Comparison of Pervaporation and Vapor Permeation Separation Processes for MTBE-methanol Systems

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Abstract : This paper deals with the separation of MTBE-methanol mixtures using crosslinked Poly(vinyl alcohol)(PVA) membranes with sulfur-succinic acid(SSA) as a crosslinking agent by pervaporation and vapor permeation technique. The operating temperatures, methanol concentration in feed mixtures, and SSA concentrations in PVA membranes were varied to investigate the separation performance of PVA/SSA membranes and the optimum separation characteristics by pervaporation and vapor permeation. And also, for PVA/SSA membranes, the swelling measurements were carried out to study the transport phenomena. The swelling measurements were carried out for pure MTBE and methanol, and MTBE/methanol=90/10, 80/20 mixtures using PVA/SSA membranes with varying SSA compositions. There are two factors of the membrane network and the hydrogen bonding. In pervaporation separation was also carried out for MTBE/methanol=90/10, 80/20 mixtures at various temperatures. The sulfuric acid group in SSA took an important role in the membrane performance. The crosslinking effect might be over the hydrogen bonding effect due to the sulfuric acid group at 3 and 5% SSA membranes, and this two factors act vice versa on 7% SSA membrane. In this case, the 5% SSA membrane shows the highest separation factor of 2,095 with the flux of 12.79 $g/m^2 \cdot hr$ for MTBE/methanol=80/20 mixtures at 30℃ which this mixtures show near the azeotopic composition. Compared to pervaporation, vapor permeation showed less flux and similar separation factor. In this case, the flux decreased significantly because of compact structure and the effect of hydrogen bonding. In vapor permeation, density or concentration of methanol in vaporous feed is lower than that of methanol in liquid feed, as a result, the hydrogen bonding portion between the solvent and the hydroxyl group in PVA is reduced in vapor permeation. In this case, the 7% SSA membranes shows the highest separation factor of 2,187 with the flux of 4.84 $g/m^2 \cdot hr$ for MTBE/methanol=80/20 mixtures at 30℃.

1. 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 petroleum refiners to 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 limitations of the available options [1,2].

Oxygenated compounds like 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 Clean Air Act amendments of the United States government [3,4].

Pervaporation has been considered as an alternative separation process. Doghieri et al. [5] studied the pervaporation separation of methanol-MTBE mixtures through modified poly(phenylent oxide) membrane under the various operating conditions. In cases where the methanol concentrations in feed varied from 1.1 to 20.9 wt%, the selectivities showed from 23.4 to 7.7 while the MTBE transmembrane flux initially decreased from 232 to 120 $g/m^2 \cdot hr$ when the alcohol concentration in the feed increased from 0 to 3.2%; then it decreased up to 210 $g/m^2 \cdot hr$ for 21% methanol. Park et al. [2] and Park [6] investigated the pervaporation separation of MTBE-methanol mixture using poly(vinyl alcohol) (PVA) and poly (acrylic acid) (PAA) blended membranes. As the contents of PAA in the blend increased, the electivity toward methanol increased. They showed that the selectivity of about 300 at the composition of 10% methanol was obtained for 20 wt% PAA membrane in the blend. Chen et al. [7] 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 methanol concen-

tration, temperature, and membrane type in the MTBE/methanol binary system. Pastermak et al. [8] at Texaco Inc. developed the PVA membranes crosslinked with glutaraldehyde and the fluorinated resins to separate MTBE and methanol mixtures. The PVA membrnaes showed the separation factor 233 (99.9 wt% in permeate) with the permeation rate of 0.43 $kg/m^2 \cdot hr$ for 81.1 methanol wt% in feed. The fluorinated membranes, however, were exposed to the lower methanol concentration, 11 to 16 wt%, in feed. In this case the separation factors of 4.7 to 50.9 were obtained while the flux showed 0.02 to 0.23 $kg/m^2 \cdot hr$. Therefore, they concluded that PVA membranes would be preferred for a high concentration of methanol and the preferred membranes for a low concentration may be ion exchange membranes. Craig [9] developed the composite poly (4-vinyl pyridine) membranes crosslinked with dibromobutene mounted onto polyacrylonitrile for the purpose of the separation of MTBE/methanol/C₅ mixture. Typically the separation factor 442 and the flux 2.06 $kg/m^2 \cdot hr$ were obtained when the feed concentrations of MTBE/methanol/C₅ were 19.8, 12.2 and 67.9 wt%, respectively. Park et al [2,6] investigated the separation of MTBE and methanol mixtures using PVA/PAA blended and crosslinked membranes with gradual increasing of PVA concents. When the feed concentration of methanol was 20%, PAA/PVA=70/30 blended membrane showed the selectivity, about 170 and the flux, about 0.3 $kg/m^2 \cdot hr$ while the crosslinked membrane with same composition gave almost same results with those of the blended membranes. Lee et al. [10] 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 methanol than that of MTBE. The perm-selectivity of methanol/MTBE was in the order of CA>PC>PA. As a result, the membrane reactor showed better performance than the corresponding fixed bed reactor.

Vapor permeation is one of new technically feasible membrane processes and an interesting

technical alternative to pervaporation. In vapor permeation [11-13], the whole feed mixture is in a vapor state, so that the separating component just has to permeate through a permselective and non-porous membrane, and the driving force relies on a vacuum on the permeate side which is maintained by an efficient permeate vapor condensation as in pervaporation process. Compared to pervaporation vapor permeation has the advantage that no phase change occurs while going from the feed to the permeate side and therefore the problems involved in supplying the enthalpy of evaporation in the separation process are avoided.

Disadvantage of the separation by vapor permeation, however, are the strong dependence of transmembrane flux and separation characteristics on the feed pressure, the sensitivity to friction losses in the feed stream and the possibility of condensation and hence of the formation of stagnant condensate films partially covering the membrane on the feed side. Furthermore, depending on the state conditions of the feed vapor, the annoying problem of concentration polarization on the feed side of the membrane is often not as distinct as in pervaporation.

This paper deals with the separation of MTBE-methanol mixtures using crosslinked PVA membranes with sulfur-succinic acid (SSA) by pervaporation and vapor permeation technique. The operating temperatures, methanol concentration in

feed mixtures, and SSA concentrations in PVA membranes will be varied to investigate the separation performance of PVA/SSA membranes and the optimum separation characteristics. And also, for PVA/SSA membranes, the swelling measurements are carried out to study the transport phenomena.

2. Experimental

2.1. Materials

Fully hydrolyzed Poly(vinyl alcohol) (PVA) with a molecular weight of 89,000-98,000 was purchased from Showa Chemical Co. (Tokyo, Japan) and Sulfur-succinic acid (SSA) with a formula weight of 198 (70 wt% solution in water) as a crosslinking agent were purchased from Aldrich Co. (Milwaukee, USA), respectively, MTBE, and MeOH were analytical grade from Aldrich Co. The ultrapure water used was the ultrapure water produced from the SK system.

PVA has been studied intensively as a membrane because of its good film-forming, highly hydrophilic, and good chemical-resistant properties. Membrane selectivity can generally be increased through the modification of the chemical structure of polymers by crosslinking, grafting, etc.

Prichard and Finch described the chemical/physical properties and applications of PVA in some detail, and Prichard has tried to introduce several modification methods. Table. 1 summarize

Table 1. Crosslinking Methods of PVA polymer published in the literature for membrane application.

Crosslinking agent or method	Crosslinking or condition	Application	Ref.
Formaldehyde	$H_2SO_4/Na_2SO_4/H_2O$	RO[a]	19-21
Glutaraldehyde	HCl/H_2O	RO	22,23
Oxalic acid/boric acid	$KCr(SO_4)_2H_2O$	RO	24
Heat treatment	120-175℃	RO	25
γ-irradiation	0.5-2.0 mrad	RO	26
Electron-beam irradiation	–	GAS[b]	27
Dicarboxylicacid/Cr(Ⅲ)solution/ketones	–	RO	28
Maleric acid	Heat treatment at 150℃	PV[c]	29
	Triethanoamine/H_2O	PV	17
Amic acid	Heat treatment	PV	18
Poly(acrylic acid)(MW 2,000)	150℃ for 1h	PV	14-16

RO : reverse osmosis, GAS : gas separation, PA : pervaporation

the crosslinking methods published in the literature for membrane applications.

2.2. Membrane Preparation

Aqueous 10 wt% PVA solutions were prepared by dissolving preweighed quantities of PVA in ultrapure water and heating at 90°C for at least 6hrs. Aqueous 75 wt% SSA solutions were diluted to 10 wt% solutions. Then two polymer solutions (in case of PVA:SSA=95:5, PVA 95 g and SSA 5 g were mixed together since each polymer solution had 10 wt% polymer concentration) were mixed together by varying each component composition to form a homogeneous solution for at least a day at room temperature. Homogeneous membranes were casted onto a Plexiglass plat using a Gardner knife with predetermined drawdown thickness. The membranes were allowed to dry in air at room temperature, and completely dried membranes were then peeled off. The dried and blended membranes were then heated in a thermosetted oven at the desired reaction temperature, 150°C, and time, an hour. The thickness of the resulting membranes showed 15~20 μm. The prepared membranes were then stored in solutions, such as 10 and 20 wt% MeOH, to be separated for further use. The amount of SSA solution was very small about PVA polymer solution, therefore the exact weight of SSA solution was mixed together about PVA polymer solution by wt.%. Figure 1. shows the postulated crosslinking mechanism between PVA and SSA

2.3. Swelling Measurement

The sorption capacity of the membrane was measured by immersing the membrane samples in the pure MTBE, methanol and the mixtures of MTBE and methanol at 30, 40 and 50°C. 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 swelling slab was taken out and then wiped with the cleansing tissue. Both ends of the slab were marked with a pen
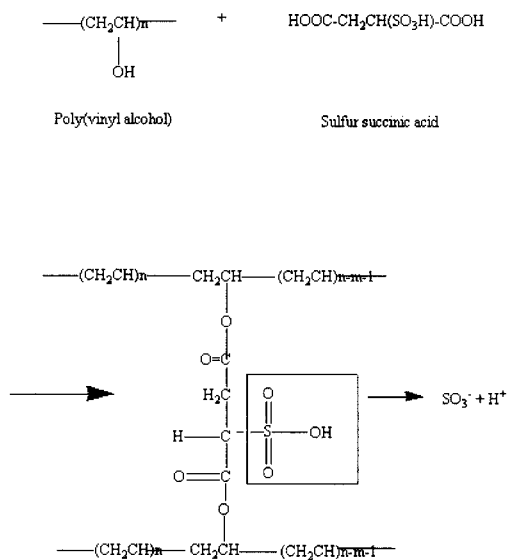
PVA[*] : poly(vinyl alcohol) SSA[**] : sulfur-succinic acid J[1] : permeation rate α[2] : separation factor

Fig. 1. Reaction mechanism of PVA and SSA.

as quickly as possible and the distance (L) between the marks was measured with Vernier Caliper with an accuracy of ±10 μm. After drying, the length (L₀) the dry slab were checked. The solubility of the mixtures in the swollen membrane, Φ, was calculated from

$$\Phi = \frac{R_L^3 - 1}{R_L^3}, \quad (R_L = \frac{L}{L_o})$$

L : The length of the swollen sample
L₀ : The original length of sample

This procedure was repeated about 20 times until satisfactory reproducibilities were obtained.

2.4. Pervaporation

The membrane cell and the experimental apparatus used in this study are illustrated in Figures 2 and 3, respectively. The pervaporation separation experiments were performed employing two stainless steel pervaporation cell(Figure 2). A feed mixture enters the cell through the center opening, flows radially through the thin channel and leaves the cell through the side opening,
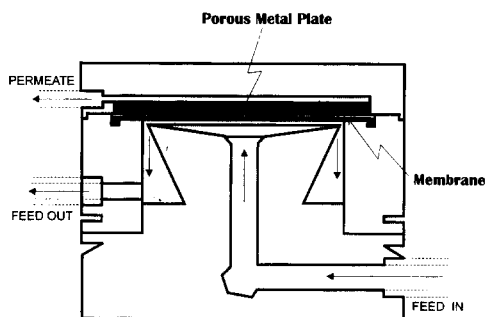
Porous Metal Plate

PERMEATE

Membrane

FEED OUT

FEED IN

Fig. 2. Configuration of the pervaporation cell used in this study.

a - Stirrer　　　　　m - Vacuum Pump
c - Feed Tank　　　　b - Temperature Controller
e - Permeation Cell　d - Micro Pump
g - Trap　　　　　　f - Vacuum Manometer
i, j - Cold traps for　h - Drying tube
　collecting sample k.l - Cold Traps
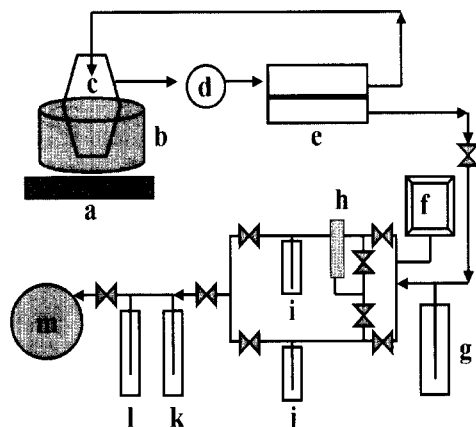
Fig. 3. Schematic diagram of pervaporation apparatus used in this study.

which allows relatively high fluid velocity parallel to a membrane surface. The effective membrane area was 14.2 cm². The four-necked feed tank has a solution capacity of approximately 1,000 mℓ. From the feed tank, which was kept at a constant temperature by the water bath, the feed mixture was circulated through the cell. The pervaporation experiments of MTBE-methanol mixtures were conducted at 30, 40 and 50℃. 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 and with thermal conductivity detector. The following relationship was used to calculate the separation factor

$$\alpha_{i/j} = \frac{(y_i/y_j)}{(x_i/x_j)}$$

where x is the feed composition, y is the permeate composition, and component i is the preferentially permeating component. Permeate flux(J) is defined as following relationship was used to calculate.

$$J = \frac{Q}{A \times T} \ [g/m^2hr]$$

where Q is the weight of permeate(g), A is effective membrane area(m²) and T is operating time(hr), respectively.

2.2. Vapor Permeation

The membrane cell and the experimental apparatus used in this study are illustrated in Figures 4 and 5, respectively. Basically, this apparatus has the same frame as the pervaporation equipment elsewhere except the membrane cell. The membrane cell was designed to produce the saturated vapor of a feed liquid at a feed temperature as depicted in Figure 4. The effective membrane area was 14.2 cm². The four-necked feed tank has a solution capacity of approximately 1,000 mℓ. The feed mixture enters the cell through the lower opening, leaves the cell through the higher opening with enough flow rate for the liquid level not to exceed the position of the higher opening. During circulating the feed mixture through the membrane cell, the saturated vapor in equilibrium with feed mixture at feed temperature could be produced in the cell. The cell was placed in a heating oven. By the heating oven, the temperature of the produced vapor
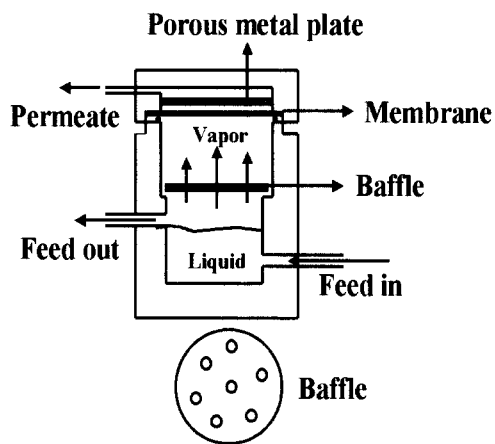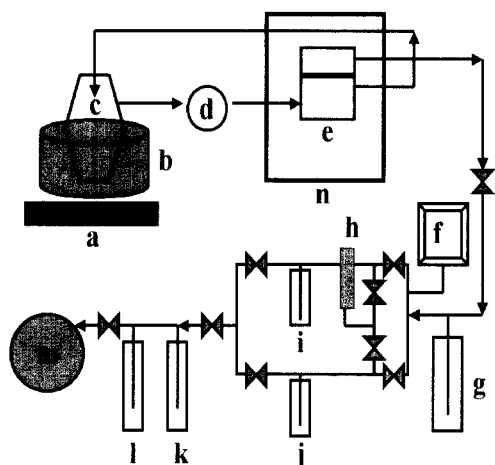
Fig. 4. Configuration of the vapor permeation cell used in this study.

a – Stirrer   b – Temperature Controller
c – Feed Tank   d – Micro Pump
e – Permeation Cell   f – Vacuum Manometer
g – Trap   h – Drying tube
i, j – Cold traps for k.l – Cold Traps
    collecting sample n – Heating Oven
m – Vacuum Pump

Fig. 5. Schematic diagram of vapor permeation apparatus used in this study.

could be controlled higher above the feed temperature to prevent the vapor from condensing in the cell.

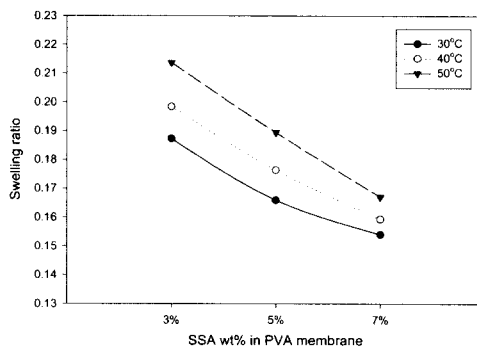During the experiments, the downstream pressure, 0.3~1 torr, was maintained. The composition

Fig. 6. Swelling ratio of PVA/SSA membranes for pure methanol with varying SSA contents.
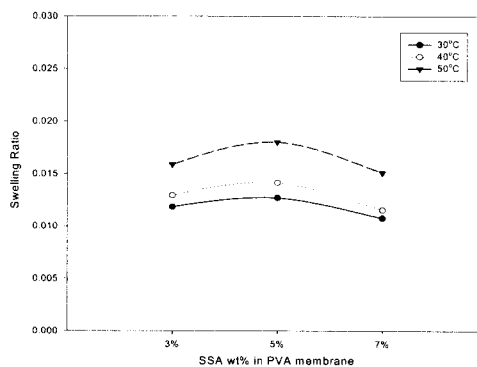

Fig. 7. Swelling ratio of PVA/SSA membranes for pure MTBE with varying SSA contents.

analysis of the permeate was done using gas chromatography(GC) equipped with Porapak Q column and with thermal conductivity detector. Permeate flux(J) and Separation factor(α) were defined as relationship was used in pervaporation.

3. Results and Discussion

3.1. Swelling Measurement

Figures 6 and 7 show the swelling ratio of pure methanol and MTBE with varying SSA contents in PVA membranes. The membrane network would be more compact when the crosslinking degree gets higher while the more addition of the hydrophilic crosslinking agent attracts more solvents, in general, As a result, the former would lead to be less space to be physically occupied in the

membranes while the latter would give a higher swelling ratio. For pure methanol, the swelling ratio decrease with increasing the crosslinking 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 crosslinking reaction rather than the increase of hydrophilicity with SSA addition on the swelling ratio is more severe. However, this analysis could not be applied to the case of pure MTBE as can be seen Figure 7. First of all, it is worth nothing that the swelling degree of MTBE is much lower than methanol case since pure MTBE is moderately high hydrophobic (see Table. 2). And the swelling ratio 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 crosslinking reaction increased with the more addition of SSA, 3 to 7% but the hydrogen bonding effect with the solvents may be reduced. The sulfuric acid group($-SO_3H$) in sulfur succinic acid could have the hydrogen bonding force with MTBE and methanol, and also PVA as well. First, a number of this sulfuric acid group could form the hydrogen bonding force with the hydroxyl group($-OH$) in PVA rather than with the organic solvents in question. As a result there are not much chances to have the hydrogen bonding with solvents when the membranes were exposed to the solvents.

However, a slight increase of the swelling ratio for 3% to 5% SSA might result in the effect of SSA which is not forming the hydrogen bonds with solvents. Particularly, the crosslinking degree could be balanced with the hydrophilic compound,

SSA, at this composition. For 7% SSA, the swelling ratio 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 crosslinking reaction does not allow the sorption of the solvents into the membranes. In summary, there are two factors of the polymer network and the hydrogen bonding in this swelling study. And this factors act interdependently on the membrane swelling.

The next two figures(Figures 8 and 9) illustrate the swelling ratio for the different compositions of MTBE-methanol mixtures at same temperatures. The swelling ratio lies the values of between pure methanol and MTBE. When the methanol concentration in the mixtures increases, the higher concentration of methanol in feed swells the membranes more since higher concentration of methanol contacts the membranes more than
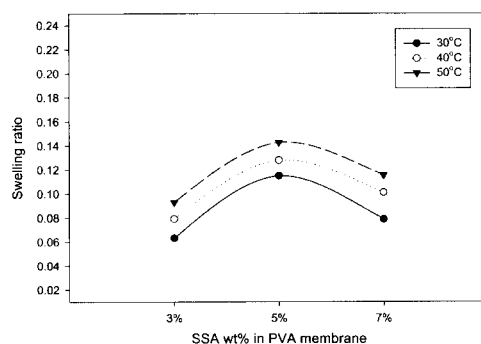

Fig. 8. Swelling ratio of PVA/SSA membranes for MTBE/methanol=80/20 mixture with varying SSA contents.

Table 2. Solubility parameters of polymers and feed components used in this study.

	δ_d	δ_p	δ_h	δ_t	V**
methanol	7.4	6.0	10.0	14.5	40.7
MTBE*	7.6	1.7	2.4	8.1	119.0
PVA*	16.0	14.3	23.9	32.1	35.0

* Solubility parameters ($cal^{1/2}/cm^{3/2}$) calculated by the group contribution method proposed by van Krevelan[30]
** Molar volume (cm^3/mol) calculated by the group contribution method proposed by van Krevelan[17]
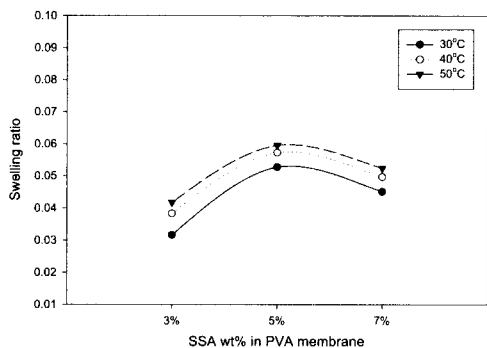
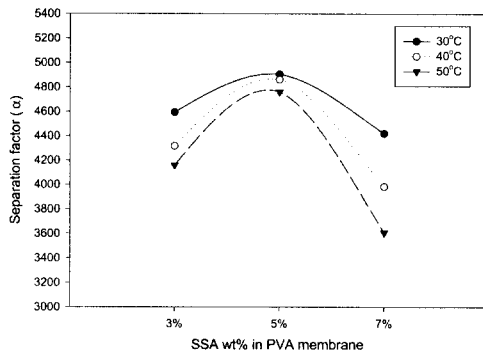**Fig. 9.** Swelling ratio of PVA/SSA membranes for MTBE/methanol=90/10 mixture with various SSA contents.
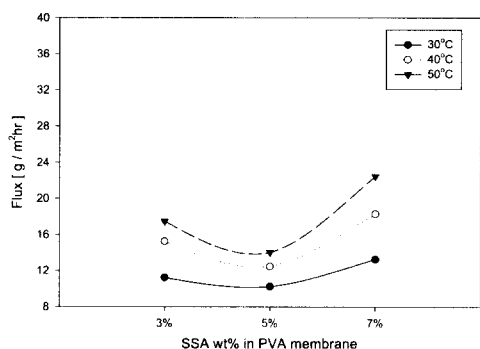

Fig. 10. Permeabilities of PVA/SSA membranes for MTBE/methanol=90/10 mixtures with varying SSA contents by pervaporation.

lower concentration of methanol and, meanwhile, the other component, MTBE, penetrates into the swollen membranes under the existence of methanol at the same time. Therefore, the swelling ratio of MTBE/methanol=80/20 mixture is larger than that of MTBE/methanol=90/10 mixture. And it could be considered that the reason why the swelling ratio at 5% SSA shows the maximum is the affection of MTBE which indicates the same trend at 5% SSA for pure MTBE.

3.2. Pervaporation

Figures 10 and 11 illustrates the permeabilities and separation factors for MTBE/methanol=90/10 mixtures, respectively. The swelling measurement indicates the maximum at 5% SSA as shown in Figures 8 and 9 while the flux shows the minimum.

Fig. 11. Separation factor of PVA/SSA membranes for MTBE/methanol=90/10 mixtures with varying SSA contents by pervaporation.

Since the permeability, 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, and the hydrogen bonding effect is over the crosslinking effect at 7% SSA. As described in '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 crosslinking 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 10. Therefore, it could be concluded that the crosslinking 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. 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 temperatures, as expected, leads the flux to increase as the operating temperature increases due to the increase of the chain mobility. And also th separation
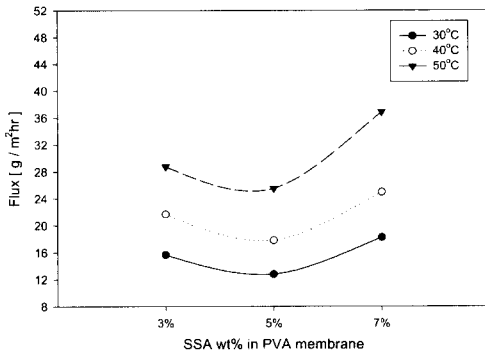
Fig. 12. Permeabilities of PVA/SSA membranes for MTBE/methanol=80/20 mixtures with varying SSA contents by pervaporation.
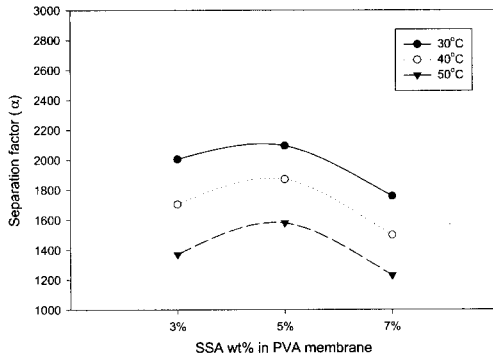

Fig. 14. Permeabilities of PVA/SSA membranes for MTBE/methanol=90/10 mixtures with varying SSA contents by vapor permeation.

Fig. 13. Separation factor of PVA/SSA membranes for MTBE/methanol=80/20 mixtures with varying SSA contents by pervaporation.

Fig. 15. Separation factor of PVA/SSA membranes for MTBE/methanol=90/10 mixtures with varying SSA contents by vapor permeation.

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 4,900 with the flux of 10.23 $g/m^2 \cdot hr$ for 5% SSA membrane at 30℃.

The next Figures. 12 and 13 illustrate the flux and the separation factor for MTBE/methanol=80/20 solution. The curve shapes are same as Figure 10 and 11, respectively, The separation factor is lower than those for MTBE/methanol=90/10 solution while the flux is higher. As described above, the flux could increase since the membrane contacts more methanol in feed. The 5% SSA membrane shows the highest separation factor of 2,095 with the flux of 12.79 $g/m^2 \cdot hr$.
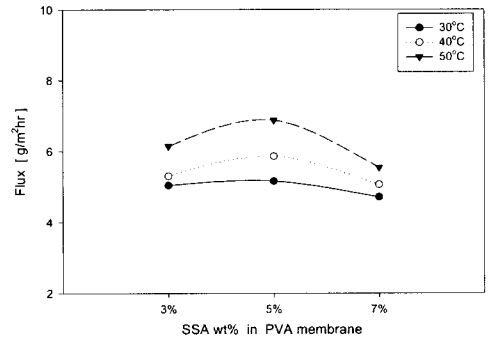
3.3 Vapor Permeation

For a comparison of the two membrane processes, membranes prepared at the same batch were used and the same operating conditions were employed. The results are shown from Figure 14 to Figure 17. On a whole, fluxes were smaller in vapor permeation than in pervaporation but separation factors were similar in two membrane processes. It was reported [31] that a remarkable resistance to mass transfer at the feed-side interface of membrane could be developed in vapor permeation to reduce flux, and thereby flux in vapor permeation could be lower than in pervaporation. Schehlmann et al. [12] also attributed the different membrane performance to differences in density and/or in concentration of

Fig. 16. Permeabilities of PVA/SSA membranes for MTBE/methanol=80/20 mixtures with varying SSA contents by vapor permeation.

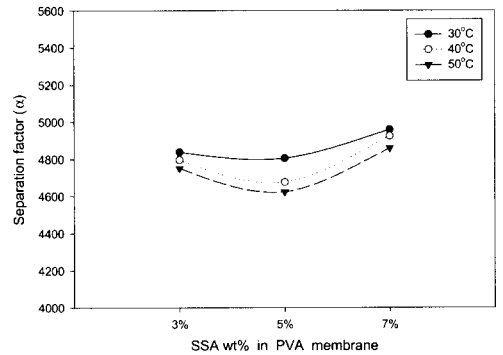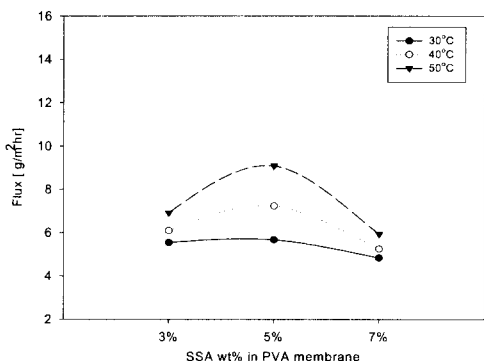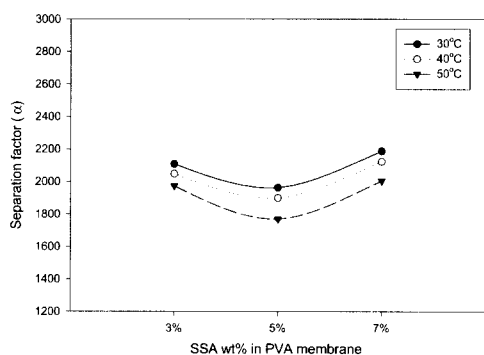**Fig. 17.** Separation factor of PVA/SSA membranes for MTBE/methanol=80/20 mixtures with varying SSA contents by vapor permeation.

the liquid or vaporous feed.

Figures 14 and 15 illustrates the permeabilities and separation factors for MTBE/methanol=90/10 mixtures, respectively. The swelling measurement indicates the maximum at 5% SSA as shown in Figures 8 and 9 while the flux shows the same trend in vapor permeation. As described in pervaporation, the flux shows the minimum at 5% SSA oppositely. As explained in 'pervaporation' the membrane network would be more compact when the crosslinking degree gets higher while the more addition of the hydrophilic crosslinking agent(SSA) attracts more solvents. It could be considered that the hydrogen bonding effect. In this case, the density or concentration of methanol in vaporous feed may be lower than that of

methanol in liquid feed, and the hydrogen bonding effect with the solvents may be reduced. In pervaporation, the hydrogen bonding effect at 7% SSA is over the crosslinking effect, but in vaporous feed, the hydrogen bonding portion between the solvent and the hydroxyl group in PVA is less than that in pervaporation as a result, the flux was reduced in vapor permeation.

As feed temperature increased, as expected, leads the flux to increase as the operating temperature increases due to the increase of the chain mobility. Also it might be explained that higher feed temperature could produce a higher saturated vapor pressure which would increase the solubility of feed vapor into the membrane and thus the difference in densities of the saturated vapor and the equilibrated liquid could be reduced or the interfacial resistance could be lowered to increase a net flux across the interface between feed and membrane. In this case, from the viewpoint of the separation factor, the best result of the PVA/SSA membranes shows about 4,959 with the flux of 4.71 $g/m^2 \cdot h$ for 7% SSA membrane at 30℃(in case of pervaporation – α : 4,900, flux : 10.23 $g/m^2 \cdot hr$).

The next Figures 16 and 17 illustrate the flux and the separation factor for MTBE/methanol=80/20 solution. The curve shape same as Figures 14 and 15, respectively. The separation factor is lower than those for MTBE/methanol=90/10 solution while the flux is higher. As described above, the flux could increase since the membrane contacts more methanol in vaporous feed. The 7% SSA membrane shows the highest separation factor of 2,187 with the flux of 4.84 $g/m^2 \cdot hr$.

4. Conclusions

Several conclusions can be drawn from this studies as followings

(1) The swelling measurements were carried out for pure MTBE and methanol, and MTBE/methanol=90/10, 80/20 mixtures using PVA/SSA membranes with varying SSA compositions. There are two factors of the

membrane network and the hydrogen bonding in the swelling measurements of PVA/SSA membranes. This factors act interdependently on the membrane swelling.

(2) Pervaporation separation was also carried out for MTBE/methanol mixtures using PVA/SSA membranes at various operating temperatures. The sulfuric acid group in SSA took an important role in the membrane performance. The crosslinking effect might be over the hydrogen bonding effect due to the sulfuric acid group at 3 and 5% SSA membranes, and this two factors act *vice versa* on 7% SSA membrane. In this case, the 5% SSA membranes shows the highest separation factor of 2,095 with the flux of 12.79 $g/m^2 \cdot hr$ for MTBE/methanol=80/20 mixtures at 30℃ which this mixtures show near the azeotropic composition.

(3) Vapor permeation separation was also carried out for MTBE/methanol mixtures using PVA/SSA membranes at various operating temperatures. Compared to pervaporation, vapor permeation showed less flux and similar separation factor. In this case, the flux decreased significantly because of compact structure and the effect of hydrogen bonding. In vapor permeation, Density or concentration of methanol in vaporous feed is lower than that of methanol in liquid feed, as a result, the hydrogen bonding portion between the solvent and the hydroxyl group in PVA is reduced in vapor permeation.

In this case, the 7% SSA membranes shows the highest separation factor of 2,187 with the flux of 4.84 $g/m^2 \cdot hr$ for MTBE/methanol=80/20 mixtures at 30℃.

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