Pervaporation Separation of Binary Organic–Aqueous Liquid Mixtures Using Crosslinked Poly(vinyl alcohol) Membranes. IV. Methanol–Water Mixtures

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SYNOPSIS

The pervaporation separation of methanol–water (M/W) mixtures was carried out using crosslinked poly(vinyl alcohol) (PVA) membranes with the low molecular weight of poly(acrylic acid) (PAA) as the crossinking agent. The PVA/PAA ratio in the crosslinked membrane was 90/10, 85/15, and 80/20 by weight. The operating temperatures were 50, 60, and 70°C, and the compositions of methanol–water mixtures to be separated were 70/30, 80/20, 90/10, and 95/5 (M/W) solutions. In all cases, the PVA/PAA = 80/20 membrane showed the best results. For M/W = 90/10 solution, the separation factor, $\alpha_{w/m} = 465$, and the permeation rate, 0.109 kg/m^{2}h, at 70°C were obtained using the PVA/PAA = 80/20 menbrane. The permeation rate and the separation factor for M/W = 95/5 solution showed 0.033 kg/m^{2}h and $\alpha_{w/m} = 2650$, respectively, when PVA/PAA = 80/20 membrane was used. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation is an emerging membrane separation process, in which the feed mixture is directly in contact with one side of a dense or a composite membrane under atmospheric pressure while a low partial pressure of the permeate species is maintained on the other side of the membrane by vacuum or a swept inert gas. The advantages of the simplisity, the low costs, the acceptable flux, and the high selectivity have shown it to be a promising process.

This article is a continuation of publications on the pervaporation separation of phenol–water and ethanol–water mixtures[1,2] using crosslinked poly(vinyl alcohol) (PVA) membranes with poly(acrylic acid) (PAA) as a crosslinking agent.[3] The pervaporation membrane separatiom of methanol–water mixtures has not been considered extensively because this mixture does not have an azeotropic point even if methanol is a practical interest in industries. However, since the molecular size of meth-

anol is smaller than that of ethanol and the hydrogen bonding force of methanol with water is larger than that of ethanol, it is worthy of research. Will and Lichtenthaler[4] found that the comparison of the pervaporation separation and vapor permeation separation process is much better than the pervaporation separation process for the alcohol–water mixtures. Nguyen et al.[5] stuided the applicability of PVA/PAA blended films for the pervaporation separation of acetic acid–water mixtures. They investigated the film-forming properties of the blended PVA/PAA membranes in detail.[6,7]

This article deals with the separation of methanol–water mixtures having various composisions using PVA/PAA = 90/10, 85/15, 80/20 crosslinked membranes at 50, 60, and 70°C.

EXPERIMENTAL

Materials

Fully hydrolyzed PVA with molecular weight of 50,000 and PAA with molecular weight of 2000 (25 wt % in water) were purchased from Showa Chem-
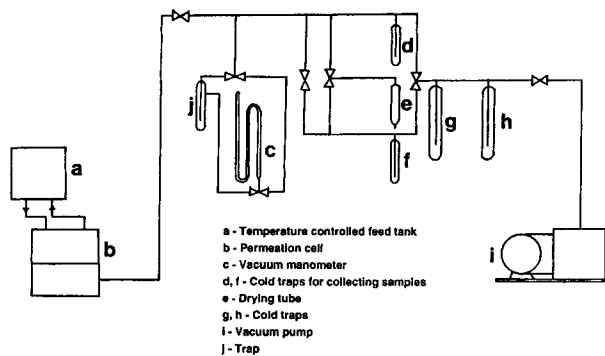
Figure 1 Schematic diagram of pervaporation apparatus used in this study.

ical Co. The methanol was analytical grade from Merck. Water used was the ultrapure water produced from the MPI 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. 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 thermosetted oven for desired re-

action times and temperatures. The resulting membranes were then stored in solutions to be separated for further use.

Pervaporation

The apparatus used in this study is illustrated in Figure 1. The pervaporation separation experiments were performed employing two stainless steel pervaporation cell (Fig. 2). The detailed descriptions can be found in ref. 2. The pervaporation experiments of methanol–water mixtures were conducted at 50, 60, and 70°C. Upon reaching steady-state flow conditions, product samples were collected with timed intervals, isolated from the vacuum system, and weighed. The composition analysis of the permeate was done using gas chromatography. The following relationship was used to calculate the separation factor:

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

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

RESULTS AND DISCUSSION

In general, it could be said that the hydrogen bonding force between water and PVA is stronger than that between organic chemical and PVA, since the PVA material shows the preferential water permeation rather than that of organic component in the feed
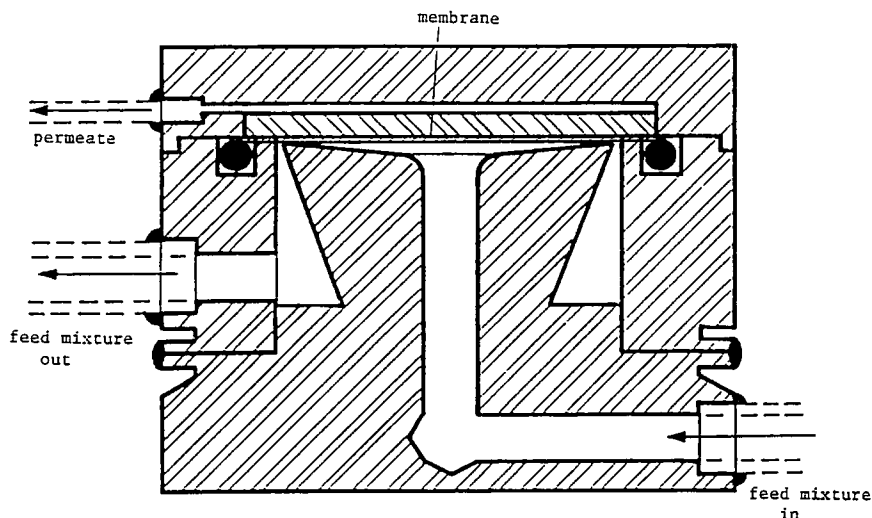

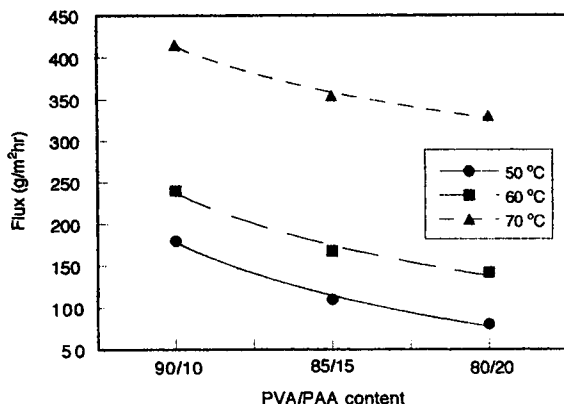**Figure 2** Configuration of the pervaporation cell used in this study.

Figure 3 Permeation rates for methanol : water = 70 : 30 solutions with varying PAA contents at 50, 60, and 70°C.

Figure 4 Separation factors for methanol : water = 70 : 30 solutions with varying PAA contents at 50, 60, and 70°C.

mixture. However, in the case of PAA used as the crosslinking agent, the carboxylic group can also form the hydrogen bonding between the polymer and the individual organic component in the feed mixture. Yoshikawa et al.[8] investigated the hydrogen bonding abilities of water, ethanol, and acetonitrile toward the carboxylic acid group. Their results showed that this ability decreased in the following order: water > ethanol > acetonitrile. This implies that the carboxylic acid group in the membrane material may interact with water stronger than ethanol and acetonitrile. However, it is well known that the methanol is more hydrophilic than the ethanol. Therefore, the hydrogen bonding ability of the methanol could lie between water and ethanol. This means that the flux of the methanol through the hydrophilic membrane would be smaller than that of water and larger than that of ethanol. As a result, it could be expected that the separation factor for the methanol–water mixture is smaller than that for the ethanol–water mixture.

As the crosslinking density in a polymer increases, the resulting membrane has a more compact network (i.e., less chain mobility and free volume). This leads to a sizing effect of the feed mixtures. In the case of the feed mixture in question, the methanol component would cause less permeability than water. Therefore, it might be said that the separation factor toward water should be larger than 1 at least.

Figure 3 shows the permeation rates for methanol/water (M/W) = 70/30 solutions at 50, 60, and 70°C using PVA/PAA = 90/10, 85/15, and 80/20 membranes. As can be seen, the more PAA contents in the membranes and the lower the operating temperatures are, the less flux can be observed. While the former might be due to the cross-
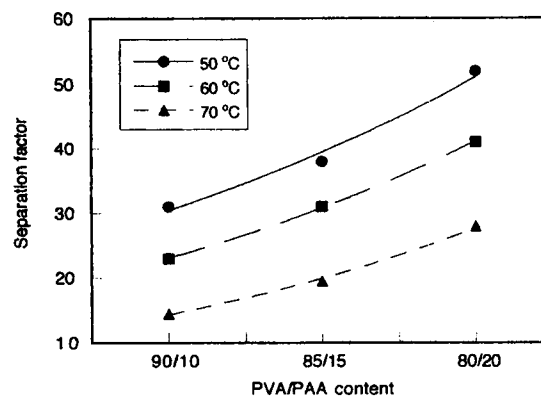
linking degree effect, the latter case could result from the hydrogen bonding ability between the water and the membrane. Since this interaction ability becomes strong as the operating temperatures are lowered, the flux decreases. As a result, the selectivity toward water increases, while the permeation rate decreases. The PVA/PAA = 80/20 membrane at 70°C shows ca. 0.33 kg/m²h. Figure 4 illustrates the separation factor at the same experimental conditions. The PVA/PAA = 80/20 membrane shows the separation factor of $\alpha_{w/m} = 28$ at 70°C. This indicates the methanol concentration of 7.7 wt % in the permeate. In contrast with this result, the commercial GFT membrane, in which the base polymer PVA is crosslinked with dicarboxylic acid and maleic acid and which is manufactured by GFT Co. in Germany,[9] shows ca. 5.2 wt % in the permeate by the pervaporation technique.[4]

The separation results for M/W = 80/20 solution are shown in Figures 5 and 6. As expected, the permeation rates are less than the case of M/W = 70/
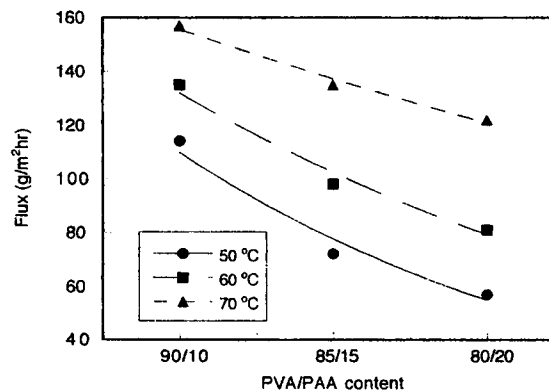

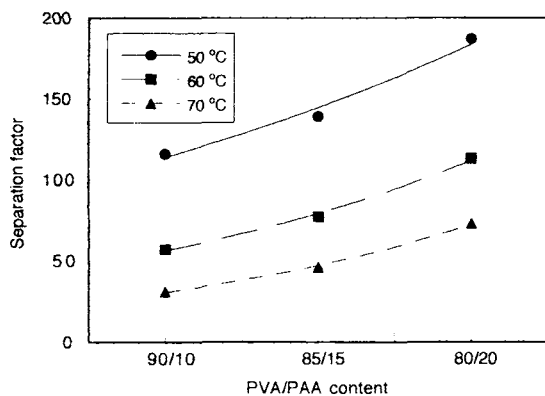**Figure 5** Permeation rates for methanol : water = 80 : 20 solutions with varying PAA contents at 50, 60, 70°C.

Figure 6   Separation factors for methanol : water = 80 : 20 solutions with varying PAA contents at 50, 60, and 70°C.

Figure 8   Separation factors for methanol : water = 90 : 10 solutions with varying PAA contents at 50, 60, and 70°C.

30 solution, while the separation factors are higher. This is due to the water contents in the feed mixtures. In general, the absorption ability of the water in the hydrophilic membrane would increase as the water concentration in the feed mixtures increases. The PVA/PAA = 80/20 membrane shows the permeation rate, 0.122 kg/m^{2}h, and the separation factor, $\alpha_{w/m}$ = 73, at 70°C.

Figures 7 and 8 illustrate the permeation rates and the separation factors for M/W = 90/10 solution. As can be seen, the permeation rates decrease and the separation factors increase when comparing with the case of M/W = 80/20 solution. The permeation rate, 0.109 kg/m^{2}h, and the separation factor, $\alpha_{w/m}$ = 465 (methanol concentration in the permeate = 1.9 wt %), were obtained at 70°C when the PVA/PAA = 80/20 membrane was used. The selectivity, again, is relatively higher than the GFT membrane results. The methanol concentration in the permeate from the pervaporation is around 80
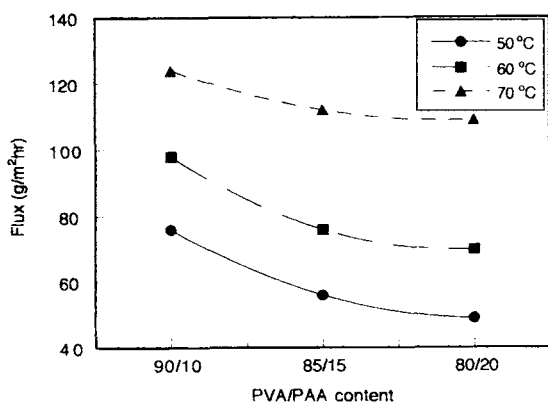
wt % at 60°C and that from the vapor permeation is around 20 wt % at 70°C.[4] However, at 80°C the GFT membrane shows the methanol concentration of ca. 2.5 wt % in the permeate. In this case, it can be said that our membrane is competitive with the GFT membrane.

Figures 9 and 10 show the separation results for the M/W = 95/5 solution. The PVA/PAA = 80/20 membrane shows the permeation rate, 0.033 kg/m^{2}h, and the separation factor, $\alpha_{w/m}$ = 2650 (methanol concentration in the permeate = 0.71 wt %) at 60°C, while the methanol in the permeate is ca. 2.5 wt % from the GFT menbrane.[4]

CONCLUSION

The pervaporation separation of methanol–water mixture was carried out using crosslinked PVA membranes with the low molecular weight of PAA as the crosslinked agent. The experiments were

Figure 7   Permeation rates for methanol : water = 90 : 10 solutions with varying PAA contents at 50, 60, and 70°C.

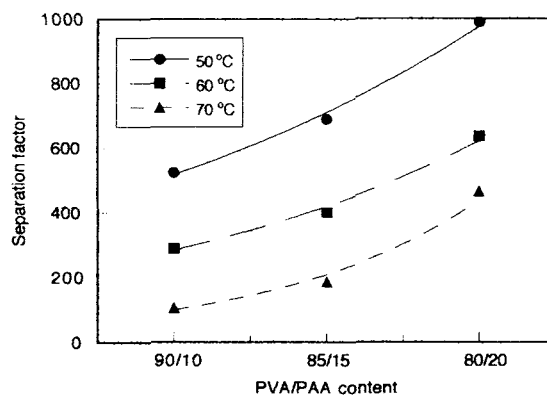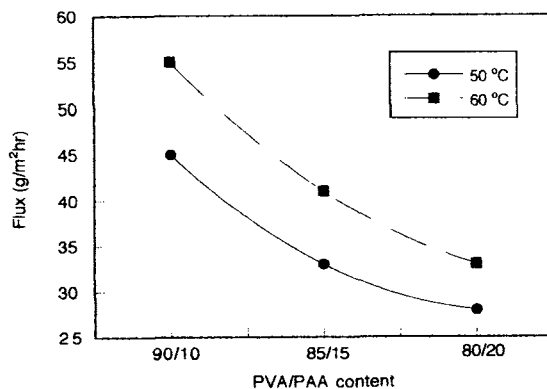**Figure 9**   Permeation rates for methanol : water = 95 : 5 solutions with varying PAA contents at 50 and 60°C.
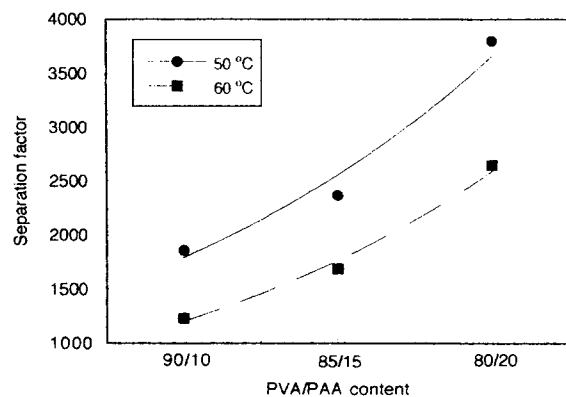
Figure 10   Separation factors for methanol : water = 95 : 5 solutions with varyings PAA contents at 50 and 60°C.

conducted at 50, 60, and 70°C for various compositions of methanol–water mixtures. In all cases, the PVA/PAA = 80/20 membrane showed the best results. For M/W = 90/10 solution, the separation factor, $\alpha_{w/m}$ = 465, and the permeation rate, 0.109 kg/m^{2}h, at 70°C were obtained using PVA/PAA = 80/20 membrane. The permeation rate and the separation factor for M/W = 95/5 solution showed 0.033 kg/m^{2}h and $\alpha_{w/m}$ = 2650 at 60°C when PVA/PAA = 80/20 membrane was used.

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