Poly(acrylic acid)–Poly(vinyl alcohol) Semi- and Interpenetrating Polymer Network Pervaporation Membranes

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SYNOPSIS

A series of poly(acrylic acid) (PAA)–poly(vinyl alcohol) (PVA) semiinterpenetrating (SIPN) and interpenetrating (IPN) polymer network membranes were prepared by crosslinking PVA alone or by crosslinking both PVA and PAA. Glutaraldehyde and ethylene glycol were used as crosslinking agents for the PVA and PAA networks, respectively. The presence of PAA increases the permeability of the membranes while the presence of PVA improves their mechanical and film-forming properties. The mechanical properties of the membranes were investigated via tensile testing. These hydrophilic membranes are permselective to water from ethanol–water mixtures and to ethanol from ethanol–benzene mixtures. The IPN membranes were employed for the former mixtures and the SIPN membranes for the latter, because the IPN ones provided too low permeation rates. The permeation rates and separation factors were determined as functions of the IPN or SIPN composition, feed composition, and temperature. For the azeotropic ethanol–water mixture (95 wt % ethanol), the separation factor and permeation rate at 50°C of the PAA-PVA IPN membrane, containing 50 wt % PAA, were 50 and 260 g/m^2 h, respectively. For the ethanol–benzene mixture, the PAA–PVA SIPN membranes had separation factors between 1.4 and 1200 and permeation rates between 6 and 550 g/m^2 h, respectively, depending on the feed composition and temperature. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation can be effectively used in the separation of azeotropic, close-boiling point, and heat-sensitive mixtures. Many pervaporation membranes have been employed for the dehydration of water–organic mixtures. Typical membranes are poly(acrylic acid) (PAA), poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), and chitosan. Both the mechanical and separation properties of the membranes used in pervaporation can be improved by using graft, block, blend, and crosslinked polymers.[1-6] Few articles have been concerned with interpenetrating polymer network (IPN) membranes.[7-9] Compared to those prepared by graft, block, or blend polymerization, the IPN or semi-IPN (SIPN) membranes have higher stabilities at high temperatures and in various liquids.

The PAA membranes exhibit high water selectivity and permeation rate because of their carboxylic groups. Of course, the PAA membranes must be crosslinked to avoid their dissolution in water. However, the crosslinked PAA membrane is brittle and its film-forming capability is low. Compared to PAA, PVA has a lower hydrophilicity but higher mechanical strength and film-forming capability. For these reasons, we prepared PAA–PVA IPN membranes by the sequential IPN technique; and their pervaporation performance for ethanol–water mixtures was investigated. We also prepared PAA–PVA SIPN membranes, and their pervaporation performance was investigated for the ethanol–benzene mixture for which the boiling points of the two components are almost the same. The higher affinity of PAA for ethanol than benzene suggested that we use the above membrane for the separation of ethanol from the ethanol–benzene mixtures. In the latter case, the SIPN membrane was preferred to

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Table I Compositions of Casting Solutions Used to Prepare PAA–PVA IPN Membranes

Membrane No.	PAA/PVA (wt Ratio)	PAA (g)	PVA (g)	GAL (g)	EG (g) $\times 10^2$	HCl (1N) (mL)	H$_2$O (mL)
I	70/30	0.58	0.25	0.025	1.2	0.125	8
II	50/50	0.25	0.25	0.025	0.5	0.125	3.5
III	30/70	0.11	0.25	0.025	0.2	0.125	2
IV	10/90	0.03	0.25	0.025	0.05	0.125	—

For all membranes GAL = 0.5 wt % in the crosslinked PVA network, EG = 2.0 wt % in the crosslinked PAA network.

the IPN one, because the latter provided a permeation rate that was too low.

EXPERIMENTAL

Materials

PVA (Aldrich, molecular weight 124,000), PAA (25 wt % in water, Aldrich, molecular weight 240,000), glutaraldehyde (GAL, 25 wt % in water, Aldrich), ethylene glycol (EG, 99%, Fisher), hydrochloric acid (37 wt % in water, Aldrich), benzene (99%, Aldrich), and ethanol (99%, Aldrich) were used as received. Water was deionized and double distilled.

Preparation of PAA–PVA IPN Membranes

To obtain the PAA–PVA IPN membranes, GAL and EG were used as crosslinking agents for the PVA and PAA networks, respectively. The compositions of the casting solutions are listed in Table I. The solution was mixed with a magnetic stirrer for 10 min, cast on a glass plate, and allowed to evaporate at room temperature for 24 h. During this process, a crosslinked PVA network containing macromolecules of PAA was generated. Subsequently, the membranes were heated in an oven at 120°C for 3 h to generate the crosslinked PAA network. The membranes were dried in a vacuum oven at room temperature for 24 h. The thickness of PAA–PVA IPN membrane was in the range of 20–30 μm.

Preparation of PAA-Crosslinked PVA SIPN Membranes

The compositions of the casting solutions used to prepare the PAA–PVA SIPN membranes are listed in Table II. The solution containing PAA, PVA, the crosslinking agent GAL, and the catalyst HCl was first mixed using magnetic stirring for 10 min. Then, the solution was cast on a glass plate and allowed to evaporate at room temperature for 24 h. The transparent SIPN membranes thus obtained were dried for 24 h in a vacuum oven at room temperature. The thickness of the dry membrane was in the range 20–30 μm.

Tensile Testing

The tensile testing of the PAA–PVA SIPN and IPN samples was performed by preparing sheets of the size required by ASTM D638-58 T and using an Instron Universal Testing Instrument (model 1000) at room temperature. The extension speed of the instrument was 10 mm/min.

Pervaporation

The pervaporation experiments were performed using the apparatus described previously.[8] The membrane was located on a porous glass support. The temperature of the permeation cell was controlled using a thermostated water bath. The effective membrane area was 9.6 cm^2. The downstream pressure was kept at 3

Table II Compositions of Casting Solutions Used to Prepare PAA–PVA SIPN Membranes

Membrane No.	PAA/PVA (wt Ratio)	PAA (g)	PVA (g)	GAL (g)	HCl (1N) (mL)	H$_2$O (mL)
I	80/20	1.0	0.25	0.025	0.125	14
II	70/30	0.58	0.25	0.025	0.125	8
III	60/40	0.37	0.25	0.025	0.125	6

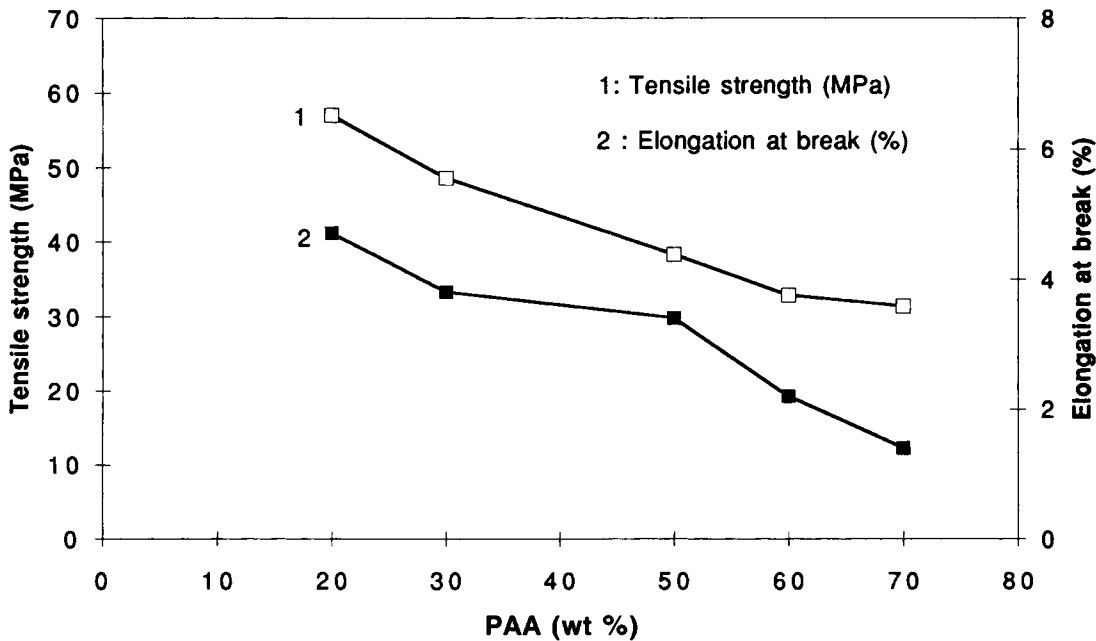For all membranes GAL = 0.5 wt % in the crosslinked PVA network.
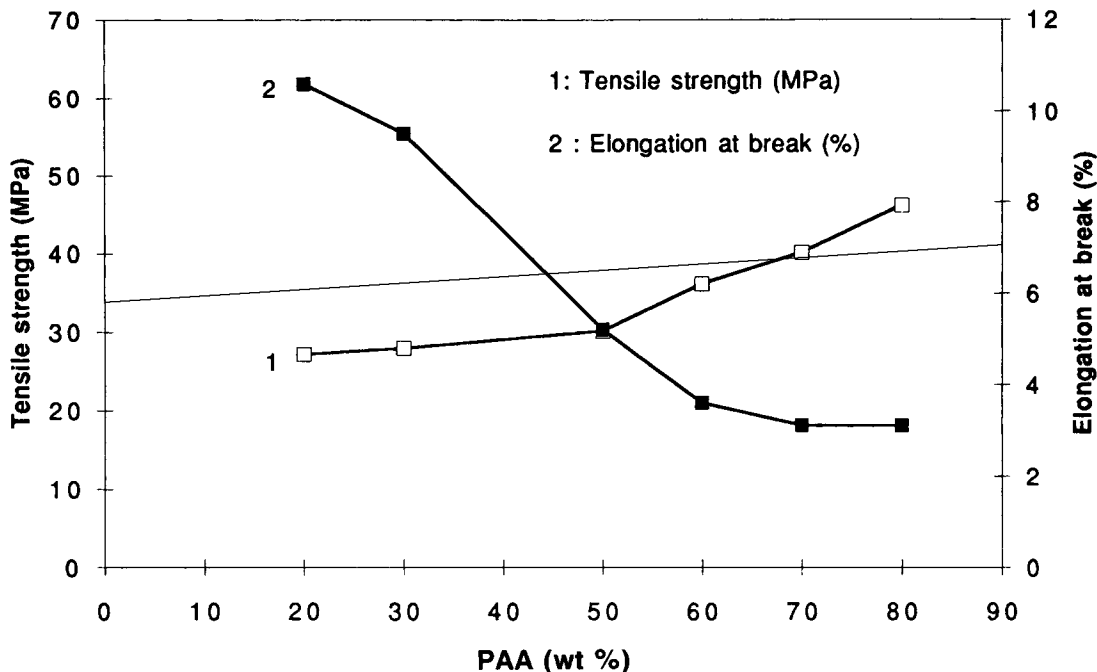
Figure 1   The tensile strength and elongation at break against the PAA content for the PAA–PVA SIPN membranes. For all membranes GAL = 0.5 wt % in the crosslinked PVA network.

± 1 torr by a vacuum pump. The steady state can be achieved after running the apparatus for about 2 h.

The permeated sample was collected in a cold trap cooled with liquid nitrogen. The composition of the sample was determined using a gas chromatograph equipped with a Porapack Q column at the temperatures of 160 and 215°C for the ethanol–water and ethanol–benzene mixtures, respectively, and a ther-

Figure 2   The tensile strength and elongation at break against the PAA content for the PAA–PVA IPN membranes. For all membranes GAL = 0.5 wt % in the crosslinked PVA network; EG = 2.0 wt % in the crosslinked PAA network.
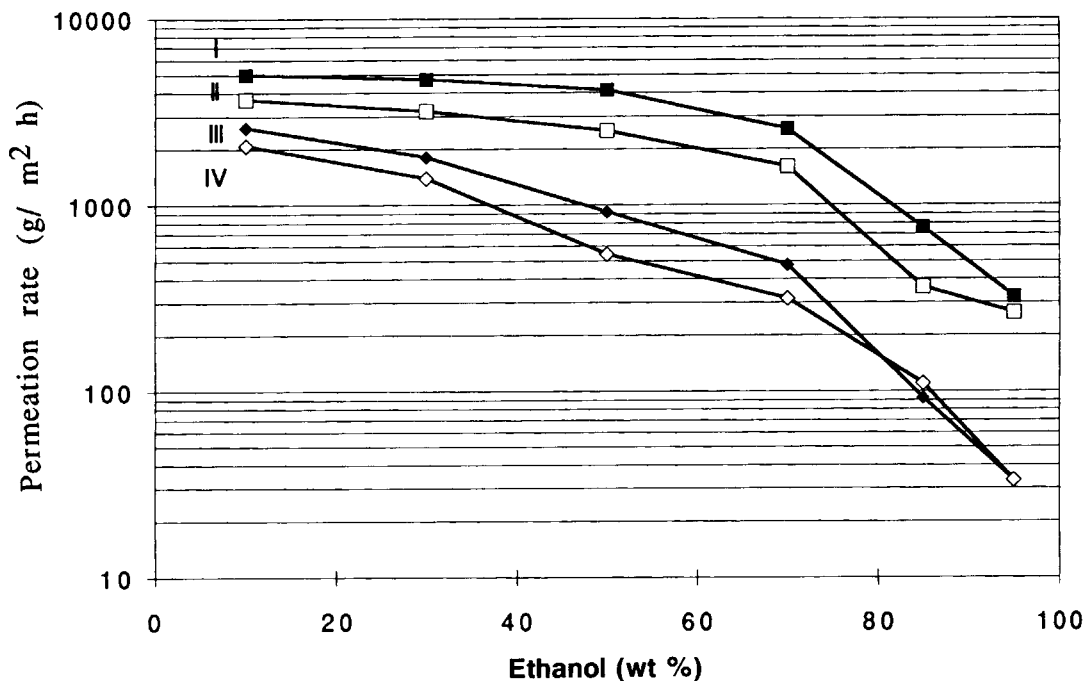
Figure 3 Effect of ethanol composition in the feed on the total permeation rate at 50°C for the pervaporation of ethanol–water mixtures. The membranes are those of Table I.
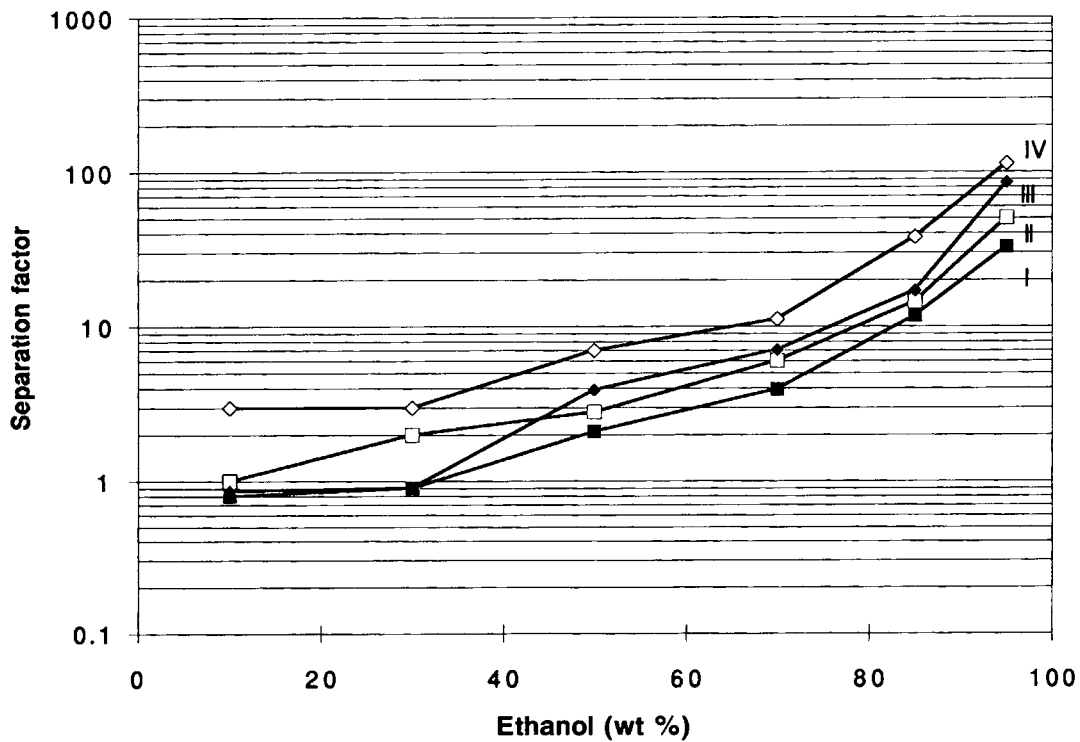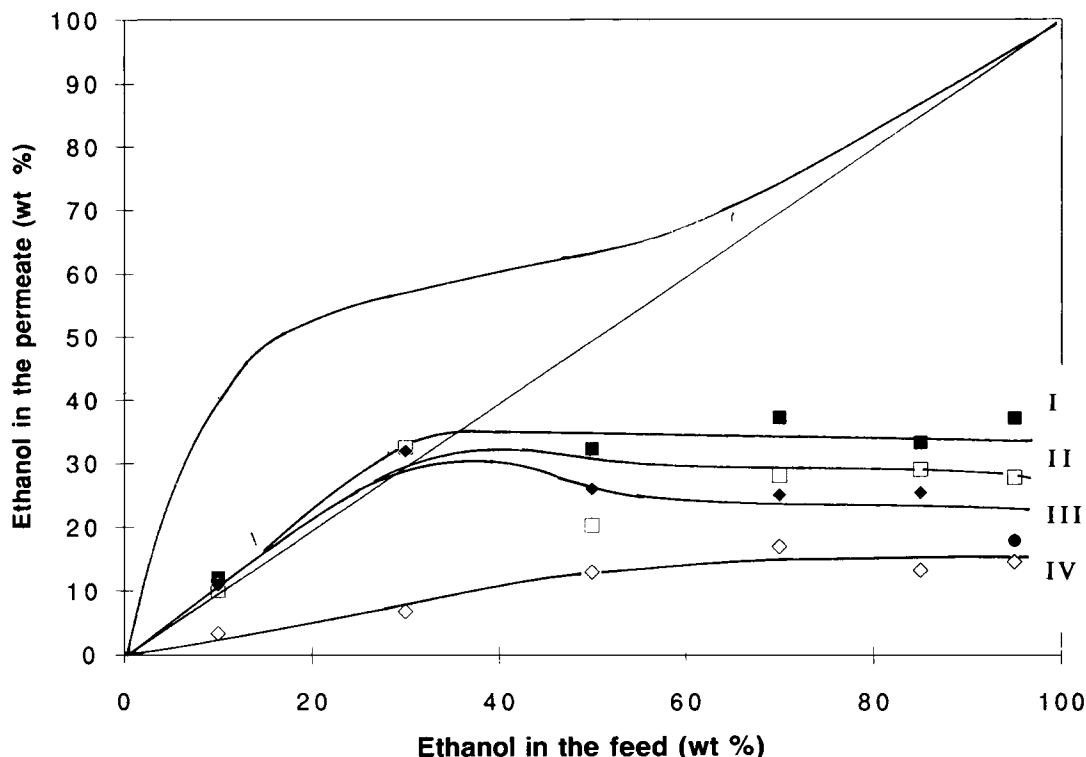

Figure 4 Effect of ethanol composition in the feed on the separation factor at 50°C for the pervaporation of ethanol–water mixtures. The membranes are those of Table I.

Figure 5 Permeate composition in the pervaporation of ethanol–water mixtures through various of PAA–PVA IPN membranes as a function of the feed composition at 50°C. The membranes are those of Table I.

mal conductivity detector. Helium was used as the carrier gas.

The permeation rate, J, can be calculated using the expression

$$J = Q/At$$

where Q is the total amount of permeate during the experimental time interval t at steady state and A is the effective membrane surface area.

The selectivity of the membrane can be characterized via the separation factor, $\alpha_{i/j}$, which is defined as

$$\alpha_{i/j} = (C_i/C_j)_{\text{permeate}}/(C_i/C_j)_{\text{feed}}$$

where $(C_i/C_j)_{\text{permeate}}$ is the weight ratio of components i and j in the permeate and $(C_i/C_j)_{\text{feed}}$ is their weight ratio in the feed. Component i is the preferentially pervaporated one.

RESULTS AND DISCUSSION

Tensile Strength and Elongation of PAA–PVA SIPN and IPN Membranes

Figure 1 shows that with increasing content of PAA in the PAA–crosslinked PVA SIPN membranes, the tensile strength increases and the elongation at break decreases. PAA is more brittle than PVA because of the rigidity caused by the strong interactions among the carboxyl groups. When the content of PAA in the SIPN was higher than 80 wt %, the membrane became so brittle that it could not be separated from the glass plate. Membranes containing about 60 wt % PAA are suitable from a mechanical point of view.

The tensile strength and elongation at break for the PAA–PVA IPN membranes are presented in Figure 2 as a function of the PAA content. One can see that with increasing PAA content both the tensile strength and the elongation at break decrease. The degree of crosslinking of the PAA–PVA IPN membranes is much higher than that of the PAA–PVA SIPN membranes, because both

Table III   Pervaporation Performances of Different Membranes for Dehydrating Water from Ethanol–Water Mixtures

| Ethanol in Feed (wt %)	Temperature (°C)	J (g/m² h)	α	Membranes	Reference
96	15	5	350	PMA	11
80	70	20	250	PVA-g-PAA	12
90	40	31	123	Chitosan	13
88	50	9	314.8	PAA-g-PVA	14
80	30	500	30	PVA-g-(PS-co-MA)	15
90	40	~ 50	150	Crosslinked PVA	16
90	40	~ 200	~ 23	Photocrosslinked PVA	17
90	75	~ 130	~ 280	Crosslinked PVA	18
90	25	78	46	Nylon 6-PAA blend	19
95	75	60	4100	PVA–PAAM IPN	8
95	50	260	50	PAA–PVA IPN	This study

PMA, poly(maleimide-co-acrylonitrile); PVA, poly(vinyl alcohol); PAA, poly(acrylic acid); PS, polystyrene; MA, malice anhydride; PAAM, polyacrylamide; IPN, interpenetrating polymer network.

polymers are crosslinked. In addition to the cross-linking in the individual networks, there are interactions among the chains, as well as some crosslinking between the two networks due to the reaction between COOH and OH. For the SIPN membranes, the tensile strength increases with increasing PAA content because of increasing interactions among the chains. For the IPN membranes, the tensile strength decreases with increasing PAA content, because the crosslinking of the latter by the EG molecules does not allow enough close contact among the chains, thus de-
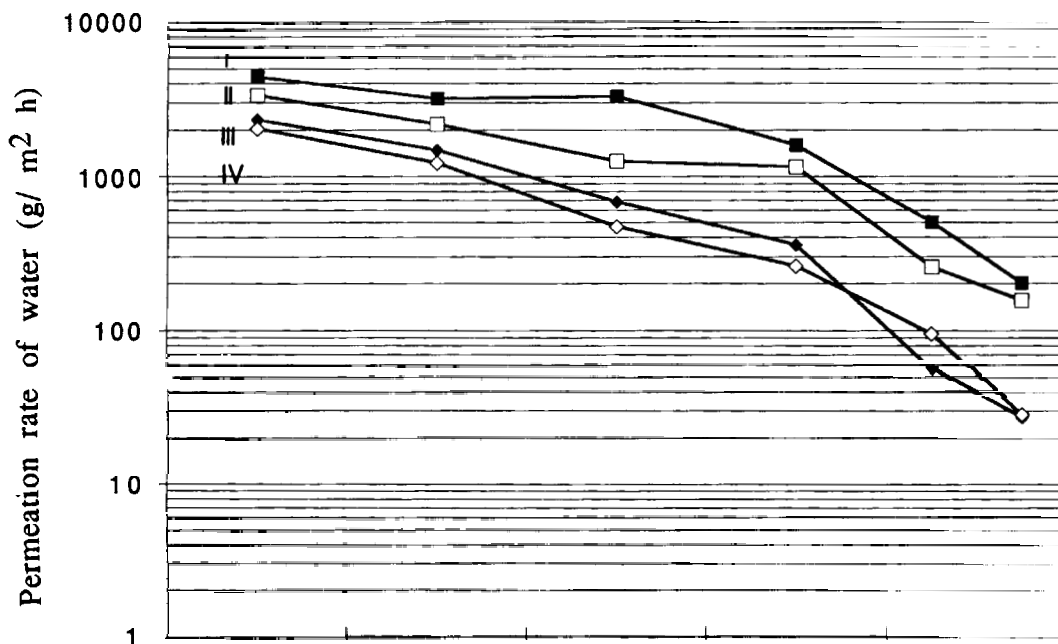

Figure 6 Effect of the ethanol composition in the feed on the permeation rate of water at 50°C for the pervaporation of ethanol–water mixtures. The membranes are those of Table I.
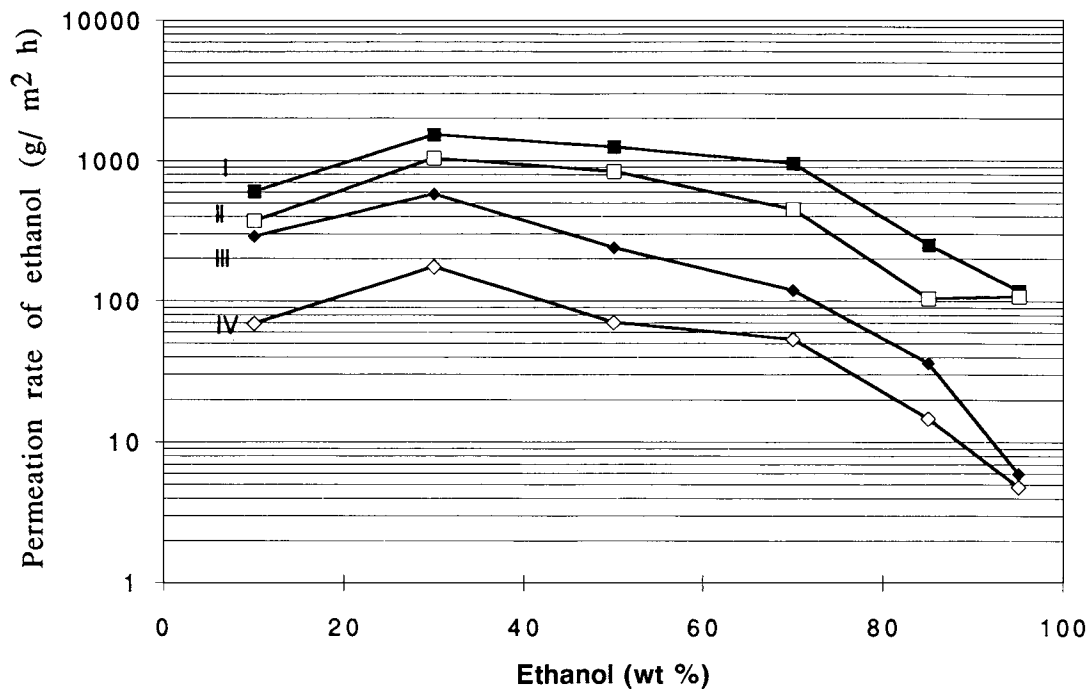
Figure 7   Effect of the ethanol composition in the feed on the permeation rate of ethanol at 50°C for pervaporation of ethanol–water mixture. The membranes are those of Table I.
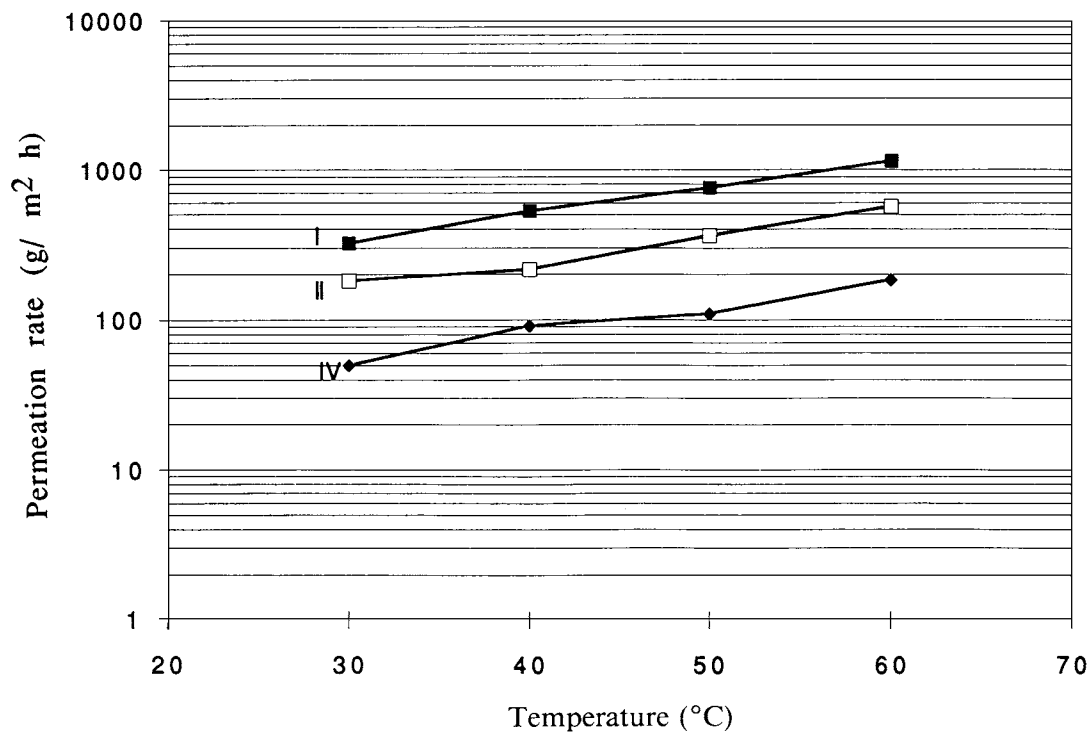
Figure 8   Dependence of the total permeation rate on the feed temperature for 85 wt % ethanol in ethanol–water mixture and membranes I, II, and IV of Table I.
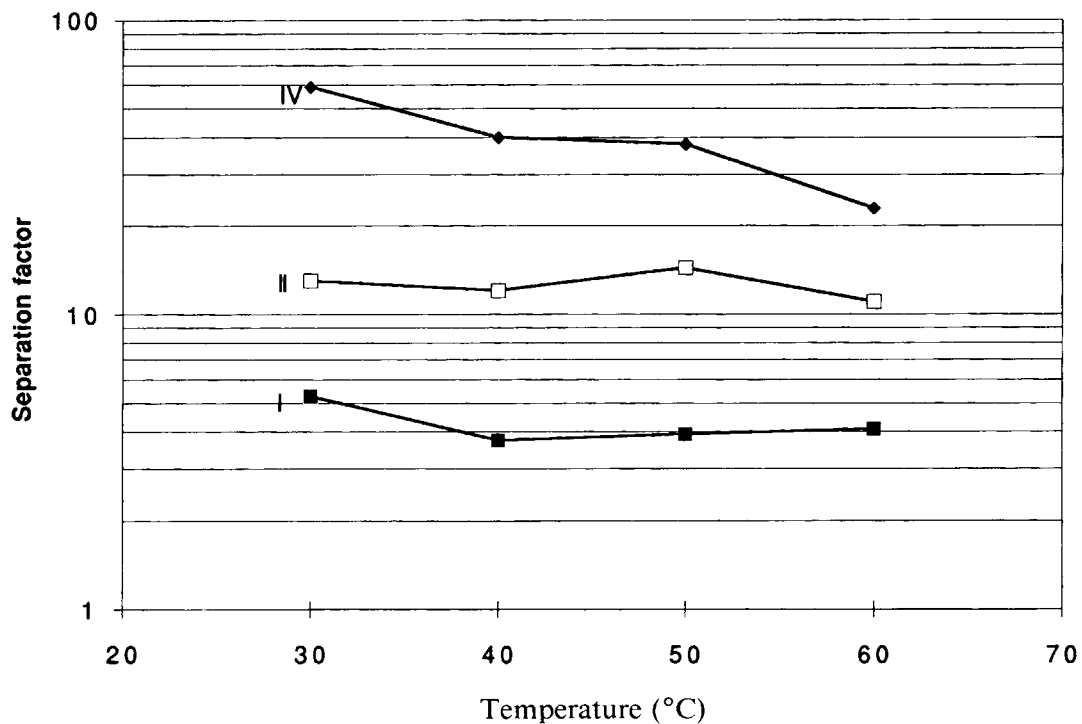
Figure 9 Dependence of the separation factor on the feed temperature for 85 wt % ethanol in ethanol–water mixtures and membranes I, II, and IV of Table I.
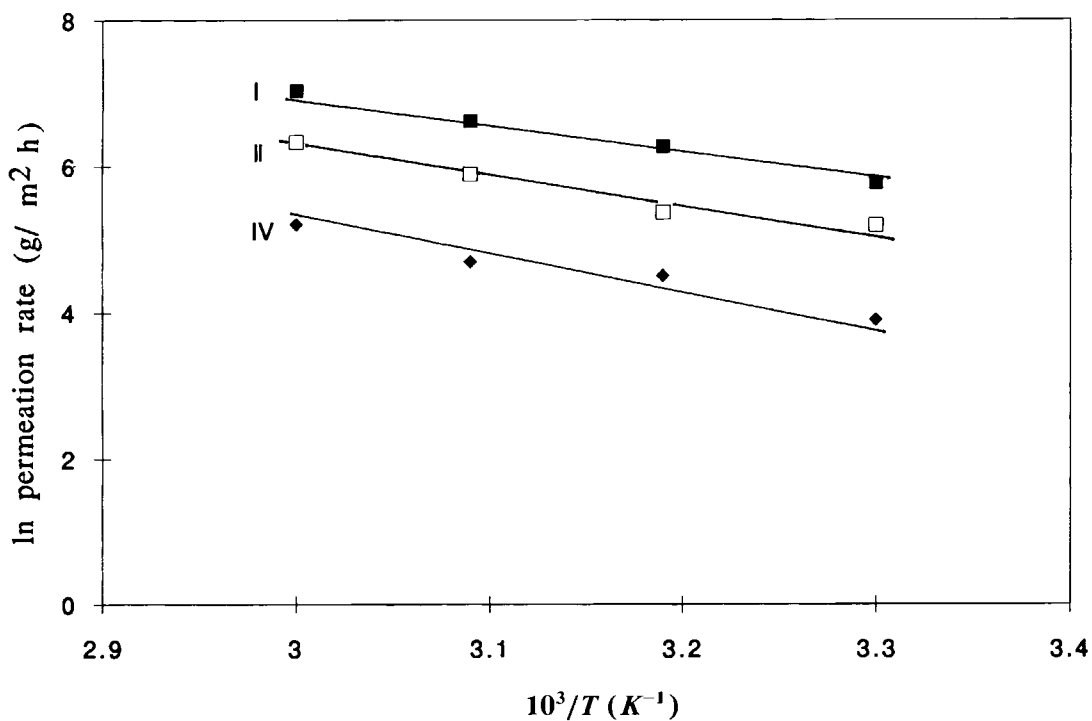
Figure 10 Arrhenius plots of the total permeation rate vs. temperature for 85 wt % ethanol in ethanol–water mixture and membranes I, II, and IV of Table I.

Table IV Activation Energies for Permeation of Ethanol–Water Mixture Containing 85 wt % Ethanol

PAA–PVA IPN Membranes (wt Ratio)	Activation Energy (kcal/mol)
70/30	7.3
50/50	7.4
10/90	9.3

For all membranes GAL = 0.5 wt % in the crosslinked PVA network, EG = 2.0 wt % in the crosslinked PAA network.

creasing the interactions among the PAA chains. The mobility of the segments is decreased, and this decreases the elongation at break with increasing PAA content for both kinds of membranes. IPN membranes containing 50 wt % PAA are suitable from a mechanical point of view.

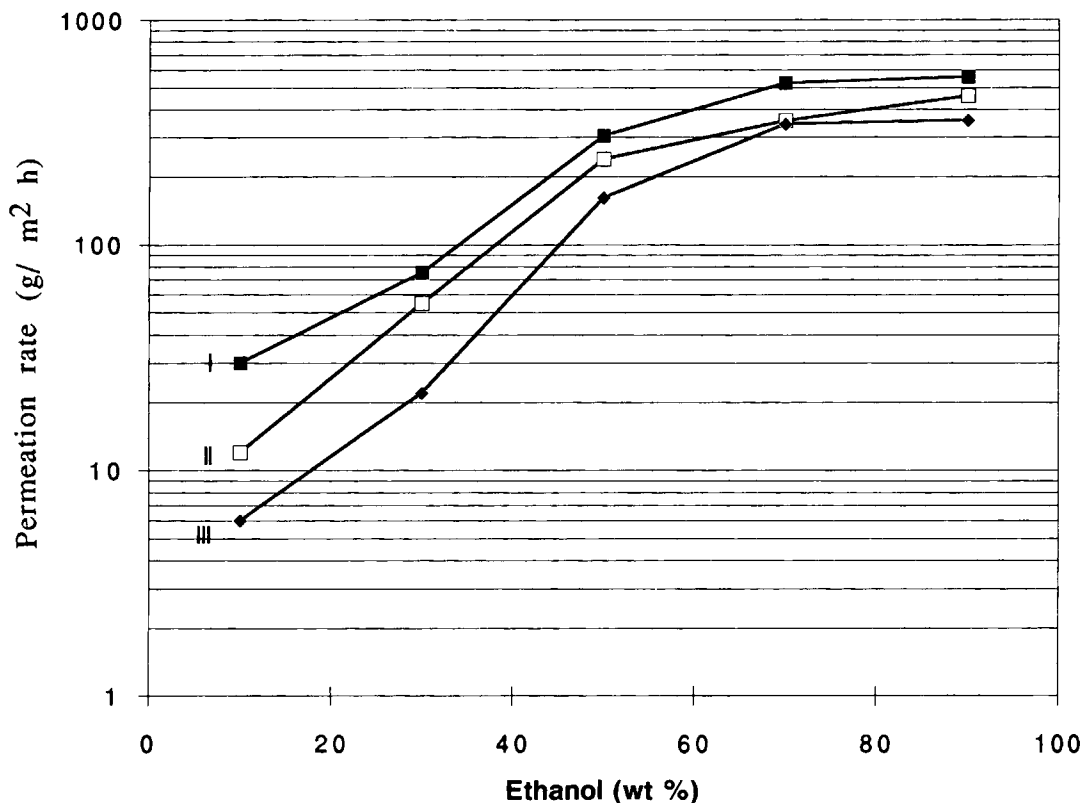## Pervaporation of Ethanol–Water Mixture Through PAA–PVA IPN Membranes

Effect of Feed Composition

Figures 3 and 4 present the total permeation rate and separation factor for PAA–PVA IPN mem-

branes of various compositions, as a function of the ethanol concentration in the feed at 50°C. The increase of the ethanol concentration in the feed increases the separation factor but decreases the permeation rate. This occurs because the hydrophilic membrane has a higher swelling at larger water contents in the feed, and this decreases the separation factor. For comparison purposes, Figure 5 presents the ethanol concentration in the permeate as a function of its concentration in the feed, together with the vapor–liquid equilibrium curve at 50°C.[10] Figures 3 and 4 also show that with increasing PAA content in the IPN membranes, the permeation rate increases but the separation factor decreases. This is because PAA is more hydrophilic than PVA, and the increase of the PAA content increases the swelling of the membrane. For the azeotropic ethanol–water mixture (95 wt % ethanol) and for a PAA–PVA IPN membrane containing 50 wt % PAA, the separation factor and the permeation rate are 50 and 260 g/m^2 h, respectively. For comparison purposes, some results regarding dehydration of ethanol–water mixtures at or near the azeotropic point obtained by various authors with various membranes are listed in Table III.[8,11–19] One can see that the PAA–PVA IPN membrane has a rel-
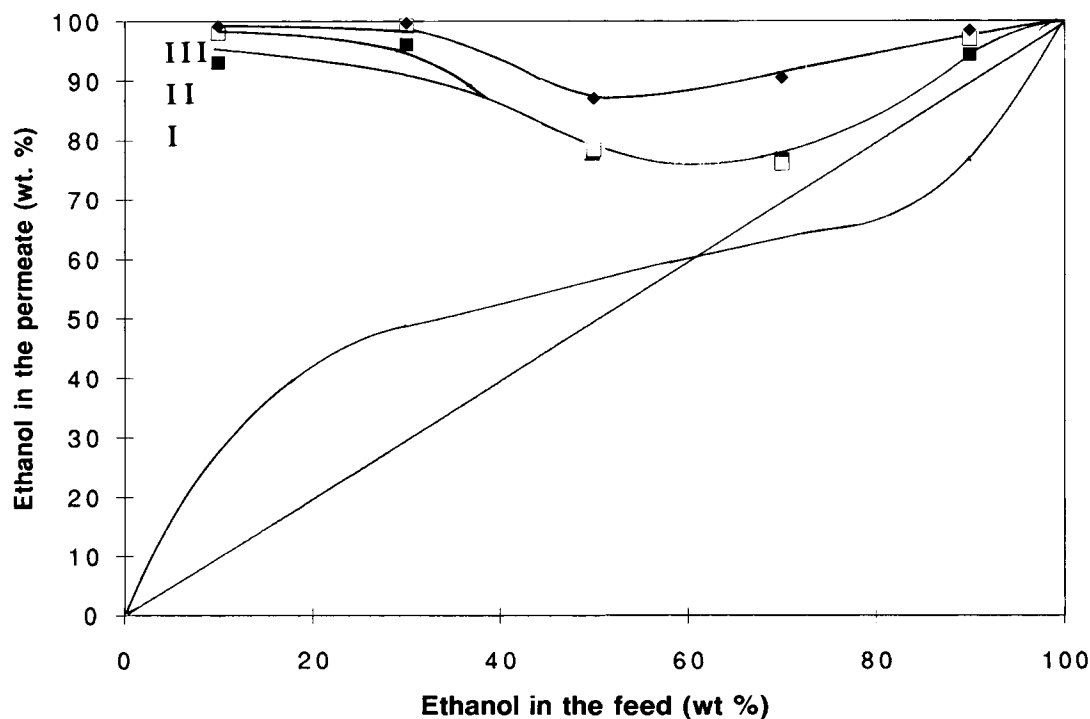
Figure 11 Permeate composition at 50°C in the pervaporation of ethanol–benzene mixtures through various PAA–PVA SIPN membranes, as a function of the feed composition. The membranes are those of Table II.
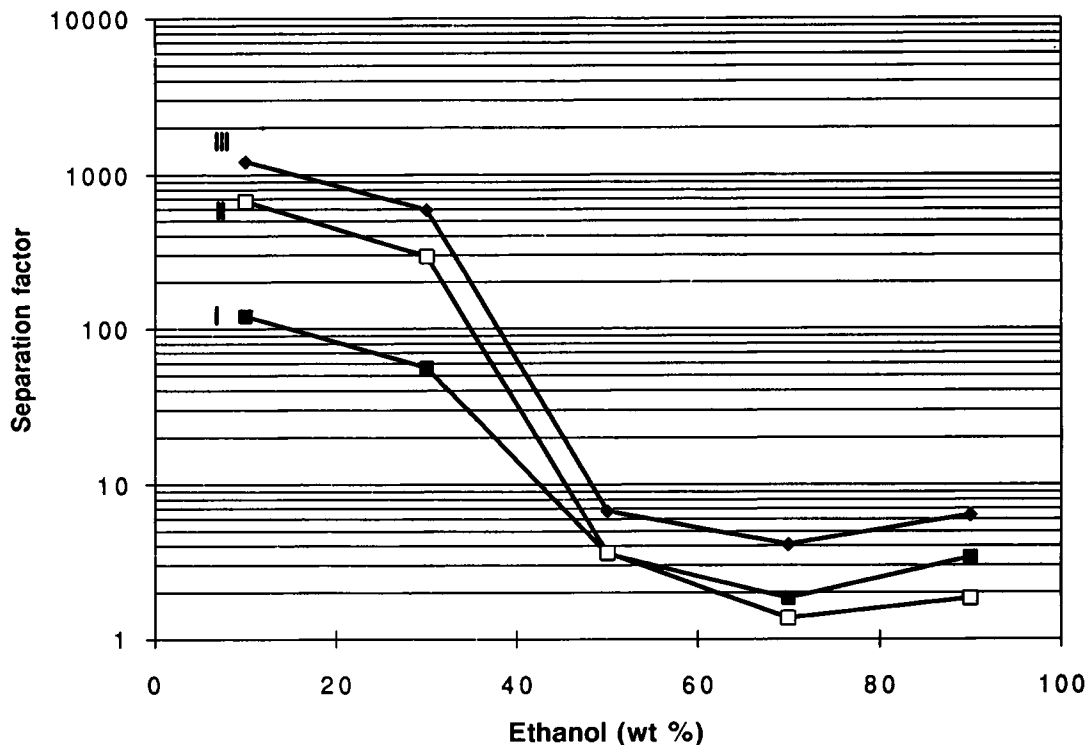
Figure 12 Effect of ethanol composition in the feed on the total permeation rate at 50°C for pervaporation of ethanol–benzene mixtures. The membranes are those of Table II.

atively high permeation rate and a good separation factor.

Figures 6 and 7 present the permeation rates of water and ethanol through various PAA–PVA IPN membranes at 50°C, respectively. The change of the permeation rate of water with the ethanol concentration in the feed has the same trend as the total permeation rate from Figure 3; that is, with decreasing ethanol concentration in the feed, the permeation rate of water increases. However, the permeation rate of ethanol first increases as the ethanol concentration in the feed decreases from 90 to 30 wt %, but decreases with the further decrease of ethanol concentration from 30 to 10 wt %. In the high ethanol concentration range, as the amount of water increases, the swelling of the membrane increases; as a result, the permeation of ethanol is enhanced. In the low ethanol concentration range, the membrane becomes so hydrophilic that the permeation rate of ethanol, which is less hydrophilic than water, is retarded.

Effect of Feed Temperature

Figures 8 and 9 present the effect of the feed temperature on the permeation rate and separation factor for various PAA–PVA IPN membranes and for 85 wt % ethanol. The permeation rate increases with increasing temperature because the increase of temperature increases both the mobility of the permeating molecules and that of the polymer segments. The effect of temperature on the separation factor depends upon the composition of the PAA–PVA IPN membranes. For the membranes with a low PAA content (PAA = 10 wt %), the separation factor decreases with increasing temperature. However, there is only a small change in the separation factor for the membranes with a high PAA content (PAA ≥ 30 wt %). This happens because the membranes with higher PAA contents have higher swelling and, consequently, both the permeating molecules and the polymer segments have higher mobility. While the increase in temperature generates additional mobility, the mobility generated by the swelling is

Figure 13   Effect of ethanol composition in the feed on the separation factor at 50°C for pervaporation of ethanol–benzene mixtures. The membranes are those of Table II.

large enough for the former increase to have small consequences.

Figure 10 contains Arrhenius plots for the total permeation rates. The activation energies are listed in Table IV, which shows that the activation energies decrease with increasing PAA content in the membrane.
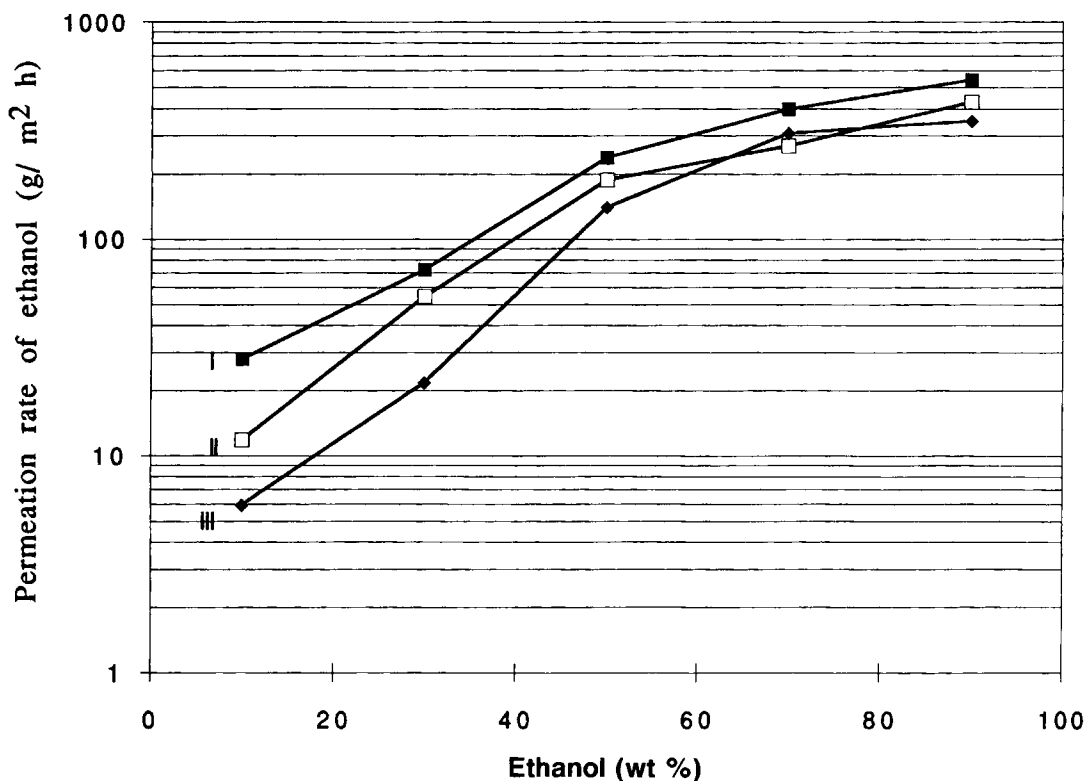
PERVAPORATION OF ETHANOL–BENZENE MIXTURES THROUGH PAA-CROSSLINKED PVA SIPN MEMBRANES

Effect of Feed Composition

Figures 11–13 present the separation characteristics of PAA–PVA SIPN membranes for the ethanol–benzene mixture at 50°C. Figure 11 shows the relationship between the ethanol concentrations in the permeate and in the feed. For comparison purposes, the vapor–liquid equilibrium curve[20] of the ethanol–benzene mixture at 50°C is also included. One can see that the SIPN membranes are permselective to ethanol over the entire range of ethanol concentrations. Figures 12 and 13 present the effect of ethanol concentration (at 50°C) on the permeation rate and separation factor, respectively. With increasing

ethanol concentration in the feed, the permeation rate increases but the separation factor decreases. The permeation rate increases with increasing PAA content in the SIPN membranes, because of the increasing hydrogen bonding between the carboxyl groups of PAA and the hydroxyl groups of the ethanol molecules. The separation factors and permeation rates of PAA–PVA SIPN membranes are in the range of 1.4–1200 and 6–550 g/m^2 h, respectively, depending on the ethanol concentration in the feed and the composition of the SIPN membrane.

Figures 14 and 15 present the effect of ethanol concentration in the feed on the permeation rate of ethanol and benzene at 50°C for various SIPN membranes. With increasing ethanol concentration, its permeation rate increases. However, the permeation rate of benzene first increases with increasing ethanol concentration from 10 to 70 wt %, and subsequently decreases as the ethanol concentration further increases from 70 to 90 wt %. In the low ethanol concentration region, the permeation of ethanol molecules through the membrane occurs with little swelling; and their adsorption on the hydrophilic sites of the membrane partially hydrophobize the membrane, thus enhancing the transfer of the benzene molecule. In the high ethanol con-

Figure 14   Effect of ethanol composition in the feed on the permeation rate of ethanol at 50°C for the pervaporation of ethanol–benzene mixtures. The membranes are those of Table II.

centration region, the swelling of the membrane increases and the membrane is increasingly hydrophilized. As a result, the permeation rate of benzene through the membrane decreases.

Effect of Feed Temperature

The dependencies of the permeation rate and separation factor on the feed temperature for 50 wt % ethanol in the feed are presented in Figures 16 and 17, respectively. With increasing feed temperature, the permeation rate increases and the separation factor decreases. Figure 18 shows that there is a linear relationship between the ln of the permeation rate and the inverse of the absolute temperature. The activation energies calculated from Figure 18 are listed in Table V. A comparison with the results of Table IV shows that, as expected, the activation energies for the SIPN membranes are lower than those for the IPN membranes.

CONCLUSION

PAA–PVA IPN membranes as well as PAA-crosslinked PVA SIPN membranes were prepared. For

the PAA–PVA IPN membranes, the tensile strength and elongation at break decrease with increasing PAA content; the tensile strength increases and the elongation at break decreases with increasing PAA content in the PAA-crosslinked PVA SIPN membranes. An explanation was proposed for the different behaviors of the two kinds of membranes. For application purposes the content of PAA should be about 50 and 60 wt % for the IPN and SIPN membranes, respectively.

The separation characteristics of IPN and SIPN membranes were investigated as a function of membrane composition, feed composition, and temperature, by dehydrating ethanol–water mixtures and separating ethanol from ethanol–benzene mixtures, respectively. In the latter case, the SIPN membranes were employed because the IPN ones provided too low permeation rates. While the overall permeation rate increases with increasing concentration of the permselective component in the feed, the permeation rate of the other component passes through a maximum. An explanation is proposed for this behavior. For the azeotropic ethanol–water mixture (95 wt % ethanol) at 50°C, the permeation rate and the separation factor of PAA–PVA IPN membrane con-
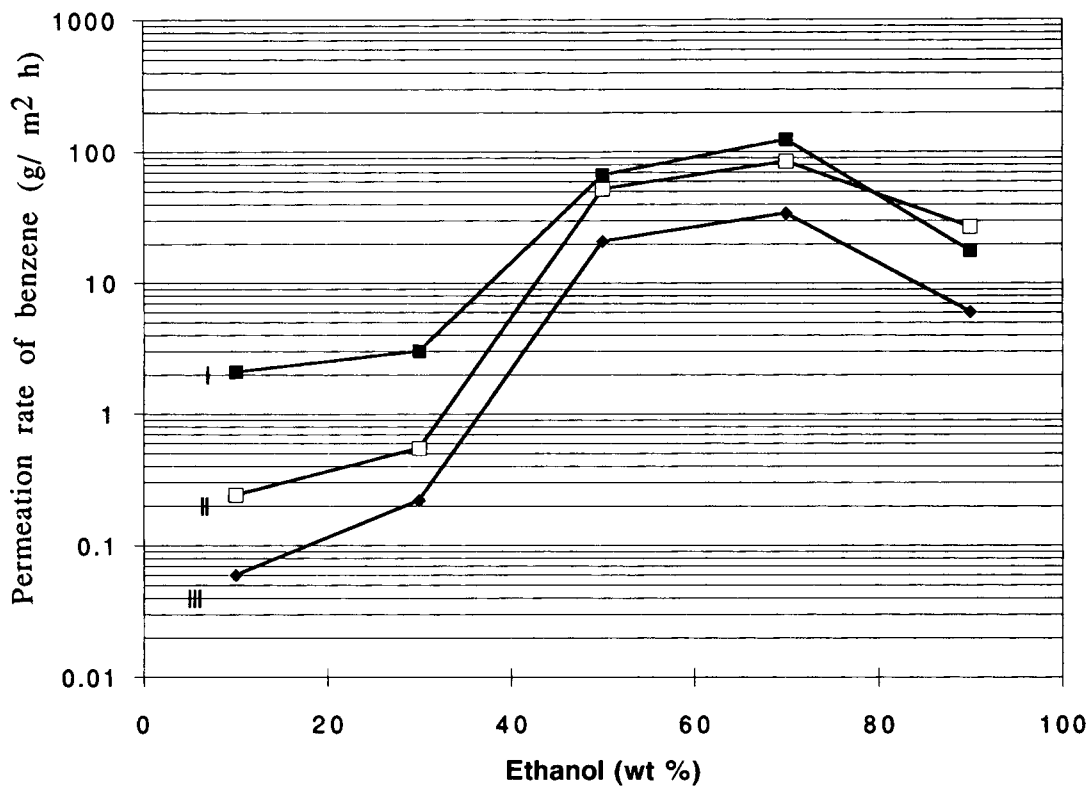
Figure 15 Effect of ethanol composition in the feed on the permeation rate of benzene at 50°C for the pervaporation of ethanol–benzene mixtures. The membranes are those of Table II.
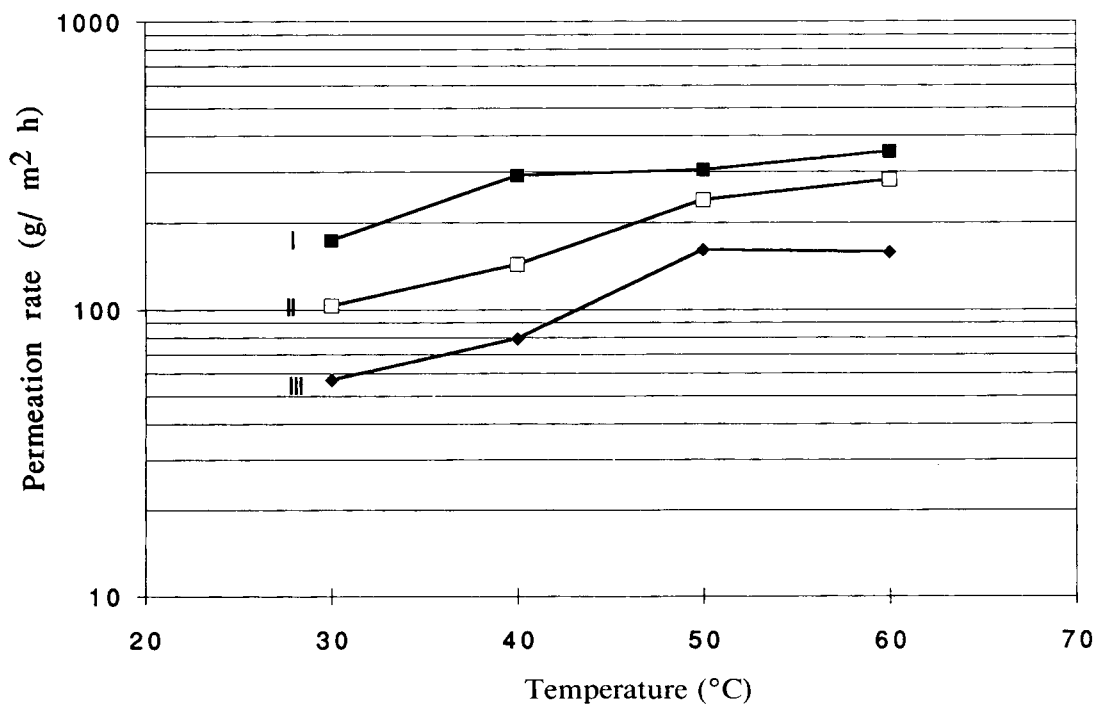
Figure 16 Dependence of the total permeation rate on the temperature for 50 wt % ethanol in ethanol–benzene mixtures. The membranes are those of Table II.
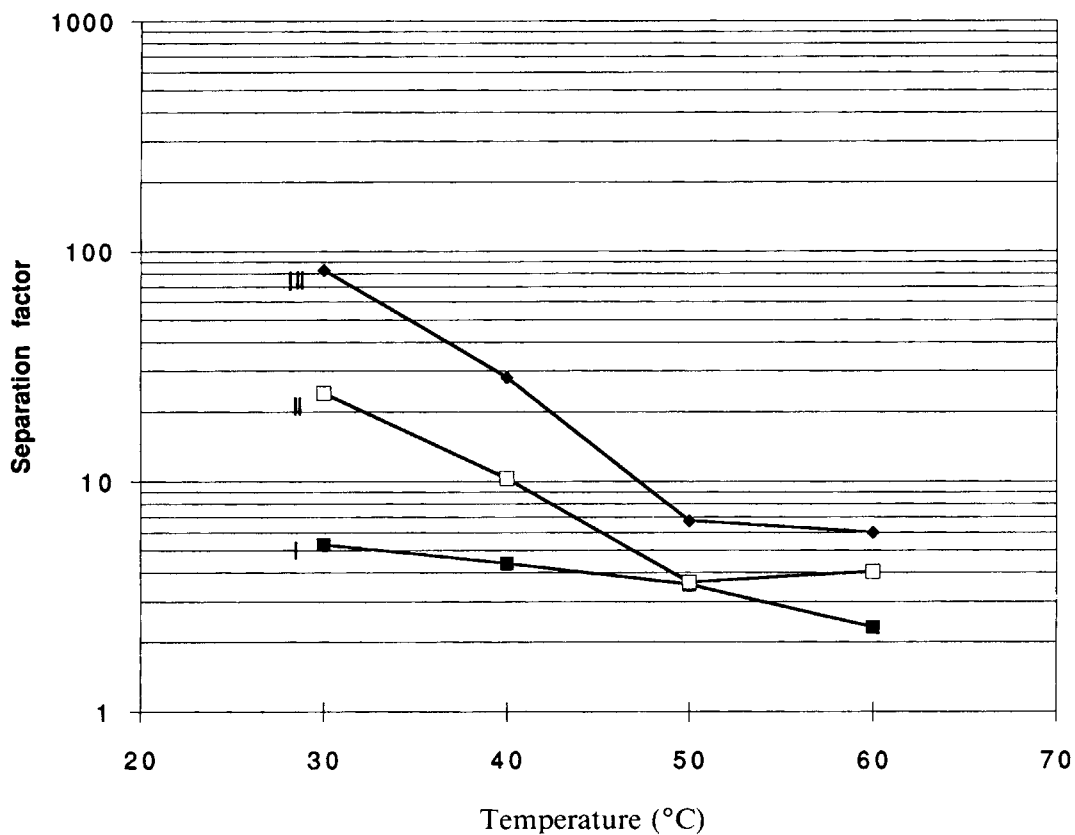
Figure 17 Dependence of the separation factor on the temperature for 50 wt % ethanol in ethanol–benzene mixtures. The membranes are those of Table II.
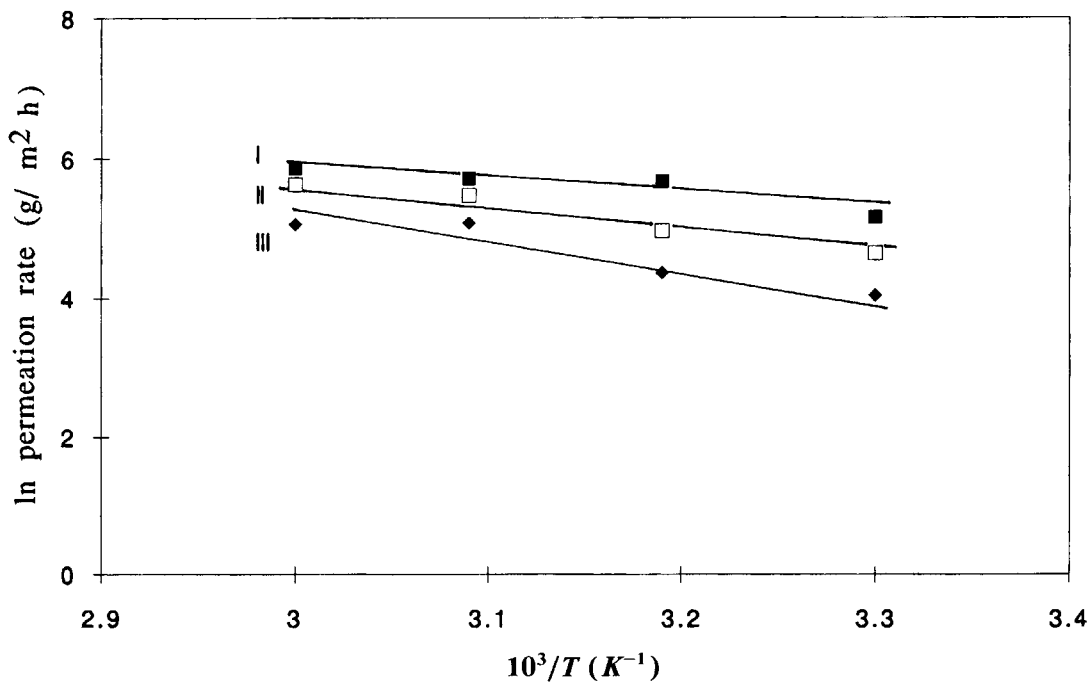
Figure 18 Arrhenius plots of total permeation rate vs. temperature for 50 wt % ethanol in ethanol–benzene mixtures. The membranes are those of Table II.

**Table V   Activation Energies for Ethanol–
Benzene Mixture Containing 50 wt % Ethanol**

PAA–PVA SIPN Membranes (wt Ratio)	Activation Energies (kcal/mol)
80/20	4.6
70/30	6.6
60/40	7.5

For all membranes GAL = 0.5 wt % in the crosslinked PVA network.

taining 50 wt % PAA were 260 g/m^2 h and 50, respectively. The PAA–PVA SIPN membranes were found to have at 50°C separation factors ranging from 1.4 to 1200 and permeation rates of about 6–560 g/m^2 h, depending on the composition of the membrane, feed composition, and temperature. The dependence of the permeation rate on the absolute temperature is consistent with an Arrhenius relationship, and the activation energies were in the range of 7.3–9.3 and 4.6–7.5 kcal/mol for PAA–PVA IPN and PAA–PVA SIPN membranes, respectively.

REFERENCES

1. J. L. Rapin, in *Proceedings of the Third International Conference on Pervaporation Processes in the Chemical Industry*, R. Bakish, Ed., Bakish Materials Corp., Englewood, NJ, 1988, p. 364.
2. H. C. Park, R. M. Meertens, M. H. V. Mulder, and C. A. Smolders, *J. Membr. Sci.,* **90,** 265 (1994).
3. Y. M. Lee and B. K. Oh, *J. Membr. Sci.,* **85,** 13 (1993).
4. H. C. Park, N. E. Ramaker, M. H. V. Mulder, and C. A. Smolders, *Sep. Sci. Technol.,* **30,** 419 (1995).
5. G. H. Koops, J. A. M. Nolten, M. H. V. Mulder, and C. A. Smolders, *J. Membr. Sci.,* **81,** 57 (1993).
6. E. Ruckenstein and F. Sun, *J. Membr. Sci.,* **81,** 191 (1993).
7. Y. K. Lee, T. M. Tak, D. S. Lee, and K. C. Kim, *J. Membr. Sci.,* **52,** 157 (1990).
8. L. Liang and E. Ruckenstein, *J. Membr. Sci.,* **106,** 167 (1995).
9. L. Liang and E. Ruckenstein, *J. Membr. Sci.,* **114,** 227 (1996).
10. J. Gmehling and U. Onken, Vapor–Liquid Equilibrium Data Collection, Vol. 1, Part 1, DECHEMA, Germany, 1977, p. 163.
11. M. Yoshikawa, H. Yokoi, K. Sanui, and N. Ogata, *J. Polym. Sci., Polym. Lett. Ed.,* **22,** 125 (1984).
12. M. Yoshikawa, N. Ogata, and I. Shimitza, *J. Membr. Sci.,* **26,** 107 (1986).
13. T. Uragami, M. Saito, and K. Takigama, *Makromol. Chem. Rapid Commun.,* **9,** 361 (1988).
14. T. Hirotsu, Jpn. Pat. 62-254807A, (1987).
15. C. Wan Yen and H. Chao Yi, *Angew. Makromol. Chem.,* **219,** 169 (1994).
16. Y. S. Kang, S. W. Lee, U. Y. Kim, and J. S. Shim, *J. Membr. Sci.,* **51,** 215 (1990).
17. T. Hirotsu, K. Ichimura, K. Mizoguchi, and E. Wakamura, *J. Appl. Polym. Sci.,* **36,** 1717 (1988).
18. R. T. M. Huang and C. K. Yeom, *J. Membr. Sci.,* **51,** 273 (1990).
19. F. Y. Xu and R. Y. M. Huang, *J. Appl. Polym. Sci.,* **36,** 1121 (1988).
20. J. Gmehling and U. Onken, Vapor–Liquid Equilibrium Data Collection, Vol. 1, Part 2a, DECHEMA, Germany, 1977, p. 409.