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Mixed Matrix Blend Membranes of NaCMC/HPC Loaded with Phosphotungstic Acid for the Dehydration of Aqueous Isopropanol by Pervaporation Technique

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ABSTRACT

Mixed matrix blend membranes of sodium carboxy methyl cellulose (NaCMC)/hydroxy propyl cellulose (HPC) were prepared using solution casting method by incorporating 5, 10, and 15 Wt. % of phosphotungstic acid (PWA) particles. The membranes thus prepared were crosslinked with glutaraldehyde and tested for the pervaporation (PV) dehydration of aqueous isopropyl alcohol (IPA) at 30 °C. The phosphotungstic acid, with its hydrophilic nature as well as its molecular sieving effect and its favorable interaction with hydrophilic NaCMC and HPC, was responsible to enhance the PV dehydration of aqueous isopropanol in terms of selectivity (α), flux (J), and pervaporation separation index (PSI). The membranes were characterized by Fourier transform infrared spectroscopy (FTIR) to confirm crosslinking and assess the intermolecular interactions present between membranes and PWA. Thermal stability and crystallinity of these membranes were determined from thermo gravimetric analysis (TGA) and X-ray diffraction (X-RD) studies. The morphology of membranes was characterized by SEM studies, which indicated good compatibility of these membranes. Swelling studies were carried out to evaluate the extent of hydrophilicity with and without PWA particles and also based on their nature. The pervaporation performance was evaluated by varying experimental parameters such as feed composition, different polymer compositions and found to be promising membrane for separation of water- isopropanol mixtures. The results pertaining to the 15 wt% PWA loaded blend membrane (M-3) had the highest selectivity 11,241 which was attributed to the combined effect of molecular adhesion between PWA and NaCMC-HPC blend matrix as well as hydrophilicity.

1. Introduction

Now a days, pervaporation (PV) with dense membranes have emerged as a promising new method for water removal from water / organic liquid mixtures. This process has been widely used for separation of liquid mixtures. The basic principles and applications of PV were reviewed in by many workers [1-9]. PV especially is utilized for dehydration of organic compounds or separation of azeotropic or close-boiling point mixtures [10, 11]. Isopropanol is a very important and commonly used solvent in biopharmaceutical and chemical industries. Aqueous isopropanol (IPA) forms an azeotrope with water in a mixture of 87.5% IPA. PV separation of water-IPA mixtures has received widespread attention [12].

Sodium carboxymethyl cellulose (NaCMC) is carboxymethyl ether of cellulose, a well-known natural polysaccharide comprising of the fibrous tissue of plants. Due to its nontoxic, biocompatible, biodegradable and abundantly availability [13-16], it is widely used in different fields ranging from technological industries to the biological, pharmaceutical, petroleum and medical fields [17-20]. It has also been used in membrane preparation for pervaporation (PV) dehydration of several-organic compounds from their aqueous feed solutions. NaCMC has also been used as a matrix material in drug delivery applications [21, 22]. However due to the poor mechanical properties of NaCMC attempts have been made to develop their blends with the other well-known polymers like HPC, chitosan etc.

Hydroxy propyl cellulose (HPC) belongs to the group of cellulose ethers which has been used already as glue and sizing material in other applications. This material is soluble in water as well as in polar organic solvents (makes it possible to combine aqueous and non-aqueous conservation method) [23]. HPC is used as a topical ophthalmic protectant and lubricant, as a food additive, a thickener and as an emulsion stabilizer with E number E463. In pharmaceuticals, HPC is used as disintegrate and is a commonly used as binder for the wet granulation method of making tablets [24]. HPC is an alkyl-substituted hydrophilic cellulose derivative that not only has a particular phase transition behavior in aqueous solution [25-27], and in some solvents [28-30], but also has many advantages such as excellent film forming properties, biodegradability, biocompatibility [31-32] etc. HPC has been a focus of research because of these unusual and desirable properties, and its prospects in industrial applications [33-35].

Blending of polymer films has the potential to improve the material strength and to modulate hydrophilic / hydrophobic characteristics as well as barrier properties to liquids [36]. In order to achieve the improved separation of water-isopropanol mixtures by the PV dehydration process, in the present study the blending of NaCMC with HPC is considered to limit the excessive swelling of NaCMC. Since NaCMC and HPC polymers are completely miscible in all proportions, due to the hydrogen-bond formation between the donor groups of NaCMC and the acceptor groups of HPC, therefore, in the blend system, it is thought that selectivity of NaCMC to water might be enhanced thus, favoring the dehydration of isopropanol [37].

Phosphotungstic acid (PWA) has been the rarely studied filler [38, 39], in developing mixed matrix membranes (MMMs). However the potential interactions between PWA and the host polymer would be responsible to achieve extraordinary separation performance of membrane. The PWA consists of Keggin unit as a primary structure, i.e., the polyanion $[PW_{12}O_{40}]^{3-}$, and a secondary structure, i.e., a regular three-dimensional assembly of the hetero polyanions with counter cations (protons) and additional water molecules [40]. This Keggin unit consists of a central PO_4 tetrahedron surrounded by four W_3O_{13} sets, linked together through oxygen atoms of which, four types can be distinguished; the central oxygen atom belonging to PO_4 tetrahedron is shared by three tungsten atoms, while the edge-sharing oxygen atoms bridge two tungsten atoms of the

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same set. The corner-sharing oxygen atoms bridge two tungsten atoms of different sets and terminal oxygen atoms are associated with a single tungsten atom. The bridging and terminal oxygen atoms are on the periphery of the structure, which are available to associate with protons or water molecules to form hydrates that are thought to enhance selectivity to water. Also, hydrogen-bonding is likely to be established between PWA and the NaCMC/HPC blend system. Due to these advantages, PWA-loaded NaCMC/HPC blend membrane is selected to investigate the PV separation of Isopropanol and the results are presented here.

2. Experimental Methods

2.1 Materials

Sodium Carboxymethylcellulose (medium viscosity) was purchased from Merck, Mumbai, India. Hydroxypropylcellulose (HPC) (MW = 1,40,000) was purchased from Aldrich Chemical Company, Milwaukee, WI, USA. Dodeca – Tungstophosphoric acid hydrate and Isopropanol were purchased from Qualigens fine chemicals, Mumbai, India. Glutaraldehyde was purchased from Merck Specialties chemicals, Mumbai, India. Acetone and Hydrochloric acid were purchased from S.D. fine chemicals, Mumbai, India. Demineralized water having a conductivity of 0.02 S/cm, was used for the preparation of feed solution, which was generated in the laboratory itself.

2.2 Preparation of (NaCMC+ HPC) Blend Membrane

Sodium carboxy methyl cellulose (2 g) and Hydroxy propyl cellulose (2 g) were individually dissolved in 45 mL of deionized water in two separate conical flasks with constant stirring for about 24 hrs at room temperature. The solutions were then filtered and mixed thoroughly in the ratio of 4:1 and cast onto a clean glass plate with the aid of doctor's blade and allowed to dry at room temperature for 1–2 days. The completely dried membrane was subsequently peeled-off and designated as M-0. To prepare Phosphotungstic acid (PWA) filled NaCMC-HPC blend membrane, a known amount of (PWA) was added into the NaCMC-HPC solution. The amount of NaCMC-HPC solution was kept constant each time. The acid filled blend solution was stirred for about 2 hrs and then it was kept in an ultrasonic bath for 30 mins at 30 °C to break the aggregated crystals of Phosphotungstic acid and enhance its dispersion in the polymer matrix. The resulting solution was poured on to a glass plate and the membrane was dried as mentioned above. The prepared membranes were then crosslinked in a bath containing with 85 vol. % acetone, 10 vol. % water, 2.5 vol. % of glutaraldehyde cross linker and 2.5 vol. % hydrochloric acid catalyst for a period of 10-12 hrs. The amount of Phosphotungstic acid with respect to NaCMC-HPC was varied as 0, 5, 10, and 15 wt. %, and the membranes thus obtained were designated as M-0, M-1, M-2 and M-3 respectively. The NaCMC-HPC blend was cross linked with glutaraldehyde to reduce the extent of swelling. Membrane thickness was measured by a micrometer screw gauge at different positions on the flat surface area of the membrane and the thicknesses of the membrane prepared were around 35-40 µ.

2.3 Swelling Measurements

The degree of swelling of PWA-incorporated membranes was determined in different compositions of water and isopropanol mixtures for 24 hrs. at 30 °C using an electronically controlled oven (WTB Binder, Germany). The masses of the dry membranes were first determined. The dry membranes were equilibrated by soaking in different compositions of the mixture in a sealed vessel, at 30 °C for 24 hrs. and then the swollen membranes were weighed immediately after careful blotting the moisture with a filter paper and weighing on a single pan Adam digital microbalance (Model, AFP 210L) having a sensitivity of ± 0.01 mg. The % degree of swelling (DS) was calculated as:

$$DS\,(\%) = \frac{(W_\alpha - W_o) \times 100}{W_o} \qquad (1)$$

where W_α and W_o are the mass of the swollen and dry membranes, respectively.

2.4 Pervaporation (PV) Procedure

Pervaporation experiments have been carried out using an indigenously designed apparatus reported in the previous articles [41, 42]. The effective membrane area in the PV cell is 34.23 cm^2 and the capacity of the PV cell is about 250 cm^3.The vacuum in the downstream side of the apparatus was maintained (1.333224x103 Pa/10 Torr) by a two-stage vacuum pump (Toshniwal, Mumbai, India).The test membrane was allowed to equilibrate for about 2 hrs while in contact with the feed mixture before performing the PV experiment. The procedure used in pervaporation (PV) experiments has been described by Chowdoji Rao et al. [43]. After the steady state, the permeate was collected in trap immersed in liquid nitrogen jar on the downstream side at a fixed time of intervals. The flux was calculated by weighing the permeate on a digital microbalance. Membrane performance in PV experiments was studied by calculating the total flux (Jp), separation factor (α). These were calculated, respectively, using the following equations.

$$Jp = Wp/At \qquad (2)$$

Here Wp represents the mass of water in permeate (kg), A is the membrane area (m^2) and t represents the permeation time (h), The selectivity of the PWA-filled membranes was evaluated by Eq. (3). Membrane selectivity, α, is the ratio of permeability coefficient of water to that of ethanol, which is calculated from their respective wt. concentrations in feed and permeate as given below:

$$\alpha = y\,(1-x)/x\,(1-y) \qquad (3)$$

Where y is the permeate weight fraction of the faster permeating component (water) and x is its feed weight fraction.

2.5 Measurement of Refractive Index (RI)

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. Temperature of the prism casing was observed with a display (±0.01 °C). The instrument was provided with two prisms placed one above and the other in front of the telescope. Upon inserting a drop of test liquid using a hypodermal syringe, the incident ray forms a line of demarcation between light and dark portions of the field, when viewed with a telescope, which moves with scale. The instrument directly gave the values of N^D. Permeate composition was determined by measuring refractive index and comparing it with the established graph of refractive index versus liquid mixture composition.

2.6 Characterization Techniques

2.6.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectral measurements were performed using Bomem MB-3000 (make: Canada) spectrophotometer equipped with KBr disc method. Each sample was finely grounded with KBr to prepare pellets under a hydraulic pressure of 400 kg and spectra were recorded between 4000 and 400 cm^{-1}.

2.6.2 Differential Scanning Calorimetric (DSC)

DSC thermo grams of nascent polymer blend membranes and PWA filled blend membranes were recorded using Differential scanning calorimeter (Model – SDT Q600, USA). Initially, the moisture was removed by heating the samples and then, thermograms were recorded from 30 to 600 °C at the heating rate of 10 °C/min under nitrogen atmosphere and at a flowrate of 30 mL/min. The sample pan was conditioned in the instrument before running the experiment.

2.6.3 Scanning Electron Microscopy (SEM)

SEM micrographs surface of the membranes were obtained under high resolution (Mag: 300 X, 5 kv) using JOEL MODEL JSM 840A Japan, Scanning electron microscope (SEM), equipped with phoenix energy dispersive. SEM micrographs were taken at Satyabhama University, Chennai.

2.6.4 X-Ray Diffraction (XRD)

A Siemens D 5000 (Germany) powder X-ray diffractometer was used to study the solid –state morphology of the MMMs of NaCMC / HPC 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. The X-RD spectra were obtained from university of Hyderabad.

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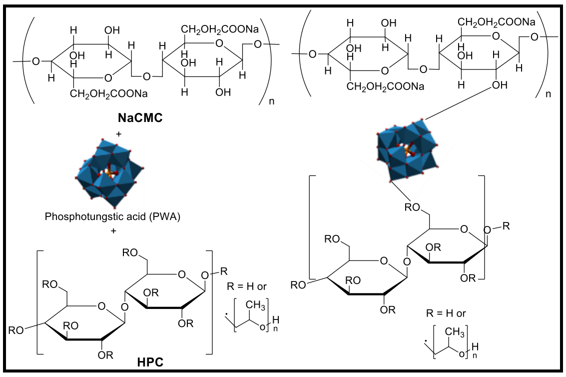
3. Results and Discussion

Scheme 1 represents the polymers used in the study and also shows the structures of PWA incorporated blend (NaCMC-HPC) membranes cross linked with glutaraldehyde, where the –CHO groups of glutaraldehyde, react with the hydroxyl groups of blend membrane incorporated with the PWA resulting in the formation of covalent bond. This can also be confirmed by FTIR studies. It was noticed that both the homo-polymers and the blend membrane incorporated with PWA were 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 temperature.



Scheme 1 Schematic diagram showing the interaction between PWA and NaCMC/HPC blend

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of PWA, Pristine blend membrane and PWA loaded blend membranes are illustrated in Figs. 1a and b.

From the FTIR spectra of pure PWA (Fig. 1a) it is clear that the symmetric and asymmetric stretching of the different kinds of W-O bonds are observed in the following spectral regions: W-Od bonds (1080-983 cm^{-1}), W-Ob-W bridges (inter bridges between corner-sharing octahedra) (983-891 cm^{-1}), W-Oc-W bridges ("intra" bridges between edge-sharing octahedra) (891-799 cm^{-1}).

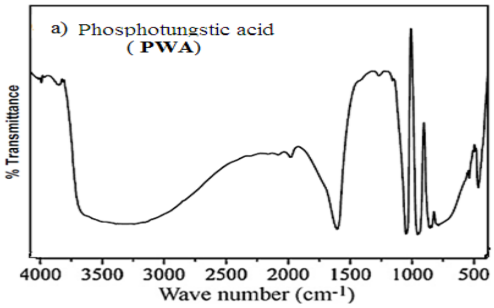


Fig. 1a FTIR spectra of Pure PWA

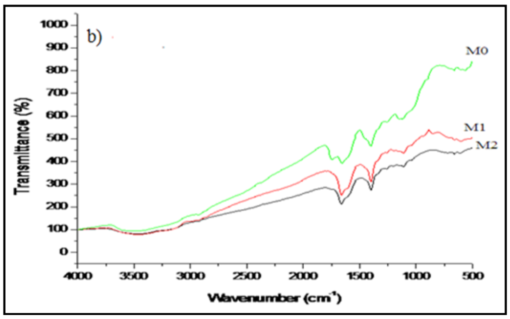


Fig. 1b FTIR spectra of Pristine blend membrane(M0) and PWA loaded blend membrane (M1, and M2)

Only the W-Od stretching can be considered as pure vibrations: the stretching involving Ob or Oc atoms present some bending character. In our study, the IR spectrum of the present compound exhibits the characteristic frequencies of structure in the range 3614-524 cm^{-1}.

A strong and broad band appearing around 3400 cm^{-1} corresponds to O-H stretching vibrations of hydroxyl groups of PWA. The spectrum of unfilled NaCMC / HPC blend membrane (M-0) and those of the filled MMMs (i.e., M-1and M-2) are displayed in Fig. 1b. The M-0 membrane has characteristic peaks at 3440, 2900, 1630 and 1020 cm^{-1} corresponding to peaks of -OH, C-H, CO and C-O stretching vibrations, respectively. In case of M-1, and M-2 membranes, no characteristic bands of Keggin unit appeared, indicating homogeneous distribution of PWA particles in NaCMC/HPC blend membranes. For M-2, the peak intensity corresponding to -OH around 3440 cm^{-1}shows a decrease in intensity compared to unfilled M-0 membrane, indicating the interaction between PWA and blend membrane through $(M_0\ O)$, $(M_0\text{-}O_c\text{-}M_0)$ and $(M_0\text{-}O_e\text{-}M_0)$ (Fig. 1b).

3.2 Differential Scanning Calorimetry (DSC)

The DSC curves of the pristine blend membrane of NaCMC / HPC (Mo) and PWA loaded MMMs (M-1, and M-2) are shown Fig. 2.

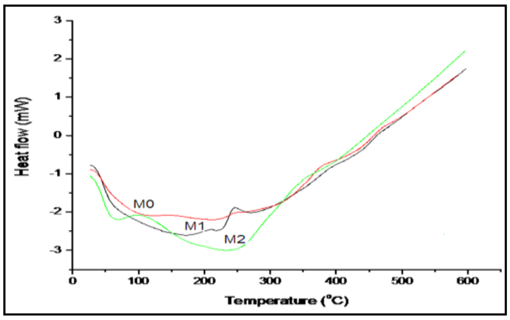


Fig. 2 DSC Thermograms of pristine blend membrane of NaCMC/HPC (Mo) and PWA loaded MMMs (M1 and M2)

From Fig. 2, it is observed that the pristine blend membrane of NaCMC/HPC (Mo) has a Tg of 79.4 °C, which is shifted to higher temperatures of 84.5 °C, and 89 °C for M-1, and M-2, respectively after the addition of PWA particles. This may be due to intermolecular hydrogen-bonding interactions between NaCMC / HPC blend and PWA particles. It can be seen from Fig. 2 that the Tg curves are quite identical, suggesting the compatibility between NaCMC / HPC blend and PWA filler particles. However at higher loading as in case of M-2 (NaCMC / HPC-10), the Tg was shifted to higher value due to micro-phase separation between the organic and inorganic phases that would allow isopropanol to transport across the membrane along with some of the water molecules, thus causing increased permeation flux exhibiting a lower selectivity.

3.3 Thermogravimetric Analysis (TGA)

TGA diagrams of NaCMC / HPC blend membrane (M-0) and PWA loaded blend membranes (M1 and M2) are shown in Fig. 3. These curves showed the thermal stability of the systems under study. These thermograms further revealed that two stage thermal degradation process.

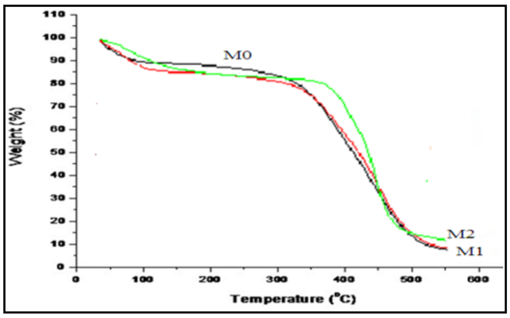


Fig. 3 TGA Spectrum of pristine NaCMC/HPC membrane and other MMMs

The first stage transition diffusion occurred in the temperature range of 40-100 °C and the second stage in the range of 100-280 °C. The weight loss in the first stage is attributed to loss of volatile products like dehydration etc. and the weight loss in the second stage is attributed to the crosslinking of polymer networks and decomposition of PWA. From the graphs it is also noticed that M2 is more stable than M1 and M1 is more stable than M0 as it contains more amount of PWA in the blend membrane.

3.4 X-Ray Diffraction (XRD) Studies

The X-RD patterns of plain PWA, plain blend membrane (M0) and PWA loaded MMMs of blend membranes (M-1 and M-2) are presented in Fig. 4.

In Fig. 4 it is observed that the curve for PWA shows strong characteristic diffraction peaks, suggesting crystalline nature of PWA. However, curves for NaCMC / HPC blend (Mo) and M_1 and M_2 show two diffraction peaks observed at various diffraction peaks at 8.20, 9.0, 18.50, 20.90 and 23.0 of 2θ showed a decrease in intensity in case of MMMs, due to random entanglement of NaCMC / HPC chains caused by the addition of

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PWA particles. After incorporating PWA particles into the NaCMC / HPC matrix, amorphous region increased, thus allowing the transport of more permeant molecules through the barrier membrane, thereby offering higher flux for MMMs than nascent NaCMC / HPC blend membrane.

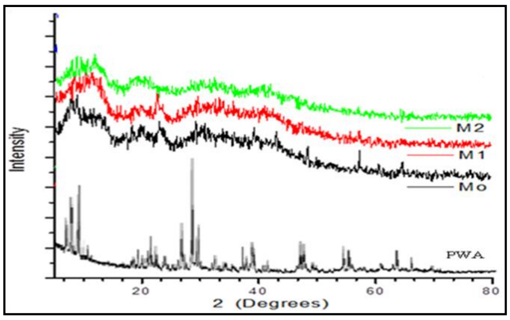

Fig. 4 XRD Spectrum of PWA, plain blend membranes (NaCMC/HPC) (Mo and PWA loaded MMMs of blend membranes M1, M2 and M3)

3.5 Scanning Electron Microscopy (SEM)

SEM images of (NaCMC / HPC) blend membrane (M0) and PWA loaded 5, 10 and 15 wt. % PWA (M1, M2 and M3) blend membranes are shown in Fig. 5.

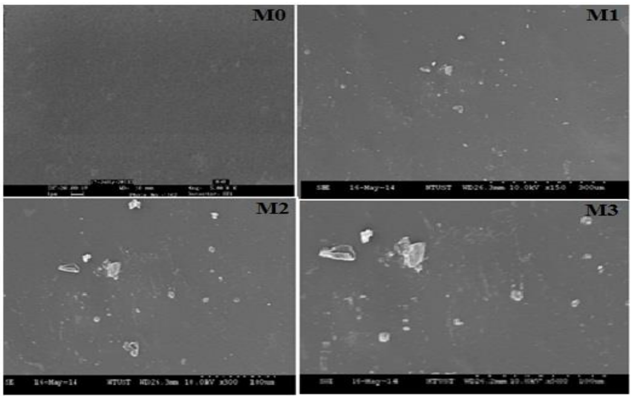

Fig. 5 SEM images of Pristine blend membrane (Mo) and PWA loaded 5 wt%(M_1), 10% wt (M2) and 15 wt% (M3) blend membranes

From Fig. 5, it is noticed that a smooth image is observed for pristine blend membrane (M0) indicating the uniform surface. From Fig. 5, it is also seen that in the case of M-1 membrane, we observe a smooth surface with uniform distribution of PWA particles. Such a homogenous 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 favorable for higher water transport than isopropanol through the membrane. With increasing loading of PWA as in M-2 and M-3 membranes, some surface roughness can be seen, but with not so much of uniform distribution of PWA particles on the surfaces of the membranes.

3.6 Swelling Results

The results of % Degree of swelling (D.S%) of pristine NaCMC-HPC blend membrane (M0) and PWA loaded MMMs of the M1, M2 and M3 at 30 °C and feed mixtures from 10 to 17.5 wt% water in the feed are presented in Table 1.

Table 1 Percentage of swelling data of blend membranes in different water in the feed / IPA mixtures at 30 °C

% of water in the feed	% of Swelling			
	M0	M1	M2	M3
10.0	20	38	42	48
12.5	32	59	62	72
15.0	41	76	82	85
17.5	46	90	92	98

The degree of swelling (%) of the membranes calculated and plotted as a function of wt. % of water in the feed mixture at 30 °C (Fig. 6).

It is observed that M-3 has the highest degree of swelling compared to all the membranes over the studied range of feed water compositions. Degree of swelling of the M-3 increased to almost double, i.e., from 45 to 96 with increasing water concentration in the feed mixture from 10 to 17.5 wt. %. These results support the higher values of flux observed in case of M-3 as compared to M-2, M-1 and the pristine blend membrane. The lowest degree of swelling for pristine blend membrane increased from 20 to 46, for 10 to 17.5 wt. % water content in the feed, but after the addition of the PWA particles into NaCMC / HPC matrix, swelling has been increased. This trend is in accordance with the flux values of the membranes in the chosen feed mixture. An increase in equilibrium swelling with increasing amount of PWA in blend membrane is due to the hydrophilic interaction of PWA with pristine blend membrane (M-0). The equilibrium swelling results vary as per the sequence: M-0 < M-1 < M-2 < M-3, i.e., higher loading of PWA, higher will be the swelling.

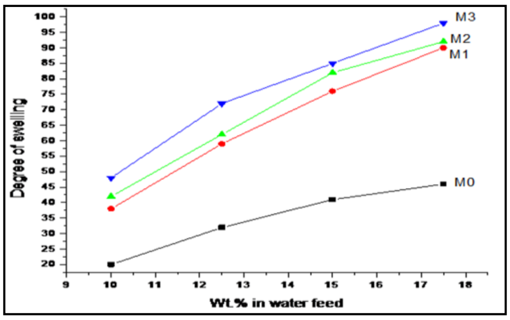

Fig. 6 Degree of swelling vs feed water composition for M0 and MMMs

3.7 Membrane Performance through PV Studies

The results of pervaporation dehydration of isopropanol interms of feed composition, permeate composition, selectivity, flux and PSI are included in Table 2.

Table 2 Pervaporation data of IPA/water mixtures for different membranes at 30 °C

Feed compositions		Permeate compositions (wt %)		Selectivity (α)	Flux (kg /m²h)	PSI
Water (x)	IPA (1-x)	Water (y)	IPA (1-y)			
M -0						
10	90	98.89	1.11	801.81	0.364	291.49
20	80	98.54	1.46	289.82	0.398	114.95
30	70	98.42	1.58	122.15	0.409	49.55
40	60	97.82	2.18	67.30	0.418	27.71
M-1						
10	90	99.72	0.28	3205.28	0.424	1358.61
20	80	99.48	0.52	765.23	0.442	337.78
30	70	99.28	0.72	321.74	0.472	151.38
40	60	99.02	0.98	151.56	0.484	72.87
M-2						
10	90	99.84	0.16	5616.00	0.464	2605.36
20	80	99.54	0.46	865.56	0.486	420.17
30	70	99.42	0.58	399.96	0.507	162.37
40	60	99.28	0.72	206.84	0.548	92.21
M-3						
10	90	99.92	0.08	11241.00	0.546	6137.04
20	80	99.77	0.23	1735.13	0.562	974.58
30	70	99.58	0.42	553.22	0.586	323.60
40	60	99.32	0.68	219.08	0.595	129.75

3.7.1 Membrane Performance Interims of Flux and Selectivity

In pervaporation, molecular transport occurs due to a concentration gradient existing between the feed and permeant mixtures as envisioned by the solution-diffusion principles [44, 45]. Permeating molecules first dissolve into the membrane and diffuse out on the product side as a result of concentration gradient. In case of mixed matrix membranes of the present study, overall separation can be explained as due to the delicate balance of solvent properties, viz., its nature and affinity towards membrane, size and vapor pressure in addition to morphological set up of the membrane. Considering the PV separation of water-isopropanol mixtures, the relative affinity of either isopropanol or water molecules towards membrane could be assessed from the sorption (swelling) measurements. When the hydrophilic PWA filler is mixed with a hydrophilic blend (NaCMC/HPC) polymer, the permeation flux of such membranes would be enhanced in proportion to the amount of filler added (see Table 2). Equilibrium swelling and/or dynamic sorption data

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described before corroborate this observation. For instance, when higher amount of PWA (15%) is present, greater would be the degree of swelling and as well as permeation flux. On the other hand, when 10% of PWA is added, membrane swelling would be higher than plain blend membrane, but lower than observed for 15 mass% loaded membrane, while flux values vary accordingly.

At low level of PWA loading, presumably the PWA spread around considerably within the blend bulk matrix (M-0), which would form the isolated islands within the matrix environment. Such a matrix is likely to absorb more of water molecules as compared to unfilled blend membrane matrix. However, at higher filling (15%: M3), the degree of swelling would be higher because the filler particles will help the matrix to absorb more of water molecules. The hydrogen-bond type inter-actions between water and hydrophilic PWA particles as well as blend polymer are responsible for higher values of flux and selectivity as compared to the pristine blend membrane. A substantial increase in selectivity and a moderate increase in permeation flux rate over that of pristine blend membrane (M-0) for 0-15 wt. % PWA loaded MMMs is due to the fact that in the swollen state, hydrophilic PWA would preferentially allow the water molecules to be sorbed faster than isopropanol, and this would increase the selectivity and flux values even at higher amounts of water in the feed.

The importance of using zeolite-filled membranes in PV separation has been well documented in the earlier literature for a variety of polymer-zeolite combinations [46, 47]. The crystalline ordered structure of hydrophilic PWA with a narrow size distribution has a higher resistivity to organic liquids than water. Thus, by dispersing PWA particles into blend polymer matrix, the increase in permeation flux of the MMMs could be the result of preferential interaction of water molecules, which would accommodate higher amount of water than isopropanol. This could be possibly due to: (1) strong adsorptive hydrophilic interaction of water molecules onto PWA particles, (2) surface diffusion from cage to cage and (3) vaporization on the permeate side. Physical adsorption involves both van der Waals type dispersion-repulsive and electrostatic interactions due to polarization, as well as dipole and quadrupole type interactions. The complimentary effects of PWA on water transport would thus improve the membrane performance. It is worth mentioning that the varying effects of flux and selectivity are attributed to the amount of PWA filler present in the blend matrix.

3.7.2 Effect of Feed Water Composition

In the present work, we find that crosslink density increases by varying the amount of PWA in the NaCMC/HPC blend, because the PWA particles will act as the reinforcing bridge between the polymer chain segments of NaCMC and HPC, while the PWA will help to establish this bridge through the electrostatic interactions. Hence, all the MMMs of this study will exhibit higher selectivity than NaCMC/HPC blend alone. However, the fluxes of all the MMMs are higher even compared to NaCMC / HPC membrane at all the compositions of water in the feed mixture (Table 2).

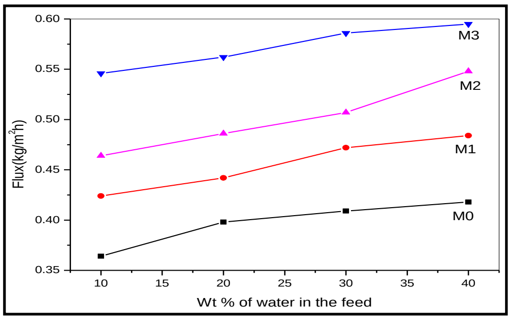

Fig. 7a Effect of wt% of water in the feed on flux for different blend membranes

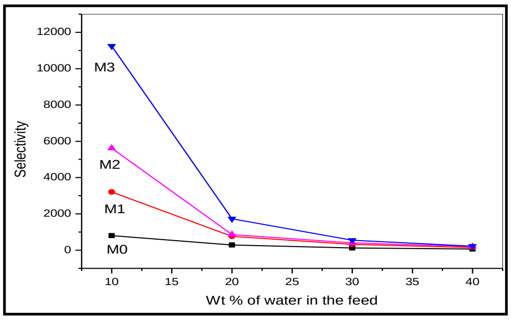

Fig. 7b Effect of wt% of water in the feed on selectivity for different blend membranes

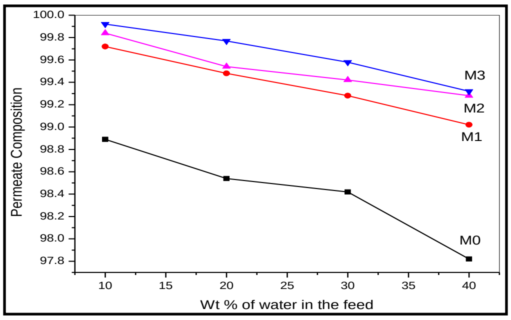

Fig. 7c Effect of wt% of water in the feed on water permeate for different blend membranes

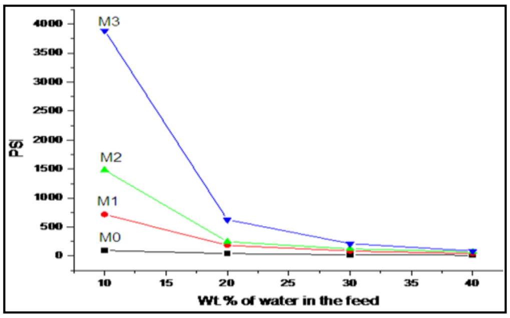

Fig. 7d Effect of wt% of water in the feed on PSI for different blend membranes

The variations of flux and selectivity with wt% of water in the feed are displayed in Figs. 7a and b respectively. The flux of pristine blend membrane has increased from 0.364 to 0.418 kg/m^2h for feeds containing 10% of water to 40% of water. However, selectivity of the pristine blend decreased from 801.81 to a considerably smaller value of 67.30 when water in the feed mixture water increased from 10 to 40%. Parallel to this effect, mass% of water in permeate also decreased from 98.89 to 97.82, water in permeate for prestine blend membrane, for 5% PWA loaded blend membrane ranged between 99.72 to 99.02 and, for 10 mass% PWA loaded blend membrane, it ranged between 99.84 to 99.28 %, while for 15% PWA loaded blend membrane, it was as high as 99.92 to 99.32 over the whole range of water compositions of the feed mixture. Since membranes of this study are highly water selective, very small differences in these compositions may cause huge differences in selectivity. Therefore, sensitivity of water measurements is plotted in Fig. 7c which shows the exact composition of water in permeate as a function of water in feed for different loadings of PWA in blend membrane matrix. This could be due to hydrophilic nature of PWA, which might have exerted high affinity to water molecules than isopropanol, since water is more polar than isopropanol. Free channels in the structure of PWA cage as well as the polymer plasticization effect could also be responsible for this effect in addition to strong molecular sieving effect induced as a result of higher amount of PWA in the blend membrane. Thus, the observed higher selectivity and high flux values for 5,10 and 15 mass% of PWA loaded blend membranes as compared to the pristine blend membrane (M0) is quite possible.

3.7.3 Effect of Pervaporation Separation Index

Pervaporation separation index (PSI) values are calculated with regard to pervaporation study and are included in Table 2. PV results are also discussed in terms of pervaporation separation index (PSI) at 30 °C as shown in Fig. 7d. The PSI values follow the same trends as in the case of selectivity, these values (PSI) decrease with increasing water concentration. Pristine blend membrane exhibits the least PSI when compared to PWA loaded blend membranes. The increasing values of PSI from pristine blend membrane to PWA loaded blend membranes suggest increase in the water content in permeate. These results are particularly useful in membrane distillation processes during alcohol fermentation.

3.7.4 Influence of PWA Loading on PV Performance

Membrane performance was studied by calculating flux and selectivity at different concentrations of PWA loaded blend, and their variations are shown Figs. 8a and b respectively. The water flux for 5% PWA loaded blend membrane has increased from 0.424 to 0.484 kg/m^2h, while the water flux for 10% PWA loaded blend membrane increased from 0.464 to 0.548 kg/m^2h. Whereas in case of 15% PWA loaded blend membrane, water flux increased from 0.546 to 0.595 for all these 5,10 and 15% of PWA mixed matrix membranes, flux increases with increasing amount of water in the feed from 10 to 40%. The flux values all of the MMMs are higher than the pristine blend membrane which can be clearly observed from the values of flux in Table 2 and also from the Fig. 8a. Mainly, selectivity of 5 wt.% PWA-containing membrane (i.e., M-1) increased considerably compared to pristine NaCMC-HPC blend membrane. At the same time, it is observed from Fig. 8b that at higher concentrations of PWA i.e., M-2, M-3 membranes, the selectivity values increased considerably compared to blend membrane.

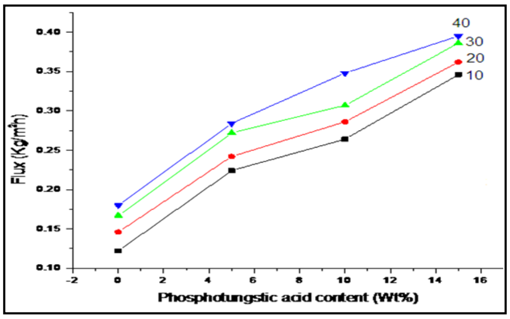

Fig. 8a Effect of PWA content on flux at different wt% of water in the feed

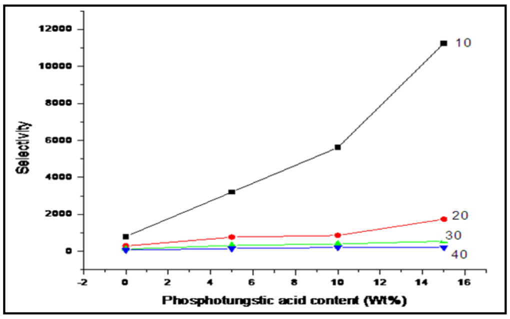

Fig. 8b Effect of PWA content on selectivity at different wt% of water in the feed

The decrease in selectivity for all the membranes with increasing water content of the feed depends upon the amount of filler added in the blend matrix. For instance, with PWA (5%) - filled membrane, selectivity dropped from 3205.28 for 10% water feed to 151.56 for 40% water feed, which is almost close to the value observed for pristine blend membrane and by this, it is evident that with a higher amount of PWA in blend membrane, the amount of water molecules could pass through the pores of PWA. For PWA (10%) - filled membrane, selectively improved greatly, i.e., the observed value is 5616.00 for 10% water in the feed, which dropped steeply to 206.84 for 40% water in the feed. On the other hand, for the mixed matrix membrane containing 15% of PWA, even though there was a slight improvement in flux, but selectivity values are quite higher over the entire range of feed mixture compositions. For instance, a value of 11241.00 for selectivity was obtained with 15% PWA loaded blend membrane at 40% water in the feed and decreased to 219.08 for the same. It is thus evident that the presence of higher amount of PWA in the blend membrane, higher number of water molecules would transport through the pores of PWA, thereby increasing its selectivity to water, but not for isopropanol.

4. Conclusion

This investigation clearly demonstrates the effect that by incorporating PWA particles into NaCMC/ HPC blend host matrix, it is possible to enhance remarkably the Pervaporation performance of the filled blend matrix membranes over that of unfilled NaCMC/ HPC blend membrane for isopropanol dehydration. However, higher loadings of PWA particles also increase the NaCMC/ HPC matrix less rigid with an increase in flux value but at the same time it also increased selectivity to water. Membrane characterization by XRD, SEM, DSC, FTIR and swelling studies. DSC analysis of the membranes indicated that the ordered association of pure blend membrane was decreased due to the presence of PWA .However, detailed mechanistic interpretation of pervaporation results requires a consideration of both true micro cavity uptake as well as interstitially held water molecules between crystallites of the membrane matrix. Much research is yet to be done in these areas to understand such problems, particularly choosing different PWA filled polymeric membranes.

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