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Synthesis of Chemically Modified Polyvinyl Alcohol Membranes for Dehydration of Dioxane by Pervaporation

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Abstract: Polyvinyl alcohol (PVOH) has been chemically modified by polymerizing hydroxyethylmethacrylate (HEMA) in aqueous solution of PVOH and finally crosslinking PVOH with glutaraldehyde to produce a semi-interpenetrating network (SIPN) membrane. Accordingly, three such SIPNs i.e., SIPNI, SIPNII, and SIPNIII were synthesized with different weight ratio of PVOH: HEMA i.e., 1:0.25 (SIPNI), 1:0.50 (SIPNII) and 1:0.75 (SIPNIII). These SIPN membranes were used for pervaporative dehydration of dioxane. PVOH without any chemical modification but crosslinked with the same amount of glutaraldehyde has also been used for this study for comparison. All the SIPN membranes were also characterized with various conventional methods like mechanical properties, DSC and TGA. Water permeability and water selectivity of the IPN membranes were found to be much higher than those of the crosslinked PVOH membrane which was not chemically modified. The permeability of the membranes were also found to increase with increase in the HEMA content in PVOH matrix.

Keywords: Pervaporation, dehydration, polyvinyl alcohol, semi-IPN

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INTRODUCTION

Separation of liquid mixtures by Pervaporation (PV) is used for dehydration of organics, removal of traces of organics, and organic-organic separations using mainly synthetic polymeric membranes. Among these polymeric membranes, hydrophilic membranes with good mechanical strength was commercially made (1) from Polyvinyl alcohol (PVOH). Uncrosslinked PVOH (whether fully or partially hydrolized) is soluble in water and thus, it is chemically crosslinked to get a suitable PV membrane. It may be crosslinked with any aldehyde or ketone at a certain pH or with any mono or polycarboxylic acid (2).

Yamada et al. (3) crosslinked PVOH with glutaraldehyde and formaldehyde and used it for ethanol-water separation. Polyamic acid was used by Huang and Yeom, (4) as a crosslinker for PVOH for use in ethanol/water separation. The problem with the PVOH membrane is its low permeability because of its high degree of crystallinity (5) which along with crosslinking reduces water permeability. The water permeability of the PVOH membrane can be increased by reducing its crystallinity which needs chemical modification of the PVOH membrane matrix. To increase the hydrophilicity the of the PVOH membrane by chemical modification, maleic anhydride/methyl methacrylate was grafted to these membranes and used for ethanol dehydration (6). In another study Kang et al. (7) modified the membrane surface of the crosslinked PVOH by chemical reaction with monochloroacetic acid. However, surface modification or grafting is not sufficient to reduce the crystallinity of PVOH. Further, a useful chemical modification should not only reduce the crystallinity of PVOH but it will also enhance its permeability without affecting its selectivity. Hence, in the present work the PVOH membrane has been chemically modified by polymerizing hydroxyethyl methacrylate (HEMA) in the matrix of PVOH and finally crosslinking the chemically modified PVOH with glutaraldehyde to produce an interpenetrating network (IPN) hydrophilic membrane. This kind of IPN is called semi IPN (SIPN) as in this case only one polymer of the IPN i.e., only PVOH is crosslinked (8). Thus, three SIPNs with varied weight ratios of HEMA to PVOH i.e., SIPNI (PVOH:HEMA = 1:0.25), SIPNII (PVOH:HEMA =1: 0.50), and SIPNHI (PVOH:HEMA = 1:0.75) were synthesized. The objective of this synthesis was not only to reduce the level of cystallinity of the PVOH matrix but also to enhance its hydrophilicidity by incorporating this highly hydrophilic PolyHEMA polymer in its structure. The homopolymer of HEMA i.e., polyHEMA is widely used as a hydrogel (9) after crooslinking but it can not be used as a hydrophilic membrane for PV because of its very poor mechanical integrity. Thus, in our previous works HEMA has been copolymerized with various other polymerizable monomers like acrylonitrile (AN) or acrylamide (AM)

(10,11) for better mechanical strength. However, the homopolymer of AM or AN possess a very high glass transition temperature and thus its copolymer with HEMA is not as flexible as PVOH. Crooslinked PVOH is a commercially successful PV membrane (1) because of its flexibility as well as its high tensile strength. Thus, in the present work, HEMA has been allowed to polymerize in the matrix of PVOH followed by crosslinking of PVOH with glutaraldehyde to produce a semi interpenetrating network (SIPN) polymer. The membrane made from this polymer possesses the mechanical integrity of PVOH along with added hydrophilicity due to the presence of polyHEMA in its matrix. The membranes, thus, prepared is expected to be useful for pervaporative dehydration of various organics with high concentration (>80 wt% in water) in water. Dehydration of dioxane by peraporation has been reported (12,13,14) by many authors because of its industrial importance. The SIPN membranes of PVOH was thus used for pervaporative dehydration of dioxane over the entire concentration range of 80–100 wt% dioxane in water.

EXPERIMENTAL

Materials

High purity analytical grade dioxane used for this study was purchased from E Marck, Mumbai. The monomer i.e., hydroxyethylmethacrylate (HEMA) was of synthesis grade and kindly given by Macromol Pvt. Ltd,, Kolkata. It was used as obtained without any purification. Ammonium persulfate and sodium metabisulfide were used as a redox initiator pair for the copolymerization reaction. Polyvinyl alohol (PVOH) with weight average molecular weight 1,25,000 and degree of hydrolysis 98–99% was obtained from S.D. Fine Chemicals, Mumbai. This was also used as obtained.

Synthesis of PVOH – PolyHEMA Semi IPN

Synthesis of PVOH – PolyHEMA SEMI IPN with three different weight ratios of HEMA:PVOH i.e., 0.25:1, 0.50:1, and 0.75: 1, termed as SIPNI, SIPNII, and SIPNIII, respectively, was carried out by solution polymerization in a three-necked reactor at 60°C for 3 hrs using ammonium persulfate and sodium metabisulfide (each, 0.5 wt% of the total monomer weight) as redox pair of initiators. The reactor was fitted with a stirrer, a thermometer pocket, and a condenser. At first around 5 wt% PVOH solution was made 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 HEMA was then added and the reaction mixture was added to the three neck flask placed on a constant temperature bath. The temperature was raised to 60°C and the aqueous solution of the initiators was 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 polyHEMA if any (which is soluble in ethanol), from the reaction mixtures. The polymer was dried at ambient temperature in a vacuum oven and redissolved in water.

Croslinking and Casting of Membranes from Semi-IPN (SIPN)

The aqueous solution (~5 wt%) of the resulting SIPN 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) (15). Thus, for 2 wt% crosslinking of PVOH, the aqueous SIPN 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 SIPN 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 hrs under vacuum. Subsequently, the membrane was annealed at 80 C for an additional 6 hrs under vacuum. The membrane thickness for the SIPN polymer was maintained at ~50 μm. The thickness was measured by Test Method ASTM D 374 using a standard dead weight thickness gauge (Baker, Type J17).

Membrane Characterization

Mechanical Strength

The tensile strength (T.S.) and elongation at break (E.A.B.) of the polymer film was determined by an Instron-Tensile tester (Instron 4301, Instron Limited, 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 the 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 semi IPN 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.

Swelling Study

Sorption Experiment

Membranes of known weights were immersed in different known concentrations of aqueous dioxane solutions and were allowed to equilibrate for 96 hours at 30°C. Each sample was weighed periodically until no weight change was observed. These membranes were taken out from the solutions and weighed after the superfluous liquid was wiped out with tissue paper. The increment in weight is equal to the total weight of water and organic solvents sorbed by the membrane. After measuring the total weight of the sorbed membranes from the above experiment, these thick samples were taken in a 250 ml conical flask kept in a constant temperature bath, and connected to a cold trap and vacuum pump in series (Fig. 1). The cold trap was immersed in a liquid nitrogen flask. The sorbed sample was heated under vacuum and the vapor coming out of the thick sorbed membranes were freezed and collected in the cold trap immersed in liquid nitrogen. The amount of toluene sorbed by the membranes were obtained by analyzing the composition of the liquefied vapor from the cold trap by an Abbe type Refractometer (model no. AR600, MISCO, USA) at 25°C temperatures for all the samples. From the total sorption weight and corresponding dioxane content (weight) of the membrane, the sorption selectivity of the membrane for water was calculated from the following equation

$$\alpha_S = \frac{\frac{y_{mWater}}{y_{mDioxane}}}{\frac{X_{FWater}}{X_{FDioxane}}} \quad (1)$$

Here Yi and Xi denotes membrane phase and feed concentration of "I" component.

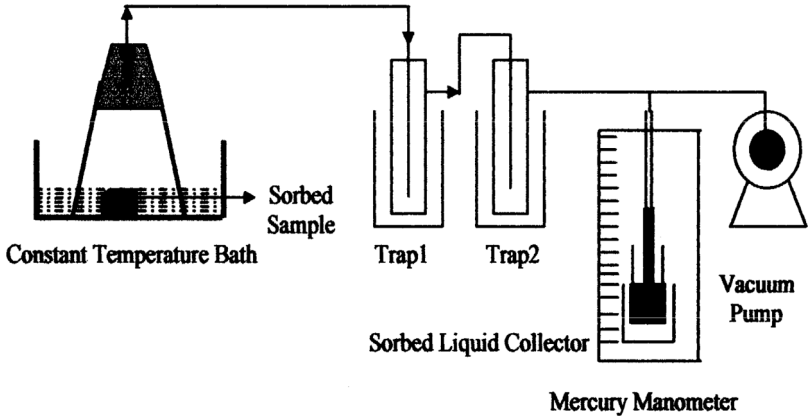


Figure 1. Experimental set up for sorption selectivity.

Permeation Study

Pervaporation Experiment

Pervaporation experiments were carried out in a batch stirred cell (10) 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. The 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-water 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 (A) of the membrane from equation-2.

$$J = \frac{W}{At} \tag{2}$$

The PV experiment was performed at a constant temperature by circulating constant temperature water around the jacket of the PV cell. The water 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. The permeation selectivity (α_{pv}) of water expressed as separation factor for water was calculated from a similar type of equation as sorption selectivity i.e., equation-3 as given below.

$$\alpha_{PV} = \frac{\frac{y_{water}}{y_{Dioxane}}}{\frac{x_{water}}{x_{Dioxane}}} \quad (3)$$

Here y_i and x_i are the weight fraction of component i (water) in membrane and feed, respectively. The performance of the membrane was also evaluated in terms of permeation separation index (PSI) as obtained from the following equation-4.

$$PSI = J_W(\alpha_{PV} - 1) \quad (4)$$

Here J_w is water flux.

RESULTS AND DISCUSSION

Membrane Synthesis

The objective of chemically modifying the PVOH matrix with HEMA was two-fold. By incorporation of HEMA in the PVOH matrix, the crystallinity of PVOH would be reduced to give enhanced water permeability. Further, the highly hydrophilic PolyHEMA would give added hydrophilicity to the modified PVOH membranes. After homopolymerization of HEMA within the matrix of PVOH, the latter is crosslinked with glutaraldehyde to produce a semi interpenetrating network polymer (SIPN). Accordingly, in this present work three SIPN membranes were synthesized with an increasing amount of HEMA in PVOH matrix. The crosslinking of the PVOH matrix was fixed at 2 mol% and not increased as it would give decreased permeability. In fact, an increase in crosslinking density gives higher selectivity with reduced flux. Thus, for most of the crosslinkable polymeric membranes, the crosslink density is varied to obtain a value which would give optimum flux and selectivity. However, for a crystalline polymer like PVOH, its crystallinity acts like crosslining and even the uncrosslinked PVOH can be used for pervaporative dehydration of an organic component with more than 99 wt% concentration in water. 2 mol% crosslinking of PVOH produces a membrane which remains intact even after 48 hour of dipping in pure water (unlike uncrosslinked PVOH which becomes soluble in pure water) and thus can be used for PV dehydration of an organic component with lower concentration in water unlike the uncrossinked PVOH membrane.

Membrane Characterization

Mechanical Strength

For a good pervaporation polymeric membrane, there should be a good balance between the tensile strength (T.S.) and elongation at break (E.A.B). The T.S and EAB of the PVOH membrane is changed as it is chemically modified with HEMA. HEMA being a very soft and low T_g polymer, reduces the T.S. of PVOH while EAB is increased with increasing amount of HEMA from SIPNI to SIPNIII. The values of T.S., E.A.B, and T_g (as obtained from DSC) is given in Table 1.

Membrane Characterization by DSC

DSC curves of polyvinyl alcohol (PVOH) and the three SIPN membranes are shown in Figs. 2a–d respectively. From the DSC it is observed that the second order transition temperature or Tg decreases in the following order PVOH(102°C) > SIPNI(98°C) > SIPNII(96°C) >SIPNIII(92°C). Similarly the first order transition temperature i.e., melting peak also decreases in the same order i.e., PVOH(331°C)>SIPNI(314°C)> SIPNII(263°C) >SIPNIII (257°C). The chemical modification of the PVOH matrix by forming an IPN with HEMA influences both of these glass transition (T_g) temperature and melting temperature. Incorporation of HEMA in the matrix of PVOH reduces its crystallinity and hence decreases both T_g and melting peak. As the amount of HEMA increases from SIPNI to SIPNIII, both of these transition temperatures decrease.

Membrane Characterization by Thermogravimetric Analysis (TGA)

The TGA of PVOH and the three IPN membranes are shown in Figs. 3a–d., respectively. All of these membranes exhibit two major weight loss regions

Table 1. Properties of the membranes

Name of the polymer	Tensile strength (kg/mm2)	Elongation at break (%)	Glass transition temperature T_g (°C)
PVOH	8.21	215	102
SIPNI	6.23	224	98
SIPNII	5.77	275	96
SIPNIII	4.21	304	92

with an onset of maximum weight loss at its melting temperature i.e., at around 200°C which continues up to around 425°C. The weight losses of these SIPN polymers in different temperature regions are associated with the splitting of the main chain and the final decomposition of the polymer.

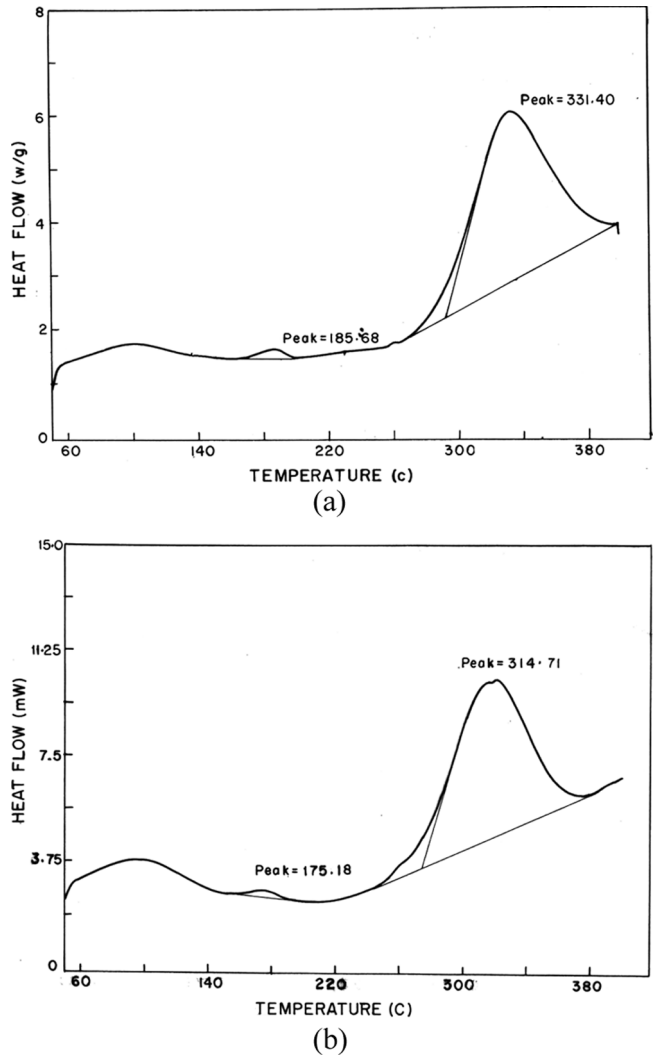
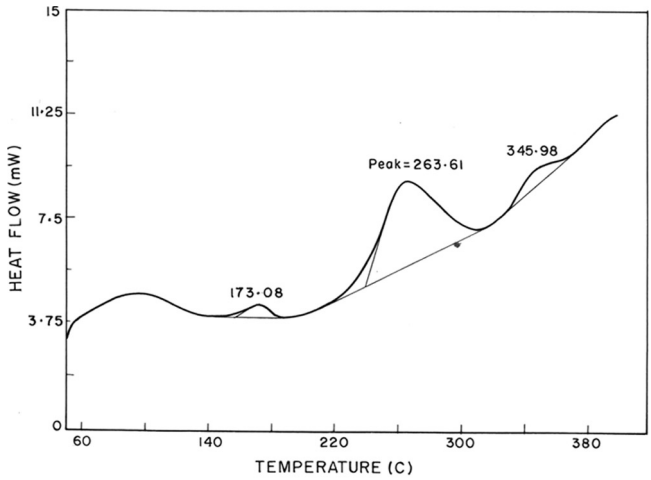


Figure 2. DSC of the membranes. (a) DSC of PVOH; (b) DSC of SIPNI; (c) DSC of SIPNII; (d) DSC of SIPNII.



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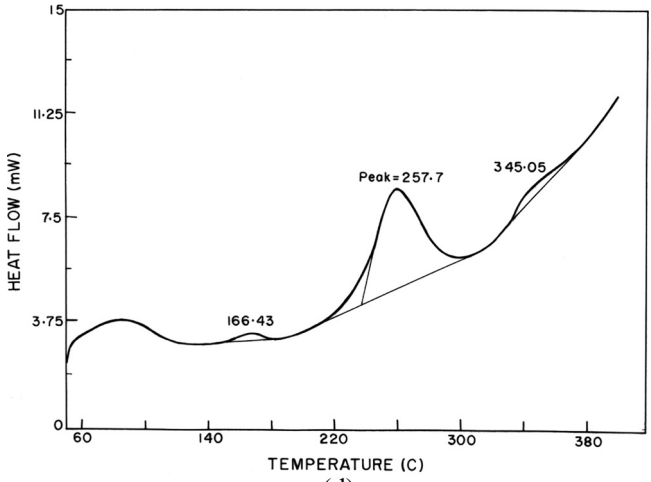


(d)

Figure 2. Continued.

Swelling Studies

Effect of Feed Concentration on Sorption Isotherms

Figure 4a shows the variation of the total sorption of dioxane and water of PVOH and the three chemically modified PVOH membranes i.e., SIPNI, SIPNII, and SIPNIII with a feed concentration of water at 25°C. Similar kind of trend lines were also observed at the other two

temperature of sorption experiments i.e., at 40 and 50°C. From this figure it is found that the total sorption increases initially up to 15 wt% water in feed almost linearly in the following order: SIPNIII > SIPNII > SIPNI > PVOH. The increase in the total sorption with increase in feed concentration of water may be attributed to increased hydrophilicity of the chemically modified PVOH membranes. As the wt% of HEMA

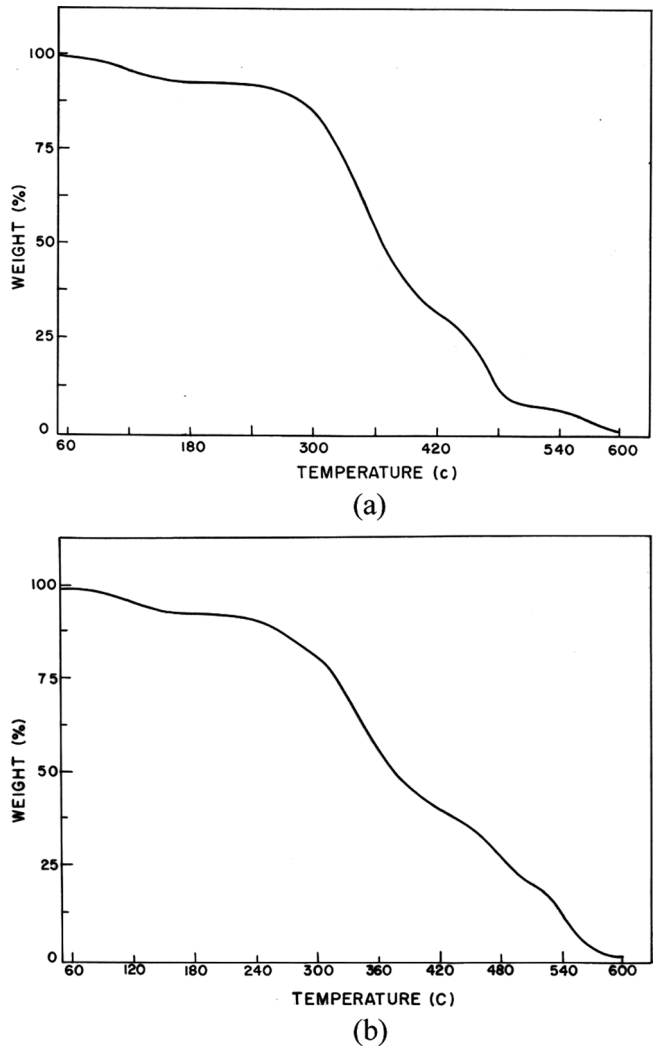
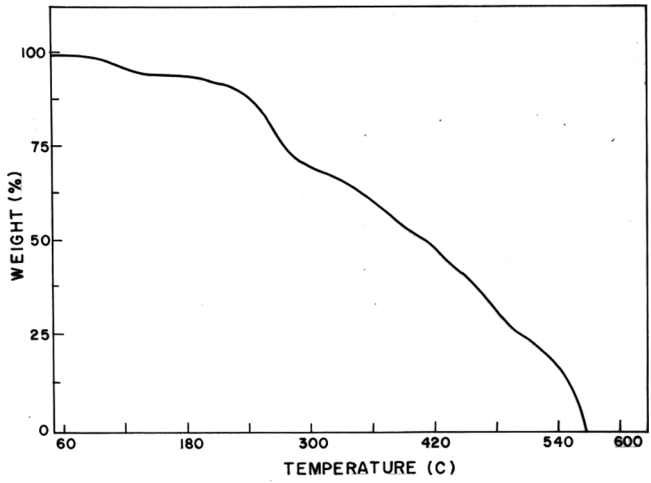


Figure 3. TGA of the membranes; (a) DSC of PVOH; (b) DSC of SIPNI; (c) DSC of SIPNII; (d) DSC of SIPNII.



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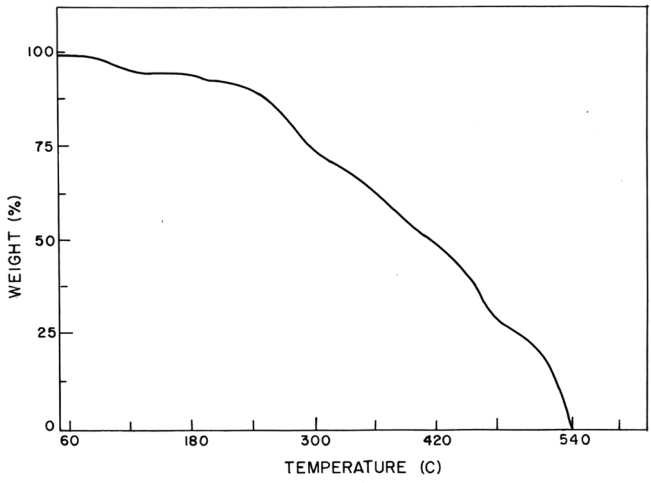
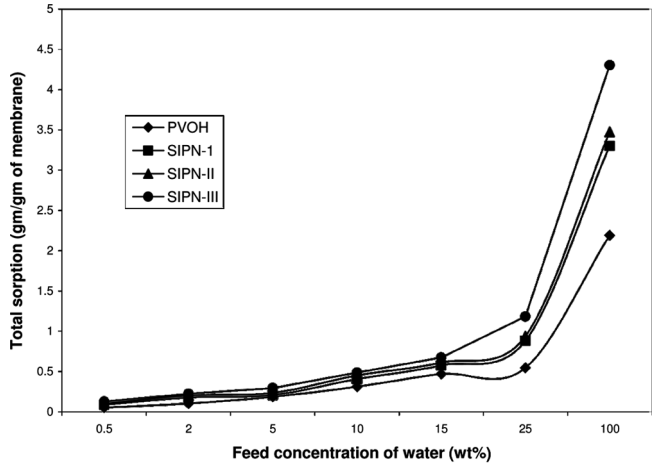


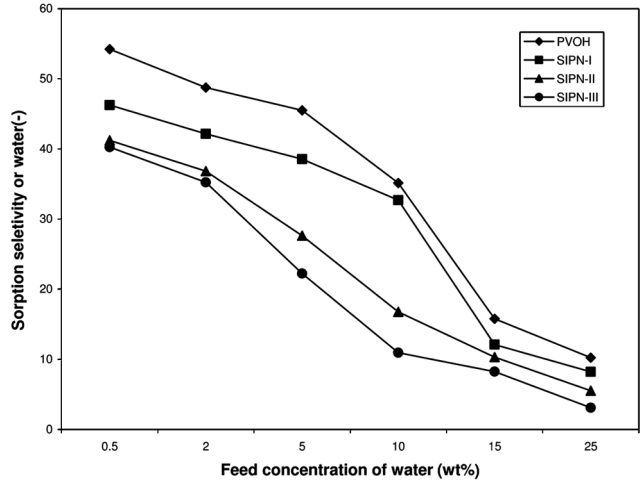
(d)

Figure 3. Continued.

increases from SIPNI to SIPNIII, the total sorption increases due to increasing extent of hydrophilicity in the membranes. All the SIPN membranes also show much higher sorption than the chemically unmodified PVOH membrane at a higher feed concentration of water because of increased water-membrane interaction through extensive hydrogen bonding between water and the hydroxyl groups of membranes. It is also observed that at a lower range of feed concentration (up to around



(a)



(b)

Figure 4. (a) Sorption isotherm at 25°C. ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII; (b) Sorption selectivity of water and feed concentration at 25°C; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII.

5 wt%) of water, the sorption isotherm of all the membranes are very close to one another; however, at a higher feed concentration of water the difference in the total sorption for these membranes are quite high and above 15 wt% water in feed the increment is extensive showing an exponential trend. In the higher concentration range, the hydrophilic membranes swell too much to maintain its integrity. It is also evident from the figures that

these sorption isotherms closely resemble Rogers Type-III sorption (16). The drastic increase of sorption above 15 wt% water in feed as shown in the figure may be ascribed to the mutual interaction of the sorped particles which is greater than their interaction with the membrane polymer and these sorped particles form a cluster within the polymer matrix.

Feed Concentration and Sorption Selectivity

From Fig. 4b it is observed that the sorption selectivity of water for all the membranes decreases almost exponentially with increase in the feed concentration of water. It is also observed that for all the membranes with increase in feed concentration of water, the sorption selectivity decreases in the following order: PVOH > SIPNI > SIPNII > SIPNIII.

In comparison to the total sorption the opposite trend in sorption selectivity is due to loss in crystalline symmetry of the chemically modified PVOH membranes. The incorporation of HEMA in PVOH matrix enhances the hydrophilicity but reduces the crystallinity of PVOH matrix and hence increases the sorption of both water and dioxane. Thus, the SIPN membranes show lower sorption selectivity. However, at a higher feed concentration of water i.e above 15 wt% of water in feed, the sorption selectivity of all the membranes including PVOH drastically decreases due to extensive plastiization of these membranes by water.

Effect of Feed Temperature on Total Sorption and Selectivity

Figure 5a and b shows the effect of temperature on total sorption and sorption selectivity respectively, for the four different membranes i.e., PVOH, SIPNI, SIPNII, SIPNIII at 5 wt% of dioxane in water. From these figures it is observed that with increase in temperature the total sorption increases almost linearly from PVOH to SIPNIII(PVOH < SIPNI < SIPNII < SIPNIII) while the sorption selectivity decreases in the opposite order.

Pervaporation (PV) Studies

Effect of Feed Concentration on Dehydration

Figure 6a shows the variation of wt% of water in permeate against wt% of water in feed for dehydration of dioxane with PVOH and the three SIPN membranes at 30°C. Similar kind of relationships were observed

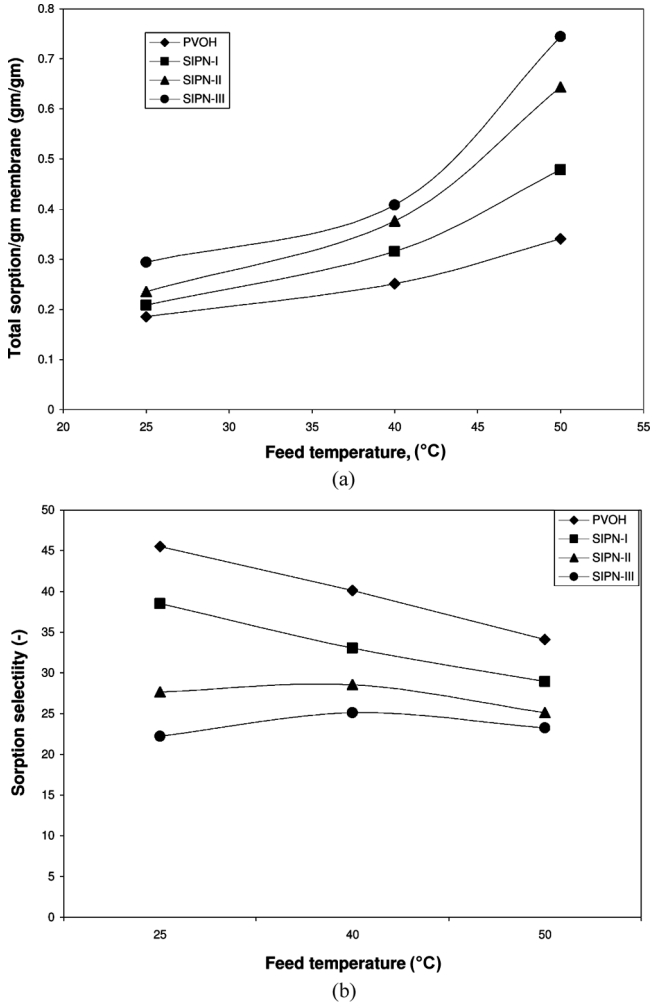
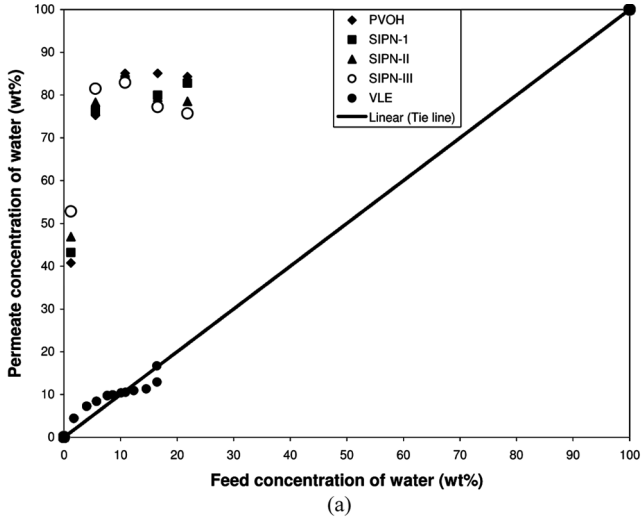
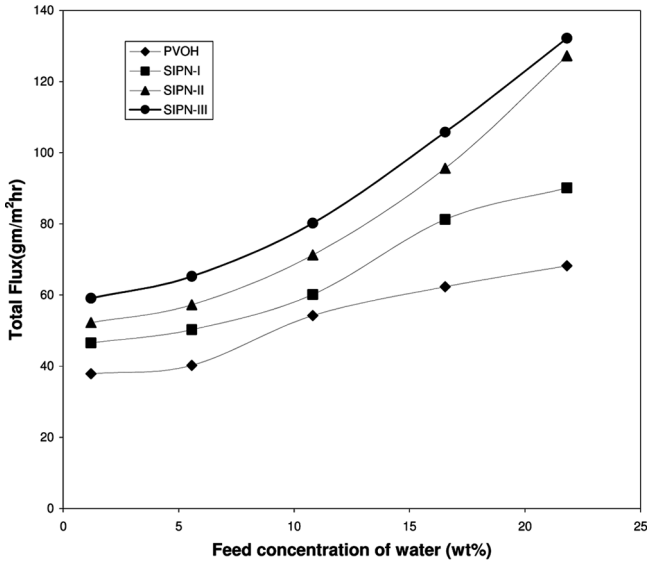


Figure 5. (a) Total sorption and Feed temperature. Feed concentration 5 wt% water; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII; (b) Sorption selectivity of water and feed temperature. Feed concentration 5 wt% water; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII.

at the two other PV temperatures i.e., at 40 and 50°C. The atmospheric vapor-liquid equilibrium (VLE) data of the dioxane-water binary system is also given for comparison. It appears from these McCabe-Thiele type xy diagrams that all the membranes show measurable dehydration characteristics over the entire concentration range without any pervaporative

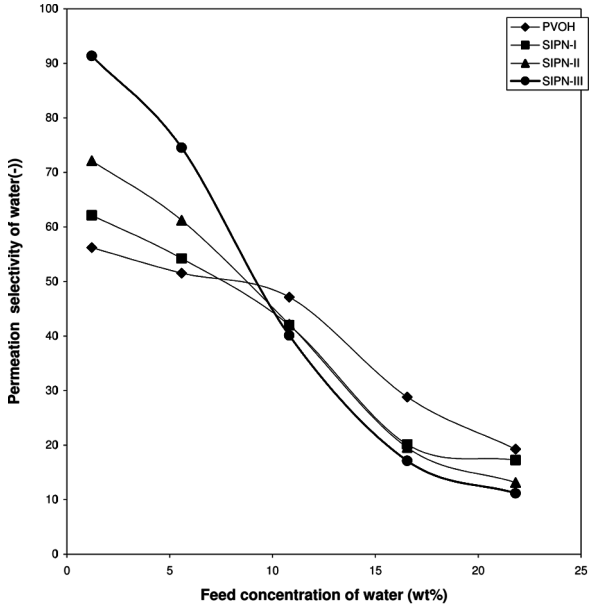


(a)



(b)

Figure 6. (a) Feed concentration and total Flux at 30°C; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII; (b) Feed concentration and water selectivity at 30°C; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII; (c) Variation of permeate concentration of water with its feed concentration at 30°C; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII; (d) Variation of permeate selectivity of water with feed temperature. Feed concentration 5.5 wt%. Water; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII.



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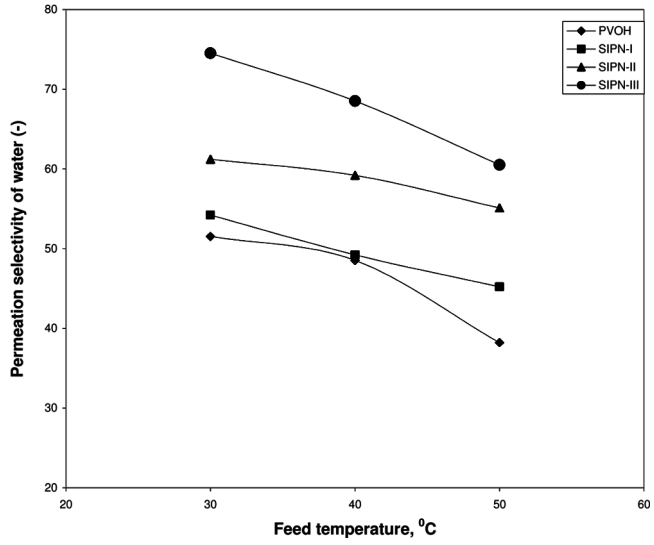


(d)

Figure 6. Continued.

azeotrope. The VLE data for the water-dioxane system show that the separation of dioxane-water by conventional distillation yields azeotrope points and for the same feed concentration of water PV separation by all the membranes are much higher than its separation by distillation. It is also observed from the figure that at low water% in feed (up to 10 wt% water) SIPNIII shows maximum water dehydration and for the same feed concentration, it decreases in the following order:

SIPNIII > SIPNII > SIPNI > PVOH.

Incorporation of HEMA reduces intramolecular hydrogen bonding of PVOH in SIPN and adds to increase the number of hydroxyl groups (OH) available for preferential hydrogen bonding with water. Thus, SIPNIII with the maximum number of such OH groups shows maximum dehydration or water selectivity. However, at around 10 wt% feed concentration of water, the highly hydrophilic SIPN membranes become plasticized and water selectivity of SIPN membranes decreases at a much higher rate than water selectivity of PVOH membrane. Thus, the selectivity order changes in the above order.

Effect of Feed Concentration on Flux

The effect of feed concentration of water on total flux at 30°C is shown in Fig. 6b for PVOH and the three SIPN membranes. Similar kind of trend lines were also observed at the other two temperatures of PV experiments i.e., at 40 and 50°C. From this figure it is observed that with increase in feed concentration of water the total flux increases almost linearly signifying the hydrophilicity of the membranes. Like total sorption, it is also seen that for the same feed concentration the flux shows the following trend SIPNIII > SIPNII > SIPNI ≫ PVOH. The lowest flux of PVOH may be ascribed to its crystallinity which comes from extensive intramolecular hydrogen bonding in its structure. Incorporation of HEMA increases the hydrophilicity as well as void space in SIPN membranes because of loss in crystallinity. Thus, the flux increases from SIPNI to SIPNIII with an increasing amount of HEMA.

Effect of Feed Concentration and Temperature on Permeation Selectivity

Permeation selectivity of all the membranes (Fig. 6c) for water decreases almost exponentially with feed concentration and up to 10 wt% water in feed permeation selectivity decreases from SIPNIII to PVOH due to an increasing extent of preferential hydrogen bonding in the same order.

At a higher feed concentration of water i.e., above 15 wt% water the decrease in selectivity is more drastic and for the same feed concentration the order becomes reverse i.e., it decreases from PVOH to SIPNIII. At higher feed concentration of water the SIPN membranes with higher amount of HEMA become more plasticized allowing the permeation of both dioxane and water. The effect of temperature on water selectivity is similar i.e it also decreases from SIPNIII to PVOH as shown for all the membranes in Fig. 6d for 5.5 wt% water in feed.

Permeation Selectivity versus Sorption Selectivity

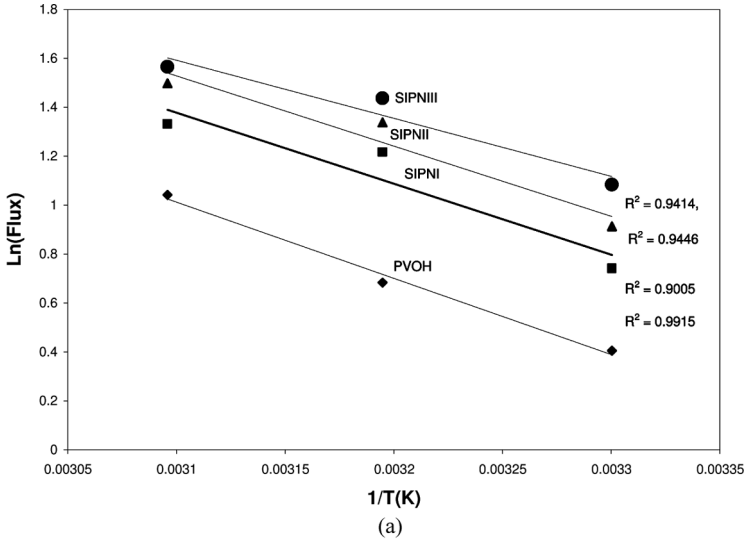
The much higher permeation selectivity (Fig. 6c) in comparison to sorption selectivity (Fig. 4b) is due to a higher diffusion rate of water than dioxane. The kinetic diameter (>0.65 nm) of dioxane (17,18) is greater than that of water (0.265 nm). Thus, the diffusion rate of dioxane through the membranes is much slower. Hence, for any feed concentration, the permeation selectivity of water is increased to a great extent due to a higher diffusion rate of water.

Activation Energy For Permeation of the Membranes

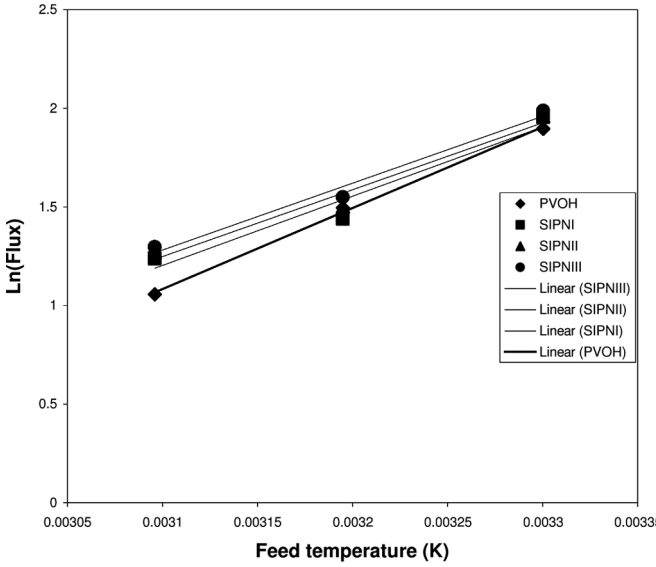
With increase in temperature flux increases linearly for all the membranes. The activation energy for permeation (Ep) can be obtained from the slope of the Arrhenius type linear plot of logarithmic of flux (Q) against inverse of absolute temperature (1/T) from the following equation

$$\ln Q = \ln A - \left(\frac{E_P}{RT}\right) \tag{5}$$

Here 'A' is a preexponential factor and 'R' is universal gas constant. Thus, the activation energy for permeation of water and dioxane could be calculated at several feed concentrations from similar plots. Water and dioxane flux at a particular feed concentration is calculated by multiplying the total flux with permeate concentration of water or dioxane (in wt%) at that concentration. Accordingly, in Figs. 7a and 7b an Arrhenius type plot of logarithmic of water flux (Fig. 7a) and dioxane flux (Fig. 7b) against the inverse of the absolute temperature are given for 5.5 wt% feed concentration of water. From these figures it is observed that all the polymers show linear plot with regression coefficient >0.9 and activation energy for permeation for both water and dioxane (Table 2) increases in the following order PVOH > SIPNI > SIPNII > SIPNIII.



(a)



(b)

Figure 7. (a) Arrhenious Plot for activation energy of water at 5.5 wt% feed concentration of water; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII; (b) Arrhenius plot for activation energy of dioxane for permeation at 5.5 wt% water in feed; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII.

Table 2. Activation energy of permeation with 5.5 wt% feed concentration

Name of the polymer	Activation energy for permeation of water. kcal/mol	Activation energy for permeation of dioxane. KCal/mol
PVOH	6.222	8.204
SIPNI	5.813	7.026
SIPNII	5.751	6.778
SIPNIII	4.746	6.774

SIPNIII containing maximum of HEMA needs minimum energy for permeation and as the extent of crystallinity of PVOH increases from SIPNIII to PVOH, the activation energy for permeation increases. The values of the activation energies of water and dioxane permeation for all the used polymeric membranes at 5.5 wt% feed concentration of water is given in Table 2.

Effect of Feed Concentration on PSI

Figure 8 shows a variation of PSI for water with feed concentration of water. The separation potential of a membrane is expressed in terms of permeability and selectivity which usually take place in the opposite way, i.e., when one factor increases the other decreases. PSI combines both permeability and selectivity in one equation (equation-4) which is found to be maximum at around 5 wt% feed concentration of water for all the membranes signifying optimum flux and selectivity at this concentration. Above this concentration PSI decreases almost linearly with feed concentration. Among the various membranes, SIPNIII shows maximum PSI which decreases from SIPNIII to PVOH.

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 (19) has defined this permeation ratio, θ, as a measure of the deviation of the actual permeation rate, J_{expt}, from the ideal rate, J°, to explain interactions between the membrane polymer and the permeants. Thus,

$$\theta_i = -\frac{\mathbf{J}_{\text{i expt at x conc.}}}{\mathbf{J}^{0}_{\text{i expt at x conc.}}} \tag{6}$$

$$J^0_{i(\text{at x conc.})} = J^0_{(\text{pure i})} \times x_i \quad (7)$$

Where i denote 'ith' component in the binary mixture, x is the weight fraction in the feed mixture, superscript 0 denotes ideal permeation. From Fig. 9a it is observed that at very low concentration of water i.e., at very high concentration of dioxane (around 99 wt% or more) in feed, the permeation factor of water is far above unity for all the membranes signifying a positive coupling effect of dioxane on water flux. In this case the dioxane-water interaction is more than the water-membrane interaction. As the water% in feed increases to around 5 wt%, the permeation factor of water decreases drastically for all the hydrophilic membranes and becomes close to unity, i.e the coupling effect of dioxane on water becomes negligible because of much higher water-membrane interaction (through hydrogen bonding) than dioxane-water interaction. Figure 9b shows the effect of water concentration in feed on permeation factor of dioxane. It is observed that at very low water concentration in the feed permeation factor of dioxane is much higher that that of water as seen in Fig. 9a. However, with increase in feed concentration of the water permeation factor decreases at a much higher rate and approaches unity. In the

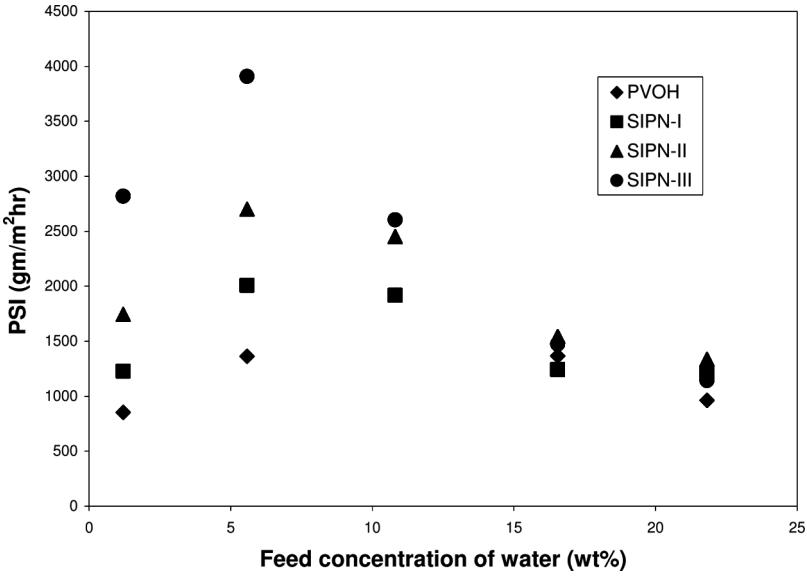
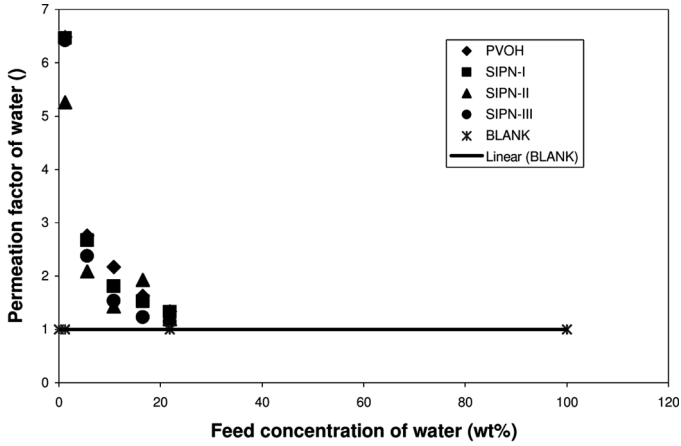
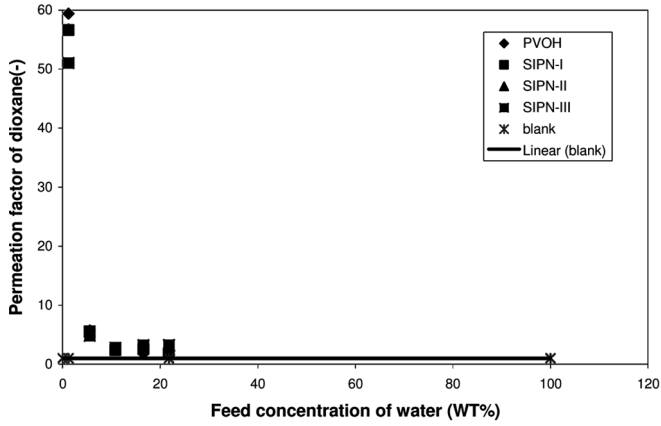


Figure 8. Feed concentration and PSI at 30°C; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII.



(a)



(b)

Figure 9. (a) Feed concentration and permeation factor of water; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII; (b) Feed concentration of water and permeation factor of DIOXANE; ◆ PVOH; ■ SIPNI; ▲ SIPNII; ● SIPNIII.

highly hydrophilic membranes, above 5wt% feed concentration of water, the dioxane flux is hardly influenced by water.

CONCLUSION

PVOH membrane was chemically modified with HEMA by polymerizing the latter in its matrix to form three semi IPN(SIPN). The membranes

were characterized by comparative DSC, TGA, and mechanical properties. With incorporation of HEMA, the SIPN membranes become softer with higher elongation at break, less tensile strength, and glass transition temperatures. In comparison to the chemically unmodified PVOH membrane, the SIPN membranes were found to show much better performance in terms of flux and selectivity for dehydration of dioxane. Among the SIPN membranes, SIPNIII with 75 wt% HEMA shows maximum flux and selectivity. However, selectivity decreases more drastically for this membrane with an increasing feed concentration of water.

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