

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

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Synopsis

The separation of water/alcohol mixtures through chitosan salt membranes was investigated. When neutralized by sulfuric acid, the separation factor increased to over 1000, but neutralized by hydrochloric acid, it was at most 50. The difference was mainly explained not only by the contraction of the "holes" due to the conformation change of chitosan molecule but also by the mobility of chitosan molecule which would correspond to the fluctuation of the "hole" size. The conformation change and the mobility of chitosan molecule were measured using CP/MAS ^{13}C -NMR. The spin-lattice relaxation time reflects the mobility of chitosan molecule. The results of the spin-lattice relaxation time obtained from NMR indicated that the mobility of chitosan sulfate was not affected much by the neutralization degree, but the mobility of the hydrochloride was markedly affected. The difference of the selectivity in these membranes could be explained by these results.

INTRODUCTION

In the previous paper,¹ we reported that the chitosan membrane neutralized by polybasic acids, for example, sulfuric acid, showed high separation factors over 1000. But when neutralized by hydrochloric acid, the marked increase of the selectivity was not observed, that is, the separation factor was at most 50. The reason of the high selectivity of the chitosan sulfate membrane was attributed to the fact that the "holes" produced by the thermal motion of chitosan molecules were contracted due to the change of the packing state of the polymer caused by the conformation change of chitosan molecules. Alcohol molecules larger than water molecule thus could not permeate through the "holes." The conformation change caused by the neutralization of amino group was observed by CP/MAS ^{13}C -NMR spectra in this paper. We would like to discuss the reason why the chitosan membrane neutralized by hydro-

chloric acid does not show high selectivity, compared with the membrane neutralized by sulfuric acid and would also like to report the method used to increase the selectivity of the chitosan membrane neutralized by hydrochloric acid.

EXPERIMENTAL

Chitosan and Its Membrane

Chitosan was supplied from Katokichi Co., Ltd. (Japan) and its deacetylation degree and weight-average molecular weight measured by GPC-LALLS (gel permeation chromatography-low angle laser light scattering) were 98 mol % and 3.0×10^5 , respectively.

Neutralized chitosan membranes were prepared in the same manner as described in the previous paper¹ and the thicknesses of the membranes were 20–25 μm .

The definitions of the words, "wet membrane" and "dry membrane" were as follows.

Wet membrane: The neutralized chitosan membrane was set onto the pervaporation cell without drying after the neutralization in water/ethanol (50/50 wt/wt) mixture, the downstream pressure was reduced to 0.3 mm Hg after the water/ethanol mixture was fed.

Dry membrane: The neutralized chitosan membrane was set onto the pervaporation cell and the membrane was dried by reduced pressure (0.3 mm Hg) for 24 h at room temperature, and, then, water/ethanol mixture was fed to the cell, keeping the downstream reduced pressure.

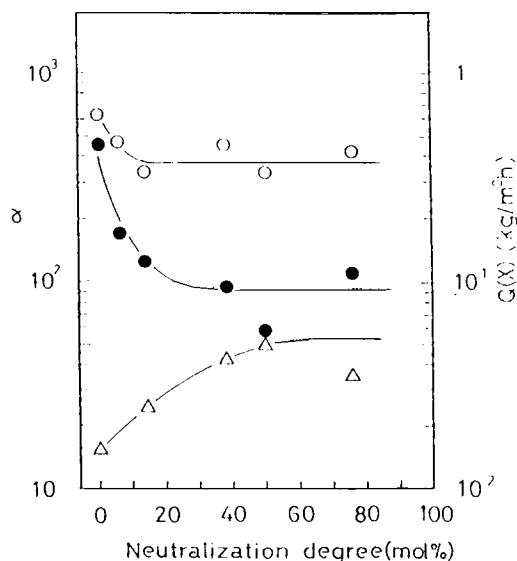


Fig. 1(a). Effect of neutralization with hydrochloric acid on permselectivity of chitosan membranes: (Δ) separation factor; (\circ) permeation rate of water; Q (water); (\bullet) permeation rate of ethanol, Q (ethanol); water/ethanol = 10/90 wt/wt; 60°C.

Neutralization Degree

The neutralization degree of chitosan was determined by ion chromatography.

Equilibrium Moisture Regain

The equilibrium regains of chitosan and its salts at 43 and 76% relative humidity were identified in the same manner reported in an earlier paper¹ using the saturated K_2CO_3 and the saturated $NaOAc$ solution at 25°C.

Pervaporation Measurements

The pervaporation separation method of water/ethanol mixture was described in another earlier paper.²

CP/MAS ^{13}C -NMR

The measurement of CP/MAS ^{13}C -NMR was described in the previous paper.³

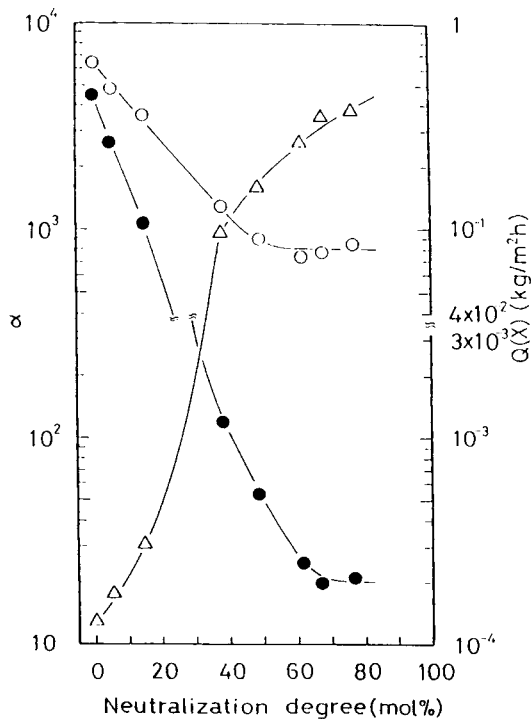


Fig. 1(b). Effect of neutralization with sulfuric acid on permselectivity of chitosan membranes: (Δ) separation factor; (O) permeation rate of water, Q (water); (●) permeation rate of ethanol, Q (ethanol); water/ethanol = 10/90 wt/wt; 60°C.

TABLE I
Relationship Between Swelling Degree and Equilibrium
Moisture Regain of Chitosan Salts

Salt	Neutralization degree (mol %)	Swelling degree (%) ^a	Neutralization degree (mol %)	Equilibrium regain (%) ^b
Sulfate	86	17 ^c	80	15 (43%RH)
	72	34 ^d	70	26 (76%RH)
Chloride	80	19 ^c	75	19 (43%RH)

^a25°C.

^b25°C.

^cWater/ethanol = 10/90 wt/wt.

^dWater/ethanol = 50/50 wt/wt.

RESULTS AND DISCUSSION

As has been described in an earlier paper,¹ the selectivity of the chitosan membrane neutralized by hydrochloric acid is lower than that neutralized by sulfuric acid throughout the entire range of the neutralization degree as shown in Figure 1 when the wet membranes were used. In the case of chitosan hydrochloride membrane, the separation factor increases to about 50 with increasing neutralization degree from 0 to 40 mol % but it does not increase in the range over 40 mol %. In chitosan sulfate membrane, it increases markedly to over 1000 with increasing neutralization degree from 0 to 30 mol %.

To analyze the difference of the permselectivity between the chitosan hydrochloride and chitosan sulfate membranes, the affinities of both chitosan

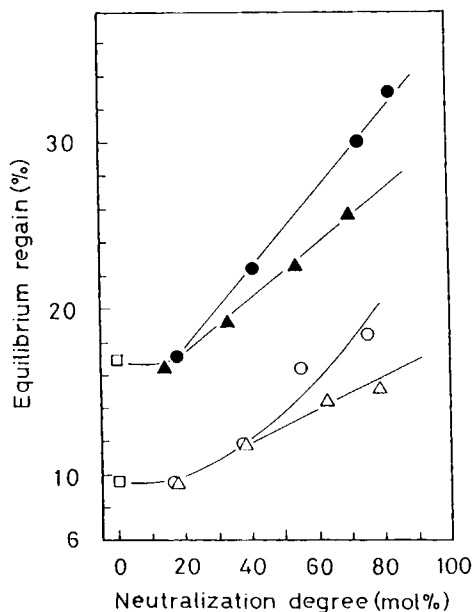


Fig. 2. Equilibrium moisture regain of chitosan neutralized by sulfuric acid or hydrochloric acid: (Δ , \blacktriangle) neutralized by sulfuric acid, 43 and 76% relative humidity at 25°C, respectively; (\circ , \bullet) neutralized by hydrochloric acid, 43 and 76% relative humidity at 25°C, respectively.

salts toward water were investigated by measuring their equilibrium moisture regains at 43 and 76% relative humidity, which will correspond to the swelling degree of the salts in 50 and 90 wt % ethanol solutions as shown in Table I. The results of the affinities are shown in Figure 2. Both the regains increase with increasing neutralization degree. In the range less than 40 mol % neutralization degree, both the regains of the hydrochloride and sulfate are nearly equal, and over 40 mol %, the regain of the former is larger than that of the latter but the difference seems to be small. These results indicate that the affinity of both chitosan salts toward water will be almost the same, especially in the range of 0–40 mol % neutralization degree. Therefore, the marked difference of their permselectivity, as mentioned above, cannot be explained only by the increase of the membrane's affinity toward water by the neutralization.

In previous papers,^{1–3} we proposed the new concept that the high permselectivity of polysaccharide membranes was attributed to the contraction of the “holes” produced by the thermal motion of the polymer chain and this contraction was brought about by the change of the packing state of the polysaccharide molecules due to the conformation change. Therefore, the

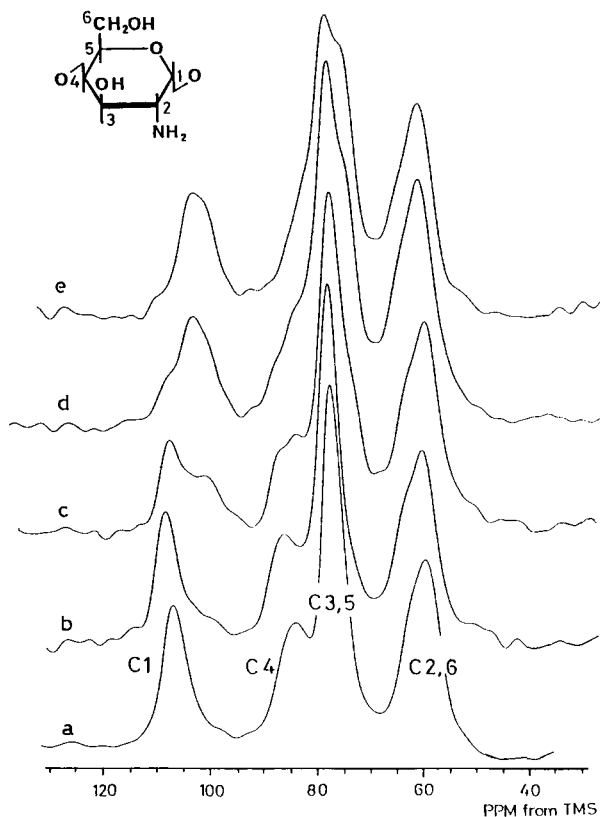


Fig. 3. CP/MAS ^{13}C -NMR spectra of chitosan neutralized by sulfuric acid. Neutralization degree (mol %): (a) 0; (b) 18; (c) 39; (d) 63; (e) 80.

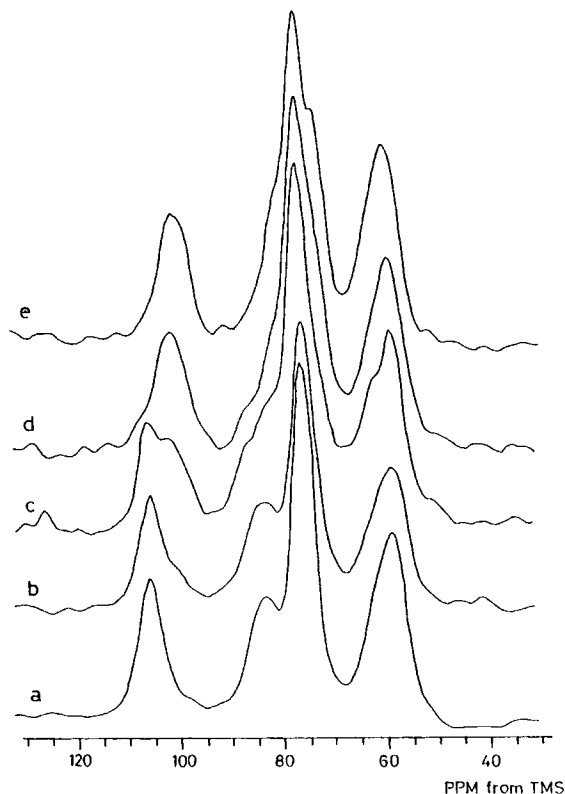


Fig. 4. CP/MAS ^{13}C -NMR spectra of chitosan neutralized by hydrochloric acid. Neutralization degree (mol %): (a) 0; (b) 16; (c) 37; (d) 55; (e) 74.

difference of the conformation between chitosan sulfate and chitosan hydrochloride would be expected, and thus those conformations were investigated using CP/MAS ^{13}C -NMR. The results are shown in Figures 3 and 4, where the salts had equilibrium regains at 43% relative humidity at 25°C . Comparing these two figures, it is apparent that the spectra of chitosan hydrochlorides are nearly equal to that of chitosan sulfates. That is, in both cases, the highfield shifts of C1 and C4 lines are observed, and this result indicates that the conformation of both chitosan salts are almost the same. Hence, the difference of the permselectivity cannot be explained only by the contraction of the "holes" due to the conformation change.

To explain the difference, the mobility of the chitosan salt molecules in the solid state which would correspond to the fluctuation of the "hole" size was examined. In the neutralized alginic acid membrane, it was made clear by the ^{13}C spin-lattice relaxation time T_1 that there was a simple relationship between its permeation rate and the mobility of the alginic acid molecules,³ so that we investigated the T_1 of chitosan sulfates and hydrochlorides which had equilibrium regains at 43 and 76% relative humidity. The observed T_1 values of ^{13}C for each chitosan salts are shown in Figure 5. T_1 values of chitosan sulfate for each carbon are increased or not affected much by the neutralization degree, while the values of chitosan hydrochloride decrease simply with increasing neutralization degree, which are observed in both the cases, i.e., the

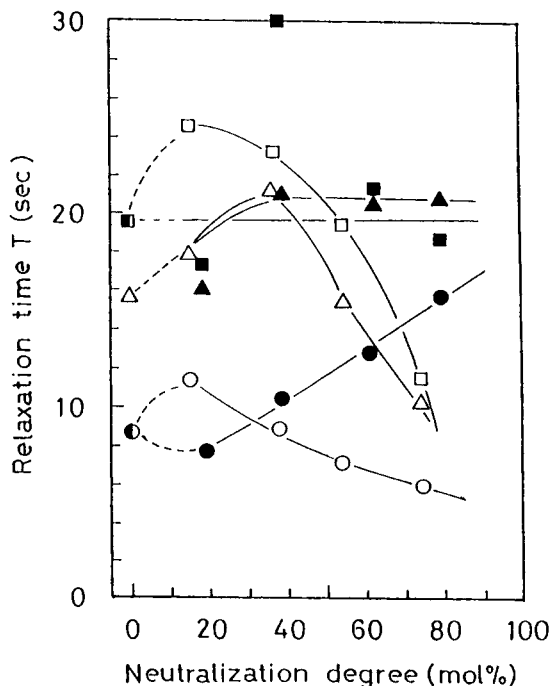


Fig. 5(a). Effect of neutralization on spin-lattice relaxation time T_1 of chitosan salts: (\square) C1, (Δ) C3, 5, and (\circ) C2, 6, which are neutralized by hydrochloric acid; (\blacksquare) C1, (\blacktriangle) C3, 5, and (\bullet) C2, 6, which are neutralized by sulfuric acid, 43% relative humidity.

salts having equilibrium regains at 43 and 76% relative humidity. In the case of chitosan sulfate, with increasing neutralization degree, the ionic crosslinking of chitosan molecules by sulfate anion occurs, so that the mobility of chitosan molecule will not increase irrespective of the increase of the equilibrium regain, which indicates the increase of water content in the membrane. But in the case of the hydrochloride, the mobility of chitosan molecules will increase with increasing neutralization degree due to the increase of the equilibrium regain since the salt has no ionic crosslinking structure. The results of the chemical shifts of each carbon and T_1 values in chitosan hydrochloride are now considered. The contraction of the "holes" caused by the conformation change due to increase of the neutralization degree will be indicated by the results for chemical shifts of C1 and C4 carbons, and, moreover, the affinity toward water increases by the neutralization. Ideally, this contraction and the increase of the affinity would bring about the increase of the selectivity, but the mobility of chitosan molecules increases with increasing neutralization degree as shown in Figure 5, which indicates the increase of the fluctuations of the contracted "holes." Therefore, ethanol molecule larger than water can permeate easily through the "holes" with increasing fluctuations, even though it is contracted by the conformation change of chitosan molecules. This will correspond to the results of the permeation rate of ethanol [Fig. 1(a)]. As the contraction of the "holes" is caused by the neutralization, the permeation of ethanol molecule larger than water would be expected to be depressed and decreased throughout all the

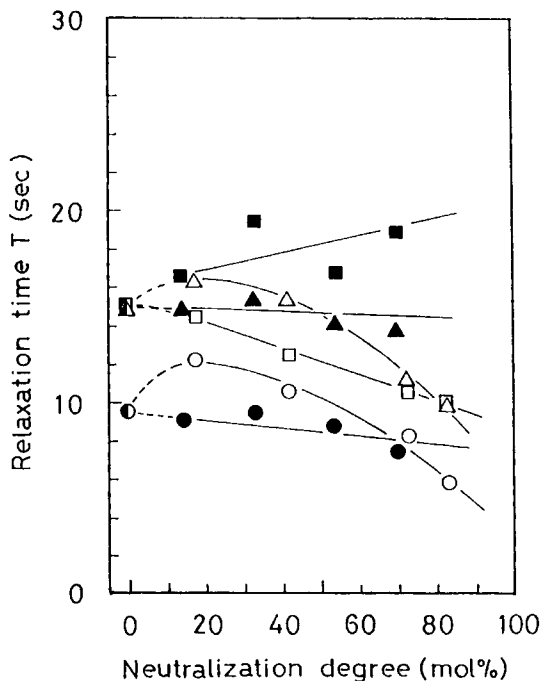


Fig. 5(b). Effect of neutralization on spin-lattice relaxation time T_1 of chitosan salts: (□) C1, (Δ) C3, 5, and (○) C2, 6, which are neutralized by hydrochloric acid; (■) C1, (▲) C3, 5, and (●) C2, 6, which are neutralized by sulfuric acid, 76% relative humidity.

neutralization degree like the case of chitosan sulfate membranes, but actually the permeation rate of ethanol is constant over 40 mol % neutralization degree. Because of the combination of the contraction of the "holes" with the fluctuations of the "holes" size, the separation factor cannot increase so high (not more than 50 at about 40 mol %) and the permeation rate is larger than that of chitosan sulfate membrane.

The permselectivity of chitosan sulfate membranes are explained as follows. The magnitude of the conformation change of chitosan molecules are low when the neutralization degree is less than 20 mol %, because high-field shifts of C1 and C4 carbons are hardly observed. This indicates that the contraction of "holes" is small and, therefore, the marked increase of the selectivity is not observed in this range. The increase of the neutralization degree will bring about the contraction of the "holes" and the increase of affinity toward water as shown, in Figures 2 and 3, but does not affect the mobility of the chitosan molecule as shown in Figure 5, that is, the fluctuation of the "holes" for each neutralization degree is nearly equal. Therefore, the sudden marked increase of the selectivity is observed over 30 mol % neutralization degree because of the contraction of the "holes" [Fig. 1(b)].

On the other hand, it is observed that the relaxation time T_1 of the dried chitosan sulfate and hydrochloride salts increase with increasing the neutralization degree as shown in Table II. This tendency of chitosan hydrochlorides is reversed for the case having the equilibrium regains. These results indicate that the mobility of the chitosan hydrochloride molecules is not increased by

TABLE II
Spin-Lattice Relaxation Time T_1 of Dry Chitosan Salts

Salt	Neutralization degree (mol %)	Relaxation time T_1 (s)		
		C1	C3, 5	C2, 6
Hydrochloride	83	30.6	32.5	12.0
	73	30.7	31.0	14.8
	42	34.1	28.9	16.3
	12	28.5	28.0	14.4
Sulfate	70	30.8	35.4	13.5
	54	51.0	32.2	14.0
	33	22.7	24.1	13.4
	14	21.3	19.9	11.6
Chitosan	0	19.7	16.5	12.0

the neutralization when it is dried. This phenomenon will be caused by the physical fixation of the chitosan molecules attributed to the drying. From these results, it is expected that even the chitosan hydrochloride membrane shows high selectivity with increasing neutralization degree when it is dried, because the conformation change of chitosan molecules (the contraction of the

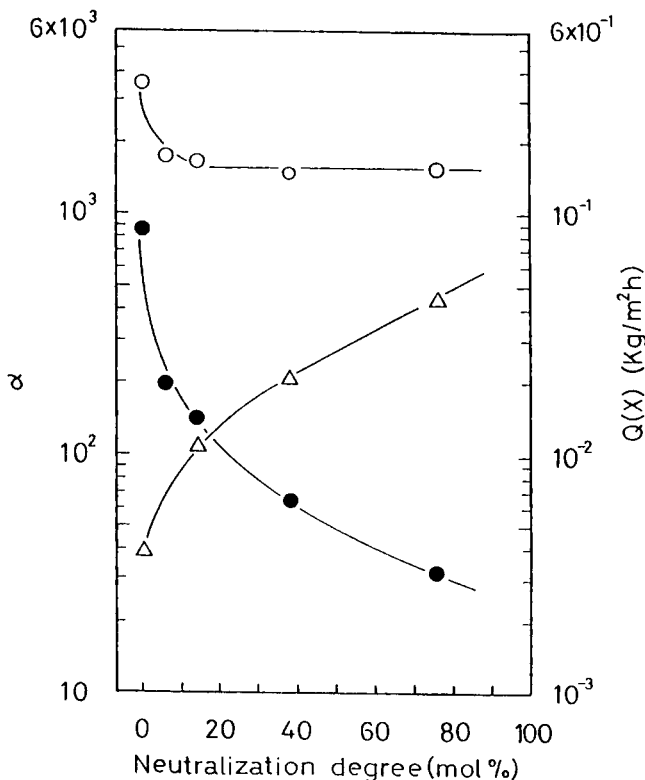


Fig. 6. Effect of drying on chitosan membrane neutralized by hydrochloric acid: (Δ) separation factor; (\circ) permeation rate of water, Q (water); (\bullet) permeation rate of ethanol, Q (ethanol); water/ethanol = 10/90 wt/wt; 60°C.

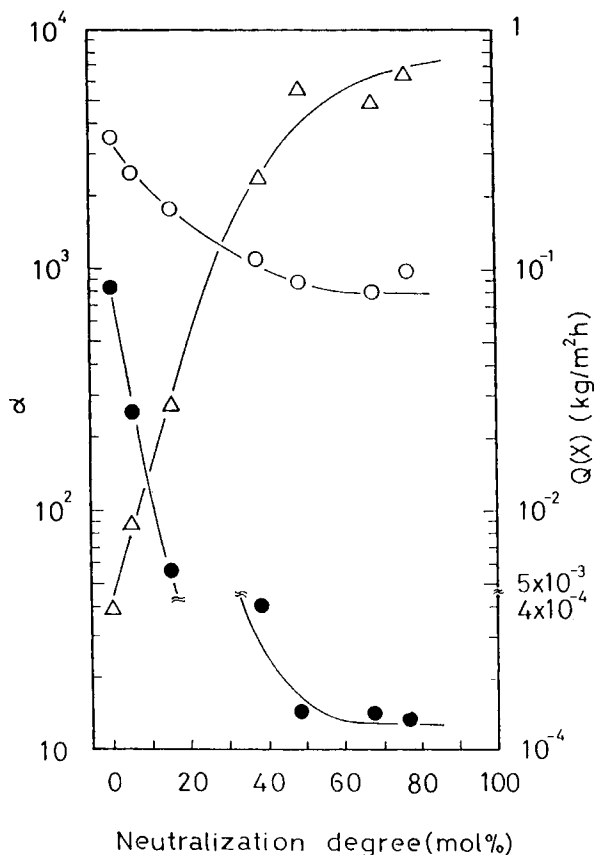


Fig. 7. Effect of drying on chitosan membrane neutralized by sulfuric acid: (Δ) separation factor; (\circ) permeation rate of water, Q (water); (\bullet) permeation rate of ethanol, Q (ethanol); water/ethanol = 10/90 wt/wt; 60°C.

“holes”) occurs and the mobility of it (the fluctuation of the “hole” size) is not decreased by the neutralization degree as in the case of wet chitosan sulfate. We investigated the permselectivity of dry chitosan membranes neutralized by hydrochloric acid and sulfuric acid using a 90 wt % ethanol mixture. The results are shown in Figures 6 and 7. In the case of dry hydrochloride membrane, the separation factor increases to over 500 with increasing the neutralization degree as shown in Figure 6. The permeation rate of water is nearly constant, about $1.5 \times 10^{-1} \text{ kg/m}^2 \text{ h}$, irrespective of the neutralization degree, but the permeation rate of ethanol decreases from 8.4×10^{-2} to $3.2 \times 10^{-3} \text{ kg/m}^2 \text{ h}$ throughout. This behavior is quite different from that of the wet membrane shown in Figure 1 and is similar to that of the sulfate membrane as had been shown in Figure 2 in the previous paper.¹ In the case of dry sulfate membrane, the separation factor is a little larger than that of the wet membrane, but the marked difference such as observed in chloride membranes was not observed. This is explained by the fact that the mobility of chitosan molecule is depressed even in the wet membrane by the ionic crosslinking of chitosan molecules due to sulfate anion.

CONCLUSION

The reasons for the marked difference of the selectivity toward water/ethanol mixtures between chitosan sulfate and chitosan hydrochloride membranes were investigated using CP/MAS ^{13}C -NMR. The similar conformation change of chitosan molecules were observed in both salts and this result would suggest that the contraction of the "holes" produced by the thermal motion of polymer molecules occurred in both the salts membranes. However, the separation factor of the hydrochloride membrane was at most 50, while that of the sulfate membrane was over 1000. Hence, it is difficult to interpret the difference of the permselectivity between them only by the "hole" theory. Therefore, the mobility of chitosan molecules in both the salts which would correspond to the fluctuation of the "hole" size was studied. The mobility of chitosan molecule increased by increasing neutralization degree when neutralized by hydrochloric acid, but it was not much affected by the neutralization degree when neutralized by sulfuric acid. This increase of the mobility in hydrochloride salts caused the increase of the fluctuation of the "holes," so that ethanol molecule larger than water could permeate through the "holes." Therefore, the separation factor did not increase in the case of the wet hydrochloride membrane. We obtained results that both the contraction of the "holes" due to the neutralization and the fluctuation of the "hole" size due to the mobility of chitosan molecules decided the permselectivity of the neutralized chitosan membranes.

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