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## Hybrid adsorbent membranes of Poly(vinyl alcohol) and Zeolite A for pervaporation dehydration of Ethanol at their Azeotropic Point

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### Abstract

The study reports on the development of hybrid adsorbent membranes of poly(vinyl alcohol) (PVA) loaded with hydrophilic sodium zeolite A i.e., 4A zeolite in different compositions from 1 to 10 wt. % that are used for pervaporation (PV) dehydration of ethanol at azeotropic point from aqueous mixtures i.e. 4.1 wt. % at 30°C. The PV performance of hybrid adsorbent membranes were much superior to that of plain PVA membrane in terms of selectivity and flux due to increased hydrophilicity of PVA membrane in the presence of 4A zeolite particles that are also hydrophilic. The membranes were crosslinked with tetraethyl ortho silicate (TEOS) and confirmed by Fourier transform infrared spectroscopy (FTIR) and ion exchange capacity (IEC). Morphology of the membranes was assessed by scanning electron microscopy (SEM). Sorption studies have been performed to evaluate the extent of interaction and degree of sorption of the prepared membranes. It is observed that flux and selectivity increased analytically with increasing amount of 4A particles in the PVA matrix. In case of hybrid adsorbent membrane containing 10 wt. % 4A, selectivity for water was 1320 and flux 0.366 kg/cm<sup>2</sup> h that was attributed to the combined effects of molecular adhesion between particle surfaces and PVA matrix as well as higher selectivity of the adsorptive membrane as compared to plain PVA membrane.

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### Introduction

Pervaporation (PV) separation has been the widely used method for separating aqueous-organic azeotropes [1]. In this method, chemical structure and physical nature of dense membranes have an effect on membrane performance and recent research efforts are moving towards developing mixed adsorbent membranes to obtain better mechanical strength and separation performance over plain polymeric membranes. In the prior literature, several hybrid adsorbent membranes loaded with inorganic zeolite particles have been developed and used for dehydrating organics [2-4]. Separation using zeolite-filled PV membranes occurs by adsorption-desorption and molecular sieving effects due to the presence of small particles [5].

The incorporation of inorganic silicate materials into a polymeric matrix has been explored extensively as an efficient way for improving various performances such as thermal stability, optical properties, electrical properties, catalytic reactivity, and transport properties of materials. Nevertheless, due to limited intrinsic compatibility between inorganic and many organic polymers, lack of adhesion at the interfaces poses challenges for applications of such hybrid materials. Better control and tailoring of the interfacial regions to optimize the desired properties would enable successful fabrication of composite materials [6].

Organic-inorganic hybrid membranes in which inorganic filler with specific physicochemical characteristics is spatially dispersed into the bulk of polymeric membranes seems a facile and feasible solution to cross the tradeoff hurdle by combining the high selectivity with desirable mechanical properties of inorganic materials and tunable flexibility with excellent

processability of polymeric materials. [1,2] Many studies have demonstrated that the dramatically improved separation properties of organic-inorganic hybrid membranes could be realized by incorporating porous or nonporous inorganic adsorbents, including zeolite, silica, carbon molecular sieve and activated carbon into the matrixes of glassy polymers and rubbery polymers. There are also some studies on incorporating mineral flakes into polymeric membranes to selectively permeable membrane [3,4] or impermeable barriers.[5] Much effort has been devoted to obtain organic-inorganic hybrid membranes with both high permeability and high selectivity. The permeability of organic inorganic hybrid membranes depends on not only the intrinsic properties of the inorganic material and polymer and the interaction between the two phases but also the inorganic content and particle size. Maxwell, [7] te Hennepe et al.,[8,9] and Koros et. al [10] have subsequently proposed and commonly employed to theoretically describe the transport behavior of hybrid organic-inorganic membranes, where inorganic particle content is the sole key variable. Recently, based on the experimental and theoretical analysis in membrane-based gas separation process, Moore and Koros proposed that the organic-inorganic interface morphologies would strongly affect the permeability and selectivity of organic-inorganic hybrid membranes [11]. They pointed out that the dispersed phase might cause an undesirable void at the interface or create varying degrees of rigidification in the surrounding polymer. Until now, no similar report specifically dealing with the pervaporation process can be found. Therefore, in this study we focus on a detailed investigation and elucidation about the organic-inorganic hybrid pervaporation membranes with simultaneously enhanced permeability and selectivity.

The purpose of this study is to find a strategy achieving simultaneous enhancement of flux and selectivity and thus establishing a set of methodologies for hybrid pervaporation membrane preparation and process development. Poly(vinyl alcohol) (PVA)-4A adsorbent membranes were prepared and characterized by FTIR, SEM, DSC and TGA techniques. The effects of 4A zeolite particle content on pervaporation properties of the adsorbent membranes for separation of Ethanol/water at azeotropic mixtures were systematically investigated. The reversal tradeoff effect was actually found and tentatively elucidated.

The development of more ecofriendly polymeric systems is a current trend. Among all the possibilities of combining different properties (polymer blends, polymer grafting, copolymerization, etc.), our attention has been focused on the use of biocompatible and biodegradable hybrid-mixed matrix membranes comprising a combination of organic base and inorganic fillers prepared by special methods [12–14]. Hybrid membranes having high crosslink density with the highest possible degree of interpenetration are the better candidates. In this direction, we thought of using poly(vinyl alcohol) (PVA), a widely used polymer, to prepare membranes by adding tetraethoxysilane (TEOS) as the crosslinking agent. PVA is an environmentally benign polymer and hence an attempt has been made to develop novel hybrid PVA membranes crosslinked with TEOS that could exhibit good oxygen barrier properties.

## Experimental

### Materials and methods

Poly(vinyl alcohol) of reagent grade sample was all from Aldrich Chemicals Ltd., USA. Tetra ethyl orthosilicate (98 % pure) was purchased from Acros Organics, India and hydrochloric acid was procured from s.d fine Chemicals, India. Deionized water, having a conductivity of 5.5  $\mu\text{S}/\text{cm}$ , was produced in the laboratory itself using the double distillation unit.

### Particle size measurement of zeolite 4A

Particle size was measured by Zetasizer (Model 3000HS, Malvern, U.K). The sizes of the completely dried zeolite 4A particles were measured by wet sample technique using wet sample adapter. Particles were dispersed in water and placed on sample cuvette and zeta average diameter was recorded. After measurement of particle size, sample cuvette was cleaned thoroughly to avoid cross contamination. Particle size was measured in triplicate, but average value was considered in data analysis.

### Membrane fabrication

#### Preparation of plain PVA membrane

PVA (5 g) was dissolved in 80 mL of deaerated distilled water at 60°C. To this solution, a known amount of TEOS was added along with 1 mL of HCl as a catalyst. The whole mixture was stirred overnight at 60°C to complete the reaction. The reaction is of sol–gel type and the resulting homogeneous solution was cast on a glass plate with the help of a doctor's knife. The membrane formed was dried at ambient temperature, and peeled off from the glass plate. During reaction, 2 wt. % of TEOS was added (i.e., 0.1 g of TEOS) for crosslinking to take place.

#### Preparation of adsorptive membrane

PVA (5 g) was dissolved in 80 mL of deaerated distilled water at 60°C; to this a known amount of TEOS was added along with 1 mL of HCl as a catalyst. The whole mixture was stirred overnight at 60 °C to complete the reaction. The known amount of zeolite 4A particles (to form 1, 2.5, 5, 7.5, and 10 wt % loading films) were first dried in a vacuum oven at 250 °C and

then dispersed in the corresponding solvent via a sonicator (model VC 50, Sonics & Materials Inc.) for 2 hrs. and added to the above prepared PVA solution. The whole mixture was stirred for about 24 h to obtain the homogeneous solution; the resultant solution was cast as a membrane with the help of doctor's knife to form membranes of uniform thickness. The cast membranes allowed drying and once dried membranes are peeled off. The hybrid adsorbent membranes are designated as 4A-PVA-1, 4A-PVA-2.5, 4A-PVA-5, 4A-PVA-7.5 and 4A-PVA-10 that contained 1, 2.5, 5, 7.5 and 10 wt % of 4A zeolite particles respectively.

The thickness of the resultant films was measured using a dial micrometer (AMES, model 56212). For each film, 10 measurements were performed and an average thickness was obtained. All the films used in this work had a thickness of around  $62 \pm 0.2 \mu\text{m}$  (the standard deviation was less than 2.5 $\mu\text{m}$ ).

### Scanning electron microscopy

SEM micrographs of the plain PVA and 4A-PVA hybrid adsorbent membranes containing 2.5 wt. % of 4A and 10 Wt. % of 4A particles were taken to study the membrane morphology. Membranes were sputtered with gold coating to make them conducting and placed on a copper stub. Scanning was done using JEOL model JSM-840A, Japan. The thickness of the gold layer accomplished by gold sputtering was about 15 nm.

### FTIR

Pristine and crosslinked membranes ground well with KBr to make pellets using a hydraulic pressure of 400–450  $\text{kg}/\text{cm}^2$ . FTIR spectra were taken for PVA, before and after modification, using Shimadzu FTIR spectrophotometers. Membranes were scanned to confirm the crosslinking reaction of PVA with TEOS.

### Pervaporation experiments

PV experiments were performed on 100 mL batch level with an indigenously built glass manifold operated at vacuum level of 0.05 mmHg in the permeate line. The effective membrane area was 20  $\text{cm}^2$  and weight of the feed mixture taken in the PV cell was 70 g. Temperature of the feed mixture was maintained constant by a thermostatic water jacket. Before starting the PV experiment, test membrane was equilibrated for about 2 to 4 h with the feed mixture. After establishment of steady state, permeate vapors were collected in cold traps immersed in liquid nitrogen for up to 4–5 h. Weight of permeate collected was measured using Mettler Balance (model B 204-S, Greifensee, Switzerland: accuracy  $10^{-4}$  g) to determine flux,  $J$  ( $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ) using weight of liquids permeated,  $W$  (kg), effective membrane area,  $A$  ( $\text{m}^2$ ) and measurement time,  $t$  (h) as:

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

The analysis of feed and permeate samples was done using Nucon Gas Chromatograph (model 5765, Mumbai, India) equipped with a Thermal Conductivity Detector (TCD) and DEGS or Tenax packed column of 1/8" ID of 2 m in length. Oven temperature was maintained at 70°C (isothermal), while injector and detector temperatures were maintained at 150°C. The sample injection volume was 1  $\mu\text{L}$ . Pure hydrogen was used as the carrier gas at 0.75  $\text{kg}/\text{cm}^2$  pressure. The GC response was calibrated for column and for known compositions of water with ethanol mixture. Calibration factors were fed into GC software to obtain the analysis for unknown samples. The selectivity,  $\alpha$  and separation index, PSI, were calculated as:

$$\alpha = \left( \frac{P_A}{1 - P_A} \right) \left( \frac{1 - F_A}{F_A} \right) \quad (2)$$

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

where  $F_A$  is weight % of water in feed and  $P_A$  is weight % of water in permeate. A minimum of three independent readings on flux and  $\alpha$  were taken under similar conditions of temperature and feed compositions to confirm steady-state pervaporation.

#### Degree of sorption

Swelling experiments were performed gravimetrically on all membranes in 10, 20 and 30 wt. % water-containing feed mixtures at 30°C as per the procedure published before [14]. Initial weights of the circularly cut (dia = 2.5 cm) Pristine PVA and 4A incorporated PVA hybrid adsorbent membranes were taken on a single-pan.

Digital microbalance (model AE 240, Mettler, Switzerland) to an accuracy of  $\pm 0.01$  mg. Samples were placed inside the specially designed airtight test bottles containing 30 cm<sup>3</sup> of the test media. Test bottles were transferred to oven maintained at constant desired temperature. Dry membranes were equilibrated by soaking in different compositions of feed mixtures in a sealed vessel at 30°C for 48 h. The swollen membranes were weighed immediately after carefully blotting them in between soft filter paper wrappings. The % degree of swelling, DS was calculated as:

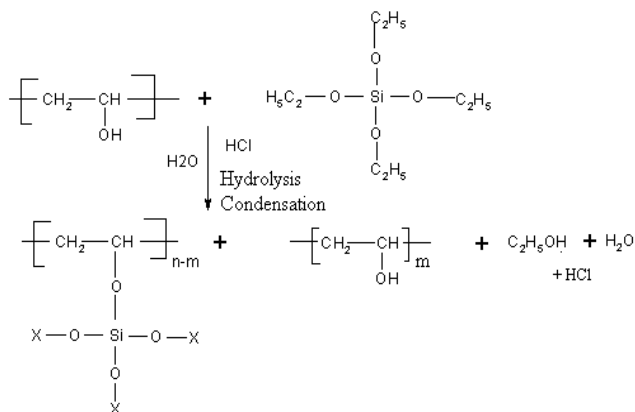
$$\% DS = \left( \frac{W_\infty - W_0}{W_0} \right) \times 100 \quad (4)$$

where  $W_\infty$  and  $W_0$  are the weights of swollen and dry membranes, respectively.

## Results and Discussion

#### Reaction of PVA and TEOS

The scheme of crosslinking reaction between PVA and TEOS are shown in Fig. 1. Polycondensation reaction was carried out as per the procedure reported earlier [12, 14]. While preparing PVA/TEOS hybrid matrix membranes, TEOS was hydrolyzed in the presence of an acid catalyst (HCl) producing the silanol groups. The resulting silanol groups yielded siloxane bonds due to dehydration or dealcoholysis reaction with other silanol or ethoxy groups during the membrane drying process. These reactions have led to cohesive type interactions between siloxane and hydroxy groups of PVA as shown in Scheme I.



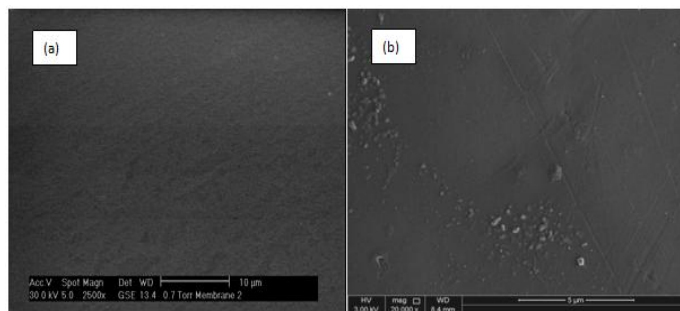
**Figure 1:** Reaction scheme of poly(vinyl alcohol) and tetraethoxysilane.

#### Sorption Studies

Incorporation of 4A zeolite as a adsorbent material into PVA matrix resulted in the formation of dense homogeneous membranes those are quite stable enough upon standing at ambient temperature up to a month or even more. The zeolite-incorporated membranes have been tested for sorption studies in water-ethanol mixtures at their azeotropic point viz., 95.9: 4.1 water: ethanol mixture to check their suitability in PV experiments.

#### Scanning Electron Microscopy (SEM)

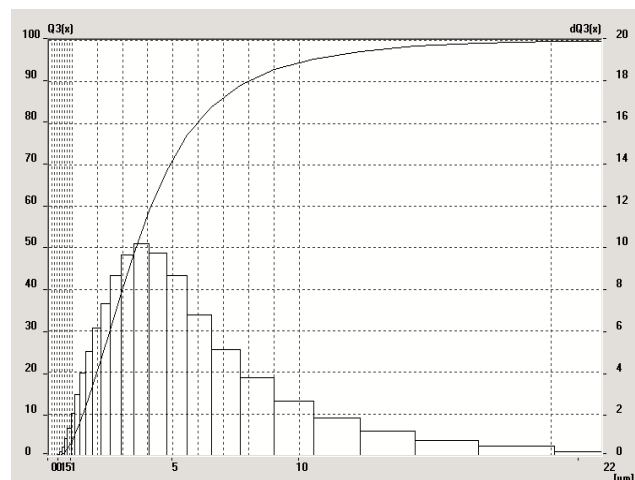
SEM image of the surfaced of the pristine PVA and 5 wt. % 4A loaded PVA hybrid membranes as shown in Figure 2. Fig. 2 (a) shows the SEM surface images of pristine PVA membrane, and Fig. 2 (b) shows 5 wt. % 4A loaded crosslinked PVA membranes. Notice that particles of 4A are distributed uniformly at the surface in PVA matrix. During PV experiments, most of water molecules get adsorbed onto 4A particles and transported through the pores of the particles that are uniformly embedded in the PVA matrix. However, it is necessary that these particles are to be uniformly dispersed in PVA matrix so that the filled membrane will exhibit enhanced effects of flux as well as selectivity. We can observe the 4A particle size will be around 3-7  $\mu$ m. This data was supported by particle size analysis.



**Figure 2:** SEM images of (a) pristine PVA and (b) 5 wt. % 4A loaded PVA.

#### Particle size and distribution

The particle size distribution of a material can be important in understanding its physical properties of the material. The histogram of particle size distribution is shown in Fig. 3. 4A zeolite particles vary in the size between 3 and 7  $\mu$ m. SEM picture of the membrane displayed in Fig. 1 also supports this analysis and distribution of particles in the membrane matrix.



**Figure 3:** Particle size histogram of zeolite 4A.

### FTIR Studies

Crosslinking of PVA with TEOS is confirmed by FTIR spectra displayed in Fig. 4. A broad peak at  $3200\text{ cm}^{-1}$  for plain PVA represents O-H stretching vibrations of the hydroxyl group. Broadness of this peak was decreased for the hybrid matrix membrane because of the incorporation of TEOS group, since the -OH groups of PVA could participate in the condensation reactions with the silanol groups of TEOS, resulting in the formation of a covalent crosslinking bond with -OH of PVA. In the region of  $1000\text{--}1100\text{ cm}^{-1}$ , multiple bands have appeared for plain PVA due to C-O stretching vibrations. In case of hybrid matrix membrane, the intensity of this peak was increased, indicating the formation of Si-O-C bonds between linear alkyl chain (-CH<sub>2</sub>-CH-) of PVA. However, -Si-O- stretching is also observed in the same region as that of C-O stretching.

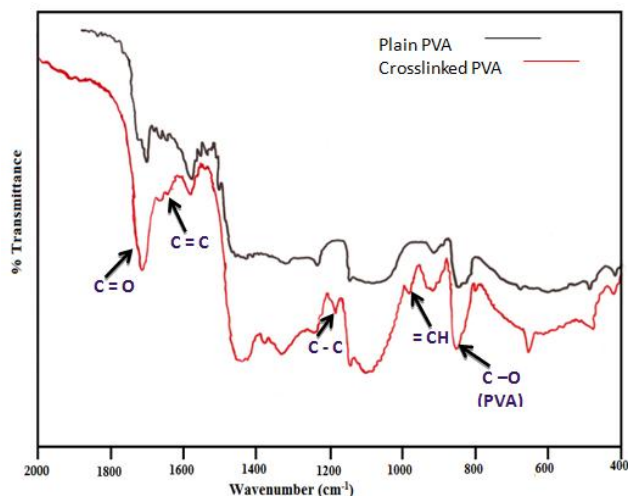


Figure 4: FTIR tracings of PVA before and after crosslinking

### Degree of Sorption

Degree of sorption was measured using the equation 4 considering weights of the wet membrane and sorbed membrane at equilibrium as a function of time and the data of water-alcohol mixtures sorbed by the zeolite 4A loaded PVA membrane was displayed in figure 5 suggesting that the sorption of the membrane is significant, showing the rigid nature of prepared membrane. Pervaporation results are greatly influenced by membrane swelling. Figure 5 compare the plots of % degree of swelling of the plain PVA and 4A loaded PVA hybrid adsorbent membranes at ambient temperature for 95.9:4.1 mass % of water in the feed mixtures containing ethanol. Notice that comparatively membranes swell to a lesser extent in zeolite loaded PVA membrane as compared to plain PVA membrane. This is due to a space occupied by the zeolite particles in the membrane matrix and they will not swell in the aqueous-organic media. However, in the feed mixtures, swelling decreases linearly with increasing loading of 4A particles in PVA. For 1 wt. % 4A-loaded PVA membrane, a slight decrease in % DS is observed over that of plain crosslinked PVA membrane. However, for 10 wt. % 4A containing mixed matrix membrane, % DS was very low of all the membranes studied in the present case.

In addition, filler particles will tend to occupy the free volume spaces of PVA matrix that otherwise are held by the hydroxyl groups of PVA. The reason for decrease in DS value is though water forms stronger hydrogen bond clusters with ethanol and hence, more energy is required for the dissociation of water molecules from ethanol-water mixture for sorption to occur within the polymer matrix. In general, four types of interactions

seem to dominate the PV results. These include membrane-water, membrane-organic, water-organic and membrane-mixed solvent media [13]. The extent of sorption depends upon the strength of these interactions and it appears that the interactions between membrane and mixed solvent media dominate over other effects.

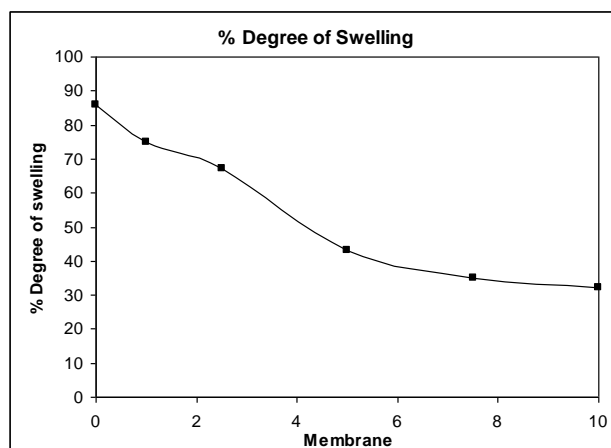


Figure 5: % Degree of sorption for the different membrane.

### Pervaporation separation Index

Figure 6 displays the variation of PSI with the extent of loading zeolite 4A in the PVA membrane. The PSI values increased linearly with increasing 4A content, signifying that membranes that contained a higher amount of filler would show improved PV performance for water-ethanol feed mixtures. The incorporation of 4A particles into the PVA membrane would not only affect membrane hydrophilicity, but also its rigidity. Thus, increased hydrophilic-hydrophilic interactions between 4A and PVA exert a significant effect on diffusion of water through composite membranes by retaining organic components on the feed side.

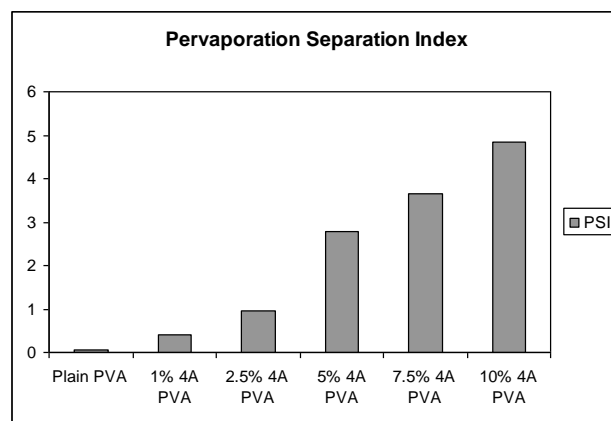
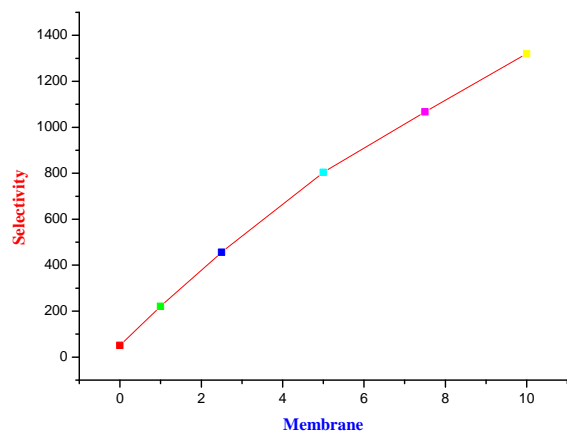


Figure 6: Pervaporation separation index.

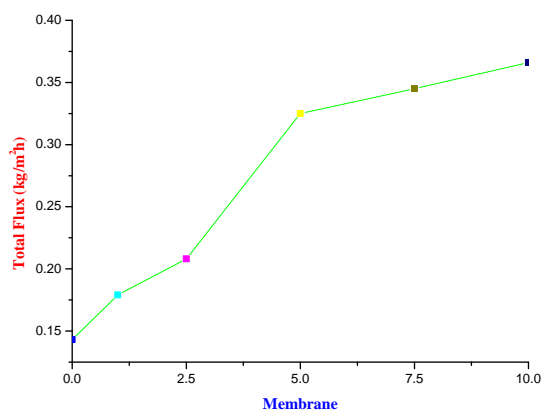
### Membrane performance

Since transport is very sensitive to subnanometer defects due to the angstrom-sized liquid molecules, it is ideally suited to probe the interfacial integrity between the inorganic and polymer phases. In addition to the improvement of mechanical properties, remarkable changes have been observed in liquid transport properties of adsorbent membrane using zeolite 4A particles. Zeolite 4A is a well-known molecular sieve with a pore diameter of  $3.8\text{ \AA}$  and a 3-dimensional pore network of interconnected cages that is ideally suited to the binary liquid separation systems.

In PV experiments, membrane performance is studied in terms of flux and selectivity [13]. The membranes prepared in this study are hydrophilic in nature and hence, are water selective. As a result, they would preferentially attract more of polar water molecules than the less polar ethanol. However, the presence of 4A zeolite particles into PVA matrix would increase the free water channels to facilitate transport of large number of water molecules through the mixed matrix membranes than with the plain PVA membrane. The transport of organic component is hindered in the presence of large excess of water due to their hydrophilic interactions with the membrane. As seen in Fig. 7 (a) and (b), for plain crosslinked PVA membrane, flux and selectivity data for ethanol–water are much lower than those observed for adsorbent membranes.



(a)



(b)

**Figure 7:** Total Flux and selectivity with respect to Membrane.

However, a systematic effect can be seen for flux and selectivity with the filled adsorbent membranes. Both flux and selectivity values of PVA adsorbent membranes increase with increasing amount of 4A zeolite particles, indicating an increased hydrophilicity of the hybrid adsorbent membranes due to the presence of 4A zeolite particles. Notice that the extent of water extracted on the permeate side of the membrane increases systematically with increasing amount of filler loading. Thus, 5, 7.5 and 10 wt. % 4A zeolite loaded PVA adsorbent membranes are able to remove >97 wt. % of water on the permeate side, whereas only smaller amount of water (up to 69 % of ethanol) were extracted through the crosslinked plain PVA. Whereas 1 wt. % 4A zeolite loaded mixed matrix PVA membranes was able to remove 91 % of water from feed (see also Table-1 for numerical data). On the other hand, for the 10 wt. % 4A zeolite

loaded PVA membrane, selectivity becomes 1320 and 98 wt.% of water could be extracted on the permeate side, suggesting the effectiveness of the mixed matrix membranes containing higher amount of 4A zeolite. The organic components of the feed mixtures were not effectively transported across the membrane due to electrostatic repulsive interactions between water molecules and hydrophilic sites of 4A zeolite filler particles. Thus, membranes of this study are more water selective than organic component selective. This is clearly demonstrated by increased performances of the PVA membranes after incorporation of 4A zeolite particles.

**Table 1:** Pervaporation Results of the Membranes in terms of flux and selectivity at 30°C

Membrane	Water (wt. %)		Flux (kg/m <sup>2</sup> h)	Selectivity ( $\alpha$ )
	Feed	Permeate		
Plain PVA	4.2	69.2	0.143	51.2
PVA + 1 wt.% 4A	4.9	91.3	0.179	221
PVA + 2.5 wt.% 4A	4.1	95.0	0.208	456
PVA + 5 wt.% 4A	4	97.2	0.325	804
PVA + 7.5 wt.% 4A	4.3	97.4	0.345	1067
PVA + 10 wt.% 4A	3.2	97.7	0.366	1320

Flux and selectivity results presented in Table-I and displayed graphically in figure 6 for feed containing 4.1 wt.% water (azeotropic point) exhibit the sequence: plain crosslinked PVA < PVA/1 wt.% 4A zeolite < PVA/2.5 wt.% 4A zeolite < PVA/5 wt.% 4A zeolite < PVA/7.5 wt.% 4A zeolite < PVA/10 wt.% 4A zeolite. It was noticed that addition of 4A zeolite particles into PVA matrix could increase the PV performance of the mixed matrix membranes than those of plain crosslinked PVA membrane. Experimental data displayed in figure 6 suggest that both flux and selectivity increase simultaneously with increasing loading of 4A zeolite particles; such effects are somewhat difficult to achieve in PV dehydration studies. In the present study, it is observed that as the amount of 4A zeolite increased, its intercalation with the base PVA matrix will also increase in addition to increase in the hydrophilicity of PVA membrane. As explained before, this effect is a manifestation of increase in preferential free volume channels created in PVA matrix after the addition of 4A zeolite particles, thus allowing an easy transport of water, since large number of water molecules are being adsorbed onto 4A zeolite particles than merely on plain crosslinked PVA membrane. Fluxes of filled membranes are higher than plain crosslinked PVA membrane. It is found that for ethanol–water mixture, selectivity values increased from 51.2, 221, 456, 804, 1067 and 1320, also flux values increased from 0.143, 0.179, 0.208, 0.325, 0.345 and 0.366 kg/m<sup>2</sup> h. This type of enhancement in membrane performance is attributed to increased preferential interaction of water molecules with the filled matrix membranes as explained before.

## Conclusions

To improve membrane performance, one can generally follow two distinct strategies, i.e., either to synthesize new polymers with specific chemical architectures or to modify the existing polymers by incorporating suitable fillers. This paper reports results obtained according to the latter route. It is realized from

the literature that fillers like zeolites can improve separation properties of membranes, provided that appropriate zeolite and polymer combinations are chosen. The 4A zeolite filled PVA hybrid adsorbent membranes of this study had not been previously reported in the literature. The hybrid adsorbent membranes studied here were effective in PV dehydration of ethanol at its azeotropic point with water. The addition of even a small amount of 4A zeolite particles into PVA membranes has improved both flux and selectivity to water over that of the plain PVA membrane. Such improvements are attributed to hydrophilic nature of 4A particles, whose addition to another hydrophilic polymer like PVA greatly improved the overall membrane performance.

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