투과증발 PAA-PVA 막을 통한 초산-물
혼합물의 투과거동에 관한 연구

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A Characterization of Permeation Behavior of Acetic Acid-Water Mixtures
Through Crosslinked PAA-PVA Membranes in Pervaporation Separation

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요   약 : PVA의 수산화기와 PAA의 카르복실산기 사이의 반응에 의해 가교구조를 갖는 PAA-PVA 막을 제조하였으며 팽윤실험을 통해 순수물, 순수초산 그리고 이들의 혼합물하에서의 가교막들의 팽윤거동을 각각 살펴보았다. 90wt% 초산 수용액하에서의 팽윤실험에서 막에 PAA함량이 높을때 물의 팽윤거동이 초산보다 더 촉진됨이 관찰되었는데 이는 팽윤과정에서의 각 구성 성분간의 짝짓기(coupling) 결과로 사료되며 또한 막의 팽윤비와 가교밀도는 경쟁적으로 투과물의 투과거동에 서로 상반되게 영향을 끼침이 관찰이 되었다. 온도에 따른 투과속도의 Arrhenius 관계에서 구한 투과활성화에너지를 통해 투과성분의 투과거동을 분석하였다.

Abstract: poly(acrylic acid)(PAA)-poly(vinyl alcohol)(PVA) membranes have been prepared by crosslinking reaction between the carboxylic acid groups of PAA and the hydroxylic groups of PVA. In the measurements of the swelling and preferential sorption of the membranes, sorption behaviors of the membranes in pure water, pure acetic acid and a mixture of them have been investigated, respectively. From the measurements of the preferential sorption in 90wt% acetic acid of aqueous mixture, the sorption of water component was found to be more enhanced at high PAA content in the membrane than that of acetic acid component due to the interaction of water with acetic acid. The sorption behavior and the degree of crosslinking influenced competitively the permeation behavior of permeants. Permeation behavior of permeants through the membranes was analyzed by using permeation activation energies which had been obtained from the Arrhenius plots of fluxes.

1. Introduction

In recent years, there have been increased inter-ests in the application of the pervaporation membrane separation process to the separation of organic aqueous mixtures, since the pervaporation tech-

nique is proved to be an energy-saving process. Compared to the separation of ethanol-water mixture on which most research efforts on the pervaporation process have concentrated, the separation of other mixtures has received relatively little attention. Acetic acid is known as an important basic chemical to rank among the top 20 organic intermediates. Because of the small differences in the volatilities of water and acetic acid in dilute solution, azeotropic distillation is used. Therefore, the acetic acid separation from water is an energy-expensive process[1]. The pervaporation process can be considered to be one of alternative process candidates from the view-point of energy saving.

Yoshikawa et al.[2] have studied the separation of the acetic acid-water system by pervaporation technique using poly(acrylic acid- acrylonitrile) membranes. They achieved the high separation factors but very low permeation rates. Nguyen et al.[3] reported the selection of membrane materials for the dehydration of water-acetic acid mixtures, using poly(vinyl alcohol)(PVA) as a base polymer. They also used blended films of PVA and poly(acrylic acid)(PAA). They obtained the results with those membranes that, when the ratio of PVA and PAA in the blend was 1:1, the selectivity and permeation rate of 90wt% acetic acid content of aqueous mixture through the resulting membrane were in the range of 6~6.6 and 0.06~0.30kg/(m²hr), respectively. Huang et al.[1] investigated the separation of water-acetic acid mixtures using PAA-Nylon 6 blended membranes. These membranes showed relatively high separation factor of 82.3 for a feed concentration of 24.18mol.% H₂O at 15℃. They concluded that balancing of the hydrophilicity and hydrophobicity of membrane material by blending hydrophilic polymer and hydrophobic polymer could be one of techniques to optimize the selectivity and permeation rate of the membrane. The introduction of crosslinked structures into polymeric membrane to improve the pervaporation separation properties as well as the stability of the membrane for aqueous solutions has been reported[4-7]. Huang and Rhim [4] have tried the chemical modification of PVA

crosslinked with maleic acid under triethanolamine/ water catalyst. (factor 7.8 at 70wt% water in the feed at 25℃). Yeom and Huang[5] have developed PVA membranes crosslinked with two types of amic acids obtained from the reactions between 3,3',4,4'-benzophenone tetracarboxylic dianhydride(BTDA) and p-phenylene diamine(p-PDA), and between BTDA and m-PDA. These membranes gave excellent pervaporative properties : fluxes of 79~722g/ (m²h) and separation factors of 34~176 for the dehydration of water-acetic acid mixtures depending on operating temperature and feed composition. Recently, Yeom et. al[6, 7] have developed a new solution technique which is able to fabricate a dimension-stable PVA membrane by the crosslinking reaction of PVA with glutaraldehyde(GA) under a catalyst and non-solvent reaction medium. Good pervaporation results were obtained from the membrane which yielded separation factors of 120~420 and fluxes of 29~263g/(m²h) for the separation of 70~90wt% of acetic acid contents of aqueous mixtures.

This paper is a continuation of the previous papers which dealt with the membranes characterization[8], pervaporation separations of water-phenol mixtures[9], and water-alcohol mixtures[10, 11]. In this paper, the swelling and preferential sorption measurements were made with the crosslinked PVA -PAA membranes with different PAA content, and the sorption behavior of acetic acid-water mixtures is to be characterized. The pervaporation separation of 90wt% acetic acid content of aqueous mixture with the membranes was carried out at 30~50℃ of operating temperature. Pervaporation activation energies were obtained from the Arrhenius plots of the fluxes and used to analyze the permeation behavior of permeants through the membranes along with the sorption data.

2. Experimental

2. 1. Materials

Fully hydrolyzed PVA with molecular weight of 50,000 and PAA with molecular weight of 2,000

(25wt% in water) were purchased from Showa Chemical Co.(Japan). The methanol and acetic acid were analytical grade from Merck. Water was the ultra-pure produced from MPI system.

2.2. Membrane preparation

10wt% of PVA aqueous solution was prepared by dissolving preweighed quantities of dry PVA in ultra-pure water and heating at 90℃ for at least 6h. 25wt% of PAA aqueous solution was diluted to 10wt% PAA content of solution. The two polymer solutions were mixed together with a certain ratio and then stirred to form a homogeneous solution for at least 1 day at room temperature. The resulting casting solution was cast onto a Plexiglas plate with the aid of a Gardner knife and dried at room temperature in a fume hood. The dried membrane was peeled off and heated in a thermostated oven for 1 hour and 150℃. The resulting membranes were then stored in the solutions to be separated for further use.

2.3. Measurements of swelling ratio and preferential sorption

Swelling ratio can be measured from changes in length before and after equilibrium swelling for the uniformly crosslinked membranes which go through isotropic length change during swelling process[13]. The dense membranes were cut into a shape of strip with dimension of 10×70(mm). The dry membrane strips were immersed in both water and acetic acid thermostated at 40℃ for 48 hours to allow the strips to reach an equilibrium sorption. After measuring the swollen length, l of a strip at equilibrium sorption, the strip was dried for 30 hours at room temperature under vacuum and then the dry length, l_o was measured. The swelling ratio, R and the volume fraction of liquid absorbed in the swollen membrane, S are defined as

$$R = \frac{l}{l_o} \tag{1}$$
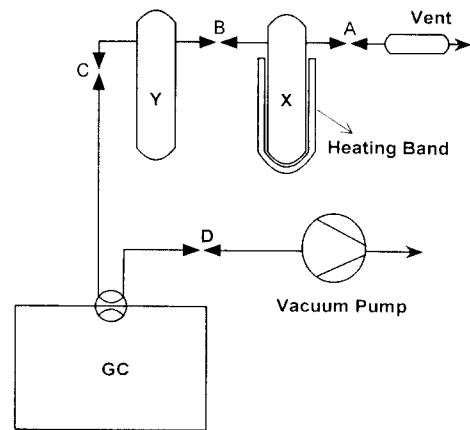
$$S = \frac{R^3 - 1}{R^3} \tag{2}$$

Fig. 1. Device for preferential sorption measurement.

For the measurement of preferential sorption, the swollen strips were taken out of the solution after equilibrium swelling, wiped off with tissue paper as quickly as possible and then they were placed into the glass tube X which, subsequently, was fitted to the device as shown Fig. 1. While the glass tube was heated up by the heating band, the liquids absorbed in the slabs were collected in the glass tube Y by liquid nitrogen under vacuum with the valves B and C opened. The collected liquids were vaporized by applying heat on the glass tube Y with the valves B and D closed so that the region between the valves could be filled with the vapours of the liquids. The vapours were analyzed by a gas chromatograph(Shimadzu, model GC-14B) which was equipped with an integrator(Shimadzu, model C-R6A), two auto sample injectors, a thermal conductivity detector(TCD), a Flame Ionization Detector(FID) and two packed columns. Each sample injector was actuated by compressed air. The columns were 5 ft long with 1/8 inch inside diameter packed with a Poropak Q. The vapours were automatically injected to the gas chromatograph by the injector. Ultrapure helium was used as carrier. For the measurement of swelling ratio, the swollen slab was taken out and put on a paper wetted by the same solution, and then both ends of the slab were marked on the paper with a pen as quickly as possi-
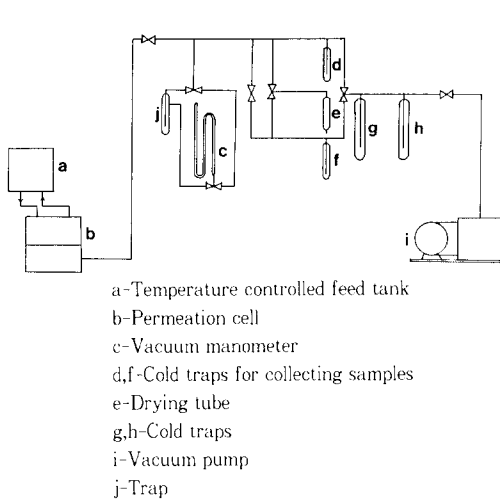
a–Temperature controlled feed tank
b–Permeation cell
c–Vacuum manometer
d,f–Cold traps for collecting samples
e–Drying tube
g,h–Cold traps
i–Vacuum pump
j–Trap

Fig. 2. Schematic representation of pervaporation apparatus.

ble and the distance L between the marks was measured with Vernier Caliper with an accuracy of ± 10μm. After drying, the length l_o of the dry slab was measured. The solubility of the liquid in the swollen membrane S was calculated eq.(2). Each measurements of preferential sorption and swelling ratio were repeated 3~5 times.

2. 4. Pervaporation

The apparatus used in this study is illustrated in Fig. 2. The pervaporation separation experiments were performed employing two stainless steel cell (Fig. 3). The feed mixture enters the cell through the side opening, which allows relatively higher fluid velocity parallel to the membrane surface. The effective membrane area is 14.2cm². The 4-necked feed tank had a solution capacity of approximately 1000 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 pressure at the downstream side was kept below 2mmHg by vacuum pump. The pervaporation experiments were conducted at 30~50℃ Upon reaching steady state flow conditions, permeate samples were collected with time intervals, isolated from the vacuum system, and weighed. The composition analysis
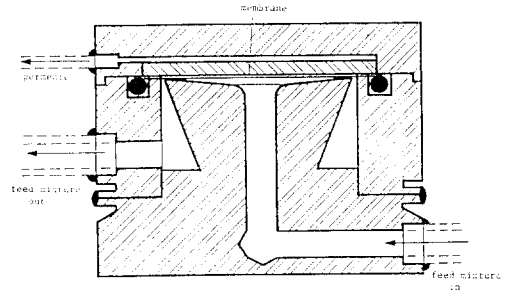

Fig. 3. Schematic presentation of membrane cell.

of the permeate was made using a gas chromatography. The following relationship was used to calculate the separation factor:

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \tag{3}$$

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

3. Results and Discussion

3. 1. Swelling Measurement

In this study, the swelling property of a membrane was used as a measure of the affinity to each components. Some basic but important parameters can be reliably obtained by separately studying the swelling behaviors of each pure components of which feed mixture will be made, avoiding too many factors to be elucidated in the case of the permeation of the multicomponent mixture. Therefore, swelling measurements were carried out in pure water and pure acetic acid on the PAA–PVA membranes fabricated in different composition. The result is shown in Fig. 4. All measurements were repeated 4 or 5 times and the resulting data had standard deviation of ±7%. The water was observed to be absorbed much larger into the membrane than acetic acid regardless of PAA content in the membrane, showing a good affinity of the membrane material toward water. Both water and acetic acid contents in the swollen membranes show a tendency to decrease monotonously with increasing the PAA
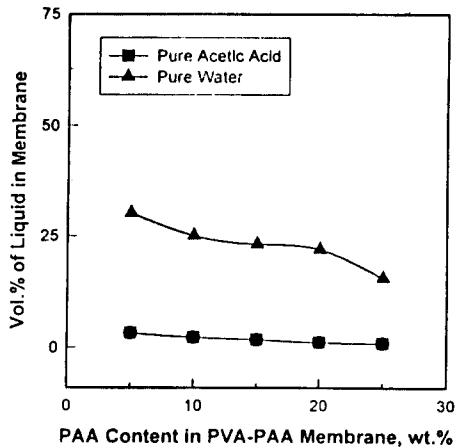
Fig. 4. Pure water and acetic acid vol.% absorbed in PVA-PAA membrane against PAA content in the membrane at 30℃.
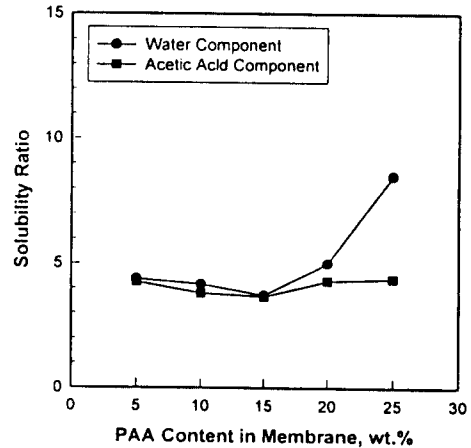

Fig. 5. Water and acetic acid vol.% absorbed in PVA-PAA membrane against PAA content in the membrane : solution=90wt% acetic acid content, temperature=30℃.

content, as a result of an increase in crosslinking density in the membranes which was observed in the previous work[8]. Usually, as crosslinking density in a membrane increases, the membrane has a more compact network structure and less chain mobility. So, the amount of solvent absorbed in the membrane decreases. The solubility data of the membranes in 90wt% acetic acid content of feed

Fig. 6. Solubility ratios of each components absorbed in PVA-PAA membrane against PAA content in the membrane : solution=90wt% acetic acid content, temperature=30℃.
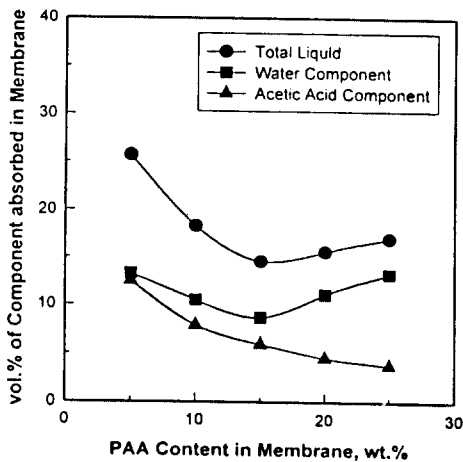
mixture are presented in Fig. 5. It is very unexpected to note that the water content absorbed in the membrane decreases until 15wt% PAA content and then increases whereas the acetic acid content decreases continuously with PAA content. More detail on it can be obtained through the analysis of the so-called solubility ratio of each component(SR_i) as shown in Fig. 6. The solubility ratio of a component which is a measure of the deviation of the actual sorption from the ideal sorption of the component in a membrane can be defined as the ratio of actual solubility(S_i) to ideal solubility(S_i') of a component.

$$SR = \frac{S_i}{S_i'} \tag{4}$$

$$S_i' = x_i S_{io}$$

where x denotes the weight fraction in the feed mixture and S_{io} solubility of pure component i in the membrane. The ideal solubility is the solubility proportional to the concentration of the component in feed mixture. It is already reported[14] that, in the case of the permeation of a polar-polar mixture through a polar membrane material, the coupling behavior can exist in sorption step as well as in diffusion step due to very strong interaction between
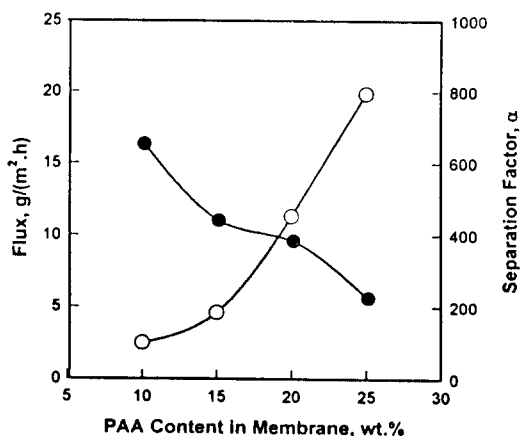
Fig. 7. Plots of flux and separation factor through PVA-PAA membranes with different PAA content in the separation of 90wt% acetic acid content of feed at 30℃.
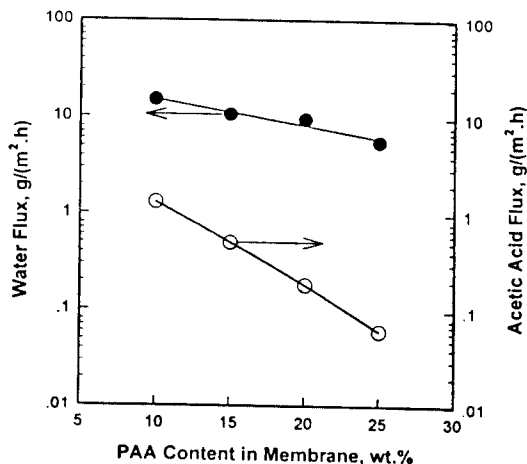

Fig. 8. Plots of individual component flux through PVA-PAA membranes with different PAA content in the separation of 90wt% acetic acid content of feed at 30℃.

the permeant molecules and the membrane material. The solubility ratio should be equal to unity when the system exhibits ideal permeation behavior. When either $SR_i > 0$ or $SR_i < 0$, the interactions between permeant-permeant and polymeric material-permeant affect the sorption of the membrane positively or negatively, respectively. On the whole, the solubility ratios of both the components are higher than unity and as the PAA content increases, the solubility ratio of water component becomes higher than that of acetic acid component. It reveals that the solubility of a component in the presence of the other component is higher than the solubility of the pure component because of interactions between the components and the polymeric membrane, causing coupled sorption. The enhancement of water solubility by the coupled sorption is more significant at higher PAA content. Thus, the coupled sorption has more effect on the water solubility, predominating over the effect of crosslinking density which will affect the solubility in the opposite way. This change in sorption behaviors with the PAA content can, in turn, influence the permeation of the mixture because the pervaporation process is controlled by both sorption and diffusion according to the solution

-diffusion mechanism[14]. It will be discussed in the following section.

3. 2. Pervaporation

Fig. 7 presents the plots of total flux and separation factor with PAA content in membrane in the permeation of 90wt% acetic acid content of feed at 30℃. The crosslinking density in the membrane increases with the PAA content as mentioned previously. Generally speaking, as the crosslinking density in a membrane increases, the free volume in the membrane is decreased and the amount of solvent swelling as well as mentioned in the previous section. Thus, the solubility of the liquid mixture declines and the diffusivity, which is governed mainly by the free volume, decreases due to the rigidity of the polymeric chains. This causes the permeation rate through the membrane to decrease and the separation factor to decrease. The increase of the separation factor is also related to the increase of the solubility ratio of water component relative to that of acetic acid component as explained in Fig. 6. A close insight into the permeation can be made through an analysis of each component flux which
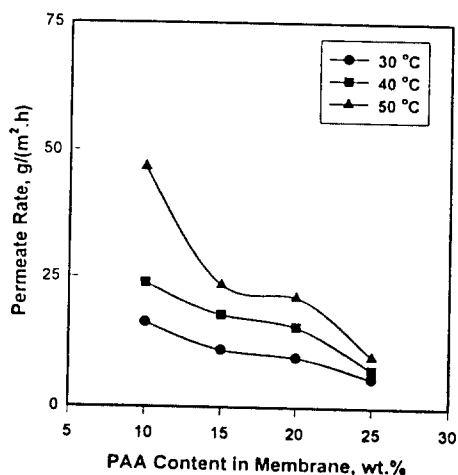
Fig. 9. Plot of flux through PVA-PAA membranes against different PAA content in the separation of 90wt% acetic acid content of feed at different temperatures.

Fig. 10. Plot of separation factor through PVA-PAA membranes with different PAA content in the separation of 90wt% acetic acid content of feed at different temperatures.

is presented in Fig. 8. With increasing the PAA content in the membrane, the water flux decreases less than does acetic acid flux, which is attributed to more enhancement of the sorption of water component than that of acetic acid component as well as permeation through the compact network structure of the resulting membrane. That is why the selectivity could increase with the PAA content.

Figures 9 and 10 show the total flux and separation factor at different operating temperature, respec-tively. All of the curves have similar shapes to those shown in the Fig. 7. As temperature increases, the frequency and amplitude of polymeric chain jumping increase and the resulting free volume becomes larger, whereas the interaction between permeant molecules becomes weak to increase the number of isolated molecules or of less associated permeating molecules, to such an extent that the size of the diffusing unit can be reduced. Therefore, in pervaporation in which the permeating molecules can diffuse through these free volumes, the diffusion rates of both the isolated and associated permeating molecules increase with temperature so that flux can be higher and separation fac-
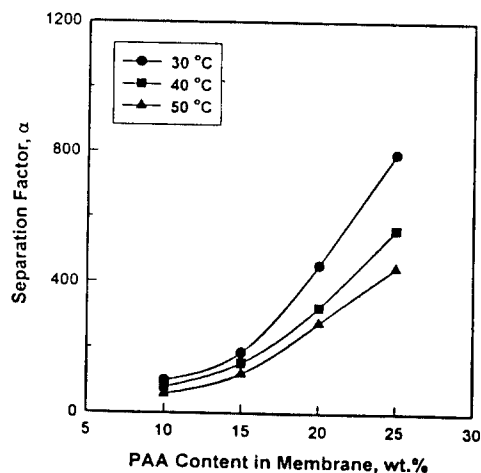
tor lower. The temperature dependence of permeation rate can be expressed by an Arrhenius type of relationship[13] in which a logarithmic form of flux is proportional to inverse temperature. The Arrhenius plots of water flux through the crosslinked PVA-PAA membranes are presented in Fig. 11, and show a good linearity in the given temperature range. Each permeation activation energies E_p were determined from the slope of each plots, respectively, and plotted against PAA content in membrane in Fig. 12. The permeation activation energy tends to decrease with the PAA content, i.e. crosslinking density. Since flux through a membrane is determined by both the solubility and diffusivity of a permeant, E_p value should be dependent on both the diffusive activation energy, E_d in diffusion step and the heat of sorption, ΔH in sorption step as follows.

$$E_p = \Delta H + E_d \tag{5}$$

In pervaporation process, if there is a significant change in membrane structure by crosslinking reaction, the heat of sorption and the activation energy of diffusion will be changed resulting from changing
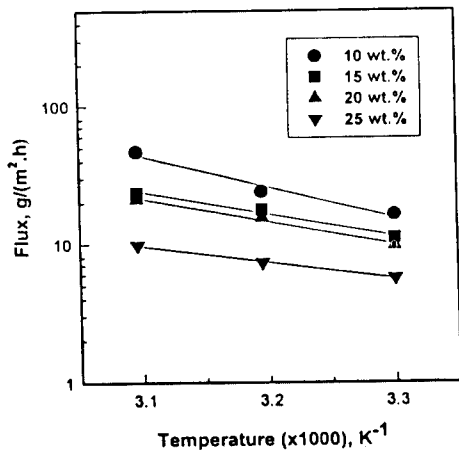
Fig. 11. Arrhenius plots of flux through PVA-PAA membranes with different PAA content in the separation of 90wt% acetic acid content of feed.
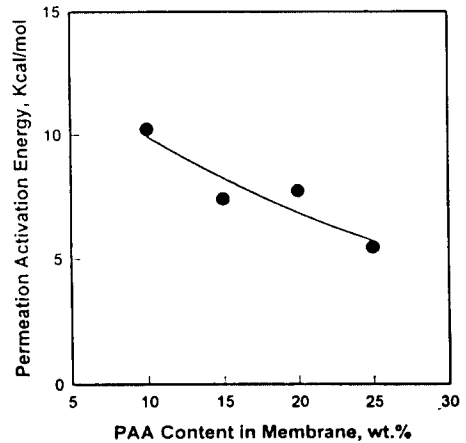

Fig. 12. Permeation activation energies in permeation through PVA-PAA membranes with different PAA content in the separation of 90wt% acetic acid content of feed.

solubility and the mobility of chainsegments, respectively, so that an analysis of the permeation activation energy with crosslinking agent content can provide some clues on the permeation behaviour. Interaction between permeant molecules is thought to be a positive factor to the E_p because associate molecules having large diffusing size require more energy for permeation than isolated molecules while the plasticization action of permeants influences negatively the E_p because of making polymeric chain segments more flexible[13]. More crosslinks make the membrane more rigid and compact, thereby increasing a energy required for diffusive transport through the membrane to reduce the diffusivity of permeant and increasing a energy for the sorption of permeant into the membrane to reduce the solubility of permeant. However, Fig. 12 shows the decline of the permeation activation energy although the crosslinking density increases with PAA content. Going back to Fig. 6, the solubility ratio of water which is a selectively diffusing component is higher at higher PAA content, resulting in the significant plasticization action of water on the membrane material and a decrease in the permeation activation energy. On the other hand, the more

the acetic acid is absorbed in the membrane, the higher the permeation activation energy is reported to be[5]. It was explained in terms of the more possibility of the association between acetic acid and water molecules, and more absorbed acetic acid which is a component with less affinity toward the membrane material. From Fig. 5, the solubility of acetic acid is found to be higher at lower PAA content. In this case, it is more likely to associate the acetic acid molecules with water molecules. As a result, the diffusing size would be increased and higher energy for the associated permeants to diffuse through the membrane could be required. That is why the permeation activation energy increases with decreasing the PAA content.

4. Conclusions

The crosslinked PVA-PAA membranes have been prepared by crosslinking reaction between carboxylic acid groups of PAA and hydroxyl groups of PVA. The solubilities of the pure components in the membrane decreased with increasing PAA content in the membrane, as a result of an increase in crosslinking density. The swelling behavior of the mem-

brane in 90wt% acetic acid content of aqueous mixture was analyzed through a parameter, so-called "solubility ratio". The enhancement of water sorption was more significant than that of acetic acid at higher PAA content in the membrane.

With increasing PAA content in the membrane, the flux was observed to decrease due to the formation of rigid polymer chains by crosslinks while separation factor increases because of the enhancement of water sorption by the coupled sorption. Permeation activation energies were used to analyze the permeation behavior of the permeants through the membranes with different crosslinking density. The significant plasticization of water on the membrane material at high PAA content causes the permeation activation energy to reduce while the large diffusing size due to the association between water and acetic acid molecules and the high solubility of acetic acid which is a component of less affinity to the membrane material could result in higher permeation activation energy at lower PAA content.

Acknowledgment

References

1. R. Y. M. Huang, A. Moreira, R. Notarfonzo, and Y. F. Xu, *J. Appl. Polym. Sci.*, **35**, 1191 (1988).

2. M. Yoshikawa, Y. Takahashi, K. Sanui, and N. Ogata, *Membrane(Japan)*, **10**(4), 247(1985).

3. T. Q. Nguyen, A. Essamri, R. Clement, and J. Neel, *Makromol. Chem.*, **188**, 1973(1987).

4. R. Y. M Huang and J. W. Rhim, *Polymer International*, **30**, 129(1992).

5. C. K. Yeom, "Pervaporation of Binary liquid Mixtures Using Modified Poly(vinyl alcohol) Membranes and Mathematical Modeling", Ph. D. Thesis, University of Waterloo, Waterloo, Ontario(May 1991).

6. Choong-Kyun Yeom and Kew-Ho Lee, *J. Membr. Sci.*, **109**, 257(1996).

7. C. K. Yeom and K.-H. Lee, *J. Appl. Polym. Sci.*, **59**, 1271(1996).

8. J. W. Rhim, M.-Y. Sohn, H.-J. Joo, and K.-h. Lee, *J. Appl. Polym. Sci.*, **50**, 679(1993).

9. Ji-Won Rhim, Min-Young Sohn, H.-J. Joo, and K.-Ho Lee, *J. Appl. Polym. Sci.*, **52**, 1217(1994).

10. Kew-Ho Lee, Hae-Kyung Kim, and Ji-Won Rhim, *J. Appl. Polym. Sci.*, Accepted for publication.

11. Ji-Won Rhim, Hae-Kyung Kim, and Kew-Ho Lee, *J. Appl. Polym. Sci.*, Accepted for publication.

12. E.Ruckenstein and F. Sun, *J. Membr. Sci.*, **95**, 207(1994).

13. R. Y. M. Huang and C. K. Yeom, *J. Membr. Sci.*, **51**, 273(1990).

14. C. K. Yeom and R. Y. M. Huang, *J. Membr. Sci.*, **67**, 39(1992).