

Annexure – VIII

UNIVERSITY GRANTS COMMISSION
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PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING
THE FINAL REPORT OF THE WORK DONE ON THE PROJECT

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4. UGC APPROVAL NO. AND DATE: F.No. 37-336 / 2009 (SR) dated 11 JAN 2010.
5. DATE OF IMPLEMENTATION: 01. 02 .2010.
6. TENURE OF THE PROJECT: Three Years.
7. TOTAL GRANT ALLOCATED : Rs.10,11,900/-
8. TOTAL GRANT RECEIVED: Rs.9,31,540/-
9. FINAL EXPENDITURE : Rs.10,05639/-
10. TITLE OF THE PROJECT: **Synthesis and application of polymer membranes as a methanol barrier in fuel cell.**
11. OBJECTIVES OF THE PROJECT:

Preparation of polymeric membranes and application as a methanol barrier in fuel cells. The main factors of using polymeric membrane in direct methanol fuel cells as an electrolyte is the facilitated proton conduction and hindered methanol permeation. The general operating temperature of proton exchange membrane fuel cells is around 80°C which offers some difficulties in their application. The conductivity depends on the water content in the membrane which at a temperature around 80°C dries out and requires supply of humidified inlet gasses. The disadvantage of such wet inlet gasses leads to gas dilution and flooding of gas diffusion layer at high current densities thus creating parasitic loss of efficiency. To

overcome these difficulties attempts have been made to improve both hydrophilicity and conductivity of the membranes by incorporating inorganic compounds into the polymeric matrix. Polyoxometalates (POMs) are such a class of inorganic compounds which fulfill both the criteria as they possess acidity more than a mineral acid and are hydrated to a large extent. Although the conductivity of pure POMs in the solid state is very high they cannot be used as electrolytes in the fuel cell as they are highly soluble in both water as well as in common organic solvents like acetonitrile. To overcome the dissolution of the POMs in water their insoluble salts have also been used as electrolytes and the conductivity was found to depend on the temperature with highest conductivity at 100°C under humidified conditions which limit their application. Therefore, various investigations were carried out to incorporate them in a polymer matrix. The POM filled Nafion membranes have shown very good conductivity than that of the pristine membrane but their casting requires mixing of both the components in a high boiling solvent followed by sonication. The limitation of these Nafion/POM membranes is the solubility of the POMs and the particle size of the incorporated POMs which is comparatively larger. Therefore, due to advantages like hydrophilicity, stability, compatibility and good film forming properties, polyvinyl alcohol (PVA) has been used as polymer for fuel cell applications. The arrangement of terminal oxygen in the structure of these POMs is such that they can easily interact with various functional groups of organic molecules especially with the polymers containing hydroxyl groups like polyvinyl alcohol. The pure PVA has a low conductivity but introduction of POM's like tungstogermanic acid increases the conductivity up to 2.0×10^{-2} S/cm with 80% wt loadings. The Keggin structure has also been found to intact in such membranes through the bonding between the terminal oxygen and hydroxyl groups of PVA has also been confirmed by spectroscopic methods. The PVA membranes, as already mentioned are hydrophilic thus leading to large swelling in water. Such swelling nature of PVA membranes leads to problems like leaching of the POM and also methanol permeation. The POMs, which contain hydrated hydrogen ions also interact with methanol and reducing its size thus increasing its permeation through the composite membranes. Therefore, attempt was made to add silica into to PVA/POM membranes with highest proton conductivity for the optimized membrane of 1.7×10^{-2} S/cm and lowest methanol permeability of 3.5×10^{-9} cm²/s. The precursor used for silica incorporation into PVA matrix is tetraethoxysilane and the silica network formed from the self-condensation of silanol groups of TEOS led to macroscopic phase separation between silica and the polymer domain due to lack of covalent bonding. In addition, the fast self-

condensation reaction rate of TEOS brought some inconveniences for the preparation of stable hybrid materials. To enhance the polymer-silica compatibility by decreasing the self-condensation rate other precursors like phenyltriethoxysilane and γ -glycidoxypropyltrimethoxysilane (GPTMS) [22] have also been used. Due to moderate self condensation rate introduction of GPTMS into effectively prevented the macro-phase separation during the formation of membrane. This is possible because GPTMS has an organically modified alkoxide moiety containing an epoxy ring. The opening of the epoxy ring allows the formation of hydroxyl group, rendering the inorganic sols with higher hydrophilicity and thus better compatibility, to be achieved between the organic and the inorganic phases.

In this project, an attempt will be made to suppress swelling ability of PVA and also the selectivity of the membrane towards methanol separation in water by using interpenetrating polymer network method. The leaching of POM, phosphotungstic acid(PWA) will be reduced by converting it into a cesium salt which decreases its solubility in water. The preparation of PVA IPN membranes with suitable silicon precursor and insoluble salt CsPWA and sulfosuccinic acid (SSA) as a cross linking agent will be prepared. The performance of the prepared IPN membrane will be tested for its DMFC applications by studying the selective pervaporation separation of methanol from methanol-water mixtures along with proton conductivity measurements.

12. WHETHER OBJECTIVES WERE ACHIEVED: Yes.

Four different nanocomposite polymeric membranes were prepared and characterized for understanding their thermal and mechanical stability and also morphological changes. The hydrophilicity of the membranes was analyzed by means of measuring contact angles. These membranes were tested for their pervaporation separation of alcohols from water. The conductivity measurements were also carried out to investigate their suitability for fuel cell applications. All the membranes prepared are hydrophilic in nature and are highly selective to water hindering the diffusion of alcohols through them and also have good conductivity values. Therefore, these membranes can be successfully used for fuel cell applications.

13. ACHIEVEMENTS FROM THE PROJECT: Two papers published and another two are communicated. Two other papers are under preparation.

14. SUMMARY OF THE FINDINGS:

Initially nanocomposite membranes (NCMs) were prepared by using the solution casting technique by incorporating the different amounts like 6, 8, 10 wt. % of Preyssler type heteropolyacid nanoparticles to the sodium alginate. Prepared NCMs were utilized for the sorption and permeation studies for the aqueous isopropanol solutions at different concentrations. Flory-Huggins interaction parameters between the permeating molecules and polymer and solubility parameters were determined to explain the sorption behaviour of the NCMs. Permeation properties of the NCMs were tested by applying them for pervaporation dehydration of IPA at different concentrations. Different PV parameters like separation factor, flux, Permeance and selectivity were calculated to explain the permeation behaviour of the NCMs. In this study, increased sorption, permeation and selectivity was observed for the NCMs than pristine sodium alginate membrane, indicating that NCMs are efficient for PV dehydration of the IPA.

Then nanocomposite membranes of chitosan prepared by incorporating different concentrations of Preyssler type heteropolyacid, $H_{14} [NaP_5W_{30}O_{110}]$ (H14-P5) nanoparticles have been characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TGA) and dynamic mechanical thermal analysis (DMTA). Proton conductivity data of these membranes measured at varying temperatures have shown a systematic improvement in proton conductivity over that of the nascent chitosan membrane. Arrhenius activation parameter values obtained have been discussed in terms of the conduction transport mechanisms.

Another attempt was made for preparing nanocomposite membranes of poly(vinyl alcohol) (PVA)/3-glycidyloxypropyl trimethoxysilane (GPTMS) incorporated with 3, 6 and 9 wt. % chemically modified cesium salt of phosphotungstic acid (Cs-PWA) nanoparticles (NPs) crosslinked with sulfosuccinic acid (SSA). The membranes were employed for methanol dehydration via pervaporation (PV) technique as a function of filler concentration, feed methanol composition and temperature. The membranes were characterized by a variety of analytical techniques. At the highest loading of 9 wt.% of Cs-PWA, the membrane showed optimum selectivity of 22386 compared to a value of 7958 for nascent membrane with a slight decrease in flux from $1.686 \text{ kg/m}^2\cdot\text{h}$ to $1.561 \text{ kg/m}^2\cdot\text{h}$ for the separation of 10 wt.% methanol + 90 wt.% water feed mixture at 30°C . Diffusion and permeability coefficients

computed from the Fick's equation gave higher diffusion coefficients for water ($4.27 \times 10^{-9} \text{ m}^2/\text{s}$) than methanol ($2.35 \times 10^{-10} \text{ m}^2/\text{s}$), suggesting water-selective nature of the membranes.

In an another attempt high performance organic/inorganic nanocomposite membranes of chitosan/hydroxyethylcellulose (CS/HEC) blends incorporated with 2, 4 and 6 wt.% phosphotungstic acid (PWA) nanoparticles have been prepared by solution casting method. Membranes were characterized by a variety of techniques and pervaporation (PV) separation performance of the MMMs was shown to be exceedingly higher than the nascent CS/HEC blend membrane for ethanol dehydration, giving the highest separation factor of 39991 for 2 wt. % PWA loaded membrane compared to a value of 203 for nascent CS/HEC blend membrane. Any further increase of PWA loading reduced the membrane performance, but flux increased with increasing PWA concentration, feed water composition and temperature. The change in driving force, nanoparticle cluster formation and membrane swelling are responsible for the observed trends.

15. CONTRIBUTION TO THE SOCIETY

The membranes prepared were highly water selective and hinder the diffusion of ethanol, methanol and isopropanol from their mixture with water. The membranes are capable of separating alcohols from water from their aqueous mixtures even at their azeotropic composition. Therefore, these membranes have potential application in pervaporation dehydration of aqueous mixtures of alcohols. The membranes also have good conductivity values which can be used for their application in fuel cells as membrane electrolytes for the proton transfer.

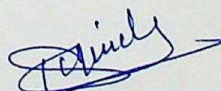
16. WHETHER ANY PH.D. ENROLLED/PRODUCED: Yes
OUT OF THE PROJECT

17. NO. OF PUBLICATIONS OUT OF THE PROJECT: 02. (Find the attached reprints)



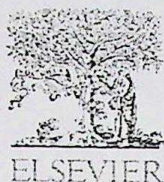
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Proton conducting properties of nanocomposite membranes of chitosan

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ABSTRACT

Nanocomposite membranes of chitosan prepared in our earlier paper (see Ref. [1]) by incorporating different concentrations of Preyssler type heteropolyacid, $H_{14}[NaP_5W_{30}O_{110}]$ ($H_{14}-P_5$) nanoparticles have been characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TGA) and dynamic mechanical thermal analysis (DMTA). Proton conductivity data of these membranes measured at varying temperatures have shown a systematic improvement in proton conductivity over that of the nascent chitosan membrane. Arrhenius activation parameter values obtained have been discussed in terms of the conduction transport mechanisms.

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1. Introduction

In our previous paper [1], nanocomposite membranes (NCMs) of chitosan (CS), incorporated with the nanoparticles of Preyssler-type heteropolyacid $H_{14}[NaP_5W_{30}O_{110}]$ i.e., ($H_{14}-P_5$), have been explored for liquid separations. It was shown that membrane separation properties of NCMs have dramatically improved over that of the nascent CS membrane due to the desirable attributes of organic and inorganic components in a single composite membrane that will offer new synergistic properties [2–5]. In continuation of this work, we now report on the improvement of proton conducting properties of NCMs of CS membrane. These NCMs have been characterized by Fourier transform infrared (FTIR) spectroscopy, thermo-gravimetric analyzer (TGA) and dynamic mechanical thermal analyzer (DMTA). From the temperature dependence of proton conductivity data, Arrhenius activation parameters have been estimated and discussed in terms of conduction mechanism. The observed moderate improvement in proton conductivity by NCMs is due the conducting channels created by the added nanoparticles.

2. Experimental

All the materials and chemicals including the preparation of Preyssler type heteropolyacid as well as NCMs remain the same

as discussed in our previous publication [1]. The average thickness of the membranes was around $40 \pm 3 \mu\text{m}$. The membrane nomenclature: nascent chitosan (M-0), whereas 5, 10 and 15% $H_{14}-P_5$ loaded chitosan nanocomposite membranes as NCM-5, NCM-10 and NCMM-15, respectively.

2.1. Spectral measurements

FTIR spectra of $H_{14}-P_5$ nanoparticles, M-0 and NCM-15 membranes were scanned in the range of $400\text{--}4000 \text{ cm}^{-1}$ using Nicolet, Impact-410 (Milwaukee, WI), FTIR spectrophotometer by the KBr pellet method.

TGA thermograms were obtained using SDT 2960 (TA Instruments, USA). Measurements were done at the heating rate of $10^\circ\text{C}/\text{min}$. The sample pan was conditioned in the instrument before performing the actual experiment.

Dynamic mechanical test analysis (DMTA) was done (courtesy of Dr. K.V.S.N. Raju, Indian Institute of Chemical Technology, Hyderabad) using a Rheometric Scientific, USA, DMTA IV instrument operated in a tensile mode at the frequency of 1 Hz and at the heating rate of $6^\circ\text{C}/\text{min}$.

2.2. Ion exchange capacity (IEC)

Ion exchange capacity (IEC) indicates the number of milliequivalents of ions in 1 g of the dry polymer. The membranes of similar masses were soaked in 50 mL of 0.01 N sodium hydroxide solution for 12 h at the ambient temperature and 10 mL of the remaining solution was titrated with 0.01 N sulfuric acid. The membrane was regenerated with 1 M hydrochloric

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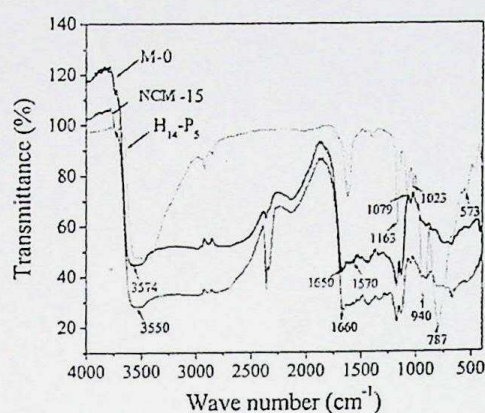


Fig. 1. FTIR spectra of $H_{14}\text{-P}_5$ nanoparticles along with chitosan (M-0) and NCM-15.

acid, washed with water until free from acid and dried to a constant mass. The IEC (mequiv/g) was then calculated as [6]:

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

where B is the volume of sulfuric acid required to neutralize the blank solution containing NaOH (mL), P is the volume of sulfuric acid required to neutralize NaOH solution in which membrane is soaked, 0.01 is the normality of sulfuric acid, 5 is a factor that corresponds to the ratio of volume of NaOH taken to dissolve the polymer and volume of NaOH used for titration and m is mass (g) of the membrane.

2.3. Proton conductivity

Proton-conductivity measurements were performed on all the NCMs using a two-probe cell by the AC impedance technique [7,8]. Conductivity cell comprised of two stainless steel electrodes, each of 50 mm dia. The membrane was sandwiched between the stainless steel electrodes fixed in a Teflon block kept in a closed glass container. Ionic conductivity of the membrane was measured under fully-humidified condition (RH=100%) by keeping de-ionized water at the bottom of the test container and equilibrating up to 24 h. Subsequently, conductivity measurements were made between 30 °C and 110 °C in a glass container that has the provision to heat. Temperature of the conductivity cell was constantly monitored with a thermometer kept inside the container adjacent to the membrane. AC impedance spectra of the membranes were recorded in the frequency range of 1 MHz and 10 Hz with 10 mV amplitude using an Autolab PGSTAT 30. Resistance of the membrane was determined from a high-frequency intercept of the impedance with the real axis. Membrane conductivity was calculated [8] from its resistance, R as:

$$\sigma = \frac{h}{RA} \quad (2)$$

where σ is proton conductivity (S/cm) of the membrane, h is its thickness (cm) and A (cm²) is the cross-sectional area.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of pure $H_{14}\text{-P}_5$, M-0 and NCM-15 (typical) displayed in Fig. 1 exhibit characteristic peaks of $H_{14}\text{-P}_5$ assigned to the Preyssler structure [8]. The P–O stretching vibrations at 1163, 1079 and 1023 cm^{−1} as well as P–O bending frequencies at 573 cm^{−1} can be seen. Stretching frequencies of W–O–W and W=O are observed

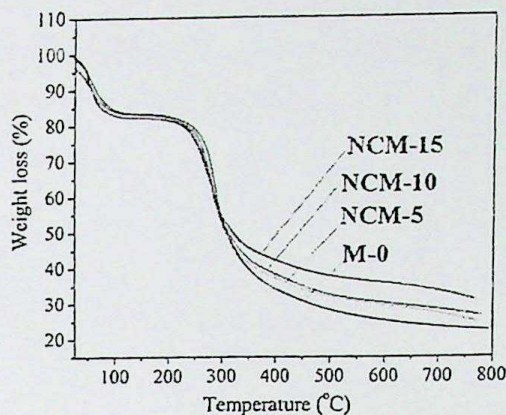


Fig. 2. TGA thermograms of M-0, NCM-5, NCM-10 and NCM-15.

at 940 and 787 cm^{−1}, respectively. A strong and broad band around 3100–3500 cm^{−1} in $H_{14}\text{-P}_5$ and CS membrane (M-0) corresponds to O–H stretching vibrations of hydroxyl groups of $H_{14}\text{-P}_5$ as well as M-0. After introducing $H_{14}\text{-P}_5$ nanoparticles into M-0 matrix, the bands for O–H of M-0 were shifted from 3574 cm^{−1} to a slightly lower value of 3550 cm^{−1} (red-shift), due to the dissociation of hydrogen bond among the hydroxyl groups of M-0, confirming the formation of hydrogen bond between –OH groups of M-0 and $H_{14}\text{-P}_5$. The bands at 1650 and 1570 cm^{−1} are assigned [9], respectively to amino-I and amino-II functional groups of M-0. However, multiple bands appearing between 900 and 1100 cm^{−1} for CS (M-0) correspond to C–O stretching vibrations [10], but these bands experience a small shift to lower frequency in NCM-15, suggesting the retainment of Keggin ion geometry of $H_{14}\text{-P}_5$.

3.2. Thermogravimetric analysis (TGA)

Thermal stability of NCMs studied by TGA displayed in Fig. 2 shows the weight loss before 110 °C for all the membranes due to sorbed water molecules and the extent of weight loss around this temperature range increased with increasing $H_{14}\text{-P}_5$ concentration in the CS matrix, implying the formation of CS– $H_{14}\text{-P}_5$ complex, due to which ion exchange capacity also increases. However, the first rapid weight loss observed at 260 °C is due to CS chain degradation, whereas the second rapid weight loss is due to the oxidative degradation of char formed from CS chain degradation. High $H_{14}\text{-P}_5$ concentrations of NCMs has resulted in high char yields around 700 °C that are almost coincident with the concentration of $H_{14}\text{-P}_5$.

3.3. Dynamic mechanical thermal analysis (DMTA)

DMTA gives important information on the microstructure of polymers. The $\tan \delta$ plot as a function of temperature is displayed in Fig. 3, wherein T_g is related to peak temperature of $\tan \delta$ curve, while the relaxation strength corresponds to the height of $\tan \delta$ peak. Storage modulus E' , cross-linking density, ν_e and number of moles of elastically effective network chains/cm³, M_c or simply molar mass between crosslinks of the network polymer are reported in Table 1.

Table 1
Results of ion exchange capacity, storage modulus, crosslink density and molar mass between cross-links.

Membranes	IEC (mequiv/g)	E' (dynes/cm ²)	ν_e (mol/cm ³)	M_c (g/mol)
M-0	1.35	3.33×10^9	0.41	1.95
NCM-5	1.64	1.19×10^{10}	1.48	0.55
NCM-10	1.80	1.35×10^{10}	1.68	0.48
NCM-15	2.10	1.40×10^{10}	1.74	0.47

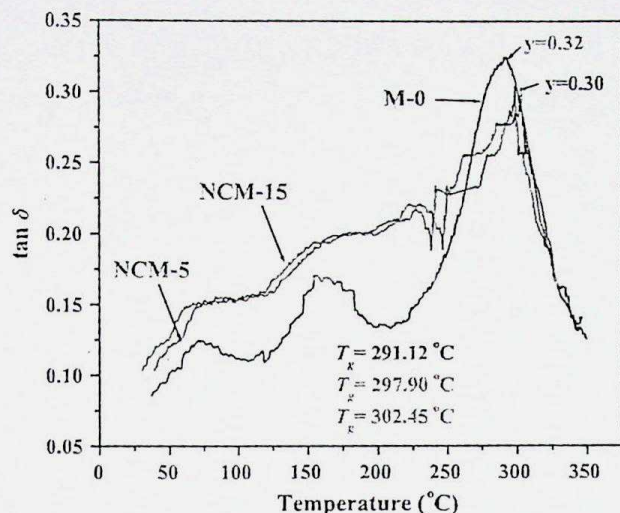
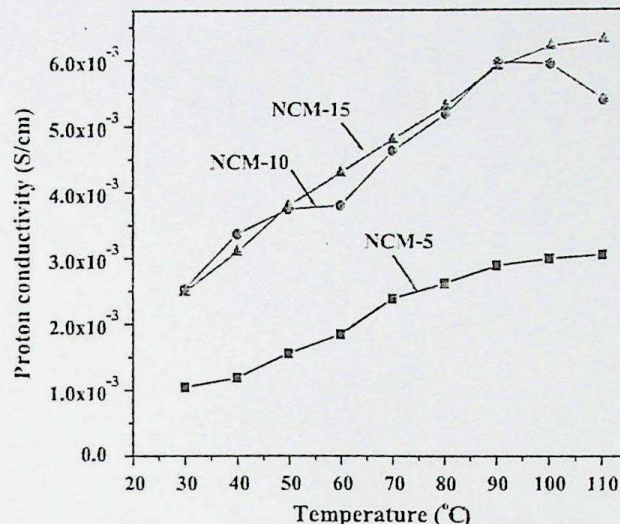
Fig. 3. Tan δ curves of M-0, NCM-5 and NCM-15.

Fig. 4. Proton conductivity of NCMs at different temperatures.

The results of ν_e indicate that NCM-5, NCM-10 and NCM-15 membranes showed much tighter network structures than the nascent chitosan (M-0); for the latter, M_c was highest, which decreased subsequently for higher loadings of the filler particles, but the ν_e values increased with increasing concentration of the filler nanoparticles, indicating that flexibility of nascent chitosan (M-0) is restricted due to the addition of H_{14} -P₅ nanoparticles in the CS matrix.

The E' values for NCMs are higher than M-0 and these values increased with increasing H_{14} -P₅ concentration such that tan δ peaks are shifted to higher temperatures, showing broader peaks. In other-words, T_g increased from 291.1 °C to 297.9, 299.4 and 302.5 °C for M-0, NCM-5, NCM-10 and NCM-15, respectively. This suggests that hydroxyl groups of CS and H_{14} -P₅ nanoparticles are responsible for increasing the cross-link density as well as T_g of the NCMs with increasing concentration of filler nanoparticles. However, the observed lower relaxation strength at higher H_{14} -P₅ concentration indicates that more of the CS segments are chemically bonded or entrapped within the H_{14} -P₅ cluster, thus restricting the mobility of CS chains.

3.4. Proton conductivity

The proton conductivity measurements were performed on NCMs at different temperatures as a function of filler concentration as displayed in Fig. 4. Proton transport occurs mainly by Grotthuss mechanism, in which proton forms hydrogen bond with water molecules to exits as H_3O^+ , thus hopping from one active component to other through a tunneling mechanism. Such proton conductivity plays an important role as fuel cell membrane [7,8,10,11]. According to the mechanisms proposed for conductivity, protons can be transported in the presence of water and hence, conductivity is influenced by water content of the polymer matrix, due to increase in the mobility of ions in the water phase. However, in case of the present NCMs, the added increase of proton conductivity is due to the presence of HPA nanoparticles acting as proton conducting centres.

Proton conductivity values of NCMs increase with increasing concentration of filler nanoparticles (see Fig. 4). The nascent CS (M-0) has excellent insulation property as a material, but proton conductivity of the hydrated plain CS upon the addition of nanoparticles has increased to 10^{-3} order; the latter was further improved by increasing the concentration of nanoparticles as observed in NCMs, due to increase in water content as well as the filler concentration in the membranes. The terminal oxygen of HPA might link

with both the hydrated hydrogen ions, thus increasing the proton conductivities at increasing concentration of H_{14} -P₅ nanoparticles as well as increase of temperature. Notice that the maximum value of proton-conductivity for NCM-15 was found to be 6.3×10^{-3} S/cm at 110 °C.

The proton conductivity data vary linearly with IEC results. As can be seen from Fig. 4 that proton conductivities of NCM-10 and NCM-15 are almost identical, but are higher than NCM-5, suggesting that higher filler concentration did not affect much of the conductivity data. To better understand the influence of temperature on proton conductivity, the Arrhenius plots of logarithmic conductivity versus $1/T$ were constructed (see Fig. 5); the Arrhenius activation parameters were calculated from the slopes of the linear plots that suggest the operation of thermally activated conduction process as explained by the conventional relationship:

$$\sigma = \sigma_0 e^{-(E_a/RT)} \quad (3)$$

where σ is proton conductivity in S/cm, σ_0 is pre-exponential factor, E_a is activation energy in kJ/mol, and RT has the usual meaning of energy. The E_a value for NCM-5 is 32.7 kJ/mol, which is higher than 22.6 kJ/mol and 25.9 kJ/mol, observed for NCM-10 and NCM-15, respectively. The calculated activation energies for proton

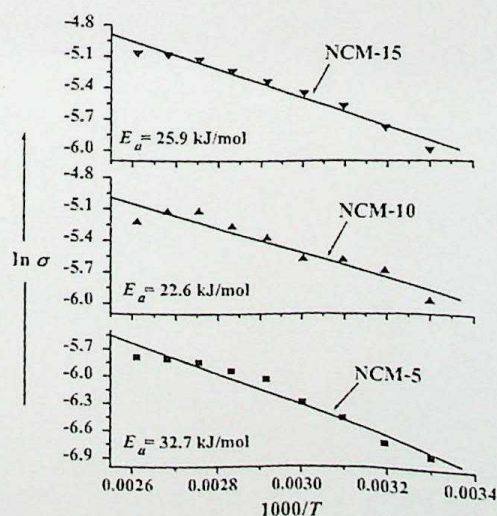


Fig. 5. Arrhenius plots of proton conductivity versus temperature.

transport are in the range of activation energies observed for Grotthuss mechanism. However, proton conductivities of the NCMs are not high enough to justify their application in fuel cell as solid electrolyte membranes, but the membranes of this study are stable at high temperature.

4. Conclusions

The results of this study suggest that NCMs of CS have improved the thermal as well as proton conducting properties compared to the nascent CS polymer, which is a perfect insulator. The NCMs showed good proton conductivity and are thermally more stable than pure CS due to proton-conducting pathways created due to the presence of H_{14} -P₅ nanoparticles in the matrix as a result of trapped H_{14} -P₅ nanoparticles or clusters acting as proton donors. The increasing concentration of filler nanoparticles as in NCMs has increased proton mobility, resulting in an increase of proton conductivity. However, the NCMs of this study may have applications as medium temperature fuel cell solid electrolyte membranes; efforts are underway to increase the proton conductivity of these membranes by an order or more of magnitude to make them useful as fuel cell membranes.

Acknowledgements

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Sorption and permeation studies for isopropanol + water mixtures using alginate based highly water selective nanocomposite membranes

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Abstract Nanocomposite membranes (NCMs) were prepared by using the solution casting technique by incorporating the different amounts like 6, 8, 10 wt.% of Preyssler type heteropolyacid nanoparticles to the sodium alginate. Prepared NCMs were utilized for the sorption and permeation studies for the aqueous isopropanol solutions at different concentrations. Sorption experiment enabled the study of interactions between the components of the mixture and the polymer. Flory-Huggins interaction parameters between the permeating molecules and polymer and solubility parameters were determined to explain the sorption behavior of the NCMs. Permeation properties of the NCMs were tested by applying them for pervaporation dehydration of IPA at different concentrations. Different PV parameters like separation factor, flux, Permeance and selectivity were calculated to explain the permeation behavior of the NCMs. In this study, increased sorption, permeation and selectivity was observed for the NCMs than pristine sodium alginate membrane, indicating that NCMs are efficient for PV dehydration of the IPA. Solution-diffusion model was adopted to study the mass transfer through the membrane by calculating the diffusion coefficients.

Keywords Pervaporation · Isopropanol-water mixture · NCMs · Sodium alginate · Preyssler HPA

Introduction

Pervaporation, a membrane based process, used for separation of liquid mixtures [1, 2] especially for azeotropic mixtures as

an alternative for the conventional energy consuming distillation process. Such distillation processes require carcinogenic entrainer like benzene to break the azeotrope which makes them environmentally less affable. These membrane separations are best explained on the basis of sorption-diffusion model [3–5] consisting of initial sorption of feed liquid, diffusion of the permeant in the membrane followed by its desorption. Therefore, the experimental data regarding sorption and diffusion is very useful while selecting a membrane or its modification for efficient separation of azeotropes. Many pharmaceutical and fine chemical synthetic procedures are often concerned with aqueous alcoholic solutions which are to be separated for their recycling. The dehydration of alcohols is also one of the important aspects of industrial applications. Generally, pristine polymeric membranes suffer many disadvantages like large swelling, lesser mechanical strength and selectivity towards the preferred component of the chosen binary liquid mixtures. Therefore, modification of these pristine membranes is essential for their application in pervaporation. Heteropolyacids (HPA) have highly stable unique crystal structure having mobile protons in the form of H_3O^+ , H_5O_2^+ , etc. [6]. Due to the presence of such hydrated protons in the discrete structure of HPA it is expected that the hydrophilicity and selectivity towards water increases than the other component of the liquid mixture as a result of enhanced interaction between water and membranes. In our earlier studies on pervaporation performance of polymeric membranes incorporating various HPAs it was found that hydrophilicity of the hybrid membranes increased and these membranes can be used for efficient dehydration of ethanol [7–9], isopropanol [10] and acetic acid [11]. Therefore, in continuation of our earlier work we have used the highly water selective [7] nanocomposite membranes of sodium alginate (NaAlg) incorporating 6, 8, 10 wt. % of Preyssler type heteropolyacid (HPA) nanoparticles for sorption and permeation studies of isopropanol-water binary mixtures.

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Isopropanol (IPA) is frequently used in industries for processes such as acetone production, manufacturing of hydrogen peroxide, solvent extraction and as a cleansing agent in semiconductor and electronic industries [12]. Due to formation of an azeotrope of IPA with water at 12.2 %, its dehydration becomes difficult without the presence of an entrainer. To overcome this difficulty, novel polymeric membranes have been developed to separate and concentrate aqueous IPA mixtures as well as other closely boiling mixtures by pervaporation (PV) technique [13–15]. Therefore, in the present study, a highly water selective membrane of sodium alginate filled with Preyssler type HPA nanoparticles was used for pervaporation dehydration of IPA. Sodium alginate, a natural polymer, has good flexibility and is also hydrophilic in nature [16–20]. Considerable swelling of NaAlg membrane in aqueous solutions leads to loss of useful mechanical properties thus limiting its application. Therefore, these membranes have been used after modification such as crosslinking with glutaraldehyde [21] or preparing two-ply membranes in combination with Chitosan [22]. Other modifications NaAlg membranes involve blending [23], grafting [24, 25], crosslinking [26], or by adding filler particles [27–29].

In this paper, nanocomposite membranes (NCMs) of NaAlg incorporating different amounts of Preyssler type HPA, $H_{14} [NaP_5W_{30}O_{110}]$ [7] are thoroughly investigated for their sorption and permeation characteristics for IPA-water mixtures. Different thermodynamic parameters like F-H interaction parameters and solubility parameters were calculated by using the sorption data in pure solvents. Surface behavior of the NCMs was studied by swelling and contact angle study. Effect of variation of HPA, feed water content and feed temperature on permeation and selectivity of the NCMs were systematically investigated in order to understand the PV performance of these prepared NCMs.

Experimental

Materials and chemicals

Sodium alginate, isopropanol, orthophosphoric acid, sodium tungstate, and potassium chloride were all purchased from s.d. fine Chemicals, Mumbai, India. All other chemicals were of reagent grade and used without further purification. Double distilled water was used throughout the study.

Synthesis of Preyssler HPA

Preyssler type HPA was (prepared) synthesized using procedure described in our previous report [8]. In brief, Orthophosphoric acid (75 cm^3 , 90 %, 1.2 mol) was slowly added to a solution containing 99 g of sodium tungstate (0.3 mol)

in 50 cm^3 water at 45°C . The resulting mixture was refluxed for 5 h, cooled to ambient temperature (30°C) and diluted with 15 cm^3 of water. Powdered potassium chloride (22.5 g, 0.32 mol) was slowly added to the vigorously stirred solution for about 35 min at ambient temperature. The pale green impure precipitate was filtered and washed off with 0.1 M potassium acetate. The white needle like crystals of potassium salt of Preyssler anion was recrystallized from hot water. The free acid was prepared by passing a solution of potassium salt of Preyssler anion in 20 cm^3 water through a column ($50 \times 1\text{ cm}$) of Dowex-50 WX in H^+ form. Evaporation of elute to dryness under vacuum afforded the desired HPA viz., $H_{14} [NaP_5W_{30}O_{110}]$. Particle size of the HPA nanoparticles is found to be 50–60 nm measured by using particle size analyzer and TEM [8].

Preparation of nanocomposite membranes (NCMs) and their characterization

NaAlg (4 g) was dissolved in 100 cm^3 of water with constant stirring. Aqueous solutions of 6, 8, and 10 wt% HPA with respect to weight of polymer were prepared separately and added to the alginate solution. Above mixture was stirred 24 h in order to get homogeneous solution. The homogeneous solution was then cast uniformly onto a glass plate with the help of a doctor's knife and dried at room temperature. The thickness of the membranes was measured by micrometer screw gauge and was around $40 \pm 2\text{ }\mu\text{m}$. The membranes containing 6, 8 and 10 wt. % Preyssler type HPA-loaded NaAlg were designated, as NCM-6, NCM-8, and NCM-10 respectively. The pristine NaAlg membrane was also prepared in the same manner in the absence of Preyssler type HPA and is designated as NaAlg. Characterizations of all the membranes have been reported in our earlier study [7].

Theory

Determination of porosity of the NCMs

Membrane samples were cut into desired size, soaked in water for 30 min and weighed immediately after the surface-adhered water was blotted with Kim wipe papers. The wet membranes were dried for 2 h at 60°C and weighed. The volume occupied by water and volume of membrane in wet state were determined to calculate membrane porosity as [30]:

$$\text{Porosity} = \frac{(W_w - W_d)}{\rho_w V_T} \quad (1)$$

Where ρ_w is density of pure water at 25°C (g/cm^3) and V_T is apparent volume of membrane in the wet state (cm^3);

W_w and W_d are weights of the membranes in wet and dry states, respectively. The V_T was calculated using:

$$V_T = \frac{(W_w - W_d)}{\rho_w} + \frac{W_d}{\rho_m} \quad (2)$$

Where ρ_m is density (g/cm^3) of the membrane in its dry state.

Swelling and sorption experiment on NCMs

Swelling experiments were performed gravimetrically at 30 °C on the membranes in 10, 20, 30 and 40 wt. % water containing feed mixtures. Initial mass of the circularly cut membranes was measured by placing them on a single-pan digital microbalance (model AE 240, Mettler, Switzerland) with sensitivity to ± 0.01 mg. Samples were then placed inside the specially designed airtight test bottles containing 30 cm^3 of the test solvent. Test bottles were maintained at 30 °C for 48 h. Mass of the swollen membranes was measured immediately by removing the test samples from the bottles and wiping the surface-adhered liquid droplets by gently pressing between the filter paper wraps. Sorbed liquids were recovered in a liquid nitrogen trap by desorbing the equilibrated sample in the purge and trap apparatus and analyzed by gas chromatography (model: Ultima-2100, Netel India Pvt Ltd., Mumbai, India). The % degree of swelling, DS was then calculated as:

$$\text{Degree of swelling} = \left(\frac{M_s - M_d}{M_d} \right) \times 100 \quad (3)$$

Where, M_s and M_d is the mass of sorbed and dry membrane respectively.

Sorption selectivity is calculated as:

$$\alpha_s = \left(\frac{M_w}{M_{IPA}} \right) \times \left(\frac{F_{IPA}}{F_w} \right) \quad (4)$$

Where, M_w and M_{IPA} represent weights of sorbed water and IPA respectively. F_w and F_{IPA} represent feed water and feed IPA respectively.

Diffusion selectivity is calculated as in Eq. (5),

$$\alpha_d = \left(\frac{\beta_{ij}}{\alpha_s} \right) \quad (5)$$

where, β_{ij} represent the separation factor.

Determination of F-H interaction and solubility parameters

Swelling experiments were performed in pure solvents and data was used to calculate the different thermodynamic

parameters. Volume-fraction values (ϕ_i) were calculated by using the following equation:

$$\phi_i = \left(\frac{W_i/\rho_i}{W_i/\rho_i + W_m/\rho_m} \right) \quad (6)$$

Where W_i is solvent uptake (g g^{-1} dry membrane) of component i at equilibrium, and ρ_i and ρ_m are the densities of the solvent and membrane, respectively.

The membrane density (ρ_m) was calculated using;

$$\rho_m = \left(\frac{M_d}{M_d - M_l} \right) \times \rho_o \quad (7)$$

The Flory-Huggins thermodynamic model expresses the dependence of the solvent volume fraction on the Flory-Huggins interaction parameter (χ_{ip}) at a given solvent activity (α_i) as [31, 32]:

$$\ln \alpha_i = \ln \phi_i + (1 - \phi_i) + \chi_{ip}(1 - \phi_i)^2 \quad (8)$$

When the membrane is immersed in pure solvent, the solvent activity becomes unity and Eq. (8) can then be rewritten as Eq. (9):

$$\chi_{ip} = - \frac{\ln \phi_i + (1 - \phi_i)}{(1 - \phi_i)^2} \quad (9)$$

The Flory-Huggins interaction parameter (χ_{ip}) is related to the chemical compatibility between the solvent and membrane. The chemical compatibility is usually expressed in terms of the difference in solubility parameters (δ) between two constituents. The relationship between the interaction parameter and solubility parameters has been reported by Bristow and Watson [33]:

$$\chi_{ip} = 0.35 + \frac{V_i}{RT} (\delta_i - \delta_p)^2 \quad (10)$$

Where V_i is the molar volume of the solvent, R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature (K), and δ_i and δ_p are the solubility parameters for the solvent and membrane, respectively. The solubility parameter of water is $47.8 \text{ J}^{1/2} \text{ cm}^{-3/2}$ and that of IPA is $23.5 \text{ J}^{1/2} \text{ cm}^{-3/2}$ [34].

F-H interaction parameters between water and IPA were determined as [9]:

$$\chi_{12} = \frac{\{x_1 \ln(x_1/v_1) + x_2 \ln(x_2/v_2) + (G^E/RT)\}}{x_1 v_2} \quad (11)$$

where ΔG^E ($\text{J} \cdot \text{mol}^{-1}$) is excess Gibbs free energy of mixing, R is gas constant ($\text{J} \cdot \text{mol}^{-1} \text{ K}^{-1}$), T is absolute temperature and x_1 , x_2 are respectively, mole fractions of components 1 and 2 of the mixture. v_i is volume fraction of the i^{th} -component in the

external liquid phase. Values of ΔG^E were calculated using activity coefficients, γ as:

$$\Delta G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (12)$$

The activity coefficients of solvent may be calculated from its molar concentration using van-Laar Eq. [9].

Solubility parameters for the membranes were obtained from the pure-solvent data from Eq. (13) by solving Eq. (10). Note that Eq. (13) has two roots, so δ_p can theoretically assume either of

$$\delta_p = \delta_i \pm \left[\frac{(\chi_{ip} - 0.35) RT}{V_i} \right]^{1/2} \quad (13)$$

two values when solvent solubility is determined in a membrane. However, with sorption measurements of membranes in two different solvents, it was possible to select the one that better matched among both the determinations.

Separation factor, flux and pervaporation separation index

Pervaporation experiments were performed in an apparatus that was indigenously designed. Effective area of the membrane in the PV cell was 26.43 cm² with a liquid volume capacity of 200 cm³. PV apparatus consists of a stainless steel cell in which the feed stock solution was maintained at the required temperature by a thermostatically controlled water jacket. PV cell consists of an efficient three-blade stirrer powered by a DC motor in the feed compartment. The feed mixture was stirred at 200 rpm, the downstream pressure was maintained around 5 mbar using a vacuum pump (Model: ED-21, Hindhivac, Bangalore, India).

Before starting the PV experiment, test membrane was equilibrated for 3 h with feed mixture and after establishment of the steady state, liquid permeate was collected and condensed in traps using liquid nitrogen. The collected permeate for about 8–10 h was weighed after allowing it to attain room temperature using a digital microbalance sensitive to ± 0.01 mg to determine the flux and was then analyzed by gas chromatography (Model: Ultima-2100, Netel India, Ltd, Mumbai.) to calculate the different PV parameters as follows.

Separation factor for the NCMs was calculated by using the following equation:

$$\beta_{ij} = \left(\frac{P_w}{P_{IPA}} \right) X \left(\frac{F_{IPA}}{F_w} \right) \quad (14)$$

Where, P_w and P_{IPA} are wt% of water and IPA in permeate, F_w and F_{IPA} are wt% water and IPA in feed respectively.

Flux of the NCMs was calculated by;

$$J = \frac{W}{A X t} \quad (15)$$

Where; W is the mass of permeate (in kg), A is the area of the membrane in (m²) which was utilized for the experiment and t is time of the experiment in hours. Pervaporation separation index is calculated by using equation: $PSI = J X \beta$. Where, J is the flux and β is the separation factor.

Permeance and selectivity

PV results obtained in this work are also analyzed on the basis of the principles of sorption-diffusion model [5], according to which mass transfer is controlled by diffusion. Since fast distribution equilibrium can be established between the bulk feed and the upstream surface of the membrane the local diffusion rate, J_i in a membrane can be described by Fick's diffusion equation [35], which under steady-state conditions for one-dimension can be written as:

$$J_i = D_i(C_{i,m}) \frac{dC_{i,m}}{dz} \quad (16)$$

where h is membrane thickness, diffusion coefficient, D_i is affected by solute concentration, but due to immobilization of the membrane, it is regarded as self-diffusion coefficient and J_i is calculated per unit of cross-sectional area of the membrane. For a planar geometry of the membrane, permeation rate, Q_i , can be calculated by integrating Eq. (16) from the upstream to downstream side across the membrane:

$$Q_i = \int_0^h J_i dz = \int_{C_{i,p,m}}^{C_{i,f,m}} D_i(C_{i,m}) dC_{i,m} \quad (17)$$

Upon solving Eq. (17), we get:

$$Q_i = J_i h = D_i(C_{i,f,m} - C_{i,p,m}) \quad (18)$$

Under steady-state conditions, J_i is constant, but at low downstream side pressure, we have: $C_{i,p,m} \approx 0$ and $C_{i,p} \approx 0$ and hence, we can simplify Eq. (18) to give:

$$D_i = \frac{J_i h}{C_{i,f,m}} \quad (19)$$

Equation (19) was used in this work to compute diffusion coefficients of permeating liquids. Distribution coefficient, K_i and permeation coefficient, P_i are calculated as:

$$K_i = \frac{C_{i,f,m}}{C_{i,f}} \quad (20)$$

$$P_i = \frac{Q_i}{C_{i,f} - C_{i,p}} \approx \frac{Q_i}{C_{i,f}} = \frac{J_i h}{C_{i,f}} \quad (21)$$

Combining Eqs. (16, 17, 18, 19, 20 and 21), the expression for permeability is written as: $P_i = D_i K_i$. For calculating membrane selectivity, α_{ij} , we prefer to use the protocol adopted before [9] and it is the ratio of two components of a mixture, is an intrinsic property of the membrane. Under certain conditions, it is the ratio of permeabilities or permeances of the components, i and j and is computed as [36]:

$$\alpha_{ij} = P_i/P_j = (D_i/D_j)(K_i/K_j) = S_d \times S_k \quad (22)$$

where $S_d = D_i/D_j$ and $S_k = K_i/K_j$. Permeation rate (J_{ij}) of water (i) and IPA (j) were calculated as: $J_{ij} = (p_{ij}^f - p_{ij}^p) / (P_{ij}/h)$ in which superscripts, f and p refer to feed and permeate, respectively; p_{ij} is partial vapor pressure of water or IPA; P_{ij} is membrane permeability coefficient of water or IPA, respectively; these are the product of diffusion (D_{ij}) and solubility coefficients (S_{ij}); h being membrane thickness, and P_{ij}/h is the permeance of water or IPA. The relationship between partial vapor pressure (p_{ij}^f), molar concentration of water (x_i), IPA (x_j) and activity coefficients of individual components of the feed mixture calculated using van Laar equation: $p_{ij}^f = x_{ij} \gamma_{ij} p_{ij}^s$, where saturated vapor pressure of water (p_i^s) or IPA (p_j^s) were calculated from Antoine equation [36].

By considering activity coefficient and molar concentrations of individual component, the saturated vapor pressure of water or IPA were calculated using $p_i^s = x_i \gamma_i p_i^o$ from which permeance of water or IPA were calculated as:

$$J_{ij} = (x_{ij} \gamma_{ij} p_{ij}^s - p_{ij}^p) / (P_{ij}/h) \quad (23)$$

Where, subscripts i and j represents the permeance for water and IPA respectively.

Results and discussion

Porosity

Percentage porosity of the all prepared membranes was calculated by the Eq. 1 and data is represented in Fig. 1. H_{14} - P_5 loading significantly affect the porosity of the NCMs. Porosity is found to increase with increasing filler loading which may be due to restricted mobility of chain segments in presence of filler nanoparticles. At 6 wt % H_{14} - P_5 loading, there is homogeneous distribution of filler nanoparticles [7] which leads to increased water selectivity due to favorable interactions between filler and membrane matrix thus allowing only water transport through the membrane while restricting the IPA. At higher loadings of H_{14} - P_5 porosity was found to be greater than pristine NaAlg

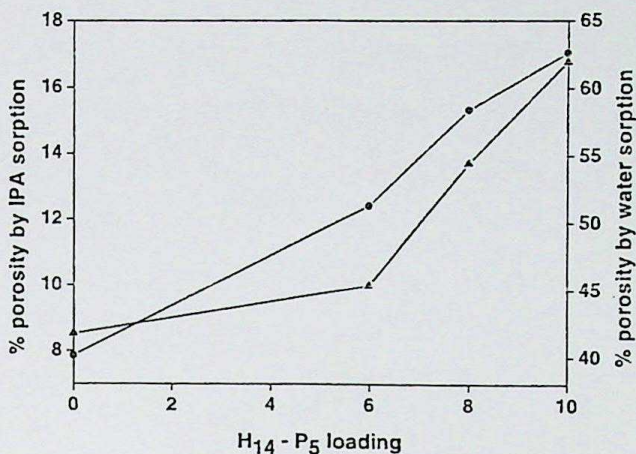


Fig. 1 Water/IPA sorption Porosity vs H_{14} - P_5 loading

membrane, may be due to aggregation of HPA, which led to permeation of IPA molecules along with water molecules thereby reducing membrane selectivity.

Swelling studies

The degree of swelling (%) of the membranes calculated from Eq. (3) for all the membranes are plotted as a function of wt. % of water in the feed mixture at 30 °C (see Fig. 2). It is observed that NCM-10 has the highest degree of swelling compared to all the membranes over the studied range of feed water compositions. Degree of swelling of the NCM-10 increased to almost double, i.e., from 61 to 132 with increasing water concentration in the feed mixture from 10 to 40 wt.%. These results support the higher values of flux observed in case of NCM-10 as compared to other membrane. The lowest degree of swelling for pristine NaAlg

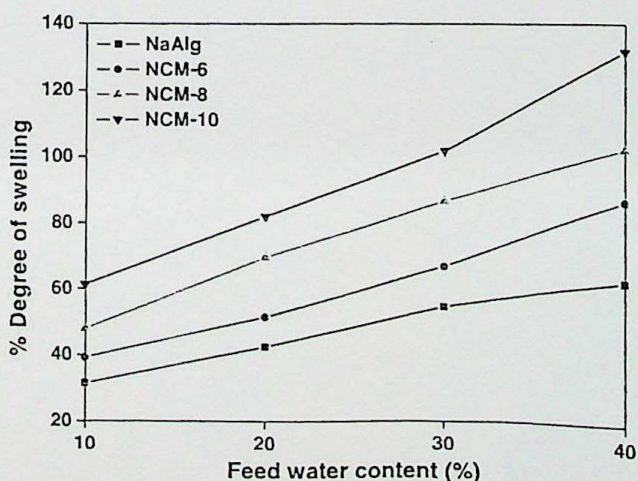


Fig. 2 Degree of swelling vs feed water composition for NaAlg and NCMs

Table 1 Contact angle, % porosity, F-H interaction and Solubility parameters, degree of swelling, flux of NaAlg and NCMs

Membrane	θ	% porosity		F-H interaction parameters		Solubility parameter (δ_p)	(δ_p, δ_s)	Degree of swelling (%)	
		Water sorption	IPA sorption	χ_{p1}	χ_{p2}			Water	IPA
NaAlg	72	40	9	0.90	1.85	56.5	8.7	69.7	10.5
NCM-6	68	51	10	0.76	1.73	55.3	7.5	118.8	12.6
NCM-8	63	58	14	0.70	1.42	54.8	7.0	158.5	21.2
NCM-10	57	63	17	0.67	1.19	54.5	6.7	189	32.7

membrane increased from 31 to 62 for 10 to 40 % water content, but after the addition of the H_{14} - P_5 nanoparticles into NaAlg matrix, swelling has been increased. This trend is in accordance with the flux values of the membranes in the chosen feed mixture. These results indicate that the hydrophilicity of the NCMs is increased with filler loading as NaAlg < NCM-6 < NCM-8 < NCM-10.

F-H interaction parameters, Solubility parameters

Table 1 displays swelling values in pure solvents for the NaAlg and NCMs. The equilibrium sorption is increased with H_{14} - P_5 loading for the permeating molecules. Sorption data obtained is utilized to calculate Flory-Huggins interaction parameters between permeating molecule and polymer membrane by using the Eqs. 9 and 10. It is observed that the F-H interaction parameter values for water-polymer interactions are lower than that of IPA-polymer interactions. Usually, stronger interaction between the mixture components would result in a smaller value of interaction parameter [37]. NCMs have shown lower F-H values for water-membrane interactions than that of pristine NaAlg membrane which indicate that NCMs interacts more preferentially with water than IPA. These preferential interactions between water molecules and the NCMs resulted in the selective sorption of the water molecules on the membrane surface, which in turn increases the permselectivity of the NCMs than pristine NaAlg membrane. Incorporation of H_{14} - P_5 nanoparticles to NaAlg causes hydrophilic-hydrophilic interactions which increases permeation flux for the NCMs. In present study, NCM-6 has shown higher affinity towards water than IPA as compared to other membranes, because of uniform distribution of the filler in the membrane matrix without any aggregation [7]. Higher filler concentration leads to weakening of polymeric chains due to aggregation of filler particles in membrane matrix which may affect the sorption and permeation behavior of the membranes. Aggregation of the filler nanoparticles at higher concentrations is also noticed in our earlier report by SEM examination of the membranes [7]. F-H interaction parameters between water and isopropanol at different feed water compositions were also calculated by

using the Eq. 11 [9]. The calculated interaction parameters were found to be 1.11, 1.045, 0.98 and 0.93 for 10, 20, 30 and 40 % feed water compositions respectively indicating an increased interaction between solvents at higher feed water content. Such an increase in interaction as the water content in the feed decreases leads to higher separation factor as observed in the present study.

The solubility parameters were calculated to study the affinity between the polymer and the permeating molecule, which is determined by difference between the ($\Delta\delta$) solubility parameters of polymer and permeating molecule. Lesser difference between the solubility parameter values between solvent and polymer attributed to the stronger interactions between them. It can be seen from Table 1 that the solubility parameter (δ_p) values decreased with H_{14} - P_5 loading from NaAlg to NCM-10. Apart from solubility parameters for water ($47.85 \text{ J}^{1/2} \text{ cm}^{-3/2}$) and IPA ($23.5 \text{ J}^{1/2} \text{ cm}^{-3/2}$) [34], NaAlg and NCM6, NCM-8 and NCM-10 shows the δ_p values ranging from 56.5, 55.3, 54.8 and 54.5 respectively. Decreased δ values after incorporation of hydrophilic H_{14} - P_5 indicates increased solubility of NCMs in water than pristine NaAlg membrane. Also, the difference between the δ values of water and membrane are quite lesser than that of IPA and membrane, suggesting higher solubility of membranes in water than IPA, which

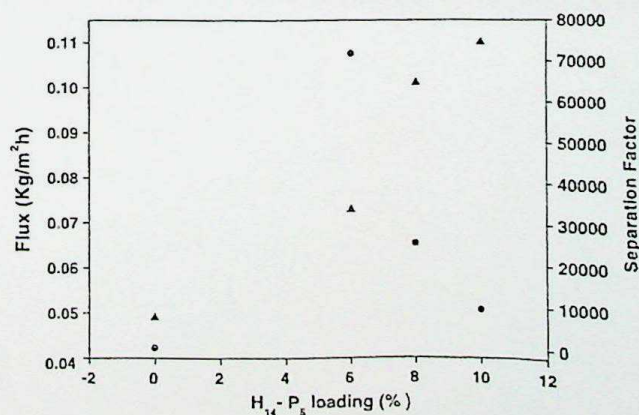
Fig. 3 Effect of variation in H_{14} - P_5 loading on PV performance NCMs

Table 2 Flux, Separation factor, sorption selectivity, diffusion selectivity and pervaporation separation index for NaAlg and NCMs (At azeotropic composition and 5 mbar pressure at 30 °C)

Membranes	Flux (kg/m ² .h)	β_{ij}	α_s	α_d	PSI
NaAlg	0.049	530	131	4.05	26
NCM-6	0.073	71960	1301	55.31	5253
NCM-8	0.101	25695	792	32.44	2595
NCM-10	0.110	9718	546	17.80	1069

might result in an increase in the water selectivity of the NCMs as compared to the NaAlg with enhanced permeation flux. These results are also supported by the contact angle measurements of the membranes (see Table 1).

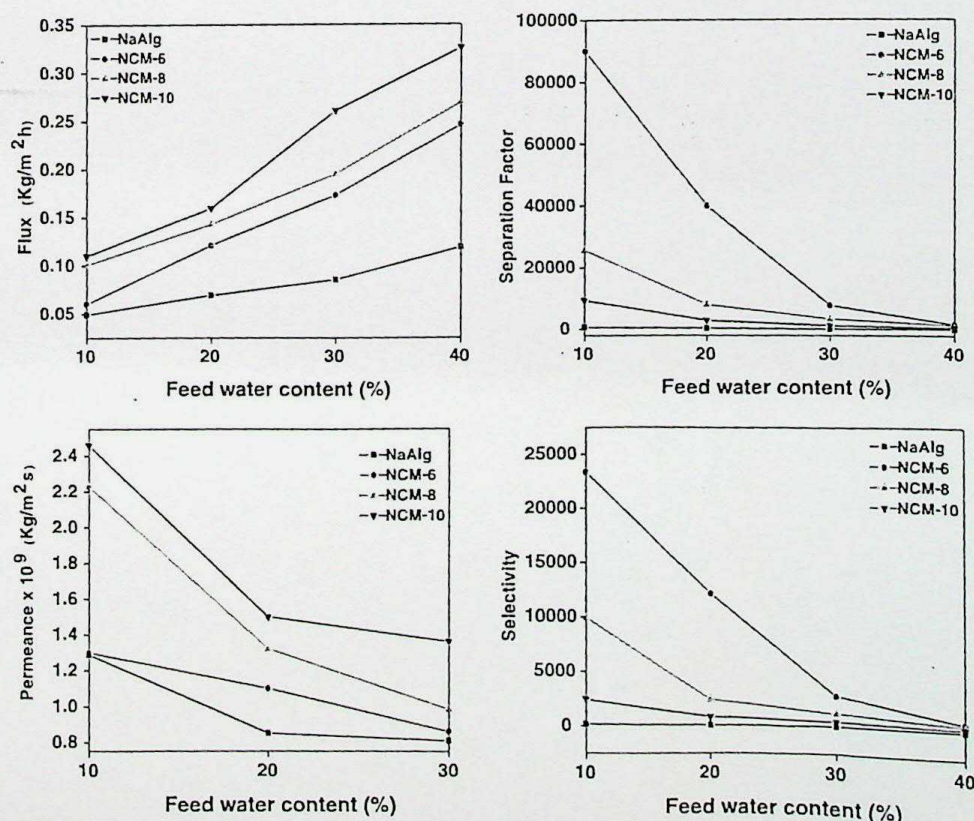
Pervaporation study

Permeation and selectivity of the membranes was studied by applying them for PV separation of IPA-water mixtures. Different PV parameters like separation factor, permeation flux, selectivity and permeance were calculated to explain the PV results. In order to understand the optimum PV performance of the membranes, the study is carried at different experimental conditions.

Effect of variation in H_{14} - P_5 loading on PV performance of NCMs

Effect of H_{14} - P_5 loading on the PV performance of NCMs studied systematically with respect to flux and separation factor. Figure 3 displays variation of separation factor and flux with the amount of filler loaded at the azeotropic composition and at 30 °C under 5 mbar pressure (Table 2), which shows that filler loading gratefully affect the performance of the membranes. NCMs have shown dramatic increase in the separation factor with increase in flux as compared to the pristine NaAlg membrane. Separation factor 530 of the NaAlg is enhanced upto 71960 for NCM-6, which further decreased to 25695 and 9718 for NCM-8 and NCM-10 respectively. Flux is increased from its base value 0.049 kg/m²h for NaAlg to 0.11 kg/m²h for NCM-10. An improved PV performance after the addition of filler is due to hydrophilic nature of the filler which absorbs more water molecules from the feed which leads to the enhancement in selectivity of the membranes. This effect is attributed to the discrete active surface sites of the HPA which makes it to behave like solutions and absorb large amount of solvent molecules particularly that of water to form HPA solvates which causes increased absorption of water by NCMs. At higher filler loadings water selectivity of the NCMs decreased due to increased free volume because of excessive

Fig. 4 Effect of variation in feed water composition in PV performance of NCMs



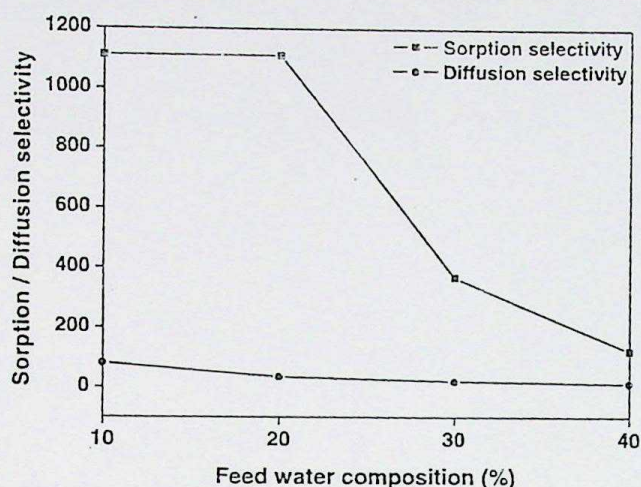


Fig. 5 Sorption selectivity (α_s) and diffusion selectivity (α_d) of NCM-6 at different feed water compositions

swelling of the NCM-8 and NCM-10. Aggregation of the filler nanoparticles at higher loadings also may leads to decreased water selectivity of NCMs.

Sorption and diffusion selectivity values were calculated by using the Eqs. 4 and 5 for the NaAlg and NCMs at azeotropic composition at 30 °C (Table 2). It is observed that sorption selectivity values are quite higher than diffusion selectivity values indicating sorption has the dominant role in PV separation. Pervaporation separation index (PSI), which is a measure of pervaporation separation ability of a membrane for the feed mixture, as displayed in Table 2, NCM-6 membrane showed highest sorption selectivity and PSI value compared to NCM-8 and NCM-10; hence one can

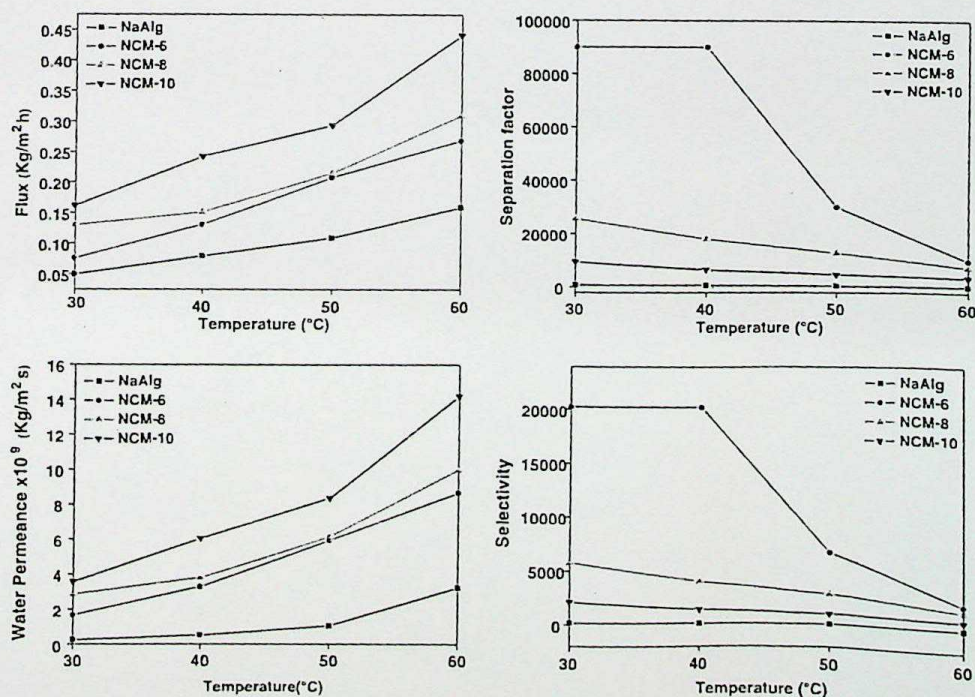
selectively separate azeotropic mixture of water and IPA by using NCM-6.

Effect of variation in feed water composition in PV performance of NCMs

Effect of feed water content variation on PV performance of NaAlg and NCMs was investigated for feed water compositions from 10 to 40 wt. % maintaining the permeate pressure at 5 mbar. Figure 4 shows the experimental results of PV which demonstrates that flux increased from 0.059 to 0.246 kg/m².h while selectivity decreased from 89991 to 1665 with rise in feed water composition from 10 to 40 wt. %. Selectivity and permeance also shows a decrease with increased feed water composition. Selectivity of the 24354 of NCM-6 at 10 % feed water content has decreased to 618 for 40 % feed water (See Fig. 4). Water permeance is also displayed in Fig. 4. Water permeance shows steady decrease for all the membranes indicating that at higher feed water concentration plasticization of polymer occur which results into transport of more IPA molecules thereby reducing membrane selectivity. On the other hand IPA permeance is still smaller by 2 orders of magnitude than water but IPA permeance increases with increased feed water content (not shown in figure) hence reduces membrane selectivity.

In case of NCM-6, selective separation of water from IPA is due to the combined effect of hydrophilic–hydrophilic interactions between H₁₄-P₅ and NaAlg with water molecules. Thus, hydrophilic H₁₄-P₅ absorbs most of the water molecules from feed and restricts IPA to crossover the barrier, which leads to increased water selectivity of the

Fig. 6 Effect of variation in temperature on pervaporation performance of NCMs



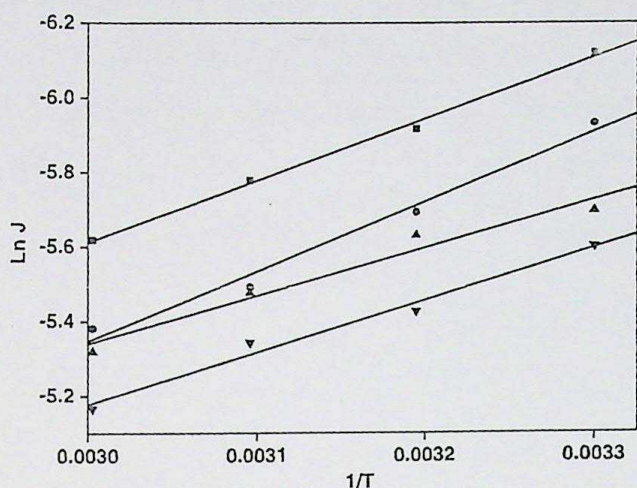


Fig. 7 $\ln J$ vs. $1/T$ for NaAlg (■), NCM-6 (●), NCM-8 (▲) and NCM-10 (▼) at 10 % feed water composition

NCM. Swelling experiments performed to determine the equilibrium swelling of NCMs, and Fig. 1 illustrates swelling behaviors of all the membranes as a function of feed water composition at 30 °C. A smaller degree of swelling of NaAlg suggests that its permeation flux during PV separation of water from IPA component is small, since swelling increases in the order: NaAlg>NCM-6>NCM-8>NCM-10. Hence, results of the feed water composition study are gratefully supported by the swelling experiments. To estimate sorption and diffusion selectivity; sorption experiments were carried out and results are displayed in Fig. 5 and it is observed that sorption selectivity dominates the diffusion selectivity. Diffusion selectivity values are much lower than that of sorption selectivity which shows that diffusion has minor role in pervaporation.

Effect of variation in temperature on pervaporation performance and diffusion coefficients

The effect of temperature variation on PV performance of NCMs was studied typically at 10 wt. % of water in feed;

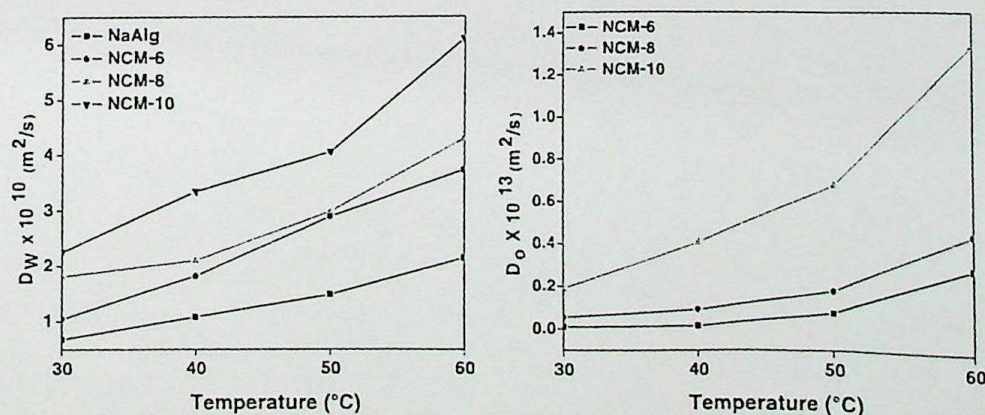
the resulting flux, separation factor, permeance and selectivity are shown in Fig. 6. It is observed that water selectivity of the NCMs decreased with increasing temperature with enhancement in permeation flux. Separation factor 89991 of NCM-6 at 30 °C decreased drastically to 9991 at 60 °C with increase in permeation flux upto 0.268 kg/m²h at 60 °C from 0.076 kg/m²h at 30 °C. Selectivity also decreased from 20227 at 30 °C to 2248 at 60 °C for NCM-6 while permeance increased upto 8.8×10^{-9} kg/m²s at 60 °C from 1.7×10^{-9} kg/m²s at 30 °C. Similarly poor PV performance of the other NCMs was observed with increase in feed temperature. As increased temperature causes the thermal mobility of the polymeric chains which produces extra void spaces in the membrane resulting in improved sorption and diffusion of the permeating molecules. Since the driving force for permeation is concentration gradient, which results from the difference in partial vapor pressure of permeant molecules between feed and permeate mixtures. As the feed temperature increases, vapor pressure in the feed compartment also increases, but vapor pressure on permeate side will not be affected, resulting in an increased concentration gradient, and hence, the driving force. Even though this driving force is closely related to phase transition in PV process, nevertheless it mandates a significant effect of temperature on permeation flux.

The temperature dependency of permeation and diffusion is studied using Arrhenius equation:

$$J = J_0 \exp\left(\frac{-E_J}{RT}\right) \quad (24)$$

Where, J represents permeation flux (J_p), J_0 is a constant representing the pre-exponential factor and E_J represents activation energy for permeation, depending upon the transport process under consideration. As the feed temperature increases, vapor pressure in the feed compartment also increases, but there is no effect on permeate vapor pressure. This would result in an increased driving force for mass transfer, consequently results in an increase in the permeation

Fig. 8 Diffusion coefficients vs temperature at 10 wt% feed water



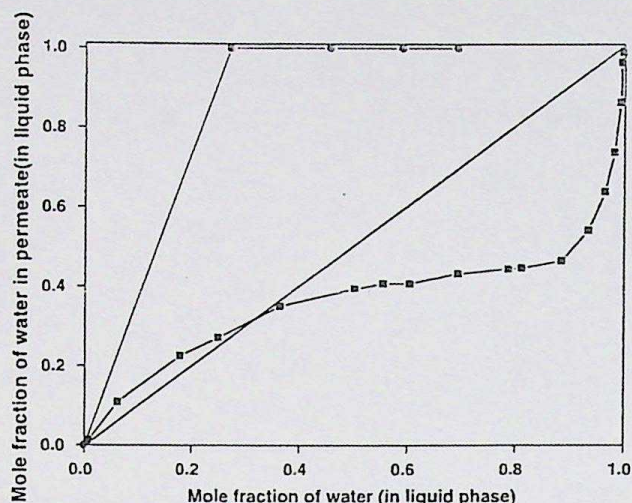


Fig. 9 Comparison of vapor liquid equilibrium curve with PV data for water and IPA mixtures

flux of penetrant. All these effects lead to an increase in flux and decrease in selectivity as feed temperature increases. Arrhenius plot of $\ln J$ vs $1/T$ is displayed in Fig. 7; exhibits linear trends for permeation; which in turn suggest that permeability follows Arrhenius rule. From the least squares fit of the linear plots of Fig. 8, activation energies of permeability (E_p) have been estimated. It is observed that the apparent activation energy value of water ($E_{pw}=36.03$ kJ/mol) is much lower than that of IPA ($E_{po}=100.36$ kJ/mol), suggesting the highly water selective nature of the membrane. The activation energy values of water permeation and total permeation ($E_p=36.04$ kJ/mol) are almost identical due to highly water selective nature of NCMs than pristine NaAlg membrane.

The diffusion coefficients of the permeating molecules are important to understand the transport across the barrier

membrane during pervaporation; generally explained by sorption-diffusion mechanism. Diffusion coefficients are estimated from equation.

$$J_i = -D_i \left(\frac{dC_i}{dx} \right) \quad (25)$$

Where, C_i is concentration of permeate (kg/m^3), D_i is diffusion coefficient (m^2/s), J_i is permeation flux/unit area ($\text{kg/m}^2.\text{s}$), subscript i stands for water or isopropanol, and x is diffusion path length. By assuming concentration profile along the diffusion pathway is linear; then diffusion coefficients, D_i can be calculated using:

$$D_i = \frac{J_i h}{C_i} \quad (26)$$

Where, h is membrane thickness ($40 \mu\text{m}$ in this study). The diffusion coefficient data is plotted in Fig. 8 as a function of temperature at fixed composition show increasing trends for water as well as IPA in case of NaAlg and NCMs at 10 wt % of water. The diffusion of water is much higher than IPA by 3 orders of magnitude throughout the entire range of feed temperature but increases with increasing feed temperature, which results in increased water flux.

Comparison with the vapor-liquid equilibrium

The concentration of permeate obtained in pervaporation is compared with the vapor-liquid equilibrium (VLE) curve obtained from distillation [38] in Fig. 9. Azeotropic mixture is very difficult to separate without adding the entrainer like benzene which is a deadly carcinogen. In, pervaporation technique membrane acts as third phase and selectivity of the membranes enhances the PV performance.

Table 3 Comparison of flux and separation factor of Present NCMs with the reported data in the literature

Sr. No	Membrane	Feed composition		Selectivity	Flux ($\text{kg/m}^2\text{h}$)	Ref.
		Water (%)	Isopropanol (%)			
1	PVA/PVP/4 % PMA	10	90	29991	0.036	[10]
2	NaAlg/Zelite K-LTL	12.6	87.4	3847	0.140	[17]
3	NaAlg-MCM-41	10	90	29991	0.106	[20]
4	NaAlg /PVA (75:25)	10	90	196	0.024	[23]
5	NaAlg—1	10	90	11241	0.039	[39]
	NaAlg—2	10	90	17991	0.027	
6	NaAlg/Activated charcoal	12.5	87.5	2326	0.41	[40]
7	PVA-PANI-III	10	90	564	0.069	[41]
8	NaAlg-HEC-10-ZSM-5(40)	10	90	30000	0.2	[42]
9	NCM-6	10	90	89991	0.059	Present work

PVA poly(vinyl)alcohol, PVP poly(vinyl)pyrrolidone, PMA phosphomolybdic acid, HEC/NaAlg hydroxyethylcellulose/sodium alginate; PVA/PANI poly(vinyl alcohol/polyaniline, NaAlg sodium alginate, MCM Mesoporous molecular sieves

Comparison of present work with the literature work for IPA dehydration

Present work of IPA dehydration is compared with the literature to understand the PV ability of the NCMs. Hence, comparisons are made in Table 3 with other important literature data on blend/composite membranes. Flux and separation factor values of the present membranes are comparable with those of other important membranes used in the literature. In some cases, the present membranes gave better performances than those published in the literature. However, the fluxes of the present NCMs are still to be improved.

Conclusion

Sorption, diffusion and permeation properties of the sodium alginate polymer as well as in its nanocomposite form are studied. It is observed that incorporation of hydrophilic H_{14} - P_5 nanoparticles to sodium alginate leads to successful dehydration of isopropanol at near azeotropic mixture composition. H_{14} - P_5 content higher than 6 wt% in membrane matrix leads to its aggregation which in turns results in the lowered water selectivity of the membranes, but still higher selectivity and flux was obtained for NCM-8 and NCM-10 than pristine NaAlg membrane. Higher values of sorption selectivity than diffusion selectivity clearly indicates that sorption plays major role in the PV. Flory-Huggins theory was used for determination of the interaction parameters and solubility parameters which are useful to study the thermodynamic processes involved in PV dehydration of IPA. PV performance of the NCMs is gratefully affected by feed water content; increase in feed water content leads to poor PV performance. Similarly increased temperature diminishes the PV performance of the NCMs. The NCMs exhibited lower Arrhenius values for water than IPA, suggesting the higher water selective nature of the NCMs. Diffusion coefficients values calculated by using Fick's law also proves the water selective nature of the NCMs.

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