키토산막을 통한 물-에탄올 수용액의 투과증발분리 : 1. 키토산-아세트산 및 키토산-금속이온 복합체막

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Pervaporation Separation of Water-Ethanol through Modified Chitosan Membranes : 1. Chitosan-Acetic Acid and -Metal Ion Complex Membranes

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요 약 : 키토산-아세트산 복합체막과 키토산-금속이온 복합체막들의 여러 공급액온도와 공급액 에탄올 농도에 대해 투과증발성능을 연구하였다. 키토산을 아세트산에 녹이고 유리판위에 캐스팅한 후 키토산-아세트산 복합체막을 얻고 이것을 수산화나트륨으로 처리하는 시간을 변화시켜 결정 화도가 각기 다른 막을 얻었다. 또한 금속이온들을 키토산막내에 주입시킨 금속이온 복합체막도 제조하였다. 알칼리 처리시간이 길어지면 유량은 감소하였는데 이것은 알칼리 처리를 통해 키토산 내의 결정성이 증가하였기 때문으로 해석된다. 금속이온들이 들어가면 물에 대한 선택성이 증가함 을 알았다.

Abstract : The pervaporation performance of chitosan-acetic acid complex membranes and chitosan-metal ion complex membranes were investigated in the present study. Chitosan was dissolved in an aqueous acetic acid solution and cast onto a glass plate to form a chitosan-acetic acid complex membrane. The chitosan-metal ion complex membranes were subsequently prepared by treating the chitosan-acetic acid membranes with NaOH solution. Pervaporation separation of water-ethanol mixture through these membranes was performed by varying the feed ethanol concentrations and temperatures. As alkali treatment time is prolonged, the flux decreased due to the increase in crystallinity as evidenced by the X-ray analysis and density measurements. Flux, however, increased with temperature. It was observed that the water selectivity could be improved in separating water-ethanol mixtures by the incorporation of metal ions in chitosan membranes.

INTRODUCTION

Pervaporation, a membrane process for separating liquid mixture, is recognized as an energy efficent alternative to distillation and other separation methods. The process involves direct contact of liquid mixture with one side of a selective membrane, while the permeated product is removed as a vapor. Pervaporation can be especially advantageous for the separation of azeotropic mixture, typified by the ethanol-water system. Several studies for the dehydration of ethanol have been conducted recently.[1~5] More recently, a combination of reverse osmosis or distillation and pervaporation process has been proposed and used in some applications.[6]

Chitosan is the deacetylation product of the alkali treatment of chitin. Chitin is one of the most abundant organic materials which can be easily obtained in the nature. The natural source of chitin is shell of crustaceans (lobsters, shrimps, etc.) or the broth from industrial fungal processes(e. g., citric acid). Chitin is similar in its chemical structure to cellulose but uses and applications have not yet been realized much as those cellulosic materials.[7~9] While chitin is insoluble in most solvents, chitosan is readily soluble in acidic solutions and quite available for industrial applications. In recent years, a basic and applied research on the effective use of chitin and chitosan derivatives has been actively conducted. Examples would be the adsorption of heavy metal ions,[10] artificial skin substrates,[11] chitosan fibers,[12] membranes[13~18] etc.

Samuels[19] first reported the solid state structure of chitosan films cast from formic acid solution and later washed with aqueous NaOH. He proposed the former(cast film) as form I crystal and the later (washed film) as form II crystal type. Sakurai et al. later extended his study on crystal structures[20] and water vapor sorption study.[21] It is assumed that the complex formation, i. e., the incorporation of fatty acid in the chitosan crystal should give crystal structure, crystallinity and crystalization behaviour different from those of chitosan itself. More recently, Mochizuki et al.[18] investigated in details the effect of metal ions in the feed on the pervaporation performance in chitosan membranes.

In the present study, the pervaporation performance of chitosan-acetic acid complex membranes and chitosan-metal ion complex membranes were investigated. Effects of alkali treatment in chitosan-acetic acid complex membranes on the separation of water-ethanol mixture were examined on the basis of molecular features. Various metal ion complex membranes were also prepared and studied to help understand the pervaporation of chitosan complex films.

EXPERIMENTAL

Materials

Chitin was prepared from crab shell according to the modified Hackmann method.[22,23] Chitin was subsequently deacetylated with NaOH soultion to obtain chitosan. It was dispersed in 47% aqueous NaOH solution and then heated for 1 hour, and washed with distilled water to remove excess NaOH. This process was repeated four times and dried at 80℃ in a vacuum oven. The degree of deacetylation was 54% measured by the titration method.[24] Acetic acid, sodium hydroxide, ethanol, were from Duksan Phamaceutical Co. Metal sulfates($Al_2(SO_4)_3$, $BaSO_4$, $NiSO_4$, $CuSO_4$, $MgSO_4$, $FeSO_4$) were from Chameleon Co.

Characterization

For structure determination, X-ray diffractometer(Rigaku Denki Model RAD-C) was used. The X-ray source was CuKα radiation (30kv, 20A) using monochromator. Density of sample was measured by density gradient column method. The solvents used were carbon tetrachloride and n-heptane.

Perparation of Chitosan Complex Membranes

3g of chitosan was added to 200ml of 2% aqueous acetic acid solution at room temperature with stirring. Polymer solution was filtered to re-

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move dust and undissolved chitosan and the cast onto a glass plate to prepare the chitosan membrane. After drying the membranes at 60℃ in an oven for more than 12 hours, they were treated with 1 N aqueous sodium hydroxide solution. Alkali treating time was controlled to be 30 min, 1, 3, 6, 9, 12, and 24 hours. Non-alkali treated sample was used as a control (cast membrane).

Chitosan-metal ion complex membranes were made by mixing 100ml of 2 wt% aqueous acetic acid solution with 1.5g of chitosan powder and 0. 1939×10^{-3} mole of metal salts were dissolved in the chitosan solution. After casting on the glass plate, acetic acid was dried in an oven controlled at 65℃, followed by treating this membrane with 1 N NaOH solution for three hours, rinsed with distilled water several times and then redried at room temperature.

Pervaporation Experiment

Permeation cell was made by stainless steel and permeating vapor was collected with two traps in liquid nitrogen. A detailed description of pervaporation apparatus was given elsewhere.[25] Effective area of the membrane was about 25.98 cm^2 and downstream pressure was 400~670 Pa(3~5 torr). Pervaporation experiment was carried out on chitosan, chitosan-acetic acid complex, and chitosan-metal ion complex membranes. Pervaporation experiment was conducted with different feed ethanol concentrations and various feed temperatures. Separation factor α was defined as follows.

$$\alpha = \frac{Y_1/Y_2}{X_1/X_2} \qquad (1)$$

where Y_i is the weight fraction of i in the permeate and X_i in the feed. 1 and 2 are water and ethanol, respectively.

RESULTS AND DISCUSSION

Effect of Alkali Treatment Time

In Fig. 1 the effect of NaOH treatment time in the chitosan complex membranes on the flux and separation factor by pervaporation is shown.

Flux generally decreased with an increase in alkali treatment time. Membrane treated with alkali for six hours shows the lowest flux values. Chitosan membrane washed with alkali for three hours has the highest selectivity of 242. The membrane alkali-washed for six hours shows a similar selectivity value with 12-hour alkali-treated membrane. The separation factor, however, decreased to about 100 for 24-hour alkali-treated membrane.

These results coincide well with the X-ray analysis. The studies of crystal structure studies on chitosan have not been made so far except those reported by Samuels[19] and Sakurai et al.[20] Samuels proposed two types of crystals denoted as the form I and form II crystals, and indicated that the unit cells of crystal form are orthorombic. The appearance of two types of crystal forms depended largely on the preparation methods of chitosan films. Form I crystal is obtained by casting the aqueous formic acid solution. Form II crystal is acquired by precipitation, i. e., by immersing the solution into an aqueous NaOH solution. Sakurai et al.[20] later extended Samuels' earlier study and prepared several chitosan membranes from formic
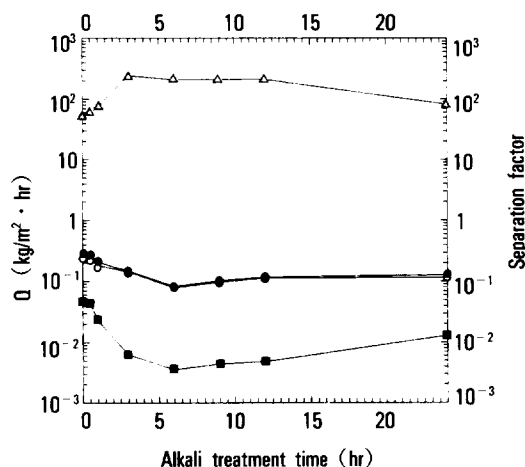
Fig. 1. Effect of NaOH treatment time on separation factor($\triangle$), total flux($\bullet$), water flux($\bigcirc$), and ethanol flux($\blacksquare$)through chitosan-acetic acid complex membrane. Feed solution, 90 wt% ethanol ; membrane thickness, 20 μm ; feed temperature, 25℃.

acid, acetic acid, butyric acid solution, and they later used these membranes for gas separation[14] and water vapour sorption study.

The tendency that alkali treatment reduces permeation rate and the amount of equilibrium solvent uptake can be explained with the increased crystalline character of alkali-washed chitosan complex membranes as evidenced by the X-ray diffraction patterns (Fig. 2). Alkali-treated chitosan complex membranes show X-ray patterns in the scattering angle (2θ) range of $9°$ to $11°$ and around $20°$. Peaks appeared at arround $10°$ are assigned to be (001) and (100) and those at around $20°$ are known to be a mixture of (101) and (002). For the present membranes, the maxima occurs at slightly different values in each films ; at $8.88°$, $9.64°$, $9.64°$, $10.10°$ and $10.64°$ in the complex membranes treated for 0, 3, 6, 9, and 24 hours, respectively. Using the formula : $n\lambda = 2 d\sin\theta$, with $n = 1$ and $\lambda = 1.54$ Å, the d spacings of the films were determined to be 9.95, 9.17, 9.17, 8.75, 8.3 Å, respectively. Accordingly, the interchain packing can be tighter in the membranes treated with aqueous alkali solution for long time.

X-ray patterns also show that alkali treatment time serves to increase the peak intensity at which 2θ is equal to around $10°$. Accordingly, we can estimate that the relative crystallinity goes up as the acetylate ions attached to amino groups in chitosan were removed. In other words, as chitosan membrane has more amino groups in the chain, it becomes more capable of hydrogen bonding between them, resulting in an increased crystallinity. This result is somewhat similar to what Sakurai et al. observed[14] for gas separation. The pervaporation of water and alcohols thus depends on the volume fraction of amorphous region (or crystallinity) since the crystalline region is usually recognized to be independant of permeation.

For some reasons, however, the peak intensity in X-ray scattering patterns and the density (Table 1) were the highest for six-hour alkali-treated sample. Also in Fig. 1, six-hour alkali-washed film has the lowest flux value. We knew from the above
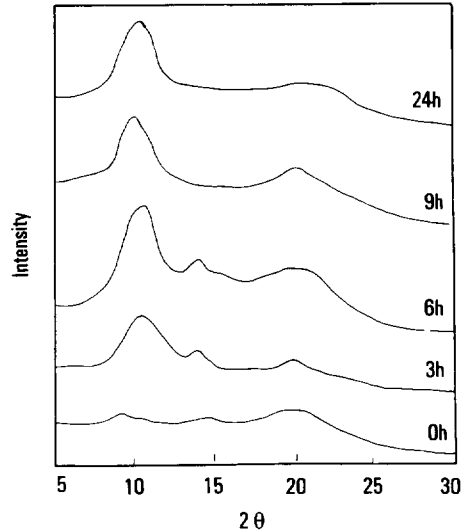

Fig. 2. X-ray scattering patterns for chitosan-acetic acid complex membranes treated with NaOH solution. Numbers on the figure indicate the duration of NaOH treatment.

X-ray analysis and density measurements that the six-hour alkali-treated membrane had the highest crystallinity. Since highly crystalline membrane receives large diffusion resistances for permeation,[28] it is understandable that flux has been decreased for six-hour alkali-treated samples. On the other hand, membrane with lower crystalline character gets smaller diffusion resistance and shows high flux such as in the cast membrane.

It was observed that the flux of washed-membrane shows relatively high flux which is 0.28 Kg /m^2 · hr and low selectivity (only about 50). As alkali treatment time increased, we knew that ion complex form was changed to amino functional groups and crystallinity may increase because of hydrogen bonding between these functional groups in the polymer chain. As a result, water and ethanol flux decreases and selectivity increases. Since the crystallinity and density of 24-hour alkali-treated membrane is a little lower than those of 12-hour alkali-treated membrane, there is an increase of ethanol flux while water flux is almost not affected. Selectivity, therefore, decreased be-

Table 1. Density of Chitosan Membranes Treated with NaOH Solution for Different Periods

| Alkali Treating Time (hr)	Density
0	1.4155
0.5	1.4176
1	1.4165
3	1.4227
6	1.4259
9	1.4217
12	1.4176
24	1.4176

cause of an enhancement of ethanol-membrane attraction.

The swelling experiment[26] also shows that the swelling becomes less as chitosan membrane was further treated with alkali solution due to an increased crystallinity with a maxima appeared at six-hour alkali treatment time, as shown in Fig. 2 and Table 1. Another possible reason for decreased absorption with prolonged alkali treatment might be that aqueous alkali solution takes time to diffuse into the cross-section of the membrane to deacetylate.

Effect of Temperature

In Fig. 3 pervaporation results for chitosan-acetic acid complex membrane obtained in various temperatures are shown. As temperature increases, the molecular thermal motion becomes active in the membrane and the permeation rate increases. An increase in ethanol permeation rate may become higher than an increase in water permeation, resulting in a decrease in selectivity when temperature is raised. In general, the reason why the flux increases with the temperature can be explained by Eyring's "holes" theory.[18] That is, as temperature increases the conformation of molecular chain is changed and holes or free volume between molecular chain are formed, resulted in an increase in permeation rate.

From Fig. 3, activation energies for permeation of water and ethanol are calculated to be 10.5, and 18 Kcal/mole, respectively. We used 90 wt%
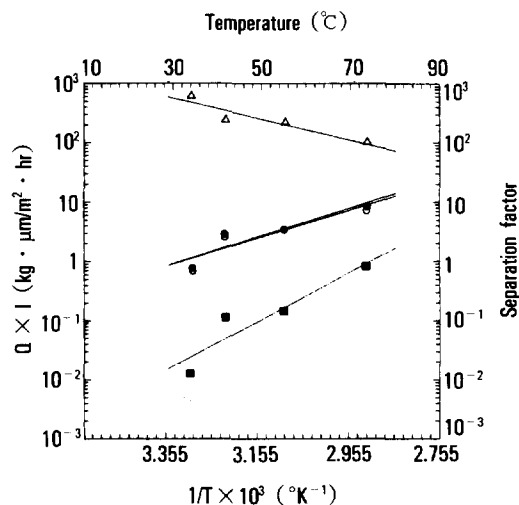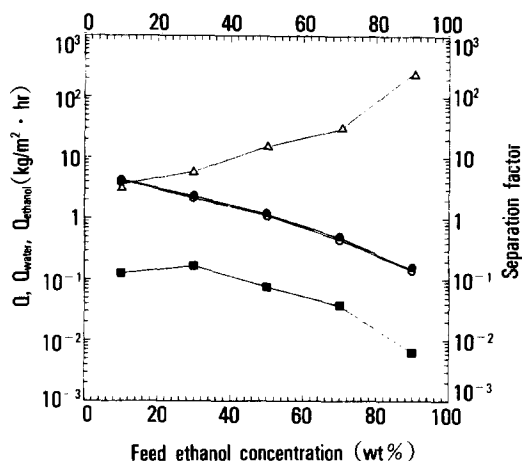

Fig. 3. Effect of feed temperature on separation factor (△), total flux(●), water flux(○), and ethanol flux (■)through chitosan-acetic acid membrane treated with NaOH solution for three hours after casting. Feed, 90 wt% ethanol ; membraned thickness, 20 μm.

ethanol as a feed. Water sorption is about three to four times greater than ethanol sorption as known from the previous swelling experiment.[26] Water is a strongly swelling media to chitosan while ethanol is not. In higher ethanol feed concentration such as in the present case, the interaction between solvents and membrane is suppressed at lower temperature. When temperature is raised this suppressed interaction between solvents and membrane become active with the aid of the thermal motion of the polymer membrane. Accordingly, the total flux increases and more so for ethanol flux increase at higher ethanol concentration.
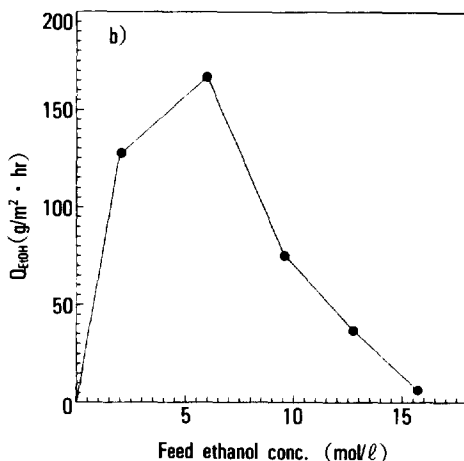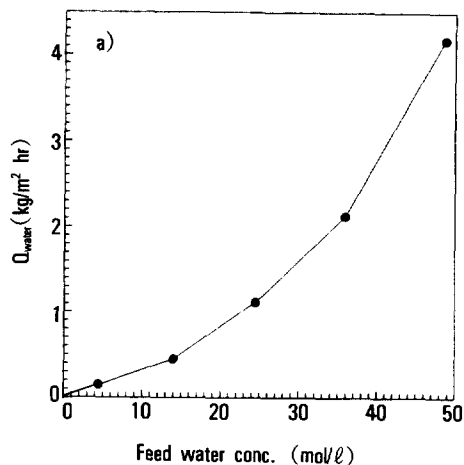
Effect of Feed Ethanol Concentration

In Fig. 4 permeation rate and selectivity of chitosan membranes measured in various ethanol concentrations are shown. To help understand the permeation mechanism we separated the flux in water and ethanol and are plotted against respective feed concentration in Figs. 5. Water permeation rate increases exponentially with feed water concentration, while ethanol flux increases and then decreases at around feed ethanol concentra-

Fig. 4. Effect of feed ethanol concentration on separation factor($\triangle$), total flux($\bullet$), water flux($\bigcirc$) and ethanol flux($\blacksquare$) through chitosan-acetic acid membrane treated with NaOH solution for three hours after casting. Operating temperature, 25℃ ; membrane thickness, 20μm.

tion of 6 mole/1. In higher water concentration of feed, swelling or plasticization due to the presence of water is obvious, resulting in a simultaneous increase in water and ethanol permeation through the membrane. In lower water concentration or higher ethanol concentration, the salting-out effect plays a role in reducing the total flux. These peculiar profiles are attributed to the presence of the ionic charges in the membrane. This kind of flux vs. feed concentration profile is also observed by Yoshikawa et al.[27] in the separation of ethanol-water mixtures through charged poly(1-methyl-4-vinylpyridinium iodide-co-acryronitrile) membrane. Cabasso,[20] Reineke[29] and Wenzlaff[30] also reported a similar tendency when they used charged membranes. We are conducting more detailed study on this subject and it will appear in the future.

In the case of 50 wt% and 30 wt% ethanol concentration, the flux of chitosan membrane appears to be above 1.2 Kg/m^2 · hr and 2.2 Kg/m^2 · hr, respectively. In Fig. 6, separation curves of chitosan membrane, and vapor/liquid equilibrium curve in all feed ethanol concentrations are shown.

Fig. 5. Effect of feed water (a) and ethanol (b) concentration on their respective pervaporation fluxes through chitosan-acetic acid complex membrane treated with NaOH solution for three hours after casting. Operating temperature, 25℃ ; membrane thicknes, 20 μm.

Permeate water concentration is above 95 wt% for chitosan membrane and at the same time the membrane has high flux. Chitosan membrane has a reasonable pervaporation performance in the 50~70 wt% ethanol concentration.

Effect of Metal Salts

It has long been known that chitosan is a good heavy metal adsorbent.[31,32] Recently chitosan-metal complex membrane was used for gas separa-
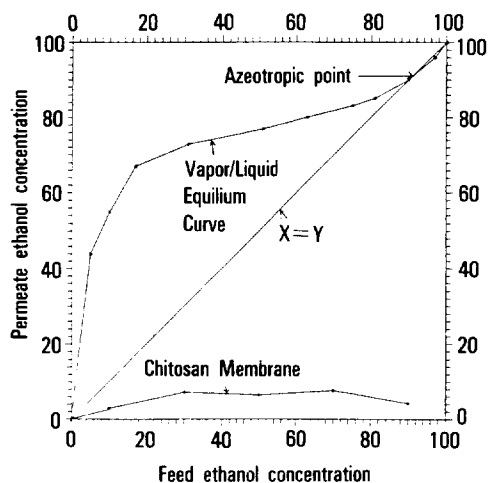
Fig. 6. Pervaporation seperation curve for chitosan-acetic acid complex membrane and vapour/liquid equilibrium curve for ethanol/water mixture.

Table 2. Effect of Addition of CoSO$_4$ in Chitosan/Acetic Acid Complex Membrane on Performance

Condition	Total Flux, Q Kg/m²·hr	Q$_w$ Kg/m²·hr	Q$_e$ Kg/m²·hr	α	C$_p$ EtOH (wt%)
Chitosan/ AcOH + 3hr NaOH Treatment	0.1488	0.1425	0.0063	242	4.259
Chitosan/ AcOH Add CoSO$_4$ + NaOH	0.097	0.0920	0.0045	169	4.726
Chitosan/ AcOH NaOH + Sorb in CoSO$_4$ 13hr	0.067	0.0645	0.00299	182	4.441

tion[15] and for pervaporation.[18] Especially, in the case of pervaporation research, Mochizuki et al.[18] reported that the chitosan membrane was sorbed in the aqueous metal salt solution and dried or they put metal salts in the feed. One of the problems for that membrane was the long-term stability because metal complex formed only on the surface.[18] The present study intends to improve this membrane stability problem and to examine the effect of various metal salts added to the membrane on pervaporation performance.

In Table 2, chitosan membrane washed for three hours in NaOH aqueous solution(control), CoSO$_4$ added into casting solution and then treated with NaOH solution for three hours (add), and the chitosan complex membrane prepared according to Mochizuki et al. (sorb) are compared. Contrary to the expectation, the pervaporation performance of the cobalt ion complex membrane is lower than that of the control without containing cobalt ions, when 90 wt% feed ethanol concentration is used. Mochizuki et al.[18] reported an enhancement of the pervaporation flux and separation factor when cobalt ions are added to the feed.[18] A possible reason for this discrepancy might be the feed

ethanol concentration difference and the macrovoid formation due to the remaining metal salts in the membrane. Cobalt sulfate added in the casting solution made complex between 2-amino groups in chitosan and cobalt ion which is expected to play as carrier sites for water. The net result was a decrease in flux and selectivity due to the formation of physical macrovoids across the membrane, as observed by scanning electron microscopy (not shown here). For most of the chitosan-metal ion complex membranes, however, the permeate ethanol concentration was below 4.7 wt%. This could be regarded as a good separation efficiency.

In Table 3, pervaporation performance of chitosan complex membranes with different metal salts added is shown. When Ba^{++} or Fe^{++} was added, selectivity was increased. In the case of Cu^{++}, flux increased to a small extent but selectivity was decreased. When Al^{+++}, Co^{++}, or Ni^{++} ions with large van der Waals radii were added, the experimental result shows a drop in flux. In the case of Ba^{++} or Fe^{++}, which have small van der Waals radii and lower electronegativity, we observed an enhanced selectivity.

In Figure 7, the ratio of diffusion coefficient multiplied by sorption coefficient, and pervaporation selectivity are compared. This figure shows a

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Table 3. Pervaporation Performance of Chitosan/Metal Ion Complex Membrane Treated with NaOH Solution for 3 Hours

Ion	Total Flux, Q $Kg/m^2 \cdot hr$	Q_w $Kg/m^2 \cdot hr$	Q_e $Kg/m^2 \cdot hr$	α
Control	0.1450	0.1425	0.0063	242
Ba^{++}	0.0462	0.0456	0.00063	609
Fe^{++}	0.0212	0.0209	0.000311	568
Co^{++}	0.0970	0.0924	0.00458	169
Ni^{++}	0.0751	0.0688	0.00624	118
Cu^{++}	0.1518	0.1386	0.01950	66
Mg^{++}	0.0346	0.0268	0.00784	40
Al^{++}	0.1039	0.0337	0.07020	4

* Feed solution = 90wt% ethanol : feed temperature = 25℃.
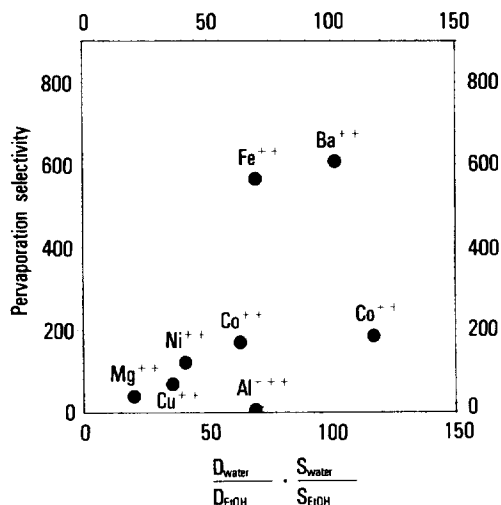
Fig. 7. Pervaporation selectivity versus diffusion selectivity times sorption selectivity for chitosan-metal ion complex membranes. Membranes are treated with NaOH solution for 3 hours.

good relationship between α_p and $\alpha_d \cdot \alpha_s$ except Co^{++} sorbed and Al^{+++} added membranes. From this result we conclude that solution-diffusion model can be applied for chitosan-metal ion complex membranes.

CONCLUSIONS

From the present study, the following several conclusions are drawn. As alkali treatment time increases, equilibrium absorption of water and alcohols decrease in chitosan-acetic acid complex membrane. Higher alcohol blocks diffusion and equilibrium sorption. Thus, as alkali treatment time increases, pervaporation flux decreases and selectivity increases. Among the alkali-washed membranes, the pervaporation flux and the selectivity for three-hour alkali-treated membrane was the highest. As temperature increases, diffusion of permeate and flux increase, and ethanol flux increased more than what water flux did. Feed water concentration affects the swelling behavior of chitosan membrane showing exponential profile. Because of swelling or plasticization of water at higher water concentration, ethanol can also be penetrated through the membrane. At higher ethanol concentration, the salting-out effect plays an important role. We found that chitosan membrane is a good barrier material for pervaporation separation of aqueous ethanol, particularly in the range of 50 to 70 wt% ethanol. Separation of water and alcohol in chitosan membrane can be enhanced by incorporating Fe^{++} and Ba^{++} ions. On the other hand Cu^{++} ion increases flux. The solution-diffusion mechanism of transport could be applicable to these membranes.

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