Acrylonitrile-Based Copolymer Membranes for the Separation of Methanol from a Methanol–Toluene Mixture through Pervaporation

Sangita Mandal Pal, Vishwas G. Pangarkar

Mumbai University Institute of Chemical Technology, Matunga, Mumbai 400019, India

ABSTRACT: The membrane selection criteria for the preferential permeation of a particular component were examined for the pervaporative separation of methanol from a mixture of methanol and toluene. One polyacrylonitrile homopolymer and five different copolymer membranes (i.e., acrylonitrile with maleic anhydride, acrylic acid, methacrylic acid, methyl methacrylate, and styrene) were prepared through emulsion polymerization. All these monomers were selected on the basis of the solubility parameter concept. The second monomer had an influence on the permselectivity and flux, and this effect was investigated. The structures of the copolymers, the features of their sorption layers, and their permeation paths were examined. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 243–252, 2005

Key words: pervaporation; PAN copolymers; organic-organic mixture solubility parameter

INTRODUCTION

Today we are witnessing important new developments that go beyond traditional chemical engineering. Some novel equipment and techniques that potentially could transform chemical plants and lead to compact, safe, energy-efficient, and environmentally friendly sustainable processes are being investigated. One such kind of developments is pervaporation (PV). Over the past 10 years, membrane PV has gained acceptance by the chemical industry as an effective process for the recovery of liquid mixtures. The three main application areas for PV are (1) the dehydration of organics, (2) the removal of organics from aqueous solutions, and (3) the separation of organic–organic mixtures. The distillation process is still dominant in the chemical process industries. Distillation is typically a high-energy-consuming process. Because of its low energy consumption and mild working conditions, PV is a promising process in the chemical industry for separating azeotropic mixtures and closely boiling mixtures and for dehydrating temperature-sensitive products.

Methanol–toluene mixtures[1] are commonly encountered in the fine chemical and pharmaceutical industries. Methanol and toluene form an azeotrope[2,3] at 78% (w/w) methanol. The presence of azeotropes complicates the design of the distillation separation process. For this type of azeotropic mixture, two-step processes are used: extraction and azeotropic distillation. PV separation has the potential to separate an azeotrope in a single step and therefore is an attractive alternative. In PV, a properly chosen membrane acts as a third component that breaks the azeotrope. However, unlike an azeotropic distillation step, in PV the third component (membrane) is regenerated *in situ*.

Factors that affect the efficiency of a given membrane for separating a given solute from a mixture are (1) sorption and (2) diffusion. When both favor a given solute, a very highly efficient separation results. Sorption is decided by the presence of the same or similar functional groups in the membrane,[4–7] whereas diffusion is affected by the nature (amorphous or crystalline) and flexibility of the chain comprising the polymeric membrane.

The selectivity and flux determine the efficiency of the process.[8] The higher the flux is, the lower the capital cost is of the membrane system. In the absence of any defects, the selectivity is a function of the material's properties.[9–11] The productivity is also a property of the material but mainly depends on the sorption–diffusion characteristics and thickness of the membrane. The lower the thickness is, the higher the productivity is. These two basic criteria are important stipulations that must be balanced against the operational cost.

THEORETICAL

The permeation of molecules through a dense, nonporous polymer matrix is generally governed by the

---

Correspondence to: V. G. Pangarkar (vgp@udct.ernet.in).

TABLE I
Properties of the Components[28]

Component	Molar volume (cc/mol)	Molecular diameter (Å)	Diffusional cross section (Å)^2	Nature of the interaction	δ (MPa$^{1/2}$)
Methanol	40.2	2.82	23.66	Polar	29.7
Toluene	106.4	4.22	41.86	Non-polar	18.2

sorption–diffusion mechanism.[12–14] The relative sorption of the permeants in the membrane depends on the relative solubility parameter value (δ; Table I) of the permeants in the membrane. The extent of the solubility or miscibility of a component with the membrane polymer can be explained by the following theories:

- Solubility parameter theory.[12]
- Interaction parameter or Flory–Huggins theory.[12]

The dissolution of an amorphous polymer in a solvent is governed by the free energy of mixing:

$$\Delta G_m = \Delta H_m - T \, \Delta S_m$$

where T is the temperature. A negative value of the free-energy change (ΔG_m) upon mixing implies that the mixing process occurs spontaneously. Because the dissolution of a high-molecular-weight polymer is always connected with a small and modest increase in the entropy (ΔS_m), the enthalpy term (the sign and magnitude of ΔH_m) is the deciding factor in determining the sign of Gibb's free-energy change. ΔH_m is given by

$$\Delta H_m / V = (\delta_1 - \delta_2)^2 \, \phi_1 \phi_2 \tag{1}$$

where V is the molar volume of the solvent and ϕ_1 and ϕ_2 are the volume fractions of the components. δ describes the attractive strength between molecules of the two materials. When δ_1 is equal to δ_2, the free energy of mixing is always less than zero, and the components are miscible in all proportions. In general, the δ difference must be small for miscibility over the entire volume fraction range.

Interaction parameter theory reveals the extent of the attraction or affinity of a solvent to a matrix. ΔG_m of a binary mixture consisting of a solvent (subscript s) and a polymer (subscript p) is given by

$$\Delta G_m / RT = \ln(1 - \phi_p) + \phi_p + \chi_{ip} \cdot \phi_p^2 \tag{2}$$

where ϕ_s is the volume fraction of the solute present in the polymer and ϕ_p is the volume fraction of the swollen polymer at temperature T. R is the universal gas constant. For equilibrium sorption, the enthalpy of mixing is zero, and the binary interaction parameter χ_{ip} (dimensionless) is obtained as follows:

$$\chi_{ip} = -(\ln \phi_s + \phi_p)/(\phi_p)^2 \tag{3}$$

$$\phi_p + \phi_s = 1 \tag{4}$$

χ_{ip} characterizes the interaction between the polymer segments and the solvent molecules and between one polymer segment with one solvent molecule. With decreasing affinity between the polymer and penetrant, χ_{ip} increases. Therefore, a lower value of χ_{ip} implies higher sorption.

SELECTION OF THE COMONOMERS FOR PV SEPARATION: A SOLUBILITY PARAMETER APPROACH

Basic factors

The membrane selection criterion[15] for a particular component from binary mixtures mainly depends on the presence of certain groups in the membrane, present either on the backbone or as pendant groups. If present on the backbone or skeleton, the interacting groups of the solute easily interact with the main polymer chain. However, if these groups are present as side or pendant groups, the probability of the aforementioned interaction decreases, but these groups attract (sorb) the corresponding solutes. For instance, the presence of the —COOH group of the polymer and secondary (hydrogen) bonding between the membrane and a solute is one such factor for selective separation by PV. The effect of these polar and hydrogen-bond forces plays an important role in sorption. Sorption is a thermodynamic phenomenon, and the concept of solubility and interaction parameters deals with this criterion. If the values of the interaction parameters of a solvent and a polymer are small, the solvent should dissolve the polymer or at least swell it significantly. On the other hand, the molecular size, shape, and mass govern the diffusion coefficient.

Different steps of morphological changes in membranes

Fluctuating microcavities or minute holes exist in the polymer matrix and are generally created[16] by the

segmental motion of the side chain. This can be considered a factor responsible for accommodation of a penetrant. The microcavity population may gradually change in the presence of a solute during sorption. Initially, the solute (methanol) is sorbed preferentially at specific sites (through hydrogen bonding with —COOH groups of the membrane), and a little perturbation of the matrix swells the upper layer. This layer immediately exerts an expansion force for the next unswollen matrix layer, and gradually the upstream part of the membrane becomes swollen with solute; methanol selectivity is highest in this region until all these specific sites are exhausted. The cooperation of the neighboring polymer segments is necessary for the penetrants to diffuse, and the redistribution of free volume caused by random fluctuations in the local density creates some void space, which leads to a tortuous path for diffusion. During this, membrane plasticization may further increase because of extensive swelling; the free volume of the membrane matrix increases with the solute-aided chain relaxation. This plasticization phenomenon reduces the selectivity for the desired component drastically if it is extensive.

Basis of the comonomer selection

Durability and mechanical integrity under the operating conditions, as well as productivity and separation efficacy, are important criteria for the selection of a membrane. For mechanical strength and very good resistance to swelling, polyacrylonitrile (PAN)[17] has been chosen. However, the presence of only one nitrile functional group (Figs. 1 and 2) in its repeating unit is not sufficient to make the membrane hydrophilic enough for use in this PV separation of methanol from toluene. Thus, several monomers have been selected on the basis of their δ values (Table II) and their group contribution effect (Table III). For this purpose, monomers such as maleic anhydride (Manh), acrylic acid (Aa), methacrylic acid (MAa), styrene (Sty), and methyl methacrylate (MMA) have been incorporated[18–22] separately in different concentrations with acrylonitrile (AN) through emulsion polymerization. In the copolymer, the AN part is expected to impart mechanical integrity, and the comonomer part is expected to impart hydrophilicity. The effect of substituted groups (Fig. 1) of the second monomer may change this trend with respect to the methanol flux, as the flux also depends on the void space and plasticization effect. For comparison, probable structures of the copolymers are drawn in Figure 2. Detailed permeation studies of methanol–toluene mixtures with all the membranes (varying in composition) have been carried out over the entire concentration range.
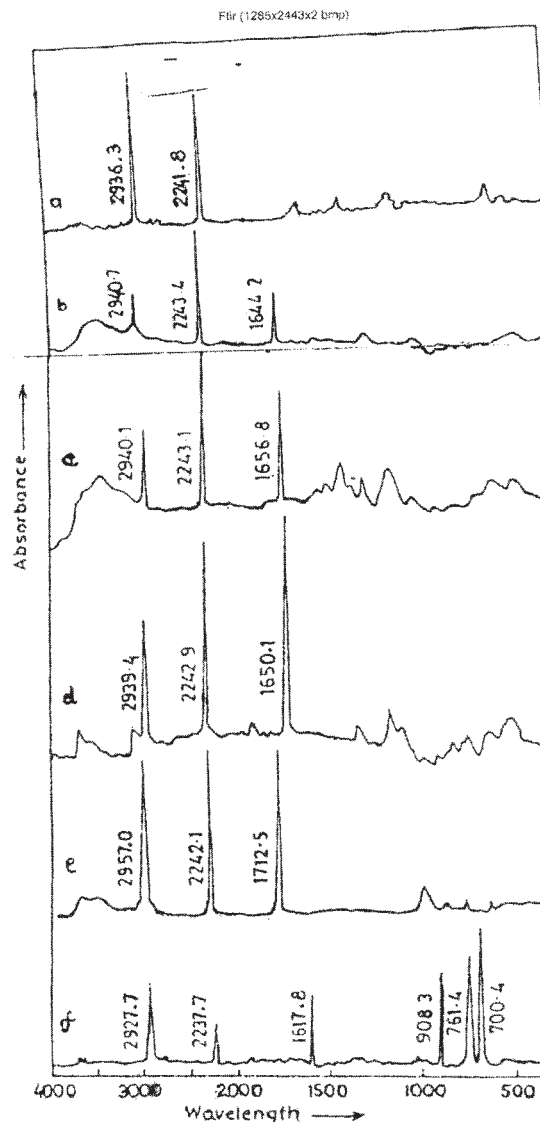

Figure 1 FTIR spectra of PAN and its copolymer membranes.

The main objective of this study is to determine the effect of δ on selective separation and its structural influence on PV separation,[23] including longevity.

EXPERIMENTAL

Materials

AN, dimethylformamide (DMF), and sodium hydroxide were supplied by S.D. Fine Chemicals, Ltd. (Mumbai, India). Thomas Baker Chemicals, Ltd. (Mumbai, India), supplied fused CaCl₂. As AN contained inhibitor, it was washed several times with a 10% NaOH solution and then with distilled water to remove traces of alkali. To make it free from water, it was kept over fused CaCl₂ overnight and distilled *in vacuo* before use. The poly(vinyl alcohol) (PVA) used, polynol 117,
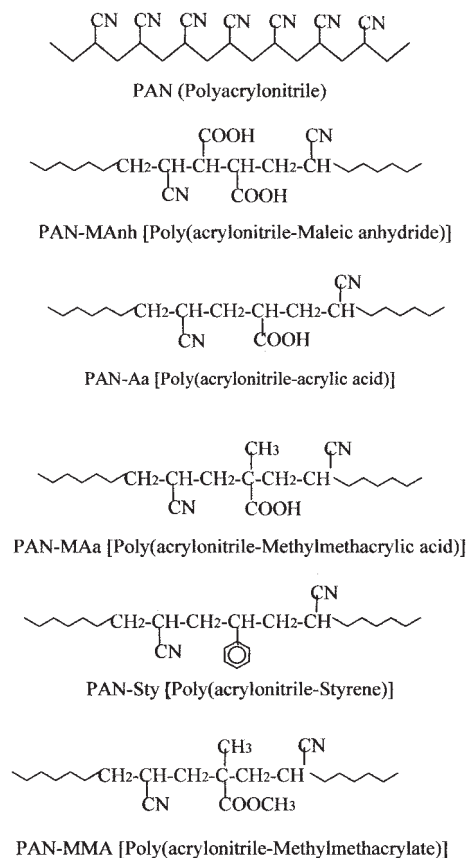
Figure 2 Structures of PAN and its copolymer membranes.

which had an average molecular weight of 75 kD and was 99% hydrolyzed, was kindly supplied by Polychem, Ltd. (Mumbai, India). Manh was procured from Loba Chemie (Mumbai, India), and Asian Paints (Mumbai, India) supplied Sty and MMA. MAa and Aa were procured from Sisco Chemicals (Mumbai, India). Aa and MAa were vacuum-distilled. Ammonium persulfate, sodium metabisulfite, and sodium lauryl sulfate (SLS) were purchased from Loba Chemie. These chemicals were laboratory-grade reagents and were used without any purification.

TABLE II
Solubility Parameters and Basic Structural Features of the Monomers[28]

Monomer	δ (MPa$^{1/2}$)	Side groups
Manh	27.8	Two—COOH
Aa	24.6	—COOH
MAa	22.7	—CH$_3$, —COOH
AN	21.5	—CN
Sty	19.0	⬡
MMA	18.0	—CH$_3$, —COOCH$_3$

TABLE III
Component Group Contribution of the Monomers[28]

Component group distribution	F_d (J$^{1/2}$ cm$^{3/2}$ mol^{-1})	F_p (J$^{1/2}$ cm$^{3/2}$ mol^{-1})	E_h (J/mol)
—CN	430	1100	2,500
—COOH	530	420	10,000
—COO—	390	490	7,000
—CH$_2$—	270	0	0
—CH$_3$	420	0	0

F_d = molar attraction due to dispersive forces; F_p = molar attraction due to polar forces

Synthesis of the copolymers

The emulsion polymerization[22] of AN with Manh, Aa, MAa, MMA, and Sty with different monomer compositions was carried out in a four-necked reactor at 70°C under a nitrogen atmosphere. Calculated amounts of SLS and PVA were dissolved in water. A predetermined amount of AN was also added with continuous stirring. Here water was used as the dispersion medium, and SLS was used as the emulsifier. Ammonium persulfate and sodium metabisulfite (0.5 and 0.25%, respectively, of the total monomer weight) were used as a pair of redox indicators. The second monomer was added slowly. The pH was adjusted with sodium bicarbonate. The reaction was carried out for 3–5 h. After polymerization, the emulsion was precipitated and washed repeatedly with water, toluene, and ethyl acetate to remove unreacted monomers and emulsifiers. The purified copolymers were then dried at 45°C for 4 h *in vacuo* and crushed into powders.

Membrane preparation

The vacuum-dried copolymer (100–150 mesh) was dissolved in DMF with continuous stirring. The homogeneous solution was spread on a clean and smooth glass plate and dried at 60°C for 2 h. Subsequently, the membrane was kept for another 6 h at 80°C.

Membrane characterization

Fourier transform infrared (FTIR) studies

The FTIR spectra[24] of the copolymer membranes were recorded on a PerkinElmer Paragon 500 FTIR instrument (Beaconsfield, Bucks, UK) with a thin (10-μm) film of each polymer.

Elemental analysis

The nitrogen contents of the copolymers were calculated (Table IV) by Duma's method.[25]

TABLE IV
Composition Nitrogen Content, and Density of the Prepared Membranes

Polymer	Comonomer composition (mol fraction; taken during the reaction)		Nitrogen content of the polymer (wt %)	Comonomer composition (mol fraction; calculated from nitrogen analysis)		Polymer code
PAN	—	—	25.8	—	—	
Poly(AN-co-Manh)	AN	Manh		AN	Manh	[PAN–Manh]
	0.953	0.047	22.5	0.914	0.086	PAN–Manh-1
	0.868	0.132	17.3	0.778	0.222	PAN–Manh-2
Poly(AN-co-Aa)	AN	Aa		AN	Aa	[PAN–Aa]
	0.936	0.064	23.1	0.9044	0.0956	PAN–Aa-1
	0.842	0.158	19.5	0.7928	0.207	PAN–Aa-2
Poly(AN-co-MAa)	AN	MAa		AN	MAa	[PAN–MAa]
	0.883	0.117	20.8	0.857	0.143	PAN–MAa-1
	0.785	0.215	17.4	0.758	0.242	PAN–MAa-2
Poly(AN-co-Sty)	AN	Sty		AN	Sty	[PAN–Sty]
	0.915	0.085	11.95	0.619	0.381	PAN–Sty-1
Poly(AN-co-MMA)	AN	MMA		AN	MMA	[PAN–MMA]
	0.75	0.25	11.84	0.615	0.385	PAN–MMA-1

Determination of the interaction parameters

Samples of dry membranes of known weights were immersed in pure solvent and were allowed to equilibrate for 3 days. These membranes were taken from the solvent, and the superfluous liquid was wiped off with tissue paper. Then, the swollen membrane was weighed. For the equilibrium sorption of a pure solvent in a polymer, χ_{ip} could be calculated from eq. (3)

Permeation studies

The experiments were carried out in a batch-stirred cell with a downstream pressure of 2 mmHg. The cell had two flanged compartments. The upper compartment, containing the liquid, had a capacity of 500 cm^3 and was provided with an outer jacket for temperature control. The effective membrane area in contact with the feed solution was 19.6 cm^2. The membrane was placed on a porous (stainless steel) supporting disc and was sealed with a rubber O-ring. The permeate vapor was collected in a trap cooled with liquid nitrogen.

The permeation selectivity is defined as follows:

$$\alpha = (Y_i/Y_j)/(X_i/X_j) \qquad (5)$$

where X and Y represent the weight fractions of the corresponding solutes in the feed and permeate, respectively. Subscript i refers to the desired component (whose selectivity is to be determined), and j refers to the second component.

Analysis of the permeants

The feed and permeate concentrations of all the mixtures were analyzed through the measurement of the refractive indices of these solutions on a Bausch and Lomb refractometer (Rochester, NY). The precision of this method was ±0.05 wt %.

RESULTS AND DISCUSSION

Characterization of the copolymer membranes by FTIR

The FTIR spectra of the PAN copolymers were obtained[24,26] with very thin (10-μm) films of the polymers. The FTIR spectra of PAN [Fig. 1(a)], PAN–Manh [Fig. 1(b)], PAN–Aa [Fig. 1(c)], PAN–MAa [Fig. 1(d)], PAN–MMA [Fig. 1(e)], and PAN–Sty [Fig. 1(f)] are given in Figure 1(a–f). The strong bands appearing in the 2242–2243.5-cm^{-1} region correspond to —CN of the AN copolymer. This band for PAN–Sty [Fig. 1(g)] can be found at 2237.7 cm^{-1}. For carboxylic acid, carbonyl carbon stretching appears at 1650 cm^{-1}, but for normal ketone, it appears at 1705–1725 cm^{-1}. The C—H stretching vibrations of methylene groups are in the range of 2926–2955 cm^{-1}. For the PAN–Sty copolymer, the bands at 700.4, 761.4, and 908.3 cm^{-1} are due to C—H stretching of the aromatic ring, whereas 1617.8 cm^{-1} is caused by the C=C skeletal of the benzene ring in the plane vibration.

Interaction parameters

The interaction parameter χ characterizes[12,27] the interaction (as discussed previously) between pairs of polymer segments, pairs of solvent molecules, and one polymer with one solvent molecule. The δ values[28] and component group contribution of the side groups (Tables II and III) have profound effects on the interaction. The compositions of the copolymer membranes are presented in Table IV. Table V shows that

TABLE V
Interaction Parameter Values for the Methanol–Toluene System with Copolymer Membranes

Polymer membrane	Code	χmethanol	χtoluene
PAN		2.82	3.11
PAN–Manh	1	2.38	3.18
	2	2.24	3.62
PAN–Aa	1	2.51	2.83
	2	2.32	2.89
PAN–MAa	1	2.62	2.78
	2	2.56	2.97
PAN–Sty	1	2.845	2.75
PAN–MMA	1	3.096	2.92

to a monomer moiety (MAa), which reduced hydrophilicity (Fig. 2). Thus, methanol sorption in the copolymer showed (Table V) results inferior to those of the aforementioned membranes.

PAN–Sty and PAN–MMA copolymer membranes

Table V shows that the methanol interaction parameter ($\chi_{methanol}$) significantly increased with these membranes. The presence of —CH$_3$ with —COOCH$_3$ groups in PAN–MMA reduced the methanol sorption, and the aromatic organophilic phenyl moiety in PAN–Sty increased its affinity for toluene because of the similarity of the phenyl group along with —CH$_3$ in

most of these membranes (except for PAN–Sty and PAN–MMA) were methanol-selective because the interaction parameters were lower than those for toluene ($\chi_{toluene}$). For example, the —COOH groups (in PAN–Manh or PAN–Aa) in the membrane formed a secondary (hydrogen) bond with methanol hydroxyls (Fig. 3), and with an increasing number of these groups, sorption increased. Methanol sorption increased with an increasing number of acid groups.

PAN homopolymer membrane

The PAN membrane contained an inert methylene backbone with only one —C≡N group as a hydrophilic part in its structure (Fig. 2). The component group contribution value of —CN for hydrogen bonding (E_h) was 2500 (Table III), which implied low methanol sorption.

PAN–Manh copolymer membranes

The high δ value of Manh (27.8 MPa$^{1/2}$) implied high polarity and a very good interaction with methanol, which was attributed to the presence of two —COOH groups, due to which methanol interacted with the matrix more than toluene.

PAN–Aa copolymer membranes

The interaction parameter value of this copolymer was less than that of the PAN–Manh copolymer membrane because of the presence of fewer —COOH groups per monomer unit of Aa. However, with an increase in the percentage of Aa in the copolymer, the interaction with methanol further increased, and this was reflected in the decreasing χ value [PAN–Aa-2 (2.32) > PAN–Aa-1 (2.51)].

PAN–MAa copolymer membranes

The presence of an extra —CH$_3$ group on the same carbon atom attached to the —COOH group in Aa led
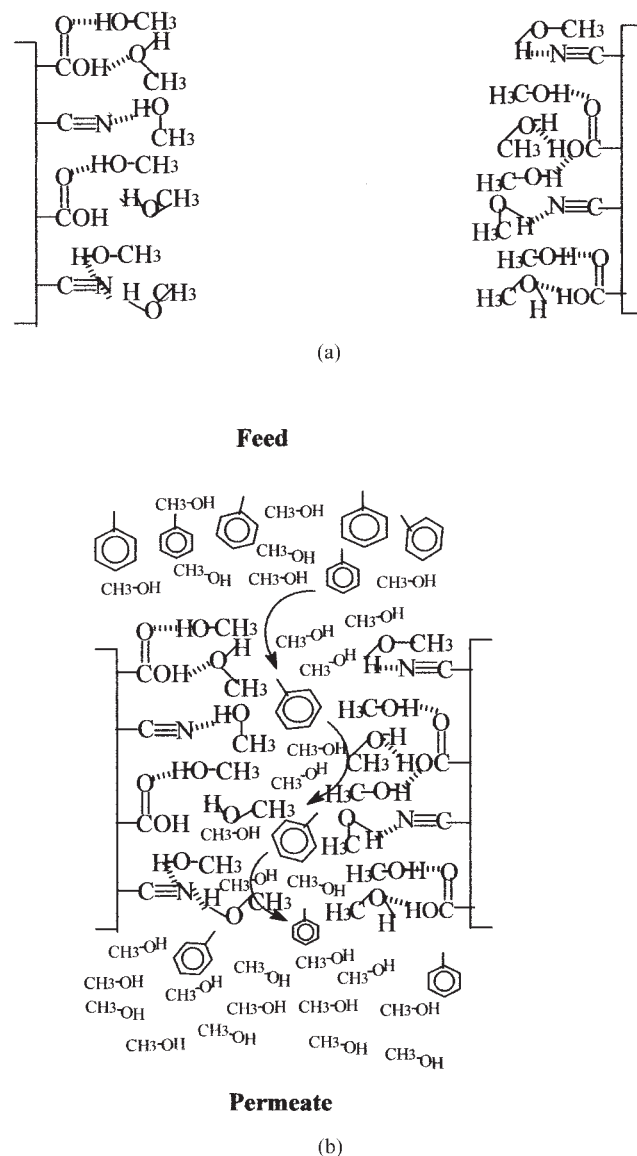

Figure 3 (a) Tentative structure of the sorption of PAN–acid copolymer membranes and (b) the probable mechanism of permeation for methanol selectivity with PAN–acid copolymer membranes.
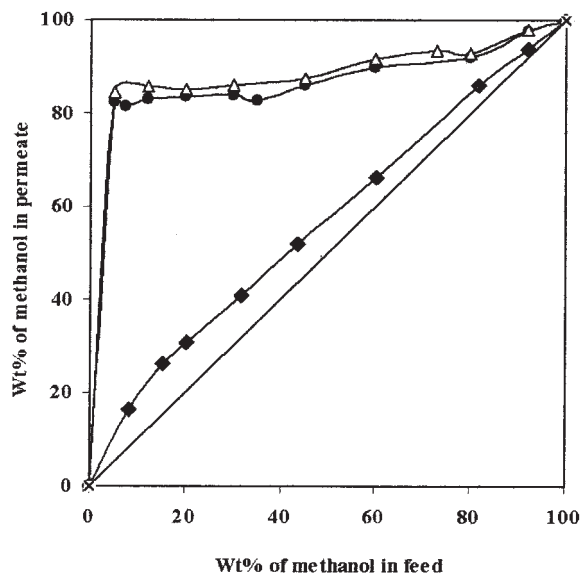
Figure 4 Variation of the concentration of methanol in the permeate with its feed concentration for the PAN homopolymer and its copolymer derivative PAN–Manh: (■) PAN, (●) PAN–Manh-1, and (△) PAN-Manh-2.

toluene. Thus, these two membranes showed no significant differences in their interaction values with methanol or toluene.

The methanol sorption criterion obeyed the following order: PAN–Manh > PAN–Aa > PAN–MAa > PAN > PAN–Sty ≅ PAN–MMA.

Effect of the feed concentration on methanol permeation

Figures 4–7 show the methanol permeation of various copolymer membranes—PAN–Manh (Fig. 4), PAN–Aa (Fig. 5), PAN–MAa (Fig. 6), PAN–MMA (Fig. 7), and PAN–Sty (Fig. 7)—from a mixture of toluene. Figures 4–6 presents nonazeotropic behavior, whereas Figure 7 shows a permazeotrope.

The polarity of a polymer mainly determines the efficiency of the distribution of electrons under certain circumstances. Figure 3 shows that the highly electronegative oxygen of carboxyl (—=O) or hydroxyl (—OH) could attract an electron toward itself, because of which it became partially negatively charged or the carbonyl carbon or hydroxyl hydrogen gained a partially positive charge. This polar nature of —COOH easily showed an affinity toward alcoholic —OH and formed strong hydrogen bonding. As the number of hydrophilic pendant groups increased, the sorption and permeation of methanol increased. For PAN–Manh, the hydrophilicity was strong enough to attract a substantial amount of methanol, and the first methanol layer did not effectively shield the polar attractive nature of the membrane, which contained a large number of —COOH groups; the number of methanol
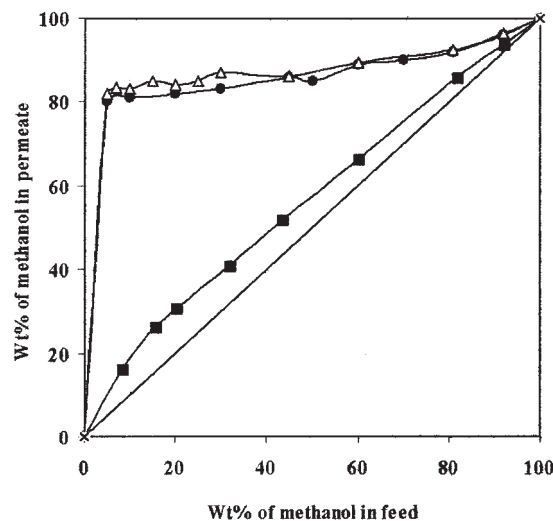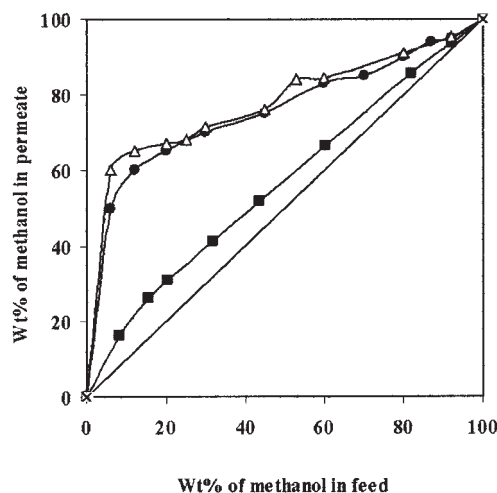

Figure 5 Variation of the concentration of methanol in the permeate with its feed concentration for the PAN homopolymer and its copolymer derivative PAN–Aa: (■) PAN, (△) PAN–Aa-2, and (●) PAN–Aa-1.

layers increased. Thus, this membrane yielded the best selective methanol permeation. However, a comparative reduction of polar groups (in PAN–Aa) or the presence of a nonpolar group (—CH$_3$ in PAN–MAa) implied that the sorbed methanol layer was effective in shielding the polar nature of the membrane, and thus methanol permeation was reduced.

Figure 7 (PAN with PAN–Sty and PAN–MMA) showed a permazeotrope. δ of AN (21.5 MPa$^{1/2}$) was slightly greater than that of Sty (19 MPa$^{1/2}$). The δ values of the polymers suggested that δ for PAN (26 MPa$^{1/2}$) was greater than δ for polystyrene (22 MPa$^{1/2}$). Thus, we expected PAN–Sty to be less hy-

Figure 6 Variation of the concentration of methanol in the permeate with its feed concentration for the PAN homopolymer and its copolymer derivative PAN–MAa: (■) PAN, (△) PAN–MAa-2, and (●) PAN–MAa-1.
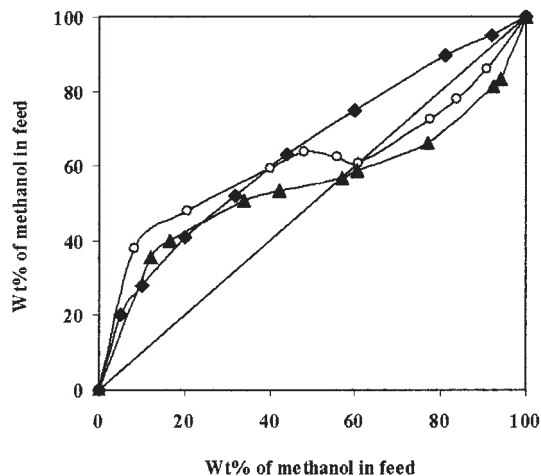
Figure 7 Variation of the concentration of methanol in the permeate with its feed concentration for the PAN homopolymer and its copolymer derivatives PAN–MMA and PAN–Sty: (■) PAN, (▲) PAN–MMA-1, and (□) PAN–Sty-1.

Figure 8 Variation of (■,●,▲) the methanol selectivity and (□,○,△) the flux for methanol and toluene systems with the methanol feed concentration for PAN and PAN–Manh membranes: (■,□) PAN, (●,○) PAN–Manh-1, and (▲,△) PAN–Manh-2.

drophilic than the PAN homopolymer, and because the δ value of MMA (18 MPa$^{1/2}$) was lower than that of Sty (19 MPa$^{1/2}$), PAN–MMA was expected to exhibit inferior results. When the copolymers were considered, it was obvious that the interactions of PAN–MMA and PAN–Sty with methanol were less than those of PAN, and this indicated a lower methanol affinity. Figure 2 shows that the presence of more methyl groups in the side chain (—COOCH$_3$) in MMA and phenyl moieties of Sty reduced the hydrophilicity of their respective copolymer membranes, and this implied a preference for toluene sorption (as discussed elsewhere); thus, the permazeotrope was observed.

Effect of the feed concentration on the methanol selectivity and flux

Figures 8–10 present the tradeoff relationship between methanol selectivity and its flux with the variation in the methanol concentration in the feed for different copolymers. At a low concentration of methanol in the feed, the interaction of membrane pendant groups with methanolic hydroxyl increased and contributed most to the sorption. Thus, high selectivity was obtained. However, with an increasing concentration of methanol in the feed, the side groups of the membranes became exhausted, and the selectivity was reduced drastically. On the other hand, because of extensive sorption by the membranes, the polar–polar interaction decreased as the attraction power of the membrane surface became shielded with the layers of methanol. Thus, the probability of aromatic sorption increased. Extensive sorption also caused membrane swelling, which allowed more toluene to sorb and diffuse, and methanol selectivity decreased.
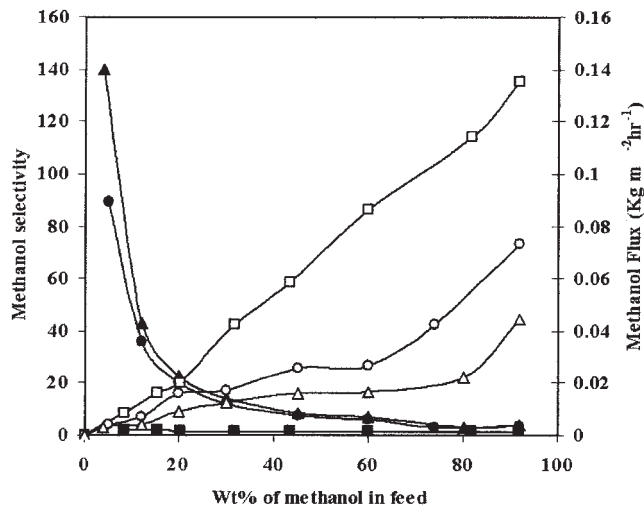
Among the various membranes, PAN–Manh (Fig. 8) yielded the best selectivity for methanol. For PAN–Manh, at a 5 wt % methanol concentration in the feed, a methanol selectivity of approximately 140 was obtained. With an increase in the number of acid moieties, the hydrophilicity increased, and vice versa. This effect was prominent in PAN–Aa (Fig. 9). Again, the lower δ value of MAa reduced the sorption of methanol and reduced its methanol selectivity (Fig. 10). For PAN–MMA and PAN–Sty (Fig. 11), the selectivity was further reduced. The order of selectivity was as follows: PAN–Manh > PAN–Aa > PAN–MAa > PAN > PAN–MMA ≅ PAN–Sty.
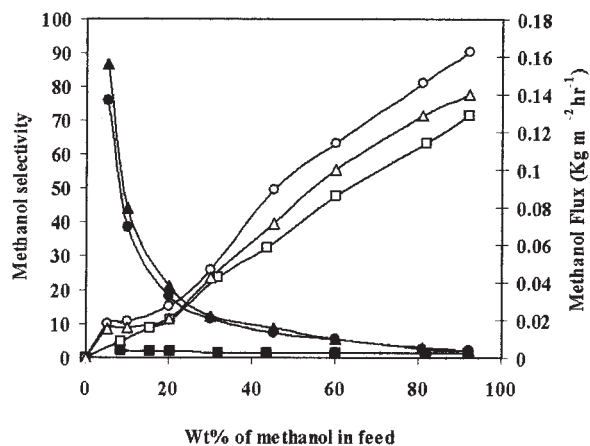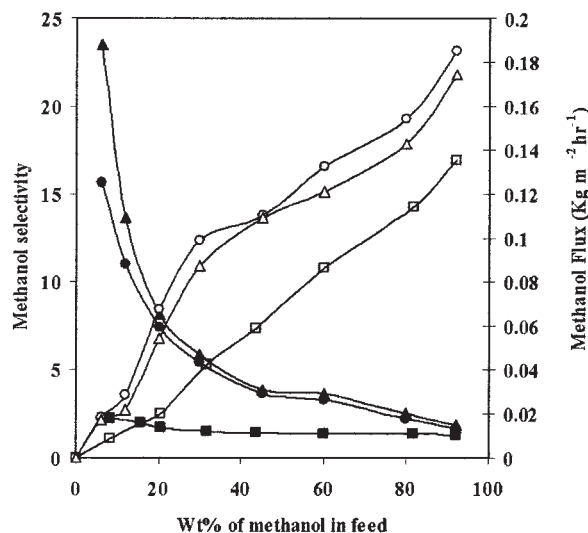

Figure 9 Variation of (■,●,▲) the methanol selectivity and (□,○,△) the flux for methanol and toluene systems with the methanol feed concentration for PAN and PAN–Aa membranes: (■,□) PAN, (●,○) PAN–Aa-1, and (▲,△) PAN–Aa-2.

Figure 10 Variation of (■,●,▲) the methanol selectivity and (□,○,△) the flux for methanol and toluene systems with the methanol feed concentration for PAN and PAN–MAa membranes: (■,□) PAN, (●,○) PAN–MAa-1, and (▲,△) PAN–MAa-2.

The second step of permeation was diffusion. The migration of the penetrant consisted of a sequence of unit diffusion steps or jumps, during which the solute had to overcome an activation barrier. The unit diffusion step involved a cooperative rearrangement of the penetrant molecule and its surrounding polymer chain segments. A certain number of van der Waals interactions between the component molecules and chain segments had to be broken to allow a rearrangement of the local structure. The amount of energy required for this rearrangement increased as the size of the solute increased. Diffusion thus depended on the factors affecting the polymer segmental mobility, which allowed the relocation of the free volume.

Structural variations that suppressed the ability to pack tended to increase diffusivity, whereas those that improved the ability to pack reduced diffusivity. The addition of symmetrical comonomers intensified the intramolecular and intermolecular interactions in PAN–Manh, which as a result exhibited the lowest flux. On the other hand, for other copolymers, methanol flux was quite high. PAN–Aa contained fewer hydrogen-bonded regions as the number of —COOH per monomer (compared to Manh) was lower, and for PAN–MAa, the addition of —CH$_3$ to the Aa monomer not only inhibited the formation of the secondary bonding but also increased the void space. In these copolymers, there were sufficient amorphous zones, which facilitated diffusion. Thus, PAN–MAa yielded better flux than PAN–Aa membranes.

The performance of the membranes increased in term of methanol selectivity when the amount of the comonomer was increased, as shown by the results of

the sorption and interaction parameter studies, permeation, selectivity, and flux. However, a balance between performance (which increases with the amount of the comonomer) and the longevity and mechanical strength (PAN contribution) of membranes is required. In this article, it has been shown that with an increasing amount of the second monomer or comonomer, the performance changes, and it varies with different types of mixtures. Thus, for a particular case, it must be optimized.

Pervaporation separation index (PSI): A criterion for membrane selection

Generally, the flux and selectivity show a tradeoff relationship. To obtain the optimum membrane configuration, Huang and Rhim[12] defined PSI as follows:

$$PSI = J_p(\beta - 1)$$

where β is Y_i/X_i and J_p is the total permeate flux.

PSI includes both flux and separation efficiency and is therefore ideal for a comparison of membrane productivity. Membranes with very high selectivity and low flux or high flux and low selectivity increase capital costs. Therefore, a compromise in the membrane configuration implies good selectivity and reasonable flux or reasonable selectivity with good flux. The PV performance of these membranes was evaluated in terms of PSI.

Figure 12 shows the PSI values with 10% methanol in the feed. The following order was found for PSI: PAN–Aa > PAN–MAa > PAN–Manh.
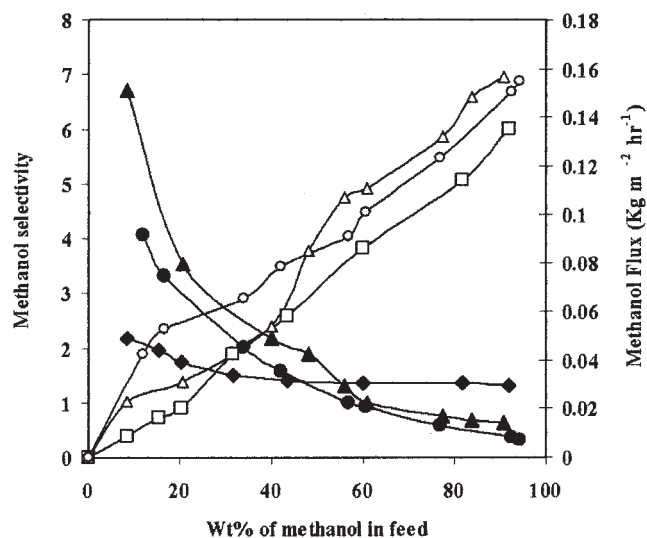

Figure 11 Variation of (■,●,▲) the methanol selectivity and (□,○,△) the flux for methanol and toluene systems with the methanol feed concentration for PAN and PAN–MAa membranes: (■,□) PAN, (●,○) PAN–Sty-1, and (▲,△) PAN–MMA-2.
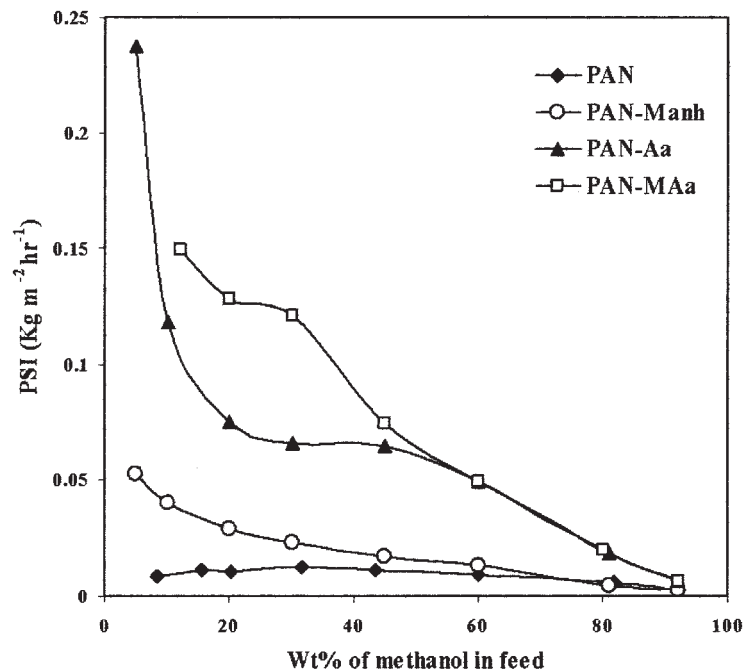
Figure 12 PSI of methanol versus the weight percentage of methanol in the feed: (■) PAN, (○) PAN–Manh, (▲) PAN–Aa, and (□) PAN–MAa.

CONCLUSIONS

This work presents the effects of the incorporation of a second monomer on the permeation behavior of a binary organic–organic mixture. The copolymer membranes showed resistance to swelling and good mechanical strength and were stable enough to prevent damage during long-term use. Some of the membranes were suitable for methanol separation, whereas others (PAN–MMA and PAN–Sty) showed azeotropic behavior, and PAN showed very low selectivity. Thus, PAN, PAN–Sty, and PAN–MMA were found to be not industrially suitable for methanol permeation. In terms of PSI, the membrane order was PAN–Aa > PAN–MAa > PAN–Manh.

References

1. Park, H. C.; Meertens, R. M.; Mulder, M. H. V.; Smolders, C. A. J Membr Sci 1994, 90, 265.
2. Burke, D. E.; Williams, G. C.; Plank, C. A. J Chem Eng Data 1964, 9, 212.
3. Gmehling, J. Azeotropic Data Book; VCH: Weinheim, 1994.
4. Kujawski, W. Sep Sci Technol 1996, 31, 1555.
5. Huang, R. Y. M.; Neil, J. R. J Appl Polym Sci 1970, 14, 2341.
6. Cabasso, I.; Jagur-Grodzinski, J.; Vofsi, D. J Appl Polym Sci 1974, 18, 2137.
7. Cabasso, I. Ind Eng Chem Prod Res Dev 1983, 22, 313.
8. Lipnizki, F.; Field, R. W.; Ten, P.-K. J Membr Sci 1999, 153, 183.
9. Lee, Y. M.; Oh, B. K.; Wang, W. J. J Appl Polym Sci 1996, 59, 227.
10. Huang, R. Y. M.; Moreira, H.; Nufarforizo, R.; Huang, Y. M. J Appl Polym Sci 1988, 35, 1191.
11. Uragami, T.; Saito, M. Sep Sci Technol 1989, 24, 541.
12. Huang, R. Y. M.; Rhim, J. W. In Pervaporation Membrane Separation Processes; Huang, R. Y. M., Ed.; Elsevier: Amsterdam, 1991; p 115.
13. Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. Regular and Related Solutions; Van Nostrand Reinhold: New York, 1970.
14. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: New York, 1953.
15. Bell, C. M.; Gerner, F. J.; Strathmann, H. J Membr Sci 1988, 36, 315.
16. Barrier Polymers and Structures; Koros, W. J., Ed.; American Chemical Society: Washington, DC, 1990.
17. Mikolajezykard, I. Krucinska Text Res J 1989, 59, 536.
18. Yosikawa, M.; Shimidzu, J.; Maeda, Y.; Magara, K.; Tsugaya, H. J Membr Sci 1993, 82, 157.
19. Borbely, J. D.; Hill, D. J.; Lang, A. P.; O'Donnell, J. H. Macromolecules 1991, 24, 2208.
20. Handbook of Polymer Synthesis; Nuyken, O.; Lattermann, G.; Kricheldorf, H. R., Eds.; Marcel Dekker: New York, 1992; Part A, p 297.
21. Andreeva, I. V.; Kotan, M. M. Vysokomol Soedin 1981, 23, 907.
22. Odian, G. Principles of Polymerization; McGraw-Hill: New York, 1970; p 268.
23. Rhim, J. W.; Huang, Y. M. J Membr Sci 1989, 46, 340.
24. Lee, Y. M.; Park, H. B.; Nam, S. Y.; Won, J. M.; Kim, H. Sep Sci Technol 1998, 33, 1255.
25. Dunke, M. Paserforsch Textiletech 1967, 18, 123.
26. Kemp, W. Organic Spectroscopy; ELBS: London, 1975; Chapter 2.
27. Sangita, M.; Pangarkar, V. G. J Membr Sci 2002, 201, 175.
28. Brandrup, J.; Immergut, E. H. Polymer Handbook, 2nd ed.; Wiley-Interscience: New York, 1975.