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Composite Membranes Comprising of Hydroxypropyl Cellulose - Poly(Vinyl Alcohol) Incorporated with Inorganic Fillers for Dehydration of Ethanol by Pervaporation

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ABSTRACT

Mixed matrix membranes (MMMs) of hydroxyl propyl cellulose/ Poly(vinyl alcohol) (HPC/PVA) blends loaded with 5, 10, 15 wt% of phosphotungsticacid (PWA) and cross linked with gluteraldehyde have been prepared by the solution casting technique. The membranes were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction study (XRD) to confirm cross linking and assess the intermolecular interactions. Thermal stability and crystallinity were determined from thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies. The morphology of membranes was characterized by SEM studies, which indicates good compatibility of these membranes. Sorption studies were carried out to evaluate the extent of interaction and degree of swelling of the membranes, in pure liquids as well as mixtures of water and ethanol. Pervaporation (PV) experiments have been performed at 30 °C to separate water - ethanol feed mixtures containing 10-17.5 wt% of water. The pervaporation performance was evaluated by varying experimental parameters such as feed composition, different polymer compositions and found to be potential membranes for separation of water-ethanol mixtures. The results reveal that the MMMs of HPC-PVA (M2) containing 10 wt% of PWA showed the flux is of the order of 0.3948 $kgm^{-1}h^{-1}$ and selectivity of the order of 1789 at 10 wt% water feed. From this it is concluded that the present blend membrane is a promising candidate for dehydration of aqueous ethanol. Flux of the blend membranes decrease with increasing concentrations of PWA. However, a significant improvement in PV performance was observed for PWA- loaded mixed matrix membranes (MMMs) compared to the pristine HPC/PVA blend membrane.

1. Introduction

Development of alternative energies gain considerable attention over the last decade due to increasing fuel consumption while petroleum reserves are being depleted. One of these alternative fuel sources is ethanol particularly when blended with gasoline to use as automotive fuel. To be compatible with gasoline ethanol must have a water content of less than 1.0 vol% [1]. To meet such specification, other methods of separation, rather than the conventional distillation method, are needed because ethanol forms an azeotropic mixture with water at 96.0 wt% [2]. One process capable of breaking azeotropes is the pervaporation. As a membrane based process, the pervaporation separates liquid mixtures by differences in the solubility and the diffusivity of each component with the membrane. In addition, without the use of heat to generate a phase change during separation the pervaporation is also suitable for close boiling point components and heat sensitive mixtures. To achieve a good separation in the membrane based separation, the membranes must possess both high permeability as well as selectivity and those qualities are strongly dependent on the characteristics of the materials used for fabricating a membrane. In a dehydration process using the polymeric membranes normally consists of polymers with water attractive functional groups in order to make them water-preferential [3].

Hydrophilic membranes are generally used for the dehydration of organic solvents because of the favourable solubility and diffusivity for selective permeation of water [4]. In particular, Poly(vinyl alcohol) has been widely used as a membrane material to solvent dehydration due to its strong affinity to water molecules, good membrane forming properties and mechanical strength [5-7]. However, PVA can be swollen easily in water, and to some extent dissolution can occur at elevated temperatures. Thus, in order to improve the membrane stability, PVA membranes need to be modified to constrain their swelling in aqueous solutions. In general, crosslinking, blending and incorporating with inorganic fillers are commonly used to reduce membrane swelling [8, 9], though a trade-off relationship between the membrane permeability and selectivity is often observed.

In recent times several workers developed MMMs by incorporating metal containing heteropoly acids (HPAs) for the PV separation of alcohol-water mixtures [10-17]. Heteropoly acids (HPAs) are the widely used inorganic materials that contain ring transition metal oxygen anion clusters, which exhibit a wide range of well-defined molecular structures, surface charge densities, chemical and electronic properties [18] in addition to their inherent catalytic properties [19-21]. The heteropoly acids (HPAs) that are strong Bronsted acids have been widely used as solid electrolytes in catalysis reactions [22, 23]. Their water solubility has been advantageously utilized in considering them as fillers in polymer matrices to improve the membrane performance [24, 25]. Among these, Keggin - type HPAs have been widely investigated as the catalytic materials [26]. Our present approach is to further explore the possibility of developing organic-inorganic hybrid membranes by incorporating HPAs that have the most potential material for pervaporation studies. HPAs are a subset of the well-known inorganic metal oxides called polyoxometalates [27, 28]. In this work, we have chosen phosphotungstic acid (PWA) that consists of Keggin unit as a primary structure, a secondary structure i.e., regular three dimensional assembly of heteropolyanions with counter cations (protons) and additional water molecules [29]. Hydrophilic membranes are widely used in PV dehydration of organic mixtures. Hydrophilic groups absorb water molecules preferentially, leading to high flux and selectivity.

Among the natural polymers, hydroxypropyl cellulose (HPC) has been widely used by several works for pervaporation studies because it is an alkyl-substituted hydrophilic cellulose derivative that not only has phase transition behavior in aqueous solution [30] but is also miscible with PVA. The material is soluble in water as well as in polar organic solvents [31], but also has many advantages such has excellent film forming properties, biodegradability and biocompatibility etc. In the present study it is

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planned to prepare blend membranes of HPC/PVA and incorporated with PWA aiming to obtain high permeability and selectivity simultaneously for pervaporation separation of ethanol-water mixtures. Ethanol is chosen in the present study, since it is a very important and commonly used solvent in biopharmaceutical and chemical industries. It is miscible with water in all proportions and forms an azeotrope at 14 wt% of water. Conventional methods for separation of ethanol-water mixtures include azeotropic distillation and extractive distillation, which are of high energy consumption and waste generation [32]. Furthermore, the present investigation also aims to study the effect of blend composition in membranes, feed concentration and the perm selectivity has also been investigated and presented here.

2. Experimental Methods

2.1 Materials

Hydroxypropyl cellulose (HPC) (MW = 1,40,000) was purchased from Sigma Aldrich Chemicals Company, Milwaukee, WI, USA. Poly(vinyl alcohol) (PVA) having a viscosity average molecular weight of 1,85,000, Acetone, hydrochloric acid and phosphotungstic acid (PWA) were purchased from SD fine chemicals, Mumbai, India. Ethanol was purchased from Qualigens fine chemicals, Mumbai, India, and Glutaraldehyde was purchased from Merck chemicals, Mumbai, India. Deionized water having a conductivity of 20 µS/cm was used for the preparation of feed solution, which was generated in the laboratory itself.

2.2 Preparation of Membranes

PWA-filled blend membranes of HPC/PVA were prepared by solution casting method. A 2g of PVA was dissolved in 45 mL of distilled water at 90 °C and 2g of HPC was dissolved in 45 mL of distilled water at room temperature (30 °C). These two solutions were mixed thoroughly by constant stirring the mixture for 30 min to form a homogeneous solution. After uniform mixing, the solution was filtered to remove any suspended particles. The 5, 10 and 15 wt% of PWA particles (with respect to the weight of the polymer) dispersed in 10 mL DI water separately by sonication for 30 min; these two solution were separately added to the previously prepared blend solution (of 90 mL) and then the whole mixture was kept under stirring for another 24 h. The blend solution was poured onto to a preleveled glass plate in dust-free atmosphere to cast the membranes with uniform thickness. Membranes thus formed were allowed to dry at ambient temperature and then peeled-off from the glass plate and then crosslinked with glutaraldehyde (2.5 mL) containing 85:10 acetone water mixture in which 2.5 mL HCl was added as activator and allowed for crosslinking reaction for 2 h. Acetone being a non-solvent prevents the initial dissolution of the membrane and water present in the feed leading to swell the membrane there by facilitating an easy penetration of GA into the membrane matrix for an effective crosslinking. Crosslinking reaction takes place between the -OH groups of PVA, HPC, and -CHO groups of GA because of formation of ether linkages by eliminating water molecules. The crosslinked membranes were removed from crosslinking bath and washed repeatedly with distilled water to remove the adhered GA and unreacted molecules and then dried in hot air oven at 50 °C to constant weight.

Membranes were designated as M0, when there was no PWA and PWA-filled membranes were prepared in the same manner by dispersing 5 wt%, 10 wt% and 15 wt% of PWA and designated as M1, M2 and M3, respectively. Membrane thickness was measured using a micrometer screw gauge and was found to be around 35- 40 µm.

2.3 Swelling Studies

The swelling experiments on the membranes were performed gravimetrically at 30 °C for ethanol-water mixture with a variable water composition of 10, 12.5, 15 and 17.5 wt%. Initial masses of the circularly cut (diameter 2.5 cm) HPC-PVA membrane and PWA loaded membranes were taken by placing them on a single-pan digital microbalance (Model AFP 210L) sensitive to ±0.01 mg. Samples were placed inside the specially designed airtight test bottles containing 30cm3 of the test solvent and these were kept in a hot-air oven maintained at constant desired temperature. Dry membranes were equilibrated by soaking in different compositions of the feed mixture in a sealed vessel at 30 °C for 24 h. The swollen membranes were weighed immediately after carefully blotting them on a digital single pan microbalance. The percentage degree of swelling, (DS) was calculated as:

$$DS\ (\%) = \left(\frac{Ws - Wd}{Wd}\right) X\ 100 \quad (1)$$

Where Ws and Wd are the mass of the swollen and dry membranes, respectively.

2.4 Pervaporation Experiments

Pervaporation experiments were performed in an indigenously built apparatus as described before [33]. This effective area of the membrane in the pervaporation cell was 28.27 cm^3 and liquid volume of 250 cm^3. The apparatus was made of a stainless steel cell in which the feed stock solution was maintained at the required constant temperature by a thermostatically controlled water jacket. The pervaporation cell consists of an efficient three-blade stirrer powered by DC motor was used in the feed compartment for stirring the mixture at 200 rpm and maintaining a down-steam pressure of 0.5 mmHg using a vacuum pump (Indvac, Model pvp-150, Peenya industrial area, Bangalore-58, India).

Before the actual measurement, the test membrane was equilibrated for 3 h with the feed mixture at room temperature. After establishment of a steady state, liquid permeate was collected, condensed in traps using liquid nitrogen for up to 3-4 h, the flux was calculated by weighing the permeate on a digital microbalance (Model ADAP 210L) sensitive to ±0.001 mg and its composition was determined by measuring its refractive index and comparing it with a standard established graph of refractive index vs mixture composition of the feed system. The permeate composition was determined at 30 °C by measuring refractive index of the liquid mixture on a refractometer (Atogo, model 3T, Tokyo, Japan). From the PV data, selectivity α was calculated using the following relation.

$$\alpha = \left(\frac{Y_A}{1 - Y_A}\right)\left(\frac{1 - X_A}{X_A}\right) \quad (2)$$

Where XA is mole fraction of water in the feed and YA is mole fraction water in the permeate. Flux, J (Kg/m^2h) was calculated from the weight of permeate, w (kg), effective membrane area, A (m2) and time, t (h) using the relation

$$J = W / At \quad (3)$$

The pervaporation separation index (PSI) was calculated using the equation

$$PSI = J (\alpha - 1) \quad (4)$$

At least three independent measurements of flux and selectivity were made under the same conditions of temperature and feed composition to confirm the steady- state pervaporation.

2.5 Fourier Transform Infrared Spectral (FTIR) Analysis

FTIR Spectra measurements were recorded in the wavelength region of 4000-400 cm^{-1} under N_2 atmosphere at a scan rate of 21 cm^{-1} using Bomem MB - 3000 (Make :Canada) FTIR spectrometer, equipped with attenuated total reflectance (ATR). About 2 mg of the sample was grinded thoroughly with KBr, and 2 pellets were made under a hydraulic pressure of 600 kg/cm^2.

2.6 Scanning Electron Microscopy (SEM)

SEM micrographs of the MMMs of HPC-PVA blends were obtained under high resolution (Mag: 300X, 5 kv) Using JOEL MODEL JSM 840A, Scanning electron microscope (SEM), equipped with phoenix energy dispersive. SEM micrographs were taken at Anna University, Chennai.

2.7 Thermo gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC)

TGA/DSC curves of MMMs at different compositions were recorded using TA instruments differential scanning calorimeter (Model - SDT Q600, USA). The analysis of the samples was performed at heating rate of 10 °C/min under N_2 atmosphere at a purge speed of 100 mL/min.

2.8 X-Ray Diffraction (XRD)

A Siemens D5000 (Germany) powder X-ray diffractometer was used to study the solid-state morphology of the MMMs of HPC/PVA blend membranes. The X-rays of 1.5406 Å wavelengths were generated by a Cu Kα radiation source. The angle of diffraction (2θ) was varied from 0° to 65° to identify any changes in crystal morphology and intermolecular distances between inter-segmental chains of the polymer.

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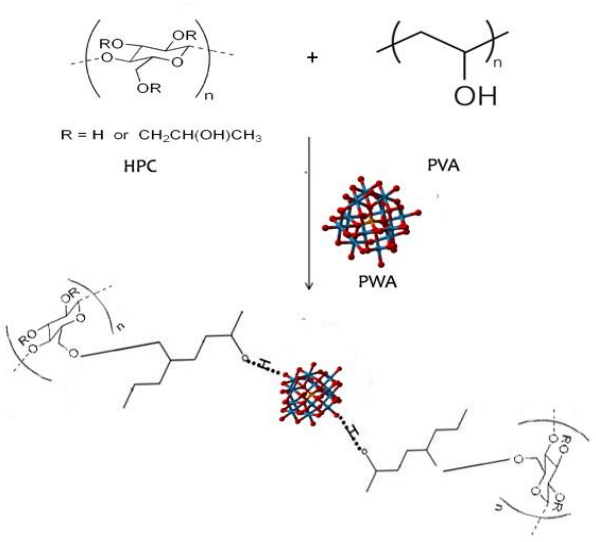
2.9 Measurement of Refractive Index

Refractive index, (N^D) for sodium-D line was measured using the thermostatically controlled Abbe Refractometer (Atago 3T, Japan) with an accuracy of ± 0.001. Refractometer was fitted with hollow prism casings through which water was circulated. The experimental temperature of the prism casing was observed with a digital display (D± 0.01 °C). The instrument directly gives the values of N. Permeate composition was determined by measuring refractive index and comparing it with the established graph of refractive index versus mixture composition.

3. Results and Discussion

Scheme 1 represents the polymers used in the study and also shows of the interaction between PWA and HPC/PVA blend.



Scheme 1 Schematic representation of the interaction between PWA and HPC/PVA blend membrane

3.1 Fourier Transform Infrared Spectroscopy

Fig. 1 shows FTIR spectrum of pure PWA (a), blend membrane without PWA (M0) (b) and PMA loaded blend membranes (M1) (c). FTIR spectra of PWA around 1084, 983, 890 and 998 cm^{-1} that are corresponding to (P-O), (W-Ot), (W-Oc-W) and (W-Oe-W) stretching respectively, wherein Ot, Oc and Oe refer to terminal, corner and edge oxygen respectively [34]. A strong and broad band appearing at 3400 cm^{-1} corresponds to O-H groups of HPC & PVA. Characteristic peaks of saccharide structure of HPC/PVA blend membrane are observed between 1630 cm^{-1} and 1450 cm^{-1}, while the majority of characteristic peaks of Keggin structure have disappeared in the spectra of mixed blend membranes indicating a homogeneous distribution of PWA nanoparticles in the blend polymer matrix. It can be observed that the peak intensity corresponding to –OH around 3410 cm^{-1} increase with the presence of filler loading (Fig. 1) indicating enhanced hydrophilicity of MMMs of blend membranes.

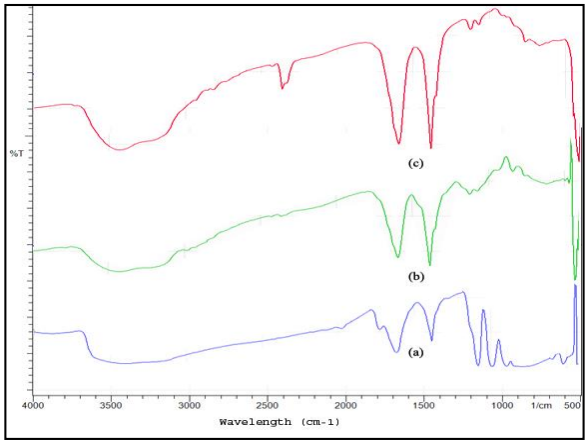


Fig. 1 FTIR spectra of (a) Pure PWA, (b) M0, (c) M1 membranes

3.2 Differential Scanning Calorimetry (DSC)

The DSC Curves of the unfilled HPC-PVA blend membrane (M0) (Fig. 2a) and that of MMM's (ie., M1) are shown in Fig. 2(b). From Fig. 2 it is observed that M0 has a Tg of 45 °C, which is shifted to higher temperatures of 75 °C – 80 °C for M1 after the addition of PWA. This may be attributed to the intermolecular H-bonding interactions between the blend polymer and the PWA particles. This would decrease molecular chain mobility of HPC-PVA blend membrane with the presence of PWA. Notice that Tg values of M1 is considerably higher than M0 due to the micro-phase separation during the membrane formation process. In the case of M0, M1, a sharp endothermic melting curves in the ranges of 275 °C and 325 °C respectively represents the melting points, which can be attributed to intermolecular hydrogen-bonding interactions between the blend polymer and the PWA particles. This may be attributed to its reduced crystallinity due to the incorporation of PWA into the M0 blend membrane.

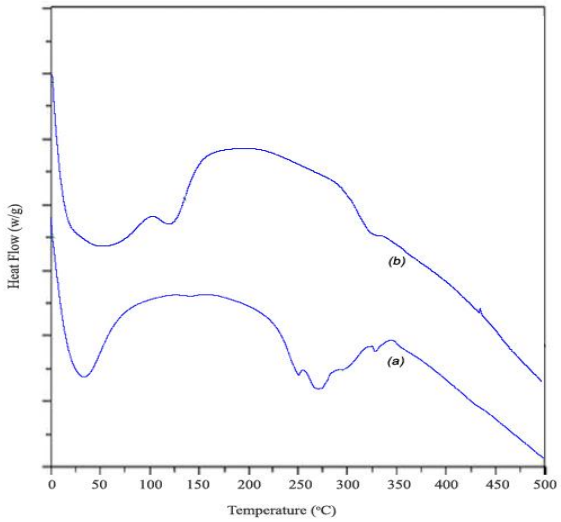


Fig. 2 DSC thermograms of unfilled HPC/PVA blend membrane (a), and PWA loaded membrane (b)

3.3 X-Ray Diffraction Studies

The XRD pattern of the PWA unfilled (M0) and filled HPC/PVA (M1&M2) blend membranes (M1&M2) are shown in Fig. 3. The pristine blend membrane exhibits characteristic XRD peaks at 2θ = 22°. All hybrid materials exhibit negligible reflections at low-angle, suggesting the absence of long-range ordering. In the wide-angle region, blend membrane exhibit only one very broad peak centered at 22°, which is a characteristic of amorphous materials. All the MMMs show the peaks around 12, 14-18° due to the presence of PWA. The absence of characteristic peaks of PWA in the XRD pattern of M1, M2 suggest that PWA units are well-dispersed in the channels of the blend membrane.

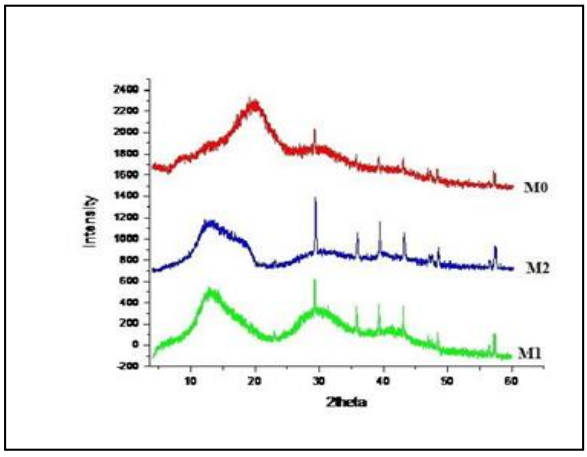


Fig. 3 XRD patterns of PWA unfilled (M0) and filled HPC/PVA blend membranes (M1& M2)

3.4 Scanning Electron Microscopy (SEM)

SEM pictures of unfilled blend membrane of HPC-PVA (50:50) (M0) (a) and 5% PWA filled blend membrane of HPC-PVA (50:50) (M1) (b) were shown in Fig. 4 and from these cross sectional images it is observed that the membranes casting were proper as they all depict non porous structures. Accordingly such membranes may be considered to be of dense structures, which are essential in pervaporation studies. The Fig. 4(b) membrane has a thick and dense top layer almost without any pores confirms a molecular level distribution of PWA particles, such a homogeneous mixing of PWA particles in the bulk of the polymer phase would facilitate higher water transport through the membrane due to the creation of channels that are more favourable to the transport of water molecules than ethanol. These typical SEM images of MMM (M1) suggest smooth surface for this membrane with no phase separation and suggesting a homogeneous and more uniform distribution of PWA particles in to MMM of HPC-PVA (M-1) can be seen in this SEM photograph.

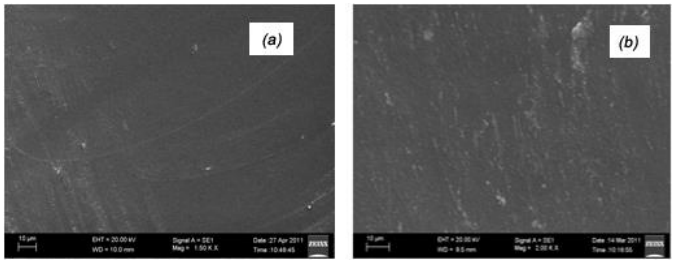


Fig. 4 Surface SEM images of unfilled (HPC-PVA) blend membrane (M0) (a) and PWA filled membrane (M1) (b)

3.5 Membrane Performance

3.5.1 Swelling Experiments

The degree of swelling obtained from sorption experiments at 30 °C for cross-linked pristine blend membrane of HPC-PVA and cross-linked mixed matrix of HPC-PVA blend membranes are measured as a function of wt% of water in the feed are displayed in Fig. 5, and are also shown in Table 1.

Table 1 Percentage swelling data of Ethanol and water mixtures at 30 °C for different blend membranes.

% of water in the feed	% of Swelling			
	M0	M1	M2	M3
10	21.49	13.32	12.43	10.42
12.5	41.84	27.46	19.64	13.46
15	46.44	36.94	20.49	16.99
17.5	54.29	45.45	30.13	20.45

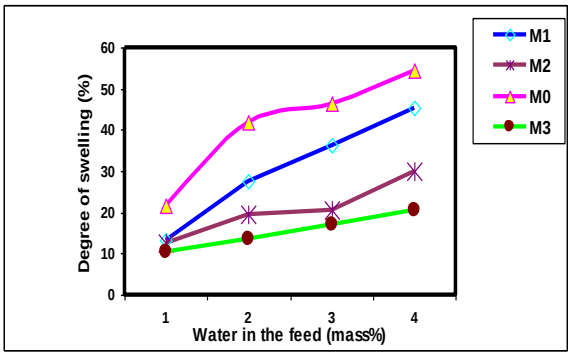


Fig. 5 Degree of swelling of prestine HPC/PVA blend membrane (M0) and Mixed Matrix Membranes of HPC/PVA blend membranes (M1, M2&M3)

A lower swelling was observed for PWA loaded membrane than for pristine blend membrane. Swelling decreased with increasing PWA content of the membranes. Swelling results are in good agreement with the observed Tg values. Degree of swelling decreased with increasing Tg of the membranes, which is dependent upon the amount of PWA added to the blend matrix. Membrane swelling influenced water flux as well as selectivity. Degree of swelling is decreased with increasing PWA loading whereas it increased with increasing water composition of the feed. This may be due to the hydrophilic nature of PWA particles, which when added to another hydrophilic HPC/PVA blend membrane would further decrease the degree of swelling. This observation is a further evidence of the more water selective nature of the MMMs than ethanol and even that of pristine blend membrane of HPC/PVA. These observations can be attributed for the increase of hydrophilic-hydrophilic interactions in the MMMs between HPC/PVA and PWA particles that are responsible for higher selectivity to water than ethanol. As a result of increased interactions between water and polymer matrix, the water selectivity also increased compared to ethanol in case of MMMs of HPC/PVA blend compared to the pristine blend membrane of HPC/PVA.

3.6 Pervaporation Studies

3.6.1 Effect of PWA Loading

Membrane performance was studied by calculating flux and selectivity at different feed compositions of water-ethanol feed mixtures. The MMMs exhibited higher selectivity than the pristine HPC/PVA (M0) blend membrane (Table 2). As can be seen in Table 2 higher selectivity 1294 at 10 wt% water feed and a lower selectivity of 58 at 15wt% water feed are observed for pristine HPC/PVA(M0) blend membrane and then the selectivity increased to 1789 at 10 wt% water feed and decreased to 420 at 15 wt% water feed, respectively for the HPC/PVA (M1) membrane, while the flux values increased from 0.2010 kg/m^{2}h at 10 wt% water feed to 0.2607 kg/m^{2}h at 15 wt% water feed for pristine blend membrane. On the other hand, for HPC/PVA (M1) membranes, selectivity increased to 1442 at 10 wt% water feed, whereas the flux value also increased to 0.3948 kg/m^{2}h as observed, suggesting somewhat lower performances at higher PWA loadings compared to 15 wt% loading. This effect can be explained as due to increased hydrophilic-hydrophilic interactions between PWA particles and the membrane matrix due to the formation intermolecular hydrogen-bonding between HPC/PVA blend membranes and the PWA particles [35] (Scheme 1). These interactions would facilitate higher water transport through the MMMs due to the creation of channels for easy transport of water molecules compared to ethanol, thus increasing the flux and selectivity values for MMMs. Thus, the present MMMs could dehydrate ethanol effectively at lower concentration of water. Since water-ethanol forms an azeotrope at 14.4 wt% of water (a value that is close to 10 wt%), hence, the present membranes are being useful in separating the azeotropic mixtures.

3.6.2 Effect of Feed Water Composition

Feed water composition also exerts an effect on the PV performance of MMMs as can be seen from flux and selectivity values given in Table 2. This effect is attributed to polymer plasticization as seen with the pristine HPC/PVA blend membrane and variations of the MMMs of HPC/PVA blend membranes due to swelling, which would facilitate transport of water molecules from feed to permeate side manifested by hydrophilic-hydrophilic interactions. Pristine HPC/PVA blend membranes have higher flux values with a reasonably good selectivity at increasing water concentration of the feed mixture. Flux and selectivity results at 30 °C are presented in Table 2. The flux for pristine HPC/PVA (M0) blend membrane has increased from 0.2010 to 0.2607 kg/m^{2}h for varying feed concentrations of water from 10 to 15.0 wt%. As the feed water concentration increases, the selectivity of pristine HPC/PVA blend membrane decreases considerably from 1294 to 68.

Similar to this observation, wt% water removed in permeate also decreased from 98.54 to 98.23. On the other hand, the PV performance of pristine HPC/PVA blend membrane was developed by incorporating with PWA (ie., 5 to 15 wt %). As the feed water composition increased from 10.0 to 15.0 wt%. With the MMMs, flux values increased with increasing feed water composition from 10 to 15 wt%. However, at lower feed water composition (10.0 wt%), there appears to be a stronger tendency for water molecules to get adsorbed onto the PWA surfaces, but further increase of feed water to 15 wt% has only declined water selectivity, but with a slight increase in flux. For instance, flux for HPC/PVA-2 membrane increased from 0.3419 to 0.3898 Kg/m^{2}h, while for HPC/PVA-3 membrane, it increased from 0.3948 to 0.4364 Kg/m^{2}h at an increasing amount of water in the feed from 10.0 to 15.0 wt%. However, at lower feed water composition (10.0 wt%), there appears to be a stronger tendency for water molecules to get adsorbed onto the PWA surfaces, but further increase of feed water to 15 wt% has only declined water selectivity, but with a slight increase in flux. Degree of swelling also has an effect on membrane performance in case of HPC/PVA-2, smaller number of water molecules might have been adsorbed, thus lowering the flux values compared to MMMs. With HPC/PVA higher loading of PWA might have caused adsorption of large amount of water molecules, thus increasing the flux. Sorption of MMMs is almost twice greater at higher feed water concentration, due to plasticization effect of the membranes as result of which more number of isopropanol molecules along with water molecules would pass through the membrane, resulting in reduced membrane selectivity. The preferential interaction with water molecules causes the

membrane to swell, leading to plasticization and unrestricted and quicker transport of both volatile components through the barrier. On swelling, the polymer chains become more flexible and hence the transport through the membrane becomes easier for both the feed components resulting in high flux [36].

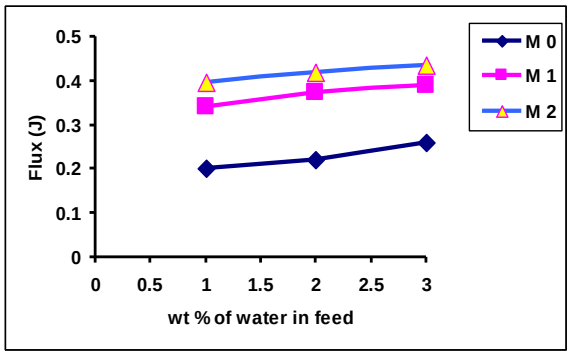


Fig. 6 Flux vs wt% of water in feed mixture for pristine HPC/PVA blend membrane(M0) and MMMs of HPC/PVA-1(M1), HPC/PVA(M2)

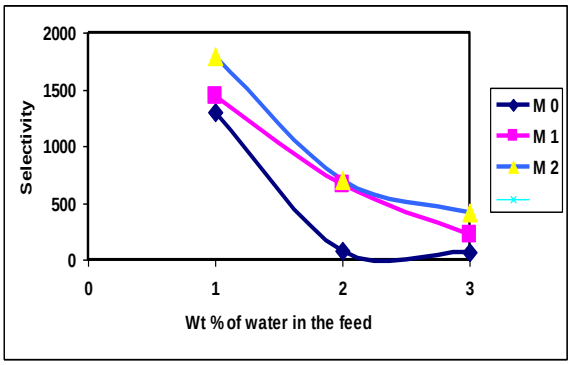


Fig. 7 Selectivity vs. wt% of water in feed mixture for pristine HPC/PVA blend membrane and MMMs of HPC/PVA-1 (M1), HPC/PVA (M2)

Table 2 Pervaporation data for feed mixture of water–ethanol at 30 °C

Wt% of water in feed	Wt% of water in permeate	Flux (J) Kg/m²h	Selectivity (α)
Pristine (HPC/PVA) (M0)			
10.0	98.54	0.2010	1294
12.5	98.35	0.2204	80
15.0	98.23	0.2607	68
HPC/PVA (M1)			
10.0	99.32	0.3419	1442
12.5	99.50	0.3719	666
15.0	99.50	0.3898	220
HPC/PVA (M2)			
10.0	99.42	0.3948	1789
12.5	99.51	0.4202	702
15.0	99.60	0.4364	420

4. Conclusion

The present study deals with the development of novel type of MMMs from the blend polymers of hydroxypropyl cellulose (HPC) and poly(vinyl alcohol) (PVA) incorporated with hydrophilic PWA nanoparticles for the use in effective ethanol dehydration. The boost in PV performance of the MMMs is attributed to hydrophilic-hydrophilic interactions between the filler nanoparticles and water. At higher loadings of PWA nanoparticles, aggregation effect may be responsible to reduce water selectivity. The flux and permeate values increased with increasing feed water composition. Sorption data suggests that membrane selectivity is mainly governed by sorption selectivity. With increasing feed water composition the membrane performance exhibited a reduction in selectivity and improvement in flux due to increased swelling. On the whole, the PV separation MMMs of HPC/PVA (M3) blend membrane is better than pristine HPC/PVA (M0) membrane as well as those MMMs of HPC/PVA (M1&M2) blend membranes. This work suggests higher water selective nature for the developed MMMs.

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