.

INTRODUCTION

The purpose of our series of research is to study the separation of aqueous organic solutions through polysaccharide membranes by the pervaporation technique.

In the previous papers,[1,2] we reported that trace amounts of some specific salts in the feed mixtures affected the permselectivity of regenerated cellulose and chitosan membranes, and then a marked increase of selectivity was observed. These unique behaviors were explained by the contraction of the "holes" produced by the thermal motion of the polymer chains due to the conformation change of the polysaccharide molecule. The new conformation was immobilized by the crosslinking of the polysaccharide molecules with the salts as shown in Figure 1(a). To keep the high selectivity of these membranes, it was necessary for the salt to be present in the feed mixture, even when chitosan membrane which interacts with the metal ions more strongly than cellulose membrane.

Considering the schematic crosslinking structure of the polysaccharide molecules [Fig. 1(a)], it is supposed that the metal ion is not necessarily important to crosslink the molecules because ionic crosslinking is possible even

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L = -OH, -NH$_2$
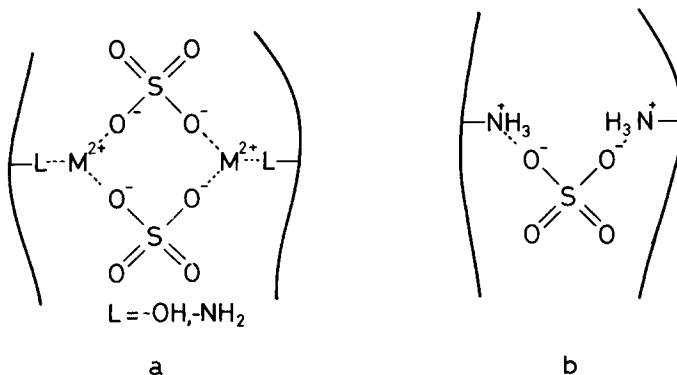
a   b

Fig. 1. Schematic crosslinking of polysaccharides by metal sulfate and sulfuric acid: (a) cellulose or chitosan; (b) chitosan.

if polybasic acids are used as shown in Figure 1(b). In addition, ionic crosslinking seeming to be stronger than the crosslinking by the coordination bond in chitosan, it would be expected to keep high selectivity for even ion-free systems when the chitosan membrane is neutralized by polybasic acids.

In this paper, we report the permselectivity of chitosan membranes neutralized by various acids and the causes of the marked increase of the selectivity due to the neutralization.

EXPERIMENTAL

Chitosan Membrane

Chitosan was supplied by Katokichi Co. Ltd. (Japan) and its deacetylation degrees were 72 and 98 mol %, and its weight-average molecular weights were 1.7×10^5 and 3.0×10^5, respectively, measured by GPC–LALLS (GPC: Waters 201D, LALLS:Chromatix CMX-100).

Chitosan membrane was obtained by the procedure described hereinafter. Chitosan–acetic acid salt membrane was prepared by casting 1 wt % chitosan aqueous solution containing 1 wt % acetic acid onto a glass plate and drying at room temperature. The thickness of the membrane was 20–25 μm. And it was treated in 3 wt % NaOH solution (50 wt % ethanol) and then washing thoroughly with aqueous ethanol solution (50 wt % ethanol).

The neutralization of chitosan membranes thus obtained was carried out by soaking the membrane in a water/ethanol mixture (50/50 wt/wt) containing the adequate amount of acids.

Pervaporation Measurements

The pervaporation measurements were conducted in pervaporation mode with a membrane surface of 7.0 cm^2 and a downstream pressure of 40 Pa (0.3 mm Hg). Water/ethanol mixture was recirculated at 120 mL/min and its temperature was kept constant by the heat exchanger and the water bath. The permeated vapor was collected in a nitrogen trap. The compositions of the feed mixture and permeate were determined by Shimazu GC-7A gas chromatograph equipped with 1-m-long column packed with Porapak Q.

Swelling Degree

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

Analysis of Solid State Structure of Chitosan

The solid state structure of chitosan was determined by CP/MAS ^{13}C-NMR spectra obtained from a JEOL FX-270 spectrometer equipped with CP/MAS unit. The matched field strengths ν 1H and ν 1C were 45 kHz and the rate of the MAS was about 3.5 kHz. The ^{13}C chemical shift was referred to TMS as zero.

RESULTS AND DISCUSSION

As has been mentioned in the introduction, chitosan has amino groups and it can be neutralized by acids.

At first, the effect of the neutralization with H_2SO_4 on the permselectivity of chitosan membrane was investigated using 50 wt % ethanol mixture. The results are shown in Figure 2, where the total permeation rates are divided into the permeation rates of water and ethanol. The separation factor increases from 10.5 for the chitosan membrane to 450 for the neutralized one with increasing the degree of the neutralization. In the latter case, the permeation rate of water holds nearly constant (about 1.8 kg/m^2 h) over 15 mol % neutralization, but that of ethanol decreases from 0.34 to 0.0039 kg/m^2 h throughout all the range, and the rate at 84 mol % is 2 orders of magnitude lower than that at 0 mol %. These results indicate that the marked improvement of the selectivity due to the neutralization is caused by the marked decrease of the permeation rate of ethanol.

The relationship between the equilibrium regain of the membrane which would correspond to the swelling degree and the neutralization degree was investigated from the viewpoint of the affinity of the membrane toward water. The results are shown in Figure 3. The regain increases with increasing the neutralization. This indicates that the affinity of the neutralized membrane toward water increases as the neutralization degree increases. Therefore, it is difficult to explain the results that the permeation rate of water is nearly constant regardless of the neutralization degree. If the selectivity of the neutralized chitosan membrane depends only on the affinity, the selectivity will increase with increasing the dissociation constant of the polybasic acids used when the membrane is neutralized by the equivalent amount of acids. The effect of the polybasic acids on the permselectivity was investigated and the results are shown in Figure 4, where the separation factor is plotted against the first dissociation constant of acids. Figure 4 shows that the dissociation constants of the acids are not necessarily correlated with the separation factor. Especially, neutralized by tribasic acids such as phosphoric acid, trimellitic acid, and trimesic acid, the separation factor is almost the same in the range of the dissociation constant from 8×10^{-4} to 6×10^{-2}.
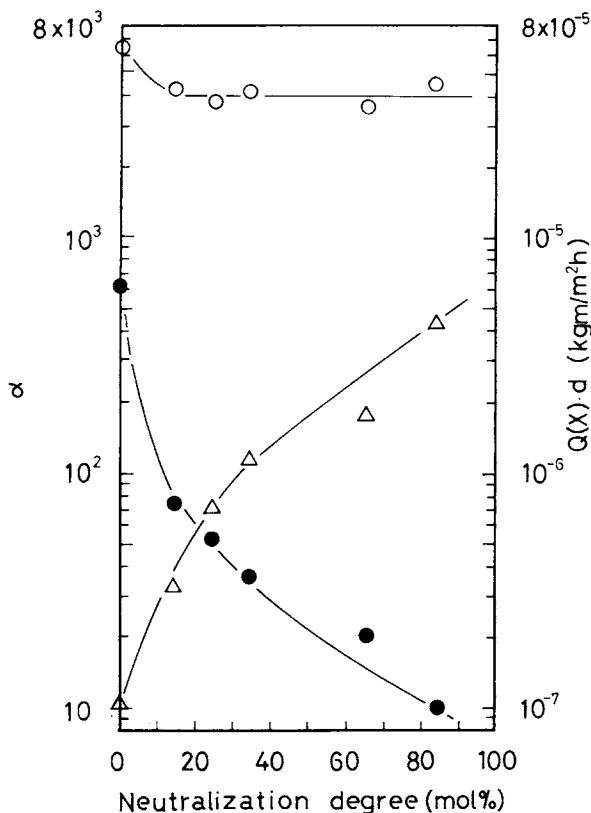
Fig. 2. Effect of neutralization with H_2SO_4 on permselectivity of chitosan membrane: (○) Q(water) · d; (●) Q(ethanol) · d; (△) separation factor; deacetylation degree = 98 mol %; water/ethanol = 50/50 wt/wt; 60°C.

In the case of dibasic acids, it is observed that chitosan membrane neutralized by a stronger acid has a higher selectivity. That is, the separation factor increases from 12 to 450 with increasing the dissociation constant from 3.71×10^{-5} for adipic acid to 5.90×10^{-2} for oxalic acid. There are, however, some exceptions which are found among the isomeric acids such as maleic acid and fumalic acid, and tere(iso)phthalic acid and phthalic acid. With respect to these isomeric acids, the separation factor of the membrane neutralized by acids having lower dissociation constant is larger than that neutralized by the isomer having higher dissociation constant. That is, the dibasic acids having carboxyl group on cis position such as maleic acid and phthalic acid prove to be less effective than other isomeric acids for the increase of the separation factor.

Considering the results of polybasic acids, the increase of the selectivity cannot be interpreted only by the increase of the affinity and the results will suggest that the structure of the neutralized chitosan molecule is important for the increase of the selectivity. In order to interpret the permselectivity of the neutralized chitosan membranes, we conceived that the conformation change of chitosan molecule affected strongly the selectivity like the cuprophan membrane reported in the previous paper. The conformation change
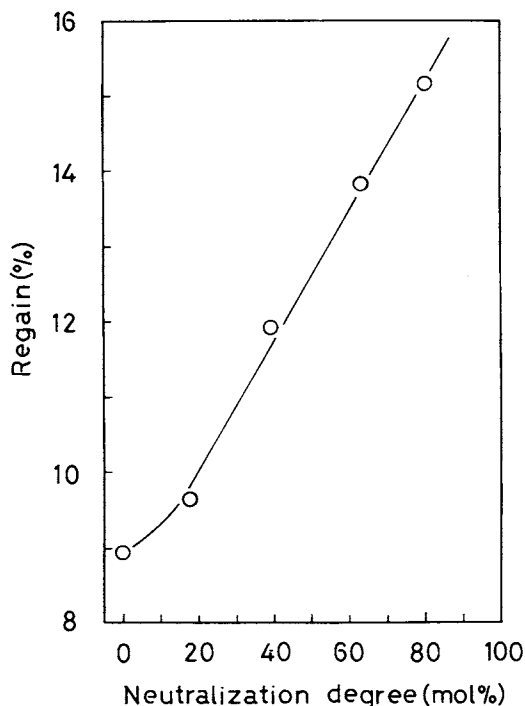
Fig. 3.   Effect of neutralization with H$_2$SO$_4$ on equilibrium regain of chitosan membrane: deacetylation degree = 98 mol %; 43% relative humidity; 25°C.

caused by the ionic and/or steric repulsion of the neutralized chitosan molecule will change the packing state of chitosan molecules, and therefore, the "holes" produced by the thermal motion of the chitosan molecule through which the permeant molecule diffuses will be contracted. So, the permeation of ethanol molecule becomes more difficult but the permeation of smaller water molecule is hardly affected by the contraction of the "holes" and the selectivity increases when chitosan membrane is neutralized by the polybasic acid. The selectivity of neutralized chitosan membranes will be also influenced by the structure of the ionic crosslinking formed by the isomeric dibasic acids, so that the selectivity does not always correlate with their dissociation constant.

The conformation change of chitosan molecule by the neutralization was confirmed by the CP/MAS ^{13}C-NMR spectra. Figure 5 shows the spectra of the sulfates of chitosan. Each peak of spectra is assigned as follows considering the assignment of cellulose molecule by Horii et al.[3] In the spectrum of chitosan, the peak at the lowest field, 106.0 ppm, corresponds to C$_1$ of glucosamine ring. The second lowest peak at 84.0 ppm corresponds to C$_4$. The chemical shifts of C$_2$ and C$_6$ are determined to be 58.1 ppm and those of C$_3$ and C$_5$ appear at 75.9 ppm. The chemical shifts of C$_1$ and C$_4$ are split into two lines by neutralization; the increase of the new lines and the decrease of the origin are observed with increasing the neutralization degree and the origin disappears over the 40–50 mol % degree. Considering the results reported by Horii et al. that there are simple relationships between ^{13}C chemical shifts of
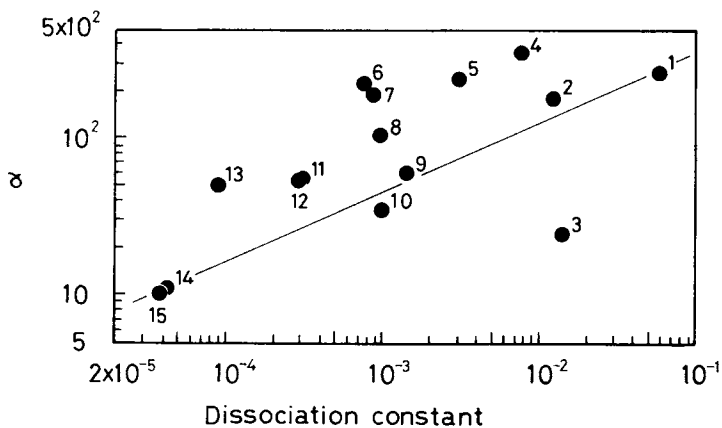
Fig. 4. Effect of acids species on permselectivity of chitosan membrane: (1) oxalic acid; (2) pyromellitic acid; (3) maleic acid; (4) phosphoric acid; (5) trimellitic acid; (6) trimesic acid; (7) citric acid; (8) fumaric acid; (9) malonic acid; (10) phthalic acid; (11) terephthalic acid; (12) isophthalic acid; (13) succinic acid; (14) glutaric acid; (15) adipic acid. Water/ethanol = 50/50 wt/wt; 60°C; deacetylation degree = 72 mol %.
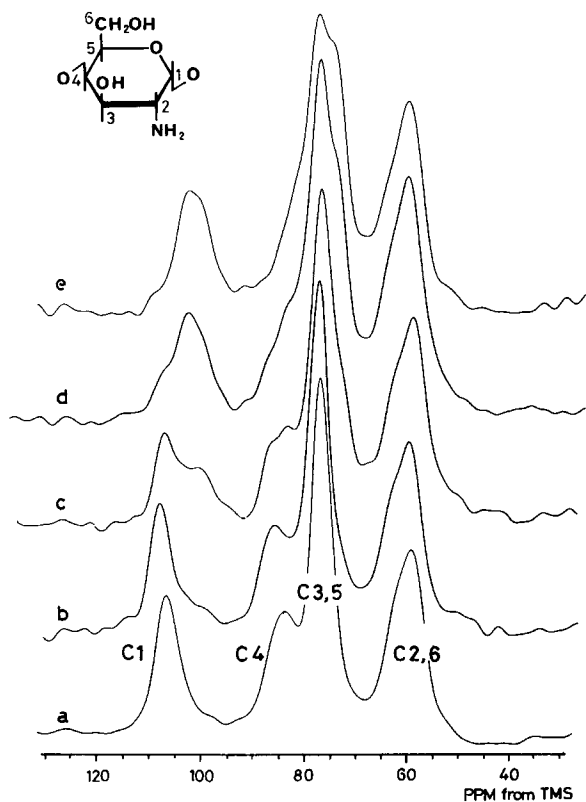

Fig. 5. CP/MAS ^{13}C-NMR spectra of neutralized chitosan: deacetylation degree = 98 mol %; neutralization degree: a = 0, b = 18 mol %, c = 39 mol %, d = 63 mol %, and e = 80 mol %.
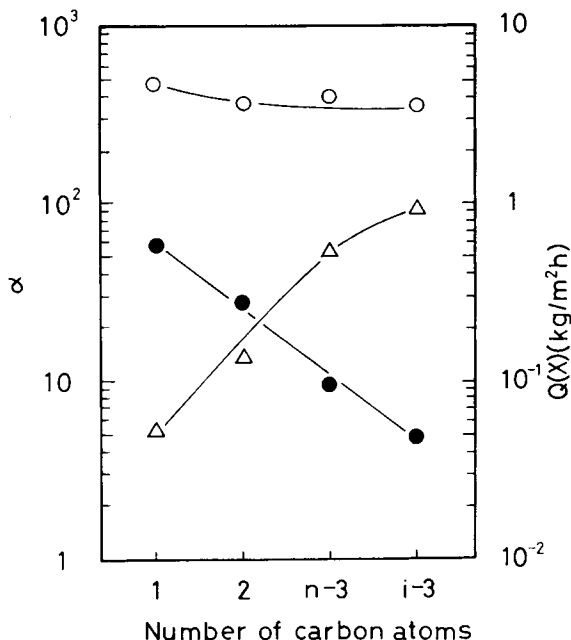
Fig. 6. Effect of molecular shape of alcohol on permselectivity of chitosan membrane: (○) Q(water); (●) Q(alcohol); (△) separation factor; number of carbon atoms: 1 = methanol, 2 = ethanol, n-3 = n-propanol, i-3 = i-propanol; alcohol concentration = 28 mol % (28 mol % ethanol = 50 wt % ethanol); 60°C; deacetylation degree = 98 mol %.

C$_1$ and C$_4$ and the dihedral angle about β-1,4-glycosidic linkage, the large highfield shifts about 3–4 ppm for the C$_1$ and C$_4$ lines with increasing the neutralization degree will indicate that the dihedral angle about β-1,4-glycosidic linkage changes. This will indicate the conformation change of chitosan molecule by neutralization.

From the point of view of molecular order, the effect of the size of alcohol molecules (methanol, ethanol, n-propanol, and i-propanol) on the permeation rates and separation factor of chitosan and chitosan sulfate membranes was investigated. The results are shown in Figures 6 and 7, where the total permeation rates is divided into the permeation rates of water and alcohol. In chitosan membrane, the permeation rate of water is nearly constant, about 4 kg/m^2 h, irrespective of the number of carbon atoms of alcohols. But the permeation rate of alcohol decreases exponentially from 0.57 kg/m^2 h for methanol to 9.7 $\times$ 10^{-2} kg/m^2 h for n-propanol. The swelling degree of chitosan membrane for each mixture is nearly constant as shown in Figure 8. The neutralization of chitosan by H$_2$SO$_4$ causes the decrease of the permeation rates of water for methanol and ethanol mixtures to about 1.7 kg/m^2 h, but for the n-(i-)propanol mixture, such a decrease can hardly be observed. The permeation rate of alcohol decreases from 6.70 $\times$ 10^{-2} kg/m^2 h for methanol to 2.95 $\times$ 10^{-3} kg/m^2 h for n-propanol.

Irrespective of the increase of the number of carbon atoms in the alcohol, the permeation rate of water is not so affected by the neutralization as has been described, but the permeation rate of alcohol is affected markedly. That
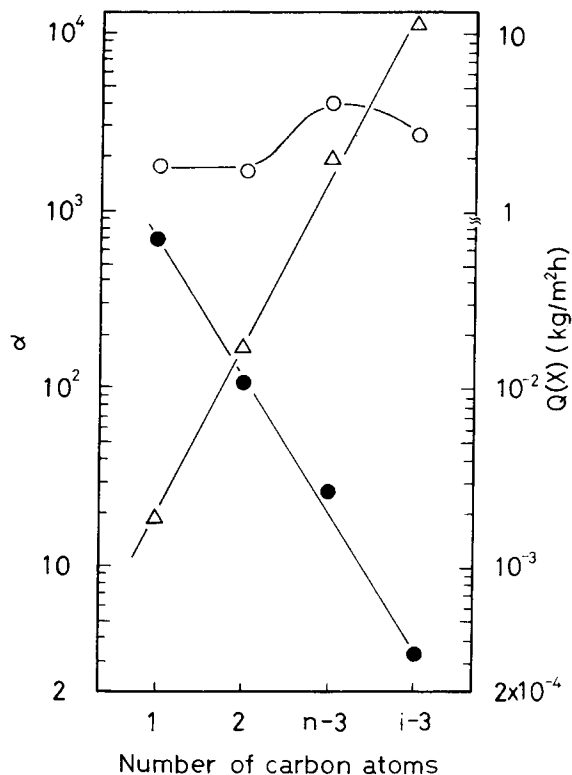
Fig. 7.   Effect of molecular shape of alcohol on permselectivity of chitosan sulfate membrane: (○) Q(water); (●) Q(ethanol); (△) separation factor. Number of carbon atoms: 1 = methanol, 2 = ethanol, n-3 = n-propanol, i-3 = i-propanol. Alcohol concentration = 28 mol % (28 mol % ethanol = 50 wt % ethanol); neutralization degree = 51 mol %; 60°C; deacetylation degree = 98 mol %.

is, the ratios of the permeation rates of alcohols [$Q(X)$(chitosan sulfate)/$Q(X)$ (chitosan)] decreases from 1.18×10^{-1} for methanol to 3.03×10^{-2} for n-propanol with increasing the alcohol's chain length from 2.9 to 5.4 Å. Moreover, when the i-propanol mixture is used, the ratio is 6.38×10^{-3}. The small ratio for the i-propanol mixture compared with n-propanol etc. will be due to a larger cross-section area of i-propanol than other alcohols as shown in Table I. These results indicate that it is more difficult for alcohol molecules having a longer chain or a larger cross-section area to permeate through the neutralized membrane and, therefore, these results are connected with the contraction of the "holes" by the conformation change of chitosan molecule.

The behaviors of the permeation rate of water will be discussed next. The increase of its rate of chitosan sulfate membrane observed in n- and i-propanol mixtures will correspond to the swelling degree for each mixture as shown in Figure 8. So, the increase of the permeation rate will be caused by the increase of the swelling degree. The reason why the swelling degrees for n- and i-propanol mixture are larger than those for methanol and ethanol mixtures is that the interaction between the water molecule in the mixture and the ammonium group of chitosan increases relatively with increasing the
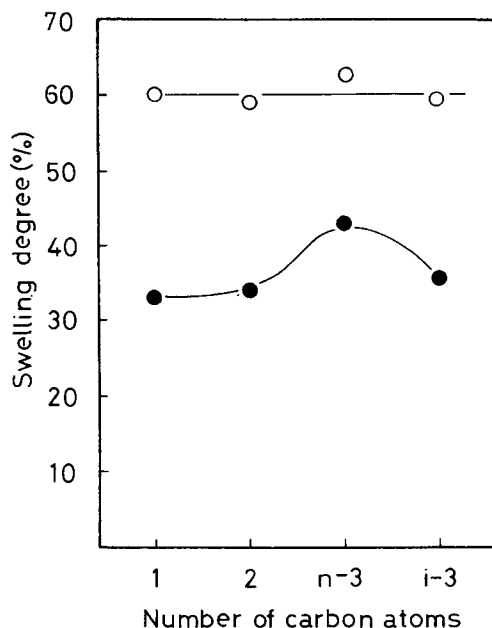
Fig. 8. Swelling degree of chitosan and neutralized chitosan membrane: (○) chitosan membrane; (●) chitosan sulfate membrane; neutralization degree = 70 mol %; alcohol concentration = 28 mol %; 25°C; deacetylation degree = 98 mol %.

hydrophobicity of the alcohols, that is, with increasing the number of carbon atoms from 1 to 3. The marked increase of the swelling degree for the n-propanol mixture in comparison with that for the i-propanol mixture may be explained as follows. Considering that n-butanol is hardly soluble in water but t-butanol is soluble, the i-propanol molecule will be more hydrophilic than the n-propanol though both alcohols are highly soluble in water. So, the interaction between water molecules in the n-propanol mixture and the chitosan molecule will be larger than that in the i-propanol mixture and this reflects the results of the swelling degree.

As has been described, when chitosan membrane is neutralized by polybasic acids, marked improvement of its selectivity is observed. Next, the effect of the neutralization by monobasic acids was investigated in comparison with

TABLE I
Molecular Length and Shape of Alcohol[a]

Alcohol	L (Å)	V/L (Å^2)
Methanol	2.9	23.2
Ethanol	4.2	23.1
n-Propanol	5.4	23.3
i-Propanol	4.3	29.6

[a]L denotes the maximum zigzag length calculated using data from *Table of Interatomic Distances and Configuration in Molecules and Ions*, Special Publication No. 11, The Chemical Society, London, 1958. V was calculated by dividing the molecular weight by the density and the Avogadro number.
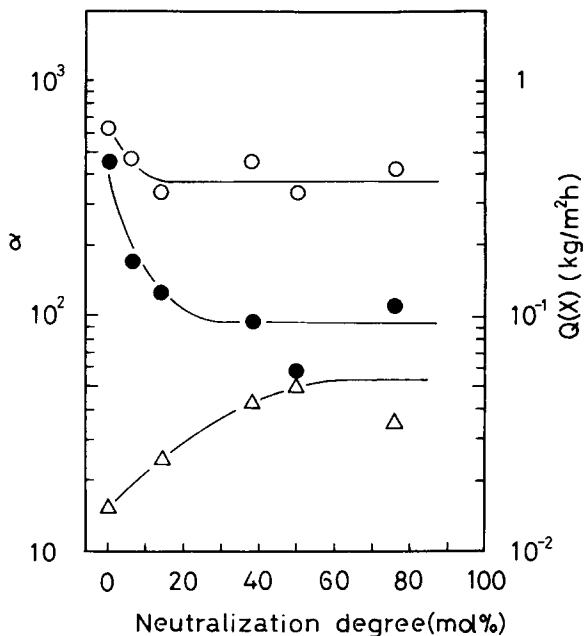
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Fig. 9. Effect of neutralization with HCl on permselectivity of chitosan membrane: (○)
Q(water); (●) Q(ethanol); (△) separation factor. Water/ethanol = 10/90 wt/wt; 60°C; deacetyla-
tion degree = 98 mol %.

the neutralization by monobasic acids was investigated in comparison with
the neutralization by H_2SO_4. These experiments were carried out using the
chitosan sulfate and hydrochloride membranes which were set onto the
pervaporation cell without drying after the neutralization in a water/ethanol
(50/50 wt/wt) mixture. A 90 wt % ethanol mixture was fed because the
chitosan hydrochloride membrane was not strong enough against low ethanol
concentration feed (50 wt %) to operate when the degree of the neutralization
increased. The results are shown in Figures 9 and 10, where the total
permeation rates are divided into the permeation rates of each component,
water and ethanol. In the case of chitosan hydrochloride membrane, the
separation factor increases to about 50 with increasing the neutralization
degree from 0 to 50 mol % and it tends to keep constant over 50 mol % degree.
The permeation rate of water shows nearly constant over 15 mol % degree and
the rate of ethanol also tends to hold constant over 40 mol % degree. In the
case of the chitosan sulfate membrane, the separation factor increases from
13.4 to 31 with increasing the neutralization degree from 0 to 15 mol % but it
increases sharply to over 900 beyond 32 mol % degree. The permeation rate of
water decreases with increasing the neutralization degree but its decrease is
small over 30 mol % degree. The permeation rate of ethanol decreases sharply
throughout all the range and its value at 77 mol % degree is 3000 times smaller
than that at 0 mol % degree.

    To analyze the difference of the permselectivity between chitosan hy-
drochloride and chitosan sulfate membrane, the solid state structure of the
hydrochloride was studied by CP/MAS ^{13}C-NMR and the highfield shifts of
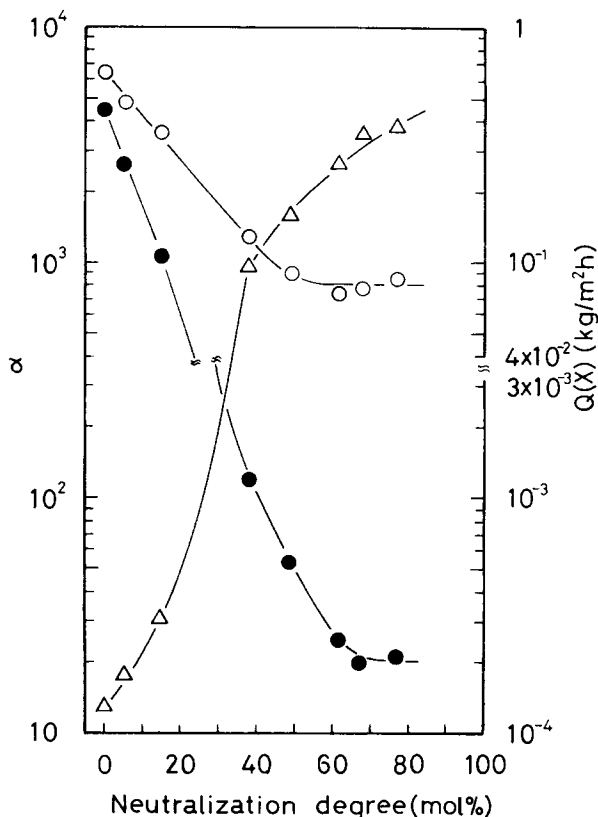C_1 and C_4 lines were observed similar to the case neutralized by H_2SO_4. So,

Fig. 10.   Effect of neutralization with H_2SO_4 on permselectivity of chitosan sulfate membrane: (○) Q(water); (●) Q(ethanol); (△) separation factor. Water/ethanol = 10/90 wt/wt; 60°C; deacetylation degree = 98 mol %.

the difference cannot be explained only by the contraction of the "holes" due to the conformation change of chitosan molecule, but will be explained by the difference of the mobility of chitosan molecule between the hydrochloride and the sulfate. Indeed, the difference of the mobility was made clear by the spin-lattice relaxation time obtained from CP/MAS ^{13}C-NMR, and it proves that the relaxation time of the hydrochloride is smaller than that of the sulfate. This indicates that the mobility of the hydrochloride is larger than that of the sulfate. Therefore, the selectivity of the hydrochloride membrane cannot increase enough. The relationships between the solid state structure of chitosan and the permselectivity will be discussed in detail in the next paper.

The effect of the temperature (30–75°C) on the permselectivity of chitosan sulfate membrane was investigated using a water/ethanol (50/50 wt/wt) mixture. The results are shown in Figure 11. The line of the separation factor has a minimum point at 45°C (3.14×10^{-3} K^{-1}). The Arrhenius plots of the permeation for each component indicate that the apparent activation energy for water permeation is 6.42 kcal/mol and that the one for ethanol permeation is 10.5 kcal/mol in the range of 30–45°C and it decreases to 3.25 kcal/mol over 45°C. As far as we know, such permeation behaviors have never been previously reported.[1,2] According to Eyring's hole theory of diffusion, the
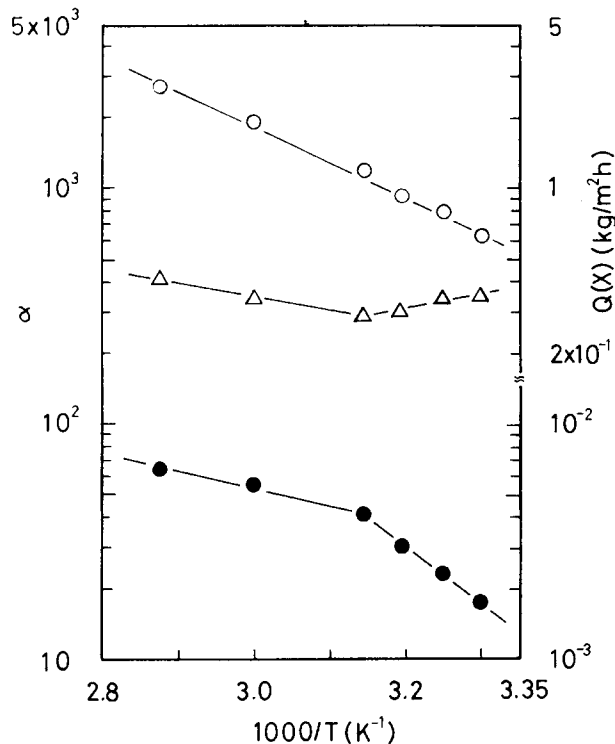
Fig. 11.   Effect of temperature on permselectivity of chitosan sulfate membrane: (○) Q(water); (●) Q(ethanol); (△) separation factor. Neutralization degree = 73 mol %, water/ethanol = 50/50 wt/wt, deacetylation degree = 98 mol %.

thermal motion of polymer chain randomly produces the "holes" through which the permeating molecules can diffuse. As the temperature is increased, the thermal agitation increases and the diffusive "holes" are expanded. Therefore, more alcohol molecules can diffuse through the membrane, and the separation factor decreases. In the case of the chitosan sulfate membrane, the permeation of each component follows Eyring's theory in the range of 30–45°C, but in the range of 45–75°C, only the permeation of ethanol is depressed in comparison with that of water and this will not be explained well by the Eyring's theory. This reason will be as follows.

In chitosan sulfate, the mobility of chitosan molecule is strongly controlled because of the crosslinking of the chitosan molecules by SO_4^{2-} anion and/or its rigid molecular structure. Therefore, only a little increase of the motion of chitosan molecule will be allowed with increasing the temperature in comparison with nonionized free chitosan as reported in the previous paper,[2] that is, the expansion of the "holes" will be controlled to a certain average. So, the increase of the temperature (to 45°C) can cause the expansion of the "holes" and the results obtained follows Eyring's theory. But in high temperature (over 45°C), the increase of the temperature hardly causes the expansion of the "holes," and so the large increase of the permeation rate of ethanol is not brought about. With respect to the permeation of water, the "holes" will be large enough for water molecule to diffuse through them, so its permeation
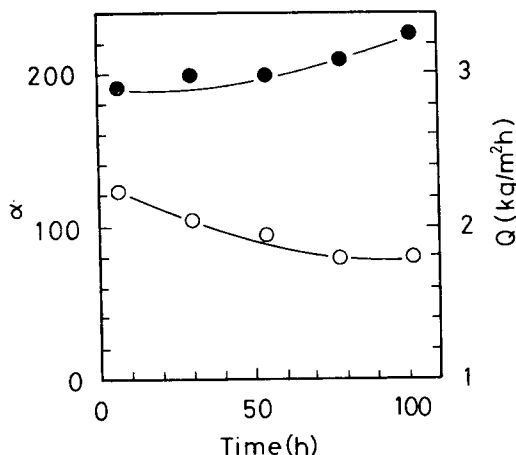
Fig. 12.   Time course of permselectivity of chitosan sulfate membrane: (○) separation factor; (●) Q, water/ethanol = 50/50 wt/wt (ion free); 60°C; neutralization degree = 73 mol % deacetylation degree = 72 mol %.

rate increases throughout all the range of the temperature, 30–75°C. Therefore, the separation factor increases over 45°C.

As described in the previous paper,[2] chitosan membranes pretreated with CoSO$_4$ solution showed high selectivity toward an ion-free water/ethanol mixture but the time course of their pervaporation caused a marked decrease of the selectivity within 15 h because of the release of Co^{2+} ion from the membrane. On the other hand, the time-course study of chitosan sulfate membrane for an ion-free water/ethanol mixture shows that high selectivity is kept over 100 h as shown in Figure 12. This result indicates that the ability of SO$_4^{2-}$ to maintain the new conformation is larger than that of the Co^{2+} complex and so the sulfate membrane is superior to the complex membrane.

CONCLUSIONS

The chitosan membrane was investigated as the pervaporation membrane. The chitosan membrane showed marked high permselectivity toward water/alcohol mixtures when the amino group of chitosan was neutralized by polybasic acids, but when neutralized by monobasic acids, high permselectivity was not observed. The high selectivity was achieved not by the increase of water permeation but mainly by the marked decrease of the permeation of alcohols. The reason for the high performance would be the contraction of the "holes" produced by the thermal motion of the polymer chain due to the conformation change of the chitosan molecule rather than the increase of the affinity toward water. This conformation change was caused by the neutralization and was confirmed by the analysis of the solid state structure of chitosan and chitosan sulfate using CP/MAS ^{13}C-NMR. The high performance of chitosan sulfate membrane could be maintained toward ion-free water/alcohol mixtures.

References

1. A. Mochizuki, Y. Sato, H. Ogawara, and S. Yamashita, *J. Appl. Polym. Sci.* (Part I of this series).

2. A. Mochizuki, Y. Sato, H. Ogawara, and S. Yamashita, *J. Appl. Polym. Sci.* (Part II of this series).

3. F. Horii, A. Hirai, and R. Kitamaru, *Polym. Bull.*, **10**, 357 (1983); F. Horii, A. Hirai, and R. Kitamaru, *Polymers for Fibers and Elastomers*, ACS Symposium Series, C. Arthur, Jr., Ed., Am. Chem. Soc., Washington, DC, 1984, p. 27.