

# Water–Ethanol Permsepation by Pervaporation through Photocrosslinked Poly(vinyl Alcohol) Composite Membranes

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## Synopsis

Water–ethanol permselectivity was investigated by pervaporation through composite membranes which were prepared by coating photocrosslinkable poly(vinyl alcohol) containing pendant styrylpyridinium group (0.86–3.93 mol %) on porous films. These membranes were water-permselective, and the selectivity was dependent on the state of membranes; namely, incorporation ratio of styrylpyridinium group on poly(vinyl alcohol), molecular weight of the base polymer, coating thickness of a photopolymer, etc. Photocrosslinkable styrylpyridinium group showed, of course, the ionic character by a pyridinium moiety to work on permsepation of water effectively as well as preventing the dissolution of membranes by crosslinking. Membranes based on the higher molecular weight poly(vinyl alcohol) ( $\bar{P} = 1700$ ) gave the higher permselectivity of water in general than those of lower molecular weight ( $\bar{P} = 500$ ) one. Swelling of the polymers reached 160%, and permeation rate through the membranes increased with the increase of swelling. Selective diffusion of water was found to take place in swelling, and to play a part in the water-permsepation through the membranes.

## INTRODUCTION

There has been much interest in recent years in water–ethanol permsepation by membrane processes, and greater efforts have been aimed toward the development of very effective membranes for this purpose. There are two types: namely, water-permselective membranes and ethanol-permselective membranes. In order to be water-permselective, membranes must be hydrophilic and attract water preferentially. Indeed, membranes derived from hydrophilic substrates such as cellulose, poly(vinyl alcohol) (PVA), and so on are water-permselective from water–ethanol mixtures. Among them, PVA membranes which were supported by substrate polymer have been applied for practical use by pervaporation recently.<sup>1</sup> We also have attempted to obtain the water–ethanol permselective membranes using plasma graft polymerization technique. Membranes prepared by graft polymerization of hydrophilic monomers like acrylic acid<sup>2,3</sup> and methacrylic acid<sup>4</sup> onto porous substrate membranes pretreated by glow discharge plasmas have revealed water-permselectivity, and the selectivity increased much by the ionization of graft polymer layers.

PVA is known as one of the popular synthetic polymers which have higher hydrophilicity. The characteristics are ascribed mainly to the hydroxy group in the side chain, and the polymer is soluble in water. In order to apply this

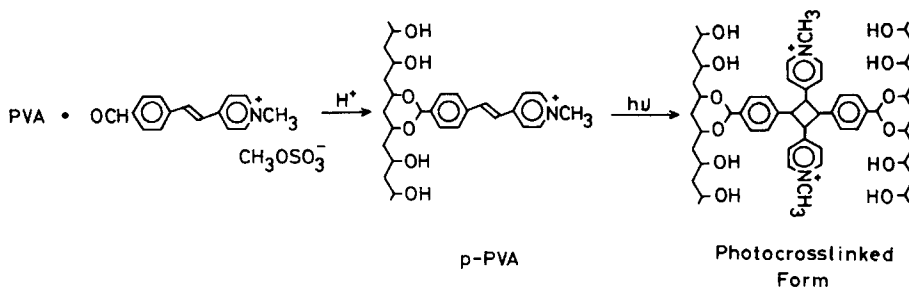
polymer to practical use, for example, to permselective membranes, some kind of crosslinking is necessary to prevent the dissolution. Heat treatment is popular for crosslinking, and another novel process lies in photocrosslinking of PVA derivatives with photosensitive groups. Ichimura, one of the authors, has developed the process with PVA-containing photocrosslinkable moieties like styrylpyridinium groups,<sup>5-7</sup> and applied these for photosensitization,<sup>8</sup> immobilization of enzymes,<sup>9</sup> and so on. One of the great merits of the process by this photopolymer is that the crosslinking proceeds under mild condition. Only exposure to room light is good enough for crosslinking of PVA, while heat treatments need to raise temperature at about 200°C.

In this study, composite membranes were prepared from the photopolymers with various amount of styrylpyridinium group on the substrate porous film, and water-ethanol permseparation was investigated by pervaporation. In the photopolymer, pendant styrylpyridinium group supplied "the olefinic double bond" which proceeded the 2 + 2 addition to lead crosslinking under exposure to light. It also should be noticed that styrylpyridinium group provided ionic character. It is well known that ionic groups in membrane work effectively to enhance the water-permselectivity as observed in some ion-exchange membranes like Nafion,<sup>10</sup> and the grafted and ionized membranes.<sup>2-4</sup> Such ionic effects on permseparation of water are due to the hydrophilicity, and in addition the permeation rate increases by the enlargement of the path by ionic repulsion.

Then we expected the similar effects with the membranes composed from the photopolymers containing ionic styrylpyridinium group. We would like to report the results on the water-ethanol permseparation by pervaporation through membranes of the photocrosslinked PVA formed on substrate porous films.

## EXPERIMENTAL

**Photocrosslinked PVAs.** Photocrosslinkable PVAs were prepared by the coupling of 1-methyl-4-(*p*-formylstyryl)pyridinium methosulfate to a base PVA according to a previous paper.<sup>5</sup> The reaction path as well as the dimerization to form crosslinked polymer is shown in Scheme I:



Scheme I. Reaction scheme for the preparation of photocrosslinkable PVAs containing styrylpyridinium group and the photodimerization.

Details of the reaction procedure have been described previously.<sup>5</sup> Six kinds of photocrosslinkable polymers as shown in Table I were used in this study, and they are abbreviated as *p*-PVA<sub>1-6</sub>, respectively. Base PVA used was mainly the one with molecular weight 1700, and the saponification ratio 88% from

TABLE I  
Photocrosslinkable Poly(vinyl Alcohol) Solutions Containing Styrylpyridium Group  
Used in This Study

Sample no.	Substrate PVA		SbQ% <sup>c</sup>	Concn (wt %)
	$\bar{P}^a$	SR% <sup>b</sup>		
<i>p</i> -PVA <sub>1</sub>	1700	88	1.97	10.3
<i>p</i> -PVA <sub>2</sub>	1700	88	1.35	10.4
<i>p</i> -PVA <sub>3</sub>	1700	88	1.18	8.8
<i>p</i> -PVA <sub>4</sub>	1700	88	0.86	10.6
<i>p</i> -PVA <sub>5</sub>	500	88	1.97	10.5
<i>p</i> -PVA <sub>6</sub>	500	100	3.93	10.5

<sup>a</sup>Degree of polymerization.

<sup>b</sup>Saponification ratio in %.

<sup>c</sup>Incorporation mol % of styrylpyridinium group in PVA (SbQ = stilbazole quarternized).

poly(vinyl acetate). In addition to this, the ones with molecular weight 500, and the saponification ratios 88% and 100% were also used. Incorporation of the styrylpyridinium group could be raised more than 4%, but was restricted due to the mechanical stability for use as membranes after crosslinking.

**Preparation of Membranes.** An aqueous solution of the photocrosslinkable PVAs was cast on a porous film using a coater. Millipore MFVS with average pore size in 0.025  $\mu\text{m}$  was used mainly for substrate films. Coated membranes were allowed to dry in air, and simultaneously the PVA layer was crosslinked with light of fluorescent lamp in the laboratory. Since the pendant styrylpyridinium was photosensitive not only to UV light but also to visible light (i.e., up to 450 nm), the wavelength of a room light source was sufficient enough for crosslinking the modified PVAs. After crosslinking, the composite membranes were soaked in deionized water for about 2 h, and soluble portions were removed. With the single step of polymer coating, composite membranes with the photocrosslinked PVA content from 1.1 mg/cm<sup>2</sup> to 1.7 mg/cm<sup>2</sup> were obtained on Millipore MFVS depending on the photopolymer solutions. By repeating the processes, composite membranes with thicker coating of photocrosslinked PVA were prepared.

**Pervaporation.** Water-ethanol separation was carried out by pervaporation. Details of the procedure were the same as described before.<sup>2-4</sup> Pervaporation was usually conducted at 40°C, and also made in the temperature range between 30 and 50°C to see the temperature dependences and to obtain the activation energies for permeation with some membranes. Concentrations of water and ethanol were obtained with gas chromatography equipped with Porapak column heated at 105°C. Permselectivity for water was evaluated by separation factor, which was given by the following equation:

$$\alpha_{\text{EtOH}}^{\text{water}} = (X_{\text{water}}/X_{\text{EtOH}})/(Y_{\text{water}}/Y_{\text{EtOH}})$$

where  $X_{\text{water}}$  and  $X_{\text{EtOH}}$  were the concentrations of water and ethanol in permeate and  $Y_{\text{water}}$  and  $Y_{\text{EtOH}}$  were those in feed, respectively. Higher values of  $\alpha_{\text{EtOH}}^{\text{water}}$  naturally correspond to the higher permselectivity of water by pervaporation.

**Swelling.** A sample of about 400 mg of the photocrosslinked PVA was obtained by casting the starting aqueous solution on a glass plate (without a substrate porous film). These polymers were dipped in aqueous ethanol solutions (0–90 wt %) at room temperature for about 2 h, and the equilibrium was reached. The swelling ratio [SR (%)] was obtained from the weights of a sample in dry state ( $W_0$ ) and in swollen state ( $W$ ), by the following equation:

$$\text{SR (\%)} = 100 \times (W - W_0) / W_0$$

## RESULTS AND DISCUSSION

### Permsepation of Water

Figure 1 shows a result of pervaporation carried out at 40°C, for a composite membrane of photocrosslinked PVA<sub>3</sub> which was prepared with a single coating of the initial solution on Millipore MFVS. Results are presented by the dependences of flux and permsepation on the feed ethanol concentration.

Water permsepation was indicated in all of these photocrosslinked PVA membranes, since the ethanol concentration was lowered in permeates. Permselectivity was, however, much dependent on the starting photopolymers. Membranes from *p*-PVA<sub>1-4</sub>, which were produced on the higher molecular weight PVA ( $\bar{P} = 1700$ ), showed better permselectivity generally, compared to those from *p*-PVA<sub>5,6</sub> on the lower molecular weight PVA ( $\bar{P} = 500$ ).

Flux or permeation rate was also dependent on the membranes, and the membranes from *p*-PVA<sub>5,6</sub> showed the higher permeation rate in general. The higher permeation rate corresponded to the lower permselectivity through the two polymeric membranes. Decrease of flux was observed in all the cases, as ethanol concentrations in feed increased. Such permeation behavior has been commonly observed in the water-permselective membranes, in which permeation took place through the swollen layer in part by the feed solutions.

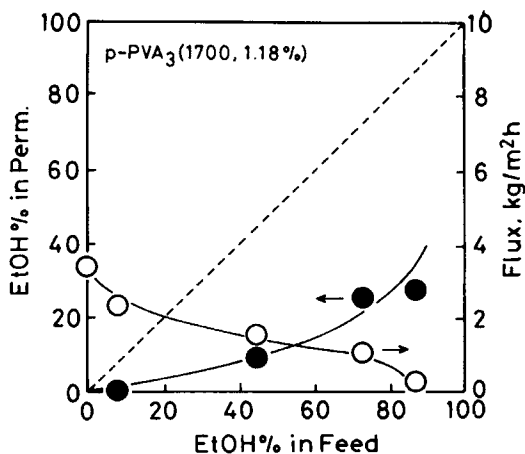


Fig. 1. Results of pervaporation at 40°C through a composite membrane from *p*-PVA<sub>3</sub>.

When water-permselectivity was evaluated with separation factor ( $\alpha_{\text{EtOH}}^{\text{water}}$ ), the maxima values were observed for the feeds with ethanol concentration in the range of 60–70%. Among the membranes, the one from  $p\text{-PVA}_3$  showed the better permselectivity generally, but the permselectivity through the membranes with a single coating of photopolymers as shown above was not enough yet for the practical use for water-ethanol separation.

### Dependences on Coating Thickness

Thickness of the permselective layer plays sometimes an important role on permselectivity. Then the dependences of permseparation were investigated with the membranes in which various coating amounts of the  $p\text{-PVA}_3$  layer were formed by repeating the coating process a couple of times on Millipore MFVS substrate.

Dependences of flux and separation factor are represented in Figures 2 and 3 for the membranes with the coating of  $p\text{-PVA}_3$  up to  $17 \text{ mg/cm}^2$ . Flux decreased as the coating thickness increased with the feed of lower ethanol concentration, and the decrease was much prominent for water and 20 wt % ethanol. When 90% ethanol was used for feed, however, permeation rate did not change practically in the coating range.

Even for the feeds with lower ethanol concentration, it should be noticed that flux did not vary inversely with the increase of coating thickness or coating weight of the PVA layer. This phenomenon supports the permeation mechanism by pervaporation that permeation proceeds through both the swollen layer and the skinned layer faced to vacuum in a membrane. Indeed, in such gas permseparation which is attained through a homogeneous membrane, the permeation rate changes inversely with the increase of the thickness, and then the permeation coefficient can be obtained. However, in

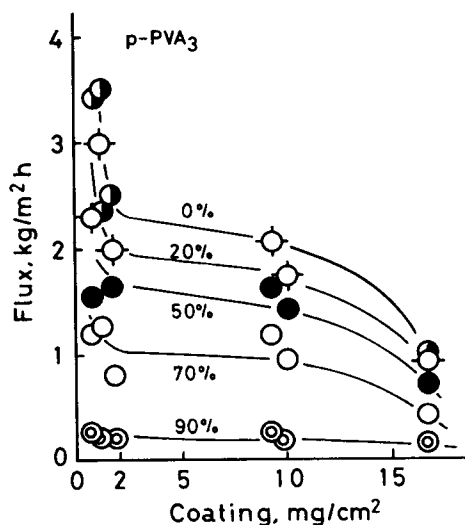


Fig. 2. Dependences of flux through composite membranes from  $p\text{-PVA}_3$  on the coating weight, respectively, for the feeds with 0, 20, 50, 70, and 90 wt % ethanol.

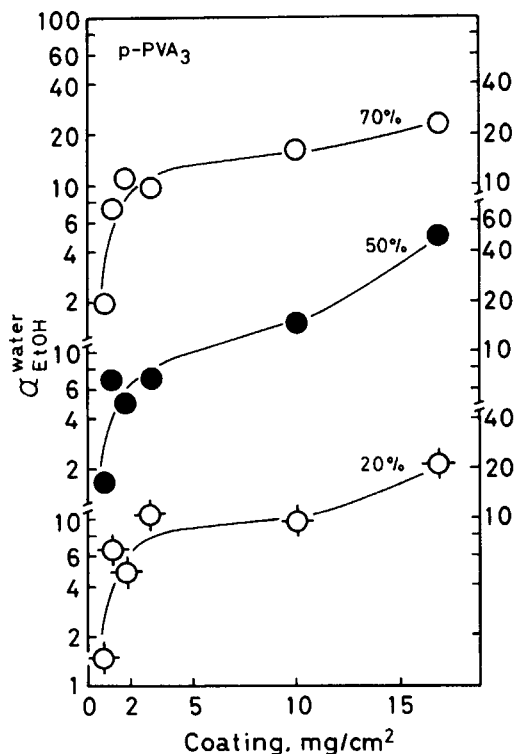


Fig. 3. Dependences of separation factor for water through the membranes from *p*-PVA<sub>3</sub> on the coating weight, respectively, for the feeds with 20, 50, and 70 wt % ethanol.

pervaporation, such a coefficient cannot be expected, as can be seen from the above results.

When the coating exceeded about 1.0 mg/cm<sup>2</sup> on the porous membrane, water-permsepation was attained, and the selectivity increased with the increase of the coating. As shown in Figure 3 for the feeds with 20, 50, and 70 wt % ethanol, the separation factor reached more than 20.

In all the above experiments, porous membranes with average pore size in 0.025 μm were used for the supporting substrate of the composite PVA membranes. It was expected that pore size of the substrate porous film might also affect the pervaporation performances from the comparison with the dependences on the coating weight of the permselective layer described above. Then, some other substrate films with the average pore sizes in 0.10 and 0.22 μm were used, and pervaporation behaviors were studied. For this purpose, coating was repeated twice, and composite membranes with coating layer weighing from 1.7 to 2.2 mg/cm<sup>2</sup> were obtained. It was observed that flux generally increased with increase of the pore size of substrate film. That was possibly due to the decrease of the effective thickness of the PVA layer on the larger pores in substrate film. Permselectivity of water was naturally lowered with the increase of flux in the composite membranes formed on the substrate films with larger pores. That was the reason why the substrate porous film with smaller pores of 0.025 μm was used mainly in this study.

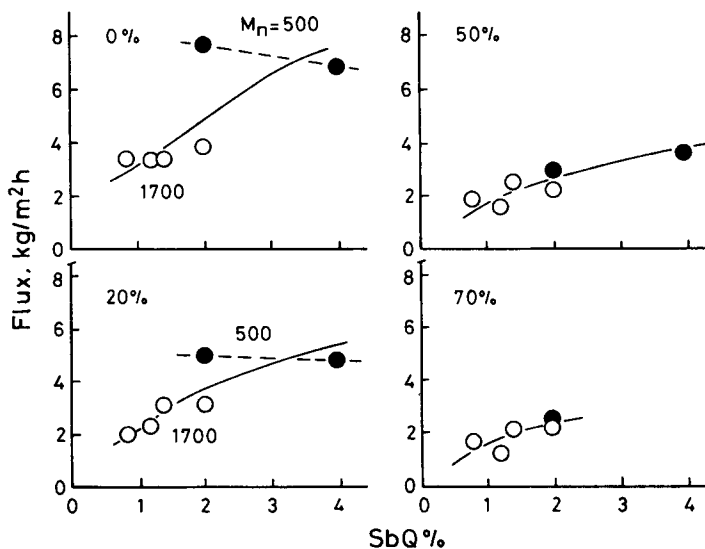


Fig. 4. Dependences of flux through the composite membranes on the incorporation mol % of styrylpyridinium group (SbQ, stilbazole quarternized) in PVA, respectively, for the feeds with 0, 20, 50, and 70 wt % ethanol.

#### Dependences on the Amount of Incorporated Styrylpyridinium Group on PVA

Permselectivity was much dependent on the species of starting photocross-linkable PVAs. One of the factors that should affect the permselectivity is the content of the pendant styrylpyridinium group on the base PVA. The styrylpyridinium group not only works as a coupling olefine source by photoirradiation, but also provides an ionic character by the pyridinium moiety. Generally, increase of the crosslinking should result in the decrease of flux, and increase of the ionic density should result in the increase of flux in pervaporation. Thus the dependences of pervaporation of water-ethanol on the incorporation ratio of styrylpyridinium group on to the base PVA chain should be interesting.

Figures 4 and 5 show the dependences of flux and separation factors respectively on the incorporation ratio of styrylpyridinium group on PVA. Some important characteristics can be pointed out. At first, flux generally increased with the content of styrylpyridinium group in spite of the increase of crosslinking by the same pendant group, and the increase of flux was generally observed with all the feeds investigated here. However, the situation seems to be a little different in the membranes derived from the lower molecular weight ( $\bar{P} = 500$ ), and the flux became smaller as the content increased for the lower ethanol feeds of 0 and 20 wt %. The results are indicated with broken lines in Figure 9.

The flux was generally higher through the membranes of the photocross-linked PVAs derived from the lower molecular weight, and this was quite evident when the flux was compared in the PVA membranes of 1.97 mol % content of the styrylpyridinium group. This was especially true for the lower

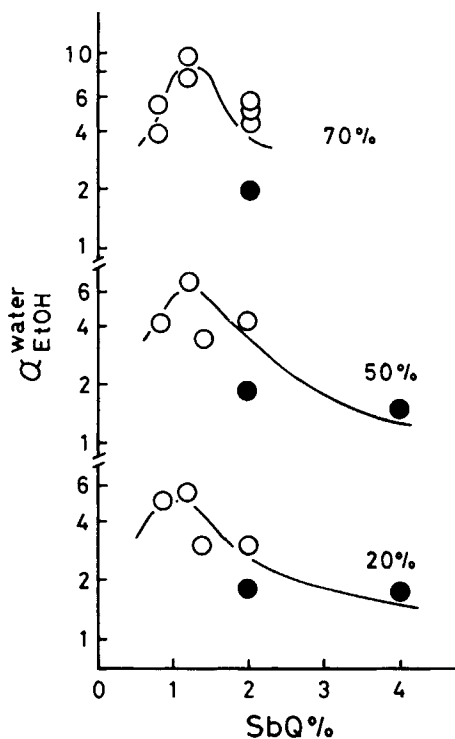


Fig. 5. Dependences of separation factor for water through the composite membranes on incorporation mol % of styrylpyridinium group (SbQ) in PVA.

ethanol feeds. Such higher permeation rates are possible due to the high affinity of the solvents to the polymer of lower molecular weights.

### Temperature Dependences

The flux was, of course, higher at higher temperatures. Pervaporation was undertaken with some membranes in the range between 30 and 50°C, and the dependences were investigated. Activation energies for permeation were obtained at first from Arrhenius plots using an equation,  $Q = Q_0 \ln(-\Delta E_a/RT)$ , where  $Q$  is the permeation rate or flux,  $R$  is a gas constant, and  $T$  is absolute temperature of measurement. Some typical results are summarized in Table II. Indeed, these values may be lacking in strictness due to the limited data of permeation rates obtained at 5°C intervals in the temperature range, but seem to be reasonable in comparison with others reported previously.<sup>2,3,10</sup> When activation energies were compared with those of the heat-treated PVA film, not so many differences were observed, while in the case of acrylic acid graft polymerized membranes the activation energies decreased much by ionization.<sup>2,3</sup> In the photocrosslinked PVA membranes as studied here, incorporation of the ionic group by pyridinium salt was, however, restricted to 2 mol %, and such lower incorporation might result in the smaller changes in activation energies. The separation factor decreased only slightly as the temperature increased.



TABLE II  
Activation Energy for Permeation of Water-Ethanol Mixtures by Pervaporation

Membrane	SbQ%	Activation energy (kcal/mol)				
		0%	20%	50%	70%	90% <sup>b</sup>
<i>p</i> -PVA <sub>1</sub>	1.97	6.4	5.1	5.4	6.3	—
<i>p</i> -PVA <sub>2</sub>	1.35	—	4.3	7.7	6.9	7.0
<i>p</i> -PVA <sub>3</sub>	1.18	6.5	5.9	6.3	6.0	5.5
PVA <sup>c</sup>	—	5.4	6.8	7.7	6.0	5.1

<sup>a</sup>Incorporation mol % of styrylpyridinium group in PVA.

<sup>b</sup>Ethanol wt % in feed.

<sup>c</sup>Thermally crosslinked 0.028-mm-thick PVA film.

### Comparison with Heat-Treated PVA Films

Membrane performances of permseparation can be obtained by the relationships between permselectivity and flux, since the two factors are closely related with each other. In other words, permselectivity decreases as flux increases in general, and vice versa. Permseparation of water was then evaluated with the relationship of the two factors, and the results for the composite membranes from *p*-PVA<sub>3</sub> with various coatings were compared with those of the thermally crosslinked PVA films that were commercially available. Figure 6 shows the relations by log values for 50 wt % ethanol feed obtained in the temperature range from 30 to 50°C. Thicknesses of the

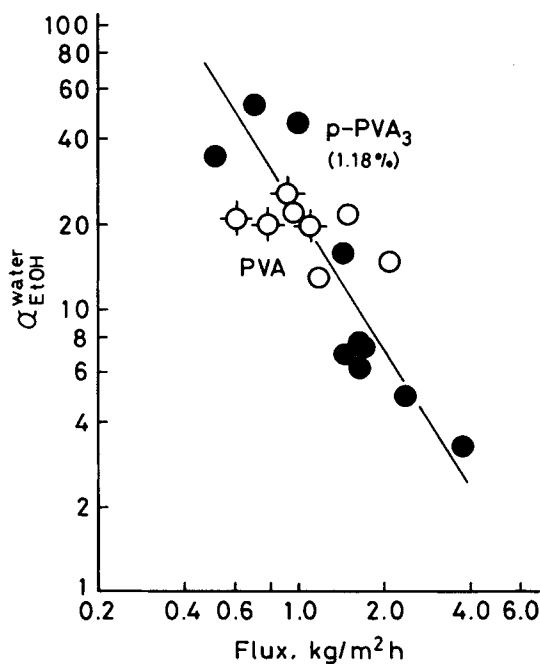


Fig. 6. Relationships between the log values of flux and separation factor to 50 wt % ethanol through the *p*-PVA<sub>3</sub> membranes (●) and the thermally crosslinked PVA films with thickness 0.028 (○) and 0.047 mm (◊).

thermally crosslinked PVA films were 0.028 and 0.047 mm, but other details, such as conditions for heat treatment and the molecular weight of starting PVA, were not known. Direct comparison may not be given accordingly, but some characteristics in the photocrosslinked PVA membranes can be pointed out from the results. For example, permseparation of water is much dependent on the membrane condition including coating thickness of  $p$ -PVA<sub>3</sub>, while the thermally crosslinked PVA films show comparatively higher separation factor with lower fluxes. Among them, a membrane with 17 mg/cm<sup>2</sup> coating of  $p$ -PVA<sub>3</sub> gave the best separation factor. At any rate, it can be stated that the permseparation of water through the composite membranes from  $p$ -PVA<sub>3</sub> parallels that through thermally crosslinked PVA films investigated here, when the performances in permseparation are judged by the relations of separation factor and flux. Thus one of the features in this type of membrane lies in the possibility of the variant flux and permselectivity of water obtained by changing the membrane condition like the coating thickness of the photopolymer layer.

### Swelling

The swelling of membranes plays an important role on permseparation by pervaporation, and accordingly we investigated the swelling behaviors of the photocrosslinked polymers from  $p$ -PVA<sub>1-4</sub>, in which the molecular weight of the base PVA was 1700 and the saponification ratio 88%. Figure 7 shows the typical results of the dependences of swelling on the ethanol concentration for  $p$ -PVA<sub>1</sub> and  $p$ -PVA<sub>3</sub> polymers obtained at room temperature. Swelling was, of course, greater in the lower ethanol feeds and reached about 160%. But the swelling decreased with the increase of ethanol concentration, and the remarkable decrease was observed when the feed ethanol concentration exceeded 50 wt %. These photopolymers were not swollen practically, when distilled ethanol was used for swelling agent.

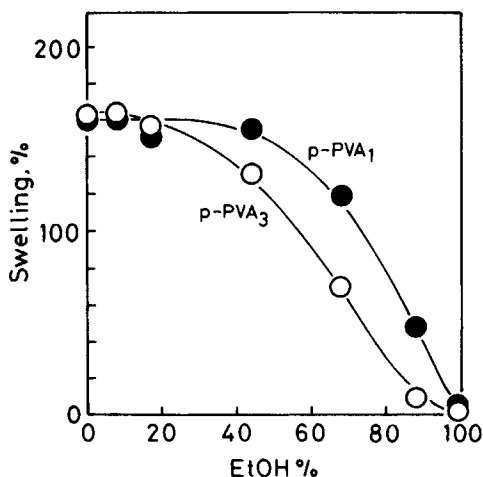


Fig. 7. Dependences of swelling of the photocrosslinked polymers from  $p$ -PVA<sub>1</sub> and  $p$ -PVA<sub>3</sub> on the feed ethanol concentration at room temperature.

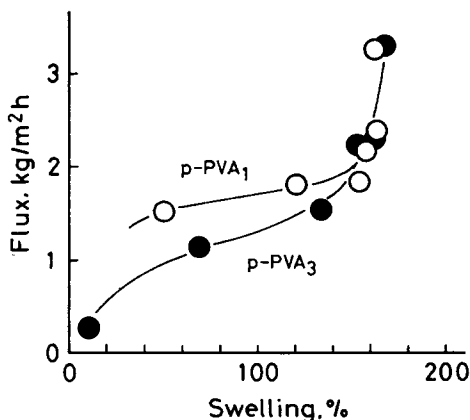


Fig. 8. Relationships between swelling of polymers from  $p$ -PVA<sub>1</sub> and  $p$ -PVA<sub>3</sub> and the permeation rates through the composite membranes with the feeds of various ethanol concentration.

Thus the partially crosslinked PVAs with the styrylpyridinium group showed the higher swelling with water and water-rich ethanolic solutions, and such greater swelling resulted in the higher flux through the membranes generally. However, the swelling ratio was variant according to feeds. Then the effects of swelling on permeation rates were investigated with the polymers from  $p$ -PVA<sub>1</sub> and  $p$ -PVA<sub>3</sub>. Figure 8 shows the relationships between the swelling ratio and permeation rates through these membranes measured at 40°C. As already indicated, both permeation rate and swelling decreased with increase of ethanol concentration in feed, but they did not seem to increase linearly. Especially the flux behavior should be noticed at about 160% of swelling; namely, permeation increased remarkably. Such an unusual increase

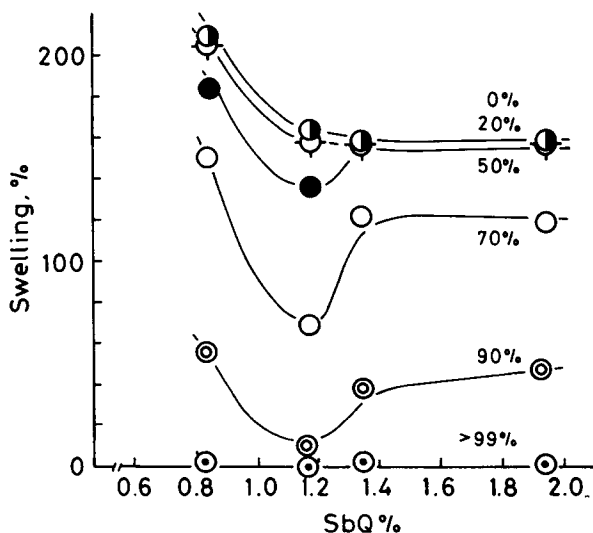


Fig. 9. Dependences of swelling on the content of styrylpyridinium group (SbQ) in the photo-crosslinked PVAs based on the higher molecular weight ( $\bar{P} = 1700$ ).

may reflect some changes of the membrane morphology due to contact to solvents, although an exact explanation cannot be given at present. At any rate, the swelling behaviors were somewhat different in the two polymers of  $p$ -PVA<sub>1</sub> and  $p$ -PVA<sub>3</sub>, which respectively had the contents of the styrylpyridinium group of 1.97 and 1.18 mol %. The permeation rate was in general higher in the former photopolymer with higher content of the pendant group, and this probably reflects the ionic effect.

Thus swelling was also dependent on the content of the coupling source, and next the dependences of swelling on the content of styrylpyridinium group in PVA were investigated. Figure 9 shows the dependences, respectively, for 0, 20, 50, 70, 90, and 99 wt % ethanol solutions. Swelling was, of course, dependent on the feed ethanol concentration. The swelling ratio was generally greater in the  $p$ -PVA<sub>4</sub> photopolymer which had styrylpyridinium group at less than 1.0 mol %, and that became almost constant when the content exceeded 1.4 mol % as shown with  $p$ -PVA<sub>1</sub> and  $p$ -PVA<sub>2</sub> photopolymers. Interestingly, the swelling ratio was smallest in the  $p$ -PVA<sub>3</sub> polymer for feeds with 50, 70, and 90 wt % ethanol. These phenomena may reflect the polymer structures balanced between the compaction of the polymer through crosslinking and the ionic repulsion by pyridinium ion.

Swelling of these polymers was next studied from the effect on permseparation of water from water-ethanol mixtures. For this purpose, the diffused liquids in the swollen polymer was extracted under vacuum, and the composition of water and ethanol was analyzed by gas chromatography. Figure 10 shows the relations between the ethanol concentrations in feed and in extract in the swollen photopolymer from  $p$ -PVA<sub>1</sub> (a), and the results are compared with those for pervaporation (b). Also in the swollen states, ethanol concentration was lowered, and the profiles were very similar to each other. This suggests that permseparation of water had already taken place during swelling of liquids by the selective adsorption of water.

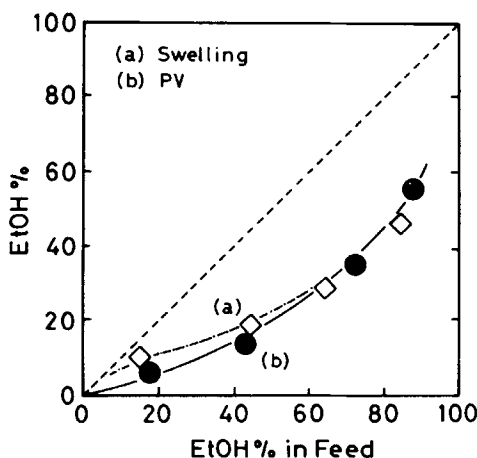


Fig. 10. Comparison of swelling (a) and permseparation of water by pervaporation (b) for the photocrosslinked products from  $p$ -PVA<sub>1</sub>.

## CONCLUSION

Composite membranes were prepared from photocrosslinked PVAs which contained the pendant styrylpyridinium group with various ratios on porous films, and water-ethanol permseparation was investigated with these membranes by pervaporation. These membranes were water-permselective, although the selectivity was dependent on the state of the membranes. In the photocrosslinkable PVAs, the pendant styrylpyridinium group had two functions; namely a photocrosslinkable olefine source by 2 + 2 addition, and an ionic source by pyridinium group. Through the investigation, the following were found:

1. Water-permselectivity was dependent on the photopolymer with respect to the molecular weight of the base PVA and the content of styrylpyridinium group.
2. Coating thickness of the photocrosslinked PVA also affected the permselectivity of water and the permeation rate, although the permeation rate did not vary inversely with the coating weight.
3. The content of the styrylpyridinium group affected the permseparation of water from two aspects: namely, through the compaction of membranes by crosslinking and through the enlargement of the permeation paths by the ionic repulsion.
4. Swelling of these photopolymers reached about 160%, and decreased with the increase of ethanol concentration in feed. Swelling was negligibly small in distilled ethanol.
5. The permeation rate through the composite membranes increased with the swelling ratio.
6. Selective diffusion of water took place already during swelling in photocrosslinked PVAs, and played an important role in the permseparation through the membranes by pervaporation.

## References

1. H. E. A. Bruschke, *Proceedings of First International Conference on Pervaporation Processes in the Chemical Industry*, Bakish Materials Co., Atlanta, 1986, p. 1.
2. T. Hirotsu, *J. Appl. Polym. Sci.*, **34**, 1159 (1987).
3. T. Hirotsu and S. Nakajima, *J. Appl. Polym. Sci.*, **36**, 177 (1988).
4. T. Hirotsu, *Ind. Eng. Chem. Prod. Res. Dev.*, **26**, 1287 (1987).
5. K. Ichimura, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1411 (1982).
6. K. Ichimura and S. Watanabe, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1419 (1982).
7. K. Ichimura and T. Komatsu, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 1475 (1987).
8. K. Ichimura, U. S. Pat. 4,272,620 (1981).
9. K. Ichimura, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2817 (1984).
10. I. Cabasso and Z.-Z. Liu, *J. Memb. Sci.*, **24**, 101 (1985).

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