# Pervaporation Separation of an Aqueous Organic Mixture Through a Poly(acrylonitrile-*co*-vinylphosphonic acid) Membrane

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ABSTRACT: Polyacrylonitrile (PAN)-based copolymers containing phosphonic acid moiety were synthesized for dehydration of aqueous pyridine solution. The *in situ* complex, formed between the vinylphosphonic acid (VP) moiety in the membrane and the pyridine in the feed, enhanced separation capacity of poly(acrylonitrile-*co*-vinylphosphonic acid) (PANVP) membranes. All the PAN-based membranes containing phosphonic acid were very selective toward water. The pervaporation performances of PANVP membranes depended on the content of the phosphonic acid moiety in the membrane and operating temperature. The pervaporation separation of water/pyridine mixtures using PANVP membranes exhibited over 99.8% water concentration in permeate and flux of  $4-120 \text{ g/m}^2/\text{h}$  depending on the content of vinylphosphonic acid and operating temperature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 83–89, 1999

Key words: pervaporation; PAN-based membranes; in situ complex and pyridine

## INTRODUCTION

Pervaporation is a membrane process in which a pure liquid or liquid mixture is in contact with the membrane on the feed or upstream side at atmospheric pressure and where the permeate is removed as vapor because of low vapor pressure existing on the permeate or downstream side.<sup>1</sup> Low vapor pressure can be achieved by using a vacuum pump. In this case, the downstream pressure must be lower than the saturation pressure of permeants at least.

Pervaporation technique through polymeric membrane has been studied to separate azeotropic mixtures, close-boiling, or aqueous organic mixture.<sup>2</sup> For the pervaporation process to be successful, several important technologies, such as

Journal of Applied Polymer Science, Vol. 74, 83–89 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/010083-07 the design of excellent membrane material, the optimization of separation system, development of module design and membrane preparation process, are necessary to be improved. Among them, the most important key technology in the pervaporation process may be the development of optimum membrane materials. The selected membrane has to be easy to prepare and selectively separate a desired component from a feed mixture.

Polyacrylonitrile (PAN) is a well-known polymer material for manufacturing of textile fibers and membranes.<sup>3</sup> PAN is very polar and the nitrile groups in side chain offer hydrogen bonding sites for strong interaction with water. The highly polar nature of PAN led to high water sorption, whereas PAN membrane<sup>4</sup> showed low permeability value of only about 8.5 g/m<sup>2</sup>/h. Although the reasons for low permeability were not clear, it was assumed that the combination of high cohesive energy density (29.4–44.5 kJ/mol) and chain stiffness would result in low permeability of PAN membrane.

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Pyridine is an important solvent or catalyst in the chemical industry and laboratory, and also is frequently present in effluents from rubber and plastics, petrochemicals, pharmaceuticals, and agrochemicals.<sup>5</sup> The recovery of pyridine from outflow is of big concern because it is often necessary to reuse relatively expensive chemicals. Pyridine form an azeotrope with water at 59.4% by weight at  $92-93^{\circ}$ C.<sup>6</sup>

Several researchers have studied the separation of water-pyridine mixture by the pervaporation method. Kujawski et al.<sup>7</sup> have reported on the pervaporation separation of azetropic mixture of pyridine using several ion-exchange and neutral membranes. Drioli et al.<sup>8,9</sup> used cation-exchange material and poly(vinyl alcohol) to dehydrate and poly(dimethylsiloxane) to separate pyridine from water-pyridine mixture. Pervaporation separation of water-pyridine mixture through several ionomer membranes by Néel et al.<sup>10</sup> showed high selectivity but rather low fluxes.

Ion-complex membranes have been known to be useful in the dehydration of organic aqueous solution by pervaporation for their high flux and selectivity toward water.<sup>11</sup> However, in long-term operation, the ion-complex membrane undergoes a transient decrease in its separation performance due to the fact that metal counterions on the surface of the membrane are washed away by the shear force of feed. To overcome this problem, an in situ complex mechanism was proposed in our previous studies<sup>12-17</sup> in which a polymer membrane was used as a counter-ion toward feed. In this case, the complexation between pyridine from the feed and acidic group in the membrane was formed.<sup>13–17</sup> Pervaporation performances of pyridine-water mixtures using in situ complex membranes were affected by the copolymerized functional acid groups.<sup>16,17</sup> Due to the formed in situ complex, it was probably assumed that water transport was accelerated and that pyridine had little chance to permeate through the *in situ* complex membrane because of its low solubility in membrane. Therefore, the selectivity toward water through in situ complex membranes was fairly high.

This study is a continuing research in a series of investigations using a phosphoric acid group containing PAN membranes for pyridine-water separation. Our previous study used the poly(acrylonitrile*co*-monoacryloxyethyl phosphate) membrane.<sup>17</sup> In the present study, the monomer containing a phosphonic acid group was copolymerized with acryloni-

Table IConditions for Synthesis of PANVPCopolymers

	AN		VP	
Sample	wt %	mol %	wt %	mol %
PANVP1	99	99.51	1	0.49
PANVP2	95	97.48	5	2.52
PANVP3	90	94.83	10	5.17
PANVP4	85	92.02	15	7.98

Water, 250 mL; KPS, 0.5 g.

trile to dehydrate the water-pyridine mixture using a pervaporation process. The phosphonic acid group was intended to form an *in situ* complex with pyridine in the feed. The objective of this study was to investigate the effect of vinylphosphonic acid (VP) content in membrane and operating temperature on separation performance and to improve the separation capacity of water-organic mixtures using an *in situ* complex membrane concept.

#### **EXPERIMENTAL**

#### Materials

Acrylonitrile (AN) (Tedia Company, Inc.) was purified by the inhibitor remover column (Aldrich) to remove hydroquinones. VP (Hoechst) and potassium persulfate (KPS) (Ajax Chemicals) were used without further purification. Toluene and dimethylformamide (DMF) were purchased from J. T. Baker and Tedia Company Inc., respectively. Pyridine was purchased from Showa Chemical Company and used without further treatment.

# Copolymerization of Acrylonitrile and Vinylphosphonic Acid

The conditions and procedures of copolymerization are listed in Table I and schematically presented in Scheme 1. Copolymers are designated as PANVP1-4 depending on the VP content in copolymers. Distilled water, 250 ml, was placed in a four-necked round flask under nitrogen atmosphere. After a sufficient nitrogen purge, surfactant, sodium lauryl sulfate (SLS), was added into the flask. Then, predetermined amounts of AN and monoacryloxyethyl phosphate monomers were poured. KPS (0.5 g) was added after heating the mixture to 70°C. Copolymerization was performed at 70°C with continuous stirring and ni-





Scheme 1 The structure of synthesized PANVP.

trogen atmosphere for 3 h. After copolymerization, the mixture was filtered and washed with toluene to remove the residue of nonpolymerized monomer. Copolymers were dried in a vacuum oven at  $50^{\circ}$ C for 2 days.

#### **Preparation of Copolymer Membranes**

Synthetic copolymers were dissolved in a 5 wt % DMF solution with stirring at room temperature. The solution was poured into a glass plate after filtration with a glass filter. Then, the solvent was allowed to evaporate at 50°C in a vacuum oven. The evaporated solution was dipped into a water bath to separate the membrane from the glass plate. Thickness of the membrane was 90–100  $\mu$ m.

#### **Pervaporation Experiment**

Equipment and procedures used to conduct the pervaporation experiments were identical to those described previously by Lee and Won.<sup>4</sup> However, the feed mixture was supplied continuously into the pervaporation cell by pumping. The effective membrane area in contact with feed was about 25.98 cm<sup>2</sup>. The downstream pressure was about 2 torr which is lower than saturation vapor

pressure of water. The operating temperature was 30, 45, 60, and 75°C. The composition of the permeate was measured by Shimadzu GC-14B equipped with a 3-m-long glass column packed with Porapak-Q. Separation factor ( $\alpha$ ) and permeate flux (J) are defined, respectively, as follows:

$$\alpha = \frac{Y_w/Y_p}{X_w/X_p} \tag{1}$$

$$J = \frac{Q}{A \times t} \tag{2}$$

where  $Y_i$  is the weight fraction in permeate and  $X_i$  is that on feed. Subscripts w and p denote water and pyridine, respectively. Q, A, and t represent the weight of permeant (g), effective membrane area (m<sup>2</sup>), and operating time (h), respectively.

#### **Characterization of PANVP Membranes**

A Fourier transform infrared (FTIR) spectrometer (Nicolet Magna-IR 550) and an elemental analyzer (Carlo Erba Instrument EA1110) were used for analysis of the structure and composition of copolymers. Molecular weight of poly(acrylonitrile-co-vinylphosphonic acid) (PANVP) copolymers was determined by using the GPC (Waters Model 510 HPLC pump, Milford, MA). Distilled water was used for the contact angle measurement of PANVP membranes. In a contact angle measurement, droplets of each water 5  $\mu$ L in size were deposited onto PANVP membrane surface with a syringe. The readings on the drop were directly taken using a cathetometer fitted with a goniometer (Erma Model G-1) evepiece at 25°C. Each value reported for the contact angle was the average of at least five measurements. X-ray (Rigaku, Dmax 2500) was used for the structural analysis of PANVP copolymers.

#### Swelling Behavior of Copolymer Membranes

PANVP copolymer membranes, completely dried under reduced pressure at room temperature and weighed, were immersed into pure water and 60 wt % aqueous pyridine solution in a sealed vessel at 30°C. When the membrane reached an equilibrium after 24 h, it was rapidly taken out of the vessel, wiped with Kimwipe paper to remove solvent residue, and weighed. The swelling ratio, *S*, is defined as

Sample	Mol % of VP in Membrane	Water Contact Angle (Degree)	${ m MW} imes 10^{-5}$ (g/mol)
PANVP1	0.64	51.2	1.6
PANVP2	1.25	50.6	1.3
PANVP3	1.43	44.4	1.1
PANVP4	1.93	40.4	1.0

Table IIPhysical Properties of PANVPMembranes

$$S(\%) = \frac{W_s - W_d}{W_d} \times 100$$
 (3)

where  $W_s$  is the weight of solvent-swollen membrane in water/pyridine mixtures and  $W_d$  denotes the weight of dried membrane.

## **RESULTS AND DISCUSSION**

#### **Properties of PANVP Membranes**

The physical properties of PANVP membranes are described in Table II. From the elemental analysis, it was shown that the content of phosphonic acid groups in PANVP copolymer membranes ranged from 0.64 to 1.93 mol %. This means that the reactivity of acrylonitrile is higher than that of the VP monomer. The molecular weight of the copolymer was  $1.0-1.6 \times 10^5$  g/mol, and decreased with increasing content of VP in copolymer. It was also found that the hydrophilicity of PANVP membranes increased with the content of phosphonic acid in the copolymer membranes as evidenced from their water contact angle values as described in Table II. Small contact angle values for a membrane containing high phosphonic acid content indicate a strong interaction of the membrane with water. After the copolymerization of VP with AN monomer, the hydrophilicity of synthesized copolymer membranes increased significantly higher than PAN membrane.

Figure 1 shows the FTIR spectra of virgin PANVP copolymer. The characteristic stretching vibration of —CN appears at 2250 cm<sup>-1</sup>. The intensity of stretching peaks of —OH at 3500 cm<sup>-1</sup> increased with the content of VP. The peaks at 1650 cm<sup>-1</sup> represent —C—N in copolymers. The bands at 1240 cm<sup>-1</sup> were developed from



Figure 1 FTIR spectra of PAN and PANVP.

P=O stretching vibrations. Also, the P-O-(H) stretching vibrations can be found at 1010 cm<sup>-1</sup>.

Wide angle X-ray diffraction (WAXD) patterns of PAN and PANVP are shown in Figure 2. PAN and PANVP exhibited a characteristic crystalline peak at around  $2\theta = 17^{\circ}$ . The intensity of PANVP copolymers at  $2\theta = 17^{\circ}$  were higher than that of PAN. It is thought that the crystalline portion in the PANVP membrane increased after an incorporation of phosphonic acidic groups in copolymer.

In Figure 3, the degree of swelling of the PANVP membranes in 60 wt % aqueous pyridine solution is shown as a function of VP content in copolymer membranes. The degree of swelling of these membranes increased with VP content in copolymer membranes except the PANVP1 membrane. These results indicated that the more VP



**Figure 2** WAXD patterns of PAN and PANVP copolymers.



**Copolymer membranes** 

**Figure 3** Swelling behaviors of PANVP membranes in 60 wt % aqueous pyridine concentration.

content in copolymer membranes, the greater the affinity of the membrane with aqueous pyridine solution. That is, the copolymerization of VP with AN enhanced the affinity with water/pyridine mixture.

#### **Pervaporation Performances of PANVP Membranes**

As shown in Figure 4, the flux through PANVP membranes for 59 wt % pyridine aqueous solution increased with the content of VP in copolymer, whereas the water concentration in permeate did not decrease much with increasing the content of VP in copolymers. The permeability of PANVP membranes tends to be similar to the result of swelling behaviors. Namely, the increase of VP



**Figure 4** Effect of VP content on pervaporation performance of PANVP membranes for water-pyridine mixtures (59 wt % feed pyridine concentration, 75°C operating temperature).



**Figure 5** Effect of operating temperature on pervaporation performance of PANVP4 membrane in 59 wt % aqueous pyridine mixtures.

content in copolymer membranes resulted in high flux.

The structure of polymer membranes generally expanded by the swelling of membranes.<sup>18</sup> Therefore, flux of swollen membrane increases. High swelling degree after copolymerization of VP with AN contributed to enhance the transport of permeants through membranes, resulting in a high flux. Despite high flux with increasing VP in PANVP membranes, the water concentration in the permeate did not decrease much, possibly due to formation *in situ* complex between pyridine in the feed and phosphonic acid in membrane. Since pyridine can be captured inside of the membrane, the transport of water through the membrane can be facilitated through the ion-dipole interaction.

Pervaporation performance of the water/pyridine mixture through the PANVP membrane was also affected by the operating temperature. As shown in Figure 5, the PANVP4 membrane was highly selective toward water from ambient temperature to  $75^{\circ}$ C when the feed was 59 wt % pyridine aqueous solution. Note that the water concentration in permeate remains >99.8%. Flux increased to a greater extent with operating temperature. Similar to our previous studies on acrylic acid-, sulfonic acid-, and phosphoric acidcontaining copolymer membranes,<sup>13-17</sup> phosphonic acid containing PAN-based copolymer membrane showed temperature-dependent permeation behaviors. However, the PAN membrane showed temperature-independent permeation behaviors.<sup>4,15-17</sup> As operating temperature increased, VP segments in PANVP membrane showed more plasticized motion than AN seg-



**Figure 6** Comparison of pervaporation performances of PANVP4 membrane with those of other PAN-based copolymer membranes.

ments and acted as the transport medium through which the permeants could penetrate easily.

Pervaporation performance of PANVP4 membrane with another *in situ* complex membrane was compared and described in Figure 6. The PANVP4 membrane represented a lower flux value but showed a higher separation factor than other *in situ* complex membranes. From this Figure, phosphorus containing PAN-based membranes had a good separation property toward water-pyridine mixture, when it is compared with our previous *in situ* complex membranes. In other words, phosphorus containing PAN-based membranes have an even higher separation factor than other acid groups containing PAN-based membranes despite low flux values. In comparison with PANPH membrane, PANVP4 membrane showed a higher separation factor but somewhat lower flux values. This is because PANPH has more bulky groups of phosphate and flexible ethylene group in the side chain. Most of all, Figure 6 indicates that the PANVP membrane has excellent affinity for water.

#### CONCLUSION

PANVP was successfully synthesized by emulsion copolymerization. Molecular weight of PANVP copolymers ranged from 100,000 to 160,000 and decreased with increased VP monomer contents. The swelling ratio of PANVP membranes in 60 wt % aqueous pyridine solution showed about twice as much as the PAN membrane. In situ complex between phosphonic acid in the membrane and pyridine from the feed enhanced water transport through PANVP membranes. The pervaporation performance of water-pyridine mixture through the PANVP membranes exhibited above 99.8% of water concentration in permeate and 4-120g/m<sup>2</sup>/h of total flux. Phosphorus containing PANbased membranes have an even higher separation factor than other acid groups containing PAN-based membranes despite low flux values. In comparison with the PANPH membrane, the PANVP4 membrane showed a higher separation factor but somewhat lower flux values. This is presumably because PANPH has a more bulky phosphate group and flexible ethylene group in the side chain. Most of all, the PANVP membrane has excellent affinity for water as indicated in Figure 6.

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#### REFERENCES

 Mulder, M., Ed. Basic Principles of Membrane Technology; Kluwer Academic Publishers: Netherlands, 1996; p. 325.

- Neel, J. In Membrane separations technology; Noble, R. D.; Stern, S. A., Eds.; Elsevier: Amsterdam, 1995; p. 143.
- 3. Brandrup, J.; Immergut, E. H. Polymer Handbook, 3rd ed.; John Wiley & Sons: New York, 1989; p. V/57.
- 4. Lee, Y. M.; Won, K. Polym J 1990, 22, 578.
- Mark, H. F.; Othmer, D. F.; Overberger, C. G.; Seaborg, G. T., Eds.; Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed.; John Wiley & Sons: New York, 1982; Vol. 19; p. 454.
- Budavari, S. The Merck Index, 12th ed.; Merck & Co.: Whitehouse Station, NJ, 1989; p. 8153.
- Kujawski, W.; Nguyen, T. Q.; Neel, J. Sep Sci Technol 1991, 26, 1109.
- Drioli, E.; Zhang, S.; Basile, A. J Membr Sci 1993, 80, 309.
- 9. Drioli, E.; Zhang, S.; Basile, A. J Membr Sci 1993,

81, 43.

- Xie, H. A.; Nguyen, Q. T.; Schaetzel, P.; Neel, J. J Membr Sci 1993, 81, 97.
- Sedlacek, B.; Kahovec, J. Synthetic Polymeric Membranes; Walter de Gruyter & Co.: Berlin, 1987, 30.
- 12. Lee, Y. M.; Oh, B. K. J Membr Sci 1993, 85, 13.
- 13. Lee, Y. M.; Oh, B. K. J Membr Sci 1995, 98, 183.
- Oh, B. K.; Wang, W. J.; Lee, Y. M. J Appl Polym Sci 1996, 59, 227.
- 15. Oh, B. K.; Lee, Y. M. J Membr Sci 1996, 113, 183.
- Lee, Y. M.; Oh, B. K. Macromol Symp 1997, 118, 425.
- Park, C. H.; Nam, S. Y.; Lee, Y. M.; Kujawski, W. J Membr Sci 1998, to appear.
- Inui, K.; Okumura, H.; Miyata, T.; Uragami, T. J Membr Sci 1997, 132, 193.