Pervaporation Separation of Tetrahydrofuran/Water Azeotropic Mixtures using Phosphorylated Blend Membranes

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Abstract
In this study, we developed novel phosphoric acid crosslinked blend membranes for the pervaporation separation of tetrahydrofuran/water mixtures. Sodium alginate and chitosan blend membranes were prepared by solution casting and solvent evaporation technique. These blend membranes were crosslinked with phosphoric acid in isopropanol/water baths and used for pervaporation separation of feed mixtures ranging from 6 to 43 wt.% water in tetrahydrofuran (THF)/water mixtures at 30 °C. Crosslinking was confirmed by Fourier transform infrared (FTIR) and Ion Exchange Capacity (IEC) study. Thermal stability and crystallinity of the membranes were determined from thermogravimetric analysis (TGA) and X-ray diffraction (XRD) studies respectively. The surface morphology of the membranes was observed using Scanning electron microscopy (SEM). Sorption studies were carried out to evaluate the extent of interaction and degree of swelling of the membranes in THF, water and binary mixtures. The effect of experimental parameters such as feed composition, membrane thickness, and permeate pressure on separation performance of the phosphorylated membranes were determined. These membranes were found to have good potential for breaking the azeotrope of 94 wt.% THF with a selectivity of 459 and normalized flux of 0.25 kg m^{-2} h^{-1} 10 μm. The membrane performance exhibited a reduction in selectivity and an improvement in flux with increasing feed water compositions. Selectivity improved and flux decreased with increasing membrane thickness. Both flux and selectivity decreased with increasing permeate pressure.

Keywords

1 Introduction

Pervaporation (PV) is a potential industrial method for the economical separation of isomers, close boiling mixtures, besides heat sensitive and hazardous compounds [1, 2]. PV is an environmentally friendly process [3] and is an efficient technique for separation of azeotropic mixtures because the separation mechanism in PV is not based on the relative volatility of the components, but on the difference between the sorption and diffusion properties of feed components, as well as on membrane properties [4]. Pervaporation separation has three steps:

1. the sorption of permeate at the membrane interface;
2. diffusion across the membrane due to a chemical potential gradient (rate-determining step);
3. desorption into a vapor phase at the permeate side of the membrane [5].

Therefore, in PV process, the membrane material is a key factor for successful separation. Hydrophilic groups absorb water molecules preferentially, which leads to both high flux and high separation factors [6].

Among the hydrophilic polymer membranes, sodium alginate (SA), which is one of the polysaccharides extracted

from seaweed, is found to have an excellent performance as a membrane material for pervaporation-based dehydration of organic solvents [7, 8]. SA has good chemical resistance, high permselectivity to water and good membrane forming properties with other polymers. However, very high hydrophilicity of carboxylic and hydroxyl groups present in SA renders the membrane unstable in aqueous solution during PV. To improve the mechanical stability of membrane, SA needs to be blended with another polymer [9]. Chitosan (CS) is deacetylated form of chitin [10], which is the second most abundant biopolymer in nature next to cellulose. CS is available in crustacean shells such as crab and shrimp. CS has been proven to have good film forming properties with mechanical and chemical resistance [6]. CS has both reactive amino and hydroxyl groups that can participate in chemical reactions such as salt formation [11]. These hydrophilic groups are considered to play an important role in preferential water sorption and diffusion through the CS membrane [9]. Sometimes, hydrophilic groups cause membrane swelling, which leads to plasticization action, resulting low selectivity [12]. Hence, modification of the polymer, in order to retain the hydrophilic groups without substantial loss in the stability is the key to prepare potentially useful pervaporation membranes [13]. The SA/CS blend membranes were crosslinked with phosphoric acid to reduce swelling and increase the structural strength of the membrane.

Tetrahydrofuran (THF) boiling point is 65 °C and at atmospheric pressure it forms an azeotrope with water at 63.4 °C [14]. THF is used in the pharmaceutical, polymer, and fine chemical industries because of its broad and high solvation power for polar and non-polar compounds [15]. THF is a relatively expensive solvent and thus being able to recover used solvent by dehydration can offer significant savings whilst also being environmentally beneficial. Since THF forms an azeotrope with water at 94 wt.% of THF, this prevents the use of simple distillation [14, 16]. THF and water mixtures can be separated by extractive distillation. 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, where chemical-free separation occurs. PV can separate azeotropic mixtures and save energy and cost, can be a substitute for traditional separation processes [17]. Therefore, the PV separation process should be suitable to be applied to THF dehydration.

In the present investigation, we aimed to develop membranes having good flux and selectivity together. In continuation of our ongoing efforts to develop new blend and crosslinked membranes [14, 18], we synthesized SA/CS blend membranes for the dehydration of THF/water mixtures. The blending of the two polymers resulted in the spontaneous formation of a polymer complex, which was further crosslinked with phosphoric acid to reduce swelling and increase structural strength besides thermal and mechanical stabilities. The work also explores the effect of varying water concentrations in the binary feed mixture on membrane flux and selectivity. Sorption studies and ion exchange capacity measurements were carried out to explain the polymers constituting the polyion complex. Different experimental parameters such as feed composition, membrane thickness, and permeate pressure on separation performance was evaluated. FTIR, XRD, and TGA analysis were used to characterize the membranes and to understand the mechanism of interaction between the polymers constituting the blend and crosslinking agent.

2 Experimental
2.1 Materials
SA and CS, having an average molecular weight of 500,000 and 300,000, respectively, were purchased from Aldrich Chemical Co., USA. THF of purity 99% and phosphoric acid were purchased from S.D. Fine chemicals, Mumbai, India and the other reagents like oxalic acid, isopropanol, hydrochloric acid, sulphuric acid, and sodium hydroxide were purchased from Loba Chemicals, Mumbai, India. Water of conductivity <0.02 S/cm was generated in the laboratory by distilling the deionized water twice in a quartz distillation plant.

2.2 Blend ratio optimization
Different blend solutions of SA and CS were prepared by mixing SA with CS in the mass ratios of 1:1, 1:2, 1:3, 2:3, 3:1, 4:1, and 5:1. Among these blended ratios, 1:3 was found to be optimum. It is noted that an increase in any one of the polymers (SA, CS) content in the blend renders the membrane brittle as evidenced by the membrane stability test. The stability of the membrane is assessed by bending the film. The membrane is considered stable if its mechanical strength is restored after bending it, i.e., the membrane does not break upon bending. Hence, among the various blending ratios of SA to CS studied, the only one mechanically stable blend membrane of SA and CS at 1:3 ratio is considered for PV studies.

2.3 Membranes preparation and cross linking

Solution casting and solvent evaporation technique was used to prepare P-SA/CS blend membranes. 2 wt.% solutions of SA and CS were prepared separately by dissolving SA and CS in 2% oxalic acid. The suspensions were stirred for 2 h at 40-50 °C, allowed to stay overnight before use to enable the gas bubbles to escape. The optimized blend solution (SA:CS at 1:3 ratio) was stirred for a period of 1/2 h for homogeneity and kept aside for 1 h to obtain a bubble free solution. The homogeneous solution was cast on to a clean glass plate and allowed water to evaporate at room temperature resulting in the formation of dense non-porous blend membranes. The SA/CS blend membranes were crosslinked in a bath containing isopropanol/water bath (90/10 vol %) with a solution of 3.5 vol % phosphoric acid as crosslinking agent and 1 vol % hydrochloric acid as a catalyst at room temperature, and a crosslinking time of 3 h is found to be optimum. The HCl added in crosslinking bath enables in inducing the ion complexation between anion group of SA and cation group of CS and helps in the covalent crosslinking involving phosphoric acid. After the membranes are prepared, the formation of crosslinked polyion complex membrane is confirmed by immersing in water to verify its insoluble nature. The membranes are expected to have low degree of swelling due to covalent crosslinking as well as reduced interaction with organic solvents (salting out effect) due to ionic crosslinking. After removing the membrane from the crosslinking bath, it is washed with water repeatedly and dried in an oven at 80 °C to eliminate the presence of residual acid, if any. Different thickness of the membranes was prepared by varying volumes of the optimized blend solution (SA:CS at 1:3 ratio).

2.4 Membrane characterization

The thickness of each membrane was measured by a micrometer screw gauge at different locations and the average values of these were taken as the thickness of a particular membrane.

FTIR spectra of SA/CS and P-SA/CS membranes were scanned in the range between 4000 and 400 cm^{-1} using Thermonicolet FTIR-200 series spectrophotometer.

A Seifert X-ray diffractometer was used to study the solid-state morphology of blended SA/CS and P-SA/CS in powdered form. X-rays of 1.546 Å radiation were generated by a CuK$_\alpha$ source at 40 kV and 20 mA.

Thermal stability of the polymer films was examined using Seiko 220TG/DTA analyzer, from 30 to 290 °C at a heating rate of 10 °C/min with continuous flushing with pure nitrogen gas at 200 mL/min. The samples were subjected to TGA to determine the thermal stability and decomposition characteristics.

The morphology of the SA/CS and P-SA/CS membranes were observed using Jeol SEM attached with x-ray energy analyzer model JSM-840A.

2.5 Determination of the ion exchange capacity (IEC)

The IEC indicates the number of milliequivalents of ions in 1 g of the dry polymer. The degree of substitution indicates the average number of acid groups present in the polymer. To determine the degree of substitution by acid groups, SA/CS and P-SA/CS specimens of similar weight were soaked in 50 mL of 0.01N NaOH solution for 12 h at ambient temperature. Then, 10 mL of the solution was titrated with 0.01N H$_2$SO$_4$. The membrane was regenerated with 1M HCl, washed with water till the washings are free from acid and dried to a constant weight. The IEC was calculated according to Eq. (1):

$$IEC = \frac{(B-P) \times 0.01 \times 5}{m},\tag{1}$$

where B was the volume of H$_2$SO$_4$ used to neutralize blank sample soaked in NaOH (mL), P was the volume of H$_2$SO$_4$ used to neutralize the membrane soaked in NaOH (mL), 0.01 was the normality of the H$_2$SO$_4$, and '5' was the factor corresponding to the ratio of the amount of NaOH taken to dissolve the polymer to the amount used for titration, and m was the sample mass (g).

2.6 Sorption studies

A pre-weighed polymer samples were soaked in THF/water mixtures of various concentrations and allowed to reach sorption equilibrium at room temperature (for at least 12 h). The swollen sample is removed from the solvent mixture, wiped with tissue paper to remove the surface liquid, and immediately weighed. The process is repeated until the films attained steady state as indicated by constant mass after a certain period of soaking time. Degree of swelling (DS) was calculated as:

$$DS = \frac{M_s}{M_d}.\tag{2}$$

The sorption represents the fraction of the extracted liquid mixture by the membrane. The percentage sorption was calculated using Eq. (3):

$$\%\text{Sorption} = \frac{(M_s - M_d) \times 100}{M_d}, \qquad (3)$$

where M_s was mass of the swollen polymer in grams, and M_d was mass of the dry polymer in grams.

2.7 Pervaporation and analytical procedure
2.7.1 Influence of operating conditions
Experiments were carried out following the procedure described in the literature [6, 9, 14, 19, 20]. The indigenously constructed 100 mL batch level PV manifold (Fig. 1) was operated at a vacuum as low as 0.5 mmHg in the permeate line. The effective area of the membrane in contact with the feed stream was 19.6 cm². The feed consisting of THF, and water was stirred vigorously at a speed of 150 rpm during experiments to minimize concentration polarization. Permeate was condensed and collected in a liquid nitrogen cold trap for 6 h. Tests were carried out at room temperature (30 ± 2 °C) and repeated twice using fresh feed solution to check for reproducibility. The collected permeate was weighed in a Sartorius electronic balance with an accuracy of 10^{-4} g to determine the flux. Analysis of permeate composition was carried out by measuring the refractive index of the mixture with an accuracy of ±0.001 units, using Abbe Refractometer (Advance Research Instruments Company, New Delhi, India). A calibration plot of refractive index versus percent composition of THF/water was obtained with the known quantities of mixture components.

2.7.2 Flux and selectivity
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:

$$J_i = \frac{W_i}{A \times t}, \qquad (4)$$

where W_i represents the mass of water in permeate (kg), A is the membrane area (m²) and t represents the experiment time (h). PV flux on a commercial level is generally reported for a membrane of 10 μm thickness. The observed flux for a membrane of any given thickness is converted to flux for 10 μm by multiplication of the corresponding factor assuming linear relationship between thickness and flux.

The membrane selectivity (α) is the ratio of permeable coefficients of water and THF and can be calculated from their respective concentrations in feed (x) and permeate (y) as given in Eq. (5):

$$\alpha = \frac{y \times (1 - x)}{x \times (1 - y)}. \qquad (5)$$

Pervaporation separation index (PSI), which is a measure of the separation capability of a membrane, is expressed as a product of flux (J) and selectivity (α):

$$\text{PSI} = J \times \alpha. \qquad (6)$$

3 Results and discussion
Scheme 1 represents the structures of the polymers used in the study and also exhibits the ionic complexation reaction between cationic group (–NH$_3$+C) of CS and anionic group (–COO$^-$) of SA [21] as well as the covalent crosslinking induced by addition of phosphoric acid. This is confirmed by FTIR spectra and IEC. It is noticed that the P-SA/CS blends are optically clear to the naked eye. No separation into two layers or any precipitation was noticed when allowed to stand for one month at room
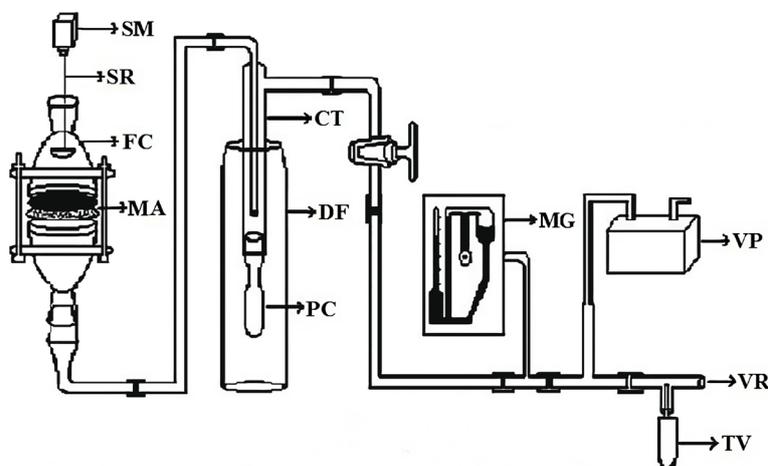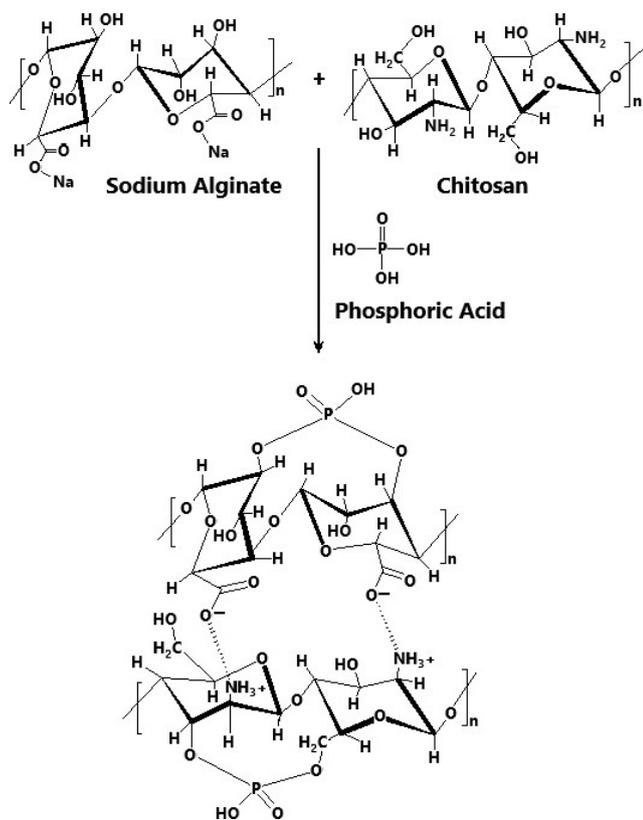

Fig. 1 Block diagram of pervaporation set-up. SM: stirring motor, SR: stirring rod, FC: feed chamber, MA: membrane assembly, CT: condenser trap, DF: Diwar flask, PC: permeate collector, MG: McLeod gauge, VP: vacuum pump, VR: vacuum release, TV: Teflon valve

Scheme 1 Structural representation of sodium alginate/chitosan blended membrane crosslinked with phosphoric acid

Fig. 2 FTIR spectra of (a) SA/CS and (b) P-SA/CS blend membranes

temperature. An estimation of the number of groups presents before and after crosslinking gives an idea of the extent of crosslinking.

3.1 Membrane characterization
3.1.1 FTIR studies
Fig. 2 shows the FTIR spectra of uncrosslinked blend polymer, SA/CS (Fig. 2(a)) and phosphoric acid crosslinked blend polymer, P-SA/CS (Fig. 2(b)). SA/CS membrane show broad characteristic peak appearing in the range 3000-3600 cm^{-1} corresponding to –O-H and –NH- stretching (in NH$_3^+$) vibrations. The peak at 1660 cm^{-1} can be attributed to the NH$_3^+$ deformation and C=O stretching of the carboxylic group. This blend shows the -C-OH stretching at 1309 cm^{-1}, asymmetric stretching of –C-O-C- at 1156 cm^{-1}. Symmetric and asymmetric stretching vibrations of carboxylate ion (COO$^-$) show the peaks at 1413 and 1565 cm^{-1}, respectively. The other bands at 1375 cm^{-1} (-CH$_2$ bending), and 907 cm^{-1} (skeletal vibrations involving the C-O stretching) are the characteristics of SA/CS blend membrane structure. The spectrum confirms the complexation between the dissociated carboxylate groups of SA (COO$^-$) and protonated amino groups from CS
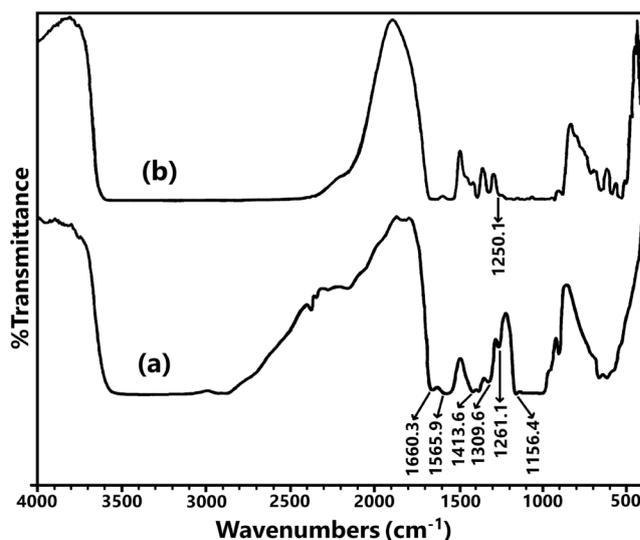
through electrostatic interaction. Moreover, as the polyion complex formation proceeds, the –O-H bonding would also be expected because of an increase in intermolecular interaction such as hydrogen bonding between SA and CS.

After crosslinking, the band appearing at 3000–3600 cm^{-1} (Fig. 2(a)) is shifted to 2300–3600 cm^{-1} (Fig. 2(b)) and the formation of new peak at 1250 cm^{-1} corresponds to the interaction of hydroxyl group of phosphoric acid with hydroxyl groups of both SA and CS resulting in the formation of –P–O–C– bond [14] as shown in the Scheme 1, and also this peak corresponds to P=O stretching and OH deformation occurring on crosslinking the polymer [19, 22]. A new peak at 1250 cm^{-1} indicates that the P=O remains intact and does not participate in the reaction. It can be concluded that phosphoric acid acts as a crosslinking agent between SA and CS. The model structure proposed in Scheme 1 is well in accordance with the FTIR spectra.

3.1.2 XRD studies
Dried membrane of thickness of 50 µm is used for XRD analysis. The angle of diffraction is varied from 5 to 80^0 to identify the change in the crystal structure and intermolecular distances between the intersegmental chains before and after crosslinking. On crosslinking, the polymer chains are in close compaction with one another and thus a reduction in the cluster space may be encountered.

The X-ray diffractograms of SA/CS and P-SA/CS blend membranes, shown in Fig. 3, have no sharp peaks indicating the amorphous nature of the membranes. The XRD spectra of the SA/CS (Fig. 3(a)) exhibits a broad peak at $2\theta = 20^0$, which may be due to the intermolecular interaction such as the formation of hydrogen bonding between SA
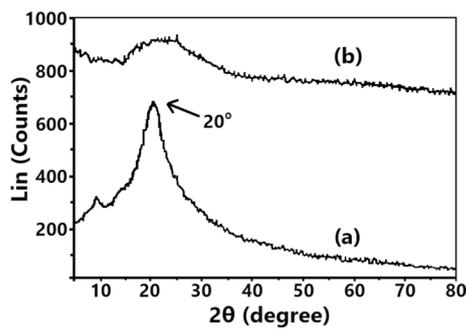
Fig. 3 X-ray diffractograms of (a) SA/CS and (b) P-SA/CS blend membranes

and CS [23]. P-SA/CS (Fig. 3(b)) membrane appears to be more amorphous than SA/CS as its diffraction pattern has no peak. On crosslinking the peak that appears at $2\theta = 20^0$ in the diffraction pattern of SA/CS disappears due to disturbance of the bonds in P-SA/CS blended membrane. Thus, XRD studies confirm crosslinking of SA/CS blend.

3.1.3 TGA studies
The TGA curves of crosslinked and uncrosslinked blends are shown in Fig. 4. The TGA curve of SA/CS blend (Fig. 4(a)) shows the beginning of weight loss at 220 °C followed by a final decomposition at 280 °C. Fig. 4(b) shows that P-SA/CS blend begins to undergo a weight loss starting at 180 °C followed by the final decomposition at 230 °C. This observation indicates that there is no considerable difference in thermal stability before and after crosslinking. Hence these membranes could be used for PV studies even at high temperatures.

3.1.4 Scanning Electron Microscopic (SEM) studies
SEM photographs of SA/CS and P-SA/CS membranes are shown in Fig. 5. It is obvious that the surface of both membranes is flat, and has no pores nor cracks. This illustrates the good compatibility between the components of SA/CS and P-SA/CS membranes.

3.2 Ion exchange capacity (IEC) studies
Ion exchange capacity provides an indication of the content of residual ionic groups present in a polymer matrix, which plays an important role in PV flux and selectivity. The amount of residual hydroxyl and acetyl groups in blend membranes are estimated from IEC studies. It is found that SA/CS blend had an IEC of 3.82 mequiv/g, whereas P-SA/CS blend polymer exhibited an IEC of 1.33 mequiv/g. The IEC results show that almost 65% of hydroxyl groups present in the SA/CS have now formed crosslinks with PA. The IEC, which is equivalent to the
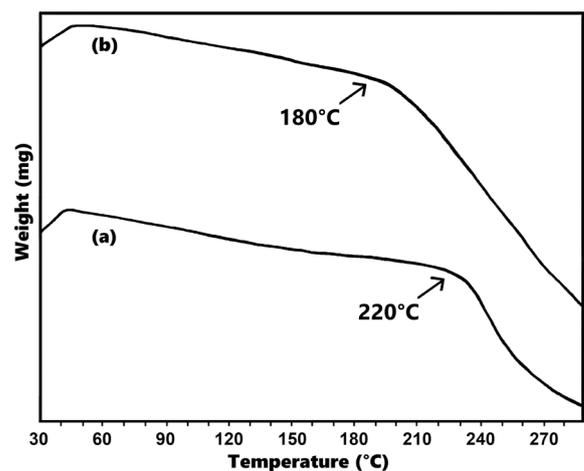

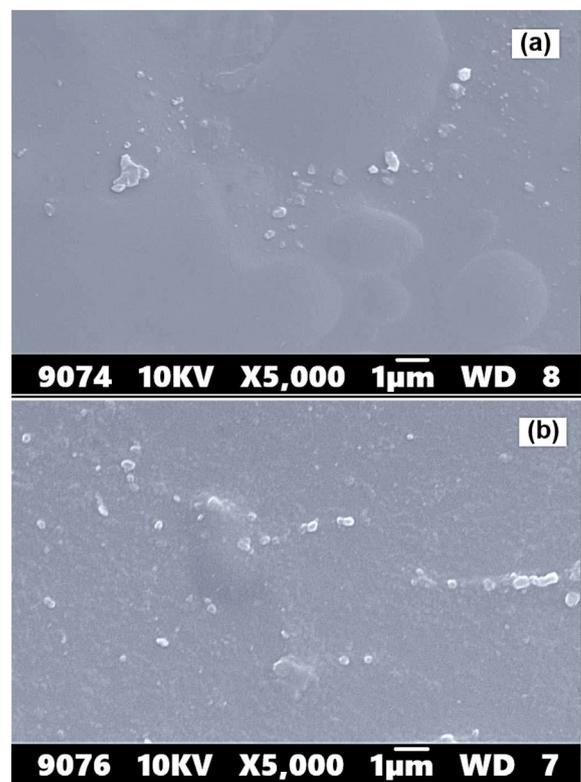**Fig. 4** TGA curves of (a) SA/CS and (b) P-SA/CS blend membranes

Fig. 5 SEM micrographs of (a) SA/CS and (b) P-SA/CS blend membranes

total number of acetyl and hydroxyl groups present in the membrane, decreases upon crosslinking because some hydroxyl groups and acetyl groups are consumed during the reaction [6, 9, 20].

3.3 Sorption studies
The effect of equilibrium sorption percentage and degree of swelling data of P-SA/CS membrane for different THF/water compositions is shown in Table 1. The amount of water sorbed in the membrane increases with water

Table 1 Effect of feed concentration on DS, % of sorption, normalized flux, selectivity, and PSI values

Feed water (wt.%)	Degree of swelling	% of sorption	Normalized flux (J)	Selectivity (α)	PSI ($J \times \alpha$)
0.0	1.01	5.6	–	–	–
6.1	1.18	17.9	0.25	459	113.9
15.0	1.29	29.3	0.31	111	34.1
24.3	1.47	47.4	0.34	46	15.7
33.1	1.60	60.3	0.38	21	8.0
43.1	1.86	85.5	0.42	11	4.6
100.0	2.36	135.8	–	–	–

content in the mixture i.e., 5.57 to 85.50 with feed water concentration from 0 to 43.05 wt.%. From Table 1, it is observed that the membranes show high sorption percentage to water at equilibrium (135.78%). The hydrophilic groups in these membranes are responsible for the preferential water sorption. Further, it is observed that degree of swelling increases from 1.0057 to 2.3578 with increasing water concentration from 0 to 100 wt.% in the mixture. As membrane swelling increases with increasing water content, more THF molecules are sorbed along with water molecules, which is called sorption coupling. P-SA/CS membrane shows high water selectivity with the maximum occurring at 93.86 wt.% content of THF in the feed mixture at 30 °C. From these data, it is apparent that P-SA/CS is an excellent pervaporative membrane for the dehydration of tetrahydrofuran mixtures.

3.4 Pervaporation results
### 3.4.1 Effect of feed composition
In this study, the effect of feed composition on PV performance was studied at 30 °C by varying feed water concentration and measuring the flux and selectivity. Downstream pressure of 0.5 mmHg and membrane thickness of 50 μm were kept constant. The data in Table 1 indicate that the permeate normalized flux increases from 0.2478 to 0.4196 kg m^{-2} h^{-1} 10 μm with an increase in water feed concentration from 6.14 to 43.05 wt.%. Mass transport through the hydrophilic blend membrane occurs by solution diffusion mechanism [24]. The plasticizing effect of water on the polymeric membrane and the movement of permeating molecules through the membrane as a coupling unit of THF and water, together contributed to the increases of THF flux and permeance with increasing feed water concentration in the THF/water mixture. Hence the selectivity decreases from 459.45 to 11.08 as the feed water concentration increases from 6.14 to 43.05 wt.% (Table 1). Higher water concentrations render greater swelling of the membranes that enables permeation of both components

into the permeate stream yielding higher normalized flux but a drop in selectivity. Thus, the swelling increases with increasing water concentration leading to reduction in membrane selectivity.

Pervaporation separation index (PSI), defined as the product of total permeation and separation factor, has been used as a performance evaluating parameter. The data in Table 1 show that the PSI values increases almost linearly from 4.65 to 113.85 with increasing THF concentration from 56.95 to 93.86 wt.%, signifying that the membranes show better performance for the separation of THF/water mixture at lower feed water concentration of 6.14 wt.%.

3.4.2 Effect of membrane thickness
The effect of membrane thickness on separation performance was studied at constant feed composition (azeotropic) and permeate pressure (0.5 mmHg) by using synthesized membranes of different thicknesses ranging from 50 to 160 μm. Fig. 6 shows a gradual decrease in the flux with an increase in the membrane thickness with other operating parameters kept constant. When the membrane thickness varied from lower to higher, the corresponding flux decreases from 0.0496 to 0.0273 kg m^{-2} h^{-1} due to increasing resistance
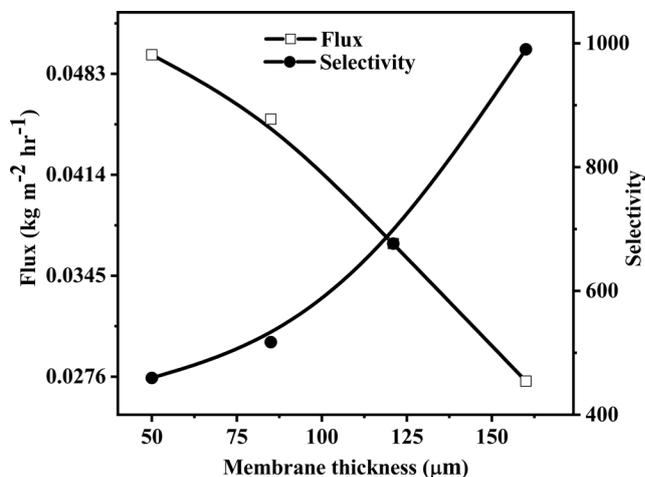
Fig. 6 Effect of membrane thickness on PV performance

to mass transfer. PV selectivity is usually independent of membrane thickness but in the present case, the selectivity increases from 459.45 to 990.41. Due to plasticization of membrane upstream layer with the feed mixture, it allows the passage of both the feed components.

At permeate side, the membrane acts as a selective barrier due to continuous evacuation, and therefore, this layer formed the restrictive barrier, thus allowing the interacting small size water molecules to pass through the membrane. It was 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.

3.4.3 Effect of permeate pressure

The permeate pressure was varied from 0.5 to 9 mmHg, to study the permeation characteristics of P-SA/CS at a constant thickness of 50 μm and an azeotropic feed composition. As the permeate pressure decreases, the driving force for diffusing molecules increases, resulting in higher permeate rates. From Fig. 7, considerable lowering
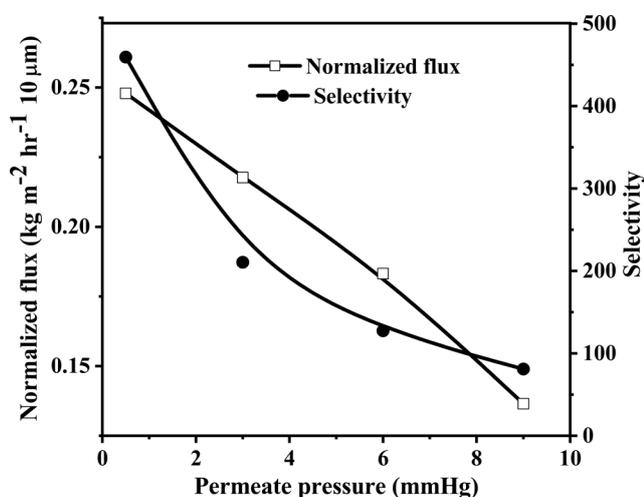
of normalized flux from 0.2479 to 0.1365 kg m^{-2} h^{-1} 10 μm and selectivity from 459.45 to 81.03, with an increase in permeate pressure from 0.5 to 9 mmHg is observed. Diffusion through the membrane is the rate determining step in the pervaporation process and the diffusing water molecules experience larger driving force under high vacuum, which enhances the desorption rate at the downstream side. A lower vacuum reduces the driving force, thus slowing desorption of molecules. In such cases, the relative volatilities of the two components of the mixture govern the separation factor of the membranes. THF having higher vapor pressure than water, permeates competitively with the latter, thus lowering the concentration of water in permeate. At low pressure (high vacuum) the influence of driving force for diffusing molecules in the membrane is high and will result in the components being swept out immediately from the permeate side with high mass transfer rates.

4 Comparison of present work with literature

There were very few reports in the literature on the PV separation of THF/water mixtures. Data from literature on flux and selectivity of different membranes for pervaporation separation of THF/water system are included in Table 2 along with those obtained in the present study [8, 15, 25–28]. From the literature, it was clearly evidenced that some of the membranes yielded higher selectivities and some of the membranes yielded higher fluxes, but no membrane was good at both selectivity and flux. From the comparison table it was found that P-SA/CS membrane showed better selectivity than many of other membranes, whereas this membrane showed comparable flux to that of others. Furthermore, the ease in fabrication of these membranes associated with low cost render them more attractive for pervaporation of THF/water separation.

Fig. 7 Effect of permeate pressure on PV performance

Table 2 Comparison of PV performance of P-SA/CS membrane with literature values at 30 °C operation temperature

Membrane	Water in feed (wt.%)	Normalized flux	Selectivity	Reference
Y-type zeolite	6.7	0.75	45	[8]
PVA/PEI	6	1.07	176	[15]
GA-PVA/PEI	6	0.37	424	[15]
SA-HEC-10 (GA + UFS crosslinked)	10	0.05	1516	[25]
SA (GA + UFS crosslinked)	10	0.05	304	[25]
PAA-*g*-SA	10	0.40	216	[26]
PVA-SA	6	1.0	291	[27]
K-LTL-type zeolite + SA	6.7	0.02	3081	[28]
P-SA/CS	6	0.25	459	Present work

SA: Sodium alginate, HEC: Hydroxyethyl cellulose, GA: Glutaraldehyde, UFS: Urea-formaldehyde-sulfuric acid, PAA: Poly(acrylic acid),
PVA: Poly(vinyl alcohol), PEI: Poly(ethyleneimine)

5 Conclusions

In the present study, the authors developed novel phosphoric acid crosslinked blend membranes for the dehydration of THF/water mixtures. The number of groups crosslinked in SA/CS blend polymer was identified from the IEC studies. Characterization of the blend membranes by FTIR and XRD confirmed the crosslinking reaction. The membranes showed adequate thermal stability to withstand the PV experimental conditions. FTIR spectroscopy confirmed the predicted interaction between the SA/CS blend and the crosslinker. With increasing feed water compositions, the membrane performance exhibited a reduction in selectivity and an improvement in flux due to increased swelling. Expectedly, with increasing membrane thickness, selectivity improved, but flux decreased. Higher permeate pressure caused a reduction in both flux and selectivity. From the results, the phosphorylated SA/CS blend membranes appear to have promising potential for dehydration of THF, especially at the azeotropic composition of 94 wt.% of THF, besides dehydrating the solvent to ≥99 wt.% purity. PV and distillation could be used together in an integrated process to achieve a final purity of ≥99% of THF.

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