

Study of enhanced physical and pervaporation properties in composite membrane

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Abstract. Novel mixed matrix membranes of Sodium Alginate (NaAlg) were developed by the incorporation of unmodified, modified Phosphomolybdic acid (PMA) then cross-linked with glutaraldehyde externally. These membranes were prepared by the solution casting technique. Pervaporation (PV) experiments have been performed with pure NaAlg, unmodified NaAlg-PMA5, NaAlg-PMA10, modified NaAlg-mPMA5, and NaAlg-mPMA10 (wt. % of PMA 5 and 10) at 30, 40 and 50°C, to separate water-isopropanol feed mixtures containing 10-30 wt. % of water. Pervaporation results of NaAlg-mPMA10 produced a highest separation factor of 9028 with a flux of 0.269 kg/m².h for 10 wt. % of water containing feed mixture. Both separation factor and flux for water increased significantly with increasing content of mPMA into NaAlg; a significant improvement in PV performance was observed for NaAlg-mPMA5 and NaAlg-mPMA10 membranes when compared to pure NaAlg & PMA-5, PMA-10 membrane.

Keywords: pervaporation; flux; azeotrope; phosphomolybdic acid; water-isopropanol mixture; sodium alginate; membrane

1. Introduction

It is of the great importance for both commercial and environmental reasons the recovery of water from organic solutions (such as process fluids or effluents). Pervaporation is an important and well established method for the recovery and recycling of many volatile organics from aqueous media (Yunxiang Bai *et al.* 2013).

Pervaporation (PV) allows separation of mixtures that are difficult to separate by conventional distillation, extraction, adsorption, etc. Therefore, in separation and purification technology, PV has advantages in separating azeotropes, isomeric components, close-boiling liquid mixtures, thermally sensitive compounds as well as removing species that are present in low concentrations. In PV, a liquid feed from upstream side of the membrane interacts with membrane surface and

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transports across the barrier membrane as a vapour on permeate side under the influence of high vacuum (low pressure). PV technique has been well recognized as an energy-intensive process compared to simple distillation because it can be performed at ambient temperature and requires lesser energy in addition to being an environmentally clean process. In general pristine polymers show low transport parameters selectivity and productivity and mechanical strength. To overcome this problem and to improve transport properties, variety of zeolites have been used as fillers (Avagimova *et al.* 2013), Bhat and Aminabhavi (2006)

Incorporation of nano-inorganic particle into common polymers leads to materials with improved physical properties (Zhanget *al.* 2008). This is due to the ability of nano-inorganic particle to reduce the mobility of the polymer chains. Polymer/nano-inorganic particle hybrids are routinely prepared by three different techniques: (1) solution blending method, (2) *in situ* polymerization method, (3) sol-gel method (Babanzadeh *et al.* 2012, Strachota *et al.* 2001).

A variety of fillers have been used to prepare the membranes that exhibit improved performances over those of the virgin polymer membranes (Teli *et al.* 2007, Lu *et al.* 2000, Gao *et al.* 1996, Bhat and Aminabhavi 2006, Bhat *et al.* 2006). Heteropolyacids (HPAs) which exhibit a wide range of well-defined molecular structures, surface charge densities, chemical and electronic properties are widely used inorganic materials that contain ring transition metal oxygen anion clusters, Pope (1983). In addition HPAs have their inherent catalytic properties (Okuhara *et al.* 1996, Misono 1987, Pizzio *et al.* 2003) as well. Among these, Keggin-type HPAs have been widely investigated as the catalytic materials Keggin (1993). The acid and redox catalytic properties of HPAs have been modified by replacing protons with metal cations and/or by changing the heteroatom or the frame work poly-atoms done by Neumann (1998), McGarvey and Band Moffat (1991).

In this study, we have made an attempt to evaluate permeation, and swelling data in pure NaAlg as well as Modified membranes of NaAlg incorporated with mPMA 5 and 10 wt. % at 30, 40 and 50°C in water-Isopropanol mixtures. By using these data, parameters for permeation and diffusion were estimated. Such data will be useful in understanding membrane-liquid/mixture interactions before seeking their successful applications in PV separation problems. In comparison to zeolite-filled membranes, published data on clay-modified hybrid composite membranes are somewhat rare Okuno (1992), Zhang *et al.* (1997). Incorporation of inorganic fillers perm selective in a polymer membrane would dramatically improve its separation performance. Earlier, Wang *et al.* (2004) prepared the polyamide/SDS-clay hybrid nanocomposite membranes and tested for PV separation of water-ethanol mixtures and found that SDS-clay content has an effect (when dispersed into a hydrophobic polyamide) on its PV performance. Among the family of polysaccharides, NaAlg has been the most widely used polymer in fabricating PV separation membranes in addition to its usage in drug delivery (Chanachi *et al.* 2000, Cao *et al.* 2000, Soppimath *et al.* 2001, Fischer *et al.* 1955, Haug *et al.* 1966). NaAlg is water-soluble having good membrane forming properties; it can be readily cross-linked with glutaraldehyde or Ca^{2+} ions. Alginate is a linear chain structure of (1-4)-linked β -d-mannuronic acid (M) and α -l-guluronic acid (G) residues arranged in a block wise fashion. These blocks are constructed in three different ways: homopolymeric MM blocks, homopolymeric GG blocks and heteropolymeric sequentially alternating MG blocks (Bhat and Aminabhavi 2006).

Inorganic fillers have a high surface area, a high void volume and a uniform pore size distribution, and so these have been used widely as shape-selective catalysis and separation media in chemical and physical processes. Thus, the incorporation of selective zeolites into a suitable polymeric membrane matrix can improve the separation performance of pervaporation membranes

because of a combined influence of molecular sieving action, selective adsorption and differences in the diffusion rates.

2. Experimental

2.1 Materials

NaAlg ($\overline{M}_w = 122,594$), ammonium carbonate, were purchased from s.d. fine Chemicals, Mumbai, India, PMA was purchased from Titan Biotech Ltd, Bhiwadi, India. Isopropanol, glutaraldehyde (GA), acetone, and HCl were purchased from Merck (Pty) Ltd Chemical Division Johannesburg, South Africa. Deionized water was produced in the laboratory.

2.2 Modification of PMA

Ammonium carbonate was used to modify PMA. Here excessive protons exchanges with larger NH_4^+ ions as described by (Bhat *et al.* 2010). Separate homogeneous solutions of PMA (1M) and ammonium carbonate (0.5M) were prepared in distilled water. Now PMA solution is treated in deionized water with a stoichiometric amount of ammonium carbonate salt solution containing the desired cation. By controlling the stoichiometry of the added ammonium carbonate solution one can control number of protons of PMA to be substituted. The transparent, homogenous PMA solution turned cloudy white as the heteropoly salt precipitated upon ion-exchange of the protons with larger cat ions like NH_4^+ present in the salt solution. The resulting mixture was sonicated in ultrasonic bath and dried in a hot air oven at 30°C.

2.3 Membrane fabrication

Using water as solvent, mixed matrix membranes of pure NaAlg and NaAlg-mPMA5, NaAlg-mPMA10 have been prepared by solution casting method, by the incorporation of modified Phosphomolybdic acid (modified with ammonium carbonate in 1:1 molar ratio) in 5 wt% and 10 wt. % with respect to the weight of the polymer. 4 g of NaAlg was dissolved in 80 mL of water with constant stirring. Separately, particles were weighed and dispersed in 20 mL of water by sonication for 120 min, and added to the previously prepared NaAlg solution, stirred for a further period of 24 h. Uniform thickness membranes were then casted by pouring the solution on a dust-free glass plate. These membranes were dried and peeled off from the glass plate. Then the membranes were immersed in a crosslinking bath containing (30:70) water: acetone mixture along with 2.5 mL of GA and 2.5 mL of concentrated HCl. After allowing 12-14 h. Cross-linked membranes were removed from the bath, washed repeatedly with deionized water and dried in an oven at 40°C. Pristine NaAlg membrane was prepared in the same manner except that clay filler particles were not added. Membrane thicknesses as measured by a micrometer screw gauge were around $50 \pm 1.0 \mu\text{m}$. The colour of the prepared hybrid composite membranes is slightly cloudy white and semi-transparent. These membranes were well characterized by SEM, DSC, TGA and UTM to understand the physical properties.

2.4 Membrane characterizations

Scanning electron microscopy (SEM) micrographs of pristine NaAlg and NaAlg-mPMA10 were obtained under a high resolution (Mag 300X 5kV) using TESCAN VEGA3 (Bruno in Check Republic). Differential scanning calorimetry (DSC) thermo grams of pristine NaAlg, NaAlg-mPMA5 and NaAlg-mPMA10 films were recorded on a Rheometric Scientific (Model DSC-SP, Ashtead, Surrey, United Kingdom) from 25 to 400°C at the heating rate of 10°C/min in nitrogen atmosphere. Tensile strength and elongation at break of the pristine NaAlg, NaAlg-mPMA 5 and NaAlg-mPMA10 filled matrix films were measured using Universal testing machine (UTM) (Model H 25KS, Hounsfield, Surrey, United Kingdom). Test specimens were prepared in the form of dumbbell shapes as per ASTM D-638 standards. Films of gauge length, 50 mm and width, 10 mm were stretched at the cross head speed of 10 mm/min. TGA thermo grams of pure NaAlg, NaAlg-mPMA5 and NaAlg-mPMA10 were obtained using SDT 2960 simultaneous DSC-TGA (TA Instruments, USA). Measurements were performed over the temperature range of 25 -600°C at the heating rate of 10°C/min. The sample pan was conditioned in the instrument before performing the experiment.

2.5 Pervaporation experiments

Pervaporation experimental setup is the same as originally described before (Adoor *et al.* 2007, Adoor *et al.* 2013). Before starting the PV experiment, the test membrane was equilibrated for about 2 h with the feed mixture. After establishment of a steady state, permeate vapours were collected in cold traps immersed in liquid nitrogen up to 2 h. Weight of the permeate collected was measured to determine flux, J (kg/m². h) using the weight of liquids permeated, W (kg), effective membrane area, A (m²) and measurement time, t (h) as

$$J = \frac{W}{At} \quad (1)$$

The analysis of feed and permeate samples was done using a MAPL Gas Chromatograph (Model 1100, Bangalore, India) equipped with athermal conductivity detector (TCD) on a DEGS packed column of 1/8" ID having 2 m length by maintaining the oven temperature at 70°C (isothermal) and those of injector and detector at 150°C using a sample injection volume was 1 μL. Pure hydrogen was used as a carrier gas at 0.75 kg/cm² pressure. GC response was calibrated for column and for known compositions of water plus organic mixtures. The calibration factors were fed into GC software to analyse for unknown samples. The GC response was calibrated for the column and for known compositions of water+isopropanol mixtures. Separation factor (α), pervaporation separation index (PSI) and enrichment factor (β) were calculated using the equations

$$\alpha = \left(\frac{P_w}{P_{org}} \right) \left(\frac{F_{org}}{F_w} \right) \quad (2)$$

$$PSI = J (\alpha - 1) \quad (3)$$

$$\beta = C_w^P / C_w^F \quad (4)$$

Here, P_w and P_{org} are wt. % of water and organic components, respectively in permeate; F_w and F_{org} are wt. % of water and organic components, respectively in the feed. A minimum of three independent measurements of flux and separation factor were taken under similar set of conditions

of temperature and feed compositions to confirm the steady-state pervaporation. Subscript w stands for water, J is water flux and C is concentration in wt. %.

2.6 Dynamic sorption

Sorption experiments were performed gravimetrically on all the membranes at the azeotropic compositions of isopropanol, at different temperatures. Sorption was also studied for different feed compositions at the ambient temperature (30°C). (Okuhara *et al.* 1996a, b) To do this, dry weight of the circularly cut (diameter=2.5 cm) pristine NaAlg, NaAlg-mPMA5 and NaAlg-mPMA10 membranes were taken on a microbalance sensitive to ± 0.01 mg, then samples were taken inside the specially designed airtight test bottles containing 20 cm³ test media. The bottles were then transferred to oven kept at the desired constant temperature. Dry membranes were equilibrated by soaking in different compositions of feed mixtures in a sealed vessel at 30°C for 48 h. Sorbed membranes were weighed immediately after careful blotting on a digital microbalance. The % sorption was calculated as

$$\% \text{ Sorption} = \left(\frac{W_{\infty} - W_0}{W_0} \right) \times 100 \quad (5)$$

Where W_{∞} and W_0 are weights (gram) of the sorbed and dry membranes, respectively.

3. Results and discussion

3.1 Scanning Electron Microscopic studies (SEM)

Fig. 1 shows the surface SEM micrograph of NaAlg 10 mixed matrix film in which mPMA particles are distributed homogeneously throughout the NaAlg matrix facilitating rough nature. However, it is compulsory that these particles are to be uniformly distributed in NaAlg matrix so that the composite film will exhibit superior effects of mechanical and thermal property. The uniform distribution of mPMA particles in NaAlg matrix is prevalent from the SEM micrograph.

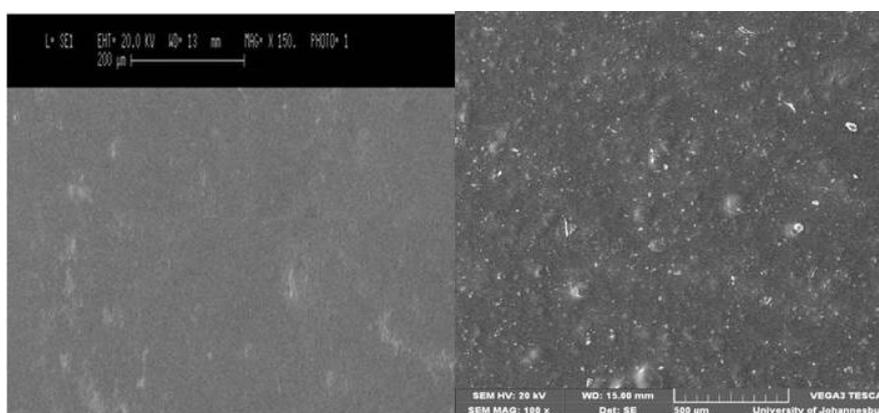


Fig. 1 Shows the surface SEM micrograph of NaAlg 10 mixed matrix membrane

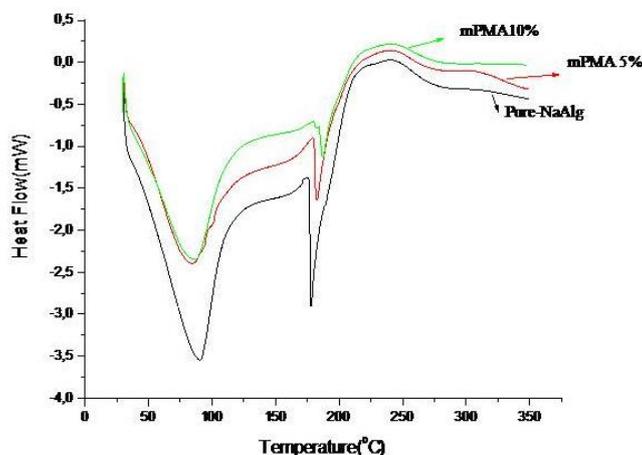


Fig. 2 Differential Scanning Calorimetric (DSC) thermo grams of the pristine and mixed matrix membrane

3.2 Differential Scanning Calorimetry (DSC) measurements

Differential Scanning Calorimetric (DSC) thermo grams of the pristine and mixed matrix films are depicted in Fig. 2. Measurements were carried out on a model DSC SP, Rheometric Scientific, UK. NaAlg-mPMA10 showed highest T_g value at 194°C which is higher than pristine NaAlg which showed at 175°C, which illustrates the importance of mPMA in the film. The higher T_g value of NaAlg-mPMA10 is the reflection of its improved thermal property.

3.3 Universal Testing Machine (UTM)

The % elongation at break for pristine NaAlg was 200 with the maximum tensile strength of 6.01 N/mm², whereas NaAlg-mPMA5 and NaAlg-mPMA10 mixed matrix film showed % elongation at break of 130 and 110, respectively with maximum tensile strengths of 28.75 N/mm² and 38.11 N/mm², respectively, indicating that mechanical strength of the mPMA film is higher than that of the pristine NaAlg film. One can also see from Table.4 that mPMA filler is more effective in increasing the tensile strength of NaAlg film as compared to other fillers like mPTA.

3.4 Thermo Gravimetric Analysis (TGA)

TGA thermo grams of pure NaAlg, NaAlg-mPMA5 and NaAlg-mPMA10 mixed films are shown in Fig. 3. One can see two major weight loss regions with an onset of maximum weight loss at its melting temperature at 210°C, which continues up to 450°C. The weight losses of these films in different temperature regions are associated with the splitting of the main chain and final decomposition of the polymer. It is observed that the extent of weight loss during melting of the polymers follows the sequence: Pure NaAlg (36.11%) > NaAlg-mPMA10 (31.41%); from this we can understand that increasing order of thermal stability from pure NaAlg to NaAlg-mPMA10 film due to filler loading. It is also observed that wt. % residue after thermal decomposition of the matrix at 470°C is higher for NaAlg-mPMA10 than pure NaAlg, signifying the existence of HPA filler in the NaAlg matrix, since HPA filler remains intact even at this temperature.

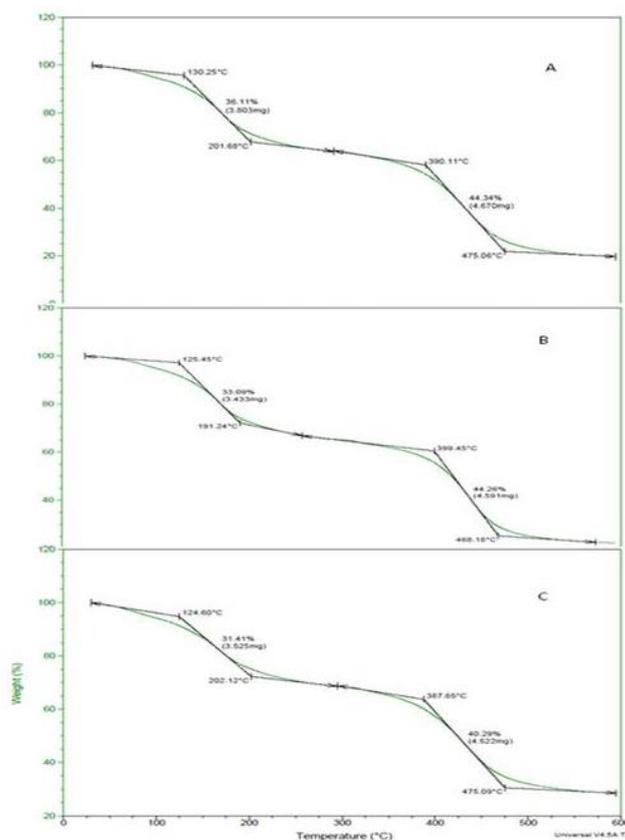


Fig. 3 TGA thermo grams of pure NaAlg, NaAlg-mPMA5 and NaAlg-mPMA10 mixed membrane

3.5 Membrane performance

Membrane performances of pristine NaAlg, NaAlg- mPMA5 and NaAlg- mPMA10 mixed matrix membranes have been studied by calculating flux, separation factor and permeation separation index for water-isopropanol mixtures. Results are given in Tables 1 and 2. In addition, a more quantitative approach was taken on for investigating membrane ability by calculating molar flux, membrane permeability and selectivity to water, which also supported the PV results. The PV results at 10 wt. % water in the feed are given in Tables 1-3 from which it is evident that mixed matrix membranes have improved PV performances compared to pristine NaAlg membrane; also, the performances of NaAlg-mPMA membranes are much superior to NaAlg-PMA membranes. At ambient temperature, pristine NaAlg membrane has the separation factor of 658 and a water flux of $0.047 \text{ kg/m}^2\cdot\text{h}$ for water-isopropanol mixture. The separation factor increased systematically from NaAlg-PMA5 to NaAlg-PMA10 viz., 2140 and $0.201 \text{ kg/m}^2\cdot\text{h}$ to 3858 and $0.251 \text{ kg/m}^2\cdot\text{h}$, respectively. Similar trends are observed for NaAlg-mPMA5 to NaAlg-mPMA10 membranes, i.e., separation factor and flux values vary from 4981 and $0.257 \text{ kg/m}^2\cdot\text{h}$ to 9028 and $0.282 \text{ kg/m}^2\cdot\text{h}$, respectively. NaAlg-mPMA10 showed >10-fold increase of separation factor to water compared to pristine NaAlg membrane. PV results at 40 and 50°C are also presented in Tables 3 for water-isopropanol feed mixtures. The separation factors of all the membranes decrease at higher

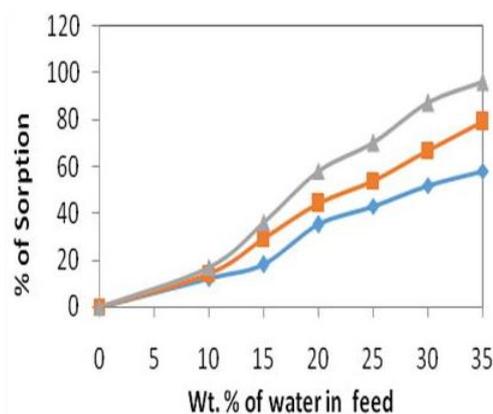


Fig. 4 % Sorption curves of pure NaAlg (▲), NaAlg-mPMA5 (■) and NaAlg-mPMA10 (◆) membranes for water-isopropanol feed mixtures at 30°C

temperatures, but flux values increase due to increase in void volume spaces of the membranes at elevated temperatures.

3.6 Sorption

Dynamic sorption curves vs. time plots are displayed in Fig. 4 for pristine NaAlg, NaAlg-PMA and NaAlg-mPMA membranes at 30°C for 10, 15, 20, and 25 wt.% water-containing feed mixtures of isopropanol. Pristine NaAlg swells in water, lowering its selectivity to water, but the presence of PMA nanoparticles in NaAlg reduces membrane swelling as the matrix becomes more rigid. Also, incorporation of modified PMA into NaAlg reduced leaching of filler particles compared to the unmodified PMA loaded mixed matrix membrane. The chemical modification of PMA using ammonium carbonate is responsible to improve the mechanical strength of mixed matrix membrane as the stoichiometric exchange of H^+ ions by the larger NH_4^+ ions helps to control the swelling. This effect can be seen in Fig. 4, wherein swelling of NaAlg-mPMA membranes is smaller than NaAlg-PMA and pristine NaAlg membranes. Furthermore, the amount of swelling in water-isopropanol, due to interactions of free terminal hydrophilic -OH groups of isopropanol with NaAlg.

3.7 Effect of feed water composition

The effect of feed water composition on pervaporation performance of both pristine and mPMA-loaded NaAlg hybrid composite membranes was investigated and results are presented in Tables 1 and 2, mPMA loaded NaAlg membranes swell to a larger extent in the presence of water as compared to pristine NaAlg membrane. The flux data of mPMA -loaded NaAlg membranes are higher than those of the pristine NaAlg membrane. For mPMA -loaded NaAlg hybrid composite membranes, flux increased with increasing water composition from 10 to 30 wt. % of the feed mixture. At 10 wt. % water in the feed mixture, a strong adsorptive effect of water molecules onto hybrid composite membranes was obtained, which would facilitate to increase the transport of water from the feed side (Teli *et al.* 2007a, b). For NaAlg-mPMA10 membrane, the observed selectivity was 9028 at 10 wt. % of water in the feed, which decreased with the increasing

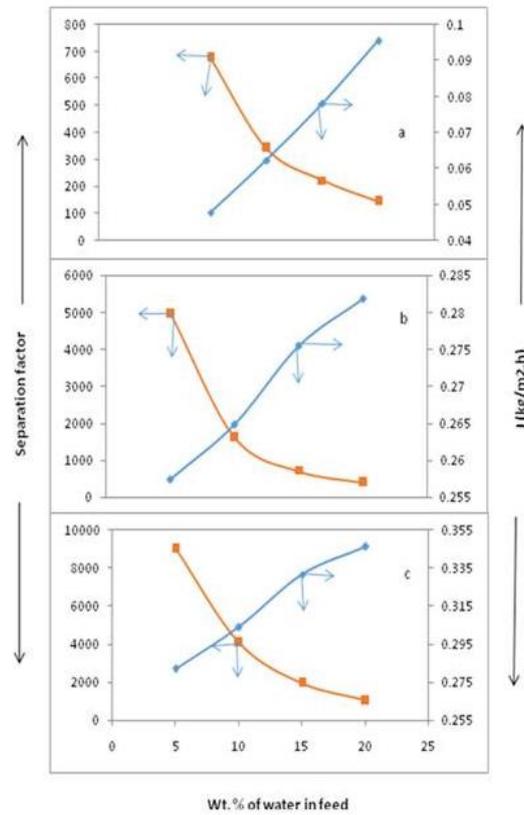


Fig. 5 Water flux and separation factor vs. wt. % of water for (a) pristine NaAlg, (b) NaAlg-mPMA5, and (c) NaAlg-mPMA10 membranes for water-isopropanol feed mixtures at 30°C. Symbols: (◆) flux and (■) separation factor

Table 1 Pervaporation data for unmodified NaAlg Membrane water + isopropanol at 30°C

Water in feed (Wt. %)	Water in permeate (Wt. %)	Water flux (J) (kg/m ² h)	Separation factor(α)	PSI
10	98.69	0.047	658	31
15	98.37	0.061	342	20
20	98.23	0.077	222	16
25	97.97	0.094	145	13
NaAlg-PMA5				
10	99.12	0.201	2140	442
15	99.07	0.208	958	205
20	98.81	0.215	470	106
25	98.69	0.226	301	72
NaAlg-PMA10				
10	99.51	0.251	3858	964
15	99.32	0.262	1314	341
20	98.91	0.275	514	139
25	98.72	0.282	308	84

Table 2 Pervaporation data for Modified NaAlg Membrane water + isopropanol at 30°C

Water in feed (Wt. %)	Water in permeate (Wt. %)	Water flux (J) (kg/m ² h)	Separation factor(α)	PSI
10	98.69	0.047	678	31
15	98.37	0.061	342	20
20	98.23	0.077	222	16
25	97.97	0.094	145	13
NaAlg-mPMA5				
10	99.62	0.257	4981	1276
15	99.52	0.264	1627	427
20	99.34	0.275	711	193
25	99.24	0.281	404	111
NaAlg-mPMA10				
10	99.79	0.282	9028	2541
15	99.78	0.304	4081	1237
20	99.71	0.331	1948	643
25	99.62	0.346	1048	361

concentration of water in the feed (see Fig. 5). At higher concentration of water in the feed mixture, NaAlg-mPMA10 membrane could absorb more amounts of water molecules when compared to Pristine, NaAlg-mPMA5 membrane due to plasticization effect of the polymer. However, selectivity has decreased, but flux increased considerably at 10 wt. % mPMA containing NaAlg membrane. For 30 wt. % water containing feed mixture, selectivity decreased to 1048, but flux was enhanced to 0.346 kg/m².h for the NaAlg-mPMA10 membrane. In case of pristine NaAlg, NaAlg-mPMA5 membrane, the respective values are much lower, i.e., 0.094 kg/m².h and 0.281 kg/m².h. In all cases, flux and selectivity of NaAlg-mPMA10 membranes are higher than that of plain NaAlg membrane. In any case, the present study demonstrates the positive role played by Phosphomolybdic acid upon incorporation into NaAlg to enhance the membrane performance over that of pristine NaAlg membrane.

3.8 Effect of mPMA on membrane performance

The variations of flux and separation factor are studied as a function of different wt. % of mPMA particles into NaAlg matrix. Pristine NaAlg membrane exhibited a separation factor of 658 with a flux of 0.047 kg/m².h at 10 wt. % of water in the feed mixture of isopropanol. Separation factor of NaAlg increased after the incorporation of mPMA particles. For NaAlg-mPMA5 membrane, the separation factor and flux were increased to 4981 and 0.257 kg/m².h respectively, while that for NaAlg-mPMA10, the values were 9028 and 0.282 kg/m².h at same content of water in the feed mixture. These increased values with increasing loading of mPMA compared to the pristine NaAlg membrane can be attributed to the fact that modification of PMA provides higher hydrophilicity and higher strength to the NaAlg.

The simultaneous increase in separation factor and flux is a difficult problem in PV separation, even though several studies have demonstrated this effect (Bhat *et al.* 2006, Mohanapriya *et al.* 2009). From the plot of separation factor and flux vs filler loading shown in Fig. 6, one can see

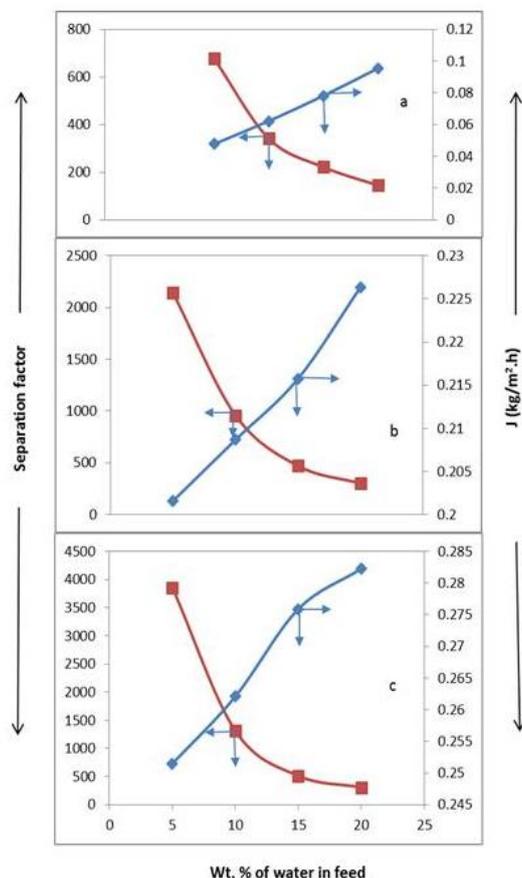


Fig. 7 Water flux and separation factor vs. wt. % of water for (a) pristine NaAlg, (b) NaAlg-PMA5, and (c) NaAlg-PTA10 membranes for water-isopropanol feed mixtures at 30°C. Symbols: (◆) flux and (■) separation factor

that separation and flux increased with filler loading, suggesting the suitability of the composite membrane for interchanging phenomena.

The selection of PMA as filler is helpful to achieve better enhancement of separation factor and flux to water in the present work. The chemical modification of PMA might be responsible for the controlled stoichiometric exchange of H^+ ions by the larger NH_4^+ ions in the original PMA. Also, the larger NH_4^+ cations provide improved strength to the framework of PMA as the excess H^+ ions act as spoil-players in the presence of higher water content of the feed mixture, resulting in a leaching of PMA particles from the membrane. As displayed in Figs. 5, 7 at 30°C, the pristine NaAlg shows the least PV performance compared to NaAlg-mPMA5, as well as NaAlg-mPMA10 offered higher separation factor and flux compared to PMA-NaAlg5, PMA-NaAlg10, NaAlg-mPMA5 and Pure NaAlg over the entire water composition range for both the feed mixtures. This notice that, NaAlg-mPMA10 membrane has higher PV values than that of NaAlg-mPMA5 membrane for the feed mixtures; this could be the result for hydrophilic-hydrophilic interactions of the filler membrane along with water molecules in the feed as shown in Figs. 5 and 7.

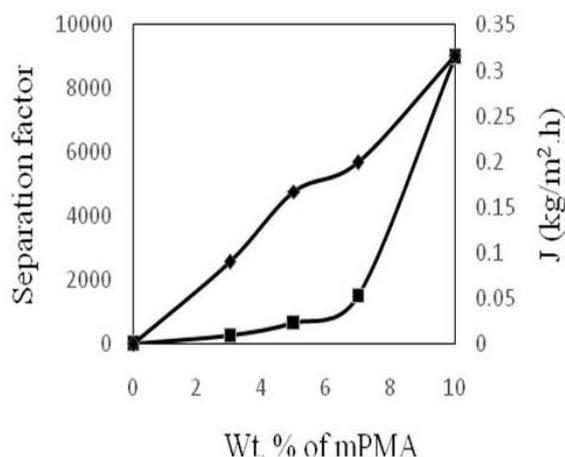


Fig. 6 Water flux and separation factor vs. wt. % of mPMA loading for water-isopropanol mixtures for 10 wt. % of water in the feed at 30°C. Symbols: (◆) flux and (■) separation factor

In this work, we established stoichiometric exchange of more susceptible protons in the Keggin structure by NH_4^+ cat ions to maintain the hydrophilicity of PMA and at the same time to reduce membrane swelling compared to NaAlg-PMA membranes (Bhat *et al.* 2010a, b), chemical modification of PMA was useful to offer improved PV data, since PMA clusters remain intact and being highly insoluble in the matrix would avoid leaching out effect as well as impart higher mechanical strength to composite membrane. The effect of using modified PMA as additive in NaAlg is demonstrated in Fig. 5 for water-isopropanol mixtures. For water -isopropanol feed mixture, NaAlg-mPMA10 membranes is quite superior to NaAlg-mPMA5, giving optimum separation factor of 9028 and flux of $0.282 \text{ kg/m}^2\cdot\text{h}$ for water-isopropanol feed mixtures at 10 wt. % of water in the feed mixture.

3.9 Effect of temperature

Pure NaAlg, and mixed matrix membrane were utilized in PV membrane. The performance was tested at different temperatures viz., 30, 40 and 50°C, typically using 10 wt. % water-containing feed mixture. Membranes were stable at all these particular temperatures; flux and selectivity values were computed at all the temperatures. The operating temperature influences both the membrane intrinsic property and the driving force for penetrant transport through the membrane during pervaporation process. As expected, the flux increased with increasing temperature, but selectivity decreased results presented in Table 3. The temperature dependency of flux was analyzed by Arrhenius equation of the type

$$J = J_0 \exp\left(-\frac{E_J}{RT}\right) \quad (6)$$

Where J_0 , E_J , R and T are the pre-exponential factor, apparent activation energy (kJ/mol) for permeation flux, molar gas constant and feed temperature (T) in Kelvin, respectively. If activation energy is positive, then permeation flux increases with increasing temperature, which has been observed in majority of PV experiments (Okuhara *et al.* 1996 a, b, Mohanapriya *et al.* 2009, Moon

Table 3 Pervaporation results for pure and mixed matrix membranes for water–isopropanol mixture at 10 wt. % of water in the feed mixture at 30–50°C

Temperature (°C)	flux, J (kg/m ² .h)	Selectivity (α)	PSI
Pure NaAlg			
30	0.047	658	31
40	0.064	342	23
50	0.101	249	18
NaAlg-PMA5			
30	0.201	2140	442
40	0.303	638	190
50	0.318	266	81
NaAlg-PMA-10			
30	0.251	3858	964
40	0.334	734	242
50	0.417	459	187
NaAlg-mPMA5			
30	0.257	4981	1276
40	0.303	747	223
50	0.318	413	127
NaAlg-mPMA10			
30	0.282	9028	2541
40	0.334	794	262
50	0.452	624	277

Table 4 Comparison with literature data: Comparisons of flux and separation factor of HPA-incorporated membranes with literature data at 30°C

Membrane	% Water	Flux	Separation factor	Reference
P- NaAlg	5.2	0.24	2182	25
NaAlg-mPTA10	10	0.316	8991	26
NaAlg	10	0.29	120	31
CS/NaAlg	13.5	0.22	436,	32
IPN-1	15	0.225	255	33
PVA/HPA-1	10	0.105	337	34
PVA/HPA-7	10	0.032	89,991	
CS/NaAlg	5wt%	0.07	1110,	35

et al. 1999), G.Y. According to free volume theory, an increase in temperature increases thermal mobility of the polymer chains, which further generates extra free volume within the polymer matrix thereby, increasing the sorption and diffusion rates of permeant molecules. This type of increase in free volume of the membrane matrix will result in an easy transport of organic component of the mixed media. Consequently, the membrane selectivity to water will be reduced,

Table 5 Comparison with literature data: Tensile strength and % elongation of pristine NaAlg and 1 and 5 wt.% mPMA incorporated Sodium Alginate hybrid composite film

Membrane	Tensile Strength N/mm ²	%elongation at break	Reference
NaAlg	6.11	210	19
NaAlg-mPTA5	14.75	150	
NaAlg-mPTA10	28.11	120	
NaAlg-0	4.4	16.2	21
NaAlg-6	4.8	18.7	
NaAlg-8	5.4	32.6	
NaAlg-12	7.2	38.1	
NaAlg	6.01	200	Present work
NaAlg-mPMA5	28.75	130	
NaAlg-mPMA10	38.11	110	

but flux will be increased. The driving force for permeation represents the concentration gradient, resulting from the difference in partial vapour pressure of the permeants between feed and permeate mixtures. As the feed temperature increases, vapour pressure in the feed compartment increases, but vapour pressure at permeate side is not affected. This would result in an increase of driving force with increasing temperature. The driving force is closely related to the phase transition in PV process and thus, is strongly dependent upon the operating temperature. This has affected the membrane performance in such a way that the flux was increased, but selectivity decreased with an increase in temperature.

4. Conclusions

Incorporation of hydrophilic mPMA particles could improve the separation characteristics of the mixed matrix membranes better than the pristine NaAlg membrane by reducing their swelling in the presence of mixed feed water + isopropanol.

- The flux and separation factor values of the mixed matrix membranes were higher than the pristine NaAlg membranes due to induced hydrophilicity of NaAlg matrices.
- Mechanical property of composite mixed matrix membranes are improved

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References

Adoor, S.G., Prathab, B., Manjeshwar, L.S. and Aminabhavi, T.M. (2007), "Mixed matrix membranes of

- sodium alginate and poly (vinyl alcohol) for pervaporation dehydration of isopropanol at different temperatures”, *Polym.*, **48**, 5417-5430.
- Adoor, S.G., Rajinekanth, V., Nadagouda, M.N., Rao, K.C., Dionysiou, D.D. and Aminabhavi, T.M. (2013), “Exploration of nanocomposite membranes composed of phosphotungstic acid in sodium alginate for separation of aqueous-organic mixtures by pervaporation”, *Sep. Purif. Technol.*, **113**, 64-74.
- Avagimova, N., Polotskaya, G., Saprykina, N., Toikka, A. and Pientka, Z. (2013), “Mixed matrix membranes based on polyamide/montmorillonite for pervaporation of methanol-toluene mixture”, *Sep. Purif. Technol.*, **48**(17), 2513-2523
- Babanzadeh, S., Mehdipour-Ataei, S., and Mahjoub, A.R. (2012), “Preparation and characterization of novel polyimide/SiO₂ nano-hybrid films by in situ polymerization”, *J. Inorg. Organomet. Polym.*, **22**(6), 1404.
- Bai, Y., Dong, L., Zhang, C., Gu, J., Sun, Y., Zhang, L. and Chen, H. (2013), “ZIF-8 filled polydimethylsiloxane membranes for pervaporative separation of n-butanol from aqueous solution”, *Separ. Sci. Technol.*, **48**(17), 2531-2539.
- Bhat, S.D. and Aminabhavi, T.M. (2006), “Novel sodium alginate composite membranes incorporated with SBA-15 molecular sieves for the pervaporation dehydration of aqueous mixtures of isopropanol and 1, 4-dioxane at 30 C”, *Micropor. Mesopor. Mater.*, **91**(1), 206-214.
- Bhat, S.D., Mallikarjuna, N.N. and Aminabhavi, T.M. (2006), “Microporous alumino-phosphate (AlPO 4-5) molecular sieve-loaded novel sodium alginate composite membranes for pervaporation dehydration of aqueous-organic mixtures near their azeotropic compositions”, *J. Membr. Sci.*, **282**, 473-483.
- Bhat, S.D., Naidu, B.V.K., Shanbhag, G.V., Halligudi, S.B., Sairam, M. and Aminabhavi, T.M. (2006), “Mesoporous molecular sieve (MCM-41)-filled sodium alginate hybrid nanocomposite membranes for pervaporation separation of water-isopropanol mixtures”, *Sep. Sci. Technol.*, **49**, 56-63.
- Bhat, S.D., Sahu, A.K., Jalajakshi, A., Pitchumani, S., Sridhar, P., George, C. ... and Shukla, A.K. (2010), “PVA-SSA-HPA Mixed-Matrix-Membrane electrolytes for DMFCs fuel cells and energy conversion”, *J. Electrochem. Soc.*, **157**(10), 1403-1412.
- Bhat, S.D. and Aminabhavi, T.M. (2006), “Novel sodium alginate-Na⁺ MMT hybrid composite membranes for pervaporation dehydration of isopropanol, 1, 4-dioxane and tetrahydrofuran”, *Sep. Sci. Technol.*, **51**, 85-94.
- Cao, S., Shi, Y. and Chen, G. (2000), “Influence of acetylation degree of cellulose acetate on pervaporation properties for MeOH/MTBE mixture”, *J. Membr. Sci.*, **165**, 89-97.
- Chanachai, A., Jiratananon, R., Uttapap, D., Moon, G.Y., Anderson, W.A. and Huang, R.Y.M. (2000), “Pervaporation with chitosan/hydroxyethylcellulose (CS/HEC) blended membranes”, *J. Membr. Sci.*, **166**, 271-280.
- Fischer, F.G., Dorfel, H. and Hoppe-Seyler's. Z. (1955), “The paper chromatographic separation and determination of hexuronic acids”, *Physiol. Chem.*, **302**, 224-234.
- Gao, Z., Yue, Y. and Li, W. (1996), “Application of zeolite-filled pervaporation membrane”, *Zeolites.*, **16**, 70.
- Haug, A., Larean, B. and Smolder, O. (1966), *Acta. Chem. Scand.*, **20**, 183.
- Keggin, J.F. (1993), “Structure of the molecule of 12-phosphotungstic acid”, *Nature*, **131**(3321), 908-909.
- Lu, S.Y., Chiu, C.P. and Huang, H.Y. (2000), “Pervaporation of acetic acid/water mixtures through silicalite filled polydimethylsiloxane membranes”, *J. Membr. Sci.*, **176**(2), 159-167.
- McGarvey, G.B. and Moffat, J.B. (1991), “Ion-exchange properties of microporous monovalent salts of 12-tungstophosphoric acid and 12-molybdophosphoric acid catalysts”, *J. Catal.*, **128**, 69-83.
- Misono, M. (1987), “Acidic and catalytic properties of heteropoly compounds”, *Mater. Chem. Phys.*, **17**(1-2), 103-120.
- Mohanapriya, S., Bhat, S.D., Sahu, A.K., Pitchumani, S., Sridhar, P. and Shukla, A.K. (2009), “A new mixed-matrix membrane for DMFCs”, *Energy. Environ. Sci.*, **2**, 1210-1216.
- Moon, G.Y., Pal, R. and Huang, R.Y.M. (1999), “Novel two-ply composite membranes of Chitosan and sodium alginate for the pervaporation dehydration of isopropanol and ethanol”, *J. Membr. Sci.*, **156**, 17-27.
- Naidu, B., Bhat, S.D., Sairam, M., Wali, A.C., Sawant, D.P., Halligudi, S.B.... and Aminabhavi, T M.

- (2005), "Comparison of the pervaporation separation of a water-acetonitrile mixture with zeolite-filled sodium alginate and poly (vinyl alcohol)-polyaniline semi-interpenetrating polymer network membranes", *J. Appl. Polym. Sci.*, **96**, 1968-1978.
- Neumann, R. (1998), "Polyoxometalate complexes in organic oxidation chemistry", *Prog. Inorg. Chem.*, **47**, 317-370.
- Okuhara, T., Mizuno, N. and Misono, M. (1996), Catalytic chemistry of heteropoly compounds", *Adv. Catal.*, **41**, 113-252.
- Pizzio, L.R., Vázquez, P.G., Cáceres, C.V. and Blanco, M.N. (2003), "Supported Keggin type heteropolycompounds for ecofriendly reactions", *Appl. Catal. A: Gen.*, **256**(1), 125-139.
- Pope, M.T. (1983), *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, New York.
- Soppimath, K.S., Aminabhavi, T.M., Kulkarni, A.R. and Rudzinski, W.E. (2001), "Biodegradable polymeric nanoparticles as drug delivery devices", *J. Control. Rel.*, **70**, 1-20.
- Strachota, A., Tishchenko, G., Matejka, L. and Bleha, M. (2001), "Chitosan-oligo (silsesquioxane) blend membranes: preparation, morphology, and diffusion permeability", *Inorg. Organomet. Polym.*, **11**(3), 165.
- Teli, S.B., Gokavi, G.S. and Aminabhavi, T.M. (2007), "Novel sodium alginate-poly (N-isopropylacrylamide) semi-interpenetrating polymer network membranes for pervaporation separation of water+ ethanol mixtures", *Sep. Purif. Tech.*, **56**, 150-157.
- Teli, S.B., Gokavi, G.S., Sairam, M. and Aminabhavi, T.M. (2007), "Mixed matrix membranes of poly (vinyl alcohol) loaded with phosphomolybdic heteropolyacid for the pervaporation separation of water-isopropanol mixtures", *Coll. Surf. A: Physico. Chem. Eng. Aspect.*, **301**(1), 55-62.
- Wang, Y.C., Fan, S.C., Lee, K.R., Li, C.L., Huang, S.H., Tsai, H.A. and Lai, J.Y. (2004), "Polyamide/SDS-clay hybrid nanocomposite membrane application to water-ethanol mixture pervaporation separation", *J. Membr. Sci.*, **239**, 219-226.
- Zhang, L., Zhou, D., Wang, H. and Cheng, S. (1997), "Ion exchange membranes blended by cellulose cuoxam with alginate", *J. Membr. Sci.*, **124**, 195-201.
- Zhang, X.K., Poojari, Y., Drechsler, L.E., Kuo, C.M., Fried, J.R. and Clarson, S.J. (2008), "Pervaporation of organic liquids from binary aqueous mixtures using poly (trifluoropropylmethylsiloxane) and poly (dimethylsiloxane) dense membranes", *J. Inorg. Organ. Polym.*, **18**, 246-252.