

Pervaporation Separation of MTBE–Methanol Mixtures Using Cross-linked PVA Membranes

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ABSTRACT: Poly(vinyl alcohol)(PVA)/poly(acrylic acid)(PAA) and PVA/sulfosuccinic acid (SSA) membrane performances have been studied for the pervaporation separation of methyl *tert*-butyl ether (MTBE)/methanol (MeOH) mixtures with varying operating temperatures, amount of cross-linking agents, and feed compositions. Typically, the separation factor, about 4000, and the permeation rate, 10.1 g/m²/h, were obtained with PVA/PAA = 85/15 membrane for MTBE/MeOH = 80/20 mixtures at 50°C. For PVA/PAA membranes, it could be considered that the flux is affected by the structural changes of the membranes due to the cross-linking and the free carboxylic acid group also took an important role in the separation characteristics through the hydrogen bonding with PVA and the feed components leading to the increase of flux. The latter membrane of the 5% SSA membrane shows the highest separation factor of 2095 with the flux of 12.79 g/m²/h for MTBE/MeOH = 80/20 mixtures at 30°C. Besides the swelling measurements were carried out for pure MTBE and MeOH, and MTBE/MeOH = 90/10, 80/20 mixtures using PVA/SSA membranes with varying SSA compositions. It has been recognized that there are two factors, the membrane network and the hydrogen bonding in the swelling measurements of PVA/SSA membranes. These two factors act interdependently on the membrane swelling. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1699–1707, 2000

Key words: pervaporation; MTBE-methanol; poly(vinyl alcohol); sulfosuccinic acid; cross-linking

INTRODUCTION

Increasing environmental pollution problems and the subsequent emergence of more strict regulations on fuel exhaust gases led to progressive changes in gasoline compositions. Among these changes, the amount of lead additive in gasoline, which is lowering the octane ratings and showing the poisonous effects on exhaust catalytic mufflers, indicates the reduction trend. This demands that petroleum refiners increase gasoline contents of other hydrocarbon components having

high octane numbers, such as benzene/toluene/xylene mixtures, and to look for other new octane enhancers. However, due to the toxicity of aromatic compounds, their levels will rather be reduced than increased limiting the available options.^{1,2}

Oxygenated compounds such as alcohols or ethers have also high octane numbers. It has been reported that the addition of oxygenated compounds into gasoline led to reduce the emissions of carbon monoxide and unburned hydrocarbons. One of oxygenated fuel additives, methyl *tert*-butyl ether (MTBE), has been extensively tested if this could be more suitable than other alcohols as octane enhancer. As a result, it has been proven that MTBE could meet the requirement of the

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Clean Air Act amendments of the United States government.^{3,4}

A typical MTBE production can be obtained from the reaction of pure methanol (MeOH) and isobutylene. The excess MeOH in MTBE reaction must be removed for recycle to the reactors and for high purity ether products and C₄ to C₇ raffinate. The effluent of the reactor contains, mainly, the MTBE produced and the untreated excess of MeOH. The effluent mixtures are first split in the debutanizer into a bottom MTBE product and a near azeotropic mixture of MeOH and MTBE, the composition of which is 14.3 wt % MeOH at 760 mmHg. This mixture is then separated by water washing, after which MeOH and the water mixture are distilled to recycle MeOH to the reactor.^{1,5} However, it is well known that this conventional separation process is both energy- and capital-intensive.

Pervaporation has been considered as an alternative separation process. Doghieri et al.⁶ studied the pervaporation separation of MeOH-MTBE mixtures through modified poly(phenylene oxide) membranes under the various operating conditions. In cases where the MeOH concentrations in feed varied from 1.1 to 20.9 wt %, the selectivities showed from 23.4 to 7.7, whereas the MTBE transmembrane flux initially decreased from 232 to 120 g/m²/h when the alcohol concentration in the feed increased from 0 to 3.2%; then it decreased up to 210 g/m²/h for 21% MeOH. Park et al.² and Park⁷ investigated the pervaporation separation of MTBE-MeOH mixture using poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) blended membranes. As the contents of PAA in the blend increased, the selectivity toward MeOH increased. They showed that the selectivity of about 300 at the composition of 10% MeOH was obtained for 20 wt % PAA membrane in the blend. Chen et al.⁸ at Air Products & Chemicals Inc. developed the Total Recovery Improvement for MTBE (TRIM) process, which is an improved esterification process for ether production, especially MTBE, by incorporating one or more pervaporation membrane steps in the purification section downstream of the esterification reactors to remove alcohol from the product stream using cellulose acetate membranes. The separation factors ranged from 14 to 400 over a wide range of feed MeOH concentration, temperature, and membrane type in the MTBE/MeOH binary system. Pasternak et al.⁹ at Texaco Inc. developed the PVA membranes cross-

linked with glutaraldehyde and the fluorinated resins to separate MTBE and MeOH mixtures. The PVA membranes showed the separation factor 233 (99.9 wt % in permeate) with the permeation rate of 0.43 kg/m²/h for 81.1 MeOH wt % in feed. The fluorinated membranes, however, were exposed to the lower MeOH concentration, 11–16 wt %, in feed. In this case the separation factors of 4.7–50.9 were obtained whereas the flux showed 0.02–0.23 kg/m²/h. Therefore, they concluded that PVA membranes would be preferred for a high concentration of MeOH and the preferred membranes for a low concentration may be ion exchange membranes. Craig¹⁰ developed the composite poly(4-vinyl pyridine) membranes cross-linked with dibromobutene mounted onto polyacrylonitrile for the purpose of the separation of MTBE/MeOH/C₅ mixture. Typically the separation factor 442 and the flux 2.06 kg/m²/h were obtained when the feed concentrations of MTBE/MeOH/C₅ were 19.8, 12.1, and 67.9 wt %, respectively. Park et al.^{2,7} investigated the separation of MTBE and MeOH mixtures using PVA/PAA blended and cross-linked membranes with gradual increasing of PVA contents. When the feed concentration of MeOH was 20%, PAA/PVA = 70/30 blended membrane showed the selectivity, about 170 and the flux, about 0.3 kg/m²/h, whereas the cross-linked membrane with same composition gave almost same results with those of the blended membranes. Lee et al.¹¹ investigated the application of polymer membranes, cellulose acetate (CA), polyarylate (PA), and polycarbonate (PC), to the catalytic decomposition of MTBE. It was revealed that all the membranes showed larger permeability of MeOH than that of MTBE. The perm-selectivity of MeOH/MTBE was in the order of CA > PC > PA. As a result, the membrane reactor showed better performance than the corresponding fixed bed reactor.

This article deals with the separation of MTBE-MeOH mixtures using cross-linked PVA membranes with PAA and sulfosuccinic acid (SSA) by pervaporation technique. The operating temperatures, MeOH concentration in feed mixtures, and the PAA and SSA concentrations in PVA membranes will be varied to investigate the separation performance of PVA/PAA and PVA/SSA membranes and the optimum separation characteristics. In addition, for PVA/SSA membranes, the swelling measurements are carried out to study the transport phenomena.

EXPERIMENTAL

Materials

Fully hydrolyzed PVA with a molecular weight of 50 000 and PAA with a molecular weight of 2000 (25 wt % in water) were purchased from Showa Chemical Co. (Tokyo, Japan) and Aldrich Co. (Milwaukee, USA), respectively. MTBE, SSA, and MeOH were analytical grade from Aldrich Co. The ultrapure water used was the ultrapure water produced from the SK system.

Membrane Preparation

Aqueous 10 wt % PVA solutions were prepared by dissolving preweighed quantities of dry PVA in ultrapure water and heating at 90°C for at least 6 h.¹² Aqueous 25 wt % PAA solutions were diluted to 10 wt % solutions and the aqueous 10 wt % SSA solutions were prepared. Then two polymer solutions were mixed together by varying each component composition to form a homogeneous solution for at least 1 day at room temperature. Homogeneous membranes were cast onto a plexiglass plate using a Gardner knife with predetermined drawdown thickness. The membranes were allowed to air dry at room temperature, and completely dried membranes were then peeled off. The dried and blended membranes were then heated in a thermosetted oven at 150°C for 1 h. The thickness of the resulting membranes showed 15–20 μm. The prepared membranes were then stored in solutions, such as 10 and 20 wt % of MeOH, to be separated for further use.

Swelling Measurement

The sorption capacity of the membrane was measured by immersing the membrane samples in the mixtures of MTBE and MeOH. The homogeneous membranes were cut into a shape of slab with dimensions of 10 × 50–80 (mm). The slab soaked in the mixtures for 2 days for an equilibrium swelling. The swollen slab was taken out and then wiped with the cleansing tissue. Both ends of the slab were marked with a pen as quickly as possible and the distance (L) between the marks was measured with Venier Caliper with an accuracy of ±10 μm. After drying, the length (L_0) the dry slab were checked. The solubility of the mixtures in the swollen membrane, ϕ , was calculated from¹³:

$$\phi = \frac{R_L^3 - 1}{R_L^3}, \quad \left(R_L = \frac{L}{L_0} \right) \quad (1)$$

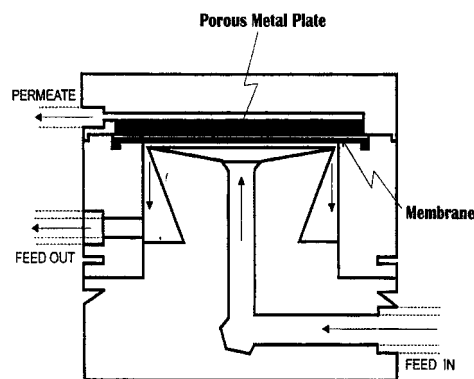


Figure 1 Configuration of the pervaporation cell used in this study.

Pervaporation

The membrane cell and the experimental apparatus used in this study are illustrated in Figures 1 and 2, respectively. The pervaporation separation experiments were performed employing two stainless steel pervaporation cell (Fig. 1). A feed mixture enters the cell through the center opening, flows radially 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 14.2 cm². The detailed descriptions can be found in reference 14. The pervaporation experiments of MTBE-MeOH mixtures were conducted at 25, 35, and 45°C. Upon reaching steady-state flow conditions, product samples were collected with timed intervals, isolated from the vacuum system, and weighed. During the experiments, the downstream pressure, 0.3–1 torr, was maintained. The composition analysis of the permeate was done using gas chromatography equipped with Porapak Q column. The following relationship was used to calculate the separation factor:

$$\alpha_{ij} = (y_i/y_j)/(x_i/x_j) \quad (2)$$

where x is the feed composition, y is the permeate composition, and component i is the preferentially permeating component.

RESULTS AND DISCUSSION

PVA/PAA Cross-Linked Membranes

The resulting PVA/PAA cross-linked membranes have been successfully applied to the pervapora-

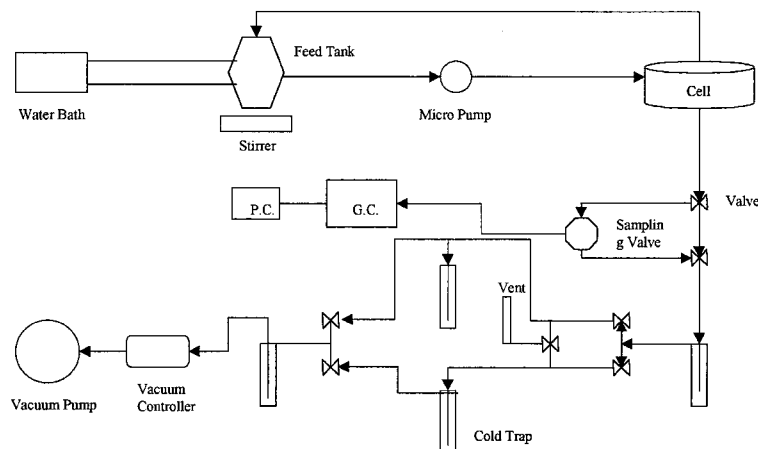


Figure 2 Schematic diagram of pervaporation apparatus used in this study.

tion separations of water-alcohol^{14,15} and water-acetic acid mixtures.¹⁶ According to this studies, the flux of alcohols was observed to increase in the order of water > methanol > ethanol > *iso*-propyl alcohol. This result was coincided with Yoshikawa et al.'s studies,¹⁷ which indicated that the hydrogen bonding abilities toward the hydroxyl and carboxyl groups decreased in the following order: water > methanol > ethanol > acetonitrile. Therefore, it is expected that the methanol flux has to be larger than the MTBE flux.

First, the PVA/PAA = 75/25 membrane, which showed the highest separation factor for water-alcohol mixtures, was exposed to investigate the effect of the operating temperatures for MTBE/MeOH = 80/20. This results are illustrated in Figure 3. Generally speaking, as the cross-linking density in a polymer increases, the resulting membrane has a more compact network, resulting in less chain mobility. Therefore, the free vol-

ume in the polymer decreased. As a result, the solubility of the liquid mixtures declines and the diffusivity, which is governed by the free volume, decreases due to the rigidity of the polymer chains. This might cause the permeation rate through the membrane to decrease as the operating temperature is lowered. Furthermore, because the interaction ability between the each component and the membrane becomes strong as the operating temperatures are lowered, the flux decreases. As can be seen in Figure 3, the permeation rate increases while the separation factor decreases as the operating temperature increases. This figure shows the typical trend of the pervaporation experiments. At 30°C, the separation factor and the permeation rate show 2350 and 10 g/m²/h, respectively.

The effect of the feed composition using PVA/PAA = 80/20 membrane is shown in Figure 4. As the MeOH concentration in the feed decreases,

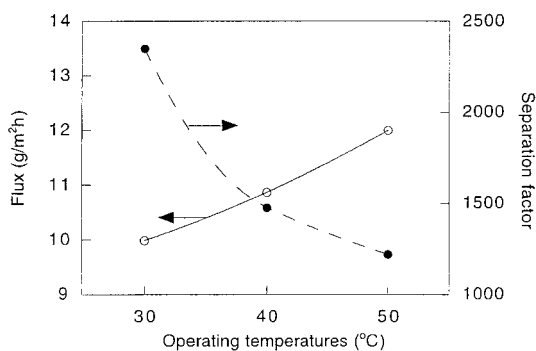


Figure 3 Effect of the operating temperatures for MTBE/MeOH = 80/20 using PVA/PAA = 75/25 membrane on the permeation rate and the separation factor.

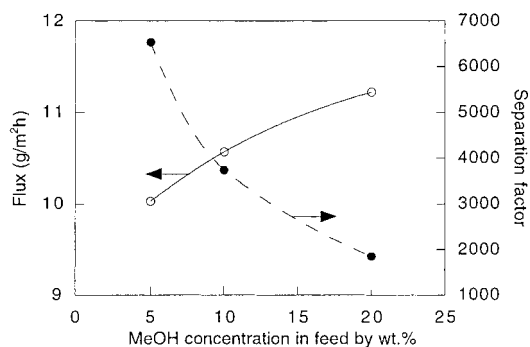


Figure 4 Effect of the feed composition using PVA/PAA = 80/20 membrane on the permeation rate and the separation factor at 30°C.

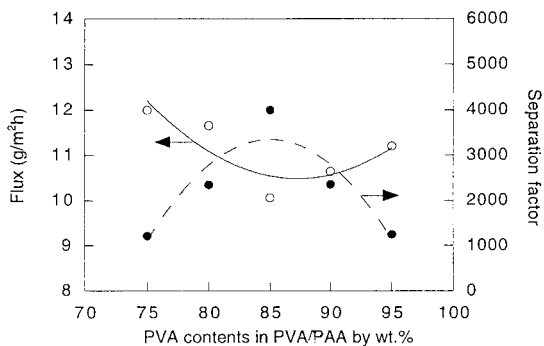


Figure 5 Permeation rate and separation factor for MTBE/MeOH = 80/20 mixtures with varying PAA contents at 50°C.

the flux decreases while the separation factor increases. When the membrane has less chances to contact with the more preferential composition, MeOH, in the feed, the membrane swells less and, as a result, the permeation rate becomes less. Typically the PVA/PAA = 80/20 membrane shows the permeation rate, 11.2 g/m²/h, and the separation factor, 1850, for MTBE/MeOH = 80/20 feed composition at 30°C.

Figure 5 illustrates the effect of the amount of the cross-linking agent, PAA, on the pervaporation characteristics for MTBE/MeOH = 80/20 solution at 50°C. As the amount of PAA increases, the permeation rate decreases up to 15% of PAA and then increases whereas the separation factor shows vice versa. As described above, it is natural that the flux could decrease because the membrane network forms more compact due to the more cross-linking effect. However, the erratic result of the increase of flux can be observed in the ranges of >15 wt % PAA even though it could be expected that the flux has to decrease with more addition of PAA, or in other words, more cross-linking reaction. It has been published that there could exist the unreacted carboxylic acid groups in PAA due to the less chain mobility when the amount of PAA is more added.¹⁶ In fact, the esterification reaction between the carboxylic acid in PAA and the hydroxyl group in PVA could occur each other when they are near enough as can be seen in Figure 6. Therefore, the unreacted carboxylic acid group would form the hydrogen bonding with the near hydroxyl group in PVA and also the individual component in feed. The unreacted carboxylic acid group is partly captured in the membrane network whereas the rest could freely exist. This free carboxylic acid group form the hydrogen bonding with the solvents in ques-

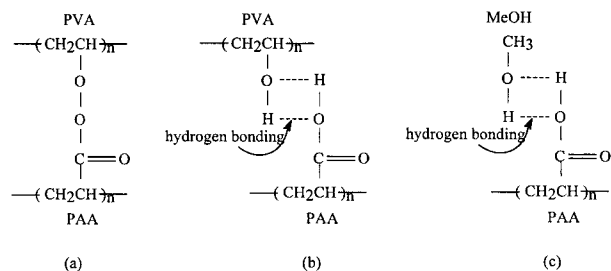


Figure 6 Schematic diagram of (a) cross-linking reaction between PVA and PAA; (b) hydrogen bonding between PVA and PAA; and (c) hydrogen bonding between MeOH and PAA.

tion when the membranes are exposed to the feed so that the membrane swells more than the membrane prepared by just previous composition of PAA (see Fig. 6). Therefore, it leads the flux increase even though the membrane network is quite compact.

PVA/SSA Cross-linked Membranes

Swelling Measurements

Figures 7 and 8 show the solubility, ϕ , of pure MeOH and MTBE with varying SSA contents in PVA membranes, respectively. As explained above, the membrane network would be more compact when the cross-linking degree gets higher whereas the more addition of the hydrophilic cross-linking agent attracts more solvents, in general. As a result, the former would lead to be less space to be physically occupied in the membranes whereas the latter would give a higher solubility. For pure MeOH, the solubility,

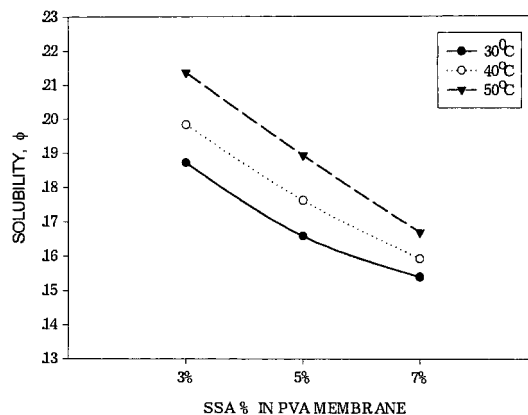


Figure 7 Swelling ratio of PVA/SSA membranes for pure MeOH with varying SSA contents at the operating temperatures.

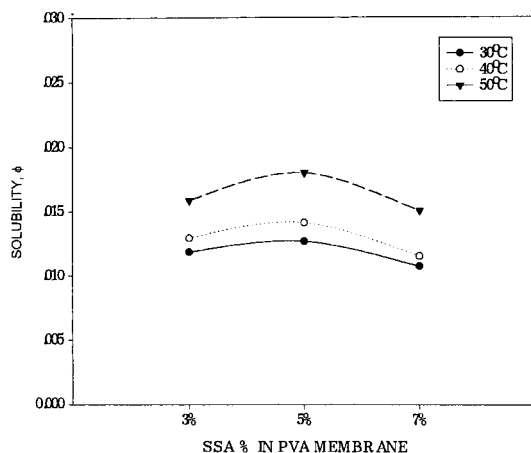


Figure 8 Swelling ratio of PVA/SSA membranes for pure MTBE with varying SSA contents at the operating temperatures.

ϕ , decreases with increasing the cross-linking agents in the membranes even though more hydrophilic group, SSA, is introduced. In this case, the effect of the structural change of the PVA membrane due to the cross-linking reaction is more severe rather than the increase of hydrophilicity with SSA addition on the swelling behavior. However, this analysis could not be applied to the case of pure MTBE, as can be seen Figure 8. First of all, it is worth noting that the ϕ values of MTBE are much lower than the MeOH case because pure MTBE is moderately hydrophobic (see Table I). And the solubility shows the maximum at 5% SSA in PVA membranes whereas the solubilities of 3 and 7% SSA are lower than the value at 5% SSA. It could be considered that the effect of the structural change, i.e., more compact network due to the cross-linking reaction, increased with the more addition of 3–7% SSA, but the hydrogen bonding effect with the solvents may be reduced. The sulfuric acid group in SSA could have the hydrogen bonding force with MTBE and MeOH, and also PVA as well. First, a number of this

Table I Solubility Parameters ($\text{cal}^{1/2}/\text{cm}^{3/2}$) of Solvents and Polymer

Solvent or Polymer	δ_t	δ_d	δ_p	δ_h
Methanol	14.5	7.4	6.0	10.9
MTBE ^a	8.1	7.6	1.7	2.4
PVA ^a	27.0	20.2	9.6	15.1

^a Calculated by the group contribution method proposed by Hoftyzer and van Krevelan.¹⁸

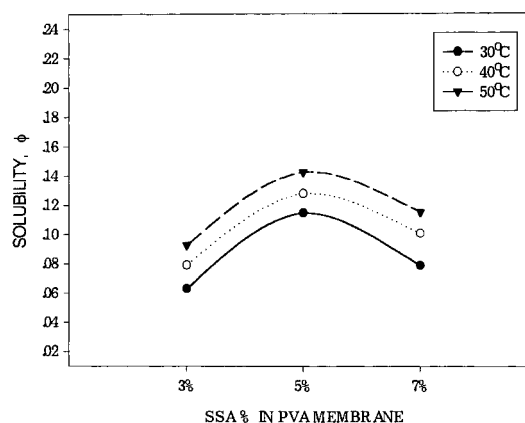


Figure 9 Swelling ratio of PVA/SSA membranes for MTBE/MeOH = 90/10 solutions with varying SSA contents at the various operating temperatures.

sulfuric acid group could form the hydrogen bonding force with the hydroxyl group in PVA rather than with the organic solvents in question. As a result there are not many chances to have the hydrogen bonding with solvents when the membranes were exposed to the solvents. However, a slight increase of the solubility for 3–5% SSA might result in the effect of SSA that is not forming the hydrogen bonds with solvents. Particularly, the cross-linking degree could be balanced with the hydrophilic compound, SSA, at this composition. For 7% SSA, the solubility is lower than the values of 3 and 5% SSA. The hydrogen bonding portion between the sulfuric acid group and the hydroxyl group in PVA might be formed more than the other compositions. And also the more compact network due to the more cross-linking reaction does not allow the sorption of the solvents into the membranes. In summary, there are two factors, the polymer network and the hydrogen bonding in this swelling study. And these factors act interdependently on the membrane swelling behavior.

Figures 9 and 10 illustrate the solubilities for the different compositions of MTBE-MeOH mixtures at same temperatures. The solubilities lies between the values of pure MeOH and MTBE. When the MeOH concentration in the mixtures increases, the higher concentration of MeOH in feed swells the membranes more because higher concentration of MeOH contacts the membranes more than lower concentration of MeOH and meanwhile the other component, MTBE, penetrates into the swollen membranes under the existence of MeOH at the same time. Therefore, the

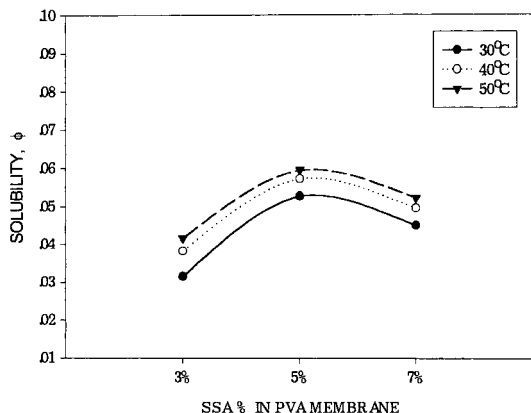


Figure 10 Swelling ratio of PVA/SSA membranes for MTBE/MeOH = 80/20 solutions with varying SSA contents at the various operating temperatures.

solubility of MTBE/MeOH = 80/20 mixture is larger than that of MTBE/MeOH = 90/10 mixture. And it could be considered that the reason why the solubility at 5% SSA shows the maximum is the effect of MTBE that indicates the same trend at 5% SSA for pure MTBE.

Transport Properties

Figures 11 and 12 illustrates the permeabilities and separation factors for MTBE/MeOH = 90/10 mixtures, respectively. The flux and the separation factor shows the same trend as PVA/PAA membranes shown in Figure 5. The swelling measurement indicates the maximum at 5% SSA, as shown in Figures 9 and 10, whereas the flux shows the minimum. Because the permeability,

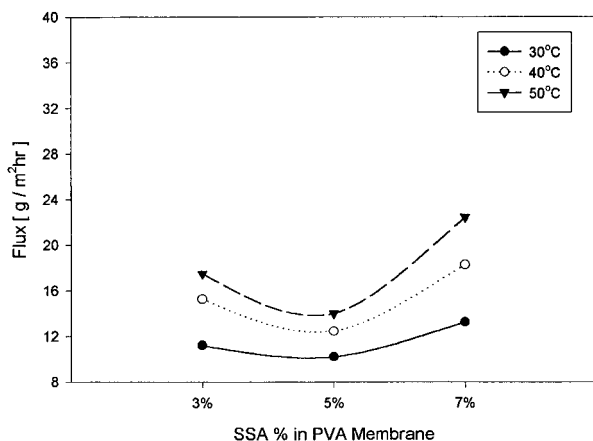


Figure 11 Permeabilities of PVA/SSA membranes for MTBE/MeOH = 90/10 solutions with varying SSA contents at the various operating temperatures.

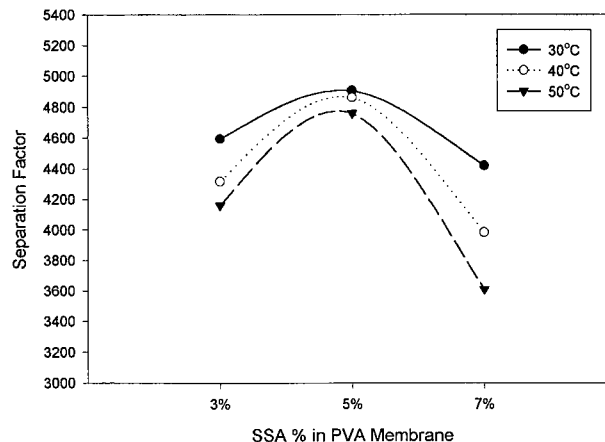


Figure 12 Separation factors of PVA/SSA membranes for MTBE/MeOH = 90/10 solutions with varying SSA contents at the various operating temperatures.

P , is defined as diffusivity (D) times solubility (S), i.e., $P = D \times S$, the effect of the diffusivity may be much lower than that of the solubility at 5% SSA. If it is assumed that the cross-linking effect is over the hydrogen bonding effect at 3% SSA, it could be said that these two factors are balanced at 5% SSA, and the hydrogen bonding effect is over the cross-linking effect at 7% SSA. As described in the section “Swelling Measurement,” the sulfuric acid group pending on PVA chain could form the hydrogen bonding partly with the hydroxyl group in PVA. If the membrane network becomes more compact as the cross-linking reaction proceeds, the sulfuric acid group can form the hydrogen bonding only with the neighbor hydroxyl group due to the less chain mobility. Therefore, according to this description, the flux at 5% SSA may increase or at least maintain the initial flux at 3% SSA, and then the flux at 7% SSA probably has to increase. However, the flux at 5% SSA decreases from the flux at 3% SSA and then increases to the flux at 7% SSA as can be seen in Figure 11. Therefore, it could be concluded that the cross-linking effect might be over the hydrogen bonding effect on the flux at 3% and 5% SSA membranes and this two effects are shown vice versa at 7% SSA membrane. However, when the flux of PVA/SSA membranes is compared with that of PVA/PAA membranes as shown in Figure 5, the former is larger than the latter in the whole range of the cross-linking agent concentrations. This fact would remind of us that the membrane of 3% SSA still has the effect of hydrogen bonding on the flux. The effect of the operating tempera-

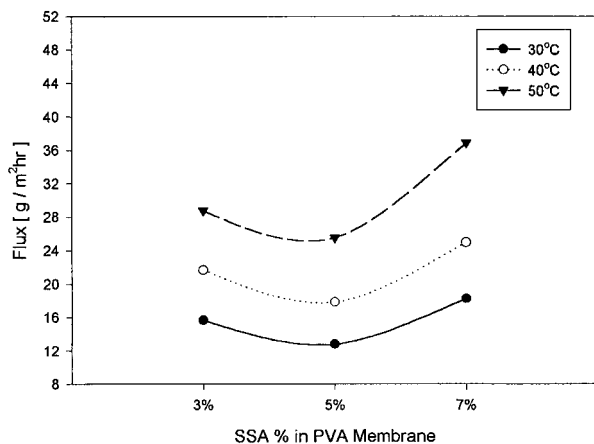


Figure 13 Permeabilities of PVA/SSA membranes for MTBE/MeOH = 80/20 solutions with varying SSA contents at the various operating temperatures.

tures, as expected, leads the flux to increase as the operating temperature increases due to the increase of the chain mobility. And also the separation factor shows the typical trend in pervaporation. In this case, from the viewpoint of the separation factor, the best result of the PVA/SSA membranes shows about 4900 with the flux of 10.23 g/cm²/h for 5% SSA membrane at 30°C.

Figures 13 and 14 illustrates the flux and the separation factor for MTBE/MeOH = 80/20 solution. The curve shapes are the same as in Figures 11 and 12, respectively. The separation factor is lower than those for MTBE/MeOH = 90/10 solution whereas the flux is higher. As described above, the flux could increase because the membrane contacts more MeOH in feed. The 5% SSA membrane shows the highest separation factor of 2095 with the flux of 12.79 g/cm²/h.

CONCLUSIONS

Several conclusions can be drawn from this study as follows:

1. PVA/PAA membranes have been investigated for the pervaporation separation of MTBE/MeOH mixtures, focusing on the effects of operating temperatures, amount of cross-linking agents, and feed compositions. Typically, the separation factor, about 4000, and the permeation rate, 10.1 g/m²/h, were obtained when PVA/PAA = 85/15 membrane was exposed to MTBE/MeOH = 80/20 mixtures at 50°C. Up to 15

wt % of PAA addition to PVA, it could be considered that the flux is affected by the structural changes of the resulting membranes due to the cross-linking. The free carboxylic acid group also took an important role in the separation characteristics through the hydrogen bonding with PVA and the feed components leading to the increase of flux.

2. The swelling measurements were carried out for pure MTBE and MeOH, and MTBE/MeOH = 90/10, and 80/20 mixtures using PVA/SSA membranes with varying SSA compositions. There are two factors, the membrane network and the hydrogen bonding, in the swelling measurements of PVA/SSA membranes. These two factors act interdependently on the membrane swelling.
3. The sulfuric acid group in SSA took an important role in the membrane performance. The cross-linking effect might be over the hydrogen bonding effect due to the sulfuric acid group at 3 and 5% SSA membranes, and these two factors act vice versa on 7% SSA membrane. In this case, the 5% SSA membranes shows the highest separation factor of 2095 with the flux of 12.79 g/m²/h for MTBE/MeOH = 80/20 mixtures at which this mixtures show near the azeotropic composition.
4. Pervaporation separation was also carried out for MTBE/MeOH mixtures using PVA/SSA membranes at various operating tem-

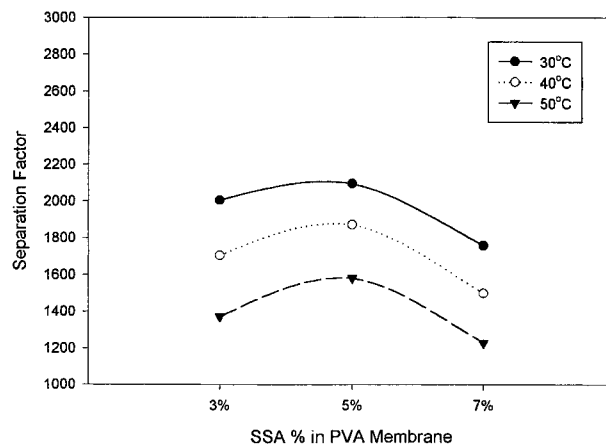


Figure 14 Separation factors of PVA/SSA membranes for MTBE/MeOH = 80/20 solutions with varying SSA contents at the various operating temperatures.

peratures, 30, 40, and 50°C. Both flux and separation factor show the typical trend in pervaporation at each operating temperatures. At 50°C, the flux, 36.9 g/m²/h, and the separation factor, 1230, were obtained for MTBE/MeOH = 80/20 solution and 7% SSA in PVA membrane.

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