

# Dehydration of Tetrahydrofuran by Pervaporation Using Crosslinked PVA/PEI Blend Membranes

P. Srinivasa Rao,<sup>1</sup> S. Sridhar,<sup>2</sup> A. Krishnaiah<sup>1</sup>

<sup>1</sup>Biopolymers and Thermophysical Laboratories, Department of Chemistry, Sri Venkateswara University, Tirupati 517502, India

<sup>2</sup>Membrane Separations Group, Chemical Engineering Division, Indian Institute of Chemical Technology, Hyderabad 500007, India

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**ABSTRACT:** Dense blend membranes were prepared by blending hydrophilic polymers poly(vinyl alcohol) (PVA) and poly(ethyleneimine) (PEI), which were then crosslinked by glutaraldehyde (GA) in a mixture of solvents under the catalysis of hydrochloric acid (HCl) for the dehydration of tetrahydrofuran (THF) by pervaporation. The effect of experimental parameters such as feed water concentration, permeate pressure, and membrane thicknesses on permeate parameters, i.e., flux and selectivity were determined with feed water concentration less than 40 wt %. The membranes were found to have good potential for breaking the azeotrope of 94 wt % THF with a flux of 1.072 and 0.376 kg/m<sup>2</sup> h for plane PVA/PEI and crosslinked PVA/PEI blend membrane, which exhibited high selectivity of 156 and 579 respectively. Selectivity was found to improve with decreasing feed water concentration and increasing membrane

thickness, whereas flux decreased correspondingly. High permeate pressure causes a reduction in both flux and selectivity. These effects were clearly elucidated with the aid of the known relationship among plasticization effect, degree of swelling, permeate pressure, and feed water concentration. These blend membranes were also subjected to sorption studies to evaluate the extent of interaction and degree of swelling in pure as well as binary feed mixtures. Further ion exchange capacity studies were carried out for all the crosslinked and uncrosslinked membranes to determine the total number of interacting groups present in the membranes. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1152–1161, 2006

**Key words:** pervaporation; PVA/PEI blend; THF/water mixture; glutaraldehyde

## INTRODUCTION

Pervaporation (PV) is a potential industrial method for the separation of aqueous organic mixtures, close boiling point mixtures. PV appeared far more selective due to its simplicity, energy-saving efficiency compared with conventional azeotropic distillation. PV with polymeric membranes with high perm selectivity were used for effective dehydration of organic mixtures and separation of organic–organic mixtures.<sup>1–5</sup> The permeation process consists of three consecutive steps: (i) sorption of the feed components at the upstream layer of the membrane, which swells due to absorption of feed components in the membrane; (ii) diffusion of the feed components through the membrane; and (iii) desorption of these components at the downstream surface of the membrane. Therefore, the membrane material is the key factor for successful separation. The disadvantage of dense homogeneous membranes for PV separation is low permeation rate, especially with high selective membrane material. For industrial use PV with flux

and high selectivity are desired; therefore, several methods of membrane preparation like blending, copolymerization, and grafting<sup>6–10</sup> have been used to improve the separation. Blending provides desired permeability characteristics in the PV experiments.<sup>11,12</sup>

The boiling point of tetrahydrofuran (THF) is 65°C, and at atmospheric pressure, it forms an azeotrope with water at 63.4°C. THF is frequently utilized as a solvent in many pharmaceutical synthetic procedures because of its broad solvency for polar and nonpolar compounds. THF is particularly capable of dissolving many ionic species and organometallics which are commonly used in specialty syntheses. THF is a relatively expensive solvent, and thus, being able to recover used solvent by dehydration can offer significant savings while also being environmentally beneficial. Since THF forms an azeotrope with water at 94 wt %, this prevents the use of simple distillation.<sup>13</sup> Adding an entrainer to the mixture to break the azeotrope results in an impure THF product containing some of the entrainer, rendering it unsuitable for many applications where pure THF is required. Therefore, dehydration of THF up to > 99% purity from their aqueous solutions has been attempted in the PV experiments. The blend membrane performance was studied by

Correspondence to: A. Krishnaiah (abburikrish@yahoo.com).

calculating selectivity and permeation flux for varying membrane thickness at 30°C at azeotropic composition.

Synthesis of novel membranes with good separation capability is still a major research goal in membrane science. More than a decade ago, the GFT company (now Sulzar Chemtech) first commercialized PV technology for ethanol dehydration using composite membranes based on crosslinked poly(vinyl alcohol) (PVA) on microporous poly(acrylonitrile) substrate.<sup>14–16</sup> Wesslein et al.<sup>17,18</sup> studied the dehydration of aqueous organic mixtures, separation of organic–organic mixtures through PV by using commercial PVA membranes. Innumerable synthetic polymers have been attempted as membranes for different PV-based separation studies with varying degrees of success.<sup>19–21</sup>

PVA is a very effective material for PV dehydration because of its good film forming, high hydrophilicity, and good chemical resistance. Since PVA has poor stability in aqueous solution, several techniques such as crosslinking and grafting are used to create a stable PVA membrane with good mechanical properties and selective permeability to water. Currently, PVA membranes used for PV are crosslinked with glutaraldehyde (GA), poly(acrylic acid), citric acid etc. Though PVA membranes are proven materials for the dehydration of alcohols, their performance has not been satisfactory for the separation of water from organics such as THF or 1,4-dioxane, due to low selectivities and flux at water concentrations below 9.9 wt %.<sup>22</sup>

The present investigation is an attempt to enhance the performance of PVA membranes for dehydrating THF–water mixtures by blending the polymer with poly(ethyleneimine) (PEI). PEI is a branched chain cationic hydrophilic polymer with a lot of amine groups and has been extensively used to modify membrane surfaces.<sup>23</sup> Because of its amino functional groups, PEI is used to prepare blend membranes with anionic polymers like cellulose acetate, poly(*p*-chloro methyl styrene) and poly(methacrylate).<sup>24–27</sup> The blend membrane was crosslinked with GA to reduce swelling and increase the structural strength of the membrane along with its thermal and mechanical stability. The work also explores the separation performance for varying water compositions in the binary feed mixture. Sorption studies and ion exchange capacity (IEC) measurements were carried out to explain the polymers constituting the polyion complex. Effect of permeate pressure and membrane thickness on separation performance was evaluated.

## EXPERIMENTAL

### Materials

PVA, of weight-average molecular weight ( $M_w$ ) of 1,25,000, degree of hydrolysis of 98–99% was purchased from Loba Chemie, Mumbai, India. The degree

of polymerization of PVA was  $1570 \pm 50$  and the saponification degree was 99%. PEI ( $M_n = 70,000$ ) 50 wt % aqueous solution from Aldrich was used as such. The ratio of primary, secondary, and tertiary amino groups in PEI were approximately equal to 1 : 2 : 1. Solvent THF of purity 99% used in the study was reagent grade sample purchased from S.D. Fine Chemicals, Mumbai. Double distilled water of conductivity 0.02 S/cm was used for the preparation of feed solutions.

### Membrane preparation

PVA/PEI membrane was prepared by solution casting and solvent evaporation technique. PVA (7 g) was dissolved in 93 mL of deionized water to form a 7 wt % solution at 90°C. PEI (7 wt %) solution was prepared by dissolving 3.5 g of 50 wt % aqueous solution of PEI in 23.25 mL of water and mixed with 7% PVA solution in the ratio of 1 : 3 respectively. The mixture was then stirred for a period of half an hour to form a homogeneous solution. The bubble-free polymer solution was cast to the desired thickness on a clean glass plate, and solvent was allowed to evaporate slowly at room temperature for a period of 24 h. The resultant membrane was removed from the glass plate and dried in vacuum oven at 50°C for 6 h. Scheme 1 is a structural representation of the reaction that takes place in the preparation of PVA/PEI blend membrane. The blend was then crosslinked with GA for which the possible interactions are shown as Scheme 2.

### Pervaporation procedure

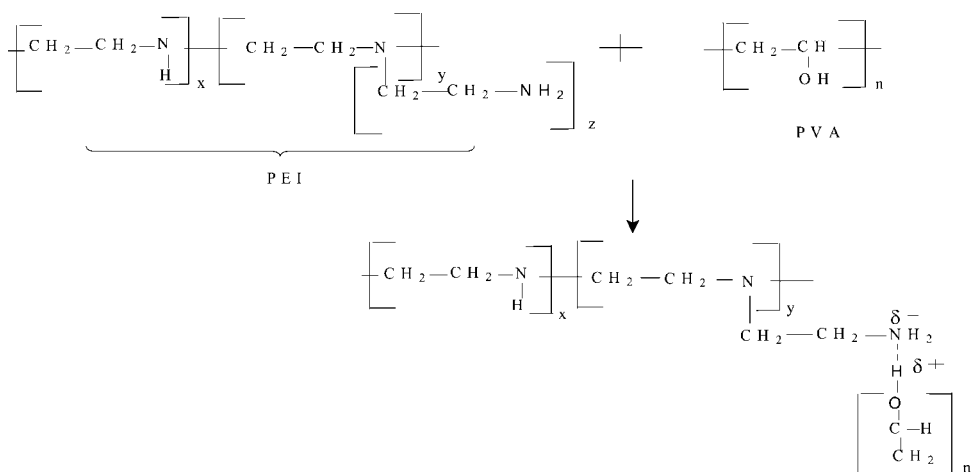
Experiments were carried out on a 100 mL batch level with an indigenously constructed PV manifold (Fig. 1) operated at a vacuum as low as 0.25 mmHg in the permeate line. The membrane area in the PV cell assembly was  $\sim 20$  sq. cm. The experimental procedure is described in detail elsewhere.<sup>28</sup> Permeate was collected for a duration of 6–8 h. Tests were carried out at room temperature ( $30 \pm 2^\circ\text{C}$ ) and repeated twice using fresh feed solution to check for reproducibility. The collected permeate was weighed after allowing it to attain room temperature in a Sartorius electronic balance (accuracy:  $10^{-4}$  g) to determine the flux and then analyzed by gas chromatography to evaluate the membrane selectivity.

### Flux and selectivity equations

In PV, the flux  $J$  of a given species, say faster permeating component  $i$  of a binary liquid mixture comprising of  $i$  (water) and  $j$  (THF) is given by

$$J_i = \frac{W_i}{At} \quad (1)$$

where  $W_i$  represents the mass of water in the permeate (kg),  $A$  is the membrane area ( $\text{m}^2$ ), and  $t$



**Scheme 1** Structural representation of PVA/PEI blend.

represents the evaluation time (h). PV flux on a commercial level is generally reported for membrane of 10  $\mu\text{m}$  thickness. The observed flux for membrane of any given thickness is converted to flux for 10  $\mu\text{m}$  by multiplication of the corresponding factor, assuming linear relationship between thickness and flux.

The membrane selectivity is the ratio of permeable coefficients of water and THF and can be calculated from the respective concentrations in feed ( $X$ ) and permeate ( $Y$ ) as follows

$$\alpha = \frac{Y_{\text{H}_2\text{O}}/Y_{\text{THF}}}{X_{\text{H}_2\text{O}}/X_{\text{THF}}} \quad (2)$$

### Analytical procedure

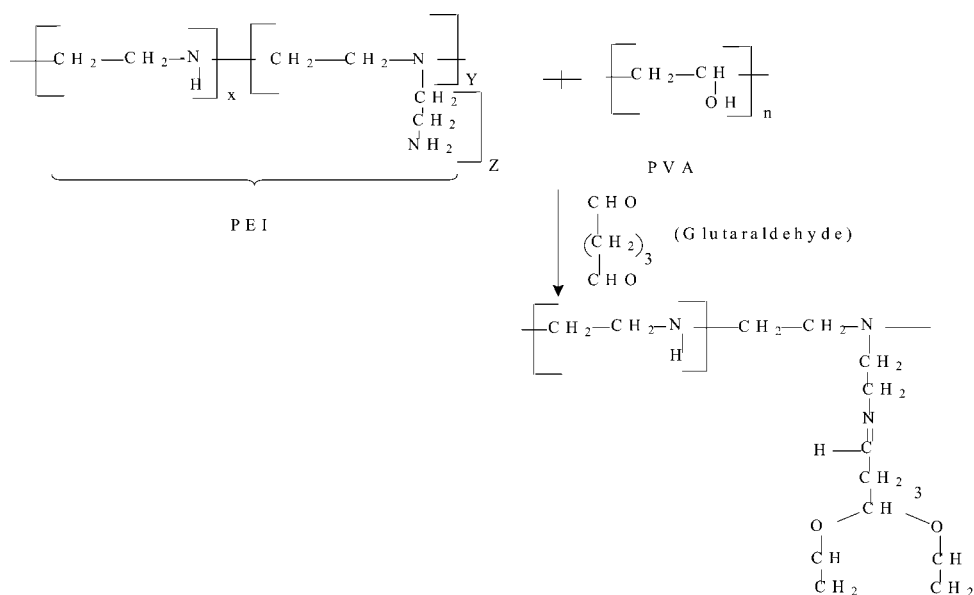
The feed and permeate samples were analyzed using a Nucon Gas Chromatograph (Model 5765) installed

with thermal conductivity detector and packed column of 10% DEGS on 80/100 Supelcoport of 1/8" ID and 2 m length. The oven temperature was maintained at 70°C (isothermal) while the injector and detector temperatures were maintained at 150°C. The sample injection size was 1  $\mu\text{L}$  and pure hydrogen was used as the carrier gas at a pressure of 1 kg/cm<sup>2</sup>. The GC response was calibrated for this particular column and analytical conditions using known compositions of THF–water mixtures. The calibration factors were fed into the software to obtain correct analysis for unknown samples.

### Membrane characterization

#### Sorption characteristics

To determine polymer–liquid interaction, pre-weighed samples of circular pieces of the polymer



**Scheme 2** Structural representation of crosslinked PVA/PEI blend with GA.

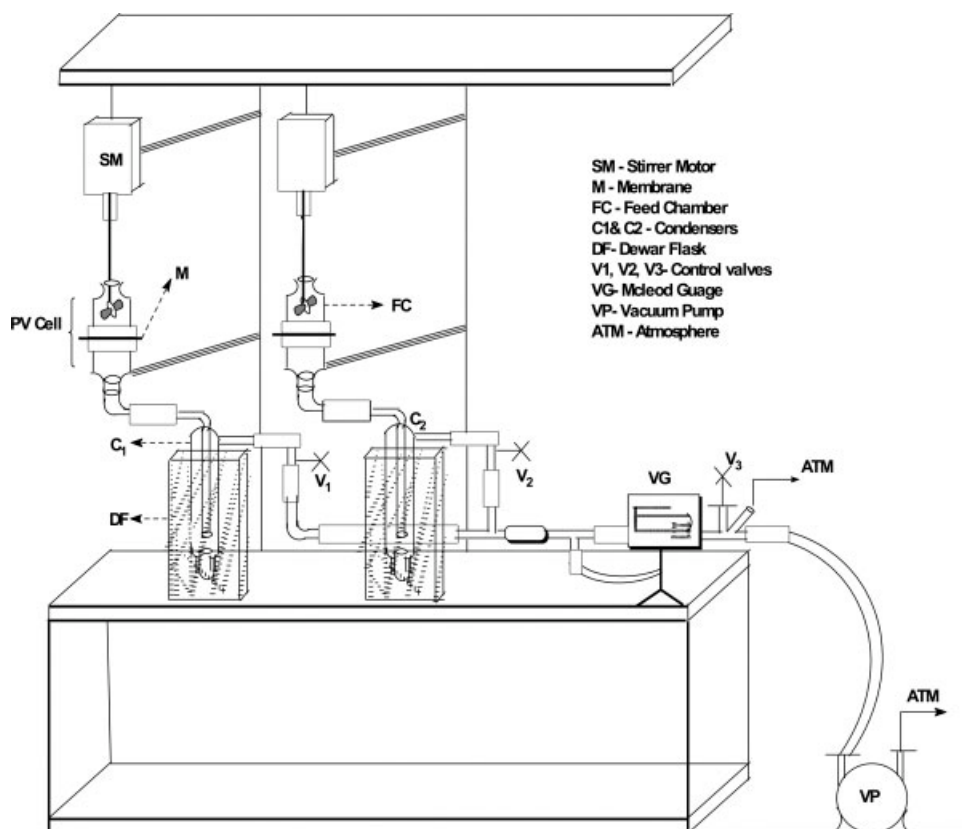


Figure 1 Laboratory PV setup.

films (3 cm diameter) were soaked in deionized water and THF as well as mixtures. The films were taken out after different soaking periods and quickly weighed after carefully wiping out excess water to estimate the amount absorbed at the particular time "t." Films were then quickly placed back in the solvent. The process was repeated until the films attained steady state as indicated by constant weight after a certain period of soaking time. The percentage sorption was calculated from the equation:

$$\text{Sorption [\%]} = \frac{M_s - M_d}{M_d} \times 100 \quad (3)$$

where  $M_s$  is mass of the swollen polymer in g,  $M_d$  is mass of the dry polymer in g.

$$\text{Degree of swelling} = \frac{M_s}{M_d} \quad (4)$$

#### Determination of ion exchange capacity

To determine the effect of crosslinking on the blend, the IEC of the blend was estimated. IEC indicates the number of groups present before and after crosslinking, which gives an idea of the extent of crosslinking. The IEC indicates the number of milli-equivalents of ions in 1 g of the dry polymer. To determine the IEC,

the specimens of similar weight were soaked in 50 mL of 0.1N sodium hydroxide solution for 12 h at ambient temperature. Then, 10 mL of this per sample solution was titrated with 0.1N sulfuric acid. The sample was regenerated with 1N hydrochloric acid, washed, and dried to obtain constant weight. The IEC was calculated according to the equation:

$$\text{IEC} = \left[ \frac{(B - P) \times 0.1 \times 5}{m} \right] \quad (5)$$

where  $B$  is sulfuric acid used to neutralize the blank sample,  $P$  is sulfuric acid used to neutralize the PV membrane, 0.1 is the normality of sulfuric acid, the number 5 represents the factor corresponding to ratio of the amount of NaOH taken to dissolve the polymer to the amount used for titration and  $m$  represents the sample mass (g).

## RESULTS AND DISCUSSION

Schemes 1 and 2 represent the structures of the polymers synthesized in the present study and also show the interactions occurring on blending the two polymers with GA. They have several polar sites such as amine, hydroxyl, and acetal moieties for binding with water. The interactions include hydrogen bonding between hydrogen ion of hydroxyl group of

PVA and nitrogen ion of amine group of PEI as well as covalent crosslinking induced by addition of GA. The solubility behavior of the membranes synthesized in the present work is studied by dissolving in different solvents such as dimethyl formamide (DMF), isopropyl alcohol (IPA), diethyl ether (DEE), and chloroform along with distilled water. PVA is soluble in water and DMF, PEI is soluble in water, IPA and DEE but their blend is insoluble in all the solvents including water. However, their blend undergoes swelling to some extent in water. This nonsolubility of the blend may be due to the formation of a weak force of interaction, resulting on blending the two homopolymers.

PVA/PEI blend membrane is highly hydrophilic in nature and it preferentially absorbs water owing to extensive intra- and intermolecular hydrogen bonding and dipole-dipole interactions between water and the functional groups of PVA/PEI membrane such as amine, acetal, and hydroxyl besides unreacted amine moieties. In the present study, the blend of PVA and PEI is crosslinked by GA to reduce excessive swelling and to increase the selectivity. The HCl added enables in inducing the covalent crosslinking involving GA. After the membranes were prepared, the formation of crosslinked membrane was confirmed by immersing in water to verify its insoluble nature. The membranes were expected to have a low degree of swelling due to covalent crosslinking as well as reduced interaction with organic solvents.

There were very few reports in literature on PV-based separation of THF-water mixtures. Table I gives the comparison of present work with literature, which indicates that the present study gives the

better flux and selectivity for PVA/PEI and GA-crosslinked PVA/PEI (XPVA/PEI) membranes than other membranes reported. To the best of our knowledge, it is the first kind of study wherein PVA/PEI membrane was employed to withstand the solvent environment and PV condition employed in this study.

### Characterization

The membranes were extensively characterized before and after crosslinking by FTIR, XRD, TGA, and tensile testing respectively, to verify crosslinking, and observe its effects on intermolecular interactions, crystallinity, temperature resistance, and mechanical strength of membranes. Detailed characterization of the uncrosslinked and crosslinked membranes of PVA/PEI are given elsewhere.<sup>41</sup>

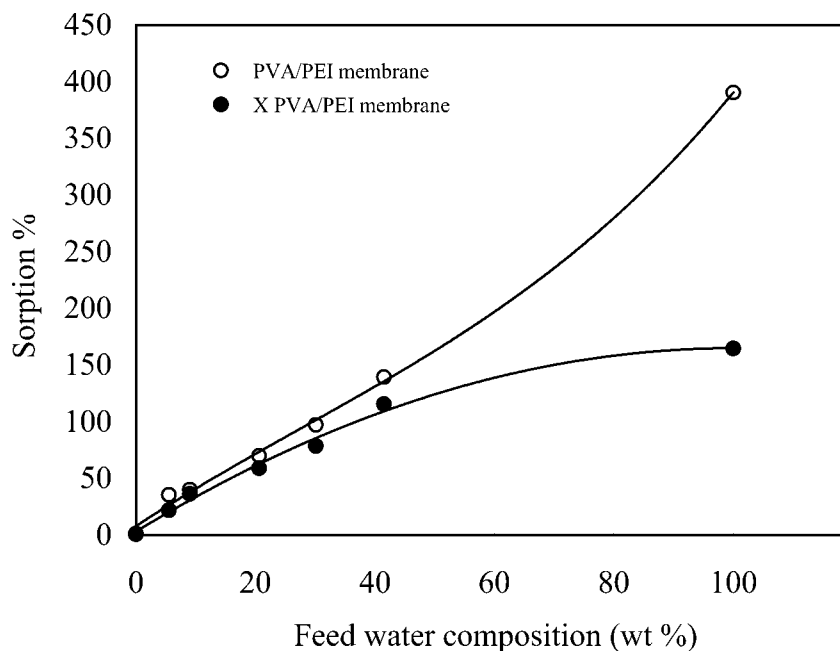
### Sorption studies

The effect of equilibrium sorption percentage of PVA/PEI blend membrane and GA-crosslinked membrane in THF-water mixtures at different compositions are shown in Figure 2. From the graph, it is evidenced that the sorption percentage increases steadily from 35.46 to 139.1 for PVA/PEI membrane and from 21.77 to 115.48 for GA-crosslinked membrane with increasing water concentration 5–40 wt %. At 100 wt % water composition, the sorption was very high for both the membranes, i.e., 390.28 for PVA/PEI membrane and 164.44 for GA-crosslinked PVA/PEI membrane respectively. This shows the hydrophilic nature of the membrane, which has affinity for water and is capable of being selective towards the same during separation. Comparatively,

TABLE I  
Comparison of Flux and Selectivity of PVA/PEI and GA-Crosslinked PVA/PEI Membranes with Literature

Membrane	Temperature (°C)	Water in the feed (%)	Flux (kg/m <sup>2</sup> h 10 μm)	Selectivity	Reference
PTFE-PVP	25	5.7	1.59	18.4	29
PAN-PVP	20	5.9	0.64	10.4	30
PVP-PTFE	25	5.9	0.45	8.5	31
Composite PVA	50	6	0.6	28	32
Y-type zeolite	30	6.7	0.75	45	33
Y-type zeolite	60	5	3.15	360	33
NaAlg.	60	5	1.96	970	34
Poly(acylhydrozone)	25	6.7	0.37	1518	35
NaAlg.(GA + UFS crosslinked)	30	10	0.72	304	36
PAA-g-NaAlg.	30	10	0.40	216	36
PVA-PVP	40	5	0.68	–	37
PVA-NaAlg.	30	6	1.0	291	38
Zeolite-NaAlg. (commercial)	45	7	0.43	1240	39
CMC-VP-31 (commercial)	25	10	0.60	191	40
PVA/PEI	30	6	1.07	176	Present work
XPVA/PEI	30	6	0.37	424	Present work

PTFE, poly(tetrafluoroethylene); PVP, poly(vinyl pyrrolidone); PAN, poly(acrylonitrile); PVA, poly(vinyl alcohol); NaAlg, sodium alginate; PAA, poly(acrylic acid).



**Figure 2** Effect of feed water composition on sorption.

the sorption percentage was more for PVA/PEI membrane than for GA-crosslinked PVA/PEI membrane due to compact nature of the membrane after crosslinking. However, increased swelling has a negative impact on membrane selectivity, since the swollen and plasticized upstream membrane layer allows some THF molecules also to escape into the permeate side along with water.

### Ion exchange capacity

The amount of residual amine and hydroxyl groups present after crosslinking was estimated from the IEC studies. It was noted that uncrosslinked blend showed an IEC of 0.30 meq/g, whereas the crosslinked blend membrane exhibited an IEC of 0.13 meq/g. The IEC, which is equivalent to the total number of free amino groups (considering the fact that amino groups in the blend are more reactive when compared to hydroxyl groups), decreased after crosslinking.<sup>42</sup> This shows that almost 60% of the amine groups present in the unmodified blend have now formed crosslinks with GA and there are still a few amine and hydroxyl groups left for sorption and diffusion of water molecules through the blend, thereby excluding the possibility of formation of the homolinks.

### Pervaporation studies

#### Effect of feed composition

The variation of PV performance over a wide range of feed mixtures at 30°C was investigated using both the uncrosslinked and crosslinked blend membranes.

For this study, the membrane thickness and permeate pressure were kept constant at 50  $\mu\text{m}$  and 0.25 mmHg respectively. The PV performance of PVA/PEI membrane crosslinked with GA was investigated for varying feed compositions comprising 5 to 45 wt % water.

Figures 3 and 4 show the variation of flux and selectivity of the blend membrane with varying feed water concentration. Expectedly, a rise in the feed concentration of water produced an increase in the water flux from 1.07 to 2.12  $\text{kg}/\text{m}^2 \text{ h}$  10  $\mu\text{m}$  for PVA/PEI membrane and from 0.37 to 0.75  $\text{kg}/\text{m}^2 \text{ h}$  10  $\mu\text{m}$  for GA-crosslinked PVA/PEI membrane, and mass transport through the hydrophilic blend membrane occurs by solution diffusion mechanism.<sup>26</sup> In addition to the sorption percentage for binary feed mixtures presented in Figure 2, it was also found that the membranes showed a high degree of sorption in pure water (390% for PVA/PEI and 164.4% for XPVA/PEI) but relatively negligible sorption (1.12% for PVA/PEI and 0.58% for XPVA/PEI) in pure THF. The preferential affinity of the membrane towards water causes swelling, which allows rapid permeation of feed molecules. The degree of swelling correspondingly rises with an increase in the feed water concentration, resulting in enhanced flux. However, increased swelling has a negative impact on membrane selectivity, since the swollen and plasticized upstream membrane layer allows some THF molecules also to escape into the permeate side along with water. Therefore, the permeate concentration indicates a drop in selectivity from 176 to a lower value of 3.05 for PVA/PEI membrane and from 424 to 3.62 for XPVA/PEI membrane over the same feed concentration range of 5–45% water.

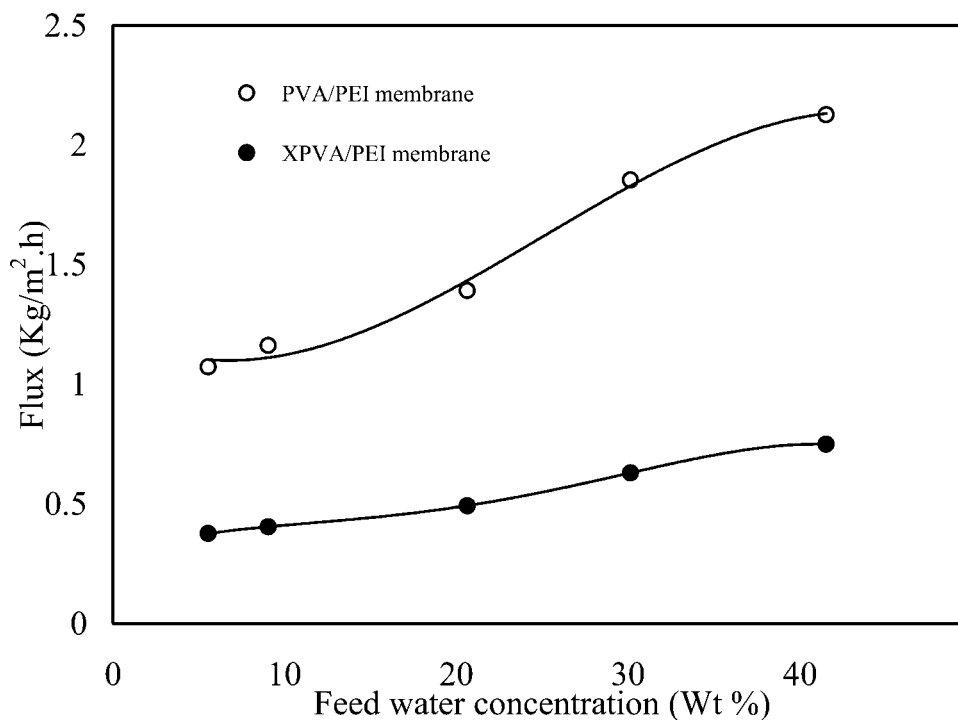


Figure 3 Effect of feed water composition on flux.

Kurkuri et al.<sup>36</sup> used sodium alginate-based membranes to separate THF–water mixtures. The membranes produced from the grafted sodium alginate were dense films and thus showed poor fluxes of  $\sim 0.1$  kg/m<sup>2</sup> h, slightly greater than that of the pure sodium alginate membrane and separation factors ranged between 216 and 591. PVA/poly(vinyl pyrrolidone) (PVA/PVP) blends of different compositions were

used by Lu et al.<sup>37</sup> and crosslinked with UV at elevated temperature. They found that permeation flux increased with increasing PVP content without a loss of selectivity and that a PVP content of 80 wt % was optimal for the process as this gave a high flux of around 0.33 kg/m<sup>2</sup> h when dehydrating a 95 wt % THF solution at 40°C but was far less fragile than a pure PVP membrane. Urtiaga et al.<sup>39</sup> studied by dehydrating

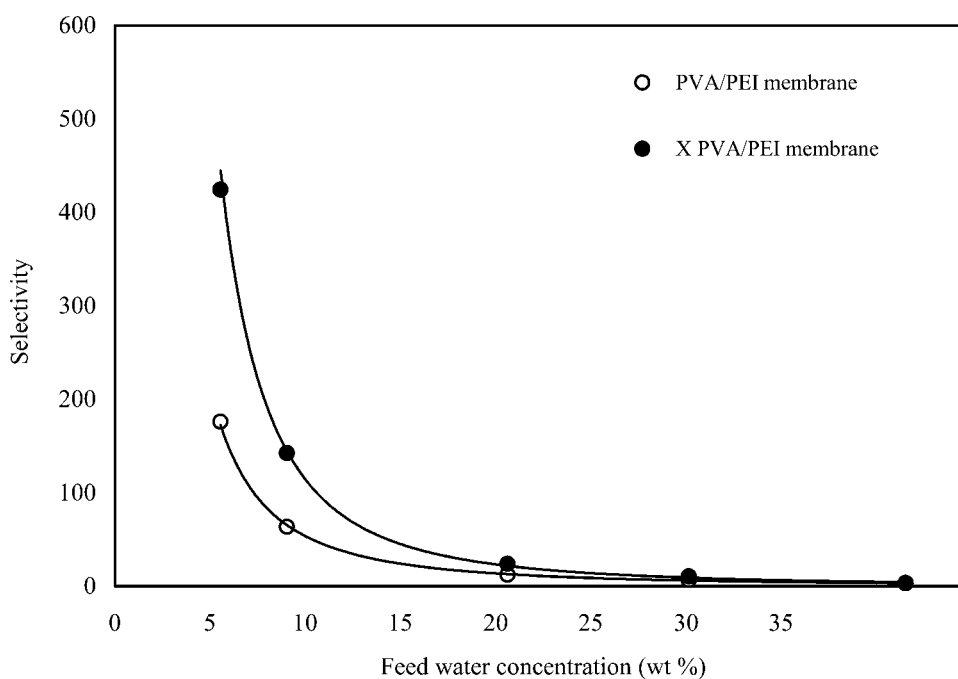


Figure 4 Effect of feed water composition on selectivity.

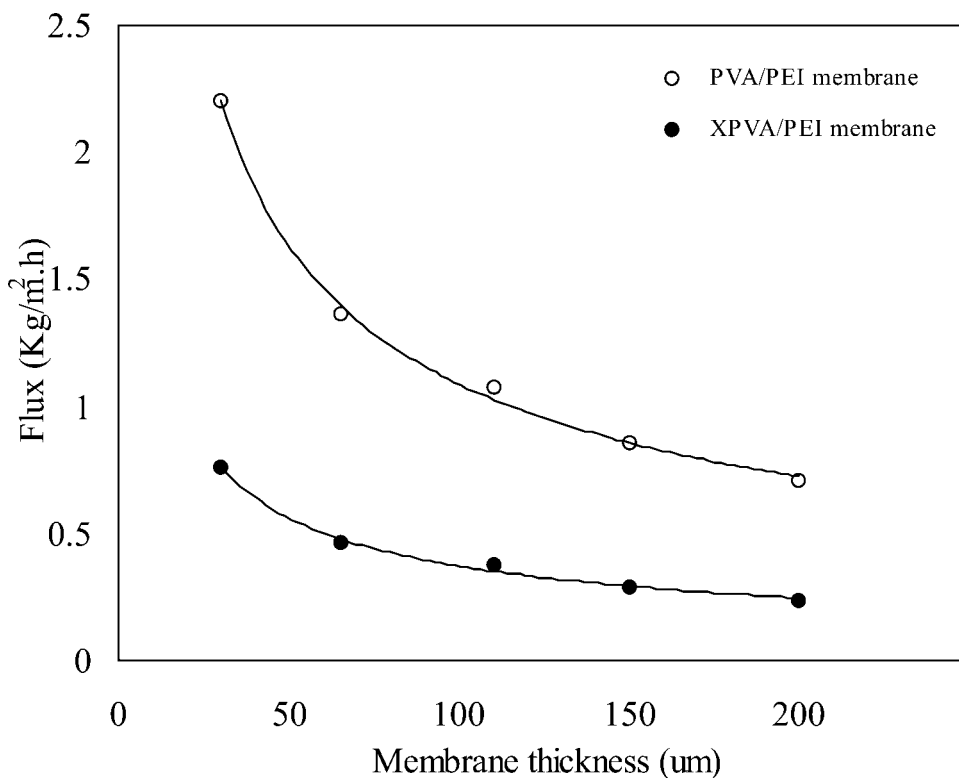


Figure 5 Effect of membrane thickness on flux.

THF using a zeolite-based membrane. They found that the separation factor was as high as 20,000, increasing with decreasing water content in the feed down to 0.15 wt % water at which point the permeate becomes enriched in THF. The flux was also reasonable, above  $0.3 \text{ kg/m}^2 \text{ h}$  at all water concentrations and as high as  $1 \text{ kg/m}^2 \text{ h}$  at the relatively low chosen operating temperature of  $45^\circ\text{C}$ . Li et al.<sup>34</sup> looked at four types of zeolite membranes, A, Al-ZSM-5, Y, and mordenite. They showed that the Y-type membrane had the highest flux and selectivity of  $2.4 \text{ kg/m}^2 \text{ h}$  and 290, respectively, at  $60^\circ\text{C}$ . Ortiz et al.<sup>43</sup> looked at the dehydration of THF with two different types of commercial membranes, the poly layer of  $\sim 1\text{--}2 \text{ m}$  with a sponge-like gutter layer on a nonwoven support.

However, it is worth mentioning that the membranes showed promising results for dehydrating feeds having 5–15 wt % water. Moreover, the azeotropic composition of 96 wt % THF was easily broken by PV, since a comparable high flux of  $0.37 \text{ kg/m}^2 \text{ h}$   $10 \text{ }\mu\text{m}$  and selectivity of 424.5 was obtained using GA-crosslinked PVA/PEI membrane.

#### Effect of membrane thickness

The effect of varying membrane thickness on separation performance was studied at constant feed composition (azeotropic) and permeate pressure ( $0.25 \text{ mmHg}$ ) by synthesizing membranes of thickness ranging from

30 to  $200 \text{ }\mu\text{m}$ . With an increase in the membrane thickness, a gradual reduction in the flux from  $2.2$  to  $0.7 \text{ kg/m}^2 \text{ h}$   $10 \text{ }\mu\text{m}$  for PVA/PEI membrane and from  $0.75$  to  $0.23 \text{ kg/m}^2 \text{ h}$   $10 \text{ }\mu\text{m}$  for XPVA/PEI membrane can be clearly evidenced from Figure 5. Though the availability of polar groups enhances with an increase in the thickness, flux decreases, since diffusion becomes increasingly retarded as the feed molecules have to travel a greater distance to reach the permeate side. With an increase in membrane thickness from 30 to  $200 \text{ }\mu\text{m}$ , the selectivity increased from 61.3 to 294.2 for

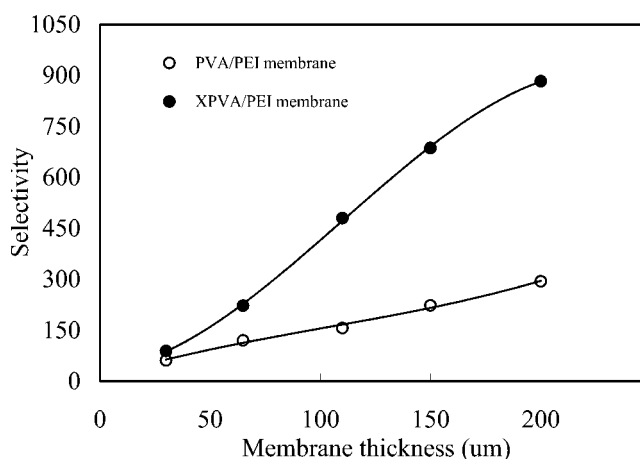


Figure 6 Effect of membrane thickness on selectivity.



PVA/PEI membrane and from 89.38 to 883 for XPVA/PEI correspondingly (Fig. 6). In PV process, the upstream layer of the membrane is swollen and plasticized due to absorption of feed liquid and allows unrestricted transport of feed components. In contrast, the downstream layer is virtually dry because of continuous evacuation in the permeate side, and therefore, this layer forms the restrictive barrier which allows only interacting and smaller sized molecules such as water to pass through. It is expected that the thickness of the dry layer would increase with an increase in the overall membrane thickness, resulting in improved selectivity as observed in the present case.

#### Effect of permeate pressure

The permeate pressure was varied from 0.25 to 10 mmHg to study the permeation characteristics at a constant membrane thickness of 50  $\mu\text{m}$  and azeotropic feed composition. At lower pressures (high vacuum), the influence of the driving force on the diffusing molecules in the membrane is high and will result in the components being swept out immediately from the permeate side, resulting in high mass transfer rates. Figures 7 and 8 show that the membrane exhibits considerable lowering of flux from 1.07 to 0.64  $\text{kg}/\text{m}^2 \text{ h}$  10  $\mu\text{m}$  for PVA/PEI membrane and from 0.37 to 0.17  $\text{kg}/\text{m}^2 \text{ h}$  10  $\mu\text{m}$  for XPVA/PEI membrane as well as a reduction in selectivity from 156 to 46 for PVA/PEI membrane and from 579 to 78 for XPVA/PEI membrane, with an increase in permeate pressure from 0.25 to 10 mmHg. Under high vacuum conditions (lower pressures), diffusion through the membrane is the rate determining step of the PV process and the diffusing water molecules experience larger driving force, which enhances the desorption rate at the downstream side. Lower vacuums reduce the driving force, thus slowing the desorption of molecules. In

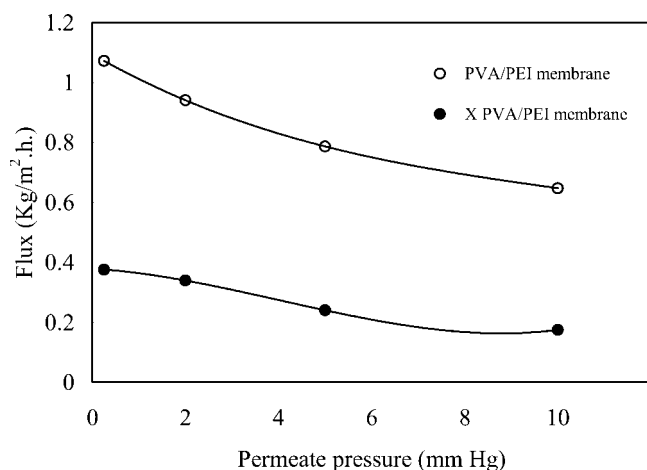


Figure 7 Effect of permeate pressure on flux.

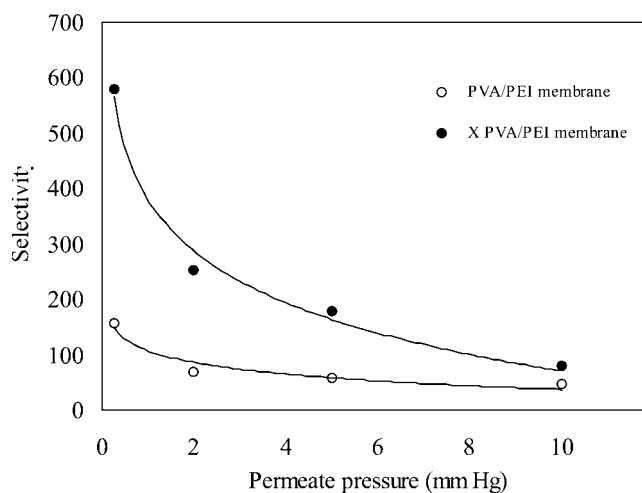


Figure 8 Effect of permeate pressure on selectivity.

such cases, the relative volatilities of the two components of the mixture govern the separation factor of the membrane. THF being more volatile (b.p. 65°C) than water permeates competitively with the latter, thus lowering membrane selectivity.

#### CONCLUSIONS

Blend membranes were prepared from PVA and PEI by mixing the respective polymer solutions in 1 : 3 weight ratio. PVA/PEI blend membrane and GA-crosslinked PVA/PEI blends appear to have promising potential for dehydration of THF, especially at the azeotropic composition of 6 wt % of water besides dehydrating the solvent to >99 wt % purity. With increasing feed water concentration, the membrane's performance was found to be affected substantially because of increase in the extent of swelling of the polymer. This resulted in an increase in flux and decrease in selectivity. The GA-crosslinked PVA/PEI membrane was found to show promising performance for dehydration of THF when compared to uncrosslinked PVA/PEI membrane containing smaller amounts of water ( $\leq 9.9$  wt %). Varying thickness showed a considerable effect on the flux and selectivity. Increase in permeate pressure caused a reduction in both flux and selectivity for both the membrane types. In actual practice, PV could be effectively combined with distillation in a hybrid process, where THF could be distilled up to azeotropic composition from where on PV could be applied to achieve a final purity of  $\geq 99\%$  of THF.

#### References

1. US Department of Energy. Membrane separation systems—A research need assessment; Washington, DC, April 1990. US DOE Report No. DE 90-011770.

2. Baker, R. W.; Cussler, E. L.; Eykamp, W.; Koros, W. J.; Riley, R. L.; Strathmann, H. *Membrane Separation Systems: Recent Developments and Future Directions*; Noyes Data Corp.: Park Ridge, NJ, 1991.
3. Cabasso, I. *Indian Eng Chem Prod Res Dev* 1983, 22, 313.
4. Huang, R. Y. M., Ed. *Pervaporation Membrane Separation Processes*; Elsevier: New York, 1991.
5. Helsel, R. W. *Chem Eng Prog* 1977, 73, 55.
6. Anilkumar, S.; Gedam, P. H.; Kishan, V. S.; Kumaran, M. G.; Thomas, S. *J Appl Polym Sci* 1996, 60, 735.
7. Chanachai, A.; Jiratananon, R.; Uttapap, D.; Moon, G. Y.; Anderson, W. A.; Huang, R. Y. M. *J Membr Sci* 2000, 166, 271.
8. Chen, X.; Li, W.; Shao, Z.; Zhong, W.; Yu, T. *J Appl Polym Sci* 1999, 73, 975.
9. Yeom, C. K.; Lee, K. H. *J Appl Polym Sci* 1998, 67, 209.
10. Jegal, J.; Lee, K. H. *J Appl Polym Sci* 1999, 71, 671.
11. Moon, G. Y.; Pal, R.; Huang, R. Y. M. *J Membr Sci* 1999, 156, 17.
12. Yeom, C. K.; Lee, K. H. *J Appl Polym Sci* 1998, 67, 949.
13. Horsley, L. H. In *Advances in Chemistry Series, Vol. 116: Azeotropic Data III*; Gould, R. F., Ed.; ACS: Washington, DC, 1973; p 218.
14. Feng, X.; Huang, R. Y. M. *J Membr Sci* 1996, 116, 67.
15. Nawawi, M.; Ghazali, M.; Huang, R. Y. M. *J Membr Sci* 1997, 124, 53.
16. Ren, J.; Jiang, C. *Sep Sci Technol* 1998, 33, 517.
17. Wesslein, M.; Heinmiz, A.; Lichtenthaler, R. N. *J Membr Sci* 1990, 51, 169.
18. Wesslein, M.; Heinmiz, A.; Lichtenthaler, R. N. *J Membr Sci* 1990, 51, 181.
19. George, S. C.; Ninan, K. N.; Thomas, S. *J Membr Sci* 2000, 176, 131.
20. Yoshikawa, M.; Shimada, H.; Tsubouchi, K.; Kondo, Y. *J Membr Sci* 2000, 177, 49.
21. Feng, X.; Huang, R. Y. M. *J Membr Sci* 1996, 109, 165.
22. Yeom, C. K.; Lee, K. H. *J Membr Sci* 1996, 109, 257.
23. Lee, K. H.; Kim, H. K.; Rhim, J. W. *J Appl Polym Sci* 1995, 58, 1707.
24. Nguyen, Q. T.; Essamri, A.; Clement, R.; Neel, J. *Makromol Chem* 1987, 188, 1973.
25. Hu, H.; Arbor, M. A.; Hou, C. J.; Pensacola, F. U.S. Pat. 5,277,812 (1994).
26. Chen, Z.; Deng, M.; Chen, Y.; He, G.; Wu, M.; Wang, J. *J Membr Sci* 2004, 235, 73.
27. Say, L.; Tuncel, A.; Denizli, A. *J Appl Polym Sci* 2002, 83, 2467.
28. Sridhar, S.; Ravindra, R.; Khan, A. A. *Indian Eng Chem Res* 2000, 39, 2485.
29. Neel, J.; Nguyen, Q. T.; Clement, R.; Le Blanc, L. *J Membr Sci* 1983, 15, 43.
30. Nguyen, Q. T.; Le Blanc, L.; Neel, J. *J Membr Sci* 1985, 22, 245.
31. Aptel, P.; Challard, N.; Cuny, J.; Neel, J. *J Membr Sci* 1976, 76, 271.
32. Mencarini, J., Jr.; Coppola, R.; Slater, C. C. *Sep Sci Technol* 1994, 29, 465.
33. Shi, Y.; Wang, X.; Chen, G. *J Appl Polym Sci* 1996, 61, 1387.
34. Li, S. G.; Tuan, V. A.; Noble, R. D.; Falconer, J. L. *Indian Eng Chem Res* 2001, 40, 4577.
35. Oikawa, E.; Tamura, S.; Arai, Y.; Aoki, T. *J Appl Polym Sci* 1995, 58, 1205.
36. Kurkuri, M. D.; Kumbar, S. G.; Aminabhavi, T. M. *J Appl Polym Sci* 2002, 86, 272.
37. Lu, Q. N. J.; Zhou, J.; Ping, Z. H. *J Appl Polym Sci* 2003, 89, 2808.
38. Aminabhavi, T. M.; Naidu, B. V. K.; Sridhar, S. *J Appl Polym Sci* 2004, 94, 1827.
39. Urriaga, A.; Gorri, E. D.; Casado, C.; Ortiz, I. *Sep Purif Technol* 2003, 32, 207.
40. Chapman, P. D.; Tan, X.; Livingston, A. G.; Li, K.; Oliveira, T. *J Membr Sci* 2005, 268, 13.
41. Rao, P.S.; Smitha, B.; Sridhar, S.; Krishnaiah, A. *Sep Purif Technol* 2006, 48, 244.
42. Igarashi, K.; Nakano, Y. *J Appl Polym Sci* 2002, 86, 901.
43. Ortiz, I.; Gorri, D.; Casado, C.; Urriaga, A. *J Chem Technol Biotechnol* 2005, 80, 397.