

Pervaporation Separation and Swelling Measurement of Acetic Acid–Water Mixtures Using Crosslinked PVA Membranes

JI-WON RHIM,^{1,2,*} SEOK-WON YOON,² SUN-WOO KIM,² and KEW-HO LEE¹

¹Membranes and Separation Laboratory, Korea Research Institute of Chemical Technology, P.O. Box 9, Daedeog-Danji, Taejon 305-606, Korea and ²Department of Chemical Engineering, Hannam University, 133 Ojung-Dong, Daedeog-Ku, Taejon 300-791, Korea

SYNOPSIS

The pervaporation separation and the swelling behavior of acetic acid–water mixtures were investigated at 30, 40, and 50°C using the crosslinked poly(vinyl alcohol) (PVA) membranes with varying the poly(acrylic acid) (PAA) contents and the acetic acid concentration in the feed mixture. Typically, for the pervaporation separation of 90 wt % acetic acid in the feed, the PVA/PAA = 75/25 membrane gives the separation factor of 795 and the flux of 5.6 g/m² h at 30°C, respectively. The swelling degree decreases as the PAA content in the membrane decreases to 20 wt % of PAA due to the increase of the crosslinking portion in the membrane and increases beyond this PAA content. The swelling degrees show fairly high at the operating temperatures and the total range of the liquid mixtures in question. The overall activation energy of permeation was also calculated using an Arrhenius type relationship. From this study, it could be concluded that the diffusion step is dominant over the sorption step. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

In recent years there has been increased interest in the use of the pervaporation membrane separation process for separation of organic liquid mixtures, since the pervaporation technique is considered to be an energy-saving process. Compared to the ethanol–water system on which many pervaporation researchers have focused, the separation of other mixtures has received relatively little attention. Acetic acid is known to rank among the top 20 organic intermediates in the chemical industry.¹ 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

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 the permeation rates obtained were very low. Nguyen et al.³ reported the membrane material selection for the dehydration of water–acetic acid mixtures using poly(vinyl alcohol) (PVA) as the base polymer. They also used the blended film of PVA and poly(acrylic acid) (PAA). When, however, the ratio of the PVA and PAA blends was 1 : 1, the selectivity and the permeation rate for the mixture of water–acetic acid 10 : 90 (wt %) was in the range of 6–6.6 and 0.06–0.30 kg/m² h, respectively. They concluded that the PVA-poly(hydroxycarboxylic acid) blended membrane which selectivity and permeation rate showed 7.9 and 0.06 kg/m² h, respectively, was the most suitable membrane material for the dehydration of water–acetic acid mixtures. Huang et al.¹ also investigated the separation of water–acetic acid mixtures using PAA–Nylon 6 blended membranes. They showed the relatively high separation factor of 82.3 for the feed concentration of

* To whom correspondence should be addressed.

24.18 mol % H₂O at 15°C. And also they concluded that blending a hydrophilic polymer with a relatively hydrophobic polymer could be a useful technique for producing improved permselective membranes. Huang and Rhim⁴ have tried the modification of PVA using maleic acid in triethanolamine/water catalyst solution and to separate the entire range of the water–acetic acid solution. They obtained the separation factor 7.8 at 70 wt % water in the feed at 25°C. Yeom⁵ has developed the noble crosslinked PVA membranes using two types of crosslinking agent resulted from the reactions between 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and *p*-phenylene diamine (*p*-PDA), and between BTDA and *m*-PDA. The applications of these membranes to the dehydration of water–acetic acid mixtures at fairly high operating temperatures showed relatively high separation factors which ranged from 75 to 150 for the feed composition of 10 wt % water. And also, very recently, the Korea Research Institute of Chemical Technology (KRICT) investigated to develop the crosslinked PVA membranes using glutaraldehyde (GA) as the crosslinking agents and applied to the separation of water–acetic acid mixtures.^{6,7} In their investigation, the separation factor and the permeation rate using the membrane crosslinked with 5 vol % GA solution showed 420 and 30 g/m² h, respectively, at 35°C for 90 wt % acetic acid in the feed.

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.^{10,11,12} In this paper, the pervaporation separation of water–acetic acid mixtures using various PVA membranes crosslinked with PAA as the crosslinking agent was investigated experimentally at 30, 40, and 50°C. Also, the swelling measurement was carried out at the same experimental conditions with the pervaporation experiment. The overall activation energy of permeation was calculated using an Arrhenius type relationship.

EXPERIMENTAL

Materials

Fully hydrolyzed PVA with molecular weight of 50,000 and PAA with molecular weight of 2,000 (25 wt % in water) were purchased from Showa Chemical Co., respectively. The acetic acid was

analytical grade from Merck. Used water was the ultra-pure produced from MPI system.

Membrane Preparation

Aqueous 10 wt % PVA solutions were prepared by dissolving preweighed quantities of dry PVA in ultra-pure water and heating at 90°C for at least 6 h. Aqueous 25 wt % PAA solutions were diluted to 10 wt % solutions. 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 Plexiglas plate 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 blended membranes were heated in a thermoset oven for desired reaction time, 1 h, and temperature, 150°C. The resulting membranes were then stored in solutions to be separated for further use.

Swelling Measurement

The sorption capacity of the membrane was measured by immersing the membrane samples in the same range of acetic acid–water mixtures at 30, 40, and 50°C. After wiping with the cleansing tissue, the membranes were weighed as quickly as possible. This procedure was repeated about 20 times until satisfactory reproducibilities were obtained. Then the samples were dried in a vacuum oven at room temperature to a constant weight. The swelling degrees, Q , were calculated by using

$$Q = \frac{m - m_0}{m_0} \times 100$$

where m is the mass of the swollen sample and m_0 is the original mass.

Pervaporation

The apparatus used in this study is illustrated in Ref. 2. The pervaporation separation experiments were performed employing two stainless steel pervaporation cell (Ref. 2). The detailed descriptions can be referred to ref. 2. The pervaporation experiments of acetic acid–water mixtures were conducted at 50, 60, and 70°C. Upon reaching steady state flow conditions, product samples were col-

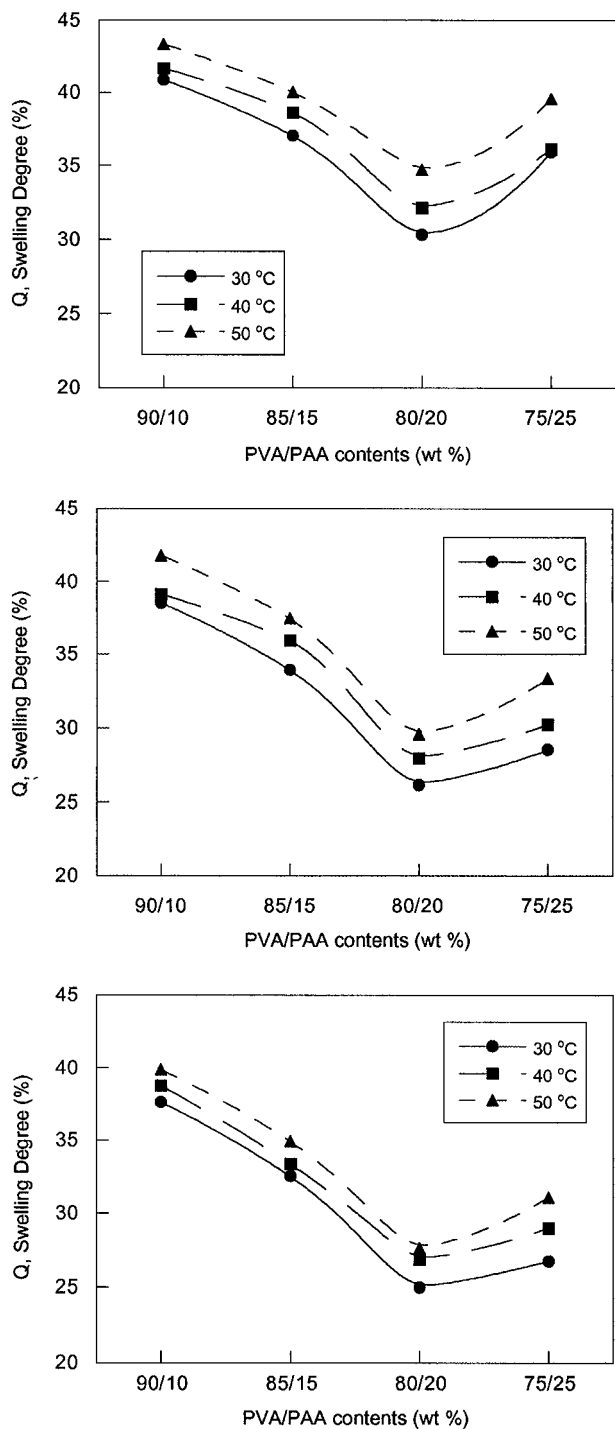


Figure 1 Swelling degrees for (a) 70 wt % acetic acid in the feed, (b) 80 wt % acetic acid in the feed, and (c) 90 wt % acetic acid in the feed at 30, 40, and 50°C using the crosslinked PVA membranes with varying PAA contents.

lected with timed intervals, isolated from the vacuum system, and weighed. The composition analysis of the permeate was done using gas chroma-

tography. 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.

RESULTS AND DISCUSSION

Swelling Behavior of Crosslinked PVA Membranes

Generally speaking, as the crosslinking density in a membrane increases, the resulting membrane has a more compact polymeric network structure leading to less solubility of a single component in a liquid mixture and less polymeric chain mobility due to less free volume in the membrane. Therefore, both the solubility and diffusivity of a permeant through the crosslinked membrane have a tendency to decrease in the pervaporation process. However, the solubility property could be changed not only by the chemical properties of the crosslinked agent but by the immersion of the membrane in the liquid mixture. Furthermore, an increase in the swelling degree results in the increase of the diffusivity due to the plasticizing effect, which means the decrease of an energy required for diffusive transport through the membrane.

Figure 1(a) shows the swelling behavior of the various crosslinked PVA membranes with the

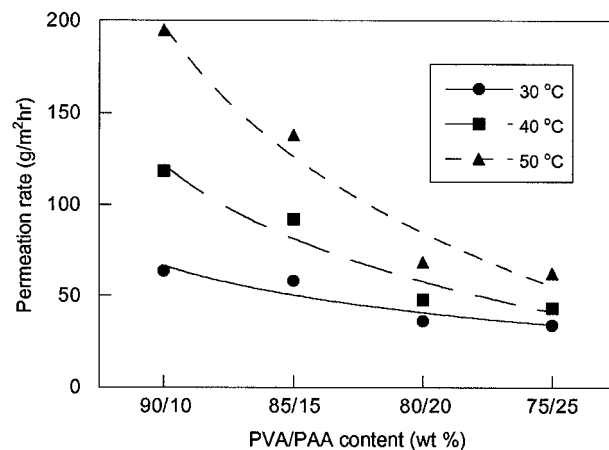


Figure 2 Permeation rates for 70 wt % acetic acid in the feed at 30, 40, and 50°C using the crosslinked PVA membranes with varying PAA contents.

PAA as the crosslinking agent for acetic acid : water = 70 : 30 mixture at 30, 40, and 50°C. As the temperature increases, the swelling degree, Q , increases slightly for the same membrane. This could be explained by the free volume concept described in the above. Since the swelling ratio indicates 1.36 to 1.41 at 30°C, this membrane has a high affinity to the liquid mixture in question. With increasing the PAA content, the swelling ratio of the membranes in acetic acid–water mixture decreases until 20 wt % of PAA and then increase beyond this point. Yeom and Lee⁶ reported that the aldehyde group has an affinity to both acetic acid and water. Therefore, it can be said that the crosslinking density and the aldehyde groups affect the swelling behavior of the resulting membranes, i.e., more crosslinks make the membrane more swollen while fewer crosslinks make it less swollen. It is clear from the previous IR studies⁸ that the crosslink portions increase quantitatively in the resulting membrane beyond 20 wt % PAA, but it is not proportional to the quantity of PAA content. This means that there would be still unreacted carboxylic acid in the resulting membrane. However, it can be seen that the swelling ratio increases even if the crosslinking degree increases. Since both polymers, PVA and PAA, and both solvents, acetic acid and water, are donors and acceptors of hydrogen bonds in these systems, it is practically impossible to realize what the dominating interactions would be.

Figure 1(b) and (c) illustrate the same trend with the previous Fig. 1(a). As can be seen, the water concentration in the mixture decreases, the swelling degree decreases. Since the membrane used in this study is highly hydrophilic, this phenomenon is very general in the pervaporation area, i.e., the solution uptake would be smaller when the water concentration is smaller in the mixture.

Pervaporation Analysis

Fig. 2 shows the permeation rates for acetic acid 70 wt % in the feed at various operating temperatures. As can be seen, the permeation rate increases with increasing the operating temperatures, while it decreases with increasing the PAA content in the resulting membrane. As the crosslinking density in a polymer increases, the resulting material has a more compact network structure, resulting in less chain mobility. Therefore, the free volume in the polymer and the

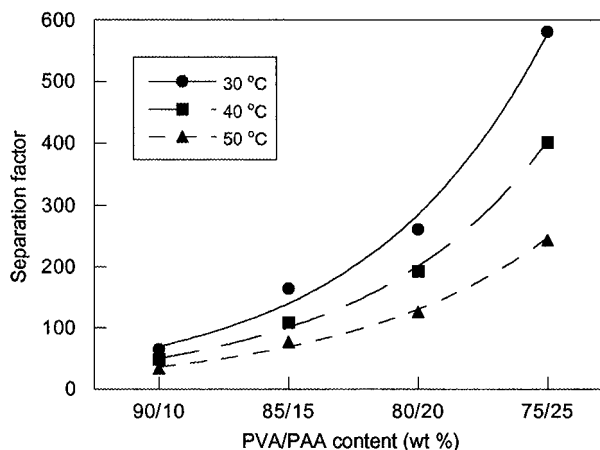


Figure 3 Separation factors for 70 wt % acetic acid in the feed at 30, 40, and 50°C using the crosslinked PVA membranes with varying PAA contents.

amount of solvent swelling decrease,¹⁰ since PVA is a well-known water-soluble polymer, in other words, highly hydrophilic material. In fact, as the hydroxyl content in PVA increases, the content of water in the permeate increases.³ Also, Nguyen et al.³ reported that the polyacid component favored the transport of water over that of acetic acid by preferential interactions. Therefore, the resulting just-blended polymer, PVA and PAA, would give more water permeation than the acetic acid permeation. They also reported that the blends with the polyacid lead to a more cohesive network in the liquid mixture due to the interactions between the two polymer species. However, when the flux is combined with the swelling ratio, it is consistent below the 20 wt % PAA content in the membrane, and not at 25 wt % PAA. It could be considered that the kinetic effect would affect the total flux rather than the thermodynamic effect at this point. Since the molecular size of the acetic acid is larger than that of water, the more compact network by the increase of the crosslinking degree due to the increase of PAA content hinders the transport of larger component in the feed. Therefore, the separation factor increases even though the swelling degree increases as can be seen in Figure 3. At this composition, the separation factor 581 and the permeation rate 33.7 g/m² h are obtained, respectively.

Figure 4 illustrates the permeation rates for 80 wt % acetic acid in the feed, the same trend as in Figure 2 can be obtained. However, the flux itself is less than that for 70 wt % acetic acid in the feed, as expected. The decrease of weight fractions of water in the feeds causes a strong hydrogen

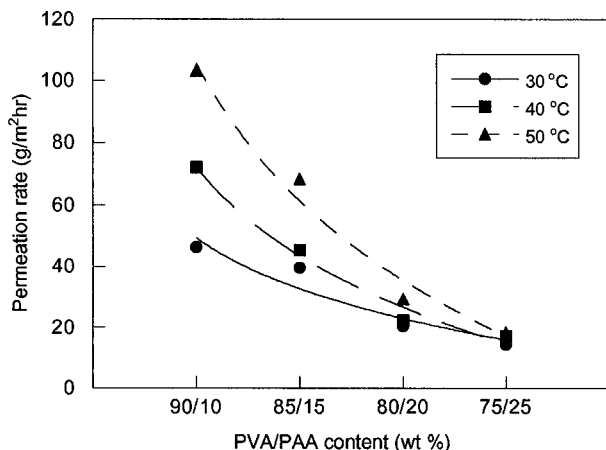


Figure 4 Permeation rates for 80 wt % acetic acid in the feed at 30, 40, and 50°C using the crosslinked PVA membranes with varying PAA contents.

bonding interaction among carboxyl or carbonyl groups. This strong self-interaction hinders the incorporation of water into the membrane. As a result, the flux decreases with decreasing the water concentration in feed. The separation factors are shown in Figure 5. When compared to the case of 70 wt % acetic acid in the feed, the flux is smaller, while the separation factors are larger. The separation factor and the flux give 602 and 14.4 g/m² h, respectively, at 30°C when using PVA/PAA = 75/25 membrane.

The results of the separation factor and the flux for 90 wt % acetic acid in the feed are shown in Figures 6 and 7, respectively. The separation factor of 795 at 30°C is obtained while the perme-

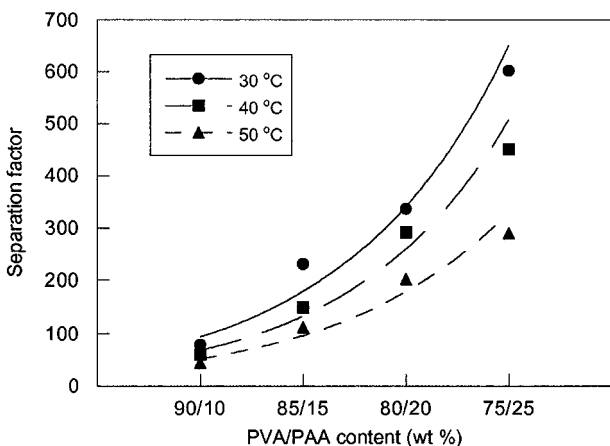


Figure 5 Separation factors for 80 wt % acetic acid in the feed at 30, 40, and 50°C using the crosslinked PVA membranes with varying PAA contents.

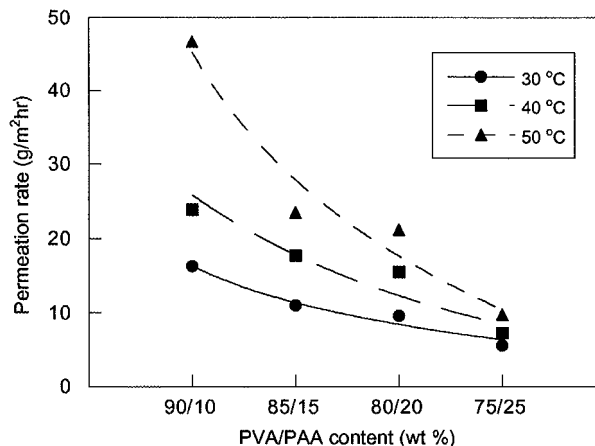


Figure 6 Permeation rates for 90 wt % acetic acid in the feed at 30, 40, and 50°C using the crosslinked PVA membranes with varying PAA contents.

ation rate is 5.6 g/m² h. This indicates that the water concentration in the permeate is 98.9 wt %.

Arrhenius Plot of Permeation Rate

The temperature dependence of the permeation rate can be expressed by an Arrhenius type relationship⁵

$$J_p = A_p \exp\left(\frac{-E_p}{RT}\right) \quad (1)$$

where A_p and E_p are the preexponential factor and the overall activation energy of permeation, respectively. Since the selectivities are governed

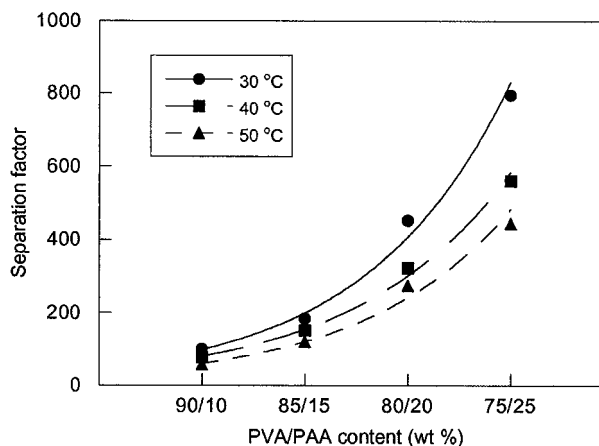


Figure 7 Separation factors for 90 wt % acetic acid in the feed at 30, 40, and 50°C using the crosslinked PVA membranes with varying PAA contents.

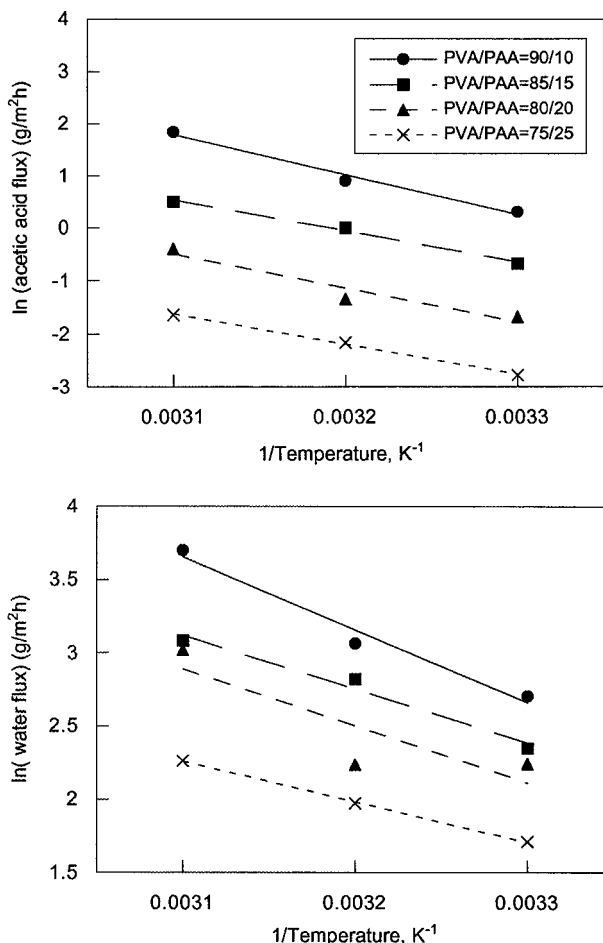


Figure 8 Arrhenius plots of individual component fluxes [(a) acetic acid and (b) water] through PVA membranes crosslinked with varying PAA contents.

by the sorption and the diffusion rates of the components at the same time, the E_p value should be dependent on both the diffusive activation energy, E_d , in the diffusion step and the heat of sorption, ΔH , in the sorption step, as follows.

$$E_p = \Delta H + E_d \quad (2)$$

Figure 8 shows the Arrhenius plots of the calculated individual component fluxes [(a) acetic acid, (b) water] using eq. (1) with varying the PAA content in the membrane for 90 wt % acetic acid concentration. Figure 9 illustrates the calculated E_p values from Figure 8. The larger solubility of the mixture leads to the smaller heat of sorption, ΔH . In the case of PVA/PAA = 90/10 membrane it could be predicted from eq. (2) that the diffusion step would be dominant over the sorption step since the solubility is quite high at this PAA con-

centration, resulting in small heat of sorption, as can be seen in Figure 1. The solubility decreases as the PAA content increases due to the increase of the crosslinking degree. Therefore, the same trend for the PAA = 10 wt % in the membrane is shown to PAA = 20 wt %. At PAA = 25 wt %, the sorption step would affect more than that of lower PAA content. However, it is not clear which step is dominant in this case from the swelling study.

CONCLUSIONS

The pervaporation separation and the swelling behavior of acetic acid–water mixtures were investigated at 30, 40, and 50°C using the cross-linked PVA membranes with varying the PAA contents and the acetic acid concentration in the feed. For the pervaporation separation of 80 wt % acetic acid in the feed, the PVA/PAA = 75/25 membrane shows the separation factor of 602 and the flux of 14.4 g/m² h at 30°C, respectively. And also, for the pervaporation transport studies of 90 wt % acetic acid solution, the same membrane gives the separation factor 795 and the flux 5.6 g/m² h, respectively. The swelling degree decreases as the PAA content in the resulting membrane decreases to 20 wt % of PAA due to the increase of the crosslinking portion and increase beyond this PAA content. The swelling degrees show fairly high at the operating temperatures and the total range of liquid mixtures in question. The overall activation energy of permeation was also calculated using an Arrhenius type relationship. From this swelling study, it could be concluded

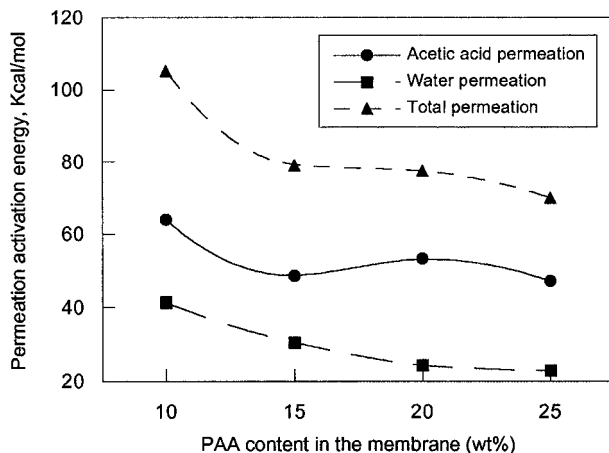


Figure 9 Permeation activation energies calculated from Figure 8.

that the diffusion step is dominant over the sorption step since the solubility is quite high at this PAA content, leading to a small heat of sorption. However, it is not clear which step is dominant for 25 wt % of PAA content.

REFERENCES

1. R. Y. M. Huang, A. Moreira, R. Notarfonzo, and Y. F. Xu, *J. Appl. Polym. Sci.*, **35**, 1191–1200 (1988).
2. M. Yoshikawa, Y. Takahashi, K. Sanui, and N. Ogata, *Membrane (Japan)*, **10**, 247–253 (1985).
3. T. Q. Nguyen, A. Essamri, R. Clement, and J. Neel, *Makromol. Chem.*, **188**, 1973–1984 (1987).
4. R. Y. M. Huang and J. W. Rhim, *Polymer International*, **30**, 129–135 (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, Canada 1991.
6. Choong-Kyun Yeom and Jew-Ho Lee, “Pervaporation Separation of Water-Acetic acid Mixtures Through Poly(vinyl alcohol) Membranes Crosslinked with Glutaraldehyde”, to appear.
7. C. K. Yeom and K.-H. Lee, “A Study on Permeation Behavior of Liquid Mixture Through PVA Membranes Having Crosslinking Gradient Structure in Pervaporation”, to appear.
8. J. W. Rhim, M.-Y. Sohn, H.-J. Joo, and K.-H. Lee, *J. Appl. Polym. Sci.*, **50**, 679–684 (1993).
9. J.-W. Rhim, M.-Y. Sohn, and K.-H. Lee, *J. Appl. Polym. Sci.*, **52**, 1217–1222 (1994).
10. K.-H. Lee, H.-K. Kim, and J.-W. Rhim, *J. Appl. Polym. Sci.*, to appear.
11. J.-W. Rhim, H.-K. Kim, and K.-H. Lee, *J. Appl. Polym. Sci.*, to appear.
12. E. Ruckenstein and F. Sun, *J. Membrane Sci.*, **95**, 207–219 (1994).

Received January 26, 1996

Accepted June 29, 1996