Pervaporation of Pyridine–Water Mixture Through Poly(acrylonitrile-co-4-styrene sulfonic acid) Membrane

BOO-KEUN OH,* WUN JAE WANG,† and YOUNG MOO LEE‡

Department of Industrial Chemistry, College of Engineering, Hanyang University, Seoul 133-791, Korea

SYNOPSIS

The modified polyacrylonitrile (PAN) membranes used in this study had sulfonic acid moiety to act as a specific functional group for the dehydration of pyridine aqueous solution. The *in situ* complex formed between pyridine in the feed and sulfonic acid moiety in the membrane could enhance the dehydration capacity of the modified PAN membranes. It was found that the pervaporation patterns were closely related to the content of the sulfonic acid in the modified PAN membranes. The effective *in situ* complex membrane can be prepared by controlling the content of sulfonic acid in the membrane. The *in situ* complex membrane shows an increase of permeation flux with a slight decrease in separation factor as operating temperature increase. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Pyridine is an important solvent or catalyst and also is frequently present in effluents from rubber and plastics, petrochemicals, and some other organo-chemical industries such as pharmaceuticals and agrochemicals.[1] The recovery of pyridine from outflow is an important problem because it is often necessary to reuse relatively expensive chemicals. Pyridine is a weak base and has pK_a of 5.23 at 20°C.[2] Pyridine forms an azeotropic point with water at 58.7% by weight at 93.6°C.[3]

Studies on the separation of pyridine–water mixture by pervaporation have been reported and evaluated by Eustache and Histi[4] and more recently by Drioli et al.[5,6] and Néel et al.[7] In the dehydration process, treated GFT membrane, which has hydrophilic support (polyacrylonitrile) and skin layer [poly(vinyl alcohol)], shows a good selectivity toward water. Ionomer membranes such as acrylic acid grafted polyethylene, the interpenetrating polymer network of polyethylene and sulfonated poly (styrene-co-divinylbenzene), Nafion, poly(tetrafluoroethylene-co-styrene sulfonic acid) and so on, all possessing special functional groups in the membranes, have high permeate fluxes but low selectivities.[7] In addition to these, Naylor et al. also reported the results of dehydration of aqueous pyridine by using BP poly(acrylic acid) membrane, which showed high permeate selectivity. The permeates contained only less than 0.2% pyridine over the feed concentration range examined (up to 40% water).[8]

Ion-complex membranes have been known to be useful ones in the dehydration of organic aqueous solution by pervaporation for their high flux and selectivity toward water.[9-11] However, in a long-term operation, the ion-complex membrane undergoes a transient decrease in its separation performance due to the fact that metal counterion on the surface of the membrane is washed away by the shear force of the feed.[11] In the case of organic compound as a counterion, it may have two problems such that the organic counterion may diffuse into the membrane and is contained in organic concentrate. If a polymer is used as a counterion, the stability of the membrane capacity can be enhanced, but the procedure of the membrane preparation is a little difficult.

In our previous studies, on the dehydration of pyridine aqueous solution through modified PAN membranes containing acrylic acid moiety, it was confirmed that the *in situ* complex formed between pyridine in the feed and the acidic functional group in the membrane showed better dehydration capacity than other membrane systems resulted from (1) a nonspecific interaction between the membrane and permeants and (2) hydrogen interaction between

---

* Present address: Central R&D Center, Samsung, Daejon, Korea.
† Present address: Hansol Institute of Science and Technology, Kyungki-do, Korea.
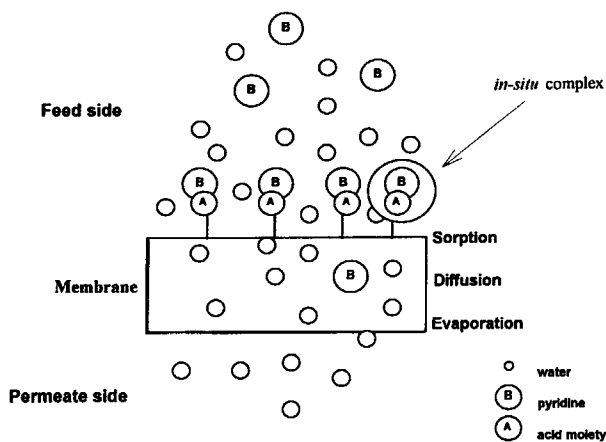‡ To whom correspondence should be addressed.

Figure 1   Schematic diagram of *in situ* complex mechanism. The permeation of water in the feed was accelerated by the formation of *in situ* complex.

the membrane and a major permeant.[12,13] In an earlier study,[14] we already proposed the *in situ* complex membrane concept in the dehydration of acetic acid aqueous solution by using a poly(acrylonitrile-*co*-4-vinyl pyridine) membrane that had a basic functional group. The proposed *in situ* complex system (see Fig. 1) has several advantages. First, since pyridine can form a strong acid–base complex or *in situ* complex with a counterionic species in the membrane, the classical problem of washing out of counterion in a long-term operation can be solved by continuous supply of counterion from the feed. Second, when the dehydration of pyridine aqueous solution is conducted with high separation factor, the diffusion of pyridine into the membrane is not a serious problem because pyridine can be captured inside of the membrane. In this case, the diffusion of pyridine can be hindered by forming an *in situ* complex with the acidic functional groups on and in the membrane. Also, the *in situ* complex can accelerate the diffusion of water through the ion–dipole interaction. From these studies, it is thought that in the ion-complex membrane system, the separation capacity can be affected by the content of the

functional groups in the membrane. That is, there exists an effective and optimum functional group content in the membrane to enhance the separation capacity because an excessive ionic content in the membrane causes an extraordinary swelling by the increased interaction with water in the feed and lowers the separation efficiencies.

In this study, the sulfonic acid group that can also form an *in situ* complex with pyridine in the feed was selected as an acidic functional group to dehydrate the pyridine–water mixture using the pervaporation process. Our objective is to study the effect of the content of sulfonic acid functional group on the separation capacity to dehydrate the pyridine–water mixture. It is our goal to investigate the effect of operating temperature on the separation performance of pyridine–water mixture using pervaporation process.

EXPERIMENTAL

Materials

Acrylonitrile (AN, Katayama Chem. Co., Japan) was purified through the inhibitor remover column (Aldrich Chem. Co., USA) to remove hydroquinone before use. 4-Styrene sulfonic acid sodium salt (SS-Na, Aldrich Chem. Co., USA) was used as received. Potassium persulfate (PPS, Wako Pure Chem. Co., Japan) was used as an initiator. Conc. HCl (Duksan Chem. Co., Japan) was used as received. Reagent grade pyridine (Junsei Chem. Co., Japan), toluene (Junsei Chem. Co., Japan), and dimethyl formamide (DMF, Junsei Chem. Co., Japan) were used without further purification. Water was distilled and deionized by a Milli-Q ultrapure water system (Millipore Co., USA).
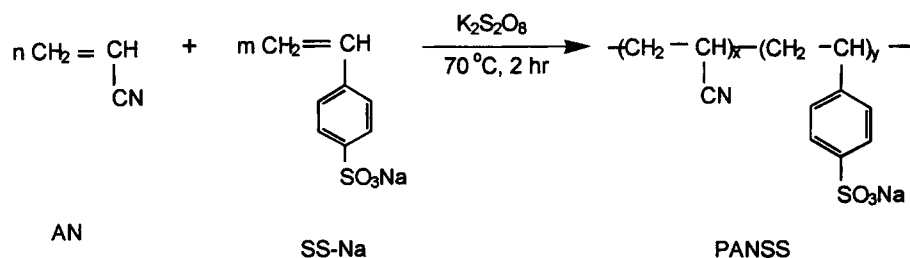
Synthesis of PANSS

The condition and the procedure of polymerization are listed in Table I and shown in Scheme 1. Two

Table I   Conditions for Preparing PAN-SS Polymers[a]

Sample	Distilled Water (mL)	AN (mol)	SS-Na (mol)	PPS (mol)
PANSS-1	230	0.471	4.70×10^{-3}	1.92×10^{-3}
PANSS-2	250	0.471	1.17×10^{-2}	1.20×10^{-3}
PANSS-3	270	0.471	2.35×10^{-2}	2.22×10^{-3}
PANSS-4	310	0.471	4.70×10^{-2}	2.55×10^{-3}

[a] The temperature of reaction media was kept at 70°C.

n CH$_2$ = CH + m CH$_2$= CH $\xrightarrow[\text{70°C, 2 hr}]{\text{K}_2\text{S}_2\text{O}_8}$ —(CH$_2$ — CH)$_x$—(CH$_2$ —CH)$_y$ —

|
CN

SO$_3$Na

|
CN

SO$_3$Na

AN   SS-Na   PANSS

Scheme 1.

hundred milliliters of distilled and deionized water, AN, and SS-Na was added into a four-necked round flask equipped with mechanical stirrer, thermometer, and nitrogen inlet tube. Potassium persulfate was added into the stirring solution while maintaining the reaction temperature at 70°C under a nitrogen atmosphere. The copolymerization was continued for 2 h to prepare poly(acrylonitrile-co-4-styrene sulfonic acid) (PANSS). PANSS was precipitated by pouring the copolymer emulsion solution into an excess 0.1N HCl aqueous solution. PANSS was filtered and washed with excess distilled and deionized water, toluene, and ethanol to remove residual monomers. For further purification, PANSS was dissolved in DMF and reprecipitated in distilled and deionized water and filtered and dried in a vacuum oven at 50°C and 10 mm Hg for 3 days.

Characterization

Elemental analyses were conducted by Carlo Erba Model EA 1108. Inherent viscosities of all polymers were determined by using Cannon-Fenske type viscometer and measured at the concentration of 0.5 g/dL in DMF at 25°C. X-ray (Rigaku D/Max-111A) and FT-IR (Nicolet Magna-IR 550) were used for the structural analysis of PANSS. Distilled water and methylene iodide were used for the contact angle measurements of PANSS membranes. In a contact angle measurements, droplets of each liquid 5 mL in size were deposited onto PANSS surface with hypodermic syringe. The readings on the drop were directly taken using a cathetometer fitted with a goniometer (Erma Model G-1) eyepiece at 25°C. Each value reported for the contact angle was the average of at least five measurements. Tensile strength and elongation were measured by Toyo Baldwin Model UTM-400 and cross-head speed was 2 mm/min.

Membrane Preparation

PANSS was dissolved in DMF and filtered with a glass filter. The 25% copolymer solution by weight

was cast onto a 0.9-mm rimmed glass plate and preheated at 60°C in an oven for 3 h, followed by a further drying at 10 mm Hg for 48 h to remove any residual solvents in a vacuum oven. It was dipped into water bath for 2 h at 30°C to separate membranes from the glass plate. The membrane was further dried at 60°C oven for 1 day before use.

Pervaporation

The equipment and procedures used to conduct the pervaporation experiments were identical to those described previously by Lee et al.[15] However, the feed mixture was continuously supplied into the pervaporation cell. The effective membrane area in contact with liquid was about 25.98 cm.^{2} The downstream pressure was lower than 1 Torr and the operating temperature was 25, 40, 55, and 70°C. The composition of the permeate was measured by Shimadzu GC-14B equipped with a 3-m-long glass column packed with GE-SE 30. Separation factor (α) 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 in feed. Subscripts w and p denote water and pyridine, respectively. Q, A, and t represent the weight of permeant (g), effective membrane area (m^2), and operating time (h), respectively.

RESULTS AND DISCUSSION

The specification and physical properties of PANSS membranes are described in Table II. The contents of sulfonic acid groups in PANSS membranes range from 0.7 to 4.2 mol % as analyzed from the elemental

Sample	Mole Percent of Sulfonic Acid	η_{inh} (dL/g)	Strength (MPa)	Elongation (%)	Water Contact Angle (°)
PANSS-1	0.7	3.79	23.68	5.92	64.2
PANSS-2	1.6	4.06	22.29	7.82	54.0
PANSS-3	3.5	4.85	24.92	4.75	52.2
PANSS-4	4.2	4.32	22.86	5.34	49.9

analysis. PANSS membranes, glassy and dense co-polymers, have tensile strengths at break of about 22–25 MPa and elongations of 5–8%. They have inherent viscosity values of 3.8–4.9 dL/g and easily form transparent membranes. It is found that the hydrophilicities of PANSS membranes increased with the content of sulfonic acid in the membrane as evidenced from their water contact angle values. The lower contact angle values of membrane means greater interaction toward water.

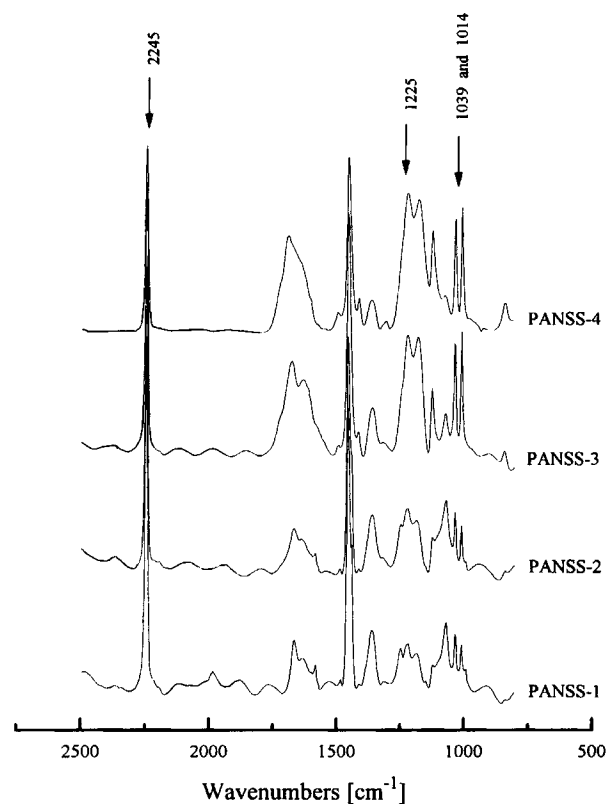Figure 2 shows the FT-IR absorbance spectra of PANSS after dipping in 56 wt % aqueous pyridine

solution for 1 day at 25°C and drying in a vacuum oven at 60°C and 5 mm Hg for 1 day. The characteristic stretching vibration of —CN appears at 2245 cm⁻¹. The symmetric and asymmetric stretching vibrations of S=O in sulfonic acid can be found at 1225, 1039, and 1014 cm⁻¹ and their intensities increased with the content of sulfonic acid group in the membrane. We can also confirm the formation of the complex between sulfonic acid moiety in the membranes and pyridine in the pyridine–water mixture as evidenced by a new peak appeared at 1129 cm⁻¹ after complex formation. X-ray diffraction patterns shown in Figure 3 show that PANSS membranes in this study do not have any distinct crystalline region.

In general, pervaporation is a useful separation system in the dehydration of azeotropic mixture with water. The pervaporation units typified with dehydration of the ethanol–water mixture are commercially available from Carbone Lorraine. An energy efficiency can be achieved by the hybrid pervapor-
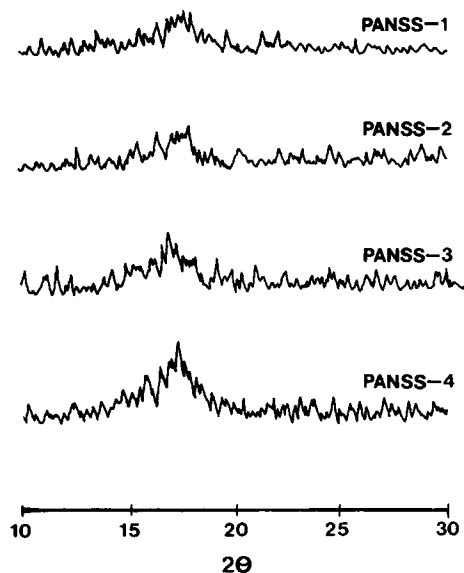

Figure 2   FT-IR absorbance spectra of PANSS membranes prepared by dipping in 56 wt % aqueous pyridine solution for 1 day at 25°C and drying in a vacuum oven at 60°C and 5 mm Hg for 1 day.

Figure 3   X-ray diffraction patterns of PANSS membranes.

ation system with distillation. In a hybrid system, the output from the distillation is transported to the pervaporation membrane in an azeotropic temperature. Therefore, if pervaporation can be conducted at an azeotriopic temperature or above, the cost for the process can be reduced because a heat exchanger is not necessary. However, most of the polymeric membranes at a higher operation temperature such as azeotropic points undergo an increase of the permeation flux and a decrease of the separation factor. Therefore, stable membranes maintaining reasonable separation performance at higher operation temperature need to be developed.

The effect of the operating temperature on the pervaporation separation capacity is shown in Figures 4–6. In Figure 4, we can classify three types of permeation behavior with the operating temperature: (1) slight temperature-dependent type (PANSS-1 and PANSS-2), (2) intermediate temperature-dependent type (PANSS-3), and (3) highly temperature-dependent type (PANSS-4). It is thought that those different permeation behaviors are closely related to the content of the sulfonic acid in the modified PAN membranes.

It was reported that in the dehydration of ethanol aqueous solution, the PAN membrane had a small change of the permeation flux with operating temperature below its glass transition temperature (around 87°C).[16] In our previous paper[13] on the dehydration of pyridine aqueous solution, the PAN membrane showed temperature-independent per-

Figure 5 Effect of the operating temperature on the concentration of water in permeate of PANSS-1 (O), PANSS-2 (△), PANSS-3 (▽), and PANSS-4 (□). The pyridine concentration in the feed was 56 wt %.

meation behavior. The possible reason might be that it did not have any specific functional groups that could enhance the hydrophilicity of the PAN membrane. The same behavior can be found in PANSS-1 and PANSS-2 membranes that have only a small amount of the sulfonic acid (below 1.6 mol %). PANSS-1 and PANSS-2 membranes also show low activation energy values (below 3.2 kcal/mol) (see
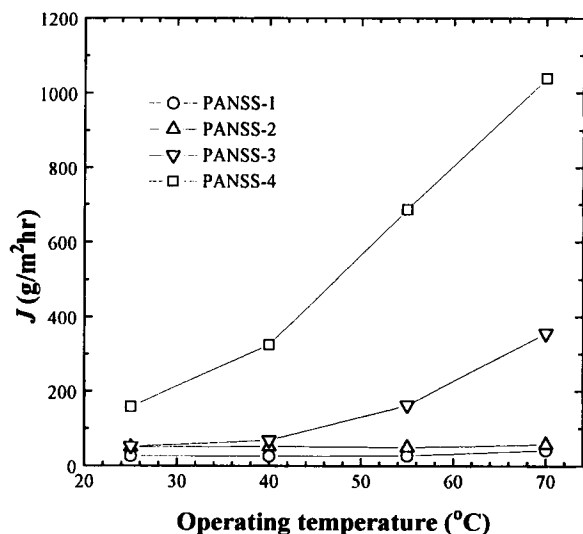

Figure 4 Effect of the operating temperature on the total permeation flux, J, of PANSS-1 (O), PANSS-2 (△), PANSS-3 (▽), and PANSS-4 (□). The pyridine concentration in the feed was 56 wt %.
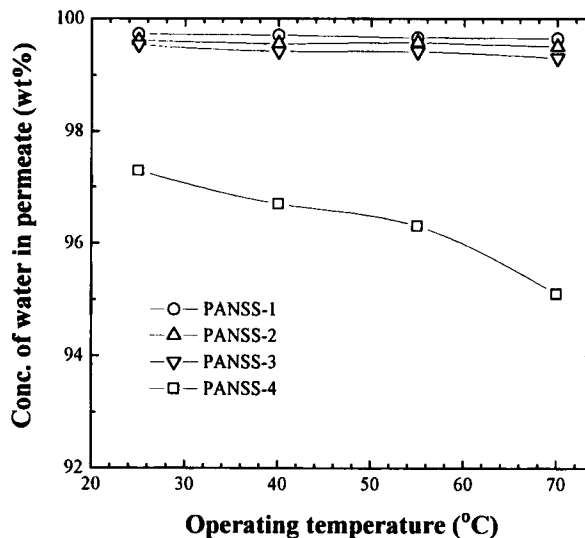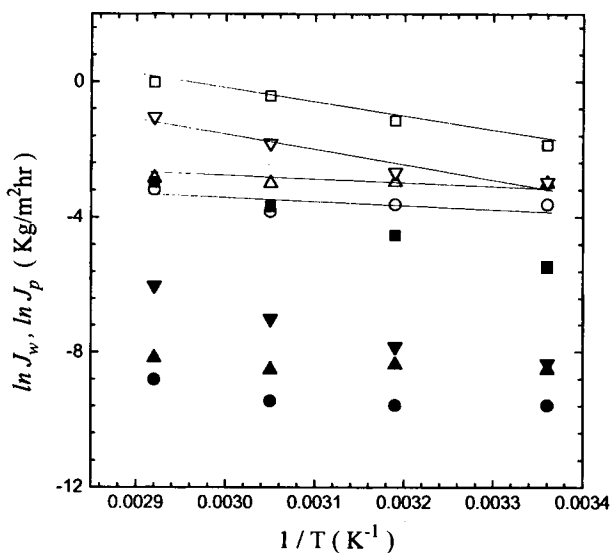

Figure 6 Arrhenius plots of PANSS-1 (O, ●), PANSS-2 (△, ▲), PANSS-3 (▽, ▼), and PANSS-4 (□, ■). Straight and dotted lines depict ln J_w and ln J_p, respectively.

Table III) for the permeation of water and pyridine as can be calculated from Figure 6 with $r^2 \geq 98\%$. Further evidence about a slight temperature dependence of these samples is that the water content in the permeate is almost the same in the operating temperature ranges in Figure 5.

The PANSS-3 membrane containing 3.5 mol % sulfonic acid group shows a typical temperature-dependent permeation behavior. However, the water concentration in the permeate ranges from 99.54 to 99.31 wt % at 25–70°C and is not greatly reduced even at 70°C. Two possible reasons are as follows. First, the increase of the permeation flux is due to the solute-induced relaxation of polymer chain in PANSS-3 by an enhanced hydrophilicity. Second, as can be seen in our previous study, the functional group (sulfonic acid) inside and on the surface of the membrane can hinder the permeation of pyridine and enhance the water permeation through the membrane, even at high temperature by forming an *in situ* complex.[12,13]

In the case of the PANSS-4 membrane, it can be found that the permeation behavior showed as those of general hydrogen bonding type dehydration membranes.[18,19] In Oh and Lee[13] it was found that the poly(acrylonitrile-*co*-acryl amide) membrane showed a temperature-dependent permeation behavior. It was thought that the hydrogen bonding could not selectively hinder the permeation of pyridine as in the case of *in situ* complex membrane. A similar behavior can be found in the PANSS-4 membrane, which shows high activation energies for water and pyridine (see Table III). The increased affinity toward water and pyridine is mainly caused by the increased amount of sulfonic acid groups in the membrane. An extensive swelling and solute-induced chain relaxation provide more free volume in the PANSS-4 membrane in higher operating temperature ranges resulting in an increase in permeation flux and a slight decrease in separation factor.

Table III   Activation Energies (E) for Water and Pyridine through PAN-SS Membranes for Dehydration of 56 wt % Pyridine Aqueous Solution

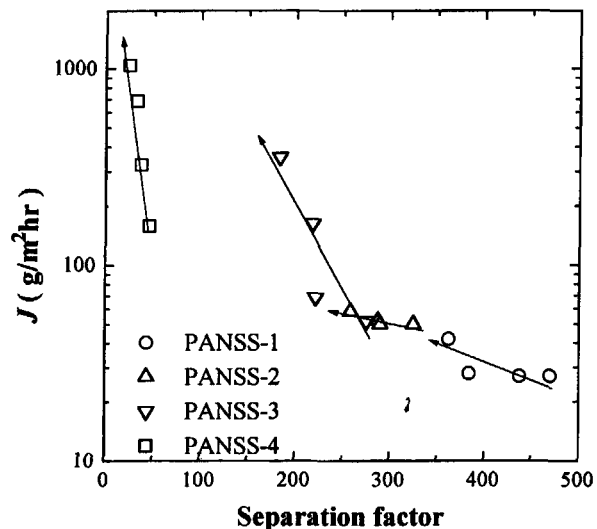| Sample	E_w (kcal/mol)	E_p (kcal/mol)
PANSS-1	1.699	3.171
PANSS-2	1.047	1.138
PANSS-3	8.875	10.453
PANSS-4	8.570	11.218

Figure 7   Trends of permeation behaviors of PANSS-1 (O), PANSS-2 (△), PANSS-3 (▽), and PANSS-4 (□). The direction of the arrow means an increase of operating temperature. The range of operating temperature was 25–70°C.

Figure 7 describes the pervaporation patterns of PANSS membranes having different content of sulfonic acid group according to the operating temperature. It is confirmed that the PANSS-3 membrane containing 3.5 mol % 4-styrene sulfonic acid shows an increase of permeation flux but only a minimum decrease of separation factor.

CONCLUSION

The polyacrylonitrile membrane was successfully modified by an emulsifier-free emulsion copolymerization with sodium 4-styrene sulfonate. It is found that the hydrophilicities of PANSS membranes increased with the content of sulfonic acid in the membrane as evidenced from their water contact angle values. In dehydration of pyridine aqueous solution, PANSS membranes showed different permeation behaviors in connection with the content of the sulfonic acid in PANSS membranes, that is (1) slight temperature-dependent type (PANSS-1 and PANSS-2), (2) intermediate temperature-dependent type (PANSS-3), and (3) highly temperature-dependent type (PANSS-4). The water concentration in the permeate was above 99 wt % for PANSS-1 to PANSS-3 membranes, while that for PANSS-4 was 97–95 wt % in 25–70°C. It could be concluded that the effective *in situ* complex membrane for the dehydration of pyridine aqueous so-

lution could be prepared by controlling the content of sulfonic acid group on and in the membrane.

REFERENCES

1. S. Akita and H. Takeuchi, *J. Chem. Eng. Jpn.*, **26**(3), 237 (1993).
2. H. F. Mark, D. F. Othmer, C. G. Overberger, and G. T. Seaborg, Eds., *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 19, 3rd ed., John Wiley, New York, 1982, p. 454.
3. J. A. Dean, Ed., *Lange's Handbook of Chemistry*, McGraw-Hill, New York, 1985, p. 63.
4. H. Eustache and G. Histi, *J. Membr. Sci.*, **8**, 105 (1981).
5. E. Drioli, S. Zhang, and A. Basile, *J. Membr. Sci.*, **80**, 309 (1993).
6. E. Drioli, S. Zhang, and A. Basile, *J. Membr. Sci.*, **81**, 43 (1993).
7. H. A. Xie, Q. T. Nguyen, P. Schaetzel, and J. Neel, *J. Membr. Sci.*, **81**, 97 (1993).
8. T. de V. Naylor, F. Zelaya, and G. J. Bratton, in *Proceedings of the 4th International Conference on Pervaporation Processes in the Chemical Industry*, R. Bakish, Ed., Bakish Materials Corp., Englewood, NJ, 1989, p. 428.
9. J. Neel, Q. T. Nguyen, R. Clement, and R. Francois, in *Proceedings of the Second International Conference on Pervaporation Processes in the Chemical Industry*, San Antonio, Texas, March 8–11, Bakish Materials Corp., Englewood, NJ, 1987, pp. 35–48.
10. R. Y. M. Huang, A. Moreira, R. Notartonzo, and Y. F. Xu, *J. Appl. Polym. Sci.*, **35**, 1191 (1988).
11. G. M. Koops and C. A. Smolders, *Pervaporation Membrane Separation Processes*, R. Y. M. Huang, Ed., Elsevier Science Pub., Amsterdam, 1991, p. 268.
12. Y. M. Lee and B.-K. Oh, *J. Membr. Sci.*, **98**, 183 (1995).
13. B.-K. Oh and Y. M. Lee, *J. Membr. Sci.* (to appear).
14. Y. M. Lee and B.-K. Oh, *J. Membr. Sci.*, **85**, 13 (1993).
15. Y. M. Lee, D. Bourgeois, and G. Belfort, *J. Membr. Sci.*, **44**(2), 161 (1989).
16. Y. M. Lee and K. Won, *Polym. J.*, **22**(7), 578 (1990).
17. R. Y. M. Huang and J. W. Rhim, *Pervaporation Membrane Separation Processes*, R. Y. M. Huang, Ed., Elsevier Science Pub., Amsterdam, 1991, p. 166.
18. M. Yoshikawa, H. Yokoi, K. Sanui, and N. Ogata, *J. Polym. Sci.: Polym. Lett. Ed.*, **22**, 125 (1984).
19. C.-M. Hu and W.-Y. Chiang, *J. Appl. Polym. Sci.*, **42**, 1829 (1991).