



Mixed Matrix Blend Membranes of Sodium Alginate-Hydroxy Propyl Cellulose Loaded with Phosphomolybdic Acid used for Pervaporation Dehydration of Isopropanol Mixture at 30°C

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ABSTRACT

Mixed matrix blend membranes (MMMs) of sodium alginate-hydroxy propyl cellulose (SA-HPC) were prepared by loading with phosphomolybdic acid (PMA) and characterized by various physico-chemical techniques like Fourier transform infrared spectral, scanning electron microscopy and thermo gravimetric analysis. Pervaporation properties of membranes were investigated for the separation of water-isopropanol feed mixtures containing 10-15 wt.% of water. Membrane performance showed dependence on the extent of PMA loading. The 0.2 wt.% PMA-loaded blend membrane had the highest selectivity of 1865, which declined considerably at higher loading. The flux of 0.2 wt. % PMA-loaded membrane was higher than that of pristine SA-HPC blend membrane. Degree of swelling was smaller after PMA loading exhibiting better separation ability. From this study, it is concluded that the selectivity of MMMs is higher than the pristine SA-HPC blend membrane.

Key words: Pervaporation, Phosphomolybdic acid, Sodium alginate-hydroxy propyl cellulose blend, Isopropanol-water mixture.

1. INTRODUCTION

Isopropanol (IPA) is widely used as a solvent in the pharmaceutical industry as well as in many chemical processes such as acetone production, solvent extraction, and in the manufacturing of hydrogen peroxide. High purity grade IPA is required as a cleansing agent in semiconductor and electronic industries [1-3]. The azeotropic composition of IPA with water is 12.2%, which makes it difficult to separate from water by the conventional distillation without recourse to carcinogenic benzene as an entrainer [4]. Alternatively, membrane-based pervaporation (PV) separation offers high separation efficiency along with high energy savings [5-7].

PV is an efficient membrane based separation technology which has been widely used in industrial processes due to its easy and effective operation and high-energy savings [8-10]. This technique has been most actively investigated for its applications in separation and purification of azeotropic liquid mixtures; particularly for dehydration of organic

solvents, separation of azeotropic or close boiling mixtures [11]. In PV separation; physical and chemical properties of the membrane play very important role. Hence, selection of the membrane material for PV applications is very important factor in order to fabricate the membranes with higher permselectivity.

Polymers with glass transition temperatures above room temperature are usually used for dehydration of alcohols. Among the many organic polymers, sodium alginate (SA), a naturally occurring hydrophilic biopolymer, has been widely used as a membrane in PV separation [12]. SA is a good example of this type of material and has been extensively studied as a hydrophilic membrane component. Sometimes SA membranes are modified by cross-linking, complexing or grafting to improve its chemical stability and separation performances, these efforts have been made to develop blend membranes of SA with other polymers. Hydroxypropyl cellulose (HPC) is another important biopolymer used in PV dehydration studies. In order to improve PV separation characteristics of

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water-isopropanol mixtures, in this work, blending of SA with HPC is considered to limit the excessive swelling of SA. HPC which is an alkyl-substituted hydrophilic cellulose derivative that not only has phase transition behavior in aqueous solution [13], but also has many advantages such as excellent film forming properties, biodegradability and biocompatibility etc.

Organic/inorganic hybrid composite materials have recently attracted considerable attention in various fields [14,15] as functional materials due to their advantages like lightness, pliability, heat-resistance due to strength of inorganic materials, hence, arising as a “next generation” membranes [16]. Usually, an inorganic component such as heteropolyacid hydrates [17-22], zeolites [23,24], silica [25] and carbon molecular sieve [26] are used as filler to fabricate the organic/inorganic hybrid polymeric membranes were used in literature for PV mediated separations of binary liquid mixtures.

In the above considerations and to get better stability of the membranes, efforts have been made to develop mixed matrix membranes (MMMs) by physical mixing of the different types of inorganic fillers [27-30]. In the past, phosphomolybdic acid (PMA) has been rarely chosen as a filler [31,32]. PMA is a heteropoly acid, having one hetero atom surrounded by four oxygen's to form a tetrahedron. The hetero atom located centrally and caged by 12 octahedral MO_6 -units linked to one another by the neighbouring oxygen atoms, thus with a total of 24 number of bridging oxygen atoms that link 12 addenda atoms. The bridging and terminal oxygen atoms on the periphery of the structure are thus available to associate with water molecules to form hydrates that are thought to enhance selectivity to water. And also, the hydrogen-bonding is likely to be the formation between PMA and SA-HPC blend membrane system. In the present study, MMMs prepared by loading different quantities of PMA into the blend systems of SA and HPC were used in the PV separation of isopropanol-water mixtures, and compared with the unfilled blend membrane.

2. EXPERIMENTAL

2.1. Materials

SA having a viscosity average molecular weight of 500,000, acetone, hydrochloric acid and PMA were purchased from S. D. Fine Chemicals, Mumbai, India. HPC with a molecular weight of $\approx 15,000$ was purchased from Aldrich Chemical Company, Milwaukee, WI, USA. Iso-propanol was purchased from Qualigens Fine Chemicals, Mumbai, India and glutaraldehyde (GA) was purchased from Merck Chemicals, Mumbai, India. Deionized water having a conductivity of $20 \mu S/cm$ was used for the preparation of feed solution, which was generated in the laboratory itself.

2.2. Preparation of Membranes

MMMs of SA-HPC blends loaded with PMA membranes were prepared by solution casting and solvent evaporation technique. In brief, different ratios of SA and HPC so as to make 4 g were dissolved in 90 mL of distilled water individually at room temperature by constant stirring on a magnetic stirrer (Remi Equipment Model 2 MLH, Mumbai, India) for 24 h to get homogeneous solution of SA-HPC blend. In separate flasks, 0.2, 0.3 g of PMA was dispersed in 10 mL of water, sonicated for 2 h, added individually to the previously prepared SA-HPC blend solution. The whole mixture was stirred for 24 h, filtered and poured onto a perfectly aligned clean glass plate in a dust free environment for casting the membranes using a doctor's blade. The membranes after drying at ambient temperature ($30^\circ C$) were peeled off from the glass plate, immersed in a cross-linking solution bath containing water and acetone mixture (30:70) along with 2.5 mL of Con. HCl, 2.5 mL of GA. After allowing for 12 h, take out the membrane from the cross-linking bath, and wash with deionized water repeatedly then dry in an oven at $40^\circ C$ to eliminate the presence of residual acid, if any. The dried MMMs were peeled off and designated as SA-HPCM-2, SA-HPCM-3 respectively. The resulting solution was mixed thoroughly and then filtered to remove any suspended particles. Membrane thickness was measured by a micrometer screw gauge at different positions on a flat surface area of the membrane, and the thicknesses of the membrane prepared were around $35-40 \mu$.

2.3. PV Experiments

PV apparatus consists of stirred stainless steel cell through which retentate is circulated to the feed tank. Effective surface area of the membrane in the cell is 28.27 cm^2 with a radius of 3.0 cm and volume capacity of the cell is about 250 cm^3 . Temperature of the feed mixture is maintained constant using a thermostatic water jacket. The PV cell is provided with an efficient three-blade stirrer powered by a DC current motor in the feed compartment. Turbulent flows were obtained even at low rotation of the stirrer, i.e., $<200 \text{ rpm}$ speed. Mass transfer limitations due to concentration polarization are negligible. The permeate is collected in a glass container, cooled in a Dewar flask with liquid nitrogen. The vacuum is maintained by a two-stage vacuum pump.

The experimental procedure remained the same as reported elsewhere [33]. Weight of the permeate vapors collected in a Dewar flask with liquid nitrogen trap was measured and its composition was determined by measuring its refractive index by comparing it with the standard graph of refractive index versus mixture composition of the feed system. The selectivity, α of a given membrane was estimated using the following equation [34].

$$\alpha_{PV} = \left(\frac{y_A}{1-y_A} \right) \left(\frac{1-x_A}{x_A} \right) \quad (1)$$

Where X_A is, mole fraction of water in feed and Y_A is the mole fraction of water in permeate. Flux, J ($\text{kg/m}^2 \text{ h}$), was calculated from the weight of liquid permeated, W (kg), effective membrane area, A (m^2) and actual measurement time, t (h)

$$J = \frac{W}{A_t} \quad (2)$$

2.4. Membrane Swelling

The swelling experiments on the circularly cut membranes were performed at 30°C gravimetrically [35] in 10, 12.5 and 15 wt. % water-containing feed mixtures. To do this, dry weight of the circularly cut (diameter=2.5 cm) disc shaped MMMs of blend samples were stored in a desiccator over anhydrous calcium chloride maintained at 30°C for about 24 h before performing the swelling experiments. MMMs of blend samples with compositions ranging from 10 wt. % to 15 wt. % water at $30^\circ\text{C} \pm 0.5^\circ\text{C}$ were soaked in IPA/water mixture of different compositions for 48 h. Membrane were removed from this swelling reaction solution and were wiped with tissue paper to remove the adhered liquid and weighed immediately to determine the amount of liquid sorbed by the membrane [36]. The degree of swelling was calculated using the following equation:

$$\text{Degree of Swelling (\%)} = \left(\frac{W_s - W_d}{W_d} \right) \times 100 \quad (3)$$

Where W_s and W_d are the mass of the swollen and dry membranes, respectively.

2.5. Fourier Transform Infrared Spectral (FTIR) Analysis

FTIR spectra measurements were recorded in the wavelength region of $4000\text{--}400 \text{ cm}^{-1}$ 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. About 2 mg of the sample was grinded thoroughly with KBr, and pellets were made under a hydraulic pressure of 600 kg/cm^2 .

2.6. 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 ($\pm 0.01^\circ\text{C}$). The instrument directly gives the values of N^D . Permeate composition was determined by measuring the refractive index and comparing it with the established graph of refractive index versus mixture composition.

2.7. Scanning Electron Microscopy (SEM)

SEM micrographs of the MMMs of SA-HPC blends were obtained under high resolution (Mag: $\times 300$, 5 kv) using JOEL MODEL JSM 840 A, SEM, equipped with phoenix energy dispersive. SEM micrographs were taken at Anna University, Chennai.

2.8. 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 $10^\circ\text{C}/\text{min}$ under N_2 atmosphere at a purge speed of $100 \text{ mL}/\text{min}$.

3. RESULTS AND DISCUSSION

3.1. FT-IR Analysis

The FTIR spectra of PMA and PMA-loaded MMMs of SA-HPC are illustrated in the Figure 1. The FTIR spectrum of PMA shown in Figure 1a exhibits four characteristic bands around 1064 , 965 , 868 and 785 cm^{-1} that are, respectively attributed to $\nu_{\text{as}}(\text{P-O})$, $\nu_{\text{as}}(\text{M}_0\text{-O}_t)$, $\nu_{\text{as}}(\text{M}_0\text{-O}_c\text{-M}_0)$ and $\nu_{\text{as}}(\text{M}_0\text{-O}_e\text{-M}_0)$ stretching vibrations, in this O_t , O_c and O_e refer to terminal, corner and edge oxygens, respectively [37]. A strong and broad band appearing around 3400 cm^{-1} represents to O-H stretching vibrations of hydroxyl groups of PMA.

The spectrum those of MMMs of SA-HPCM-2 and SA-HPCM-3 are displayed in Figure 1b. In this MMMs of SA-HPCM-2 and SA-HPCM-3 membrane, there are no characteristic bands of Keggin unit that indicates the homogeneous distribution of PMA particles in SA-HPC blend membranes. For MMMs of SA-HPCM-2 the peak intensity corresponding to $-\text{OH}$ around 3490 cm^{-1} , indicating the hydrogen bond interaction between PMA and blend membrane through $(\text{M}_0\text{-O}_t)$, $(\text{M}_0\text{-O}_c\text{-M}_0)$ and $(\text{M}_0\text{-O}_e\text{-M}_0)$. The

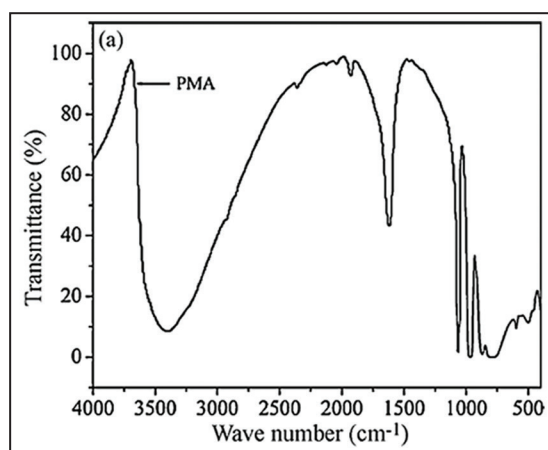


Figure 1(a): Fourier transform infrared spectra of phosphomolybdic acid showing characteristic bands.

progressive increase in PMA content as in the case of SA-HPCM-3 is due to the presence of a large number of hydroxyl groups of PMA.

3.2. SEM

Figure 2 shows the SEM pictures of SA-HPCM MMMs containing 0.2 and 0.3 wt. % PMA was taken to inspect the distribution of PMA particles. As can be seen from Figure 2a especially in the case of SA-HPCM-2 membrane, we observe a smooth surface with uniform distribution of PMA particles. Such a homogenous mixing of PMA 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 to the transport of water molecules than IPA. With increasing loading of PMA, as in Figure 2b. SA-HPCM-3 membrane, some surface roughness can be seen, but with not so much of uniform distribution of PMA particles on the surfaces of the membrane, which may not allow high water transport through this membrane.

3.3. TGA

TGA thermograms of SA-HPCM-2 and SA-HPCM-3 membranes shown in Figure 3, which shows TG curves on heating the samples up to 600°C. In this Figure 3, SA-HPCM-2 MMMs exhibit two major weight loss regions with a maximum weight loss at its melting temperature at 175°C, which continues up to 375°C. And also the

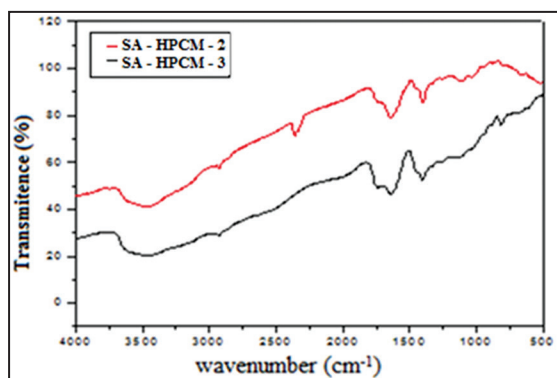


Figure 1(b): Fourier transform infrared spectral mixed matrix membranes of sodium alginate-(SA) HPCM-2, SA-HPCM-3 showing characteristic bands.

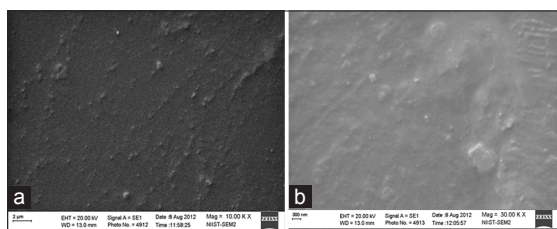


Figure 2: (a) Scanning electron microscopy (SEM) image of mixed matrix membranes (MMMs) of sodium alginate (SA) HPCM-2, (b) SEM image of MMMs of SA-HPCM-3.

other SA-HPCM-3 shows two major weight loss regions with a maximum weight loss at this melting temperature at 225°C, which continues up to 400°C. The weight loss of these membranes is accompanied by the release of moisture and other low-molecular-weight products sorbed on the membrane surface, with the weight loss of approximately 20 wt. %. It is observed that the amount of weight loss during melting of the polymers follows the order: SA-HPCM-2 (45.5%) > SA-HPCM-3 (40.5%); this tendency is attributed to increasing order of thermal stability from SA-HPCM-2 to SA-HPCM-3 membrane due to higher PMA loading.

3.4. DSC

This DSC technique provides information such as a glass transition (T_g), melting (T_m) and crystallization (T_c), in addition to the associated enthalpy for each process. DSC curves of SA-HPCM-2 and SA-HPCM-3 are shown in Figure 4. In the case of SA-HPCM-2, a sharp endothermic melting curve in the range of 185-195°C i.e., at 190.5°C represents the melting point, but the melting endothermic order has shifted to 89-98°C in case of SA-HPCM-3, which may be described to its

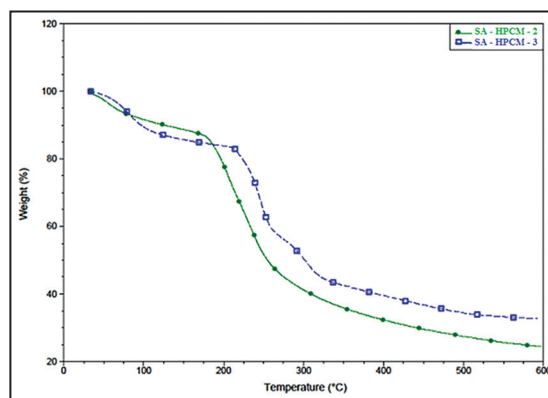


Figure 3: Thermogravimetric analysis thermograms of the mixed matrix membranes of the sodium alginate (SA) HPCM-2 and SA-HPCM-3.

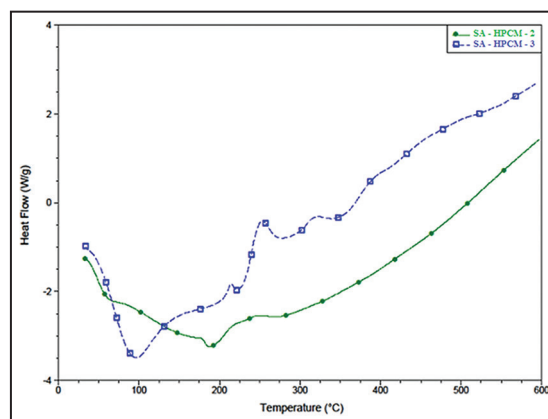


Figure 4: Differential scanning calorimetry thermograms of the mixed matrix membranes of the sodium alginate (SA) HPCM-2 and SA-HPCM-3.

reduced crystallinity due to the incorporation of higher PMA into the SA-HPC blend membrane.

4. MEMBRANE PERFORMANCE

4.1. Swelling Experiments

The degree of swelling obtained from sorption experiments at 30°C for cross-linked SA-HPC and PMA filled SA-HPC blend membranes are measured as a function of wt. % of water in the feed are displayed in Figure 5, for 10-15 wt. % water containing feeds. Degree of swelling of SA-HPCM-2 blend membranes is almost more than two times higher than that of the pristine SA-HPC blend membrane. From Figure 5, it is also noticed that degree of swelling increased with increasing PMA loading as well as with increasing water composition of the feed. This may be due to the hydrophilic nature of PMA nanoparticles, they are added to another hydrophilic of SA-HPC blend membrane would further increase the degree of swelling. This observation is a further evidence of the more water selective nature of the MMMs than isopropanol and even that of pristine blend membrane of SA-HPC. At higher filler loading, the selectivities increase, for SA-HPCM-2 and SA-HPCM-3 compared with pristine blend membrane of SA-HPC. These observations can be attributed to increasing hydrophilic-hydrophilic interactions in the MMMs between SA-HPC and PMA nanoparticles that are responsible for higher selectivity to water than isopropanol. As a result of increased interaction between water and polymer matrix, the water selectivity also increased compared with isopropanol in case of MMMs of SA-HPC blends compared to the pristine blend membrane of SA-HPC.

5. PV STUDIES

5.1. Influence of PMA Loading on PV Performance

Membrane performance was studied by calculating

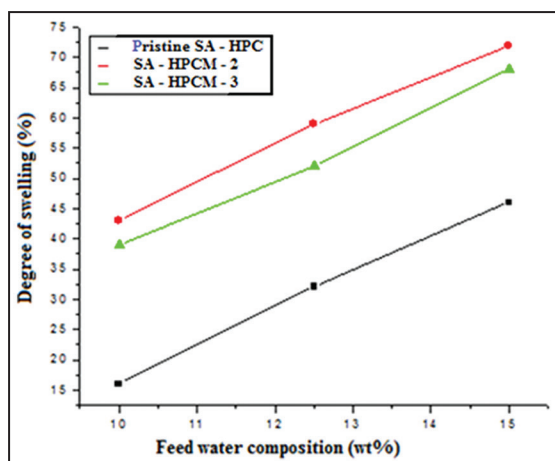


Figure 5: Degree of swelling of pristine sodium alginate (SA)-hydroxypropyl cellulose blend and mixed matrix membranes of SA-HPCM-2, SA-HPCM-3.

flux and selectivity at different feed compositions of water-isopropanol feed mixtures. The flux and selectivity were calculated by using equations (1) and (2) are described in this present work. Figures 6 and 7 displays the variation of flux and selectivity with feed water composition respectively. Mainly, selectivity of 0.2 wt. % PMA-containing membrane (i.e. SA-HPCM-2) increased considerably compared to pristine SA-HPC blend membrane. Although, at higher concentration of PMA i.e., SA-HPCM-3 membranes, the selectivity values decreased considerably, but are still higher than that observed for pristine SA-HPC blend membrane. Such a rapid decrease in membrane selectivity due to the addition of the higher amount of PMA may be due to a change in pore texture of the membrane matrix in the presence of PMA. Mainly, the high density of functional group highlighted the PV performance, but at certain concentration of PMA in the membrane phase (viz., at 0.2 wt. %), the PV performance becomes optimal. In the present work, we have to investigate in more detail on SA-HPCM-2

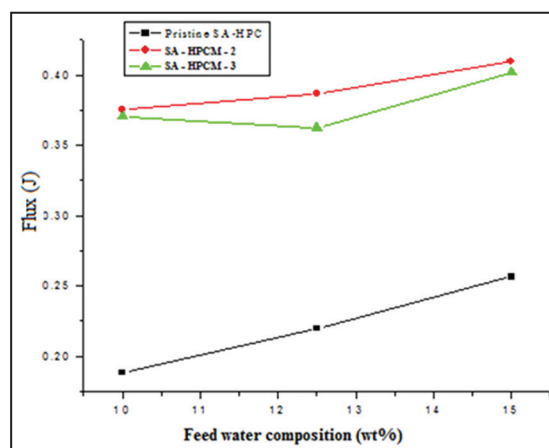


Figure 6: Flux versus wt. % of water in feed mixture for pristine sodium alginate (SA)-hydroxypropyl cellulose blend membrane and mixed matrix membranes of SA-HPCM-2, SA-HPCM-3.

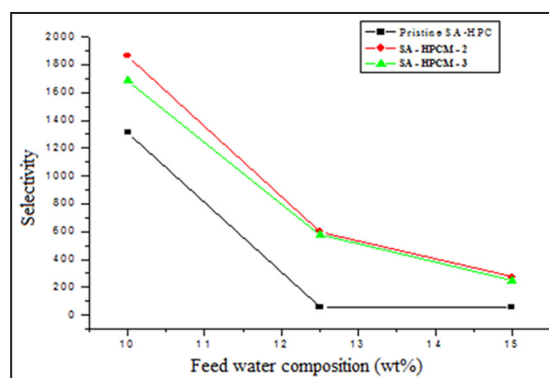


Figure 7: Selectivity versus wt. % of water in feed mixture for pristine sodium alginate (SA)-hydroxypropyl cellulose blend membrane and mixed matrix membranes of SA-HPCM-2, SA-HPCM-3.

membrane per formation that gave the optimum selectivity compared with all the membranes.

5.2. Effect of Feed Water Composition

In the present work, SA was used for blending with HPC because the bulkiness of the proposed blend membrane is an important factor as its hydrophilicity for a productive dehydration of isopropanol. Meanwhile hydrophilicity is needed for preferential attraction of water to achieve high selectivity, the high rigidity and bulkiness of the membrane are also equally essential for an easy transport of permeating water molecules [20]. The performance of pristine SA-HPC blend membrane was investigated in comparison to SA-HPCM-2 membrane as a purpose of feed water composition in order to develop PV performance over that of the pristine SA-HPC blend membrane. Table 1 displays the effect of feed water composition is 10 wt. % in the mixture on PV performance of SA-HPCM-2 and SA-HPCM-3 membranes at 30°C under the constant pressure. For the pristine SA-HPC blend membrane, percentage of degree of swelling

Table 1: PV data for feed mixture of water-IPA at 30°C.

Wt. % of water in feed	Wt. % of water in permeate	Flux (J) (kg/m ² h)	Selectivity (α)
Pristine SA-HPC			
10.0	99.32	0.1884	1314
12.5	89.52	0.2197	60
15.0	89.50	0.2567	58
SA-HPCM-2			
10.0	99.52	0.3753	1865
12.5	98.85	0.3868	601
15.0	98.00	0.4097	274
SA-HPCM-3			
10.0	99.47	0.3707	1689
12.5	98.80	0.3626	576
15.0	97.80	0.4023	248

SA = Sodium alginate; HPCM = Hydroxy propyl cellulose membrane; IPA = Isopropanol; PV = Pervaporation

Table 2: Comparison of PV performance of the present MMMs with the literature data for water-isopropanol separation.

Membrane	Temperature (°C)	Wt. % of water	Flux (kg/m ² h)	Selectivity (α)	References
SA-HEC-20	30	10	19.21	508	[38]
SA-HEC-5	30	10	16.16	543	
SA-MAS-5	30	10	0.066	1246	[39]
PVA/HPA-3	30	10	0.059	1828	[40]
SA-HPCM-2	30	10	0.3460	1865	Present work
SA-HPCM-3	30	10	0.3253	1689	

SA = Sodium alginate; HPCM = Hydroxy propyl cellulose membrane; MMMs = Mixed matrix membranes

is considerably higher than that observed for SA-HPCM-3.

5.3. Comparison of PV Results with Literature

Many reports have been made in the literature concerning the PV separation of water-isopropanol mixture with different polymer materials. Hence, it is necessary to compare our data with those of the published reports. Table 2 summarizes such data in comparison to the published reports with the literature findings of MMMs of SA-HPCM-2 membrane containing 0.2 wt. % PMA for 10 wt. % water-containing feed mixture. It is found that the present membranes exhibited a higher selectivity of 1865 than published in the literature in dehydrating isopropanol. Thus, the mixed matrix SA-HPC blend membranes of this study are very efficient in dehydrating isopropanol.

6. CONCLUSION

The present study deals with the development of the novel type of MMMs from the blend membranes of SA-HPC incorporated with hydrophilic PMA nanoparticles for the use in effective isopropanol dehydration. The boost in PV performance of the MMMs is attributed to hydrophilic-hydrophilic interactions between the filler nanoparticles and water. It is verified in this study that after incorporating 0.2 wt. % (SA-HPCM-2) of PMA particles into SA-HPC blend matrix, this can enhance the PV performance of the filled matrix membranes over that of the pristine blend membranes. The flux and permeate values decreased with increasing feed water composition. Sorption data suggests that membrane selectivity is mainly governed by sorption selectivity. On the whole, the PV separation MMMs of SA-HPCM-2 and SA-HPCM-3 blend membrane is better than pristine SA-HPC membrane. Azeotropic composition of water-isopropanol mixture was separated by the highly water-selective SA-HPCM-2 membrane, this work suggests higher water selective nature for the developed MMMs.

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8. REFERENCES

- S. Y. Nam, H. J. Chun, Y. M. Lee, (1999) Pervaporation separation of water-isopropanol mixture using carboxymethylated poly(vinyl alcohol) composite membranes, *Journal of Applied Polymer Science*, **72**: 241-249.
- G. Y. Moon, R. Pal, R. Y. M. Huang, (1999) Novel two-ply composite membranes of chitosan and sodium alginate for the pervaporation dehydration of isopropanol and ethanol, *Journal of Membrane Science*, **156**: 17-27.
- Y. L. Liu, Y. H. Su, K. R. Lee, J. Y. Lai, (2005) Crosslinked organic – inorganic hybrid chitosan membranes for pervaporation dehydration of isopropanol – Water mixtures with a long-term stability, *Journal of Membrane Science*, **251**: 233-238.
- Y. M. Lee, S. Y. Nam, B. R. Lee, D. J. Woo, K. H. Lee, J. M. Won, B. H. Ha, (1996) Dehydration of alcohol solution through crosslinked chitosan composite; preparation of chemically crosslinked chitosan composite membrane and ethanol dehydration, *Membrane (Korea)*, **20**: 37-43.
- T. M. Aminabhavi, R. S. Khinnavar, S. B. Harogopad, U. S. Aithal, Q. T. Nguyen, K. C. Hansen, (1994) Preparation separation of organic-aqueous and organic-organic binary mixtures, *Journal of Macromolecular Science, Part C Polymer Reviews*, **34**: 139-204.
- I. Blume, J. G. Wijmans, R. W. Baker, (1990) The separation of dissolved organics from water by pervaporation, *Journal of Membrane Science*, **49**: 253-286.
- P. Shao, R. Y. M. Huang, (2007) Polymeric membrane pervaporation, *Journal of Membrane Science*, **287**: 162-179.
- Q. G. Zhang, Q. L. Liu, Y. Chen, J. H. Chen, (2007) Dehydration of isopropanol by novel poly (vinyl alcohol)– Silicone hybrid membranes, *Industrial and Engineering Chemistry Research*, **46**: 913-920.
- X. Feng, R. Y. M. Huang, (1997) Liquid separation by membrane pervaporation: A review, *Industrial and Engineering Chemistry Research*, **36**: 1048-1066.
- L. M. Vane (2005) A review of pervaporation for product recovery from biomass fermentation, *Journal of Chemical Technology and Biotechnology*, **80**: 603-629.
- Q. G. Zhang, Q. L. Liu, Z. Y. Jiang, C. Yu, (2007) Anti-trade-off in dehydration of ethanol by novel PVA/APTEOS hybrid membranes, *Journal of Membrane Science*, **287**: 237-245.
- S. D. Bhat, T. M. Aminabhavi, (2007) Pervaporation separation using sodium alginate and its modified membranes—A review, *Separation and Purification Reviews*, **36**: 203-229.
- T. Cai, Z. Hu, B. H. Ponder, (2003) Synthesis and study of and controlled release from nanoparticles and their networks based on functionalized hydroxypropylcellulose, *Macromolecules*, **36**: 6559-6564.
- I. Honma, Y. Takeda, J. M. Bae, (1999) Protonic conducting properties of sol-gel derived organic/inorganic nanocomposite membranes doped with acetic functional molecules, *Solid State Ionics*, **120**: 255-264.
- H. H. Huang, G. L. Wilkes, J. G. Carlson, (1989) Structure-property behavior of hybrid materials incorporating tetraethoxysilane with multifunctional poly(tetra methylene oxide), *Polymer*, **30**: 2001-2012.
- F. B. Peng, C. L. Hu, Z. Y. Jiang, (2007) Novel (polyvinyl alcohol)/carbon nano tube hybrid membranes for pervaporation separation of benzene/cyclohexane mixtures, *Journal of Membrane Science*, **297**: 236-242.
- S. B. Teli, G. S. Gokavi, T. M. Aminabhavi, (2007) Novel sodium alginate-poly (N-isopropylacrylamide) semi-interpenetrating polymer network membranes for pervaporation separation of water+ethanol mixtures, *Separation and Purification Technology*, **56**: 150-157.
- V. T. Magalad, G. S. Gokavi, M. N. Nadagouda, T. M. Aminabhavi, (2011) Pervaporation separation of water-ethanol mixtures using organic-inorganic nanocomposite membranes, *Journal of Physical Chemistry*, **115**: 14731-14744.
- S. B. Teli, G. S. Gokavi, M. Sairam, T. M. Aminabhavi, (2007) Phosphomolybdic heteropolyacid loaded poly (vinyl alcohol) dense matrix membranes for pervaporation separation of water-isopropanol mixtures, *Colloids and Surfaces A Physicochemical and Engineering Aspects*, **301**: 55-62.
- V. T. Magalad, G. S. Gokavi, K. V. S. N. Raju, T. M. Aminabhavi, (2010) Mixed matrix blend membranes of poly (vinyl alcohol)-poly(vinyl pyrrolidone) loaded with phosphomolybdic acid used in pervaporation dehydration of ethanol, *Journal of Membrane Science*, **354**: 150-161.
- V. T. Magalad, A. R. Supale, S. P. Maradur, G. S. Gokavi, T. M. Aminabhavi, (2010) Preysslertype heteropolyacid-incorporated highly water-selective sodium alginate based inorganic-organic hybrid membranes for pervaporation dehydration of ethanol, *Chemical Engineering Journal*, **159**: 75-83.
- M. G. Mali, V. T. Magalad, G. S. Gokavi, K. V. S. N. Raju, T. M. Aminabhavi, (2011) Pervaporation separation of isopropanol-water mixtures using mixed matrix blend membranes of poly(vinyl alcohol)/poly(vinyl pyrrolidone) loaded with

- phosphomolybdic acid, *Journal of Applied Polymer Science*, **121**: 711-719.
- 23 S. D. Bhat, T. M. Aminabhavi, (2007) Zeolite K-LTL-loaded sodium alginate mixed matrix membranes for pervaporation dehydration of aqueous – Organic mixtures, *Journal of Membrane Science*, **306**: 173-185.
 - 24 M. B. Patil, T. M. Aminabhavi, (2008) Pervaporation separation of toluene/alcohol mixtures using silicalite zeolite embedded chitosan mixed matrix membranes, *Separation and Purification Technology*, **62**: 128-136.
 - 25 T. C. Merkel, B. D. Freeman, R. J. Spontak, Z. He, I. Pinnau, P. Meakin, A. J. Hill, (2003) Sorption, transport, and structural evidence for enhanced free volume in poly(4-methyl-2-pentene)/fumed silica nanocomposite membranes, *Chemistry of Materials*, **15**: 109-123.
 - 26 F. B. Peng, Z. Y. Jiang, C. L. Hu, (2006) Removing benzene from aqueous solution using CMS-filled PDMS pervaporation membranes, *Separation and Purification Technology*, **48**: 229-234.
 - 27 R. Mahajan, R. Burns, M. Schaeffer, W. J. Koros, (2002) Challenges in forming successful mixed matrix membranes with rigid polymeric materials, *Journal of Applied Polymer Science*, **86**: 881-890.
 - 28 Z. Huang, Y. Shi, R. Wen, Y. Guo, J. Su, T. Matsuura, (2006) Multilayer poly (vinyl alcohol)-Zeolite 4 A composite membranes for ethanol dehydration by means of pervaporation, *Separation and Purification Technology*, **51**: 126-136.
 - 29 Z. Huang, H. Guan, W. Tan, X. Qiao, S. Kulprathipanja, (2006) Pervaporation study of aqueous ethanol solution through zeolite-incorporated multilayer poly (vinyl alcohol) membranes: Effect of zeolites, *Journal of Membrane Science*, **276**: 260-271.
 - 30 T. T. Moore, W. J. Koros, (2005) Non-ideal effects in organic – inorganic materials for gas separation membranes, *Journal of Molecular Structure*, **739**: 87-98.
 - 31 I. K. Song, S. K. Shin, W. Y. Lee, (1993) Catalytic activity of $H_3Pm_{12}O_{40}$ -blended polysulfone film in the oxidation of ethanol to acetaldehyde, *Journal of Catalysis*, **144**: 348-351.
 - 32 J. K. Lee, I. K. Song, W. Y. J. Lee, J. Kim, (1996) Modification of 12-molybdophosphoric acid catalyst by blending with polysulfone and its catalytic activity for 2-propanol conversion reaction, *Journal of Molecular Catalysis A Chemical*, **104**: 311-318.
 - 33 B. G. Lokesh, K. S. V. Krishna Rao, K. Mallikarjuna Reddy, K. Chowdoji Rao, P. Srinivasa Rao, (2008) Novel nanocomposite membranes of sodium alginate filled with polyaniline-coated titanium dioxide for dehydration of 1,4-dioxane/water mixtures, *Desalination*, **233**: 166-172.
 - 34 K. W. Boddeker, (1990) Terminology in pervaporation, *Journal of Membrane Science*, **51**: 259-272.
 - 35 S. B. Harogopad, T. M. Aminabhavi, (1991) Diffusion and sorption of organic liquids through polymer membranes. 5. Neoprene, styrene-butadiene-rubber, ethylene-propylene-dieneterpolymer, and natural rubber versus hydrocarbons (C8-C16), *Macromolecules*, **24**: 2598-2605.
 - 36 C. Venkata Prasad, B. Yerru Swamy, H. Sudhakar, T. Sobharani, K. Sudhakar, M. C. S. Subha, K. Chowdoji Rao, (2011) Preparation and characterization of 4A zeolite-filled mixed matrix membranes for pervaporation dehydration of isopropyl alcohol, *Journal of Applied Polymer Science*, **121**: 1521-1529.
 - 37 G. Lakshminarayana, M. Nogami, (2009) Synthesis and characterization of proton conducting inorganic-organic hybrid nanocomposite membranes based on tetrethoxysilane/trimethyl phosphate/3-glycidoxy propyl trimethoxy silane/heteropoly acids, *Electrochimica Acta*, **54**: 4731-4740.
 - 38 B. V. K. Naidu, K. S. V. K. Rao, T. M. Aminabhavi, (2005) Pervaporation separation of water +1,4-dioxane and water + tetrahydrofuran mixtures using sodium alginate and its blend membranes with hydroxyethylcellulose – A comparative study, *Journal of Membrane Science*, **260**: 13-141.
 - 39 R. S. Veerapur, K. B. Gudasi, T. M. Aminabhavi, (2008) Sodium alginate-magnesium aluminum silicate mixed matrix membranes for pervaporation separation of water-isopropanol mixtures, *Separation and Purification Technology*, **59**: 221-230.
 - 40 S. B. Teli, G. S. Gokavi, M. Sairam, T. M. Aminabhavi, (2007) Mixed matrix membranes of poly(vinyl alcohol) loaded with phosphomolybdicheteropoly acid for the pervaporation separation of water-isopropanol mixtures, *Colloids and Surface A Physicochemical and Engineering Aspects*, **301**: 55-62.