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Synthesis of Novel Polymeric Membrane for Separation of MTBE-Methanol by Pervaporation

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Abstract: Polyvinyl alcohol(PVOH) has been chemically modified by crosslinking copolymerization of acrylic acid(AA) and hydroxyethylmethacrylate (HEMA) in aqueous solution of PVOH and finally crosslinking PVOH with glutaraldehyde to produce a full interpenetrating network(IPN) membrane. Accordingly, three such full crosslink IPNs i.e., PVAHI, PVAHII and PVAHIII have been synthesized with different weight ratio of PVOH:Poly (AA-co-HEMA) i.e., 1:0.25 (PVAHI), 1:0.50 (PVAHII) and 1:0.75 (PVAHIII). These IPN membranes have been used for pervaporative separation of MTBE-methanol mixtures. All the PVAH membranes were also characterized with various conventional methods like FTIR, mechanical properties, DSC and TGA. Permeability and methanol selectivity of these membranes were found to increase with increasing amount of copolymer in PVOH matrix. However, among the three membranes, PVAHIII were found to show the highest flux but lower selectivity for methanol while PVAHII membrane showed optimum performance in terms of both flux and selectivity.

Keywords: Crosslink copolymer, IPN, methanol, MTBE, pervaporation

INTRODUCTION

Methyl tertiary butyl ether (MTBE) is industrially prepared by reaction of an isoalkene (e.g., isobutene for MTBE) with excess methanol over a cation exchange resin. However, unreacted methanol forms an

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azeotrope with these ethers and thus azeotropic distillation is used to separate these ethers from methanol. A hybrid distillation system comprising in both distillation and pervaporation is being used commercially for this separation where PV is used near the azeotrope point. For this PV process cellulose acetate membrane has been commercialized. Many other polymeric membranes are being tried to achieve higher flux and selectivity for this organic-organic separation.

For organic-organic separation polymeric membranes are mainly chosen on the basis of relative solubility parameter of the organics and the membranes (2). However, for the separation of a smaller amount of methanol from ethers like MTBE, hydrophilic membranes are used (3). Apart from commercial cellulose acetate membranes (4,5) various acrylic copolymers have also been reported in recent years (6,7) for pervaporative removal of methanol from MTBE or other similar ethers. In spite of good mechanical integrity, the acrylic copolymer membranes are not as flexible as the polyvinyl alcohol(PVOH) membrane and making of the PV membrane is also not as easy as for PVOH. Most of these acrylic copolymers are prepared by emulsion polymerization technique and as a result it is difficult to remove all the impurities from these polymers which influence its PV performance. In contrast, PVOH is a chiefly available polymer and PV membrane can easily be prepared from its aqueous solution by solution casting.

Although the crosslinked PVOH membrane has been commercialized for alcohol dehydration (8), it has not been successful for MTBE-methanol separation because of very low methanol flux.

The low flux of PVOH may be ascribed to its high degree of crystallinity due to extensive intramoleular hydrogen bonding. Thus, in one of our works (9) hydroxyl ethyl methacrylate(HEMA) has been allowed to polymerize in the matrix of PVOH to reduce its crystallinity. In this case, HEMA, a monomer of a water soluble polymer (polyHEMA) also gave increased hydrophilicity and hence water flux. Among the various acrylic copolymers, crosslink copolymers like poly(acrylamide-co-HEMA) has been reported for dehydration of corrosive organics like DMF and also for the separation of methanol from MTBE (7). These copolymers can be prepared by solution polymerization in water (as both the monomers are water soluble) and the membrane can be cast from its aqueous solution by solution casting. However, high glass transition temperature of polyacrylamide gives some extent of stiffness in the membrane. To combine the flux and selectivity of acrylic copolymer with flexibility and excellent mechanical integrity of the PVOH membrane, these kinds of acrylic copolymers can be synthesized in water containing PVOH to produce an interpenetrating network (IPN) type polymer. Thus, three polymers, PVAHI, PVAHII, and PVAHIII have been synthesized with a weight ratio of

PVOH:Poly(AA-co-HEMA) of 1:0.25, 1:0.50, and 1:0.75, respectively. In each of these polymers, the molar ratio of acrylic acid(AA) to HEMA was kept constant at 10:1. Homopolymer of HEMA i.e., polyHEMA is methanol soluble but too soft (due to very low T_g) to form a durable membrane. Polyacrylic acid is also hydrophilic and soluble in water but can not form a suitable membrane. The copolymer of AA and HEMA in the matrix of PVOH would result in a suitable methanol selective membrane. The membranes cast from these polymers i.e., PVAHI, PVAHII, and PVAHIII have been used for pervaporative separation of methanol-MTBE mixture over the concentration range of 0–20 wt% methanol in MTBE.

EXPERIMENTAL

Materials

High purity analytical grade MTBE and methanol used for this study were purchased from E. Marck, Mumbai. The monomers i.e., acrylic acid and hydroxyethylmethacrylate (HEMA), both synthesis grade were procured from S.D. fine chemicals, Mumbai and used as obtained. Ammonium persulfate and sodium metabisulfide was used as redox initiator pair for the copolymerization reaction. Polyvinyl alohol (PVOH) of number average molecular weight 1,25,000 and hydrolysis of 98–99% was obtained from S.D. Fine Chemicals, Mumbai and used as obtained.

Synthesis of PVAH

The three PVAH i.e., PVAHI, PVAHII, and PVAHIII were synthesized by solution polymerization in a three-necked reactor at 65°C for 3 hrs using ammonium persulfate and sodium metabisulfide (each, 0.5 wt% of the total monomer weight) as redox pair of initiators. In all of this synthesis 10:1 molar ratio of acrylic acid and HEMA was used. The reactor was fitted with a stirrer, a thermometer pocket, and a condenser. At first 5 wt% PVOH solution was made in deionized water in a 250 ml glass beaker by gradual addition of the required amount of PVOH to boiling water in several intervals with constant stirring to obtain a viscous clear PVOH solution. Required amounts of acrylic acid and HEMA were then added to the three neck flask placed on a constant temperature bath. Temperature was raised to 65°C and aqueous solution of initiators were added to the reactor. After polymerization for some 3 hours the viscous polymer solution was taken out from the reactor and precipitated in ethanol to remove soluble monomer or oligomer if any, (which is soluble in ethanol) from the reaction mixtures. The resulting

PVAH polymer was dried at ambient temperature in vacuum oven and redissolved in water.

Crosslinking and Casting of Membranes from PVAH

The aqueous solution (containing 5 gm of PVOH) of the resulting PVAH was mixed with 25% aqueous solution of glutaraldehyde, 10% solution of H_2SO_4 (to catalyze the reaction), 50% aqueous methanol to quench the reaction, and 10% solution of acetic acid (pH controller) (9). Thus, for 2 wt% crosslinking of PVOH, the aqueous PVAH solution was mixed with 0.4 ml glutaraldehyde, 0.2 ml sulfuric acid, 0.6 ml acetic acid, and 0.4 ml methanol. The membrane was prepared by casting this aqueous solution of the PVAH with an applicator on a clean and smooth glass plate. It was kept overnight at room temperature and then dried at 60°C for 2 hours under vacuum. Subsequently, the membrane was annealed at 80°C for an additional 6 hrs under vacuum. The membrane thickness for the PVAH polymer was maintained at $\sim$50 micron. The thickness was measured by the Test Method ASTM D 374 using a standard dead weight thickness gauge (Baker, Type J17).

Membrane Characterization

Studies of F.T.I.R. Spectroscopy

The F.T.I.R. spectra of the three PVAH membranes were recorded on a Jasco (FT/IR-460 plus, Jasco Corporation, Japan) F.T.I.R. spectroscope using a thin film (10 micron) of the polymer.

Mechanical Strength

The tensile strength (T.S.) and elongation at break (E.A.B.) of the polymer film was determined by a Lloyd UTM, (England). The experiment was performed according to ASTM D 882-97. In this work, the length of the specimens was 250 mm., the thickness of the specimens was around 0.1 mm and the thickness was uniform to within 5% of the thickness between the grips. The width of the specimens was 20 mm and edges were parallel to within 5% of the width over the length of the specimen between the grips.

Differential Scanning Calorimetry (DSC)

The above three synthesized full IPN i.e., PVAHI, PVAHII, and PVAHIII were subjected to DSC for their thermal characterization. DSC thermograms were recorded on a Perkin Elmer DSC(Model DSC-7, USA) in the temperature range from 60 to 600°C at the scanning rate of 10°C/min in nitrogen atmosphere.

Thermogravimetric Analysis (TGA)

TGA thermograms of the above three samples were recorded on a Perkin Elmer (Model TGA-7, USA) instrument in nitrogen atmosphere, at the scanning rate of 10°C/min in the temperature range of 60 to 600°C.

X-ray Diffraction

Wide angle X-ray diffraction profile of polyvinyl alcohol, crosslinked polyvinyl alcohol and the three IPN membranes (sample thickness 50 micron) were studied at room temperature with a diffractometer (model: X'Pert PRO, made by PANalytical B.V., The Netherlands) using Ni-filtered Cu K_α radiation ($\lambda = 1.5418$ Å) and a scanning rate of 0.005 deg(2θ)/s. The angle of diffraction was varied from 2–72 degree to study the comparative change of the crystallinity as well as segmental spacing (d spacing) of pure PVOH, glutaraldehyde crosslinked PVOH, and the three SIPN membranes.

Permeation Study

Pervaporation Experiment

Pervaporation experiments were carried out in a batch stirred cell (9) with adjustable downstream pressure that was maintained at 1 mm Hg by liquid (mercury) column method using a manometer. The feed compartment of the pervaporation cell was equipped with a stirrer to ensure adequate mixing of the liquid feed so as to eliminate any concentration or temperature gradient. Effective membrane area(A) in contact with the feed mixture was 19.6 cm^2 and the feed compartment volume was 150.0 cm^3. The organic-organic mixtures in contact with the membrane was allowed to equilibrate for around 3 hours for the first experiment and one hour for the subsequent experiments with different feed compositions. When the steady state was reached the permeate was collected in traps immersed in liquid nitrogen. Permeation flux (J) was calculated by dividing the amount of total permeate(W) by the time (t) of experiment and area of the membrane from equation (1).

$$J = \frac{W}{At} \tag{1}$$

The PV experiment was performed at a constant temperature by circulating constant temperature water around the jacket of the PV cell. The methanol content of the permeate was determined by an Abbe type digital Refractometer (model no. AR600, MISCO, USA) at 25°C temperatures for all the samples. For quantitative analysis of methanol in feed, the permeation selectivity (α_{pv}) of methanol expressed as separation factor for methanol was calculated from a similar type of equation as sorption selectivity i.e., equation (2) as given below.

$$\alpha_{PV} = \frac{\frac{y_{methanol}}{y_{MTBE}}}{\frac{x_{methanol}}{x_{MTBE}}} \tag{2}$$

Here y_i and x_i are weight fraction of component i (methanol) in membrane and feed, respectively

The performance of the membrane was also evaluated in terms of the permeation separation index (PSI) as obtained from the following equation (3).

$$PSI = J_{methanol}\,(\alpha_{PV} - 1) \tag{3}$$

Here $J_{methanol}$ is methanol flux.

RESULTS AND DISCUSSION

Membrane Synthesis

The copolymerization of AA and HEMA produces a crosslinking copolymer of poly(AA-co-HEMA) or polyAH on heating (11). Earlier, crosslink copolymer of acrylamide and HEMA was used for separation of MTBE-methanol and dehydration of corrosive organic like DMF [7]. However, polyacrylic acid being a high T_g polymer, the copolymer polyAH would not be an effective PV membrane. In this work, thus, polyAH has been synthesized in the presence of PVOH solution in water. Apart from forming a crosslink copolymer, the carboxylic moiety of AA also reacts with hydroxyl moiety of PVOH to form an inter penetrating network (IPN). As this IPN is further crosslinked with glutaraldehyde, a full IPN of PVAH is formed where the two different polymers, i.e., PVOH and polyAH, are separately crosslinked (PVOH with glutaraldehyde and polyAH forming a crosslink copolymer) as well as interpenetration of these two polymers occurs through chemical bonding between COOH moiety of AA and OH moiety of PVOH. By this chemical modification of PVOH, hydrophilicity of PVOH was increased and with reduced crystallinity the resulting PVAH membrane yielded increased flux.

Membrane Characterization

FTIR Study

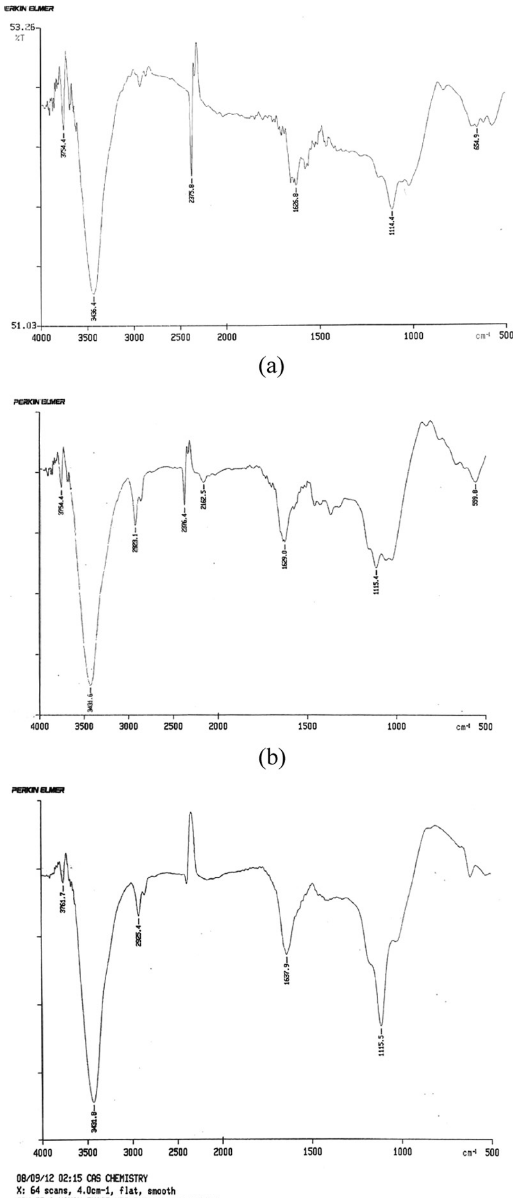
From the FTIR spectra of PVAHI i.e., Fig. 1a, we find a strong band at around 1626.8 cm^{-1} corresponding to carboxyl (COOH) peak due to acrylic acid present in all the PVAH polymers. This peak has been shifted with more intensity with increasing amount of acrylic acid in PVAHII (1629.0 cm^{-1}) and PVAHIII (1637.9 cm^{-1}). Similarly, O-H bending vibrations at around 1115 cm^{-1} correspond to poly vinyl alcohol (PVOH) as well as hydroxyethyl methacrylate comonomer of the copolymer (12). The bands at around 3436 cm^{-1} and 3754 cm^{-1} correspond to the crosslinked and the uncrosslinked hydroxyl group of PVAH polymer. These apart, the strong band at around 600 cm^{-1} and 2920 cm^{-1} are due to ($-CH_2-$) methylene (13) and C–H alkane group of the copolymer membrane (14).

Mechanical Strengths

Polyvinyl alcohol (PVOH) shows a good balance of tensile strength (TS) and elongation at break (EAB) and hence considered as a good membrane forming polymer. From Table 1 it is observed that the T.S and EAB of PVAH membrane is found to decrease with increasing amount of polyAH from PVAHI to PVAHIII. Polyvinyl alcohol (PVOH) membrane shows high TS because of its crystallinity and it also shows high elongation because of its low T_g. The increasing amount of high T_g polyAH in PVOH decreases its crystalline structure as well as increasing crosslinking of both PVOH and polyAH reduces chain flexibility of the PVAH polymer. Thus, with increasing amount of polyAH both TS and EAB of the polymer decreases.

Membrane Characterization by DSC

The glass transition temperature (T_g) and melting peak of PVOH and the three used IPNS are given in Table 1. Dry and uncrosslinked PVOH



(a)

(b)

(c)

Figure 1. (a) FTIR of PVAHI membrane; (b) FTIR of PVAHII membrane; (c) FTIR of PVAHIII membrane.

Table 1. Tensile properties of the membrane polymers

Name of the polymer	Tensile strength (MPa)	Elongation at break (%)	Glass transition temperature (°C)	Softening point (°C)
PVAHI	37.9	96.8	173	263
PVAHII	35.22	58.93	169	257
PVAHIII	25.47	45.51	166	243

membrane shows T_g at 80–85°C (15). However, the crosslinked PVOH requires much higher energy for segmental motion of its polymeric chain resulting in higher T_g (16,17). From Table 1 it is observed that the second-order transition temperature or T_g decreases marginally in the following order PVAHI > PVAHII > PVAHIII. The first-order transition temperature, i.e., melting peak decreases in the following order, i.e., PVAHI > PVAHIII > PVAHII. Incorporation of polyAH in the matrix of PVOH reduces its crystallinity and increases its free volume and segmental motion. However, the polyAH copolymer also reacts with PVOH in PVAH polymer and thus reduces its segmental motion. Thus, due to these two opposing effects, the decrease in T_g from PVAHI to PVAHIII is marginal. The decrease of melting peak in the above order may be explained by a similar reason.

Membrane Characterization by Thermogravimetric Analysis (TGA)

The PVOH membrane exhibit two major weight loss regions with onset of maximum weight loss at its melting temperature, i.e., at around 200°C which continues up to around 425°C with a residue of around 7 wt.%. Incorporation of polyAH in PVAH membranes result in three major weight loss regions with no residue in any of these membranes. It is interesting to note that in all of these IPN membranes melting starts at a much lower temperature (around 169°C) which may be attributed to loss in crystallinity of PVOH by incorporation of polyAH copolymer. The weight losses of these IPN polymers in different temperature regions are associated with splitting of the main chain and final decomposition of the polymer.

Membrane Characterization by XRD Studies

The crystallinity of atactic polyvinyl alcohol arises from extensive hydrogen bonding by the small hydroxyl groups occupying d and l sites in an atactic chain within a single crystal lattice. As this PVOH is crosslinked, there is a change in d spacing and peak intensity also decreases due to loss in crystallinity. Copolymerization of acrylic acid and HEMA in the matrix of PVOH further reduces the extent of hydrogen bonding and hence crystallinity as evident by progressive decrease of peak intensity at $2\theta = 43.6°$ from PVAHI to PVAHIII in Fig. 2.

Pervaporation (PV) Studies

Effect of Feed Concentration on Methanol Separations

Figure 3 shows the variation of wt% of methanol in the permeate against wt% of methanol in the feed for separation of methanol-MTBE mixtures with the three PVAH membranes at 24°C. Similar kind of relationships were also observed at the two other PV temperatures i.e., at 32 and 40°C. It appears from these McCabe-Thiele type xy diagrams that all the membranes show measurable separation characteristics over the used concentration range without any pervaporative azeotrope. It is also observed from the figure that over the used concentration range, all the three membranes show high methanol concentration in the permeate. Among the three membranes, PVAHII shows marginally higher methanol wt% in the permeate. Incorporation of hydrophilic crosslink copolymer polyAH in PVOH matrix increases methanol affinity of the membranes. However, it also decreases crystallinity of PVOH matrix as its intramolecular hydrogen bonding is reduced. The slightly lower methanol concentration in the permeate for PVAHIII may be due to increased void space in the membrane.

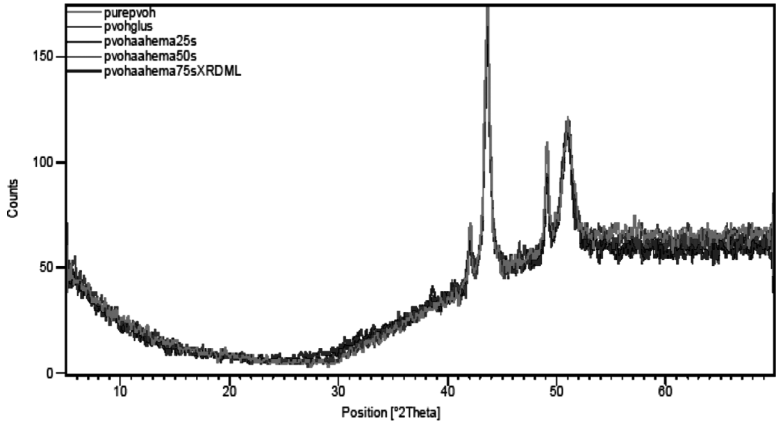


Figure 2. Comparative XRD of PVOH and IPN membranes.

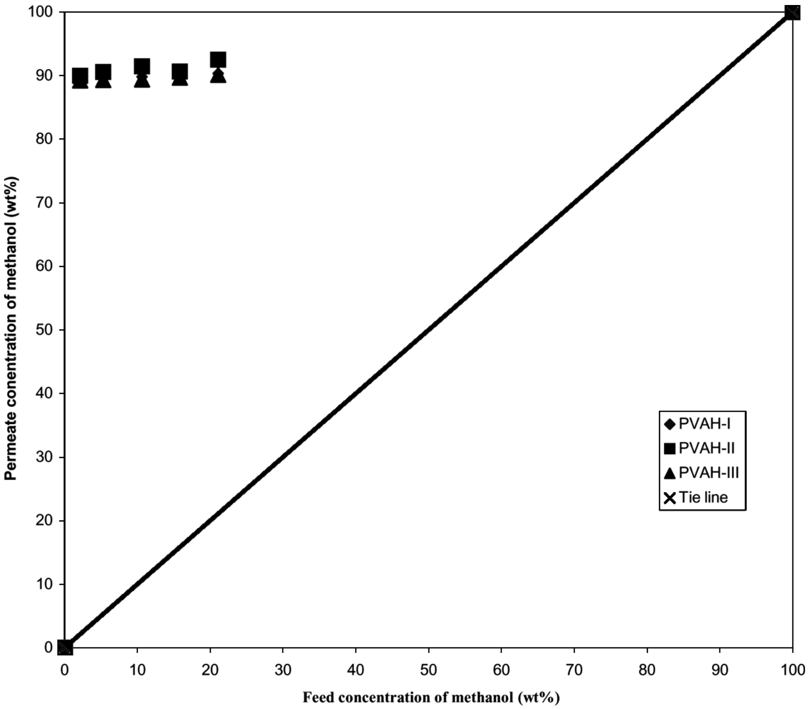


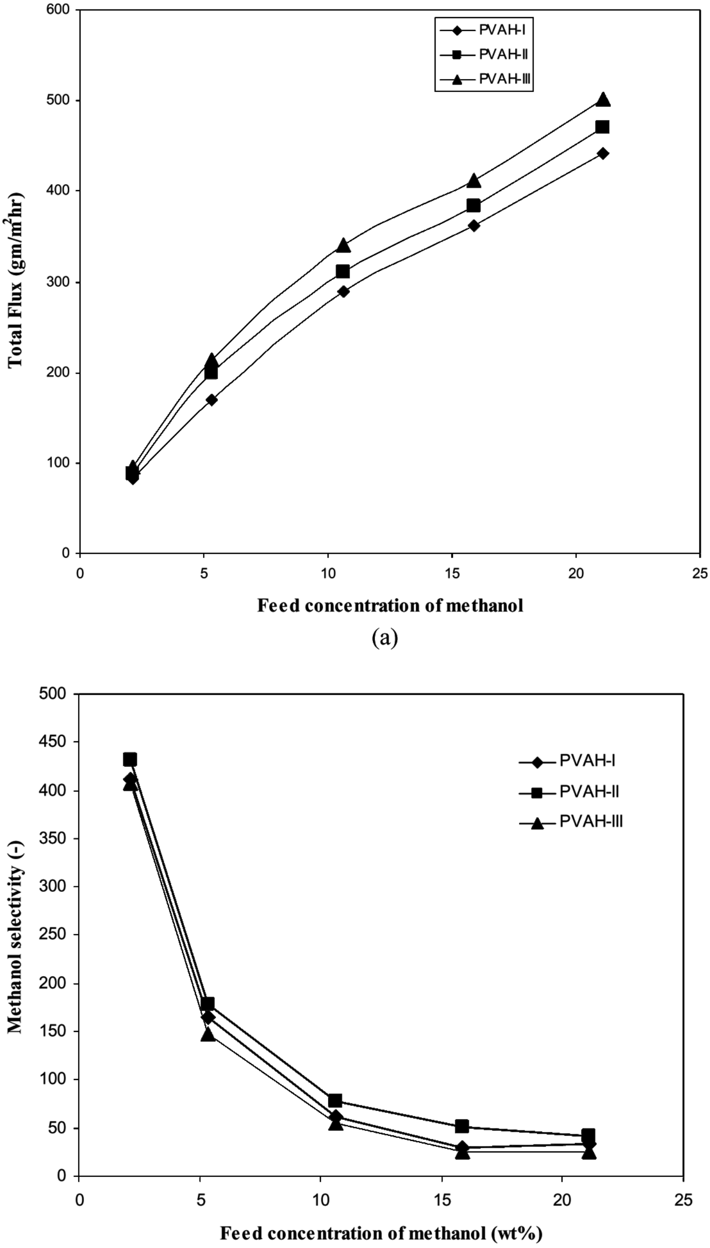
Figure 3. Variation of permeate concentration of methanol with its feed concentration at 24°C. ◆ PVAHI; ■ PVAHII; ▲ PVAHIII.

Effect of Feed Concentration on Flux and Permeation Selectivity

The effect of feed concentration of methanol on total flux and permeation selectivity for methanol is shown in Figs. 4a and 4b, respectively for the three IPN membranes at 32°C. A similar kind of relationship was also observed at the other two temperatures of PV experiments i.e., at 24 and 40°C. From these figures it is observed that with the increase in feed concentration of methanol the total flux increases almost linearly signifying methanol selectivity of the membranes. It is also seen that for the same feed concentration the flux shows the following trend

$$\text{PVAHIII} > \text{PVAHII} > \text{PVAHI}$$

The increasing order of flux from PVAHI to PVAHIII may be ascribed to a decreasing extent of crystallinity from PVAHI to PVAHIII. Incorporation of the copolymer polyAH, not only increases the hydrophilicity



(a)

(b)

Figure 4. (a) Feed concentration and total Flux at 32°C; (b) Methanol selectivity and Feed concentration at 32°C. ◆ PVAHI; ■ PVAHII; ▲ PVAHIII.

but also the void space in these IPN membranes because of loss in crystallinity. Thus, flux increases from PVAHI to PVAHIII

Permeation Selectivity and Feed Concentration

Permeation selectivity of methanol for all the membranes (Fig. 4b) decreases exponentially with feed concentration and up to around 5 wt% methanol in feed permeation selectivity decreases drastically for all the membranes. From the figure we find that the methanol selectivity of the membranes show the following order

$$\text{PVAHII} > \text{PVAHI} > \text{PVAHIII}$$

In fact, at lower feed concentration (up to around 5 wt% methanol in feed) all the three membranes show similar selectivity but the difference in selectivity increases at higher feed concentration of methanol. Incorporation of hydrophilic polyAH in PVOH matrix increases methanol selectivity and hence it increases from PVAHI to PVAHII with increasing amount of polyAH. However, the amount of polyAH in PVAHIII is very high (75 wt% of PVOH) and it causes decrease in selectivity because of increased void space.

Effect of Temperature on Flux and Selectivity

With increase in temperature flux increases linearly for all the membranes while selectivity decreases at higher temperature in the same order as shown for all the membranes in Figs. 5a and 5b for flux and selectivity respectively, with 5.5 wt% feed methanol concentration. Activation energy for permeation (E_P) can be obtained from the slope of the Arrhenius type linear plot of logarithmic of flux (Q) against the inverse of absolute temperature (1/T) from the following equation

$$\ln Q = \ln A - \left(\frac{E_P}{RT}\right) \tag{6}$$

Here ‘A’ is a preexponential factor and ‘R’ is universal gas constant. Thus, the activation energy for the permeation of methanol and MTBE could be calculated at several feed concentrations from similar plots. Methanol and MTBE flux at a particular feed concentration is calculated by multiplying the total flux with permeate concentration of methanol or MTBE (in wt%) at that concentration. Accordingly, activation energy for

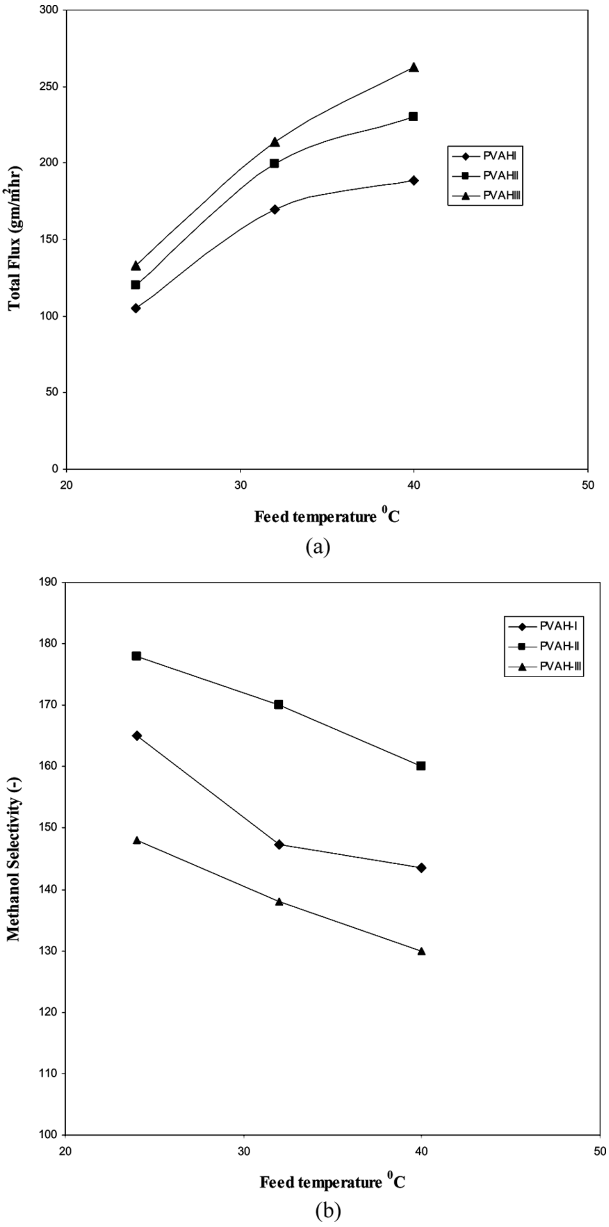


Figure 5. (a) Feed temperature and total flux. Feed conc. 5.3 wt% methanol; (b) Variation of methanol selectivity with feed temperature at 5.3 wt% feed concentration of methanol. ◆ PVAHI; ■ PVAHII; ▲ PVAHIII.

permeation of methanol and MTBE were calculated from the Arrhenius type plot of logarithmic of methanol flux and MTBE flux against inverse of absolute temperature at various feed concentration of methanol. From Figs. 6a or 6b it is observed that activation energy for permeation of methanol (Fig. 6a) or MTBE (Fig. 6b) decreases almost linearly with increasing feed concentration of methanol up to around 15 wt% methanol in feed and thereafter the change is marginal. Plasticization of the methanol selective membranes causes decrease in activation energy at higher methanol concentration. It is also observed from Figs. 8a and 8b that for the same feed concentration activation energy of methanol is lower than MTBE for all the membranes signifying methanol selectivity of the membranes.

Effect of Feed Concentration on PSI

Figure 7 shows variation of PSI for methanol with its feed concentration. PSI is found to be maximum at around 2.5 wt% feed concentration signifying optimum flux and selectivity at this concentration. Above this concentration PSI decreases almost linearly with concentration. Among the three membranes, PVAHIII shows maximum PSI which decreases from PVAHIII to PVAHI. However, at higher feed concentration PVAHII shows the highest PSI.

Effect of Feed Concentration on Permeation Ratio

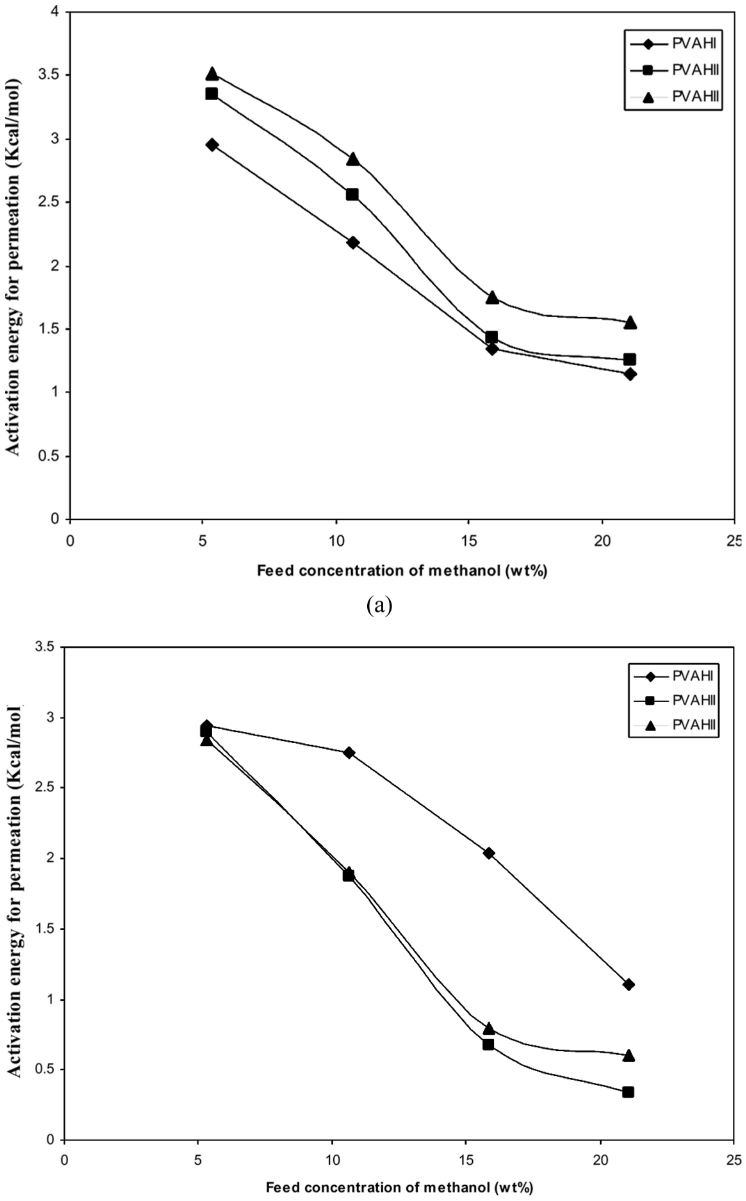
Permeation ratio gives a quantitative idea about the effect of one component on the permeation rate of the other component. Huang and Lin (18) has defined this permeation ratio, θ, as a measure of the deviation of the actual permeation rate, J_{expt}, from the ideal rate, J^0, to explain interactions between membrane polymer and permeants. Thus,

$$\theta_i = -\frac{J_{i\ \text{expt at}\ x\ \text{conc.}}}{J^0_{i\ \text{expt at}\ x\ \text{conc.}}} \tag{5}$$

$$J^0_{i\ (\text{at}\ x\ \text{conc.})} = J^0_{(\text{pure i})} \times x_i \tag{6}$$

where i denote 'ith' component in the binary mixture, x is the weight fraction in feed mixture, superscript 0, denotes ideal permeation.

From Fig. 8a it is observed that at very low concentration of methanol i.e., at very high concentration of MTBE (around 99 wt% or more) in feed, the permeation factor of methanol is far above unity for



(a)

(b)

Figure 6. (a) Vavariation of activation energy of methanol with its feed concentration; (b) Variation of activation energy of MTBE with feed concentration of methanol. ◆ PVAHI; ■ PVAHII; ▲ PVAHIII.

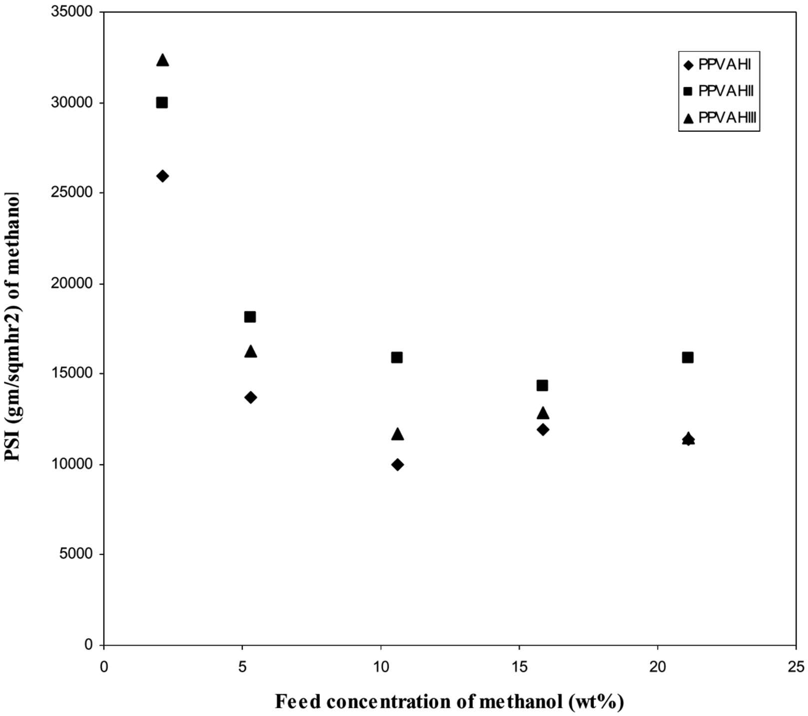


Figure 7. Variation of PSI of methanol with its feed concentration at 24°C. ◆ PVAHI; ■ PVAHII; ▲ PVAHIII

all the membranes signifying a positive coupling effect of MTBE on methanol flux. In this case MTBE-methanol interaction is more than methanol-membrane interaction. As the methanol % in feed increases to around 5 wt%, permeation factor of methanol decreases drastically for all the methanol selective membranes and becomes close to unity i.e., the coupling effect of MTBE on methanol becomes negligible because of much higher methanol-membrane interaction (through hydrogen bonding) than MTBE-methanol interaction. Figure 8b shows the effect of methanol concentration in feed on the permeation factor of MTBE. It is observed that at very low methanol concentration in feed the permeation factor of MTBE is much higher that that of methanol as seen in Fig. 8a. However, with an increase in the feed concentration of methanol, the permeation factor of MTBE decreases at a much higher rate and approaches unity. In the highly methanol selective membranes, above 5 wt% feed concentration of methanol the MTBE flux is hardly influenced by methanol.

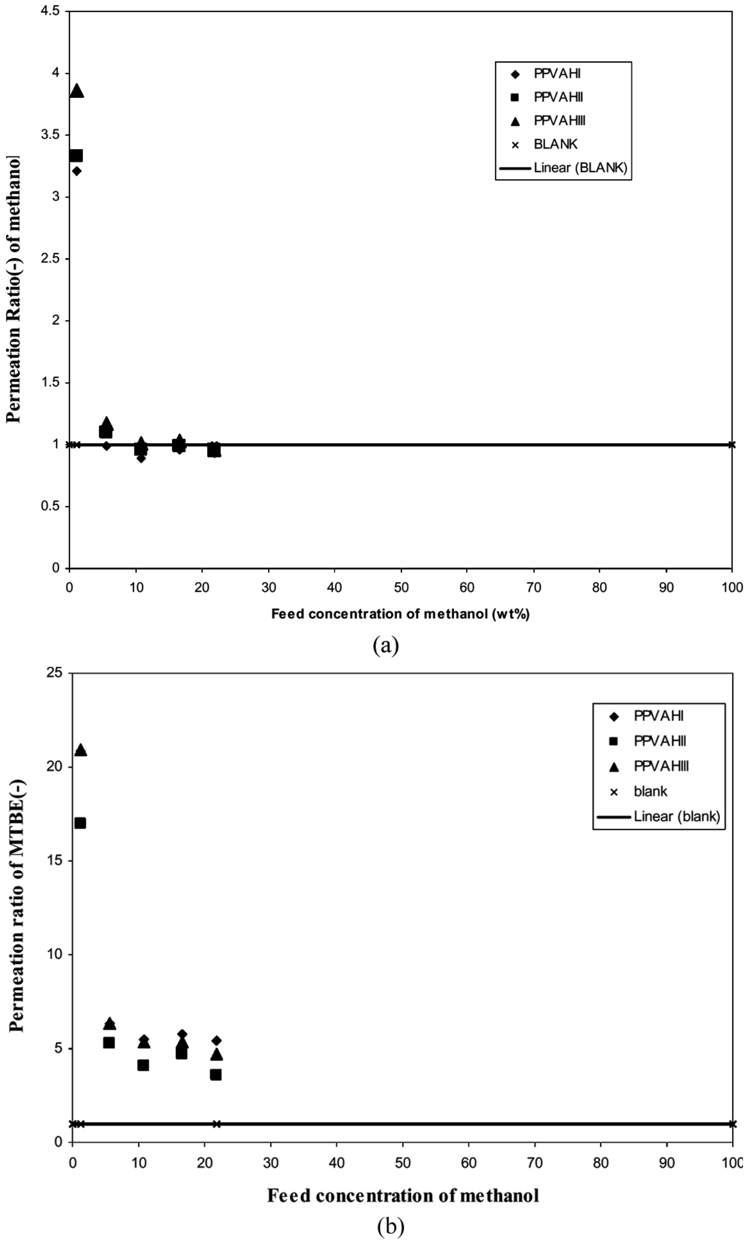


Figure 8. (a) Variation of Permeation ratio of methanol with its feed concentration at 24°C; (b) Variation of Permeation ratio of MTBE with feed concentration of methanol at 24°C. ◆ PVAHI; ■ PVAHII; ▲ PVAHIII.

Table 2. Comparison of performance of various membranes reported for pervaporative separation of methanol-MTBE mixtures

Polymer	Methanol in the feed (wt%)	Temperature of experiment (°)C	Normalized flux (kg μm/m^{2}hr)	Selectivity	ref.
PPO-OH	21	22	18.4	90	19
PAAPVA	20	35	12.2	45	20
CA	20	50	7.5	16	21
PANHEMA	15	30	0.115	2561	22
PVP/alumina	30	20	3.0	10	23
CS	20	25	8.0	200	24
PVAHII	15.87	24	16.066	51.2	Present work
PVAHIII	15.87	24	17.300	43.0	Present work

CONCLUSION

The matrix of polyvinyl alcohol(PVOH) membrane was chemically modified by copolymerizing acrylic acid with HEMA (polyAH) in aqueous solution of PVOH with three different weight ratios of PVOH: polyAH to form three full interpenetrating network(IPN) crosslink polymers i.e., PVAHI, PVAHII, and PVAHIII. The PVAH membranes were characterized with, FTIR, DSC, TGA, XRD, and mechanical properties. With the incorporation of polyAH, the PVAH membranes becomes stiff with lower elongation at break and less tensile strengths. All the membranes show measurable flux and separation factor for methanol. Among the three membranes, PVAHII with 50 wt% polyAH incorporation shows optimum performance in terms of flux and selectivity. PVAHIII membrane shows highest flux but lower methanol selectivity. Table 2 shows a comparison of the relative performances of various membranes reported for the separation of methanol-MTBE mixtures. From this table it is observed, that these PVAH membranes show significant improvement in flux and selectivity when compared to various membranes reported for this separation.

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