

Polyion Complex Composite Membranes for the Separation of Methyl *t*-Butyl Ether/Methanol Mixtures: Separation Behaviors of These Membranes

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Received 13 December 2000; accepted 8 October 2001

ABSTRACT: For the pervaporation separation of methyl *t*-butyl ether (MTBE)/methanol mixtures, polyion complex (PIC) composite membranes, composed of sodium alginate (SA) and chitosan, were prepared by alternating electrostatic adsorption of SA and chitosan on polysulfone-supporting membrane. The pervaporation experiments were carried out under various preparation and operating conditions. The results showed that the prepared membranes strongly exhibited a methanol permselectivity for the MTBE/methanol mixtures, and moreover, through certain of these membranes, only methanol was permeated. Also, by increasing the chitosan content in the reaction solution, the permeation rates and MTBE concentrations in the permeate decreased gradually because of an increase in the ionic complexation between SA and chitosan. Furthermore, raising the pervaporation temperature led to an increase in both the permeation rate and the separation factor. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1832–1842, 2002

Key words: sodium alginate; chitosan; pervaporation; MTBE/methanol mixture

INTRODUCTION

In recent years, the study of the separation of polar/nonpolar organic mixtures, such as methyl *t*-butyl ether (MTBE)/methanol or benzene/cyclohexane, was actively conducted and a study of various polymer membranes was carried out. Among the membrane materials, the hydrophilic polysaccharide polymers such as chitosan have gained special interest because they have showed the highest flux and separation factors of any hydrophilic materials tested for the pervaporation dehydration. The separation of organic mix-

ture by using the polyelectrolytes complex especially, which was focused on as one of the membrane materials because of its high chemical stability, as well as its hydrophilicity, is due to its ionic characteristic. Polyelectrolyte complexes result from the interaction of macromolecules carrying complementary ionizable groups. The expectation of polyelectrolyte complex membranes is the possibility of controlling the rate and selectivity of fluxes for solute by changes in the chemical and physical properties of the membrane induced by changing local conditions.¹ Also, they were used in the design of drug delivery systems, protein separation, anticoagulant coatings, and membranes for separating materials, or even as skin substitutes, among other applications.^{2–6} For the separating of polar components in polar/

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Journal of Applied Polymer Science, Vol. 85, 1832–1842 (2002)
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nonpolar mixtures, however, such high effective polyelectrolyte complex membranes have not yet been developed. Accordingly, to develop a membrane having an excellent pervaporation performance for the separation of MTBE/methanol mixtures, in this study, polyion complex composite membranes, composed of sodium alginate (SA) polyanion and chitosan polycation, were investigated. Chitosan, in general, is a polysaccharide polymer derived from chitin, and its repeating unit configuration is 1,4-linked 2-amino-2-deoxy- β -D-glucan. Although chitin is insoluble in most solvents, chitosan is readily soluble in acidic solutions and the cation-charged chitosan can interact with an anionic polyelectrolyte [e.g., poly(acrylic acid), pectin, and gelatin] to form polyion complexes. By contrast, sodium alginate is a polysaccharide consisting of linear chains of 1,4-linked β -D-mannuronate and α -L-guluronate residues in various proportions, and its ability to form into gel is greatly increased by the presence of divalent ions such as Ca^{2+} , which can be complexed by carboxylate groups of alginate in a tetradentate structure. Accordingly, in this study, polyion complex composite membranes composed of SA and chitosan were prepared by using their electrostatic properties. Particularly, to prepare the polyion complex composite membranes having a thin coating layer, the layer-by-layer self-assembly of oppositely charged polyelectrolytes on solid surfaces was considered and investigated for the separation of MTBE/methanol mixtures.^{7,8} MTBE shows increasing use as an oxygenate for gasoline to meet the Clean Air Act requirement. MTBE is produced by reacting isobutene with excess methanol, and the unreacted methanol is subsequently distilled off and recovered.^{9,10} However, the use of excess methanol causes a purification problem because methanol forms an azeotrope with MTBE at a composition of 14.3 wt % methanol. Pervaporation, therefore, was used to break this azeotrope. This article aims at investigating the pervaporation characteristics of polyion complex composite membranes, composed of SA and chitosan, for the separation of MTBE/methanol mixtures, and also at investigating certain studies on permeation behaviors, as well as temperature dependence.

EXPERIMENTAL

Materials

Sodium alginate (SA), methyl tert-butyl ether (MTBE), and chitosan were purchased from Al-

drich Chemicals (Milwaukee, WI). Polysulfone membrane (MWCO 30,000) for the supporters of composite membranes was purchased from U.O.P. Corp. (San Diego, CA). Methanol (guaranteed reagent) was supplied by Merck (Darmstadt, Germany). HCl (35% content, extrapure grade) and ethanol (guaranteed reagent) were purchased from Junsei Chemical Co. (Tokyo, Japan). Ultrapure deionized water was used. All chemicals were used without any further purification.

Membrane Preparation

SA was dissolved in deionized water to form a homogeneous solution of 2 wt % polymer. To prepare the composite-type polyion complex (PIC) membranes, homogeneous SA composite membranes were at first prepared by dipping the skin-layer side of polysulfone membranes into SA solution and drying them at room temperature for 24 h in a dust-free, environmentally controlled chamber. Chitosan solutions of 0.5–2.0 wt % were prepared by dissolving chitosan in water containing 5 wt % HCl. The overall prepared homogeneous SA composite membranes were then immersed in a chitosan solution for 10 min. After the polyion complexation, the membrane was taken out of the chitosan solution, washed several times with pure water to eliminate any possible residual chitosan solution, and dried at room temperature.

Swelling Ratio

The PIC membranes were completely dried under reduced pressure at room temperature and weighed. These dried membranes were immersed into a 75/25 wt % MTBE/methanol mixture, in a sealed vessel, at a selected temperature, until equilibrium was reached. After the swollen membranes were rapidly taken out from the mixture and the solution wiped carefully on the surface of the membranes with filter paper, the membranes were then weighed as quickly as possible. The swelling ratio, S , was calculated by the following equation:

$$S = (W_s - W_d)/W_d$$

where W_d and W_s are the weight of the dried membrane and the swollen membrane in a feed mixture, respectively.

Equilibrium Sorption Experiments

The composition of MTBE/methanol mixtures sorbed in the PIC membranes, after reaching ab-

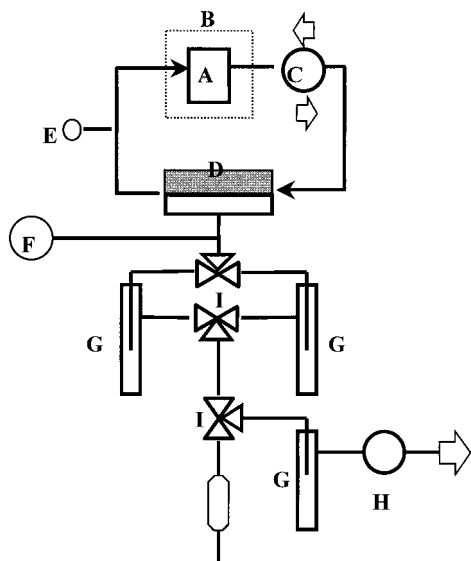


Figure 1 Schematic representation of the pervaporation device: (A) feed tank; (B) heating controller; (C) pump; (D) pervaporation cell; (E) temperature indicator; (F) pressure indicator; (G) cold trap; (H) vacuum pump; (I) three-way vacuum valve.

sorption equilibrium in the same manner as in the measurement of the swelling ratio of these membranes, were directly measured by gas chromatography (Shimadzu GC model 14B). The compositions of MTBE/methanol mixture in the membrane, and in the feed, gave the sorption selectivity, α_{sorp} , calculated by the following equation:

$$\alpha_{\text{sorp}} = (M_{\text{methanol}}/M_{\text{MTBE}})/(F_{\text{methanol}}/F_{\text{MTBE}})$$

where F_{methanol} and F_{MTBE} are the weight fraction of methanol and MTBE in the feed solution, and M_{methanol} and M_{MTBE} are those in the PIC membrane, respectively.

Pervaporation Measurements

A schematic permeation apparatus used in this study is illustrated in Figure 1. The membrane cell is made of stainless steel. A feed mixture enters the cell through the center opening, flows quickly through the thin channel, and leaves the cell through the side opening, which allows relatively high fluid velocity parallel to a membrane surface. The effective membrane area was 19.6 cm². The feed mixture was circulated from the feed tank, having a capacity of 2.5 L, through the membrane cell. The feed tank was wrapped with heating tape to heat the feed mixture. The feed-

mixture temperature was controlled by a proportional-integral-derivative (PID) temperature controller, with an accuracy of 0.5°C. A PID-type controller controlled the permeation pressure. The permeation vapor was collected in a cold trap by liquid nitrogen with a given time interval, heated up to room temperature, and weighed to determine the flux. Separation analysis was carried out by a gas chromatograph equipped with a column packed with Porapak-Q and with a thermal conductivity detector. In addition, calibration of 0.1–10 wt % MTBE/methanol mixtures was conducted with a thermal conductivity detector. In permeate, MTBE concentration of <0.01 wt % was not detected by using the thermal conductivity detector. The separation factor ($\alpha_{\text{methanol/MTBE}}$) was calculated by the following equation:

$$\alpha_{\text{methanol/MTBE}} = (Y_{\text{methanol}}/Y_{\text{MTBE}})/(X_{\text{methanol}}/X_{\text{MTBE}})$$

where X and Y are the weight fractions of each component in feed and permeate, respectively.

RESULTS AND DISCUSSION

Swelling and Equilibrium Sorption Behaviors

Figure 2 shows the swelling ratio of the PIC membranes in a 75/25 wt % MTBE/methanol mixture

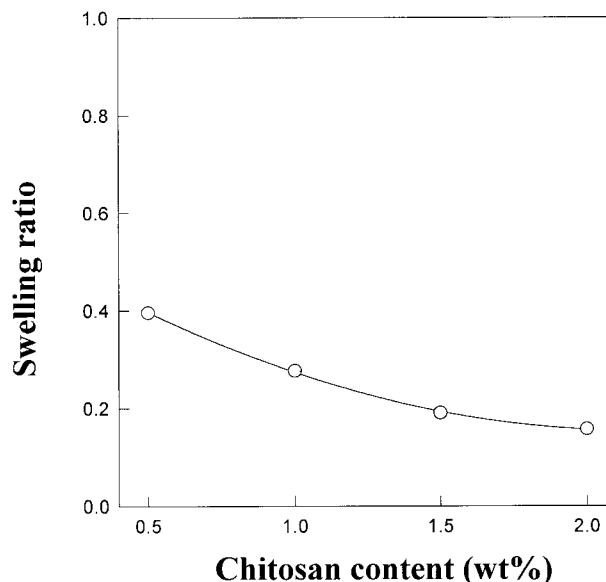


Figure 2 Swelling ratios of the polyion complex (PIC) membranes fabricated at different chitosan contents in a 75/25 wt % MTBE/methanol mixture at 40°C.

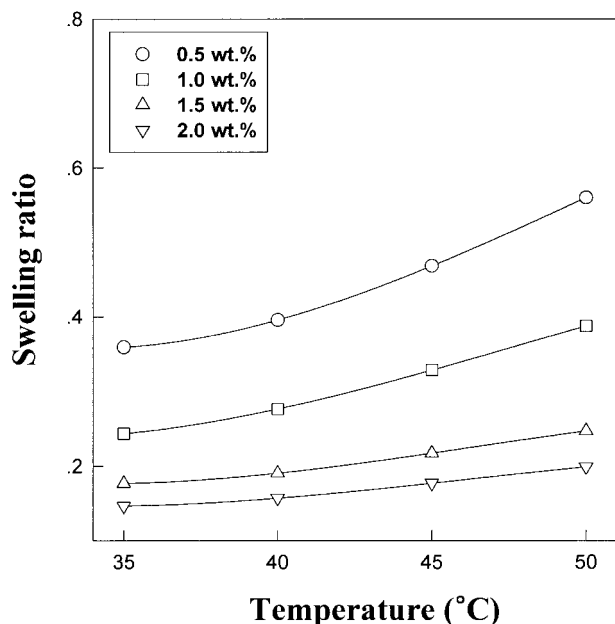


Figure 3 Influence of temperature on swelling ratio of PIC membranes.

as a function of chitosan contents in the reaction solution. The swelling ratio of the PIC membrane decreased gradually with the increase of chitosan content in the reaction solution, which could be attributed to the formation of the polyion complexes between SA and chitosan. That is why the

polyion complexes are of ionic, crosslinked network structures. Therefore, when the complexation between these polymers is raised further, the strength of the PIC membrane increases because of a greater number of SA–chitosan ionic linkages per each chain. Accordingly, the PIC membrane prepared with higher chitosan content has lesser membrane mobility and a more compact network structure, resulting in less liquid solubility, respectively.

In detail, to clarify the correlation between swelling ratio and complexation, the swelling behavior at different temperatures was measured; these results are shown in Figure 3. As can be seen from this figure, the overall swelling ratios of the PIC membrane increase with the increase in temperature. When the chitosan content in the reaction solution is raised, however, the effect of temperature in the swelling phenomenon is smaller than at low levels of chitosan content. It should be noted that the solubility of the liquid in membrane decreases with increasing chitosan content due to more ionic crosslinked structure in the PIC membrane. In addition, the MTBE concentration sorbed in the PIC membrane decreases with an increase of the chitosan content, as shown in Figure 4. In the case of this mixture, MTBE has very low affinity for the PIC membrane, and also the molecular size of MTBE is larger than that of methanol. Therefore, when the ionic complexes in

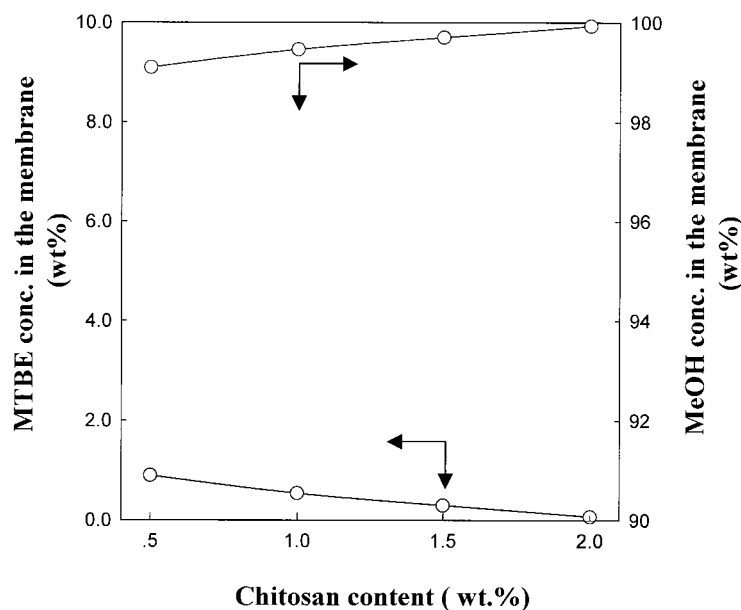


Figure 4 Equilibrium sorption for the PIC membranes fabricated at different chitosan contents in a 75/25 wt % MTBE/methanol mixture at 40°C.

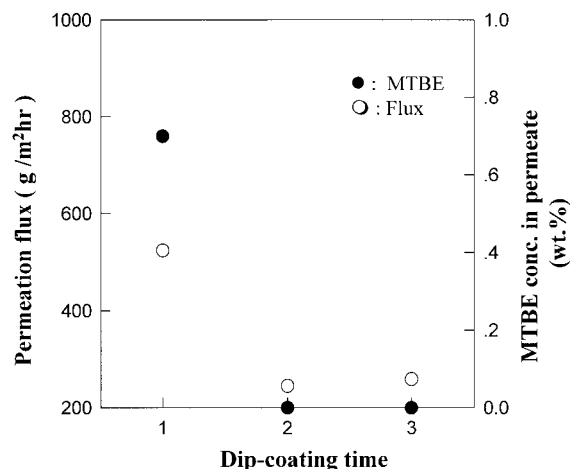


Figure 5 Permeation fluxes and MTBE concentrations in permeate through PIC composite membranes prepared at different dip-coating times in 2.0 wt % SA solution; feed: 75/25 wt % MTBE/methanol mixture; operating temperature: 40°C; chitosan content in reaction solution: 2.0 wt %.

the membrane increase, the sorption of MTBE is more highly affected by the increase in ionic complexation than that of methanol into the membrane. From this point of view, it can be concluded that the decrease in MTBE concentration would result from the increase in ionic crosslinks between SA and chitosan, as discussed above. It can also be concluded that the prepared membranes have a higher affinity for methanol than MTBE, and hence, that they are expected to separate methanol effectively from the MTBE/methanol mixture.

Influence of Membrane Preparation Conditions in Pervaporation Characteristics

Effect of Dip-Coating Time

The effects of the dip-coating conditions on the MTBE concentrations in permeate, and the permeation rates for the PIC composite membranes in a 75/25 wt % MTBE/methanol mixture at 40°C by pervaporation, are shown in Figure 5. The complex membranes were fabricated with a chitosan solution of 2.0% and complexation time of 10 min to characterize its membrane performance. As can be seen in Figure 5, the overall permeation flux, and MTBE concentration in permeate, decreased considerably with an increase in the dip-coating time, and when the dipping time was more than two times, the MTBE component was not detected by our GC. Furthermore,

in the case of the third dipping time, the permeation flux was larger than in that of the second. To investigate this permeation phenomenon, the morphology of the composite membranes prepared at different dipping times, which was analyzed by SEM, is shown in Figure 6. As the dip-coating time increased, an increase in the thickness of the coating layer appeared. However, in the case of the third dipping time, a smaller coating layer of SA than in the second was observed. It is supposed that the effect of dissolving by water component of coating solution, which acts predominantly on the formation of SA matrix. On the one hand, the overall pervaporation performances of these membranes were excellent for the removal of methanol from MTBE/methanol mixtures. This could be attributed to the physico-chemical properties of PIC membranes; that is,

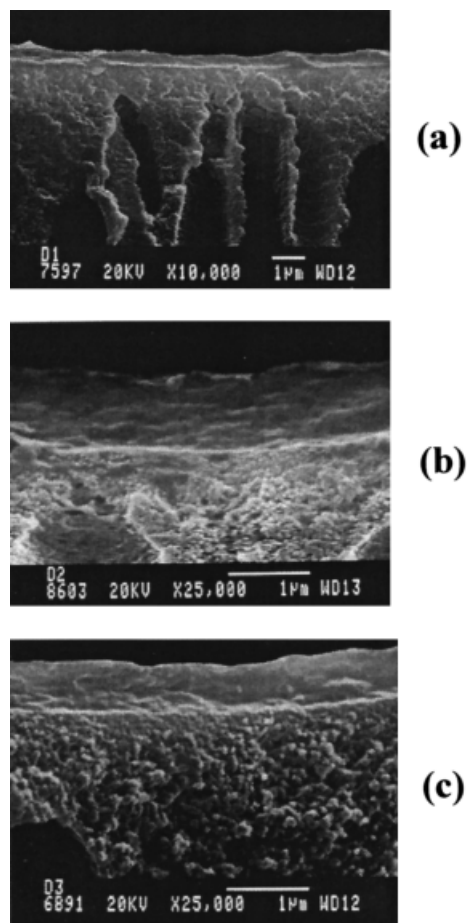
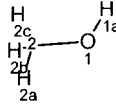
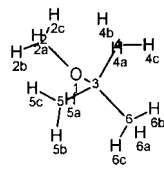


Figure 6 SEM photographs of cross section of PIC composite membranes prepared at different dip-coating time in 2.0 wt % SA solution; chitosan content in reaction solution: 2.0 wt %; (a) one time; (b) two times; (c) three times.

Table I Physicochemical Properties of Methanol and MTBE

Name	Molar Volume (cm ³)	Distance ^a (Å)	Polarizability (10 ⁻²⁴ cm ³)	3D Structure Optimized
Methanol	42.5	2.8226 (H _{2b} -H _{1a})	3.25 ± 0.5	
MTBE	117.4	5.1549 (H _{2b} -H _{6b})	10.67 ± 0.5	

^a Value was calculated by 3D program of Advanced Chemistry Development, Inc.

the methanol molecules can penetrate preferentially because of a high affinity of the PIC membrane for methanol, but MTBE is difficult to diffuse because of certain molecules that are larger than methanol, as shown in Table I. As a result, from Figures 5 and 6, it can be seen that the dipping time on the preparation of SA matrix influences the pervaporation performance of the polyion complex composite membranes.

Effect of Chitosan Solution in the Complexation

Figure 7 shows the permeation fluxes and MTBE concentration in the permeate as a function of chitosan content, for the separation of a 75/25 wt % MTBE/methanol mixture through the PIC composite membrane. With increasing chitosan content, MTBE concentration in the permeate decreased from 1.21 to 0% (no detection), and the permeation flux also decreased increasingly from 331 to 245 g/m² h. Particularly, the composite membrane prepared with 2.0/2.0 wt % SA/chitosan exhibited only methanol permeation, as well as the high flux of above 240 g/m² h. Thus, the overall prepared membranes showed excellent pervaporation performance in the separation of MTBE/methanol mixture. For this reason, it can be deduced that when the ion complex formation progresses by electrostatic interaction between the carboxyl groups (—COO⁻) of SA and the protonated amine groups (—NH₃⁺) of chitosan, the chain mobility of the membrane could be reduced more by ion complex; thereby, the resulting membrane tends to have a more rigid and compact structure as the chitosan content is increased. Consequently, the permeation rate de-

creases dramatically with the increase of chitosan content. Furthermore, these membranes are possessed of the ionic morphology such as —COO⁻NH₃⁺— and this structure appears to be the coulombic interaction for the polar components. For that reason, the preferential penetration of polar components through the charged ionic structure occurs by electrostatic interaction, rather than by hydrogen-bonding interaction. Essentially, the coulombic interactions between the carboxylic group of SA and the protonated amino group of chitosan make the charge density stronger within membrane, leading to an increase in the affinity of a membrane toward polar compo-

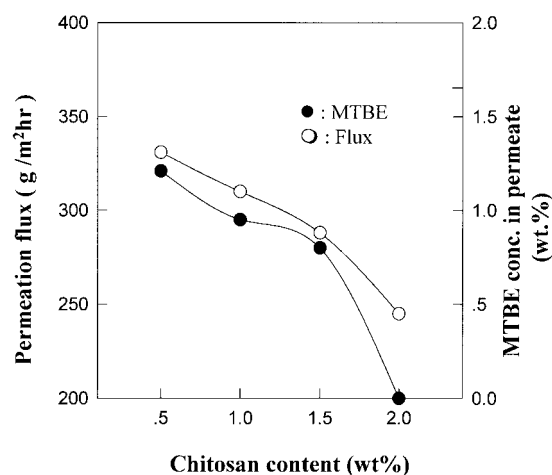


Figure 7 Permeation fluxes and MTBE concentrations in permeate through PIC composite membranes prepared at a different chitosan contents for 2.0 wt % SA content; feed: 75/25 wt % MTBE/methanol mixture; operating temperature: 40°C.

ment, and thus resulting in high selectivity of a membrane toward polar component. For this penetration behavior, it was reported previously by Mochizuki et al. that the ionic crosslinking is stronger than that by the coordination bond, and the ion holes are introduced by the ion complex formation.¹¹ Therefore, the transport phenomena happen mainly through the ion holes of the neutralized membrane, and the permeation rate and separation factor are also determined by the activity of ion holes as a result of the degree of neutralization. Therefore, the PIC composite membranes absorb methanol molecules very selectively and diffuse them. Finally, it seems that the MTBE concentration in the permeate decreases because the ionic crosslinking density of PIC composite membrane increases with the increase of chitosan content, and the permeation rate decreases. Namely, the permeation behavior of PIC composite membranes, prepared with different content levels of chitosan, is affected by the strong interaction between the membrane and methanol, as well as the difference in molecular size. Consequently, the permeation rate decreases gradually with the increase of the ionic crosslinking density in the membrane, and the MTBE concentration in the permeate also is decreased to a point of no detection. The reflections on this conduct can be confirmed by plotting individual fluxes against the concentration of methanol and that of MTBE in permeate, as shown in Figure 8. In general, the permeation rate highly depends on the thickness and crosslinking density of the prepared membrane. Accordingly, as the membrane thickness and crosslinking density greatly increase, the permeation rate decreases by the decrease in diffusion rate of permeates. In this work, when the chitosan content increases from 0.5 to 2.0 wt %, the membrane thickness increases and the permeation rate of PIC composite membrane decreases noticeably. Looking at the permeation rates of each individual component in Figure 8, the overall flux decreases linearly with the increase of chitosan content, and MTBE flux and MTBE concentration in the permeate decrease with an increase of the ion complex formation. Thus, as the degree of ion complex formation increases, the permeation rate decreases because of the increase of ionic crosslinking density. In other words, during further progressing of ion complex formation, the membrane has a more compact network structure. Therefore, as the formation of ion complex decreases the local motion of the membrane molecules, the

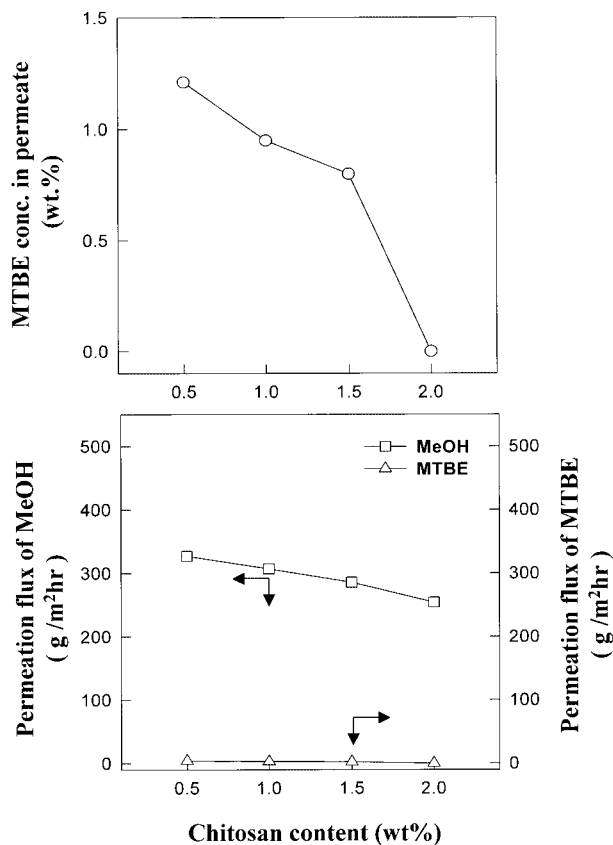


Figure 8 Individual fluxes of methanol and MTBE through PIC composite membranes prepared at a different chitosan contents for 2.0 wt % SA content; feed: 75/25 wt % MTBE/methanol mixture; operating temperature: 40°C.

larger size MTBE molecules can hardly penetrate into the membrane and diffuse out to the permeate side, which results in the increase of permselectivity.

Effect of Complexation Time

Figure 9 presents the effect of complexation time on the permeation fluxes and MTBE concentration in permeate for a 75/25 wt % MTBE/methanol mixture at 40°C. With increasing complexation time, MTBE concentration in permeates decreased somewhat, but the total permeation fluxes decreased markedly more than the complexation time of 10 min. This phenomenon can be explained by the increase of the thickness of active layers by the complexation reaction between —NH_3^+ groups of chitosan and the carboxylate groups of SA, as shown in Figure 10. In principle, flux and separation factors of the membrane are usually strongly dependent on their structure and

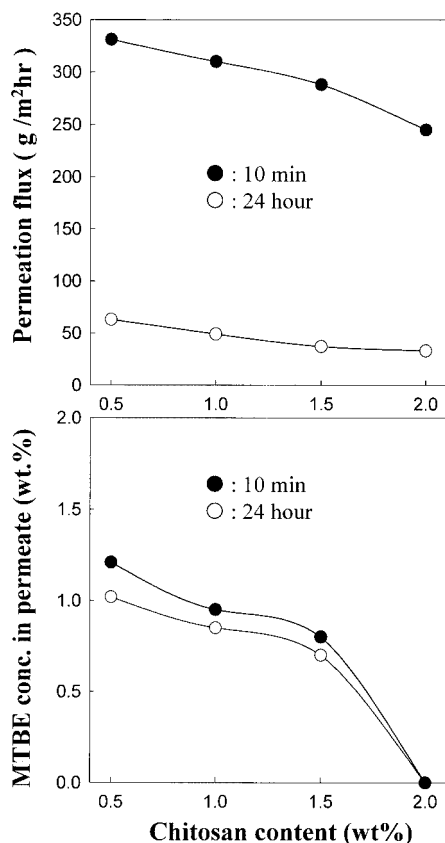


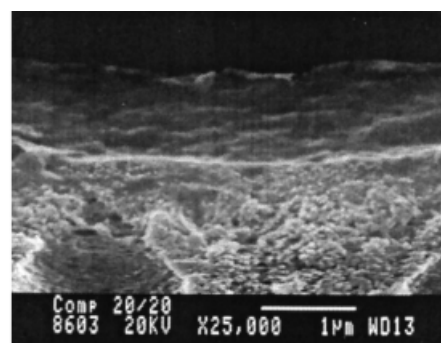
Figure 9 Permeation fluxes and MTBE concentrations, in permeate of PIC composite membranes, with the complexation time of 1 day; feed: 75/25 wt % MTBE/methanol mixture; operating temperature: 40°C.

morphology. Therefore, the membrane with higher crosslinking density has a more compact network structure and a lesser membrane mobility, resulting in less flux and less liquid solubility. Also, in the case of complexed membrane, when the complexation time is longer, the ionic crosslinking density in the membrane would increase with the reaction time, and so the above permeation results for the complexation time can be explained in terms of more compact structural changes, as well as increasing the thickness of the active layer, as shown in Figure 10. As a result, the PIC membrane prepared with longer complexation time shows lower permeant concentration and less preferential sorption toward MTBE than that which was prepared with a complexation time of 10 min, which would cause less permeation flux for a MTBE/methanol mixture. Therefore, the overall separation factor increased correspondingly with complexation time, and the total permeation flux was decreased because of the reduced chain mobility of complexed membranes.

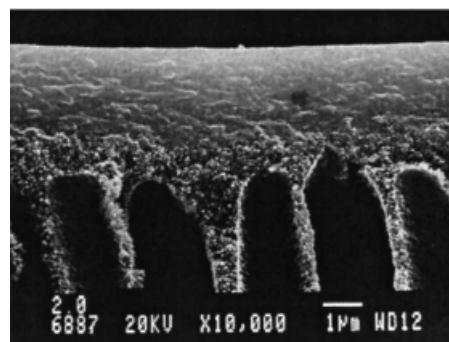
Influence of Permeation Conditions in Pervaporation Characteristics

Effect of Feed Composition

The effect of methanol concentration in the feed solution on the permeation flux and MTBE concentration in the permeate through the complex membranes at 40°C is shown in Figure 11. By increasing methanol concentration in the feed, the permeation flux increased remarkably, whereas the MTBE concentration in the permeate was so low over the entire range of MTBE/methanol mixtures that it could not be detected chromatographically. The methanol concentrations in the permeate were higher than those found in the sorption, as shown in Figure 4. In general, the separation mechanism of liquid mixtures, through polymer membrane in pervaporation, is due to the difference of the solubility of



(a)



(b)

Figure 10 SEM photographs of cross section of PIC composite membranes, with the complexation time of 10 min and 1 day; chitosan content in reaction solution: 2.0 wt %; (a) 10 min; (b) 1 day.

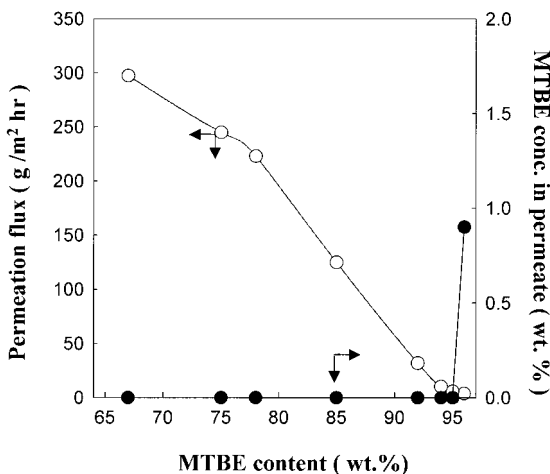


Figure 11 Effect of feed composition on the permeation flux and MTBE concentration in permeate for PIC composite membranes; feed: 75/25 wt % MTBE/methanol mixture; operating temperature: 40°C.

permeants into the polymer membrane in the sorption stage and of the diffusivity of permeants in the polymer membrane in the diffusion stage. In the case of this membrane, the methanol concentration in the permeate was higher than that in the membrane. This result suggests that the methanol permselectivity depends on both the sorption and the diffusion stage in the solution-diffusion model. As can be seen from Table I, in fact, the polarizability of methanol molecules is smaller than that of MTBE, and the molecular size of methanol is also smaller than that of MTBE. These are very important to determine both the sorption and the diffusion selectivity, to discuss the separation mechanism for the MTBE/methanol mixture through the PIC membrane. That is, in the first step, the methanol molecules are preferentially sorbed into the membrane; in the second step, the methanol molecules, which have smaller molecular size than the MTBE molecules, can predominately diffuse and, consequently, selectively permeate. From the above results, it was considered that the methanol permselectivity is significantly attributable to both high sorption selectivity and very high diffusion selectivity. On the other hand, in the case of this membrane, the usual trade-off between selectivity and permeability did not appear in the MTBE/methanol mixture. These anomalous permeation characteristics might be explained on the basis of physicochemical properties of PIC membrane, these being the strong ionic crosslinking structure and high polarity by an ionic complex struc-

ture such as $-\text{COO}^- + \text{NH}_3-$ in the backbone, which could preferentially sorb the methanol component in the feed and almost permeate only the methanol molecule. Particularly, the MTBE concentration in the membrane on the equilibrium sorption and in the permeate also was very small, as can be seen from Figures 4 and 11, and furthermore, it was unchanged despite an increase of methanol component in the feed. Therefore, it could be considered that the plasticization phenomenon did not occur in the membrane by methanol molecules because of a strong ionic crosslinking structure.

Effect of the Operating Temperature

The dependence of the MTBE concentration in the permeate and the permeation flux on the operating temperature for a 75/25 wt % MTBE/methanol mixture is presented in Figure 12. There is a general tendency that the higher temperature permeation flux is still acceptable, whereas the separation factor decreases with the temperature. This is because the frequency and amplitude of the polymer chain motions become larger with increasing operating temperature. In the case of these membranes, however, both the separation factor and the permeation flux increased with increasing operating temperatures, as shown in Figure 12. Moreover, in some cases the MTBE concentration in the permeate appeared at almost 0%. This result suggests that when the operating temperature increases, the diffusion rate of methanol molecules in the membrane increases gradually but that of MTBE decreases because of the thermal motion of the polymer chains. In addition, according to the free volume theory, increasing temperature can increase the thermal motion of polymer chain and generate more free volume in the polymer matrix to facilitate sorption and diffusion of permeant in membrane. Therefore, in the case of this result, also, the permeability of MTBE must increase but the MTBE concentration in the permeate decreased with the increasing of operating temperature, and so it is considered that the thermal motion of polymer chains in the membrane could produce to decrease the diffusivity of MTBE molecules. This assumption can be confirmed through the individual flux of methanol and MTBE plotted in Figure 13. As the operating temperature increases, the permeation flux of methanol increases but that of MTBE decreases. Accordingly, it is assumed that the thermal motion of the poly-

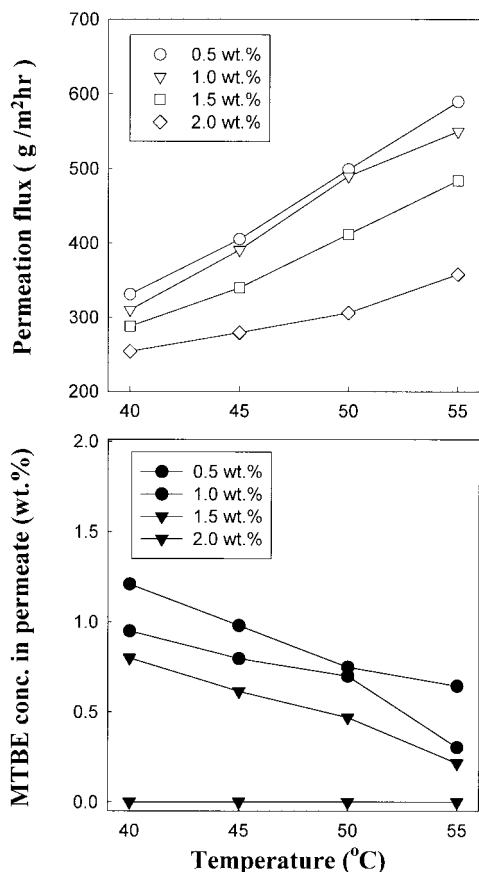


Figure 12 Effect of operating temperature on the permeation flux and MTBE concentration, in permeate for PIC composite membranes, prepared at a different chitosan content for 2.0 wt % SA content in a 75/25 wt % MTBE/methanol mixture.

mer chains could obstruct the diffusion of MTBE molecules in the membrane and play a dominant role in increasing the separation factor. Thus, permeation phenomenon of PIC membranes may be attributed to a specific characteristic, such as the rigid properties and strong ionic crosslinking structure of the PIC membranes.¹²

CONCLUSIONS

In this article, the composite membranes were prepared by alternating electrostatic adsorption of sodium alginate and chitosan on polysulfone-supporting membrane, and in the pervaporation of the MTBE/methanol mixtures, the effects of dip-coating time, complexation time, polymer concentration, feed composition, and operating temperature on the membrane per-

formance were investigated. The extent of the ionic complexation increased with the increase of chitosan content in the reaction solution and the swelling behavior also was found to depend on the degree of ionic complexation. In the case of the preparation conditions, the PIC membranes exhibited that the overall permeation flux and MTBE concentration in permeate decreased considerably with an increase in the dip-coating time, chitosan content, and complexation time. Specially, when both the dipping time and the polymer content were above two times and 2.0%, respectively, MTBE component in permeate was not detected by our GC, but the permeation flux decreased highly compared to that at the reaction time of 10 min, as the complexation time increased. This result indicates that, as the formation of ion complex decreases the local motion of the membrane

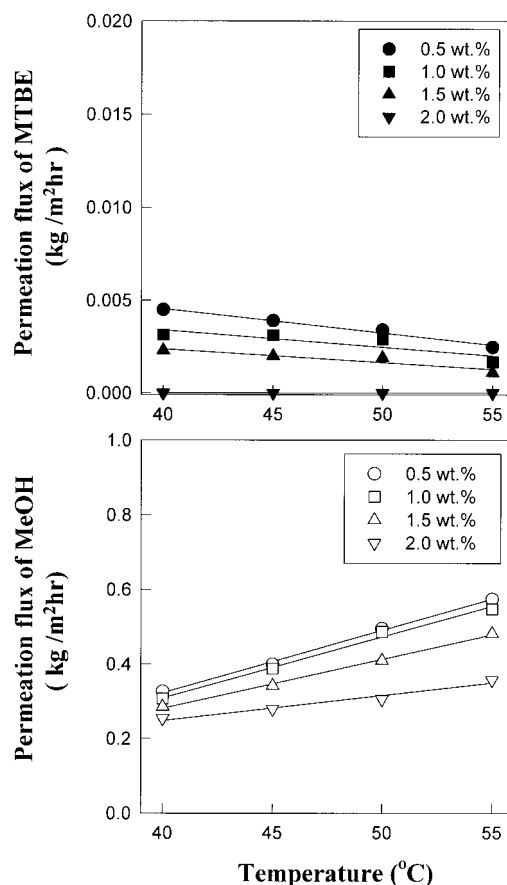


Figure 13 Effect of operating temperatures on the individual fluxes of methanol and MTBE, for PIC composite membranes, prepared at a different chitosan content for 2.0 wt % SA content in a 75/25 wt % MTBE/methanol mixture.

molecules, the larger MTBE molecules were more difficult to permeate into the membrane and to diffuse out to the permeate side, which resulted in the increase of permselectivity. Second, in the case of operating conditions, concerning the performance of their membranes, it appeared that with the increase of methanol concentration in the feed, the permeation flux increased remarkably, whereas the MTBE concentration in the permeate was so low over the entire range of MTBE/methanol mixture. Also, in the case of these membranes, the separation performance was improved as the temperature of feed solution increased.

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