Development of Methanol Selective Membranes for Separation of Methanol–Methyl Tertiary Butyl Ether Mixtures by Pervaporation

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ABSTRACT: Several copolymers of acrylonitrile (AN) were synthesized. Methanol selective membranes were prepared from these copolymers of AN. The other monomers in the copolymers were selected on the basis of their solubility parameter values relative to those of methanol. These were hydroxyethyl methacrylate, methacrylic acid, and vinyl pyrrolidone. Thus, pervaporative separation of methanol from its mixture with methyl tertiary butyl ether over the entire concentration range of 0–100% methanol was studied using these copolymer membranes of AN. For each copolymer of AN three different membranes with different copolymer compositions were prepared. Copolymers of AN with hydroxyethyl methacrylate and methacrylic acid showed high selectivity and moderate flux for methanol (2561, 773, 0.057, and 0.045 kg/m^2 h, respectively, with a membrane of 50-μm thickness for a feed mixture containing 5% methanol at 30°C). A copolymer of AN with vinyl pyrrolidone showed comparable flux, but methanol selectivity of this membrane was poor. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2645–2659, 1999

Key words: acrylonitrile; copolymers; solubility parameter; pervaporation; separation; methanol

INTRODUCTION

In recent years methyl tertiary butyl ether (MTBE) has been extensively used in gasoline instead of conventional lead additives as octane enhancers to eliminate air pollution. As a result the production of MTBE has drastically increased during the last few years. It is ranked 9th among the top 50 chemicals produced in the United States, which is up from 19th in 1992.[1]

MTBE is industrially produced by the reaction of excess methanol with isobutene from a mixed C$_4$ stream in the liquid phase over an acidic ion exchange catalyst. It has been found that an increased molar ratio of methanol to isobutene from 1 to 1.2% per pass[2] increases the MTBE conversion by 5% per pass. However, at the same time excess methanol forms azeotropes with MTBE and C$_4$ stocks.

Farnand and Sawatzky[3] first attempted reverse osmosis separation of this excess methanol. Air Product and Chemicals Inc.[2] subsequently developed a total recovery improvement process. It employs pervaporative separation of excess methanol with a Sepharex (cellulose acetate) membrane. This pervaporation (PV) unit removes methanol from the reactor effluent (reducing the concentration of methanol from 5 to 2%) and replaces the extra reactor debutanizer stage in the conventional process. In regard to the PV performance, with 5–10% methanol in the feed mixture along with MTBE/C$_4$ feed stocks, 65–90 wt % methanol in the permeate is obtained. Farnand

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and Noh[4] used cellulose acetate, Nafion 117, Nafion-417, and polyvinyl alcohol (PVA) membranes for methanol removal from a MTBE reactor effluent and got 71.4% methanol in the permeate with a cellulose acetate membrane at 50°C, 58.5% with Nafion-417 at 50°C, and 58.5% with Nafion-117 at 30°C. With the PVA membrane the permeate flux was too low to mention. When the methanol concentration in the feed was increased 1–5% the methanol flux increased and selectivity decreased, but at a higher temperature a higher methanol selectivity was found: with a cellulose acetate membrane the separation factor increased from 32 to 63 as the temperature was raised from 30 to 50°C. A PVA-poly(acrylic acid) blend membrane was tried by Park et al.[5] In this membrane with increasing PVA content the flux decreased while selectivity increased. Pasternak et al.[6] used a Nafion ion exchange membrane containing quaternary ammonium counterions or alkali metal counterions for methanol removal from its mixture with MTBE and dimethyl carbonate. In the membrane treated with the quaternary ammonium ion, methanol selectivity was found to be dependent on the length of the organic substituent of the quaternary ammonium ion. In the alkali metal cation the size of the counterion was the controlling factor for membrane performance. A high performance polymer, poly(phenylene oxide) was tried for methanol separation from its mixture with MTBE.[7] Separation performance at different feed concentrations of methanol and permeate pressure was studied. Chen and Martin[8] tried a membrane made of polystyrenesulfonate on a microporous alumina support. Membranes with an Mg^{+2} counterion showed a higher separation factor than with Na^{+2}. In the permeate 99.5 wt % methanol was obtained with this membrane. However, flux with this membrane was very poor.

From the above discussion it is evident that polar hydrophilic membranes have been used as methanol selective membranes. However, rather than being confined to a hydrophilic membrane, it is more logical to select a methanol selective membrane on the basis of the relative solubility of the polymer with respect to the permeants, including methanol.[9]

In this study copolymers of acrylonitrile with hydroxyethyl methacrylate (PANHEMA), methacrylic acid (PANMAC), and vinyl pyrolidone (PANVP) were used as methanol selective membranes for pervaporative separation of methanol from its mixtures with MTBE over the entire concentration range of 0–100% methanol. All of these polymers were chosen on the basis of their solubility parameter values relative to methanol.

EXPERIMENTAL

Materials

The AN was freed from its inhibitor by washing with sodium hydroxide solution and then with distilled water to remove traces of alkali. It was then kept over fused $CaCl_2$ overnight and distilled under a vacuum before use. The MAC, a laboratory grade reagent, was distilled under a vacuum before use. The HEMA was kindly supplied by M/s Asian Paints Ltd. (Mumbai, India) and was used as received. The VP (synthesis grade) was procured from E. Merck and was used as received. Ammonium persulfate, sodium metabisulfite, and sodium lauryl sulfate were used without any further purification.

Synthesis of Membrane Polymer

Copolymerization of AN with MAC, HEMA, and VP with different monomer compositions was carried out by emulsion polymerization[10] in a four-necked reactor at 70°C for 6 h. The reactor was fitted with a stirrer, a thermometer pocket, a condenser, and a dropping funnel. Water was used as a dispersion medium and sodium lauryl sulfate was used as the emulsifier. Ammonium persulfate and sodium bisulfite (0.5 and 0.25%, respectively, of the total monomer weight) were used as a pair of redox initiators. The pH of the solution was adjusted by adding sodium bicarbonate. The monomers with higher reactivity ratios [i.e., HEMA (for PANHEMA), MAC (for PANMAC), and VP (for PANVP)] were added dropwise from a dropping funnel. After polymerization the emulsion was precipitated and washed repeatedly with water, toluene, and ethyl acetate to remove unreacted monomers and emulsifier. The purified copolymers were then dried at 45°C for 6 h in a vacuum drier.

Membrane Preparation

Membranes were prepared by casting the corresponding copolymer from a dimethyl formamide (DMF) solution [1% (w/v)] of with an applicator on a clean and smooth glass plate and drying at 60°C for 2 h. Subsequently, the membrane was annealed at 80°C for an additional 6 h. Three membranes with increasing acid, ester, or pyrrolidone comonomers (from membrane-1 to membrane-3) were prepared from each copolymer. The membrane thickness for the copolymers ranged from 25 to 50 μm. The membrane thickness has a reciprocal relationship with the flux. Therefore, to enable a comparison with the variable membrane thickness all flux values reported in this work were normalized to a 100-μm thickness.

Copolymer Composition

Elemental Analysis

The carbon and hydrogen contents of the copolymers were determined by Praglt's method[11] while nitrogen content was calculated by the Dumas[11] method. Oxygen content was determined by subtracting these carbon, hydrogen, and nitrogen contents from the total weight of the polymer taken for analysis.

Polymer Characterization

FTIR Studies

The FTIR spectra of the PAN copolymers were recorded on a Perkin–Elmer FTIR unit using a thin (10 μm) film of each polymer.

Intrinsic Viscosity Studies

The intrinsic viscosities of the homopolymers and copolymers were determined using an Ostwald viscometer. Four dilute solutions of the polymers (0.25, 0.5, 0.75, and 1.0 wt %) in DMF were taken in the viscometer and specific viscosities were determined from the relative times taken by the polymer and the solvent in the viscometer. Reduced viscosity, which is the specific viscosity for unit concentration, was plotted against the concentration of the polymer solution and intrinsic viscosities were calculated from these plots by extrapolating the curve to zero concentration.

Glass Transition Temperature (T_g)

The T_g was determined by a Stanton Redcraft thermal analyzer. The polymer sample and an inert reference sample held in the respective holder of the analyzer were heated at a heating rate of 10°C/min. From the differential thermal analysis (DTA) curve of the temperature difference between the reference and the polymer sample (ΔT) versus temperature (T), the T_g was measured. Initially, when there was no change in the polymer, the ΔT remained constant as T increased. The temperature at which the ΔT showed the first change was recorded as the glass transition temperature.

Thermogravimetric Analysis (TGA)

TGA was carried out in the same thermal analyzer used for determining the T_g. The maximum temperature employed was 700°C with a heating rate of 10°C/min. The threshold degradation temperature was determined from the thermogram of weight loss (of the polymer sample) versus the temperature curve. As the polymer sample was heated up to a certain temperature there was no weight loss of the polymer. At the threshold degradation temperature the polymer started to degrade, which is associated with its weight loss indicated by a change in the slope of the almost linear thermogram.

Mechanical Strength

The tensile strength (TS) and elongation at break (EAB) of the polymer films were determined using an Instron tensile tester. A 4-cm length dumbbell-shaped film was cut from the membrane and the load at which it tore was noted. The TS was calculated by dividing the breaking load by the film cross-sectional area.

Analysis of Permeants

The feed, permeate, and membrane phase concentration (from the sorption experiment) of the methanol–MTBE mixtures were determined by measuring the refractive indices of these solutions with a Bausch & Lomb type refractometer.

Sorption Experiments

Membranes of known weights were immersed in different known concentrations and weights of methanol–MTBE mixtures and were allowed to equilibrate for 72 h at different constant temperatures of 30, 40, and 50°C. These membranes were then taken out of the solutions and weighed after the superfluous liquid was wiped off with tissue paper. The amount of permeants sorbed by 1 g of the membrane is given by the following expression:

$$S = \frac{S_W - S_D}{S_D} \qquad (1)$$

Table I Composition of Copolymer

Polymer	Comonomer Composition Feed (mole fraction)		Nitrogen Content of Polymer (wt %)	Copolymer Composition (mole fraction)	
PAN			25.8		
PANHEMA	AN	HEMA		AN	HEMA
PANHEMA-1	0.952	0.048	10.2	0.596	0.404
PANHEMA-1	0.910	0.090	8.7	0.543	0.457
PANHEMA-1	0.750	0.250	7.1	0.472	0.528
PANMAC	AN	MAC		AN	MAC
PANMAC-1	0.910	0.090	8.7	0.648	0.352
PANMAC-2	0.875	0.125	7.5	0.586	0.414
PANMAC-3	0.750	0.250	6.3	0.564	0.436
PANVP	AN	VP		AN	VP
PANVP-1	0.750	0.250	18.6	0.602	0.398
PANVP-2	0.670	0.330	18.1	0.570	0.430
PANVP-3	0.500	0.500	17.6	0.527	0.470

where S_W is the weight of the swollen membrane and S_D is the weight of the dry membrane, which are in grams. The swollen membrane was then desorbed under a vacuum and the amount sorbed in the membrane was collected in traps immersed in liquid N_2. The composition of this liquid was determined by the refractive index method. Sorption selectivity for the i component was determined from the following expression:

$$\alpha_{is} = \frac{\dfrac{Y_{mi}}{Y_{mj}}}{\dfrac{X_{fi}}{X_{fj}}} \qquad (2)$$

where α is the selectivity, and Y_{mi} and X_{fi} are the weight fraction of i in the membrane and feed, respectively.

Permeation

PV experiments were carried out in a batch stirred cell[12] with adjustable downstream pressure that was maintained at 1 mmHg. The effective membrane diameter in contact with the feed solution was 5.5 cm and the feed compartment volume was 150 mL. PV experiments were carried out at constant temperatures of 30, 40, and 50°C. The permeation selectivity of the ith component, α_i, was found from the following expression:

$$\alpha_{i} = \frac{\dfrac{Y_{pi}}{Y_{pj}}}{\dfrac{X_{fi}}{X_{fj}}} \qquad (3)$$

where Y_i and X_i are the weight fraction of i in the permeate and feed, respectively.

RESULTS AND DISCUSSION

Polymer Synthesis

The advantage of emulsion polymerization and the reason for choosing this method for preparing the membrane polymers are given elsewhere.[9,10]

Copolymer Composition by Elemental Analysis

The percentage of N_2 of the copolymers are given in Table I. The comonomer compositions in the copolymer were calculated from percentage of N_2 of the copolymer. The monomer composition in the feed, copolymer, and percentage of N_2 are given in Table I.

Polymer Characterization

FTIR Studies

The FTIR of PANHEMA, PANMAC, and PANVP are given in Figures 1–3, respectively. These figures show that the strong band appearing at 2240 cm^{-1} corresponds to the CN of the AN. In PANHEMA a band was found at 1240 cm^{-1} that was due to a hydroxyl group, which is apart from bands for the carbonyl of its MA ester (1740 cm^{-1}) and nitrile group (2240 cm^{-1}). For carboxylic acids the stretching frequency should be due to the carbonyl group at 1730 cm^{-1}, but in the vinyl acid copolymers of PAN (i.e., in PANMAC), apart from the nitrile band at 2240 cm^{-1}, the carbonyl band

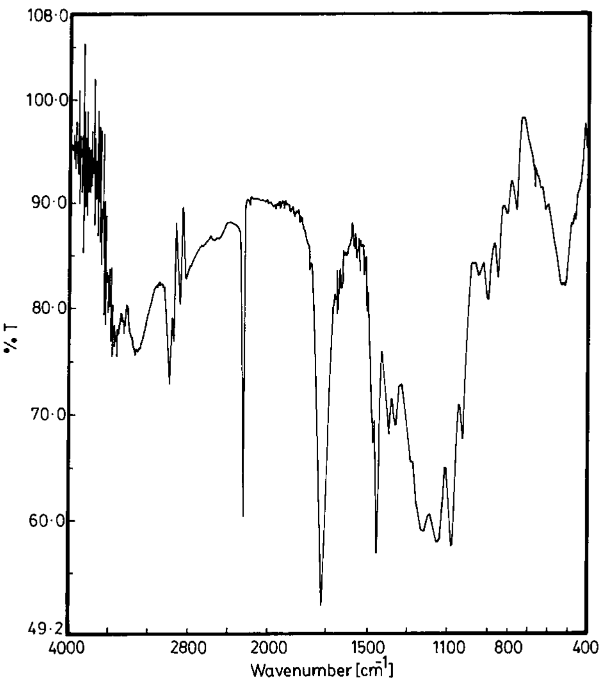

Figure 1 FTIR spectra of PANHEMA membrane.

is shifted at 1635 cm^{-1} for MAC. In PANVP, apart from the nitrile band at 2240 cm^{-1}, the band at 1675 cm^{-1} is due to its lactam carbonyl (pyrrolidone) group.

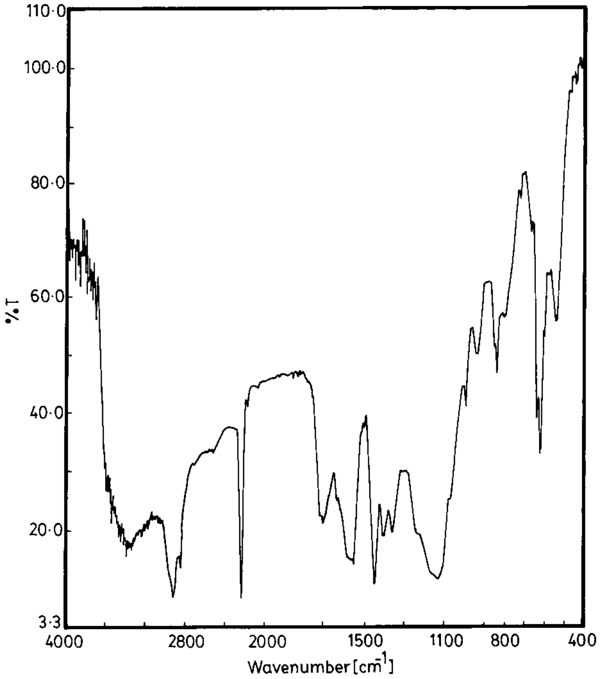

Figure 2 FTIR spectra of PANMAC membrane.

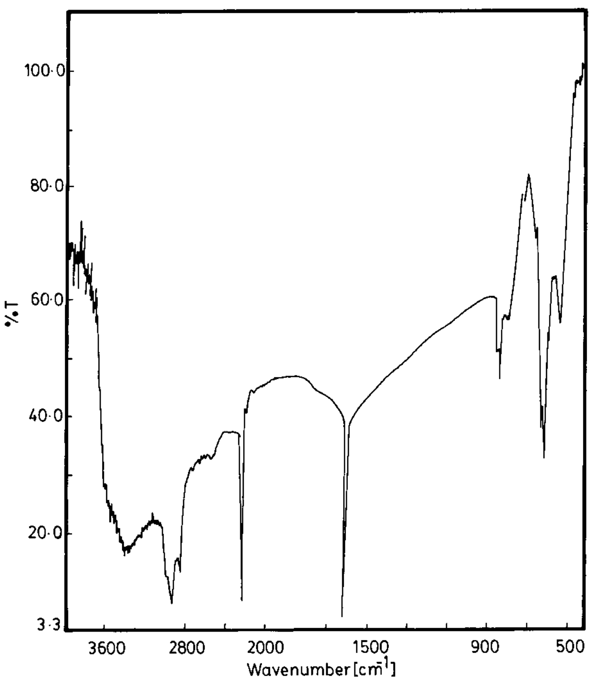

Figure 3 FTIR spectra of PANVP membrane.

Intrinsic Viscosities Studies

The intrinsic viscosities of the homopolymers and copolymers were determined by an Ostwald viscometer.

The limiting viscosity of a solution is defined as

$$[\eta] = \lim_{C \to 0} \frac{\eta - \eta_0}{\eta_0 C} \tag{4}$$

where η_0, η, and C are the solvent viscosity, solution viscosity, and concentration of the solute (g/dL of solution), respectively. Hence, the limiting viscosity will be in deciliters per gram. The quantity $[\eta]$ of a polymer solution is a measure of the capacity of a polymer molecule to enhance the viscosity, which depends on the size and the shape of the polymer molecule. These values are given in Table II. From the values of the intrinsic viscosity the molecular weight (viscosity average) of the polymer can be obtained using the following Mark–Houwink–Sakurada[13] equation:

$$[\eta] = KM^a \tag{5}$$

These K and a values vary from one polymer to another. These values also depend on the nature of the solvent used for making the polymer solution. These a and K values of the different copol-

Table II Characteristic Properties of Polymers

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Threshold Degrad. Temp. (°C)	Glass Transition Temp. (°C)	Intrinsic Viscosity [η]
PAN	78	2.5	389	92	0.98
PANHEMA-1	68.7	10.3	341	72.2	1.15
PANHEMA-2	42.3	14.2	241	65.3	1.33
PANHEMA-3	23.8	19.7	219	62.5	1.15
PANMAC-1	74.5	7.9	247	105	1.24
PANMAC-2	82.4	4.3	219	112.5	1.29
PANMAC-3	88.3	3.5	209	124	1.31
PANVP-1	82.2	4.2	217	113.5	1.12
PANVP-2	92.1	2.8	174	121.5	1.18
PANVP-3	105.3	1.2	145	142.2	1.27

ymers with different compositions are not available in the literature. Thus, the molecular weight of the copolymers cannot be obtained from the above expression. However, in any case, these K or a are always positive[13] and the value of a is such that in most of the cases $0.5 < a < 0.8$.[14] Thus, the molecular weight is proportional to its intrinsic viscosity and from these [η] values an idea of their relative molecular weight can be obtained. A polymer with a higher intrinsic viscosity will require a lower concentration of the cast solution. The concentration of the polymer in the cast solution is significant in that it affects the morphology of the membrane. A dilute polymer solution with a low viscosity will yield a porous membrane. Hence, depending on the solution viscosity, the polymer concentration of the cast solution is to be adjusted. The [η] of the copolymers are given in Table II. From these values it appears that the intrinsic viscosity of the copolymers increases as the acid, ester, or pyrrolidone content of the copolymer increases. This may be attributed to the increase in the hydrodynamic volume of the copolymer as more and more bulky acid, ester, or pyrrolidone groups are introduced in the copolymer.

Glass Transition Temperature

Determination of the T_g is a popular method of characterizing a polymer because every polymer has a specific T_g, which it owes to its amorphous region. A copolymer is characterized by a T_g that is different from both the homopolymers of its constituent monomers. For PAN it was found to be 92°C (Table II). In the PANVP copolymers the increase in T_g with the increase in the percent of pyrrolidone moiety in the copolymer (from PANVP-1 to PANVP-3) may be ascribed to the presence of the five-member rigid pyrrolidone moieties that demand high energy for the segmental motion of the copolymer. From Table II it is seen that PANVP copolymers have the highest T_g among all the copolymers. The higher T_g of PANMAC in comparison with PANHEMA may be due to the presence of the rigid methyl group in PANMAC. The presence of this additional methyl group imparts less rotational freedom of the side chain, resulting in a higher T_g. In fact, the CH_3 group is the only substituent that gives bulk without chain flexibility.[15] Thus, for substituents bulkier than CH_3, the T_g decreases because of increased chain flexibility. This is why (Table II) the T_g of PANHEMA is less than that of PANMAC.

TGA

The TGA signifies the heat resistance of the polymer. From Table II it appears that the threshold degradation temperature falls as AN is copolymerized with more and more polar monomers. This might be due to a loss of symmetry of the copolymer[16] in comparison with the homopolymer, as well as a reduction of nitrile dipolar bonding. With increasing acid, ester, or pyrrolidone comonomer percent in the copolymer the threshold degradation temperature decreases while the rate of decomposition increases. However, none of the copolymers had a threshold degradation temperature below 145°C, which is far above the tem-

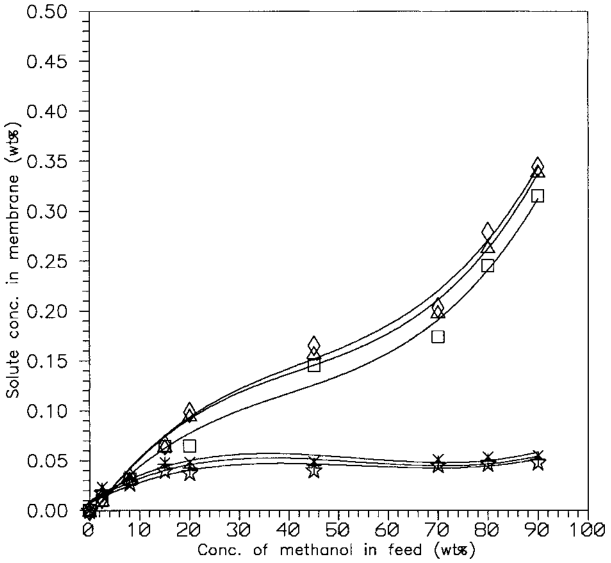

Figure 4 Sorption isotherms of methanol and MTBE for a PANHEMA membrane at 30°C. Methanol: (□) PANHEMA-1, (△) PANHEMA-2, and (◇) PANHEMA-3; MTBE: (☆) PANHEMA-1, (+) PANHEMA-2, and (×) PANHEMA-3.

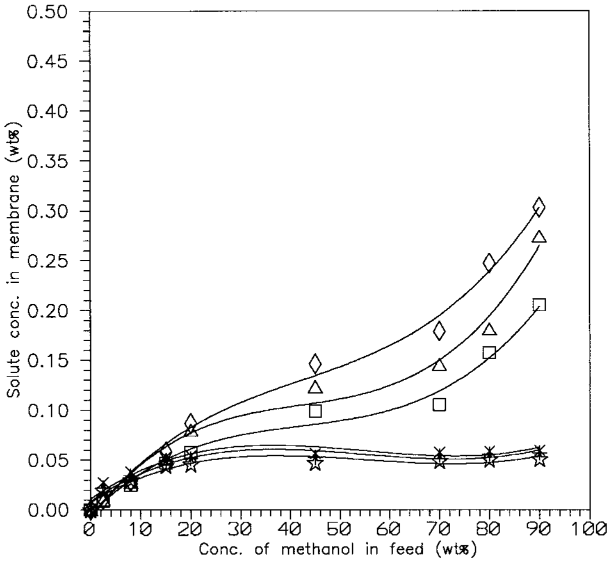

Figure 5 Sorption isotherms of methanol and MTBE for a PANMAC membrane at 30°C. Methanol: (□) PANHEMA-1, (△) PANHEMA-2, and (◇) PANHEMA-3; MTBE: (☆) PANHEMA-1, (+) PANHEMA-2, and (×) PANHEMA-3.

perature at which a pervaporation experiment is expected to be carried out.

Mechanical Strength

Too high TS or EAB results in a poor quality membrane. The TS of PAN is too high, which is evident from its high T_g. For a good membrane there should be an optimum balance between TS and EAB, which bear a trade-off relationship. On incorporation of the polar monomer HEMA, due to the increase in chain flexibility the TS decreases while the EAB increases. However, the reverse trend is observed for the PANVP or PANMAC (except for PANMAC-1) copolymer. In these cases incorporation of the five-membered stiff pyrrolidone group or methyl substituted acid group makes the resulting copolymer more glassy (as is also evident from its higher T_g values), having increased its TS and decreased its EAB. The TS and EAB values of all the copolymers are given in Table II.

Sorption

Sorption and Feed Concentration

Figures 4–6 show the variation of methanol and MTBE content of all the membranes with their corresponding feed concentration at 30°C for the AN copolymers. It is evident from these figures that methanol is sorbed much more by the membrane than by the MTBE. From the figures it is further observed that sorption isotherms for

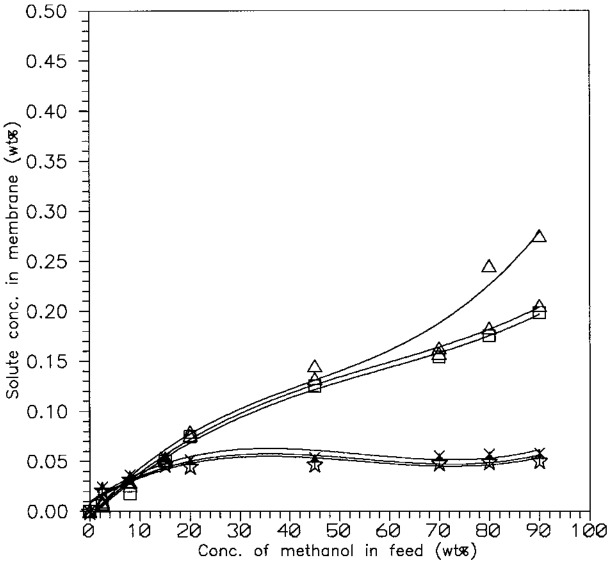

Figure 6 Sorption isotherms of methanol and MTBE for a PANVP membrane at 30°C. Methanol: (□) PANHEMA-1, (△) PANHEMA-2, and (◇) PANHEMA-3; MTBE: (☆) PANHEMA-1, (+) PANHEMA-2, and (×) PANHEMA-3.

Table III Solubility Parameters[28–30] and Other Physical Properties of Permeants and Membrane Polymers

Permeant or Polymer	Molar Volume (mL/mol)	Molecular Diameter (Å)	Diffusional Cross Section[a] (Å)^2	δ_t (MPa$^{0.5}$)	δ_h (MPa$^{0.5}$)	δ_p (MPa$^{0.5}$)	δ_d (MPa$^{0.5}$)
Methanol	40.2	2.82	23.66	29.7	22.3	12.3	15.1
MTBE	88.15	4.94	29.62	32.9	26.0	11.0	17
PAN				25.3	13.5	16.2	13.8
PMA				27–30	Strong	Strong	Strong
PVP				25.6	0	22.3	12.5
PHEMA				30.1	15.2	1.4	26.0

[a] Calculated as $[(V_m/N^*)/D_m]$, where V_m is the molar volume, D_m is the diffusional cross section, and N^* is Avagadro's number (6.023×10^{23}).

methanol are complex and do not follow any given type (Henry or Langmuir) over the entire concentration range. In fact, the isotherms are combination of type II type III isotherms at low and high concentrations, respectively, of methanol in the feed as given by Rogers.[17] The type II isotherm is obtained when there is a preference for solute–polymer interactions and type III prevails when there are solute–solute interactions. Thus, at low concentrations of methanol there is a preference of methanol molecules for certain sites on the polymer. When these sites are exhausted the methanol molecules for certain sites on the polymer. When these sites are exhausted the methanol molecules probably interact among themselves, thereby increasing the amount sorbed.

Sorption isotherms of MTBE, on the other hand, were typical Langmuir types[17] for all the copolymer membranes studied.

The much higher sorption of methanol than MTBE by all the membranes may be attributed to the comparable solubility parameter values (δ, Table III) of the membranes and methanol. On the other hand, the δ of MTBE and the membranes are far apart (Table III). Thus, methanol is sorbed much more than MTBE by the membrane polymers. Thus, for any given membrane matrix it is easier to accommodate a methanol molecule than a MTBE molecule due to the much lower molar volume (Table III) of the former.[18] These may be the reasons for the much higher sorption of methanol than MTBE (Figs. 4–6).

Sorption and Copolymer Composition

For the three copolymer membranes the increasing percent of ester (HEMA), acid (MAC), or pyrrolidone (VP) from copolymer-1 to copolymer-3 at the same feed concentration caused the equilibrium sorption of methanol to increase in all the copolymers. This can be attributed to the greater solubility of methanol in the membrane with the increasing percent of these monomers in these copolymers. Pure poly(HEMA) (PHEMA), poly(MAC) (PMAC), and poly(VP) (PVP) are soluble in methanol.[19] This is also evident from the solubility parameter values of these polymers that are similar to those of methanol (Table III). Thus, as the percent of these monomers is increased from copolymer-1 to copolymer-3, the resulting copolymer shows increased sorption of methanol. In contrast to methanol sorption, for a low feed concentration of methanol the MTBE sorption remains almost constant from copolymer-1 to copolymer-3. However, at high feed concentration of methanol in the feed increased solubility and plasticization of the membranes by methanol causes an increment in MTBE sorption from copolymer-1 to copolymer-3.

Sorption and Nature of Copolymer

The relative sorption of the permeants by the copolymer membranes follows the following order:

$$\text{PANHEMA} > \text{PANMAC} \gg \text{PANVP}$$

On the basis of their solubility parameter values (Table III), the relative solubility of the homopolymer of the copolymer membrane in methanol or MTBE has the following trend:

$$\text{PHEMA} > \text{PMAC} \gg \text{PVP} > \text{PAN}$$

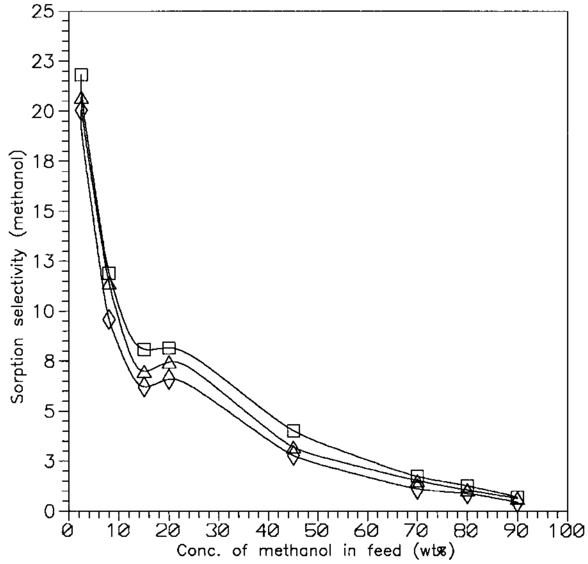

Figure 7 Variation of the sorption selectivity of methanol with its feed concentration at 30°C for a PANHEMA membrane: (□) PANHEMA-1, (△) PANHEMA-2, and (◇) PANHEMA-3.

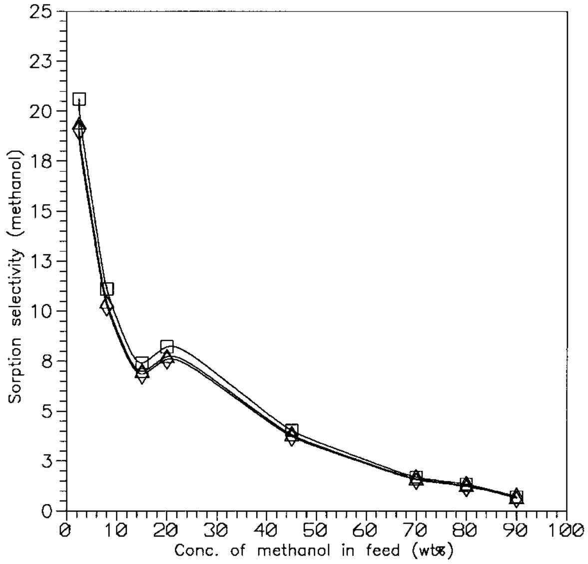

Figure 8 Variation of the sorption selectivity of methanol with its feed concentration at 30°C for a PANMAC membrane: (□) PANMAC-1, (△) PANMAC-2, and (◇) PANMAC-3.

Solubility parameters of copolymers with different copolymer compositions are not available in the literature. However, Fuchs and Suhr[20] indicated that the solubility parameter of a copolymer is similar to that of the homopolymer of its predominant monomer. Thus, the solubility of PANHEMA in methanol is maximum, resulting in maximum equilibrium sorption of methanol by this polymer. In comparison to PANHEMA or PANMAC, the equilibrium sorption by the copolymer PANVP is much less because its solubility parameter is substantially different from that of methanol.

Sorption Selectivity and Feed Concentration

Figures 7–9 show the variation of the sorption selectivity of methanol with its feed concentration. From these figures it is observed that at low feed concentration of methanol the sorption selectivity for methanol is very high for all the membranes. Near the vapor–liquid equilibrium (VLE) azeotrope point (14.7% methanol) there is a drop in the sorption selectivity for methanol. At this point because of the strong permeant–permeant interaction methanol and MTBE are both sorbed almost to the same extent by the membranes, resulting in decreased sorption selectivity for methanol. At a high feed concentration of methanol the swelling of the membranes by methanol causes increased sorption of MTBE (although MTBE is sorbed very little on its own due to its very poor solubility in the membrane). Thus, at a high feed concentration of methanol the sorption selectivity for methanol decreases.

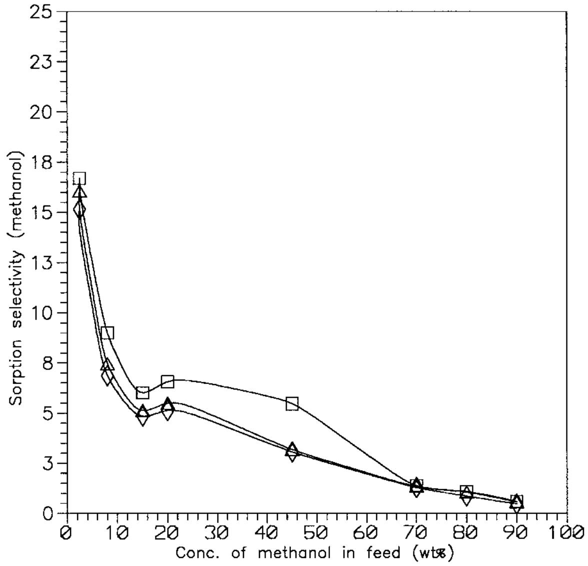

Figure 9 Variation of the sorption selectivity of methanol with its feed concentration at 30°C for a PANVP membrane: (□) PAVP-1, (△) PANVP-2, and (◇) PANVP-3.

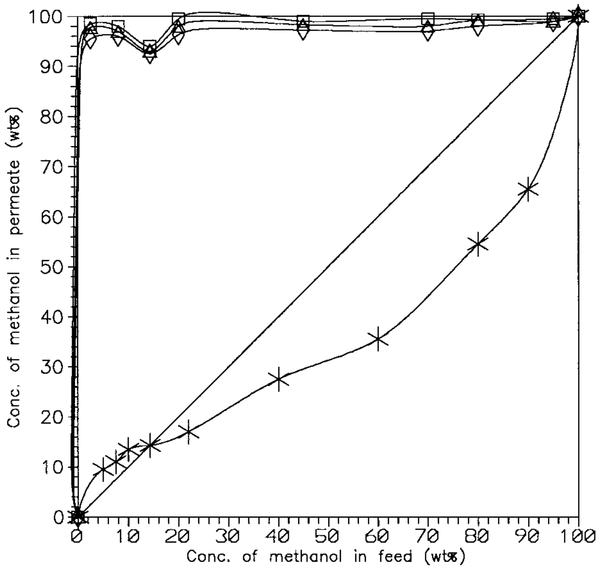

Figure 10 Variation of the permeate concentration of methanol with its feed concentration at 30°C for a PANHEMA membrane: (□) PANHEMA-1, (△) PANHEMA-2, (◇) PANHEMA-3, and (★) VLE curve.

Sorption Selectivity and Copolymer Composition

From Figures 7–9 it is further observed that for a certain feed concentration as the solubility of the membrane increases from copolymer-1 to copolymer-3 with increasing acid, ester, or pyrrolidone content, the sorption selectivity for methanol decreases because of increased plasticization of the membrane. Thus, the sorption selectivity for methanol for the same type of copolymer follows the following trend:

copolymer-1 > copolymer-2 > copolymer-3

Sorption Selectivity and Nature of Copolymer

Preferential sorption of the permeants (i.e., sorption selectivity) by a membrane depends on their relative hydrogen bonding and polar components $\delta\,(\delta_h,\,\delta_d)$ values.[21] On the basis of these δ_h and δ_d values, for the different polymers and the permeants (Table III) the sorption selectivity for methanol among the different copolymers has the following trend:

PANHEMA > PANMAC > PANVP

This was also observed in our experiments and is evident in Figures 7–9.

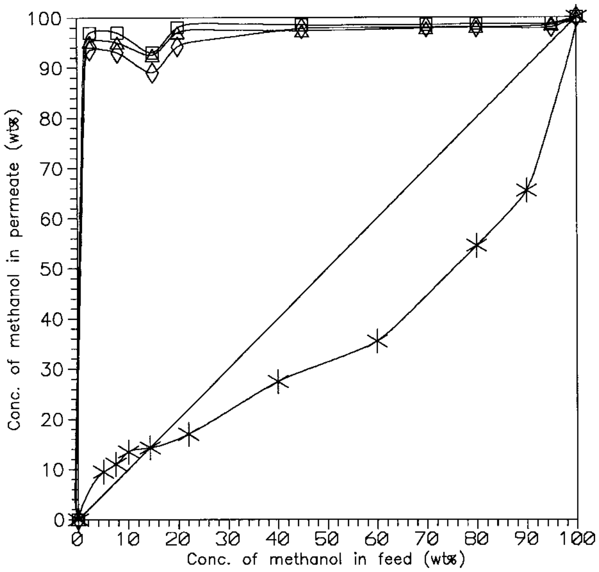

Figure 11 Variation of the permeate concentration of methanol with its feed concentration at 30°C for a PANMAC membrane: (□) PANMAC-1, (△) PANMAC-2, (◇) PANMAC-3, and (★) VLE curve.

Permeation

Separation and Feed Concentration

Figures 10–12 give the separation performance of the various copolymer membranes at 30°C where the weight percent of methanol in the feed is

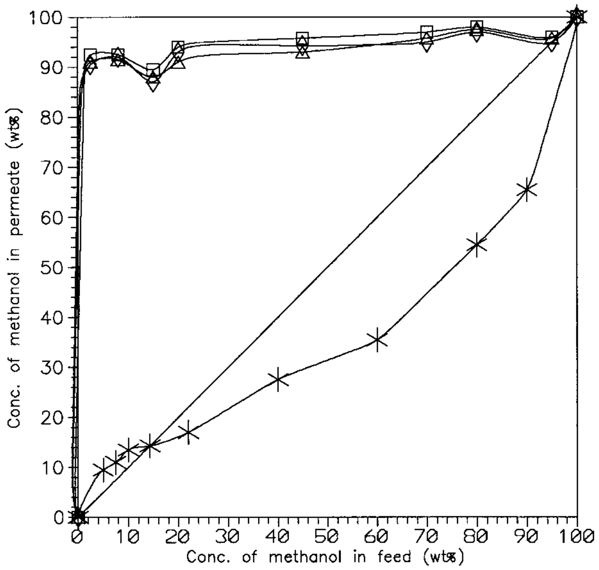

Figure 12 Variation of the permeate concentration of methanol with its feed concentration at 30°C for a PANVP membrane: (□) PANVP-1, (△) PANVP-2, (◇) PANVP-3, and (★) VLE curve.

Table IV Diffusion Coefficients of Methanol and MTBE (D_{oME}, D_{oMT}) and Diffusion Selectivity for Methanol Through All Membranes at Infinite Dilutions

Polymer	$D_{oME} \times 10^{11}$ (m^2/s)	$D_{oMT} \times 10^{11}$ (m^2/s)	Diffusion Selectivity for Methanol
PANHEMA-1	12.30	4.25	28.9
PANHEMA-2	10.57	3.76	28.1
PANHEMA-3	9.58	3.17	30.2
PANMAC-1	10.65	3.96	26.8
PANMAC-2	9.27	3.55	26.1
PANMAC-3	9.05	3.21	28.2
PANVP-1	7.83	4.58	17.01
PANVP-2	6.89	4.15	16.6
PANVP-3	6.15	3.75	16.4

plotted against the same in the permeate obtained in the PV experiments. The VLE[22] is also shown for comparison. From these figures it is clear that the membranes are highly methanol selective (for any feed concentration of methanol, permeate concentration is in the range of 87–99 wt % methanol for the different membranes) and their PV feed permeate (composition) diagram shows better separation performance than their VLE diagram. However, for all the membranes there is a low in permeate concentration of methanol at the VLE azeotrope point (14.3 wt % methanol) that is evident from the drift observed in these figures at the VLE azeotrope point (Figs. 10–12). This decrease in methanol concentration at the azeotrope point may be due to the close association of methanol and MTBE at this point, which results in permeation of both methanol and MTBE. It is further seen from these figures that for the same feed composition the methanol percent in the permeate increases with a decreasing percent of ester (for PANHEMA membranes, Fig. 10), acid (PANMAC membrane, Fig. 11), or pyrrolidone (PANVP membrane, Fig. 12) from copolymer-3 to copolymer-1 of the corresponding membranes. A drift is observed near the VLE azeotrope point (14.3% methanol) for all the membranes. Permeation selectivity for methanol for the above membranes follow the same trend as the sorption selectivity:

$$\text{PANHEMA} > \text{PANMAC} > \text{PANVP}$$

Diffusion Coefficient and Diffusion Selectivity

The diffusion coefficients of methanol and MTBE were both obtained by numerical analysis of the experimental flux and sorption data by Greenlaw et al.'s[23] model described elsewhere.[10] The diffusion coefficient of these components for all the membranes at infinite dilution along with the diffusion selectivity are given in Table IV. From Table IV it is evident that the diffusion coefficient of methanol is much higher than that of MTBE. In the diffusion stage methanol permeates faster than MTBE because the molecular diameter (calculated by optimizing the molecular mechanics energy of the permeants in Chem-X software[24]) and diffusional cross section[25] of the former is lower than that of the latter (Table III). This accounts for the higher diffusion coefficient and hence the higher diffusion selectivity for methanol. Although the relative diffusion depends mainly on the diffusional cross section of the permeants, increased sorption of the permeants from copolymer-1 to copolymer-3 causes loosening of the polymer matrix (and hence a decrease in T_g), easing the diffusion of both the permeants. This is evidenced by the marginal increase in the diffusion coefficient of the permeants from copolymer-1 to copolymer-3 for all the copolymers.

Effect of Feed Concentration on Flux and Selectivity

Figures 13–15 show the results of PV through all three copolymer membranes at 30°C. It is observed that with an increase in methanol concentration in the feed the methanol flux increases. Permeation selectivity for methanol is very high at a low feed concentration of methanol. Figures 13 to 15 also show that there is a low in selectivity at the azeotrope point. This may be due to close permeant–permeant interaction at this point, which also allows permeation of a substantial

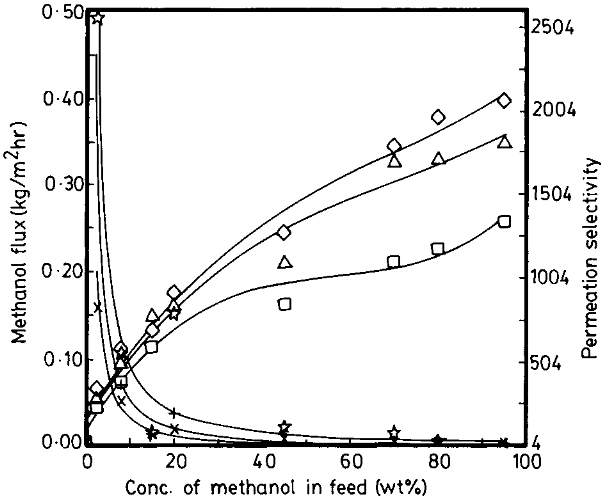

Figure 13 Variation of the flux and permeation selectivity of methanol with its feed concentration at 30°C for a PANHEMA membrane: (□) PANHEMA-1, (△) PANHEMA-2, and (◇) PANHEMA-3.

amount of MTBE, resulting in decreased selectivity. As the feed concentration of methanol exceeds the azeotrope point, selectivity again increases. The decreased selectivity at a very high feed concentration of methanol is due to plasticization of the membrane.

The increase in methanol flux with an increase in the percent of acid, ester, or pyrrolidone groups in the copolymer may be due to the greater solubility of methanol in the membrane. The relative fluxes and permeation selectivity for methanol in the copolymer membranes are similar to the relative sorption behavior of these membranes:

$$\text{PANHEMA} > \text{PANMAC} > \text{PANVP}$$

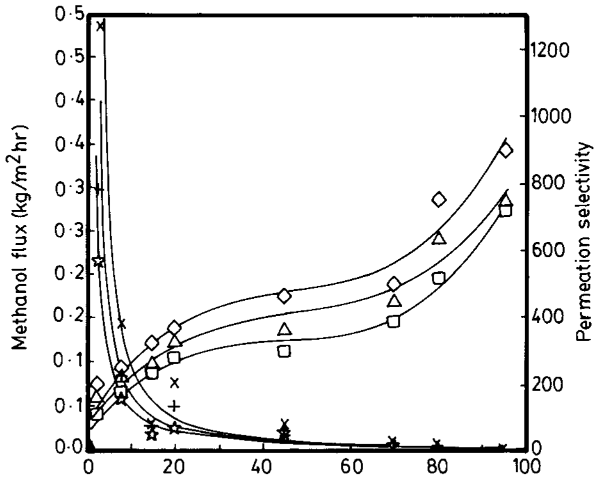

Figure 14 Variation of the flux and permeation selectivity of methanol with its feed concentration at 30°C for a PANMAC membrane: (□) PANMAC-1, (△) PANMAC-2, and (◇) PANMAC-3.

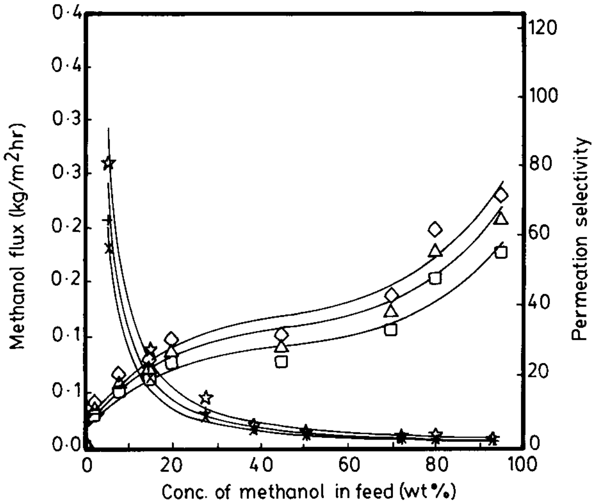

Figure 15 Variation of the flux and permeation selectivity of methanol with its feed concentration at 30°C for a PANVP membrane: (□) PANVP-1, (△) PANVP-2, and (◇) PANVP-3.

It is worth mentioning that compared to the other membranes used for methanol–MTBE separation, much better performance was achieved with the membranes studied in this work. From Table V it is clear that the flux and selectivity of the present membranes are better than those reported for the same system.

Permeation Selectivity and Feed Concentration

Figures 13–15 show that the permeation selectivity of all the membranes for methanol is much higher than the corresponding sorption selectivity. Permeation selectivity is a combination of sorption selectivity and diffusion selectivity. The high sorption and diffusion selectivity for methanol accounts for the very high methanol permeation selectivity of the membranes. However, at very high methanol content in the feed, high sorption of the permeants causes loosening of the polymer matrix, easing diffusion of both the permeants. Thus, permeation selectivity decreases at high methanol content in the feed.

Effect of Feed Temperature on Permeation

In general, the effect of temperature on the permeation flux is positive. This is due to the fact

Table V Comparison of Flux and Selectivity of Different Membranes for Pervaporative Separation of Methanol–MTBE Mixture

Membrane	Feed Concn of Methanol	Selectivity for Methanol	Flux (kg/m^2 h)	Exp. Temp. (°C)	Reference
Cellulose acetate	0.83–6.9	13.9–454	0.048–0.141	22.5–48.9	Pasternak et al.[6]
Modified PVA	5–30	~ 150	~ 0.250	25	Park et al.[5]
Nafion 417	3.2–5.3	25	0.189	50	Farnand and Sawatsky[3]
PSS/Al$_2$O$_3$	5–14.3	25,000–35,000	0.0230–0.001	25	Chen and Martin[8]
PANHEMA-2	5–15	89–2,561	0.057–0.115	30	This work
PANMAC-2	5–15	70–773	0.045–0.0907	30	This work

that although the amount sorbed by the polymer decreases with increasing temperature, this is more than offset by the increase in the diffusion coefficient of the solute due to the increase in temperature. The latter is brought about by the increased thermal motions of the polymer chain at higher temperatures. Both the processes involved in permeation, sorption, and diffusion are activated processes and the temperature effect can be described by an Arrhenius type relationship. The overall activation energy for permeation is[12]

$$\Delta E_p = \Delta E_d + \Delta H_s \tag{6}$$

where ΔE_p and ΔE_d are the activation energies for permeation and diffusion, respectively, and ΔH_s is the heat of sorption. The ΔE_p and ΔH_s values were obtained from the Arrhenius type plot of the ln(flux) and sorption, respectively, at different feed concentrations of methanol. However, recently Feng and Huang[26] argued that during PV the latent heat of vaporization (ΔH_v) required by the liquid feed mixture for its transition to the vapor state is included in ΔE_p if it is calculated from an Arrhenious type plot of ln(flux) versus $1/T$. Accordingly, the pseudo-activation energy for permeation (ΔE_p) is a mere ΔE_j, which is related to the actual activation energy for permeation (ΔE_p) as

$$\Delta E_p = \Delta E_j - \Delta H_v \tag{7}$$

The ΔE_j was obtained from an Arrhenius type plot of ln(flux) versus $1/T$, ΔH_v for methanol was obtained by the Pitzer[27] method, and the ΔH_v was calculated from the Viteres and Watson equation because of the nonavailability of a parameter value for MTBE.[27] These values were substituted in eq. (7) to get the values of ΔE_p. The ΔE_d values were calculated from the values of ΔE_p and ΔH_s from eq. (6).

Figures 16 and 17 show the variation of ΔE_p, ΔH_s, and ΔE_d of methanol and MTBE, respectively, at different feed concentrations of methanol for the PANHEMA membrane. Similar results were obtained with the other two types of copolymers. It is observed from these figures that with increasing methanol concentration in the feed mixture the ΔH_s increases and ΔE_p decreases. It is further seen that for the same type of copolymer, the ΔH_s value increases from copolymer-1 to copolymer-3. The opposite trend is observed for ΔE_p and ΔE_d values of the copolymer: it decreases from copolymer-1 to copolymer-3.

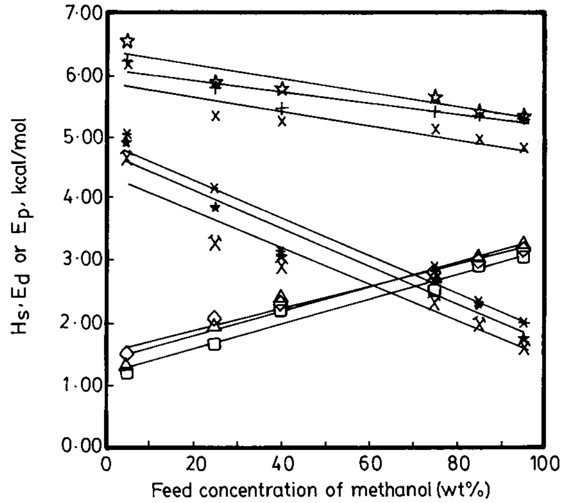

Figure 16 Variation of the heat of sorption (ΔH_s), activation energy for diffusion (ΔE_d), and activation energy for permeation (ΔE_p) of methanol with its feed concentration for a PANHEMA membrane. (□) PANHEMA-1, (△) PANHEMA-2, and (◇) PANHEMA-3; ΔE_d: (☆) PANHEMA-1, (+) PANHEMA-2, and (×) PANHEMA; ΔE_p: (*) PANHEMA-1, (★) PANHEMA-2, and (✚) PANHEMA-3.

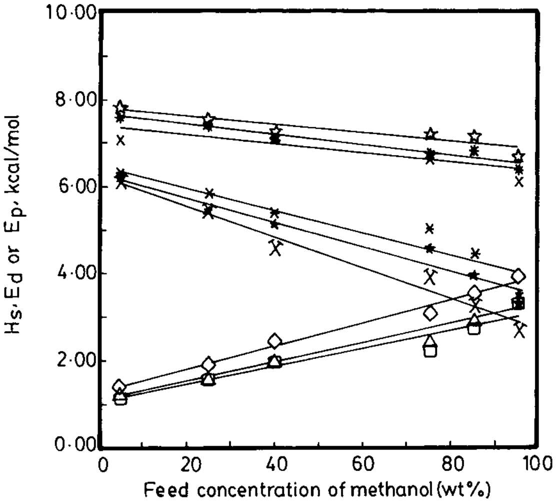

Figure 17 Variation of the heat of sorption (ΔH_s), activation energy for diffusion (ΔE_d), and activation energy for permeation (ΔE_p) of MTBE with its feed concentration for a PANHEMA membrane. (□) PANHEMA-1, (△) PANHEMA-2, and (◇) PANHEMA-3; ΔE_d: (☆) PANHEMA-1, (+) PANHEMA-2, and (×) PANHEMA; ΔE_p: (*) PANHEMA-1, (★) PANHEMA-2, and (✚) PANHEMA-3.

Sorption is an exothermic process and heat liberated during sorption will be high for a membrane that is more permeable (membrane-1 to membrane-3). Similarly, with increasing methanol concentration in the feed mixture the membrane swells and sorbs more of the permeants, having increased the ΔH_s. On the other hand, activation energy required for permeation or diffusion will depend on the nature of the polymer matrix of the membrane. Incorporation of the five-membered pyrrolidone moiety (in PANVP) or methyl substituted acid (in PANMAC) increases the chain stiffness of the resulting copolymers, but this effect is more than offset by increased solubility of the membranes from copolymer-1 to copolymer-3; thus, the activation energy for permeation or diffusion decreases from copolymer-1 to copolymer-3. The values of ΔE_p, ΔE_d, and ΔH_s for all the membranes at 5% methanol feed concentration is given in Table VI. Table VI shows that for the same copolymer the ΔE_p or ΔE_d for MTBE is higher than those for methanol while its ΔH_s is less than that of methanol. This may also be ascribed to the greater diffusional cross-sectional area of MTBE, which demands higher activation energy for diffusion (i.e., ΔE_d). The ΔE_p incorporates both the effects of ΔE_p and ΔH_s . However, the much lower ΔH_s in comparison to the ΔE_d yields a ΔE_p of MTBE that is greater than that for methanol (Table VI).

CONCLUSIONS

Copolymerization of AN with HEMA, MAC, and VP with different comonomer compositions resulted in several methanol selective membranes.

All the membrane polymers were characterized by their spectral analysis and their intrinsic viscosity, T_g, TS, and EAB. As the percent of pyrrolidone or the acid increased from membrane-1 to membrane-3, the T_g and TS of the resulting membrane increased. On the other hand, for the PANHEMA membrane the T_g and TS both decreased with an increasing percent of the ester group from membrane-1 to membrane-3.

Incorporation of ester, acid, or the pyrrolidone group imparted increased solubility of methanol in the resulting copolymer membranes. Thus all

Table VI $\Delta H_{s\mathrm{ME}}$, $\Delta H_{s\mathrm{MT}}$, $\Delta E_{p\mathrm{ME}}$, $\Delta E_{p\mathrm{MT}}$, $\Delta E_{d\mathrm{ME}}$, and $\Delta E_{d\mathrm{MT}}$ of All Membranes at 5% Methanol Concentration in Feed

Membranes	$\Delta H_{s\mathrm{ME}}$ (kcal/mol)	$\Delta H_{s\mathrm{MT}}$ (kcal/mol)	$\Delta E_{d\mathrm{ME}}$ (kcal/mol)	$\Delta E_{d\mathrm{MT}}$ (kcal/mol)	$\Delta E_{p\mathrm{MT}}$ (kcal/mol)	$\Delta E_{p\mathrm{ME}}$ (kcal/mol)
PANHEMA-1	1.19	1.11	6.23	7.57	6.46	5.03
PANHEMA-2	1.33	1.12	6.20	7.41	6.28	4.91
PANHEMA-3	1.47	1.39	6.15	7.14	5.75	4.67
PANMAC-1	1.15	1.03	6.65	7.69	6.66	5.48
PANMAC-2	1.26	1.22	6.51	7.61	6.38	5.24
PANMAC-3	1.41	1.36	6.37	7.52	6.15	4.96
PANVP-1	1.03	0.572	7.87	8.32	7.75	6.83
PANVP-2	1.15	0.960	7.29	8.11	7.15	6.14
PANVP-3	1.32	1.43	7.17	7.91	6.48	5.83

the membranes showed substantial sorption of methanol. The high sorption and diffusion selectivity for methanol resulted in high permeation selectivity for methanol by all the membranes. There was a decrease in selectivity of methanol for all the membranes at the VLE azeotrope point. However, methanol selectivity still remained high at these points.

In terms of flux and selectivity the best result was obtained for PANHEMA and PANMAC membranes.

The temperature had a positive effect on flux. However, with increasing temperature the selectivity of the membranes decreased.

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