

Pervaporation Separation of Water-*iso*-Propyl Alcohol Mixture Using PVA/PAA Membranes

Ji-Won Rhim[†], Sun-Woo Kim, and Kew-Ho Lee*

Dept. of Chem. Eng., Hannam Univ., 133 Ojung-dong, Daedeog-ku, Taejon 300-791, Korea

*Membranes and Separation Laboratory, Korea Research Institute of Chemical Technology
Daedeog-Danji P.O. Box 9, Taejon 305-606, Korea

(Received August 28, 1996, Accepted October 22, 1996)

PVA/PAA 막을 이용한 물-이소프로필알코올 혼합물의 투과증발 분리

임 지원[†] · 김 선 우 · 이 규 호*

한남대학교 공대 화공과, *한국화학연구소 분리소재연구실
(1996년 8월 28일 접수, 1996년 10월 22일 채택)

Abstract: The crosslinked PVA/PAA membranes developed in our laboratory have been characterized for water-*iso*-propyl alcohol mixture in terms of permeabilities and separation factor. When the feed mixture was 12wt% water, the permeability and the separation factor for PVA/PAA=75/25 membrane show 63g/m²h and 1520 at 80°C, respectively. In case of 5wt% water in feed mixture, the permeability for PVA/PAA=75/25 membrane is 56g/m²h at 80°C while the separation factor is 1563.

요 약 : 본 연구는 가교된 PVA/PAA 막을 이용하여 5와 12wt%를 포함하는 물-이소프로필알코올 계에 대한 투과증발 실험을 60, 70 및 80°C의 작업온도에서 수행하였다. PVA/PAA=75/25 막을 사용했을 경우 공급액의 조성이 물 12wt%에서 투과도 및 선택도가 온도 80°C에서 63g/m²h과 1520을 각각 나타내었으며, 물 5wt%에서는 같은 온도에서 투과도 56 g/m²h을 그리고 선택도는 1563을 얻었다.

1. Introduction

Separations of azeotropic mixtures have been industrially carried out by means of either distillation or recrystallization techniques, which require much heat energy. On the other hand, separations by membranes are one of the most promising processes as an energy-saving technology. Pervaporation technique is one of the potential methods for specific and selective separation of neutral substances,

particularly azeotropic mixtures, including water-*iso*-propyl alcohol(IPA) mixture which azeotropic point is at 87.8wt% of IPA at 80.4°C.

Because of practical interest of this mixture in industries, a number of membranologists have carried out the pervaporation separation experiments. Table 1 summarizes the pervaporation separation characteristics in terms of the permeability and the separation factor for various membrane materials.

This paper is a continuation of the investigation

Table 1. Summary of Pervaporation Separation Characteristics for Various Membrane Materials Published in the Literature

Membrane materials	Feed composition	Temperature (°C)	Permeability (kg/m ² hr)	Separation factor ($\alpha_{w/IPA}$)	Ref.
Cellophane	12	60	0.7	15.6	1
Modified cellulose acetate	12	80	3.7	20	2
PVA-PAN composite	~25	70~90	0.6~1.4 (water flux)	99.0% (permeate conc.)	3,4
Nafion	11.5	24~40	0.46~0.76	15.9~15.3	5
Sulfonated Polyethylene	10.6~11.2	26	0.2~1.041	28709~5.5	6
Cellophane	20 mol%	60	0.03~0.12	3~20	7
Poly(maleimide-co-acrylonitrile)	15	15	0.0051	11330	8

of the pervaporation separation characteristics for various liquid mixtures using developed poly(vinyl alcohol) / poly(acrylic acid) (PVA/PAA) membranes varying PAA contents. The experiments are conducted for 88 and 95wt% of IPA in water at 60, 70, and 80°C.

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., respectively. The *iso*-propanol was analytical grade from Merck. Used water was the ultra-pure produced from MPI system.

2.2. Membrane preparation

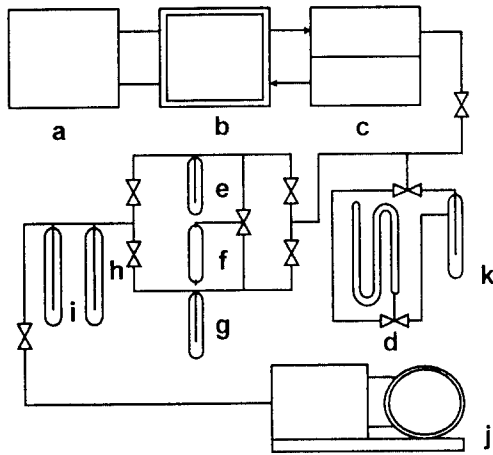
Aqueous 10wt% PVA solutions were prepared by dissolving preweighed quantities of dry PVA in ultra-pure water and heating at 90°C for at least 6 h. Aqueous 25wt% PAA solutions were diluted to 10wt% solutions. Then two polymer solutions were mixed together by varying each component composition to form 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, 1hr, and temperature, 150°C. The resulting dense non-porous membranes with ca. 200µm were then stored in solutions to be separated for further use. The details would be referred in ref.[9].

2.3. Pervaporation

The apparatus used in this study is illustrated in Fig. 1. The pervaporation separation experiments were performed employing two stainless steel pervaporation cell(Fig. 2). The detailed descriptions can be referred to Ref.[3]. The pervaporation experiments of *iso*-propyl alcohol-water mixtures were conducted at 60, 70 and 80°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 a gas chromatography. The following relationship was used to calculate the separation factor :

$$\alpha_{w,i} = \frac{(y_i/y)}{(x_i/x)}$$



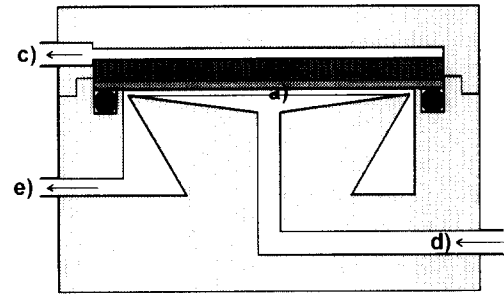
- | | |
|---|------------------|
| a : Temperature Controller | f : Drying tube |
| b : Feed tank | h,i : Cold traps |
| c : Permeation cell | j : Vacuum pump |
| d : Vacuum manometer | k : Trap |
| e,g : Cold traps for collecting samples | |

Fig. 1. Schematic diagram of pervaporation apparatus used in this study.

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

3. Results and Discussions

In general, 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 is decreased and the amount of solvent swelling as well. This principle can be applied to the separation process of crosslinked polymer membranes : as the crosslinking density in the membrane increases, the solubility of the liquid mixture declines and the diffusivity, which is governed by the free volume, decreases due to the rigidity of the polymer chains. This might cause the permeation rate through the membrane to decrease. And, from the viewpoint of the separation factor, PVA is a well-known water-



- | | |
|-------------------|---------------------|
| a) membrane | d) feed mixture in |
| b) porous support | e) feed mixture out |
| c) permeate | |

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

soluble polymer, in other words, highly hydrophilic material. This means that the hydroxyl group in PVA causes the strong hydrogen bonding with the feed mixtures to be separated. The hydrogen bonding force between water and PVA is stronger than that between *iso*-propyl alcohol and PVA since the PVA material shows preferential water permeation rather than alcohol permeation[10-12]. And also, the carboxylic acid group in PAA, which is used as the crosslinking agent in this study forms the hydrogen bonding between the polymer and the individual component in the feed mixture, i.e., water and *iso*-propyl alcohol. The water-soluble polymer, PAA, could be considered that the interaction force with alcohol decreases as the carbon number increases. As a result, the PVA/PAA membrane could absorb selectively water rather than alcohol and also permeate mainly water.

Figs. 3 and 4 illustrates the permeabilities and the separation factor for 12wt% water in feed mixture at various operating temperatures including azeotropic temperature, 80°C. As expected, the permeability decreases as the PAA content in PVA increases, while the separation factor increases. And also, as mentioned in the above paragraph, the permeability increases as the operating temperature increases. The permeability and the separation factor for PVA/PAA = 75/25 membrane show 45g/m²h

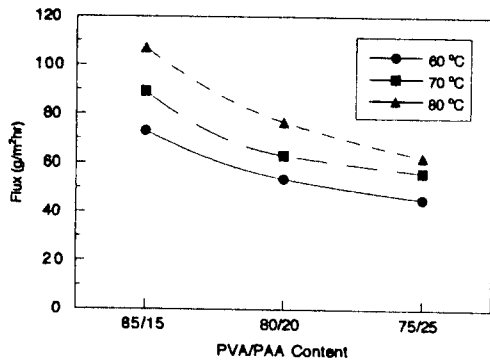


Fig. 3. Flux for 12wt% water in *iso*-propyl alcohol-water mixture using various PVA/PAA membranes by weight.

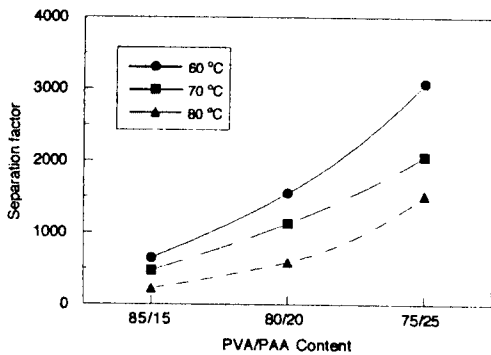


Fig. 4. Separation factor 12wt% water in *iso*-propyl alcohol-water mixture using various PVA/PAA membranes by weight.

and 3077 at 60 °C, respectively, and 63g/m²h and 1520 at 80 °C, respectively.

Figs. 5 and 6 show the permeabilities and the separation factor for 5wt% water in feed mixture at same operating temperatures. It could be predicted in this case that the total permeability is less than that for 12wt% water in feed mixture since the sorption capability for 5wt% water in the feed is smaller. As can be seen in Fig. 5, the permeability for PVA/PAA=75/25 membrane is 38.3g/m²h at 60 °C while the separation factor is 3860. And the permeability and the separation factor at 80 °C are 56g/m²h and 1563, respectively. Since the thicknesses of the prepared membranes are ca. 200 μm, the flux is much smaller than that of PVA-PAN mem-

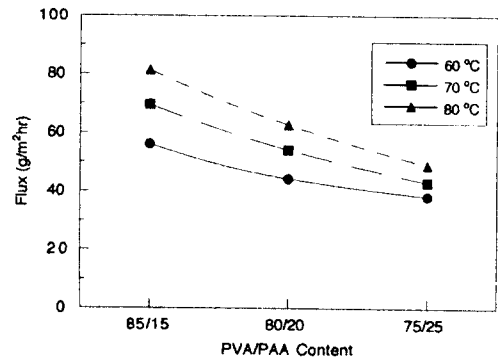


Fig. 5. Flux for 5wt% water in *iso*-propyl alcohol-water mixture using various PVA/PAA membranes by weight.

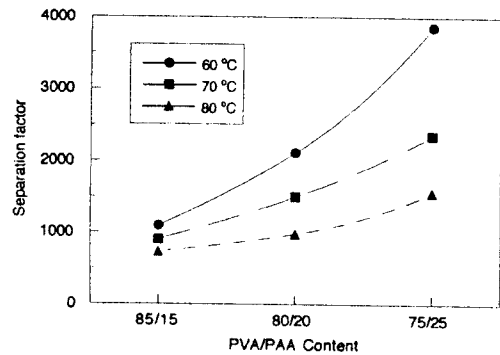


Fig. 6. Separation factor 5wt% water in *iso*-propyl alcohol-water mixture using various PVA/PAA membranes by weight.

branes which thickness is ca. 1 μm. However, this results could be competitive with the results summarized in Table 1 if the thickness is as thin as PVA-PAN's.

4. Conclusions

The pervaporation separation of water-*iso*-propyl alcohol mixture using crosslinked PVA/PAA membranes which contains PAA as the crosslinking agent from 15 to 25wt% to PVA have been carried out at 60, 70 and 80 °C. When the feed mixture was 12wt% water, the permeability and the separation factor for PVA/PAA=75/25 membrane show 45g/m²h and 3077 at 60 °C, respectively, and 63g/m²h

and 1520 at 80°C, respectively. In case of 5wt% water in feed mixture, the permeability for PVA/PAA=75/25 membrane is 38.3g/m²h at 60°C while the separation factor is 3860. And the permeability and the separation factor at 80°C are 56g/m²h and 1563, respectively.

References

1. J. W. Carter and B. Jagannadhaswamy, *Brit. Chem. Eng.*, **9**, 523(1964).
2. V. M. Manedova, Z. N. Bagrova, G. P. Bitkova, and G. A. Galustjan, *Neftepererab. Neftekhim.*, **10**, 36(1969).
3. R. Rautenbach, M. Franke, and S. T. Klatt, *J. Membrane Sci.*, **61**, 31(1991).
4. B. Will and R. N. Lichtenthaler, *J. Membrane Sci.*, **68**, 119(1992).
5. I. Cabasso and Z.-Z. Liu, *J. Membrane Sci.*, **24**, 101(1985).
6. I. Cabasso, E. Korngold, and Z.-Z. Liu, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 577(1985).
7. E. Nagy, O. Borlai, and A. Ujhidy, *J. Membrane Sci.*, **7**, 109(1980).
8. M. Yoshikawa, H. Yokoi, K. Sanui, and N. Ogata, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2159 (1984).
9. J. W. Rhim, M. Y. Sohn, H. J. Joo, and K. H. Lee, *J. Appl. Polym. Sci.*, **50**, 679(1993).
10. J. W. Rhim, M. Y. Sohn, and K. H. Lee, *J. Appl. Polym. Sci.*, **52**, 1217(1994).
11. K. H. Lee, H. K. Kim, and J. W. Rhim, *J. Appl. Polym. Sci.*, **58**, 1707(1995).
12. J. W. Rhim, H. K. Kim, and K. H. Lee, *J. Appl. Polym. Sci.*, will appear soon.