Journal of Advanced Scientific Research

Available online through http://www.sciensage.info/jasr

ISSN
0976-9595
Research Article

DEVELOPMENT OF NOVEL MIXED MATRIX MEMBRANES USING 13X ZEOLITE FILLED SA/WPI FOR THE PERVAPORATION DEHYDRATION OF ISOPROPANOL

Maruthi Y.[1], Kumara Babu P.[1], Sudhakar H.[1], Veerapratap S.[1], Sajankumarji Rao U.[2], Subha M.C.S.[2], Chowdoji Rao K.[1] *

[1]*Department of Polymer Science & Tech, Sri Krishnadevaraya University, Anantapuramu, AP, India.*
[2]*Department of Chemistry, Sri Krishnadevaraya University, Anantapuramu, AP, India.*
**Corresponding author: chowdojirao@gmail.com*

ABSTRACT

Novel polymeric membranes were prepared by incorporating different amounts of 13X Zeolite into Sodium alginate/Wheat protein isolate (SA/WPI) blend matrix. The resulting composite membranes were characterized by Fourier transform infrared spectroscopy and the results were used to analyze the possible chemical reaction between SA/WPI and glutaraldehyde. X-ray diffraction, Scanning electron microscopy, and Differential scanning calorimeter were used to analyze the crystallinity, surface morphology and thermal stability of the membranes, respectively. The membranes were tested for pervaporation studies for water /IPA mixtures at different feed water compositions at 30°C. The experimental results showed that both flux and selectivity increased with increase in zeolite content. Membrane containing 20 wt% of zeolite shows the highest separation selectivity of 4991 with a substantial flux of 0.120 $Kg/m^2/h$ at 30°C containing 10 wt% of water in the feed, suggesting that the membranes could be used effectively to break the azeotropic point of water-IPA mixture, so as to remove small amount of water from IPA.

Keywords: Pervaporation, SA/WPI, Isopropanol-Water, Azeotrope, Zeolite, Mixed Matrix Membrane

1. INTRODUCTION

Chemical separation by pervaporation (PV) technique is one of the most popular areas of current membrane research [1]. PV is a combination of preferential permeation followed by evaporation. On one side of the membrane the preferentially sorbed fluid is in the liquid state, and it is withdrawn through the membrane as preferentially sorbed vapor by applying a vacuum on the other side of the membrane [2]. The possible application areas for PV separation in industry are numerous, including separation of azeotropic mixtures [3-4], separation of mixture of organic liquids [5-6], dehydration of organic solvents [7-8] and continuous removal of one of the products of reaction from a bioreactor [9]. Separation of the liquids is governed by the chemical nature of the permeating species as well as that of the membrane material, and the morphology of the membrane itself together with the experimental conditions of process operation [10-11].

Purification of organic solvents such as isopropanol (IPA), containing a small amount of water is of vital significance in the area of organic synthesis. Isopropanol is one of the important solvents used on a large scale in chemical industry as well as in pharmaceutical laboratories. Further, it has also been used in semi-conductor and liquid crystal display industries as a water-removing agent [12-13]. IPA and water form an azeotropic mixture at a concentration of 87.5 wt% (IPA) [14] and hence, the separation of these mixtures by conventional methods such as solvent extraction and rotavapor or by distillation could prove uneconomical. Several membrane materials have been modified recently for the selective separation of water from aqueous mixtures of isopropanol [15]. However, the membranes employed in such separation studies often yield compromised results of flux and selectivity due to trade-off phenomenon existing between the flux and separation factor in PV process.

The successful performance of PV process largely depends on the physical and chemical properties of the membrane material. Hydrophilic membranes are widely used in PV dehydration of organic mixtures. Hydrophilic groups absorb water molecules preferentially, leading to high flux and selectivity. Particularly, Sodium alginate (SA), due to its high hydrophilicity, good membrane applications and excellent chemical / thermal resistance properties, has been used as a membrane in PV dehydration studies. Sodium alginate (SA), which is one of the polysaccharides extracted from seaweed, is found to have an excellent performance as a membrane material for pervaporation-based dehydration of organic solvents [16]. However, a very high hydrophilicity of sodium alginate resulting from both of its carboxyl and hydroxyl groups, leads to a significant swelling of membrane in aqueous solution. Yeom and Lee [17] improved the membrane strength and stability of SA by crosslinking with GA. Huang et al. [18] prepared stabilized SA membranes using a relatively simple method of ionic crosslinking. It has a linear chain structure of β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues arranged in block wise fashion [19] and may be modified for improvement in its stability nature even by blending it with various other natural polymers. Because the recent trend is to develop fully sustainable, biodegradable, eco-friendly and easily disposable materials. Therefore in the past decades extensive studies have been made for the potential use of polymeric materials derived from renewable resources, such as carbohydrates, starch and proteins, [20]. Plant proteins from soy [21, 22], corn, whey protein [23] cotton seed and wheat [24] have been studied because of their abundance, low cost, good biodegradability and sustainable properties for usage as films and plastics.

Another natural polymer we chose for blending was Wheat Protein Isolate (WPI) obtained from wheat seeds of an annual plant. It contains 90% protein and is higher than that of wheat protein products such as wheat gluten (76.5% protein) and defatted wheat flour. Wheat gluten is a general term for water insoluble proteins of wheat flour which is composed of a mixture of polypeptide molecules considered to be globular proteins. WPI is a byproduct of wheat gluten. Cohesiveness in them facilitates film formation. Wheat gluten contains the prolomine and glutelin fractions of wheat flour proteins, typically referred to as gliadin and glutenin respectively. Wheat gluten has been studied as a film former due to its cohesive and elastic properties and physical, chemical or enzymatic treatments have been applied to modify gluten as film forming materials [25, 26]. Several studies have been carried out on wheat gluten protein films [27, 28].

In the present study SA/WPI blend membrane was incorporated with 13X zeolite (particle size: 2.67 μm, pore size: 7.4 Å Si/Al ratio: 1.43). Glycerol was chosen as plasticizer and glutaraldehyde as a cross linking agent regardless of their edibility because protein films should be intended for non-food uses. Aiming for obtaining high permeability and selectivity simultaneously for pervaporative separation of isopropanol-water mixture. Furthermore, the effect of blend composition in membranes, feed concentration and the perm selectivity has been investigated.

2. EXPERIMENTAL

2.1. Materials

Wheat protein isolate powder was obtained from Honey Ville food products, Salt Lake city, Utah, USA. According to the manufacturer, WPI supplied consists of 90% protein, 4% fat, about 5% ash and 1% remaining unknown constituents. Sodium alginate (SA), Glutaraldehyde (GA) solution (25%), Hydrochloric acid (HCl), Isopropanol (AR- grade sample) and Acetone were purchased from S.d.fine chemicals, Mumbai, India. 13X zeolite was received as a gift sample from M/S Zeolite and Allied products Pvt. Ltd., Mumbai. All the chemicals were of analytical grade used without further purification. Deionized water with a conductivity of 20 μS / cm was produced in the laboratory using Techno pilot plant (Vadodara, India.) through a nano filtration membrane module and used for all the experiments.

2.2. Membrane Preparation

13X zeolite without loaded and with loaded SA/WPI blend membranes were prepared by solution casting and evaporation method. In brief, by dissolving each 4gm of SA and WPI in 90 ml of distilled water individually at room temperature by constant stirring on a magnetic stirrer (Remi Equipment Model 2MLH, Mumbai, India) for 24 h. A typical mixed solution of SA and WPI was prepared by the following steps. (1) The desired amounts of WPI powder and glycerol were weighted separately, mixed with 20 times (by wt. of WPI powder) distilled water and the mixture was stirred at 75°C for 40 min to obtain a homogeneous suspension. After 20 min of stirring, the desired amount of 1 N NaOH solution was added to adjust the pH value to 10 of the pure WPI suspension. The pH of the solution was monitored with an electronic pH-meter (Model LI 127, Elico,Ltd, and Hyderabad, India.). This stir-heating process denatures the WPI and is called ''pre-curing.'' The procured WPI suspension was used to prepare the films (solution A). (2) The required amount of SA was dissolved in 2% deionized water by stirring with a magnetic stirrer (Model-Remi elektrotechnik limited, Vasai-India) for 24 h (solution B). Both solutions A and B were mixed in 3:1 ratio on volume basis and stirred for about 8 hours to get homogeneous solution of SA/WPI blend. In separate flasks, 0.2, 0.4, 0.6 and 0.8 g of 13X zeolite was dispersed in 10 ml of water, sonicated for 2h, added individually to the previously prepared SA/WPI blend solution.

The mixed solution was stirred for about 24 h and then, it was kept in an ultrasonic bath for about 30 min to break the aggregated crystals of zeolite and so as to improve the dispersion of zeolite in the polymer matrix. It was then filtered and left overnight to get a homogeneous solution. The resulting solution was poured onto a glass plate and the membrane was dried at 30°C for about 24hrs. The prepared membranes were then crosslinked in a bath containing, 84 vol. % isopropanol, 10 vol. % water, 5 vol. % of glutaraldehyde, as the crosslinker and 1 vol. % hydrochloric acid, as the catalyst for a period of 2 hours. The amount of 13X zeolite with respect to SA/WPI varied as 0, 5, 10, 15 and 20%, and the membranes thus obtained were designated as SA/WPI-0, SA/WPI-5, SA/WPI-10, SA/WPI-15 and SA/WPI-20 respectively. The crosslinked membranes were washed and rinsed repeatedly with deionized water and dried at room temperature for about 24 h. Membrane thickness as measured by a micrometer screw gauge ranged between 35 and 40 μm.

2.3. Pervaporation Experiments

The equipment used to perform the PV experiments remained the same as described earlier by Sudhakar et al. [29-30]. The pervaporation cell consisted of two bell-shaped B-24 size glass column reducers/couplers clamped together with external padded flanges by means of tie rods to give a vacuum tight arrangement. The top half was used as the feed chamber and the bottom one worked as the permeate chamber. The membrane was supported by a stainless steel porous plate which was embedded with a mesh of the same material to provide a smooth uniform surface. Teflon gaskets were fixed by means of high vacuum silicone grease on either side of the membrane and the sandwich was placed between the two glass column couplers and secured tightly. The effective membrane area that was in contact with feed was 20 cm^2. After fixing the membrane, the cell was installed in the manifold and connected to the permeate line by means of a B-24 glass cone which was fixed on one side to a high vacuum glass valve followed by a glass condensor trap which consisted of a small detachable collector. The trap was placed in a Dewar flask containing liquid nitrogen for condensing the permeate vapors. A rotary vacuum pump was used to maintain the permeate side pressure which was measured with an Edward's Mcleod gauge of scale in the range 0.01-10 mmHg. High vacuum rubber tubing was used to connect the various accessories to the experimental manifold. All glass cone–socket joints were fixed with good quality high vacuum grease (Dow Corning, USA).

Initially the membrane was soaked in the feed solution overnight to attain equilibrium. During the experiments the membrane upstream side was maintained at atmospheric pressure and the downstream side pressure was controlled by adjusting the value for vacuum release (vent). The permeate was condensed in the trap for a period of 6-8 hrs and then collected in a simple bottle for evaluation of its weight to determine the flux and analyzed by refractive index data to calculate the selectivity. Flux (*J*i) was calculated using the Eq. (1). The feed was kept in continuous stirring mode using an overhead stirring motor to minimize the concentration polarization.

$$Ji = Wi/At \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Here *Wi* represents the mass of water in permeate (kg), *A* is the membrane area (m^2) and *t* represents the permeation time (h). The selectivity of the 13X zeolite-filled membranes was evaluated by Eq. (2). Membrane selectivity, α, is the ratio of permeability coefficient of water to that of isopropanol, which is calculated from their respective wt. concentrations in feed and permeate as given below:

$$\alpha = y\,(1-x)/x\,(1-y) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

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

2.4. Sorption Experiments

The sorption experiments on the circularly cut membranes were performed at 30 ^{0}C gravimetrically [31] in 10, 12.5, 15 and 17.5 wt. % water-containing fed mixtures. MMMs of Blend samples with compositions ranging from 10 to 17.5 wt % water at 30 ^{0}C ± 0.5 ^{0}C in an electronically controlled incubator (WTB Binder, model BD-53, Tuttilgen, Germany) as per procedures reported previously [32]. To do this, dry weight of the circularly cut (dia=2.5 cm) disc shaped MMMs of blend membranes were stored in a desiccators over anhydrous calcium chloride maintained at 30^{0}C for about 24 h before performing the swelling experiments. This dry weight of the circularly cut (dia = 2.5cm) MMMs of blend membranes were taken inside the specially designated air tight test bottles containing 30cm^3 of the test solvent and mass of the soaked samples were measured using a single-pan Adam digital microbalance (model AFP 210L) having a sensitivity of ±0.01mg. The swollen membranes were weighed immediately after careful blotting to remove surface adhered water. The percent degree of swelling (DS) was calculated using eq. 3.

$$DS\,\% = \left(\frac{Ms - Md}{Md}\right) x100 \qquad \ldots\ldots\ldots(3)$$

Where, M_S and M_d are the mass of the swollen and dry membranes, respectively.

2.5. Measurement of refractive index

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

2.6. Characterization techniques

2.6.1. Fourier Transform Infrared (FTIR) Spectroscopic Studies

FTIR Spectra measurements were recorded in the wavelength region 4000-400 cm^{-1} under N_2 atmosphere at a scan rate of 25 cm^{-1} using equipped using FTIR spectrometer (Bomem MB: 3000, Canada), equipped with attenuated total reflectance. About 2 mg of the sample was grind thoroughly with KBr, and pellets were made under a hydraulic pressure of 600 kg/cm^2.

2.6.2. X-Ray Diffraction (XRD) Analysis

A Siemens D 5000 (Germany) X-ray diffractometer was used to study the solid-state morphology of SA/WPI-0 and SA/WPI blend membranes. X-rays of 1.5406 Å wavelength was generated by a Cu-Kα source for this study. The angles of diffractions were varied from 0° to 65° in order to identify any changes in the crystal structure and intermolecular distances between intersegmental chains after modification.

2.6.3. Differential Scanning Calorimetry (DSC) Studies

DSC curves of the polymer films was examined using TG instruments (Model: SDT Q600, U.K) in the temperature range of 40-600 ºC at a heating rate of 10 ºC/min, with nitrogen flushed at 100 ml/min. The samples were subjected to DSC for both before and after incorporation of zeolite to determine the thermal stability and decomposition characteristics.

2.6.4. Scanning Electron Micrograph (SEM) Studies

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

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

Fig. 1 Shows the FTIR spectra of plain SA/WPI, and crosslinked zeolite filled MMM's membranes. The spectra illustrates the changes signifying a successful cross linking reaction. A characteristic peak at the range of (3433-3201) cm^{-1} in all the membranes corresponds to O-H stretching vibrations of SA/WPI polymers. A sharp peak in the range of (1589 -1596 cm^{-1}) is seen which corresponds to C=O stretching of the carboxylic groups of SA. The peaks appearing in the range of 1126-1072 cm^{-1} are seen for the membranes corresponding to C-O-C linkage vibrations. This band appears due to the formation of an ether linkage as a result of the reaction between the hydroxyl groups of SA and SPI with CHO groups of glutaraldehyde. Such changes in the spectra confirmed the successful cross linking of glutaraldehyde with both natural polymers.

The -OH stretching vibration bands around 3440cm^{-1} in SA membrane broadened and shifted to a lower wave number in the blend membranes as a result of the introduction of wheat protein composition into SA to form new intermolecular hydrogen bonds. As shown in Fig.1 SA and WPI have carbonyl groups at 1589 cm^{-1} and the FTIR analysis of membranes were based on the identification of bands related to the functional groups presenting SA and wheat, among others [33, 34]. The main characteristics absorption bands of SA appears at 1589 cm^{-1}(C=O stretching), 3440 cm^{-1}(O-H stretching) and 1118 cm^{-1}(C-O-C- in glycosidic linkage) [33]. The wheat protein spectrum showed an amide I band at 1654 cm^{-1} and amide II band at 1536cm^{-1} [34]. The amide I can be composed of several overlapping components due to various segments with different secondary structure [34]. As can be seen in the spectra of the blended membranes, the characteristic absorption bands of both SA and Wheat protein appears in proportion to the ratio between the components of the blend. As a result, the absorbance of NH and CO deformation bands appear in the range 1388-1400 and 1589-1596 cm^{-1}, respectively, showing an increase with increase in wheat content of the blend.

The FTIR spectra of 13X zeolite filled and crosslinked SA/WPI membranes are shown an additional peak was observed at 952 cm^{-1}, this is due to the presence of silonal group of the 13X zeolite and this peak was shifted to higher wavelength and the intensity increases with increase in the zeolite content (b, c, d and e) due to the increase in the zeolite content (increase in silonal groups).

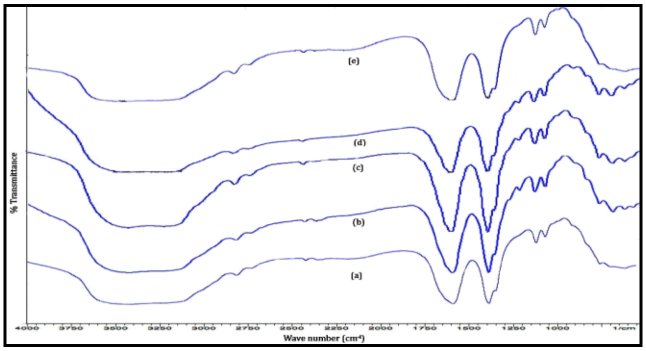

Fig. 1: FTIR patterns of (a) SA+WPI-0 cross linked membrane and 13X zeolite loaded (b) SA+WPI-5 (c) SA+WPI-10 (d) SA+WPI-15 and (e) SA+WPI-20

3.2. X-ray diffraction

In general, it is important to take into account the crystalline changes in the polymer matrix which occurs due to the presence of zeolites. In this study, the crystalline structures of the zeolite incorporated membranes were investigated by X-ray diffraction. The X-ray diffraction patterns of the zeolite filled membranes are shown in Fig. 2 (a-c). The gain in crystallinity due to the incorporation of zeolites is also evident from Fig. 2 where a progressive increase in peak intensity is observed with increasing zeolite loading from 15 to 20 wt.%.

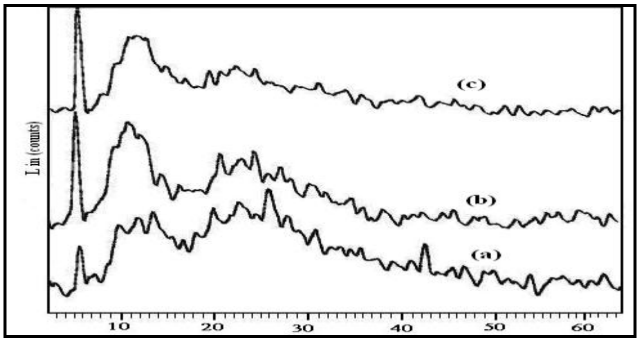

Fig. 2: Wide angle X-ray Diffraction Patterns of Zeolite filled SA+WPI membranes: (a) SA+WPI-0 (b) SA+WPI-15 and (c) SA+WPI-20.

3.3. SEM analysis

The SEM photographs of the surface of the plain SA/WPI and zeolite filled SA /WPI membranes are shown in

Fig. 3 (a-c) respectively. This figure shows the typical surface SEM micrograph of zeolite filled SA/WPI membranes in which zeolite particles are distributed homogeneously throughout the SA/WPI matrix. This uniform distribution of zeolite particles in SA/WPI matrix facilitates an easy penetration of water. The zeolite content and the swelling effects on pervaporation performance of composite membranes have been investigated in detail. Zeolite loading was only used for the present study of sorption and permeation as it showed uniform zeolite distribution.

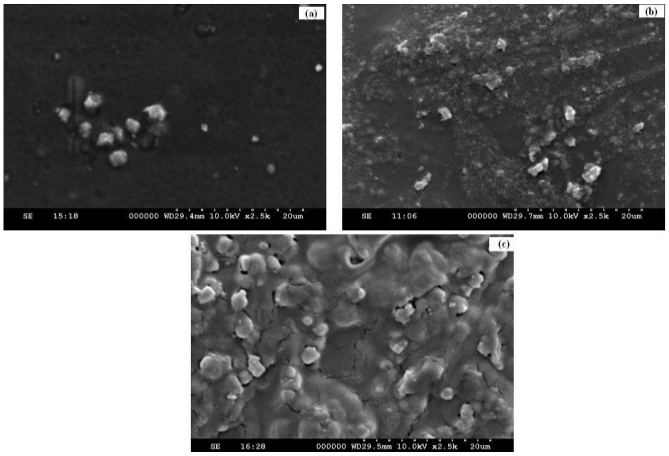

Fig. 3: SEM pictures Surfaces of the Zeolite filled SA+WPI membranes: (a) SA+WPI-0 and (b) SA+WPI-15 and (c) SA+WPI-20.

3.4. DSC studies

DSC curves of plain SA/WPI and zeolite filled SA/WPI membranes are shown in Fig. 4. The DSC curve for plain SA/WPI membrane shows a sharp endothermic melting point of 190^{0}C. The melting endotherm range shifted to higher values, i.e. 210-230 ^{0}C in zeolite filled SA/WPI membranes with increase in zeolite content in the composite membranes. This substantiate that the increase in thermal stability of the composite membrane increases with increasing zeolite content.

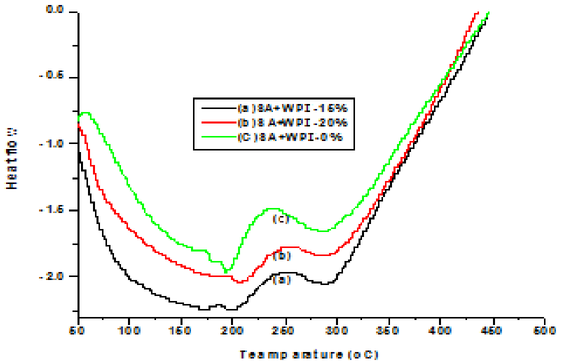

Fig. 4 : DSC analysis of Zeolite filled SA+WPI membranes: (a) SA+WPI-15 (b) SA+WPI-20 and (c) SA+WPI-0

3.5. Effect of 13X zeolite content on membrane sorption studies

The mass transport through membrane is a complex phenomenon because the interaction between liquid feed components and the membrane would result in membrane swelling affecting the PV data. The results are presented in Table 1. The variation of degree of sorption v/s percentage of feed of water through plain SA/WPI and zeolite filled SA/WPI membranes are shown in Fig. 5.

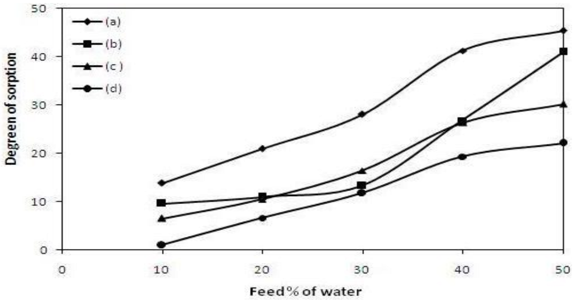

Fig. 5: Plots of Degree of sorption vs Percentage of feed of water (a) SA+WPI-0 and (b) SA+WPI-10 (c) SA+WPI-15 and (d) SA+WPI-20 incorporated 13X zeolite crosslinked membranes.

Fig. 5 compares the plots of %degree of sorption of plain SA/WPI and zeolite incorporated composite membranes at 30^{0}C for 10–50 wt. % water containing feed of water. Notice that membranes are swollen to a higher extent in IPA-water feeds due to stronger interactions (hydrogen bond type) between IPA and water with all the membranes for all the feed mixtures. Also, at the same time from the results given in Table 1 it is noticed that zeolite incorporated SA/WPI membranes were swollen to a lesser extent in all the feeds mixtures than the plain SA/WPI membrane.

Table 1: Percentage sorption data of IPA and water mixtures in SA/WPI and zeolite filled SA/WPI membranes at 30^{0}C.

% of water in the feed	% sorption in different membranes			
	SA+WPI-0	SA+WPI-10	SA+WPI-15	SA+WPI-20
10	13.81	9.55	6.49	1.03
20	20.94	10.98	10.49	6.64
30	28.04	13.31	16.44	11.76
40	41.17	26.78	26.29	19.32
50	45.33	40.89	30.14	22.03

3.6. (a) Effect of zeolite 13X content on flux and selectivity

The efficacy of the membranes in PV process is generally assessed based on the permeation of individual components. Therefore, the extent of permeation of individual components was determined by plotting the flux of water as a function of zeolite content in the membrane for different (10, 20, 30 and

40) mass% of water in the feed is shown in Fig. 6a**.** From the plot, it is clearly noticed that the flux of water increased with increase in zeolite content for all membranes over the entire range of water composition in the feed studied indicating that the membranes developed in the present study are highly water selective. This clearly reveals that the amount of zeolite incorporated in the membrane prominently enhances the membrane performance by increasing the selective transport.

Table 2: Pervaporation data of IPA and water mixtures at 30^0C and at 1 mmHg permeate pressure.

Mass % of water in feed (wt%)	Water flux J [kg m^{-2} h^{-1}]	Mass % of water in the permeate (wt %)	Selectivity (α)
SA+WPI – 0			
10	0.091	99.71	3094
20	0.123	99.81	2282
30	0.198	99.84	1453
40	0.260	99.87	1152
SA+WPI – 5			
10	0.094	99.78	4081
20	0.163	99.84	2496
30	0.260	99.86	1561
40	0.320	99.90	1298
SA+WPI – 10			
10	0.098	97.60	4491
20	0.186	96.40	2662
30	0.318	95.35	1661
40	0.371	94.50	1498
SA+WPI – 15			
10	0.112	98.80	4727
20	0.191	97.60	3072
30	0.325	96.40	1939
40	0.383	95.10	1665
SA+WPI – 20			
10	0.120	99.60	4991
20	0.206	98.50	3072
30	0.329	97.80	2115
40	0.402	97.20	1873

Fig. 6b shows the effect of zeolite content on selectivity of the membranes at different mass% (10, 20, 30 and 40%) of water in the feed. From Fig. 6b it is clearly evident that the selectivity increased significantly from membrane SA/WPI-5 to SA/WPI-20 upon increasing the 13X zeolite content in the membrane. Generally, with increasing packing density of the membrane by increasing the zeolite content in the polymer matrix, the selectivity increases [35, 36].

In the present study selectivity increased upon increasing the zeolite content in the membrane. A significant enhancement of hydrophilicity, selective absorption and molecular sieving action by the creation of pores in the membrane matrix this may be due to introducing porous zeolite particles in the membrane matrix. This can be explained in such a way that when we use water selective zeolite-incorporated membranes, the transport of water molecules through the membrane takes place in a straight path through the zeolite pores with subsequent adsorption at the feed side followed by desorption at the permeate side, which in turn is responsible for higher water flux. If enough water is present inside the membrane, the zeolite pores will be largely occupied by water molecules, prohibiting the isopropanol molecules from entering the pores of zeolite. Thus, on its way through the membrane the isopropanol molecules have to travel around the zeolite pores. The higher water concentration inside the polymer close to the permeate side of the membrane and the fact that water can travel along the straight path while isopropanol has to follow a more tortuous path act together in explaining the way in which membrane performance is enhanced in selectivity when zeolite is added to the polymer matrix [37].

Calculated results of flux and selectivity for different wt% of water in the feed are measured at 30^0C for different compositions with respect to zeolite loading in the membranes are presented in Table 2. It is observed that there is a systematic increase of water flux with increasing zeolite loading and water composition in the feed.

3.6. (b) Effect of feed composition on pervaporation performance

Pervaporation studies have shown that membrane performance is affected by water content in the feed mixture. The effect of feed composition on PV performance of SA/WPI and its MMM's are shown in Fig 6a and 6b.

It is noticed that an increase in water concentration results in an increase of permeation flux and thereby, a decrease in selectivity. The increase in permeation flux as a result of increase of water concentration is due to the preferential interaction of water as the selective component of the feed mixture giving a decrease in selectivity due to increased swelling [38]. PV performance of the SA/WPI blend membrane and its MMM's are investigated in various feed compositions ranging from 10 to 40% of water, while keeping permeate pressure and membrane thickness constant at 0.9 mmHg and 40μm, respectively. Expectedly, a rise in feed concentration of water produced an increase in water flux from 0.091 to 0.260 kg/m^2 h**,** for SA/WPI-0 membrane with a drop in selectivity from 3094 to 1152 as shown in Table 2, respectively**.** Such a variation in membrane performance is due to the preferential transport of feed (increase in concentration of water) components through the membrane matrix, which produces stronger interactions with the membrane material. This causes the membrane to swell excessively, producing a negative impact on membrane selectivity due to plasticizing effect [39].

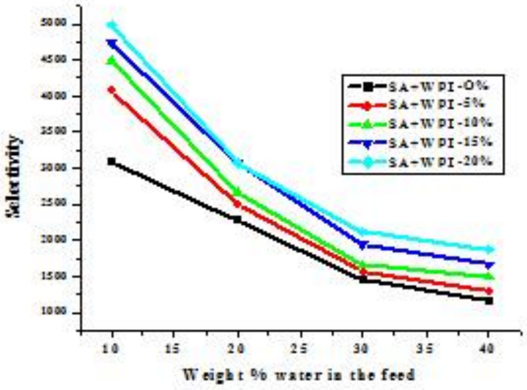

Fig. 6(a): Plots of water flux vs weight % water in feed SA/WPI-0 and SA/WPI incorporated 13X zeolite membranes

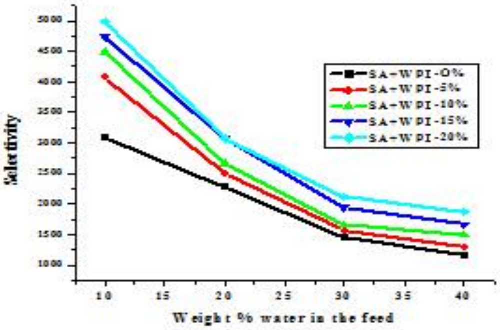

Fig. 6(b): Plots of selectivity vs weight % water in feed SA/WPI-0 and SA/WPI incorporated 13X zeolite membranes.

4. CONCLUSION

In this study, we prepared a novel hydrophilic 13X zeolite filled SA/WPI mixed matrix membrane. The unique structure of the membrane was maintained due to the strong interaction between the SA, WPI and 13X zeolite. The membranes were used to separate the IPA/water mixture. At 20% 13X zeolite content, SA/WPI maintains it's amorphous and the membrane shows the best and most stable PV separation characteristic at azeotropic compositions of water/IPA mixture.

5. ACKNOWLEDGEMENT

The authors thank the SERB, DST, New Delhi, India for providing financial support to two of the authors (Y. Maruthi & P. Kumara Babu) (DST Sanction Letter No. SR/S1/OC-53/2012, Dated: 25-04-2013) by sanctioning Major Research Project.

6. REFERENCES

1. Uragami T, Okazaki K, Matsugi H, Miyata T. *Macromolecules*, 2002; **35:** 9156-9163.
2. Tuan VA, Li S, Falconer JL, Noble RD. *J. Membr. Sci.*, 2002; **196(1)**: 111-123.
3. Neel J, "*Introduction to pervaporation*" Elsevier, Amsterdam, The Netherlands, (1994).
4. Kittur AA, Kariduraganavar MY, Toti US, Ramesh K, Aminabhavi TM. *J. Appl. Polym. Sci.* 2003; **90**:2441-2448.
5. Sarkhel D, Roy D, Bandyopadhyay M, Bhattacharya P. *Sep. Purif. Technol.* 2003; **30:** 89-96.
6. George SC, Ninan KN, Thomas S. *J. Membr. Sci*. 2000; **176 (1):** 131-142.
7. Kusumocahyo SP, Sudoh M. *J. Membr. Sci.* 1999; **161**: 77-83.
8. Kariduraganavar MY, Kulkarni SS, Kittur AA. *J. Membr. Sci.*, 2005; **247(1):** 75-86.
9. Lin X, Kikuchi E, Matsukata M. *Chem. Commun*. 2000; **11:** 957-958.
10. Haung RYM, Pal R, Moon GY. *J. Membr. Sci.* 1999; **160(1):**17-30.
11. Feng X, Haung RYM. *Ind. Eng. Chem. Res.* 1997; **36:** 1048-1066.
12. Nam SY, Chun HJ, Lee YM. *J. Appl. Polym. Sci.* 1999; **72(2):** 241-249.
13. Moon GY, Pal R, Haung RYM. *J. Membr. Sci.* 1999; **156(1):** 17-27.
14. Kulkarni SS, Kittur AA, Aralaguppi MI, Kariduraganavar MY. *J. Appl. Polym. Sci.* 2004; **94:** 1304-1315.
15. Kurkuri MD, Toti US, Aminabhavi TM. *J. Appl. Polym. Sci*. 2002; **86:** 3642-3651.
16. Shi Y, Wang X, Chen G. *J. Appl. Poly.Sci,* 1996; **61:**1387-1394.
17. Yeom CK, Lee KH. *J. Appl. Poly. Science,* 1998; **67:** 209 -219.
18. Haung RYM, Pal R, Moon GY. *J. Membr. Sci,* 1999; **160:**101-113.
19. Fischer FG, Dorfel H. [Polyuronic acids in brown algae.], Hoppe Seyler's Zeitschrift fur *Physiologische Chemie,* 1955; **302:**186-203.
20. Zhang J, Mungora P, Jane *J .Polymer* ,2001; **42:**2569-2576.
21. Preeti L, Nethravali AN. *Ind Crop Produ,* 2005; **21:**49-64.
22. Lodha P, Nethravali AN. *J Mater Sci,* 2002; **37:**3657-3665.
23. Anker M, Stading M, Hermansson M. *J Agric Food Chem,*1999; **47:**1848-1851.
24. Snchez AC, Popineau Y, Mangavel C, Larr C, Guguen J. *J Agric Food Chem,* 1998; **46:**4539-4544.
25. Hernandez PM, Kanavouras A, Ng PKW, Garava R. *J Agri Food Chemi,* 2003; **51**:7647-7654.
26. Hernandez PM, Kanavouras A, Villalobos R, Chiralt A. *J.Agri Food Chemi,* 2004; **52:**7897-7904.
27. Mangavel C, Barbot J, Bervas E, Linossier L, Feys M, Gueguen J, Opineau Y. *J Cereal Sci,* 2002; **36:**157-166.
28. Rayas Luis M, Hernandez Ruben J, Perry KE. *J Agri Food.Chem,* 1997; **20(2):**160-162.
29. Sudhakar H, Chowdoji Rao K, Sridhar S. *Desig Mono and Polym,* 2010; **13:** 287-299.
30. Sudhakar H, Venkata Prasad C, Sunitha K, Chowdoji Rao K, Subha MCS, Sridhar S. *J. of Appli Poly Sci,* 2011; **121 (5):**2717-2725.
31. Harogoppad SB, Aminabhavi TM. *Macromolecules,* 1991; **24:**2598-2605.
32. Aminabhavi TM, Phayde HTS, Ortego JD, Vergnaud JM. *Polymer,* 1996; **377:**1677-1684.
33. Pawlak A, Mucha M. *Thermo chimical. Acta.,* 2003; **396(1-2):** 153-166.

34. Dani Jagadeesh, Jeevan Prasad Reddy D, Varada Rajulu A. *J. Poly Environ (2011),* **19:**248-253
35. Kittur AA, Kariduraganavar MY, Toti US, Ramesh K, Aminabhavi TM. *J Appl Polym Sci,* 2003; **90:** 2441-2448.
36. Kurkuri MD, Toti US, Aminabhavi TM. *J Appl Polym Sci,* 2002; **86:** 3642-3651.
37. Hennepe HJC, Bargeman D, Mulder MHV, Smolders CA. *J Membr Sci,* 1987; **35(1):** 39-55.
38. Nyugen QT, Neel J, Clement R, Leblanc L. *J. Membr Sci,* 1983; 1543-1550.
39. Huang RYM, Yeom CK. *J. Membr Sci,* 1991; **62(1)**: 59-73.